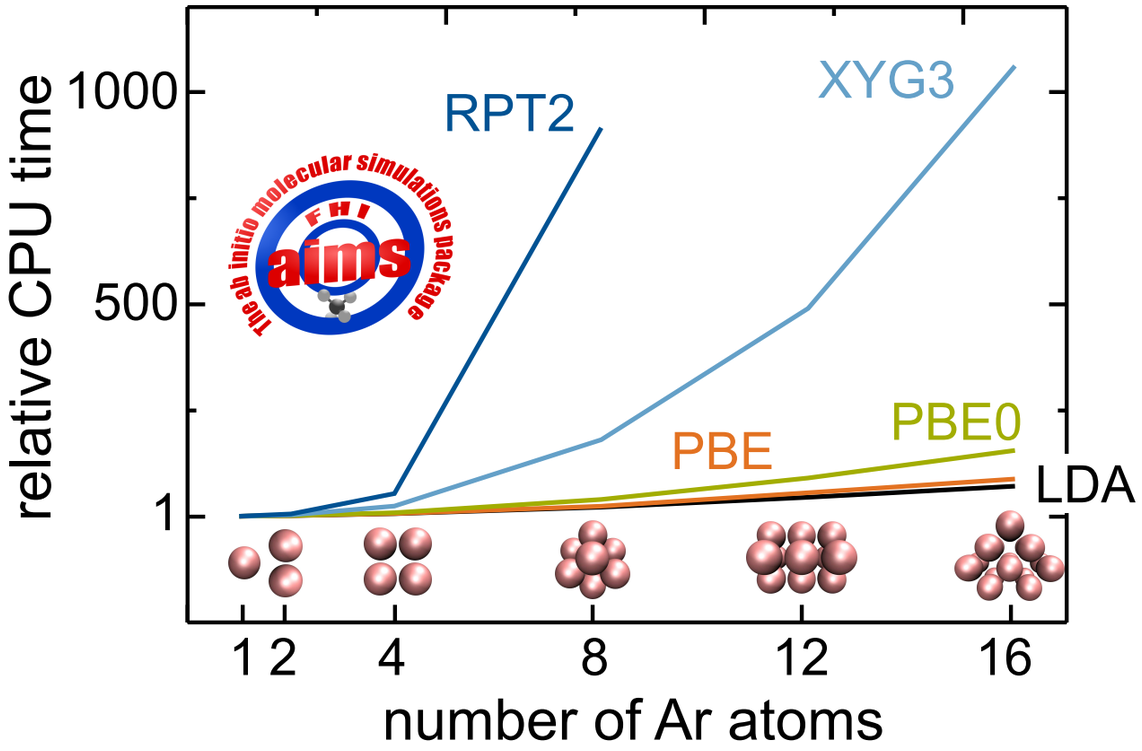
Embedding Quantum Regions in Classical Environments

Harald Oberhofer

Chair for Theoretical Chemistry, TUM

Why

scaling:



too expensive for large systems

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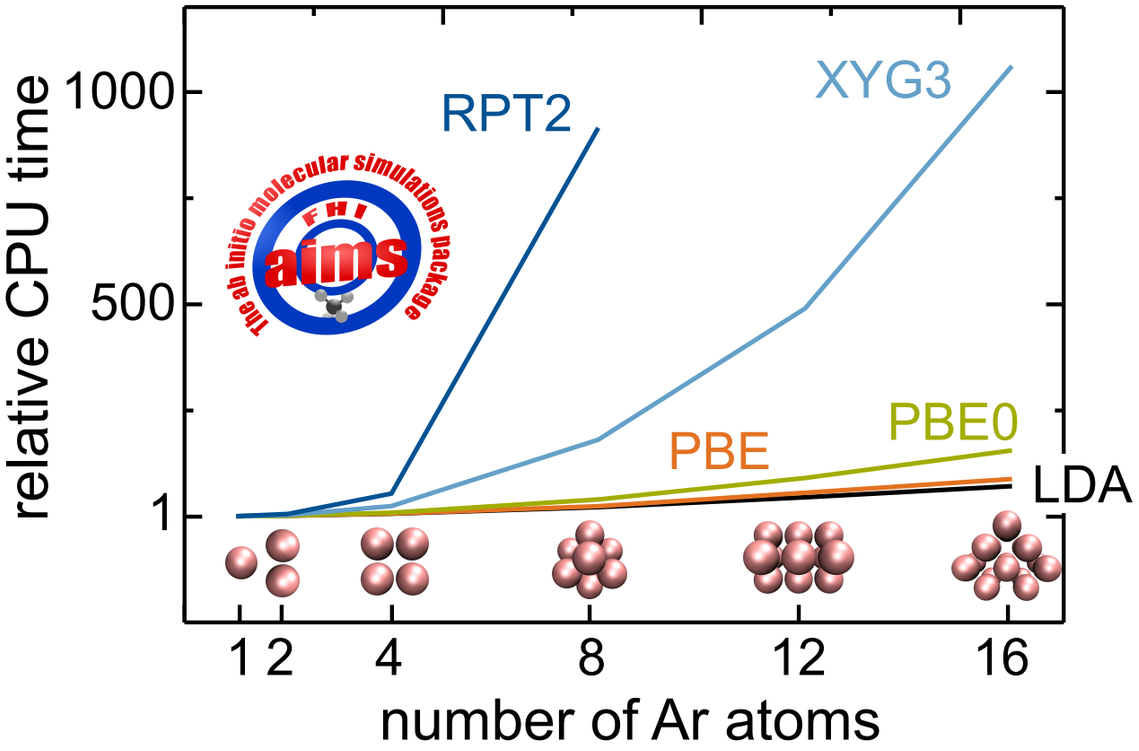

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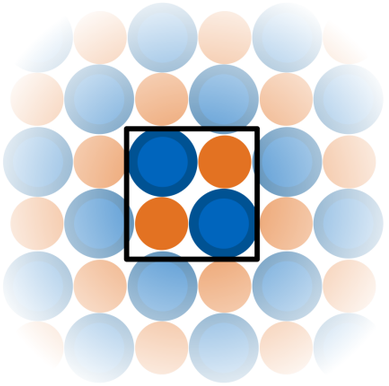

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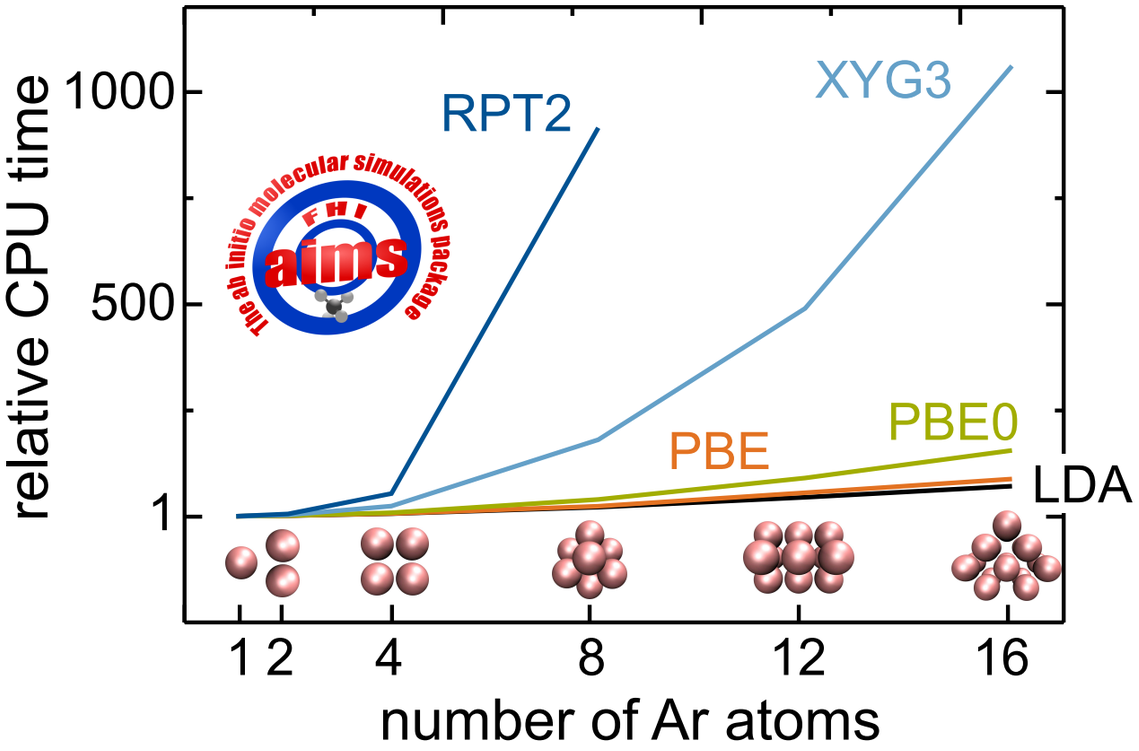

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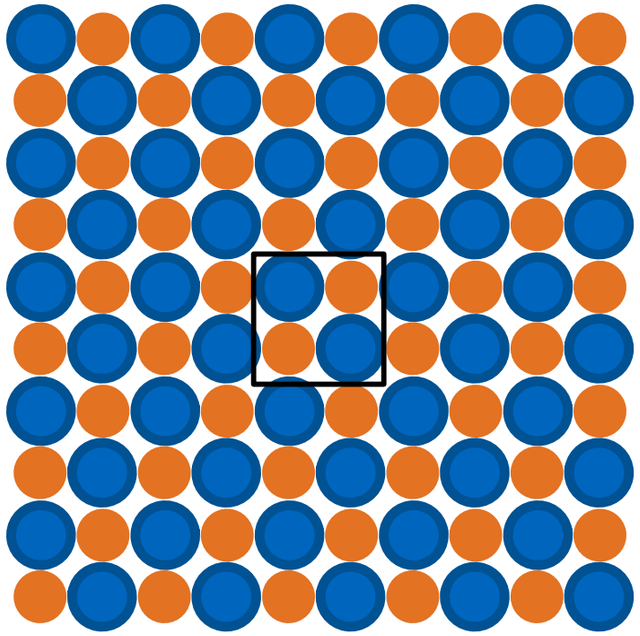

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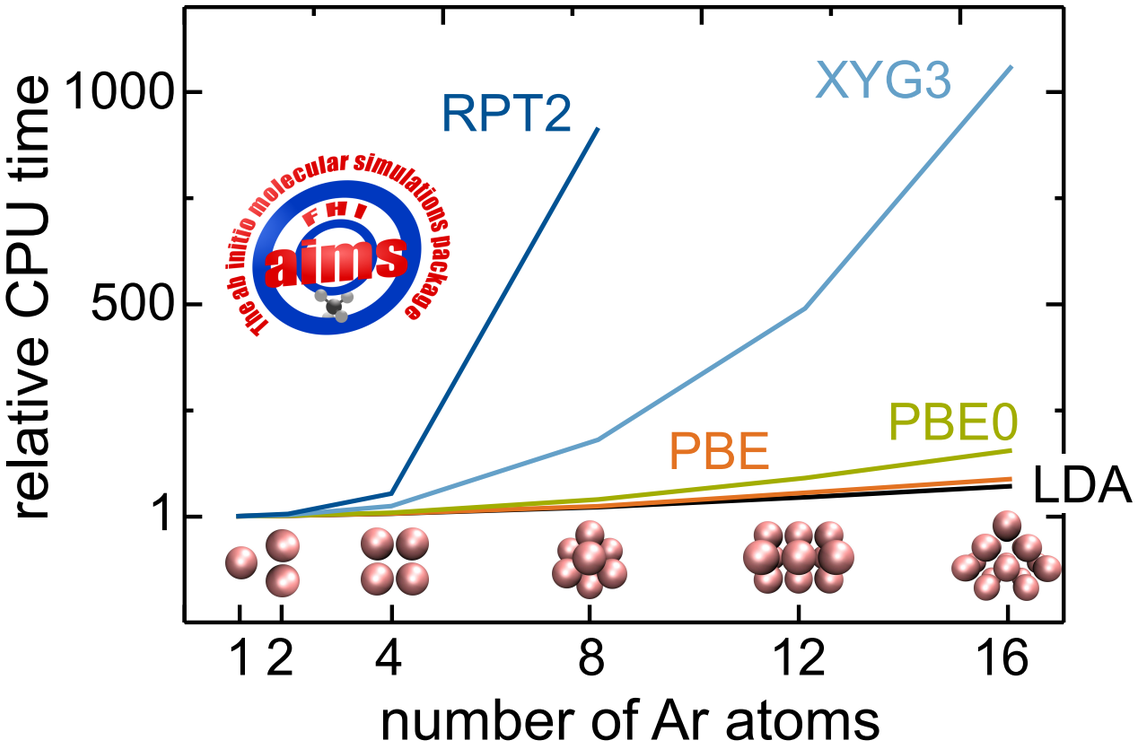

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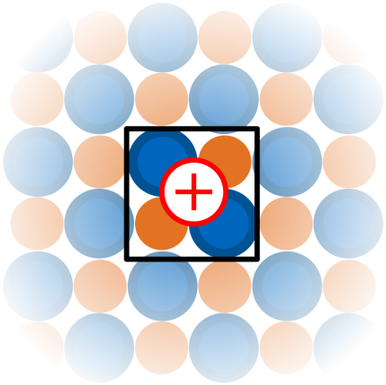

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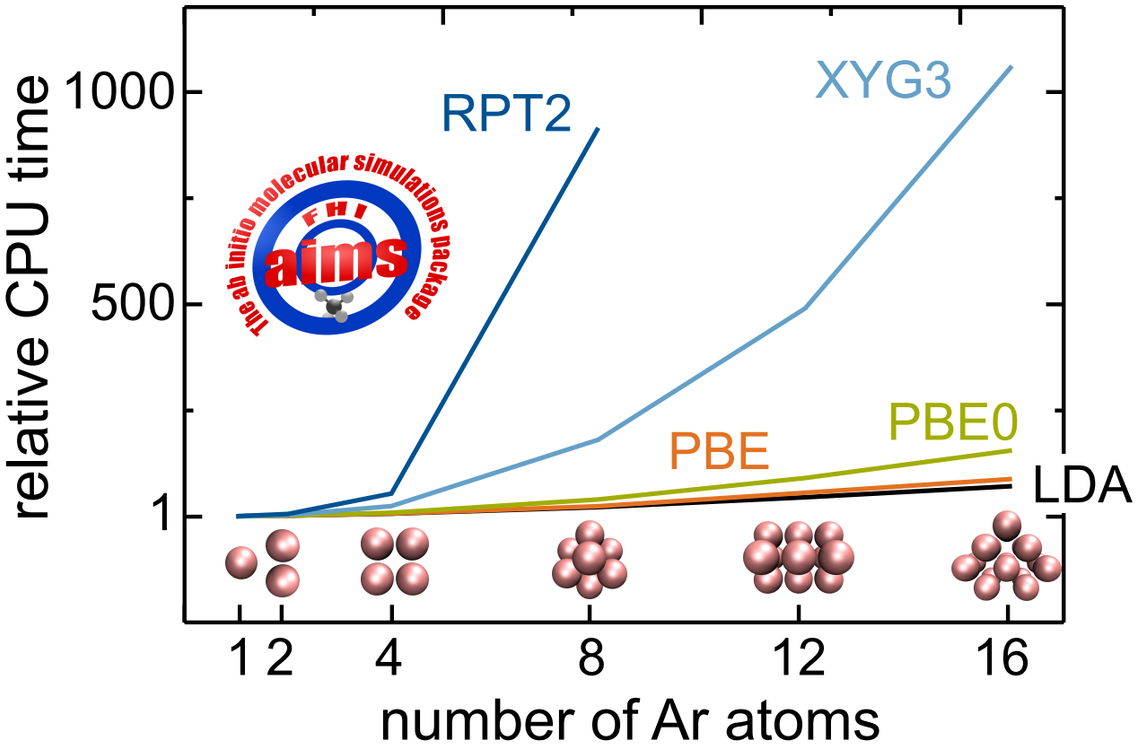

