Modeling Electrocatalysis without the Agony – Past, Present, and Future

A Roadmap to Unifying Quantum and Statistical Descriptions

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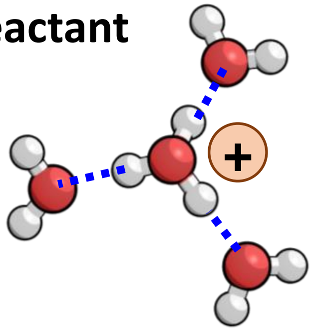
A reasonable description of solvation is necessary to compute barriers of interfacial reactions

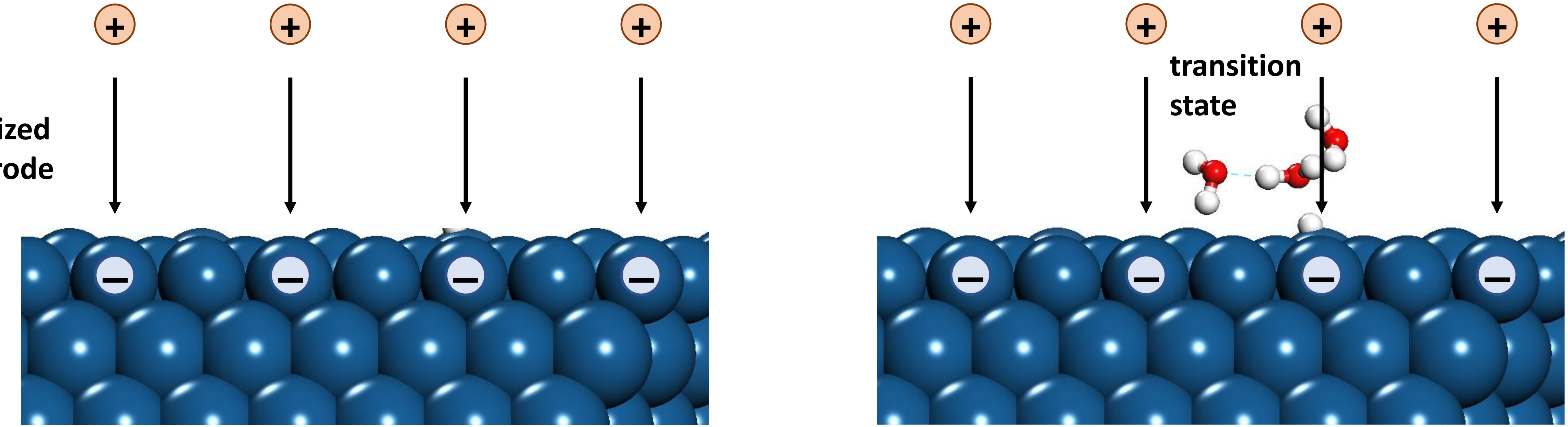
solvated reactant



Need quantum mechanics (DFT) to model bond breaking and formation

Need statistical mechanics to capture electrolyte configurations

polarized electrode



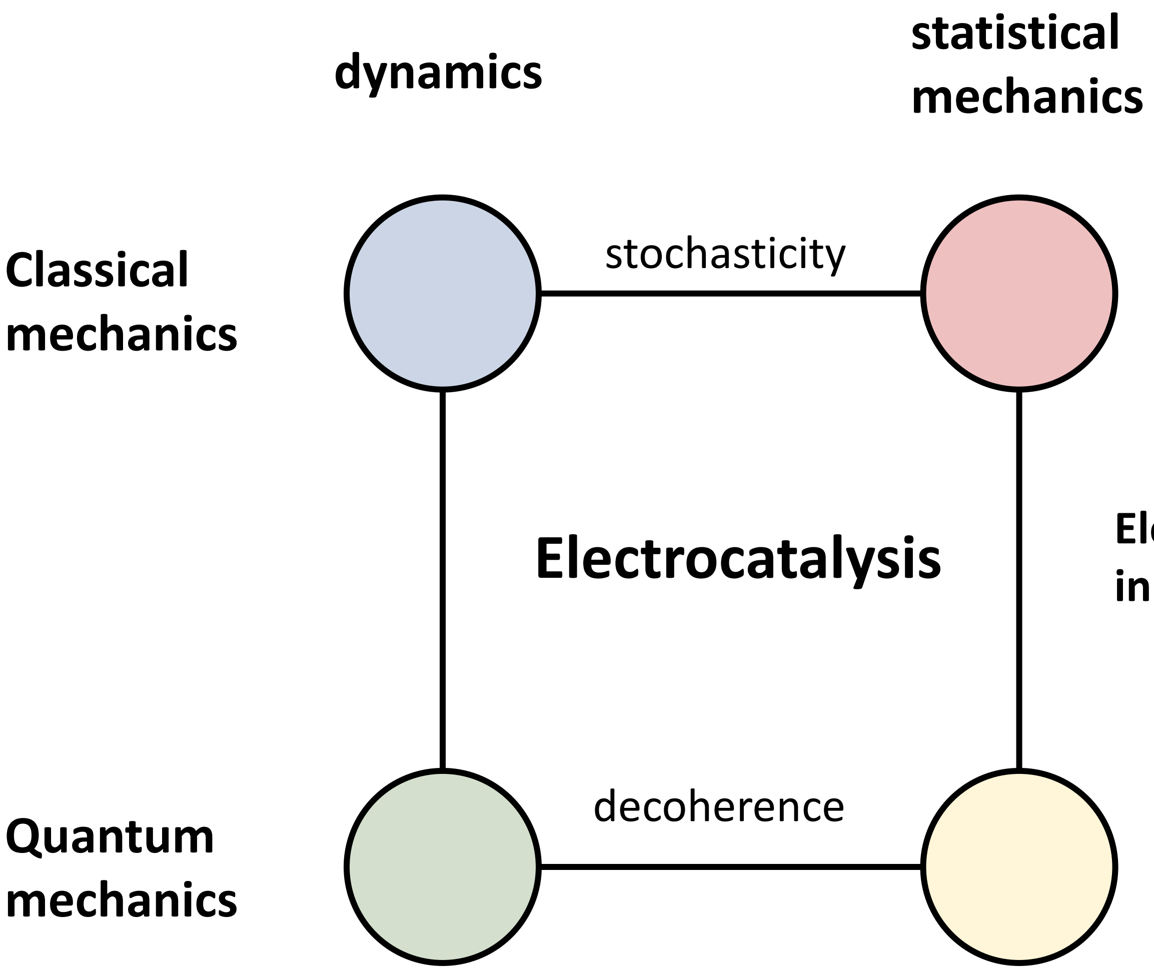
Bridging the gap …

AIMD can compute barriers while accounting for the electrolyte …

… but it is agonizing and overkill

Not appropriate for complex pathways like CO_2 electrolysis

… so we've been forced to improvise



Electrocatalysis lives right in the middle of the mess

Outline: The Past, Present, and Future

- **Past** – The computational hydrogen electrode and limiting potentials
- **Present** – Nonlinear/nonlocal hybrid solvation with VASPsol++
- **Future** – The Implicit Quantum Electrolyte

The Past

The Computational Hydrogen Electrode and Limiting Potential

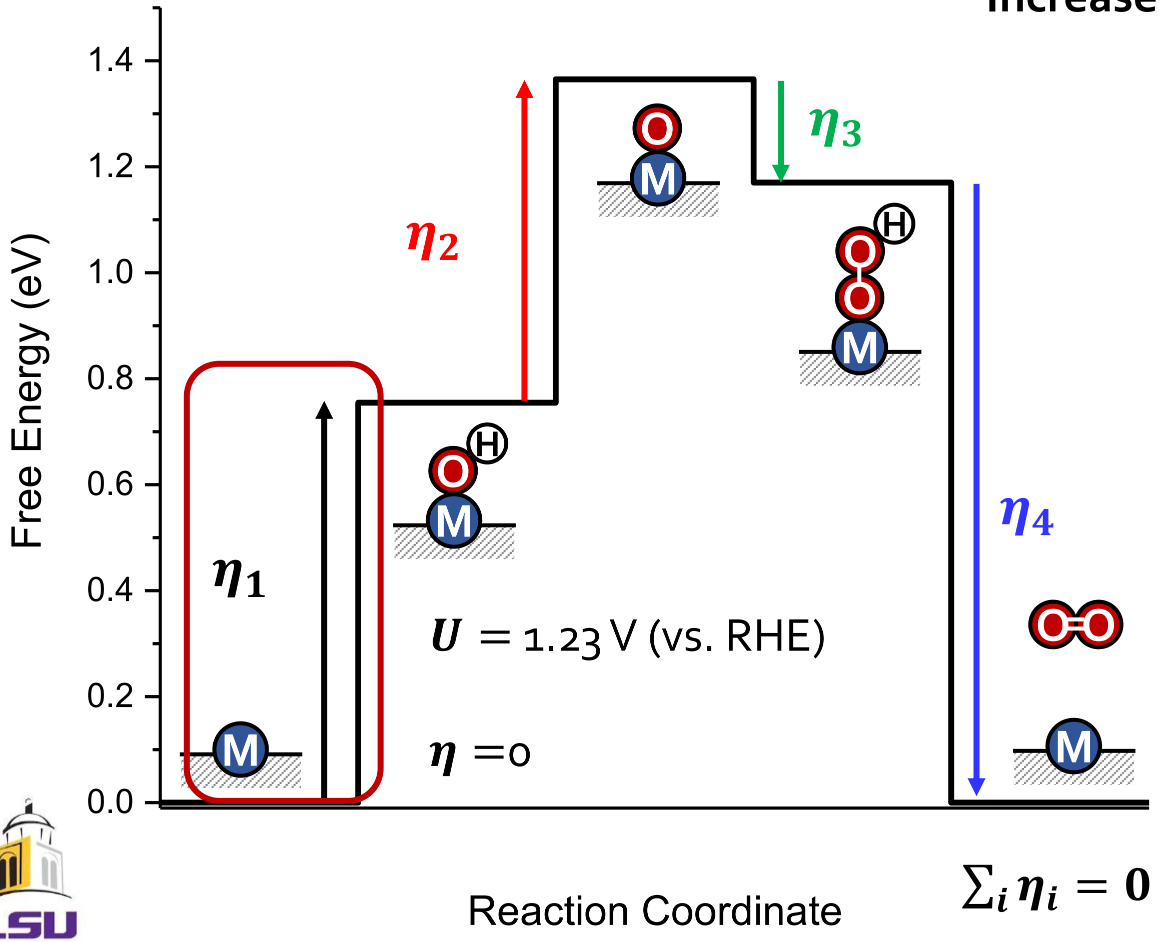
Thermodynamic Model of the OER and the importance of kinetic barriers

$$\Delta G_i(U) = \underbrace{\Delta G_i(U_{\mathrm{eq}})}_{e\eta_i} - e\underbrace{(U_{\mathrm{RHE}} - U_{\mathrm{eq}})}_{\eta} = e(\boldsymbol{\eta_i} - \boldsymbol{\eta})$$

