

Oliviero Andreussi
Q-MS School 2024



MATERIA
LAB

www.materialab.org

Continuum Models for Wet Electrified Interface



Michele Pavanello
@MkPavanello

Congratulations to the winners of the Q-MS student award! We look forward to seeing fancy @QuantumESPRESSO skills in your upcoming publications!!! @EtiennePalos @CAndreussi @fer_bononi #compchem #chemistry #physics

3:46 PM · Oct 13, 2021



Figure 2: Photos and tweet from the 2021 Q-MS School, organized in Texas. Three days intense lectures and tutorials were offered in a hybrid format, with video recording of the lectures released on the school website and on YouTube. The tutorial sessions featured challenges and awards were assigned to the most engaged participants.

Figure 3: Photos and tweet from the Embedding Hackathon (2019) and the San Diego Hackathon (2021). These intense but informal training events, with a balance of coding and social time, are crucial to build a sense of belonging for students and postdocs.

Quantum-MultiScale (Q-MS)

quantum-multiscale.org/schools

- Coding multiscale methods in condensed matter simulations
 - A modular approach
 - Collaborations through Hackathons
- Training users at the interface between Chemistry/Physics/Materials
- 2021 Q-MS School recordings available online

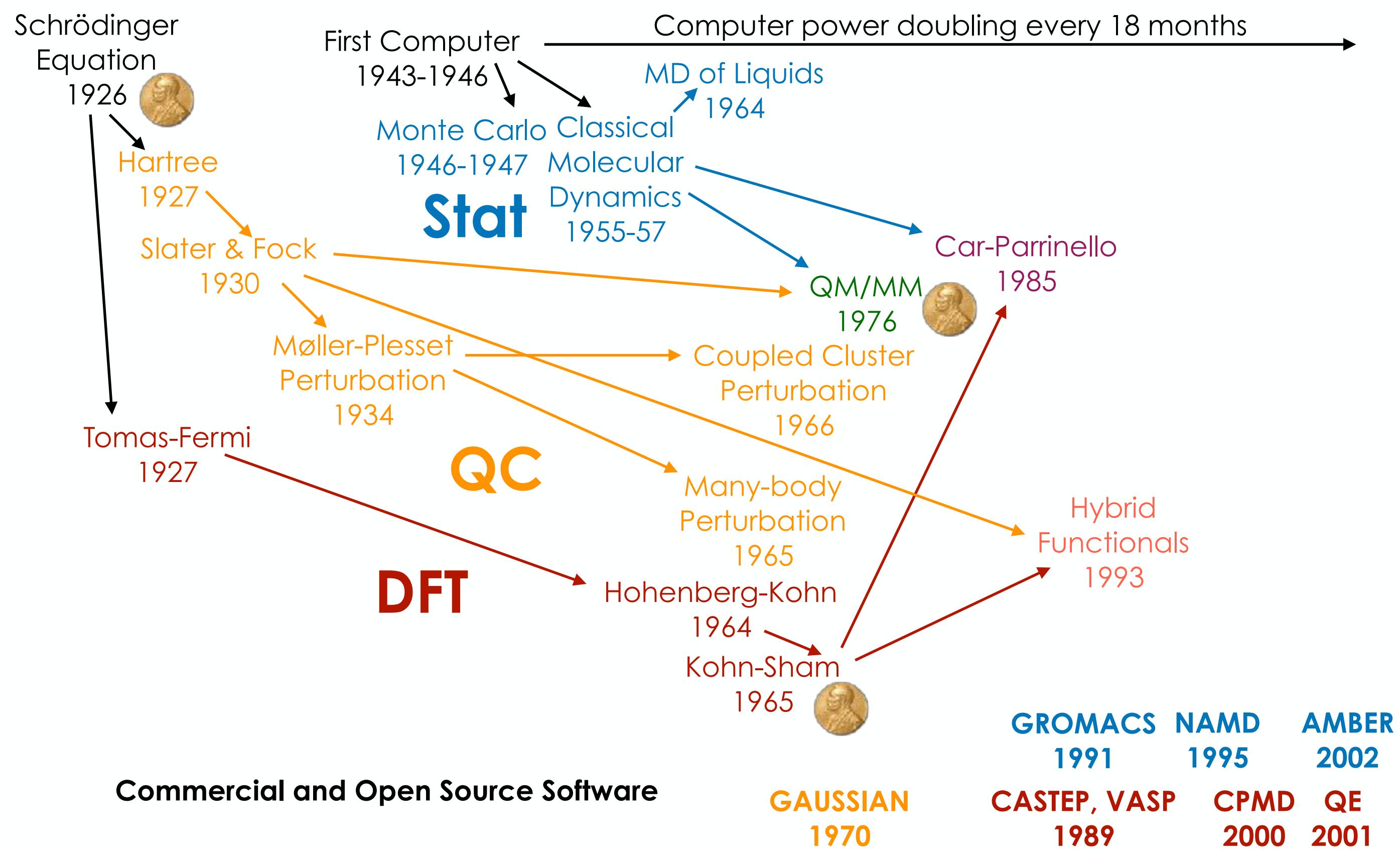


Computational Sciences

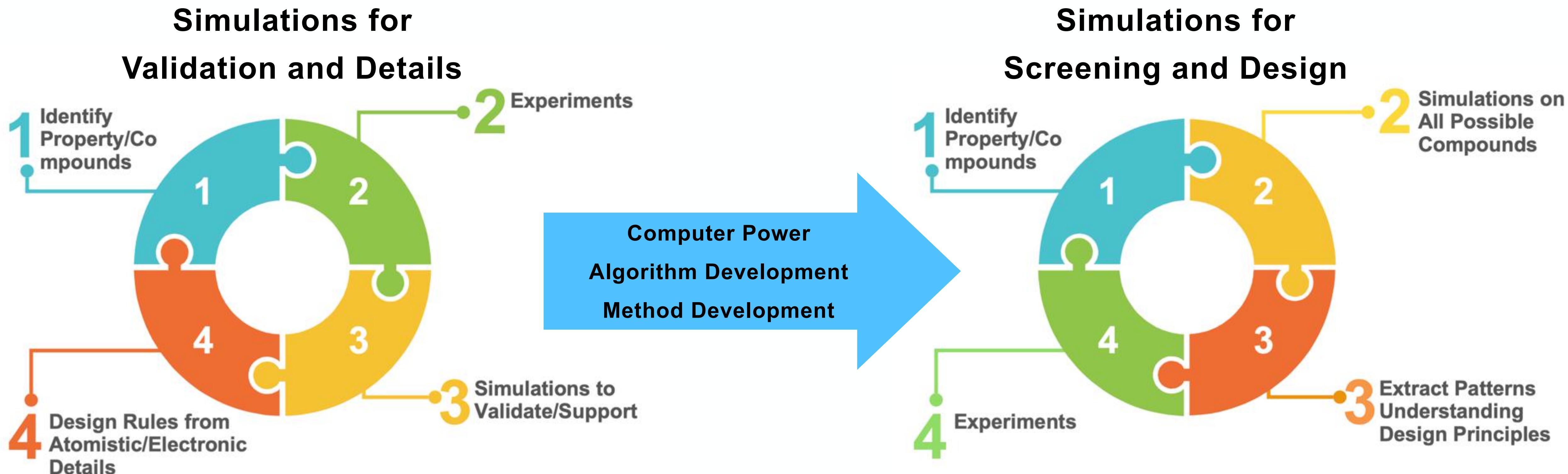
Physics, Chemistry, Materials

Timeline of Computational Matter

Non-comprehensive theories, models, and computer software developed to atomistically describe matter, molecules, materials, over the past century.



Switching the Paradigm of Simulations



An Example: Materials One-Atom Thick

- Graphene is the first known 2D material, isolated in 2004 by exfoliation of graphite, got Noble prize in 2010
- Since then a few tens of 2D materials have been exfoliated or synthesized

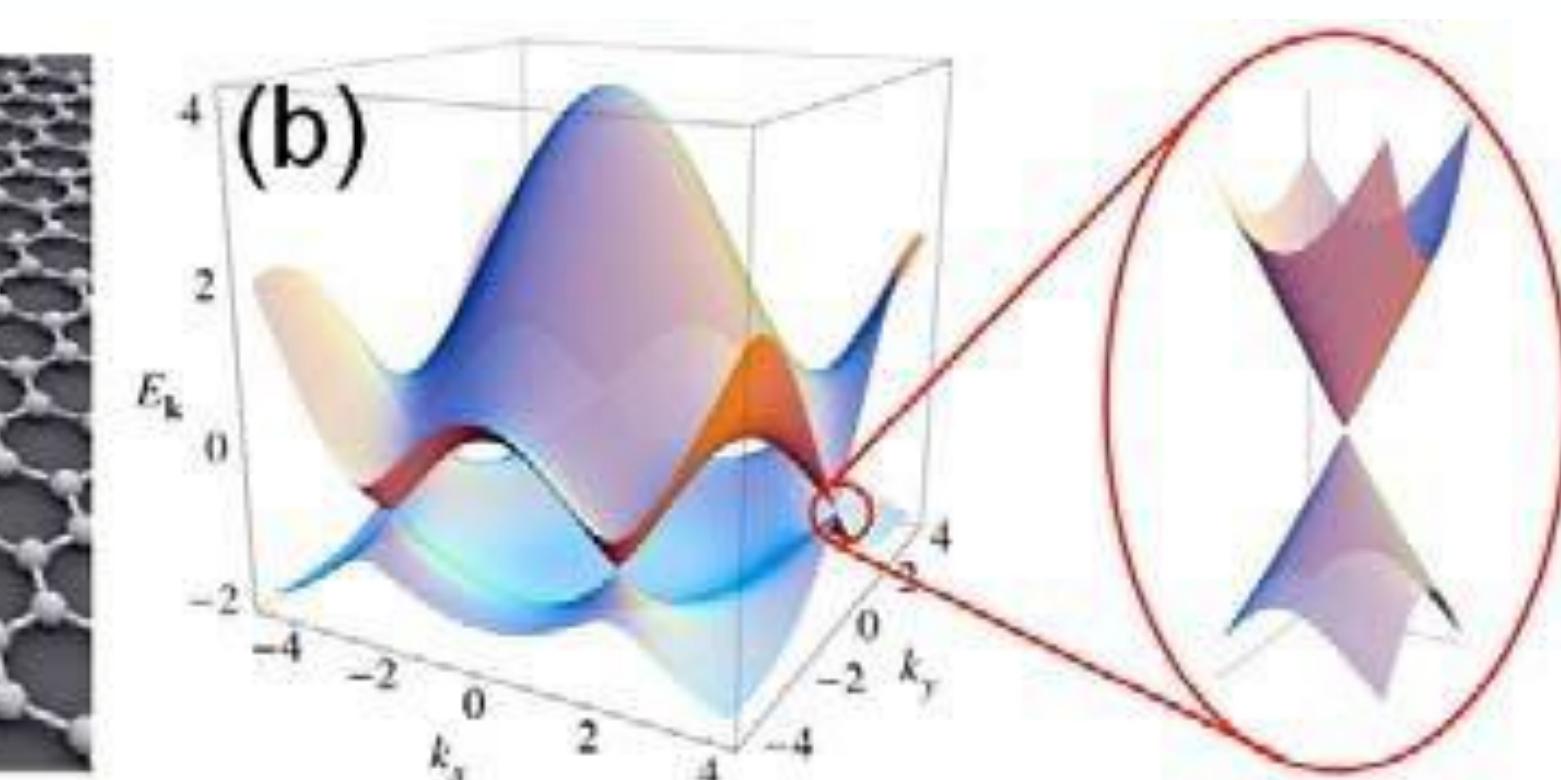
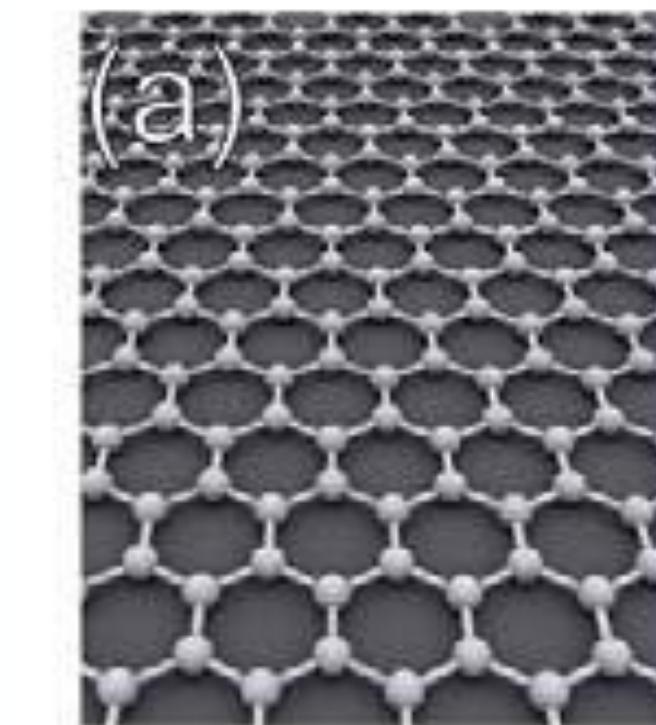
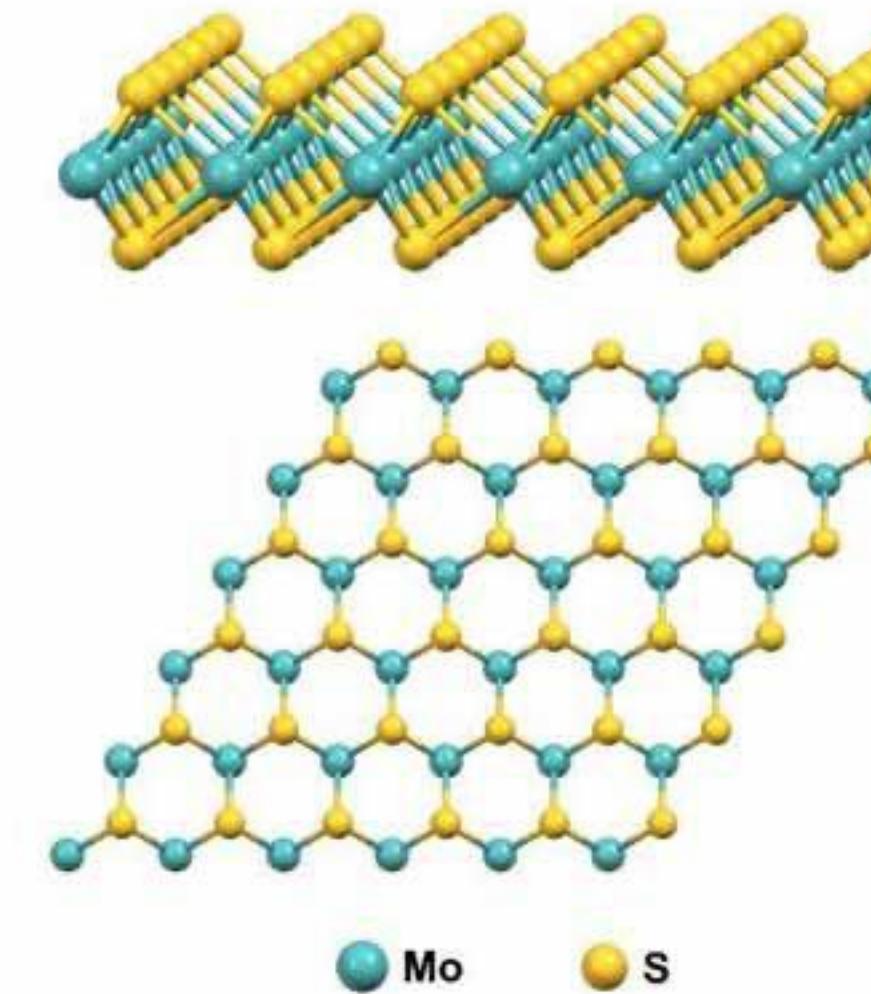
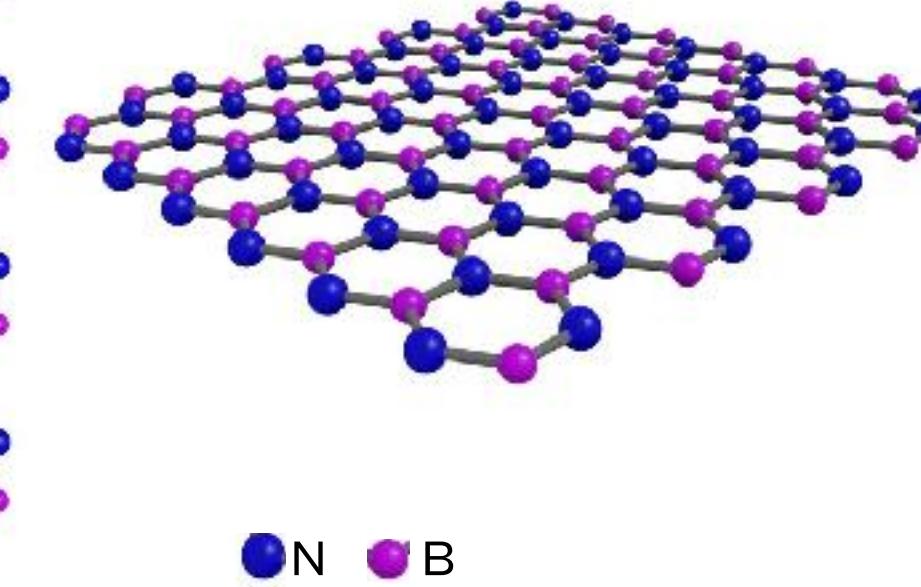
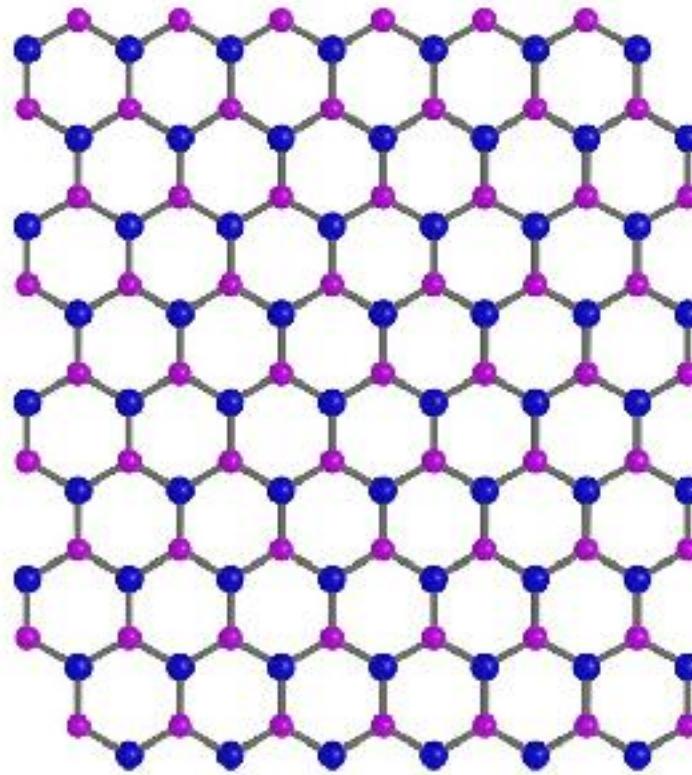


Photo: theuijunkie.com/graphene-scotch-tape-nobel-prize/

An Example: Materials One-Atom Thick

Mounet et al. Nature Nanotechnology, 13, 246, 2018

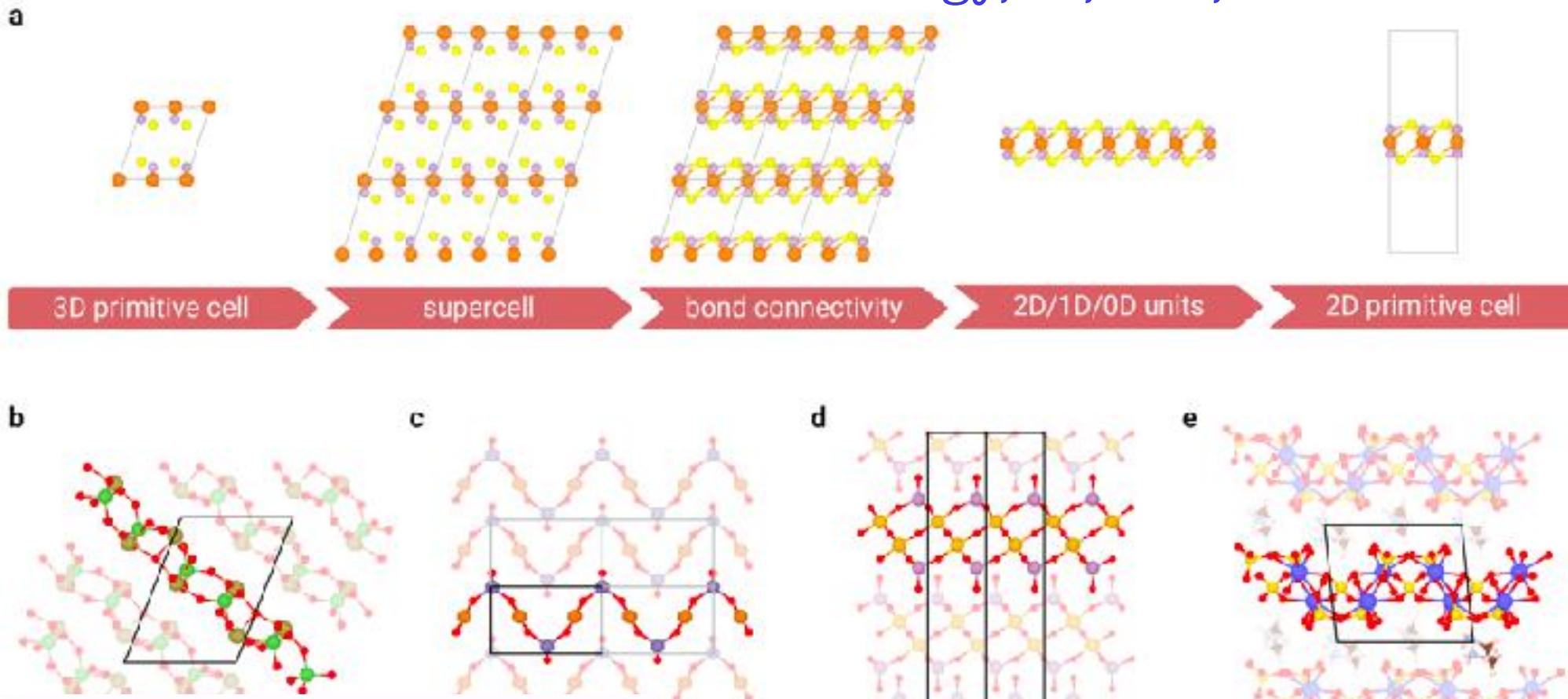
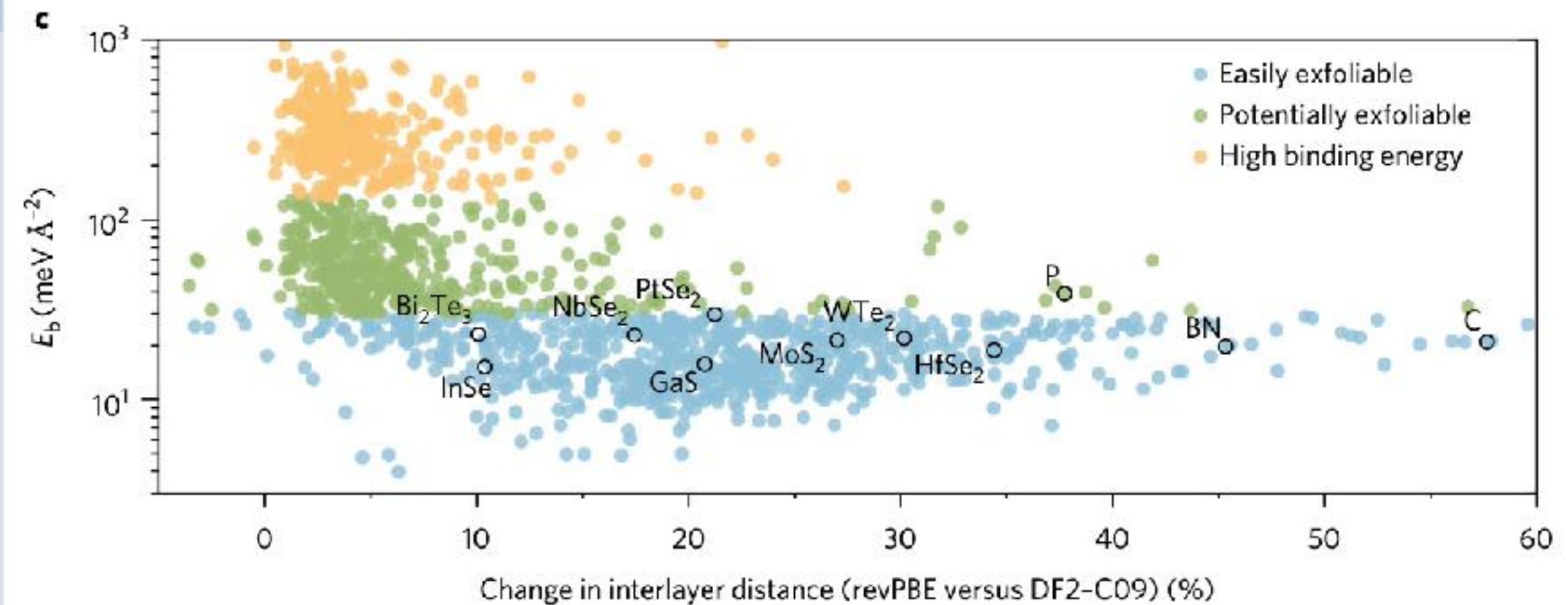
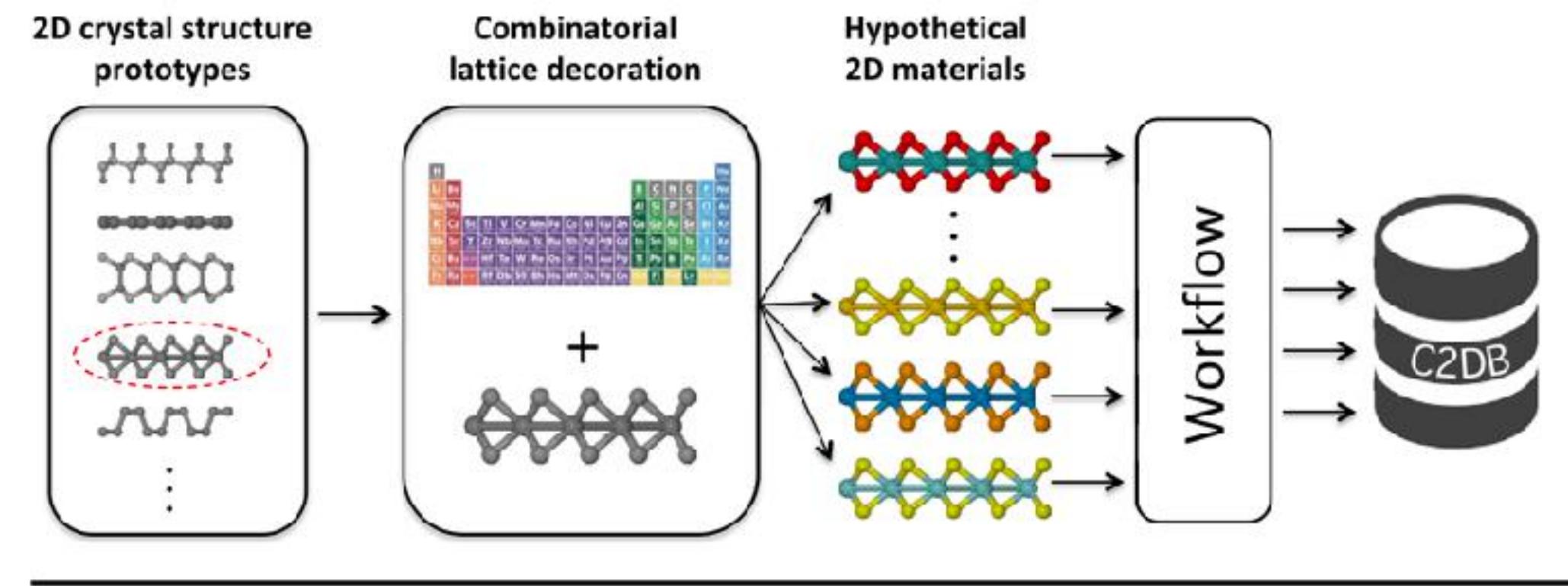


Table 1 Database statistics				
	Unique to the ICSD	Unique to the COD	Common to both	Total sum
Experimental data				
CIF inputs	99,212	87,070	13,521	186,282
Unique 3D structures (set A)	34,548	60,354	13,521	108,423
Layered 3D structures (set B)	3,257	1,180	1,182	5,619
DFT calculations				
Layered 3D, relaxed (set C)	2,165	175	820	3,210
Binding energies (set D)	1,795	126	741	2,662
2D easily exfoliable (EE)	663	79	294	1,036
2D potentially exfoliable (PE)	524	34	231	789
Total	1,187	113	525	1,825

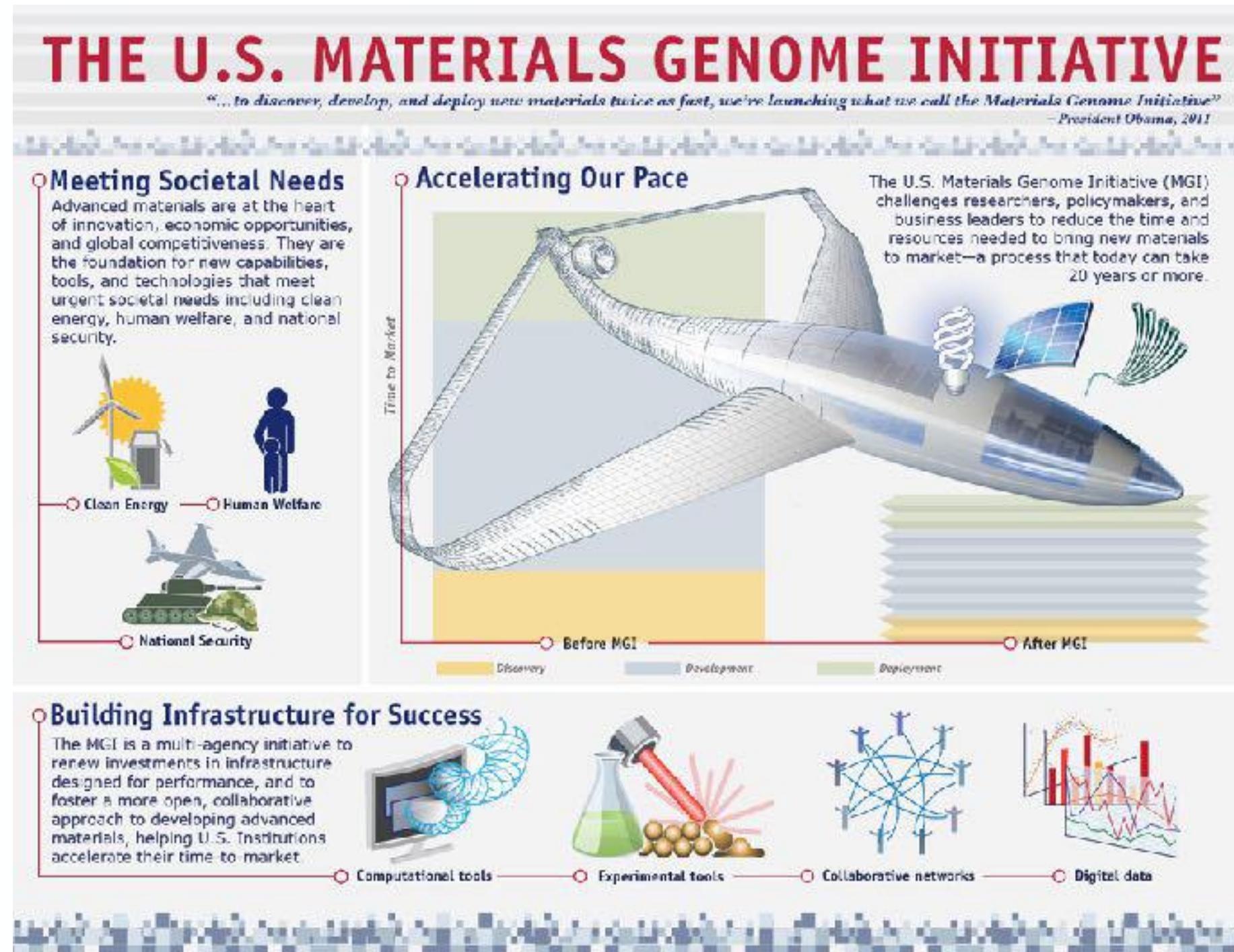
Experimental data: number of structures imported from the two databases (ICSD or COD); uniqueness not tested; number of unique 3D structures in each imported set or common to both (set A), and number of layered 3D structures identified using the geometrical criteria discussed in the text (set B). DFT calculations: number of structures that were relaxed (set C); number of structures that remain classificable layered after relaxation and for which binding energies were computed (set D); and number of easily or potentially (see text) exfoliable compounds.

Haastrup et. al. 2D Materials, 5, 042002 2018



High-Throughput Simulations for Materials Design

- Materials Genome Initiative (Obama 2011)

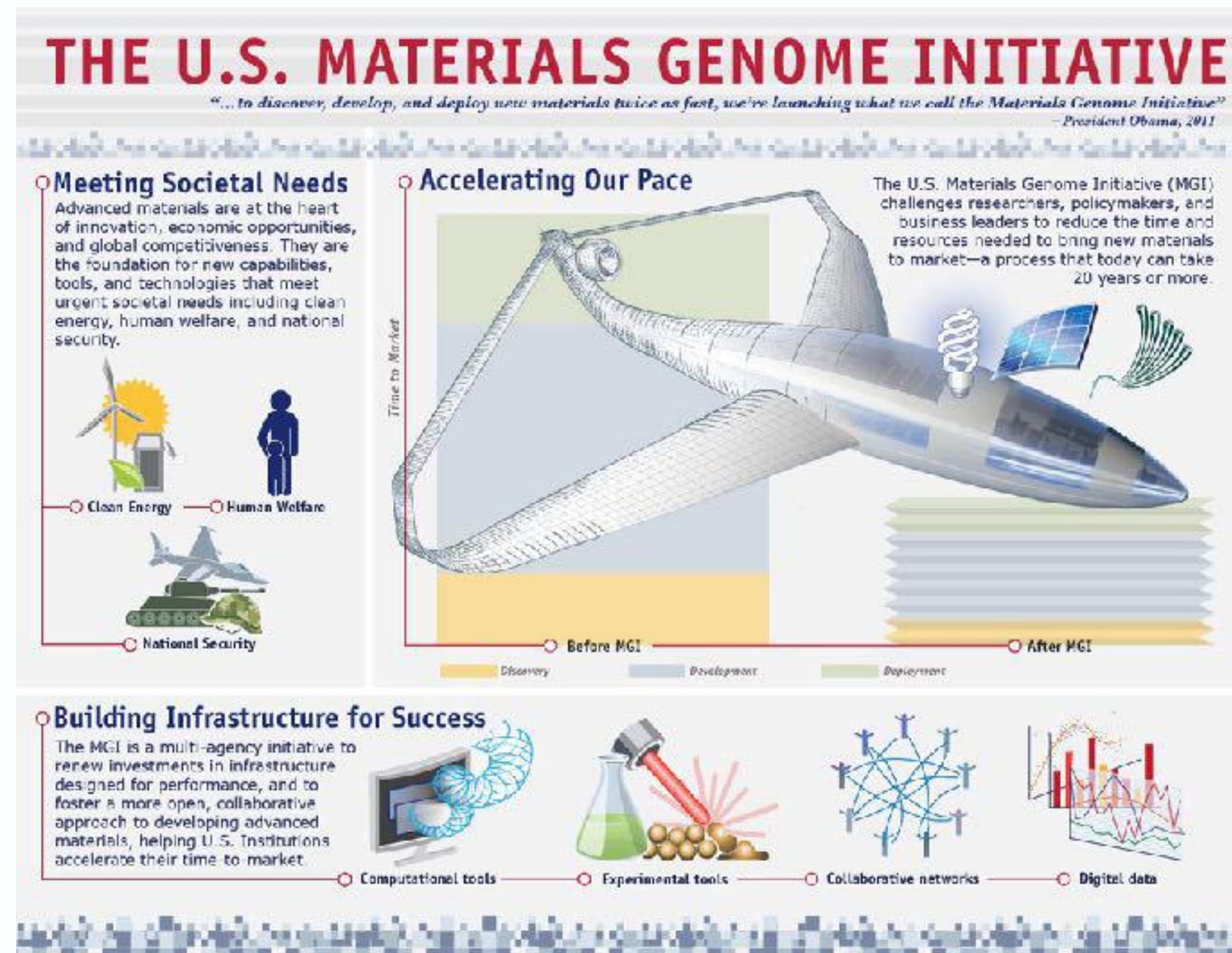


<https://www.mgi.gov/content/mgi-infographic>

- What do we need to go HT?
 - A computational infrastructure (Aiida, Nomad, Aflow, ASE, etc.)
 - Speed
 - Qualitative accuracy
 - Transferability

High-Throughput Simulations for Materials Design

- Materials Genome Initiative (Obama 2011)



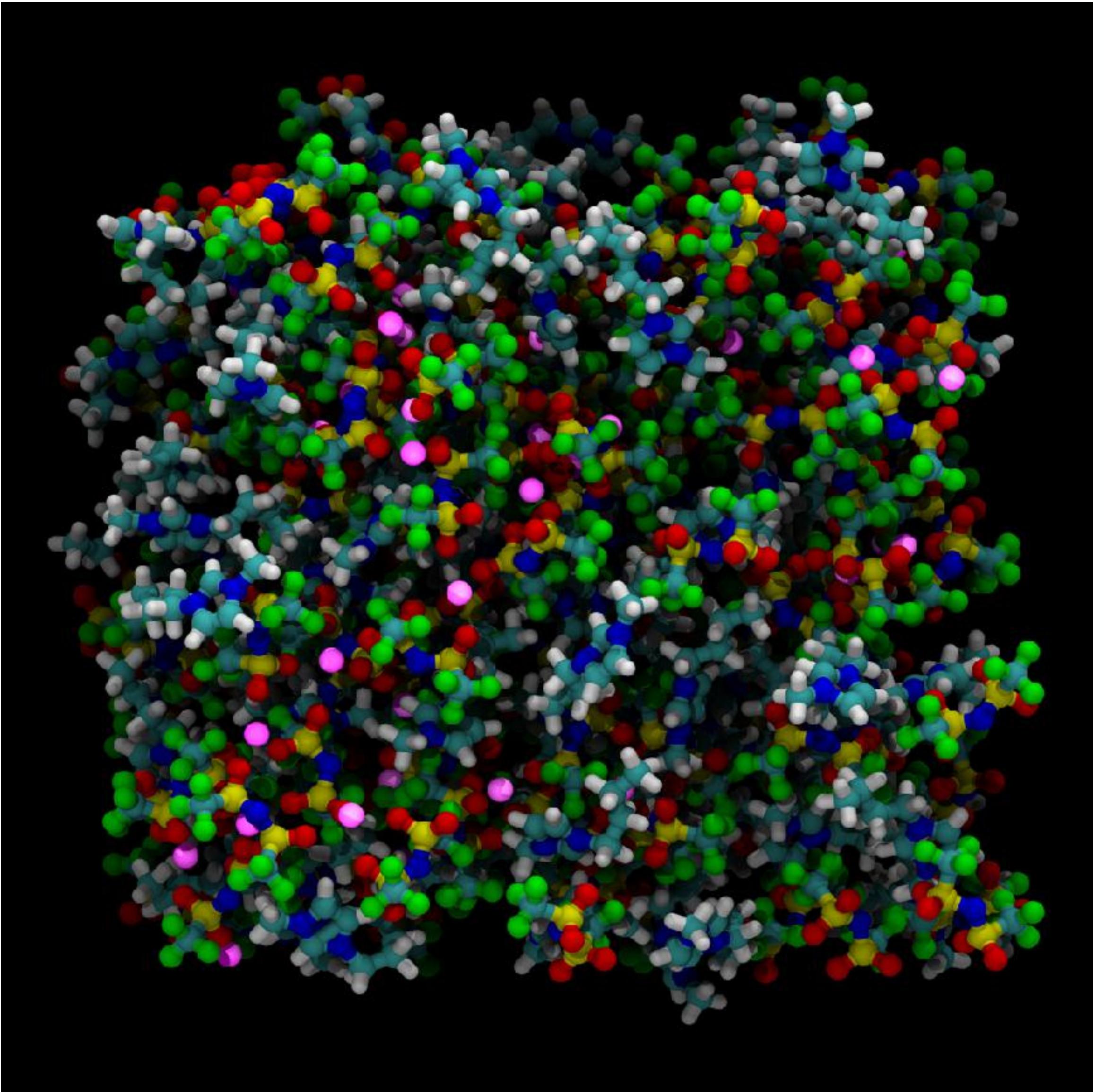
<https://www.mgi.gov/content/mgi-infographic>

- What do we need to go HT?
 - A computational infrastructure (Aiida, Nomad, Aflow, ASE, etc.)
 - Speed
 - Qualitative accuracy
 - Transferability

Electronic Structure (Density Functional Theory)

Challenges

- Length-scale bottleneck
 - DFT simulations scale as N^3 (number of electrons)
 - Disordered systems require large simulation cells
- Time-scale bottleneck
 - Statistical systems require sampling of multiple microscopic configurations



Challenges

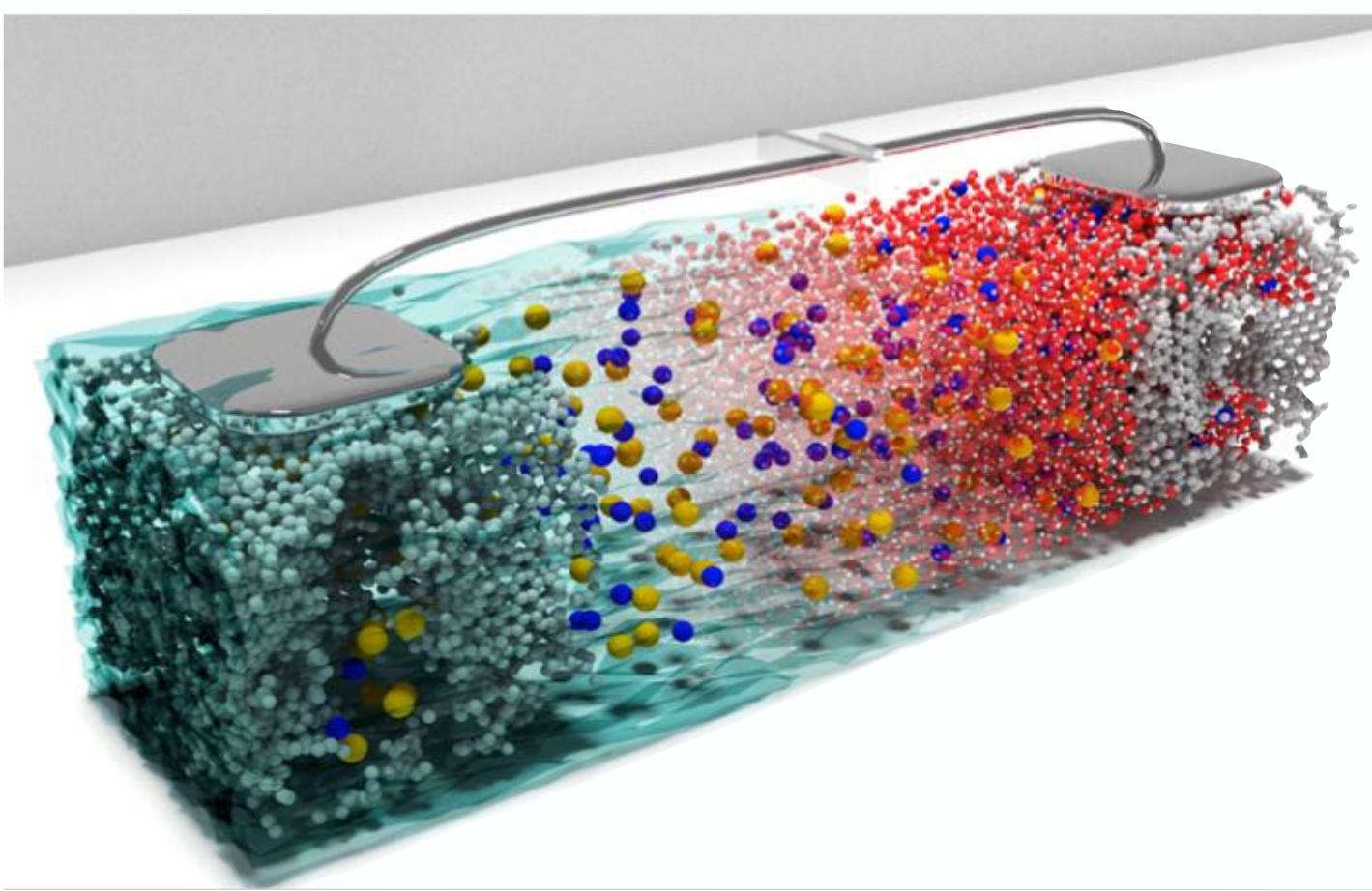
- Length-scale bottleneck
 - DFT simulations scale as N^3 (number of electrons)
 - Disordered systems require large simulation cells
- Time-scale bottleneck
 - Statistical systems require sampling of multiple microscopic configurations

Traditional High-Throughput DFT simulations focus on

- neutral bulk crystals
- slabs in vacuum
- isolated molecules

What About Wet (Electrified) Interfaces?

