

Oliviero Andreussi
i-CoMSE School 2023



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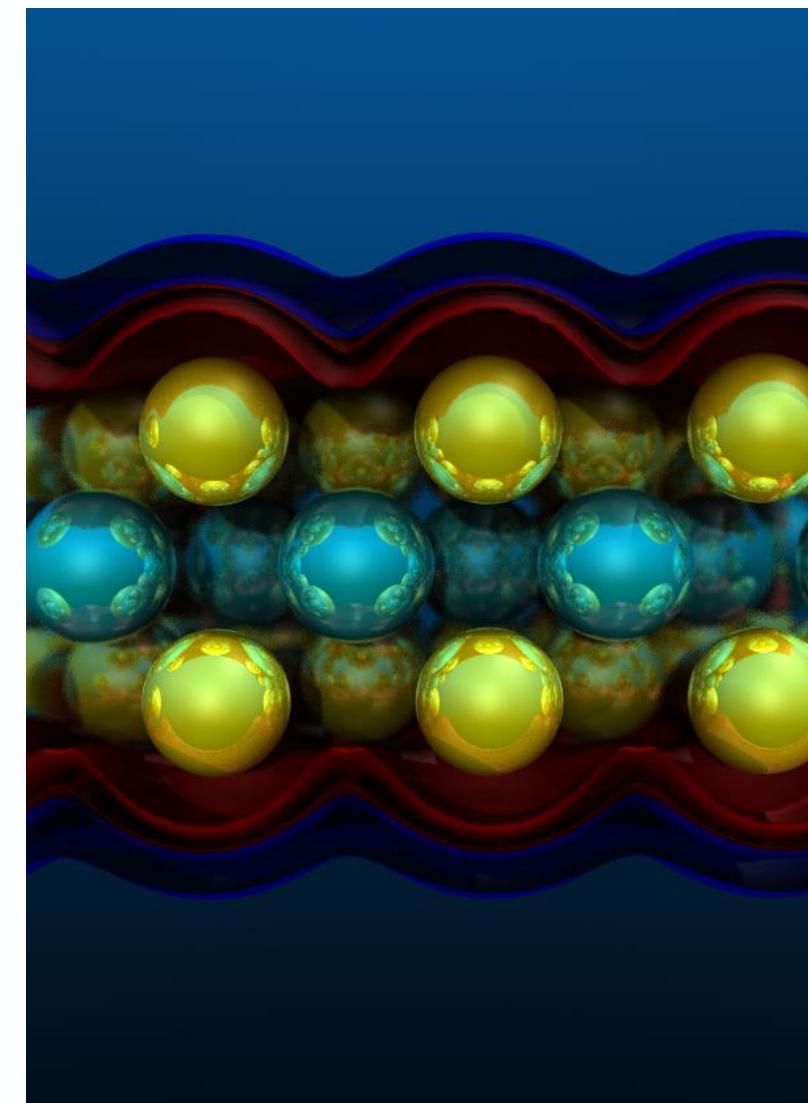
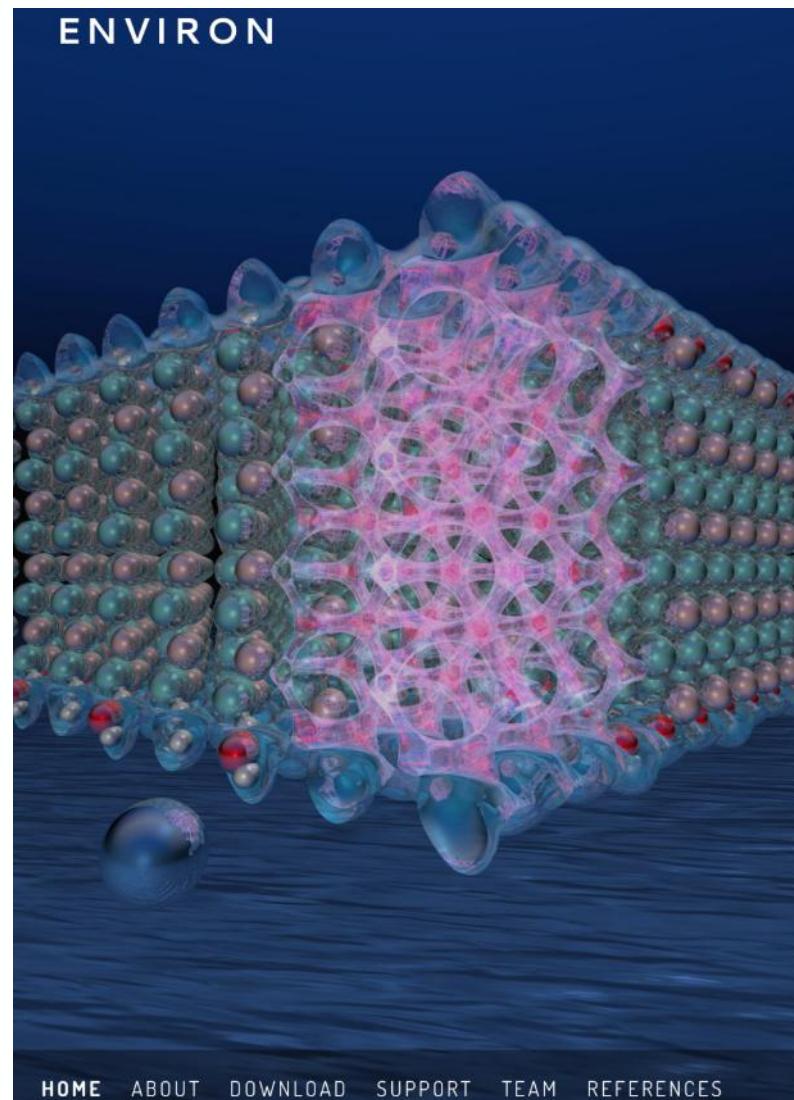
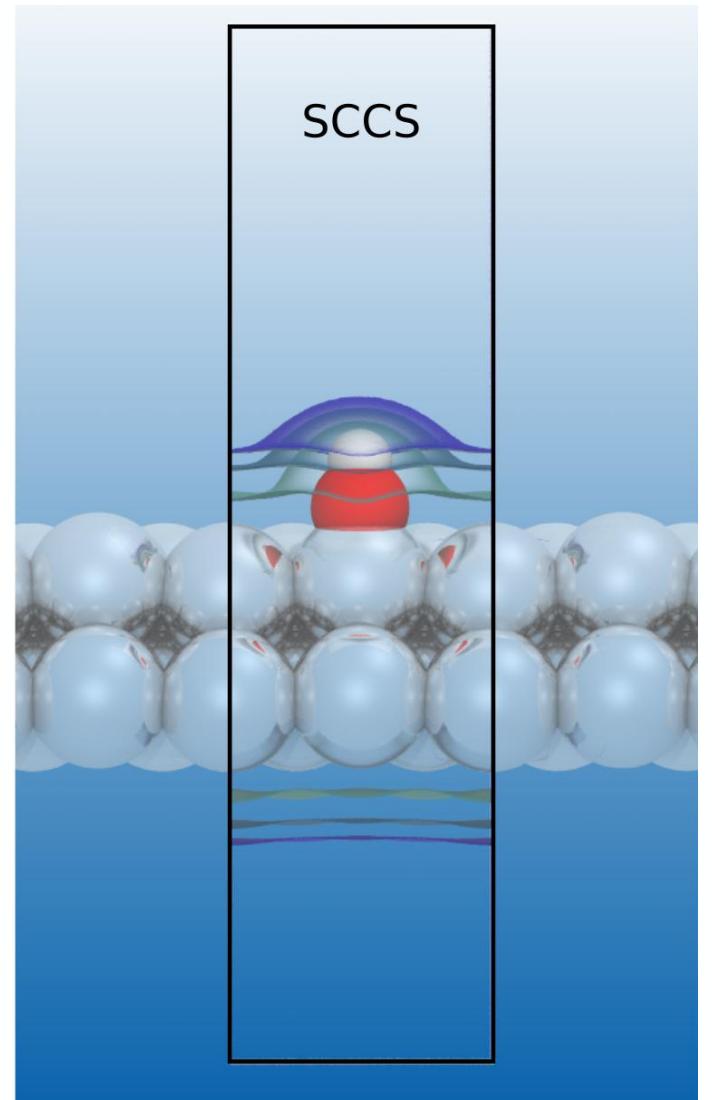
Continuum Models for Wet Electrified Interface

Multiscale and Ab initio Techniques for Energy Research and InnovAtion LAB Physics, Chemistry, Materials

www.materialab.org

www.quantum-environ.org

www.quantum-multiscale.org



1. Develop Models

- Continuum Electrochemical Environments
- Solvation Beyond the Continuum

2. Implement Codes

- Environ, PyE-C, Aiida plugins, etc.

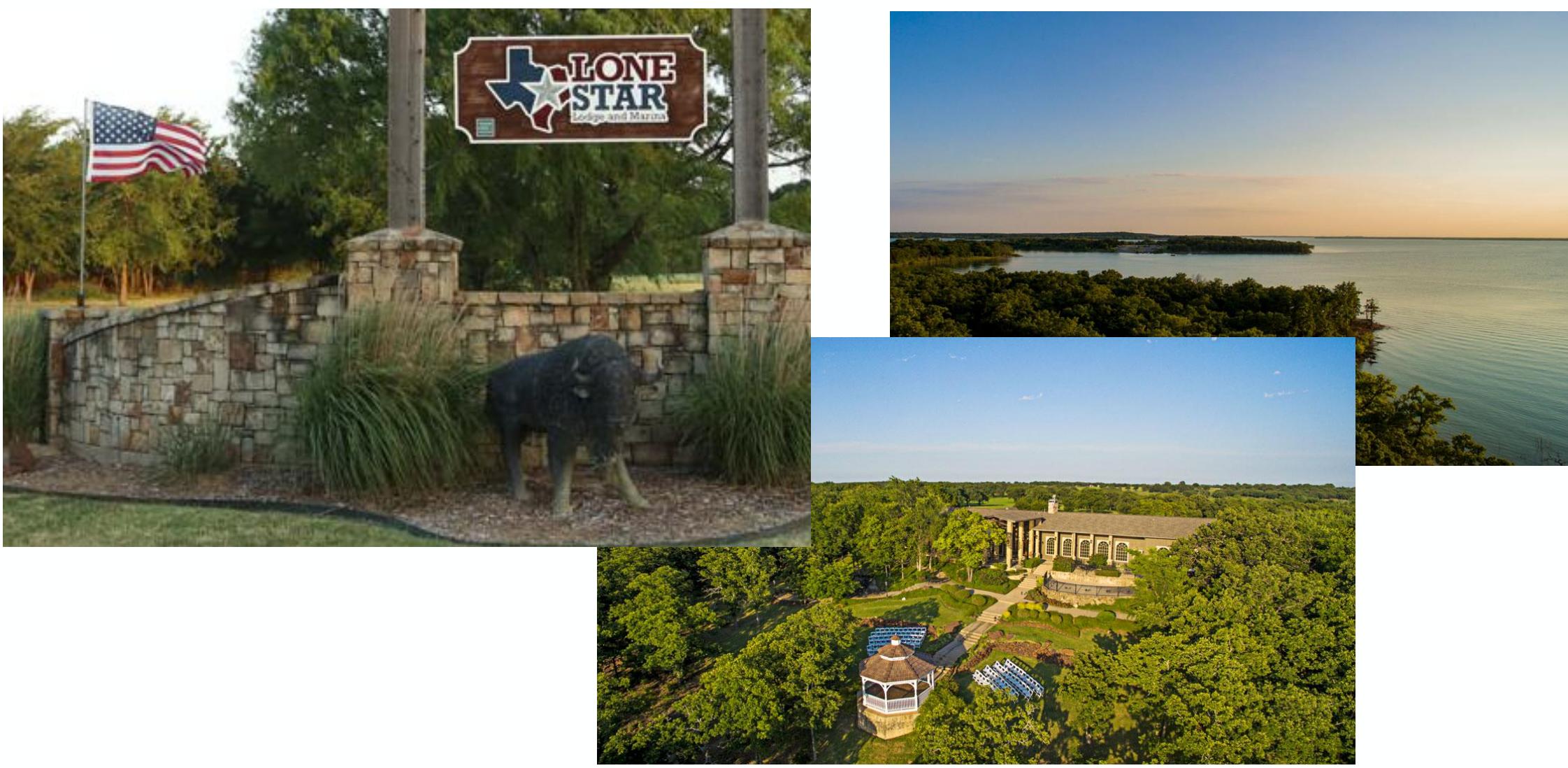
3. Simulate

- 2D Materials as Catalysts
- Inhibitors of Natural Gas Hydrates
- Metallic Glasses for Catalysis

Hackathons and Tutorials

quantum-multiscale.org/schools

- Coding multiscale methods in condensed matter simulations
 - A modular approach
 - Collaborations through Hackathons
- Quantum-MultiScale School 2021
 - Recordings available online



Electronic Structure Simulations in Materials

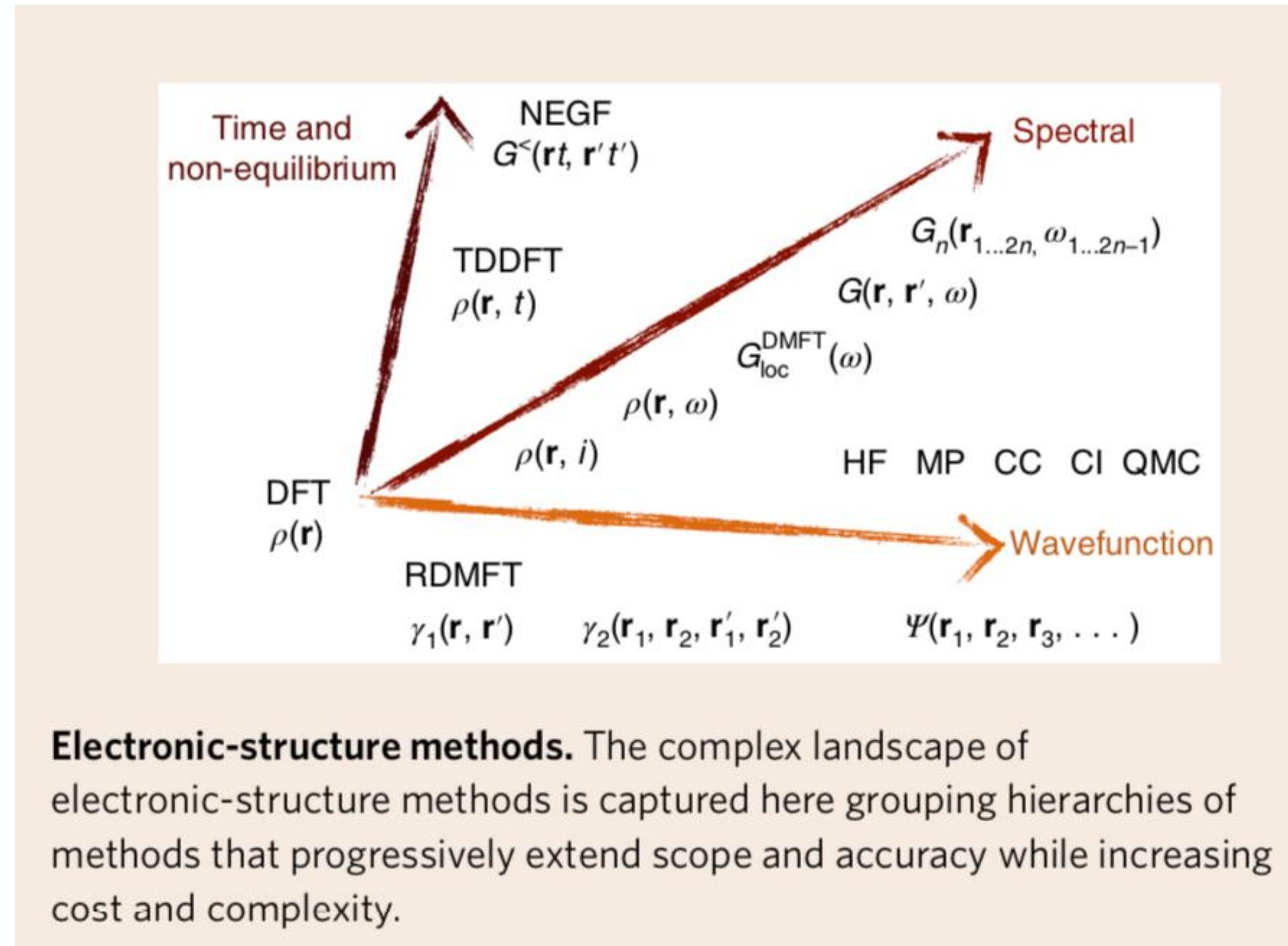


Table 1 | An overview of selected materials properties that can be obtained from DFT ground-state calculations

Materials properties	Models and theories	Electronic-structure toolbox
Atomic and cell geometries at fixed volume or pressure ^{13,166}	Hellmann–Feynman theorem	Total energy, forces and stresses
Zero-temperature stability ^{141–143} , formation energies, elastic constants, defects concentrations ¹⁶⁷	Equations of state (Murnaghan, Birch, ...), convex hulls, self-consistent chemical potentials	Total energies, forces and stresses for all different phases, defects, periodic-boundary corrections for charged defects
Chemistry and reactivity ^{84,85} , surface science ⁸⁸	Potential-energy surfaces, transition-state theory, volcano plots, kinetic Monte Carlo, rate equations, conical intersections, Marcus theory, Franck–Condon principle	Total energies and forces, van der Waals functionals, nudged-elastic-band method, constrained DFT, non-adiabatic dynamics (surface hopping, Ehrenfest)
Phonon dispersions and thermomechanical properties ¹⁸ , thermal and electrical transport ¹⁹ , superconductivity ¹⁶⁸	Linear-response theory, quasi-harmonic approximation, Grüneisen parameters, Boltzmann transport equation, equilibrium/non-equilibrium Green's functions, Allen–Dynes formula, Migdal–Eliashberg equations, superconducting DFT	Density functional perturbation theory and 2n+1 theorem for el-ph, ph-ph interactions, Born effective charges, dielectric tensor
Dielectric ¹⁸ , magnetic ¹²³ and topological properties ¹²⁵ , ferroelectrics ⁹² and multiferroics ¹⁶⁹	Linear-response theory, modern theory of polarization and of magnetization, electric enthalpy, model Hamiltonians, topological invariants	Berry phases, maximally localized Wannier functions, Wilson loops, spin-orbit coupling
Magnetic phases ⁵⁴ , magnetic anisotropy, spin waves ⁵⁵ , skyrmions ⁵⁶	Spin Hamiltonians (Ising, Heisenberg, Dzyaloshinskii–Moriya), paramagnetism as ensemble average	Spin-orbit coupling, non-collinear magnetism, force theorem, spin-density functionals
Thermodynamic ensembles ^{71,77,78} : finite-temperature properties and Helmholtz or Gibbs free energies ⁸¹ , transport coefficients ¹⁰⁸	Molecular dynamics, Monte Carlo, thermodynamic integration, metadynamics, path-integral molecular dynamics, Green–Kubo relations	Born–Oppenheimer and Car–Parrinello molecular dynamics, density functional perturbation theory, thermostats and barostats, ring-polymer mapping
Thermodynamic ensembles ^{88,129,130,170} : composition, chemical potential, partial pressure	Lattice Hamiltonians, Monte Carlo, mean-field approximation, cluster variation method, model entropies, special quasirandom structures	Cluster expansions, computational alchemy
Electrochemistry ^{86,89} , pH ⁹⁰ , operando studies	Grand-canonical simulations for electrons and ions, embedding, double-layer and diffuse-layer models	Computational hydrogen electrode, model solvents and electrolytes, Poisson–Boltzmann solvers, ensemble simulations, coupling with reservoirs
Macroscopic mechanical properties ^{109,110} (strength, fracture, and plasticity), soft matter, biomolecules	Multiscale simulations, QM-MM, dislocation dynamics, effective volumes	Force fitting, learn-on-the-fly, neural networks and kernel-regression potentials
Microscopies ¹⁷¹ : STM, AFM, TEM	Tersoff–Hamann model, electron scattering	Local density of states, first-principles molecular dynamics, all-electron charge density and potential, PAW reconstructions

If the exact functional were known, these properties would be exactly reproduced, provided all the microscopic phenomenology were included. The second column points to the broader concepts, models and phenomenology from physics, chemistry and materials science; the third column highlights the electronic-structure quantities, algorithms and theories that are typically coded. Band-structure properties require more advanced methods, but are often approximated using KS states. STM, scanning tunnelling microscopy; AFM, atomic force microscopy; TEM, transmission electron microscopy; QM-MM, quantum mechanics – molecular mechanics; el, electron; ph, phonon; PAW, projector augmented wave.

Electronic Structure Simulations in Materials

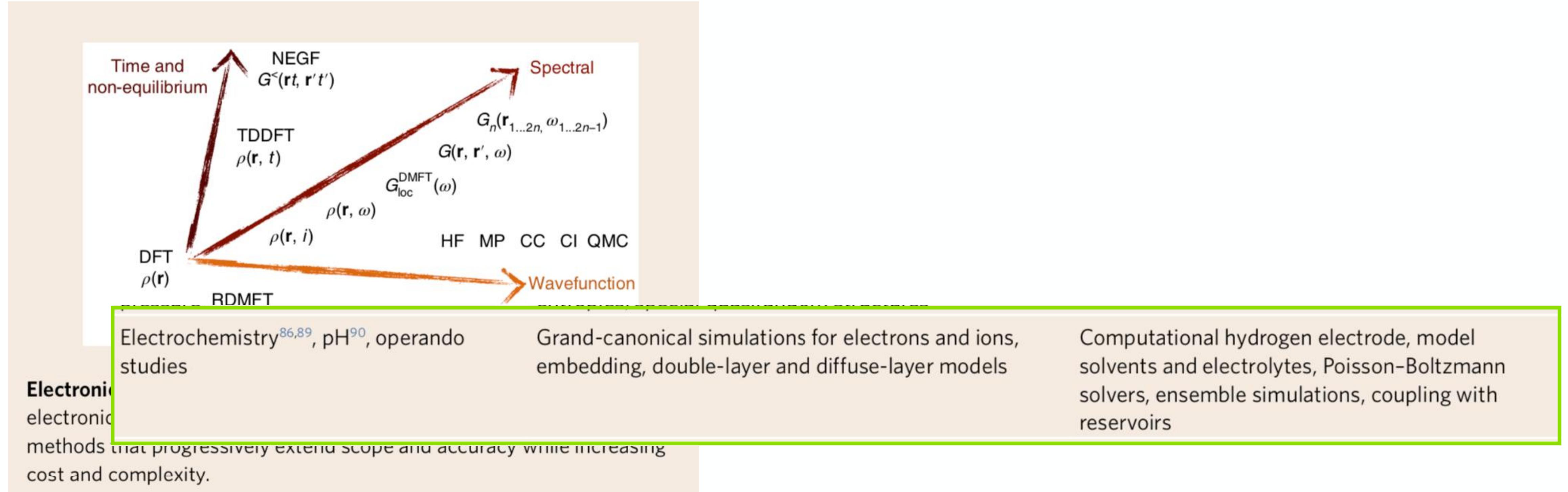


Image from M. Simoncelli acces.epfl.ch/cms/lang/en/pid/152725

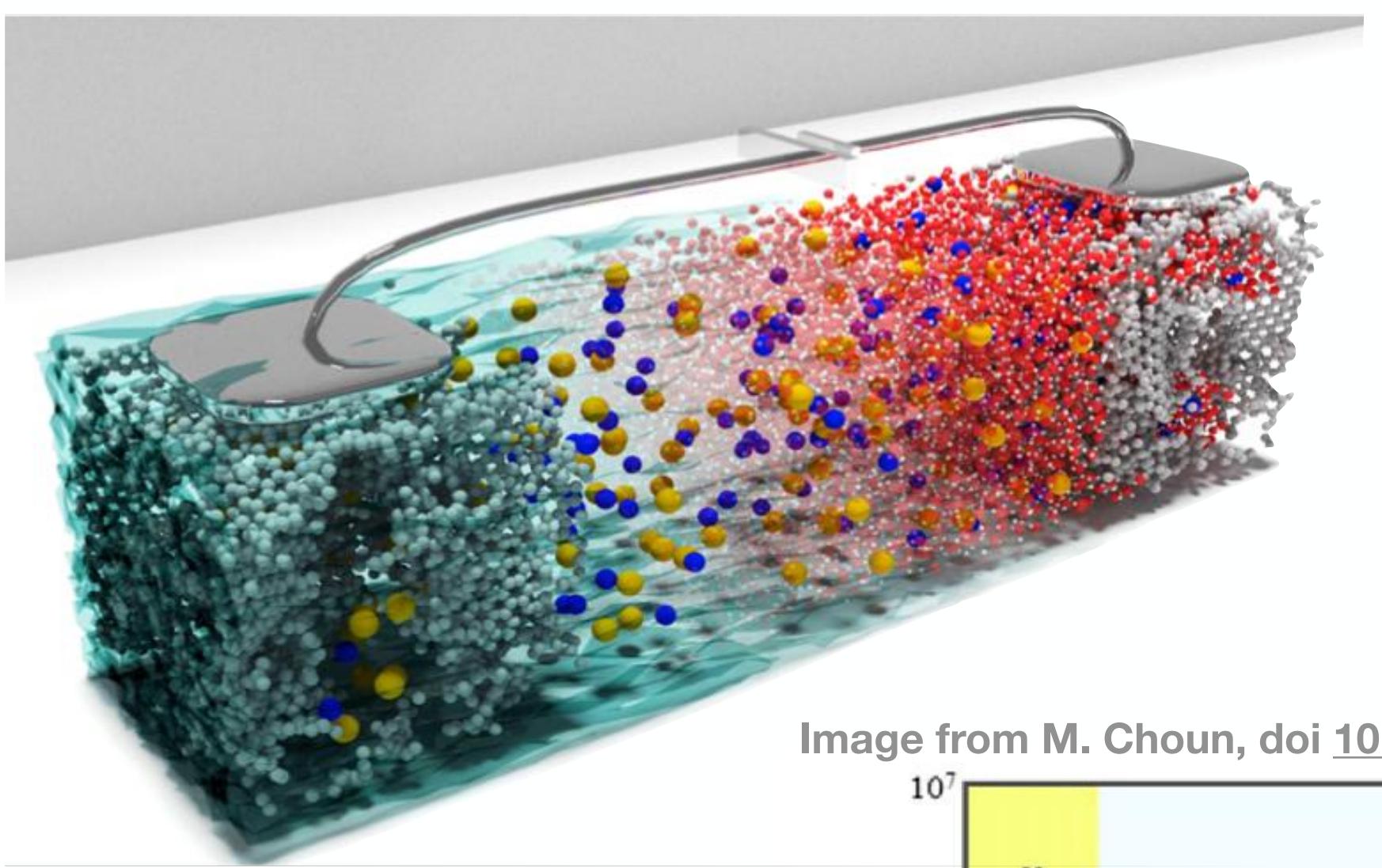
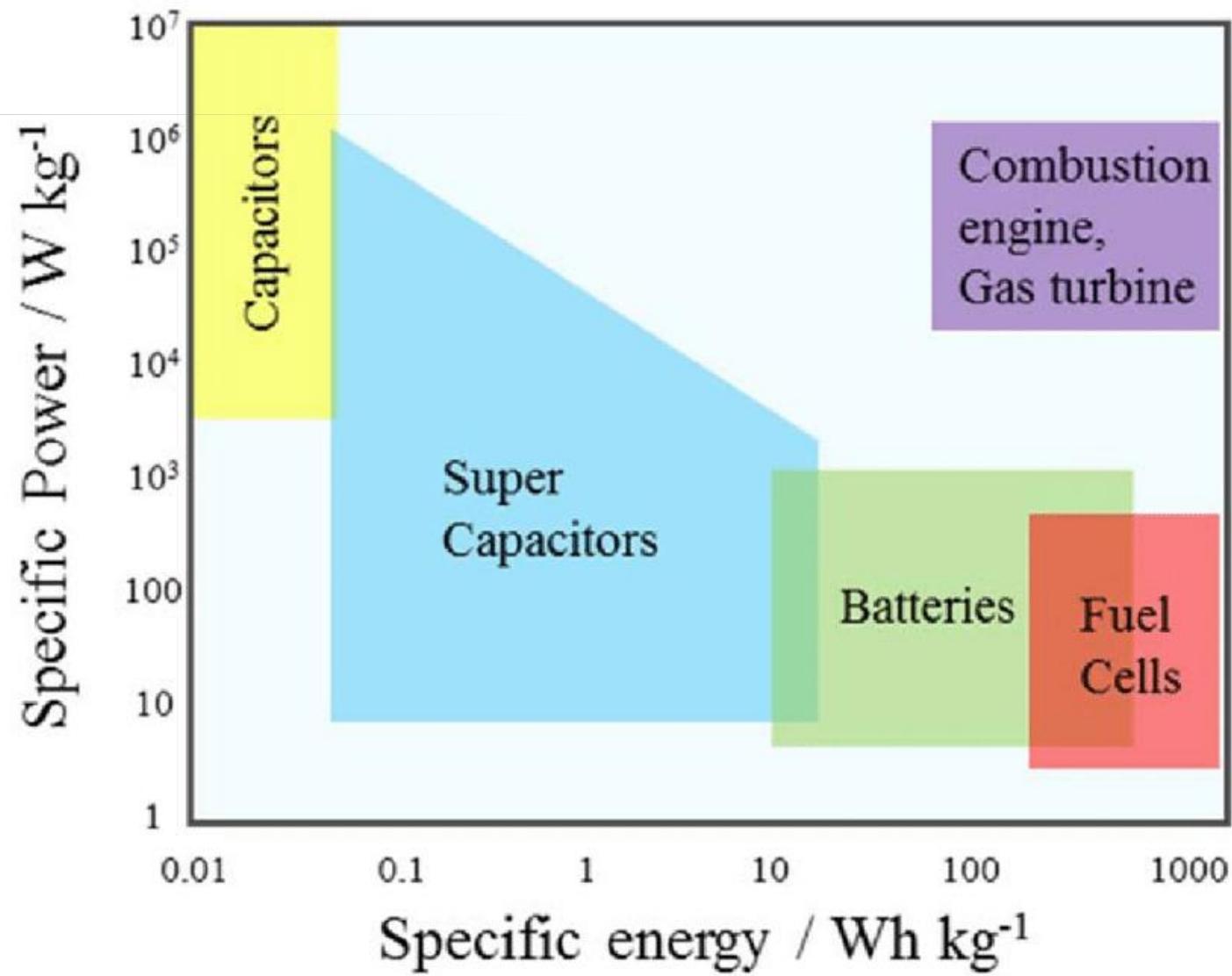


Image from M. Choun, doi [10.13140/RG.2.2.32153.42088](https://doi.org/10.13140/RG.2.2.32153.42088)



Energy Storage and Conversion

- Convert electrical energy into fuels (possibly starting from waste products)
- Convert solar energy into electrical energy
- Convert fuels into electrical energy
- Store energy via charge separation (capacitors, batteries)
- But also sensors and chemical devices

