Embedded-Cluster Calculations in a Numerical Atomic Orbital Density-Functional Theory Framework

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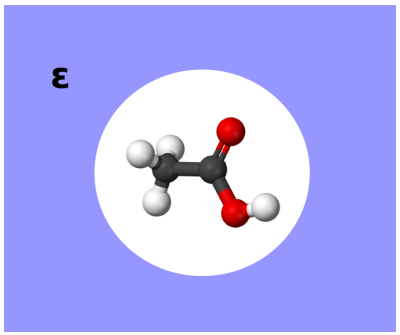
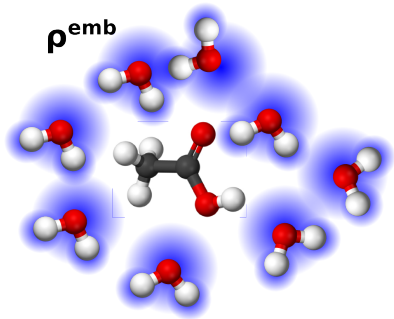
Embedding - a hierarchical approach

Solvation Models



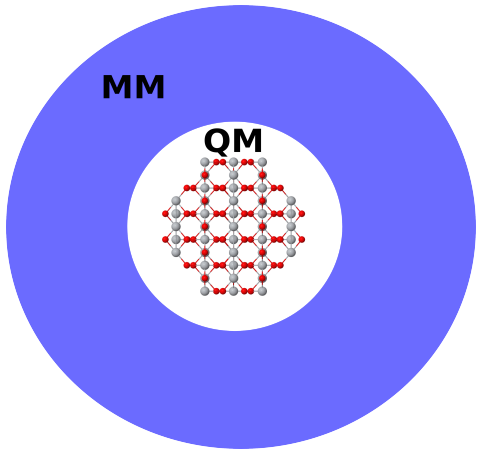
- Born, Onsager, ...
- Polarization of solvent
  $\rightarrow G_{solv}$

Density embedding



- Frozen density embedding [1]
- Embedding in $V[\rho^{emb}]$

QM/MM

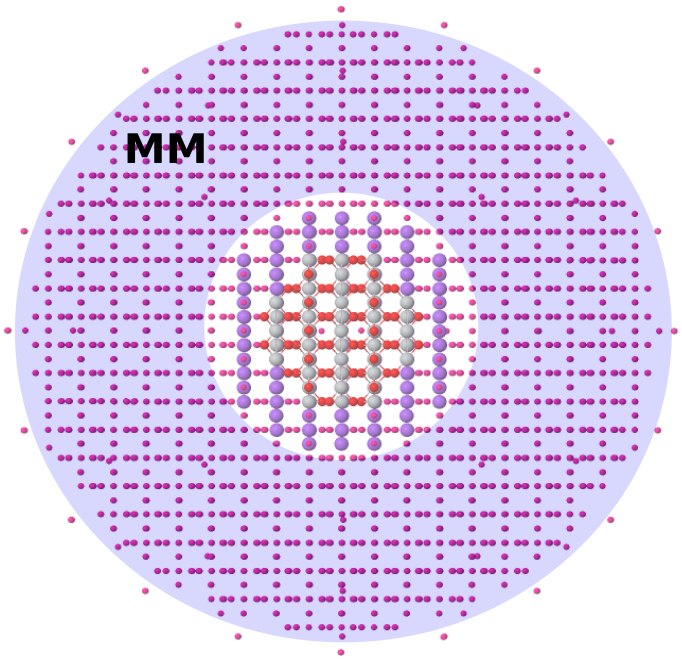


- coupling QM cluster with force fields
- for solids/crystals:

Embedded clusters

[1] T.A. Wesolowski and A. Warshel J. Phys. Chem. 97, 8050–8053 (1993)

Embedded clusters



Seamless coupling

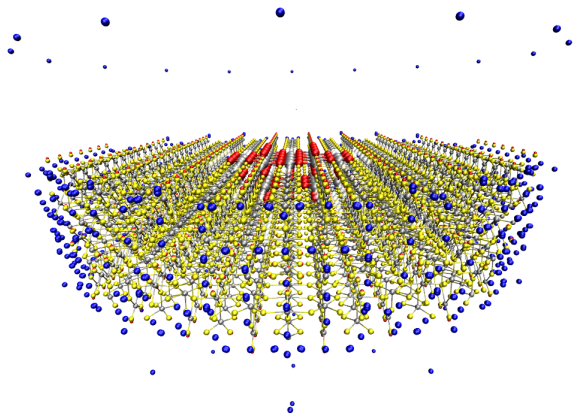
between
quantum mechanics (QM)
and
molecular mechanics (MM)

QM: explicit electrons, accurate, expensive, ...

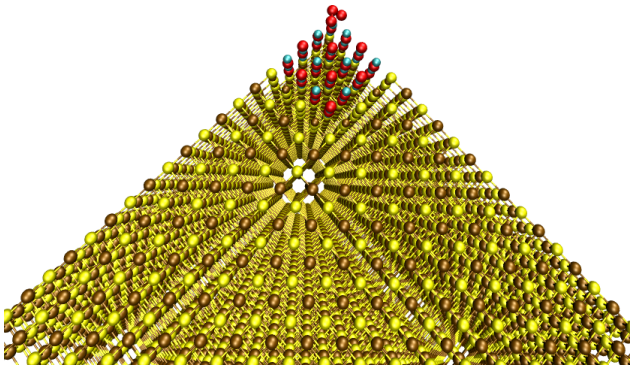
MM: classical (no explicit electrons), cheap, polarizable force field, pseudopotentials ...