Image from M. Simoncelli acces.epfl.ch/cms/lang/en/pid/152725



- Energy storage and conversion
- Corrosion
- Sensing devices
- ...

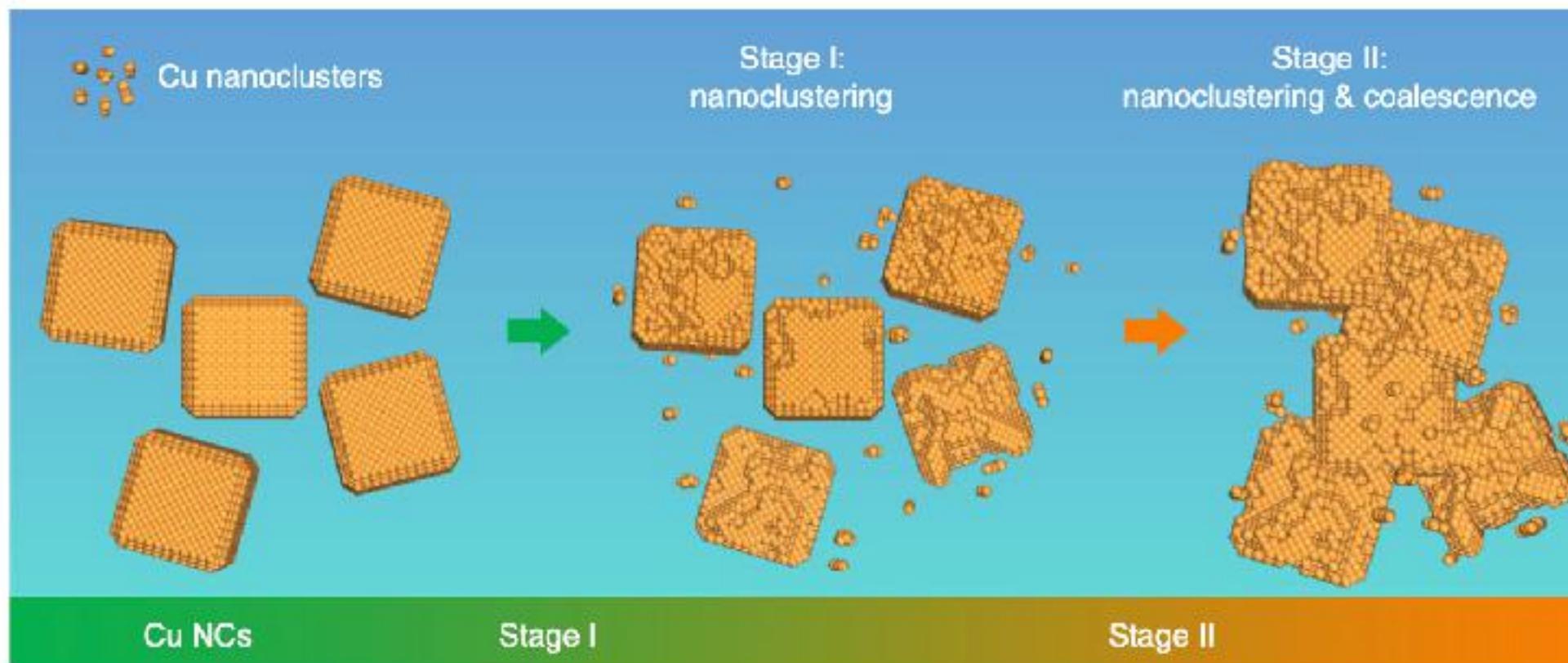


Image from J. Huang et al. Nature Communications (2018)

Can we get away with individual methods?

- Simulations on isolated molecules:
 - EA and IP from DFT can be used to estimate electrochemical window of electrolytes
- Simulations on bulk materials:
 - Band-gap, ion mobility, voltage-concentration curves
 - **Pourbaix diagrams**
 - **Catalytic descriptors**
- Simulations of liquid electrolytes:
 - Ionic conductivity, ionic capacitance
- Simulations on materials surfaces
 - **Interfacial Pourbaix diagrams**
 - **Catalytic activity and descriptors**

Computational Hydrogen Electrode¹

High-throughput electro-chemistry and catalysis

$$\frac{1}{2}H_{2(g)} = e^- + H_{(aq)}^+$$
$$\Delta G = 0 \quad \text{at} \quad pH = 1 \quad \& \quad U = V^{SHE}$$

$$\mu_e + \mu_H = \frac{1}{2}G(H_2) - k_B T \ln(10)pH - e(U - U_{SHE})$$

- Assume a proton-coupled red/ox reaction



$$\Delta G = G(B) - G(A) + \mu_e + \mu_H$$

$$G(A) = E^{DFT}(A) + ZPE(A) + TS(A)$$

$$S(A) = ?$$

- Catalytic activity
 - Multiple possible intermediates and pathways
- Pourbaix diagrams
 - Multiple possible phases
- Vacuum neutral DFT of bulk or interfaces

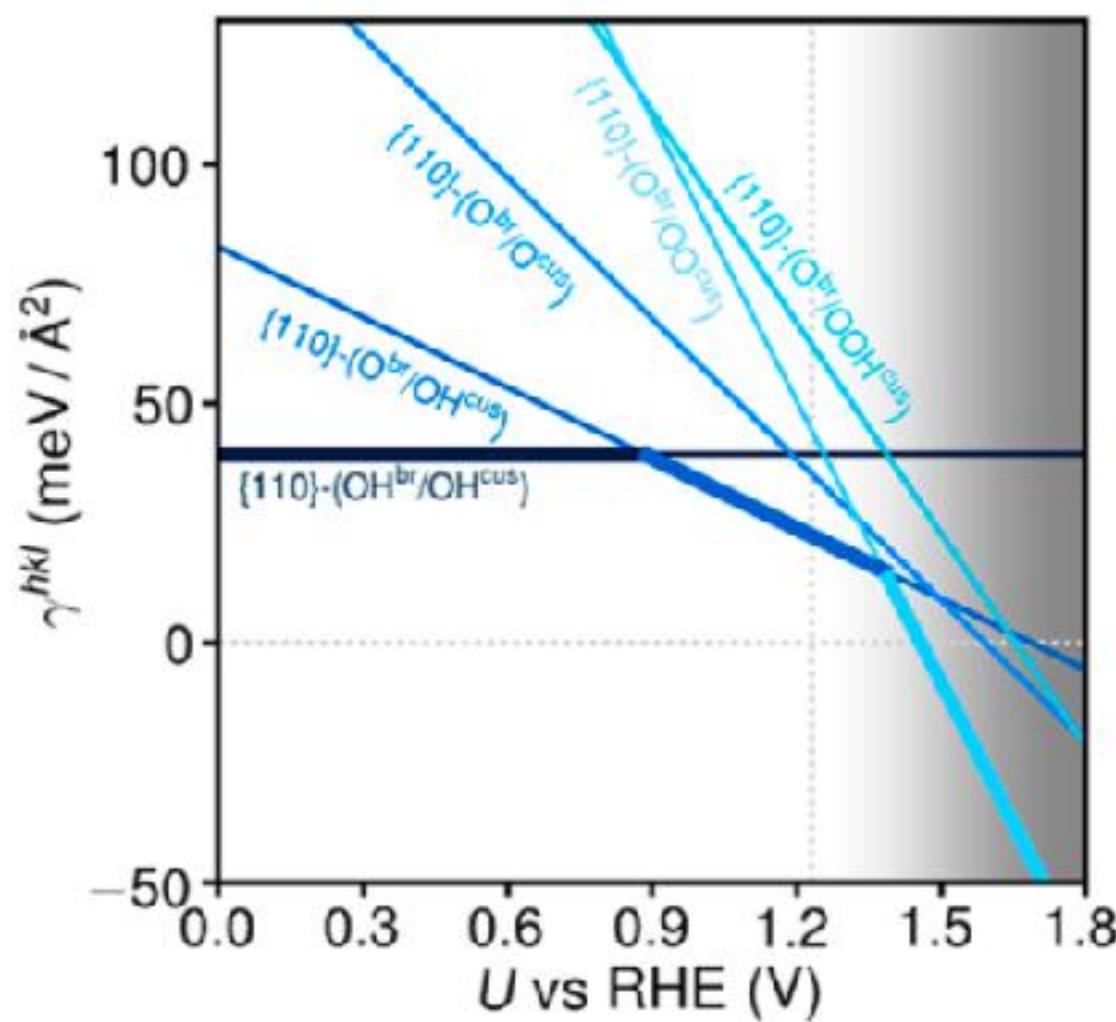
¹ Norskov et al., *J. Phys. Chem. B*, **108**, 17886 (2004)

Stability & Catalysis

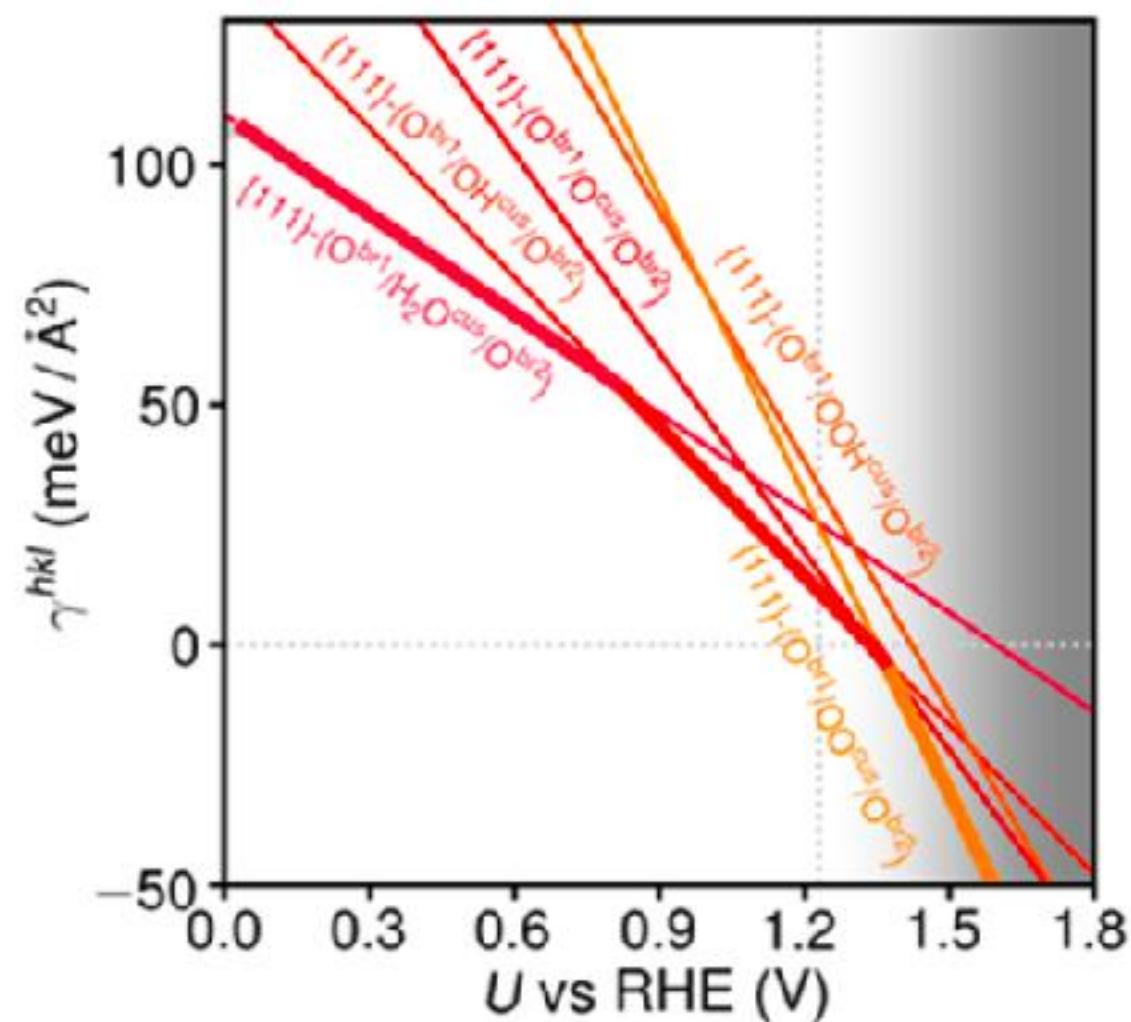
O, OH, H, etc.

From DFT to Pourbaix Diagrams

Interface Free Energies of (110) and (111) rutile IrO₂ as a function of applied potential.



D. Opalka et. al ACS Catal. **9**, 4944–4950 (2019)



- Interface Free Energy

$$\gamma = \frac{1}{2A} \left(G_{surf} - n \cdot G_{bulk} - m \cdot \mu_{H_2O} + n_{H^+} \cdot \mu_{H^+} + n_{e^-} \cdot \mu_{e^-} \right)$$

- G_{surf} and G_{bulk} can be approximated by ZPE-corrected DFT energies
- Computational Hydrogen Electrode¹
 - Neutral interfaces (PCET)

$$\bullet \quad \mu_{H^+} + \mu_{e^-} = \frac{1}{2} \mu_{H_2} - k_B T \ln(10) \text{pH} - e\Phi_{\text{SHE}}$$

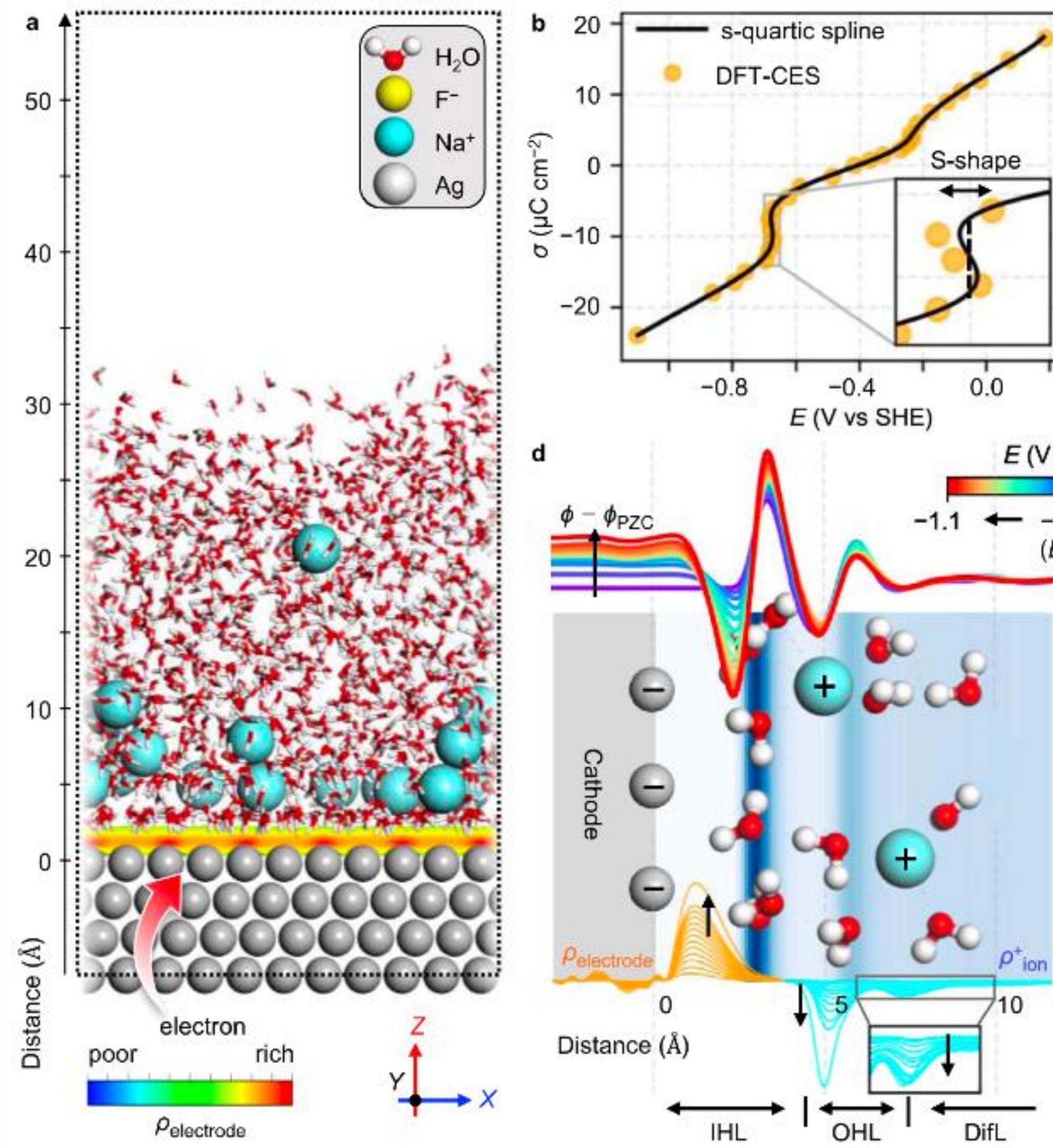
¹ Norskov et al., J. Phys. Chem. B, **108**, 17886 (2004)

What is Missing in the CHE?

What is Missing in the CHE?

- Solvent/Electrolyte
- Effects of the electric field on catalysis/relaxation
- Forces proton-coupled electron transfers

Modeling a Wet Electrified Interface What challenges?



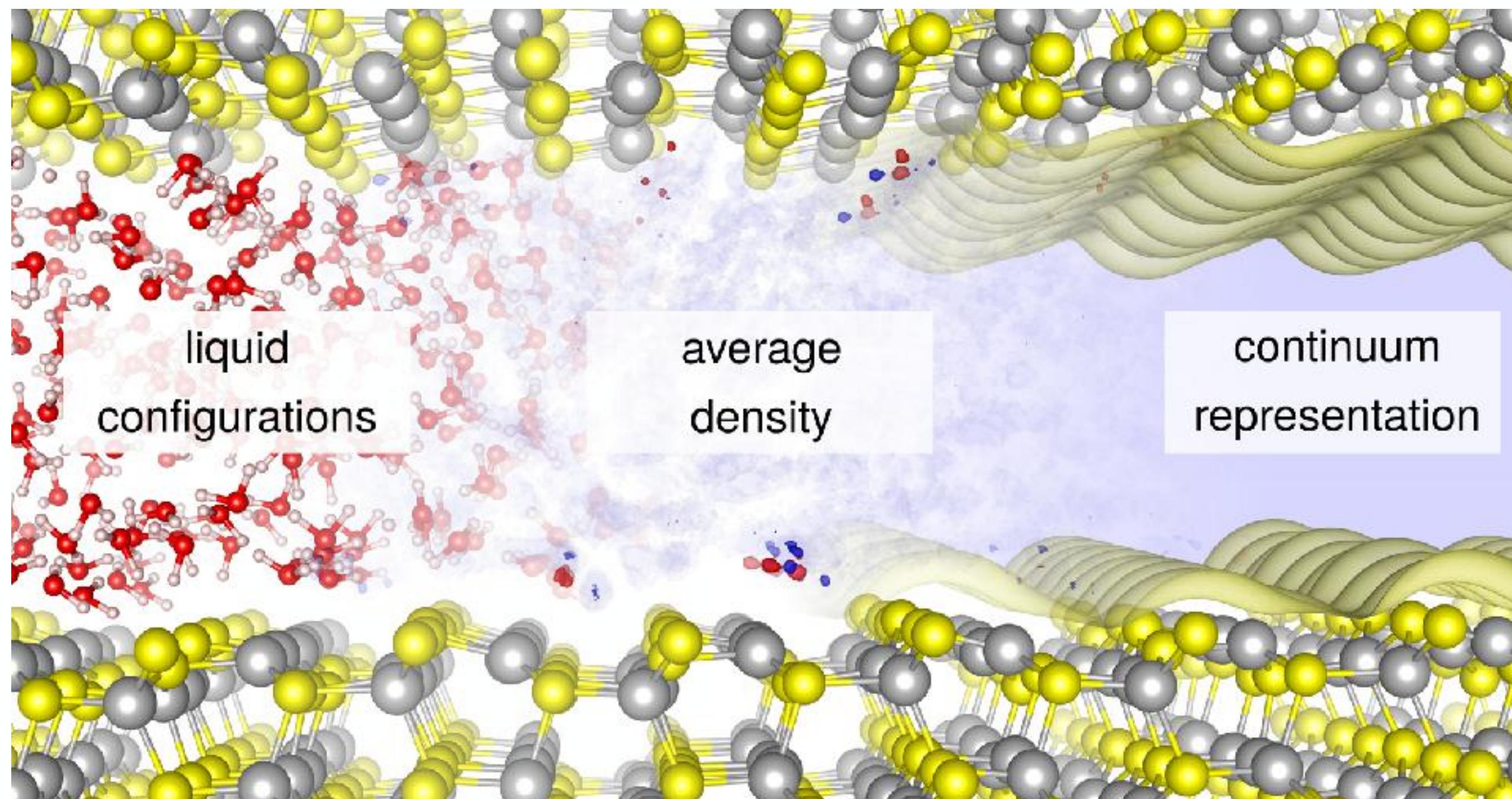
Shin et al., Nature Comm. 13, 174 (2022)

Modeling a Solvent

Explicit vs. Implicit vs. Hybrid

From Explicit to Implicit

Semiconductor-Water interface, as modeled via full ab-initio molecular dynamics simulations vs. continuum solvation



AIMD simulations by Pasquarello and coworkers. Figure by N. Hörmann.

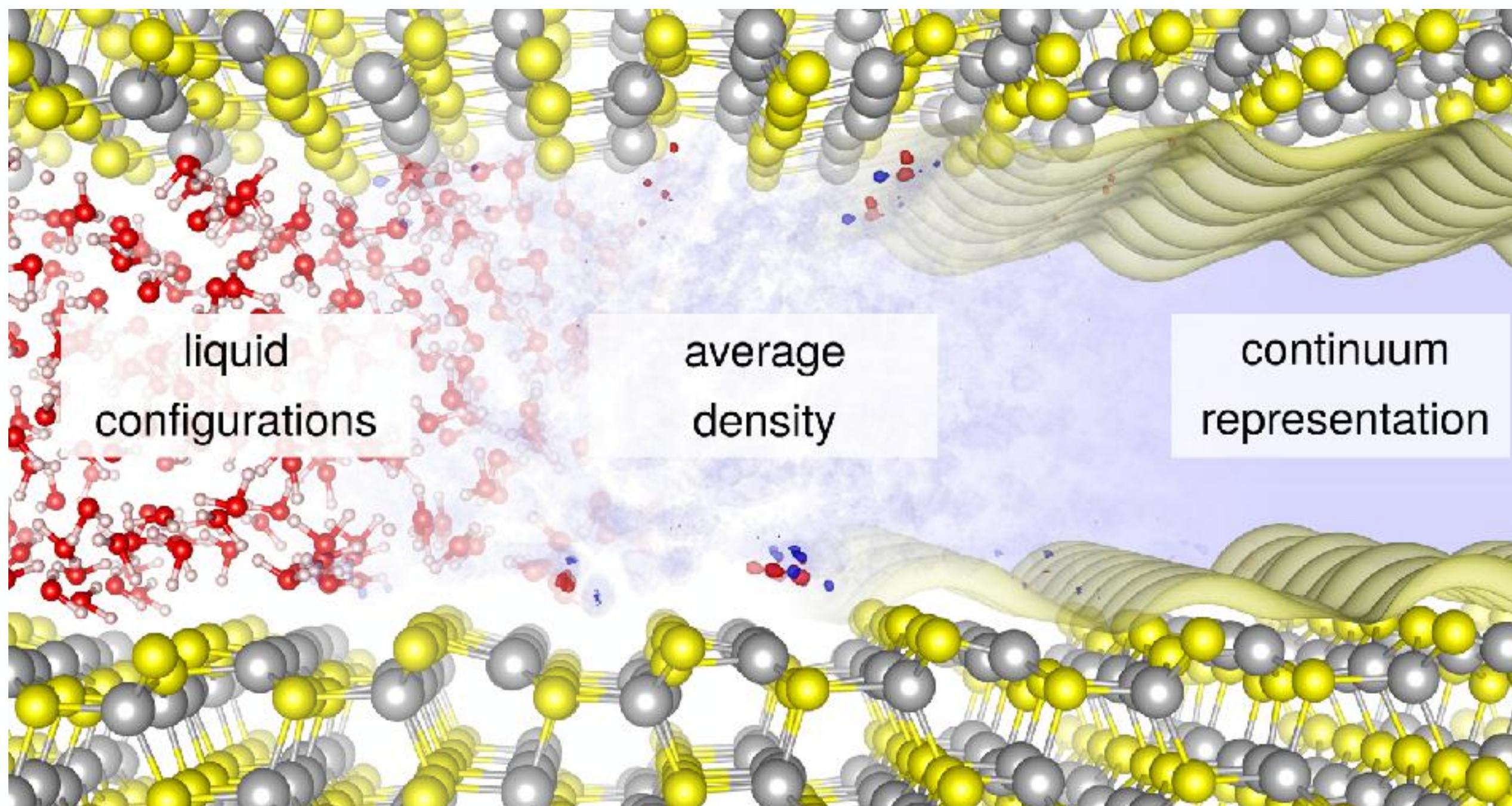
- Full ab-initio MD
- Classical QM/MM
- Continuum
- Hybrid approaches

Continuum Models

Ingredients

From Explicit to Implicit

Semiconductor-Water interface, as modeled via full ab-initio molecular dynamics simulations vs. continuum solvation



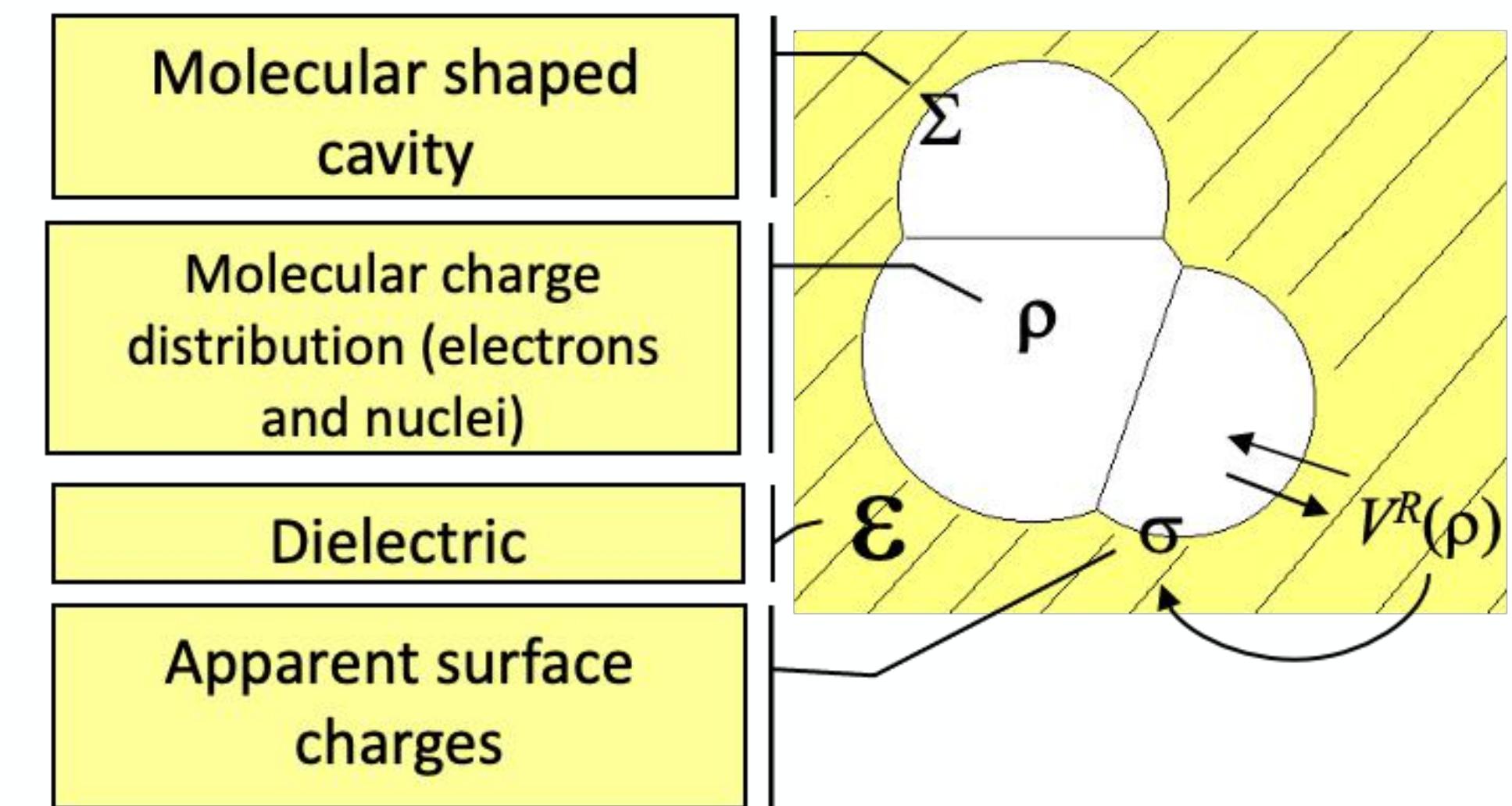
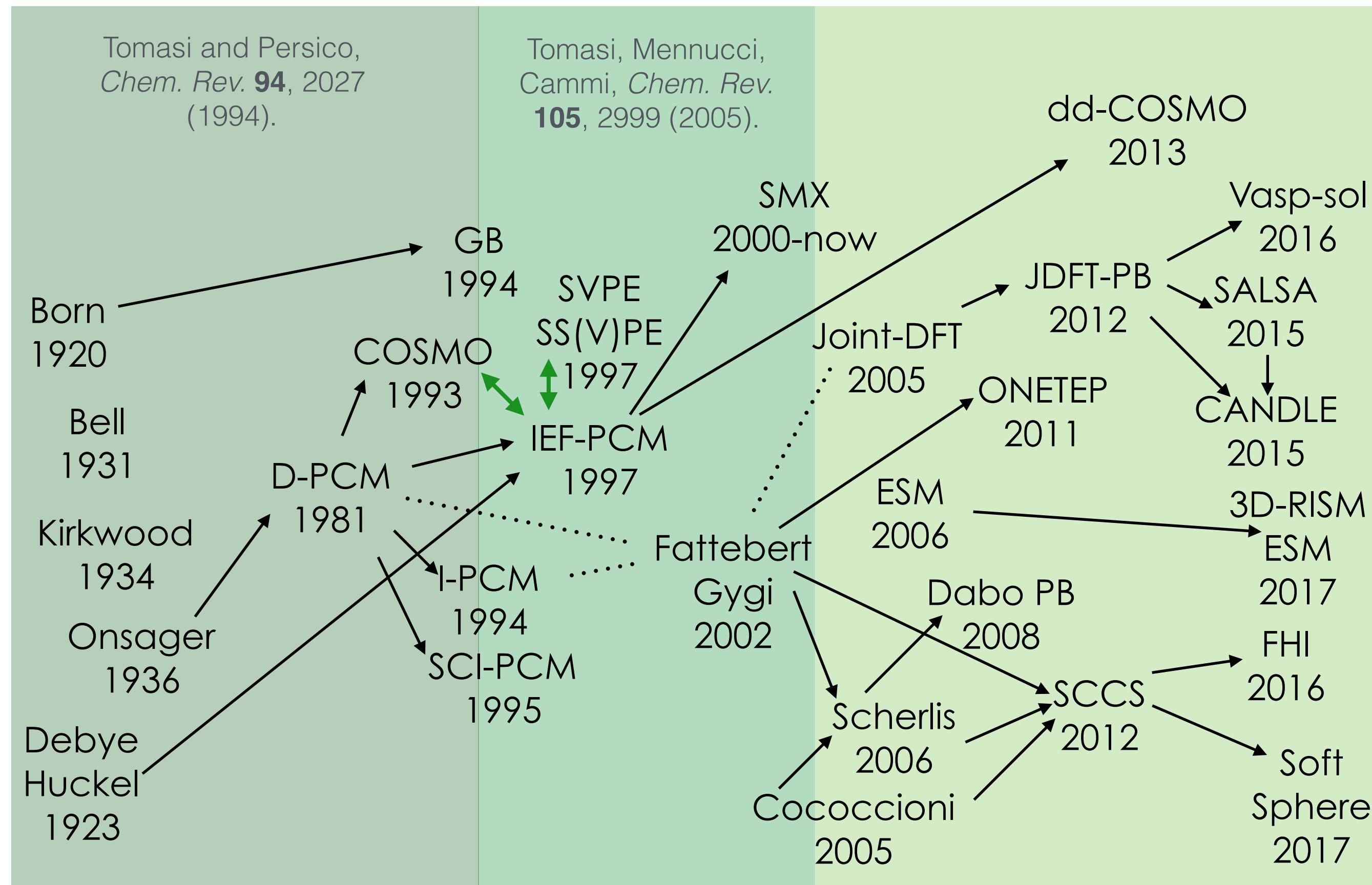
AIMD simulations by Pasquarello and coworkers. Figure by N. Hörmann.

- Interface function
- Interactions

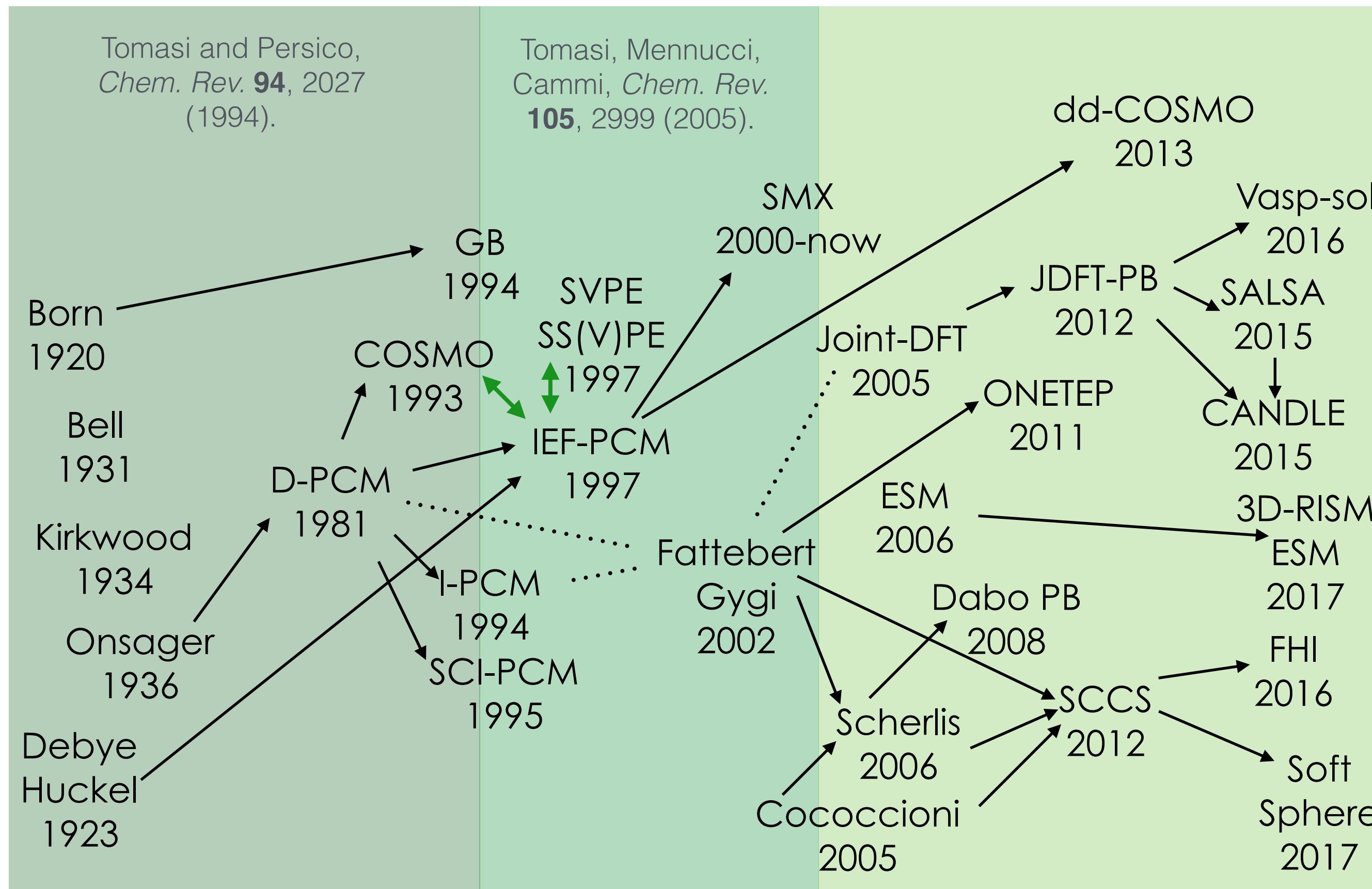
Tutorial Review on Continuum Embeddings in Condensed Matter Simulation

Andreussi and Fisicaro, *Int J Quantum Chem.* e25725 (2018).

Polarizable Continuum Model (PCM) and Co



Polarizable Continuum Model (PCM) and Co



PROs

- Fast
- Mostly accurate
- For most molecular properties (geometry, spectra, etc.)

CONS

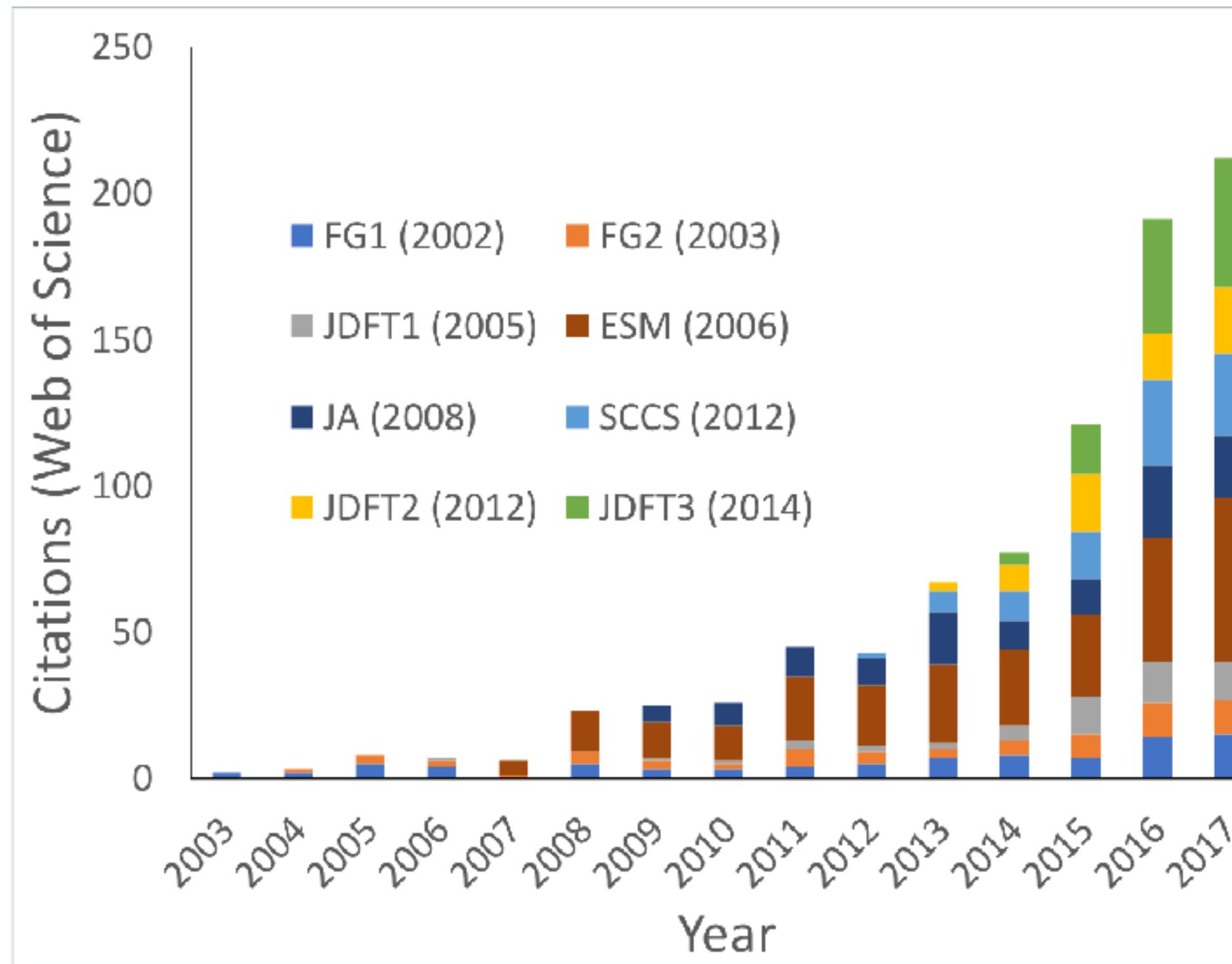
- Just mostly accurate
- Empirical
- Scaling, artifacts, ...