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

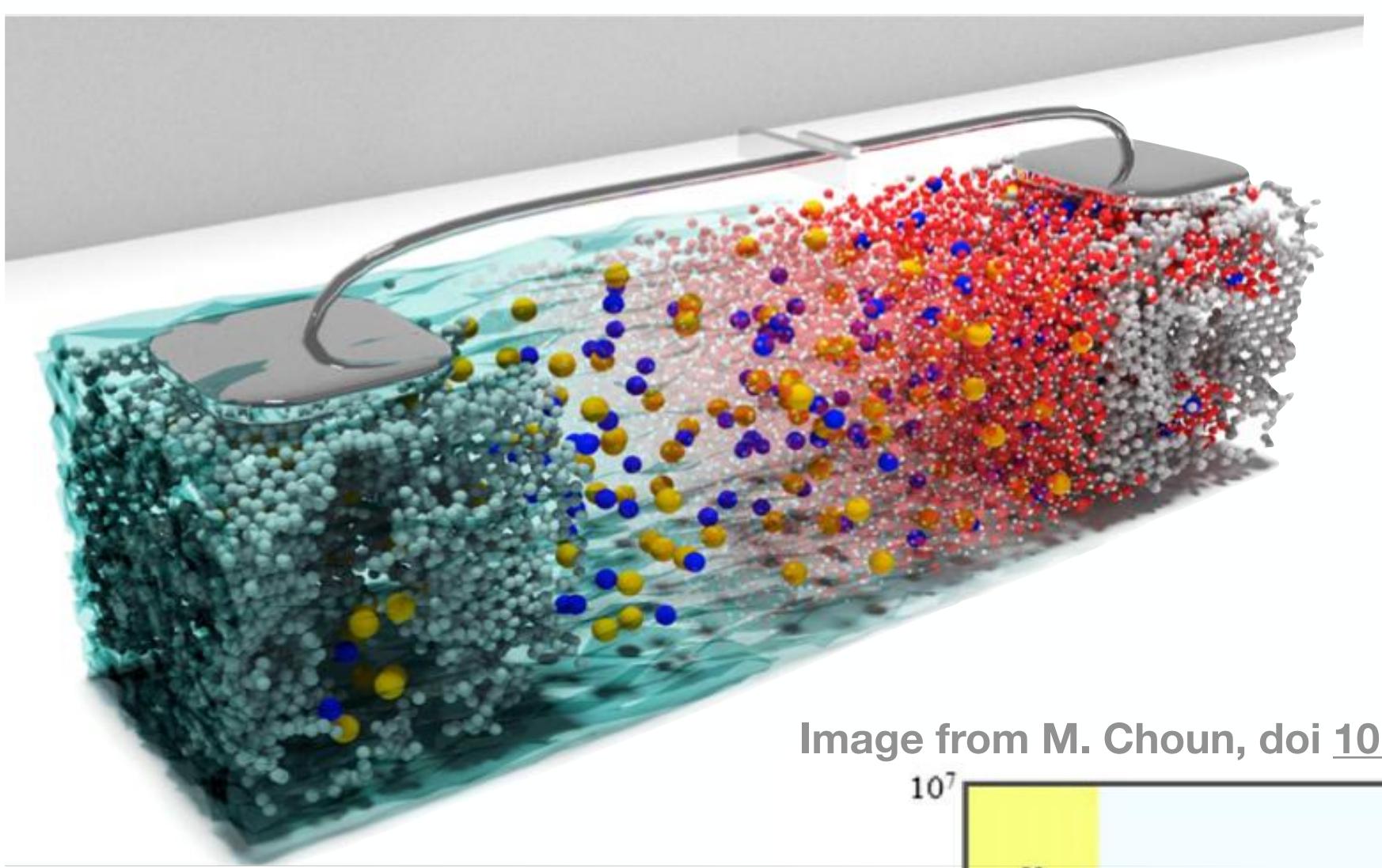
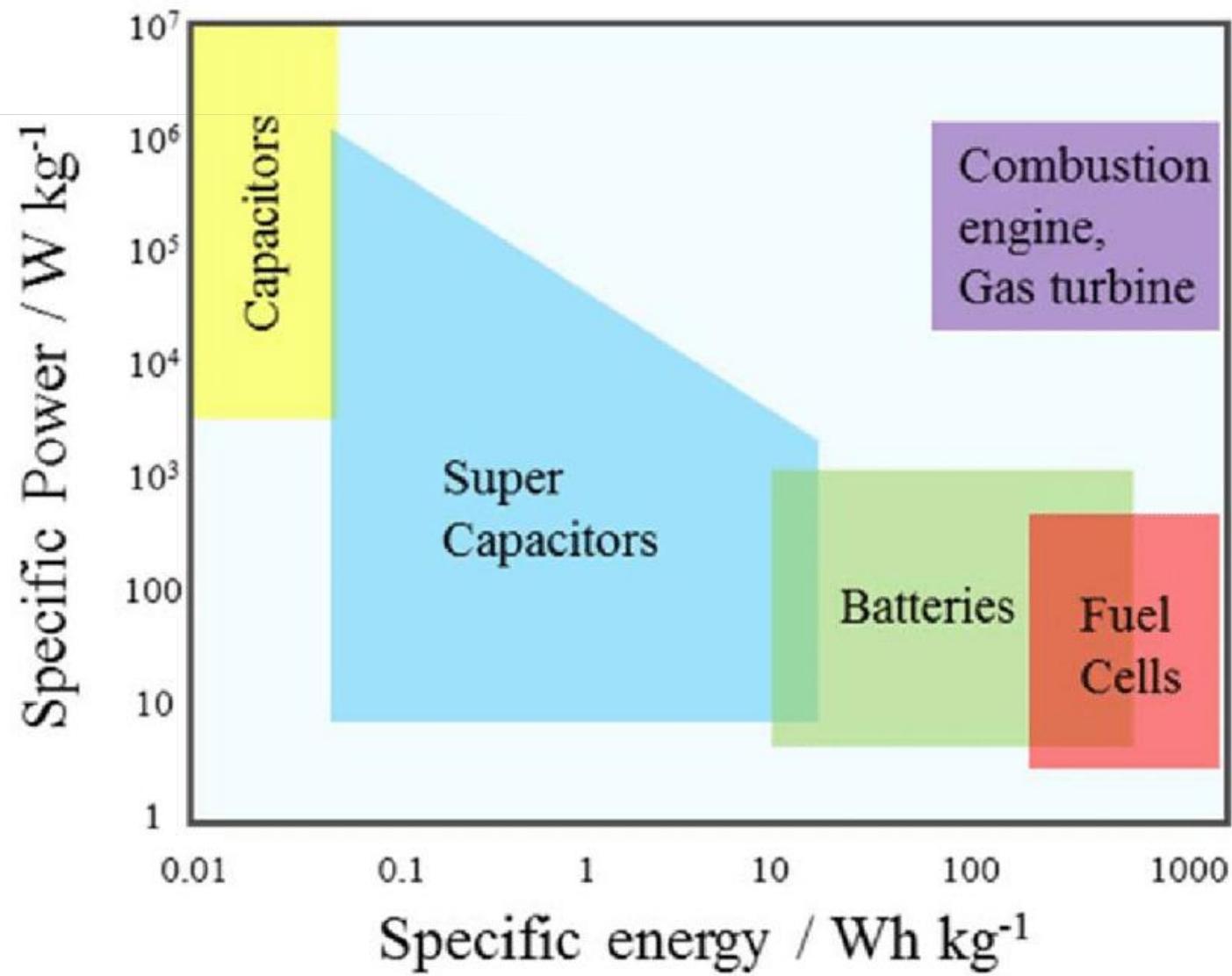


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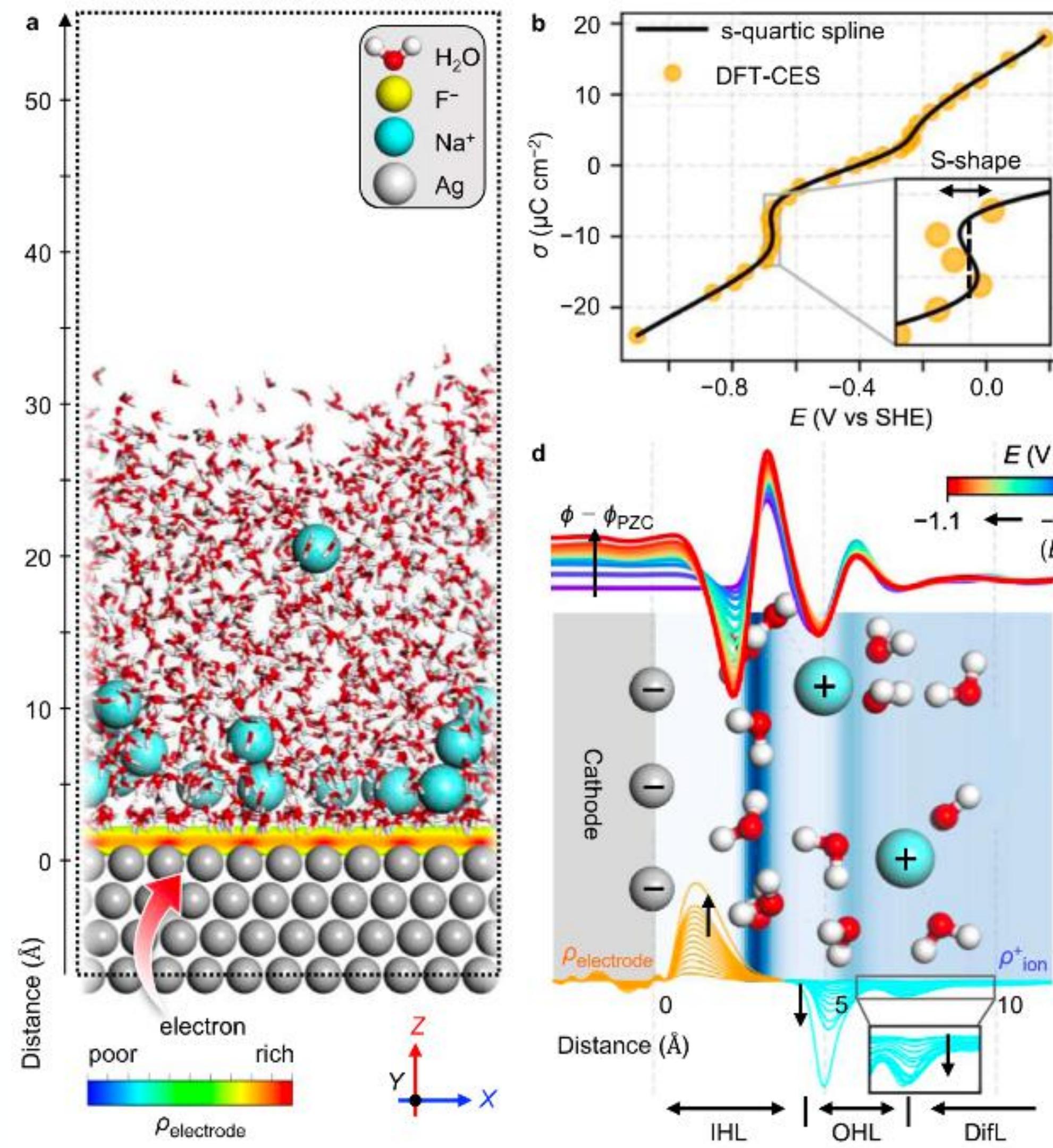
Energy Storage and Conversion

- Ordered electronic conductor
- Disordered ionic conductor
- Redox chemical species

THE INTERFACE IS THE DEVICE

- Electronic and atomistic details at the interface are important
- Environment is important

Modeling a Wet Electrified Interface What challenges?



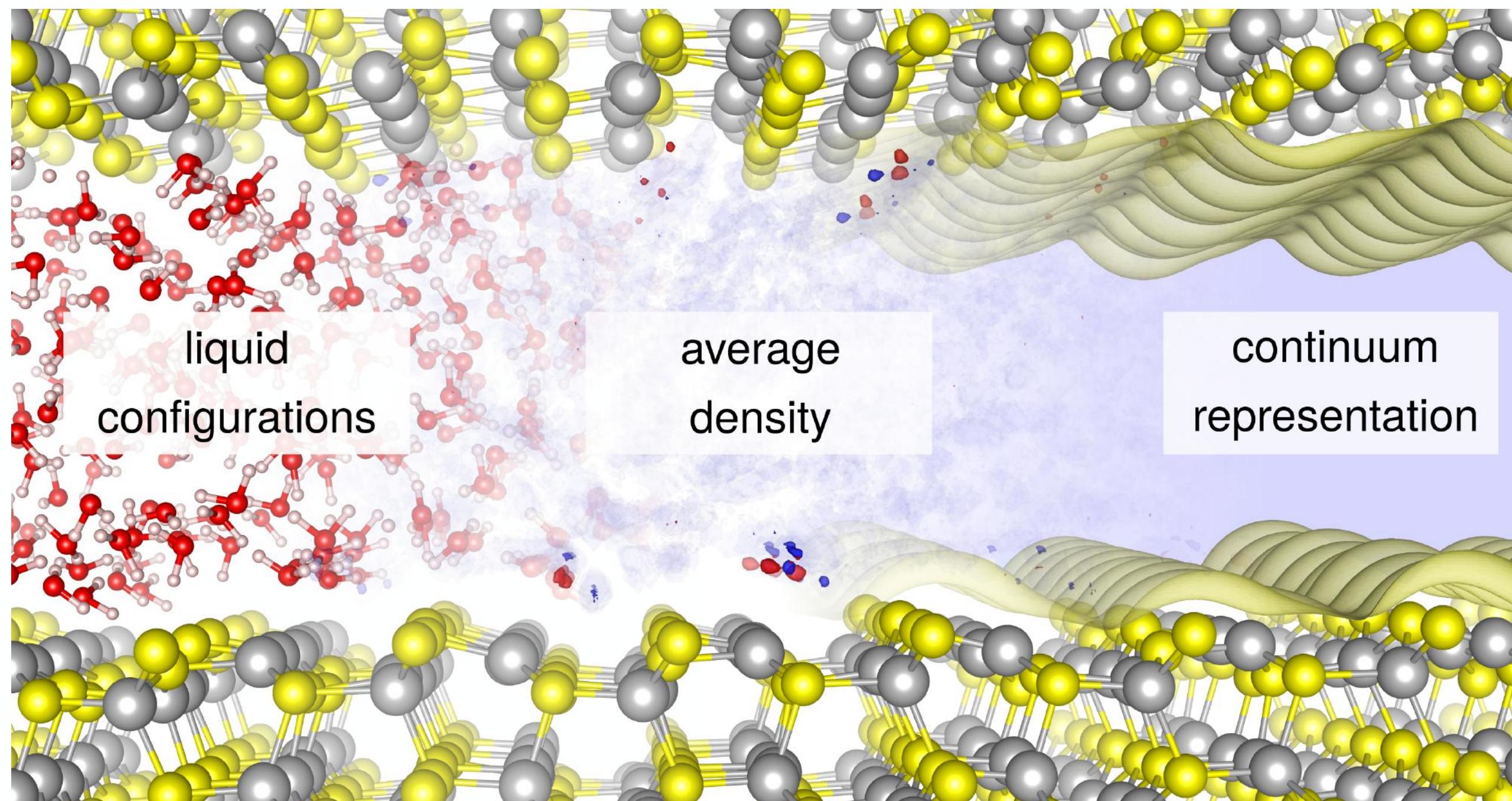
Shin et al., Nature Comm. 13, 174 (2022)

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.

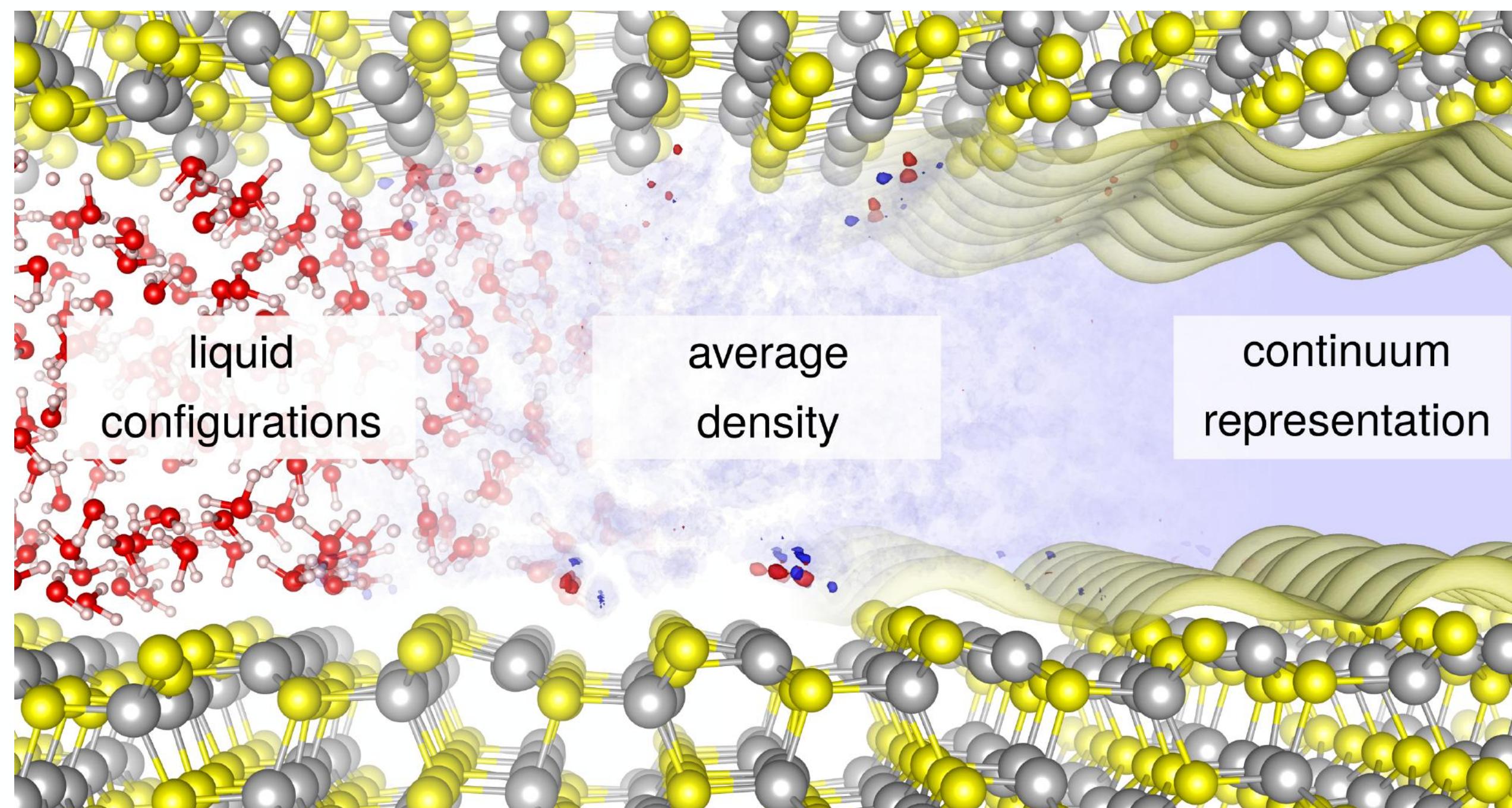
- Full ab-initio MD
- Classical QM/MM
- Continuum
- Hybrid approaches

Continuum Models

Ingredients

From Explicit to Implicit

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



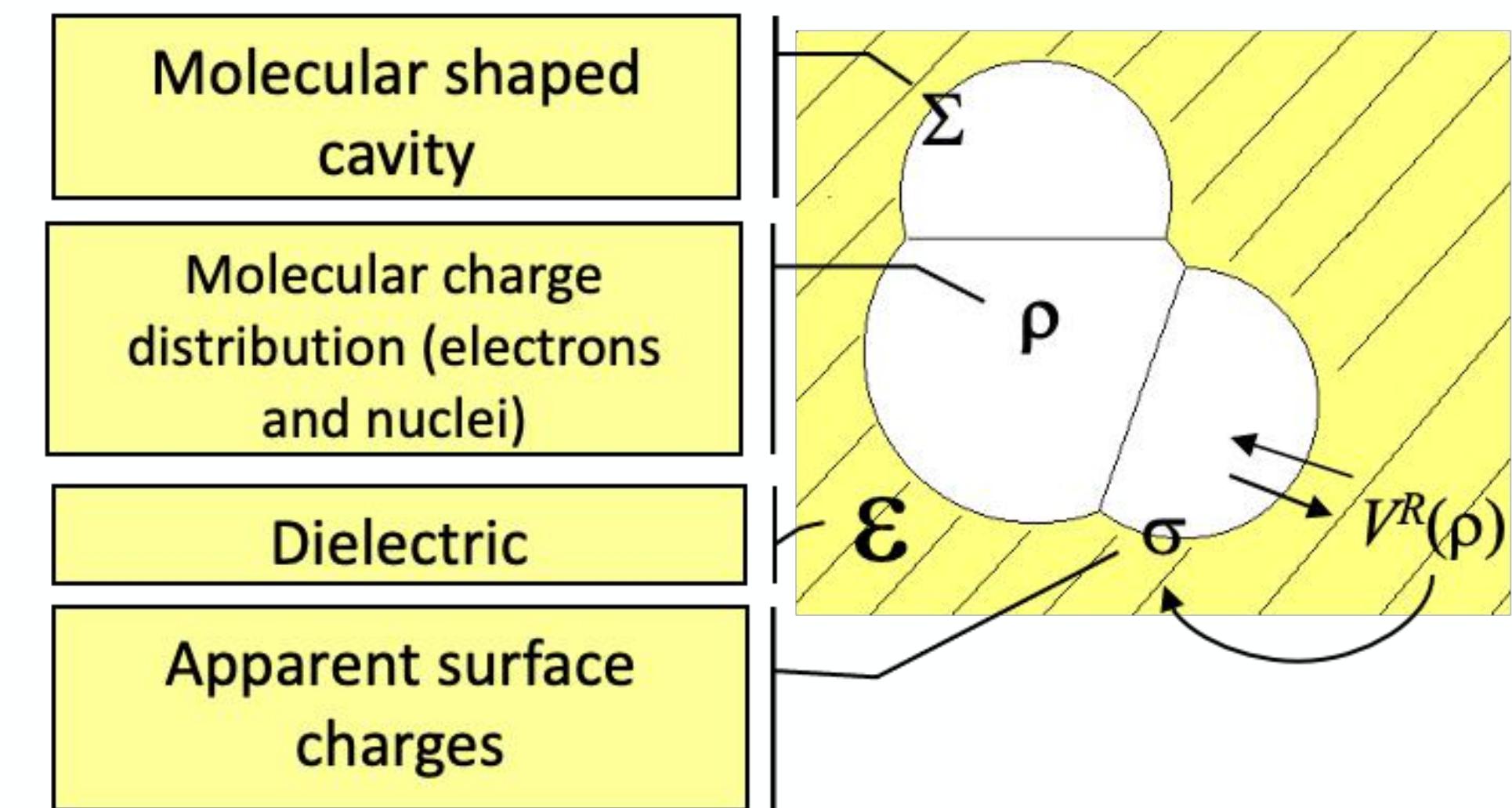
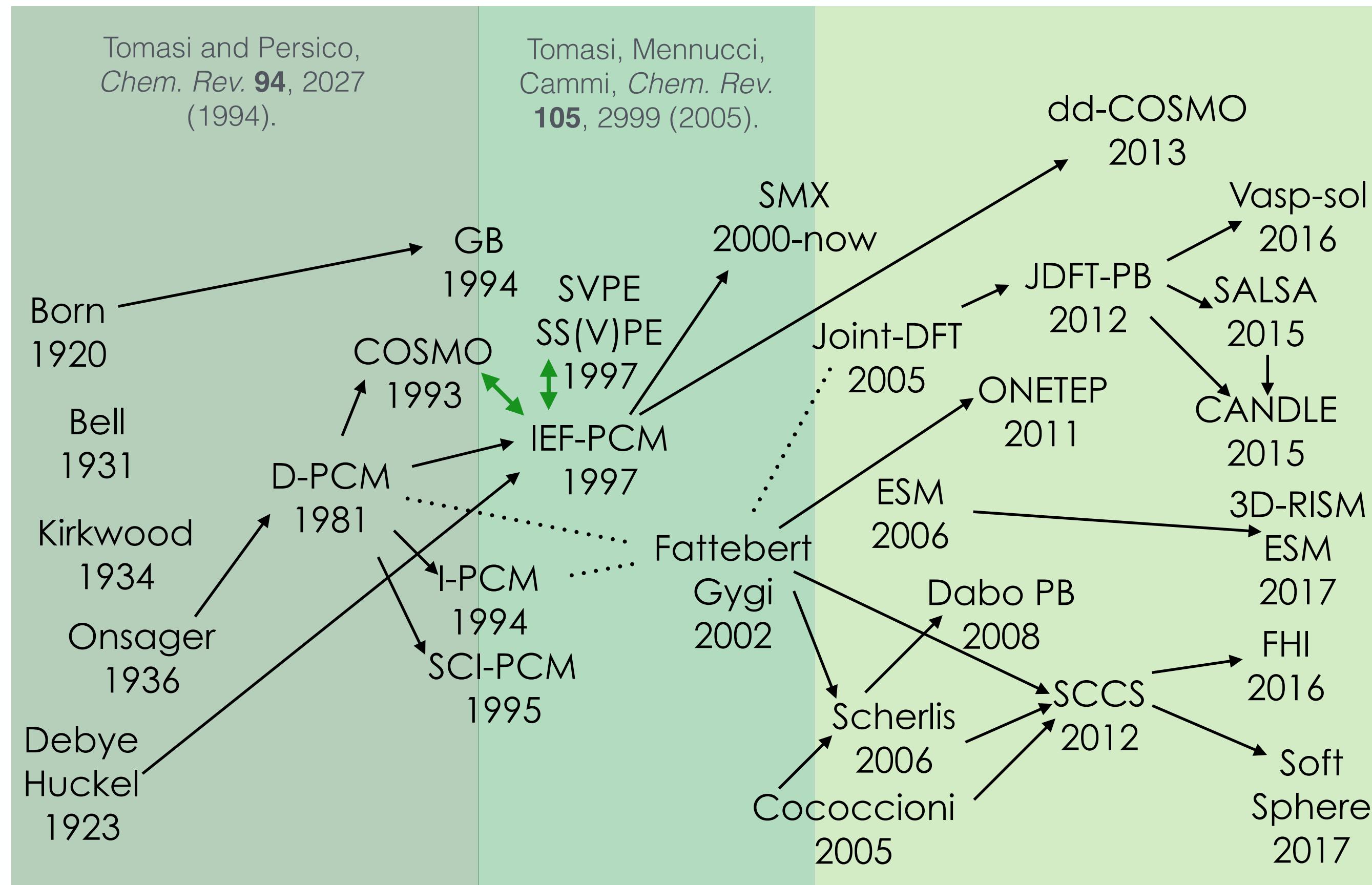
AIMD simulations by Pasquarello and coworkers. Figure by N. Hörmann.

- 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

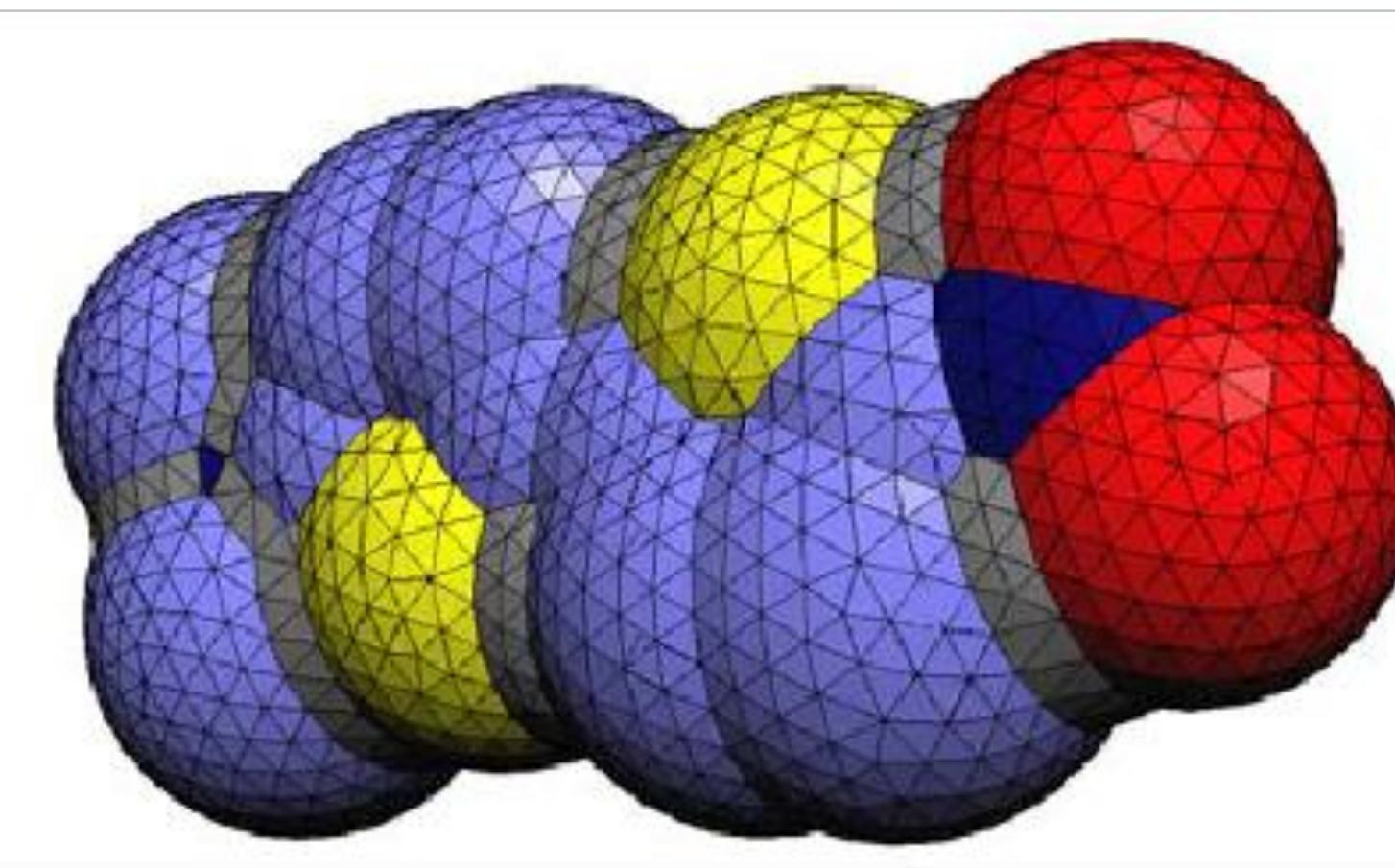
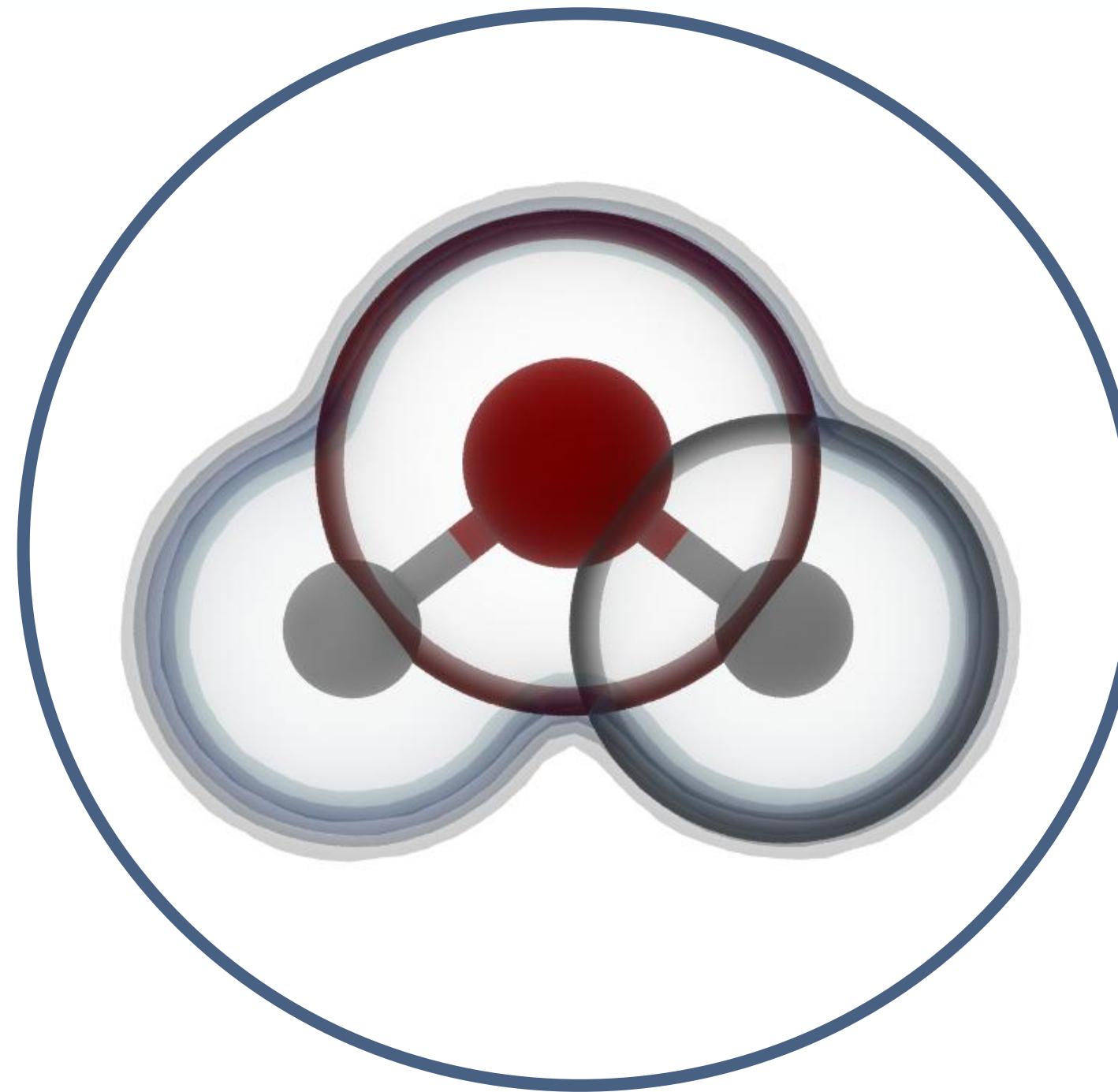


Continuum Interfaces

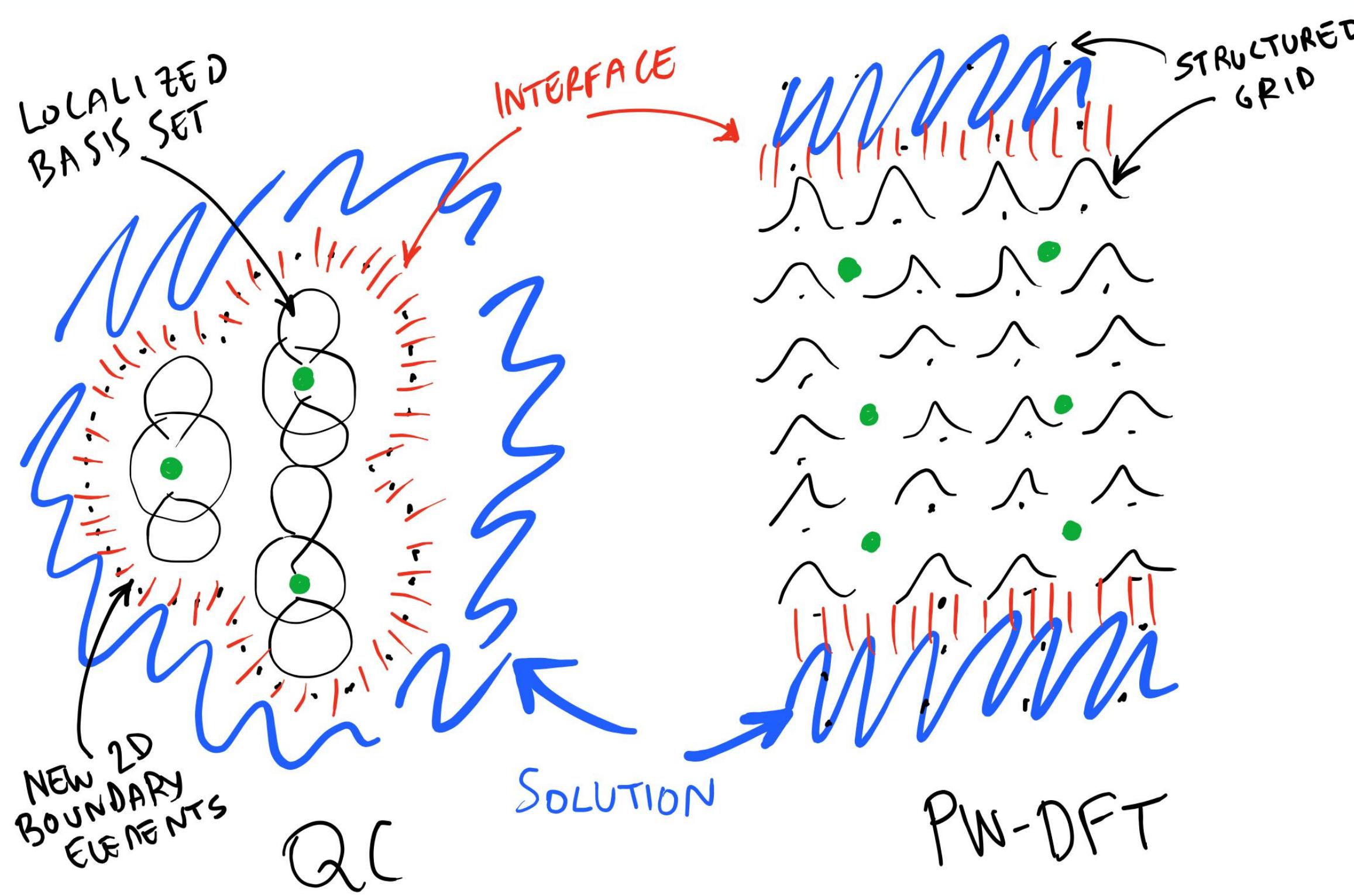
Not a single right way

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

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



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.