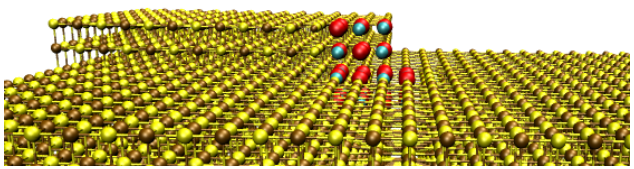
Outline

1. Motivation, Issues with PBC
2. Ingredients
   - Recovering the potential of infinite ionic background
   - Transition between QM and MM (pseudopotentials)
   - Polarization response from MM region (force fields)
3. Photocatalytic water splitting with TiO_2
4. Stability of Surface Defects



Motivation





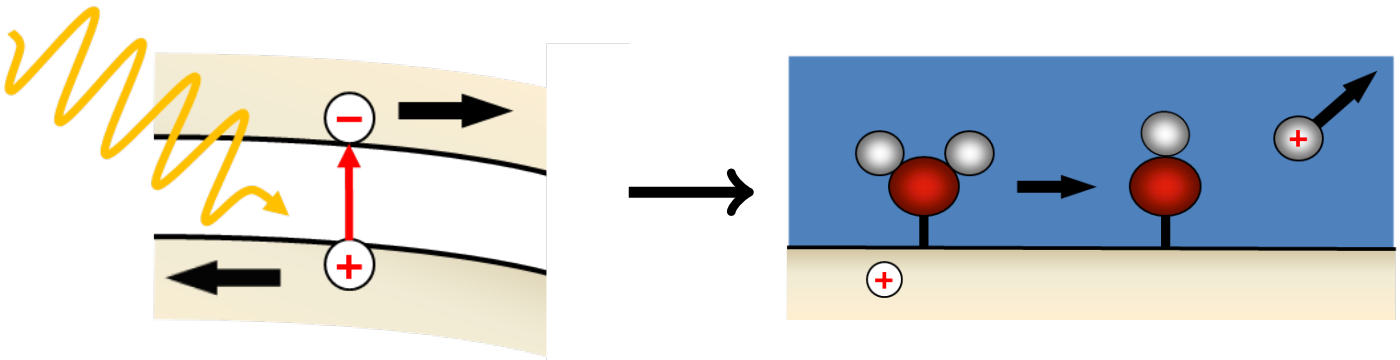
Corner, kink or step sites can offer interesting chemistry!

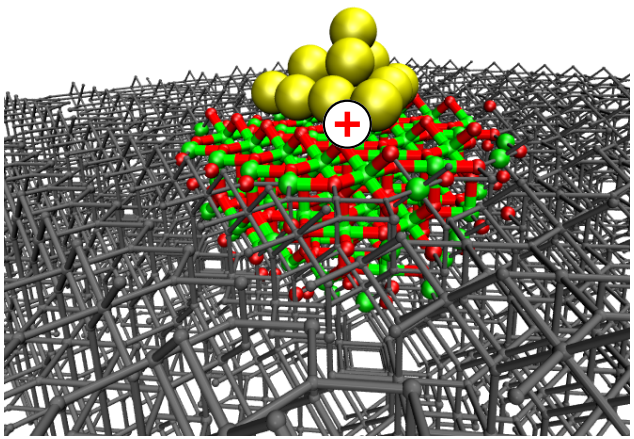
But, how to choose a supercell for that?

Motivation

Photocatalysis at nanostructured surfaces

carrier-driven redox chemistry

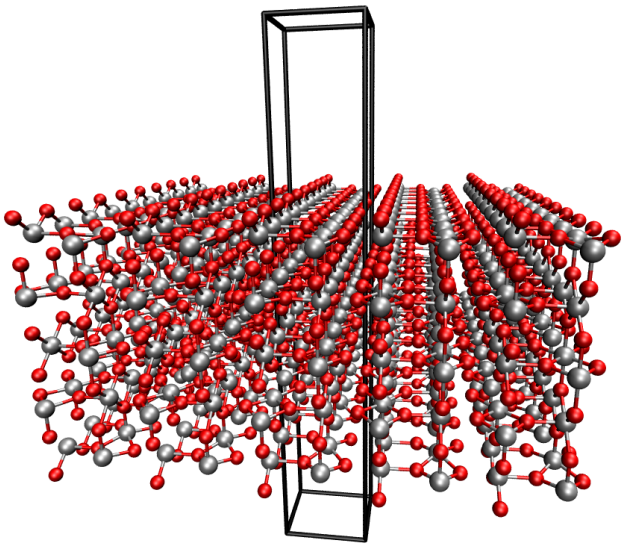


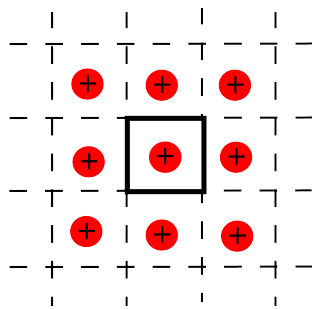


Challenges:

- bond making and breaking
- hybrid functionals
- not necessarily long-range periodicity
- charged systems

Issues with PBC



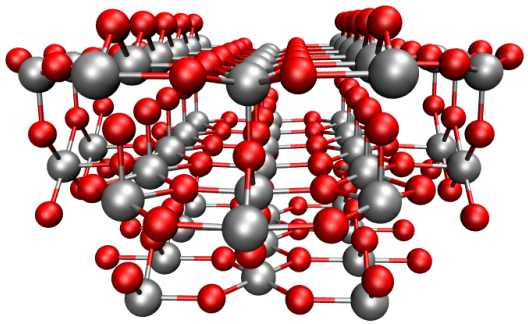


- nonperiodicities: large supercells to avoid finite size effects
- net charges are problematic
- large number of basis functions

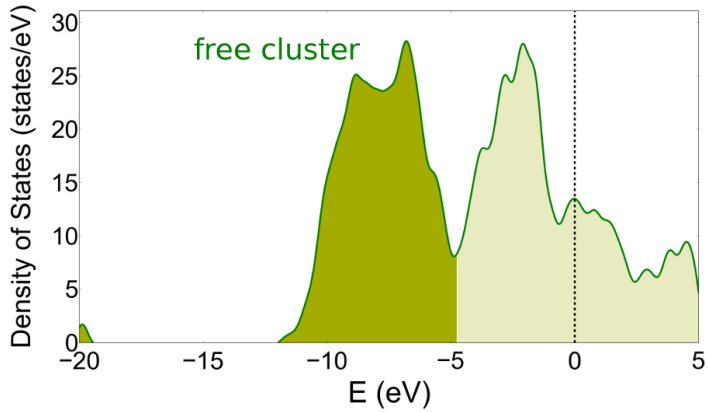
$\rightarrow$ potentially prohibitive memory demand