Translating Continuum Models in Condensed Matter Comes with Additional Challenges and Solutions

A Shared Effort

Multiscale Models of Electrochemical Environments in Condensed-Matter Simulations

Citation records for the most cited methodological articles in the field of continuum embedding methods in condensed-matter simulations.
Only articles with more than 50 total citations are reported.



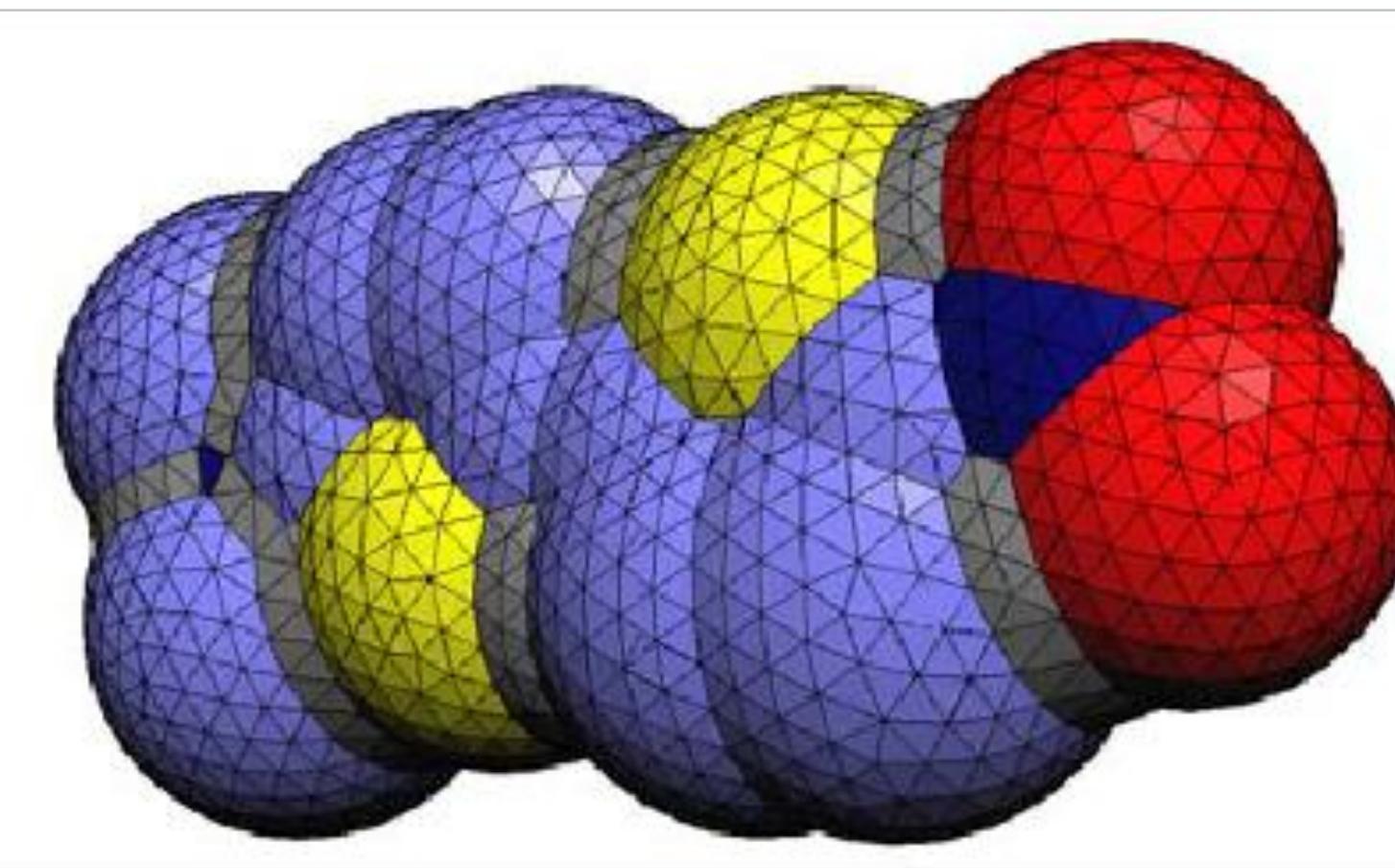
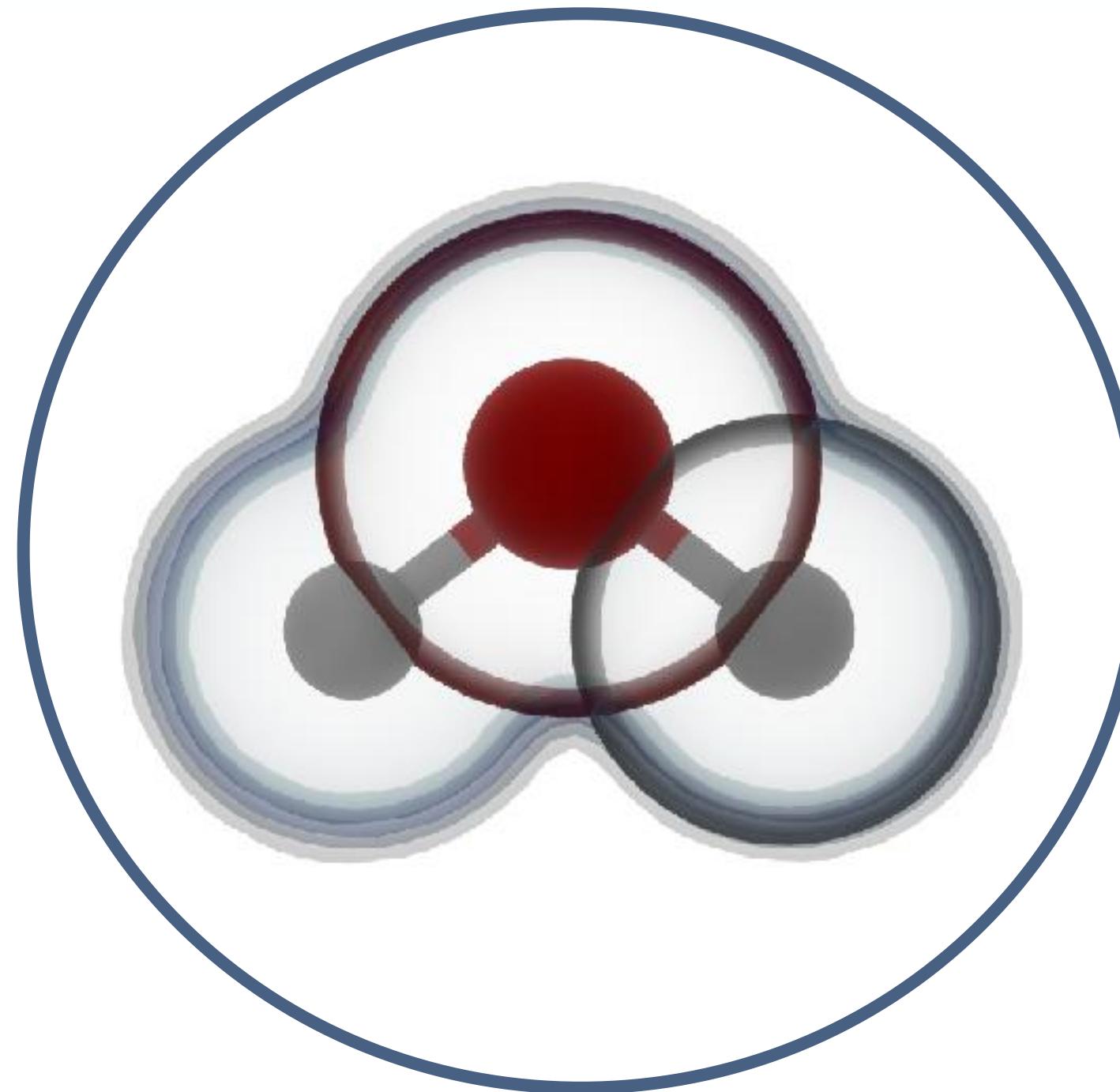
- Fattebert and Gygi (2002-2003)
- Jinnouchi and Anderson (2005)
- Otani et al (ESM, ESM-RISM, 2006-present)
- Arias and collaborators (JDFT, 2012-present)
- Hennig et al (VaspSol, 2014)
- Reuter et al (FHAIMS 2016-present)
- And others

Continuum Interfaces

Not a single right way

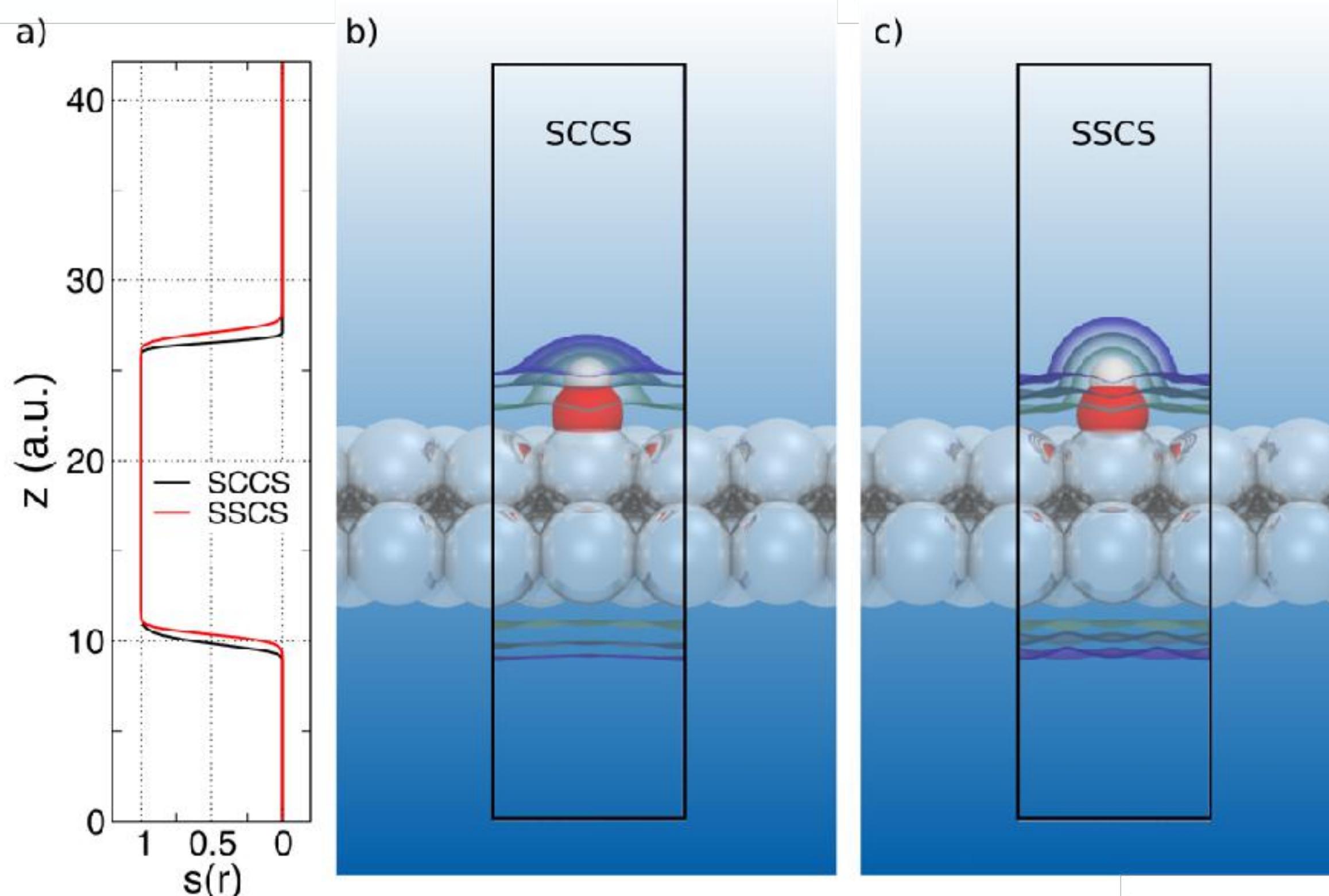
- Simple or atomistic?
- Sharp or smooth?
- Rigid or soft?

$$s(\mathbf{r}) = \begin{cases} 1 & \mathbf{r} \in \text{system} \\ 0 & \mathbf{r} \in \text{continuum} \end{cases}$$



Shape of Interface Functions

Hydroxyl adsorbed on Pt (111) surface with examples of continuum interface functions



O. Andreussi, N. Hörmann, F. Nattino, Chapter in “Atomic-Scale Modelling of Electrochemical Systems”, under review

Interfaces

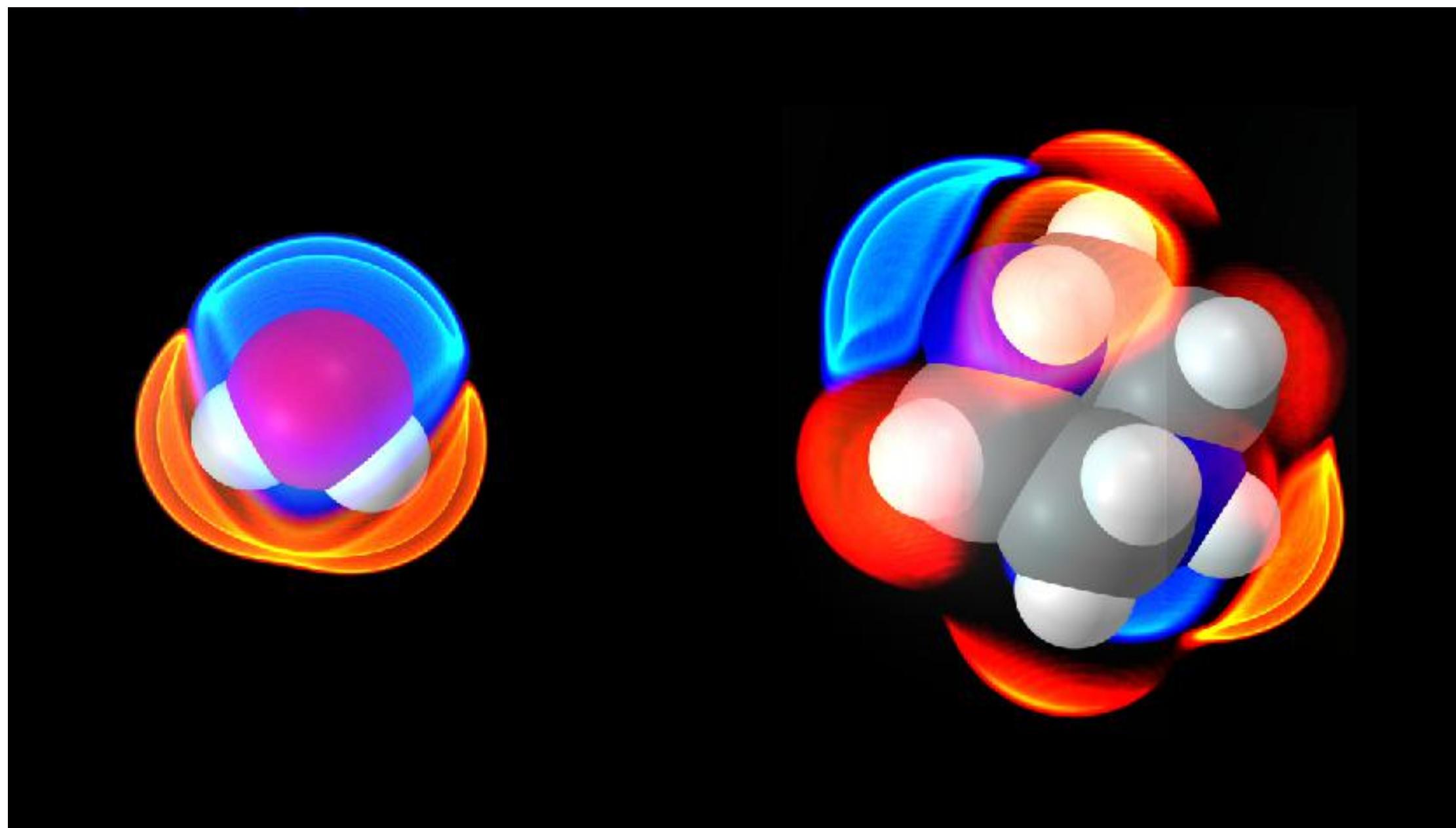
Smooth Functions: Pros and Cons

- Based on electrons (soft, self-consistent, SCCS)
- Based on ions (rigid, SSCS)
- Non-local

Interactions Electrostatics et al.

Dielectric Polarization Charges

Positive (blue) and negative (orange) polarization charges induced by the molecular solutes on the embedding continuum dielectric.



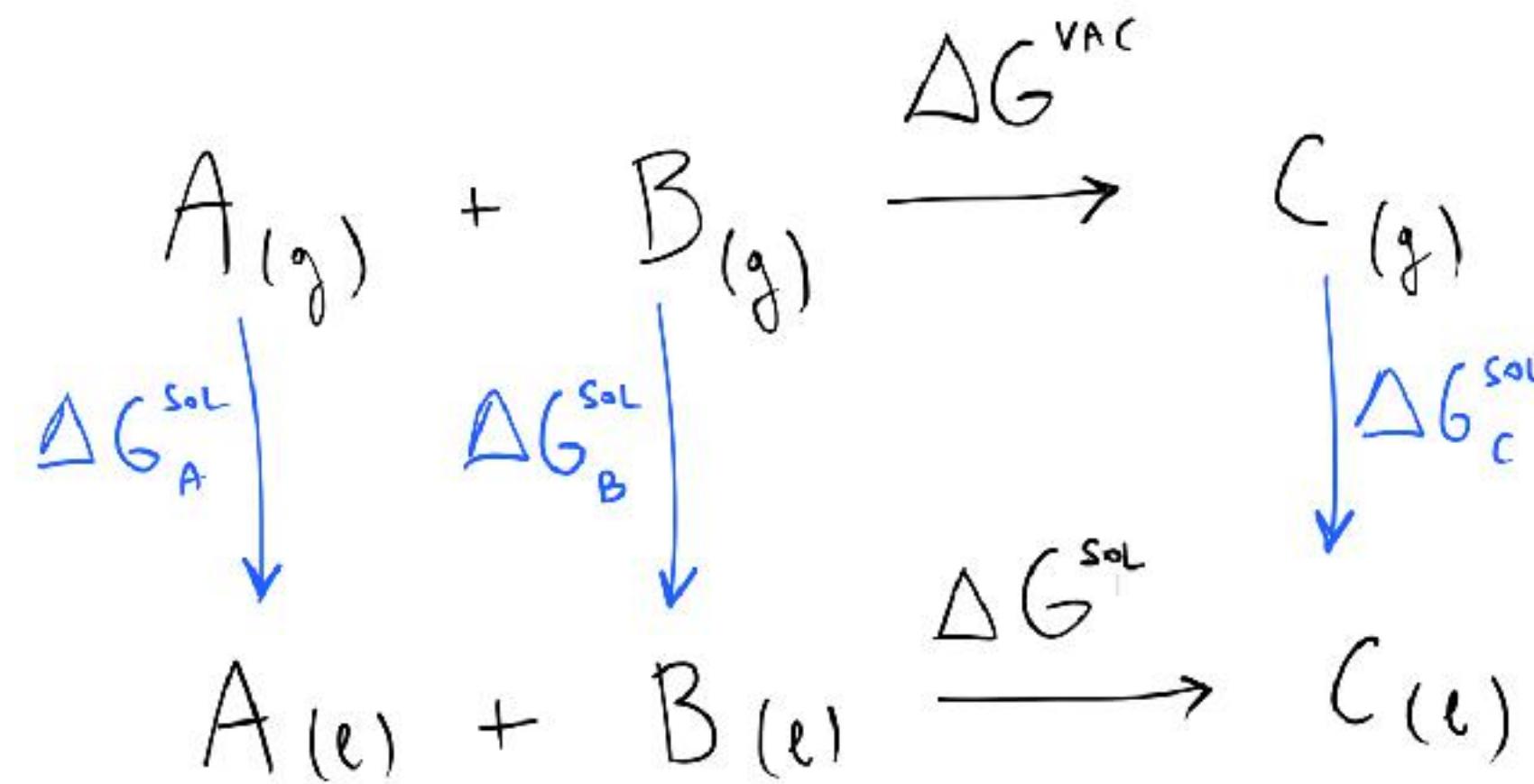
- Dielectric medium
- Electrolyte
- Pressurizing medium
- Surface tension
- Confining medium
- ...

O. Andreussi, I. Dabo, N. Marzari, *J. Chem. Phys.* **136**, 064102 (2012)

Use of Continuum Models

Not Just Solubilities

Reaction free energies in vacuum can be converted into reaction free energies in solution by means of individual solvation free energies.

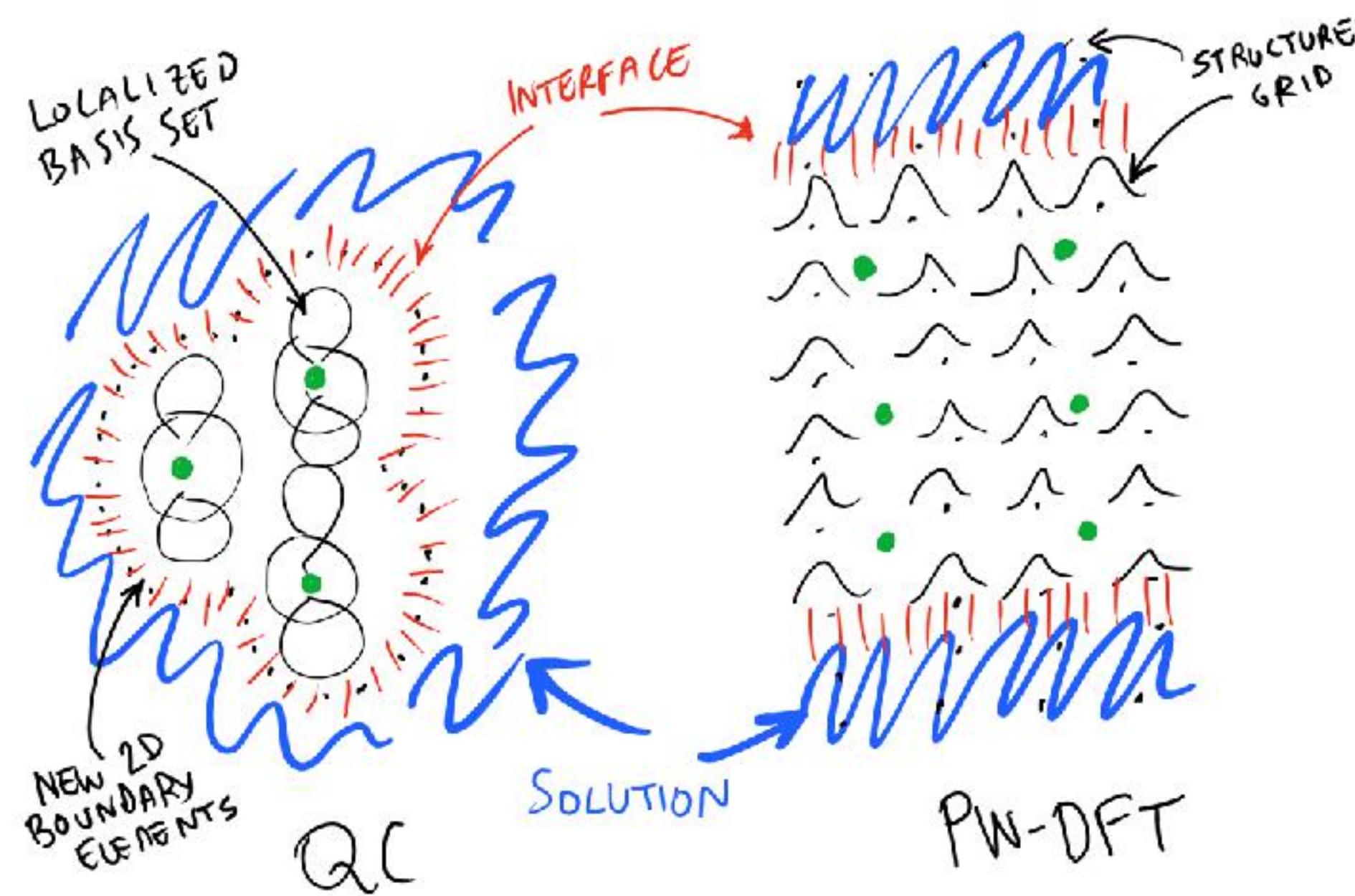


- Environment Effects on Atomic and Electronic Structure
 - Restructuring
 - Band-gap, Optical/IR/Core/Magnetic Spectra
- Solvation Free Energies
 - Solubilities
- Interface Free Energy
- Stability
 - Shape, morphology, decomposition
- Catalytic Activity

More Details on Continuum Models in Condensed Matter

When Numerical Aspects Dictate the Model

Sharp-interface continuum solvation was made convenient by the localized nature of the basis set used in quantum-chemistry codes. In plane-waves DFT, structured grids lend themselves to modeling the continuum problem on the same footing of the electronic one.



- Electrostatics (from Fattebert and Gygi¹)

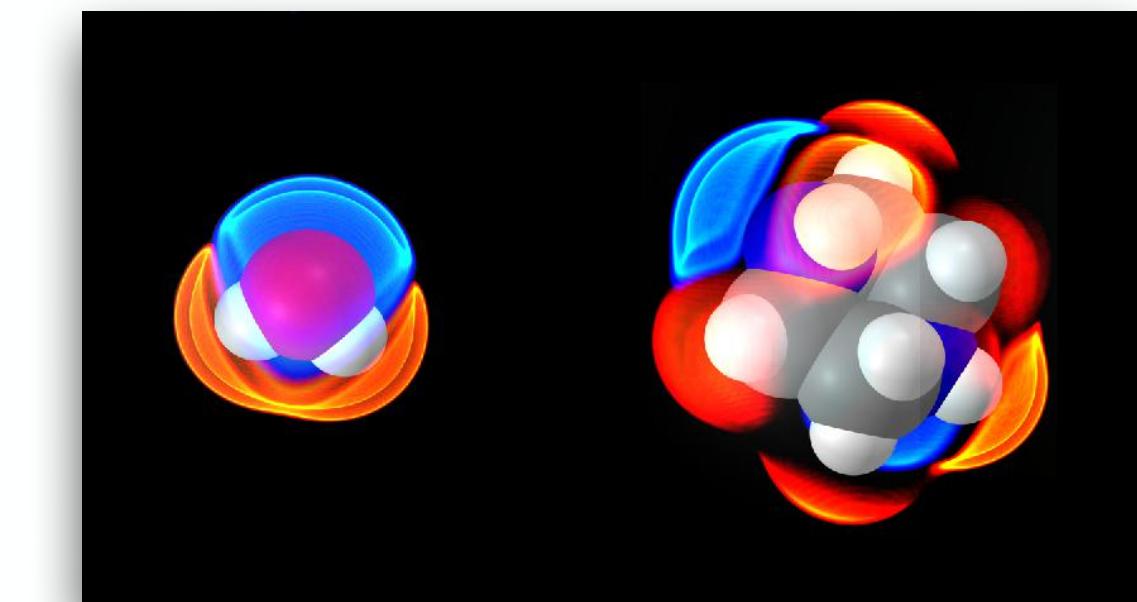
$$F^{el} (\rho^{el}, \{R_a\}) = \int \left(\rho^{el}(\mathbf{r}) + \sum_a \rho_a^{ion}(\mathbf{r} - \mathbf{R}_a) \right) \phi(\mathbf{r}) d\mathbf{r} - \int \frac{1}{8\pi} \epsilon(s(\mathbf{r})) |\nabla \phi(\mathbf{r})|^2 d\mathbf{r},$$

$$\frac{\delta}{\delta \phi(\mathbf{r})} F^{el} = 0 \rightarrow \nabla \cdot \epsilon(\mathbf{r}) \nabla \phi(\mathbf{r}) = -4\pi \rho^{tot}(\mathbf{r}).$$

- Interface function for smooth polarization charges

$$s(\rho^{el}(\mathbf{r})) = \begin{cases} 1 & \rho > \rho^{max} \\ s(\log(\rho^{el}(\mathbf{r}))) & \rho < \rho^{min} \\ 0 & \end{cases}$$

$$\epsilon(\mathbf{r}) \equiv \exp(\ln \epsilon_0 (1 - s(\mathbf{r})))$$



- Solved using iterative gradient descent (preconditioned CG)

1. J.-L. Fattebert and F. Gygi, *J. Comput. Chem.* **23**, 662, (2002) and *Int. J. Quantum Chem.* **93**, 139 (2003)

More Details on Continuum Models in Condensed Matter

- Non-Electrostatic
 - Surface and volume (still as functionals of interface function)

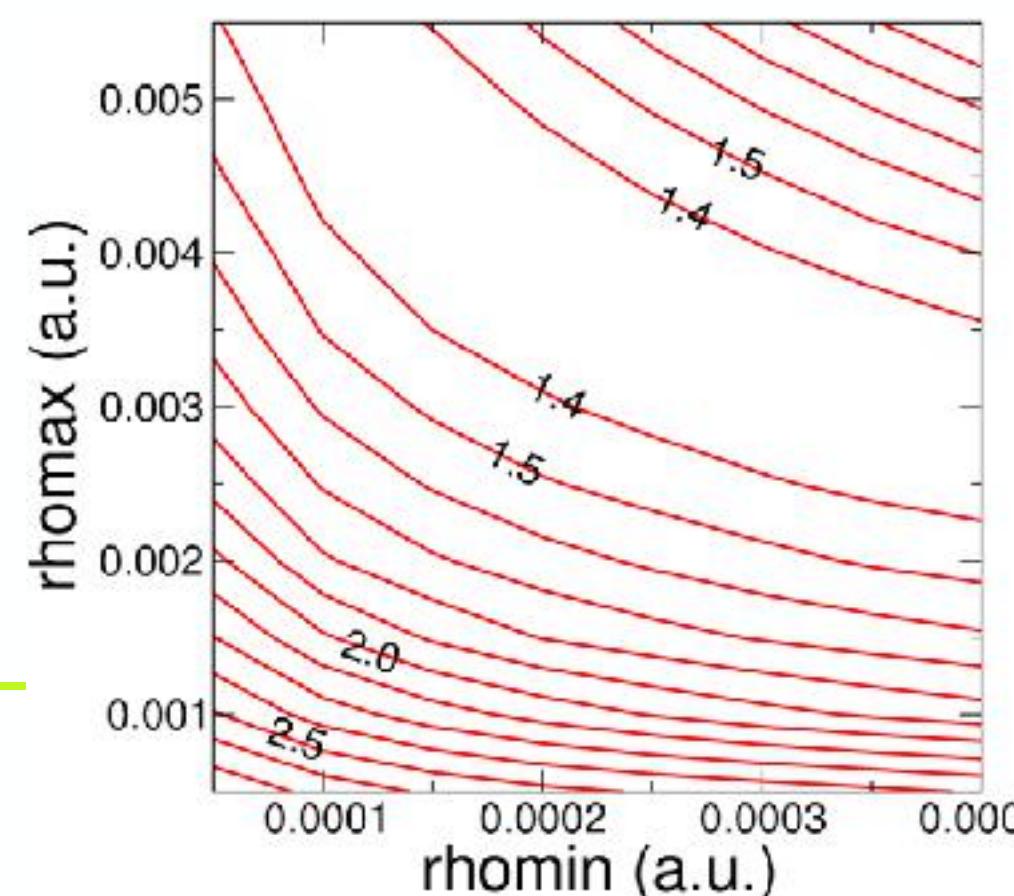
$$\Delta G^{non-el} = (\alpha + \gamma) S[s] + \beta V[s]$$

$$S[s(\mathbf{r})] = \int |\nabla s(\mathbf{r})| d\mathbf{r}$$

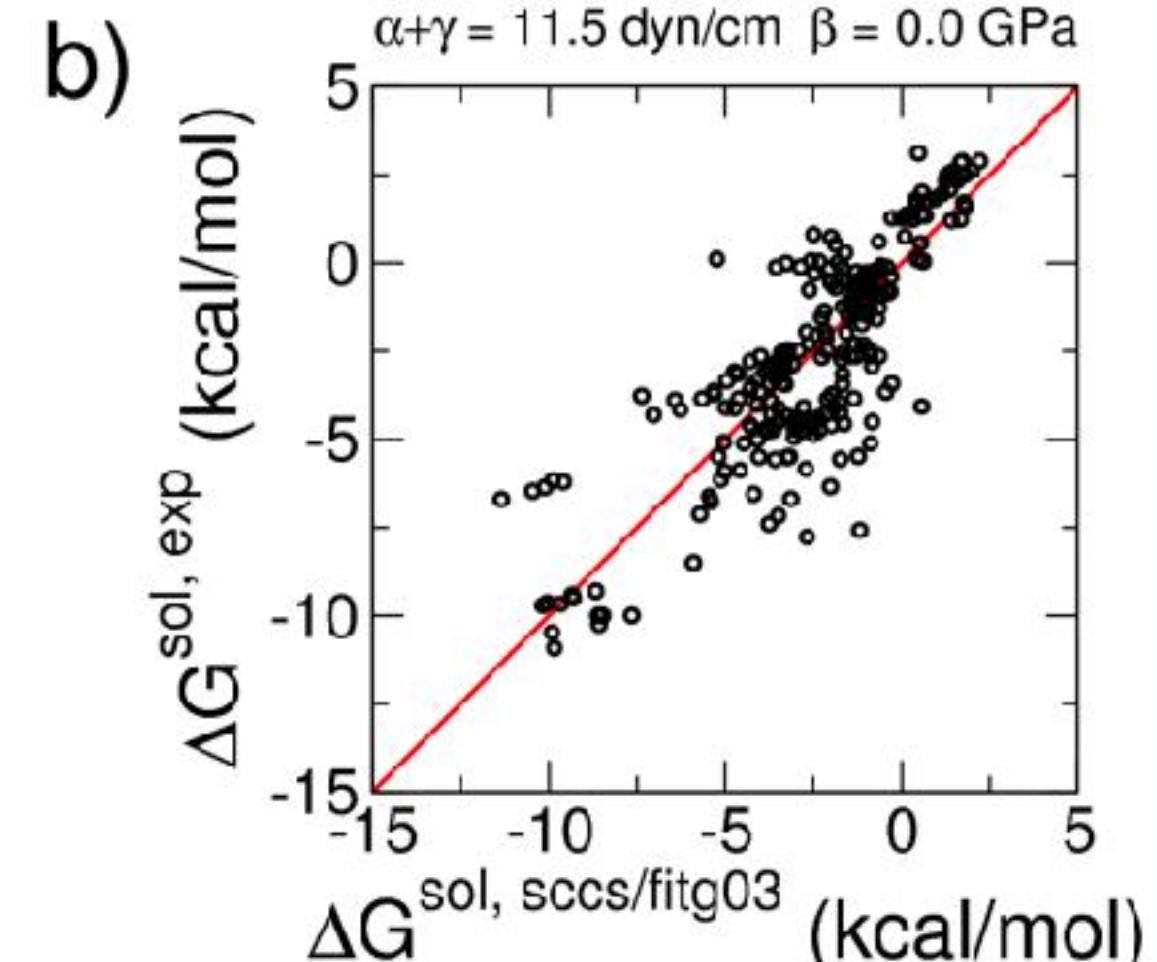
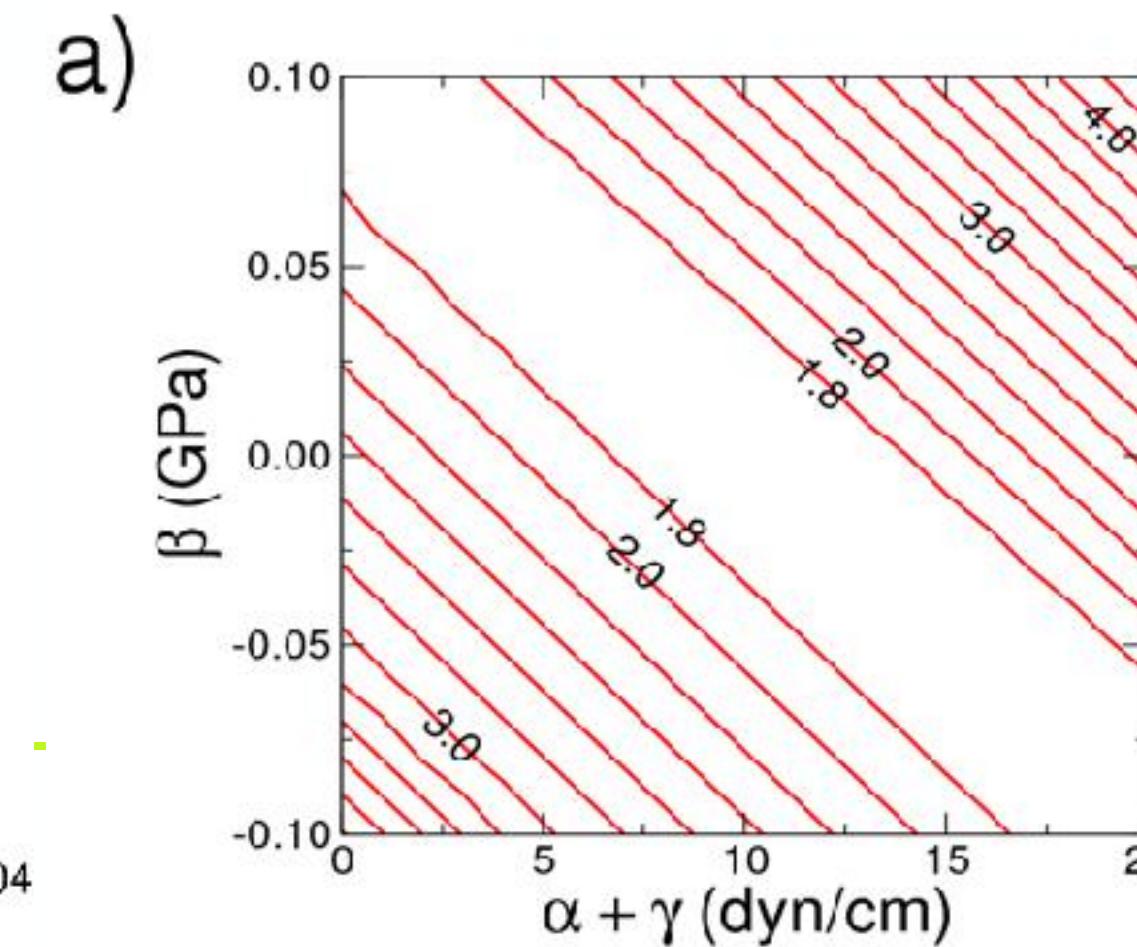
$$\frac{\delta S}{\delta s}(\mathbf{r}) = \nabla \cdot \left(\frac{\nabla s(\mathbf{r})}{|\nabla s(\mathbf{r})|} \right)$$

$$V[s(\mathbf{r})] = \int s(\mathbf{r}) d\mathbf{r}$$

$$\frac{\delta V}{\delta s}(\mathbf{r}) = 1$$



- 3-5 Parameters
 - 2 cavity parameters (2 threshold of the electronic density or 1 threshold and 1 spread)
 - Dielectric permittivity (usually from experiments)
 - Surface and volume coefficients

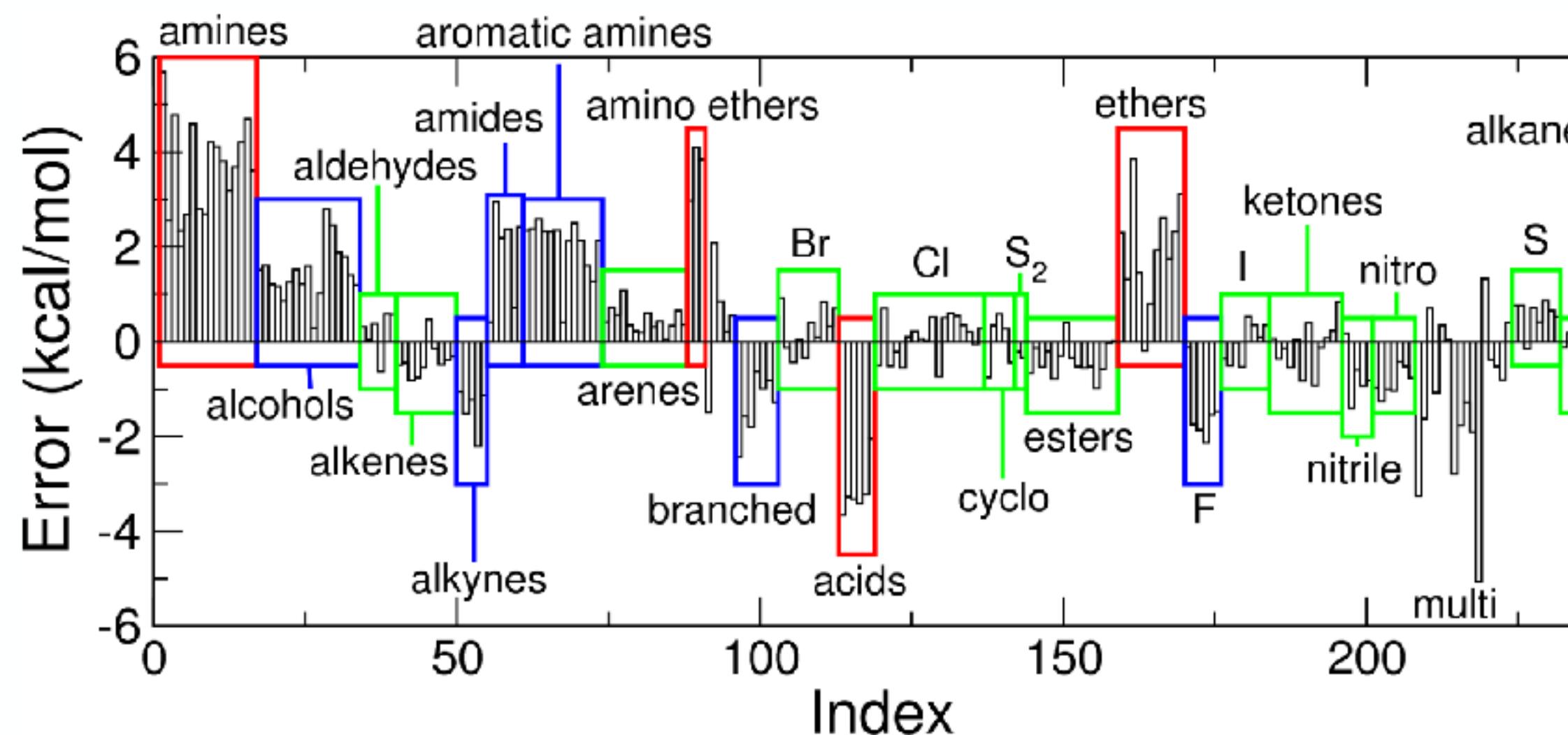


Solvation Models Combining Ingredients and Parametrization

- Self-consistent continuum solvation (SCCS)
- Soft-sphere continuum solvation (SSCS)
- With 2-3 parameters a MAE of ~1.1-1.2 kcal/mol for aqueous solvation of neutrals

Accuracy vs. Functional Groups

Errors with respect to the experiments in aqueous solvation free energies for neutral organic molecules



O. Andreussi, I. Dabo, N. Marzari, *J. Chem. Phys.* **136**, 064102 (2012)

Tuning Smooth-Interfaces Continuum Models

Table 2. MAEs in Aqueous Solvation Free Energies (kcal/mol) for Several Solvation Models (MAEs from ref 38)^a

method	neutrals	cations	anions
soft-sphere ^b	1.12	2.13	2.96
sccs ²³	1.14 ^c	2.27 ^d	5.54 ^d
SM8 ³⁸	0.55	2.70	3.70
SM12 ³⁹	0.59	2.90	2.90
PB/Jaguar ³⁸	0.86	3.10	4.80
IEF-PCM ³⁸	1.18	3.70	5.50
C-PCM/GAMESS ³⁸	1.57	7.70	8.90
GCOSMO/NWChem ³⁸	8.17	11.00	7.00

^aModel benchmarks refer to same set of 274 neutrals, 60 anions, and 52 cations of the Minnesota Solvation Database, version 2012.²⁸

^bParametrization of row 2 Table 1. ^cThe sccs implemented in BigDFT.