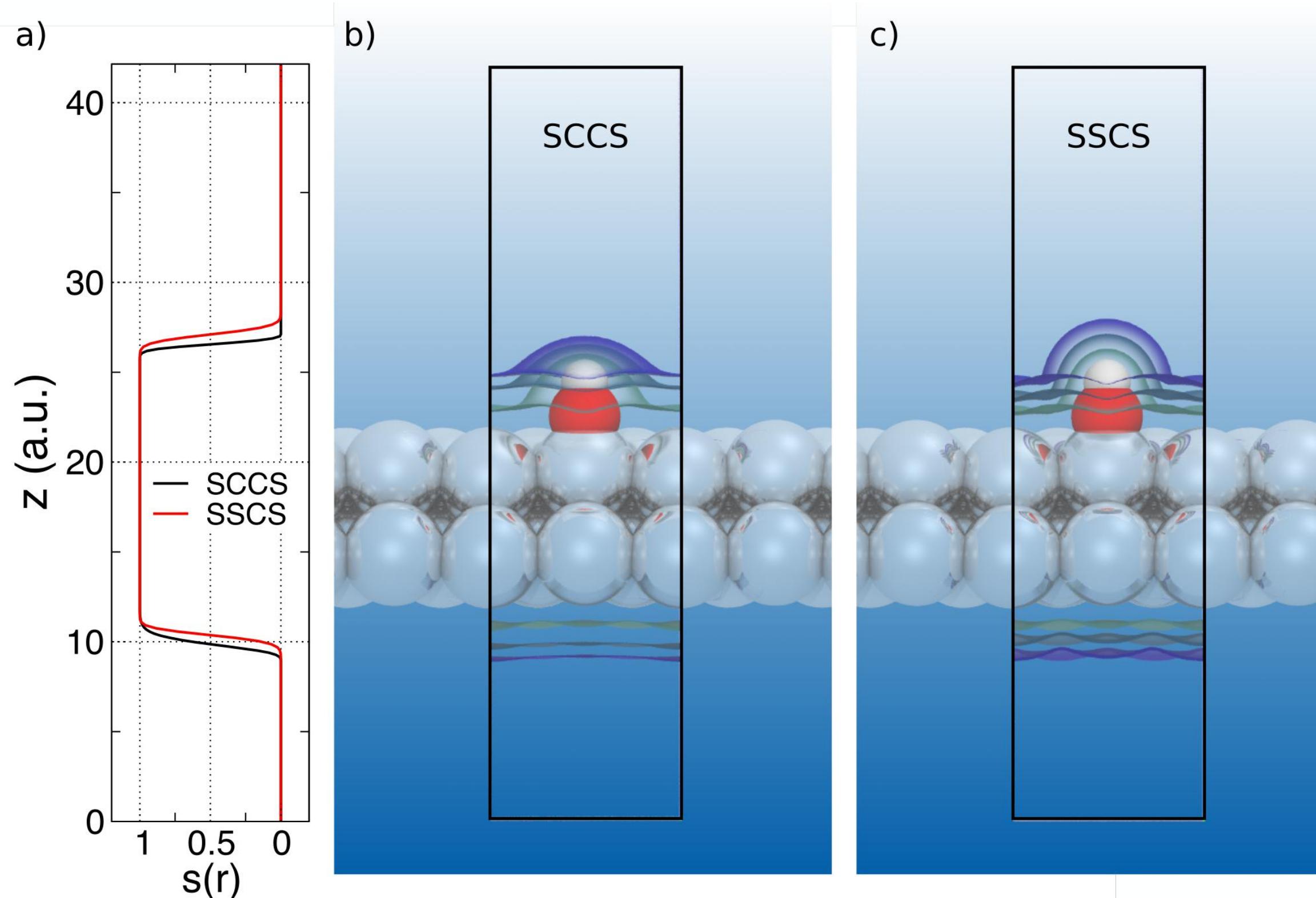
Continuum Interfaces

When Numerical Aspects Dictate the Model

- Sharp
 - Smaller 2D domain
 - Can allow direct solution
 - Only feasible for regular shapes (unions of spheres)
- Smooth
 - Reuse existing numerical domain (intrinsically variational)
 - Feasible for complex shapes
 - Allows non-local corrections

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

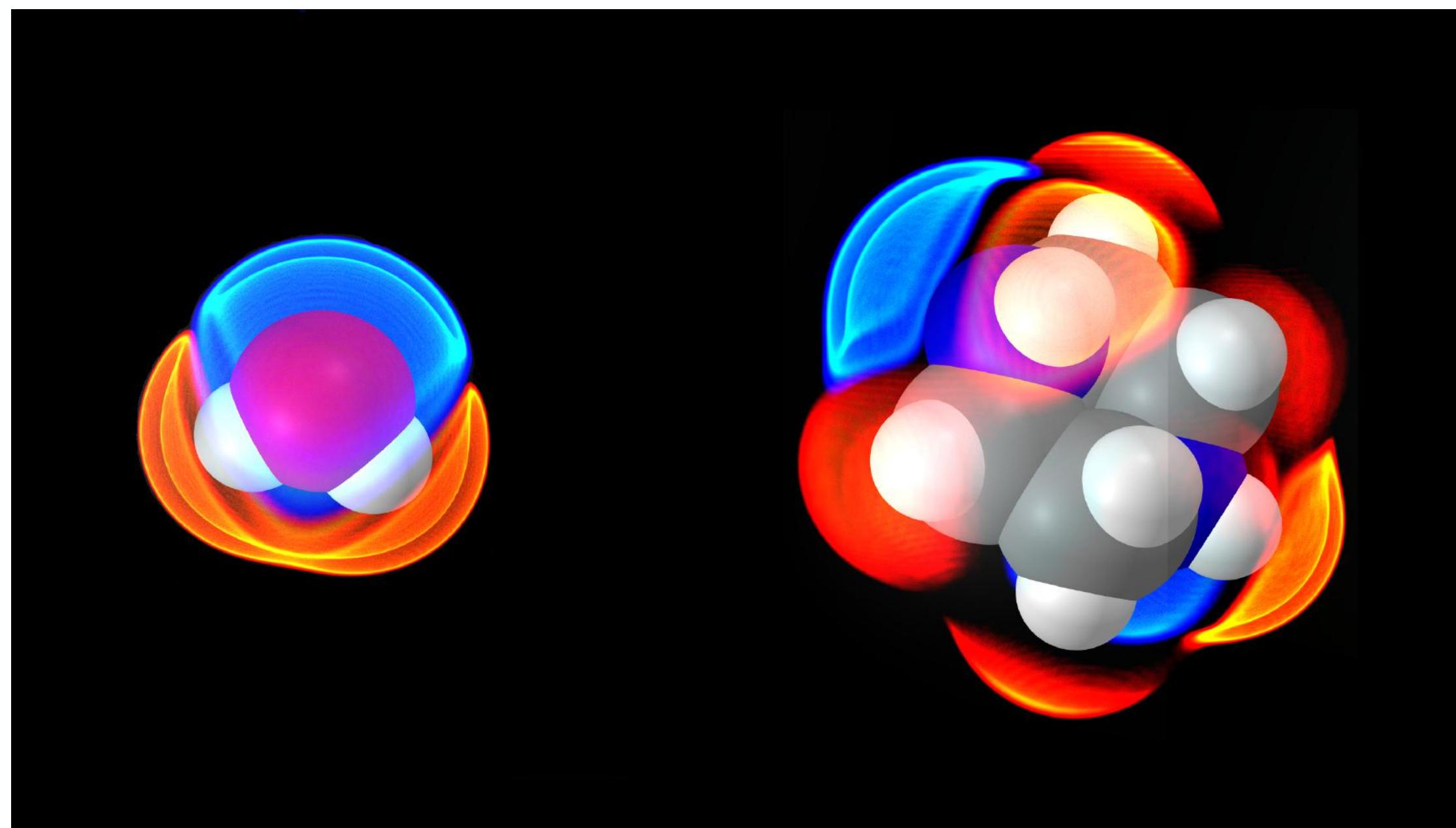
Smooth Functions: Pros and Cons

- 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.



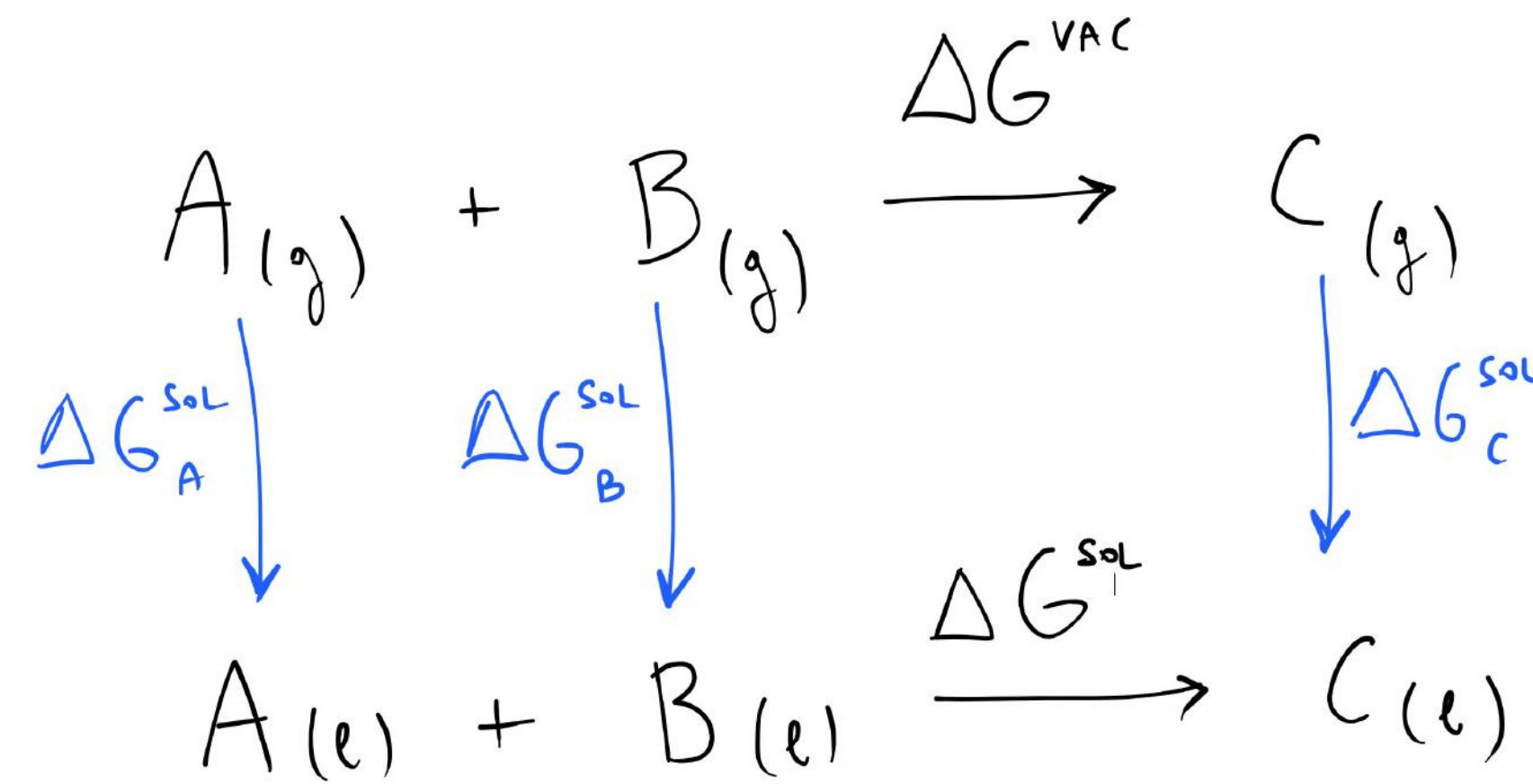
- Dielectric medium
- Electrolyte
- Pressurizing medium
- Surface tension
- Confining medium
- ...

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.

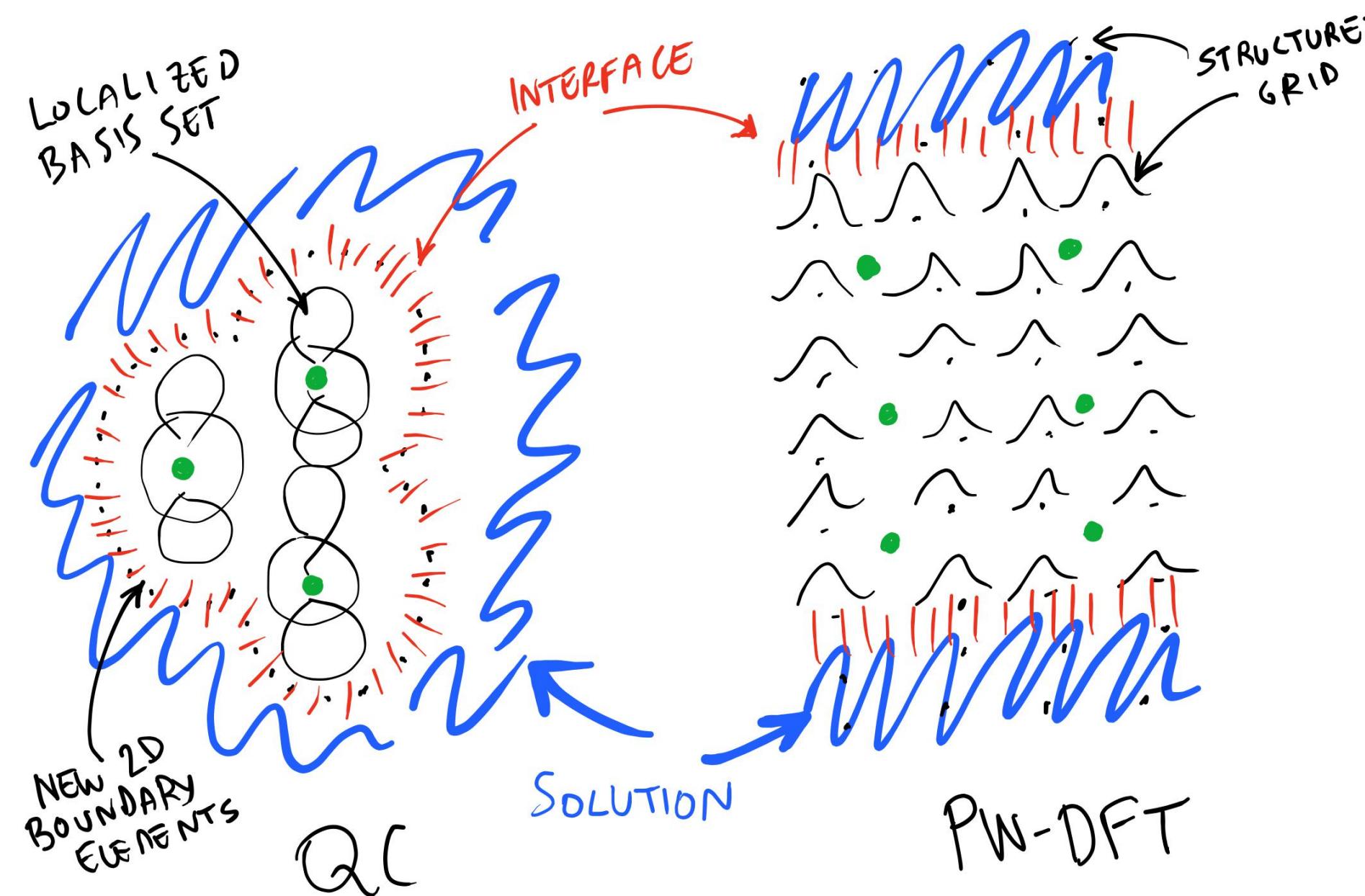


- Environment Effects on Atomic and Electronic Structure
 - Restructuring
 - Band-gap, Optical/IR/Core/Magnetic Spectra
- Solvation Free Energies
 - Solubilities
- Interface Free Energy
- Stability
 - Shape, morphology, decomposition
- Catalytic Activity

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)

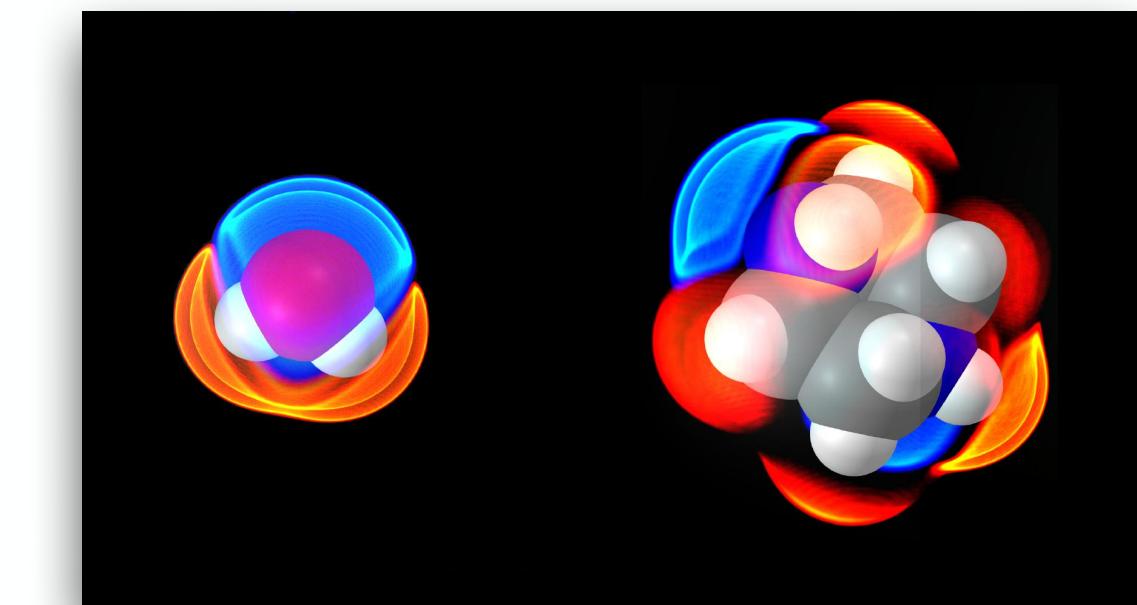
$$F^{el} (\rho^{el}, \{\mathbf{R}_a\}) = \int \left(\rho^{el}(\mathbf{r}) + \sum_a \rho_a^{ion}(\mathbf{r} - \mathbf{R}_a) \right) \phi(\mathbf{r}) d\mathbf{r} - \int \frac{1}{8\pi} \epsilon(s(\mathbf{r})) |\nabla \phi(\mathbf{r})|^2 d\mathbf{r},$$

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

- Interface function for smooth polarization charges

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

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



- 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)

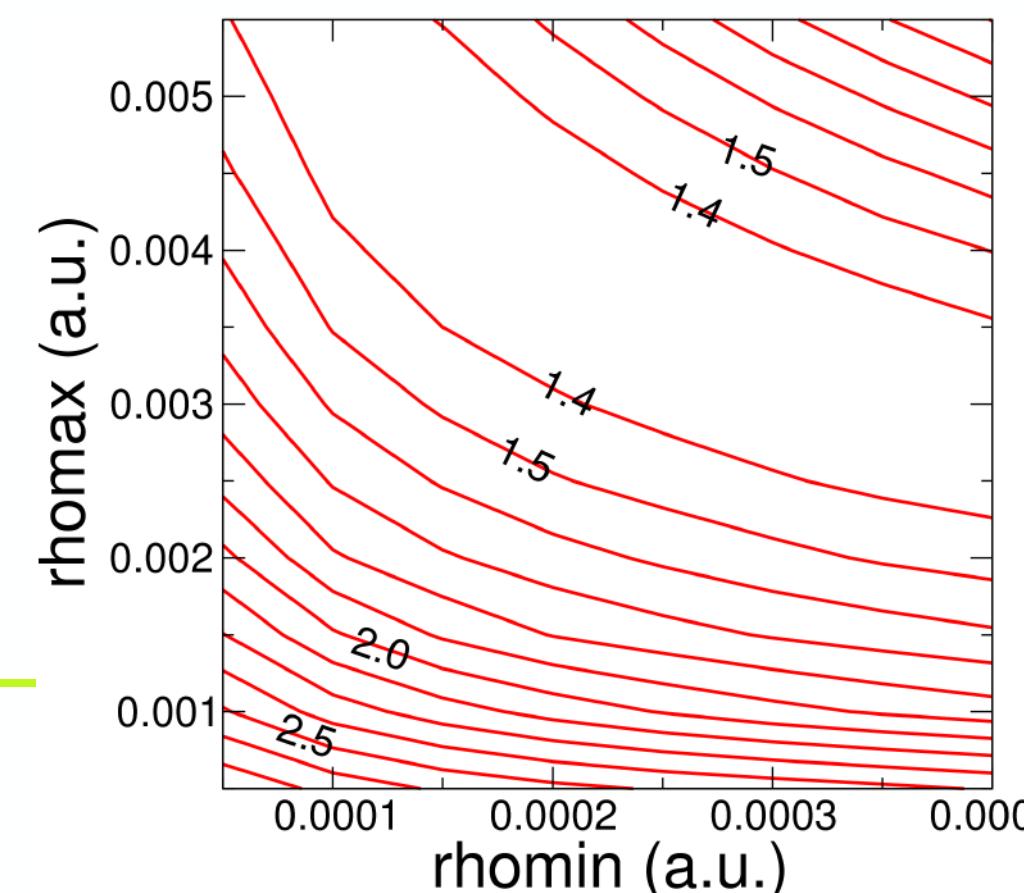
$$\Delta G^{non-el} = (\alpha + \gamma) S[s] + \beta V[s]$$

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

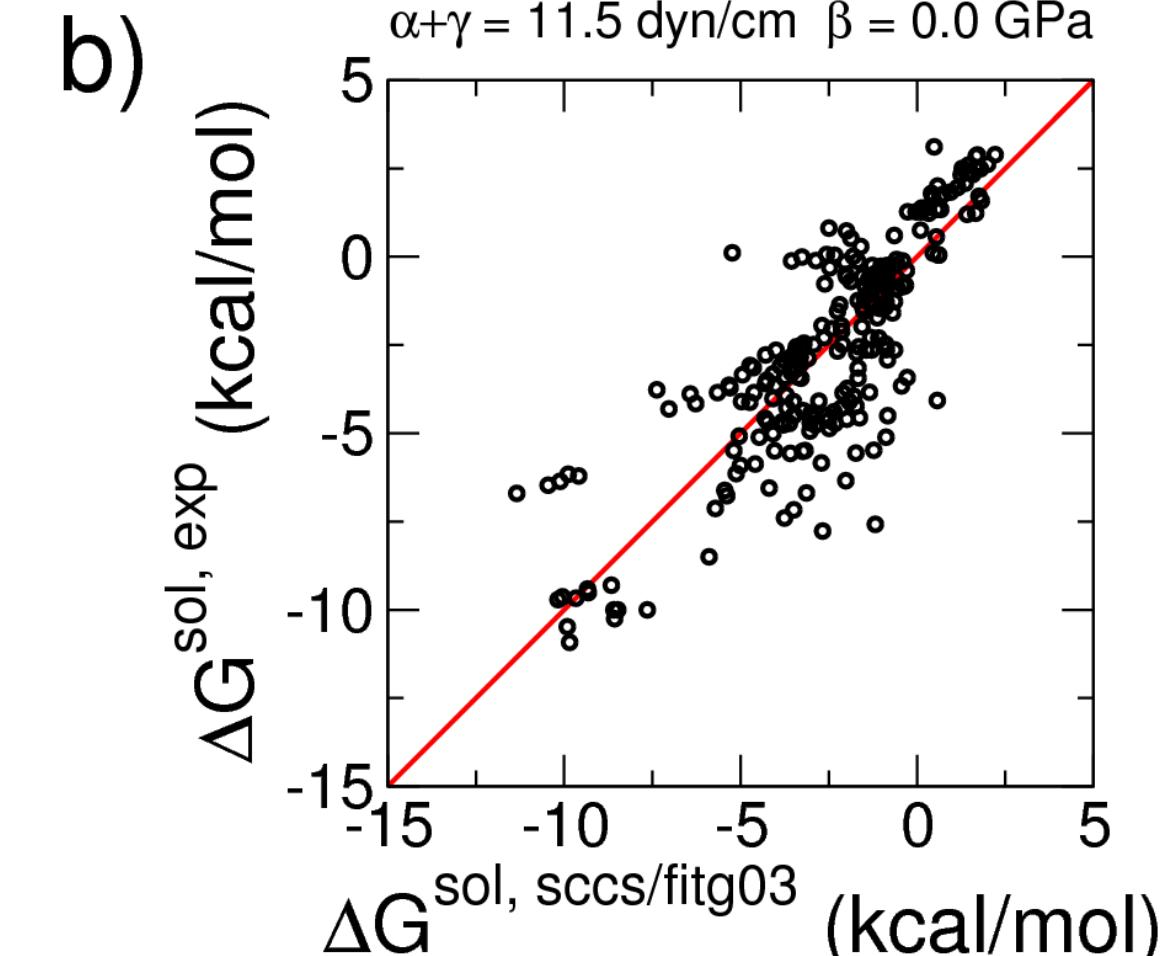
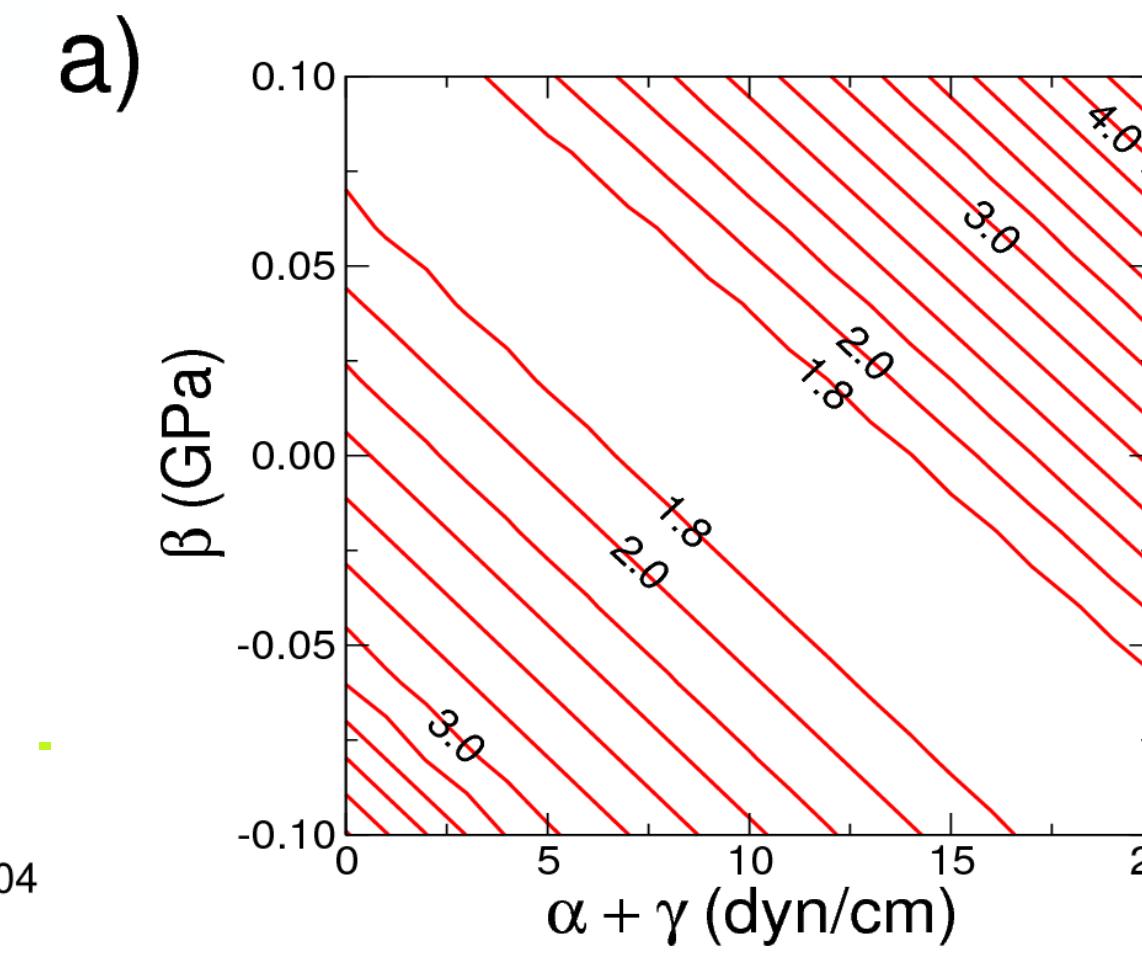
$$\frac{\delta S}{\delta s}(\mathbf{r}) = \nabla \cdot \left(\frac{\nabla s(\mathbf{r})}{|\nabla s(\mathbf{r})|} \right)$$