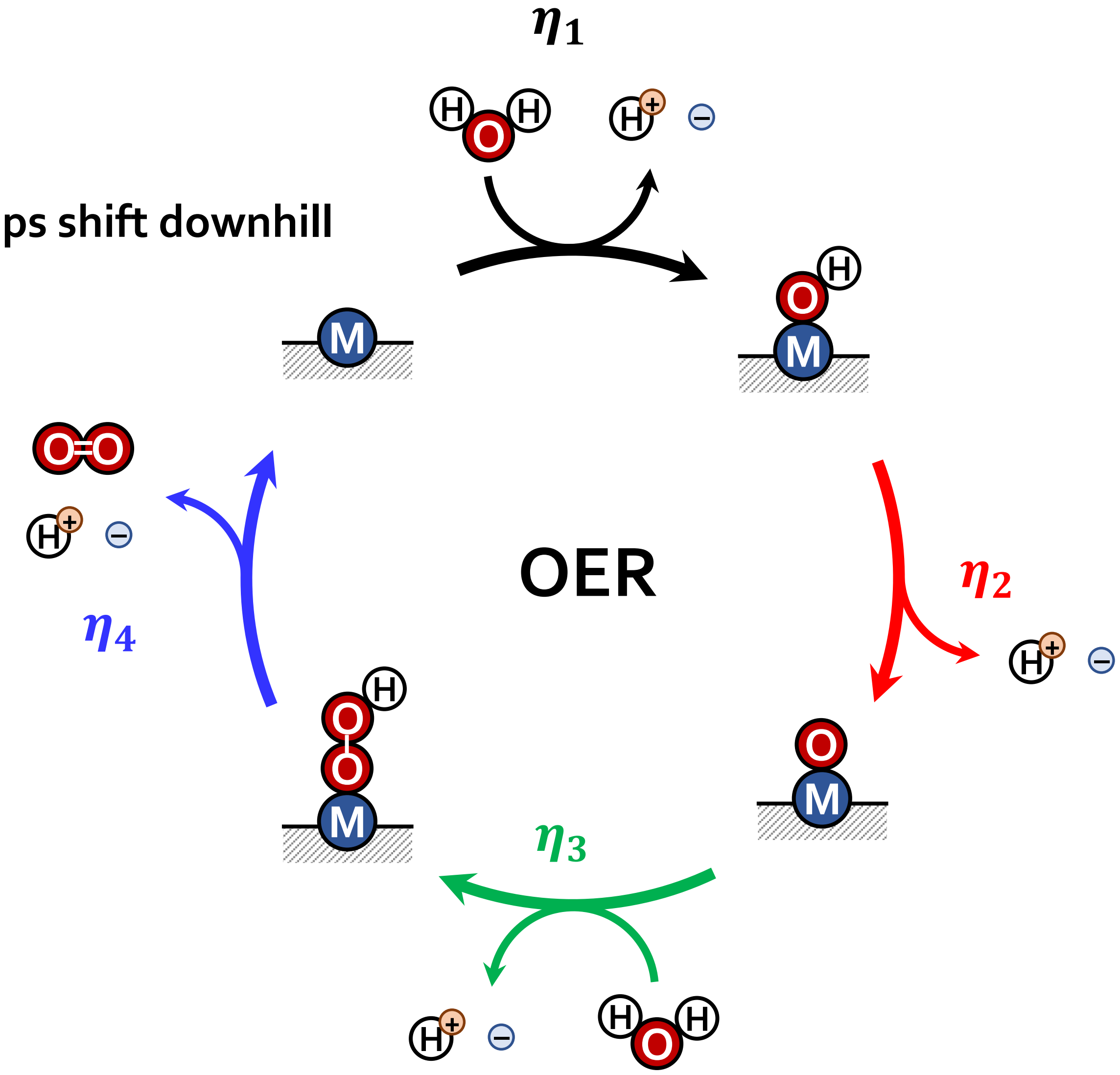
redox overpotential

electrode overpotential

Increase η, all steps shift downhill

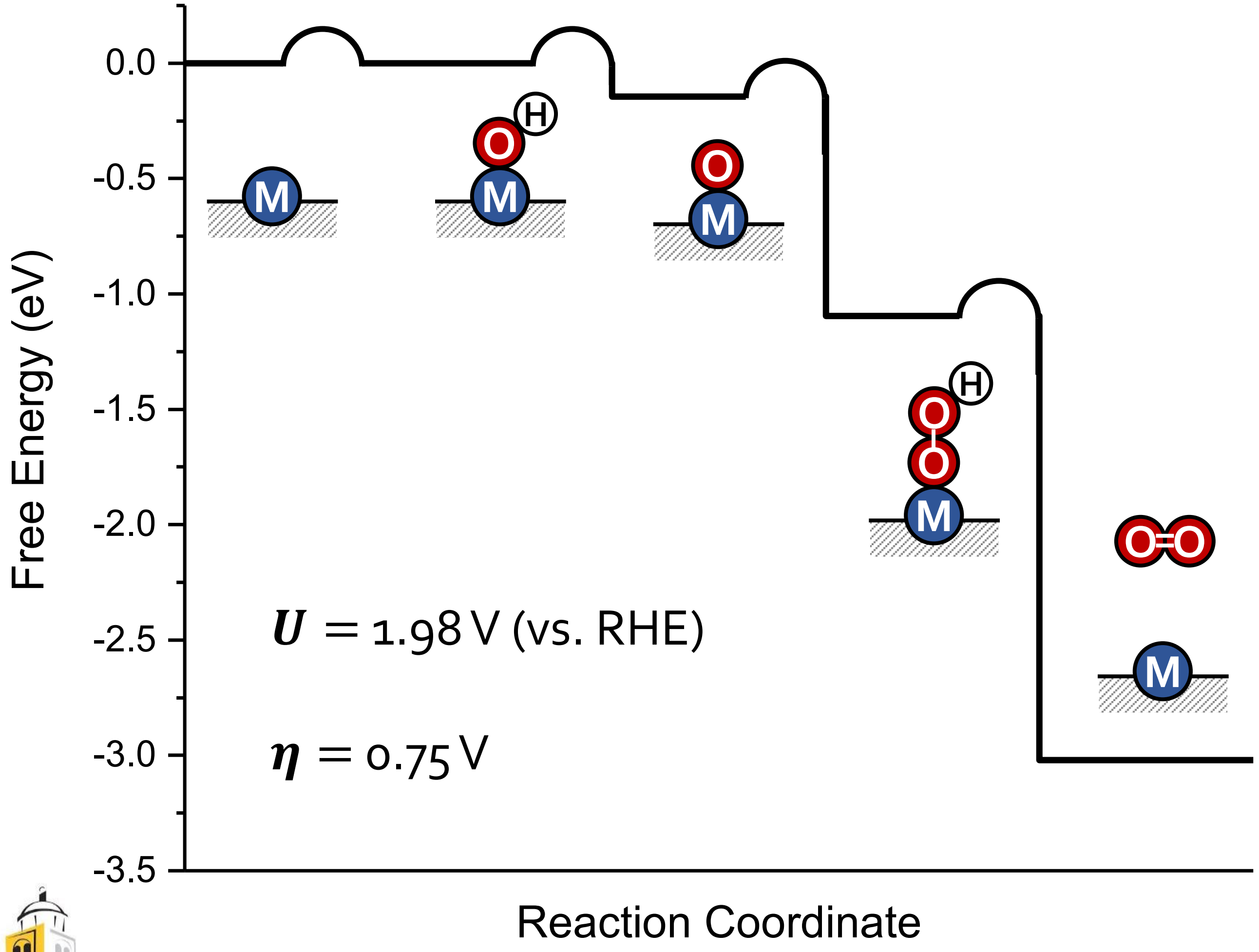


$\sum_i \eta_i = 0$



Rossmeisl et al., *J. Electroanal. Chem.* ***607***, 83 (2007)

