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Q-MS School 2021



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# Continuum Models for Wet Electrified Interface

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October 2021

Image from M. Simoncelli [acces.epfl.ch/cms/lang/en/pid/152725](http://acces.epfl.ch/cms/lang/en/pid/152725)

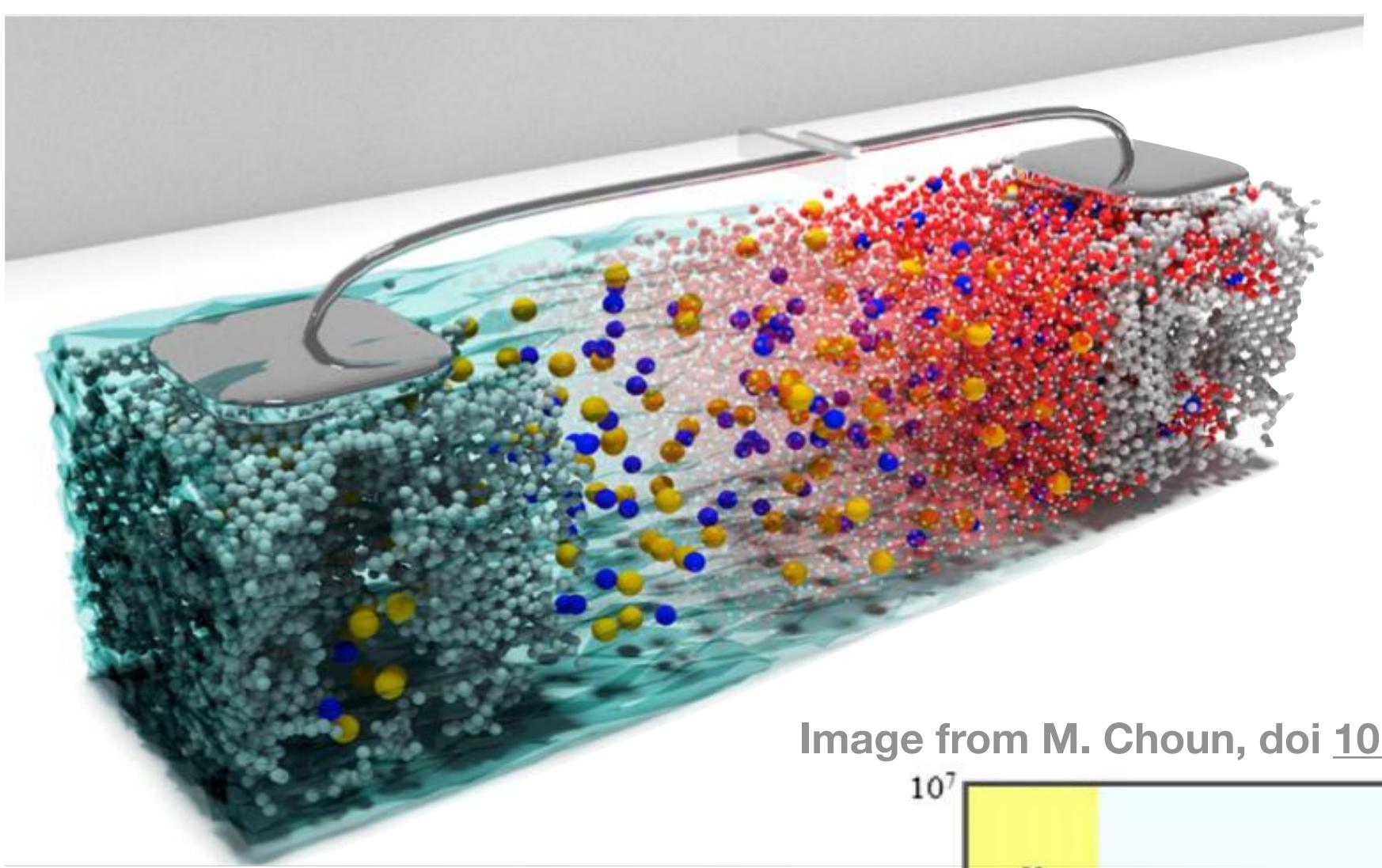
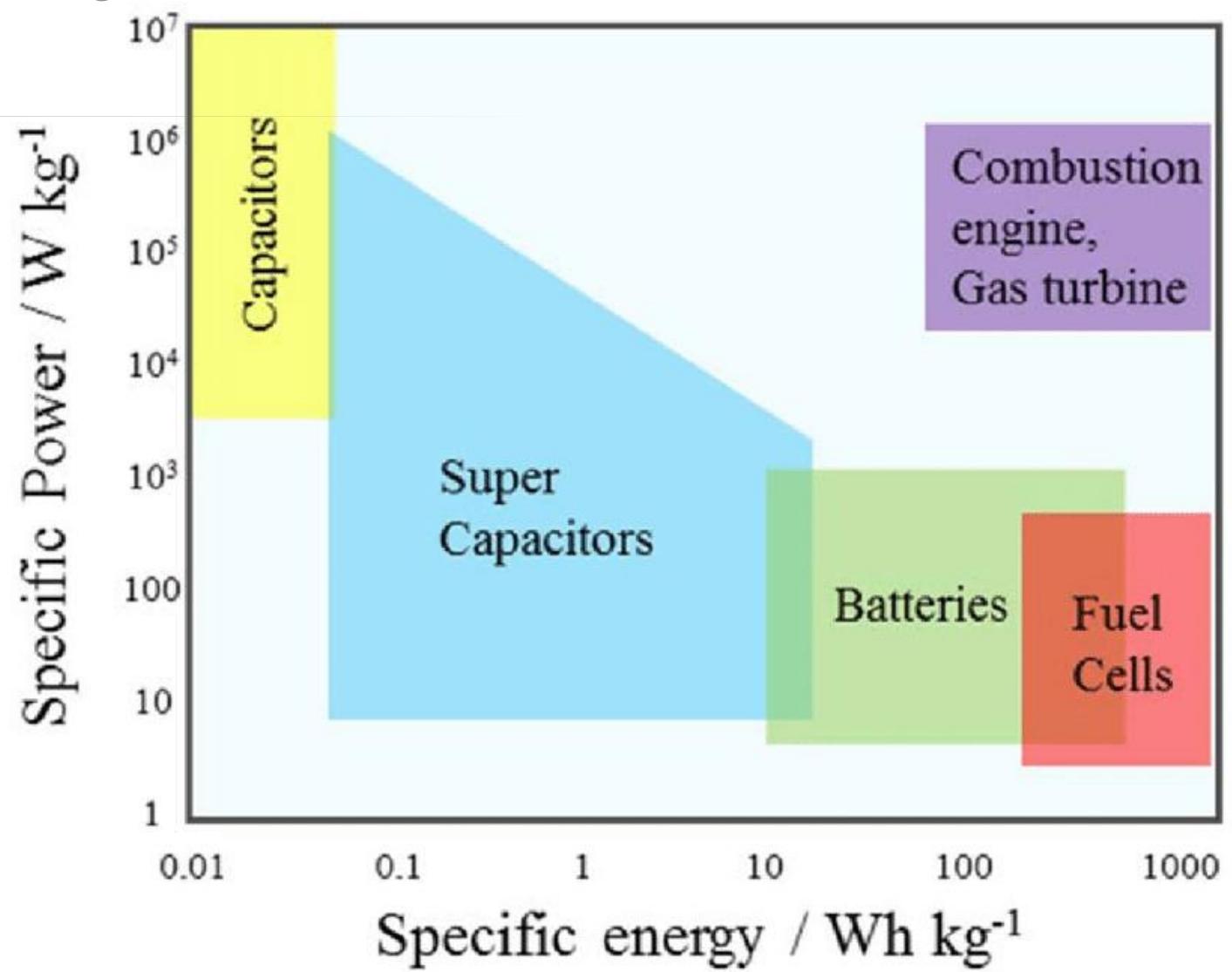


Image from M. Choun, doi [10.13140/RG.2.2.32153.42088](https://doi.org/10.13140/RG.2.2.32153.42088)



# 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](http://acces.epfl.ch/cms/lang/en/pid/152725)

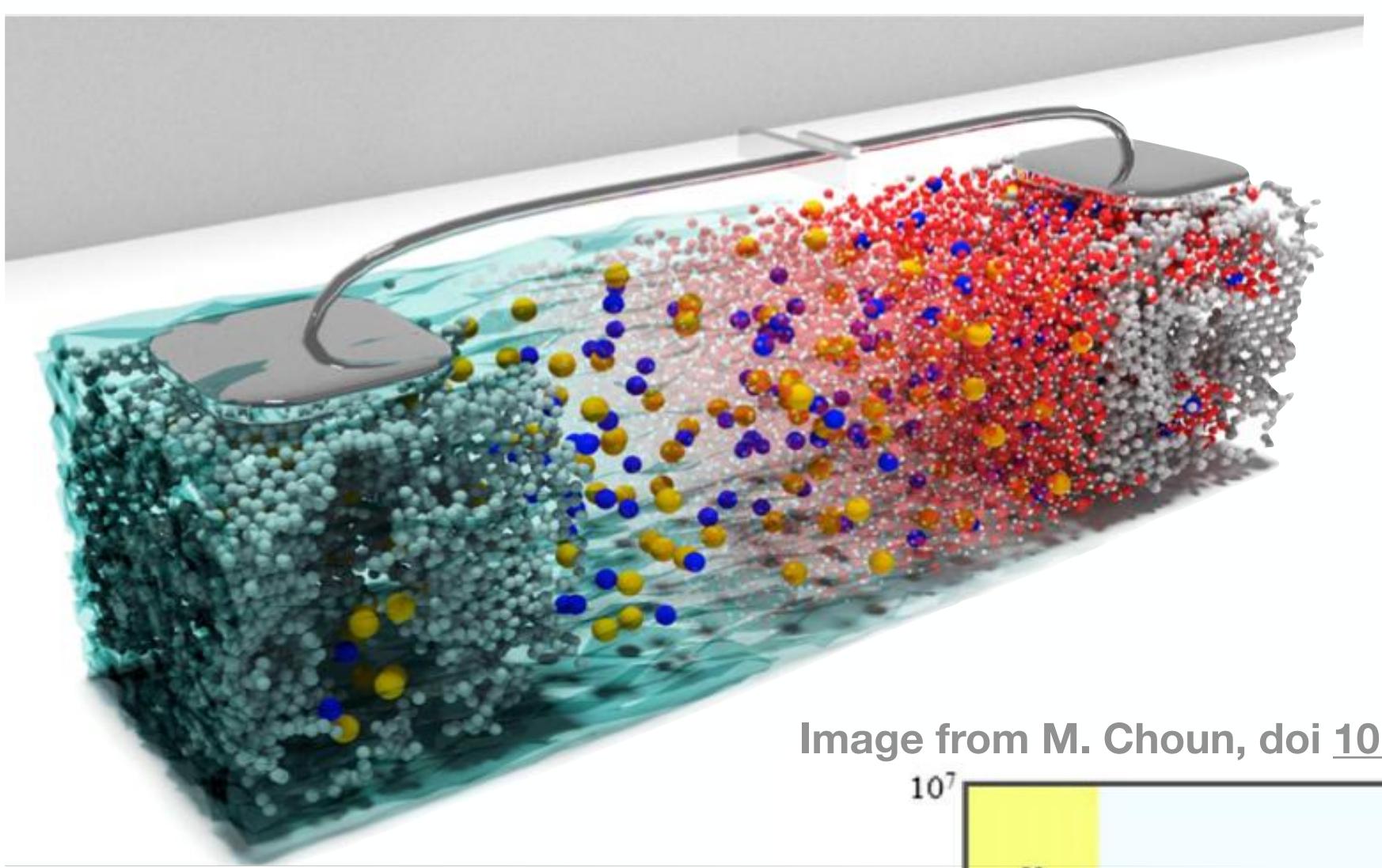
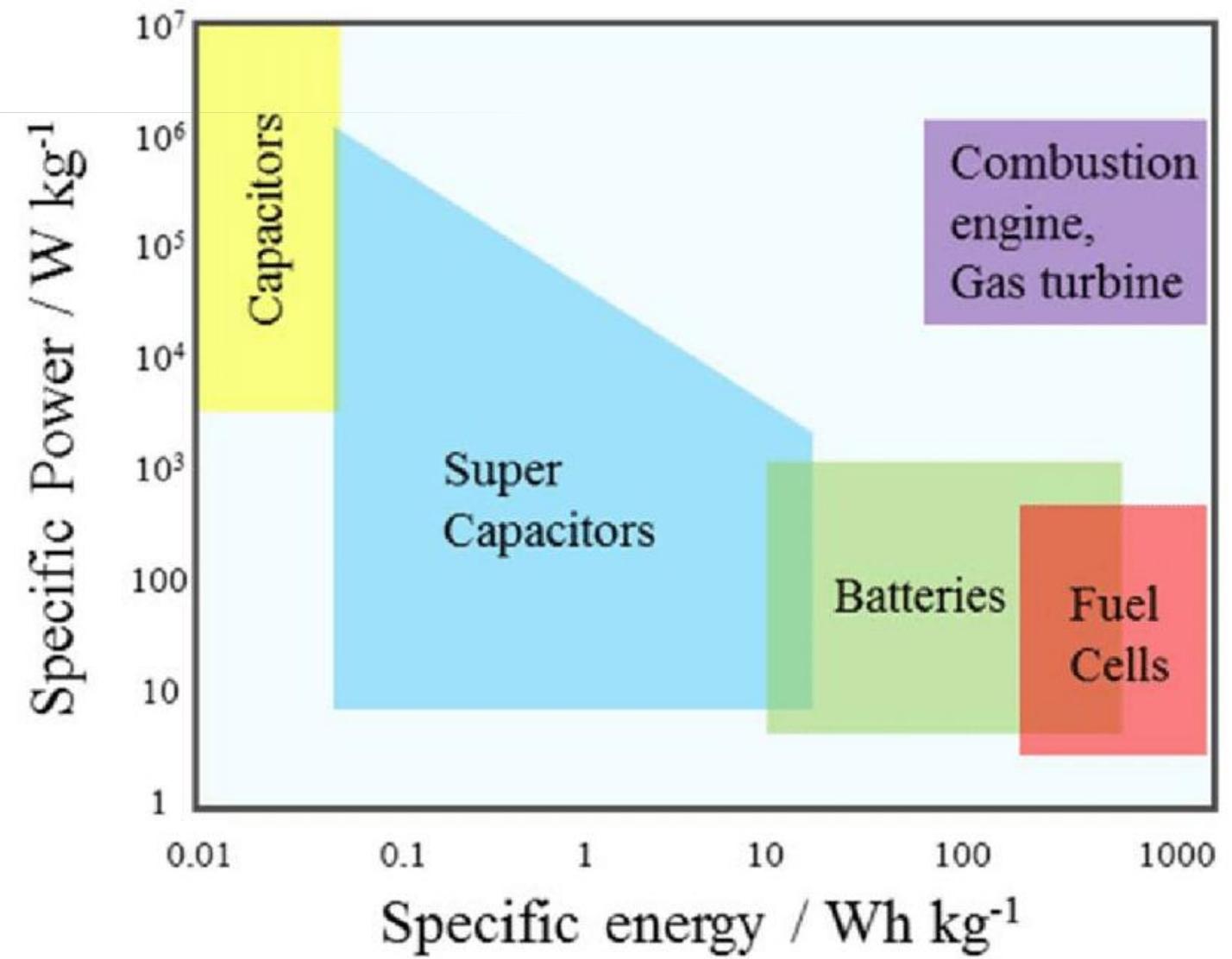


Image from M. Choun, doi [10.13140/RG.2.2.32153.42088](https://doi.org/10.13140/RG.2.2.32153.42088)



# Energy Storage and Conversion

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

**THE INTERFACE IS THE DEVICE**

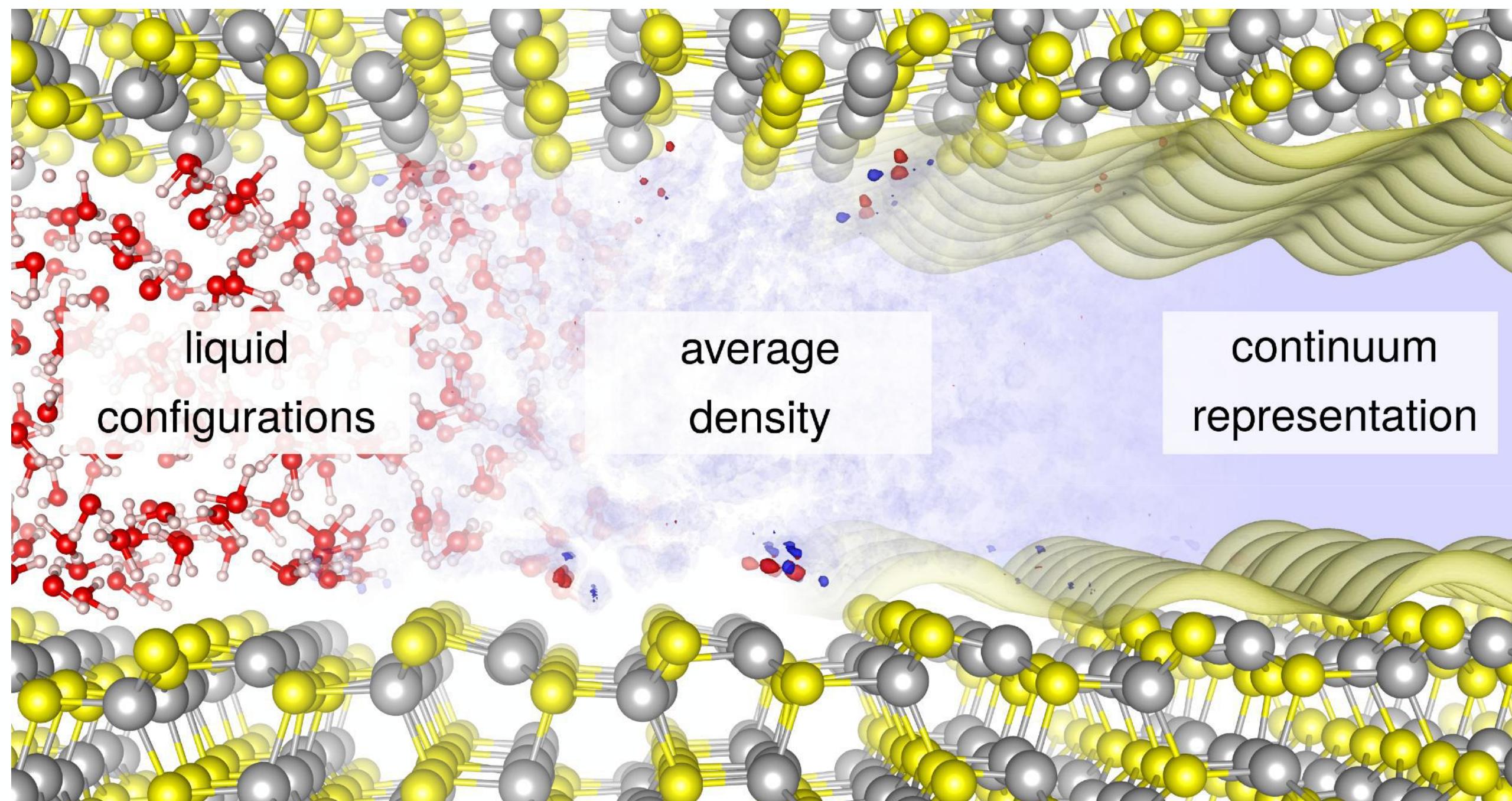
- Electronic and atomistic details at the interface are important
- Environment is important

# Modeling a 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



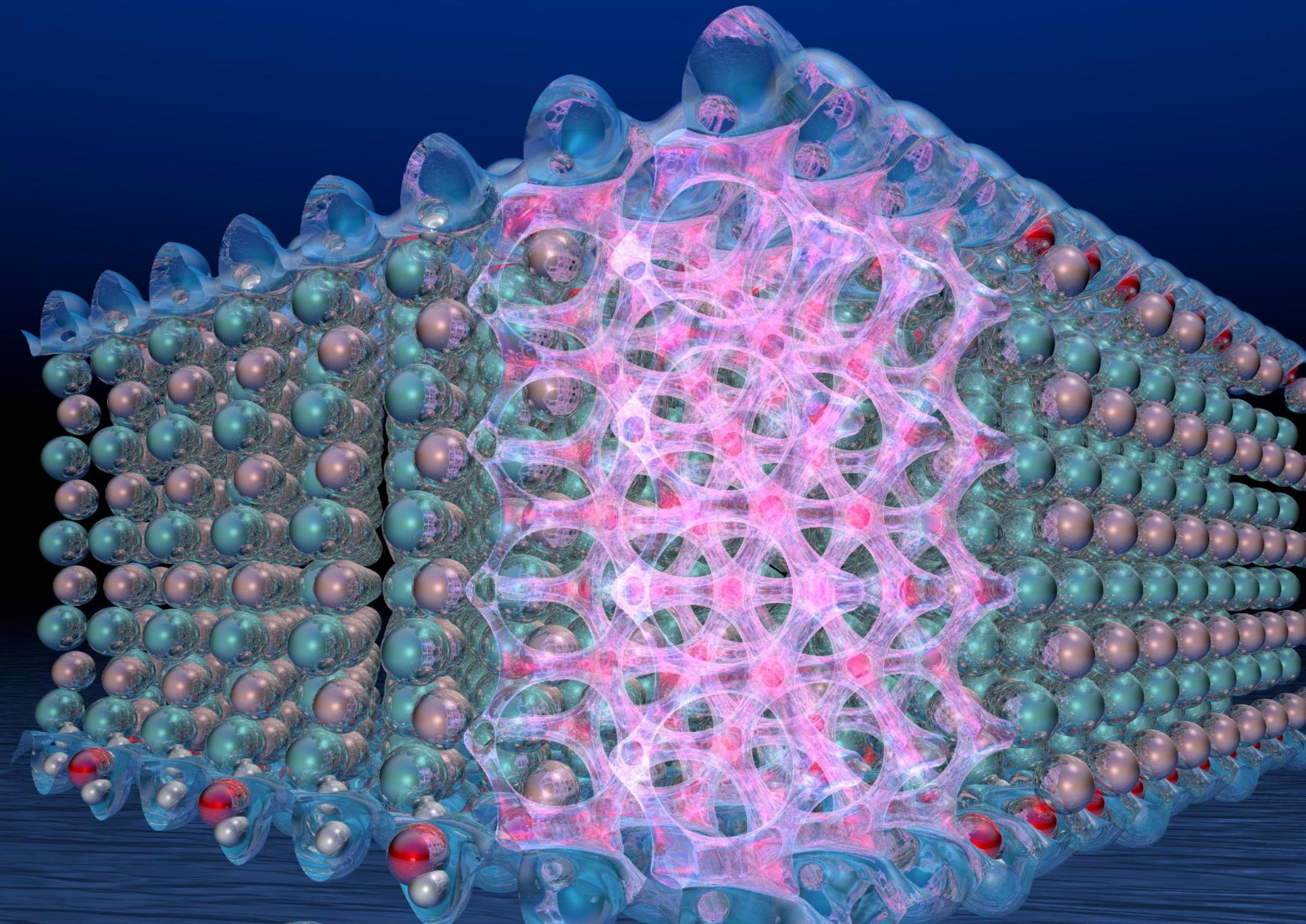
AIMD simulations by Pasquarello and coworkers. Figure by N. Hörmann.