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

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



- 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



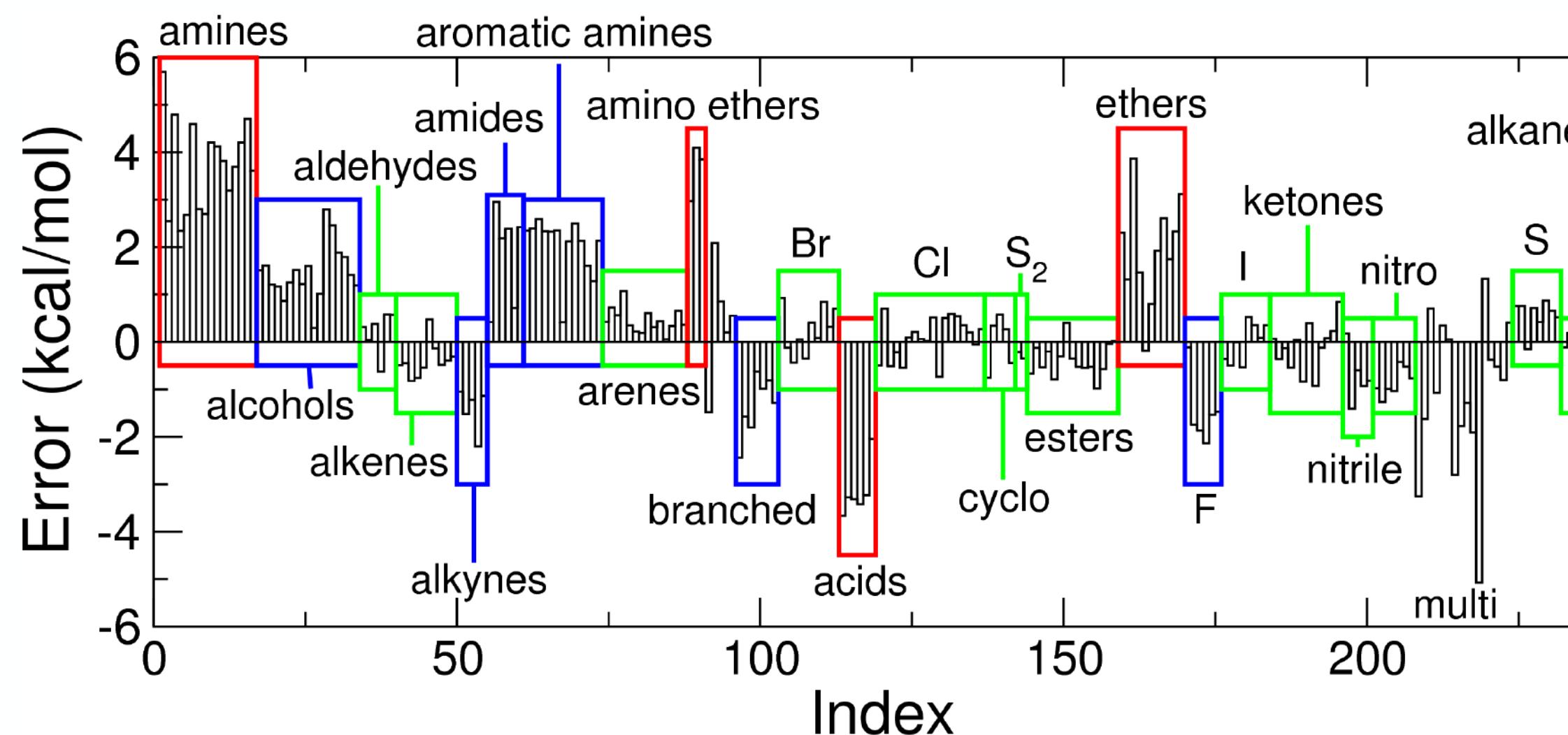
Solvation Models

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

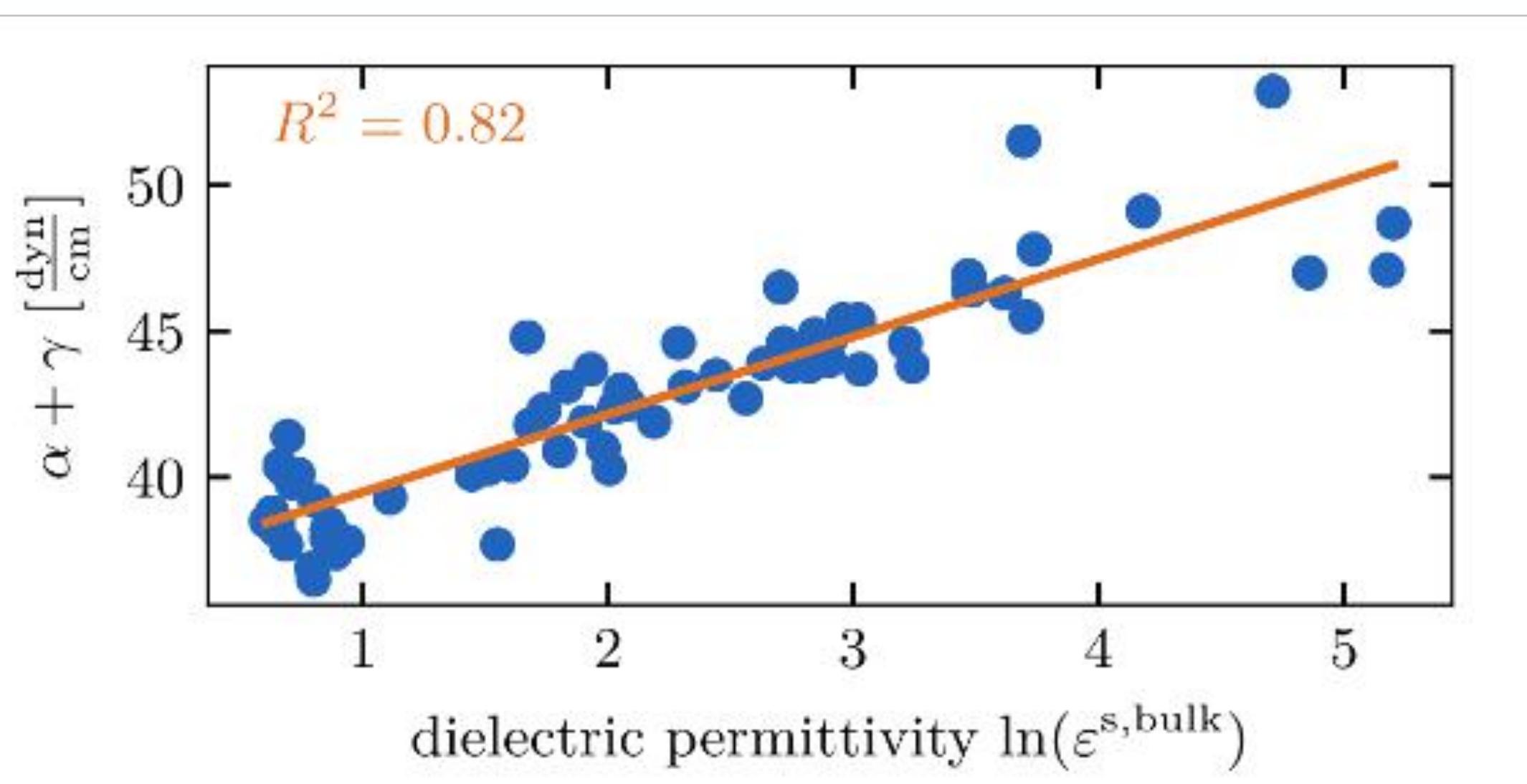
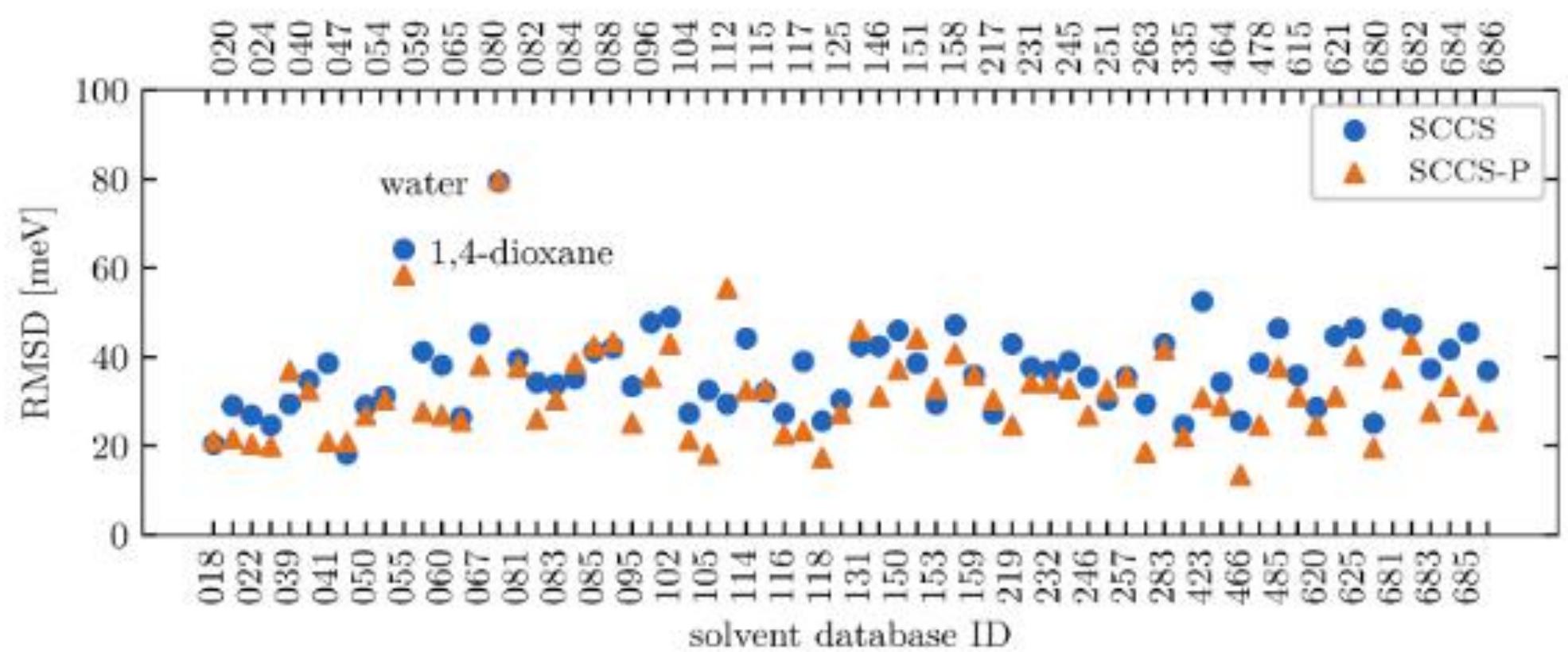
^bParametrization of row 2 Table 1. ^cThe sccs implemented in BigDFT.

^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

Towards Single-Parameter Models

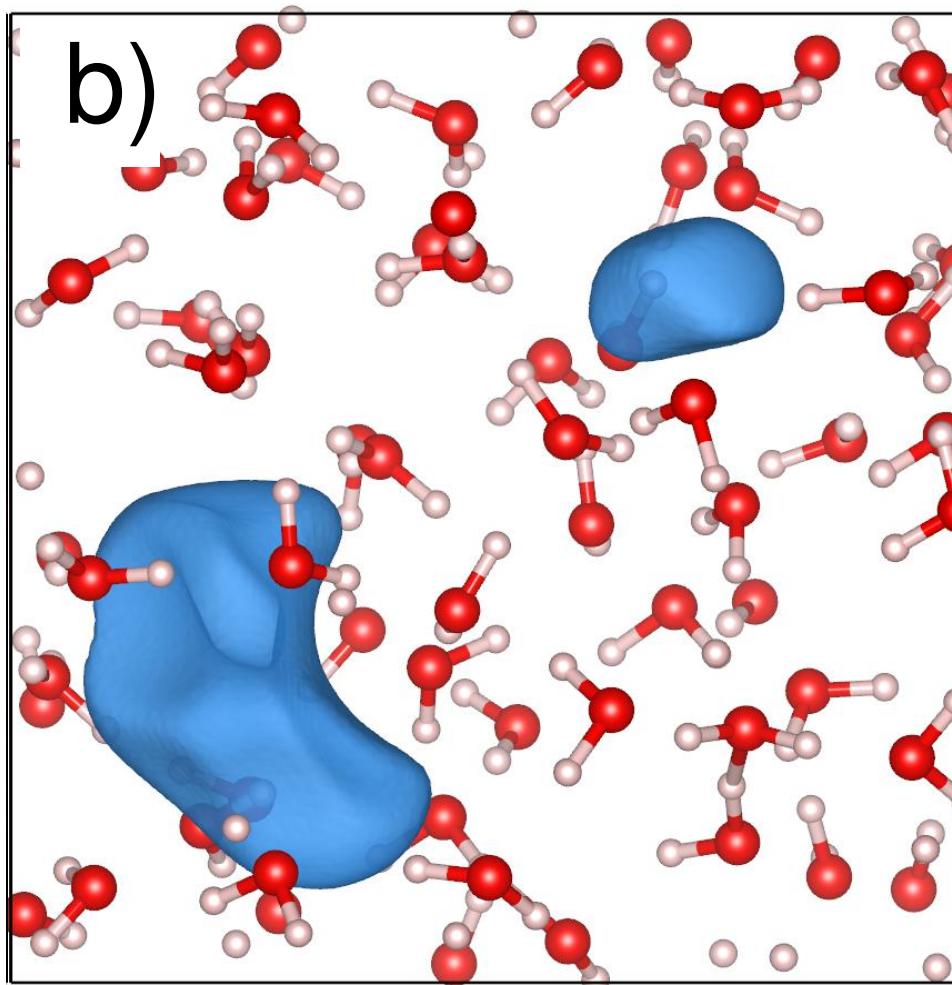
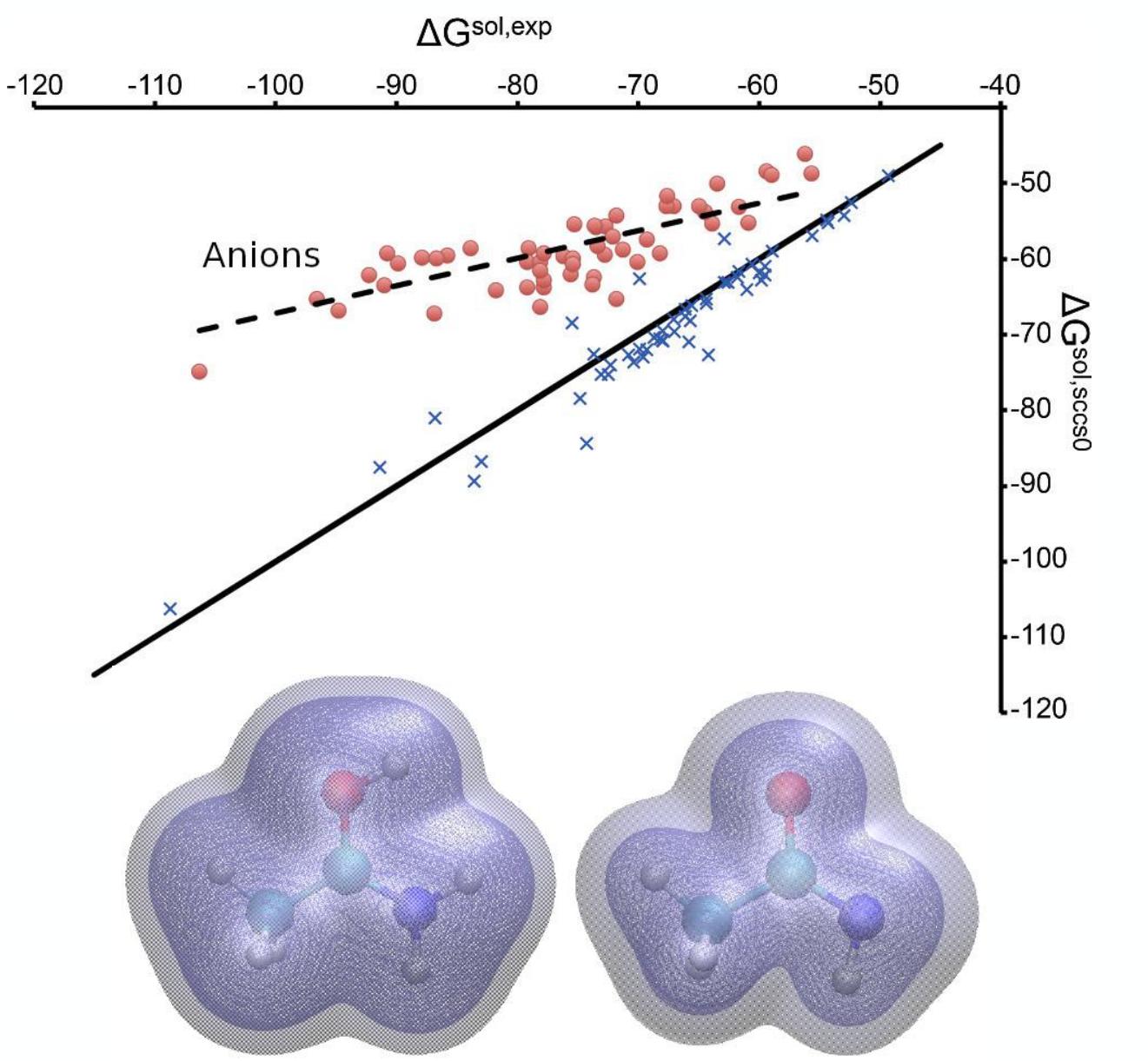
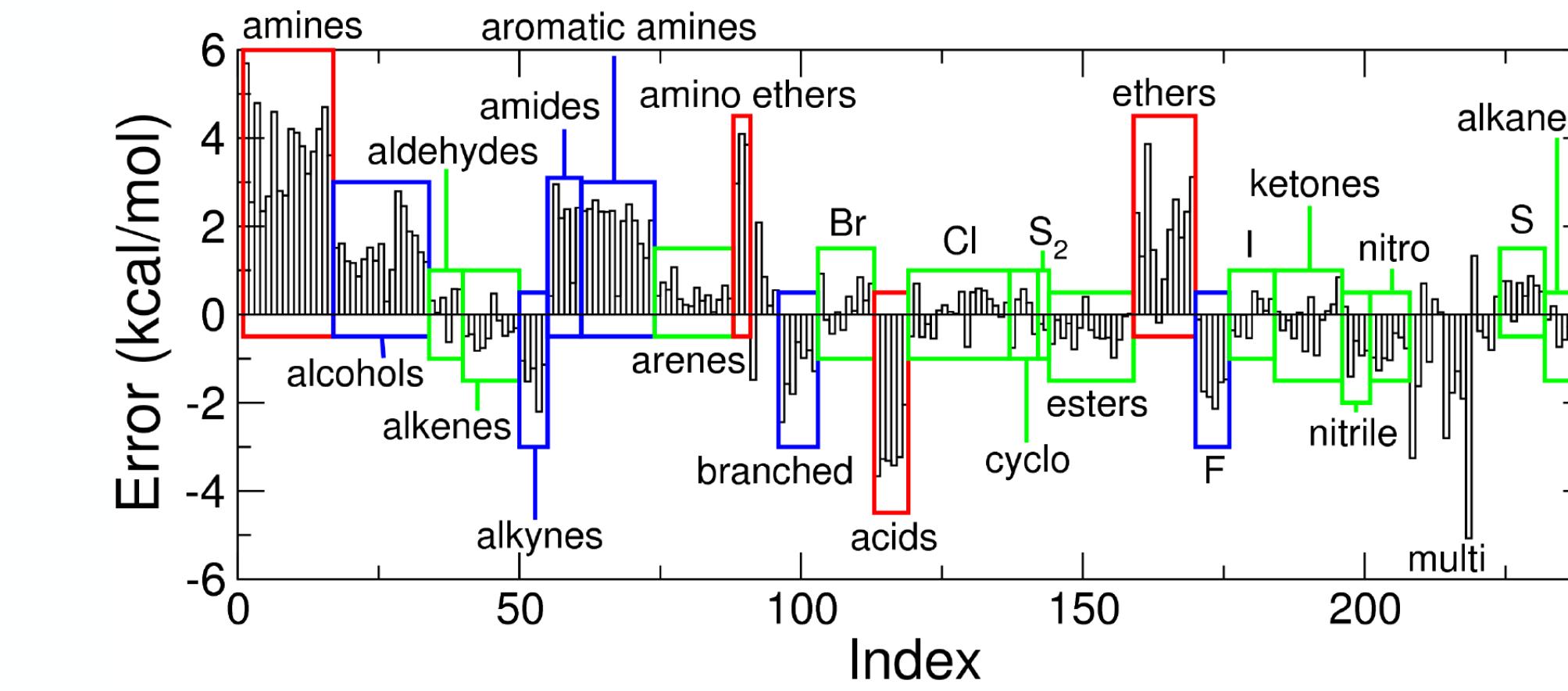


- Fixing some of the SCCS parameters (pressure and cavity thresholds) does not affect accuracy significantly
- Optimizing the remaining parameter (surface tension) on experimental solvation free energies provides a linear dependence on the dielectric permittivity.
- Knowing epsilon for a solvent we can predict its solvation free energies within chemical accuracy.

What is Under the Carpet

Challenges

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

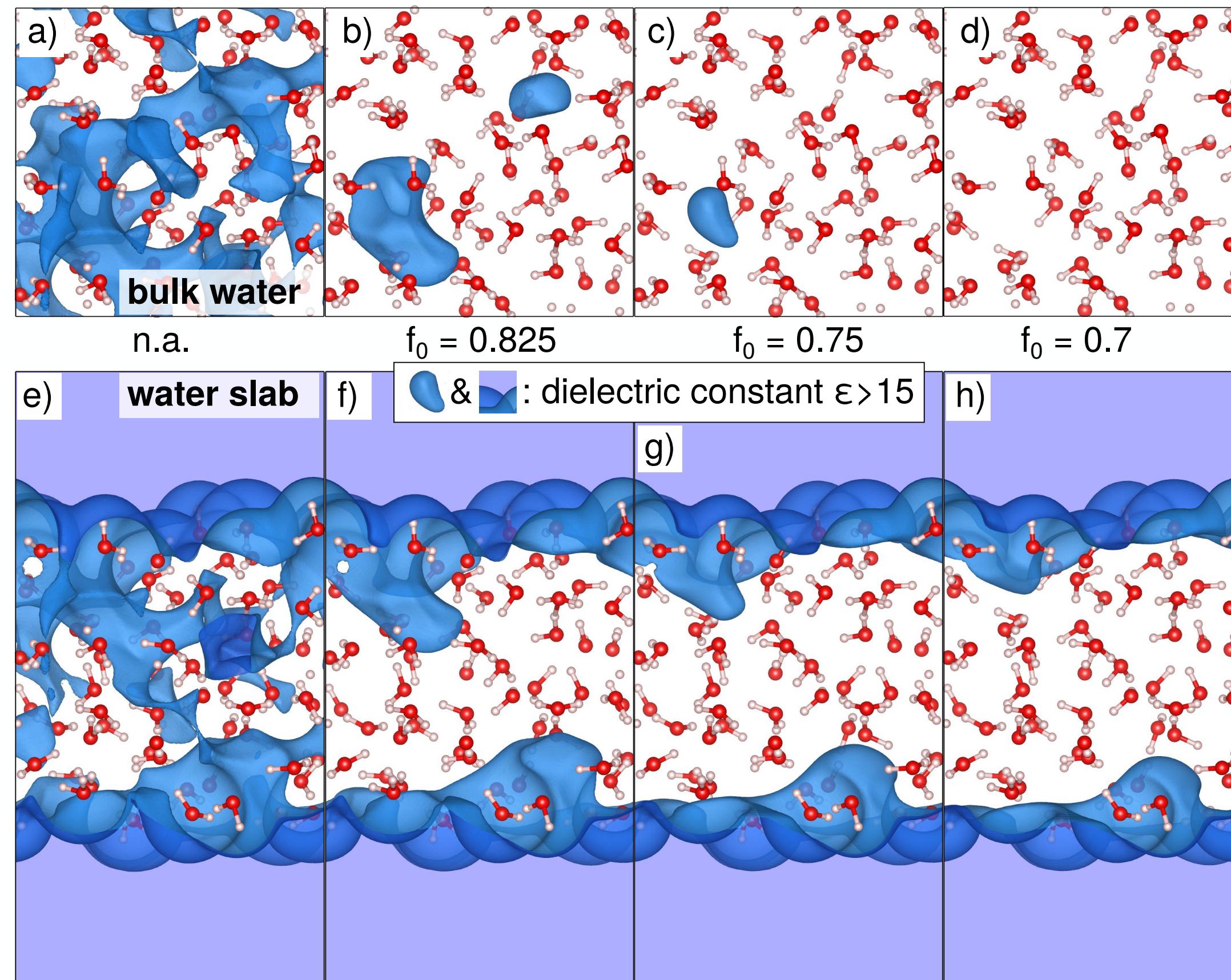


Interfaces

Non-local corrections

Filling the Voids via Solvent-Awareness

Continuum interfaces as a function of filled fraction threshold f_0

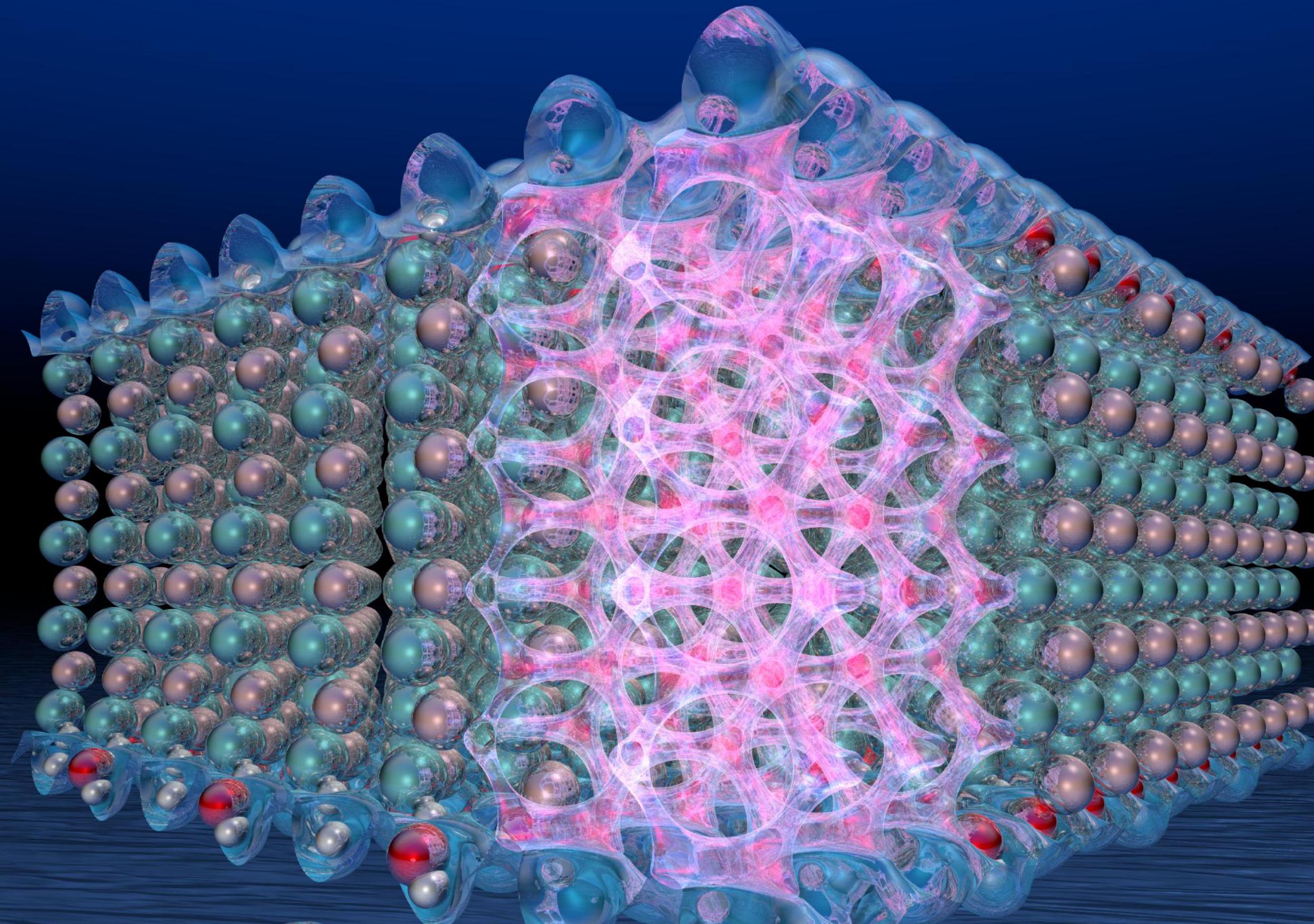


- Solvent-aware interfaces
 - Correction to remove continuum pockets inaccessible to the solvent
 - Based on spherical convolution of local interface function
- Field-aware interfaces
 - Correction to shrink the interface near charged atom/residues
 - Based on electric field flux through local interface

What About Materials?

Surfaces Can Be Hard

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



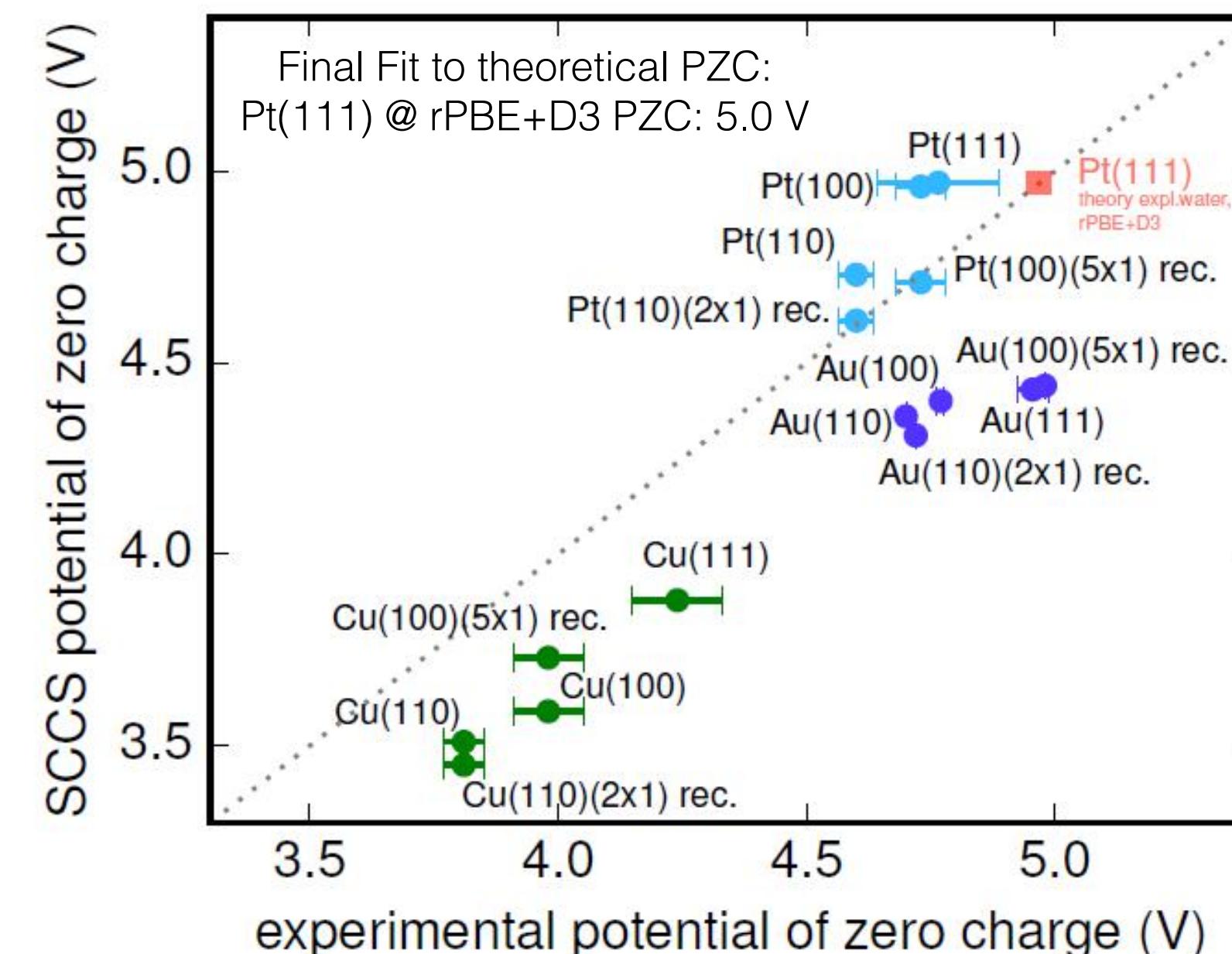
Parametrization on What?