Thermodynamic Model of the OER and the importance of kinetic barriers



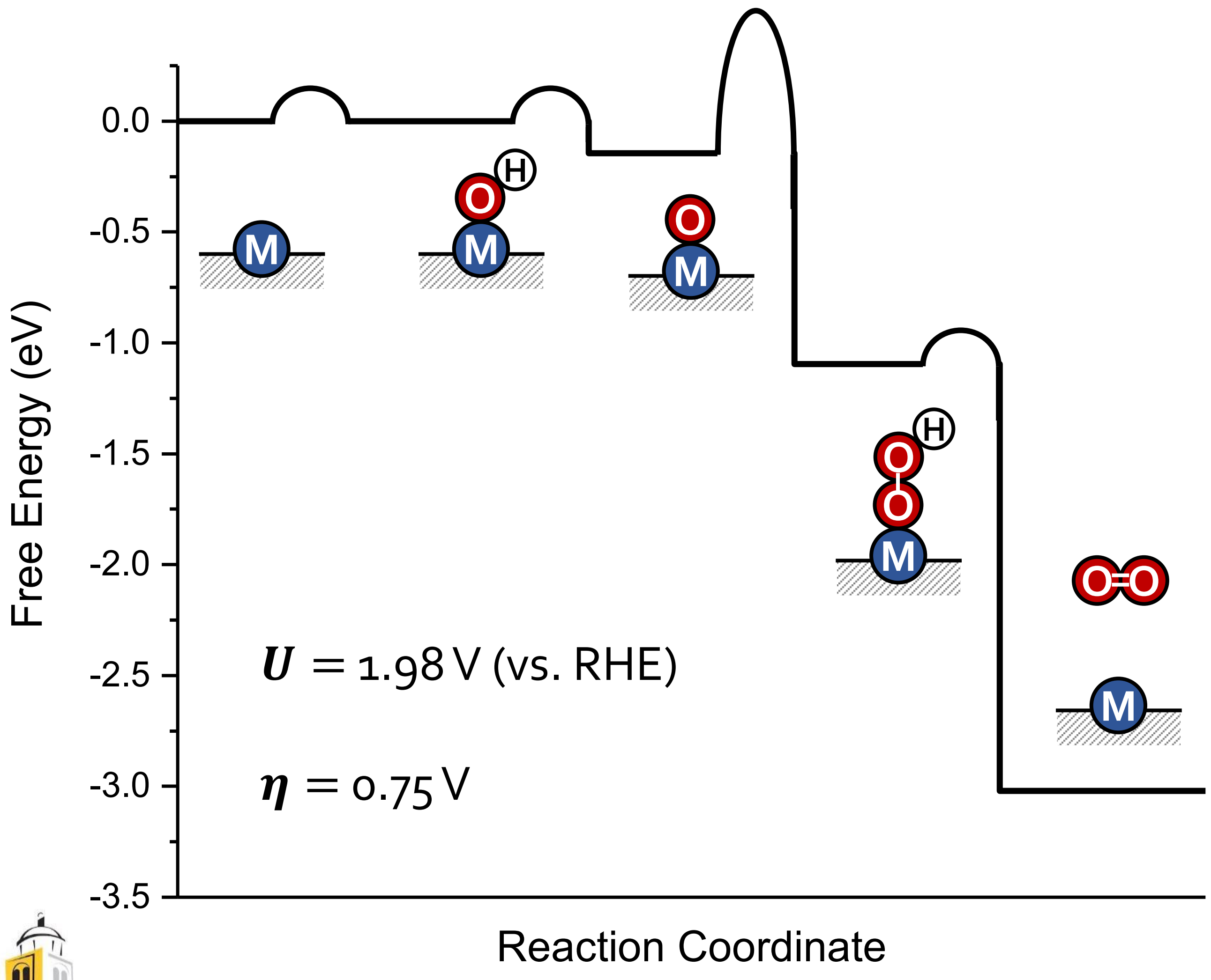
Thermodynamic Overpotential

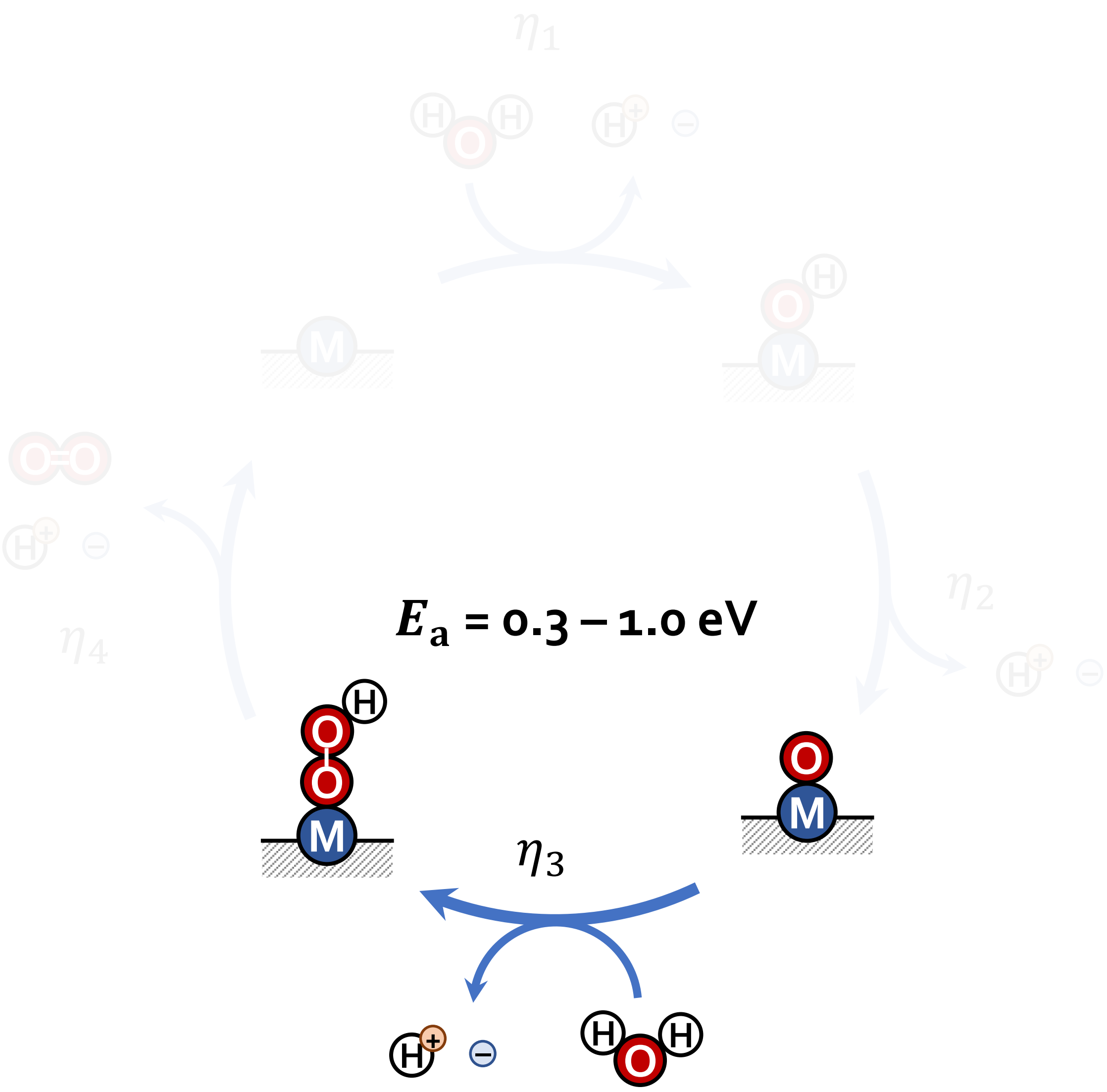
- Minimum electrode overpotential that makes all steps downhill
- $\eta_T = \max(\eta_i)$
- Proton transfer has low kinetic barriers (0.1 – 0.2 eV)*
- When $\eta > \eta_T$, all steps have barriers on order of 0.1 – 0.2 eV
- Occurs at lower electrode potential for catalyst with lower η_T – a more efficient, better catalyst
- "Optimal catalyst": all $\eta_i = 0$, $\eta_T = 0$

*T. Stecher et al., Phys. Rev. Lett. **117**, 276001 (2016)

Thermodynamic Model of the OER and the importance of kinetic barriers

… but not all barriers as small as those for simple PT





Plaisance et al., *JACS* ***137***, 14660 (2015)

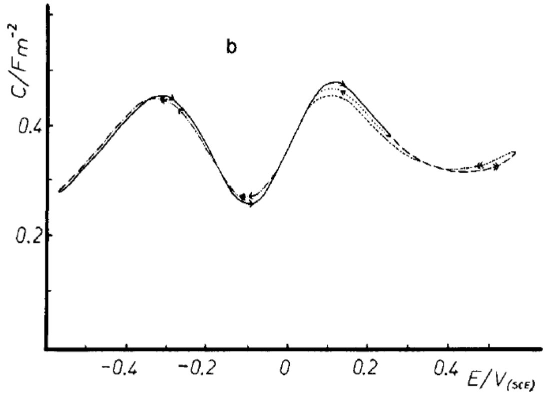
The Present

Nonlinear/Nonlocal Hybrid Solvation with VASPsol++

Implicit solvation models and their deficiencies

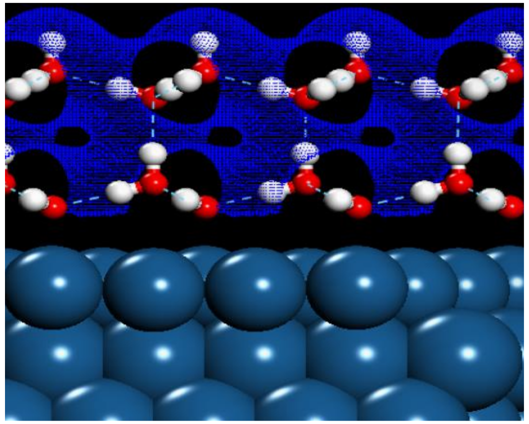
- Implicit solvation models represent the electrolyte as a continuum
- Most implementations only consider linear dielectric and ionic screening (<u>can't reproduce 'double hump' capacitance curve</u>)
- Most implementations in PW DFT codes construct the solute cavity from a local function of the solute electron density (<u>leads to 'solvent leakage'</u>)
- Most complex models exist, including ones based on classical DFT (JDFTx), but are <u>not available in widely used PW DFT codes like VASP</u>
- Previously, the only implicit electrolyte model that can be used in VASP, implemented in the VASPsol code, is based on a linear+local model and additionally <u>requires a high planewave energy cutoff to avoid severe FFT truncation errors</u>
- We have rewritten VASPsol to include an <u>***extremely robust and efficient***</u> nonlinear+nonlocal model – **VASPsol++**

Capacitance of Au(111) showing 'double hump' shape



Hamelin et al., J. Electroanal. Chem. Interfacial Electrochem. 189 (1985)

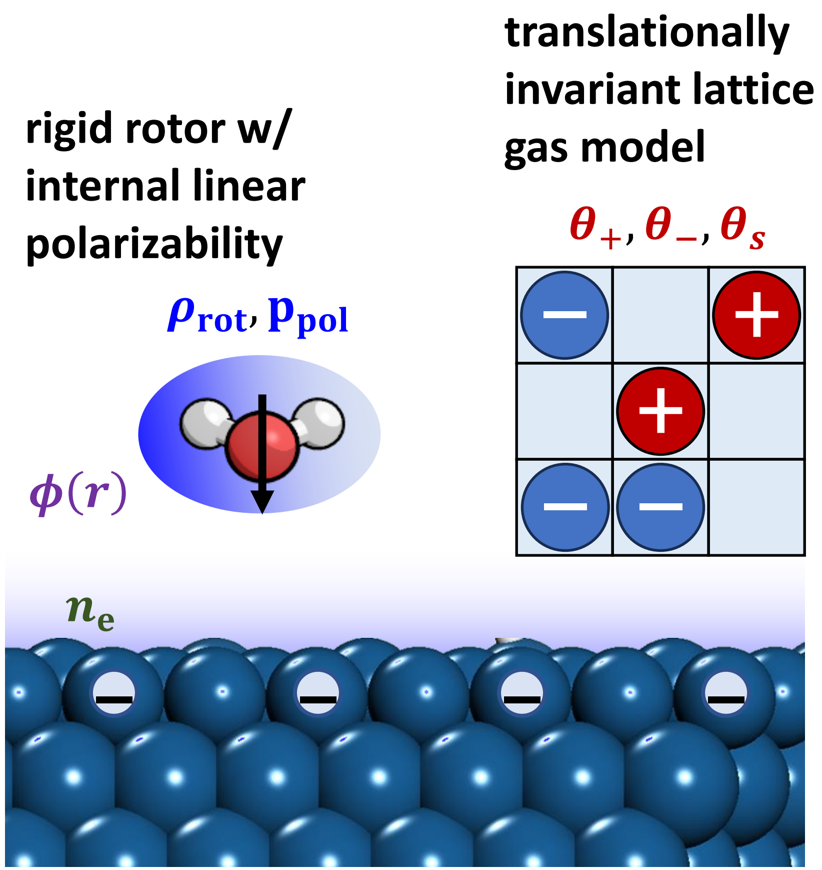
Water bilayer on Pt(111) showing 'solvent leakage'