^dThe sccs for ions corresponds to a reduced set of 55 anions and 51 cations²³ of the same Minnesota data set.

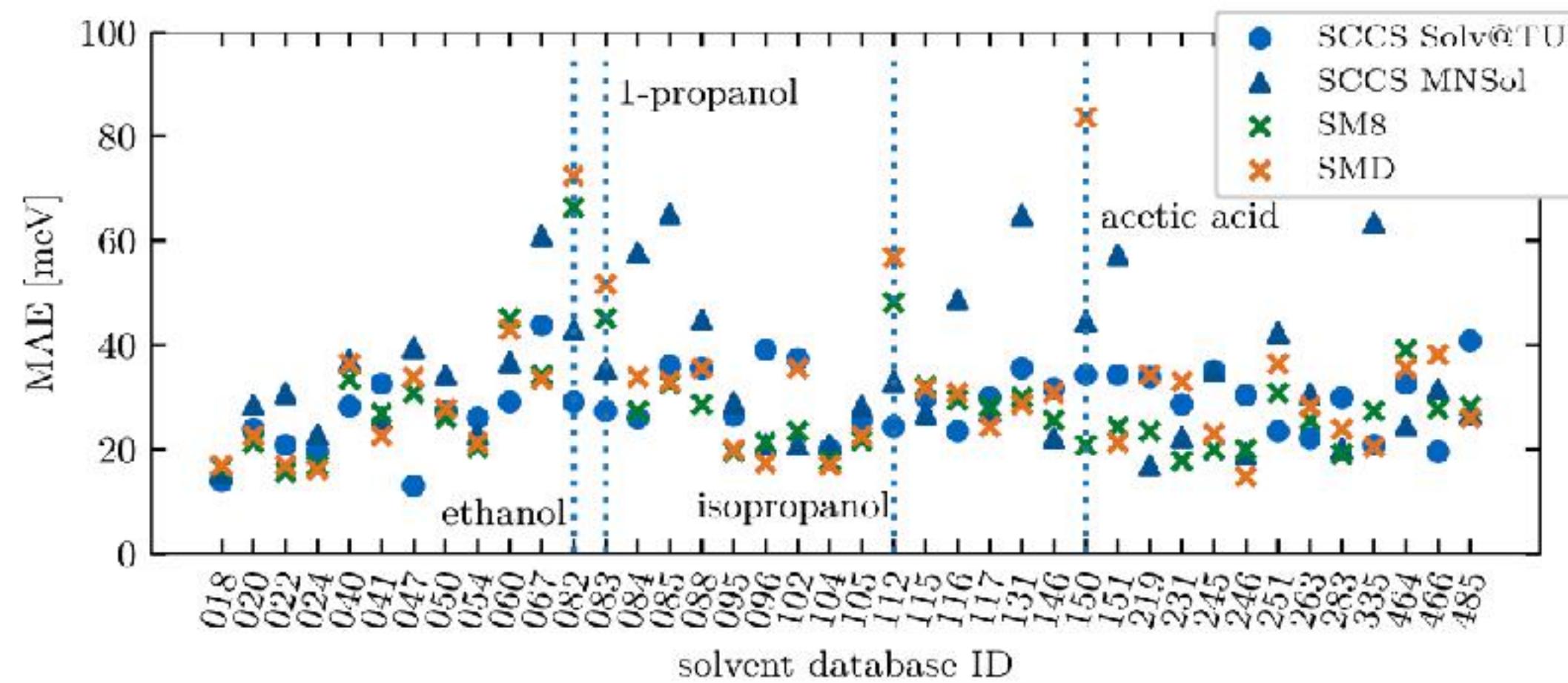
Giuseppe Fisicaro, et al. *J. Chem. Theory Comput.* **13**, 3829 (2017)

Beyond Aqueous Solvation Neutral Liquids

- Self-consistent continuum solvation (SCCS)
 - 76 non-aqueous solvents
 - Average non-aqueous MAE 0.839 kcal/mol
- Soft-sphere continuum solvation (SSCS)
 - Two experimental databases (MNSol Solv@TUM)
 - Average non-aqueous MAE 0.87 kcal/mol

Single-Parameter Models

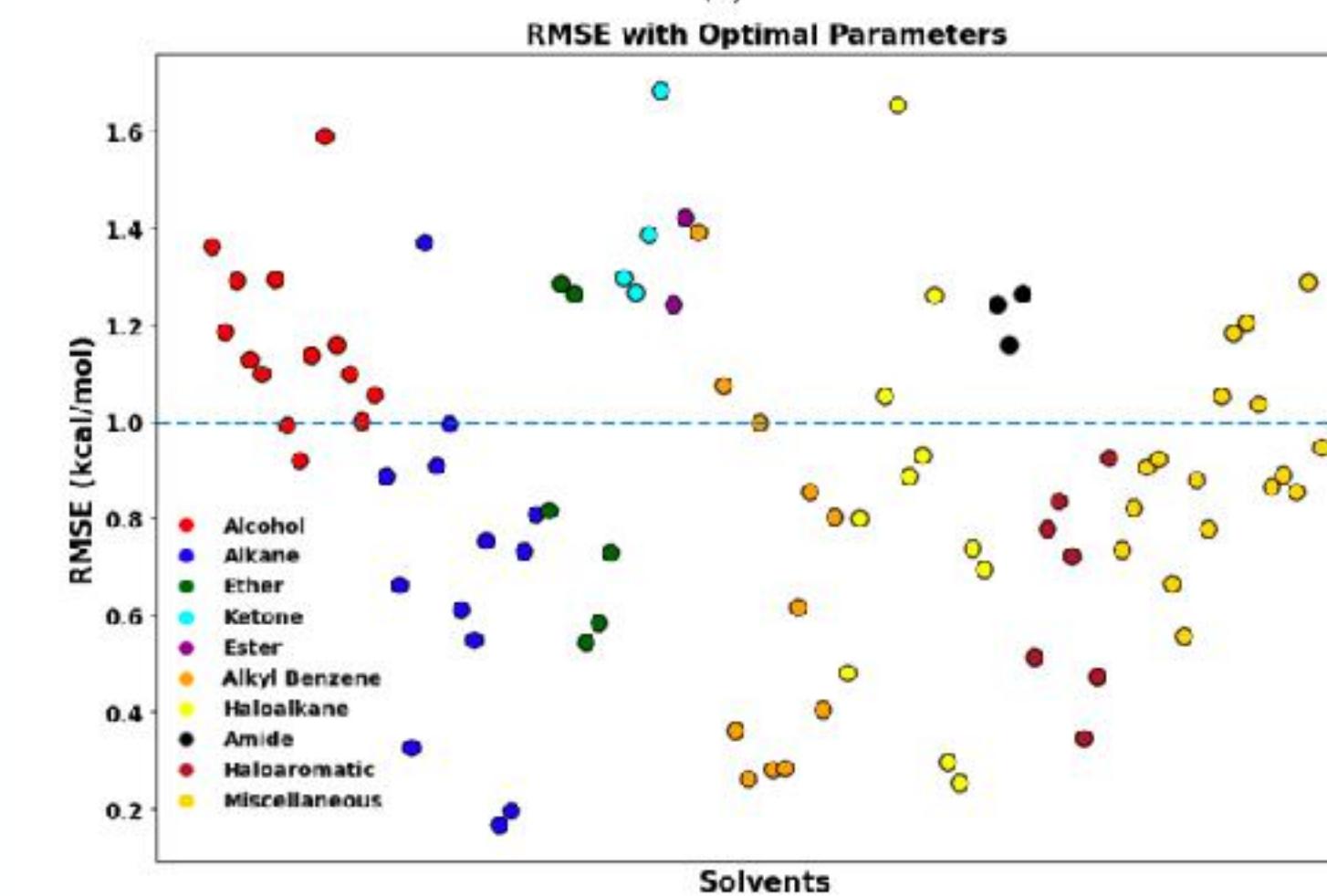
Cavity parameters appear to be transferable among solvents, so empirical tuning can focus on a single non-electrostatic parameter



C. Hille et al., *J. Chem. Phys.* **150**, 041710 (2019)

Single-Parameter Models

Using automated workflows we can tune a single non-electrostatic parameter to reproduce experimental databases of solvation free energies



P. Si, A. Jayanth, O. Andreussi, *J. Comput. Chem.* (2024)

Beyond Aqueous Solvation Neutral Liquids

Experimental ← **Fitted but strongly related to**

$$\Delta G^{\text{sol}} = \Delta G^{\text{el}}[\epsilon(s)] + \gamma S(s) + \beta V(s),$$

Transferable

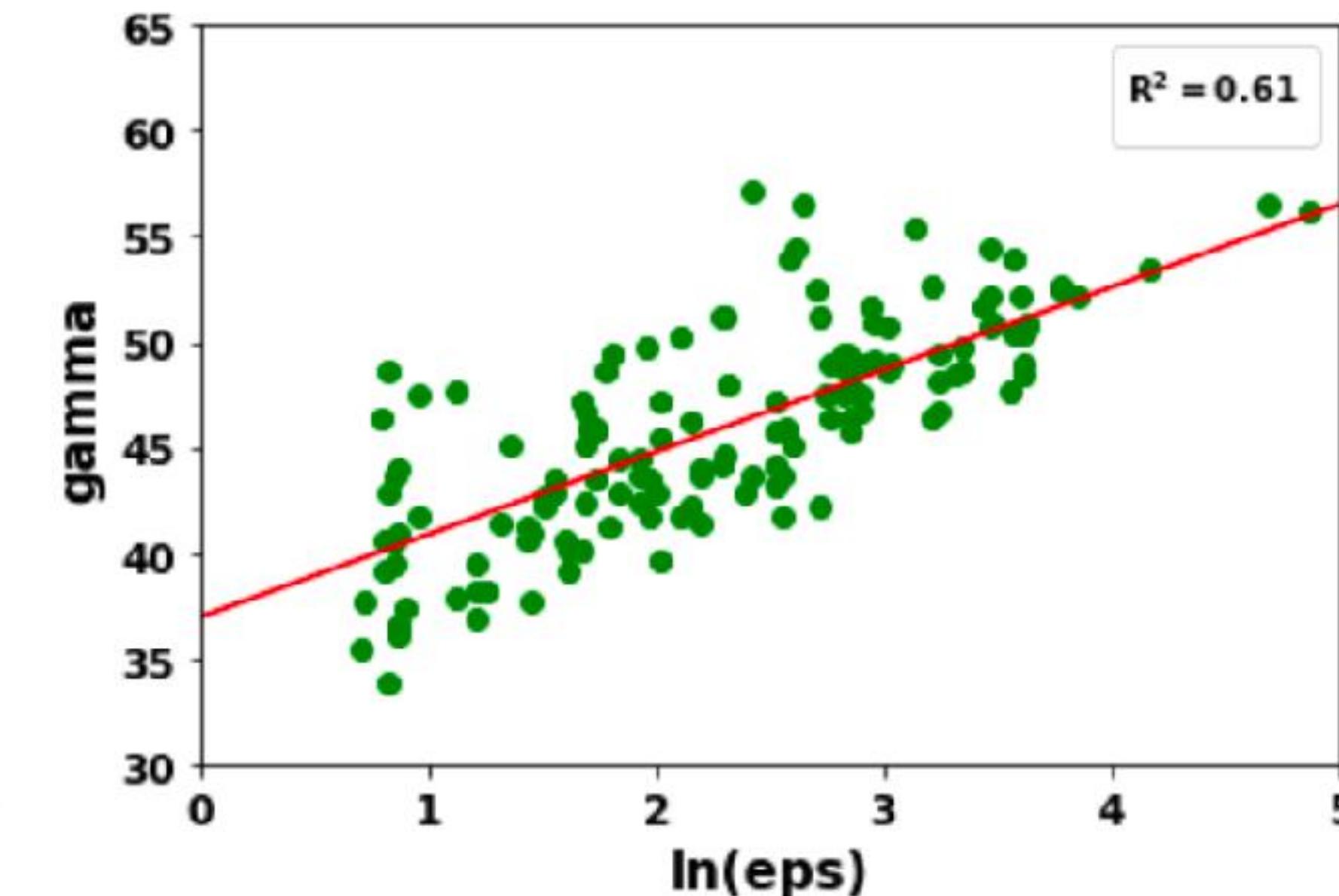
$$s_{\{\xi\}}(\{\mathbf{R}_a\}; \mathbf{r}) = 1 - \prod_a h_{\{\xi_a\}}(|\mathbf{r} - \mathbf{R}_a|)$$
$$\{\xi\} = \begin{cases} \{R_a^{vdW}\} & \text{sphere radii} \\ \alpha & \text{scaling factor} \\ \Delta & \text{softness} \end{cases}$$

Numerical

$$\text{RMSE}(\alpha, \beta, \gamma) = \sqrt{\left(\frac{1}{N} \sum_{i=1}^N (\Delta G_i^{\text{sol,pred}}(\alpha, \beta, \gamma) - \Delta G_i^{\text{sol,exp}})^2 \right)}.$$

No Tunable-Parameters Models

Comparing the optimal values of gamma vs the log of the dielectric constant reveals a **universal** solvent model that only requires the bulk dielectric permittivity



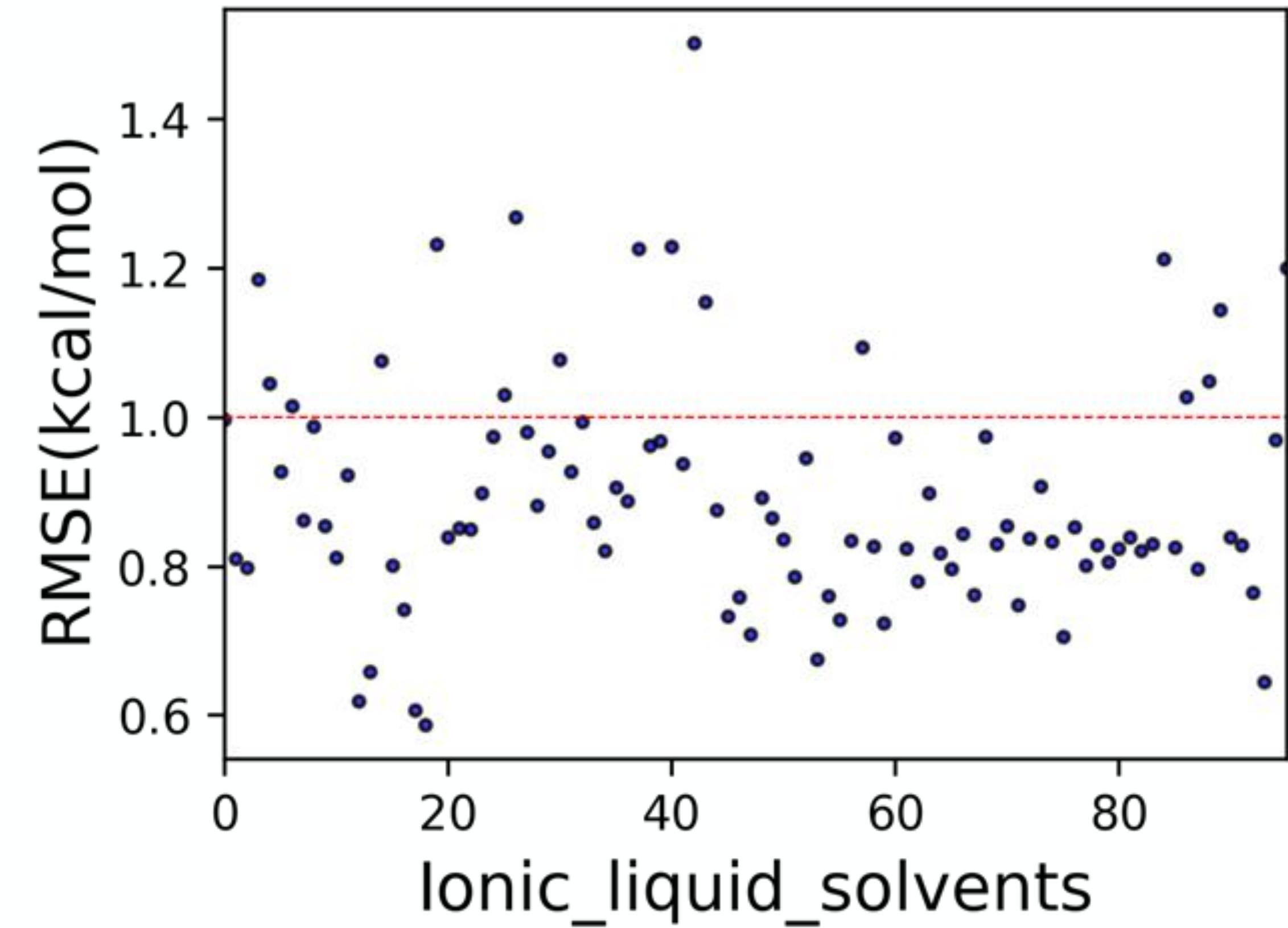
C. Hille et al., *J. Chem. Phys.* **150**, 041710 (2019)

P. Si, A. Jayanth, O. Andreussi, *J. Comput. Chem.* (2024)

Beyond Aqueous Solvation Room-Temperature Ionic Liquids

$$\Delta G_{\text{sol}} = \Delta G_{\text{el}} (C_{\text{ion}} + \epsilon(r)) + \gamma S + \beta V$$

- Soft-sphere continuum solvation (SSCS)
 - A large experimental databases on **neutral solutes** by Bill Acree (UNT)
 - One additional parameter (ionic concentration)
 - Determined from the RTIL density (that can be computed from the quantum volumes)
 - Average RMSE below 1 kcal/mol

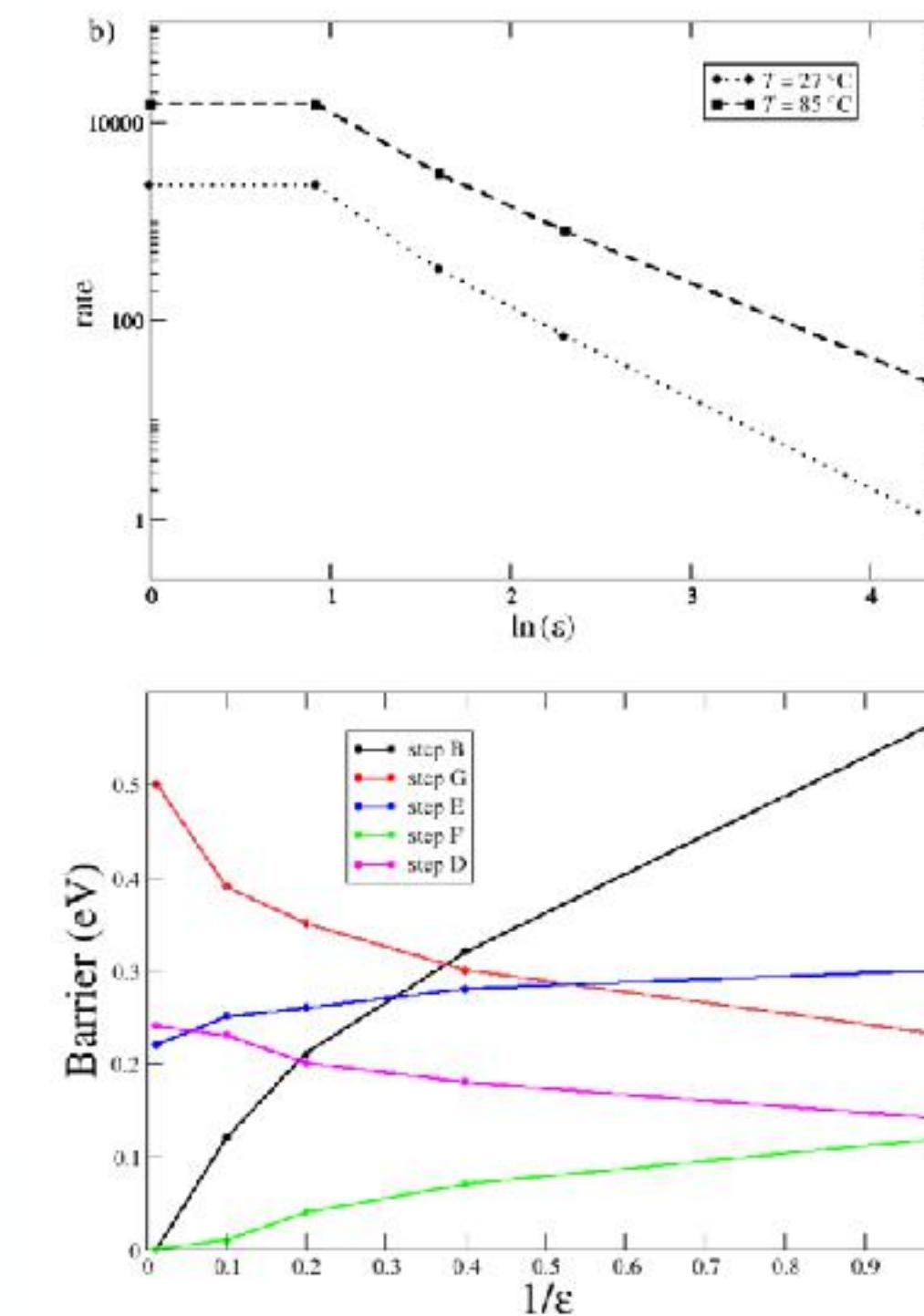
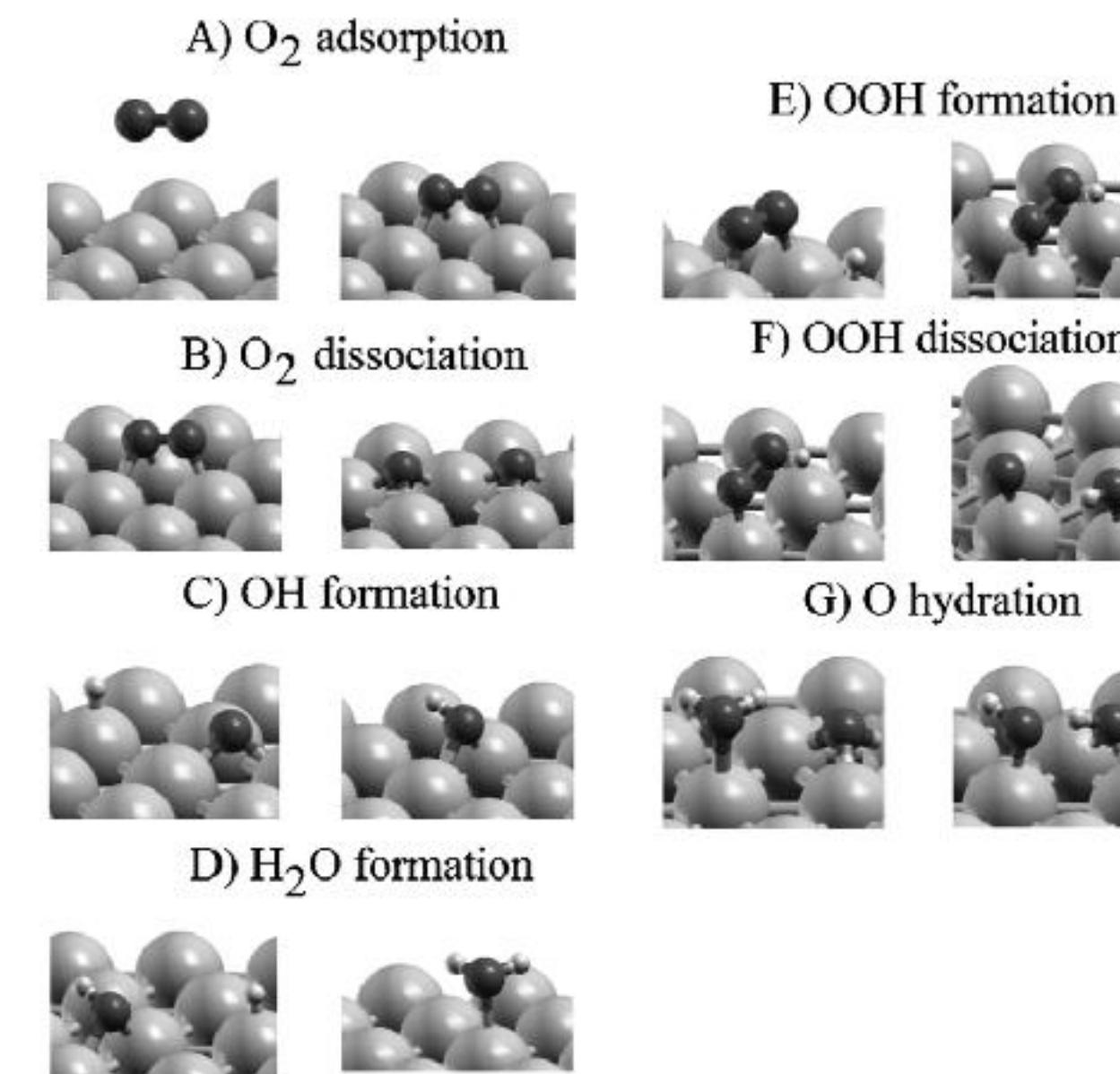


Towards the Computational Design of Solvents

1. Identify one (or more) chemical process(es)
2. Optimize over all possible continuum solvents (search over one or two parameters)
3. Identify the closest solvents that match the continuum parameter(s)
4. Refine predictions with hybrid approaches

Playing with the Model

ORR on Pt can be enhanced by orders of magnitude by changing the dielectric permittivity of the embedding electrolyte

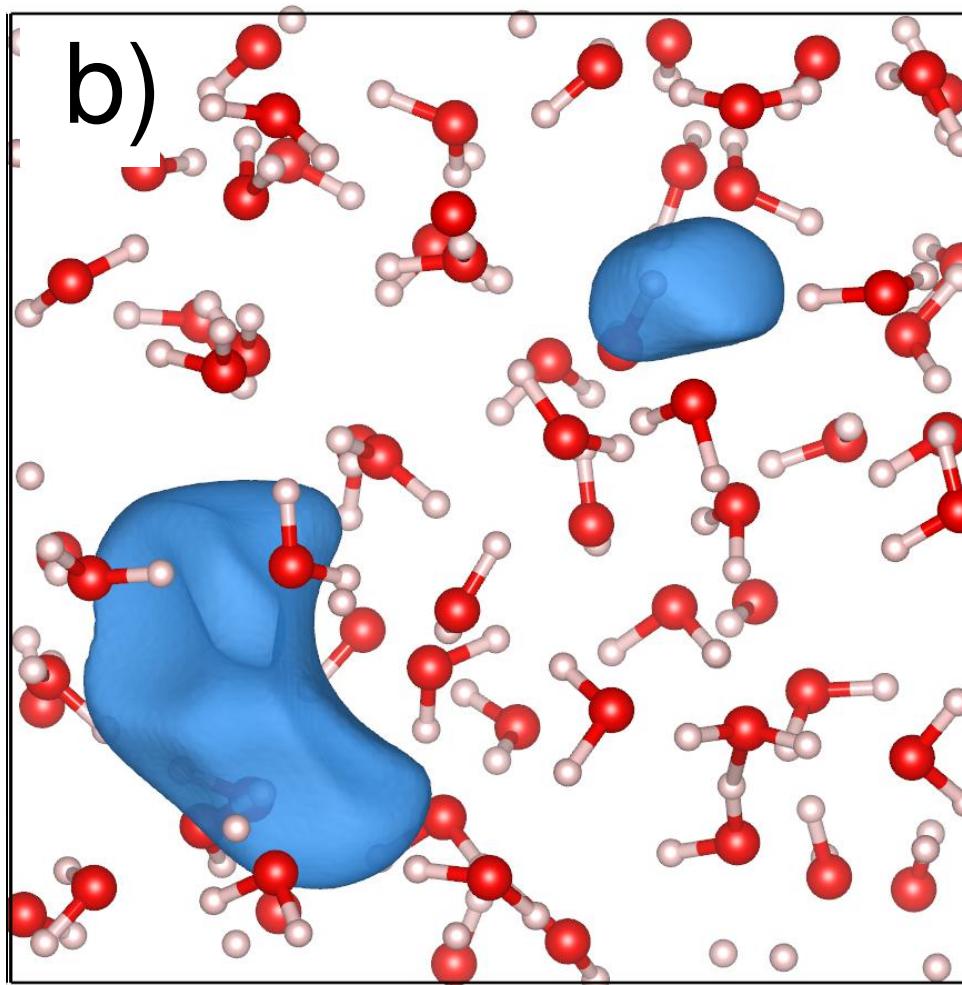
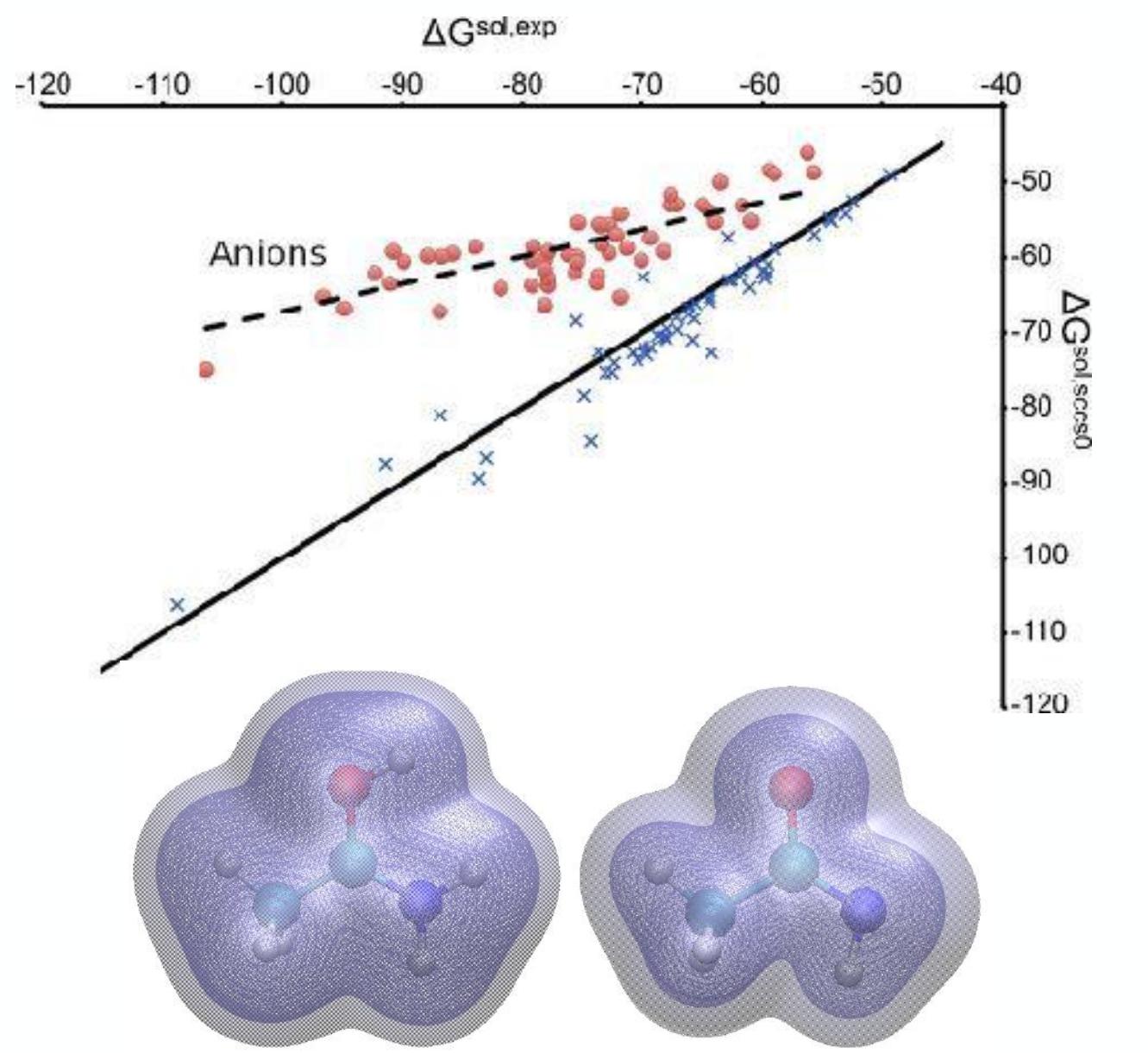
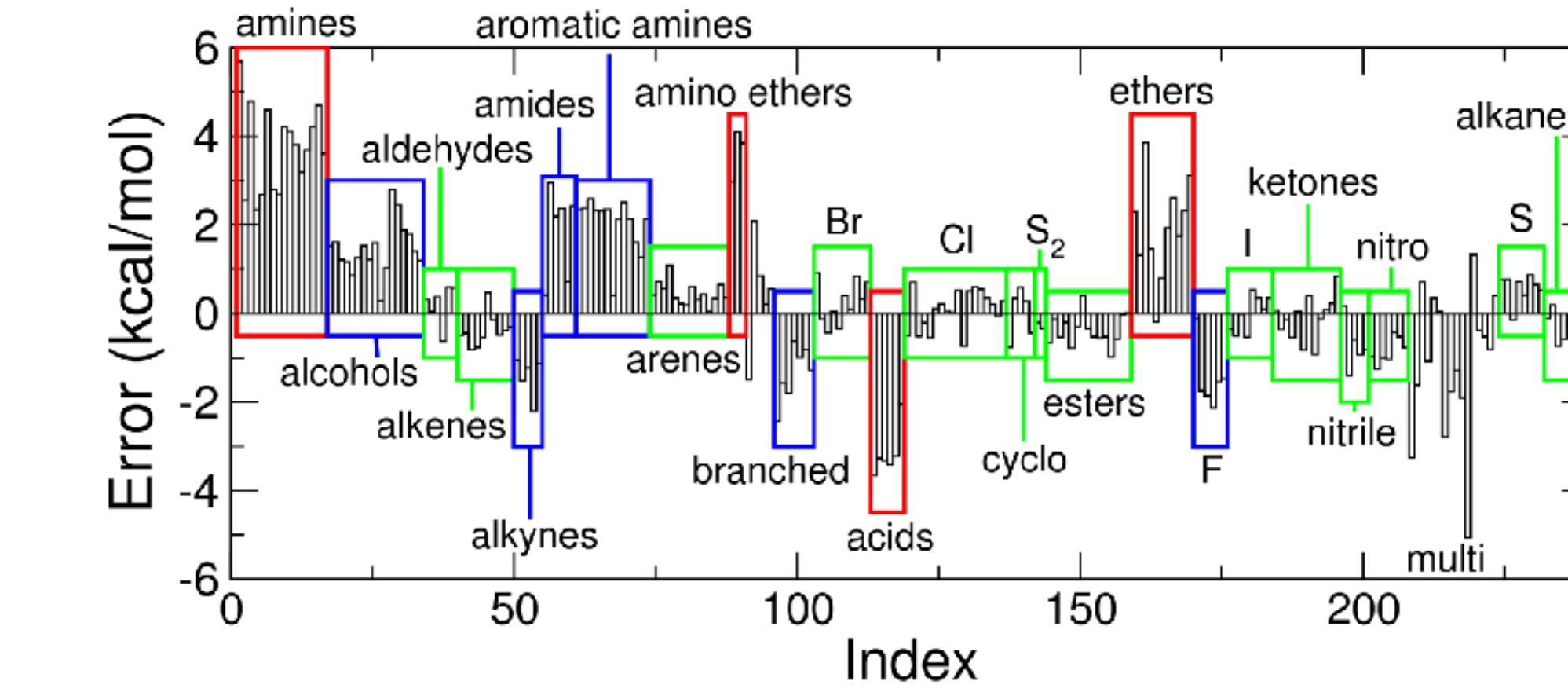


Fortunelli et al. *Angew. Chem. Int. Ed.*, **53**, 6669 (2014)

What is Under the Carpet

Challenges

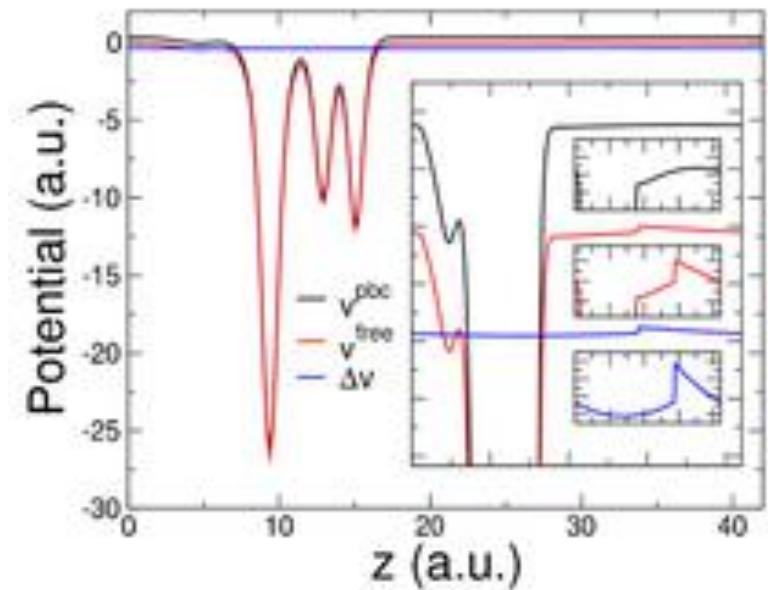
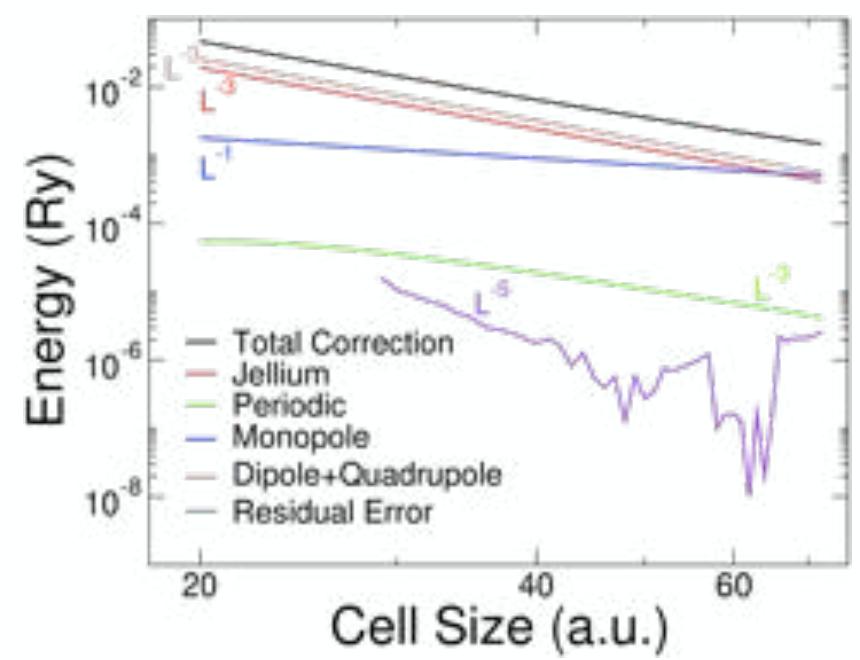
- Specific interaction
- Charged systems (anions)
- Spurious continuum in complex disordered systems