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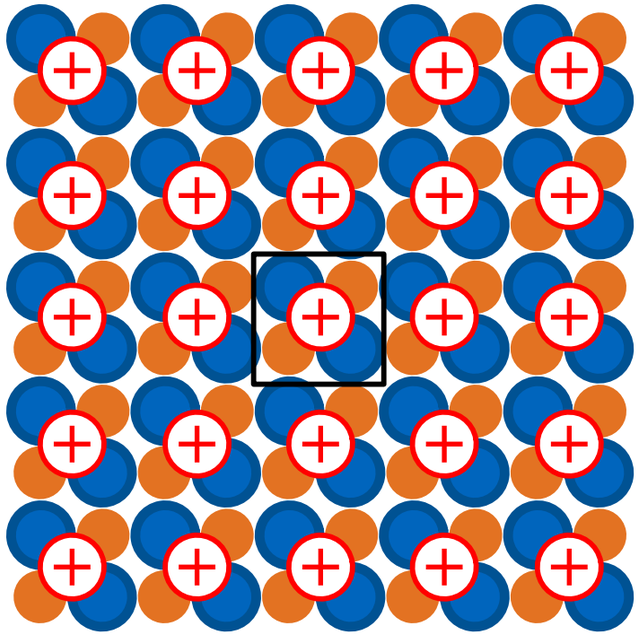

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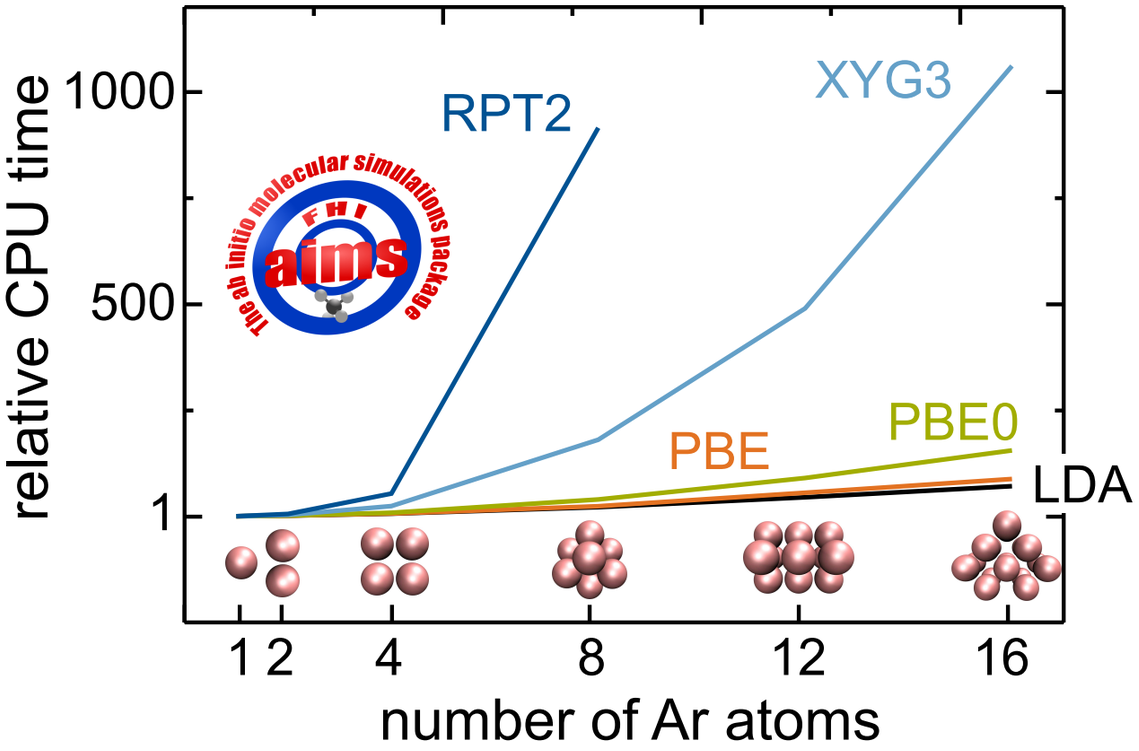

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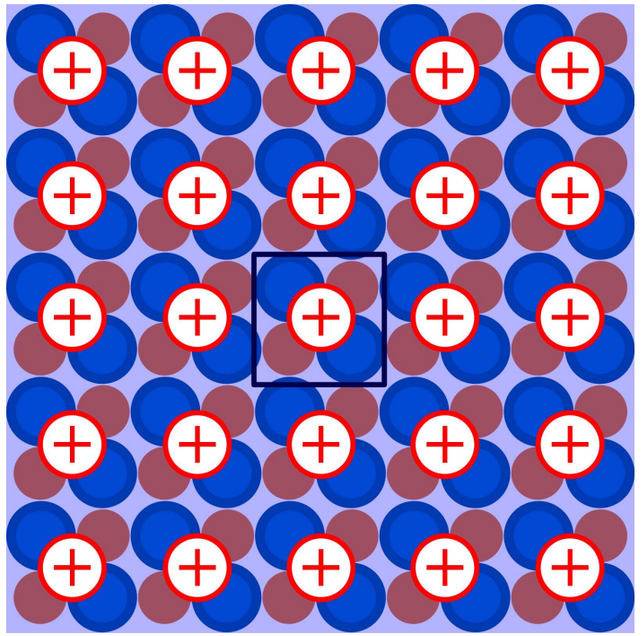

PBC charge correction

⇒ finite size effects

Levels of coarse graining

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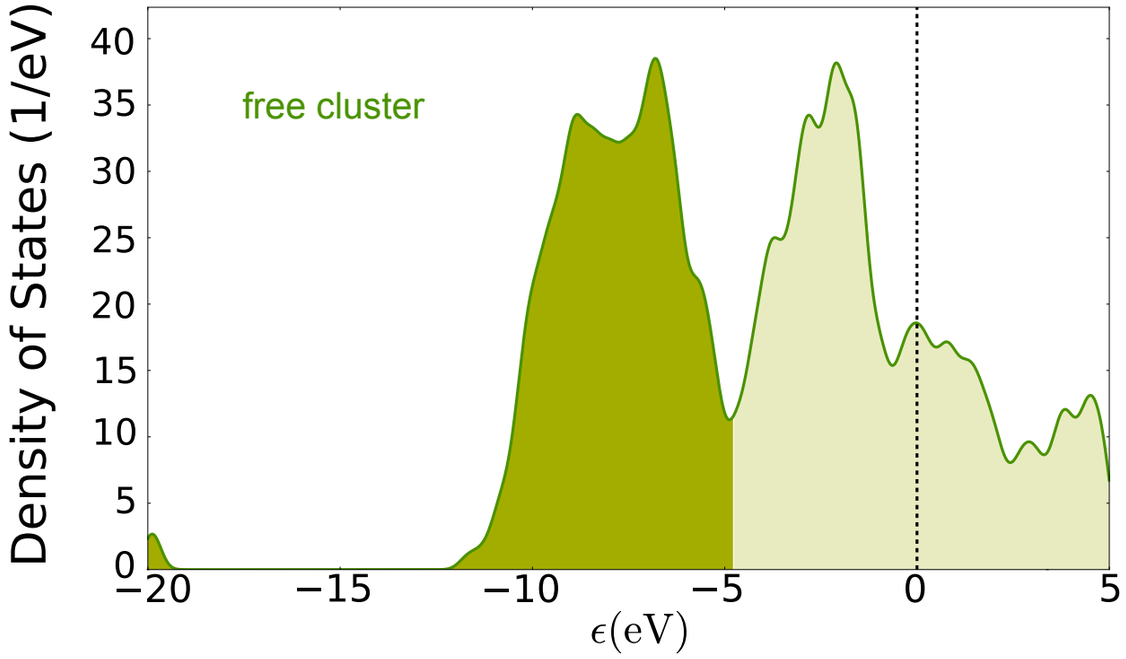
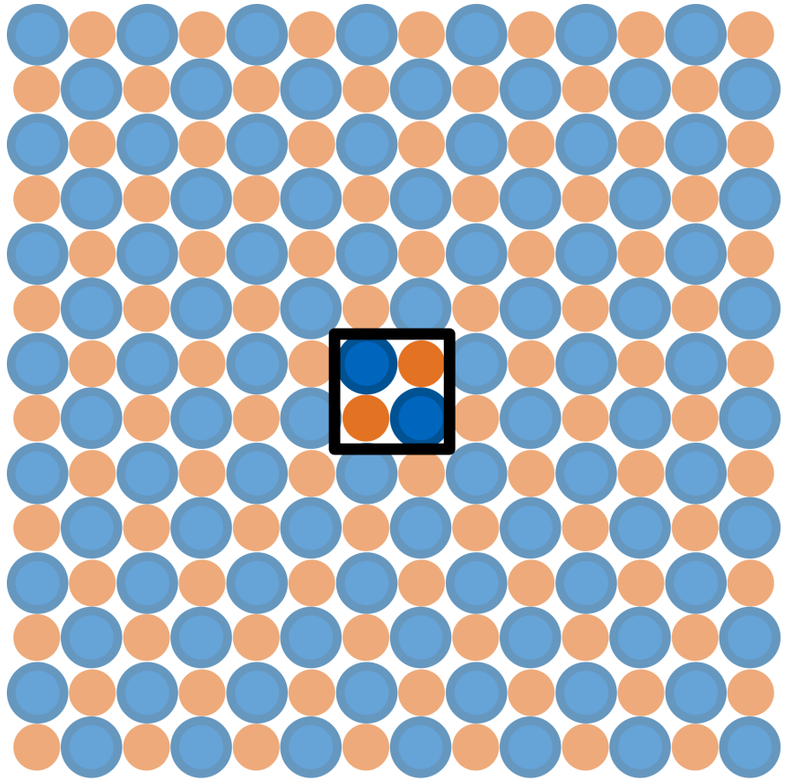


Rutile TiO_2 cluster w/o embedding

no band-gap, wrong work function

Levels of coarse graining



atomistic embedding

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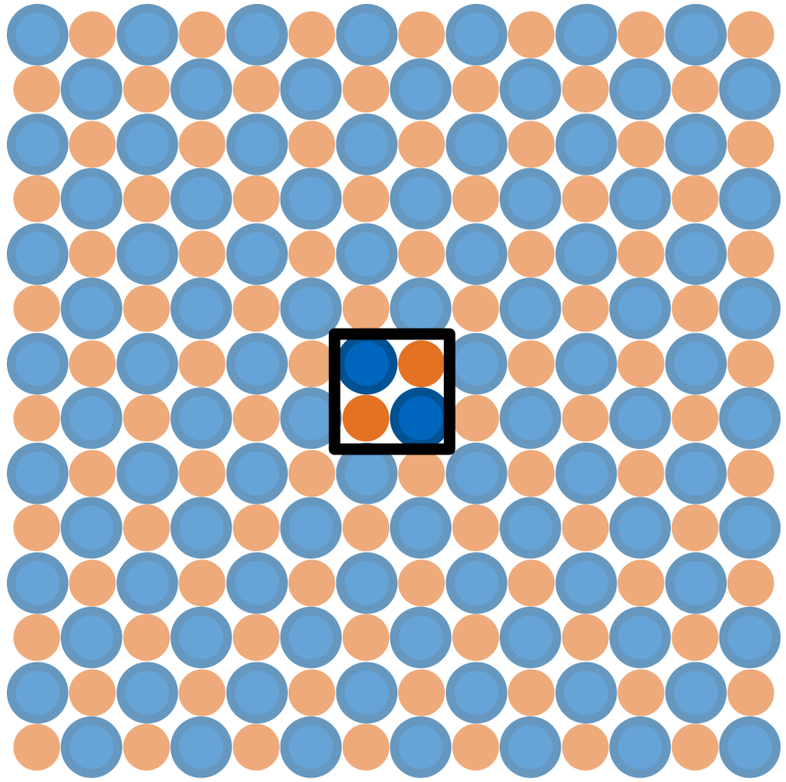

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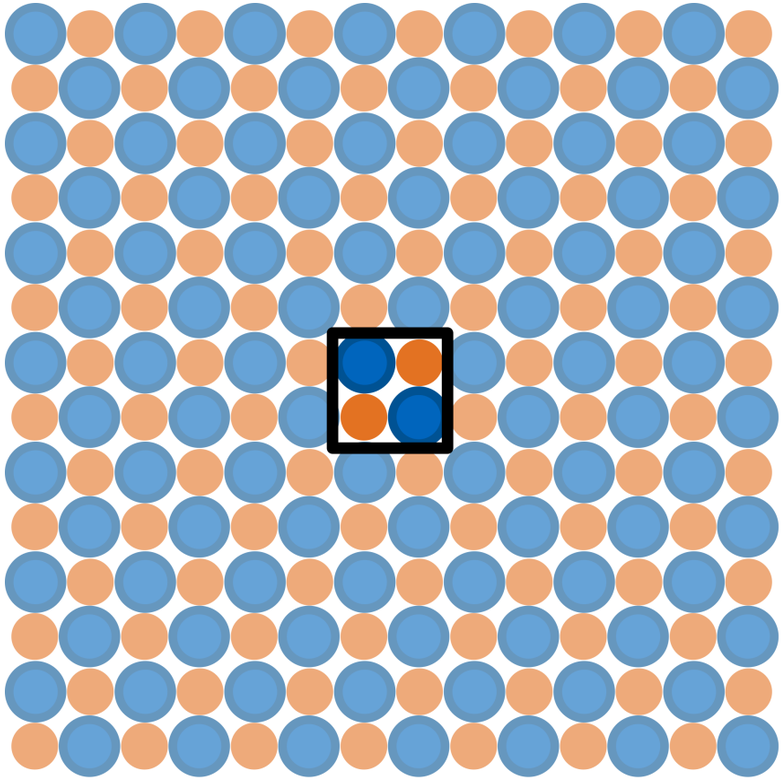

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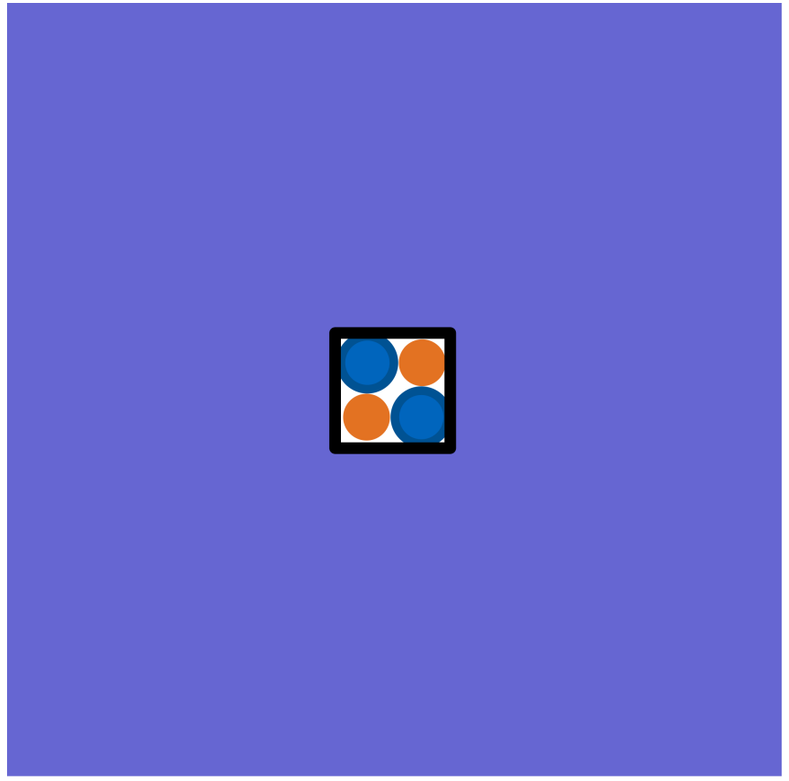

continuum embedding

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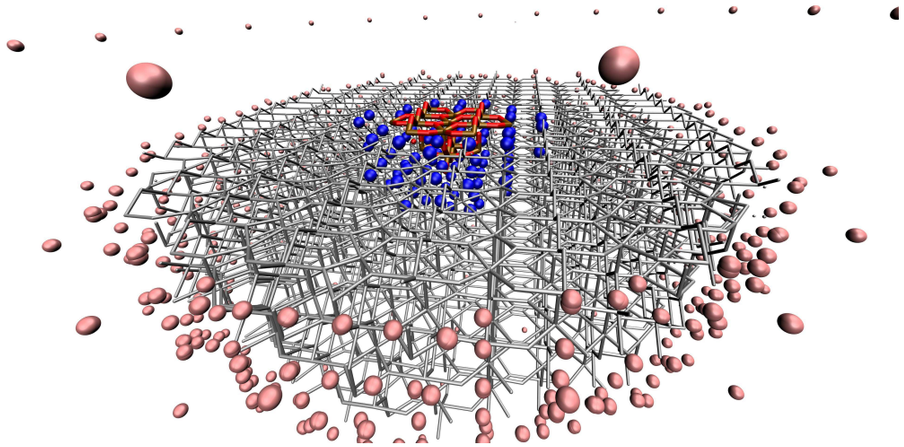