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

# More Challenges

## Surfaces Can Be Hard

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

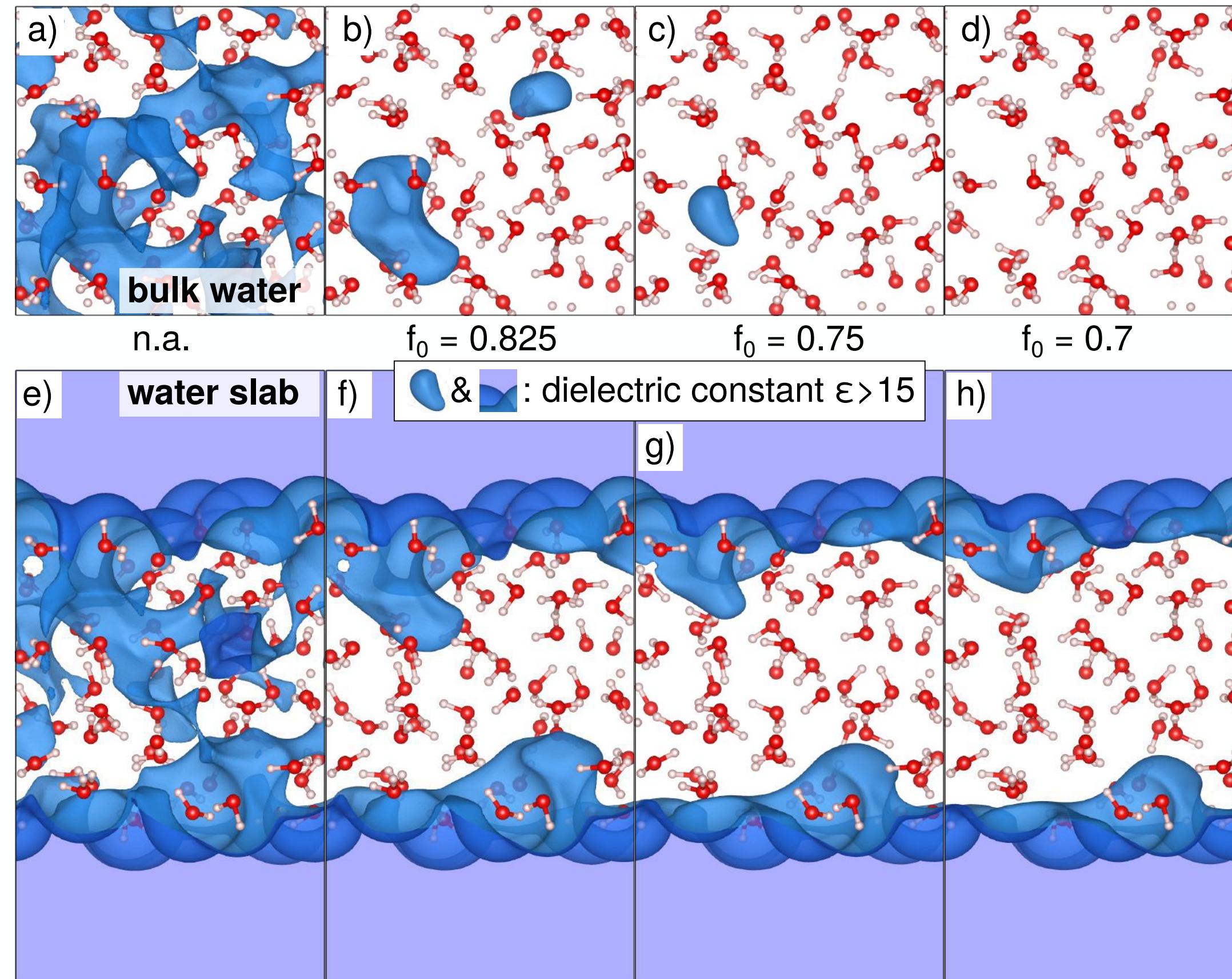


# Interfaces

## 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

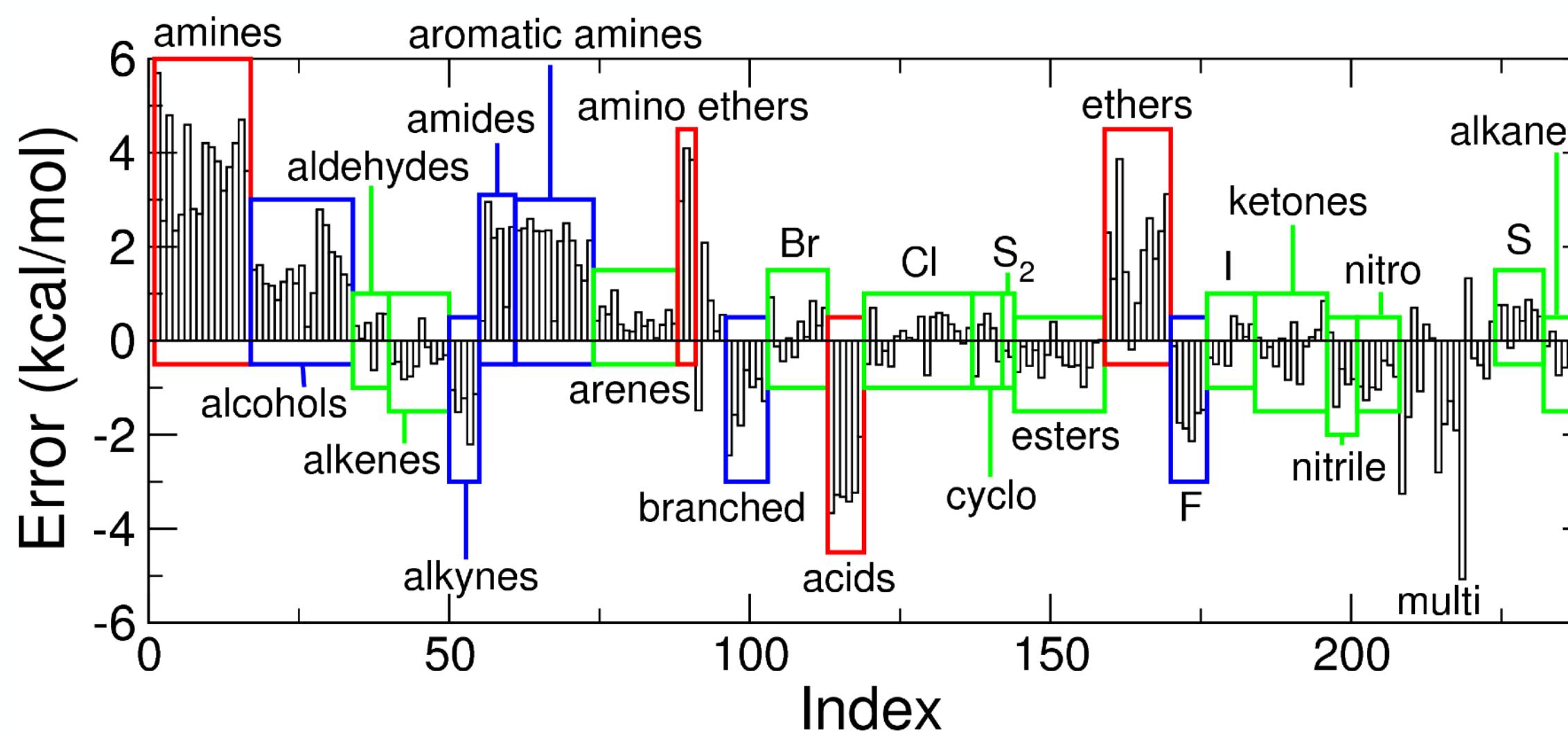
# Solvation Models

## Combining Ingredients and Parametrization

- Self-consistent continuum solvation (SCCS)
- Soft-sphere continuum solvation

### Accuracy vs. Functional Groups

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

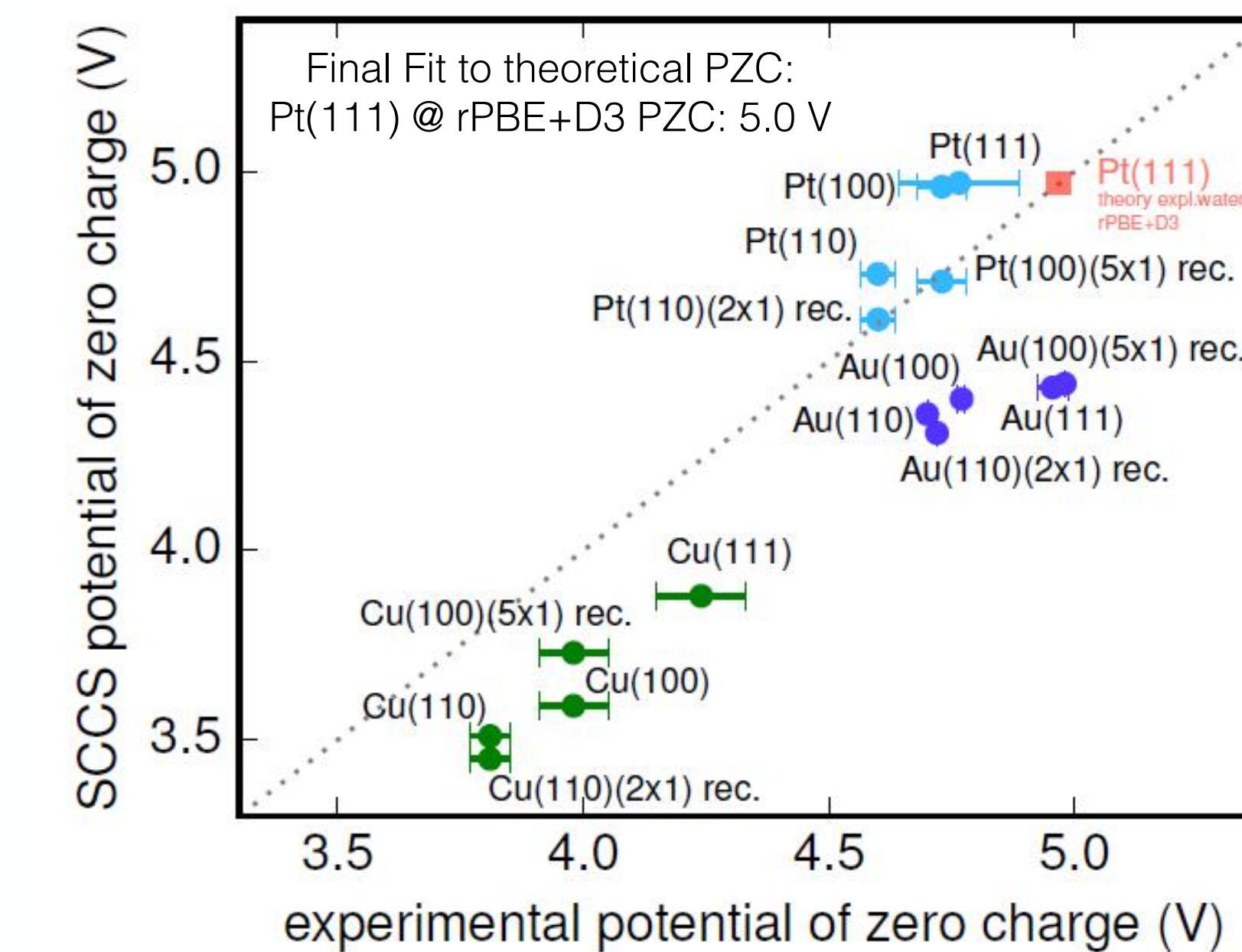


O. Andreussi, I. Dabo, N. Marzari, *J. Chem. Phys.* **136**, 064102 (2012)

- Electrochemical interfaces

### Electrochemical SCCS vs. Experiments

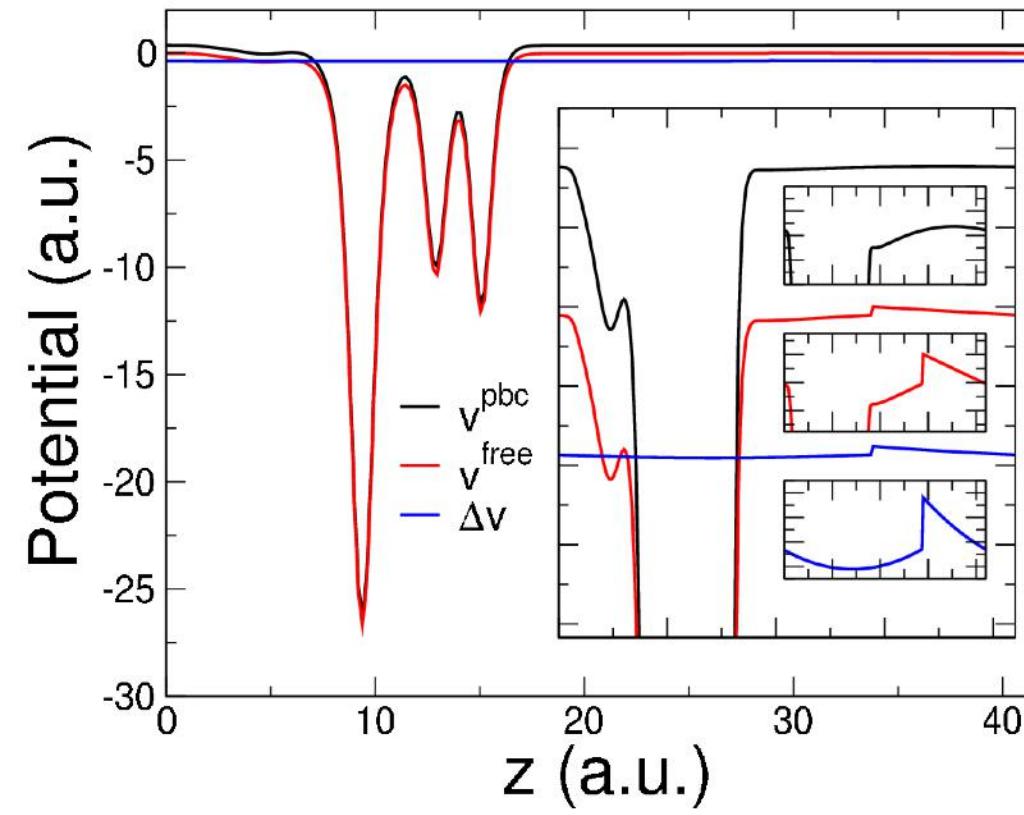
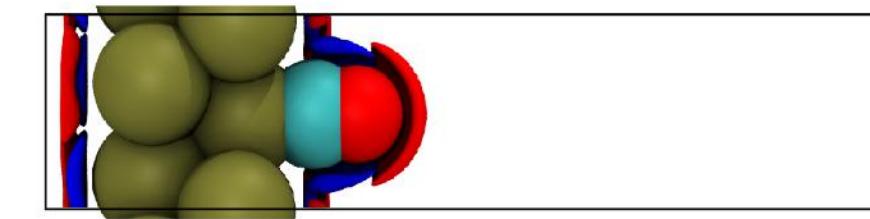
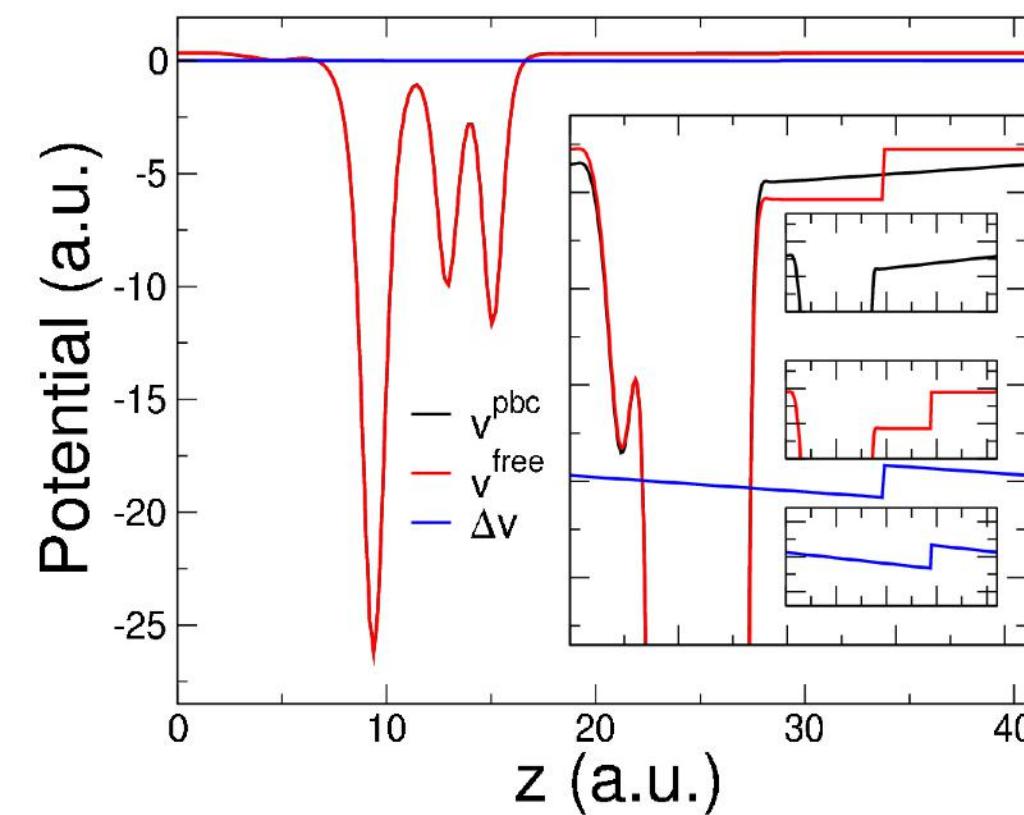
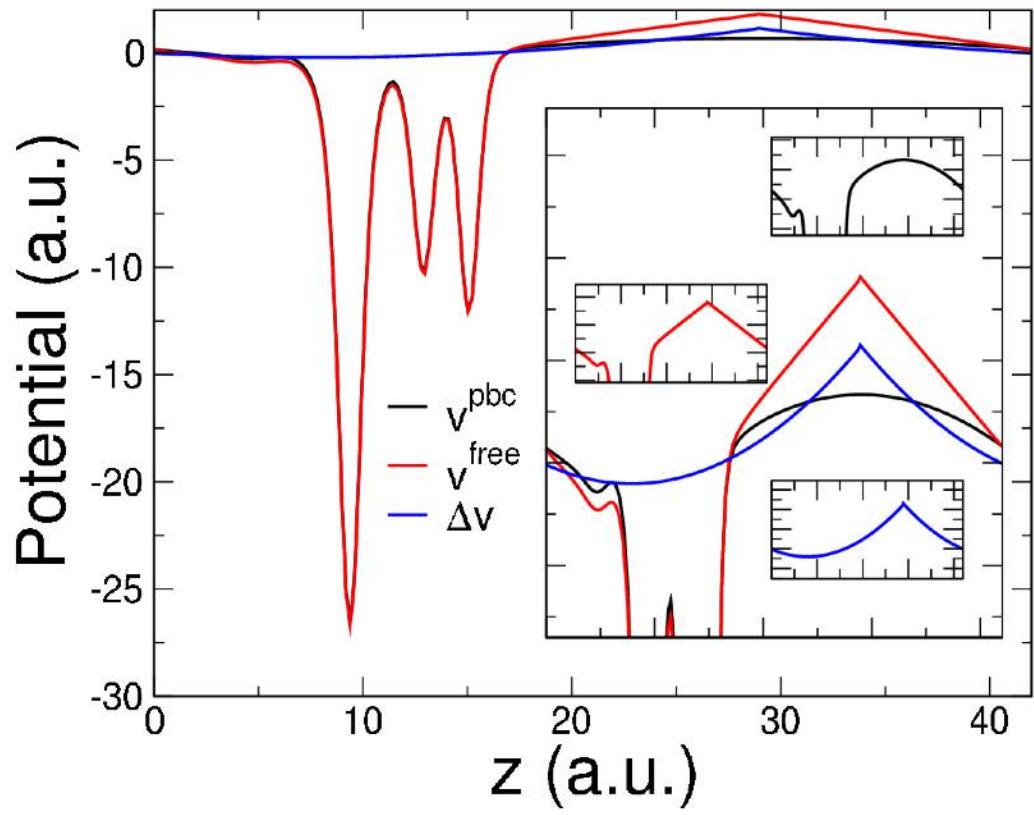
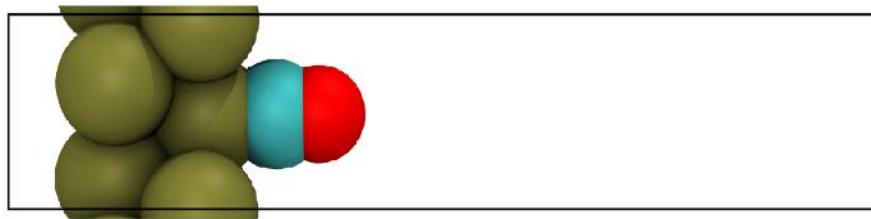
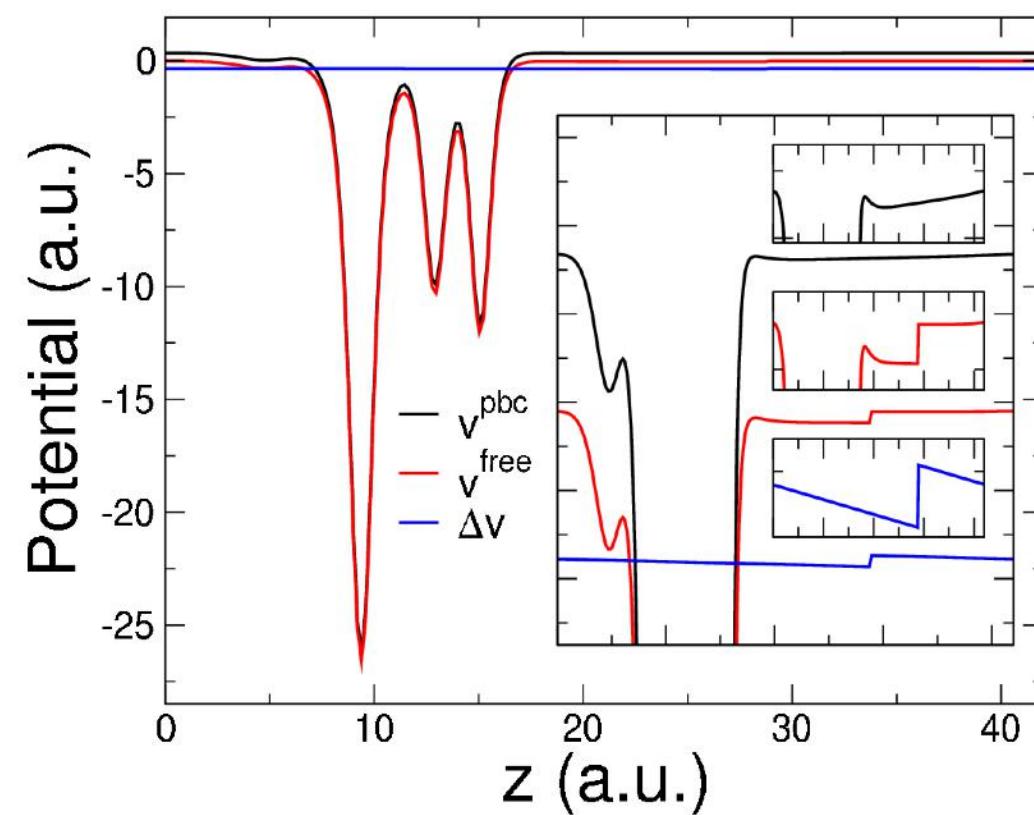
Comparison of potentials of zero charge (PZC) for continuum model with interface function parametrized on first principles results



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).