More Things to Adjust in Continuum Models in Condensed Matter

Periodic Boundaries

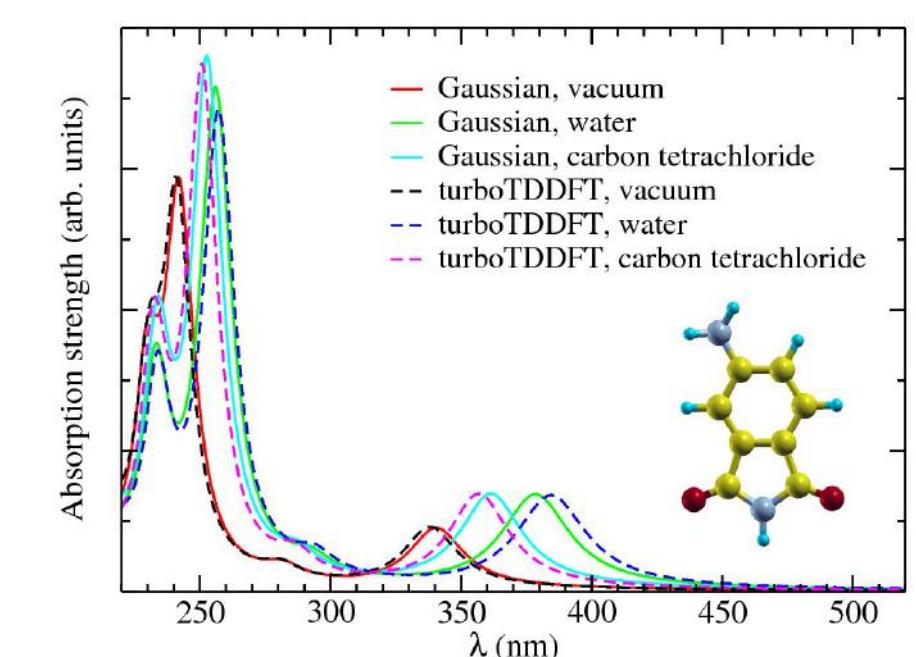
Solvent implies not full PBCs



O. Andreussi and N. Marzari,
PRB **90**, 245101 (2014)

Response Properties

Optical (TDDFT), vibrational, magnetic, core-level



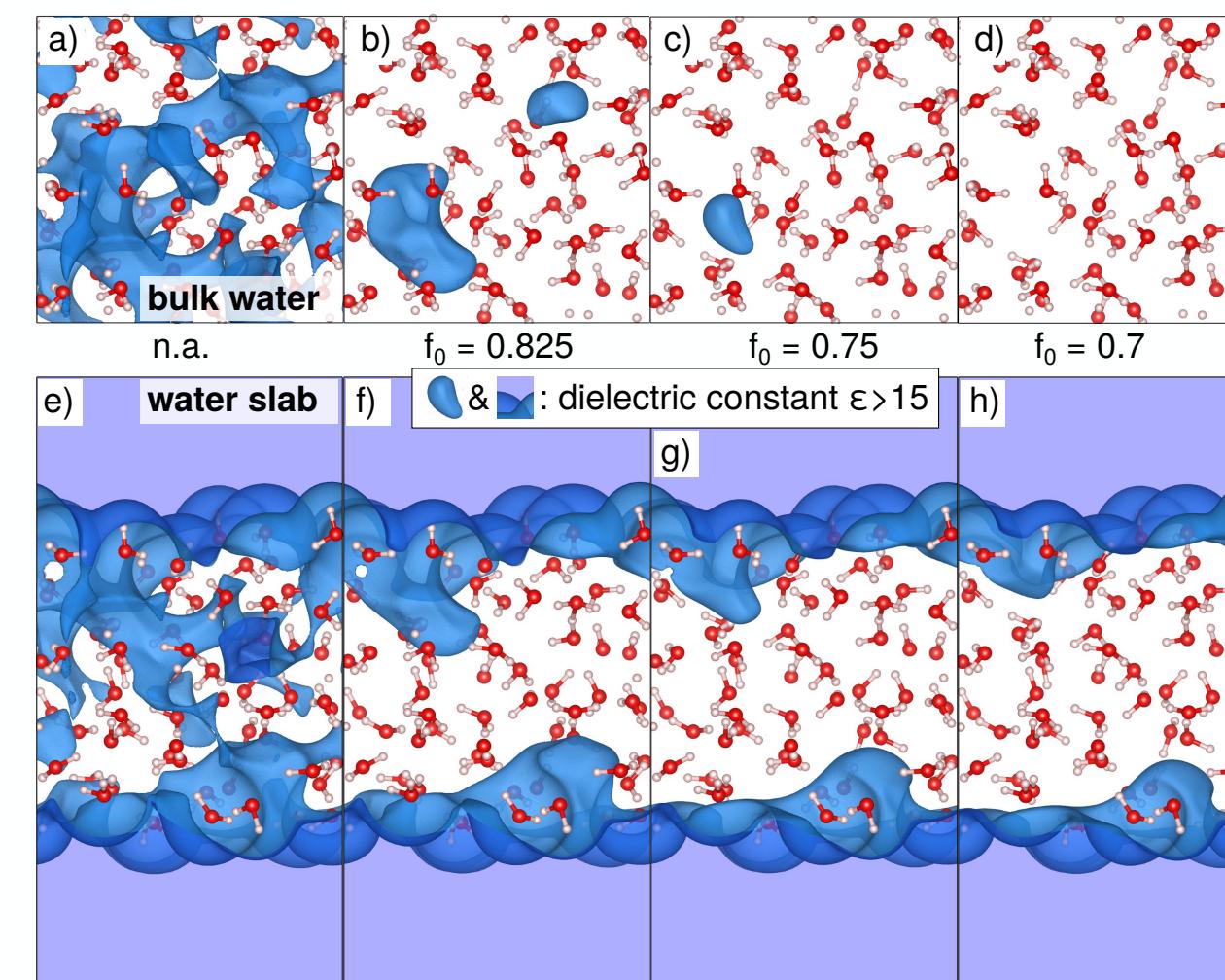
I. Timrov et al, *J. Chem. Phys.* **142**, 034111 (2015)



Y. Katayama et al, *J. Phys. Chem. C* **123** (10), 5951 (2019)

Spurious Continuum

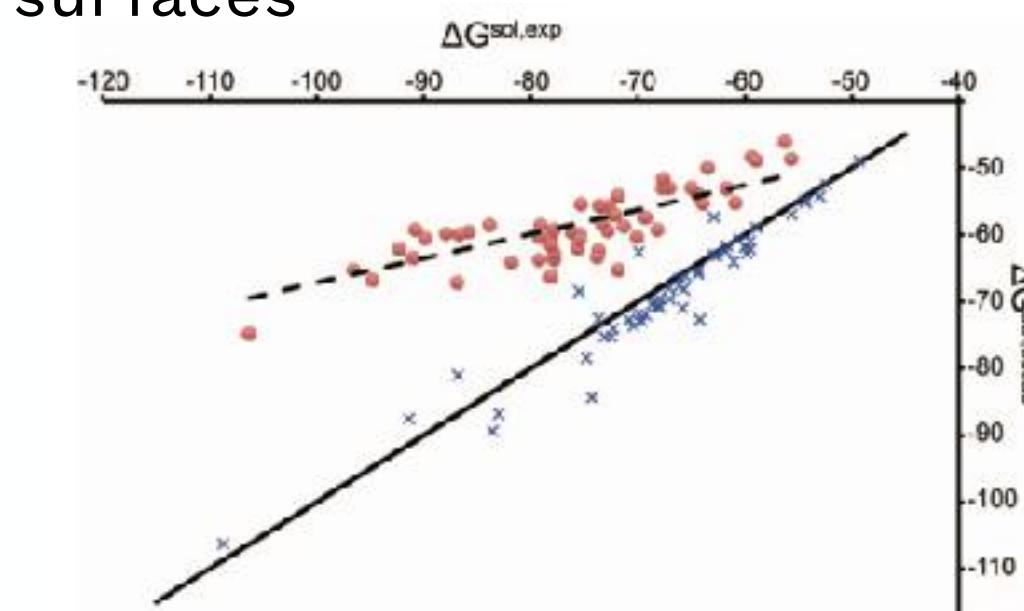
Non-local corrections to interface function to avoid unphysical regions



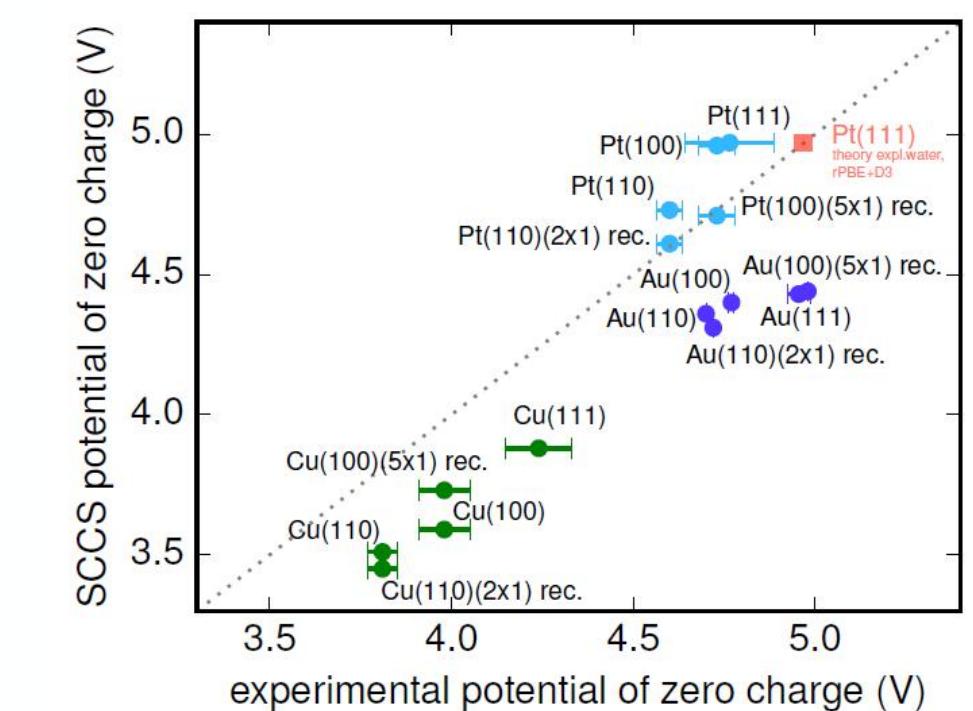
O. Andreussi et al, *J. Chem. Theory Comput.* **15** (3) 1996 (2019)

Parametrization and Benchmarking

Charged solutes and noble metal surfaces



C. Dupont et al, *J. Chem. Phys.* **139**, 214110 (2013)

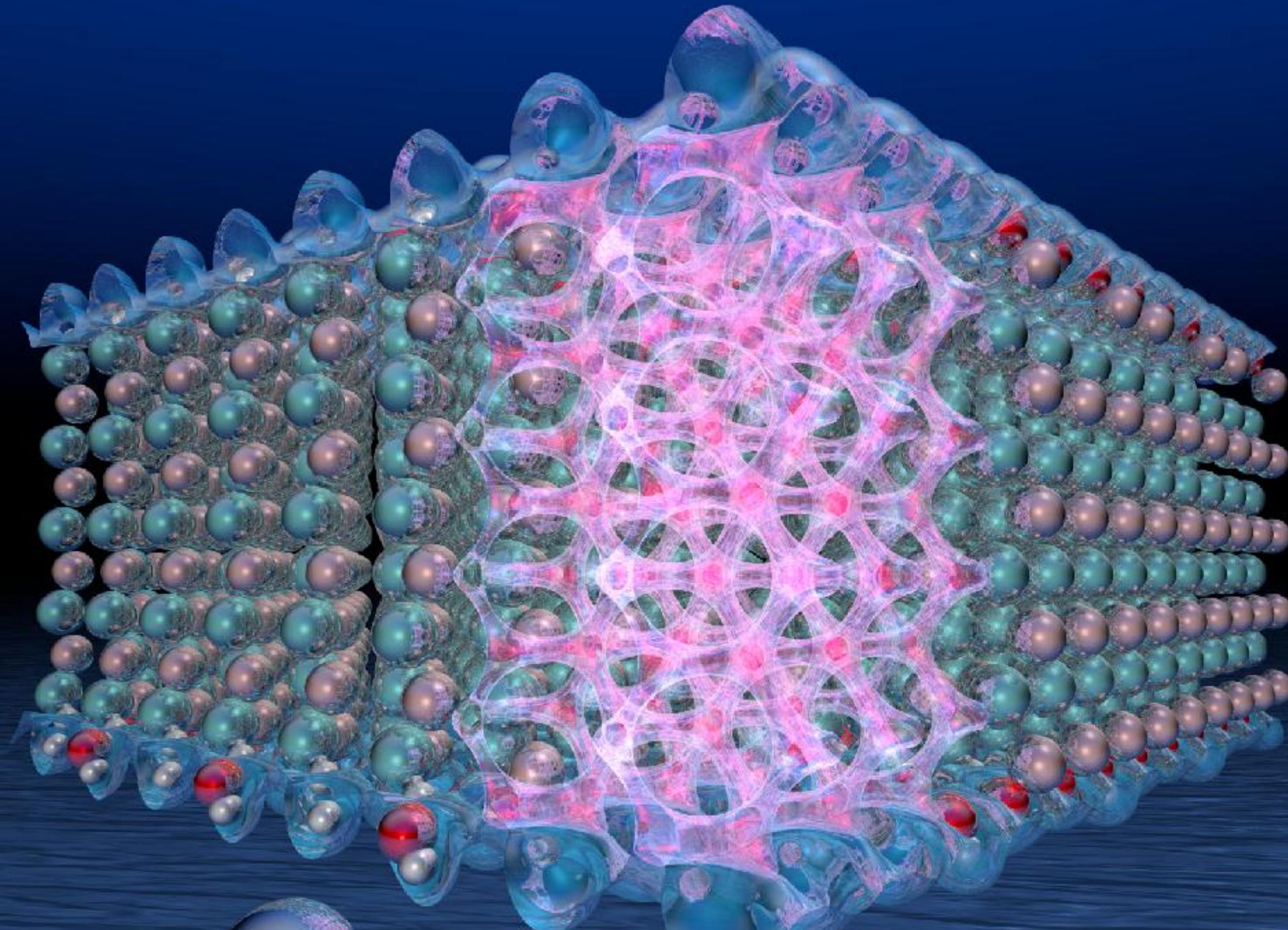


N. Hörmann, et al. *J. Chem. Phys.* **150**, 041730 (2019)

What About Materials?

Surfaces Can Be Hard

- Voids?
- Parametrization?
- Periodic Boundary Conditions?
- What about bias potentials?
- Are specific interactions important?



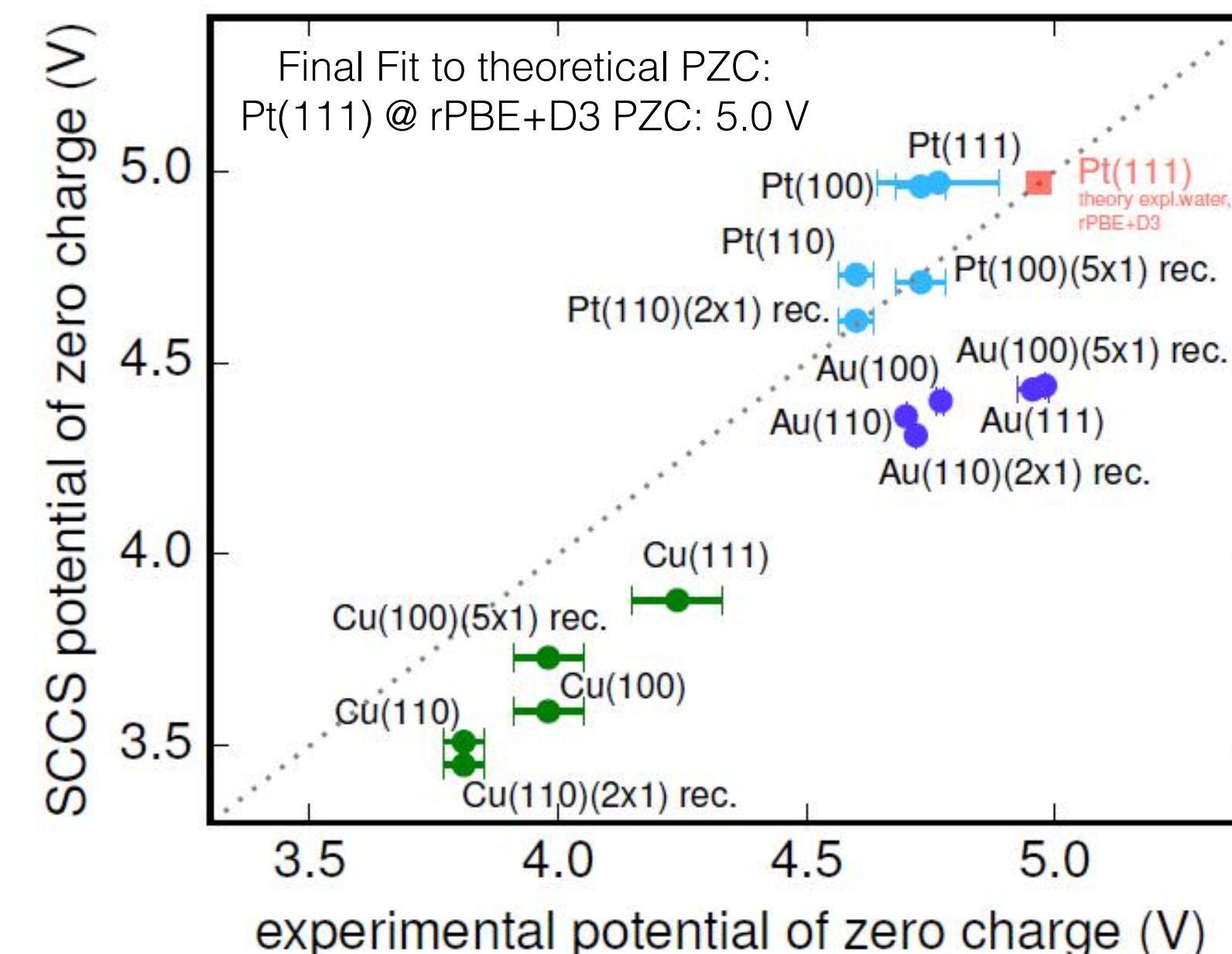
Parametrization on What?

Electrochemical Interfaces vs. Organic Molecules

- Lack of reliable and accurate experimental data on solvation effects on non-organic elements and materials
- Possible sources of parameterization:
 - Contact angles
 - Potential of zero charge
 - Differential capacitance

Electrochemical SCCS vs. Experiments

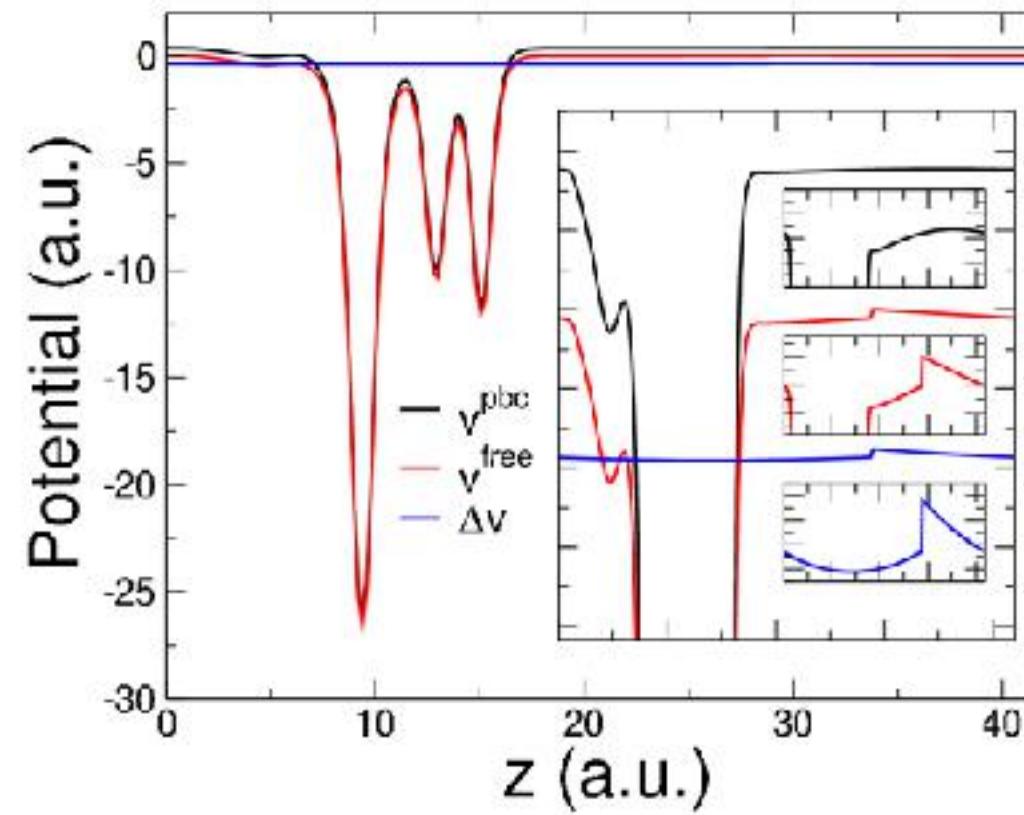
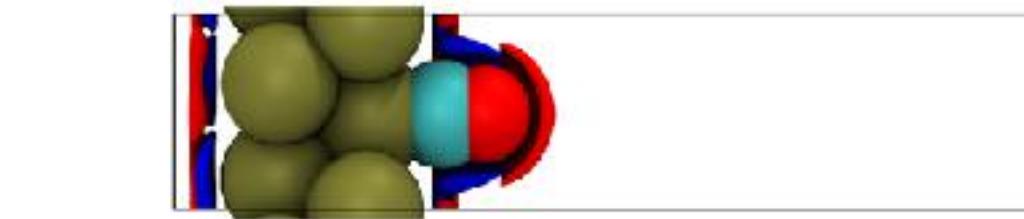
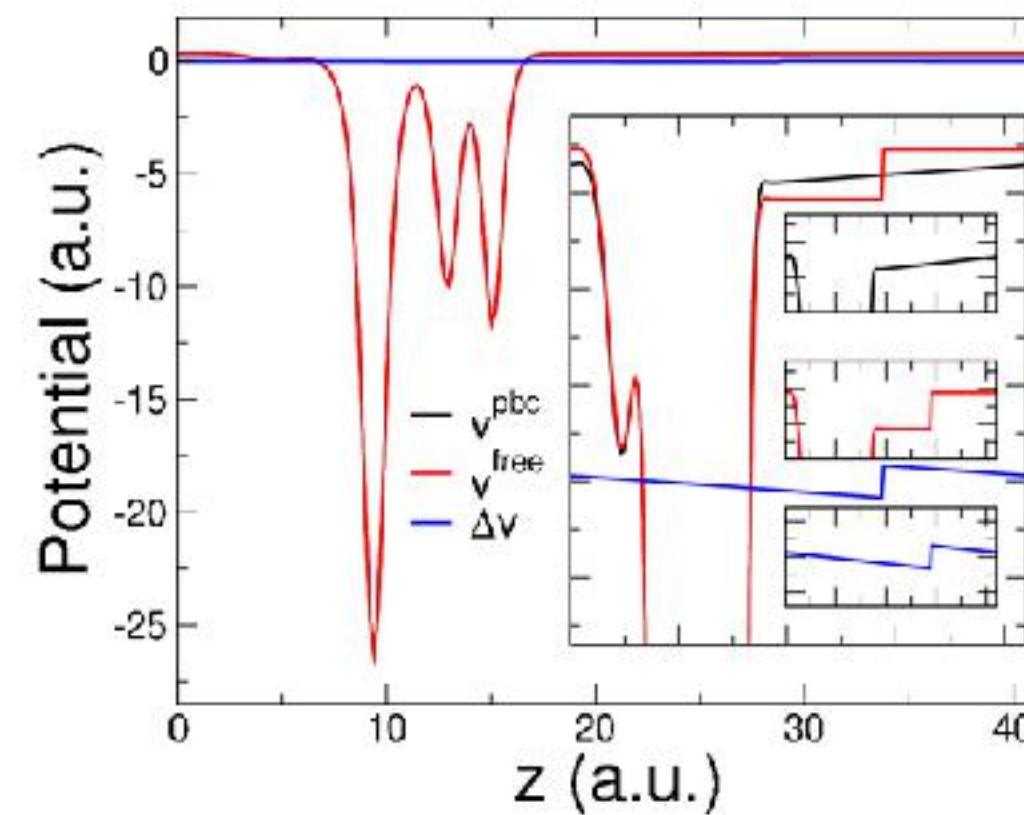
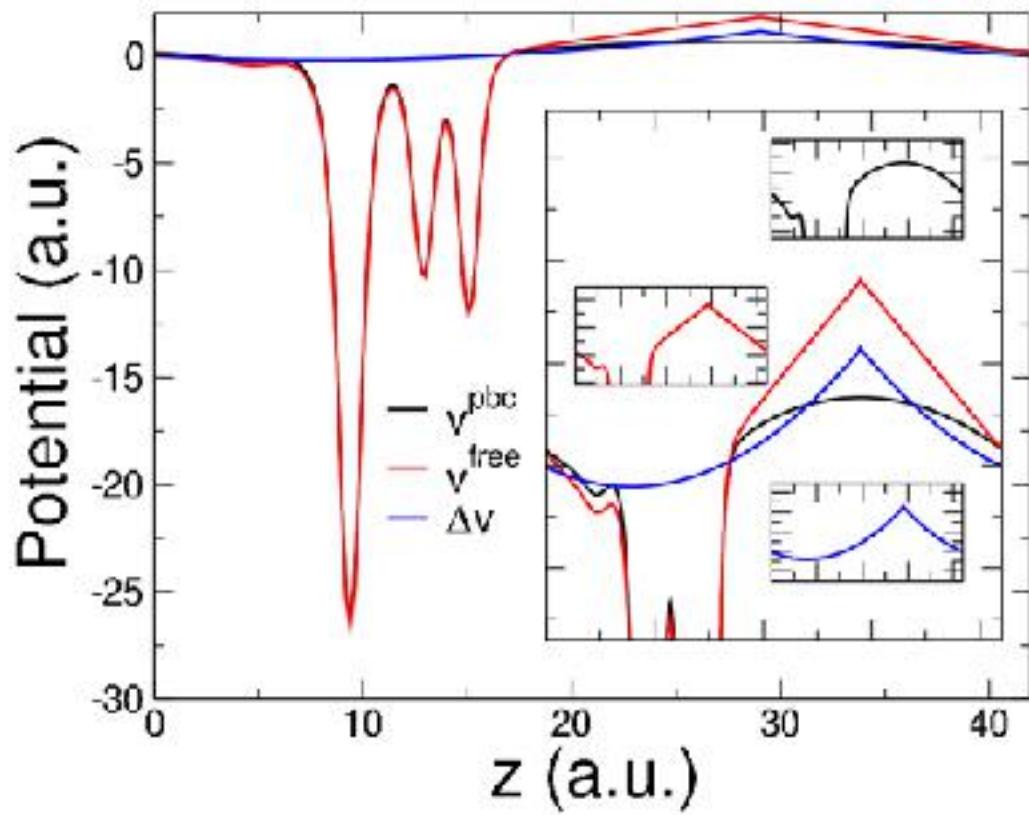
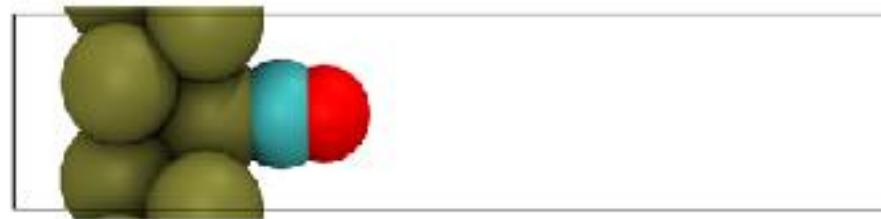
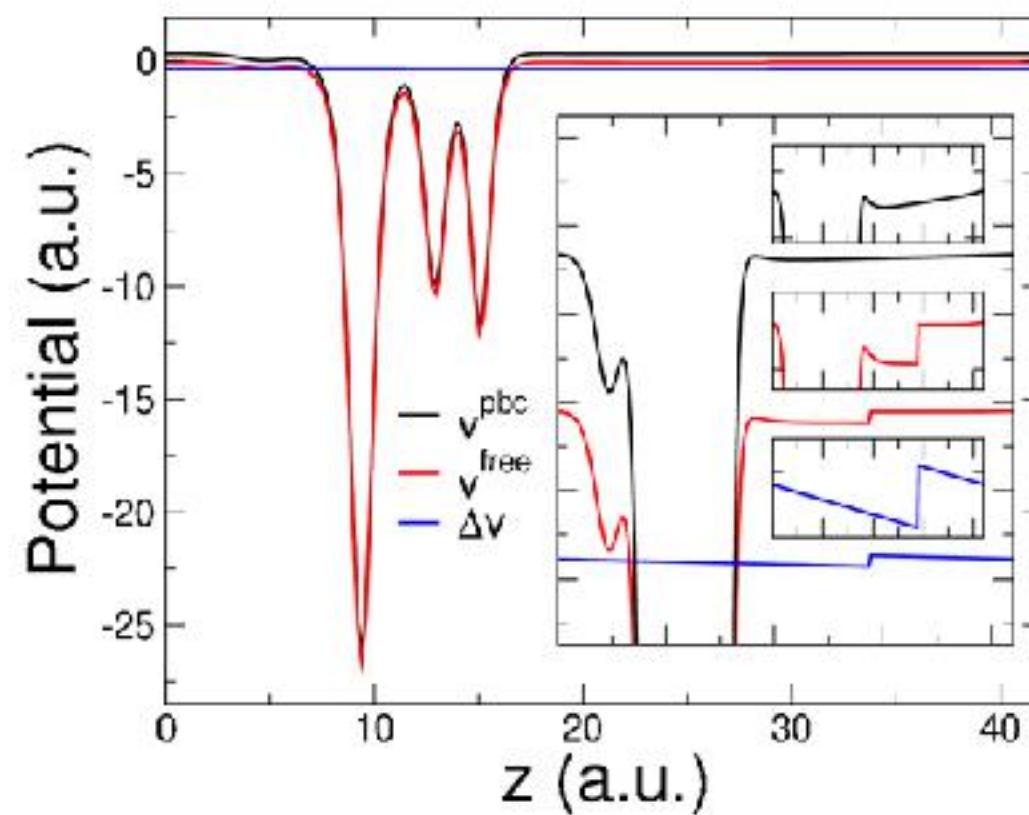
Comparison of potentials of zero charge (PZC) for continuum model with interface function parametrized on first principles results



N. Hörmann, O. Andreussi, N. Marzari, *J. Chem. Phys.*
150, 041730 (2019)

With and Without Parabolic Corrections

Corrections for neutral and charged slabs in vacuum (left) and continuum solution (right).

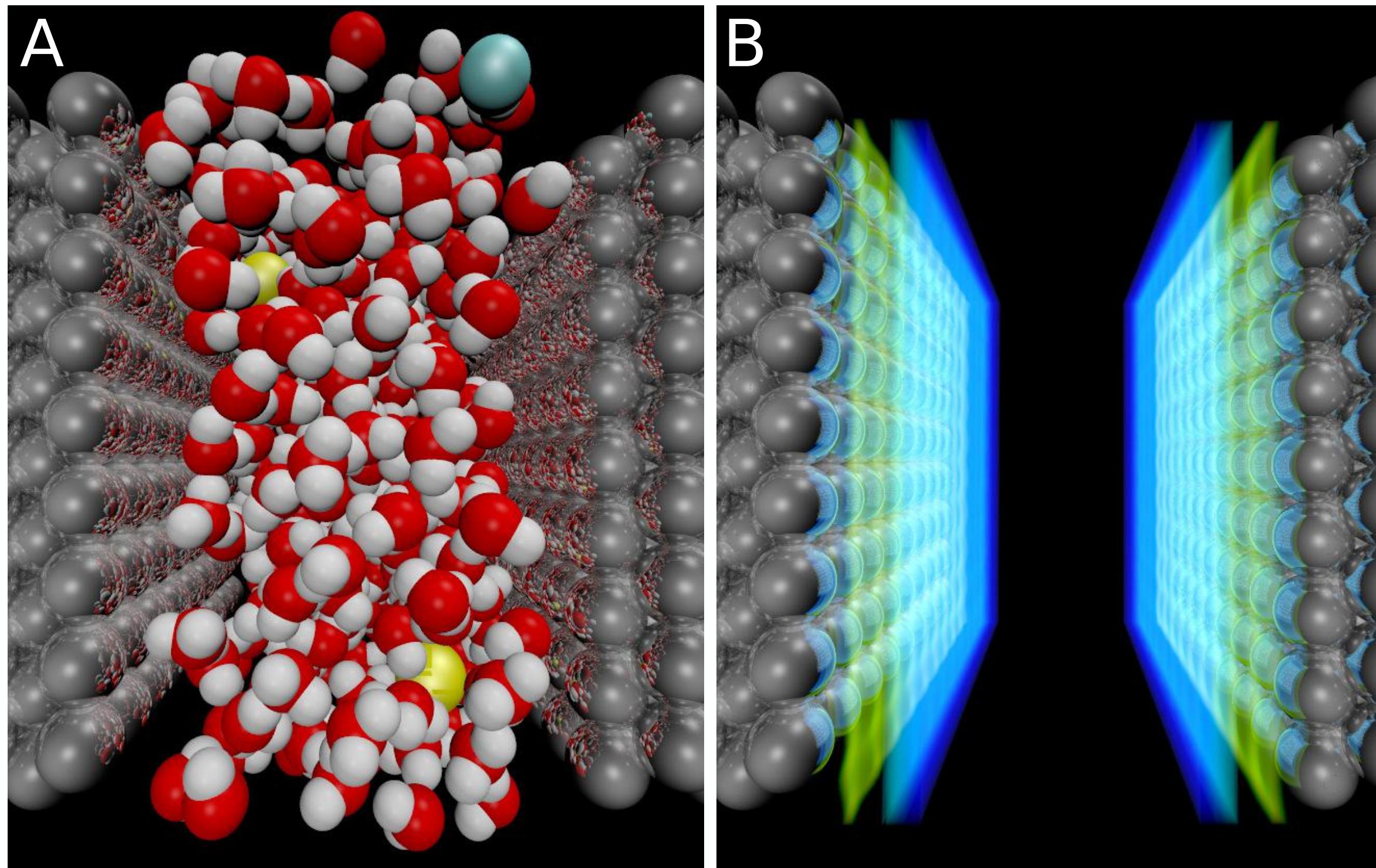


Fixing PBC in 2D Parabolic Correction

- A charged slab has infinite energy
- A dipolar slab needs a linear correction to the potential
- A shift in the potential does not change the energy of a neutral system
- But if the potential goes to zero at infinity E_f is equal to the bias

Poisson-Boltzmann (PB) Screening of Slab Potentials

In the presence of a charged slab, ions in solution will rearrange so as to flatten the electrostatic potential in the bulk of the solution, forming the so-called diffuse layer.



F. Nattino, M. Truscott, N. Marzari, and O. Andreussi, *J. Chem. Phys.*
150, 041722 (2019)

Diffuse Layer Hierarchy of Algorithms

$$\nabla \cdot \epsilon(\mathbf{r}) \nabla \phi(\mathbf{r}) = -4\pi \left(\rho^{\text{solute}}(\mathbf{r}) + \sum_i c_i(\mathbf{r}) z_i \right)$$
$$c_i(\mathbf{r}) = \frac{\gamma(\mathbf{r}) c_i^0 e^{-\frac{z_i(\phi(\mathbf{r}) - \phi_0)}{k_B T}}}{1 - \sum_{i=1}^p \frac{c_i^0}{c_0} \left(1 - e^{-\frac{z_i(\phi(\mathbf{r}) - \phi_0)}{k_B T}} \right)}$$

- Smooth planes of counter-charge
- Analytic solution to the planar-averaged 1D PB problem
- Linearized PB or size-modified PB
- Full non-linear PB or size-modified PB
- Specific ion-surface interactions

Differential Capacitance and Level of Theory

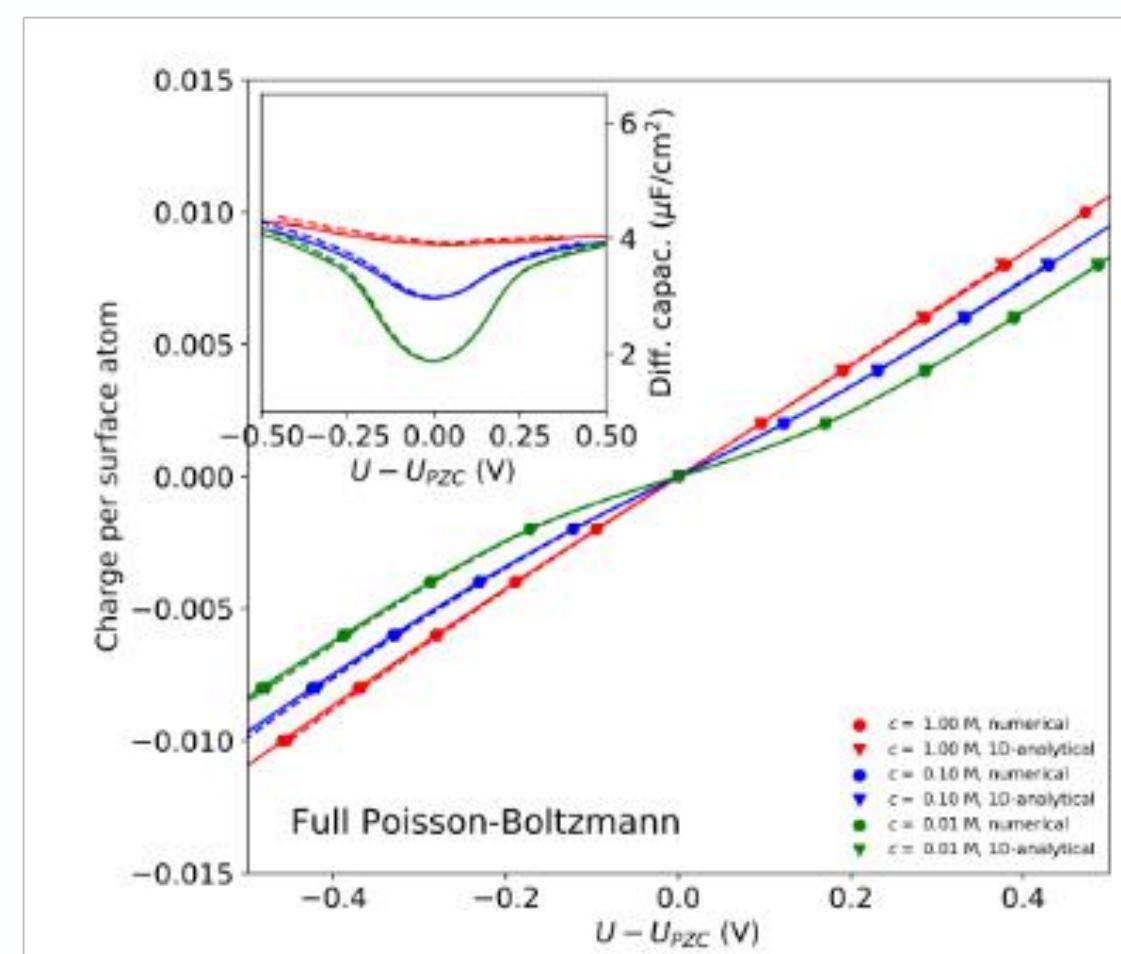
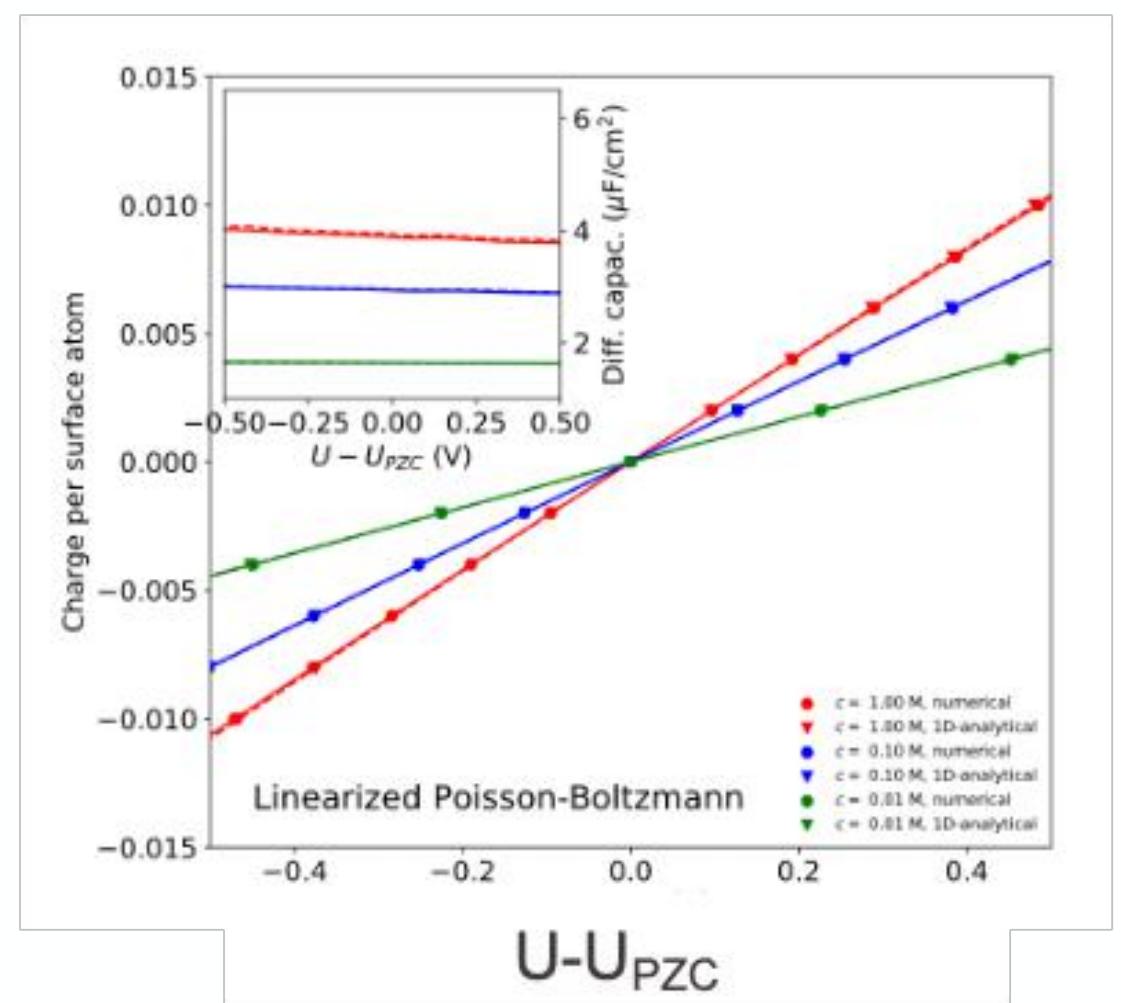
Differential capacitance of Ag (100) surface in vacuum. Variations of the Poisson-Boltzmann model of the diffuse layer are coupled with a DFT description of the substrate. Different curves correspond to different ionic concentrations