The Ingredients

Free TiO_2-cluster



e.g. $Ti_{54}O_{108}$

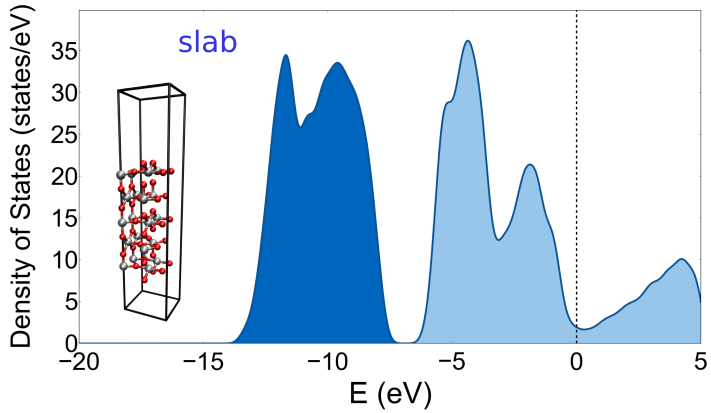


Cluster: metallic

Solving KS-equations: GGA

$$[\tfrac{1}{2}\nabla^2 + V_{nuc} + V_{Ha} + V_{xc}]\Psi_i = \epsilon_i \Psi_i$$

Slab: semiconductor

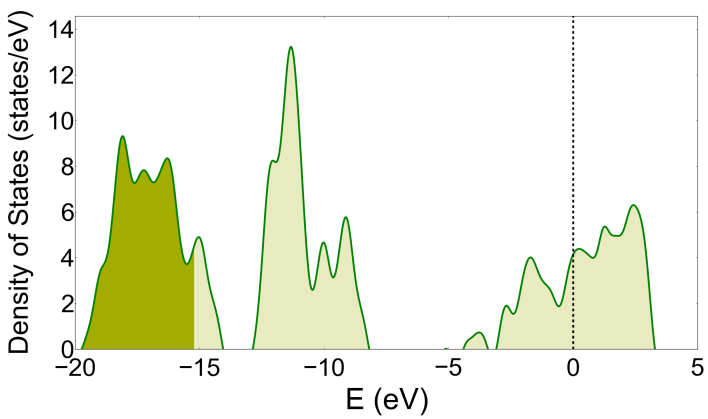


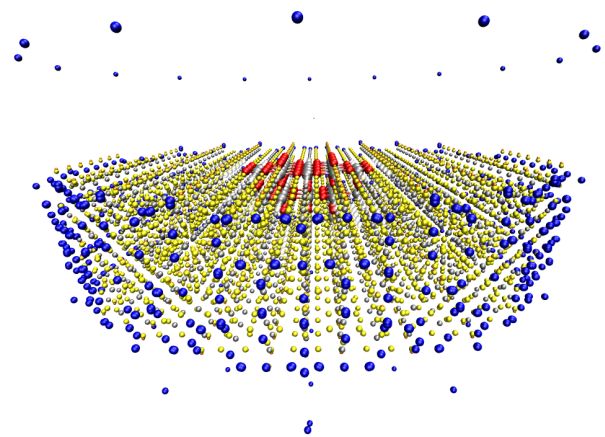
Free TiO_2-cluster + point charges

Recovering the electrostatics of the infinite ionic background:

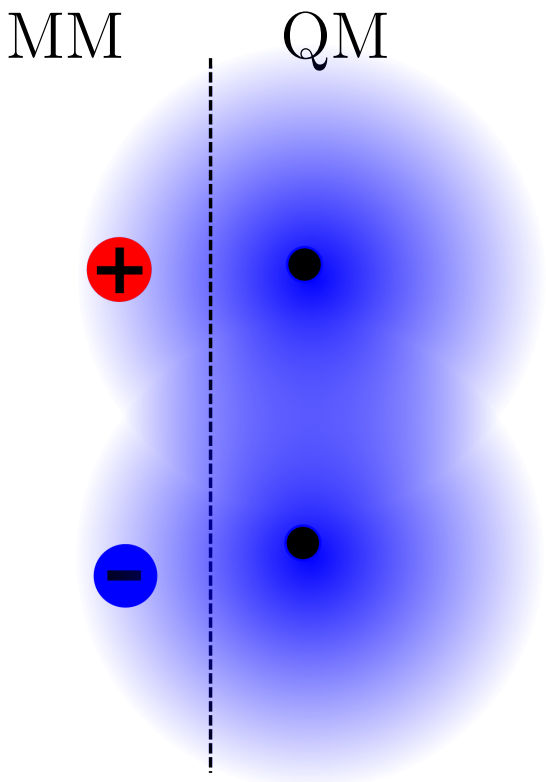
1. Supercell $\xrightarrow{\text{Ewald's method}}$ potential
2. Create finite field of point charges (+4/-2)
3. Add point charges with fitted charges (blue)

$$[\tfrac{1}{2}\nabla^2 + \mathrm{V_{nuc}} + \mathrm{V_{Ha}} + \mathrm{V_{xc}} + \mathrm{V_{PC}}]\Psi_\mathrm{i} = \epsilon_\mathrm{i}\Psi_\mathrm{i}$$



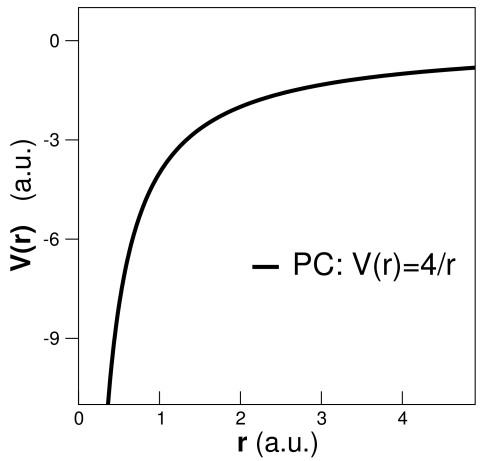


Cluster region boundary

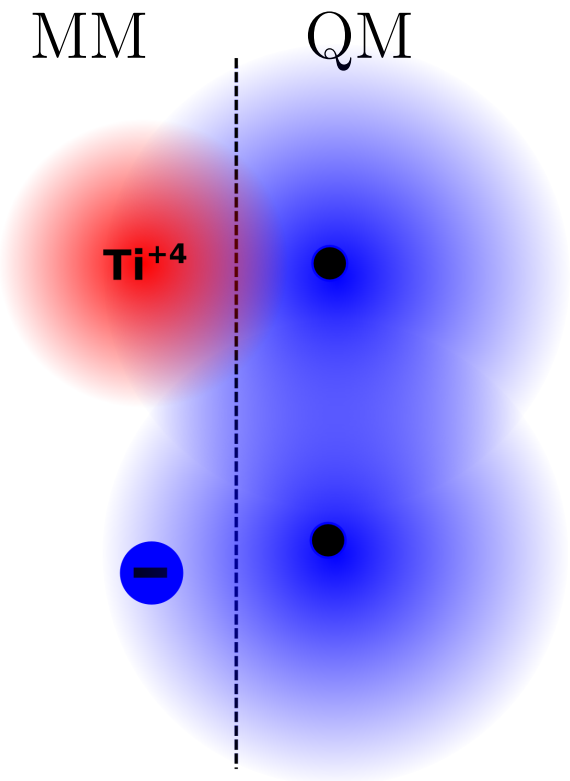


ρ_{el} overlapping with singular $\mathrm{V_{PC}(r)} = \frac{\mathrm{Q}}{\mathrm{r}}$