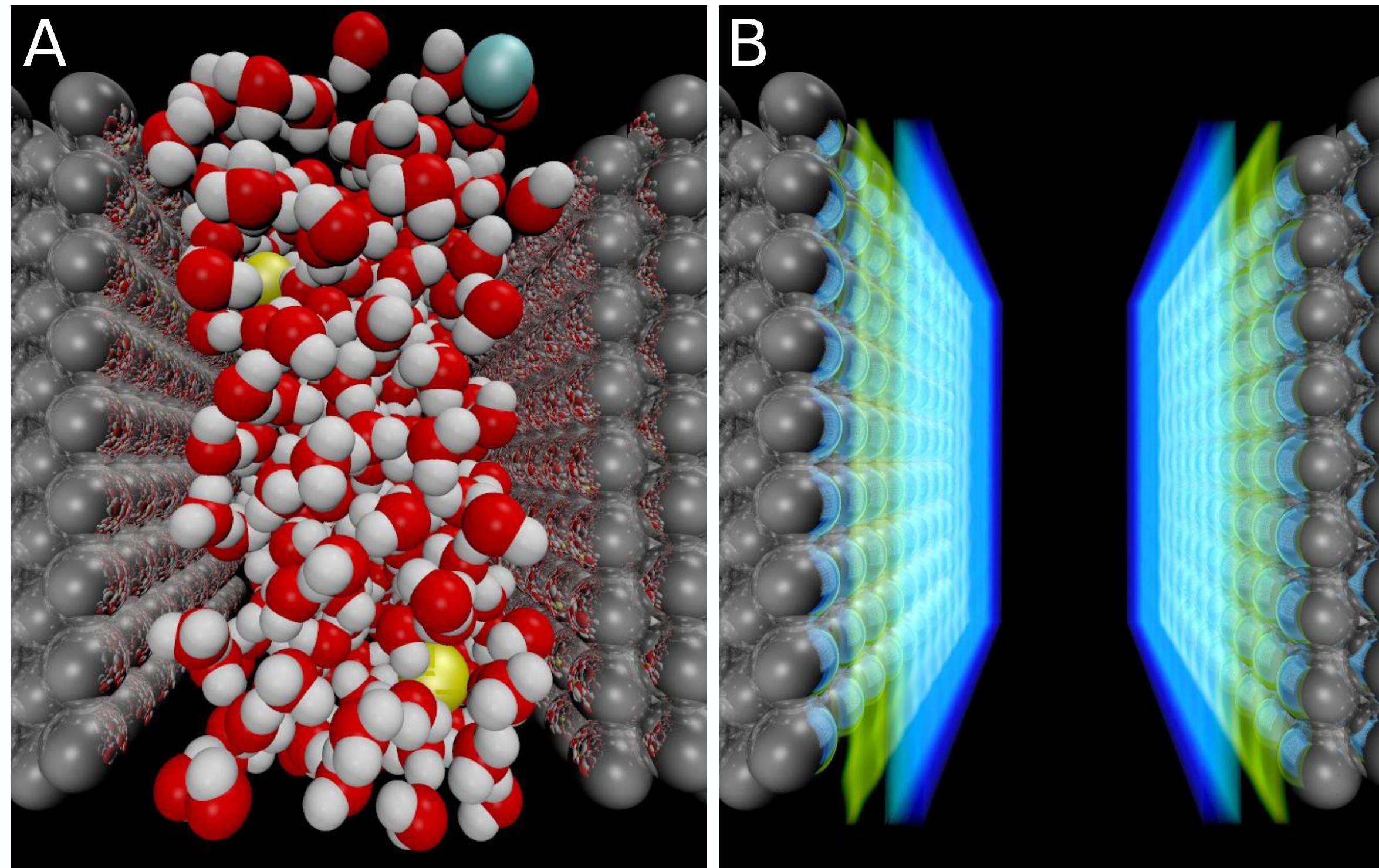


# Fixing PBC in 2D Parabolic Correction

- 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

$$\nabla \cdot \epsilon(\mathbf{r}) \nabla \phi(\mathbf{r}) = -4\pi \left( \rho^{\text{solute}}(\mathbf{r}) + \sum_i c_i(\mathbf{r}) z_i \right)$$

$$c_i(\mathbf{r}) = \frac{\gamma(\mathbf{r}) c_i^0 e^{-\frac{z_i(\phi(\mathbf{r}) - \phi_0)}{k_B T}}}{1 - \sum_{i=1}^p \frac{c_i^0}{c_0^0} \left( 1 - e^{-\frac{z_i(\phi(\mathbf{r}) - \phi_0)}{k_B T}} \right)}$$

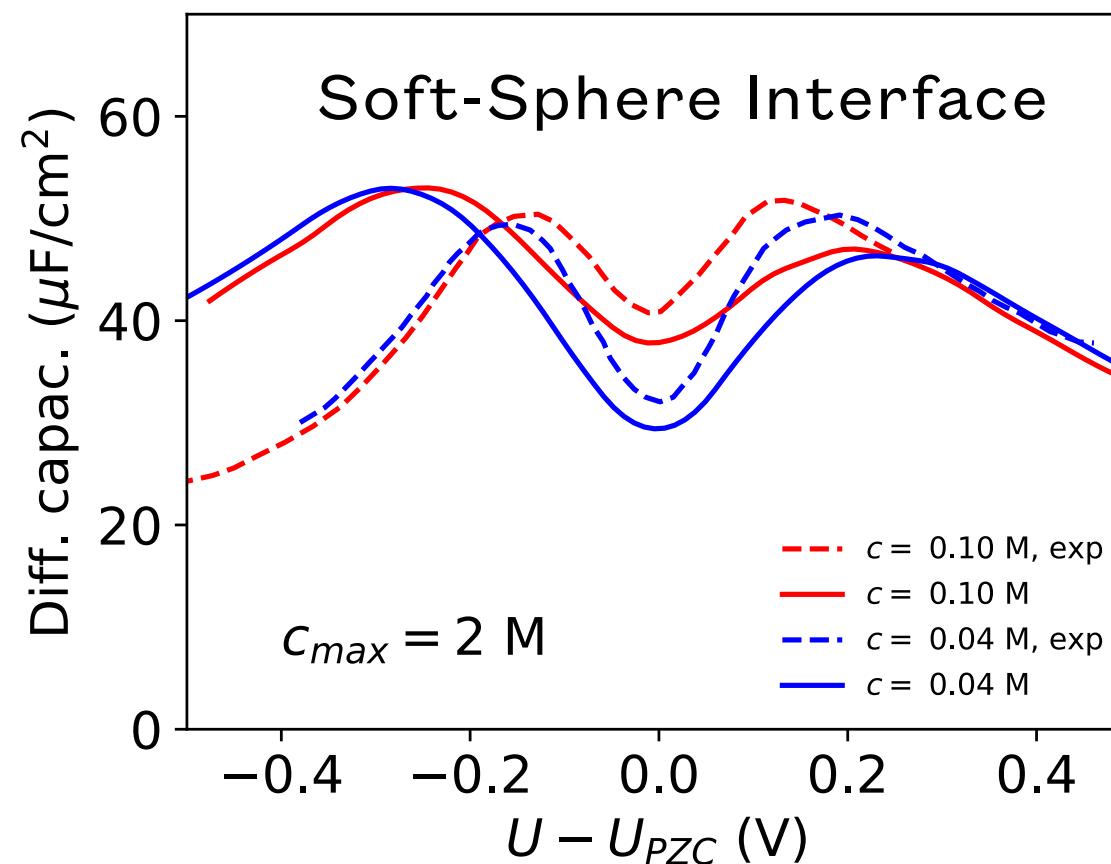
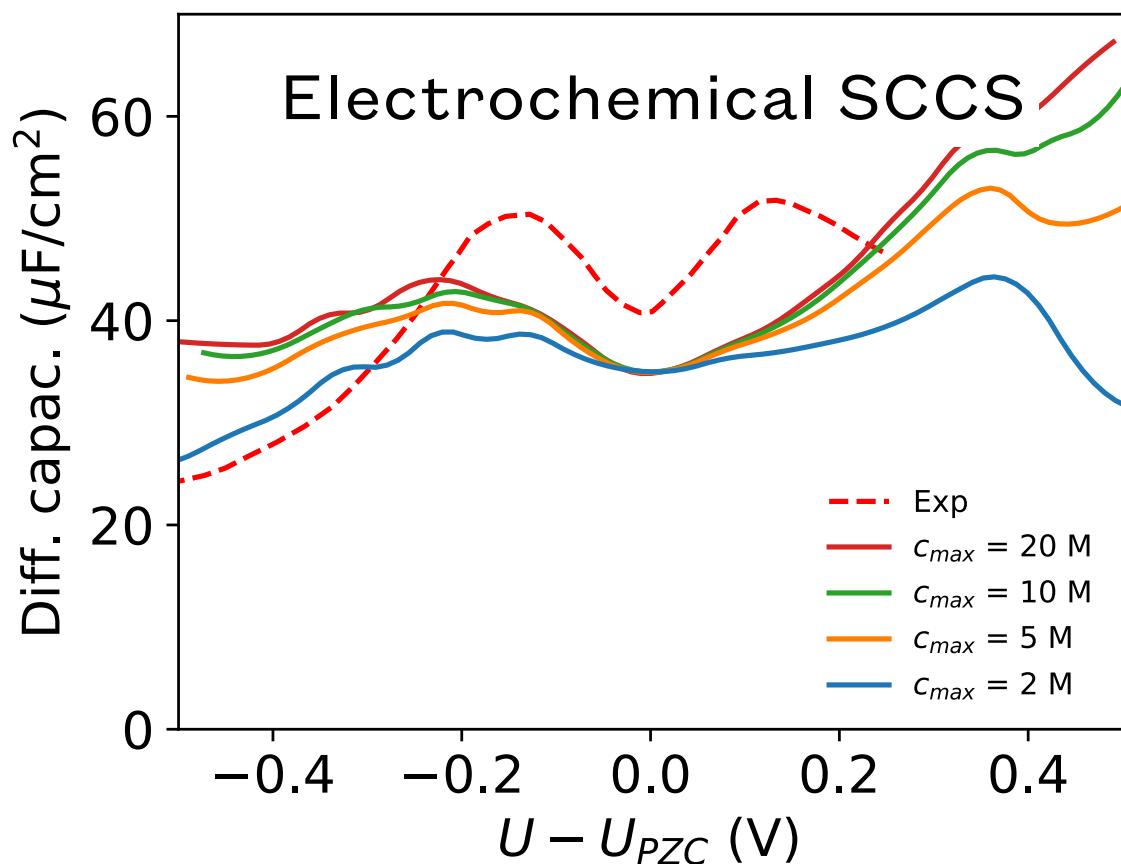
- Smooth planes of counter-charge
- Analytic solution to the planar-averaged 1D PB problem
- Linearized PB or size-modified PB
- Full non-linear PB or size-modified PB
- Specific ion-surface interactions

# Diffuse Layer Hierarchy of Algorithms

## 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.



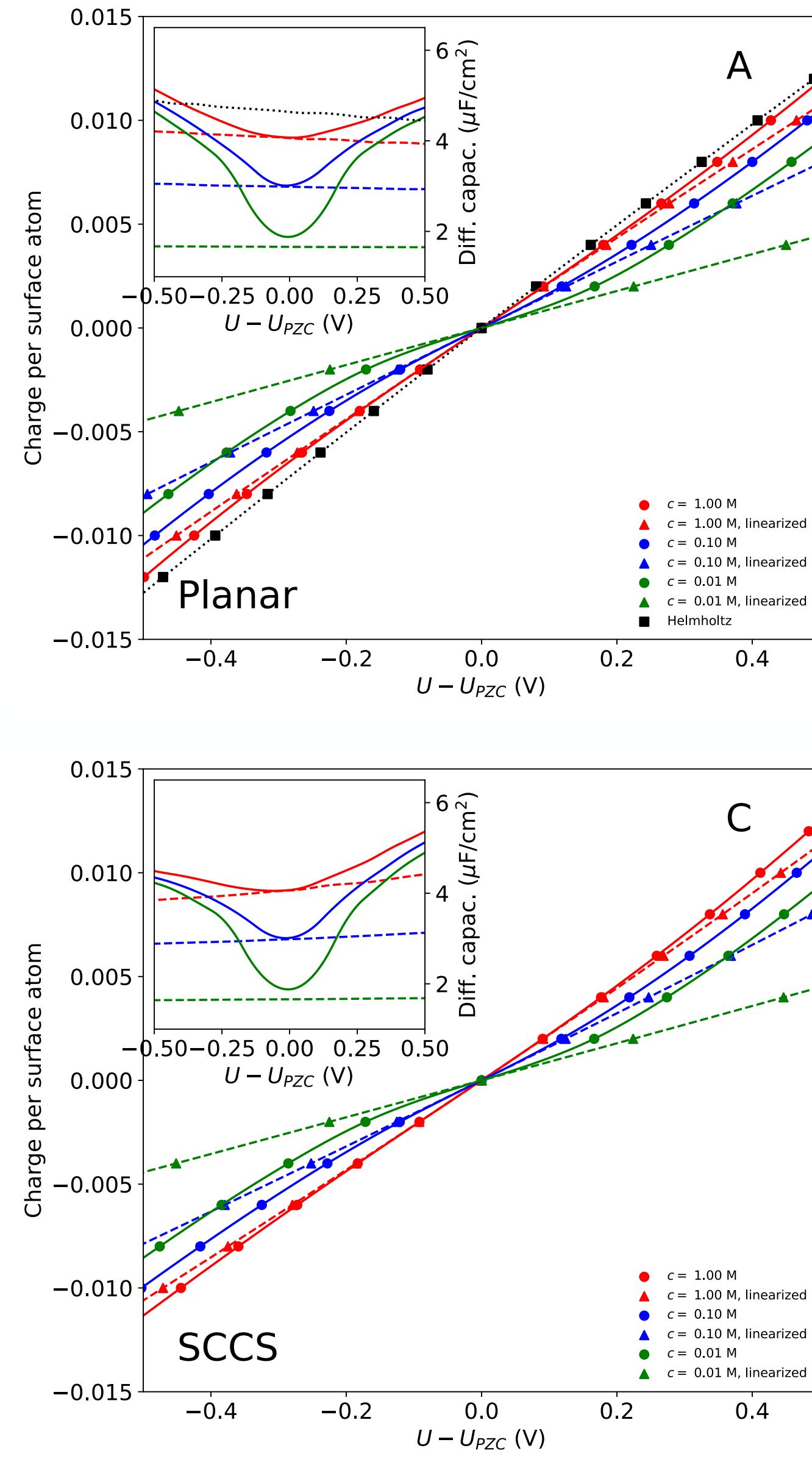
F. Nattino, M. Truscott, N. Marzari, and O. Andreussi, *J. Chem. Phys.* **150**, 041722 (2019)

$$\nabla \cdot \epsilon(\mathbf{r}) \nabla \phi(\mathbf{r}) = -4\pi \left( \rho^{\text{solute}}(\mathbf{r}) + \sum_i c_i(\mathbf{r}) z_i \right)$$

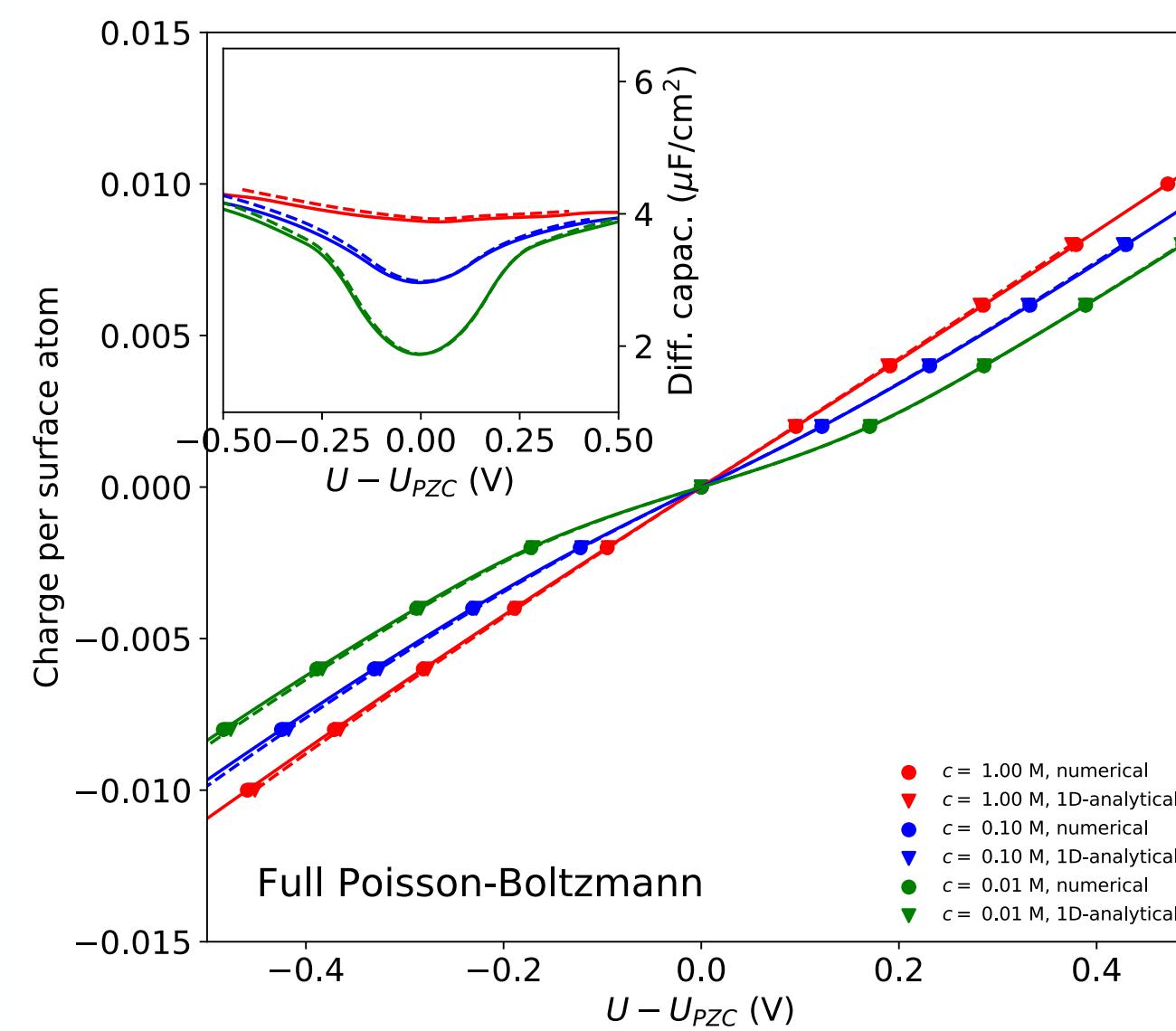
$$c_i(\mathbf{r}) = \frac{\gamma(\mathbf{r}) c_i^0 e^{-\frac{z_i(\phi(\mathbf{r}) - \phi_0)}{k_B T}}}{1 - \sum_{i=1}^p \frac{c_i^0}{c_0^0} \left( 1 - e^{-\frac{z_i(\phi(\mathbf{r}) - \phi_0)}{k_B T}} \right)}$$