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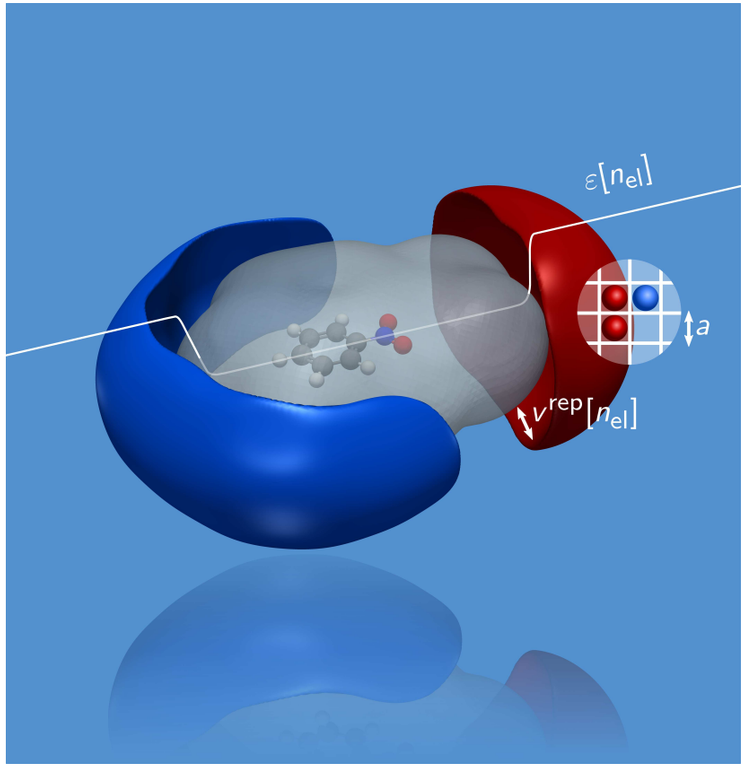
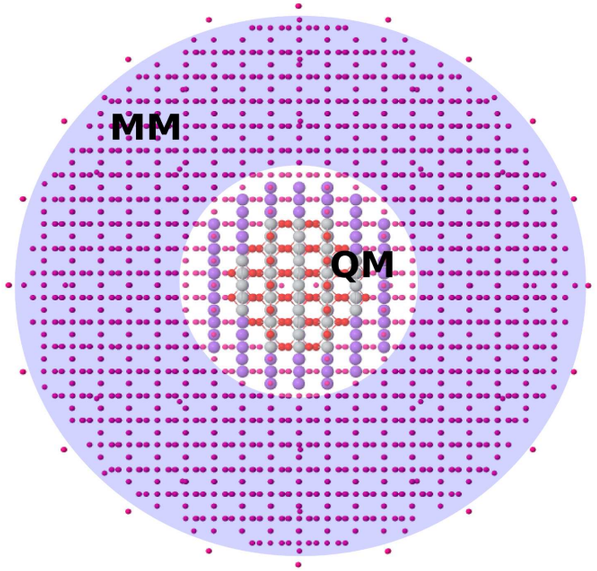


continuum embedding

Atomistic embedding (QM/MM)



seamless coupling
between
quantum mechanics (**QM**)
and
molecular mechanics (**MM**)

geometry
QM energies forces

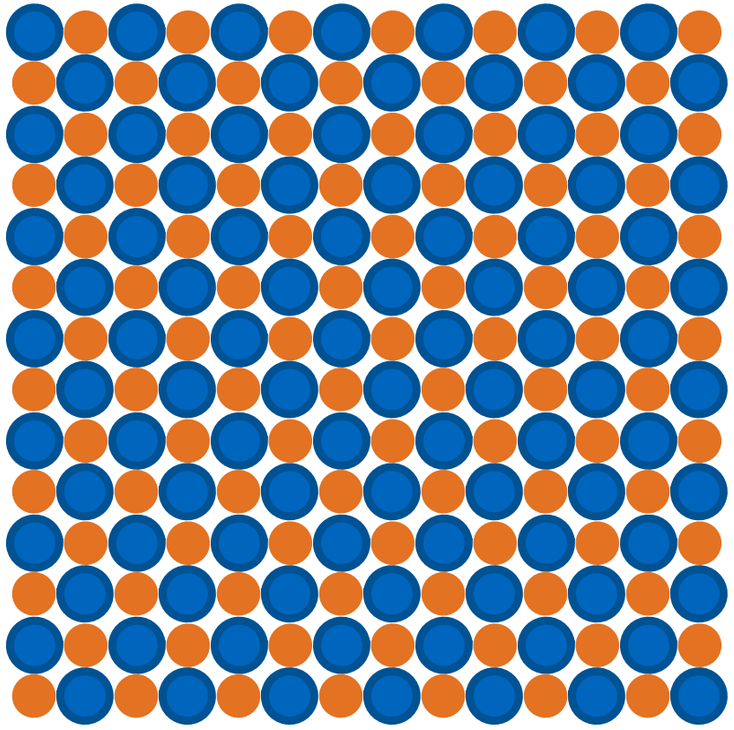
ChemShell#
www.chemshell.org

geometry
MM energies forces

GULP

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

Structure of a QM/MM simulation



Example: Crystal with positive and negative sites

- Cut large cluster
- Designate QM and MM atoms
- Positive sites near QM atoms $\Rightarrow$ charge leakage
- Replace singularities with Pseudo-potentials $\Rightarrow$ transition region
- Still missing: Periodic Madelung potential, correction for multipole moments
- Fitted charges to fix Potential in QM Zone

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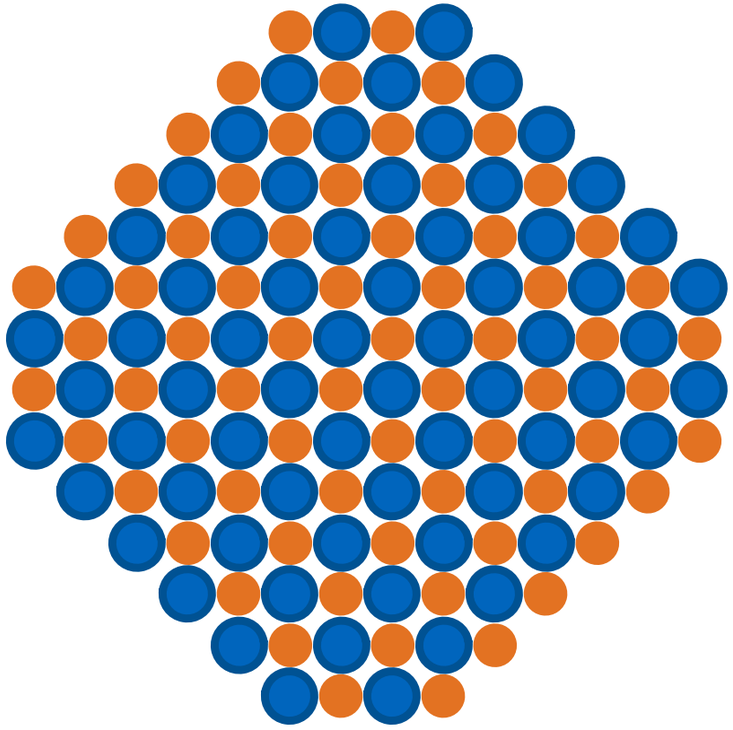

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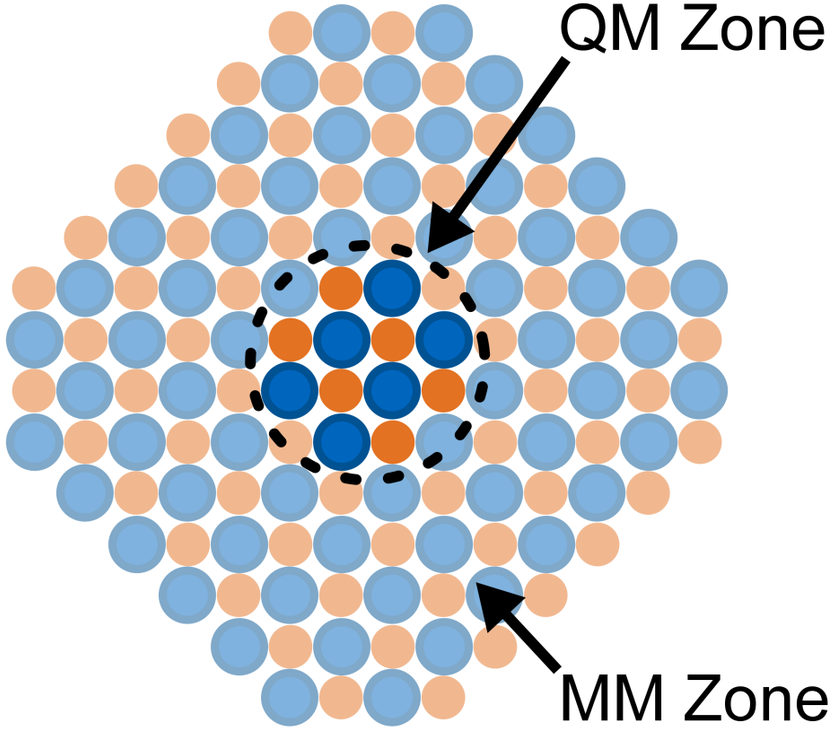

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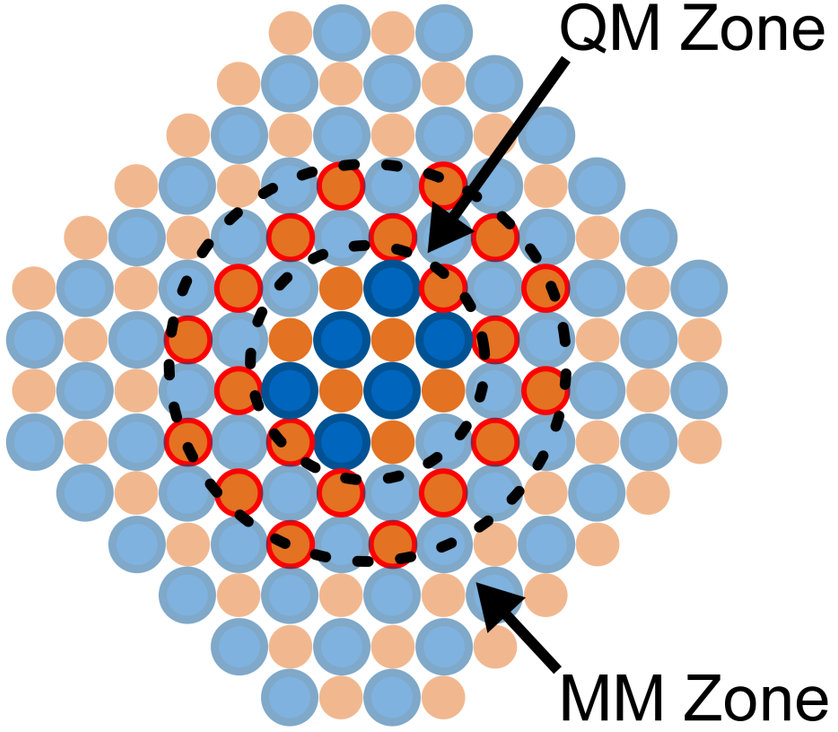

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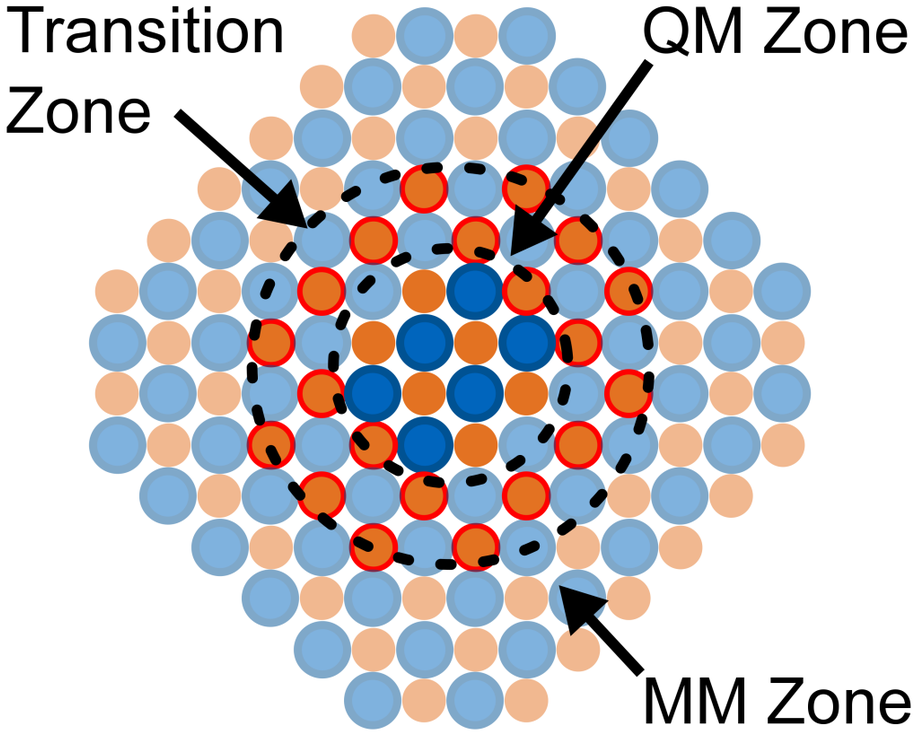

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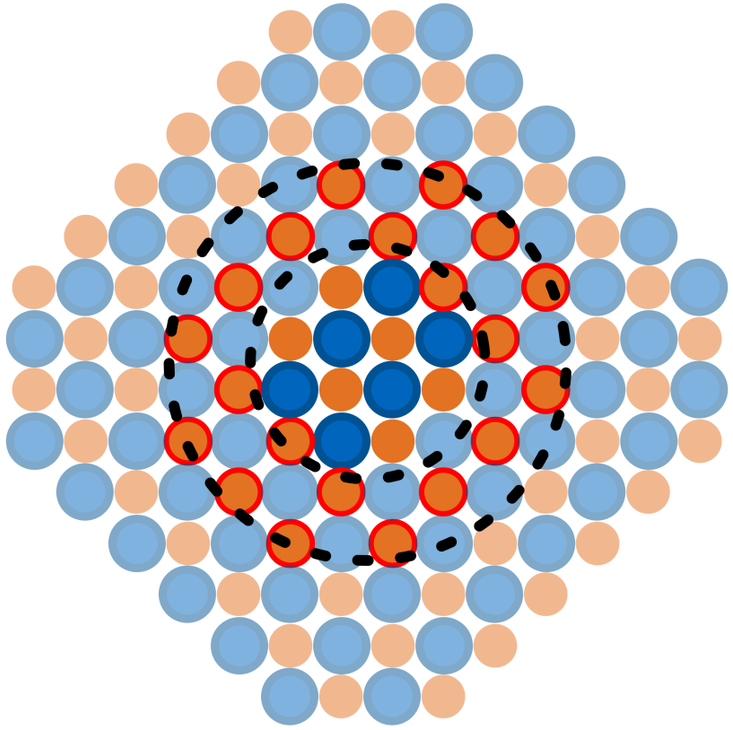