- only PC^{+} are "troublemakers"
- spurious charge leakage
- wrong scattering/dangling bonds



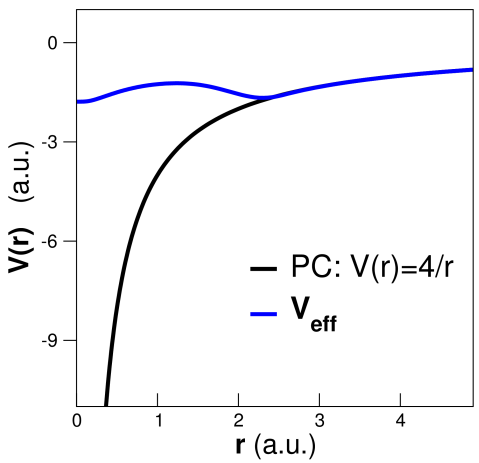
Cluster region boundary



ρ_{el} overlapping with singular $V_{PC}(r) = \frac{Q}{r}$

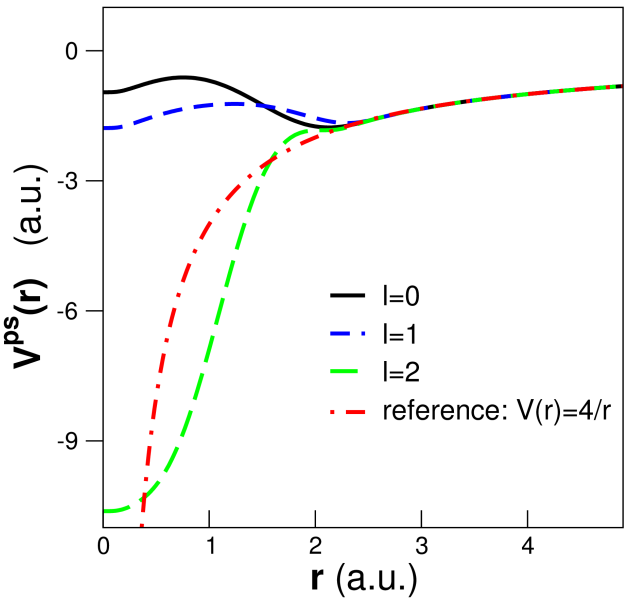
- only PC^+ are "troublemakers"
- spurious charge leakage
- wrong scattering/dangling bonds

Replace PC^+ by pseudopotential



effective potential for core and core electrons

Kleinman-Bylander Pseudopotentials



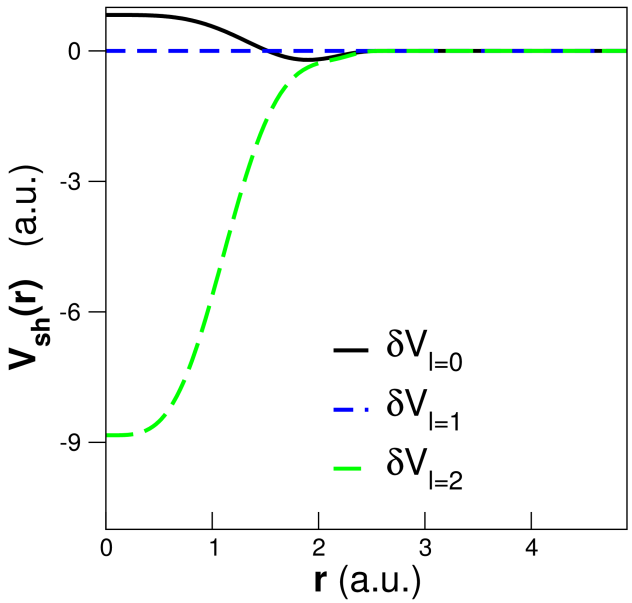
Accurate pseudopotentials:

- construct from ab-initio (FHI98PP [1])
- different potential for every l-state
- correct scattering behaviour

$$\hat{V}^{PP} = \sum_{lm} |Y_{lm}\rangle V_l(r) \langle Y_{lm}|$$

[1] M. Fuchs and M. Scheffler, Comput. Phys. Commun. 119 , 67-98 (1999)
[2] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. 48, 1425-1428 (1982)

Kleinman-Bylander Pseudopotentials



Accurate pseudopotentials:

- o construct from ab-initio (FHI98PP [1])
- o different potential for every l-state
- o correct scattering behaviour

Separation [2] : V_{loc} & $\delta V_l = V_l$ - V_{loc}

- o long-range and short-range part

$$\hat{V}^{KB} = \hat{V}_{loc}\delta(r - r') + \sum_{lm} |\chi^{KB}_{lm}\rangle E^{KB}_{l} \langle\chi^{KB}_{lm}|$$

[1] M. Fuchs and M. Scheffler, Comput. Phys. Commun. 119 , 67-98 (1999)
[2] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. 48, 1425-1428 (1982)

KB-PPs - Interaction with QM-electrons

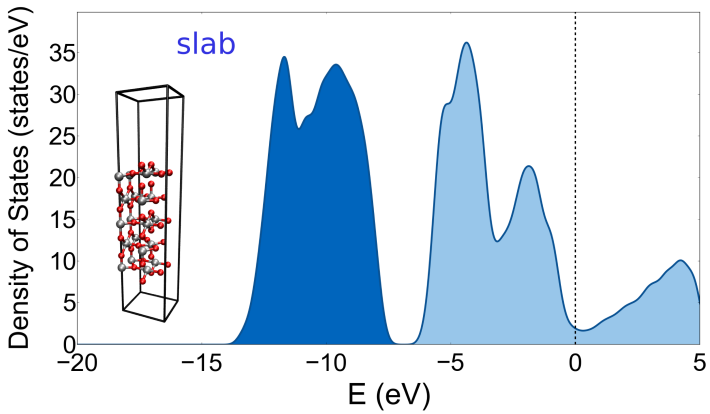
$$\hat{V}^{KB} = \hat{V}_{loc}\delta(r - r') + \sum_{lm} |\chi^{KB}_{lm}\rangle E^{KB}_{l} \langle\chi^{KB}_{lm}|$$