- 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

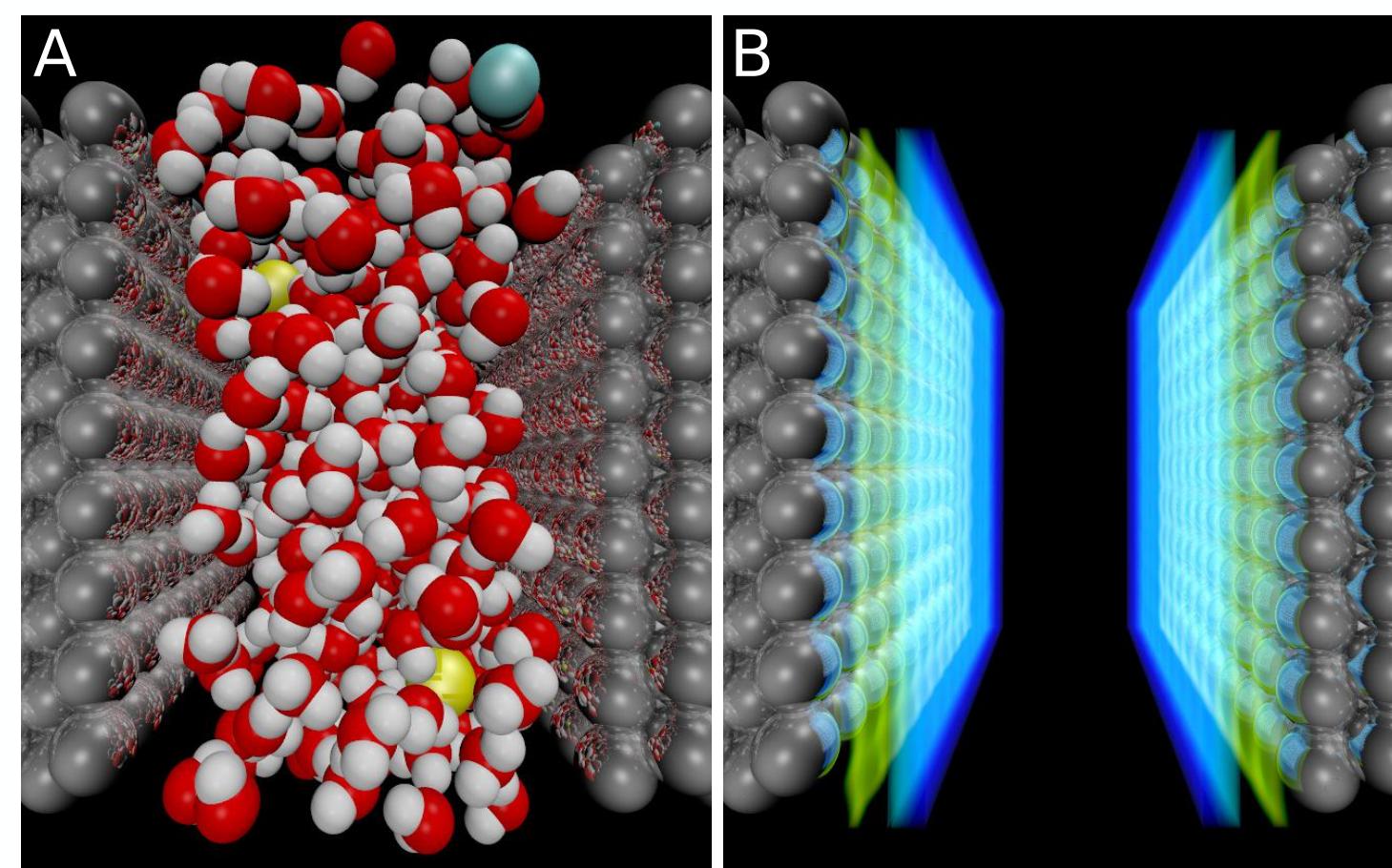
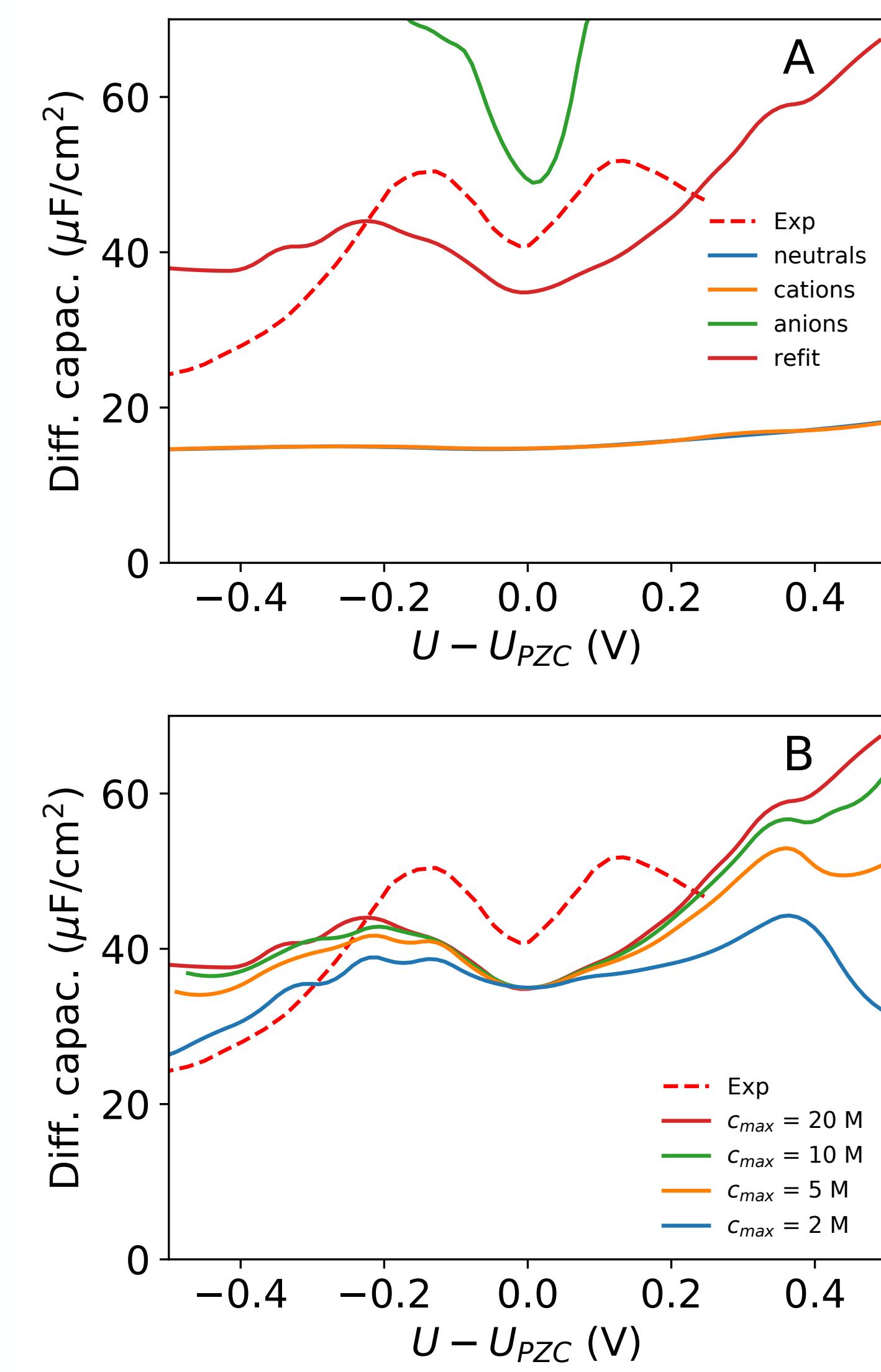
## Vacuum

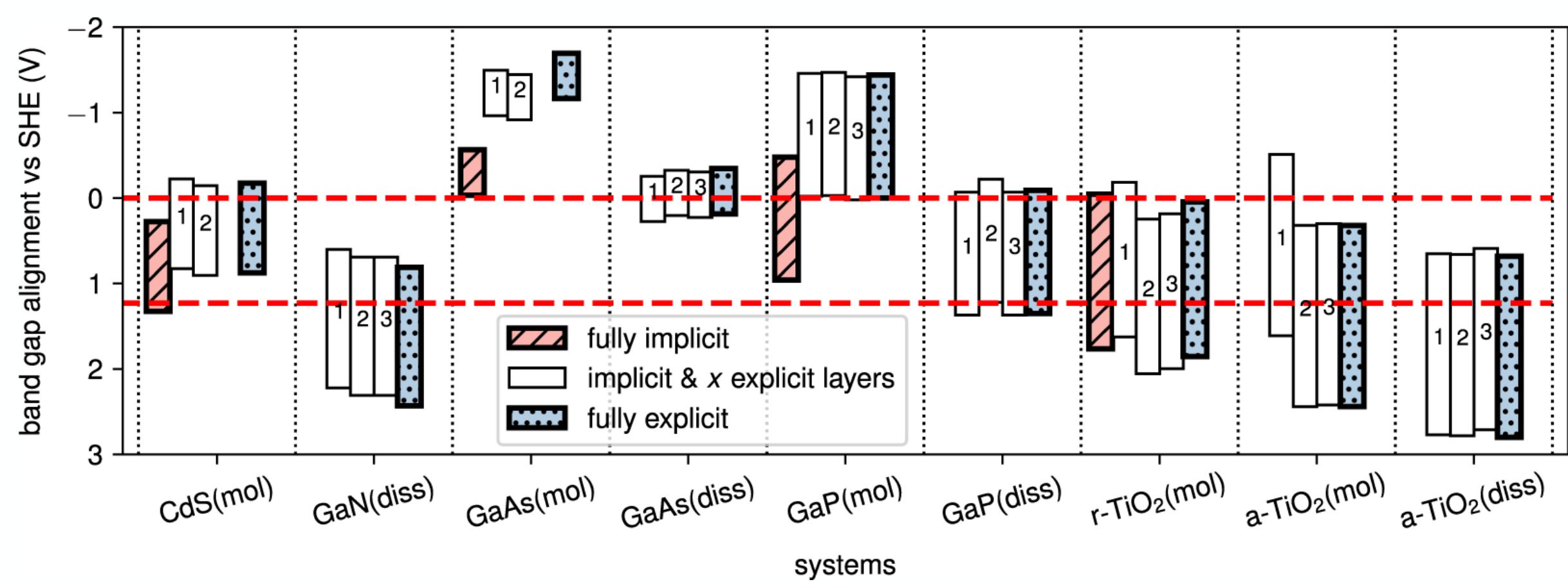
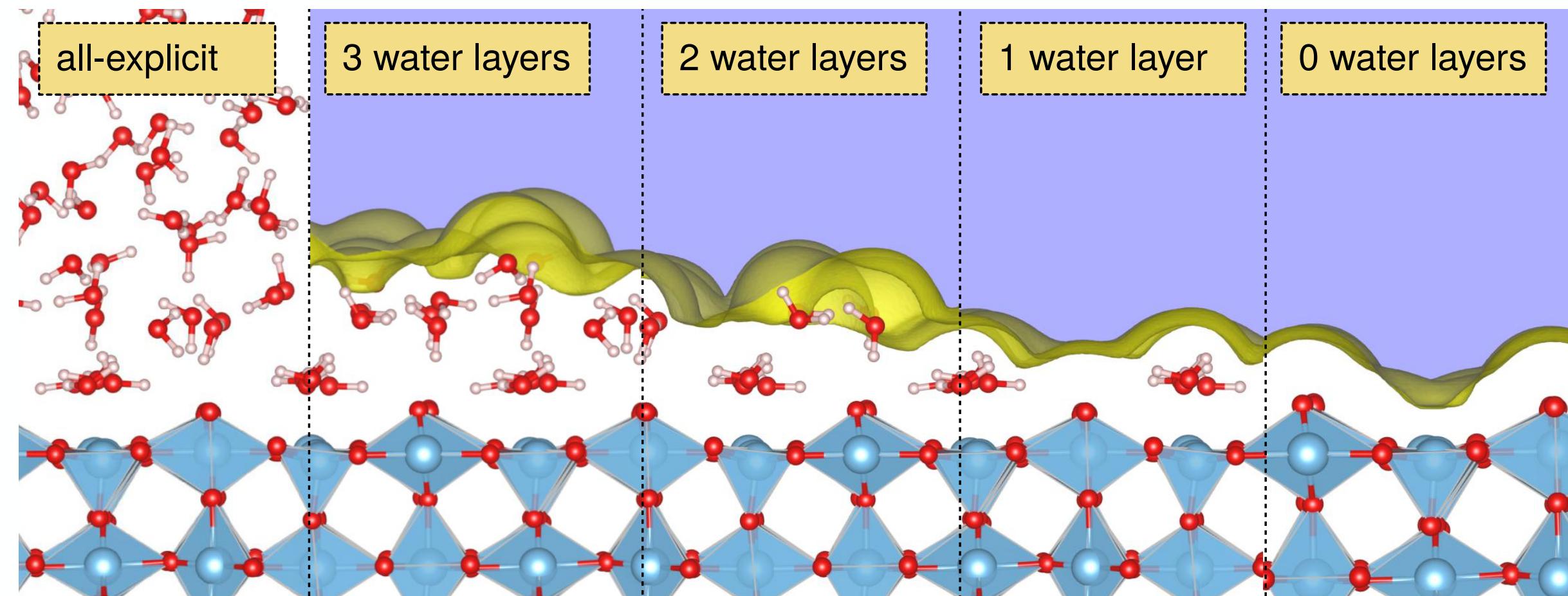


## GCS Correction



## SCCS Dielectric





# Band Alignment

## Benchmarks on Semiconductors

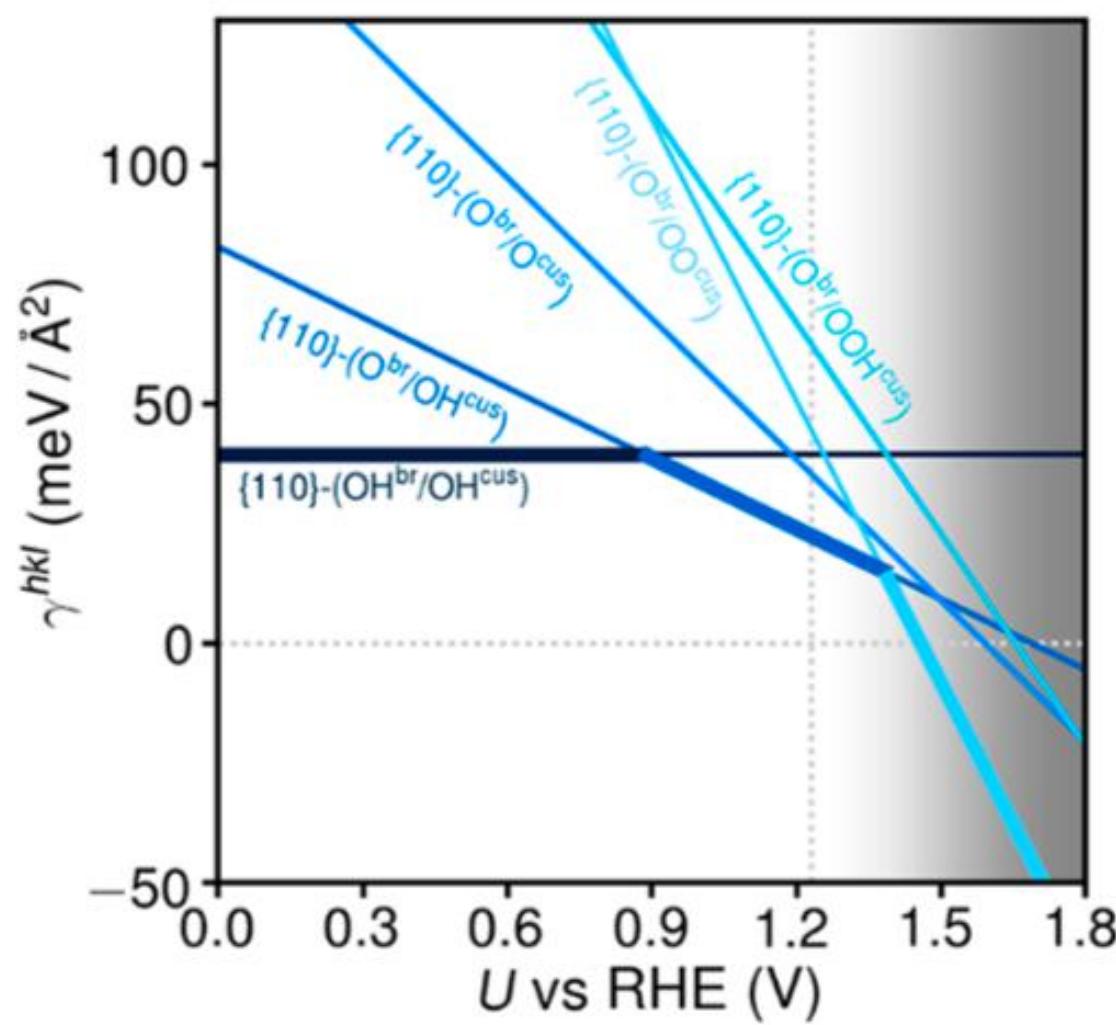
- There is a common offset when replacing explicit water with the continuum
- One explicit layer of water is necessary
- One explicit layer is often enough

# Stability & Catalysis

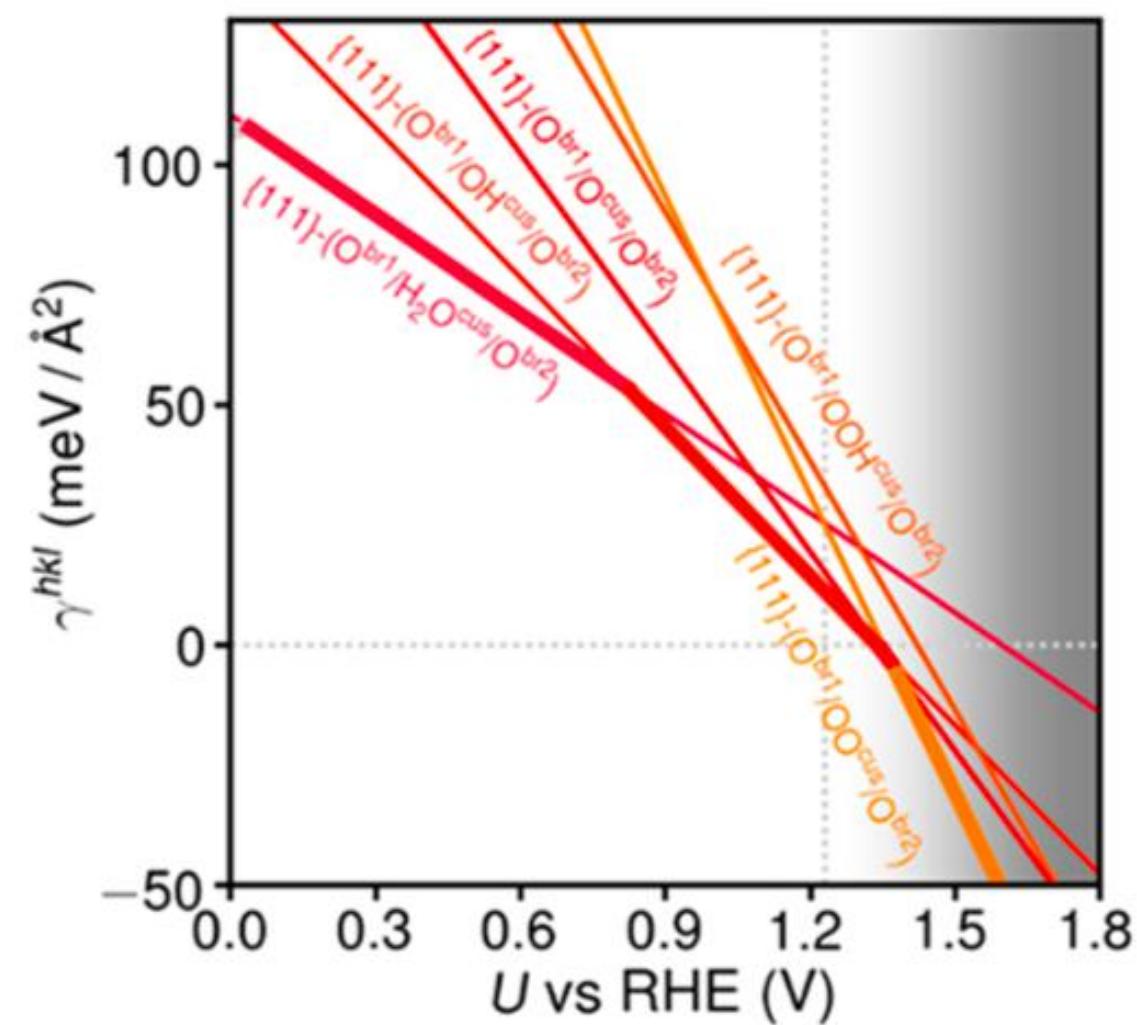
## O, OH, H, etc.