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

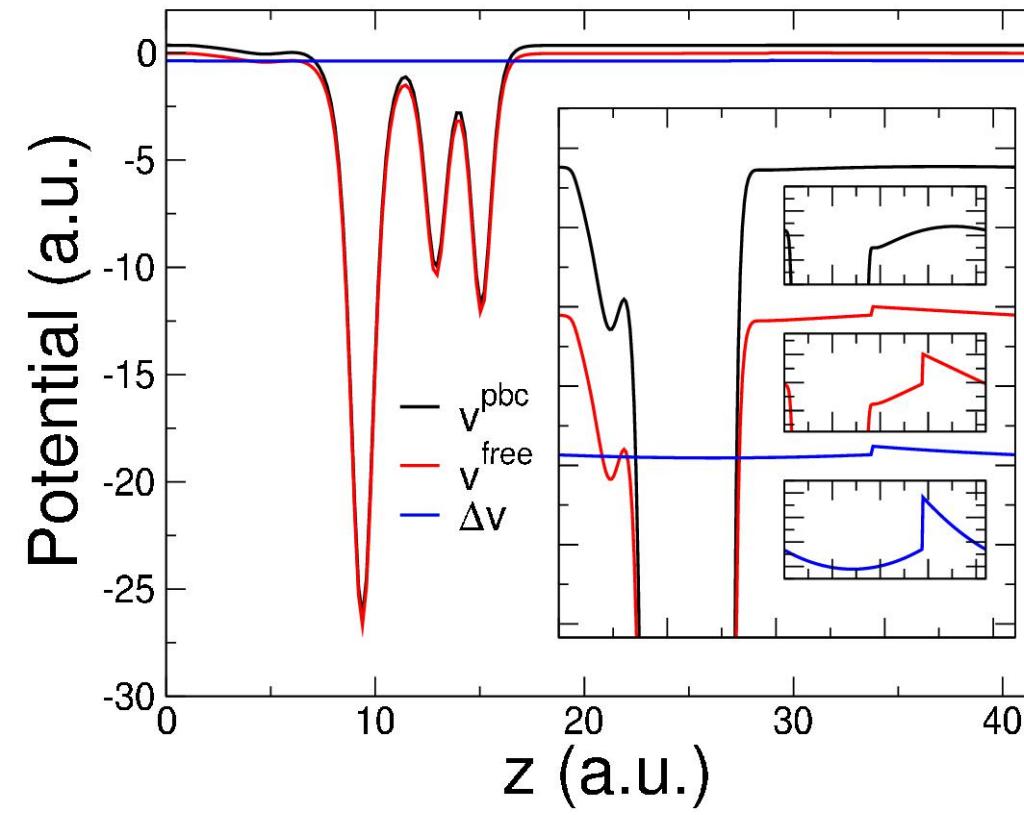
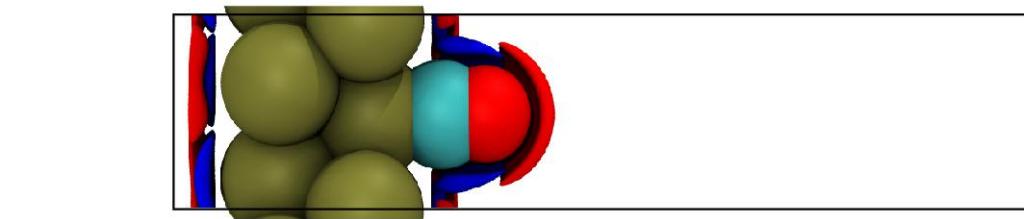
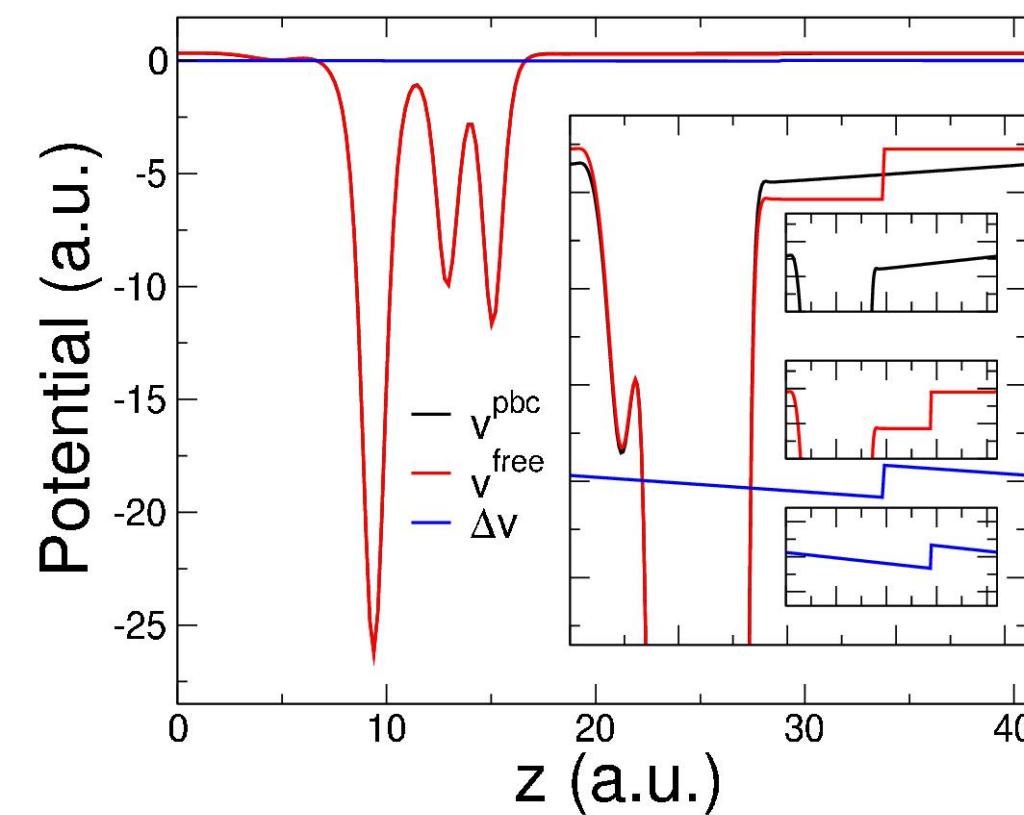
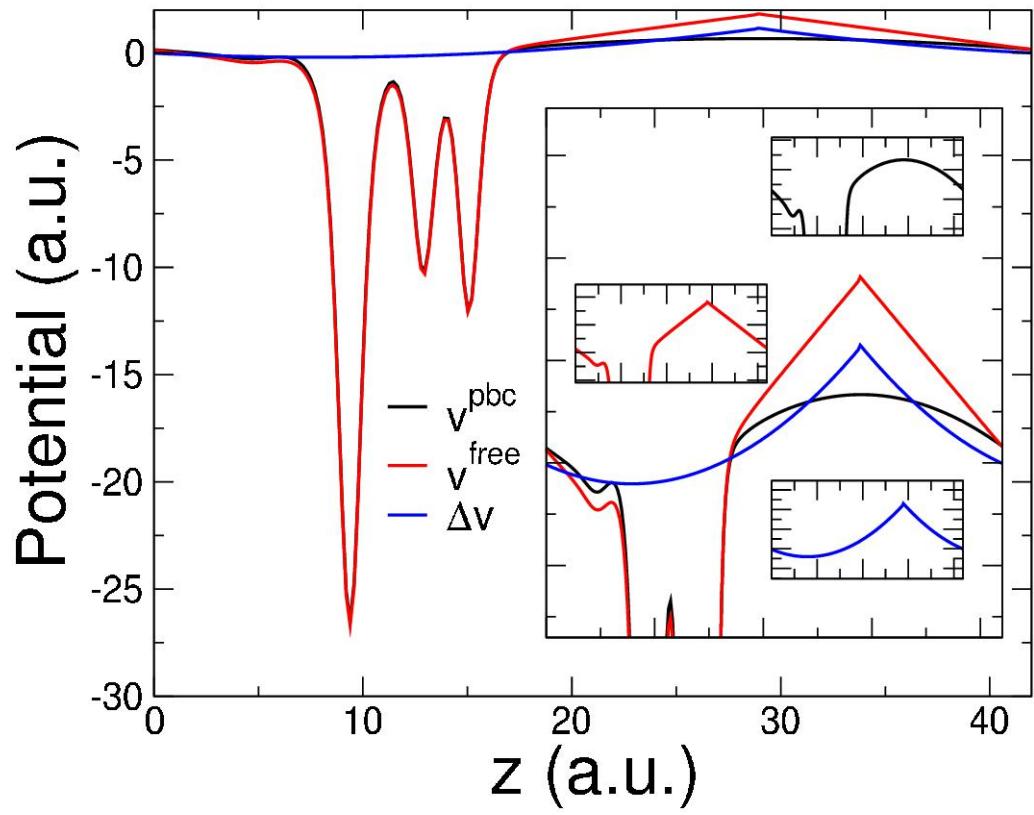
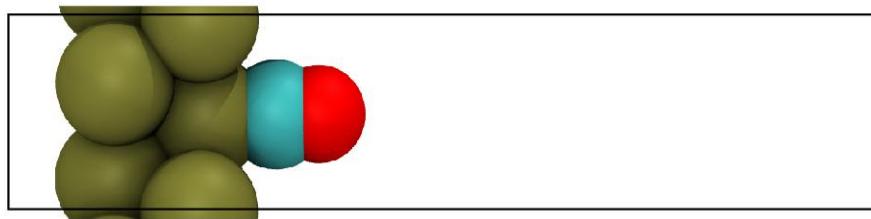
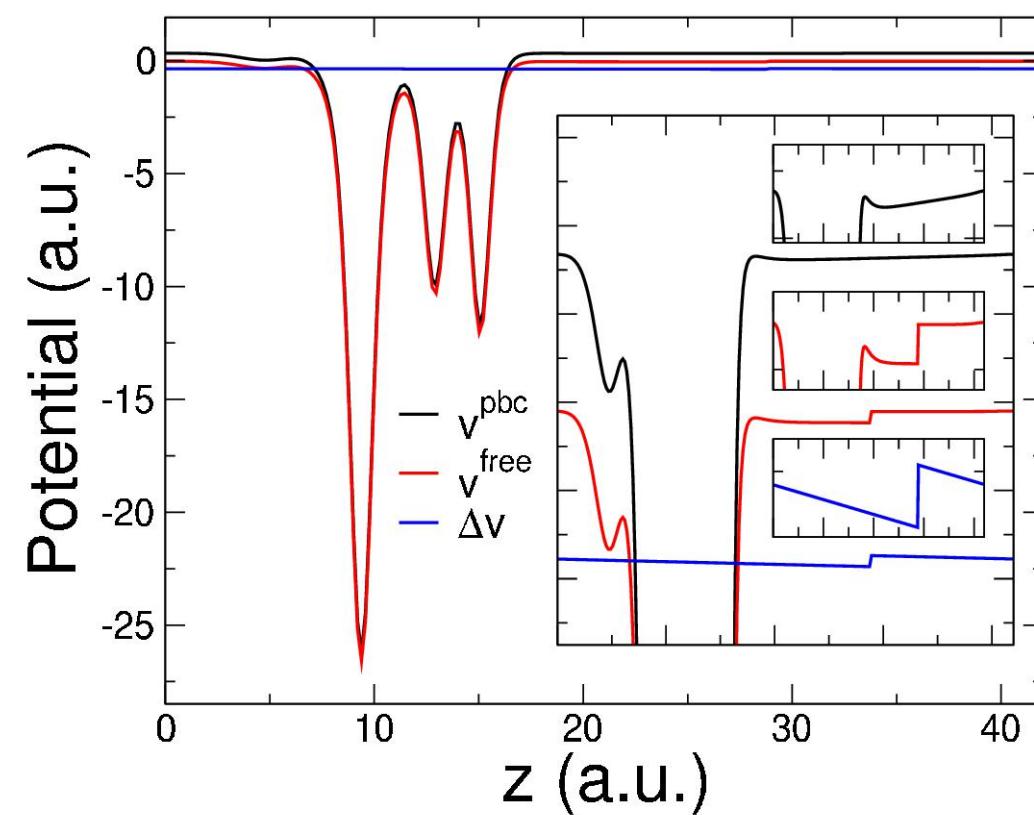
Comparison of potentials of zero charge (PZC) for continuum model with interface function parametrized on first principles results



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).

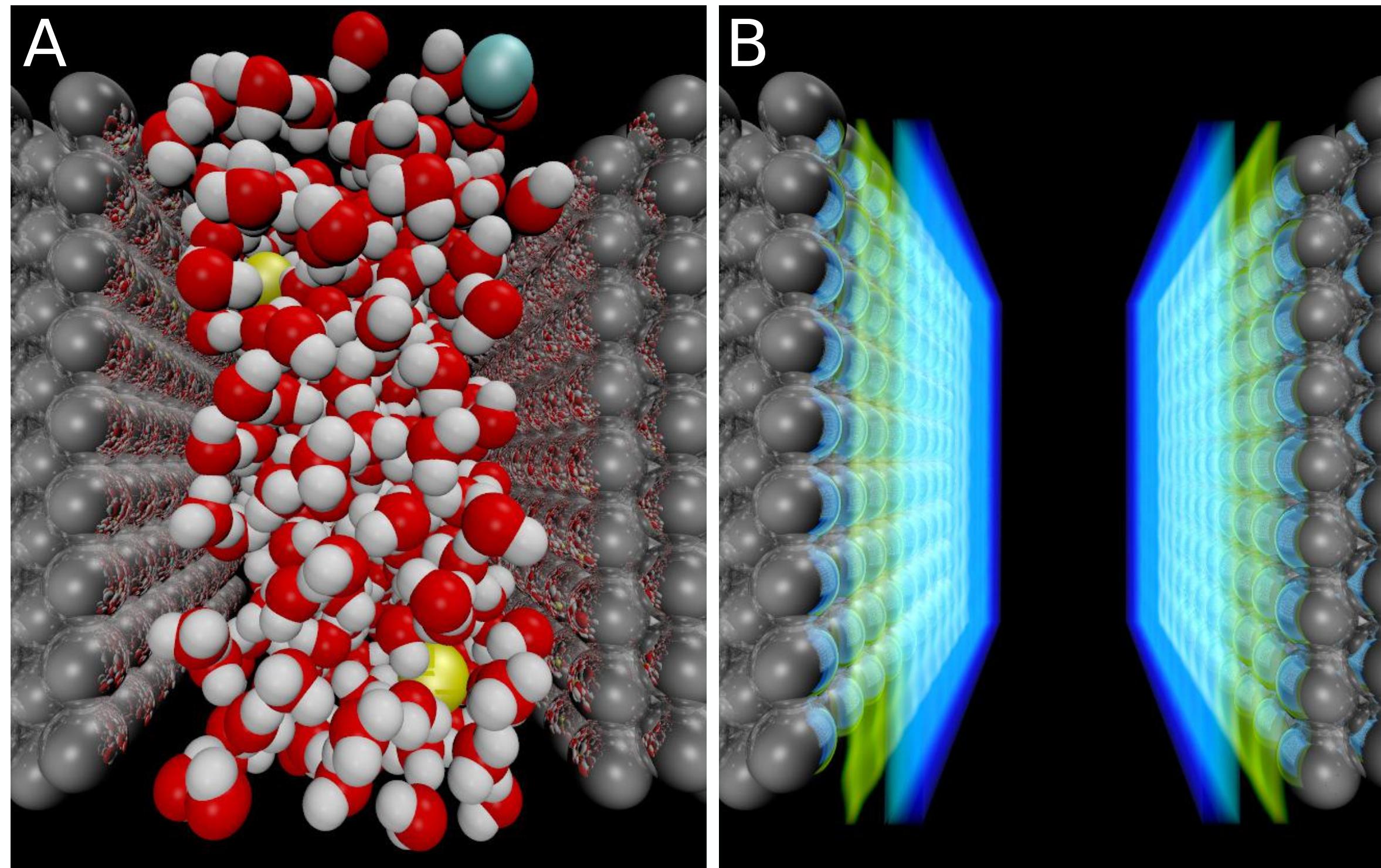


Fixing PBC in 2D Parabolic Correction

- 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

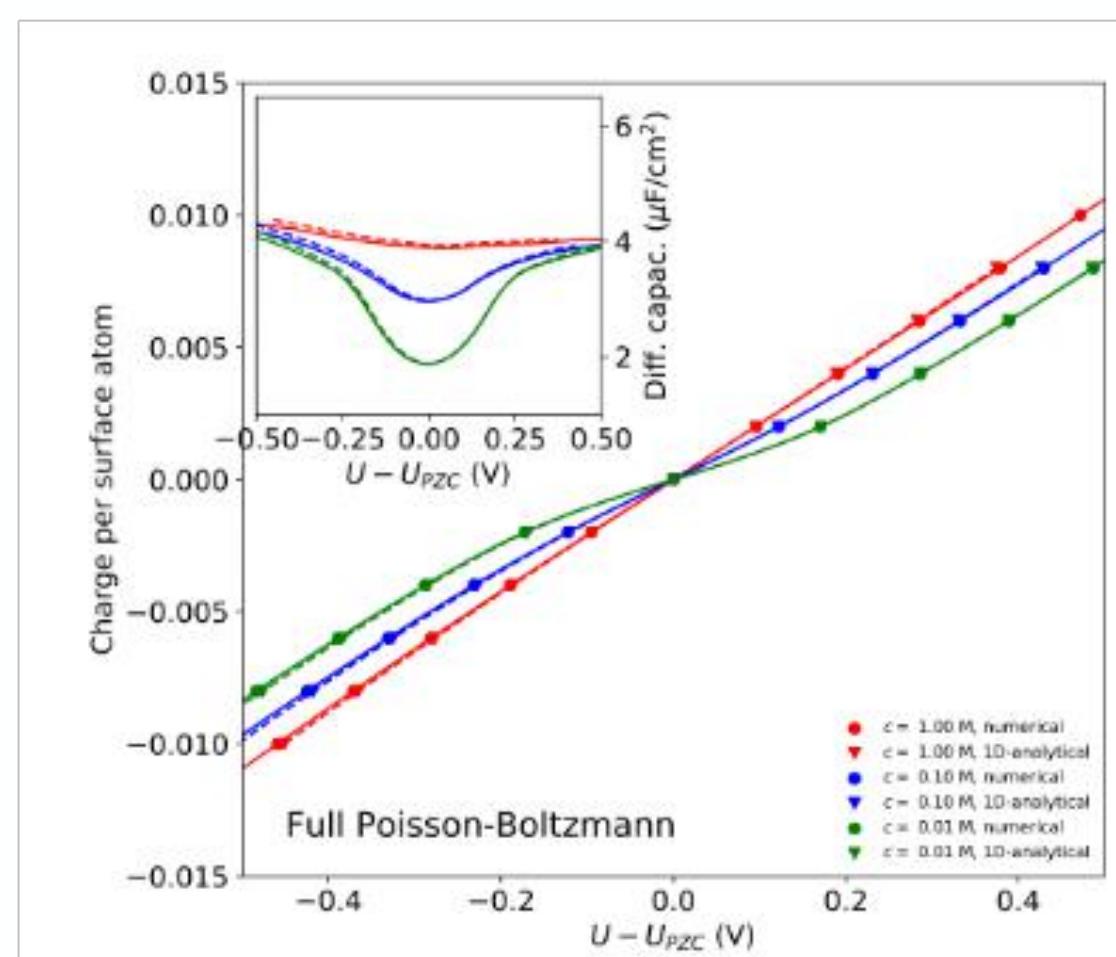
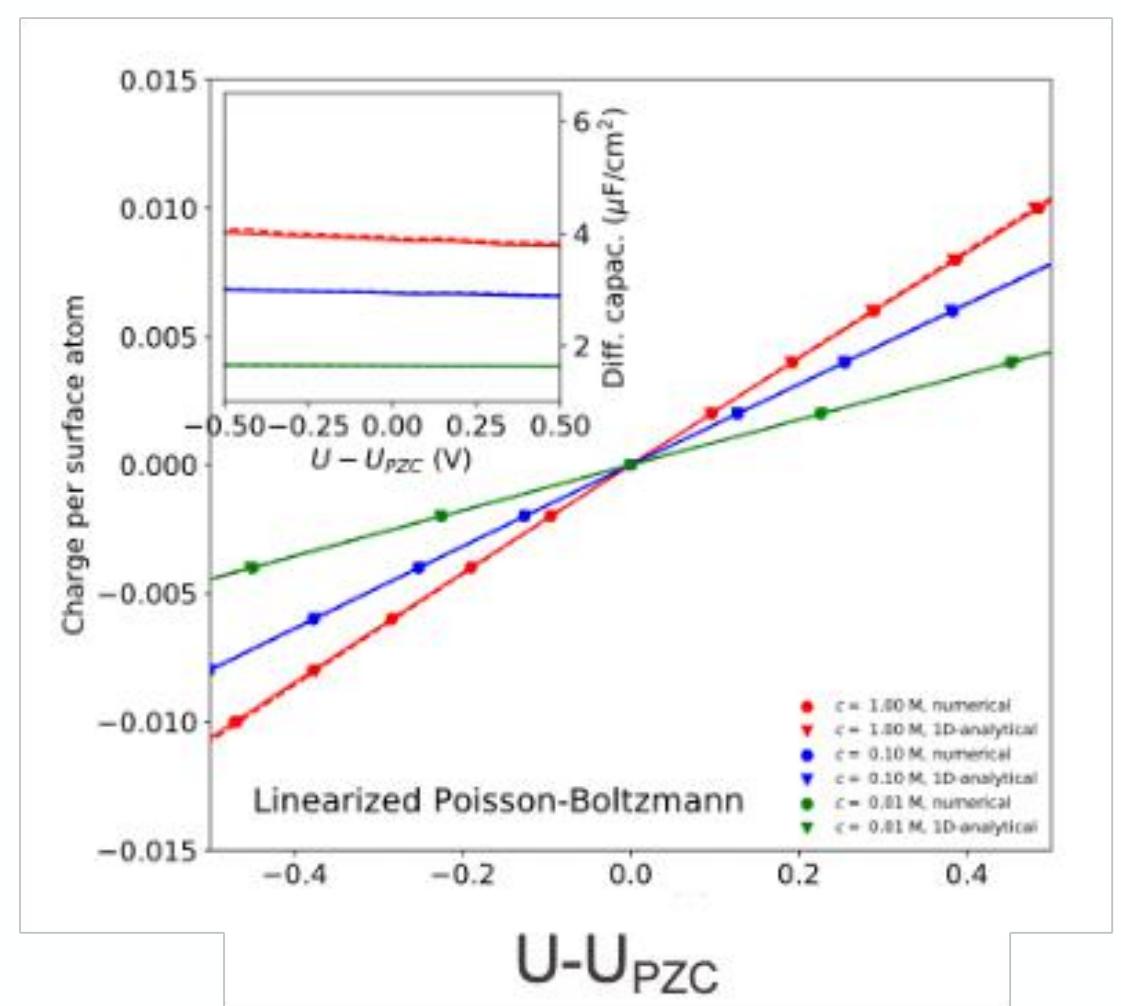
Differential capacitance of Ag (100) surface in vacuum. Variations of the Poisson-Boltzmann model of the diffuse layer are coupled with a DFT description of the substrate. Different curves correspond to different ionic concentrations

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

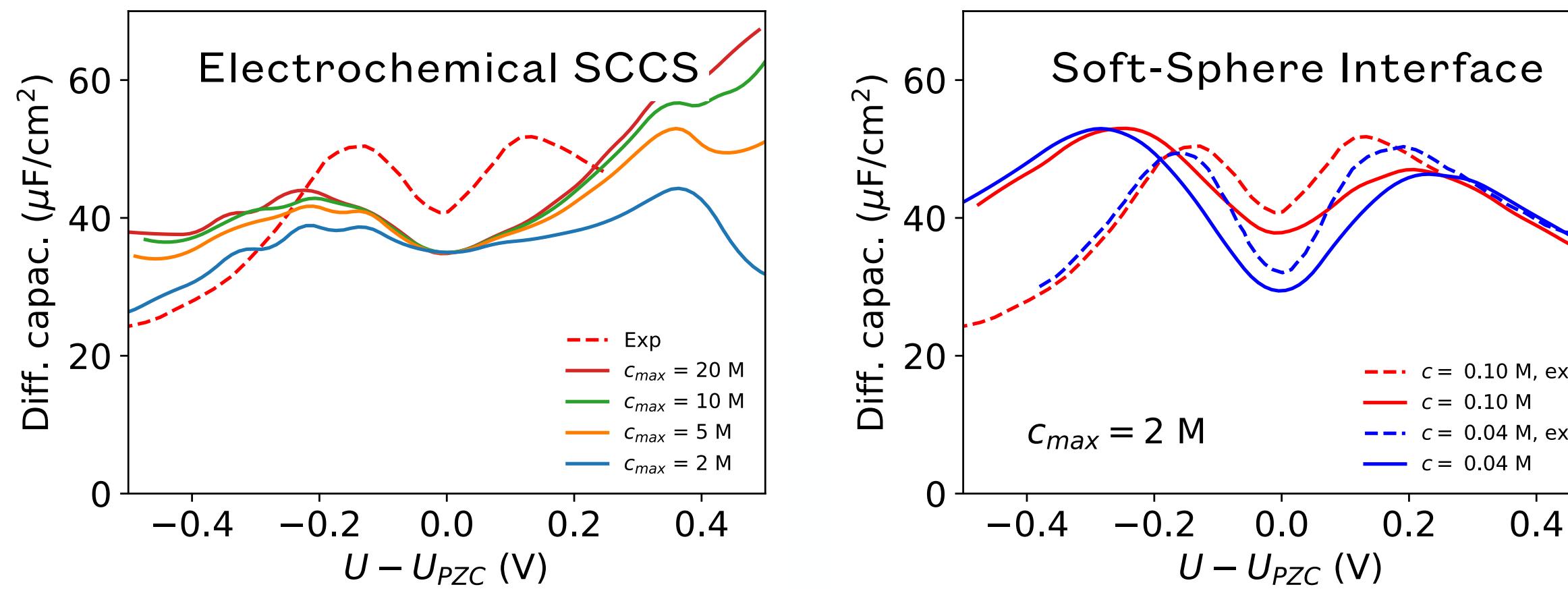
- Vary the charge on the slab and measure the potential drop (via the Fermi energy)
- Invert the variables and take the derivative of charge wrt potential

Differential Capacitance Using Environ

Tuning the Diffuse Layer Models on Experiments

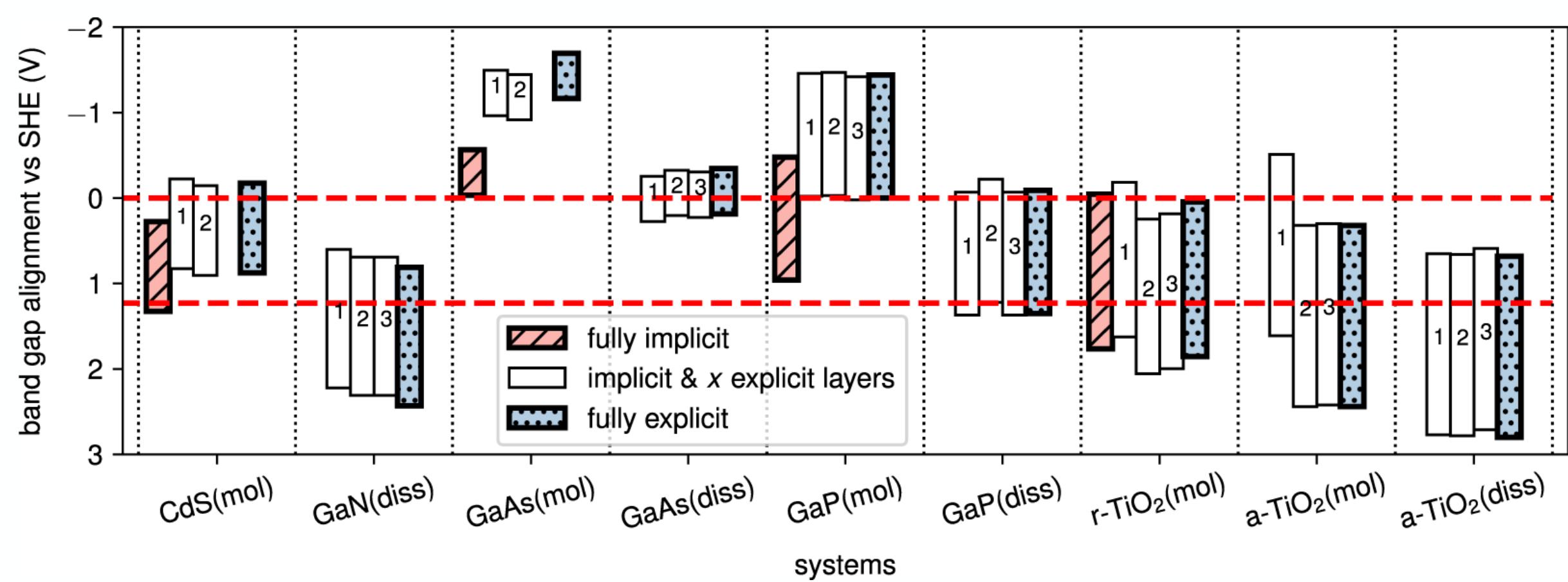
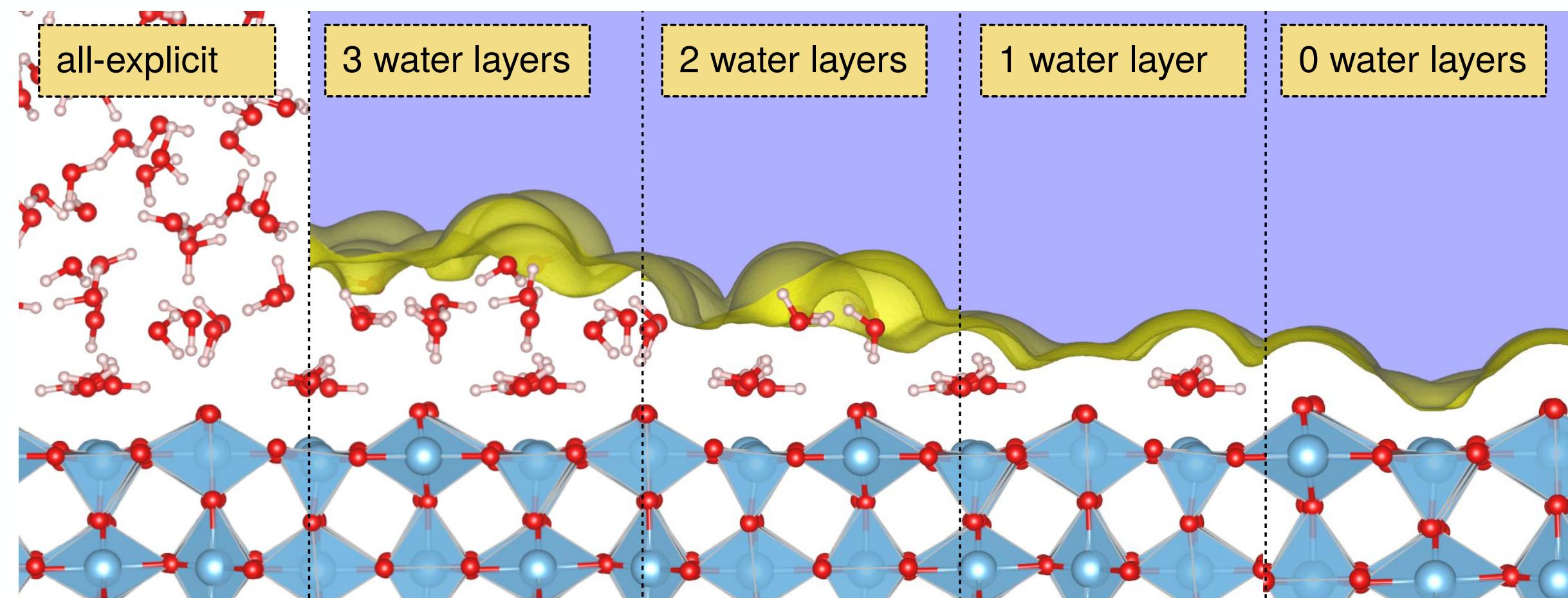
Differential capacitance of Ag (100) surface in KPF6 solution.

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

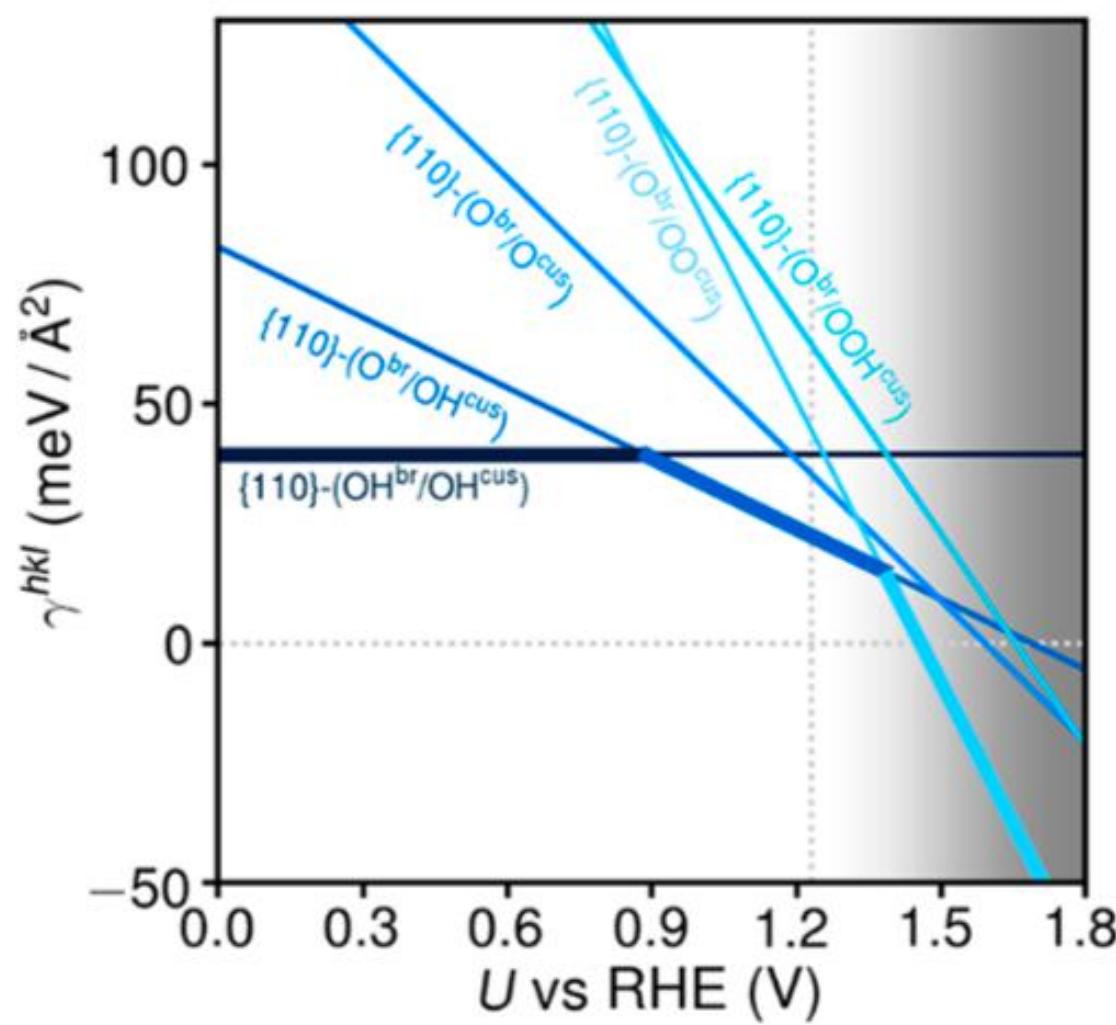
- There is a common offset when replacing explicit water with the continuum
- One explicit layer of water is necessary
- One explicit layer is often enough

Stability & Catalysis

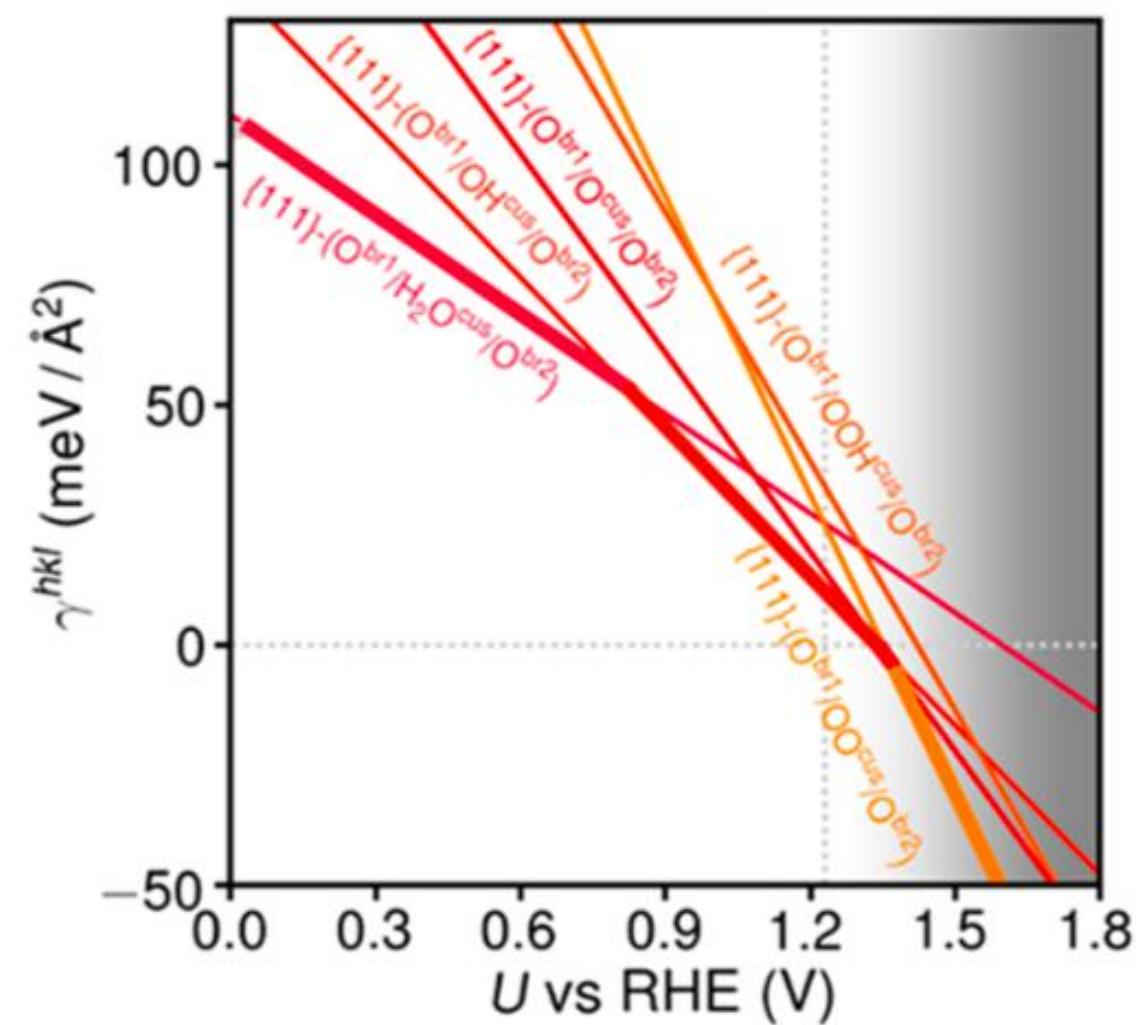
O, OH, H, etc.