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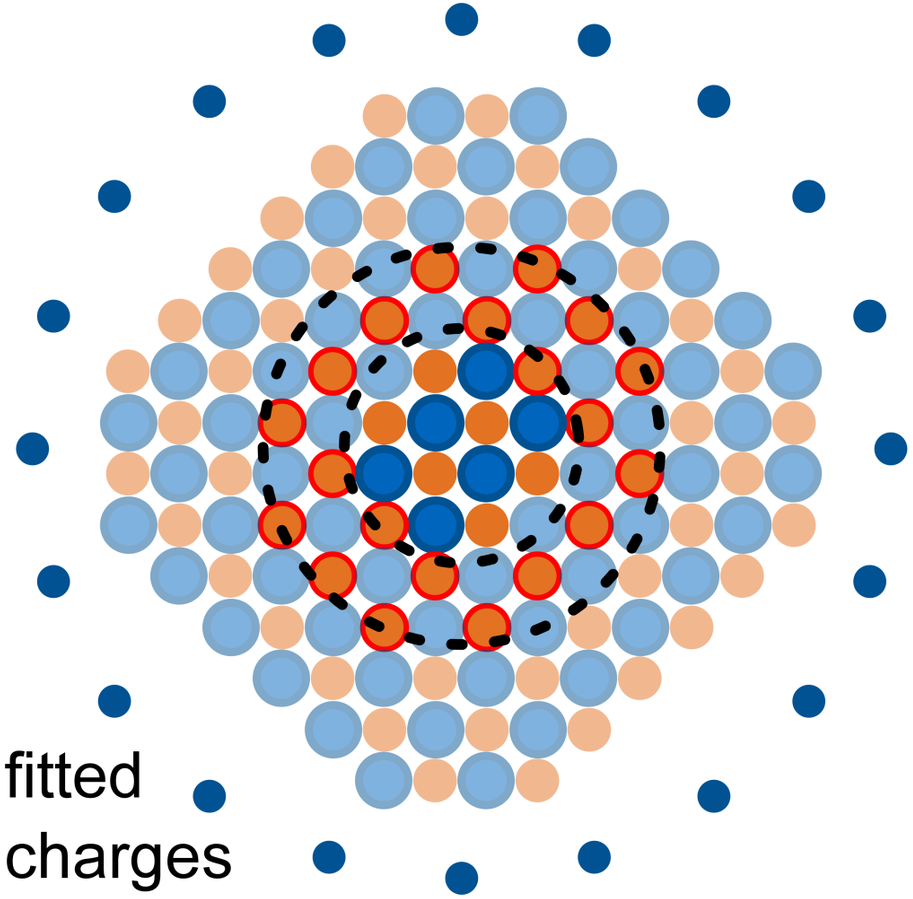

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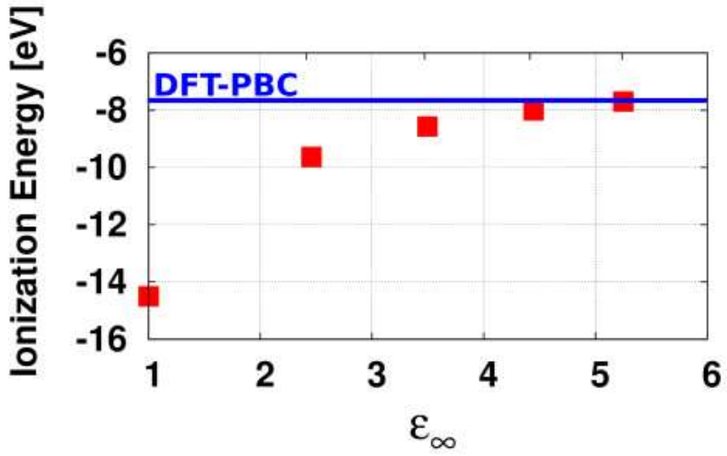
Effect of environment polarisability (MM)

IP (TiO_2)



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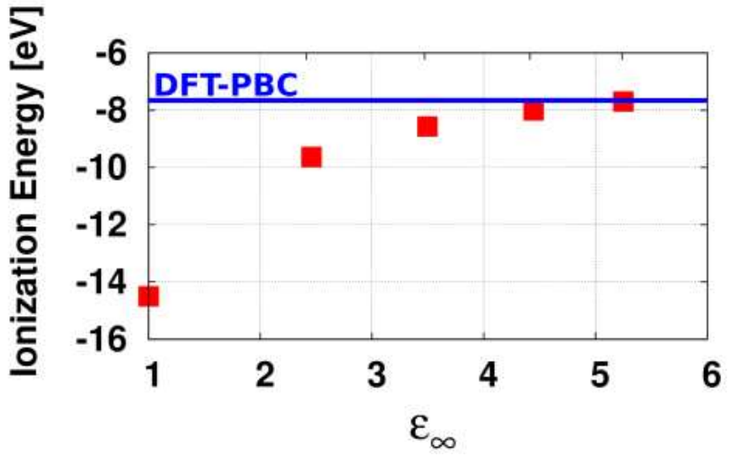
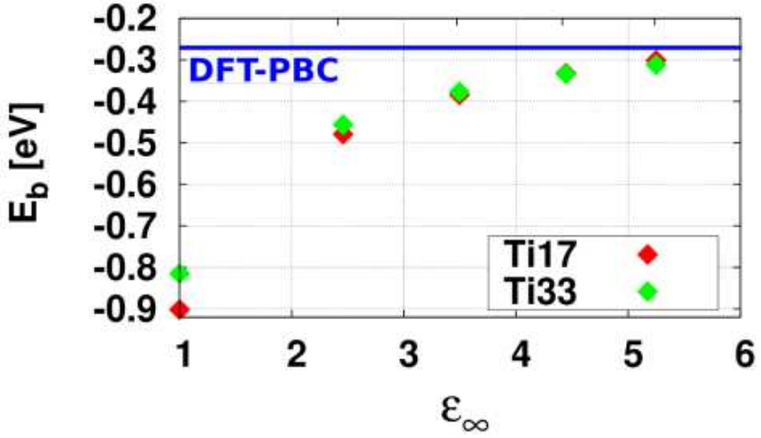


Binding Energy
$OH@TiO_2$



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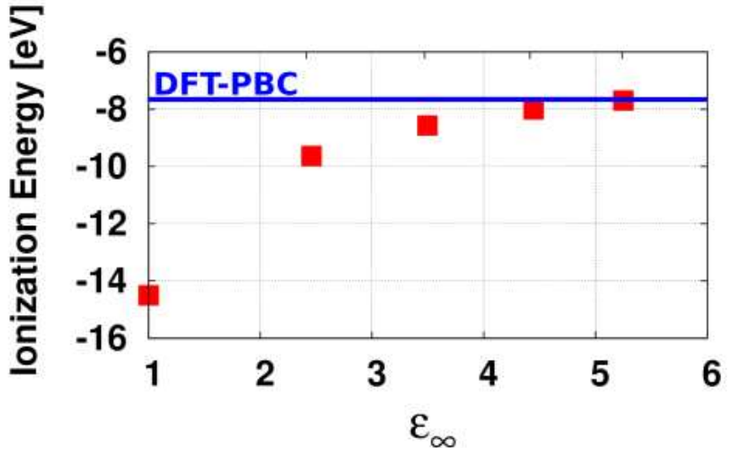

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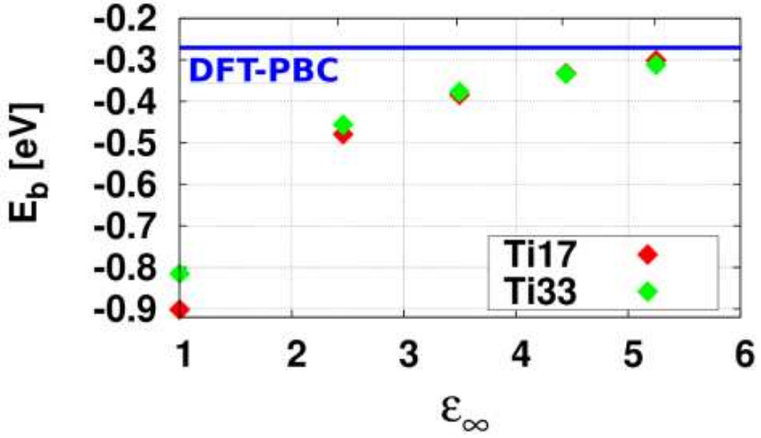
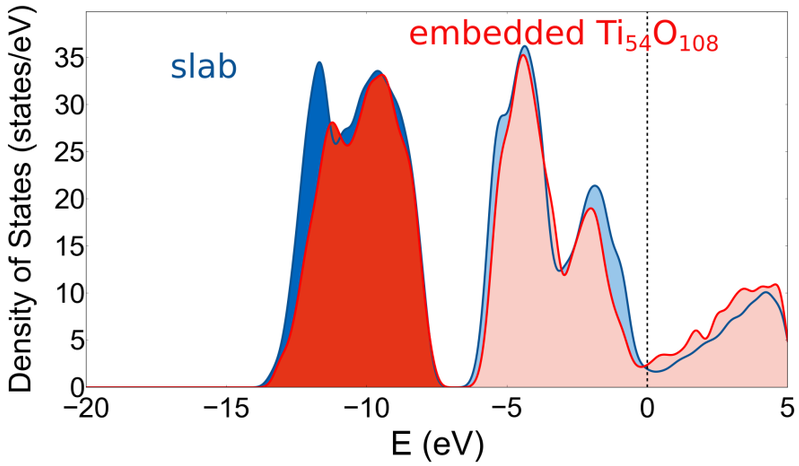




"Seamless embedding" recovers electronic structure

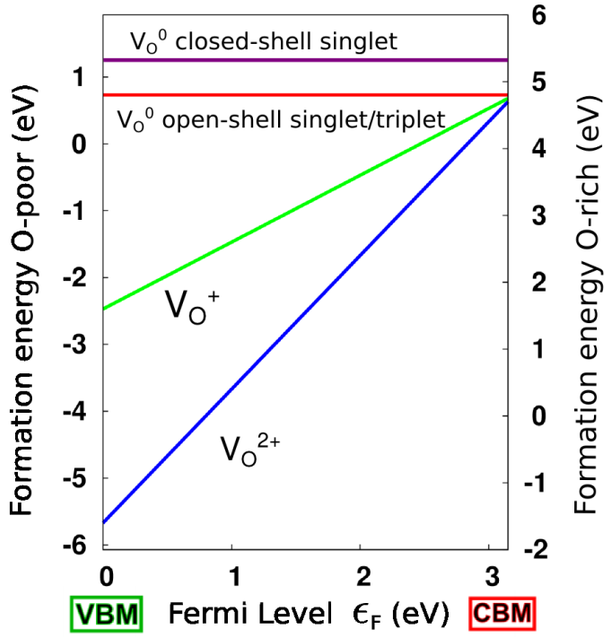
(DOS of the rutile TiO_2 110-surface)

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

Example: Rutile TiO2 (110) Surface Oxygen Vacancy

$$G_\mathrm{f}(q) \approx E_\mathrm{defect}(q) - E_\mathrm{pristine}(q) + \mu_\mathrm{O} + q\varepsilon_\mathrm{f}$$

FHI-aims HSE06, tight settings, polarisably embedded $Ti_{46}O_{92}$



Berger, Oberhofer, Reuter, Phys. Rev. B **92** 75308 (2015)

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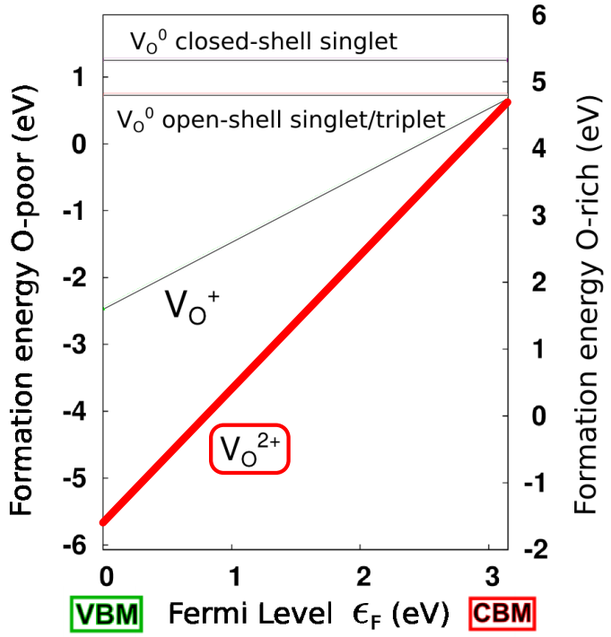
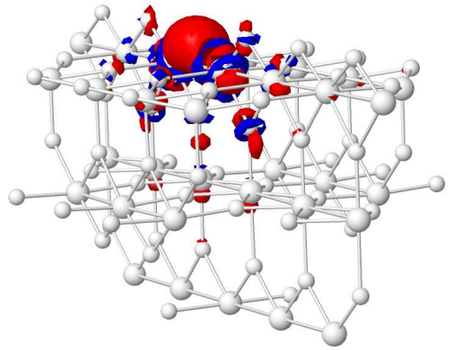
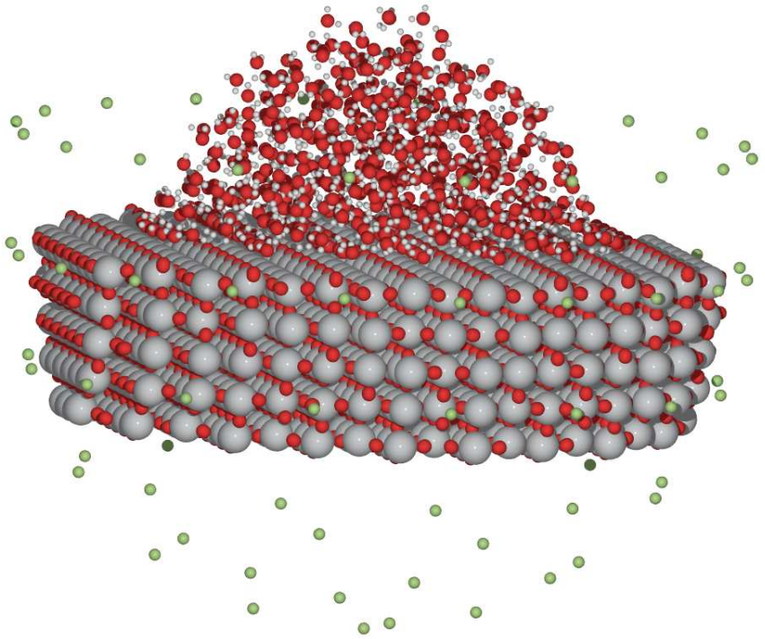


Charged defect stable over wide range of doping (ε_f) and oxidation conditions



Charges localise at defects $\Rightarrow$ photo-electrocatalysis

Example: Free Energy Barriers



Stecher, Reuter, Oberhofer, Phys. Rev. Lett. **116**, 276001 (2016)

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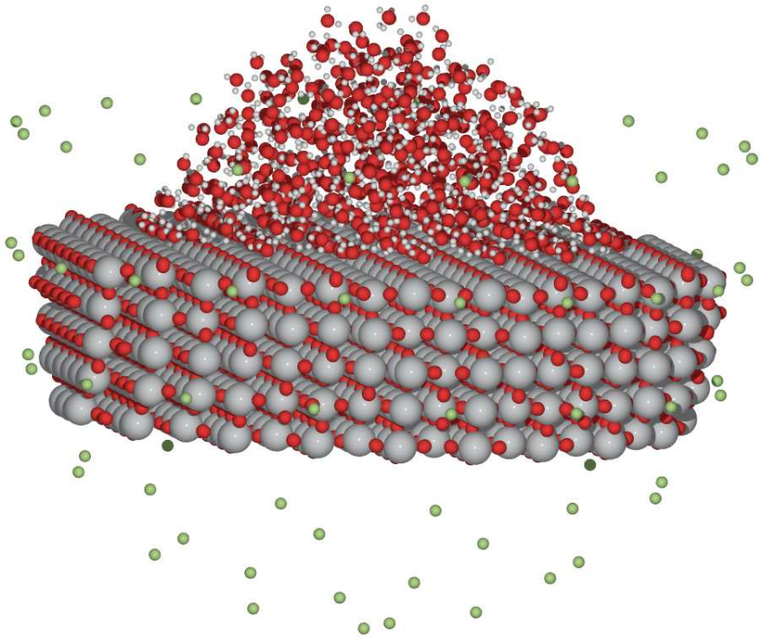