### From DFT to Pourbaix Diagrams

Interface Free Energies of (110) and (111) rutile IrO<sub>2</sub> 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 Electrode<sup>1</sup>
  - Neutral interfaces (PCET)

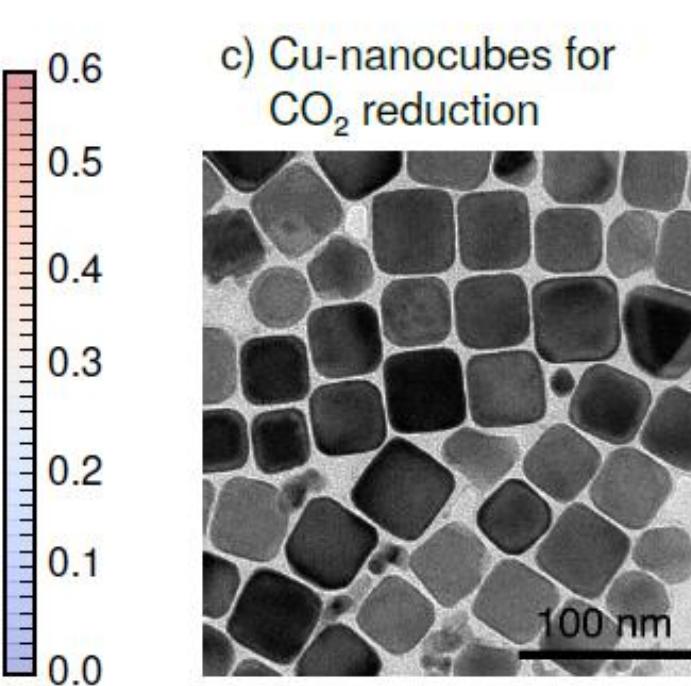
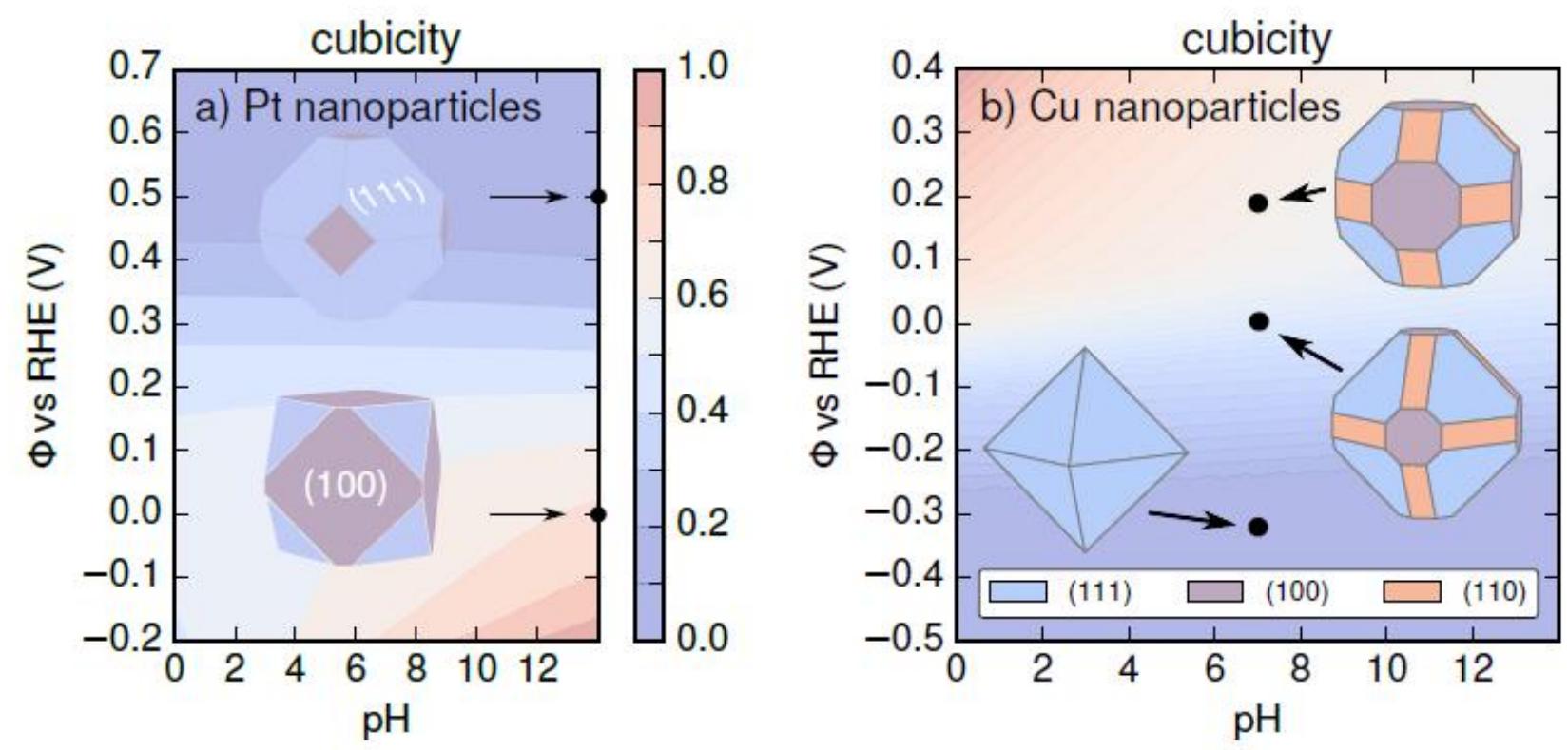
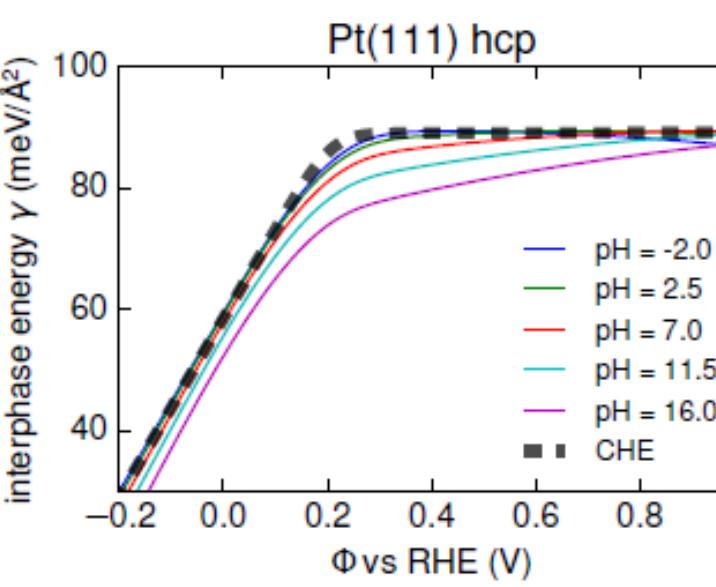
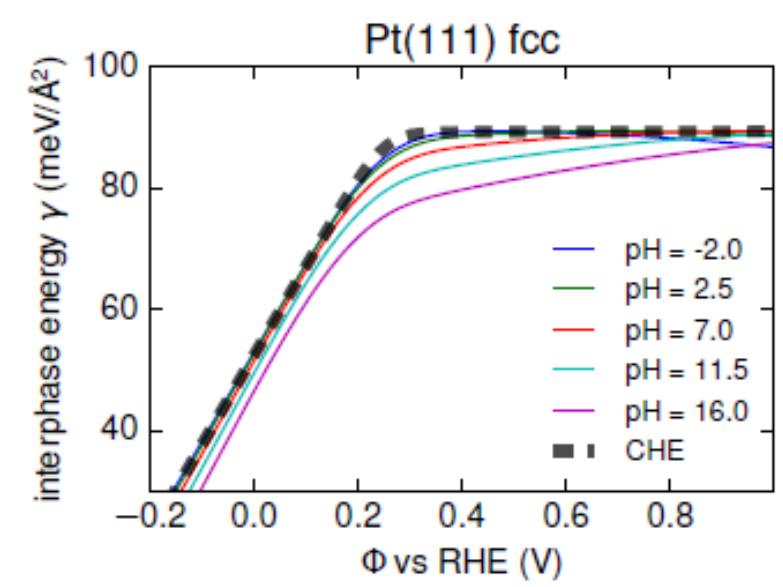
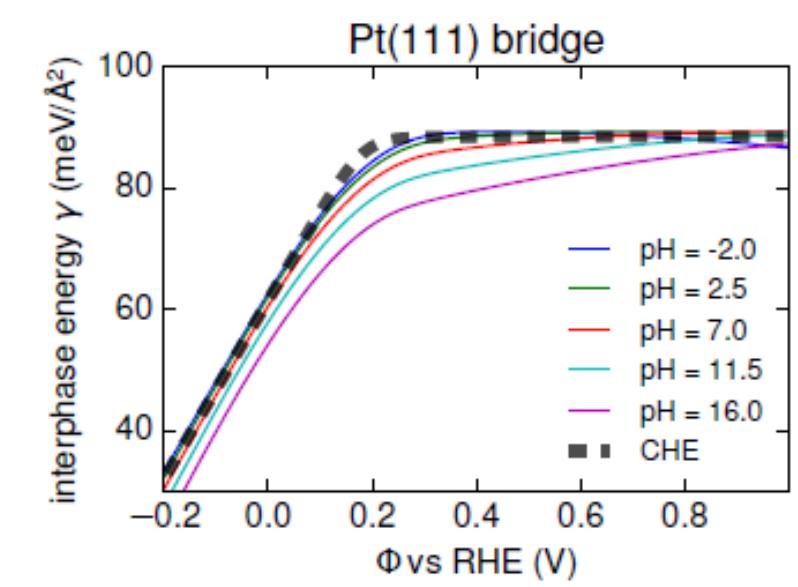
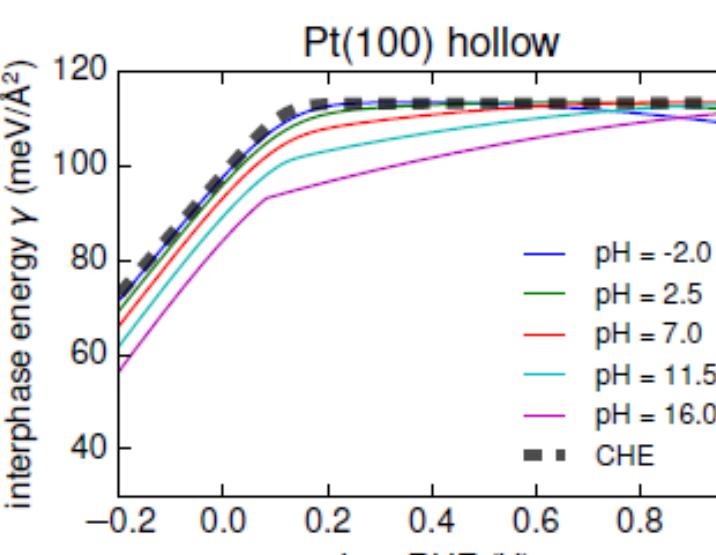
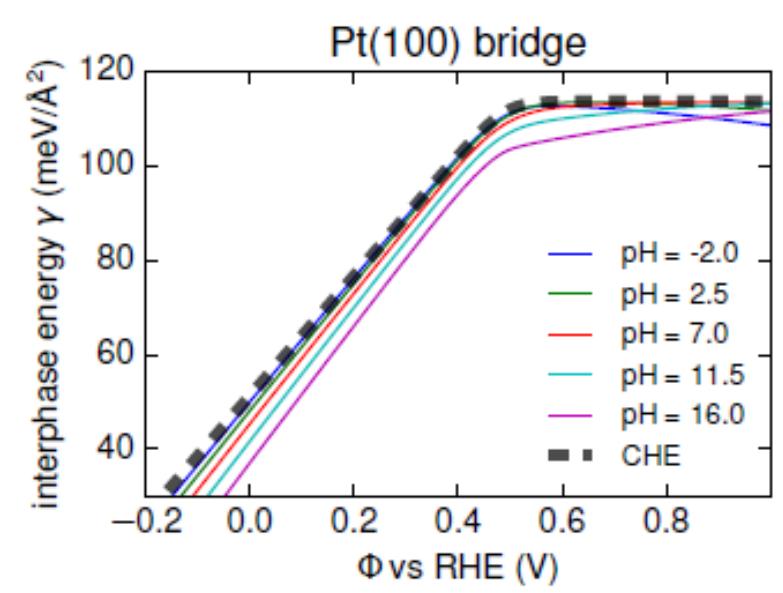
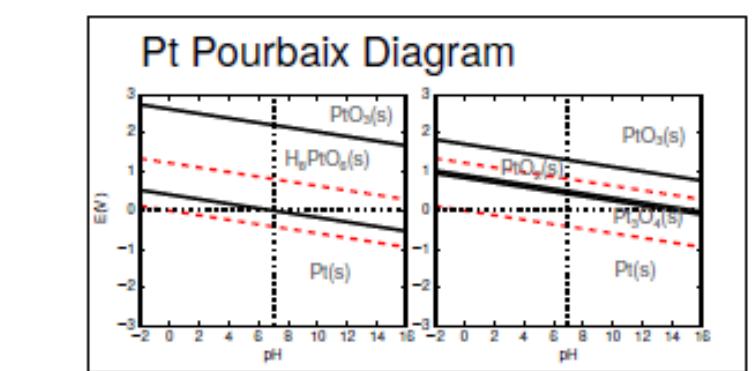
$$\bullet \quad \mu_{H^+} + \mu_{e^-} = \frac{1}{2} \mu_{H_2} - k_B T \ln(10)pH - e\Phi_{SHE}$$

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

# Grand Potential Simulations

## From extensive vs. intensive

### Pt interphase energies



c)

Cu-nanocubes for

CO<sub>2</sub> 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

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

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<sup>a</sup>

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

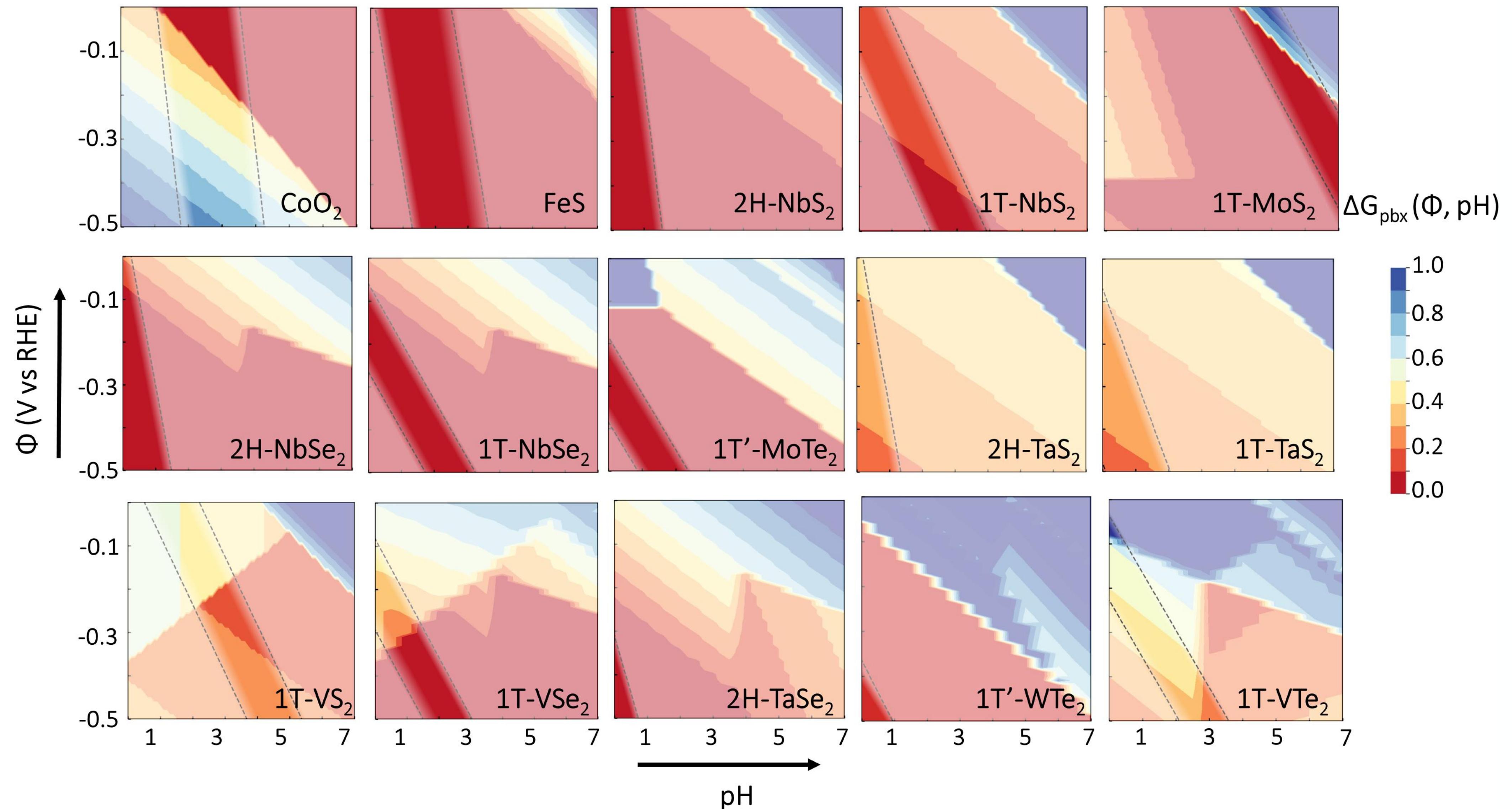
<sup>a</sup>Corresponding overpotential vs RHE for H<sup>+</sup> electrosorption ( $\Phi^{\text{over}}$  in V), aqueous stability ( $\Delta G_{\text{pbx}}(\Phi, \text{pH})$  in eV/atom), decomposition products (decomp. pdts), band gap values ( $E_{\text{gap}}$  in eV), and exfoliation (interlayer binding) energy values in aqueous medium ( $E_b^{\text{aq}}$  in meV/Å<sup>2</sup>) are reported. The pH value is 1, except for those indicated within parentheses in column 3. The exfoliation energies in vacuum ( $E_b^{\text{vac}}$ ) are given in column 7, within parentheses.

# Hydrogen Evolution Screening of 2D Materials

- Systematic simulations of about 50 materials, varying:
  - H<sup>+</sup> coverage
  - H<sup>+</sup> 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

Comparison of CHE and Grand Canonical Results for IrO<sub>2</sub>

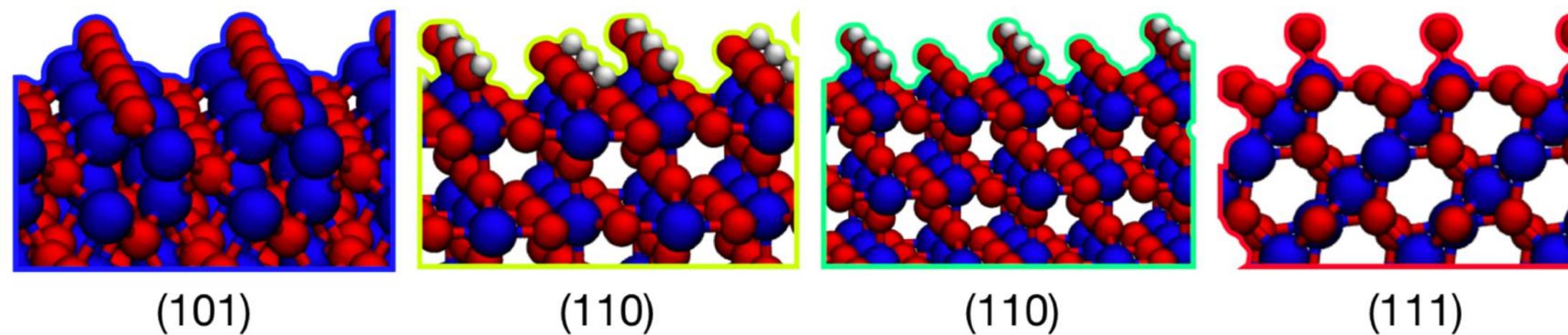
Computational Hydrogen Electrode (dashed):

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

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

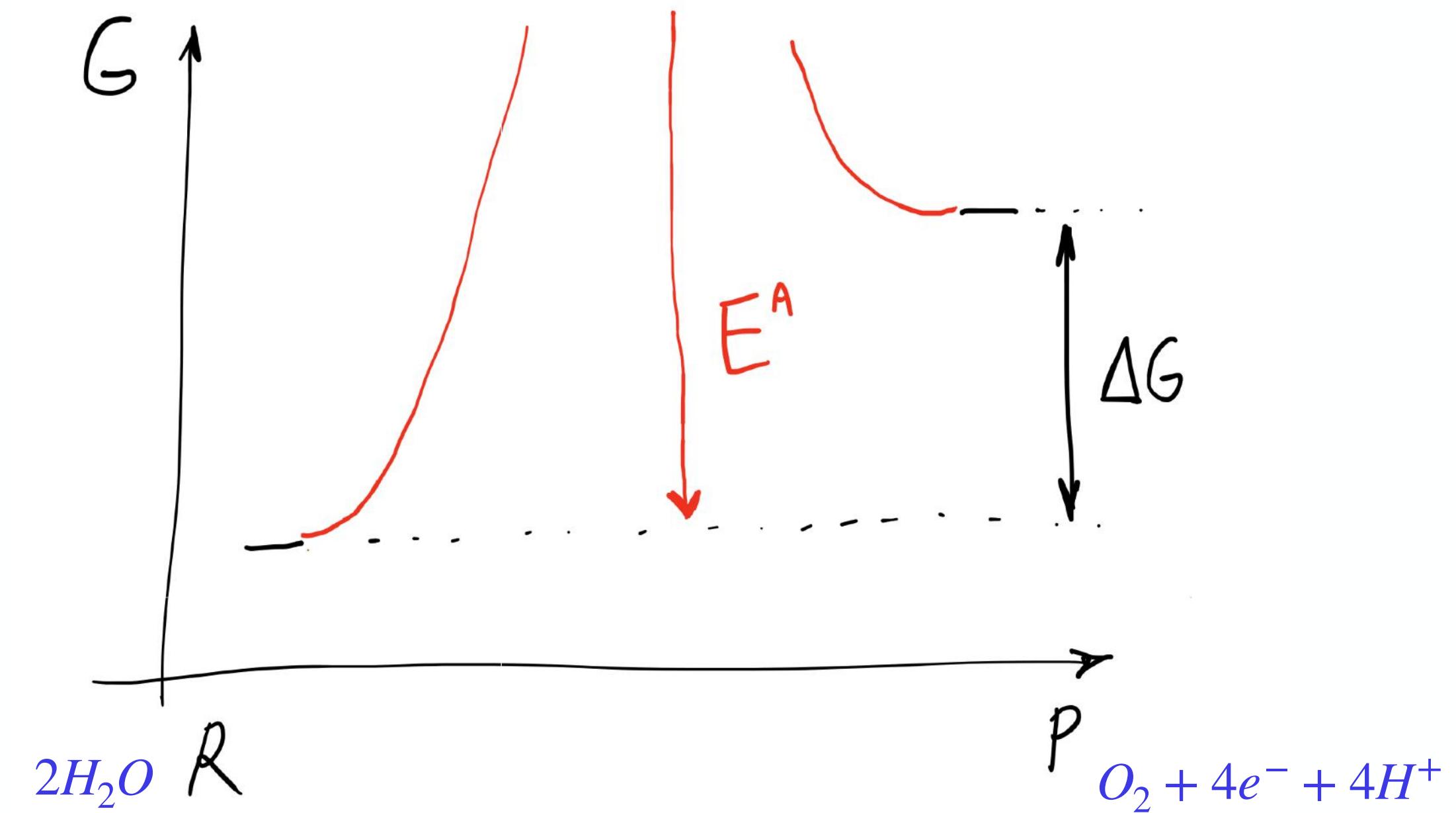
F. Nattino and N. Marzari, *Phys. Chem. Chem. Phys.*, **22**, 10807-10818  
(2020)