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)

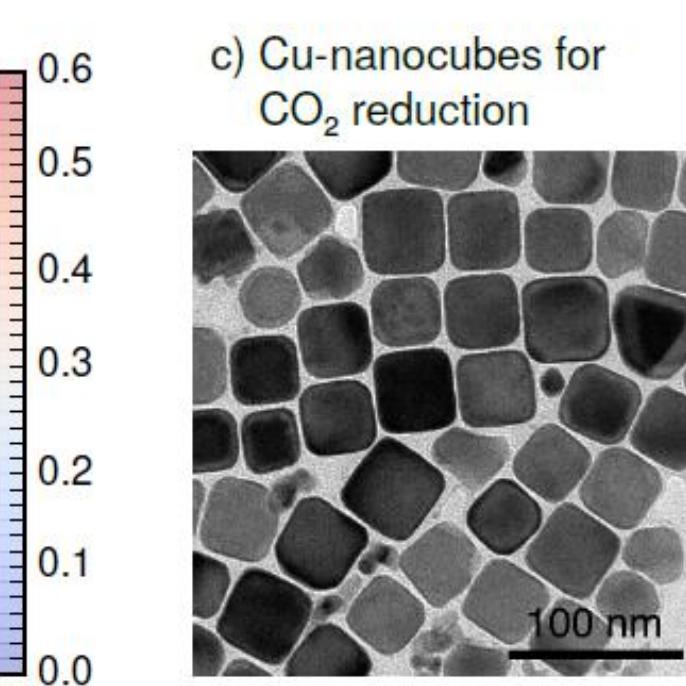
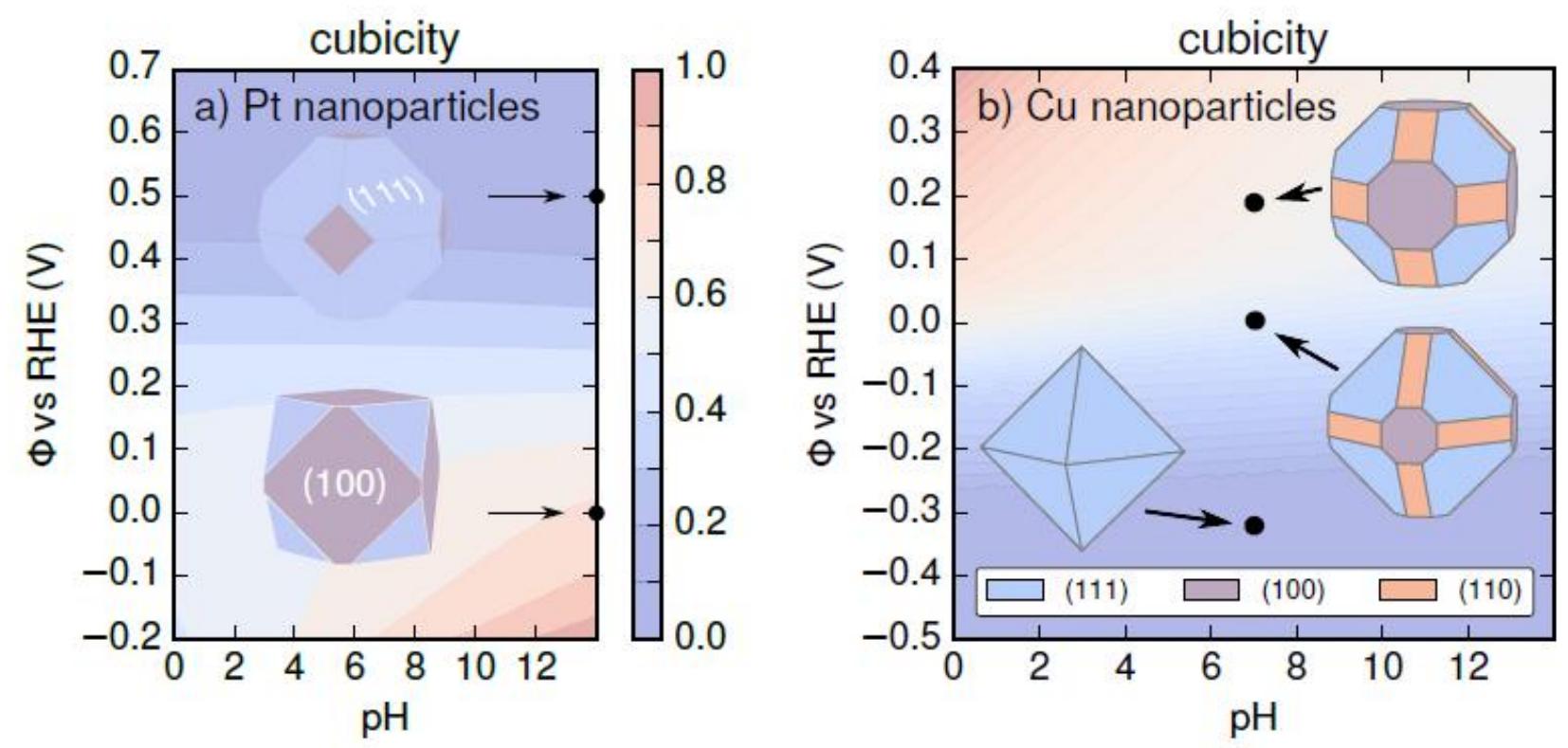
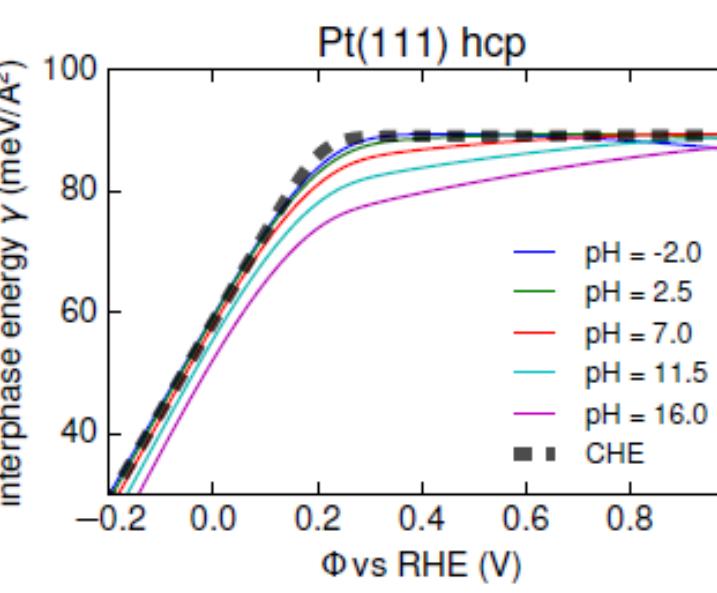
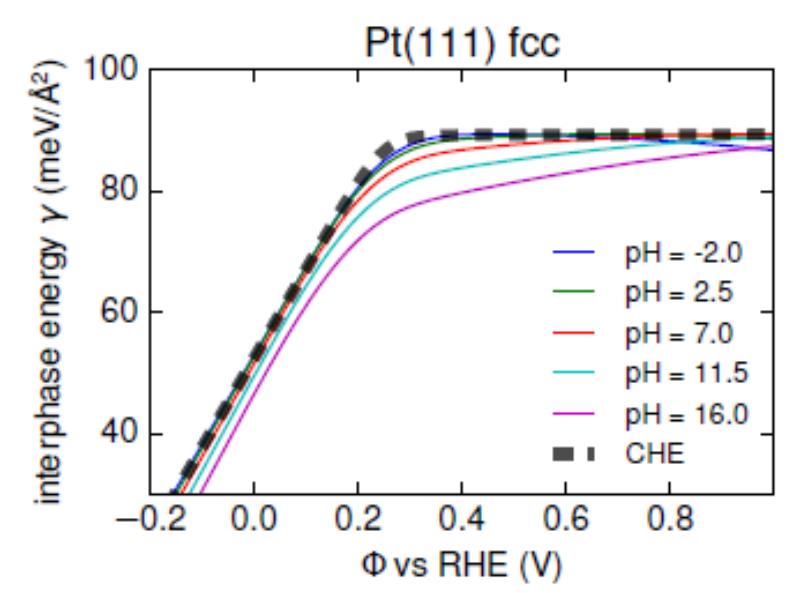
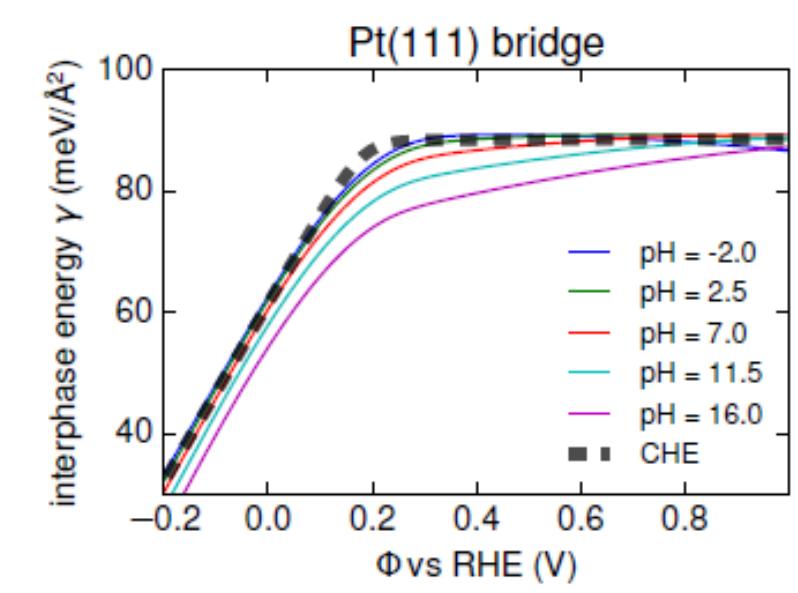
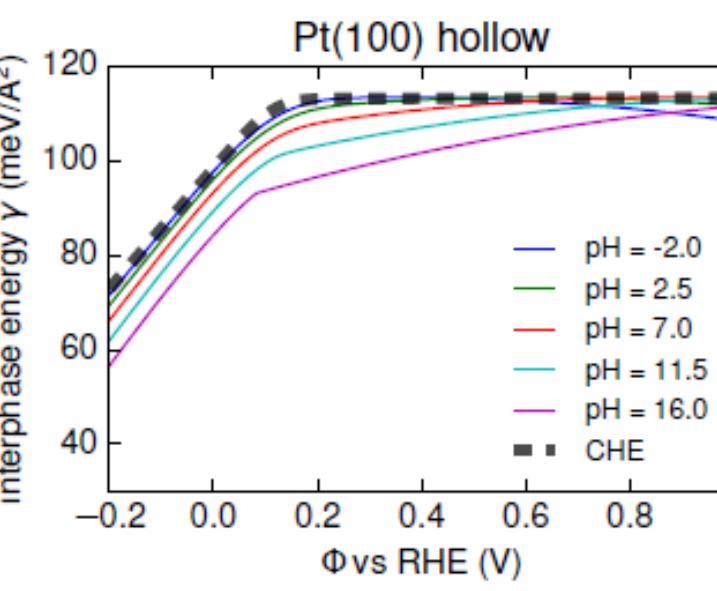
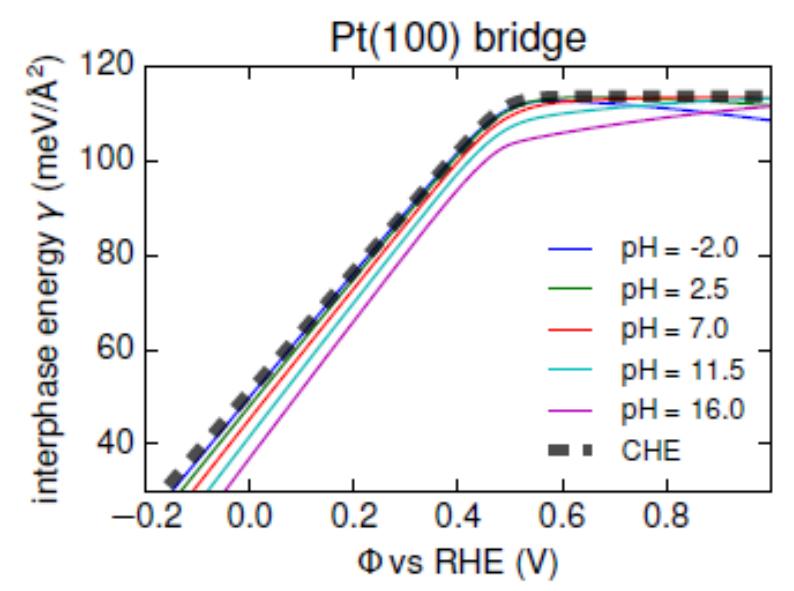
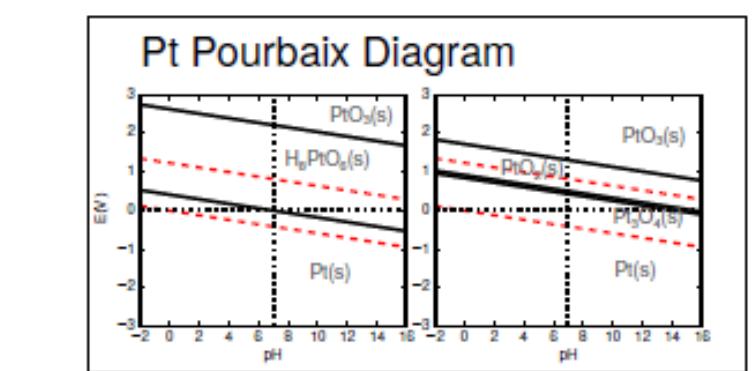
$$\bullet \quad \mu_{H^+} + \mu_{e^-} = \frac{1}{2} \mu_{H_2} - k_B T \ln(10)pH - e\Phi_{SHE}$$

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

Grand Potential Simulations

From extensive vs. intensive

Pt interphase energies



c)

Cu-nanocubes for

CO₂ reduction



- 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

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

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	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)
FeSe WTe ₂	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)
GeS	Sb ₂ Te ₃	0.5	0.06	Sb ₁₆ Te ₃ (s) + Te(s)	0.7	14.4 (25.2)
	MoTe 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	0.1(3)	0.17	HGeO ₃ ⁻ (aq) + H ₂ S(aq)	1.6	24.6 (36.2)
Cu ₂ Te	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)

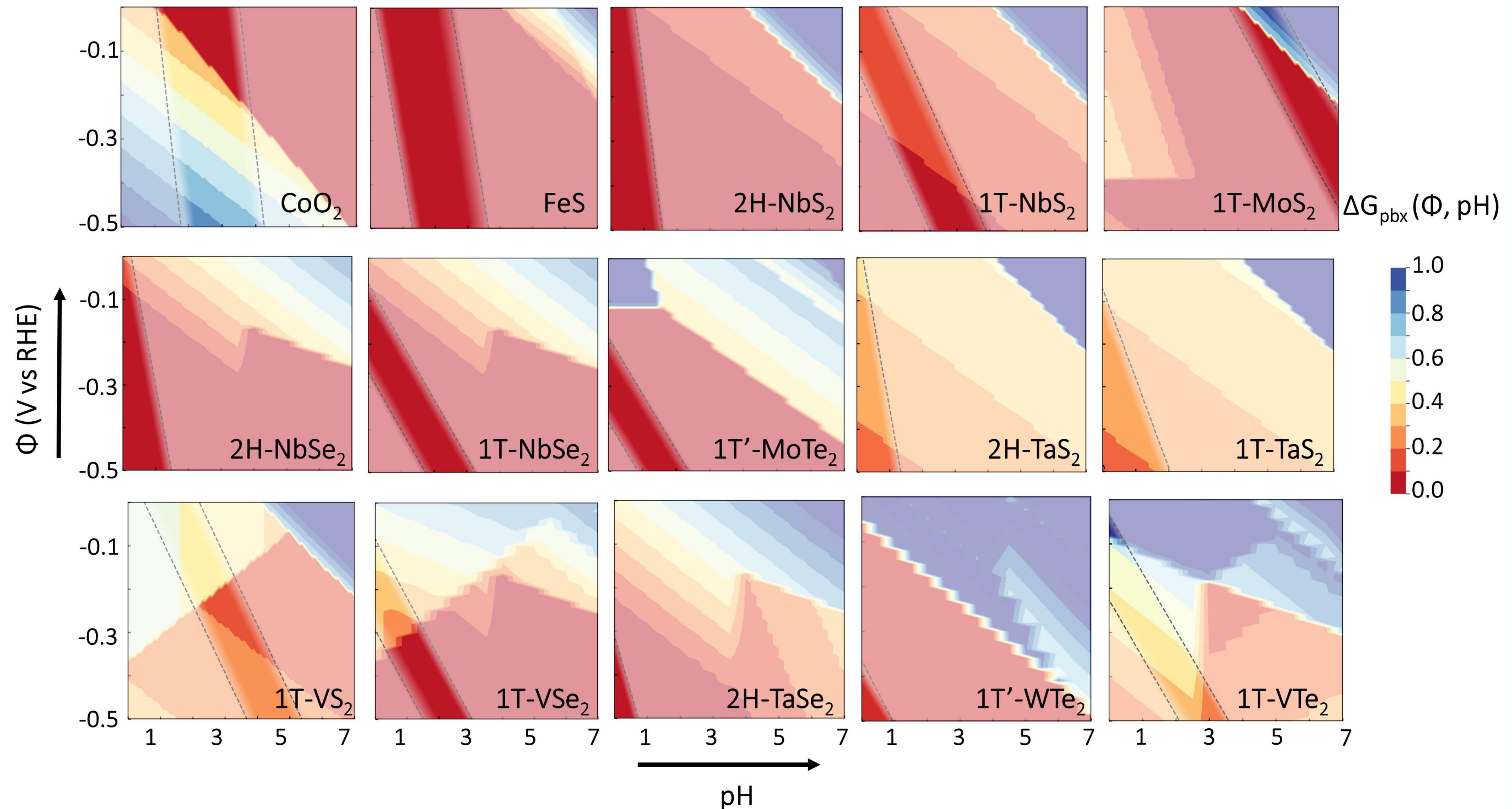
^aCorresponding overpotential vs RHE for H⁺ electrosorption (Φ^{over} in V), aqueous stability ($\Delta G_{\text{pbx}}(\Phi, \text{pH})$ in eV/atom), decomposition products (decomp. pdts), band gap values (E_{gap} in eV), and exfoliation (interlayer binding) energy values in aqueous medium (E_b^{aq} 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

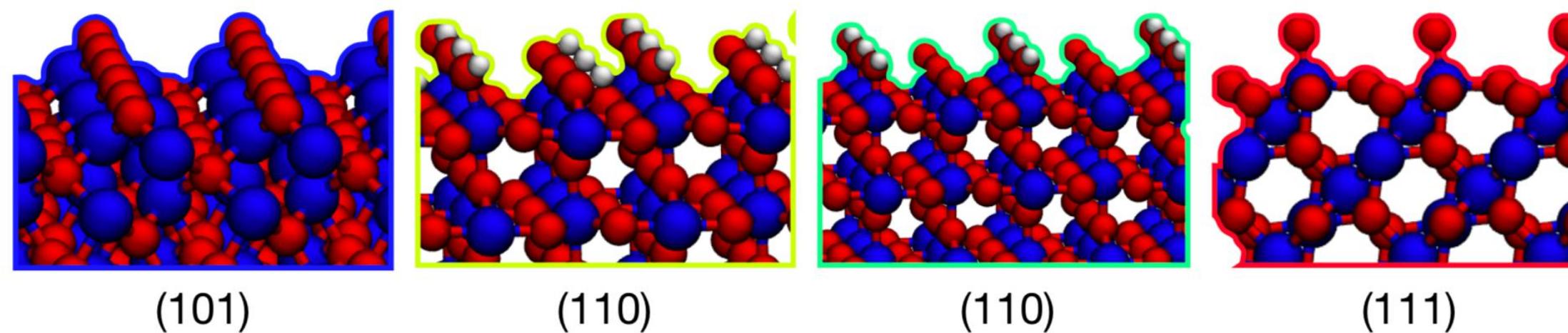
Computational Hydrogen Electrode (dashed):

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

Full Grand-Canonical (solid):

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

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



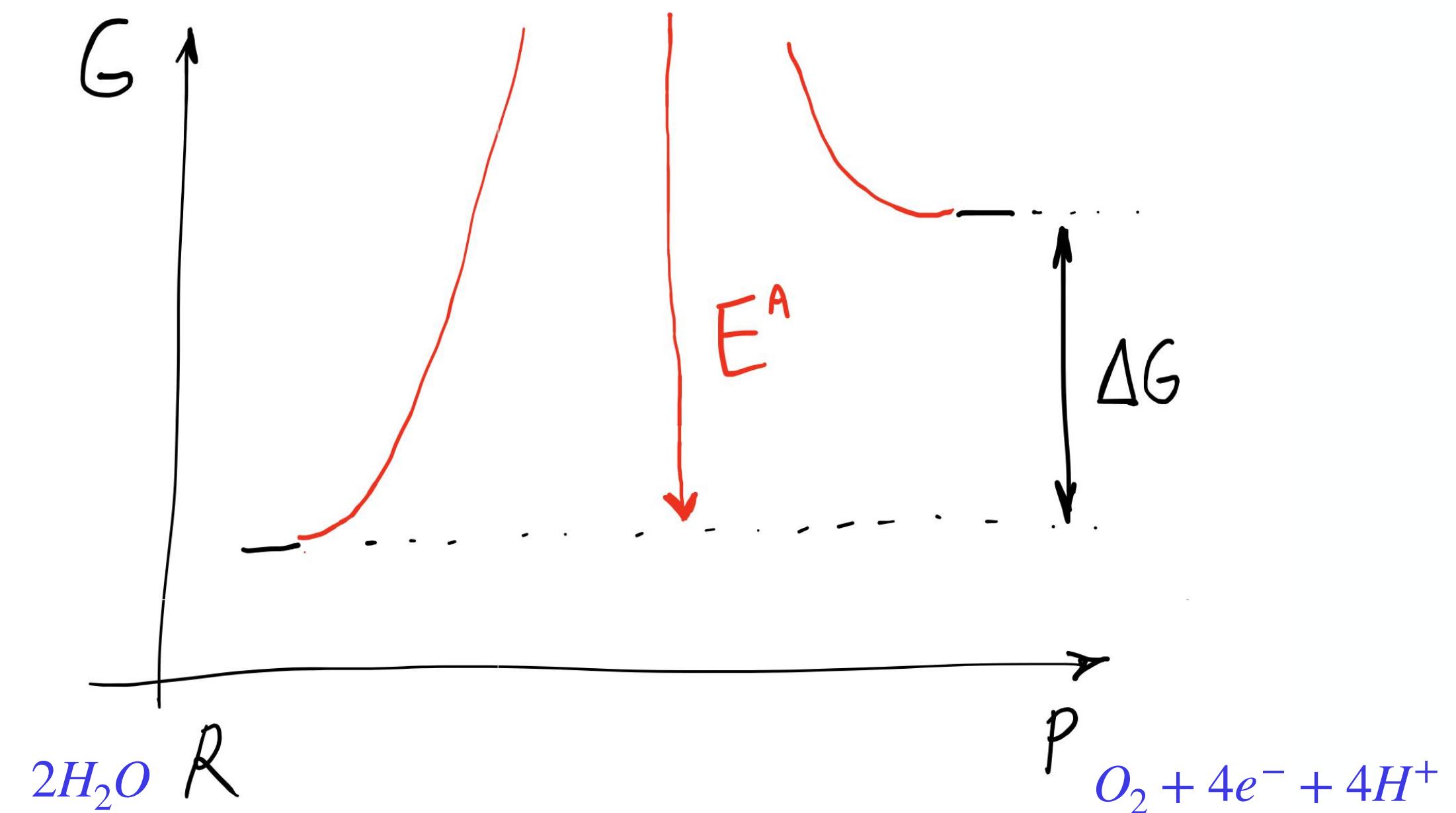
- CHE neglects effects of bias on structures
- CHE is more accurate close to PZC
- Grand Canonical requires significantly more calculations

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

Multiple Steps Conversion Catalytic Activity from Intermediates Stability

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

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

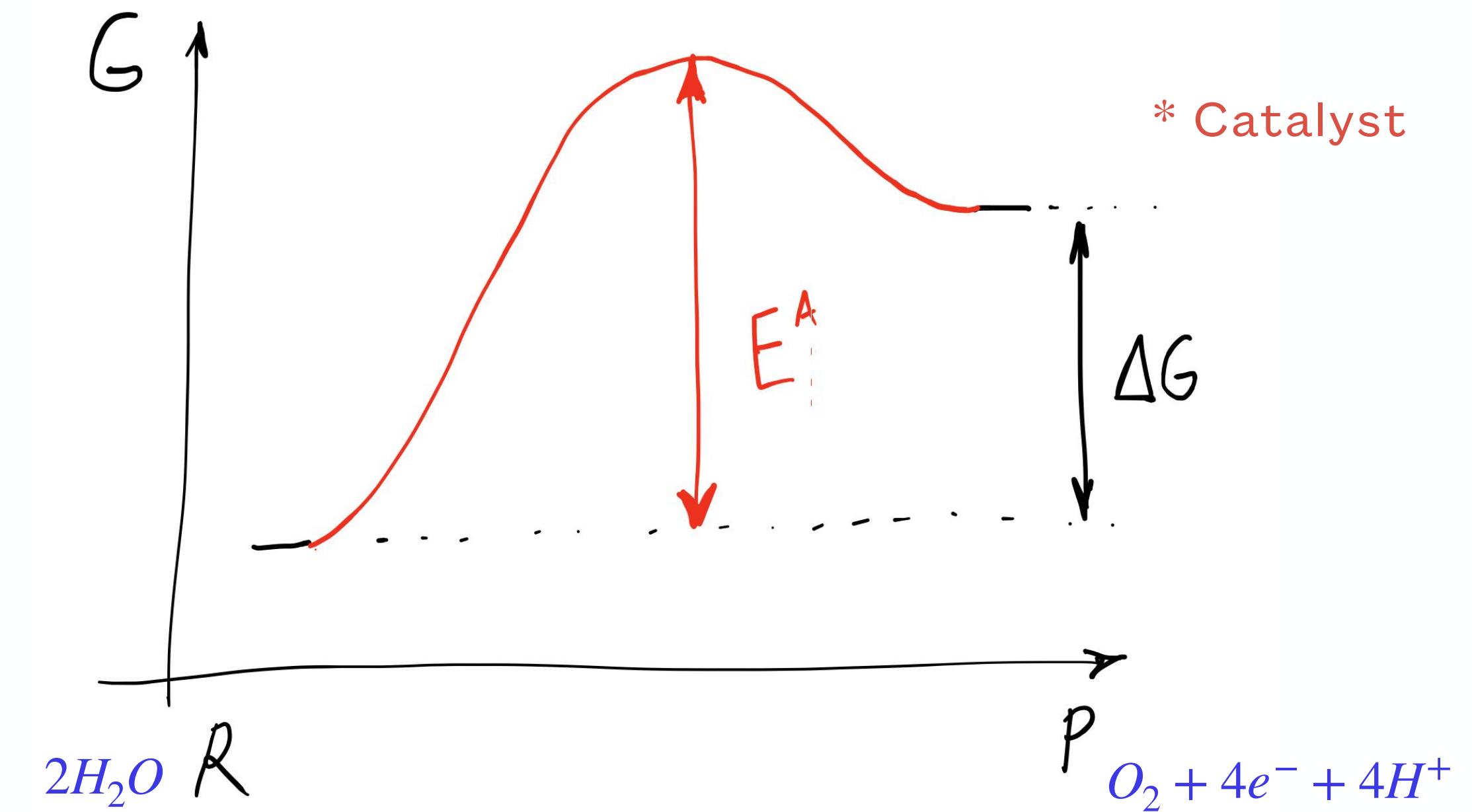


¹ Norskov et al., *J. Phys. Chem. B*, **108**, 17886 (2004)

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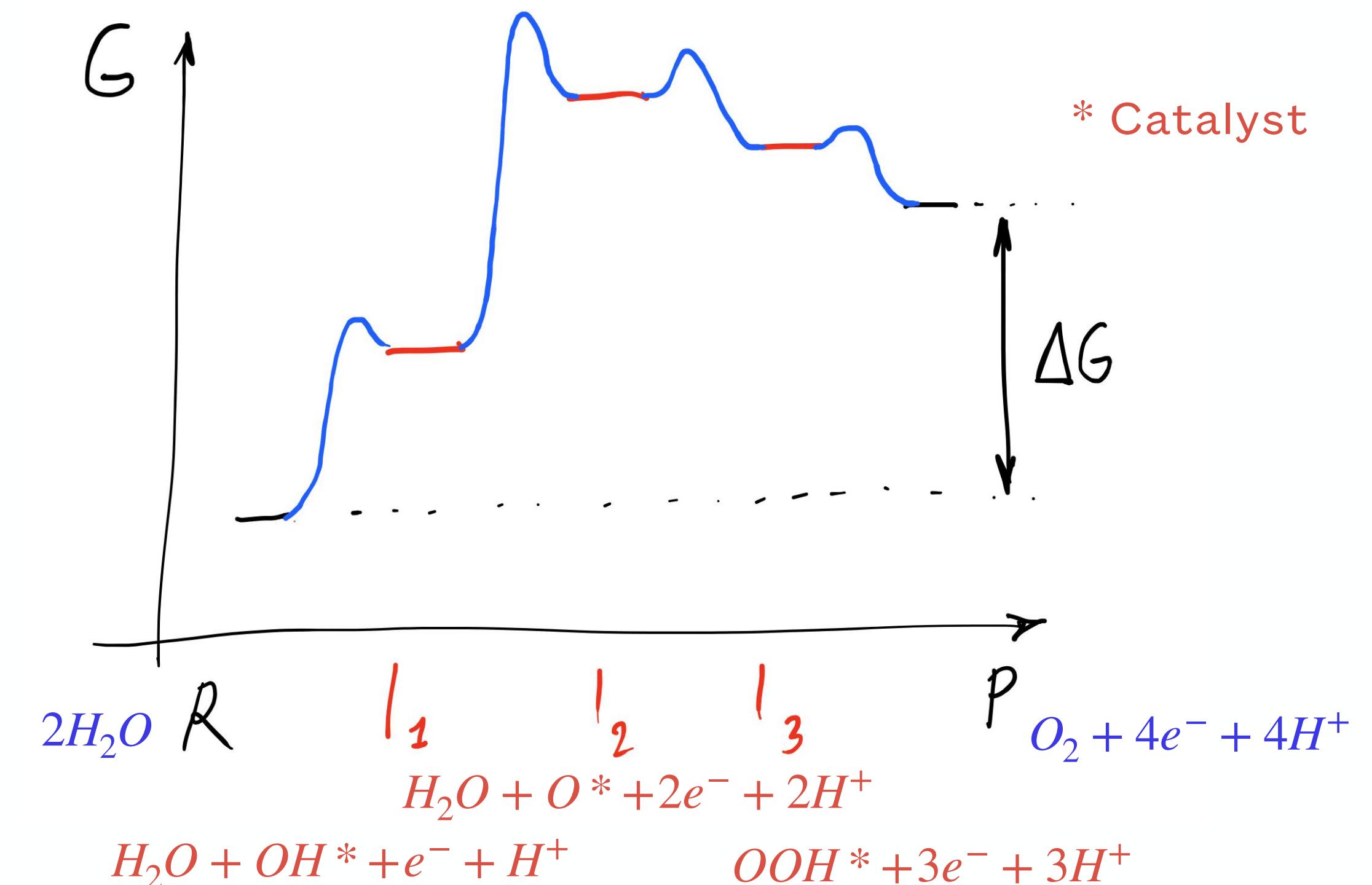