Linearized PBe

$$c_{\text{ionic}}(\mathbf{r}) \approx \sum_i c_i^\infty \left(1 - \frac{Z_i e \phi(r)}{kT} \right)$$

Full PBe

$$c_{\text{ionic}}(\mathbf{r}) = \sum_i c_i^\infty \exp \left(-\frac{Z_i e \phi(r)}{kT} \right)$$



Differential Capacitance Using Environ

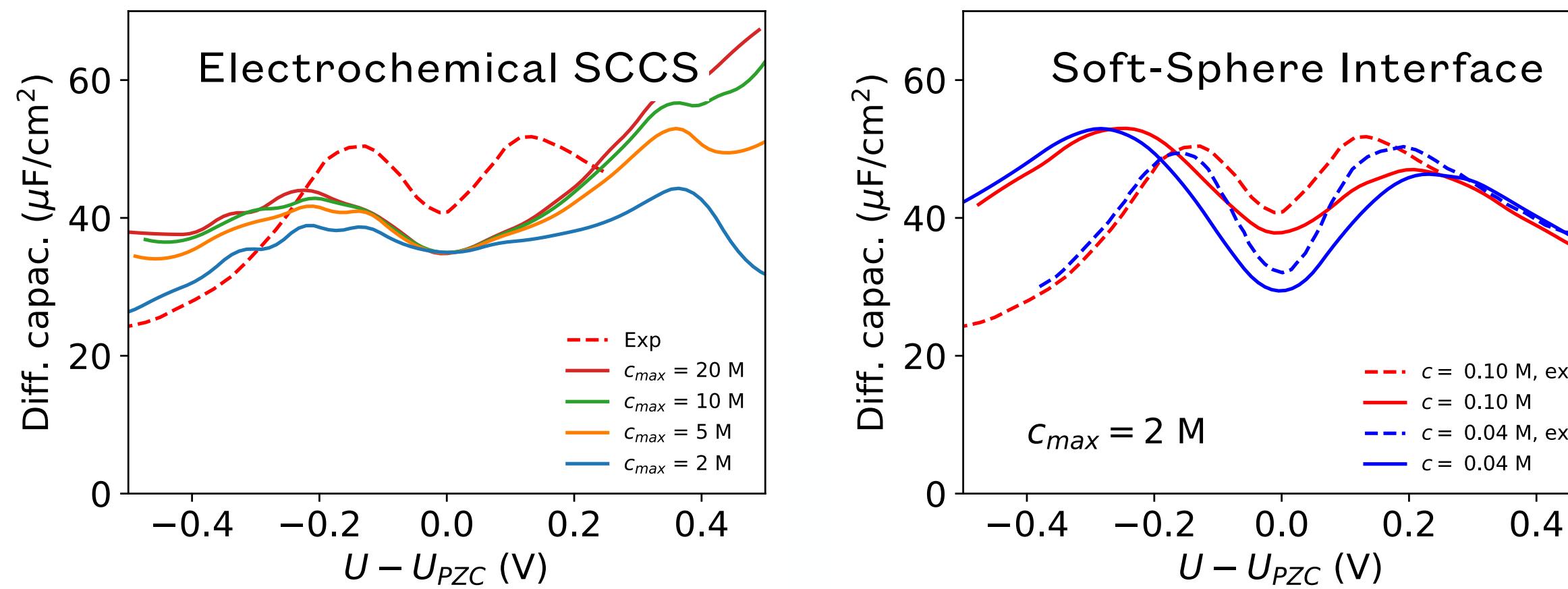
- Vary the charge on the slab and measure the potential drop (via the Fermi energy)
- Invert the variables and take the derivative of charge wrt potential

Differential Capacitance Using Environ

Tuning the Diffuse Layer Models on Experiments

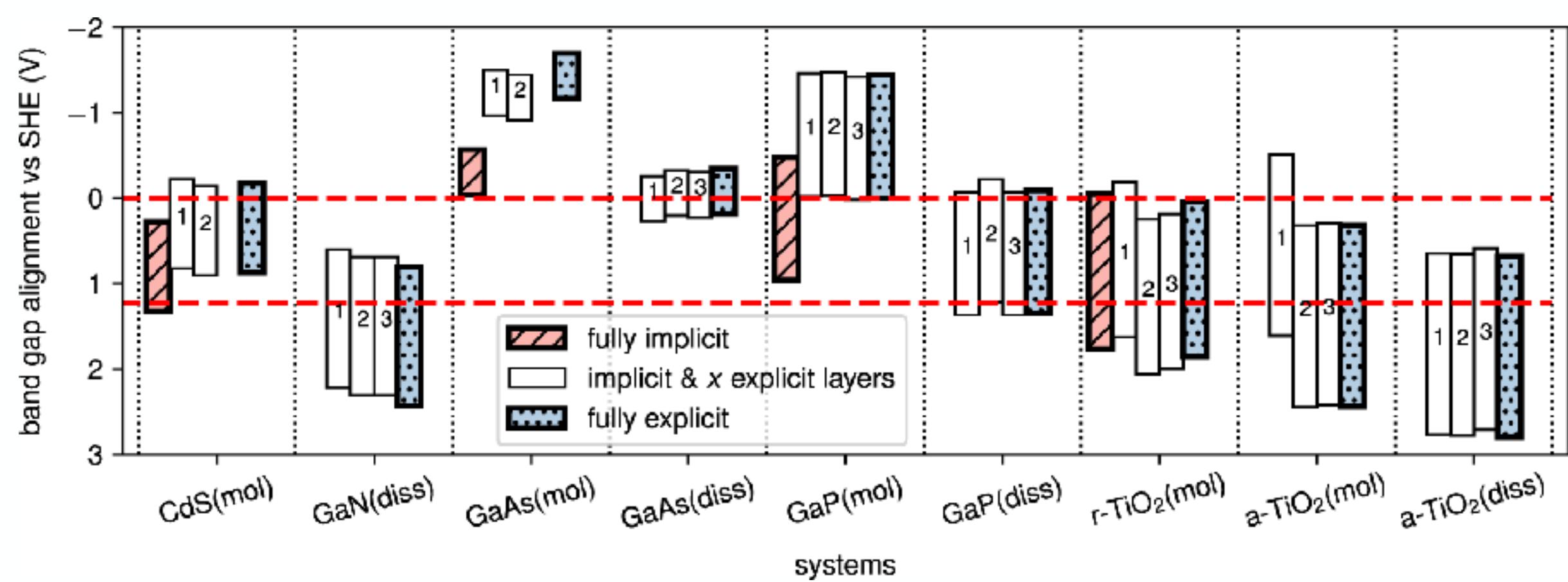
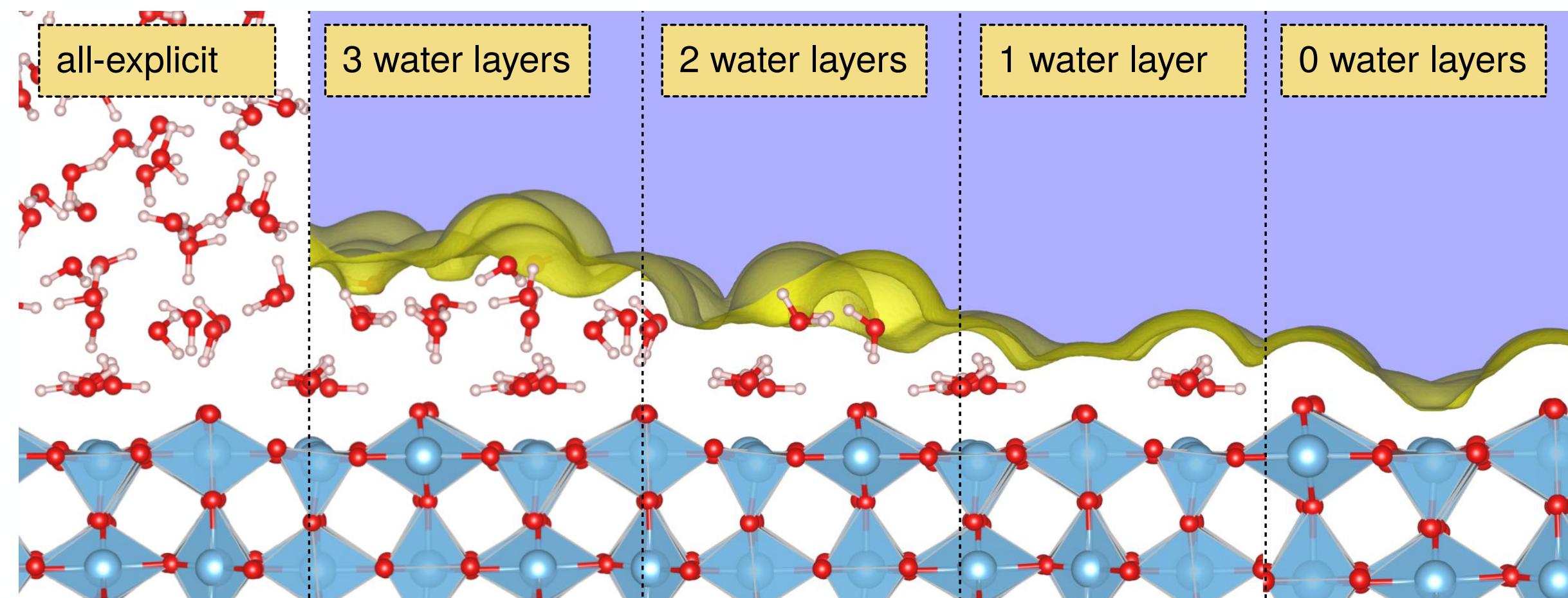
Differential capacitance of Ag (100) surface in KPF6 solution.

Modified Poisson-Boltzmann models of the diffuse layer are coupled with a DFT description of the substrate.



F. Nattino, M. Truscott, N. Marzari, and O. Andreussi, *J. Chem. Phys.*
150, 041722 (2019)

- Vary the charge on the slab and measure the potential drop (via the Fermi energy)
- Invert the variables and take the derivative of charge wrt potential



Band Alignment

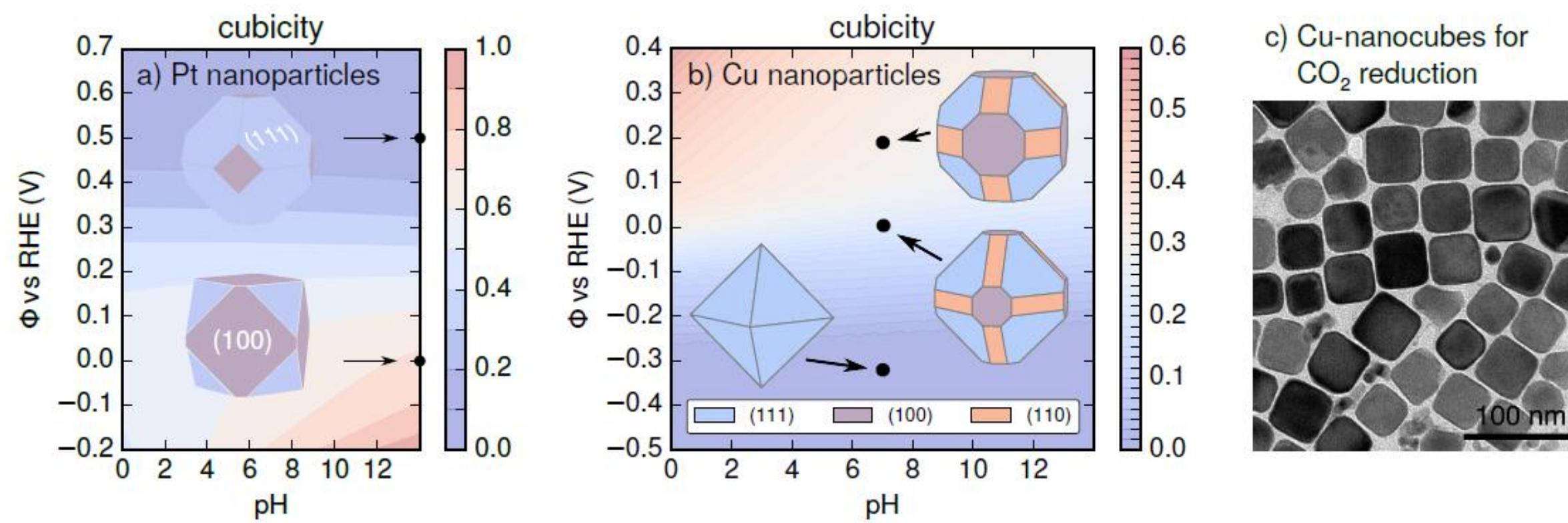
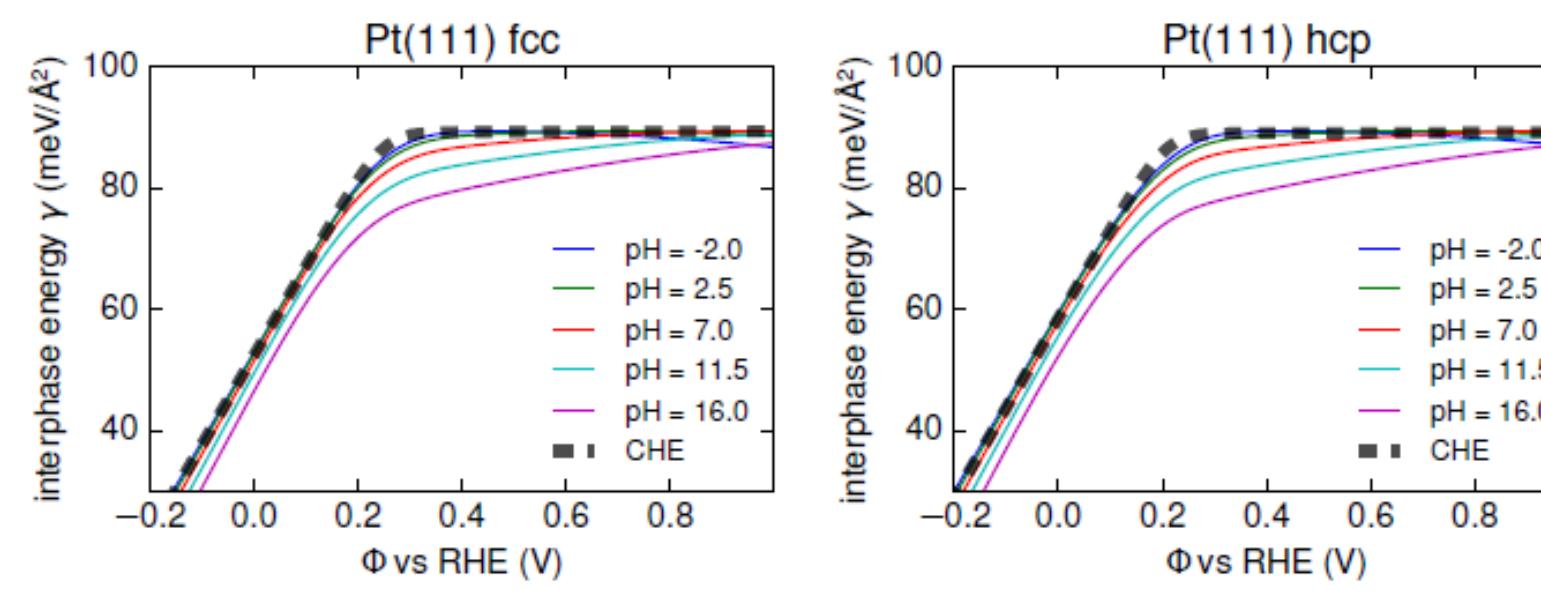
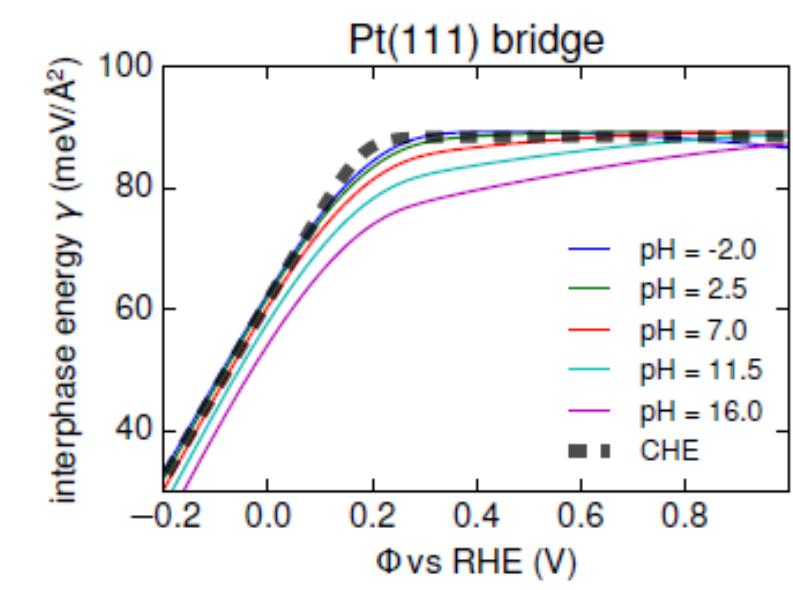
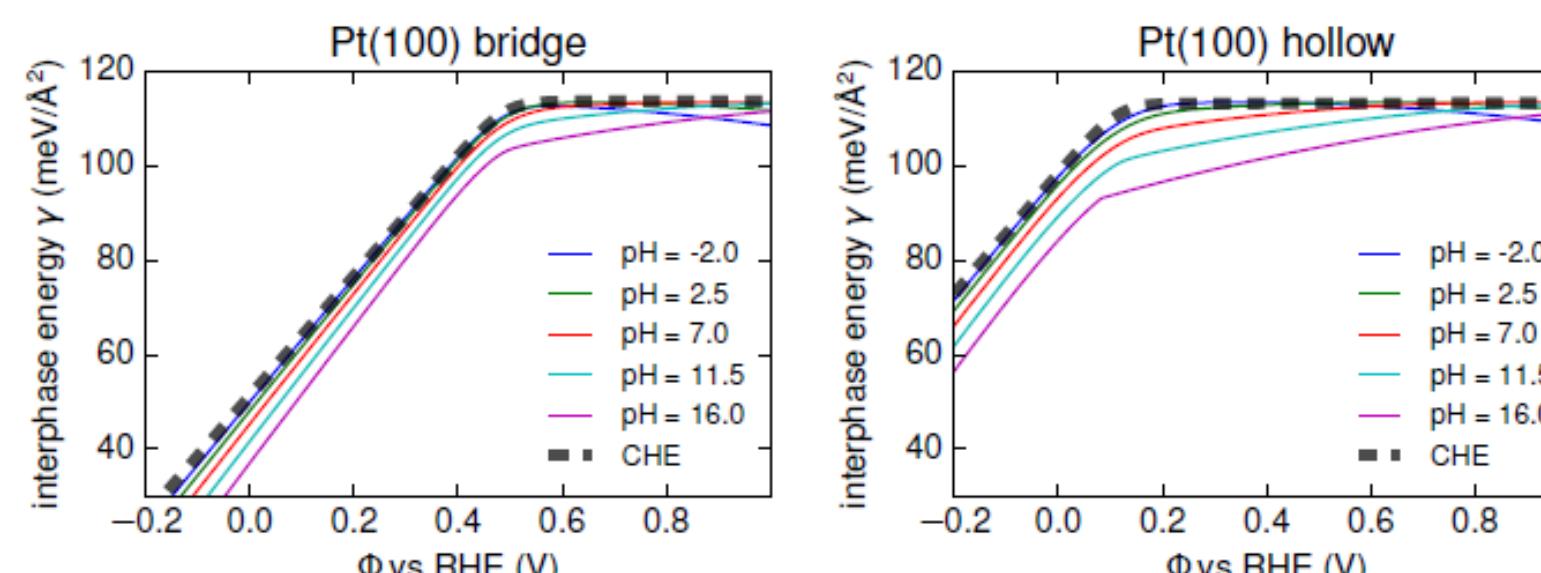
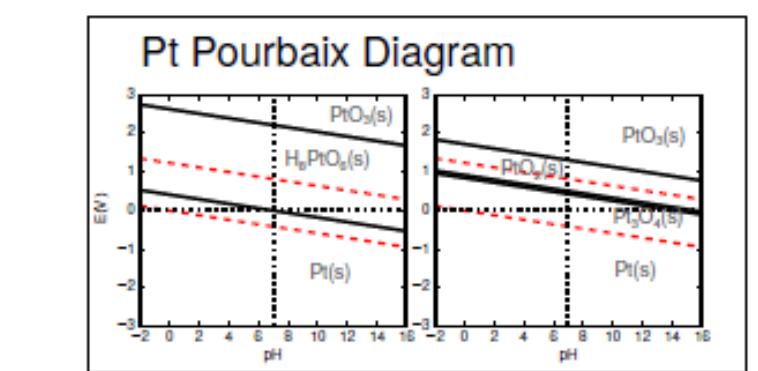
Benchmarks on Semiconductors

- There is a common offset when replacing explicit water with the continuum
- One explicit layer of water is necessary
- One explicit layer is often enough

Grand Potential Simulations

From extensive vs. intensive

Pt interphase energies



- Free energies as a function of applied potential and pH
- From Legendre transform of interfacial energies computed for a variable number of electrons and protons

$$\gamma(\Phi, \text{pH}) = \min_{\theta} \gamma_{IP}(\Phi, \theta) = \min_{\theta} \left(\min_{\sigma_{abs}} [\Delta G_{IP}(N(H^+_{\text{ads}}), N(e)_{\text{abs}})) / 2A] \right)$$

J. Huang et al. *Nature Communications* (2018)

N. Hörmann, O. Andreussi, and N. Marzari, *J. Chem. Phys.* (2019)

Table 1. 2D Materials Identified as Potential Catalysts for the HER, as Obtained from the First Three Steps of the Computational Screening Workflow Reported in Figure 1^a

prototype	compound	Φ^{over}	$\Delta G_{\text{pbx}}(\Phi, \text{pH})$	decomp. pdts	E_{gap}	$E_b^{\text{aq}} (E_b^{\text{vac}})$
Unary Compounds						
graphite As	C	0.3	1.31	CH ₄ (g)	0.0	17.2 (20.3)
	P	0.1(4)	3.36	H ₃ PO ₄ (aq)	1.9	20.8 (38.2)
	Bi	0.2	0.17	Bi(bulk)	0.6	– (20.1)
	Sb	0.1	0.15	Sb(bulk)	1.2	– (31.5)
Binary Compounds						
MoS ₂ (2-H) CdI ₂ (1-T)	NbS ₂	0.1	0.07	Nb(OH) ₅ (aq) + H ₂ S(aq)	0.0	19.0 (24.2)
	NbSe ₂	0.2	0.0	Nb(OH) ₅ (aq) + Se(s)	0.0	17.6 (23.4)
	TaS ₂	0.2	0.33	Ta ₂ O ₅ (aq) + H ₂ S(aq)	0.0	17.8 (23.1)
	TaSe ₂	0.5	0.02	Ta ₂ O ₅ (aq) + H ₂ Se(aq)	0.0	16.6 (22.5)
CoO ₂ MoS ₂ NbS ₂ NbSe ₂ NbTe ₂ SiTe ₂ SnSe ₂ TaS ₂ TiS ₂ TiSe ₂ TiTe ₂ VS ₂ VSe ₂ VTe ₂ ZrTe ₂ FeSe Bi ₂ Te ₃ WTe ₂ GeS Cu ₂ Te Bi ₂ Te ₂ Se	CoO ₂	0.1	0.43	Co(s)	0.0	13.2 (22.5)
	MoS ₂	0.1(4)	0.1	MoO ₂ (s) + H ₂ S(aq)	0.0	23.2 (28.1)
	NbS ₂	0.1	0.17	Nb(OH) ₅ (aq) + H ₂ S(aq)	0.0	17.8 (23.3)
	NbSe ₂	0.2	0.0	Nb(OH) ₅ (aq) + Se(s)	0.0	17.6 (27.4)
	NbTe ₂	0.3	0.64	Nb ₂ O ₅ (s) + Te(s)	0.0	20.0 (28.4)
	SiTe ₂	0.4	1.07	SiO ₂ (s) + Te(s)	0.0	12.4 (19.8)
	SnSe ₂	0.2	1.6	Sn ²⁺ (s) + Se(s)	0.8	8.8 (17.2)
	TaS ₂	0.3	0.3	Ta ₂ O ₅ (s) + H ₂ S(aq)	0.0	17.4 (22.4)
	TiS ₂	0.4	0.59	TiO ₂ (s) + H ₂ S(aq)	0.1	18.8 (23.6)
	TiSe ₂	0.5	0.27	Ti ²⁺ (aq) + H ₂ Se(aq)	0.0	18.4 (23.9)
	TiTe ₂	0.2	0.92	TiO ₂ (s) + Te(s)	0.0	20.2 (28.2)
	VS ₂	0.1	0.54	VO ²⁺ (aq) + H ₂ S(aq)	0.0	21.8 (27.9)
	VSe ₂	0.2	0.38	VO ²⁺ (aq) + Se(s)	0.0	19.0 (25.5)
	VTe ₂	0.2	0.54	V ₂ O ₃ (s) + Te(s)	0.0	18.2 (26.4)
	ZrTe ₂	0.3	1.02	ZrO ₂ (s) + Te(s)	0.0	18.4 (25.8)
	FeS	0.1	0.0	Fe ²⁺ (aq) + H ₂ S(aq)	0.0	19.6 (25.2)
	Bi ₂ Te ₃	0.5	0.06	Sb ₁₆ Te ₃ (s) + Te(s)	0.7	14.4 (25.2)
	WTe ₂	0.3	0.02	Mo ₃ Te ₄ (s) + Te(s)	0.0	11.4 (23.05)
	WTe ₂	0.5	0.04	WTe ₂ (bulk)	0.0	13.0 (21.7)
GeS Cu ₂ Te	GeS	0.1(3)	0.17	HGeO ₃ ⁻ (aq) + H ₂ S(aq)	1.6	24.6 (36.2)
	GeSe	0.1(5)	0.6	HGeO ₃ ⁻ (aq) + HSe ⁻ (aq)	1.1	21.9 (31.9)
	Cu ₂ Te	0.1	0.07	CuTe(s) + Te(s)	0.2	– (16.1)
Trinary Compounds						
Bi ₂ Te ₂ Se	Zr ₂ PTe ₂	0.1	2.07	ZrO ₂ (s) + PH ₃ (g) + Te(s)	0.0	19.2 (26.5)

^aCorresponding overpotential vs RHE for H⁺ electrosorption (Φ^{over} in V), aqueous stability ($\Delta G_{\text{pbx}}(\Phi, \text{pH})$ in eV/atom), decomposition products (decomp. pdts), band gap values (E_{gap} in eV), and exfoliation (interlayer binding) energy values in aqueous medium (E_b^{aq} in meV/Å²) are reported. The pH value is 1, except for those indicated within parentheses in column 3. The exfoliation energies in vacuum (E_b^{vac}) are given in column 7, within parentheses.

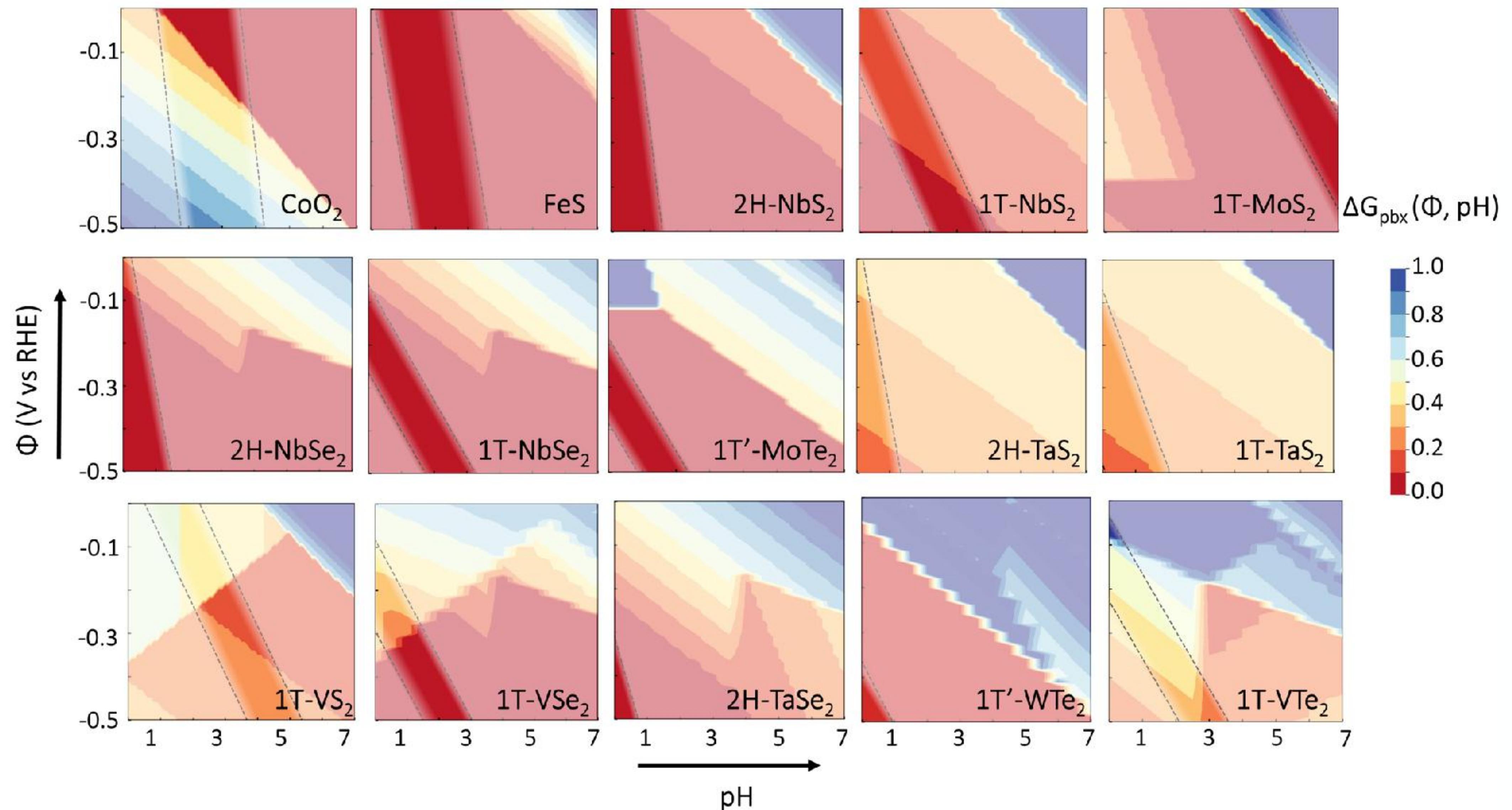
Hydrogen Evolution Screening of 2D Materials

- Systematic simulations of about 50 materials, varying:
 - H⁺ coverage
 - H⁺ adsorption sites
 - Number of electrons
- Looking for:
 - Reversibly bind hydrogen on surface

$$|\Delta G_{\text{ads}}^{\text{sol}}(\Phi, \text{pH})| < 0.1 \text{ eV/H atom}$$
 - In electrochemical regions of interest (small overpotentials and low pH)
- Compare stability of materials vs. possible degradation products

Electrochemical Stability and Catalytic Activity of Best Performing 2D Materials

Aiming for stable materials (dark red) with reversible hydrogen electro-sorption (unshaded) at low over potentials



CHE vs Grand Canonical

An Upper Limit

CHE May be Enough

$$\gamma = \frac{1}{2A} \left(G_{surf} - n \cdot G_{bulk} - m \cdot \mu_{H_2O} + n_{H^+} \cdot \mu_{H^+} + n_{e^-} \cdot \mu_{e^-} \right)$$

Comparison of CHE and Grand Canonical Results for IrO₂

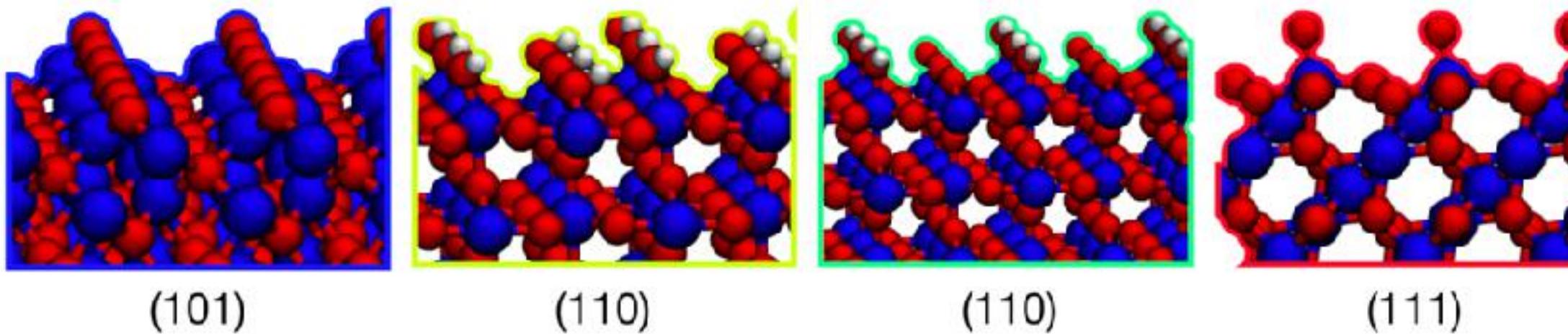
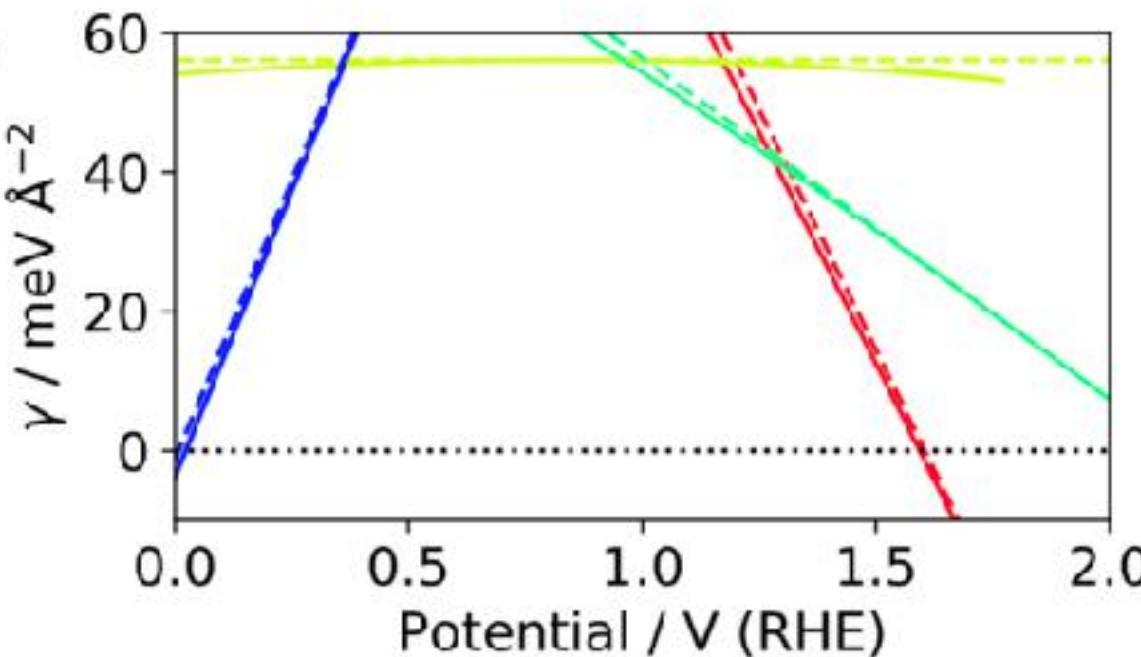
Computational Hydrogen Electrode (dashed):

$$\mu_{H^+} + \mu_{e^-} = \frac{1}{2} \mu_{H_2} - k_B T \ln(10) \text{pH} - e\Phi_{SHE}$$

Full Grand-Canonical (solid):

$$\mu_{H^+} = \frac{1}{2} \mu_{H_2} - k_B T \ln(10) \text{pH} + 4.44 \text{ eV}$$

$$\mu_{e^-} = -e\Phi_{abs}$$

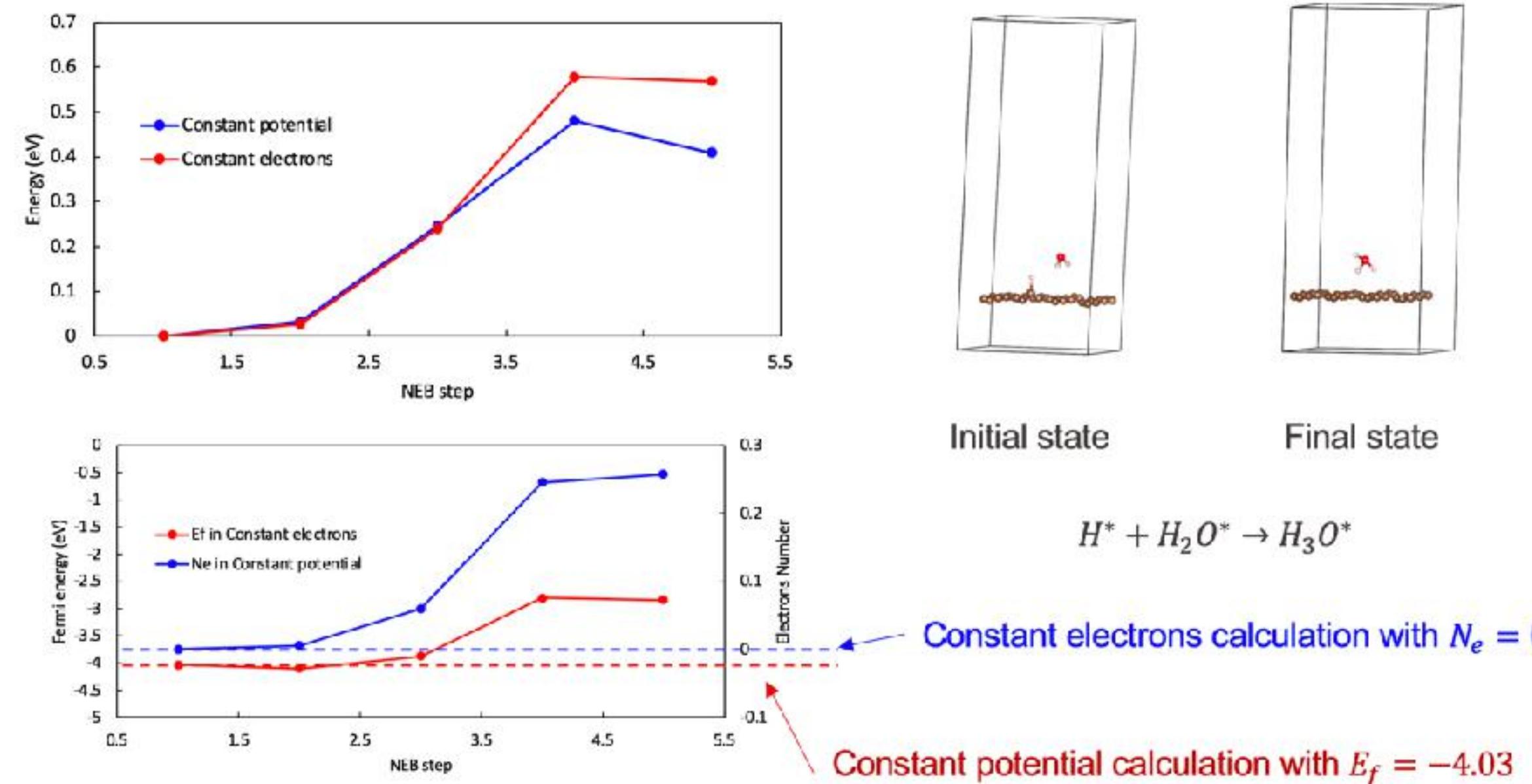


- CHE neglects effects of bias on structures
- CHE is more accurate close to PZC
- Grand Canonical requires significantly more calculations

F. Nattino and N. Marzari, *Phys. Chem. Chem. Phys.*, **22**, 10807-10818
(2020)

Comparing Constant Charge vs. Constant Potential

Nudged Elastic Band (NEB) calculations of water protonation on graphene using the two flavors of Grand Canonical simulations and Environ



W. Mouyi and N. Marzari, Barrier and Raman frequency calculation with implicit solvent and electrochemical potential (EPFL 2023)