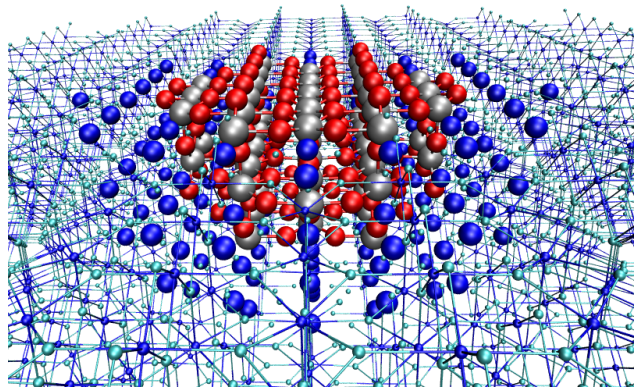
$$\hat{V}^{KB}_{SR}|\Psi_i\rangle = \sum_{\alpha} \sum_{lm} c_{i\alpha} |\chi^{KB}_{lm}\rangle E^{KB}_{l} \langle\chi^{KB}_{lm}|\varphi_{\alpha}\rangle$$

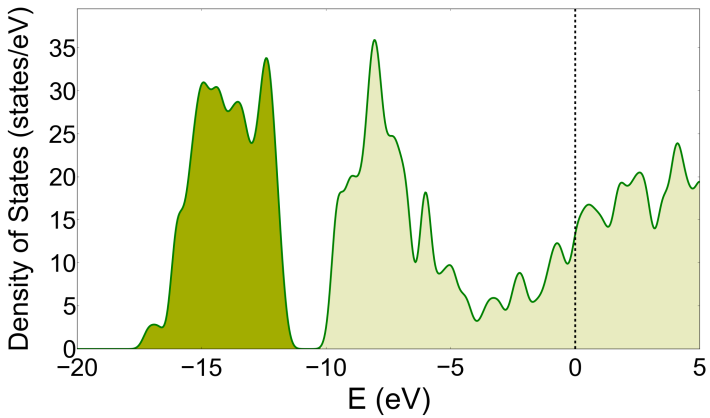
φ: basis functions (NAOs)
$c_{i\alpha}$: KS coefficients

$\langle\varphi_{\alpha}(r)|\chi^{KB}_{lm}(r')\rangle$:
- computed efficiently using RI-L infrastructure
- exploit locality (many overlaps are zero)

Free TiO_2-cluster + point charges + PP







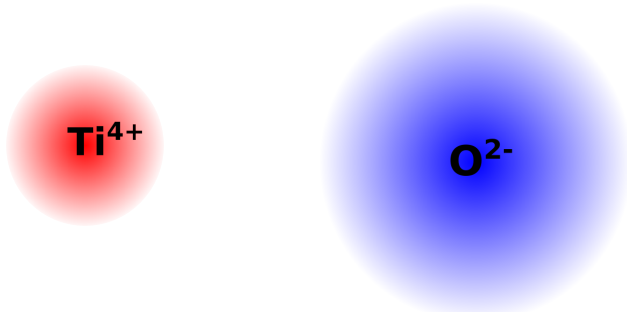
We can recover the band gap!

but: Fermi energies do not match!

Reason: - no polarization

MM region - Force fields

MM atoms/ions: interact via 2-body potentials



MM region - Force fields

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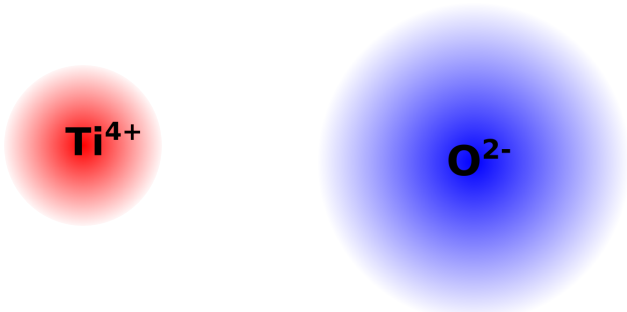
Example: Polarizable Force Field for TiO_2



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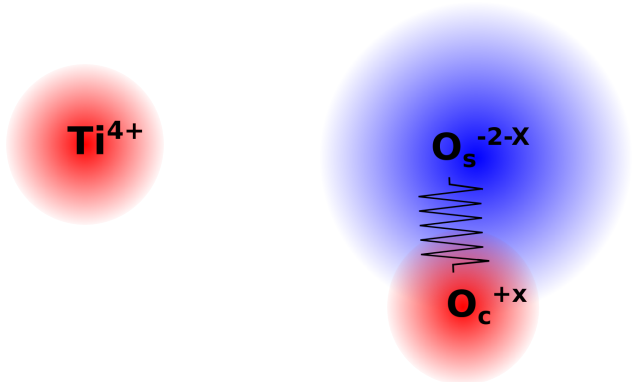


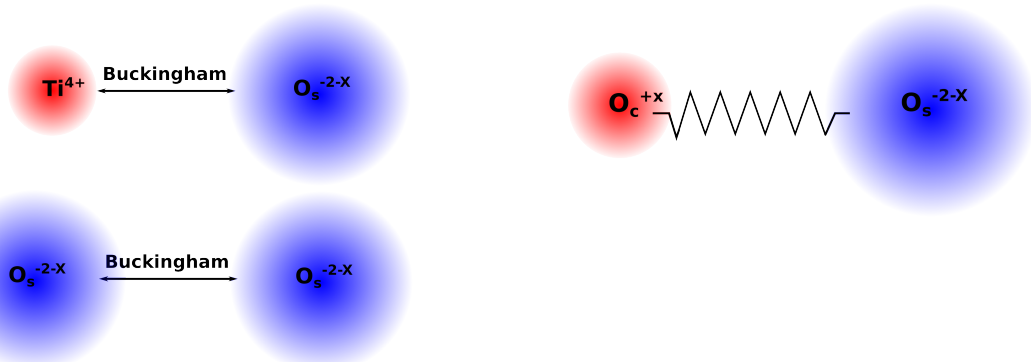
polarizable oxygen

MM region - Force fields

Example: Polarizable Force Field for TiO_2

$$U_{ij}^{coulomb} = \frac{Q_i Q_j}{r_{ij}} \quad \& \quad U_{ij}^{buck} = Ae^{-r_{ij}/\rho} - C/r_{ij}^6 \quad \& \quad U_{ij}^{spring} = \frac{1}{2} k r_{ij}^2$$