# Multiple Steps Conversion

## Catalytic Activity from Intermediates Stability

An Effective Approximation (a.k.a. the Computational Hydrogen Electrode, CHE<sup>1</sup>)

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



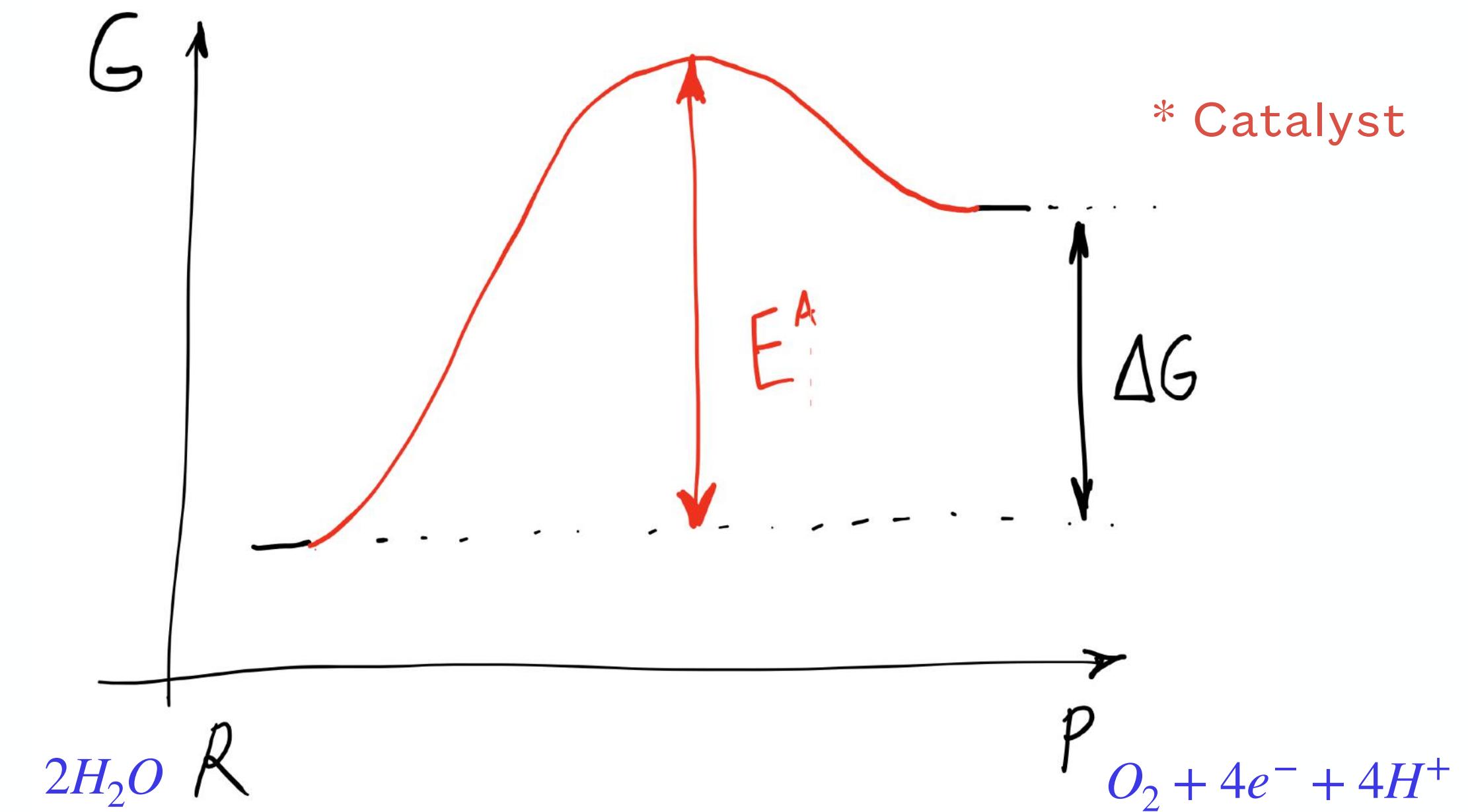
<sup>1</sup> Norskov et al., *J. Phys. Chem. B*, **108**, 17886 (2004)

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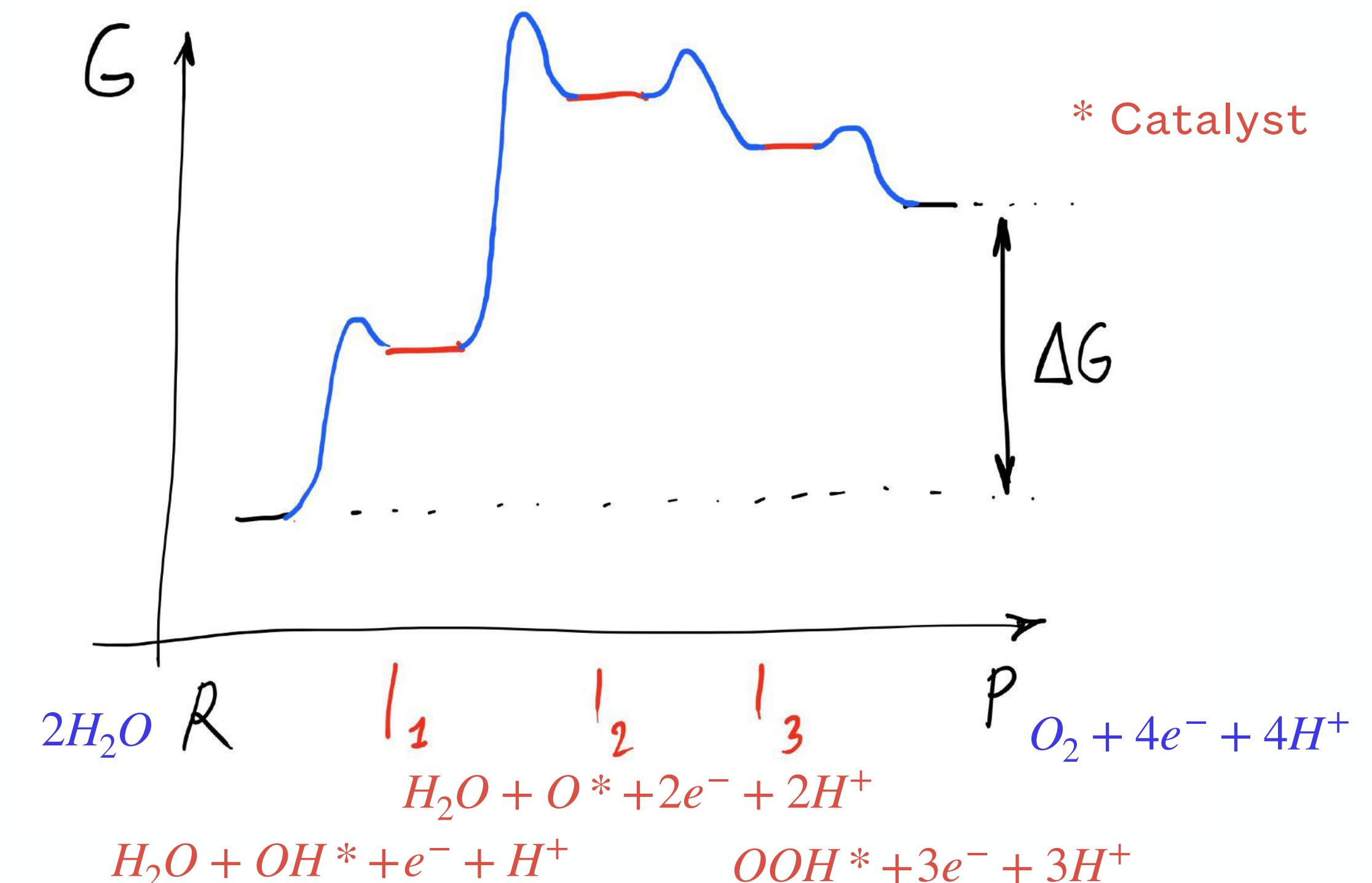


<sup>1</sup> Norskov et al., *J. Phys. Chem. B*, **108**, 17886 (2004)

# Multiple Steps Conversion Catalytic Activity from Intermediates Stability

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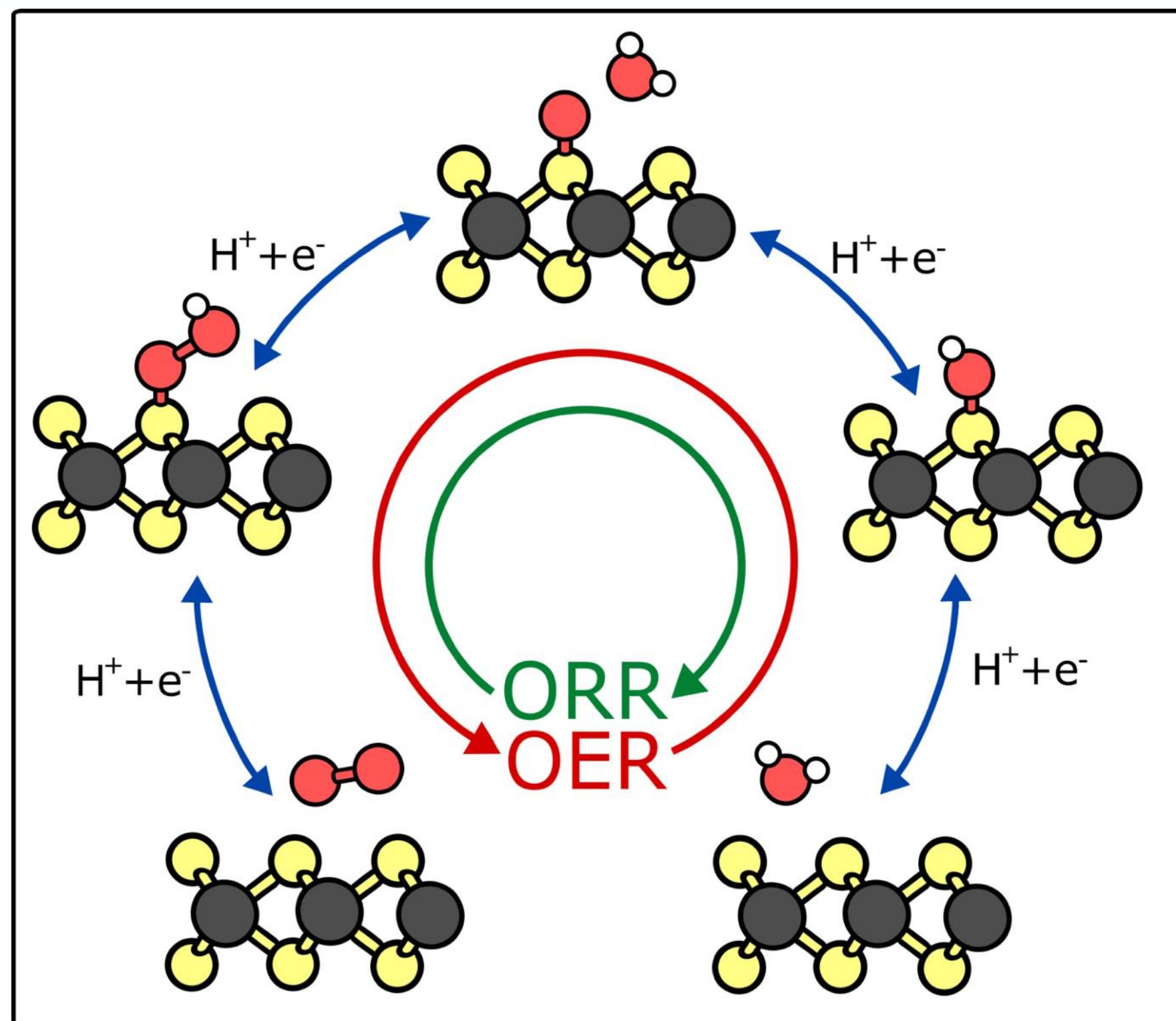
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# Multiple Steps Conversion

## Catalytic Activity from Intermediates Stability

### Oxygen-Water Conversion

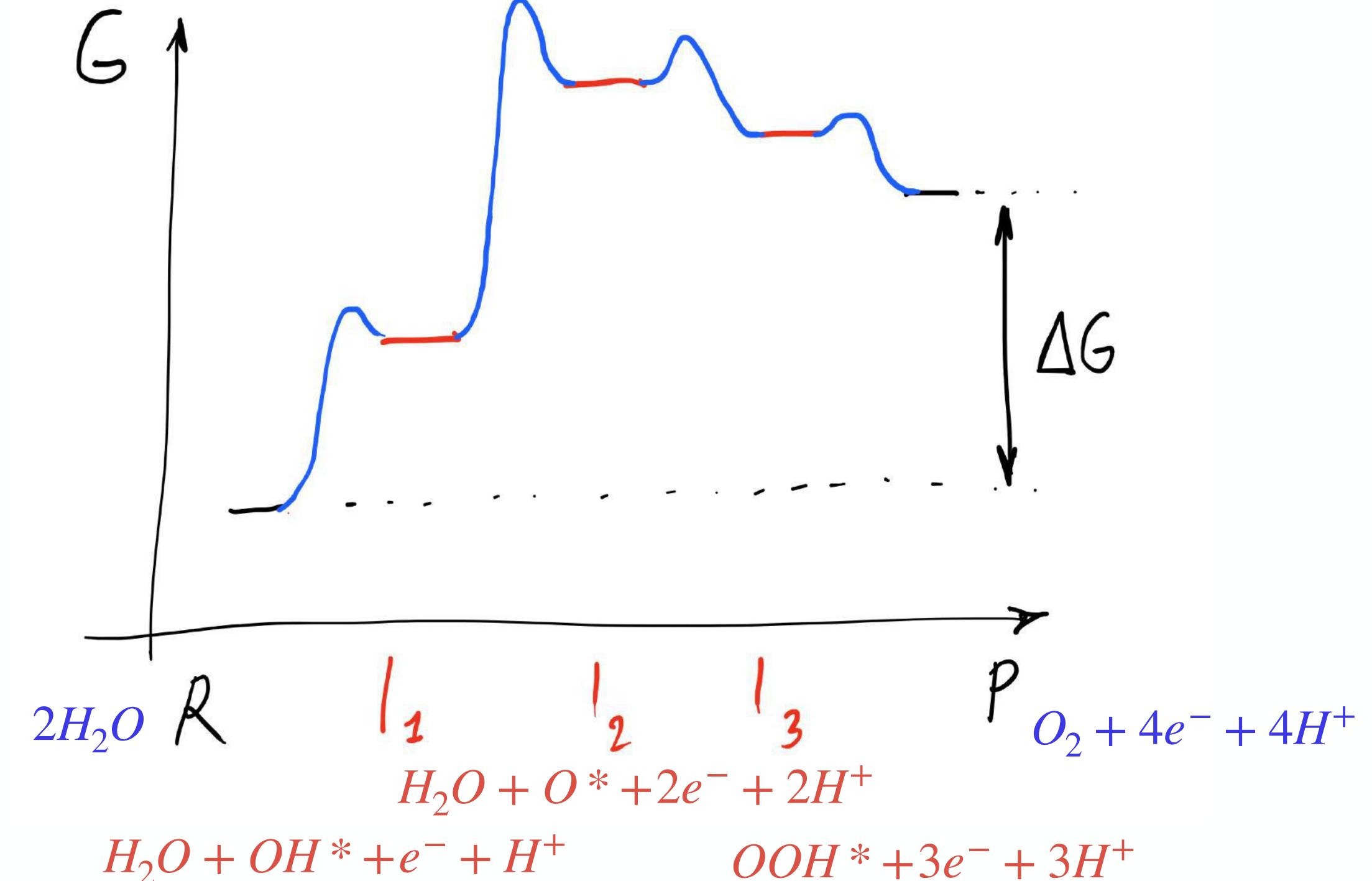
Schematic catalytic steps involved in single-site Oxygen Reduction and Oxygen Evolution reactions on a 2D material.



Karmodak and Andreussi, *in preparation* (2020)

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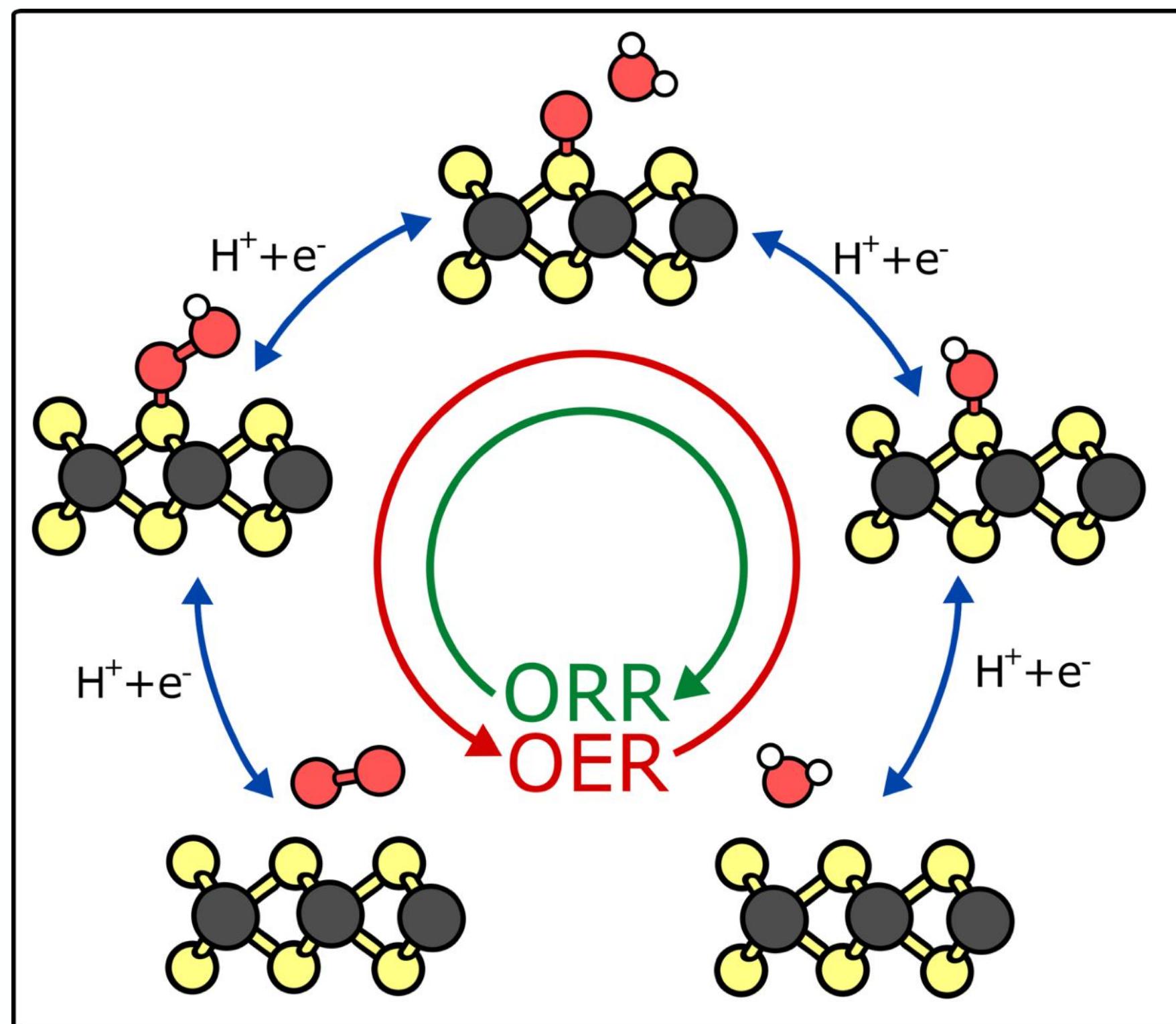
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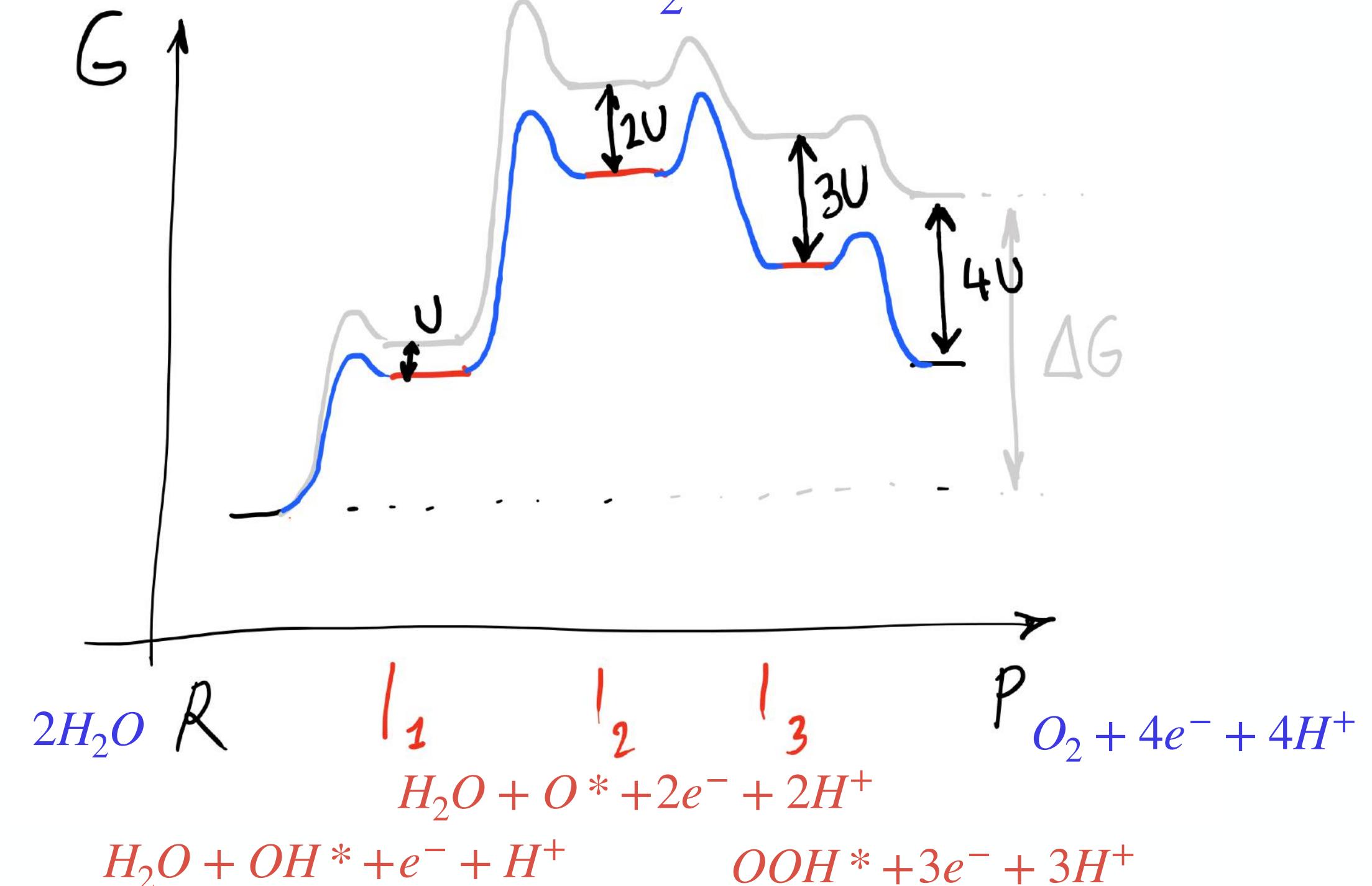