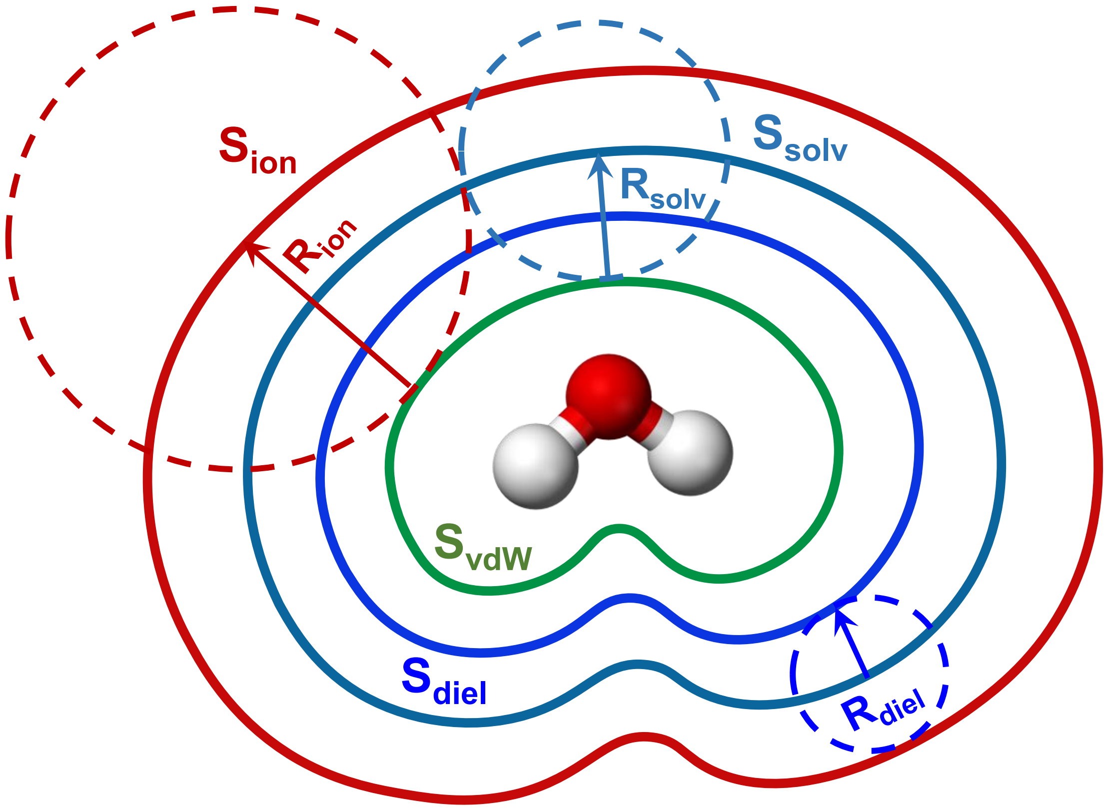
Nonlinear free energy functional and degrees of freedom

$$A_{\text{tot}} = A_{\text{KS}}[n_e, \phi] + A_{\text{diel}}[n_e, \phi, \rho_{\text{rot}}, \mathbf{p}_{\text{pol}}] + A_{\text{ion}}[n_e, \phi, \theta_+, \theta_-, \theta_s] + A_{\text{cav}}[n_e]$$

$n_e(r)$	solute electron density	solute DOFs
$\phi(r)$	electrostatic potential	coupling
$\rho_{\text{rot}}(r, \omega)$	solvent rotational distribution	solvent DOFs
$\mathbf{p}_{\text{pol}}(r)$	solvent internal polarization	solvent DOFs
$\theta_+, \theta_-, \theta_s$	electrolyte 'site' occupancies of cations, anions, and solvent	ionic DOFs



Nonlocal definitions for the dielectric and ionic cavities



S_{vdW} **van der Waals cavity** defines region occupied by solute electron density

S_{solv} **Solvent cavity** defines region occupied by solvent molecular centers

S_{diel} **Dielectric cavity** defines region where dielectric response is present

S_{ion} **Ionic cavity** defines region where counterion centers can occupy

van der Waals cavity is equivalent to the cavity in VASPsol

$$S_{vdw} = \boldsymbol{S}(n_e)$$

$$\boldsymbol{S}(n) = \frac{1}{2}\,\mathrm{erfc}\left[\frac{1}{\boldsymbol{\sigma}\sqrt{2}}\ln\frac{n}{\boldsymbol{n_c}}\right]$$

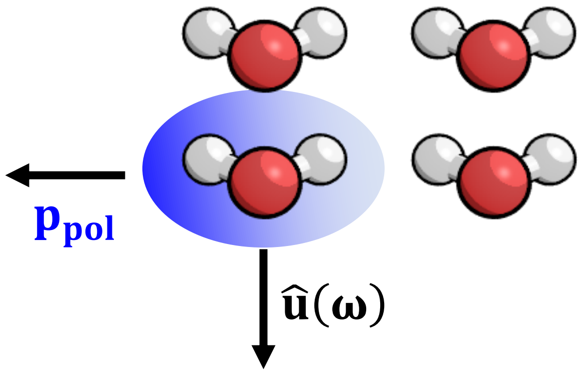
$\boldsymbol{n_c} =$ electron density cutoff

$\boldsymbol{\sigma} =$ cavity smoothness

Nonlinear dielectric free energy

rotational free energy

$$\bar{A}_{\mathrm{diel}}\{\phi, \boldsymbol{\rho}_{\mathrm{rot}}, \mathbf{p}_{\mathrm{pol}}\}(r) \equiv \underbrace{\frac{1}{\beta}\int \frac{d\boldsymbol{\omega}}{4\pi}\rho_{\mathrm{rot}}(r,\boldsymbol{\omega}) \ln \rho_{\mathrm{rot}}(r,\boldsymbol{\omega})}_{\text{rigid rotor entropic free energy}} - \underbrace{\lambda_{\mathrm{rot}}(r)\int \frac{d\boldsymbol{\omega}}{4\pi}\left(\rho_{\mathrm{rot}}(r,\boldsymbol{\omega}) - 1\right)}_{\text{normalization constraint}}$$



$$+ \underbrace{\frac{2\pi}{\epsilon_0 \alpha_{\mathrm{pol}}} p_{\mathrm{pol}}^2(r)}_{\text{internal polarization energy}} - \underbrace{\frac{2\pi}{\epsilon_0 \alpha_{\mathrm{sic}}} p^2(r)}_{\text{self-interaction and correlation correction}} + \underbrace{\mathbf{p}(r)\cdot(w_b * \nabla\phi)(r)}_{\text{interaction with electric field}}$$

$$\mathbf{p}(r) = \overbrace{\int \frac{d\boldsymbol{\omega}}{4\pi}\hat{\mathbf{u}}(\boldsymbol{\omega})\rho(r,\boldsymbol{\omega})}^{\mathbf{p}_{\mathrm{rot}}} + \mathbf{p}_{\mathrm{pol}}(r)$$

net polarization of a solvent molecule

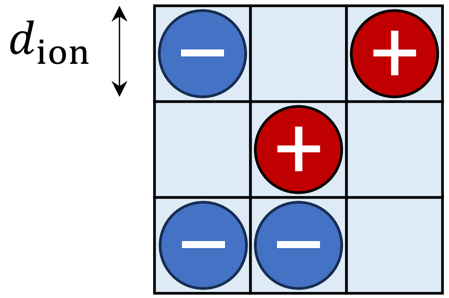
Nonlinear ionic free energy

$$\bar{A}_{\text{ion}}\{\boldsymbol{\phi},\boldsymbol{\theta}_+,\boldsymbol{\theta}_-,\boldsymbol{\theta}_s\}(r) \equiv \underbrace{\sum_{i=\{+,-,s\}} \theta_i(r)\left[\frac{1}{\beta}\ln\theta_i(r)-\mu_i\right]}_{\text{translational free energy}} - \underbrace{\lambda_{\text{ion}}(r)\left[\sum_{i=\{+,-,s\}}\theta_i(r)-1\right]}_{\text{normalization constraint}}$$

$$+ \quad \bar{\rho}_{\text{ion}}(r)\phi(r)$$

interaction with electrostatic potential

Translationally invariant lattice gas model



net charge of electrolyte 'site'

$$\bar{\rho}_{\text{ion}}(r) = ze[\theta_-(r)-\theta_+(r)]$$

Ground state dielectric and ionic respo

dielectric response:

$$\frac{\delta \bar{A}_{\mathrm{diel}}(r)}{\delta \rho_{\mathrm{rot}}(r, \boldsymbol{\omega})} = 0$$

$$\mathbf{p}(r) = \frac{\epsilon_0}{4\pi}\left[\alpha_{\mathrm{rot}} \underbrace{g_{\mathrm{rot}}(\beta p_{\mathrm{mol}} \mathcal{E})}_{\text{rotational saturation}} + \alpha_{\mathrm{pol}}\right] \mathcal{E}(r)$$

$$\frac{\delta \bar{A}_{\mathrm{diel}}(r)}{\delta \mathbf{p}_{\mathrm{pol}}(r)} = 0$$