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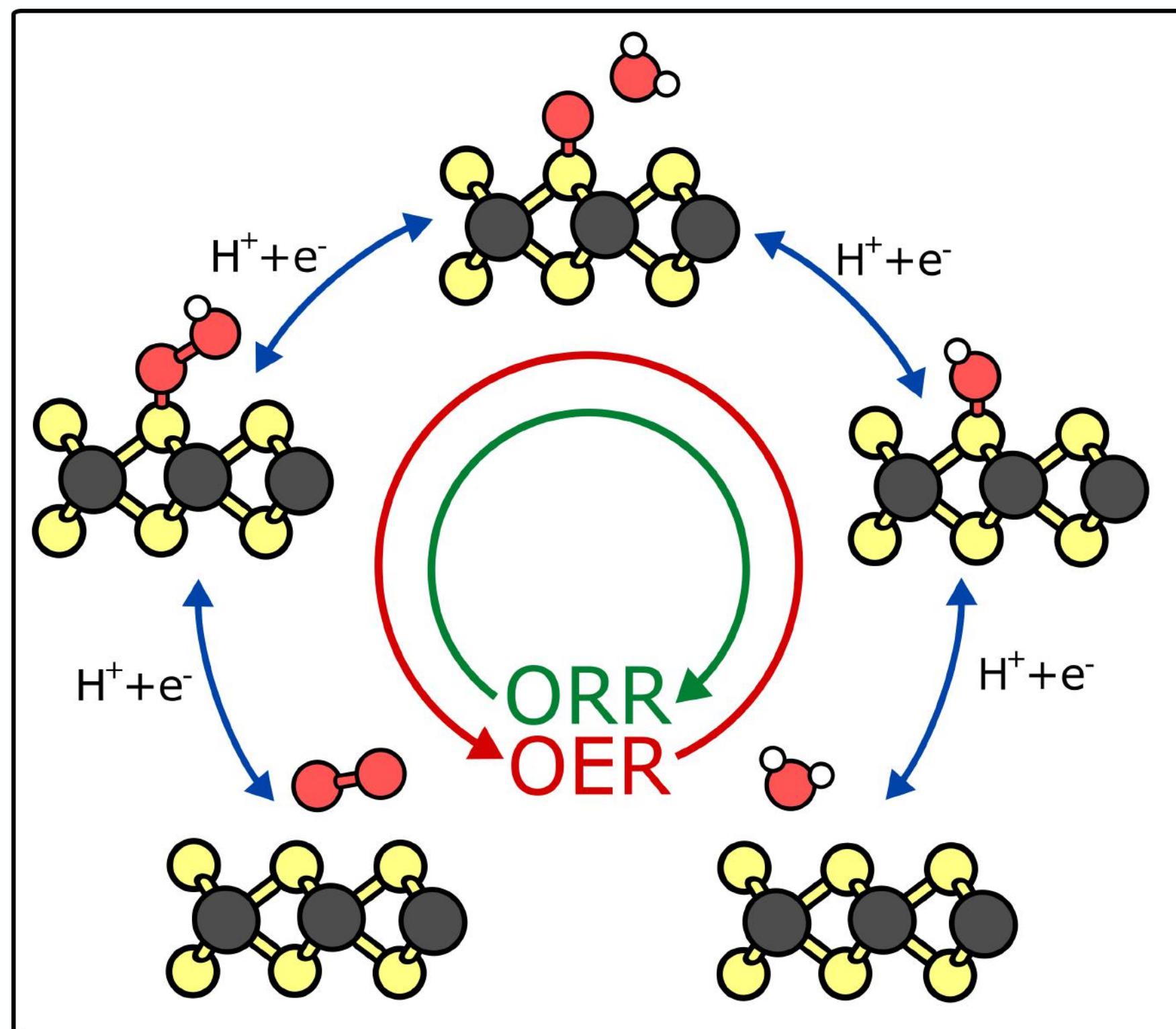
¹ Norskov et al., *J. Phys. Chem. B*, **108**, 17886 (2004)

Multiple Steps Conversion

Catalytic Activity from Intermediates Stability

Oxygen-Water Conversion

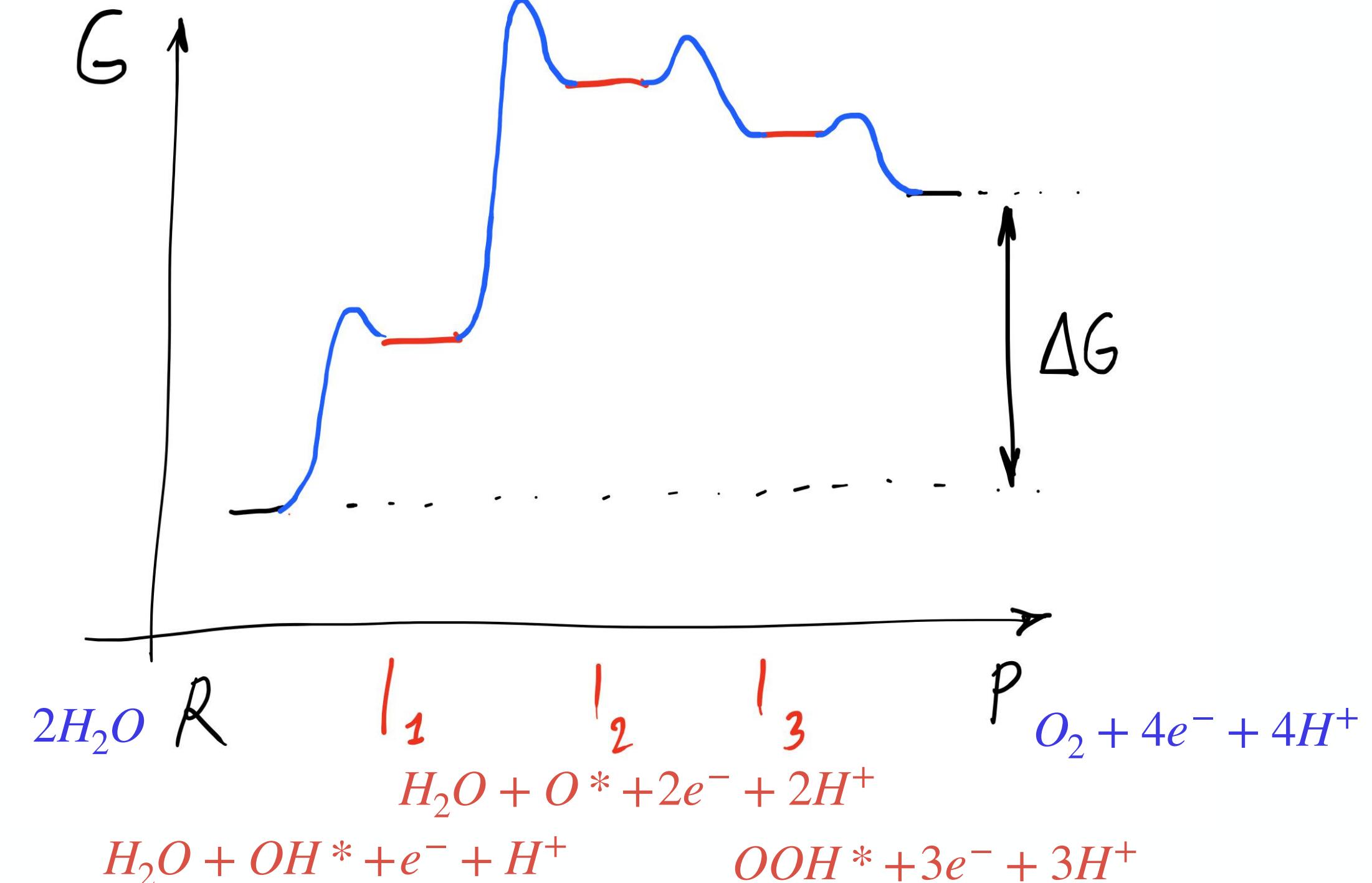
Schematic catalytic steps involved in single-site Oxygen Reduction and Oxygen Evolution reactions on a 2D material.



Karmodak and Andreussi, *in preparation* (2020)

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

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



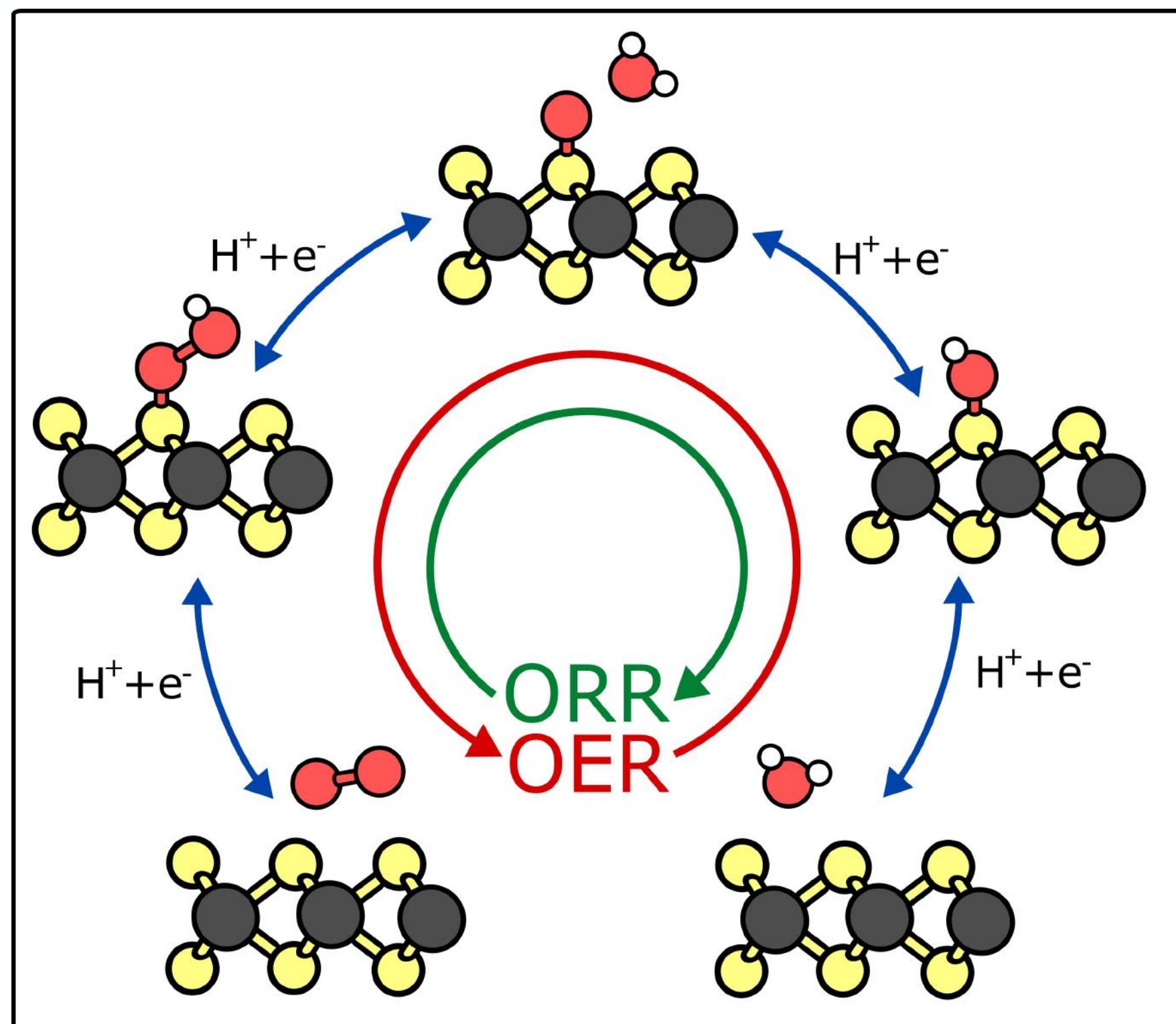
¹ Norskov et al., *J. Phys. Chem. B*, **108**, 17886 (2004)

Multiple Steps Conversion

Catalytic Activity from Intermediates Stability

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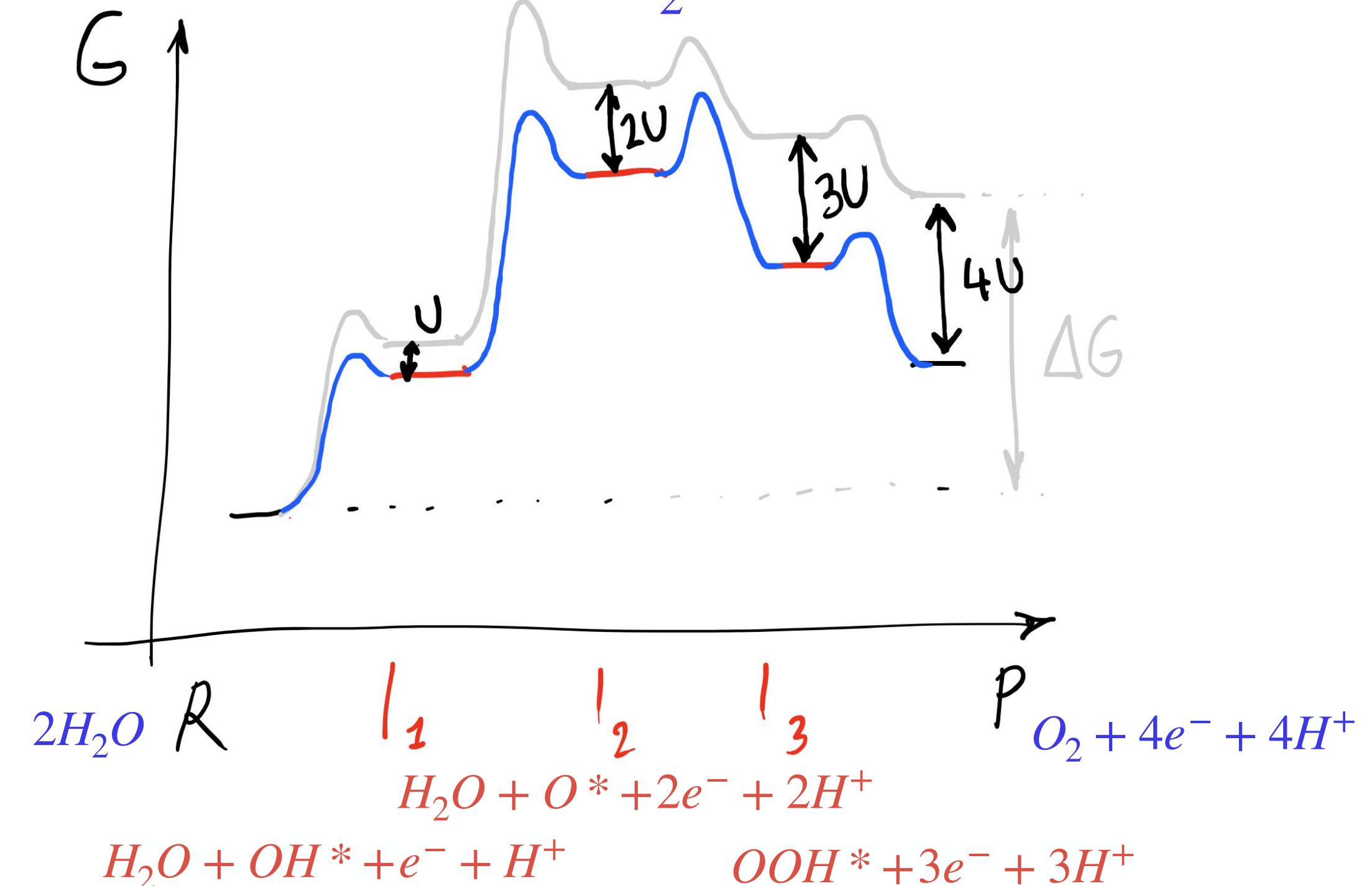


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$$\Delta G^{OER} = G(O_2) + 4\mu_e + 4\mu_H - G(H_2O)$$

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



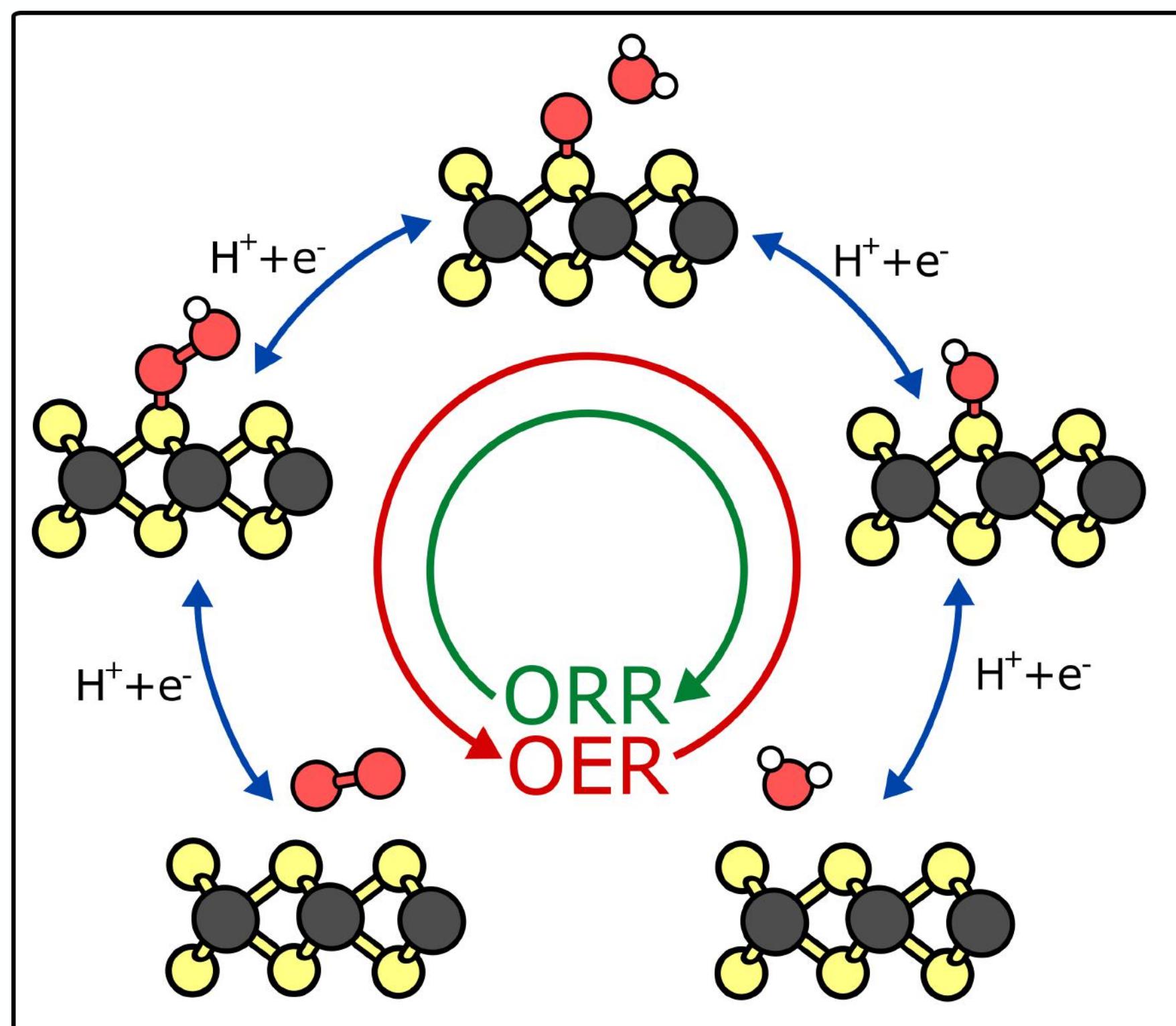
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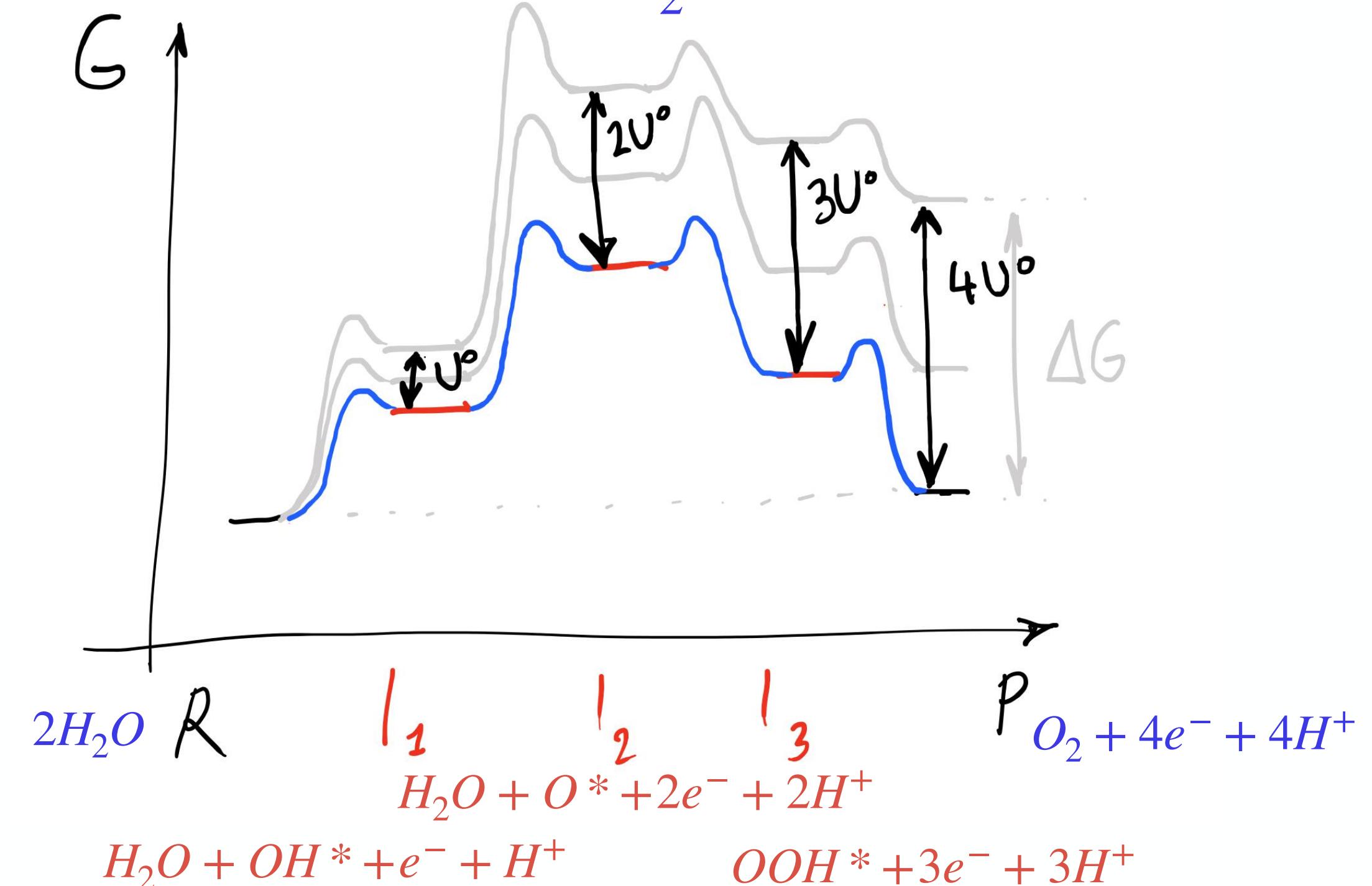


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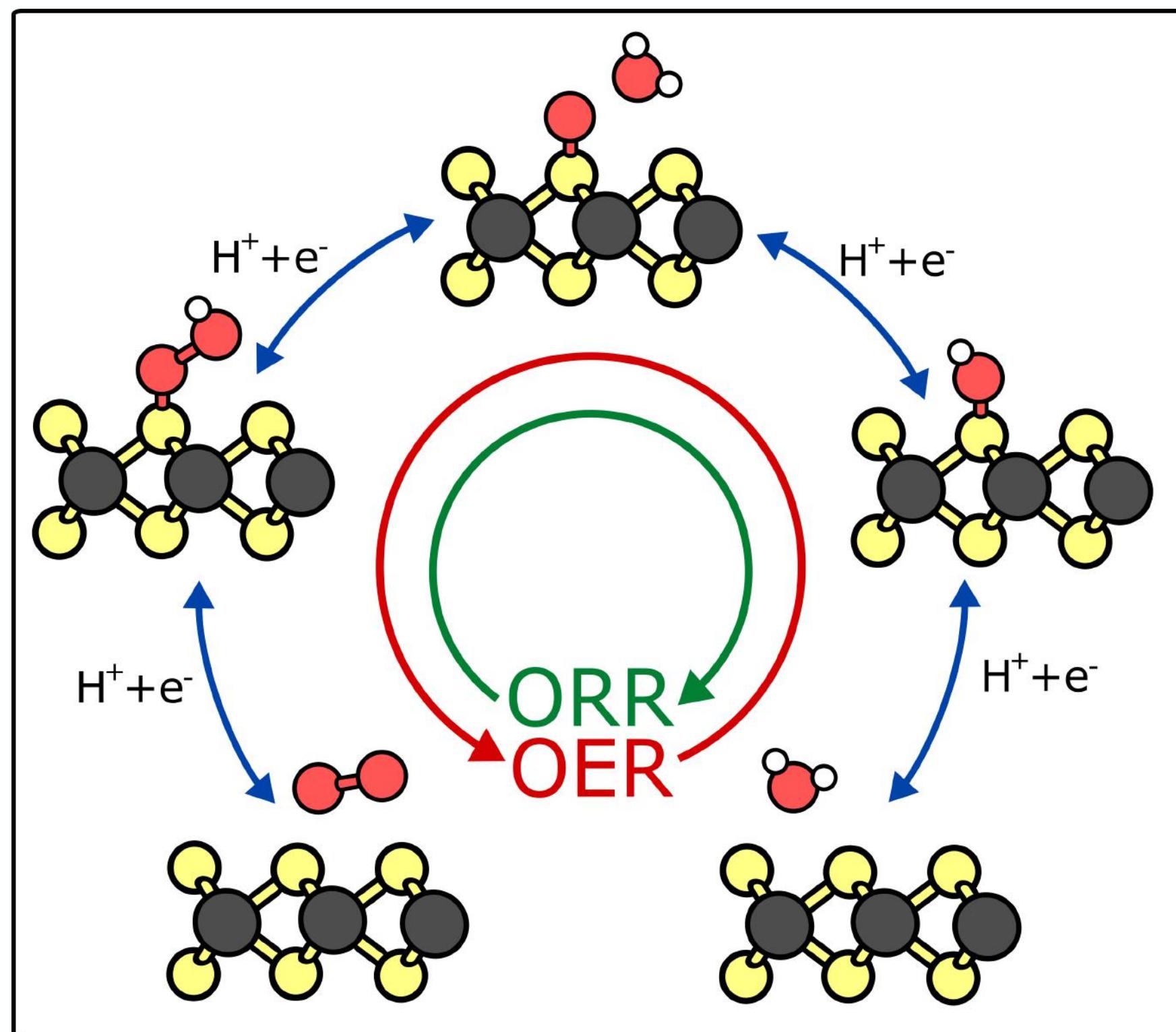
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Multiple Steps Conversion

Catalytic Activity from Intermediates Stability

Oxygen-Water Conversion

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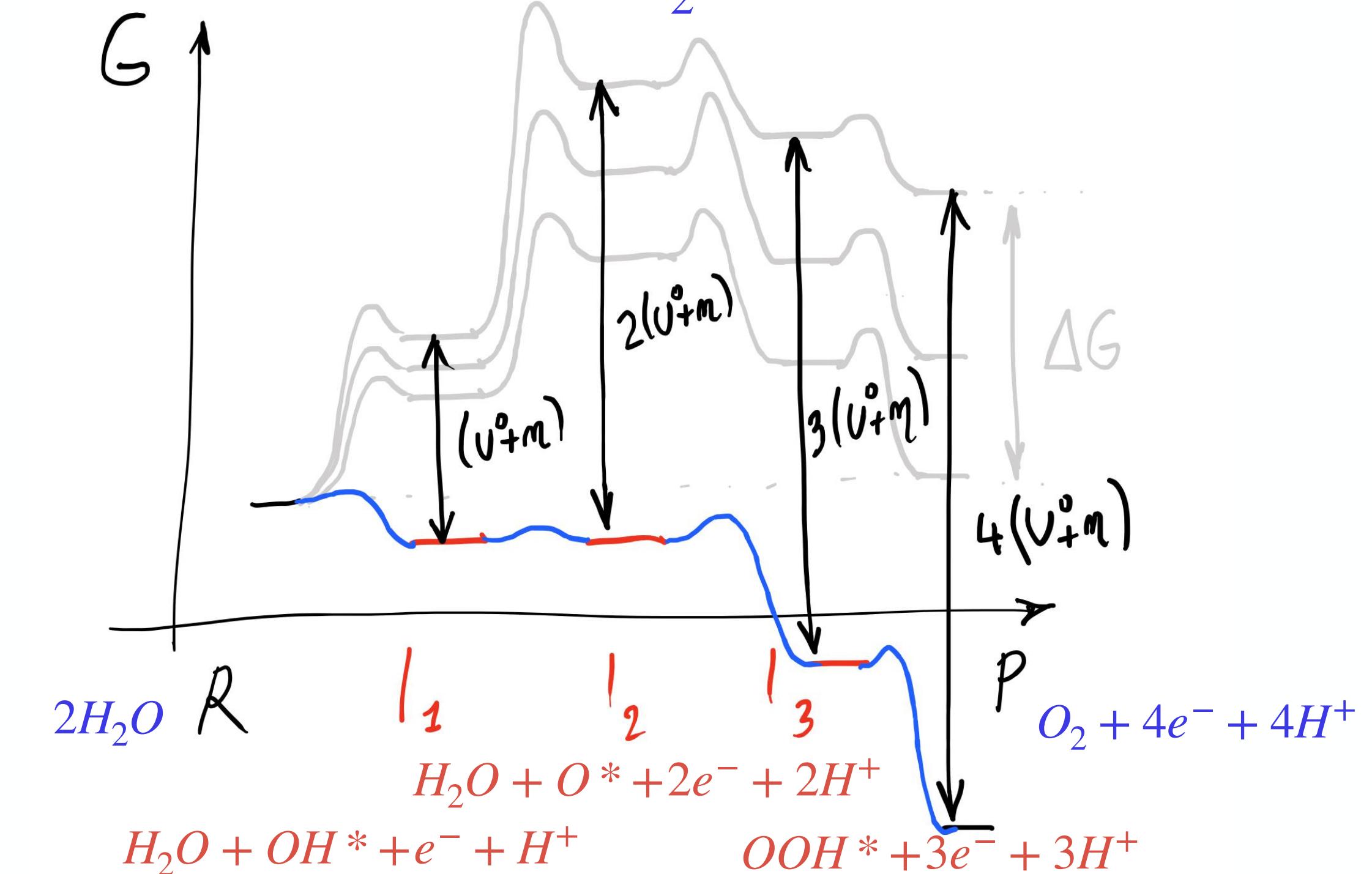


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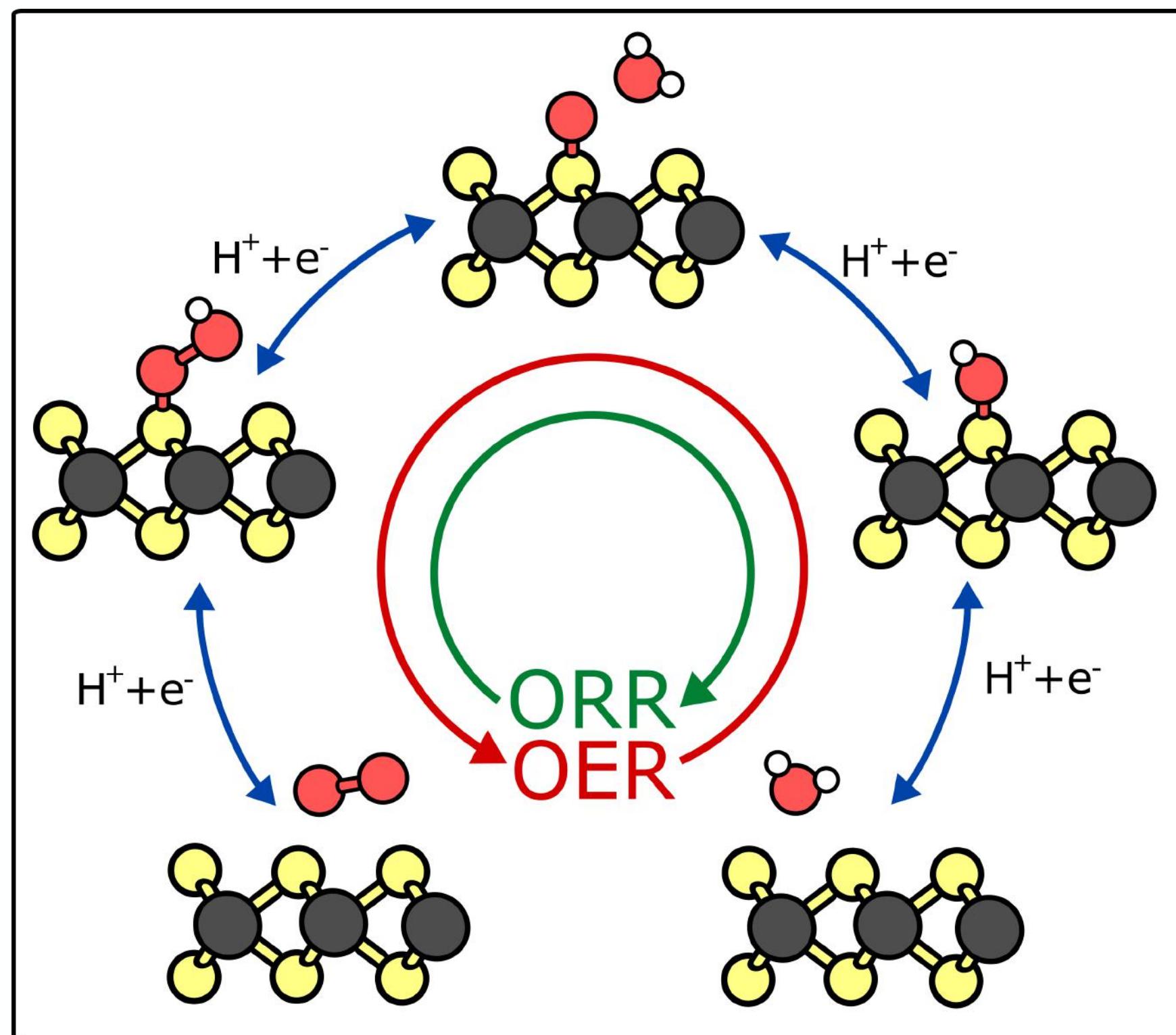
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Multiple Steps Conversion