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$$\Delta G^{OER} = G(O_2) + 4\mu_e + 4\mu_H - G(H_2O)$$

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



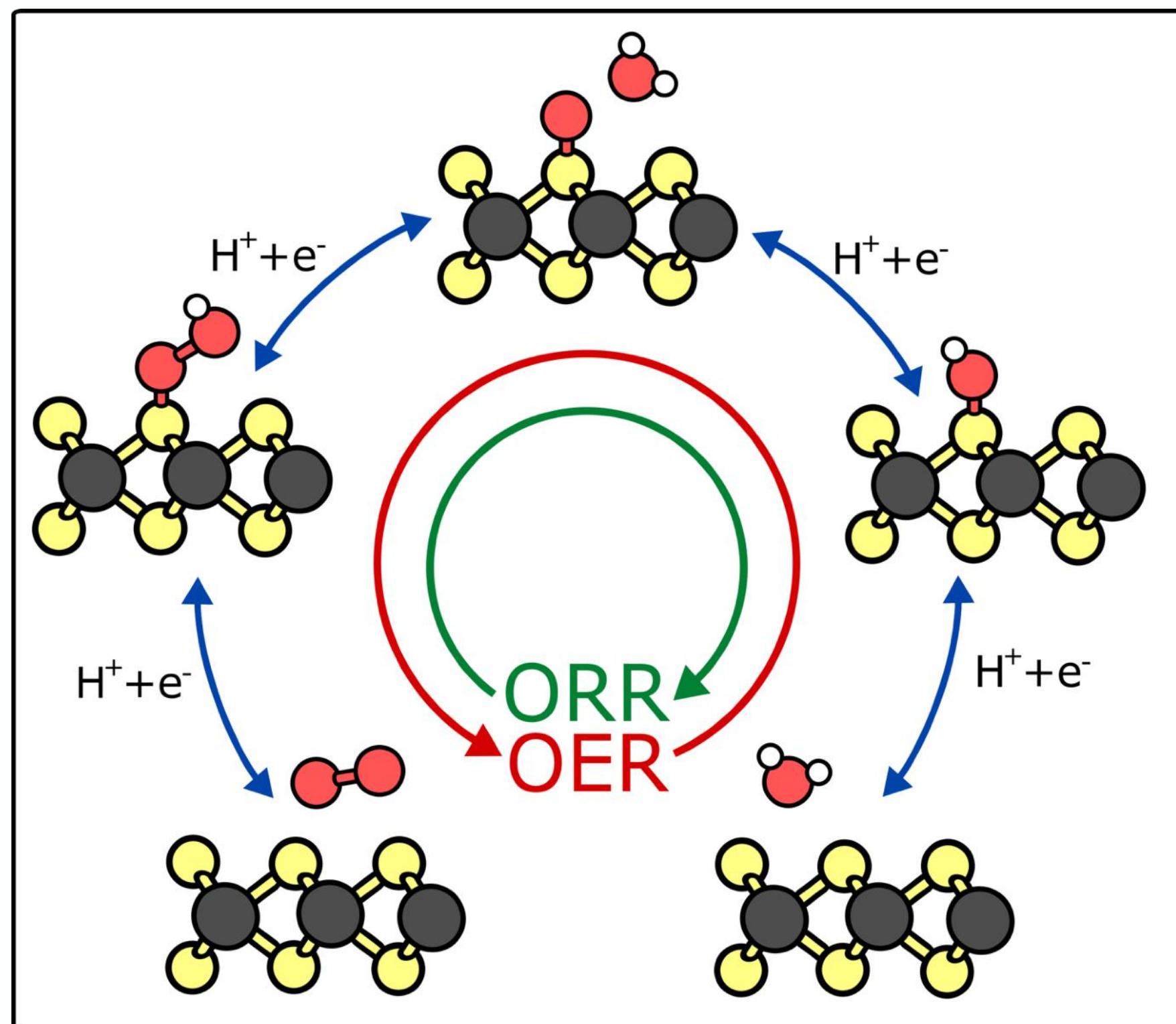
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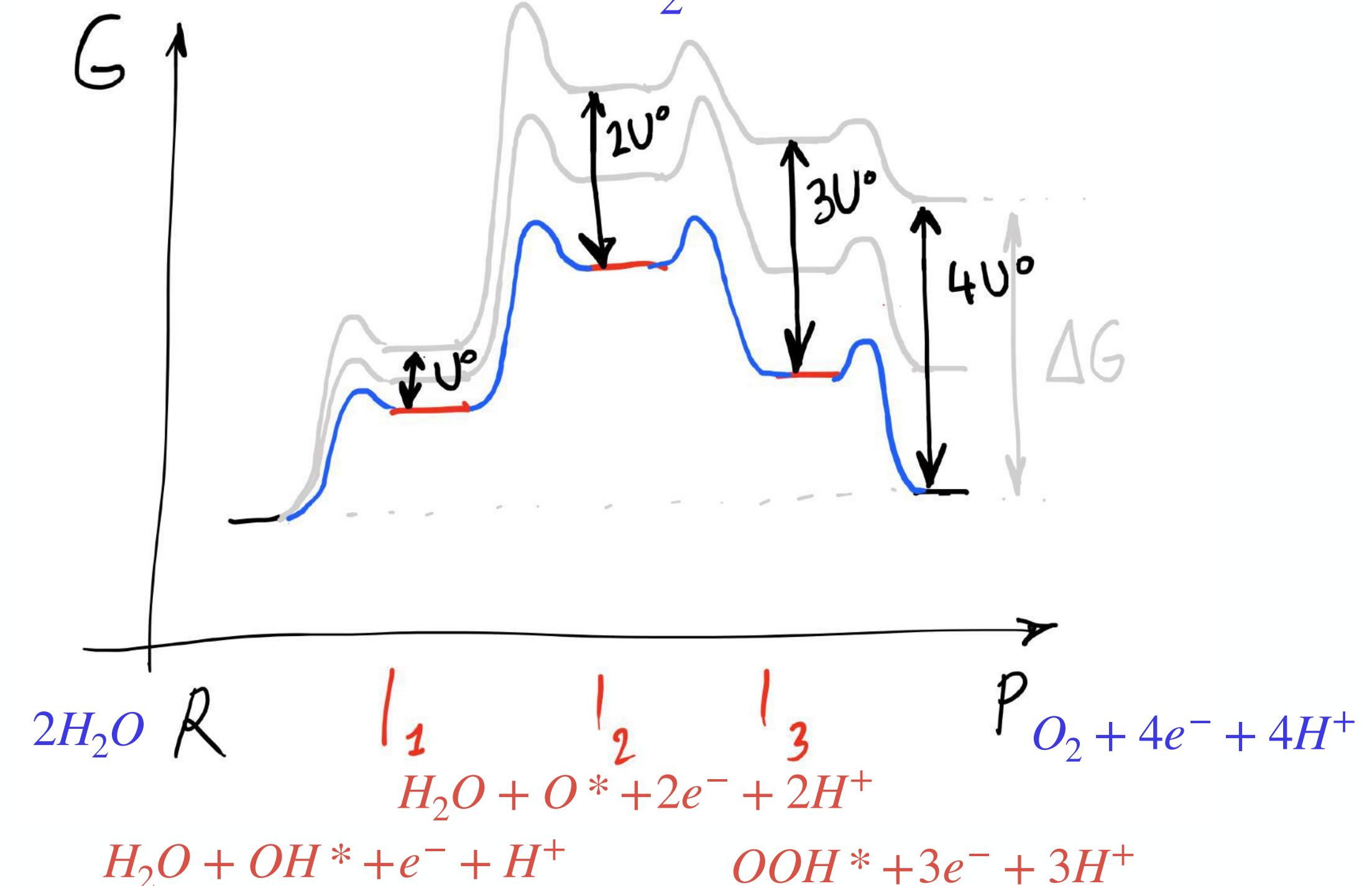


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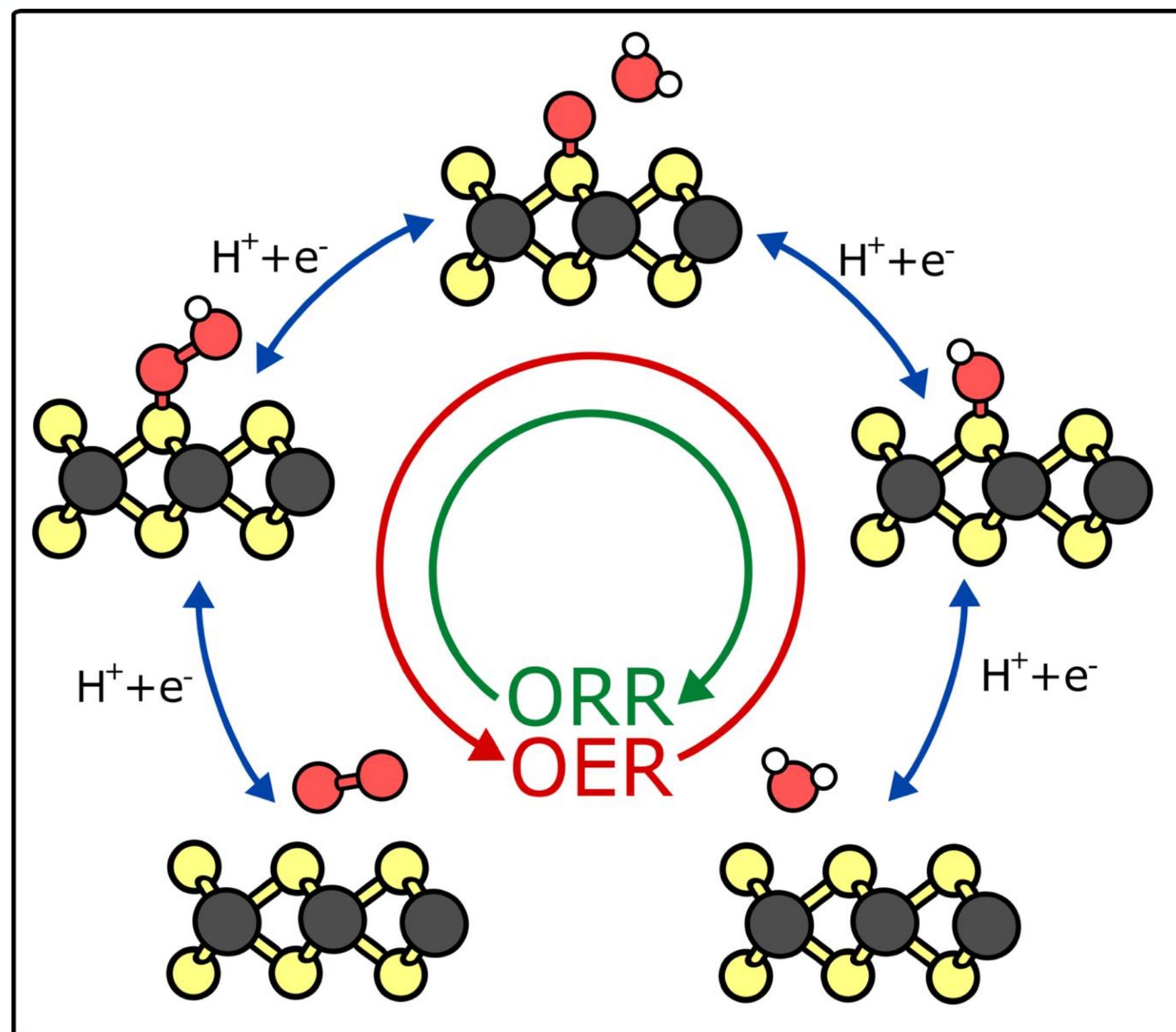
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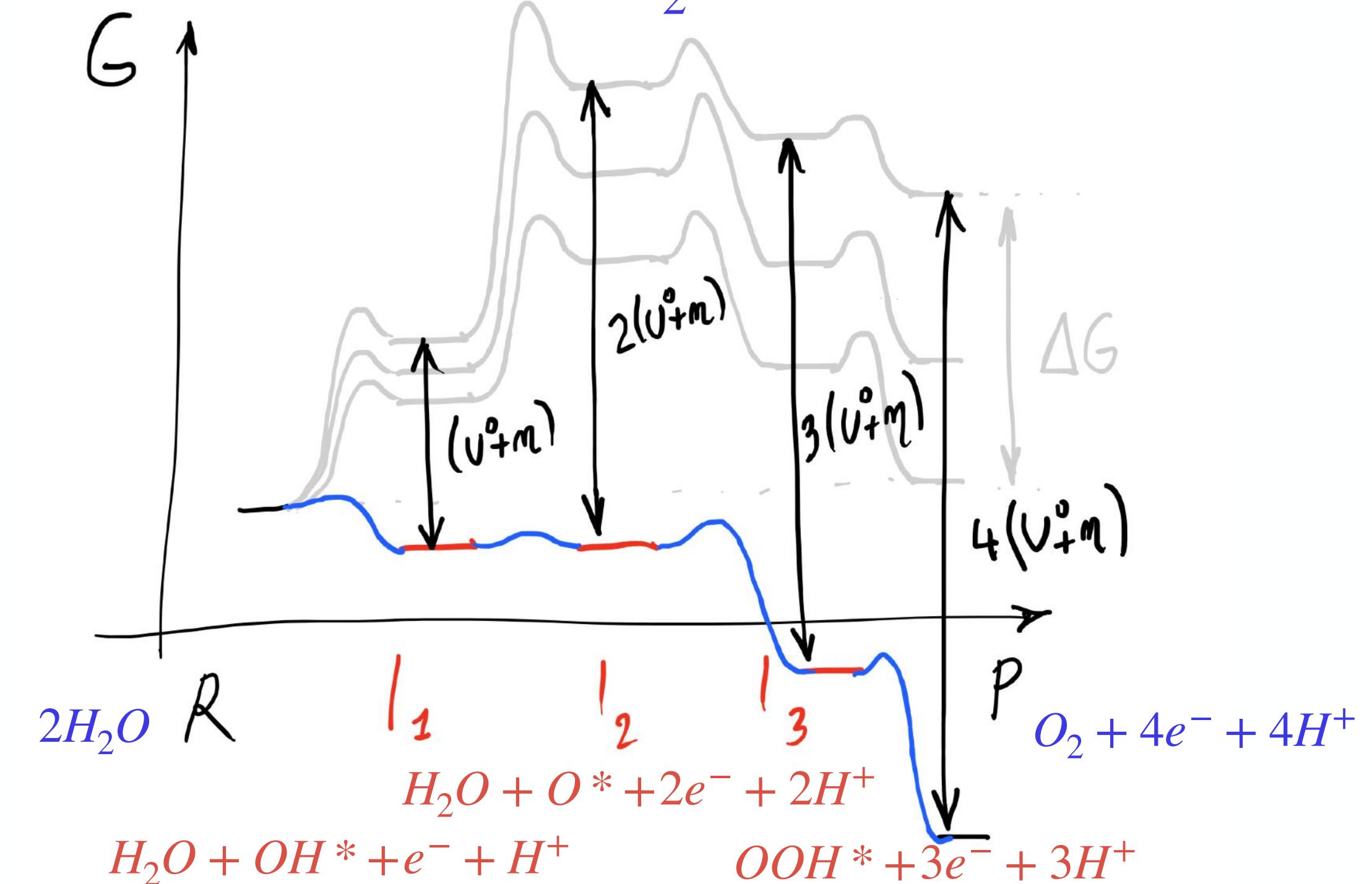


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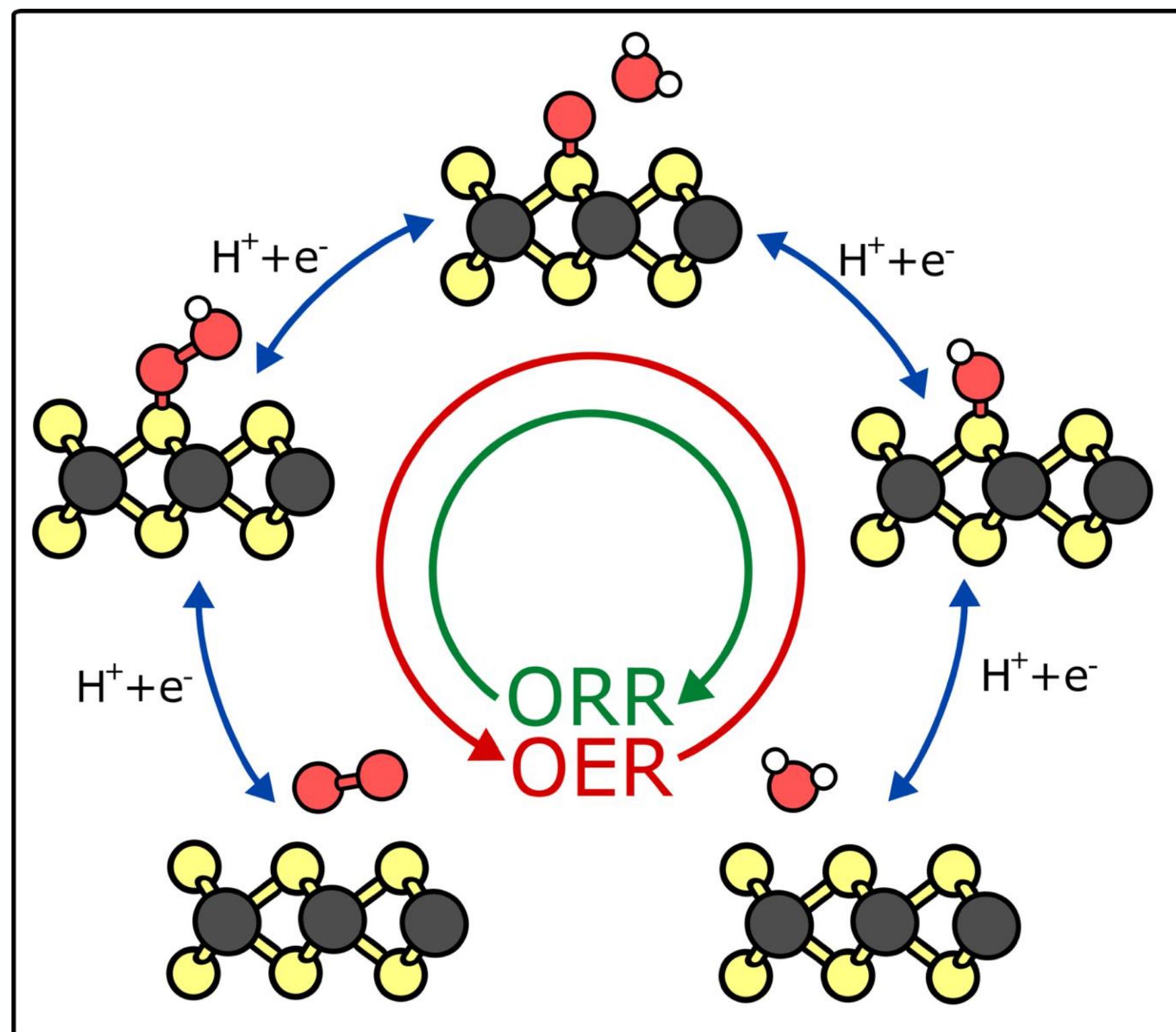
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# Multiple Steps Conversion