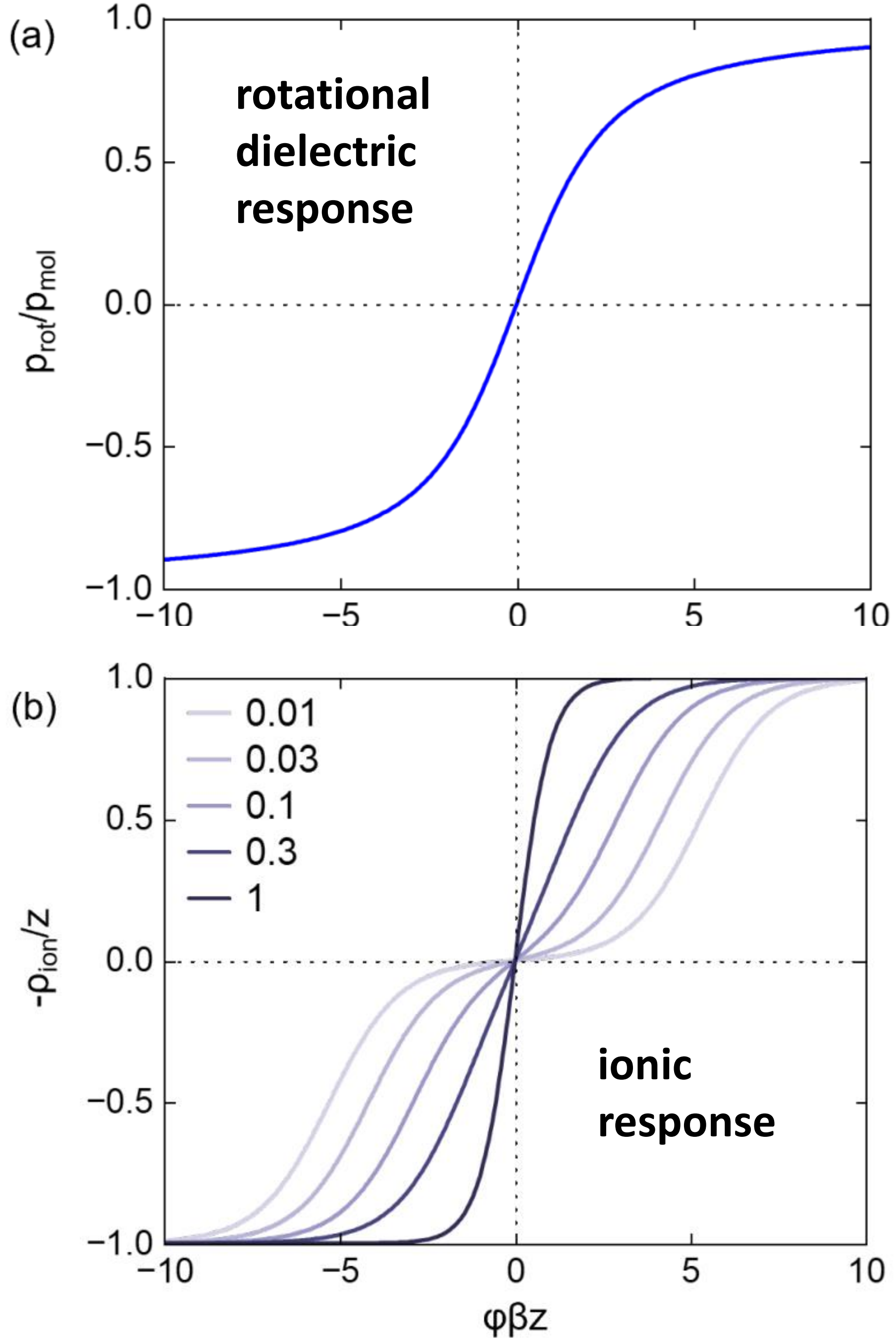
local electric field

$$\mathcal{E}(r) = -(w_b * \boldsymbol{\nabla}\phi)(r) + \frac{4\pi}{\epsilon_0 \alpha_{\mathrm{sic}}} \mathbf{p}(r)$$

ionic response:

$$\frac{\delta \bar{A}_{\mathrm{ion}}(r)}{\delta \theta_i(r)} = 0$$

$$\bar{\rho}_{\mathrm{ion}}(r) = -\frac{\epsilon_0}{4\pi} \alpha_{\mathrm{ion}}^{\mathrm{b}} \underbrace{g_{\mathrm{ion}}(\beta z \boldsymbol{\phi})}_{\text{ionic enhancement and saturation}} \boldsymbol{\phi}(r)$$



Nonlinear Poisson-Boltzmann equation

$$\frac{\delta A_{\mathrm{tot}}}{\delta \phi(r)} = \frac{\delta A_{\mathrm{KS}}}{\delta \phi(r)} + \frac{\delta A_{\mathrm{diel}}}{\delta \phi(r)} + \frac{\delta A_{\mathrm{ion}}}{\delta \phi(r)} = 0$$

Total free energy is maximized w.r.t. the electrostatic potential

Nonlinear Poisson-Boltzmann equation (solve for ϕ)

$$\underbrace{-\frac{\epsilon_0}{4\pi}\nabla^2\phi(r) = \rho_{\mathrm{sol}}(r)}_{\text{From } A_{\mathrm{KS}}} + \underbrace{\underbrace{n_{\mathrm{mol}}[-w_b * \nabla\cdot(S_{\mathrm{diel}}\,\mathbf{p})](r)}_{\text{bound charge density, } \rho_{\mathrm{b}}} + \underbrace{n_{\mathrm{max}} S_{\mathrm{ion}}(r)\bar{\rho}_{\mathrm{ion}}(r)}_{\text{ionic charge density, } \rho_{\mathrm{ion}}}}_{\text{nonlinear in } \phi(r)}$$

Linearized Poisson-Boltzmann equation

$$\frac{\delta A_{\text{tot}}}{\delta \phi(r)} = \frac{\delta A_{\text{KS}}}{\delta \phi(r)} + \frac{\delta A_{\text{diel}}}{\delta \phi(r)} + \frac{\delta A_{\text{ion}}}{\delta \phi(r)} = 0$$

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Nonlinear Poisson-Boltzmann equation (solve for ϕ)

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Linearization around ϕ

$$\rho_{\text{b}}\{\phi + \Delta\phi\} \approx \rho_{\text{b}}\{\phi\} + \frac{\epsilon_0}{4\pi} \nabla \cdot \left[w_b * \chi\{\phi\} \cdot \left(w_b * \nabla(\Delta\phi) \right) \right]$$

dielectric susceptibility tensor

$$\rho_{\text{ion}}\{\phi + \Delta\phi\} = \rho_{\text{ion}}\{\phi\} - \frac{\epsilon_0}{4\pi} \epsilon_b \kappa^2\{\phi\} \Delta\phi$$

effective inverse Debye length

Linearized Poisson-Boltzmann equation

$$\underbrace{-\frac{\epsilon_0}{4\pi}\left[\nabla\cdot\boldsymbol{\epsilon}_{\mathbf{r}}\{\phi\}\cdot\nabla-\boldsymbol{\epsilon}_{\boldsymbol{b}}\boldsymbol{\kappa}^{\mathbf{2}}\{\phi\}\right]}_{\text{Linearized Poisson-Boltzmann operator, } \hat{L}_{\mathrm{LPB}}\{\phi\}}\boldsymbol{\Delta\phi}=\underbrace{\boldsymbol{\rho}_{\mathbf{sol}}+\boldsymbol{\rho}_{\mathbf{b}}\{\phi\}+\boldsymbol{\rho}_{\mathbf{ion}}\{\phi\}+\frac{\epsilon_0}{4\pi}\nabla^2\boldsymbol{\phi}}_{\text{NLPB Residual, } R}$$

effective dielectric tensor

$$\boldsymbol{\epsilon}_{\mathbf{r}}\{\phi\}=1+w_b*\boldsymbol{\chi}\{\phi\}\cdot w_b*$$

Linearization around $\boldsymbol{\phi}$

$$\boldsymbol{\rho}_{\mathbf{b}}\{\phi+\Delta\phi\}\approx\boldsymbol{\rho}_{\mathbf{b}}\{\phi\}+\frac{\epsilon_0}{4\pi}\nabla\cdot\left[w_b*\boldsymbol{\chi}\{\phi\}\cdot\left(w_b*\nabla(\Delta\phi)\right)\right]$$