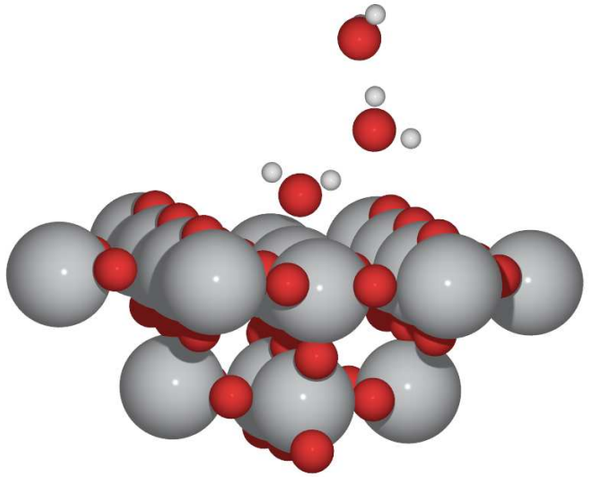

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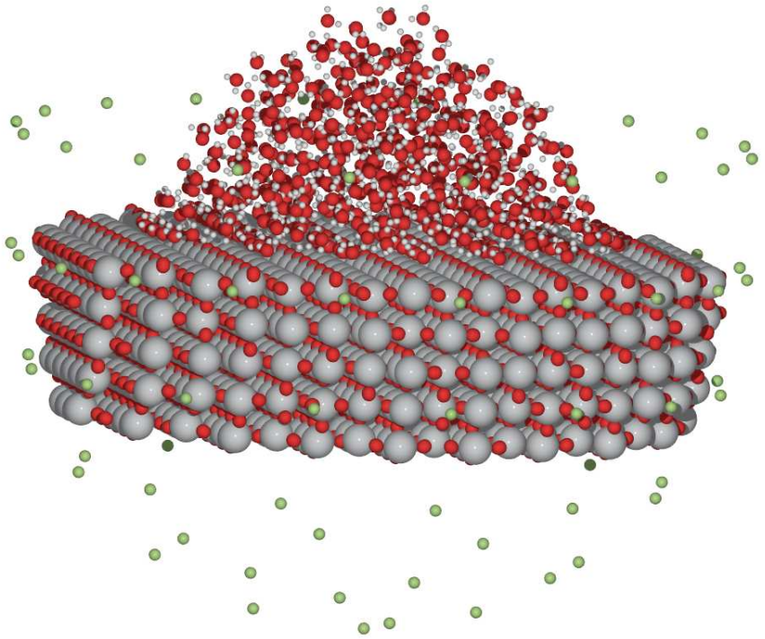
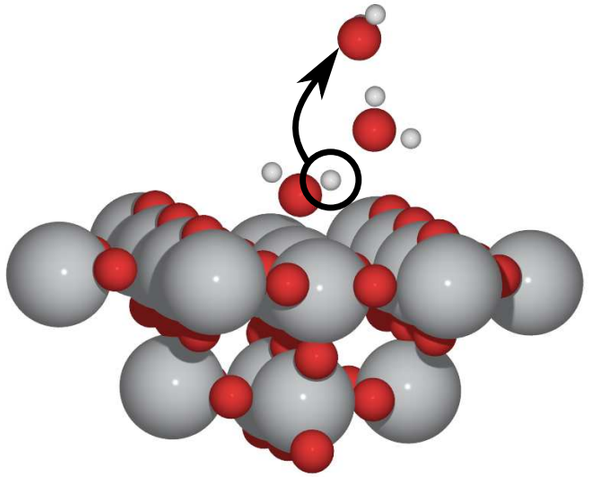


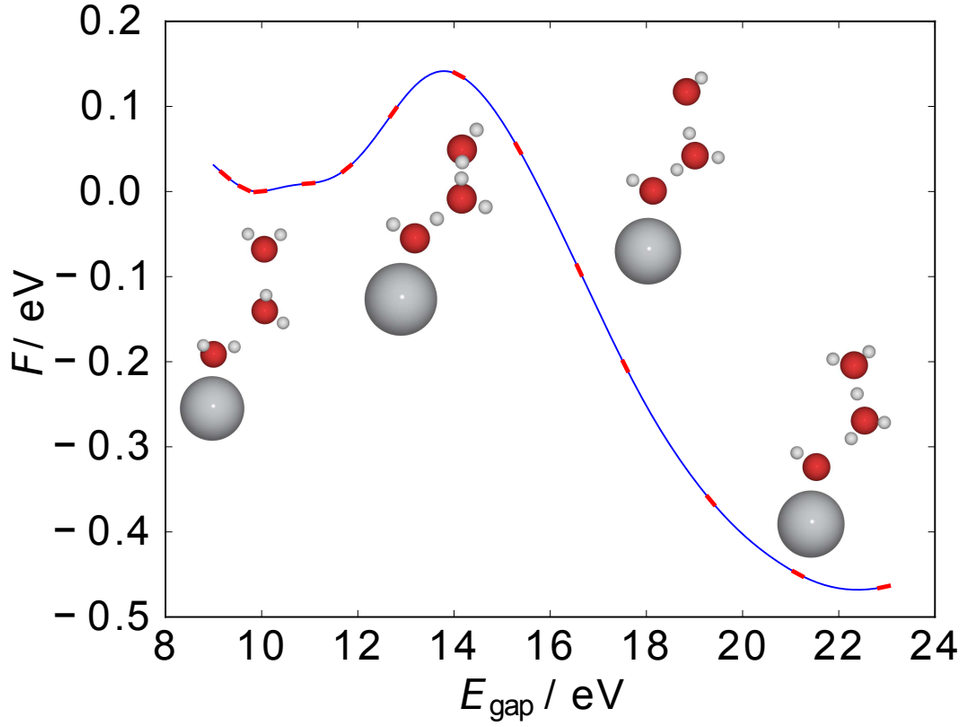


Stecher, Reuter, Oberhofer, Phys. Rev. Lett. **116**, 276001 (2016)

Example: Free Energy Barriers

Initial proton abstraction driven by electron hole:

FHI-aims HSE06, tight settings, umbrella sampling/energy gap reaction coordinate

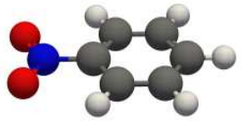


Basis-set corrected
barrier 200 ± 40 meV

Stecher, Reuter, Oberhofer, Phys. Rev. Lett. **116**, 276001 (2016)

Continuum embedding

$$\nabla \cdot [\quad\quad\quad \nabla v(\boldsymbol{r})] \;=\; -4\pi n_{\mathrm{sol}}(\boldsymbol{r})$$

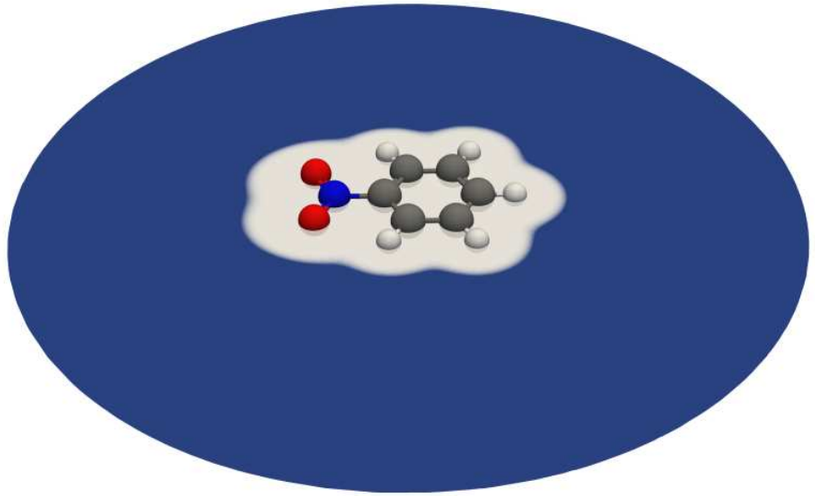


Parameters:

Poisson equation in **vacuum**

Continuum embedding

$$\nabla \cdot [\varepsilon[n_{\mathrm{el}}(\boldsymbol{r})]\nabla v(\boldsymbol{r})] \;=\; -4\pi n_{\mathrm{sol}}(\boldsymbol{r})$$



Parameters:

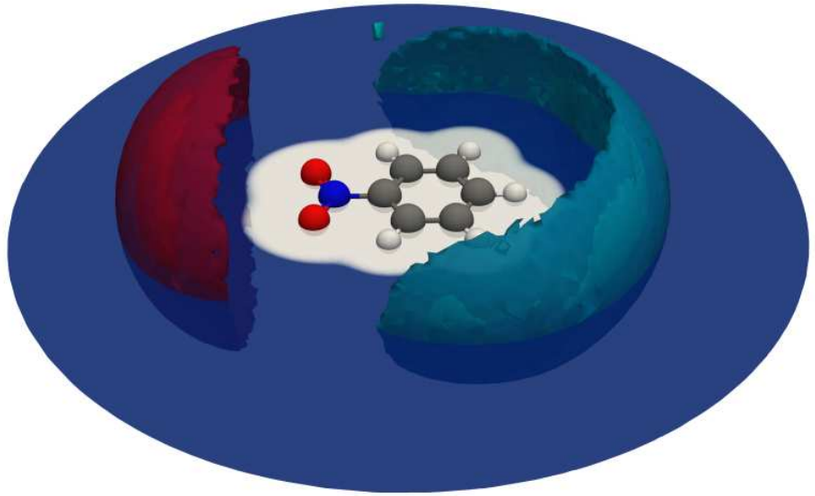
$\{n_{\mathrm{min}}, n_{\mathrm{max}}\}$ solvation cavity shape

$\{\alpha, \beta, \gamma\}$ non-electrostatics

Poisson equation in a **dielectric continuum**

Continuum embedding

$$\nabla \cdot [\varepsilon[n_{\mathrm{el}}(\boldsymbol{r})]\nabla v(\boldsymbol{r})] = -4\pi n_{\mathrm{sol}}(\boldsymbol{r}) - 4\pi n_{\mathrm{ion}}^{\mathrm{PB}}(\boldsymbol{r})$$



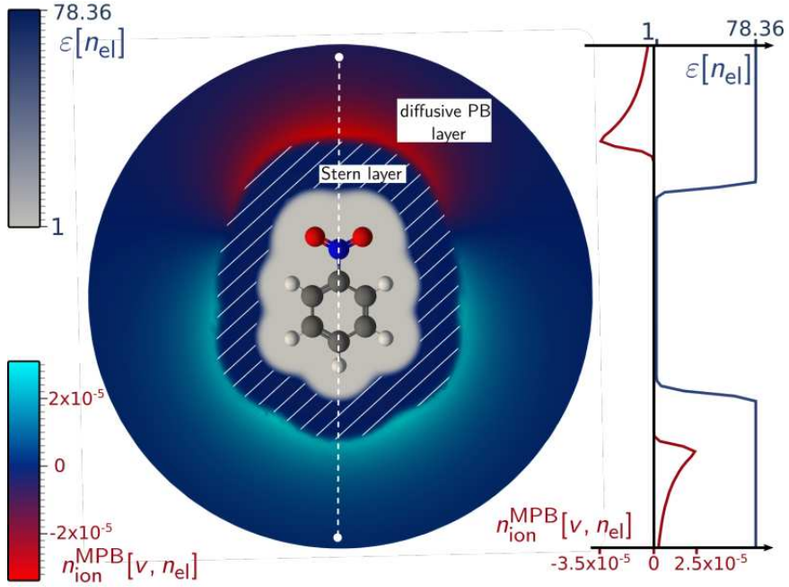
Parameters:

$\{n_{\mathrm{min}}, n_{\mathrm{max}}\}$	solvation cavity shape
$\{\alpha, \beta, \gamma\}$	non-electrostatics
$\{a\}$	ion size
$\{n_{\mathrm{min}}^{\alpha}, n_{\mathrm{max}}^{\alpha}\}$	ion cavity shape (Stern layer)

(modified) Poisson Boltzmann equation in a **dielectric continuum**

Continuum embedding

$$\nabla \cdot [\varepsilon[n_{\mathrm{el}}(\boldsymbol{r})]\nabla v(\boldsymbol{r})] = -4\pi n_{\mathrm{sol}}(\boldsymbol{r}) - 4\pi n_{\mathrm{ion}}^{\mathrm{PB}}(\boldsymbol{r})$$



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$\{\alpha, \beta, \gamma\}$	non-electrostatics
$\{a\}$	ion size
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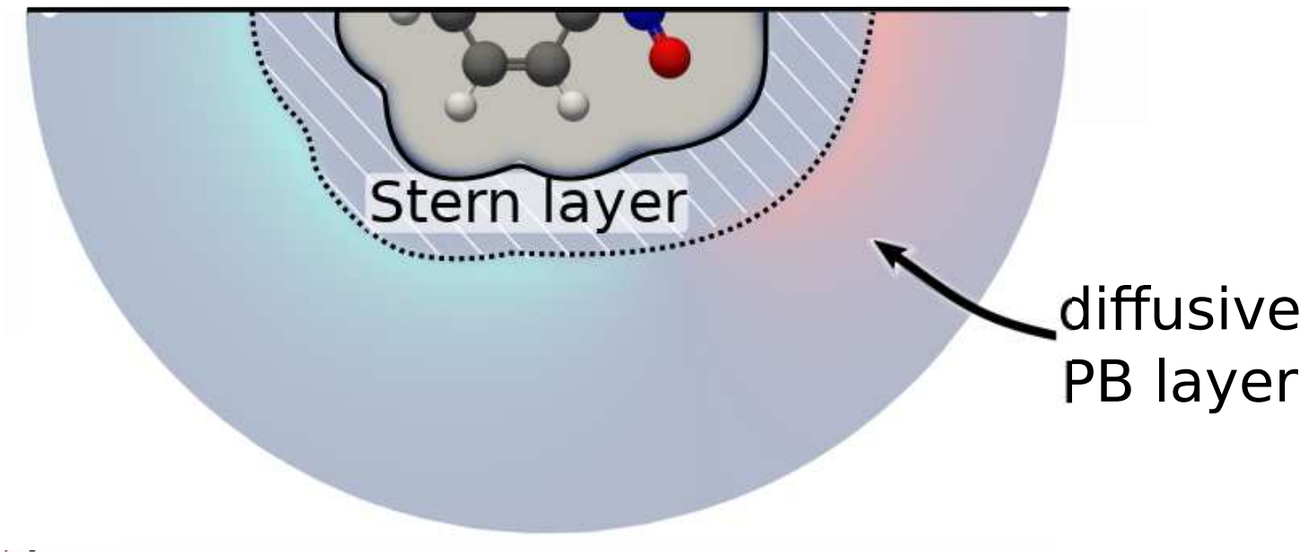
ionic “cavity” not necessarily same as solvation cavity $\Rightarrow$ **8 parameters in total**

Borukhov, Andelman, and Orland, Electrochim. Acta **46**, 221 (2000)
Ringe, Oberhofer, Hille, Matera, and Reuter, J. Chem. Theor. Comput. **12**, 4052 (2016)

Significance of the parameters

Example: Nitrobenzene in H_2O with 1M NaCl



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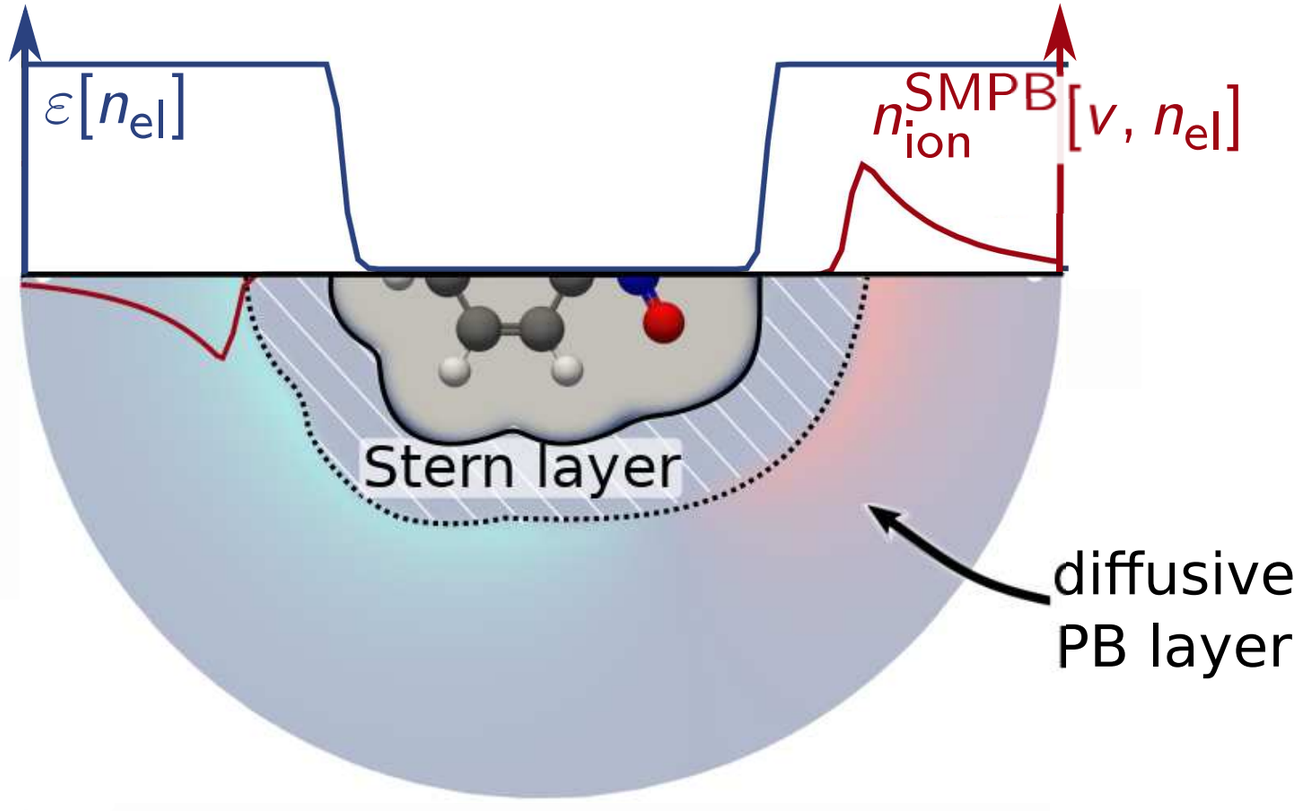