Catalytic Activity from Intermediates Stability

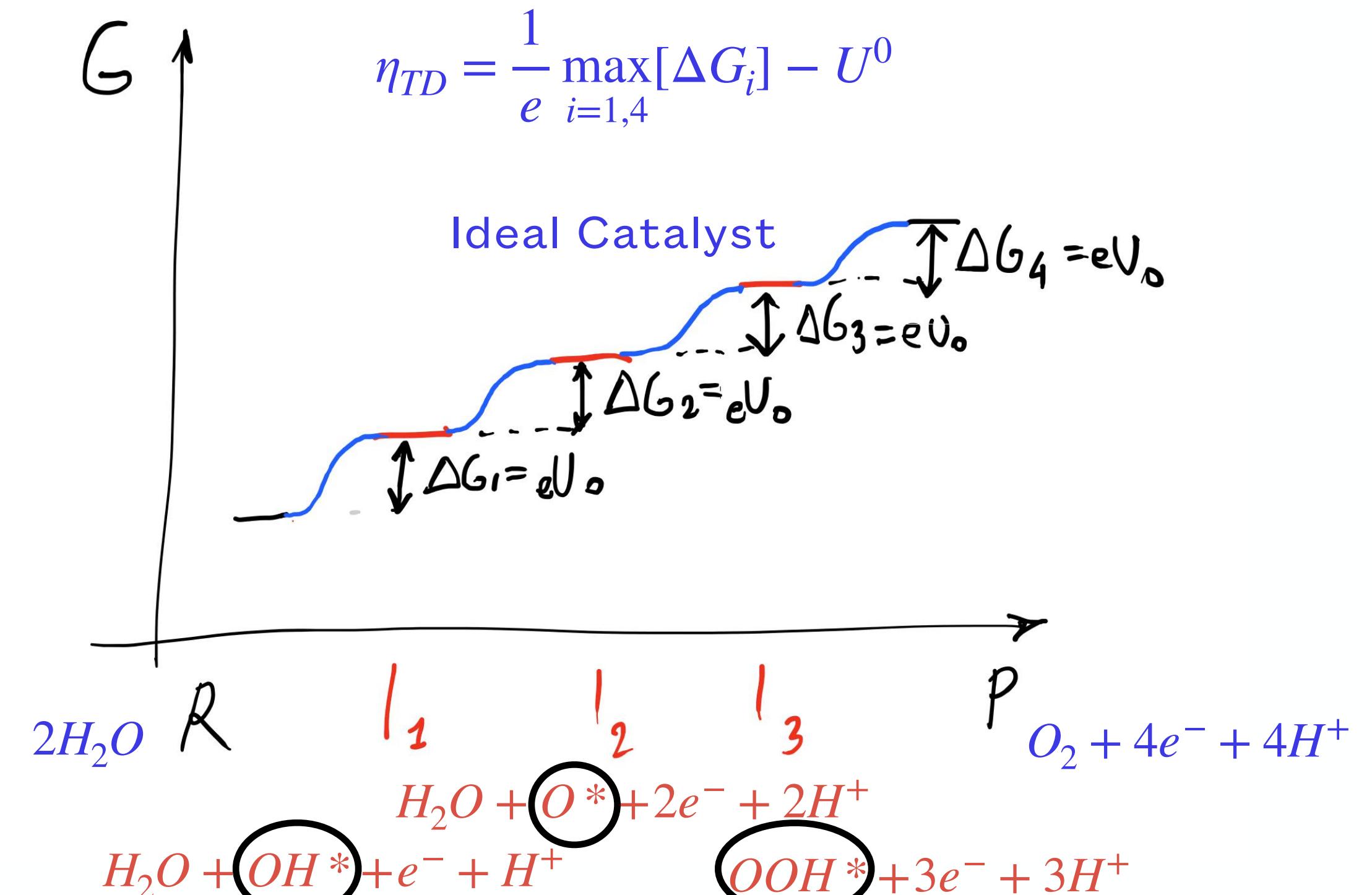
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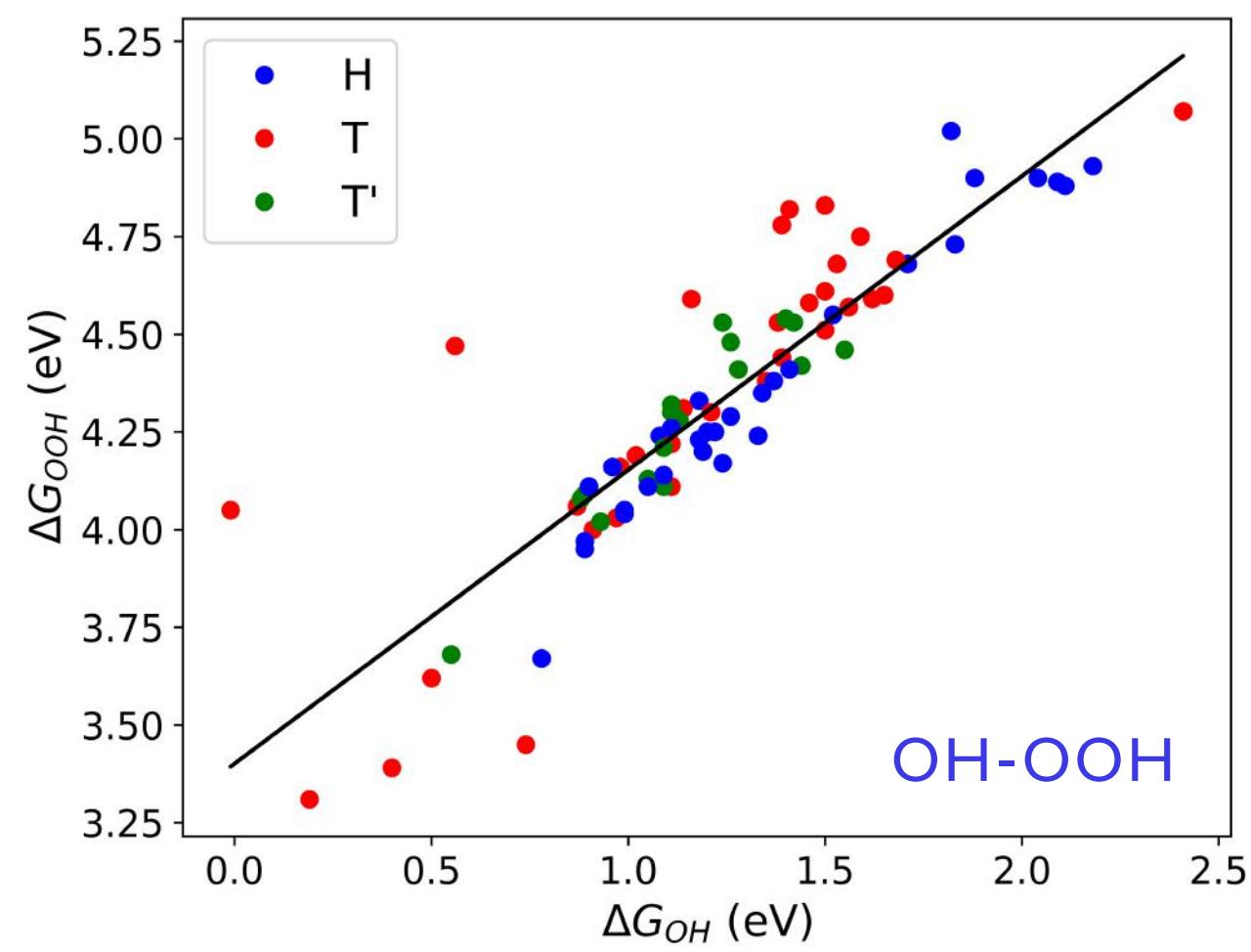
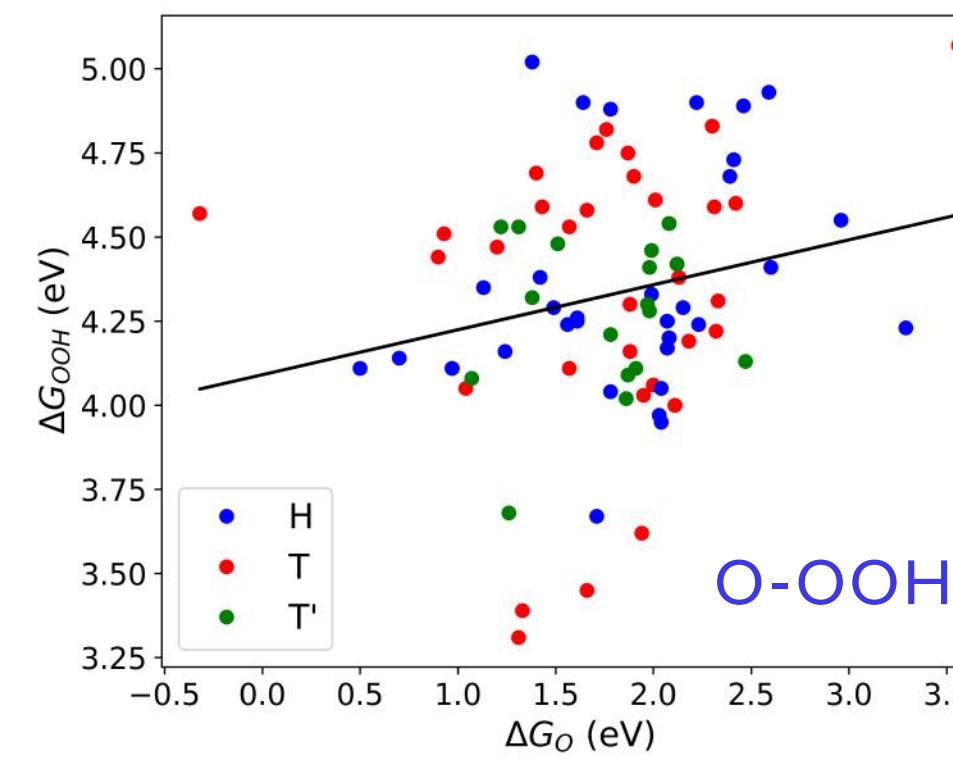
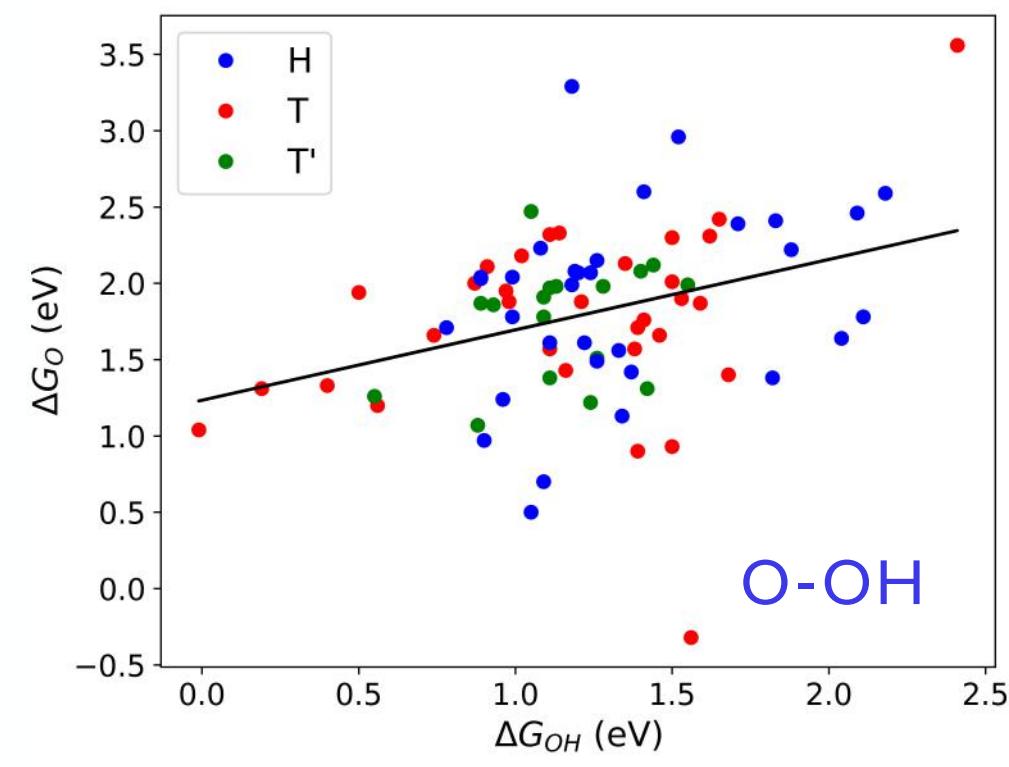
Karmodak and Andreussi, *in preparation* (2020)

- 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.



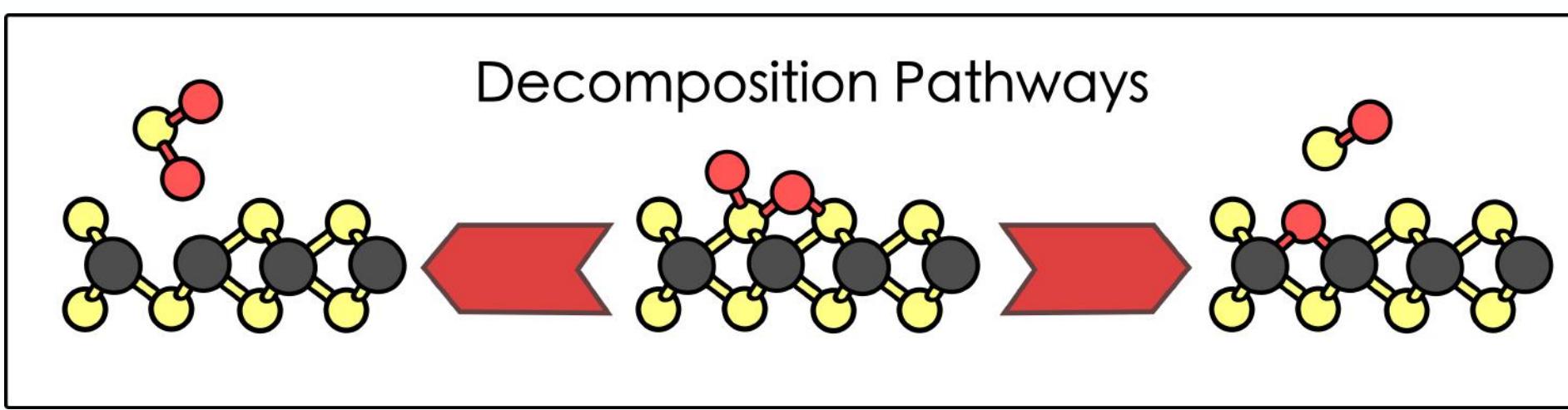
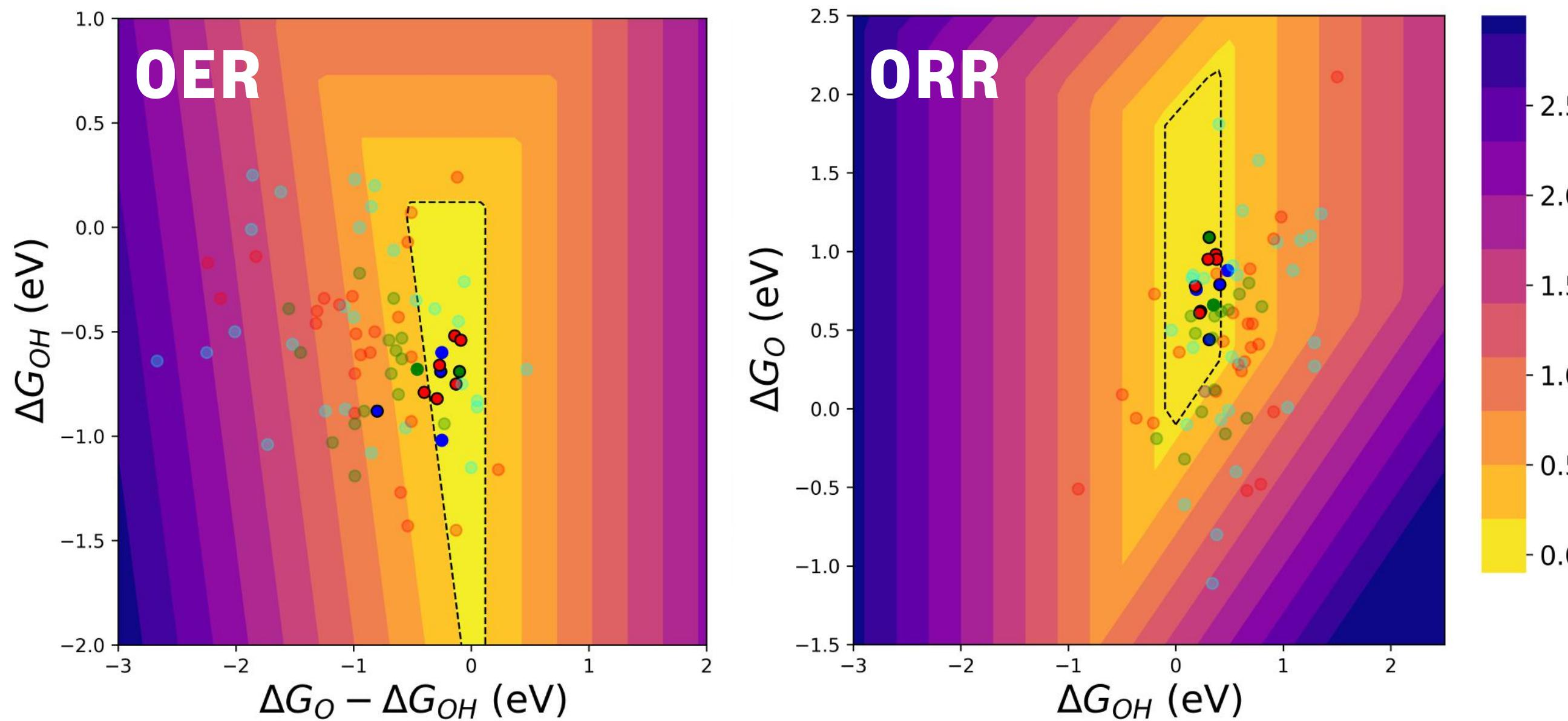
Materials Constraints

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

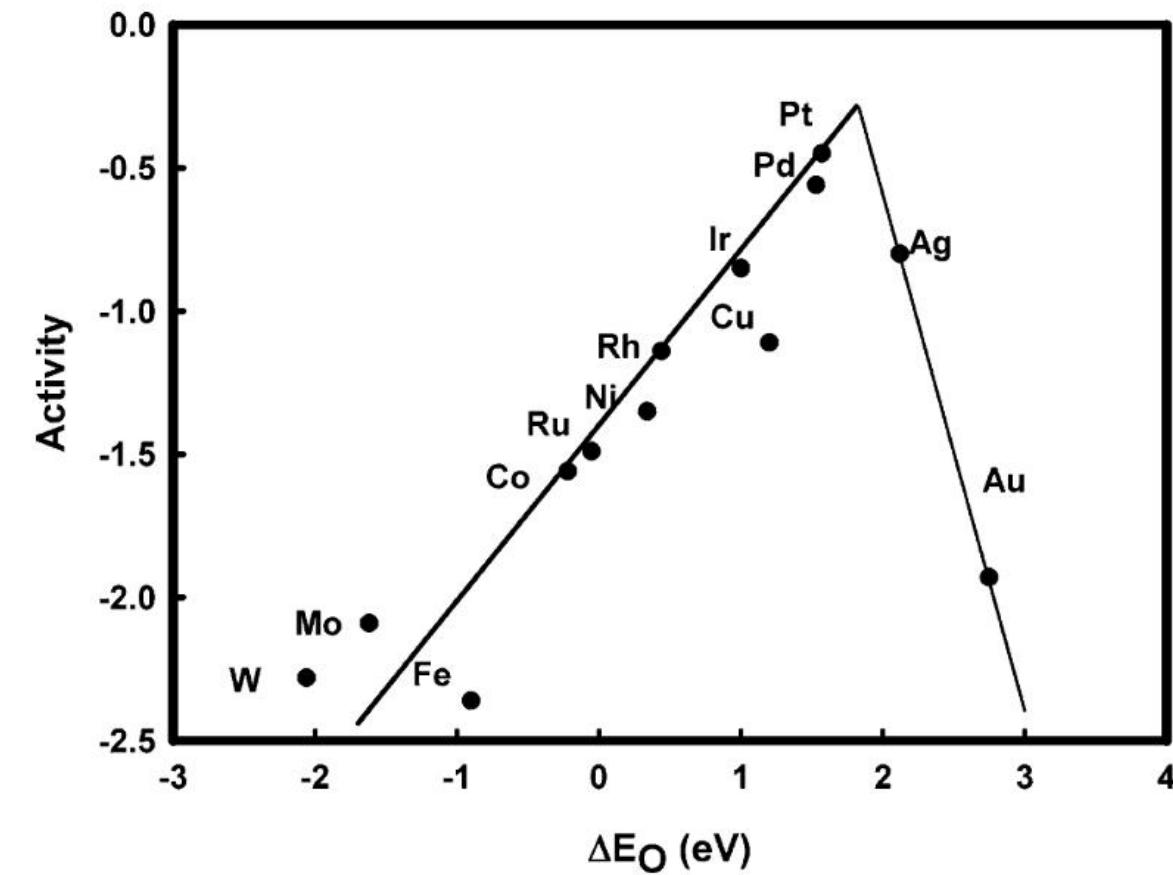
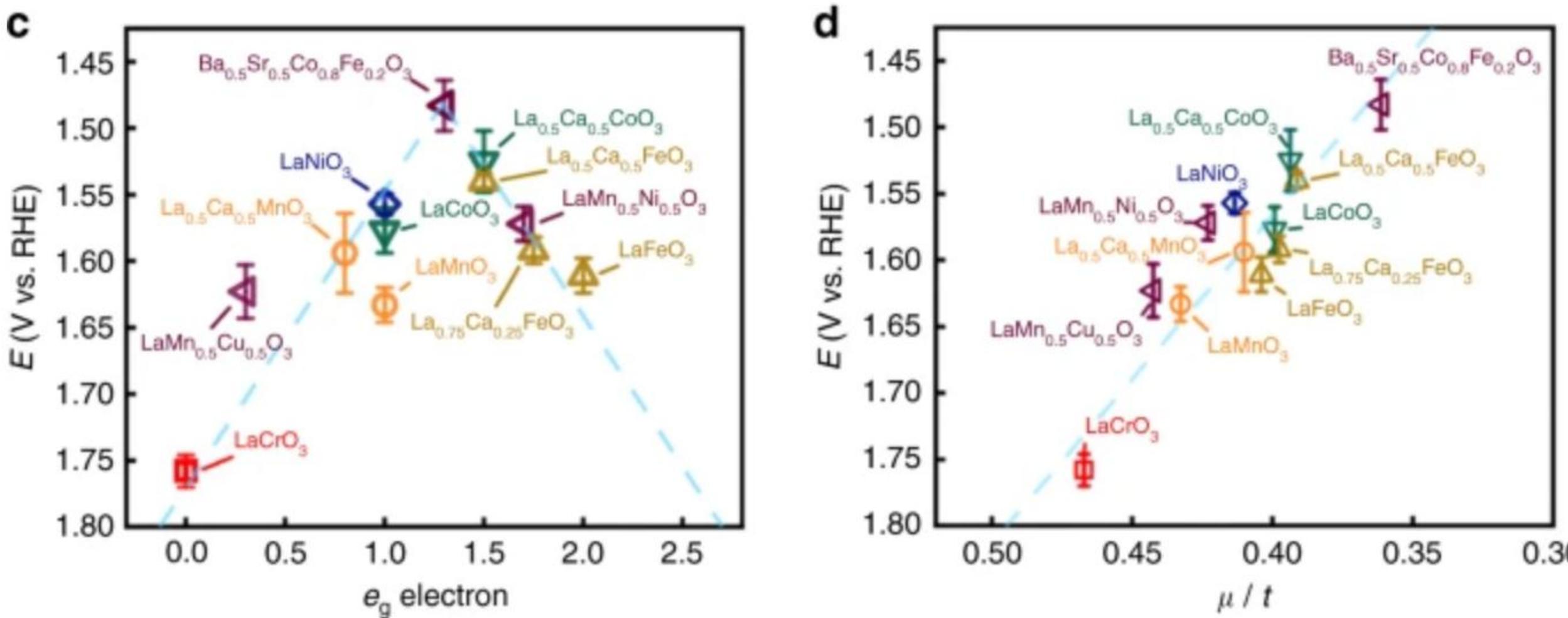
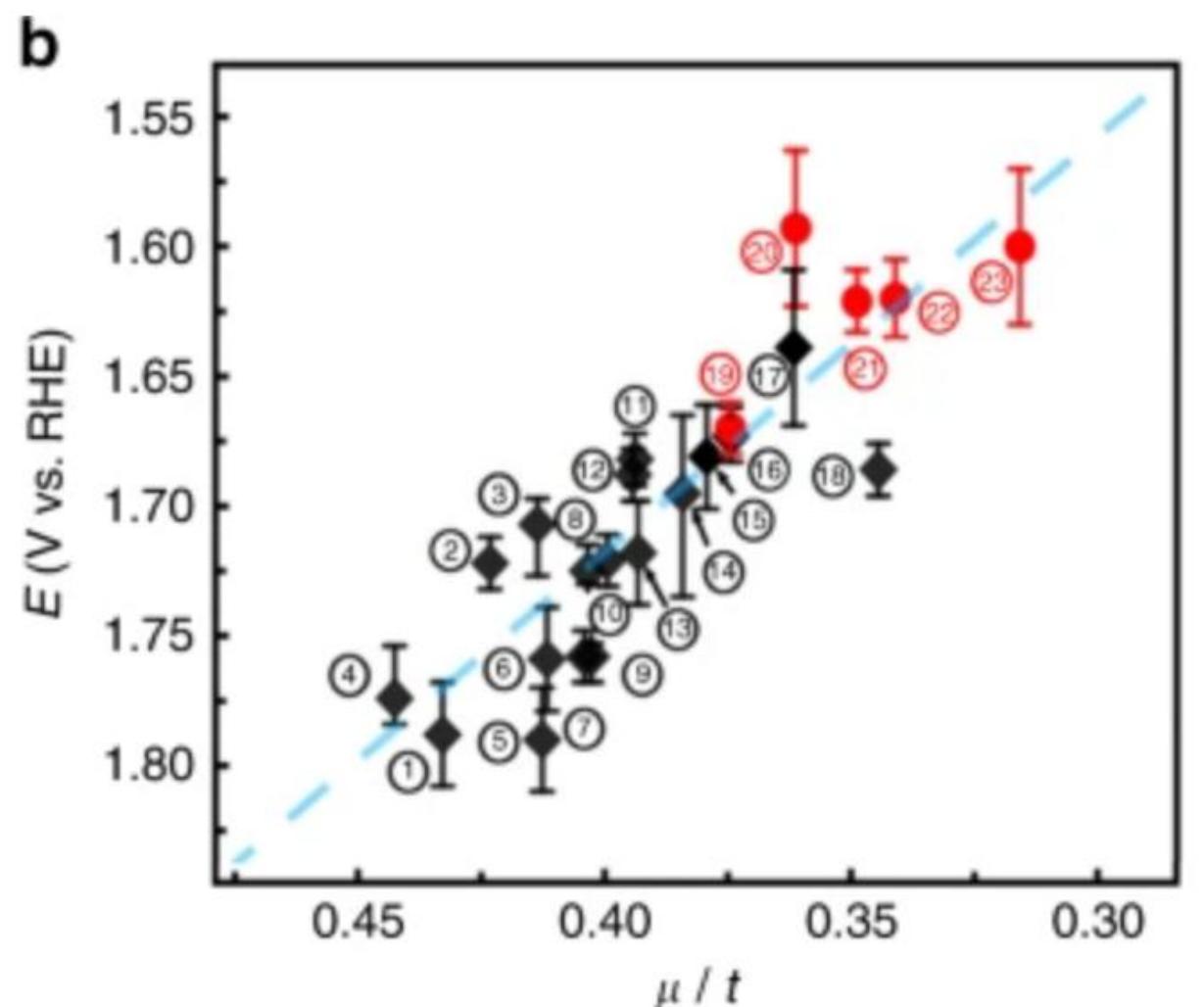


Figure 4. Trends in oxygen reduction activity (defined in the text) plotted as a function of the oxygen binding energy.

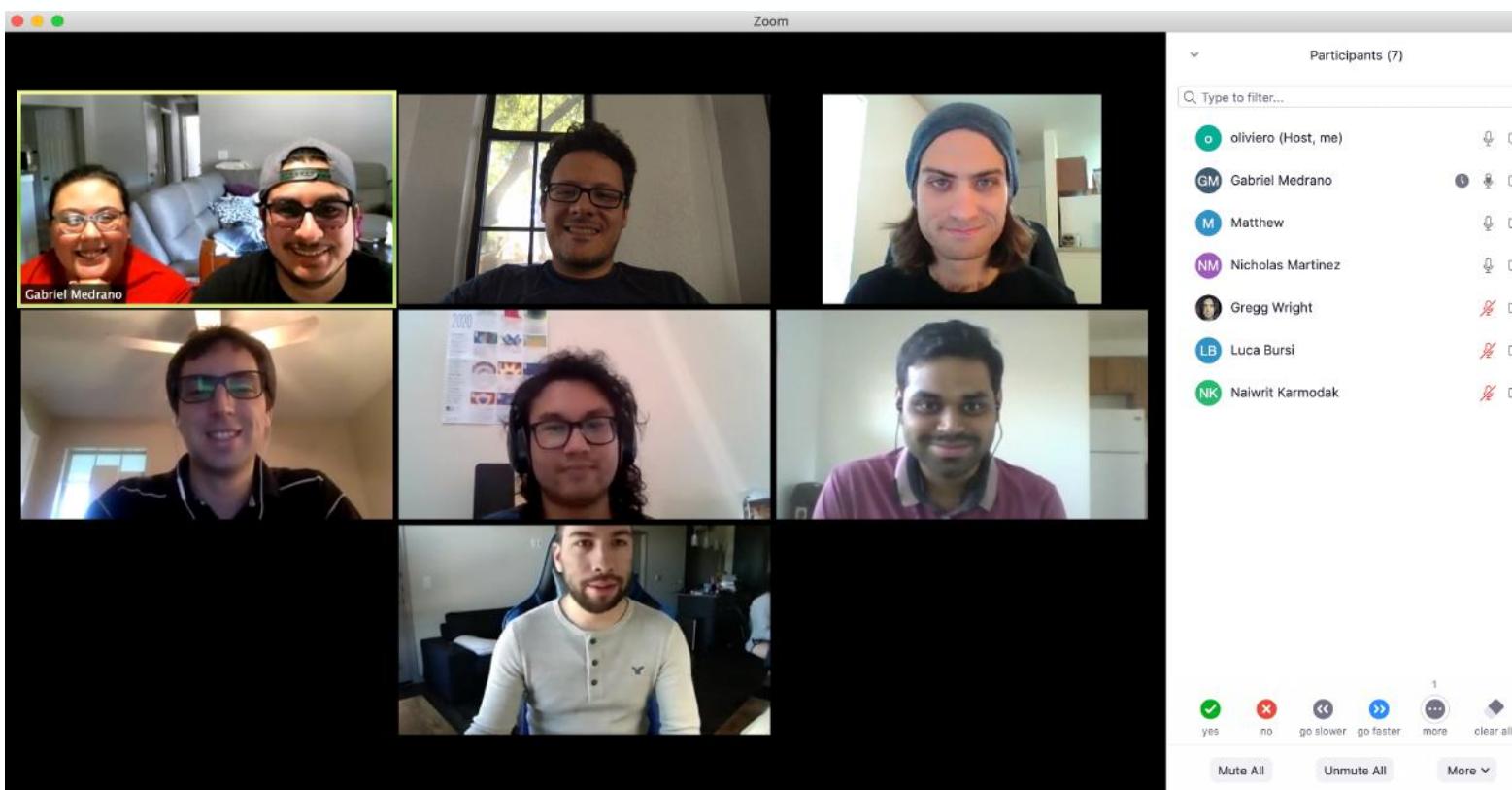




www.materialab.org

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)



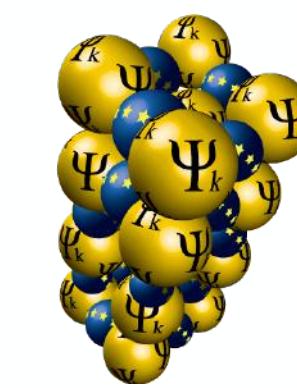
Former Members

- 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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Funding

- NSF CAREER CHE #1945139
- NSF CSSI OAC #1931479
- ACS PRF
- Computing Time
 - ORNL CNMS
 - TACC
 - UNT HPC



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OAK RIDGE
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TACC