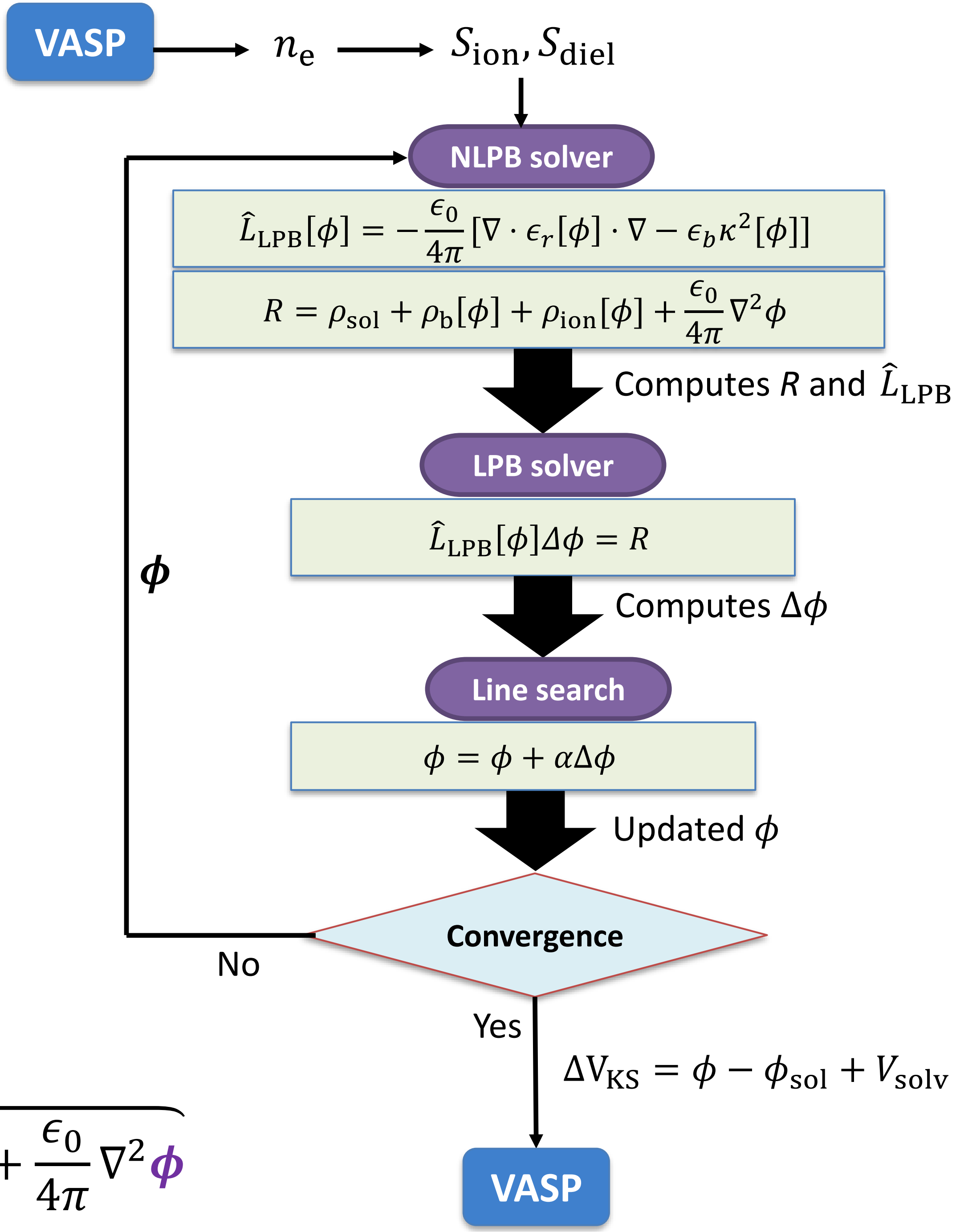
dielectric susceptibility tensor

$$\boldsymbol{\rho}_{\mathbf{ion}}\{\phi+\Delta\phi\}=\boldsymbol{\rho}_{\mathbf{ion}}\{\phi\}-\frac{\epsilon_0}{4\pi}\boldsymbol{\epsilon}_{\boldsymbol{b}}\boldsymbol{\kappa}^{\mathbf{2}}\{\phi\}\boldsymbol{\Delta\phi}$$

effective inverse Debye length

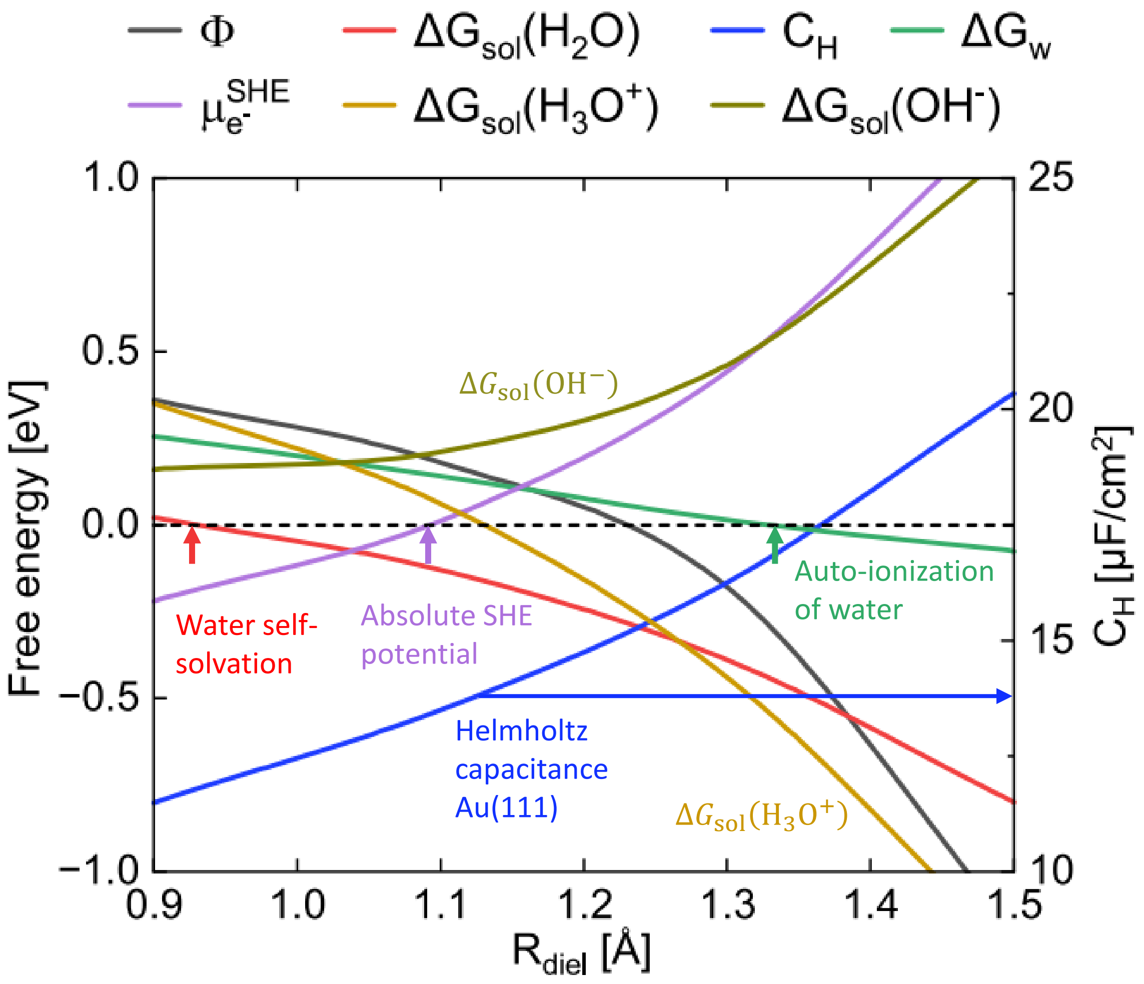
Implementation in VASP

- **Newton solver** to solve the NLPB equation (from Ringe et al.)
- Linearized PB equation solved using **preconditioned conjugate gradient** algorithm (as in original VASPsol)
- **Backtracking line search** to take care of the pathological form of the dielectric and ionic response functions (new addition)



$$\overbrace{-\frac{\epsilon_0}{4\pi}\left[\nabla \cdot \epsilon_{\mathrm{r}}\{\phi\} \cdot \nabla - \epsilon_b \kappa^2\{\phi\}\right]}^{\text{Linearized Poisson-Boltzmann operator, } \hat{L}_{\mathrm{LPB}}\{\phi\}}\Delta\phi = \overbrace{\rho_{\mathrm{sol}} + \rho_{\mathrm{b}}\{\phi\} + \rho_{\mathrm{ion}}\{\phi\} + \frac{\epsilon_0}{4\pi}\nabla^2\phi}^{\text{NLPB Residual, } R}$$

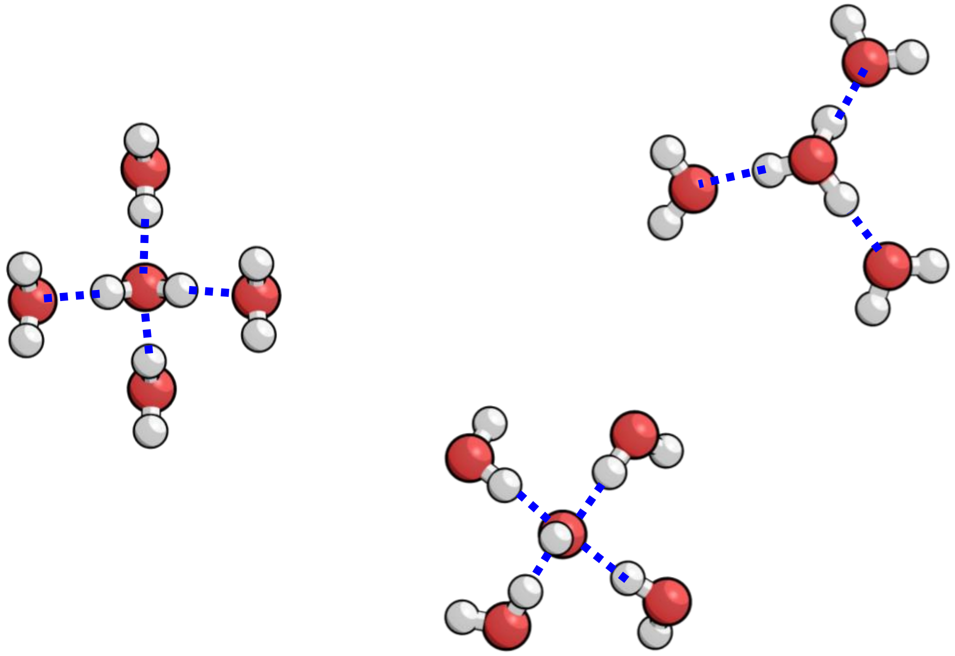
Important properties for electrocatalysis



Increasing dielectric radius …
- solvates H_3O^+ stronger
- solvates OH^- weaker

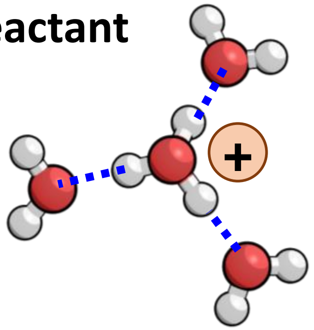
… compared to H_2O

Possibly due to bound charge penetration (even seen on alkanes)