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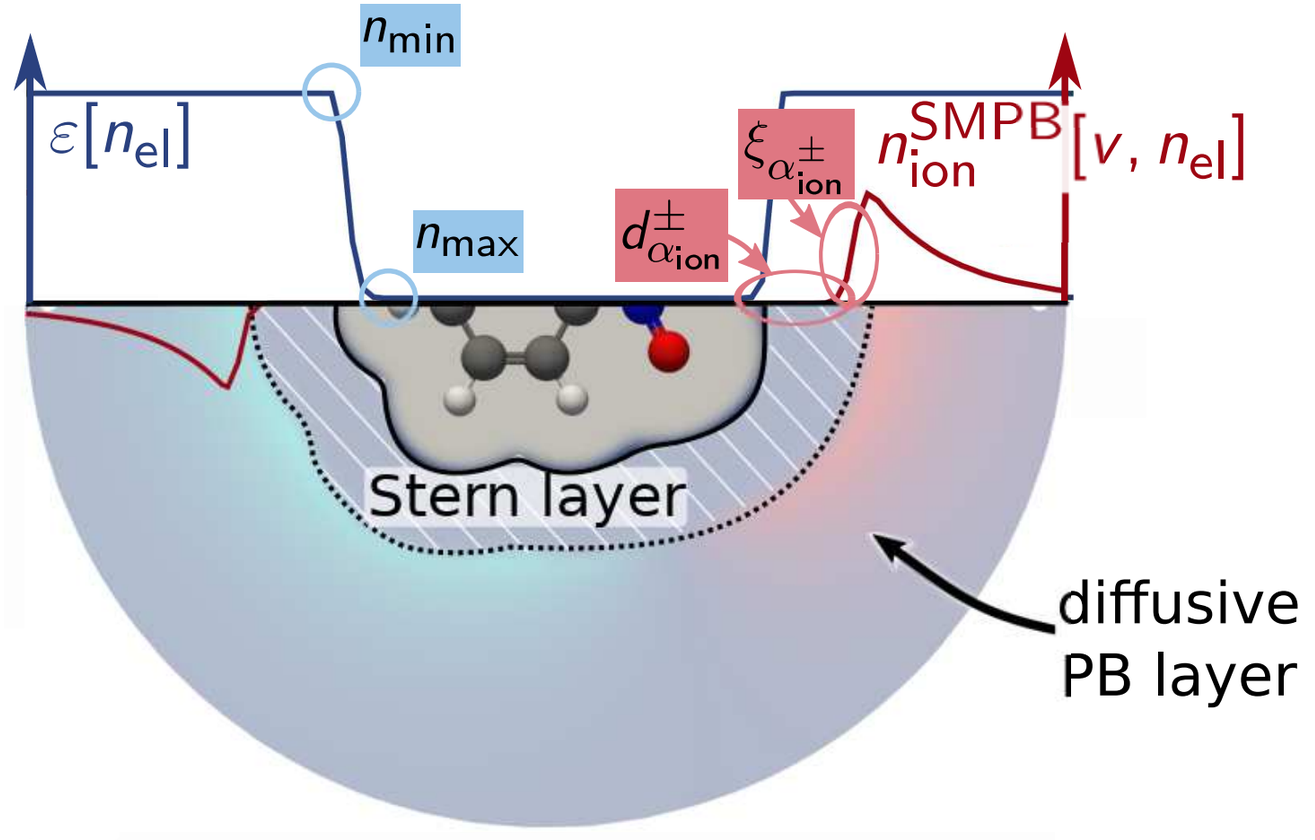

With four parameters I can fit an elephant,
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J. von Neumann via E. Fermi

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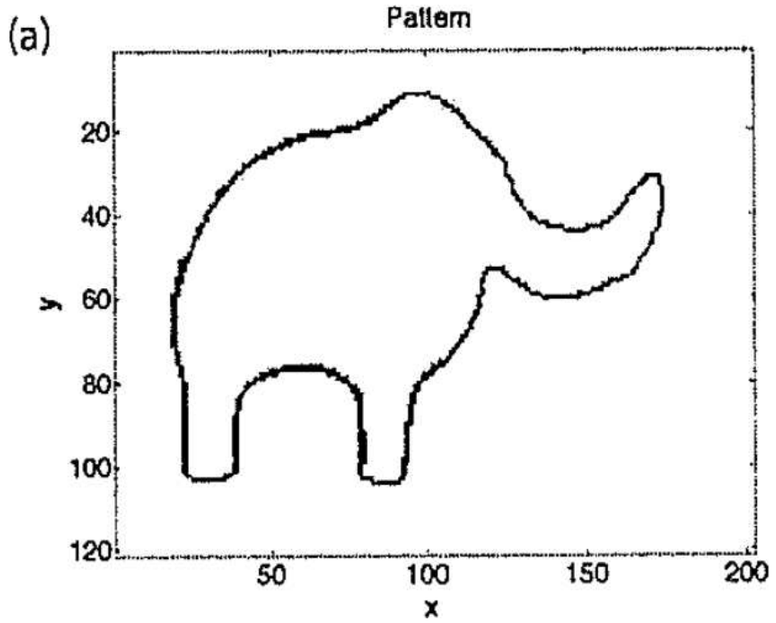
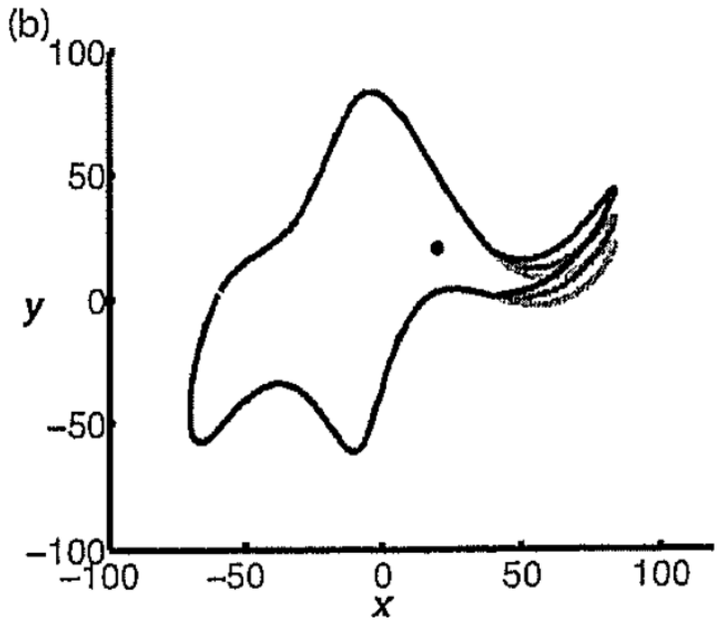


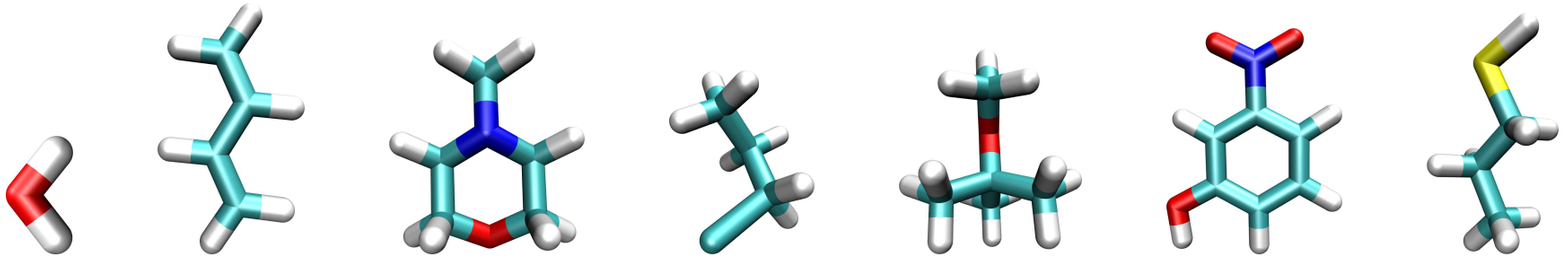
An elephant pattern.



5 parameter fit output, note the trunk wiggling.

Mayer, Khairy, and Howard, Am. J. Phys. **78**, 648 (2010)

Fixing solvation parameters



240 molecule test-set with known
experimental solvation free energies

$\Rightarrow$ fit solvation parameters

Andreussi, Dabo, and Marzari, J. Chem. Phys. **136**, 064102 (2012)
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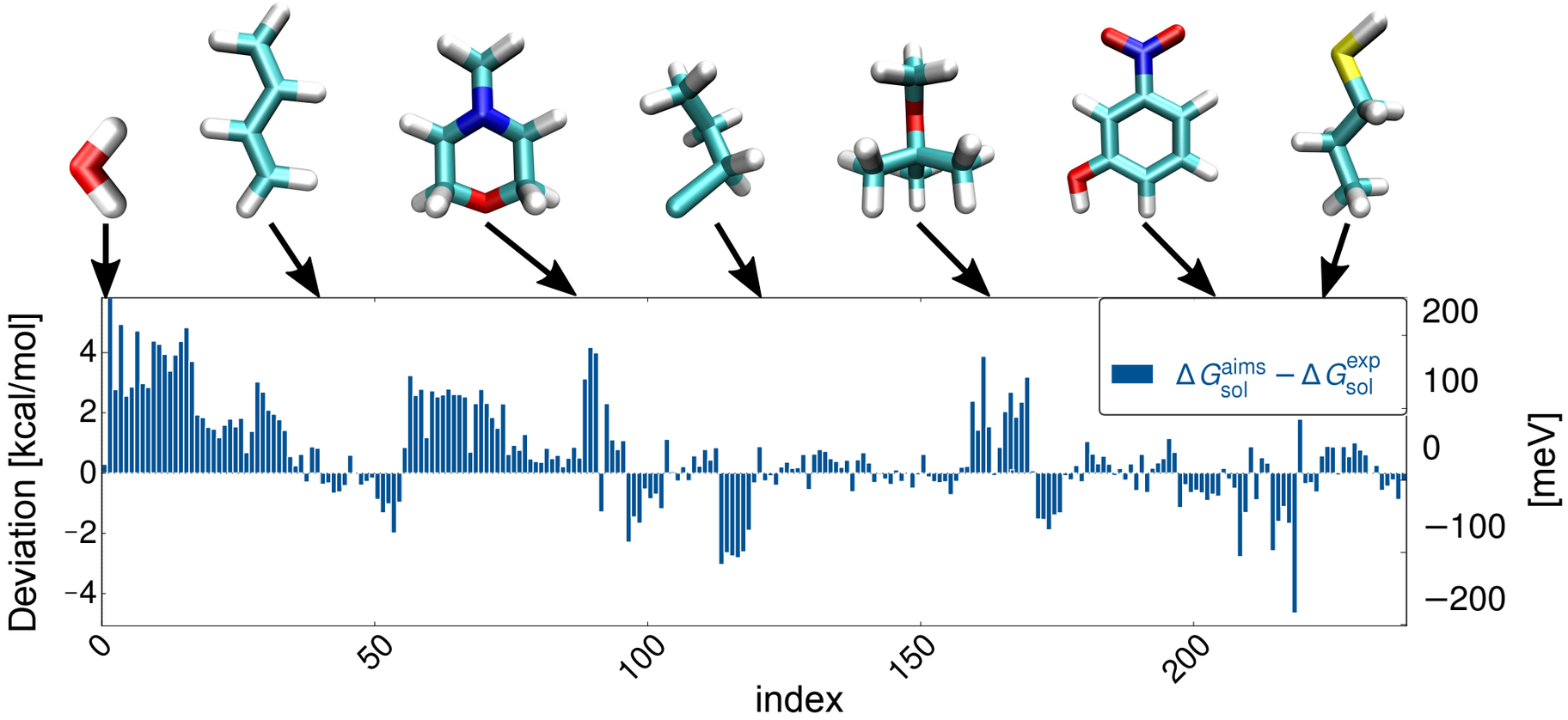

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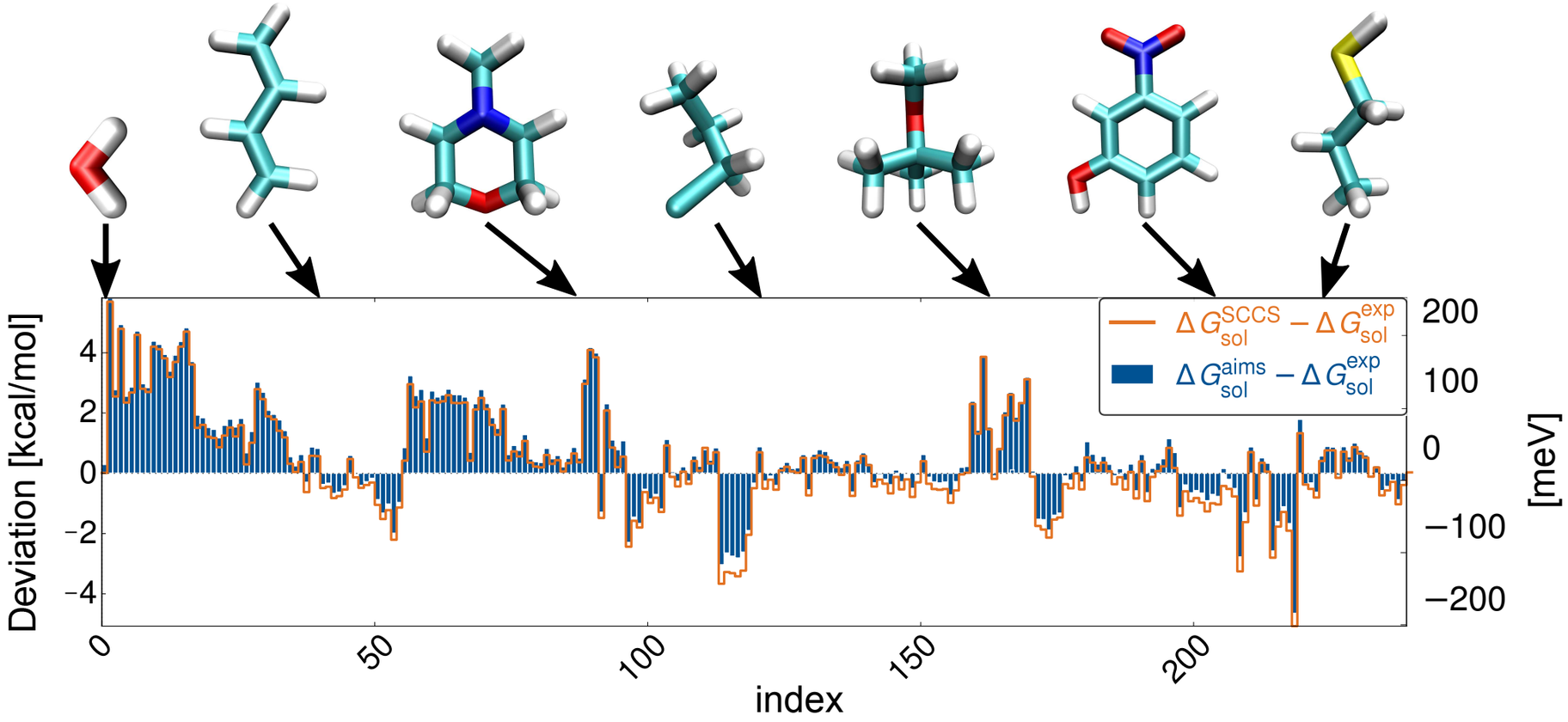