Beyond the CHE

Grand Canonical Simulations Constant Potential

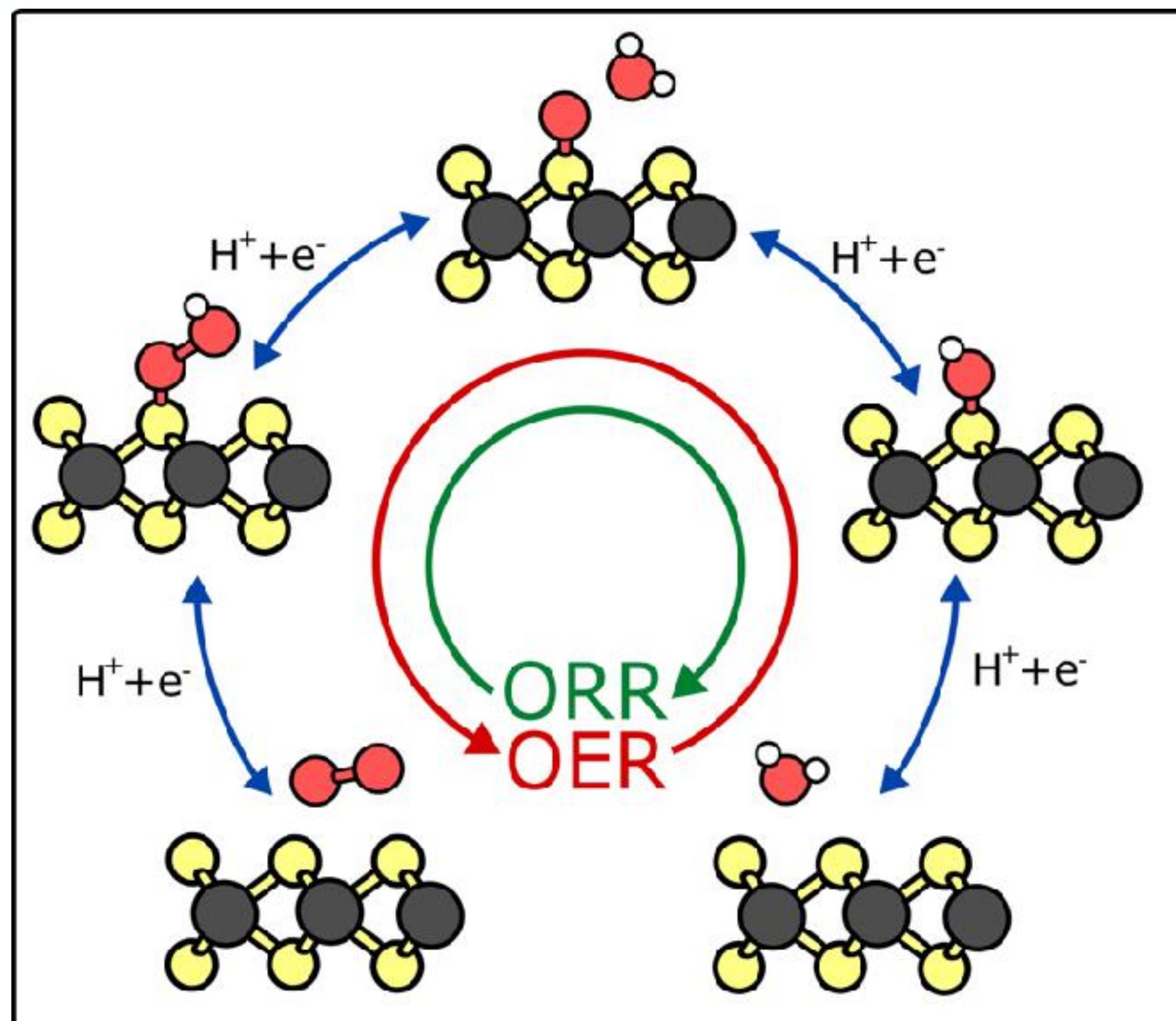
- Modified Pulay mixing¹
- Reduces the number of calculations
- Better suited for dynamic processes, reaction paths, barriers, vibrational frequencies
- However the continuum solvent is always instantaneously equilibrated

Multiple Steps Conversion

Catalytic Activity from Intermediates Stability

Oxygen-Water Conversion

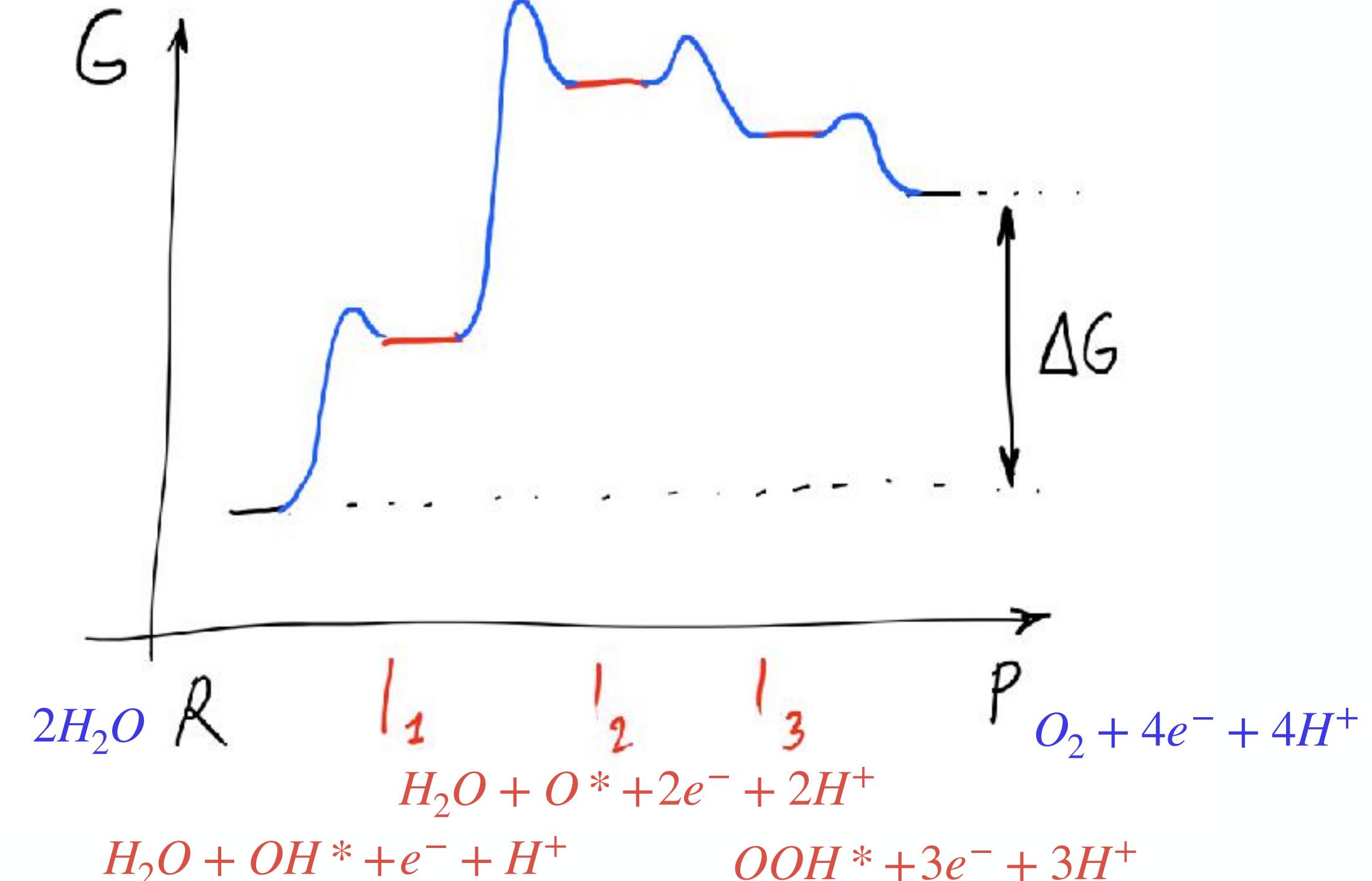
Schematic catalytic steps involved in single-site Oxygen Reduction and Oxygen Evolution reactions on a 2D material.



Karmodak, Brusi, and Andreussi, *J. Phys. Chem. Lett.* **13**, 58 (2022)

An Effective Approximation (a.k.a. the Computational Hydrogen Electrode, CHE¹)

$$\Delta G^{OER} = G(O_2) + 4\mu_e + 4\mu_H - G(H_2O)$$



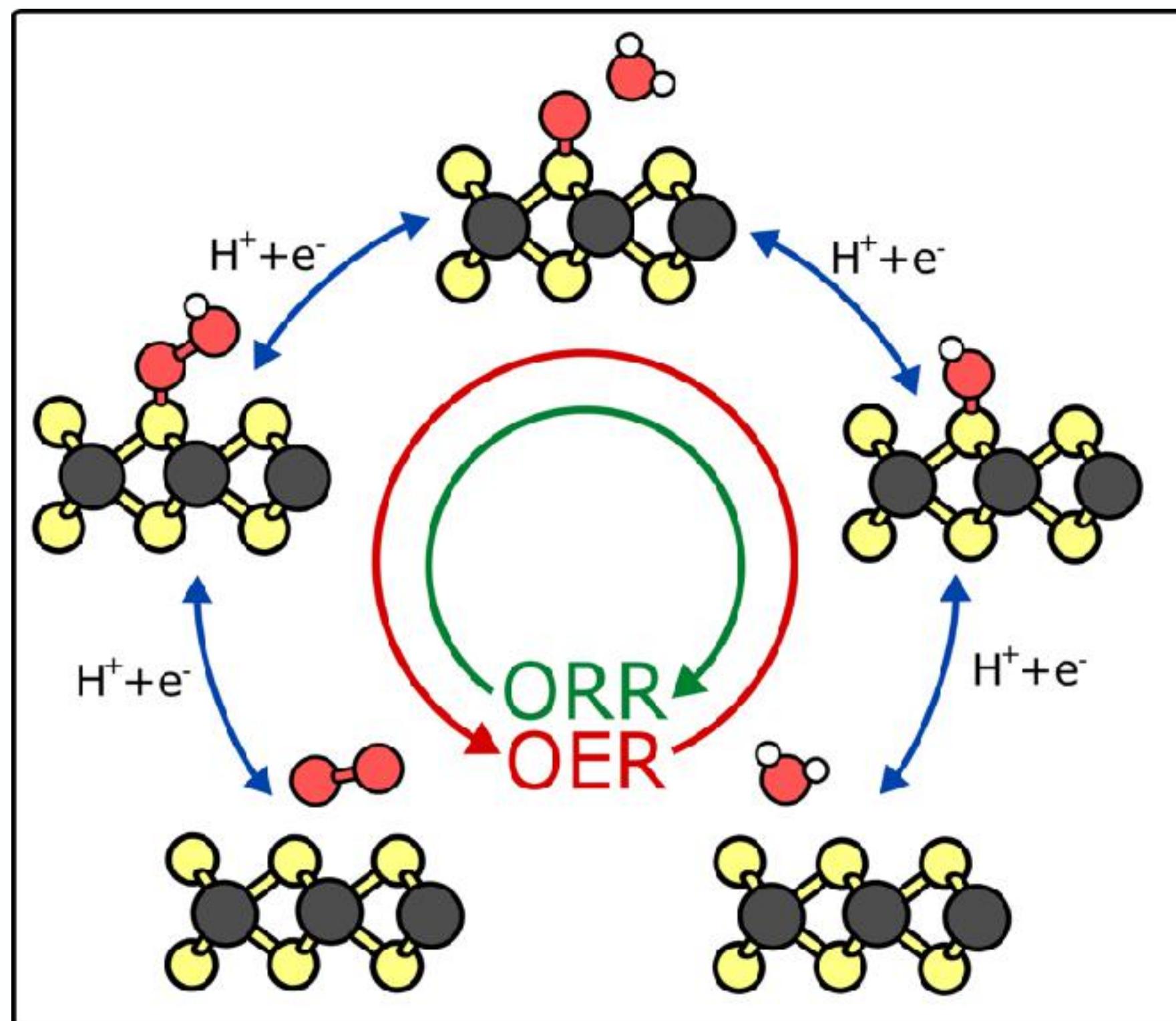
¹ Norskov et al., *J. Phys. Chem. B*, **108**, 17886 (2004)

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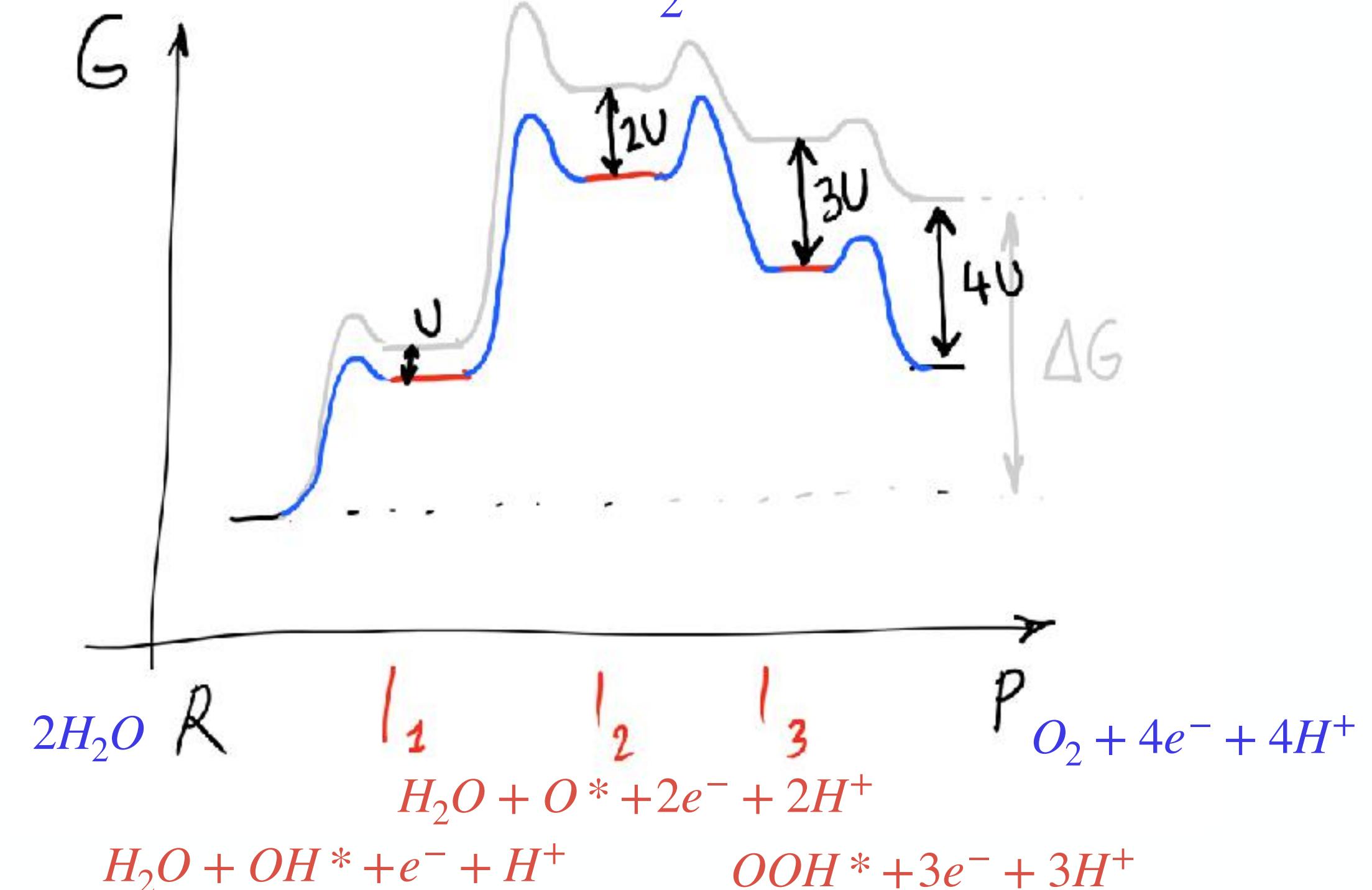


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$$\mu_e + \mu_H = \frac{1}{2}G(H_2) - k_B T \ln(10)pH - e(U - U_{SHE})$$



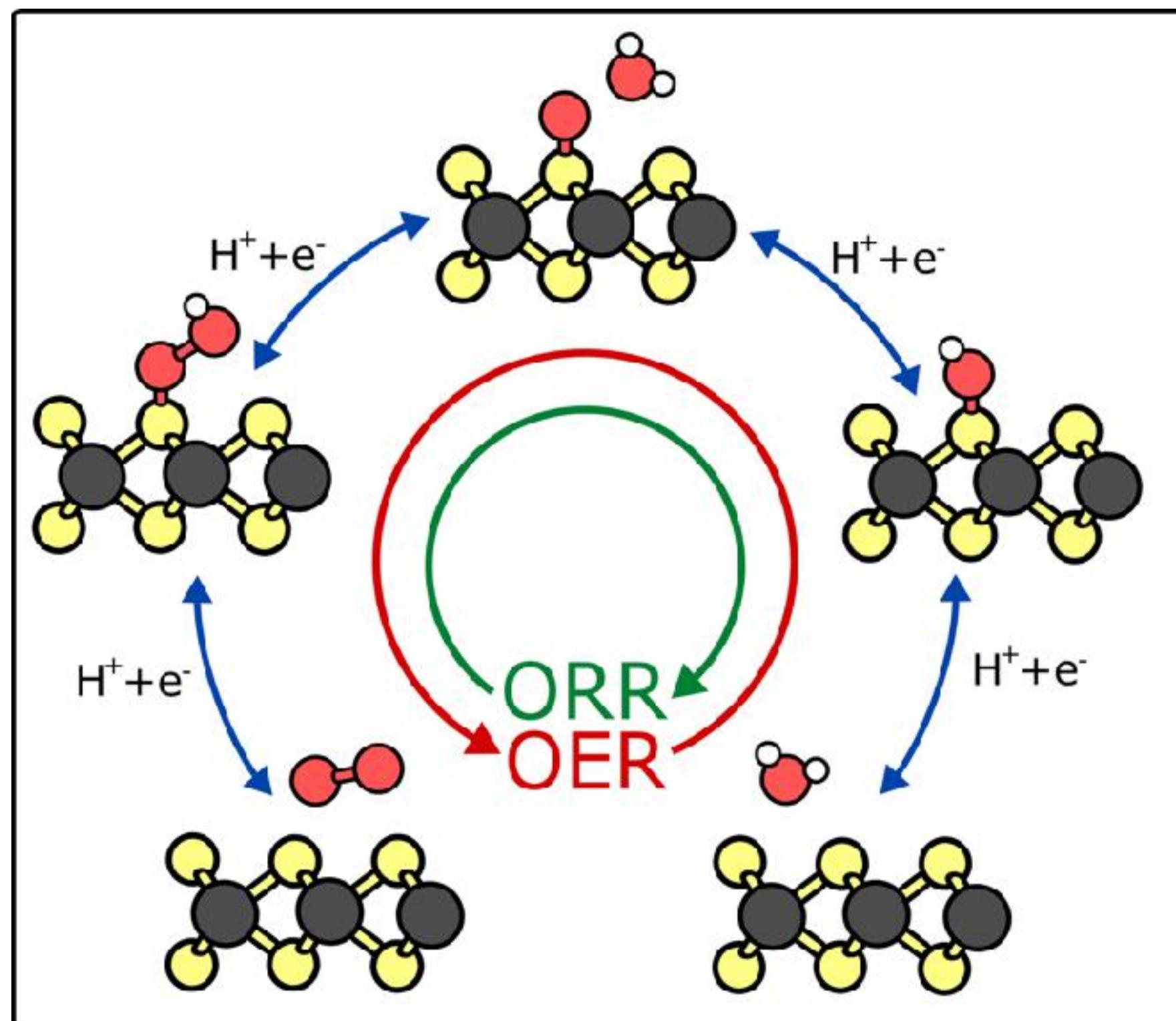
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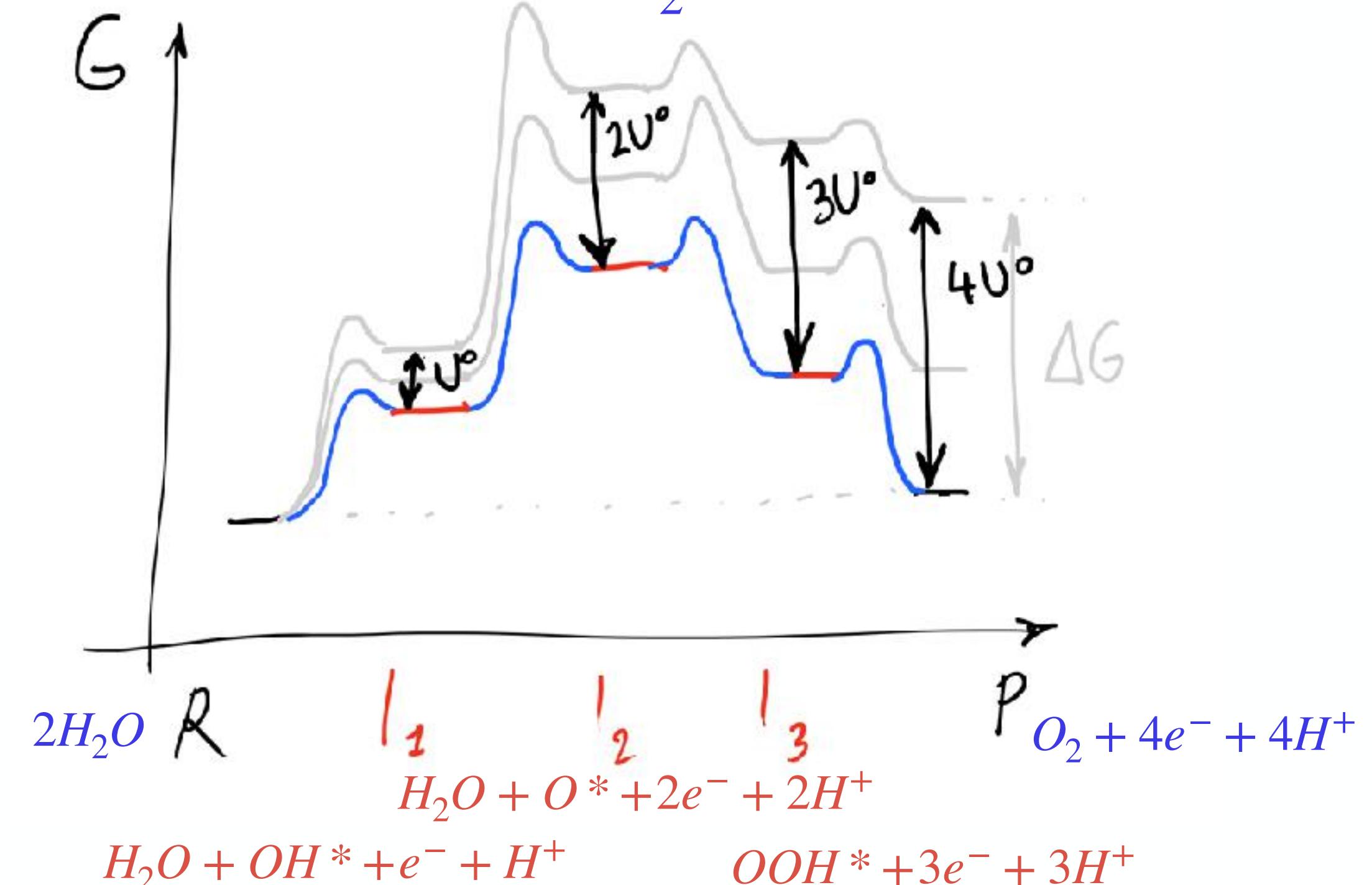


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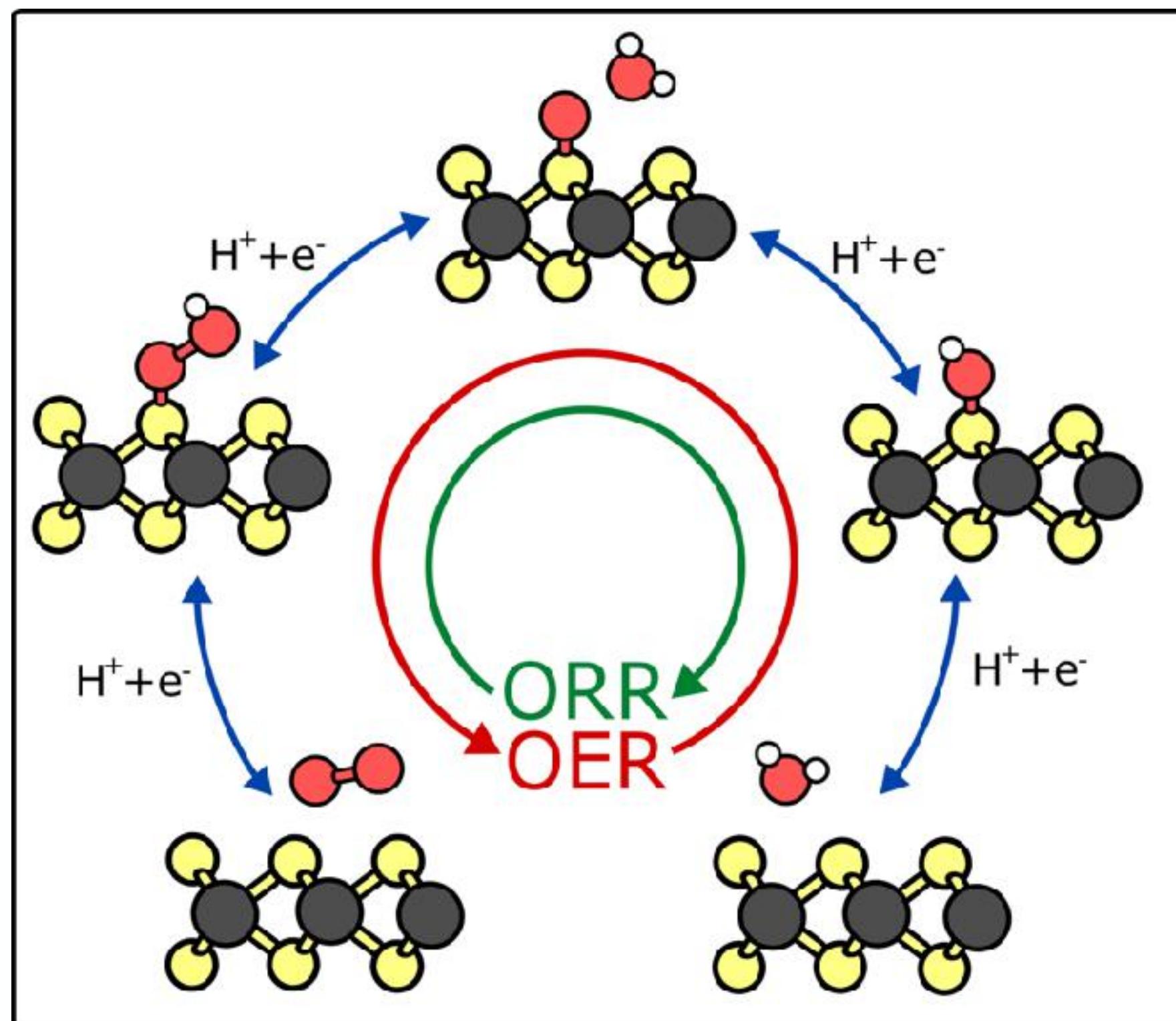
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Oxygen-Water Conversion

Schematic catalytic steps involved in single-site Oxygen Reduction and Oxygen Evolution reactions on a 2D material.

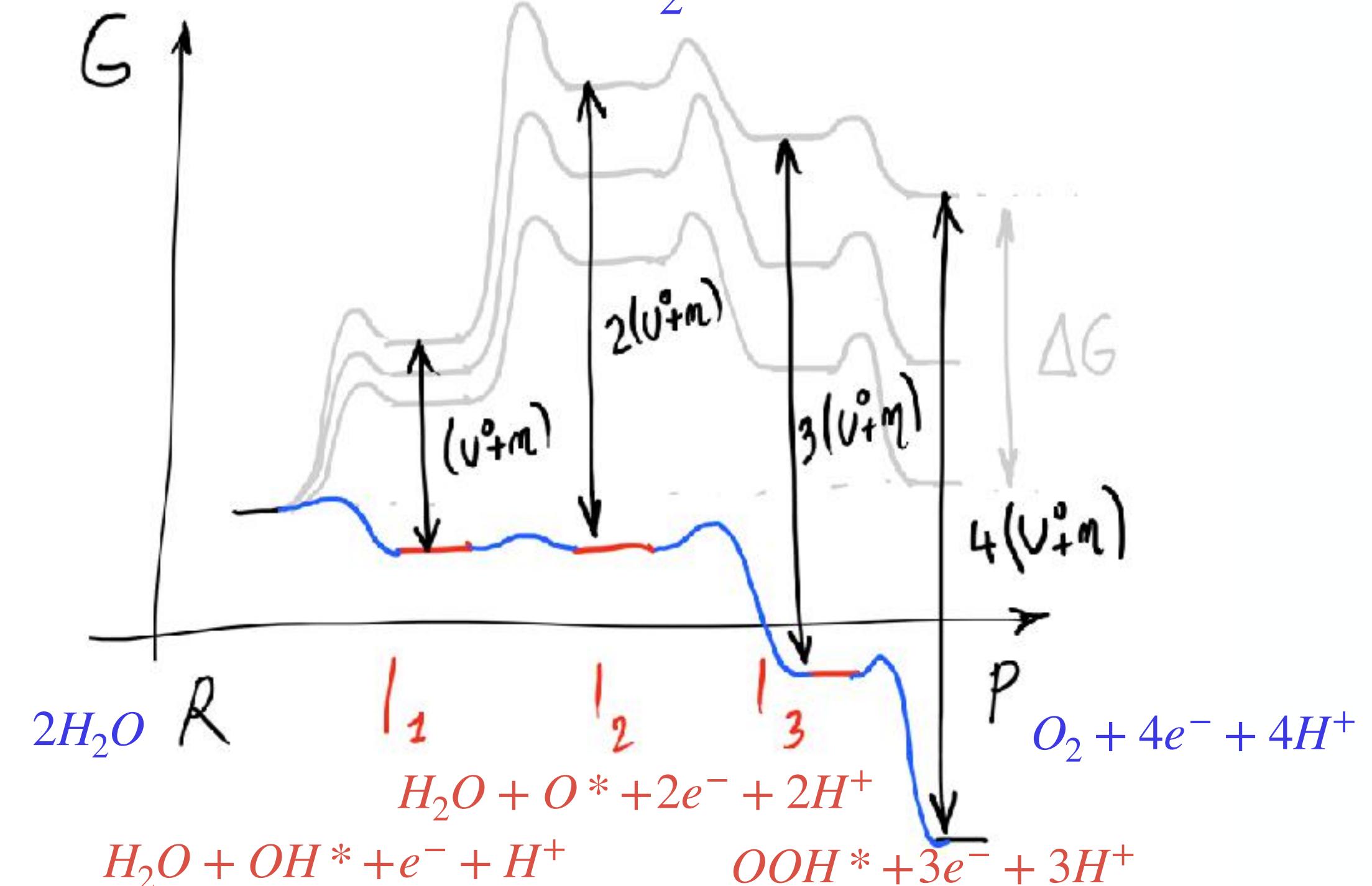


Karmodak, Brusi, and Andreussi, *J. Phys. Chem. Lett.* **13**, 58 (2022)

An Effective Approximation (a.k.a. the Computational Hydrogen Electrode, CHE¹)

$$\Delta G^{OER} = G(O_2) + 4\mu_e + 4\mu_H - G(H_2O)$$

$$\mu_e + \mu_H = \frac{1}{2}G(H_2) - k_B T \ln(10)pH - e(U - U_{SHE})$$

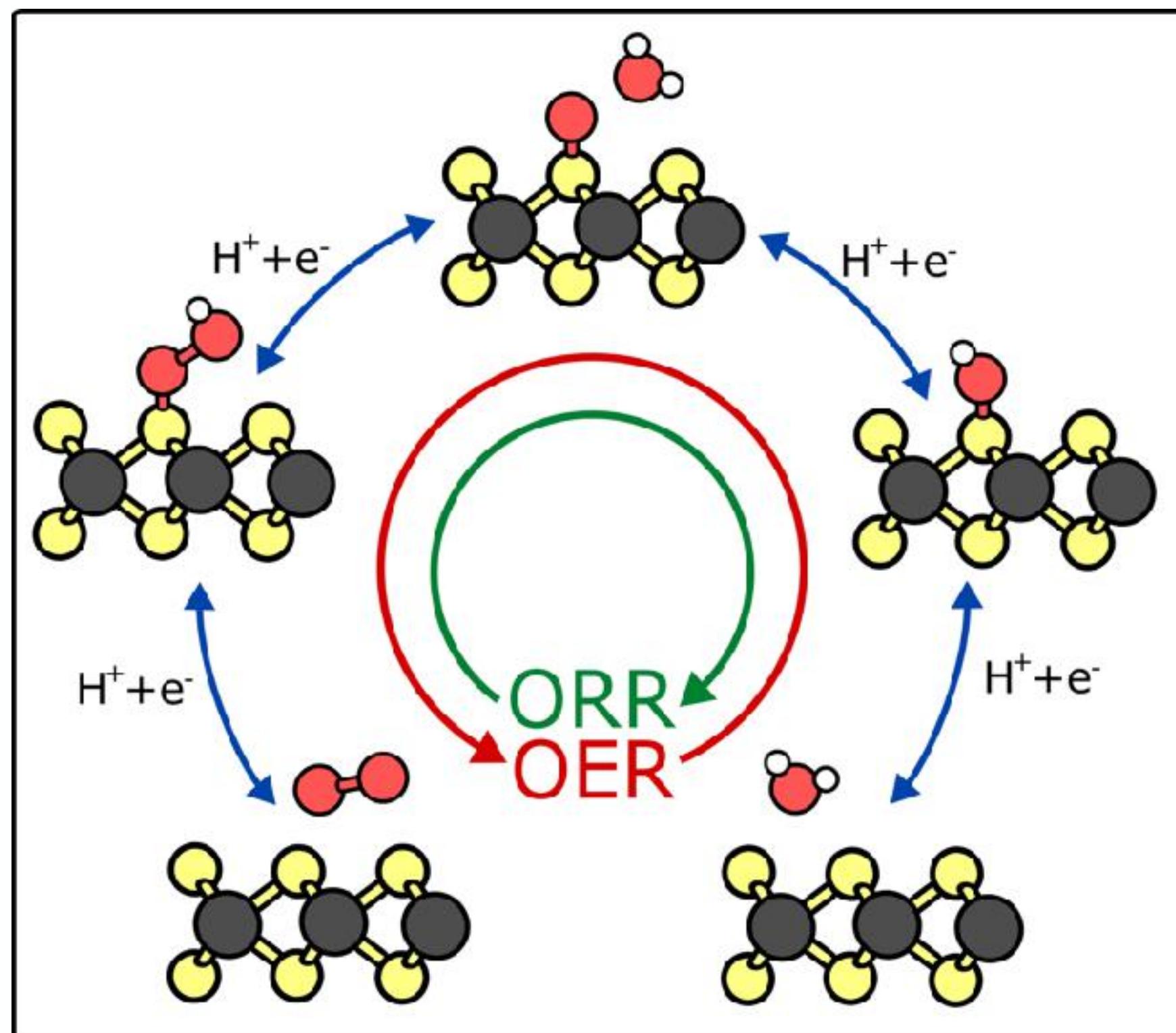


¹ Norskov et al., *J. Phys. Chem. B*, **108**, 17886 (2004)

Multiple Steps Conversion Catalytic Activity from Intermediates Stability

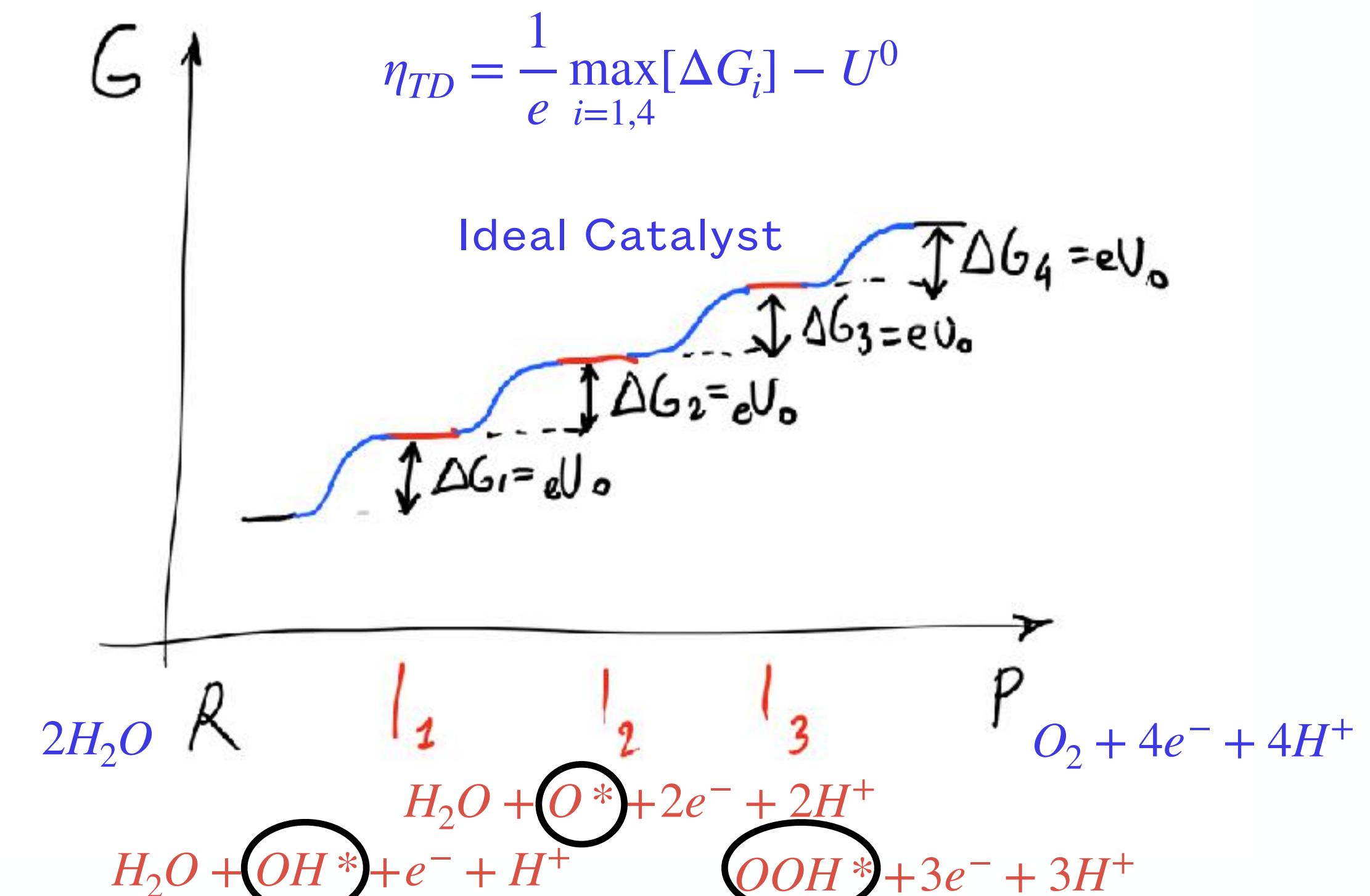
Oxygen-Water Conversion

Schematic catalytic steps involved in single-site Oxygen Reduction and Oxygen Evolution reactions on a 2D material.



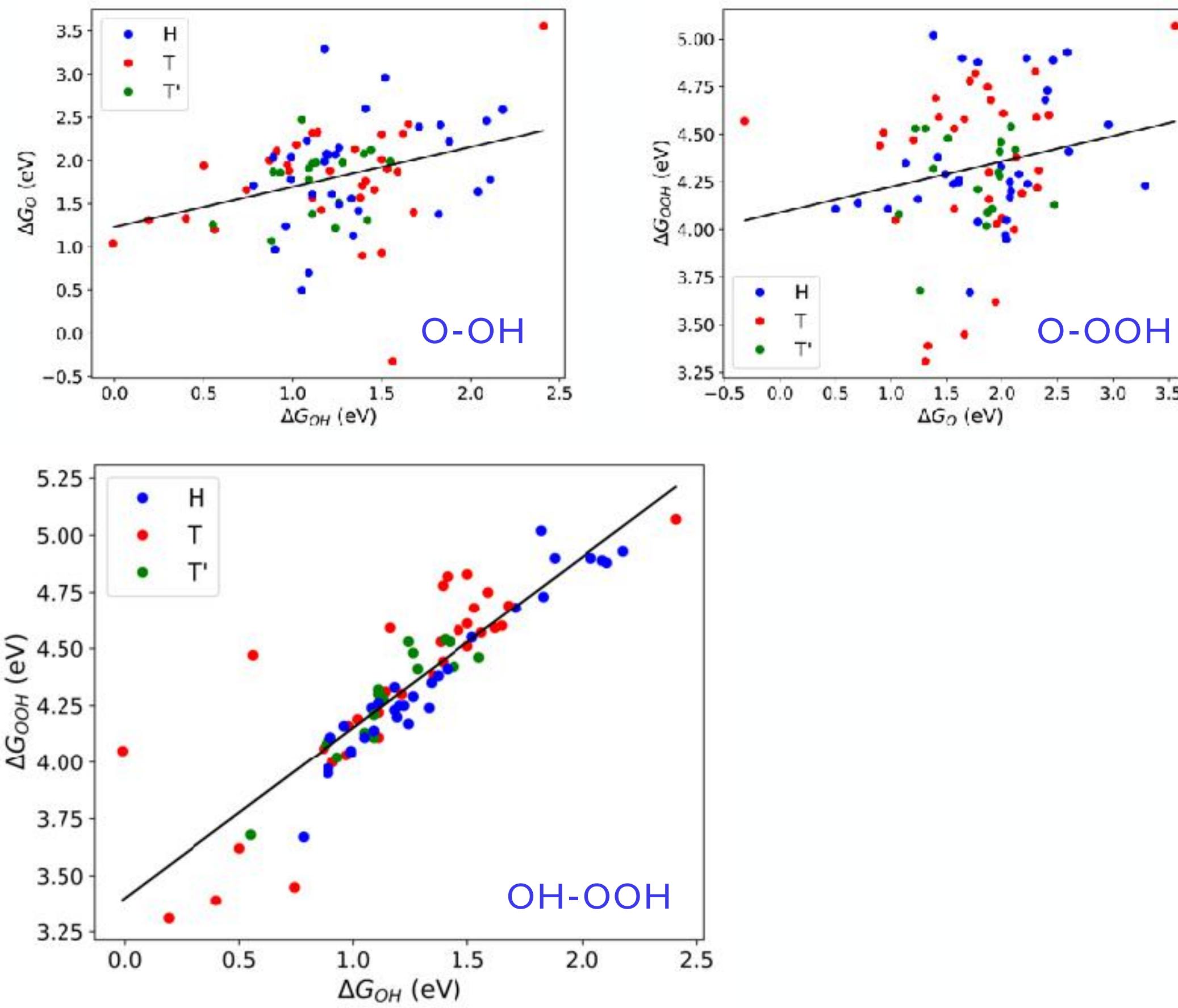
Karmodak, Brusi, and Andreussi, *J. Phys. Chem. Lett.* **13**, 58 (2022)

- Identify optimal catalysts from intermediates' energies
- Constraints (scaling relations, single-site vs. multi-sites)
- Beyond neutral interfaces (grand-potential scheme)



Scaling Relationships in 2D TMD

Relationships between electrosorption free energies of intermediate species on 2D transition metal dichalcogenides. A linear relationships between the first and third intermediates is observed.