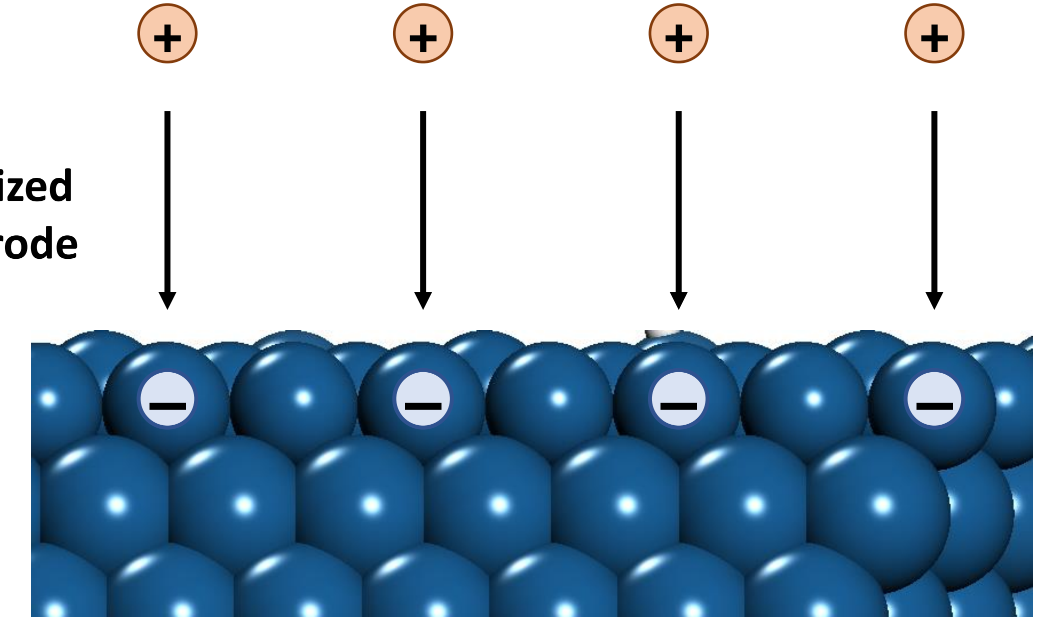
Framework for computing kinetic barriers of electrocatalytic reaction steps

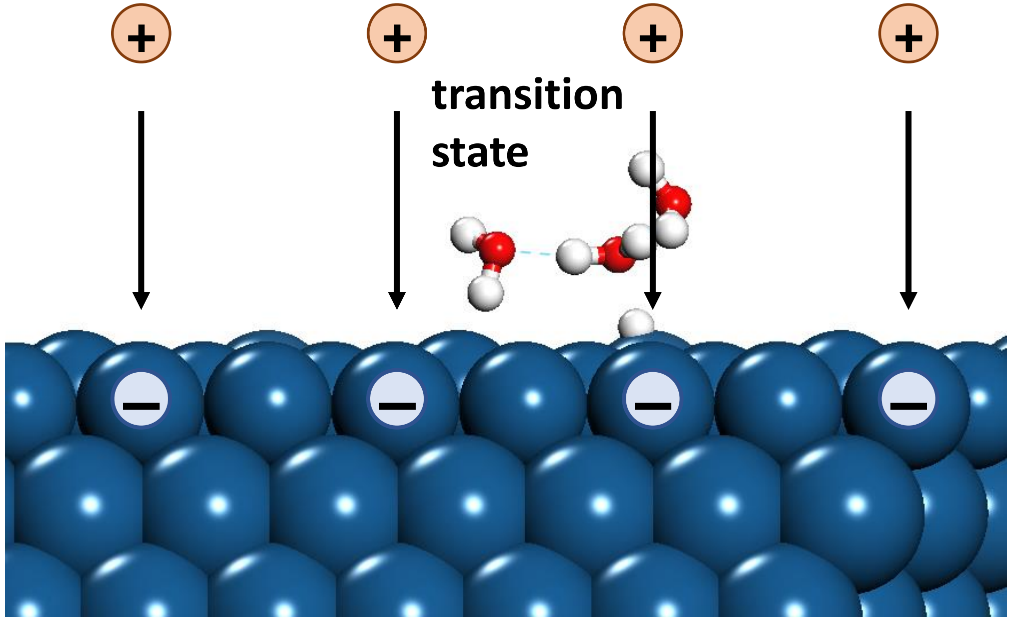
solvated reactant



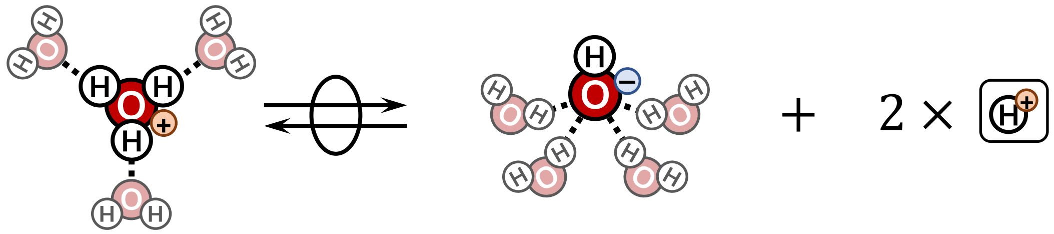
- Implicit electrolyte model takes care of the electric field at the interface and long-range electrostatic screening of charged species in the electrolyte
- Implicit electrolyte cannot accurately represent strong H-bonds that stabilize charged species like H_3O^+ and OH^-
  - This requires explicit water molecules (thermodynamic nightmare)

polarized electrode

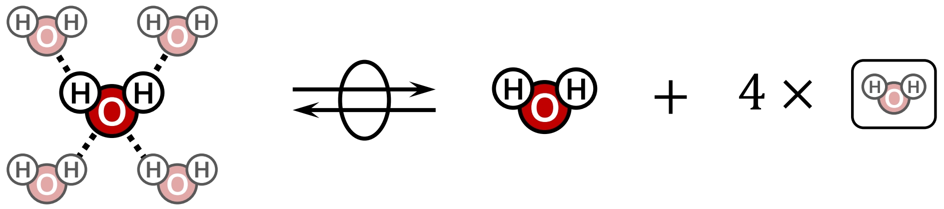




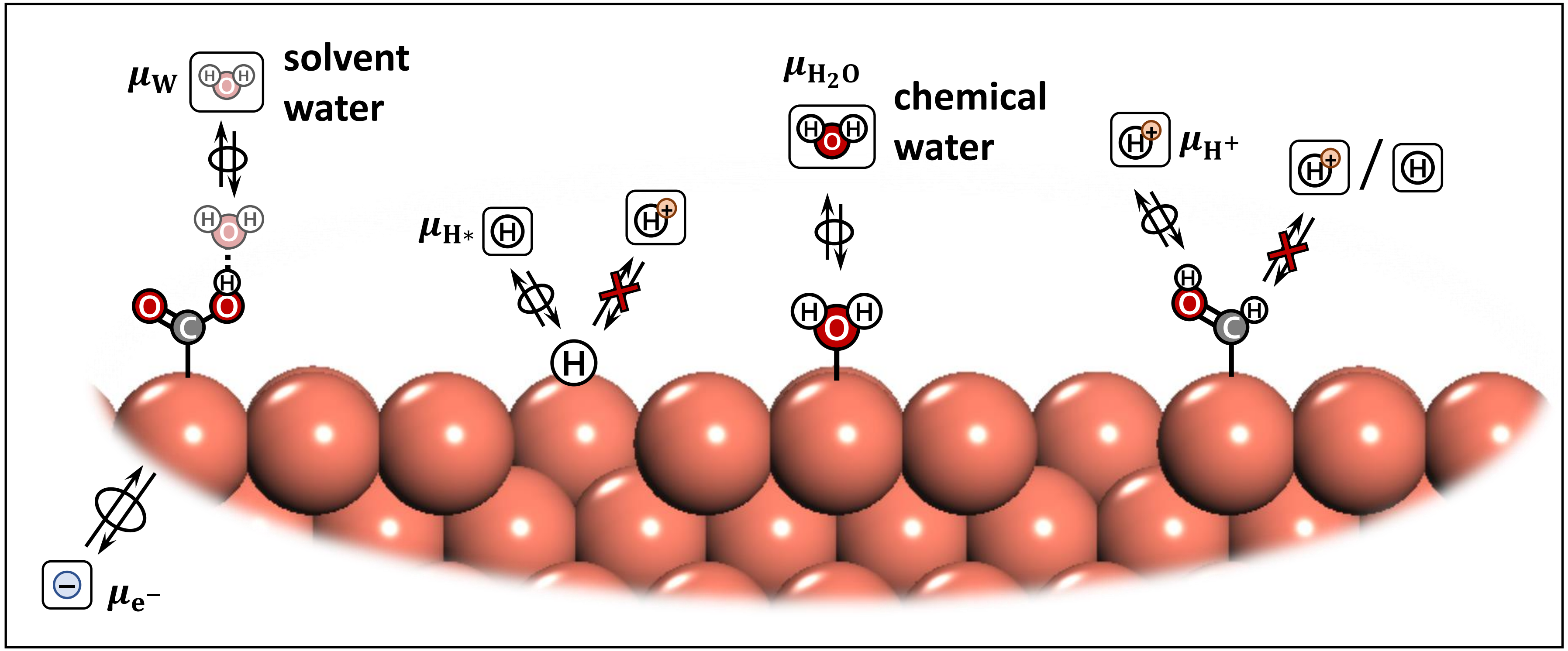
Superbasins and reservoirs in the grand canonical formalism

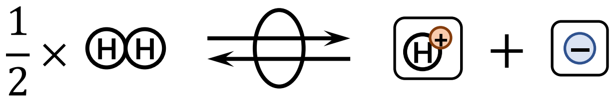


$$\boldsymbol{\mu}_{\mathbf{H}^+} = \frac{1}{2}\left[G^\circ(\mathrm{H_3O^+}) - G^\circ(\mathrm{OH^-})\right] - k_\mathrm{B}T \ln 10 \times \mathbf{pH}$$



$$\boldsymbol{\mu}_{\mathbf{W}} = \frac{1}{4}\left[G^\circ(\mathrm{H_2O}) - \boldsymbol{\mu}_{\mathbf{H_2O}}\right]$$





$$\boldsymbol{\mu}_{\mathbf{H^+/e^-}} = \frac{1}{2}G^\circ(\mathrm{H_2}) - e\boldsymbol{U}_{\mathbf{RHE}}$$

$$\boldsymbol{\mu}_{\mathbf{e^-}} = \mu_{\mathrm{H^+/e^-}} - \mu_{\mathrm{H^+}}$$

Free energy diagrams in the grand canonical formalism

$$\Omega = \Omega_{\mathrm{SCF}} + E_{\mathrm{ZPVE}} + G_{\mathrm{vib}} + n_{\mathrm{H^+/e^-}}\mu_{\mathrm{H^+/e^-}} - n_{\mathrm{H*}}\mu_{\mathrm{H*}} - n_{\mathrm{W}}\mu_{\mathrm{W}}$$