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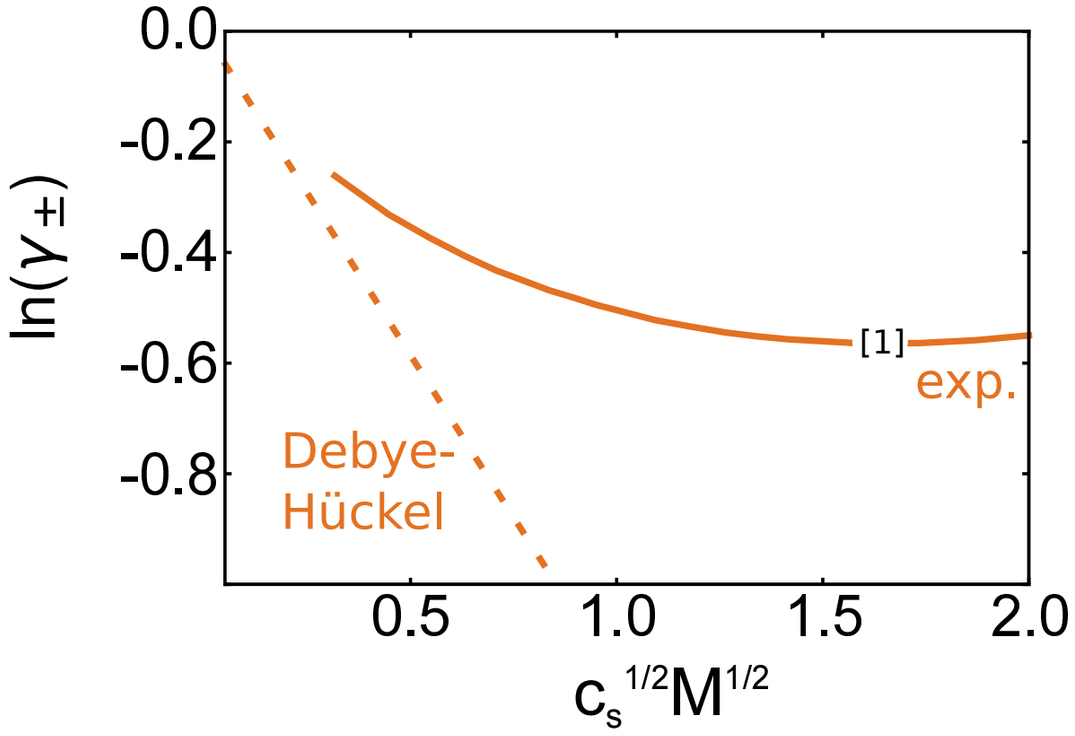
Fixing ionic parameters

First approach **salt activity coefficients** (KCl)



Robinson and Stokes, *Electrolyte Solutions, 2nd ed.*; Butterworths Publications Limited: New York (1959)
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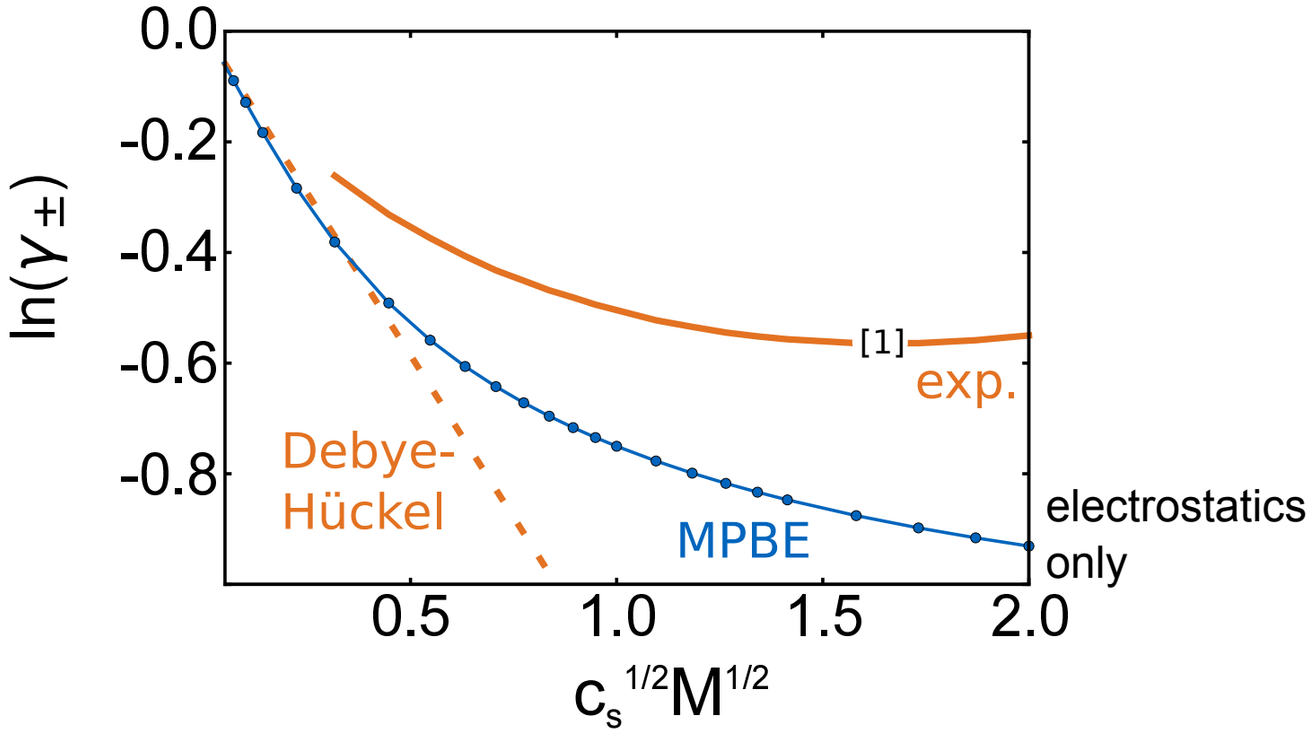

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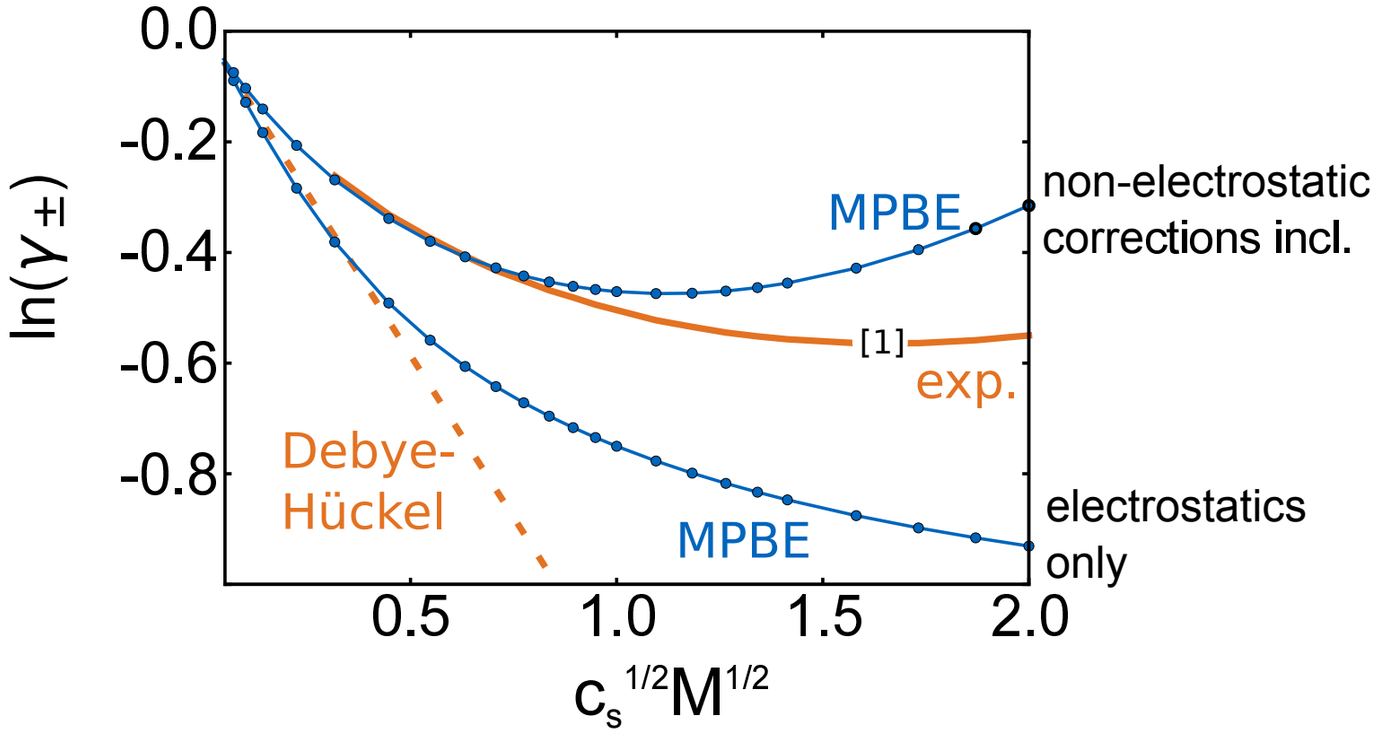

⇒ ion parameters can be fit to **physical observables**

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Molecular test-set, **Setschenow coefficients**

Linear relationship of solvation free energy of (neutral) molecules with salt concentration

$$\Delta\Delta G_{\text{ion}} \propto \mathbf{k_S}\, c_{\text{S}}$$

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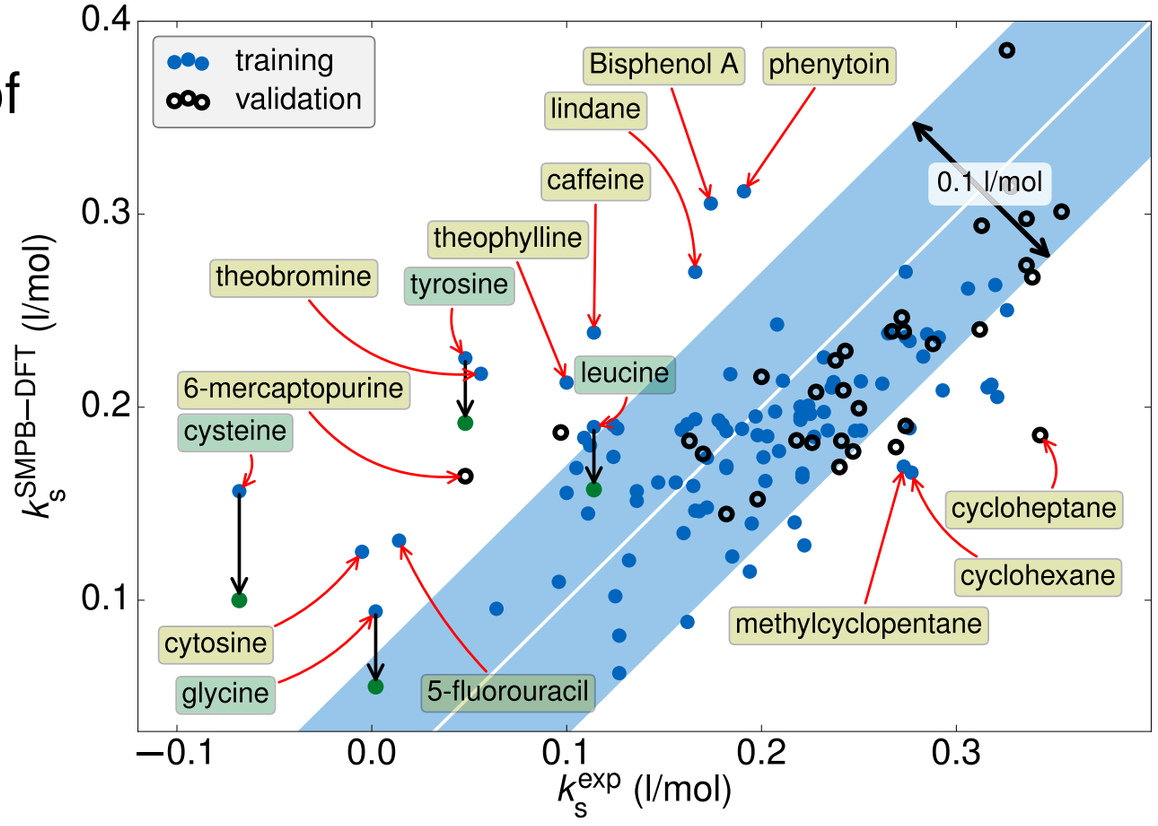

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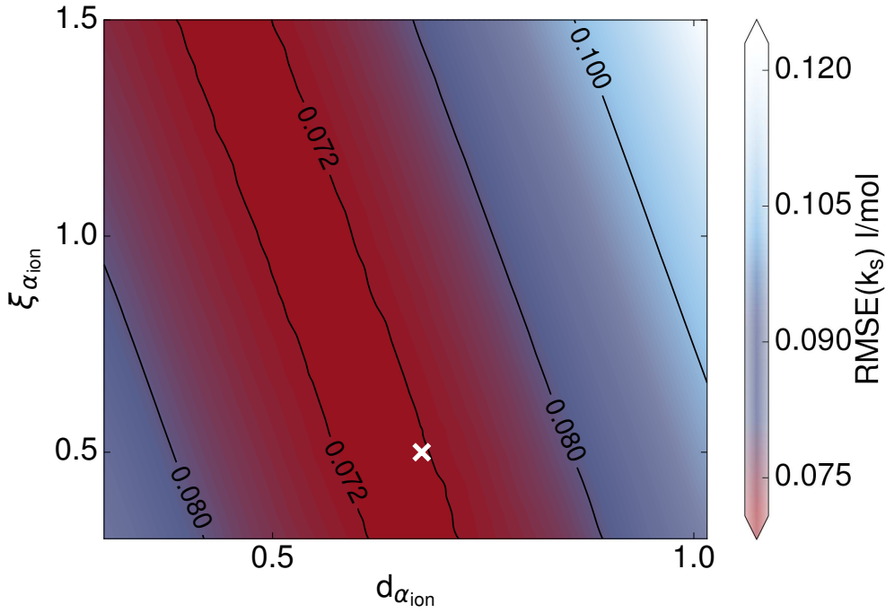

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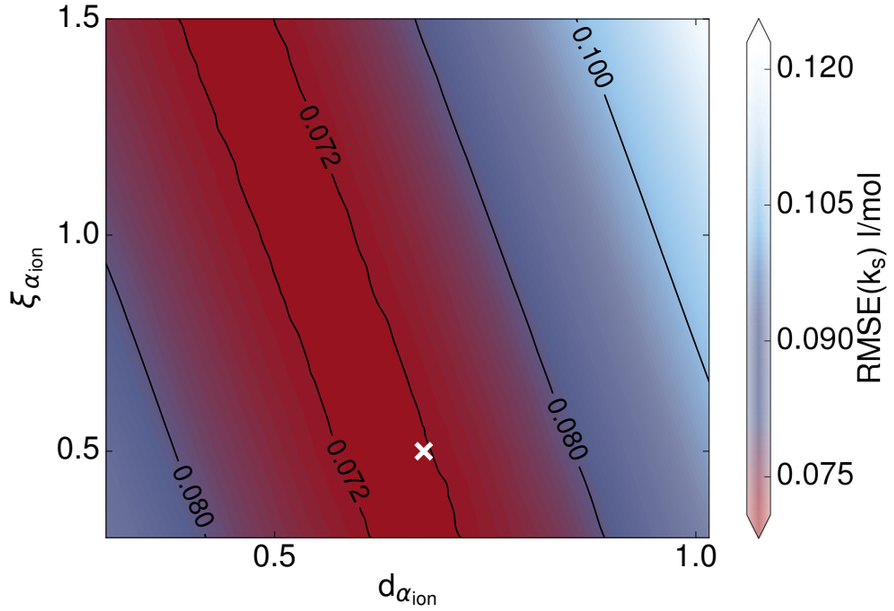
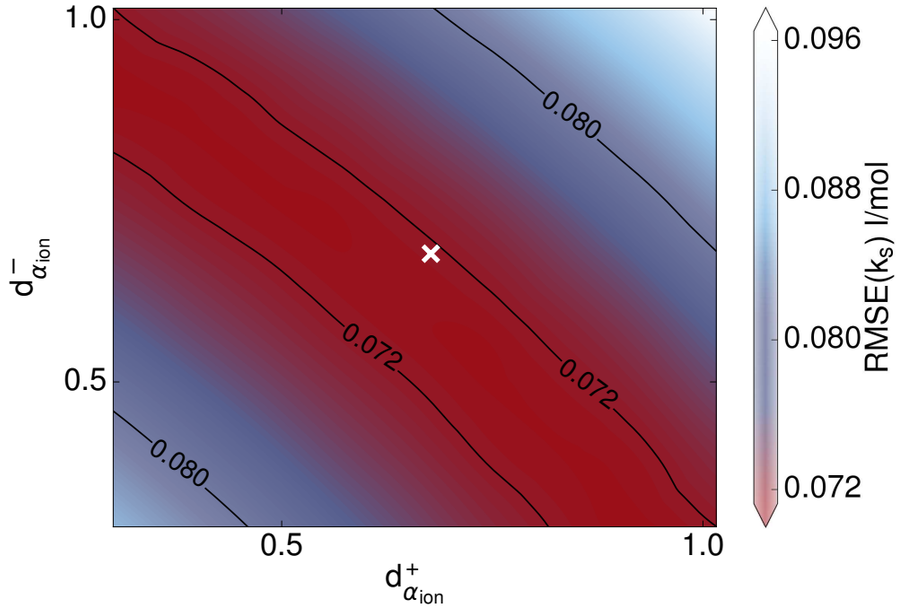


Stern layer sizes for anions d_α^- and cations d_α^+.