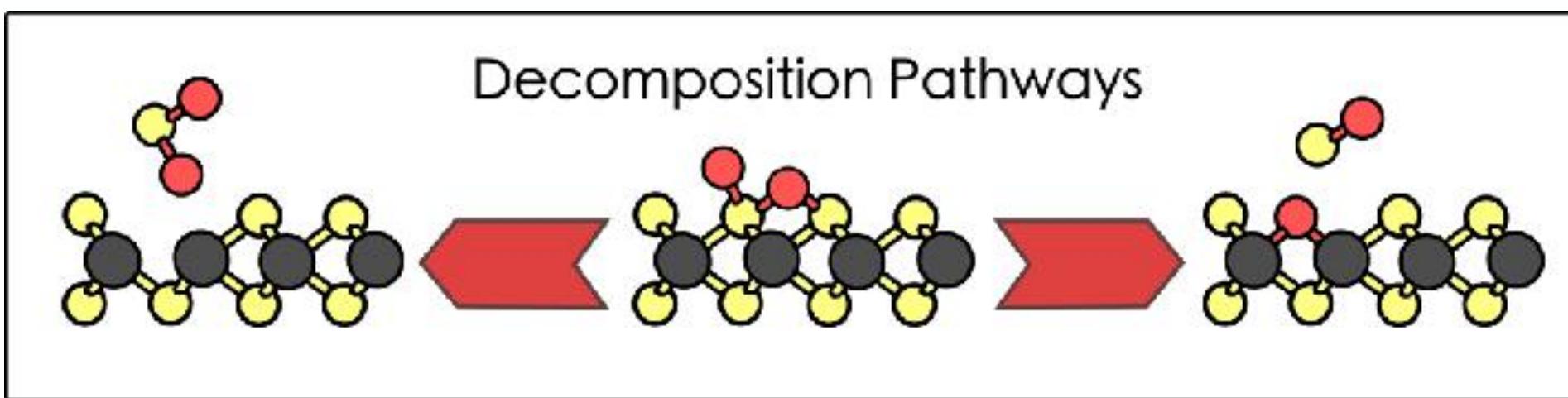
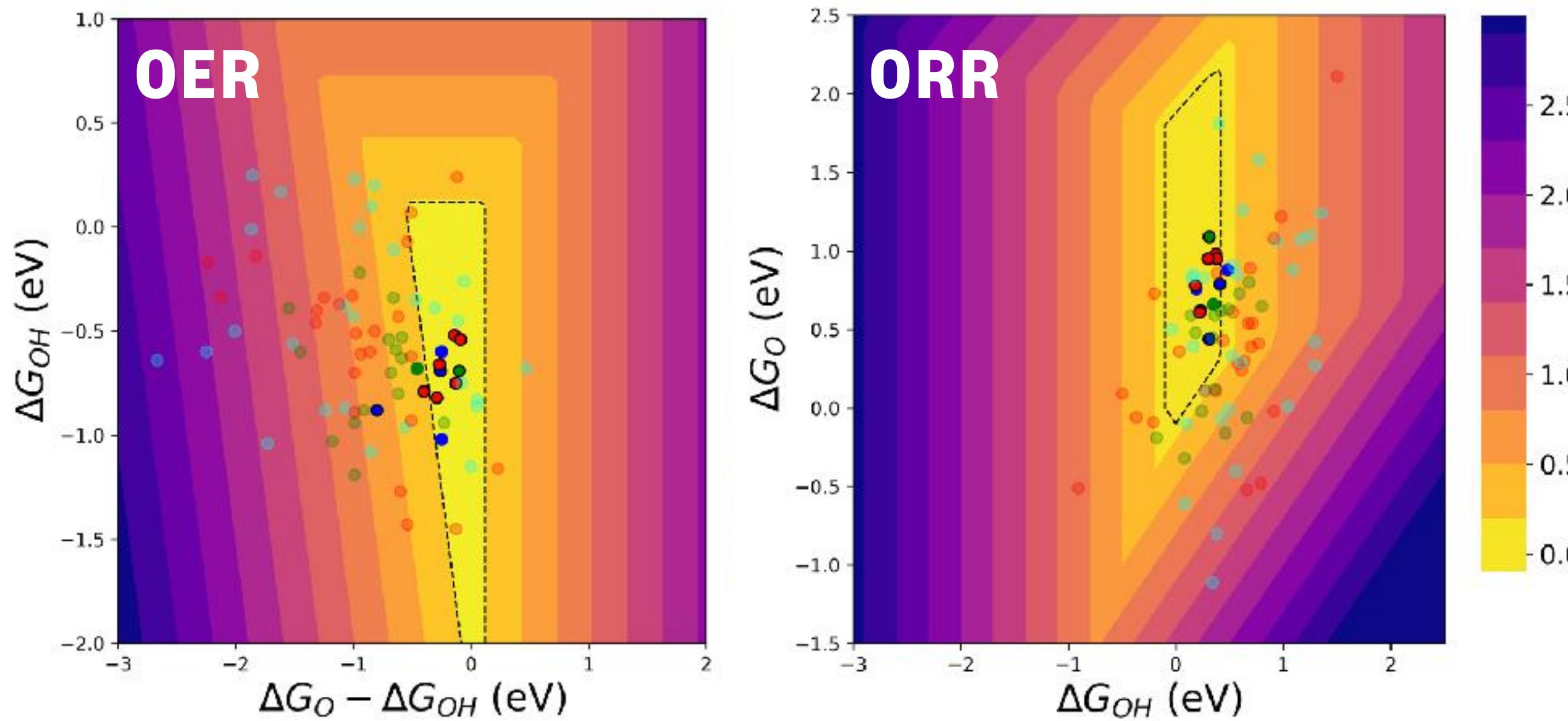
Materials Constraints

Scaling Relationships

- Highly correlated OH—OOH energies across different materials
 - One less degree of freedom
- OER potential determining steps:
 - Formation of O^* and OOH^*
- ORR potential determining steps:
 - Formation of OOH^* and release of H_2O

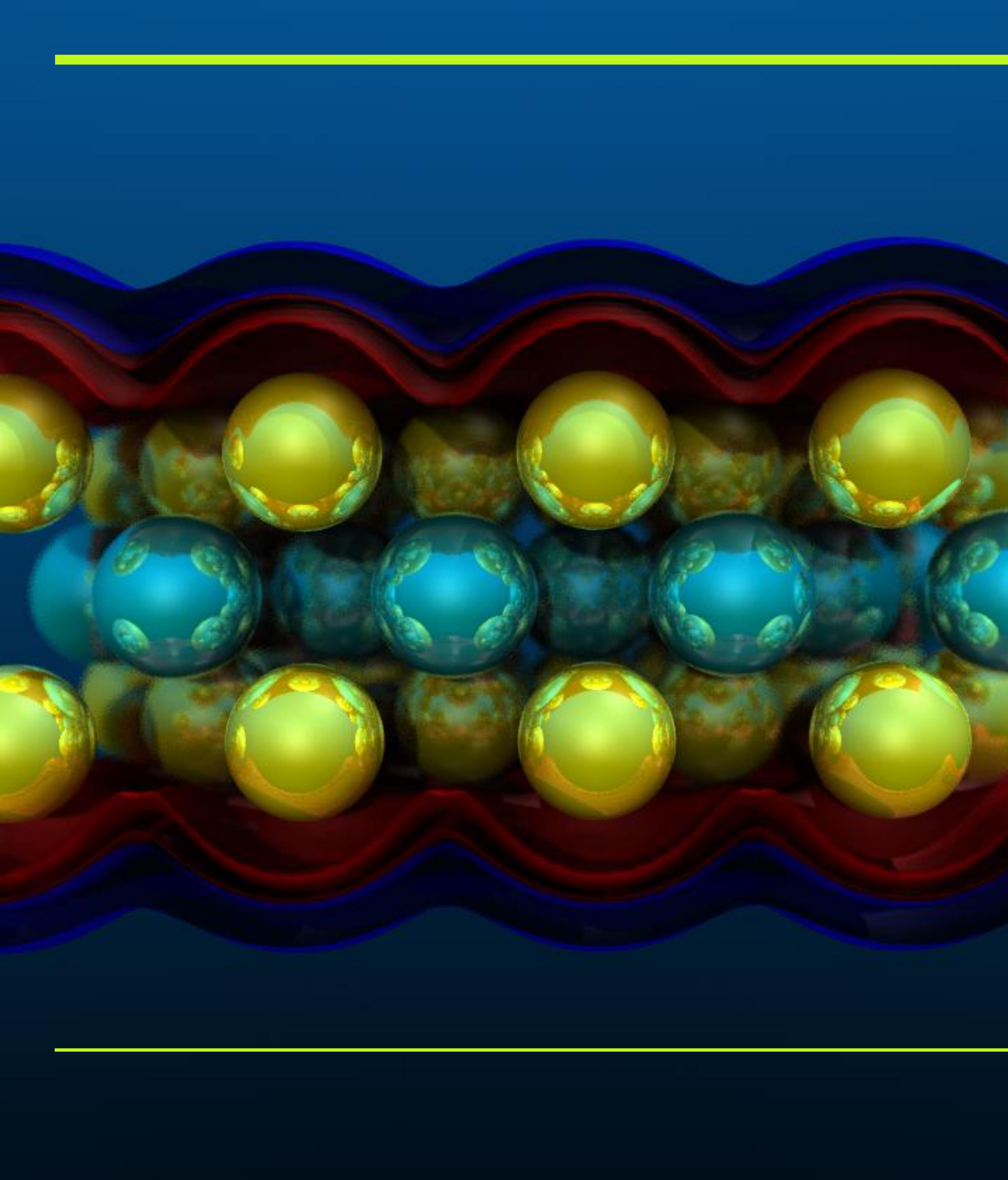
Climbing to the Top of the OER Volcano

OER free energy (in eV) at an over potential of 0.5V, as a function of intermediates-based descriptors. Solid points correspond to **stable** experimentally available compounds. Blue/Red/Green colors correspond to 2H/1T/1T' structures.



Volcanoes Stability and Activity

- OER:
 - 18 active materials (η_{TD} as low as 0.24 V)
 - 12 thermodynamically or kinetically stable
 - 8 reported experimentally
- ORR
 - 21 active materials (η_{TD} as low as 0.29 V)
 - 13 thermodynamically or kinetically stable
 - 9 are reported experimentally



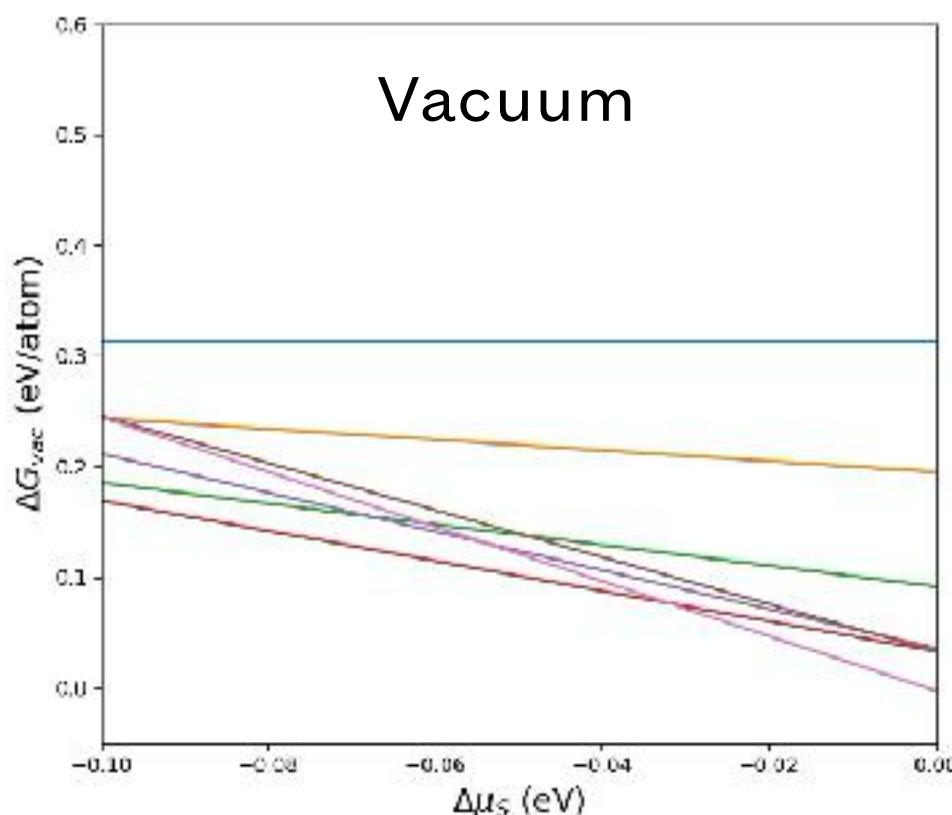
Activating 2D MoS₂

For the Oxygen Evolution Reaction (OER)

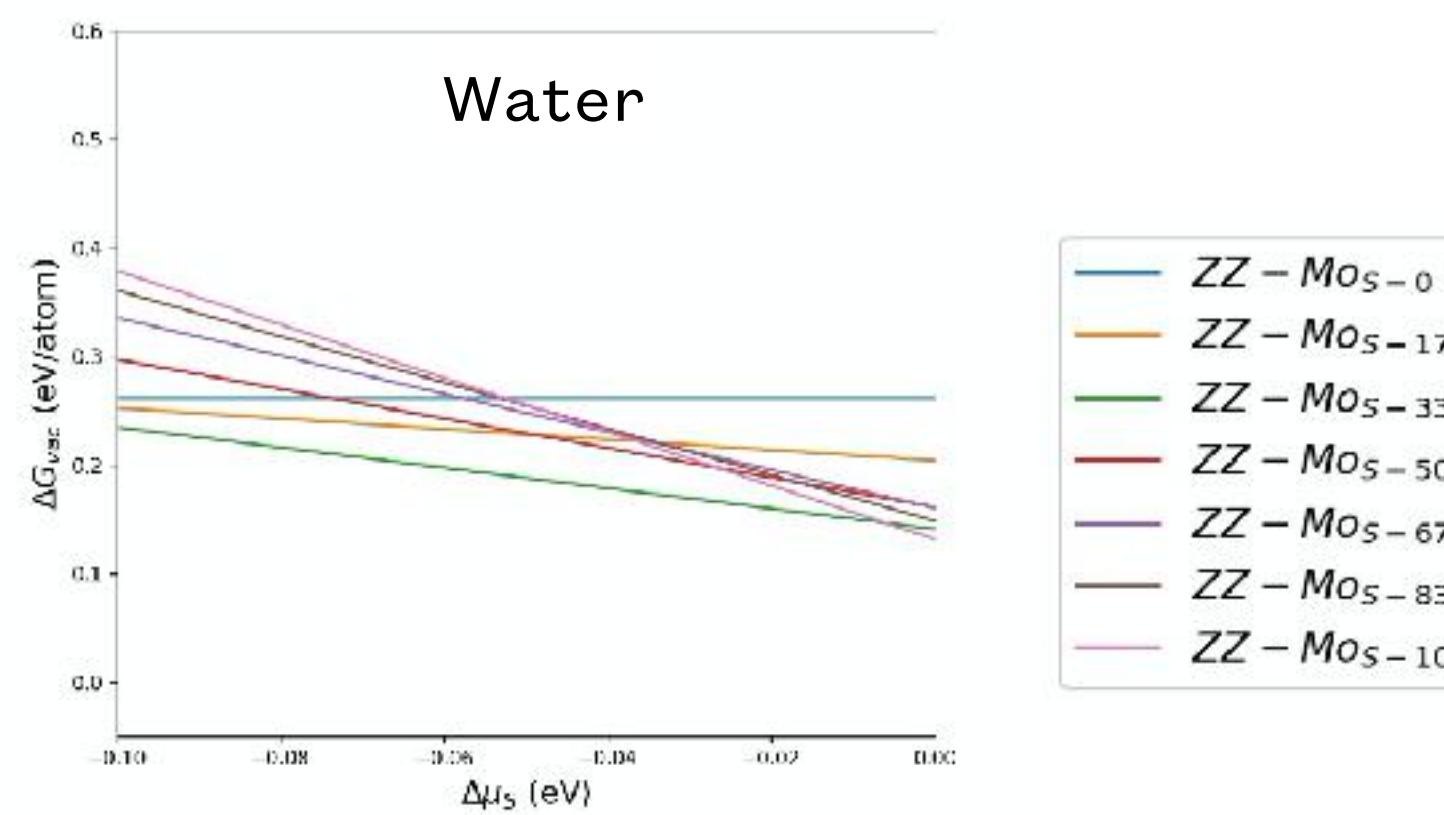
- MoS₂
 - Feasible synthesis
 - Good band alignment
- Basal plane is not active
- Promisingly small over potentials for quantum dots
- Can defects/edges and environment be used to activate the material?

Stability of MoS₂ Edges to Sulfur Concentration

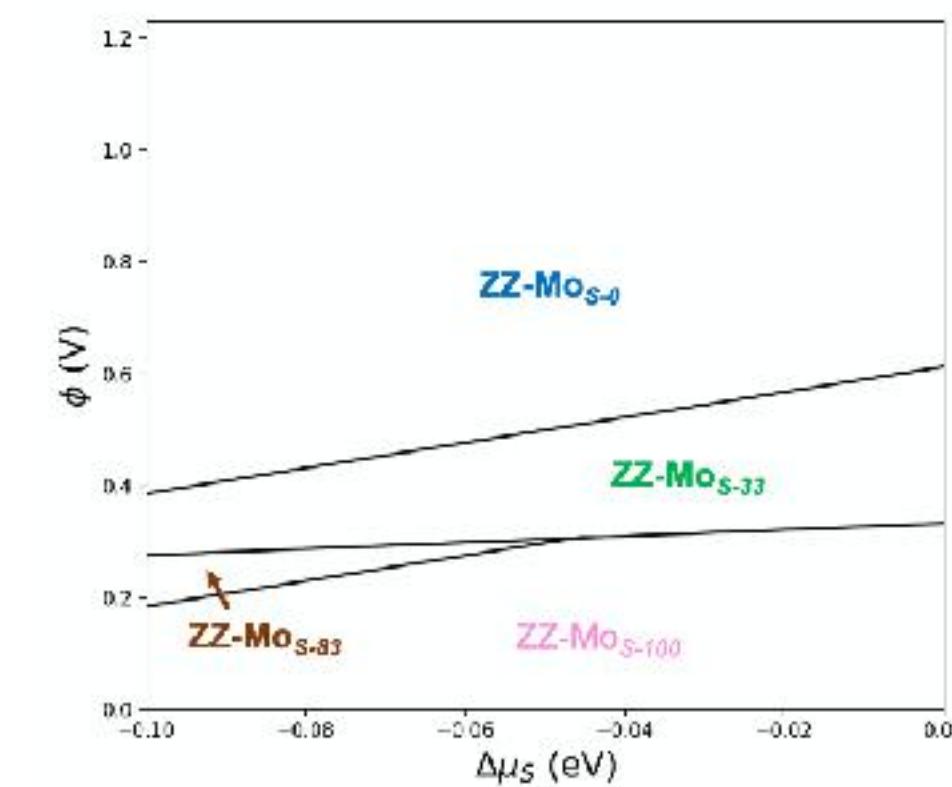
Formation energy vs. chemical potential of sulfur in vacuum and in water, as modeled by hybrid AIMD simulations



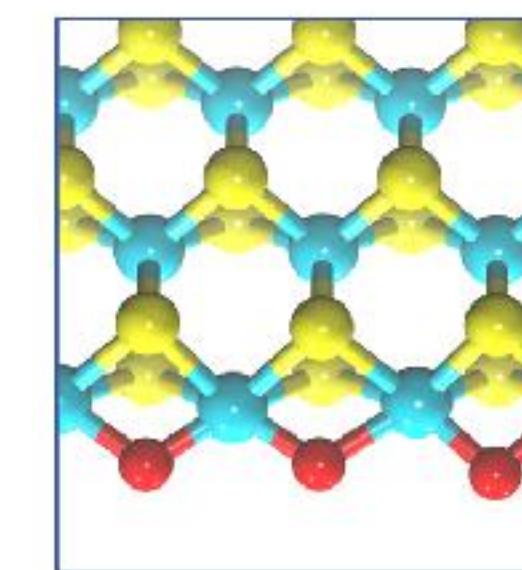
(a)



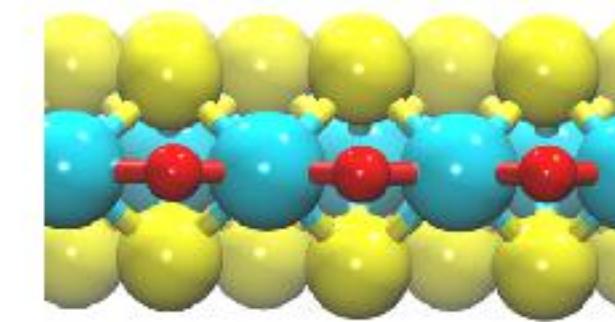
(b)



(c)

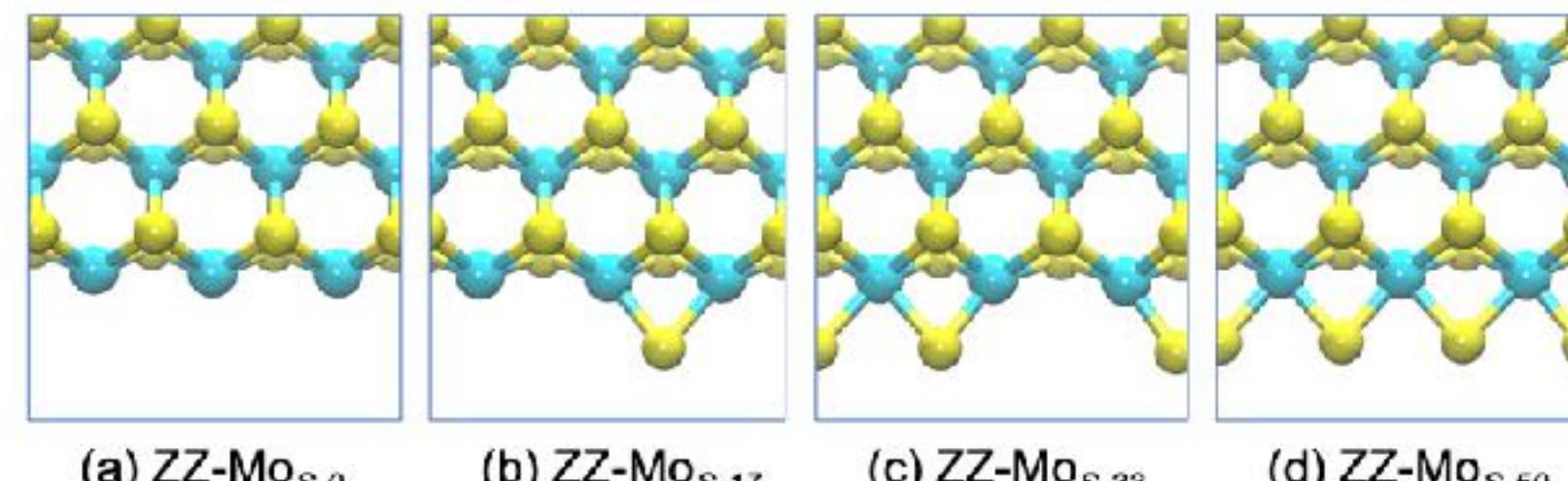


(d)



On the Edge Stability in solution

- Zig-zag edges
- Mo or S termination
- Variable S concentration

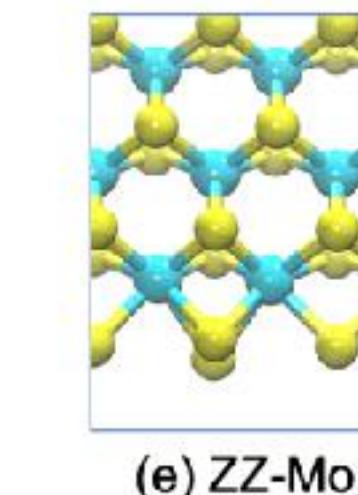


(a) ZZ-Mo_{S-0}

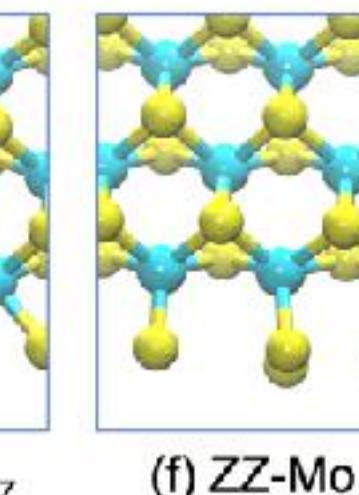
(b) ZZ-Mo_{S-17}

(c) ZZ-Mo_{S-33}

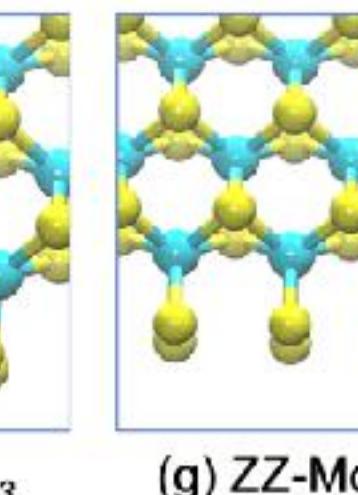
(d) ZZ-Mo_{S-50}



(e) ZZ-Mo_{S-67}



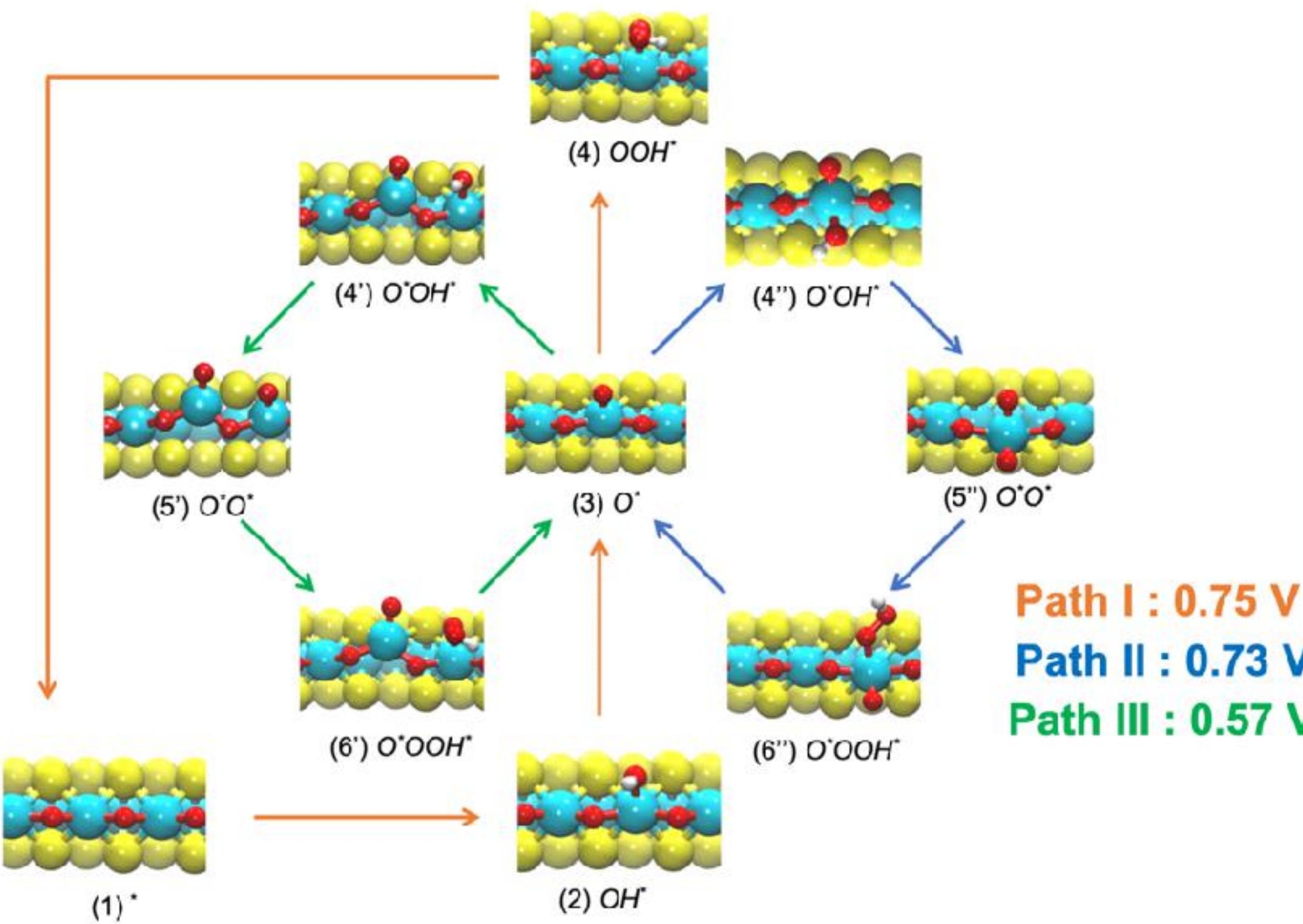
(f) ZZ-Mo_{S-83}



(g) ZZ-Mo_{S-100}

Oxygen Evolution Reaction

A single-site catalytic pathway involves the formation of three intermediate oxygen species. Basal plane and S-edges show high over potentials (>1.5 eV), with the OOH^* formation as the rate-limiting step. Instead, the oxidized edge shows alternative pathways with significantly reduced over potentials.



N. Karmodak, O. Andreussi, *J. Phys. Chem. C*, 125, 19, 10397 (2021)

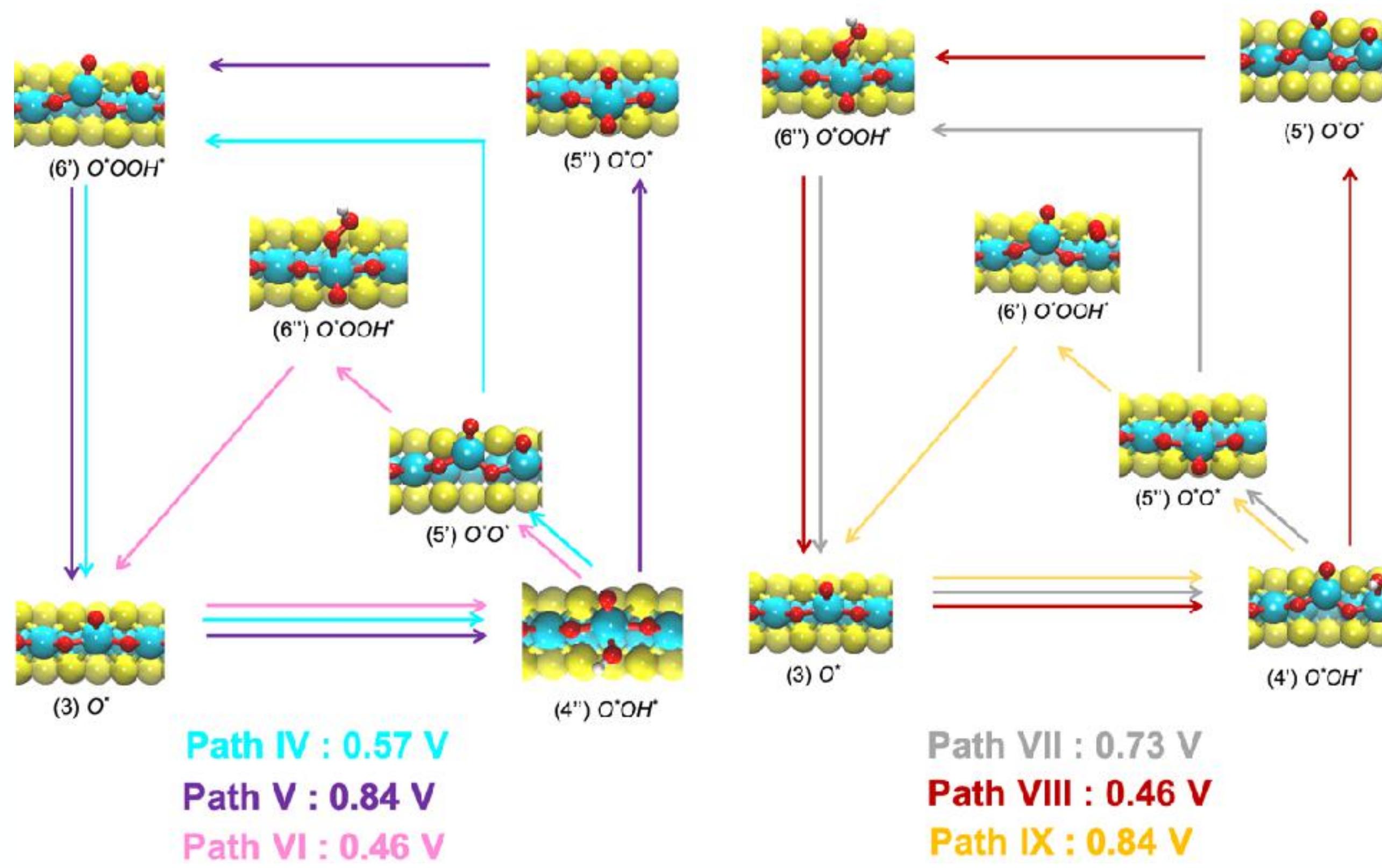
Electro-Catalytic Activity Single-site Pathways

- Hybrid simulations (one water layer + confinement)
- Molecular dynamics sampling and NEB calculations of transition states

Units: eV/V	ΔG_1	ΔG_2	ΔG_3	ΔG_4	η_{TD}
MoS₂(Basal)	1.92	-0.43	3.36	0.08	2.13
ZZ-Mos-100	1.44	0.71	3.35	-0.58	2.12
ZZ-Mos-50	1.21	0.69	2.89	0.12	1.66
ZZ-Moo I	0.10	0.97	1.87	1.98	0.75
ZZ-Moo II	0.80	1.39	1.96	0.77	0.73
ZZ-Moo III	1.31	1.15	1.80	0.66	0.57

Reconstruction Pathways

Possible pathways on a 50% S-coverage ZZ edge. Thermodynamic reorganizations followed by electrochemical steps allow to lower the over potentials.



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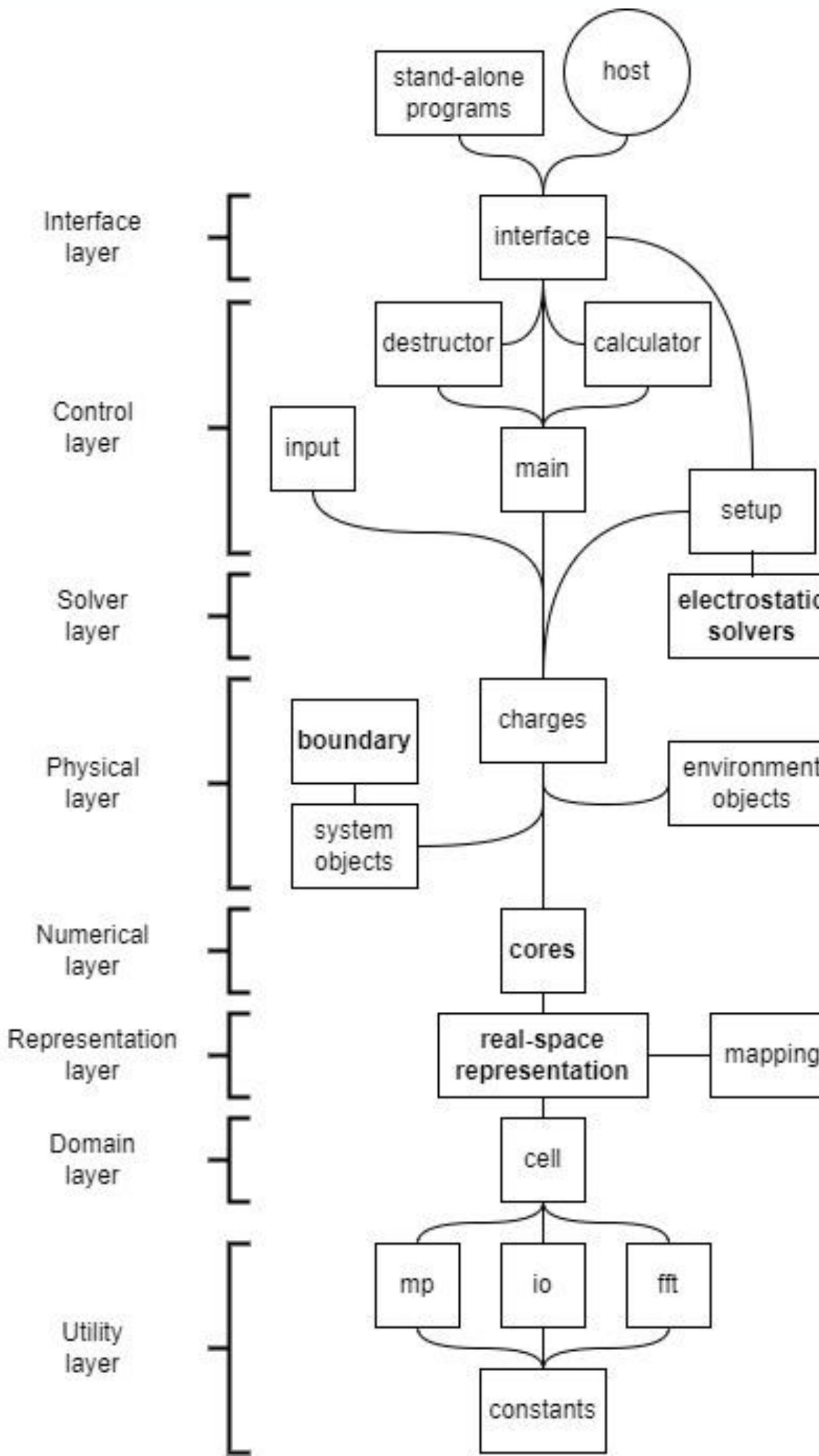
More than One Way Two-sites Pathways

- Energy gain in Mo-O formation allows structural reconstruction
- Limiting the Mo-O bond strength facilitates the OOH* formation

Units: eV/V	ΔG_1	ΔG_2	ΔG_3	ΔG_4	η_{TD}
ZZ-Moo IV	0.80	1.66	1.80	0.66	0.57
ZZ-Moo V	0.80	1.39	2.07	0.66	0.84
ZZ-Moo VI	0.80	1.66	1.69	0.77	0.46
ZZ-Moo VII	1.31	0.88	1.96	0.77	0.73
ZZ-Moo VIII	1.31	1.15	1.69	0.77	0.46
ZZ-Moo IX	1.31	0.88	2.07	0.66	0.84

Environ

www.quantum-environ.org



- From v2.0 a stand-alone library
 - Based on a FFT kernel (from Quantum Espresso)
 - Coupled with QE: ground state, geometry, vibrations, optical, magnetic, core-level spectroscopies
- In v 3.0 a new clean API
 - Coupling with DLPoly (unofficial)
 - Coupling with FHI-Aims (official, figuring out license)
- In v 3.1 Grand Canonical SCF
- In the next update (v 3.2?) pre-parametrized solvents

Don't forget to checkout the documentation and ask questions on the Google group

Envyon

A (still beta) Python Refactoring

The screenshot shows the GitHub repository page for 'Envyon'. The top navigation bar includes 'Edit Pins', 'Watch 0', 'Fork 0', 'Star 0', and a dropdown menu. Below the header are buttons for 'main' (selected), '1 Branch', and '1 Tags'. A search bar and 'Add file' button are also present.

The main content area displays a list of commits from 'olivieroandreussi':

- Merge branch 'develop' · 86f292b · 3 weeks ago · 380 Commits
- Merge branch 'develop' into documentation · 3 weeks ago
- Fix gradient modulus bug · 3 weeks ago
- Added ms-gcs input parameters · 2 years ago
- Merge remote-tracking branch 'origin/develop' into calcul... · 3 weeks ago
- Add test for QEpy + Envyon: volume embedding · 9 months ago
- Updated style rules in CI/CD · 2 years ago
- Started project · 3 years ago
- Started project · 3 years ago
- Started project · 3 years ago
- Ignoring mypy no-redef error · 2 years ago

On the right side, there's an 'About' section with a note: 'No description, website, or topics provided.' It includes links for 'Readme', 'MIT license', 'Activity', 'Custom properties', '0 stars', '0 watching', '0 forks', and 'Report repository'. Below that is a 'Releases' section with '1 tags' and a link to 'Create a new release'. The 'Packages' section notes 'No packages published' and a link to 'Publish your first package'. The 'Contributors' section lists 'edan-bainglass' and 'olivieroandreussi'.

Envyon - Python Package for Continuum Embedding
A Python implementation of Environ - a continuum embedding FORTRAN module

- Based on Python FFTs
- Coupled with QEpy
- Coupled with DFTpy and eDFTpy
- On-going coupling with MBX



www.materialab.org



Current Members

- Gabriel Medrano (PhD Physics UNT)
- Pradip Si (PhD Chemistry UNT)
- Eric Read (BS Chemistry, Boise State)
- Thiago de Silva (PhD Materials, Boise State)
- Denis Mulumba (PhD CS, Boise State)

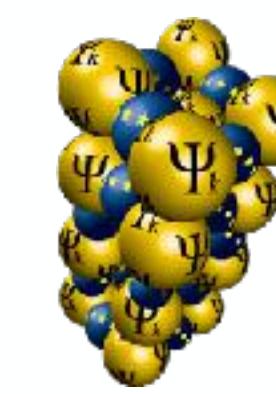
Former Members

- Dr Edan Bainglass
- Ajay Jayanth (TAMS, currently undergrad at UT Dallas)
- Nicholas Martinez (BS Physics)
- Dr Matthew Truscott (PhD Physics)
- **Dr Naiwrit Karmodak** (now Assistant Professor, Chemistry, Shiv Nadar Institute)

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