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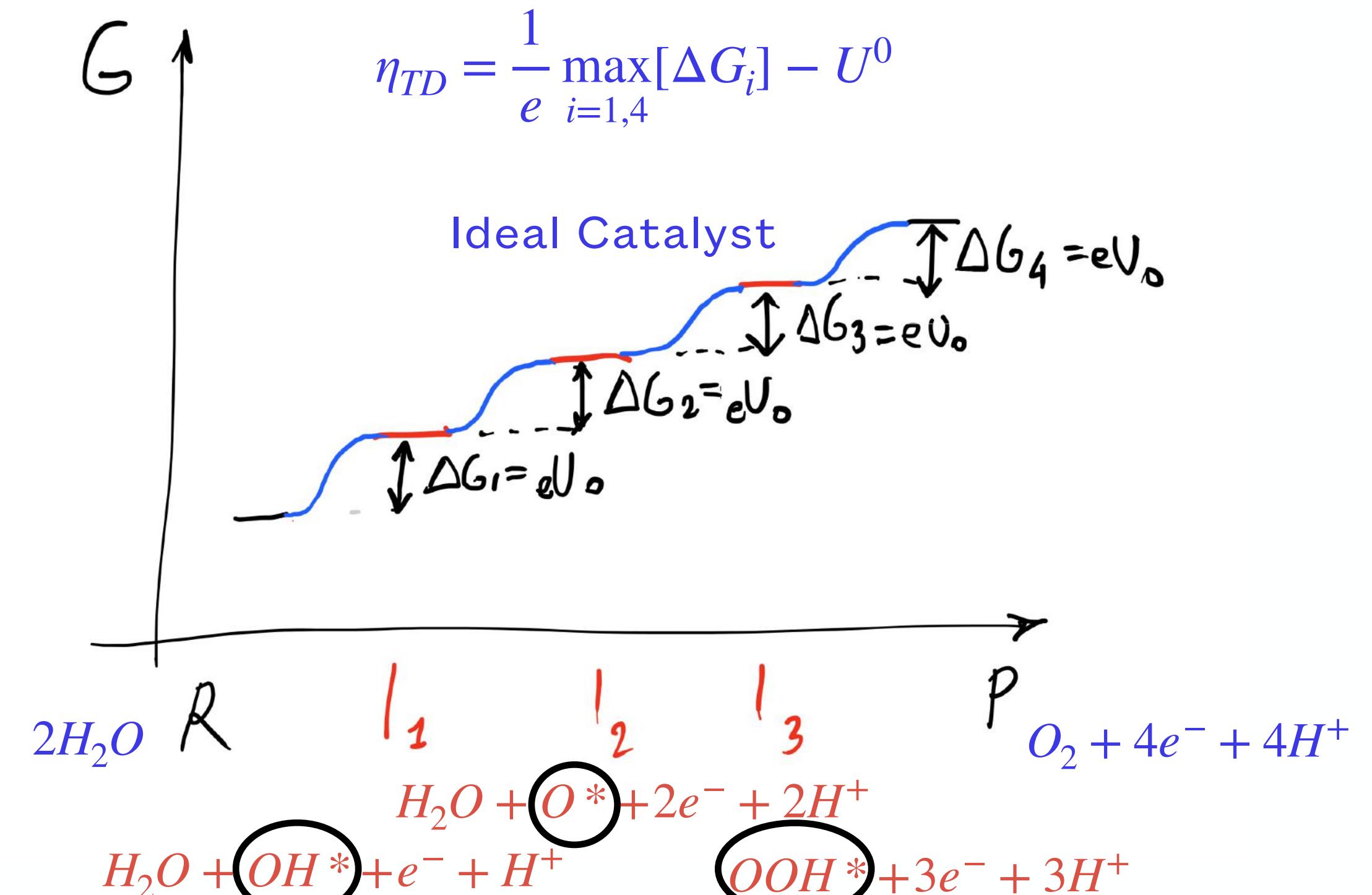
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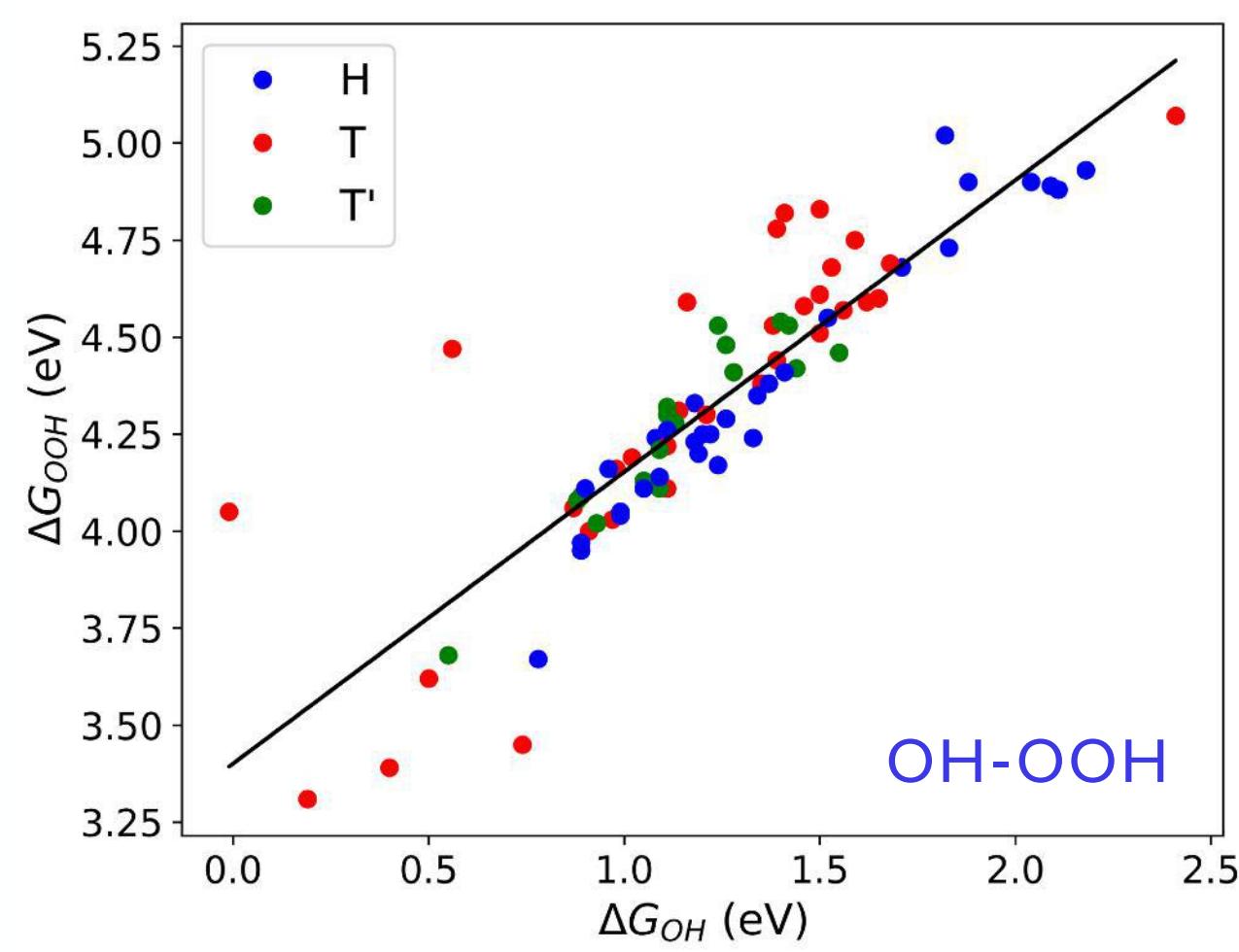
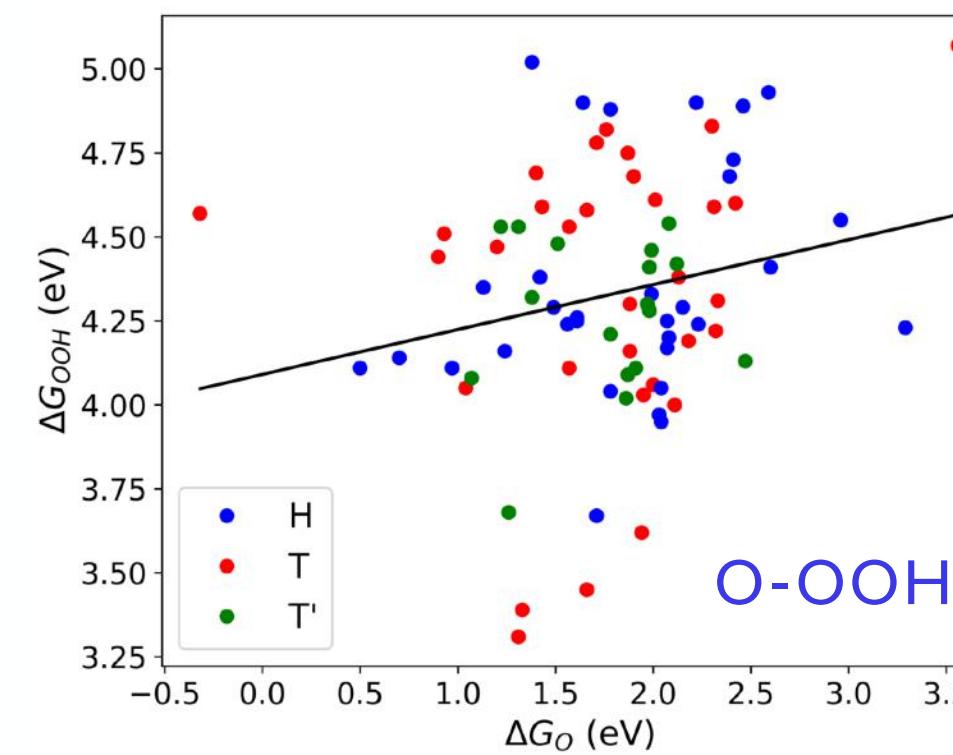
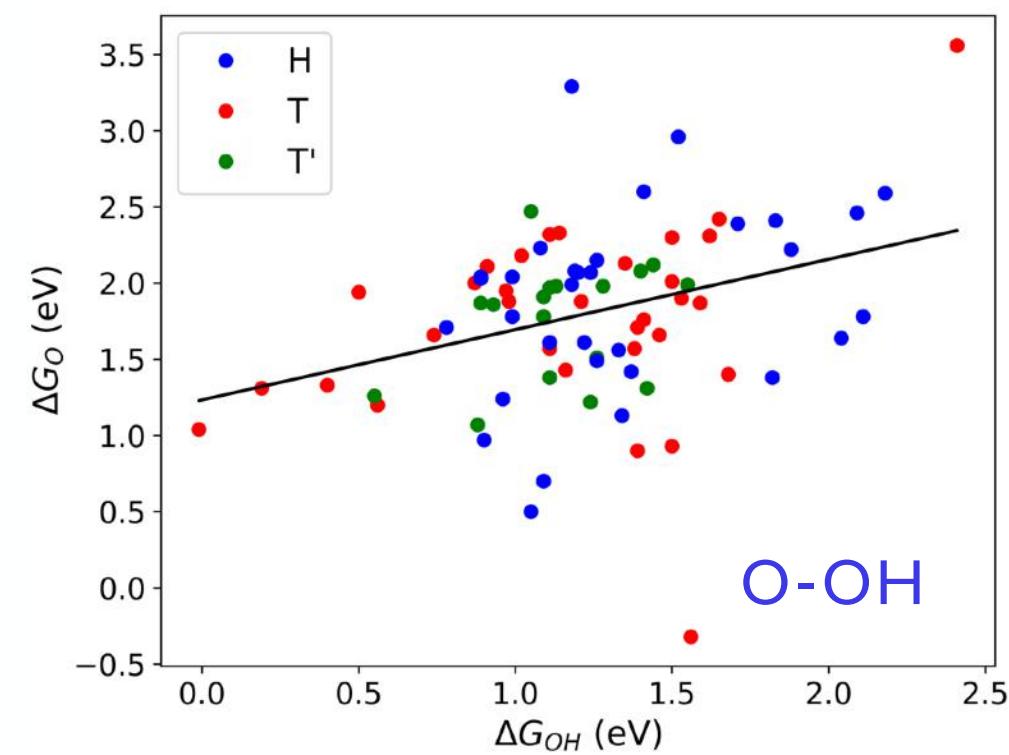
Karmodak and Andreussi, *in preparation* (2020)

- 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.



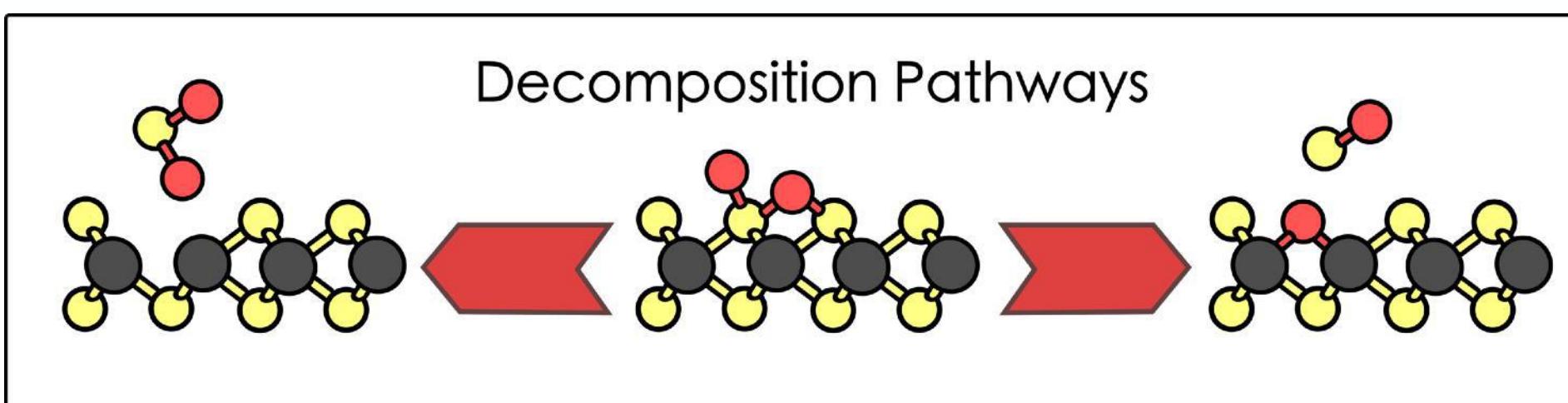
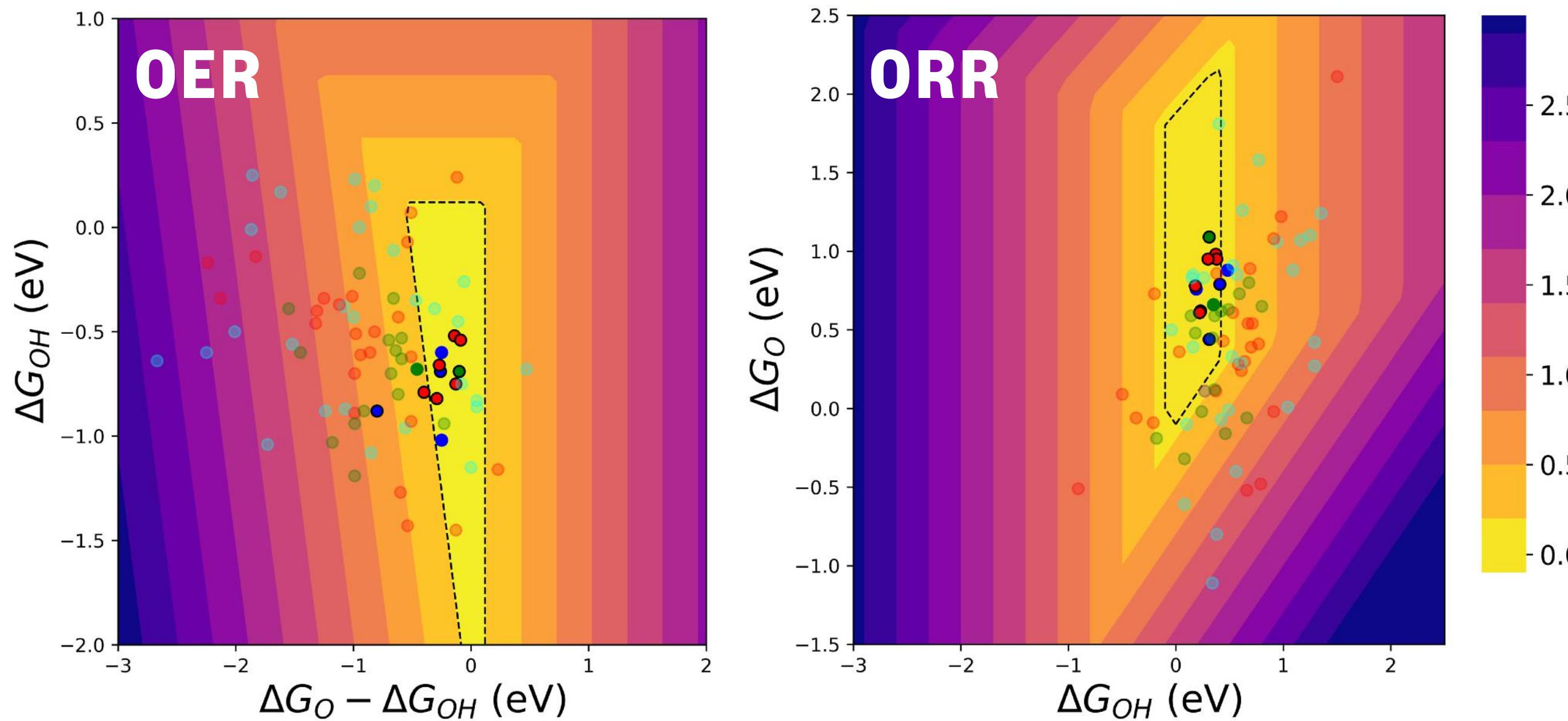
# Materials Constraints

## 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  $H_2O$

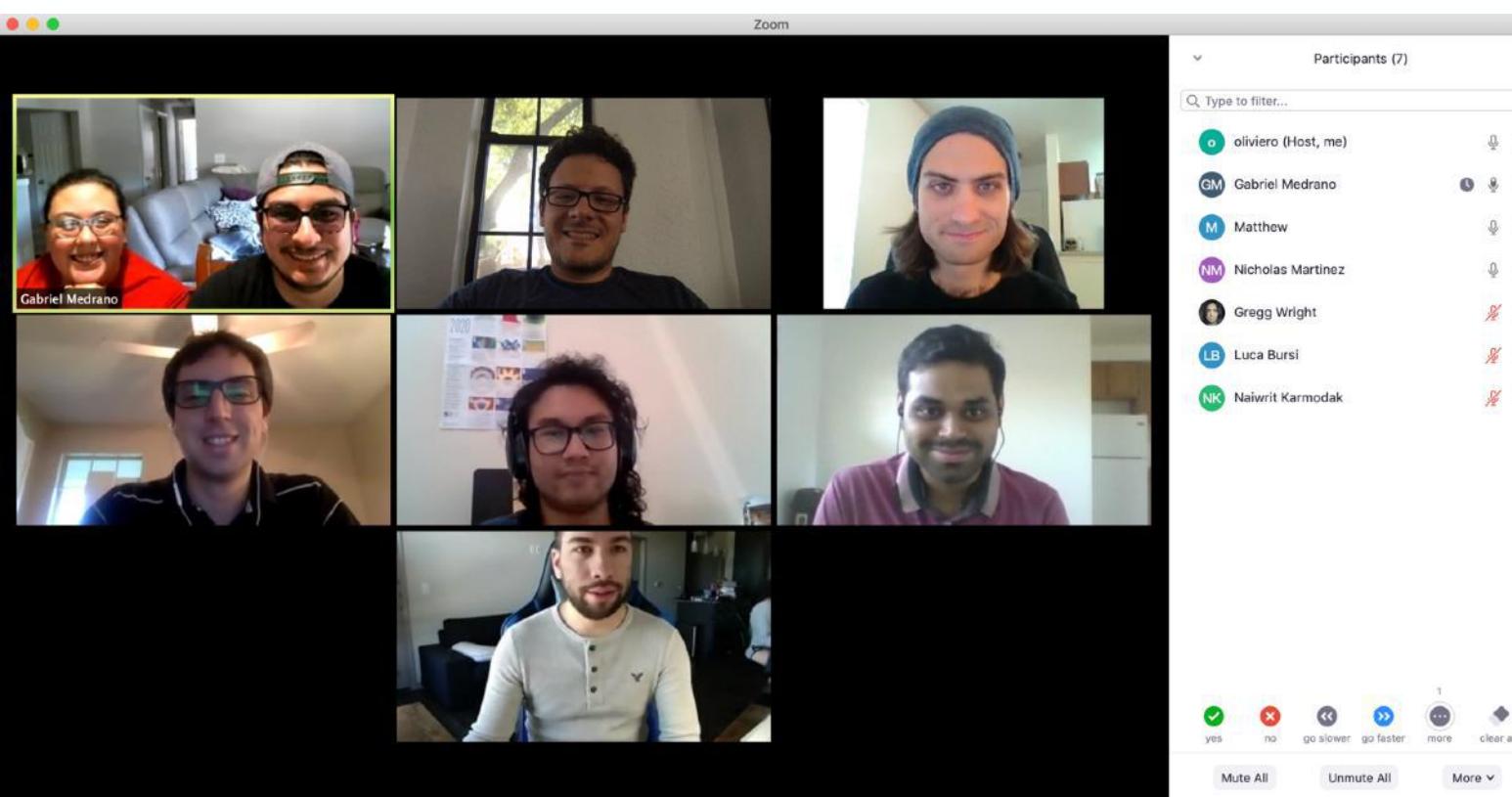
## Climbing to the Top of the OER Volcano

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 ( $\eta_{TD}$  as low as 0.24 V)
  - 12 thermodynamically or kinetically stable
  - 8 reported experimentally
- ORR
  - 21 active materials ( $\eta_{TD}$  as low as 0.29 V)
  - 13 thermodynamically or kinetically stable
  - 9 are reported experimentally



- Dr Edan Bainglass
- Dr Fernanda Bononi
- Matthew Truscott
- Gabriel Medrano
- Cristina Castillo
- Ajay Jayanth (TAMS)
- Pradip Si
- Joe Watson
- **Dr Naiwrit Karmodak (now postdoc at DTU, Denmark)**

# Acknowledgements And Funding

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