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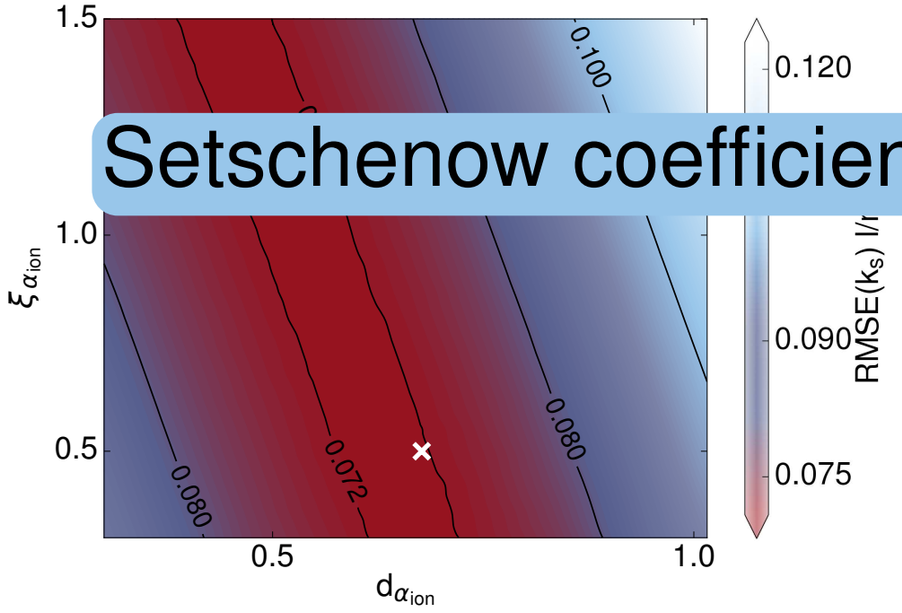

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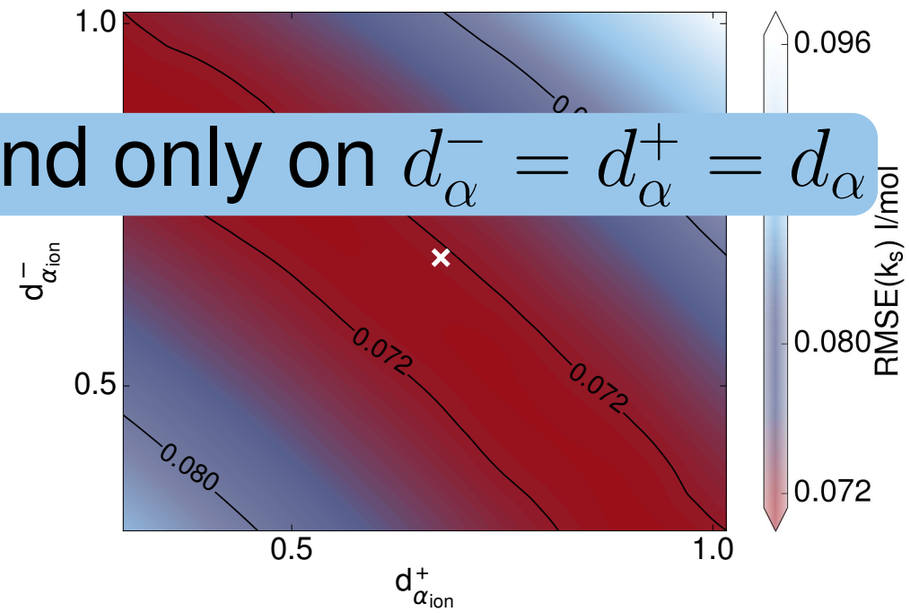

Setschenow coefficients depend only on $d_\alpha^- = d_\alpha^+ = d_\alpha$

Scaling relation for d_α (Stern Layer width)

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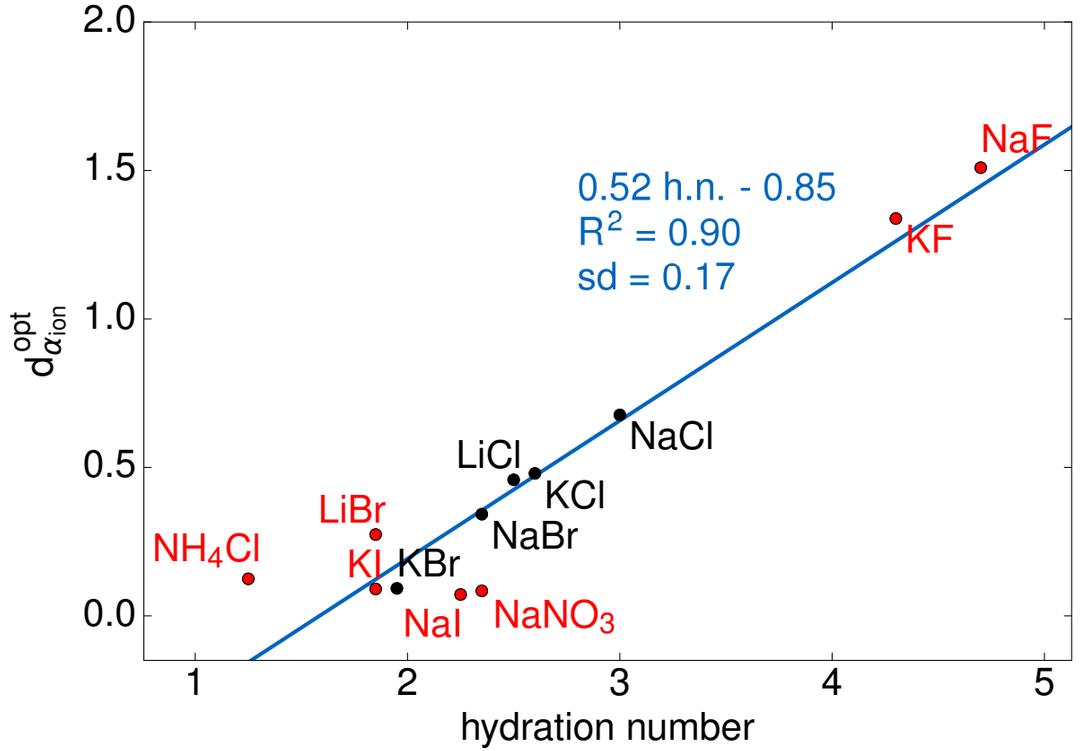
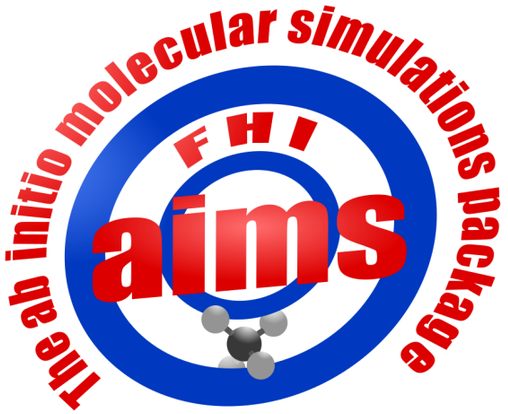


d_α correlates with the hydration number.

$\Rightarrow$ **predict ionic parameter**.

Ringe, Oberhofer, and Reuter, J. Chem. Phys. **146**, 134103 (2017)

SMPB in practice



Free energy functional

$$\Omega_{\varepsilon,\alpha^{\pm}_{\text{ion}}}[v, n_{\text{el}}] = T^{\text{S}}[n_{\text{el}}] + E^{\text{xc}}[n_{\text{el}}] + \Omega^{\text{mf}}_{\varepsilon,\alpha^{\pm}_{\text{ion}}}[v, n_{\text{el}}] + \Omega^{\text{non-mf}}_{\varepsilon}[n_{\text{el}}]$$

solute-solvent non-mf interactions

mean field interactions

$\min_{v}$ SMPBE

$\min_{n_{\text{el}}}$ modified KS-eq.

Newton-**M**ultipole-**E**xpansion **R**elaxation **M**ethod (MERM)

Solving the MPBE

Regularisation

$$v = v^{\text{free}} + \delta v$$

Rewrite SMPB as root-finding Problem

$$\mathcal{F}[v] = \nabla.[\varepsilon \nabla v] + 4\pi(n_{\text{sol}} + n_{\text{ion}}[v]) = 0$$

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Solve Integral by Multi-centre multipole expansion MERM

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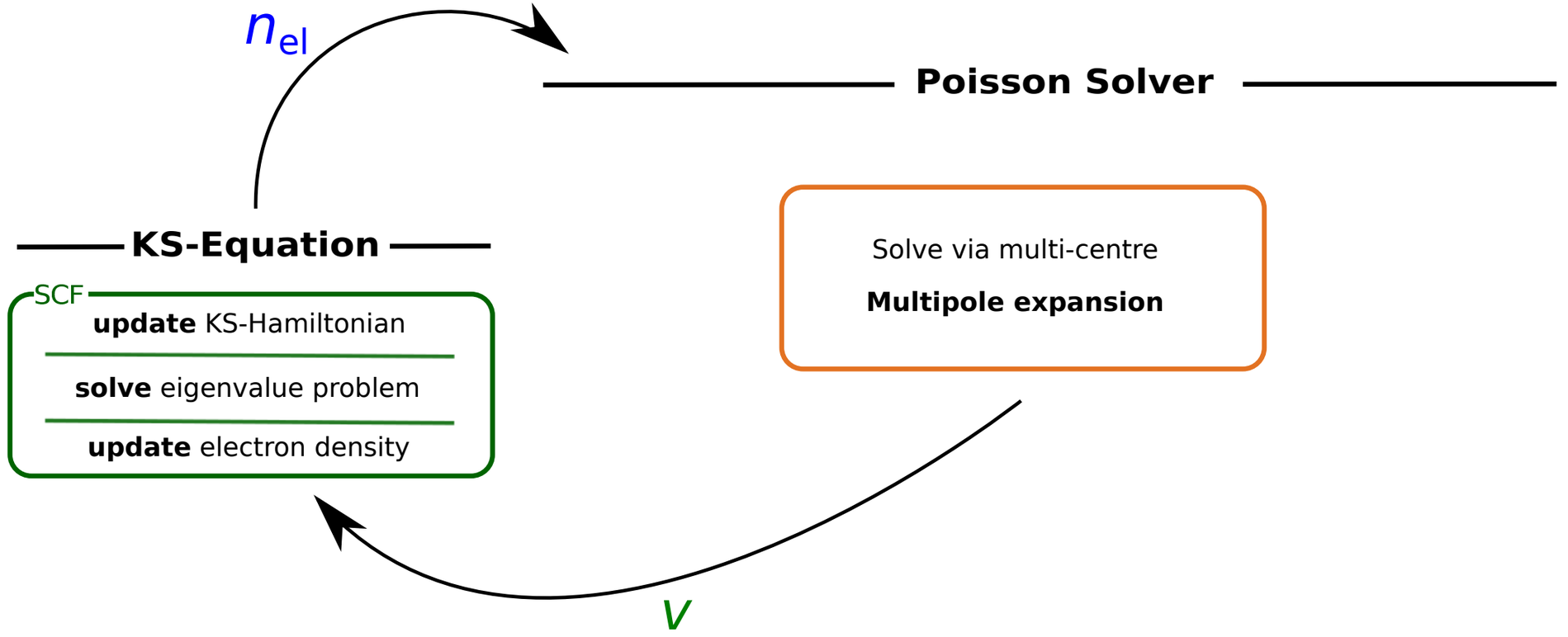
Solving the MPBE



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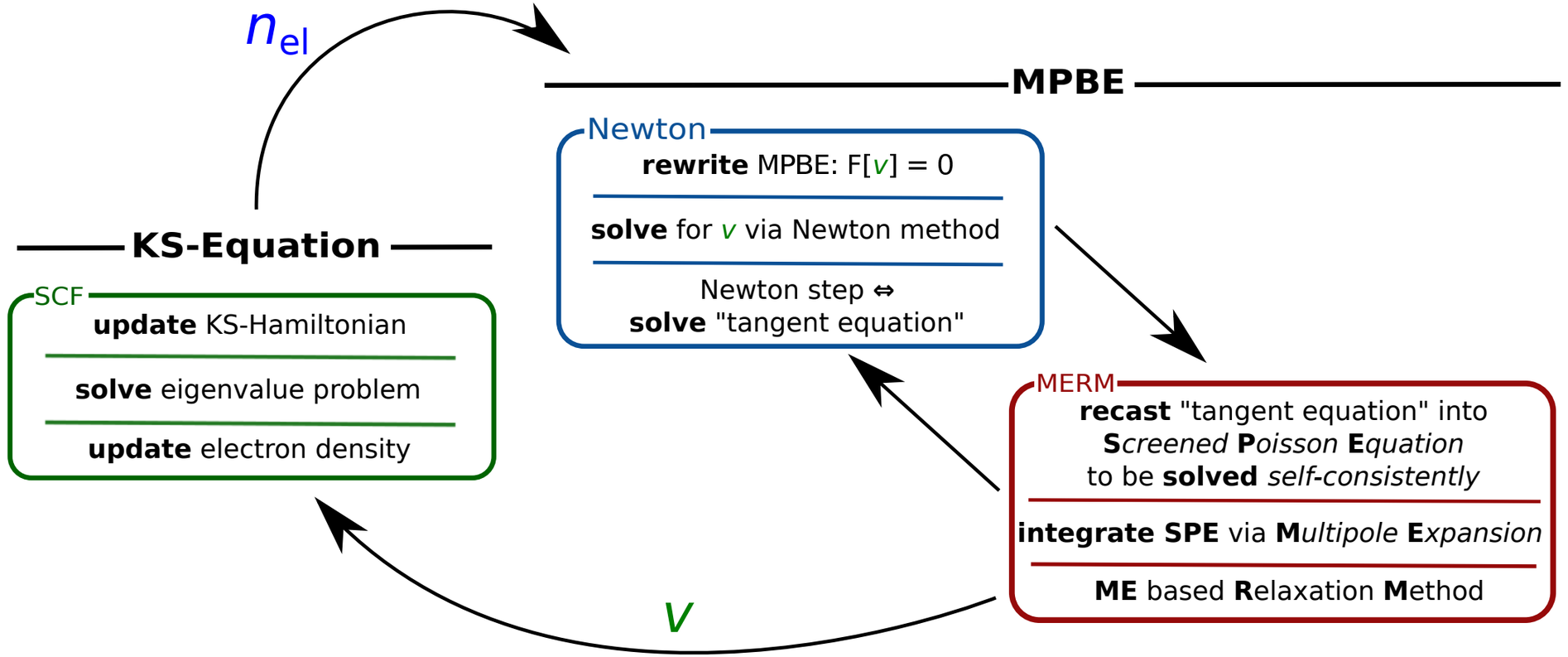

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Dr. Daniel Berger (now UCLA), embedding, defects
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Ahmad Agung, barriers
Christian Kunkel, data mining
Christoph Muschielok, MOFs
Simiam Ghan, inorganic charge transport

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Prof. Karsten Reuter
Dr. Christoph Scheurer

DFG

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