all pairs



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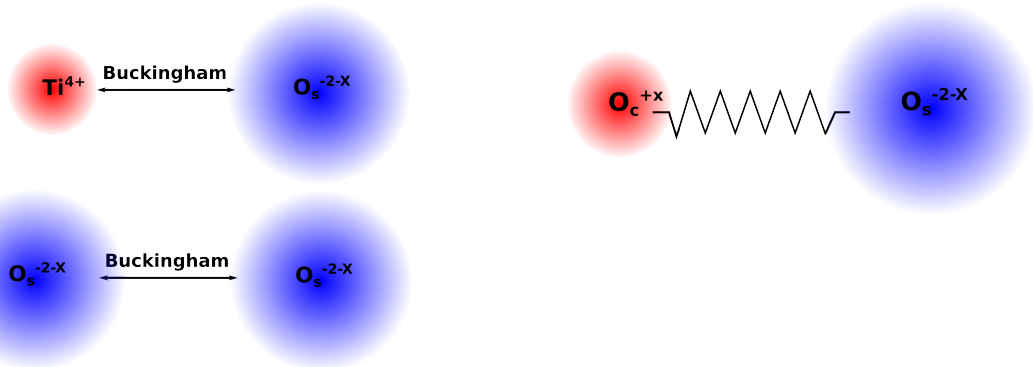

Parameters: 2×3 Buckingham, spring constant, O_c-charge

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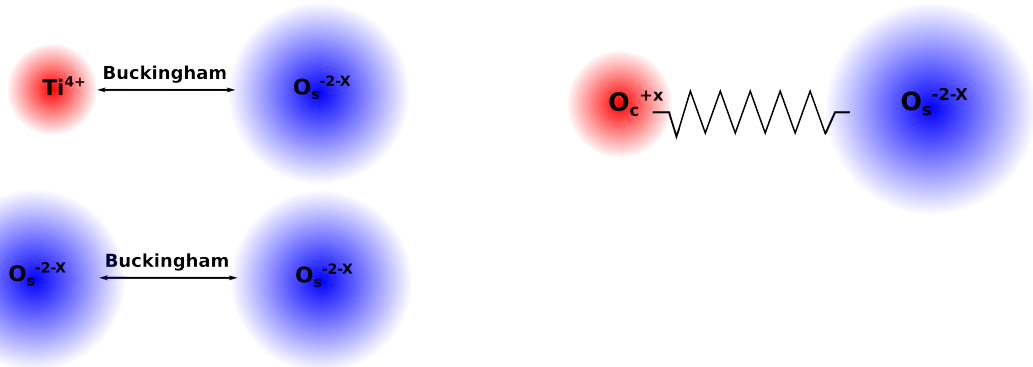


Parameters: 2×3 Buckingham, spring constant, O_c-charge

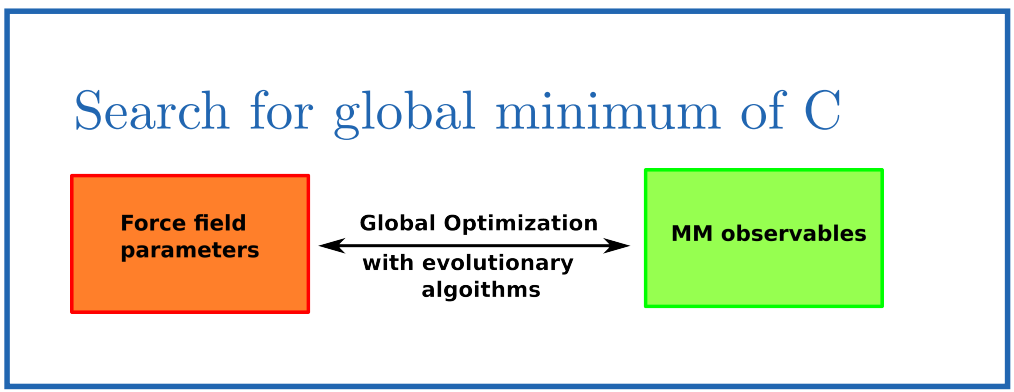
How to determine those values?

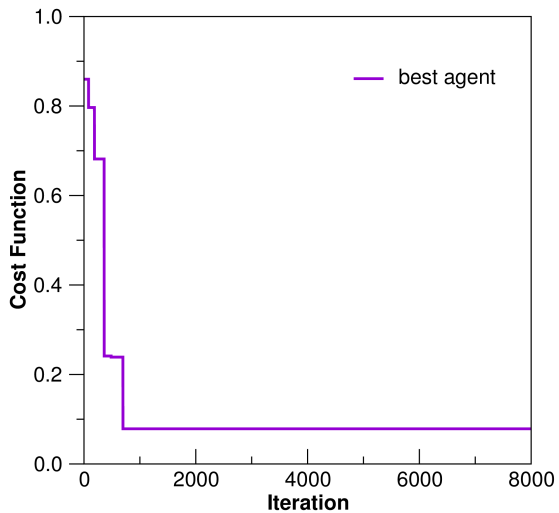
Force Field Optimization

Seamless coupling between QM and MM region:

- o avoid stress → matching lattice parameters
- o correct polarizability → matching dielectric constants

$$C = \sqrt{\sum_i \left(\frac{L_i^{MM} - L_i^{DFT}}{L_i^{DFT}} \right)^2 + \sum_j \left(\frac{\epsilon_j^{MM} - \epsilon_j^{DFT}}{\epsilon_j^{DFT}} \right)^2}$$

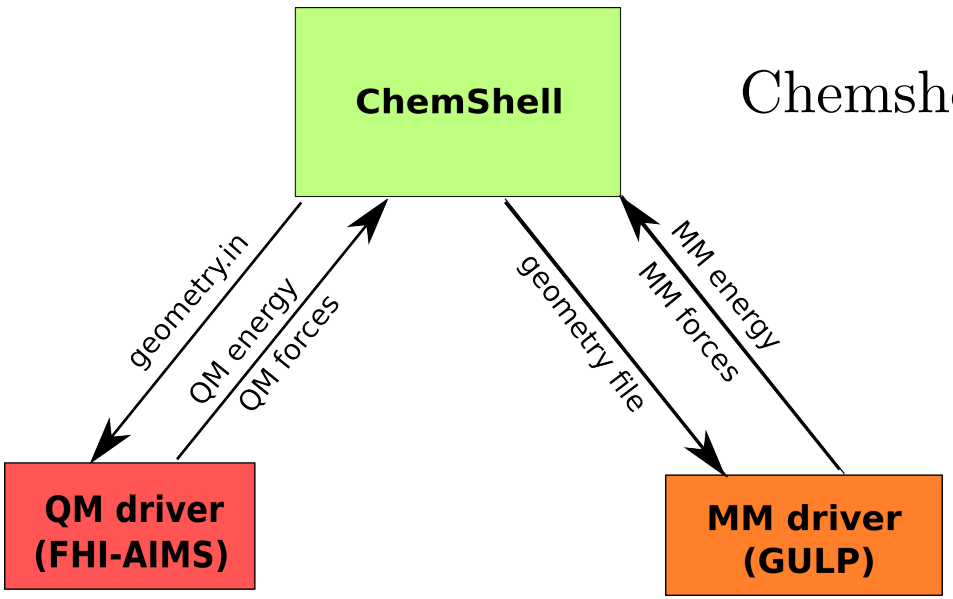




Calculating the Polarization Response

Self-consistent polarization:

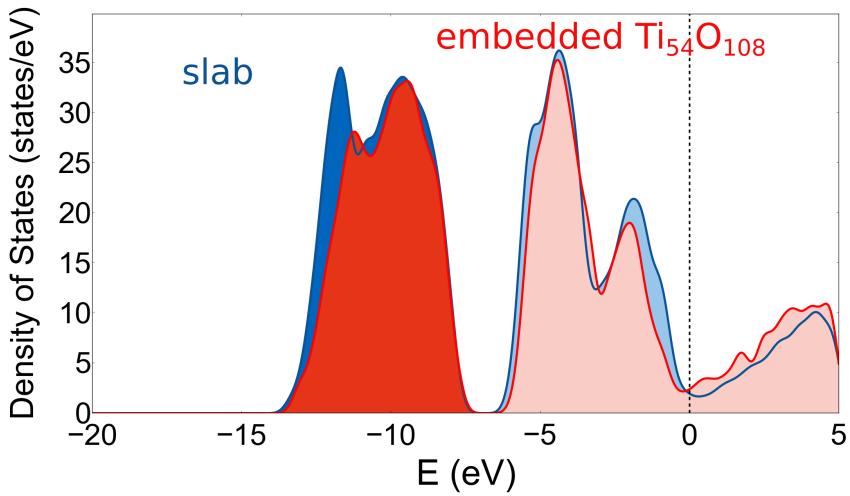
Minimizing $E_{tot} = E^{QM} + E^{MM}$ w.r.t. position of oxygen shells.



Chemshell: adding up forces,
suggesting new geometry

[Chemshell]: P. Sherwood et al., J. Mol. Struct.: THEOCHEM 632, 1 (2003)
[GULP]: J. D. Gale, J. Chem. Soc., Faraday Trans. 93, 629 (1997)

Complete and seamless embedding

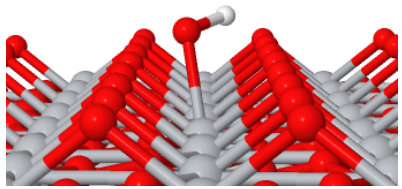


Very good agreement!

Oxygen Evolution Reaction on TiO_2

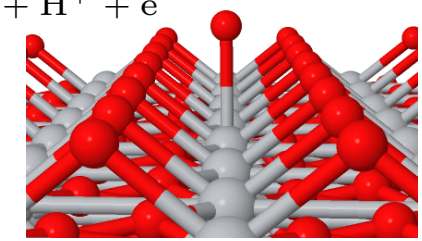
Oxygen Evolution Reaction on TiO_2 [1]

$H_2O + (^*) \rightarrow OH^* + H^+ + e^-$

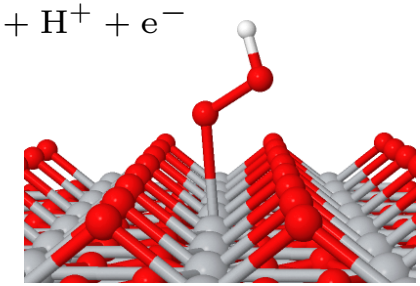


Comparing stabilities of intermediates!

$OH^* \rightarrow O^* + H^+ + e^-$



$H_2O + O^* \rightarrow OOH^* + H^+ + e^-$



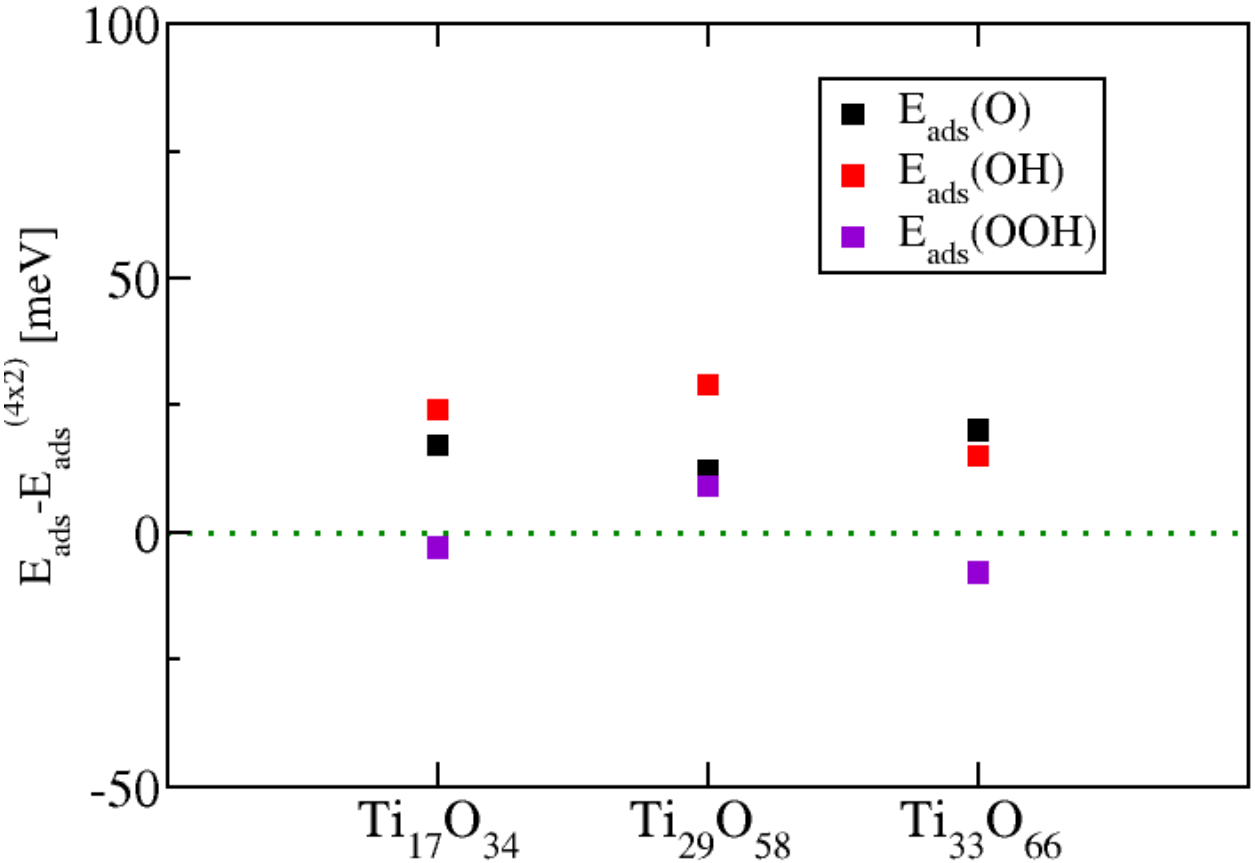
Which level of theory?

[1] Á. Valdéz et al., J. Phys. Chem C 112 (2008), 9872

$OOH^* \rightarrow O_2 + (^*) + H^+ + e^-$

Oxygen Evolution Reaction on TiO_2

Essentially converged results with $Ti_{17}O_{34}$ cluster!



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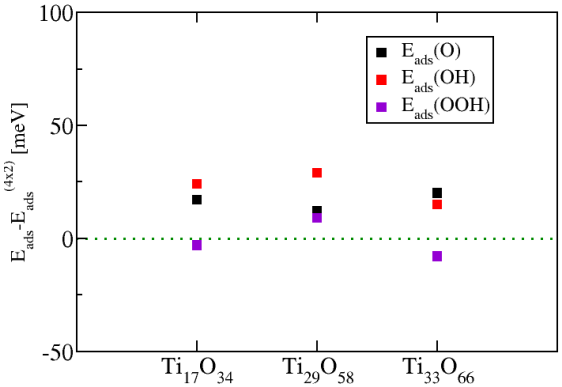
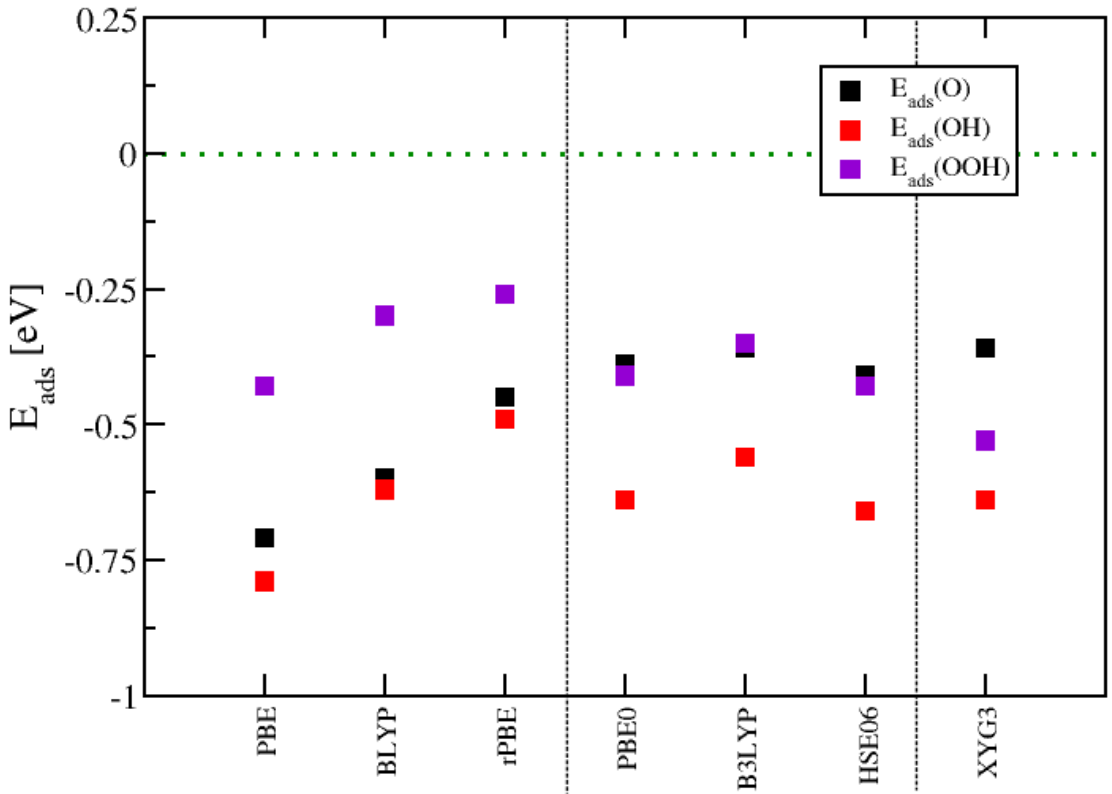


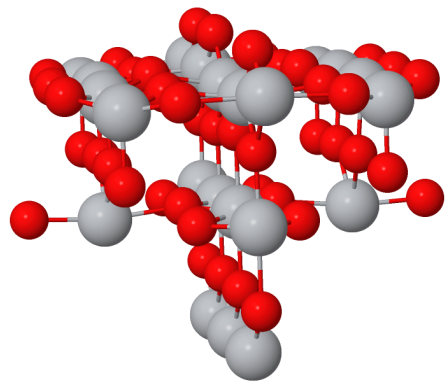
OH always
bind strongest!



Surface Defects in TiO_2

Which charge state is favored?

$$G_f \sim E_{defect}[q] - E_{pristine}[0] + \mu_O + q\epsilon_f$$



- HSE06 (localized charges)
- relaxation of cluster
- incorporating long-range polarization

(Preliminary results)

ΔG_f[eV]	q=0	q=1	q=2
$Ti_{21}O_{44}$	5.4	1.0	-2.5
$Ti_{31}O_{64}$	5.5	1.2	-2.6

Summary

Embedded-cluster calculations can be a useful method for
- o nonperidocities
- o charged systems

For seamless coupling between QM and MM one needs
- o pseudopotentials to provide correct scattering behaviour
- o force field parameters with matching MM properties

Thanks to:
Volker Blum, Andrew Logsdail & Alexey Sokol (UCL)
Harald Oberhofer & Karsten Reuter (TUM)
and IGSSE for financing.

D.Berger et al., J. Chem. Phys. 141, 024105 (2014)