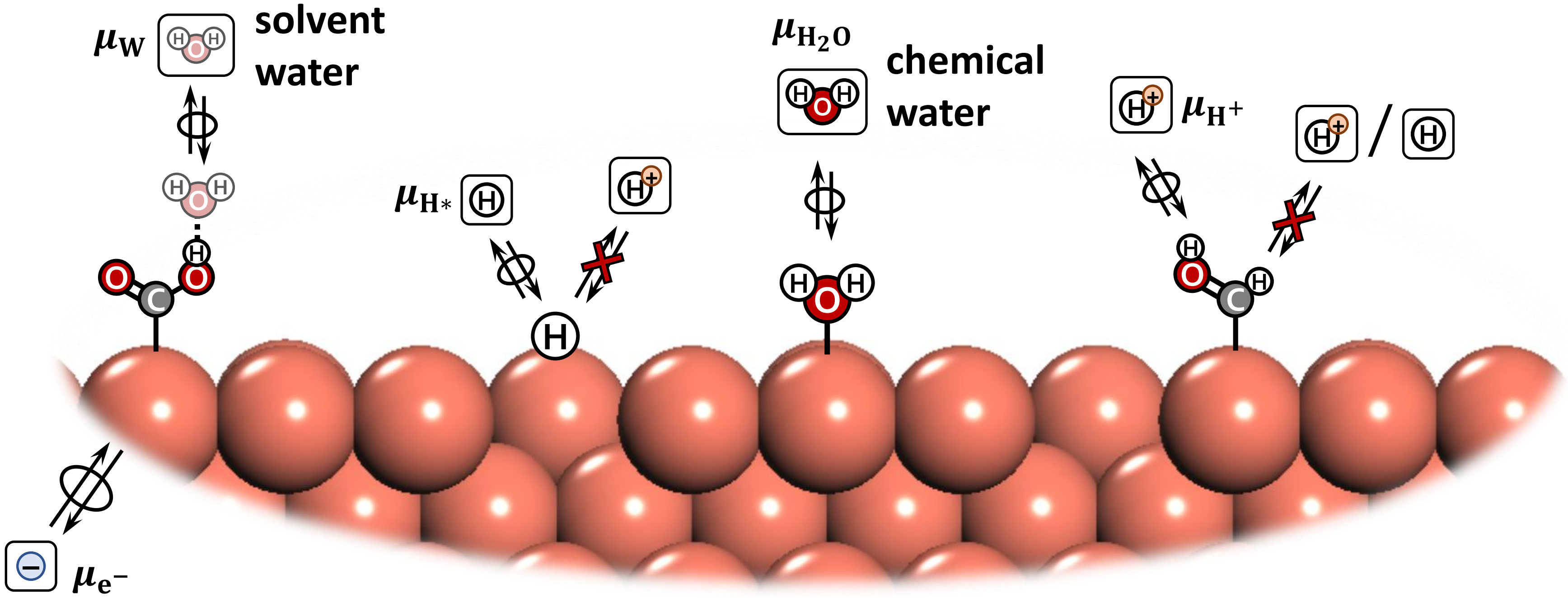
Free energy of a state

$$\Omega_{\mathrm{SCF}} = A_{\mathrm{SCF}} - q\mu_{\mathrm{e}}^{-}$$

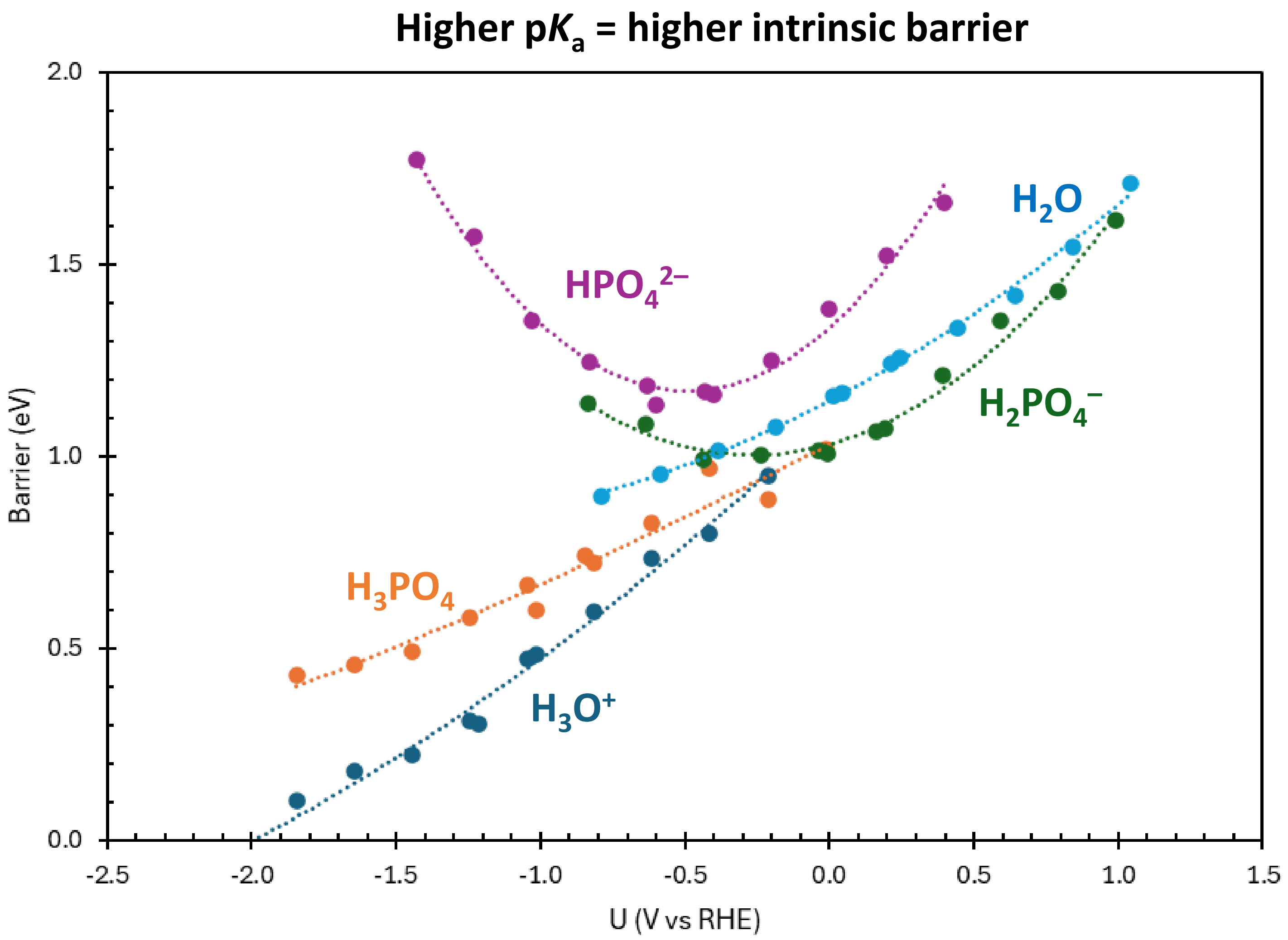
VASPsol++ GC-DFT free energy

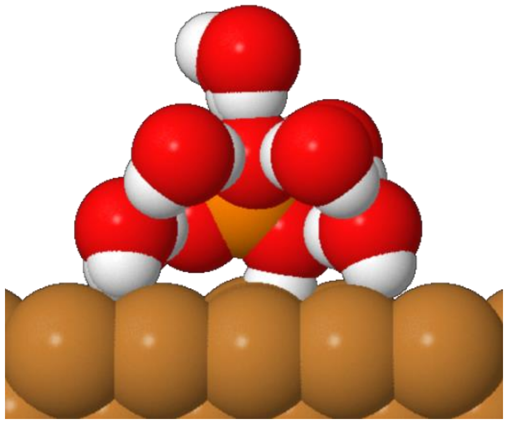
Chemical potential of intermediate $\mathbf{S}_i$

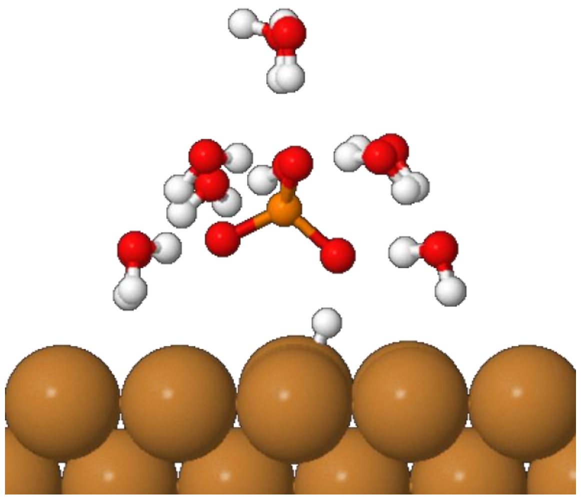
$$\mu_{\mathrm{S}_i}^{\circ} = \Omega_{\mathrm{S}_i} - \Omega_{\mathrm{ref}} - \sum_k n_{\mathrm{A}_k}^{i}\mu_{\mathrm{A}_k}$$



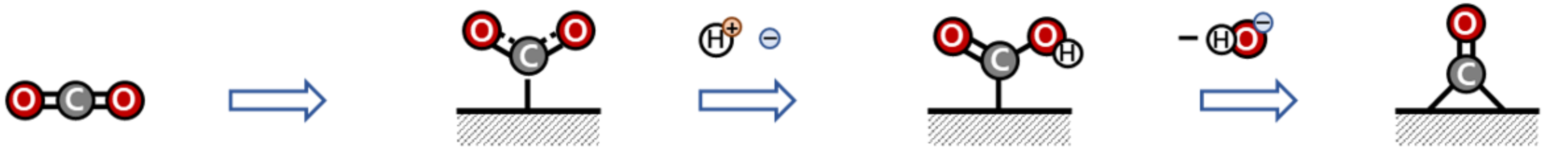
Electrochemical barriers for the Volmer step on Cu(100)





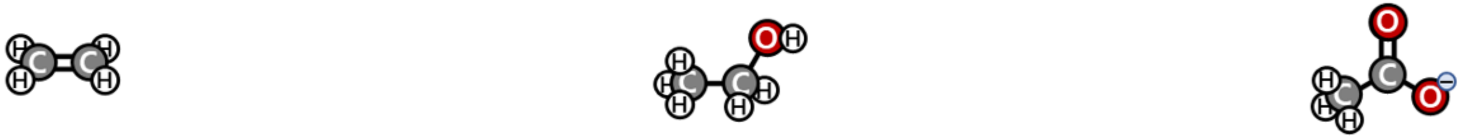


Application to electrocatalytic CO_2 reduction on Cu(100)



What controls the selectivity
to different C2 products?

71 TS calculations
37 intermediates



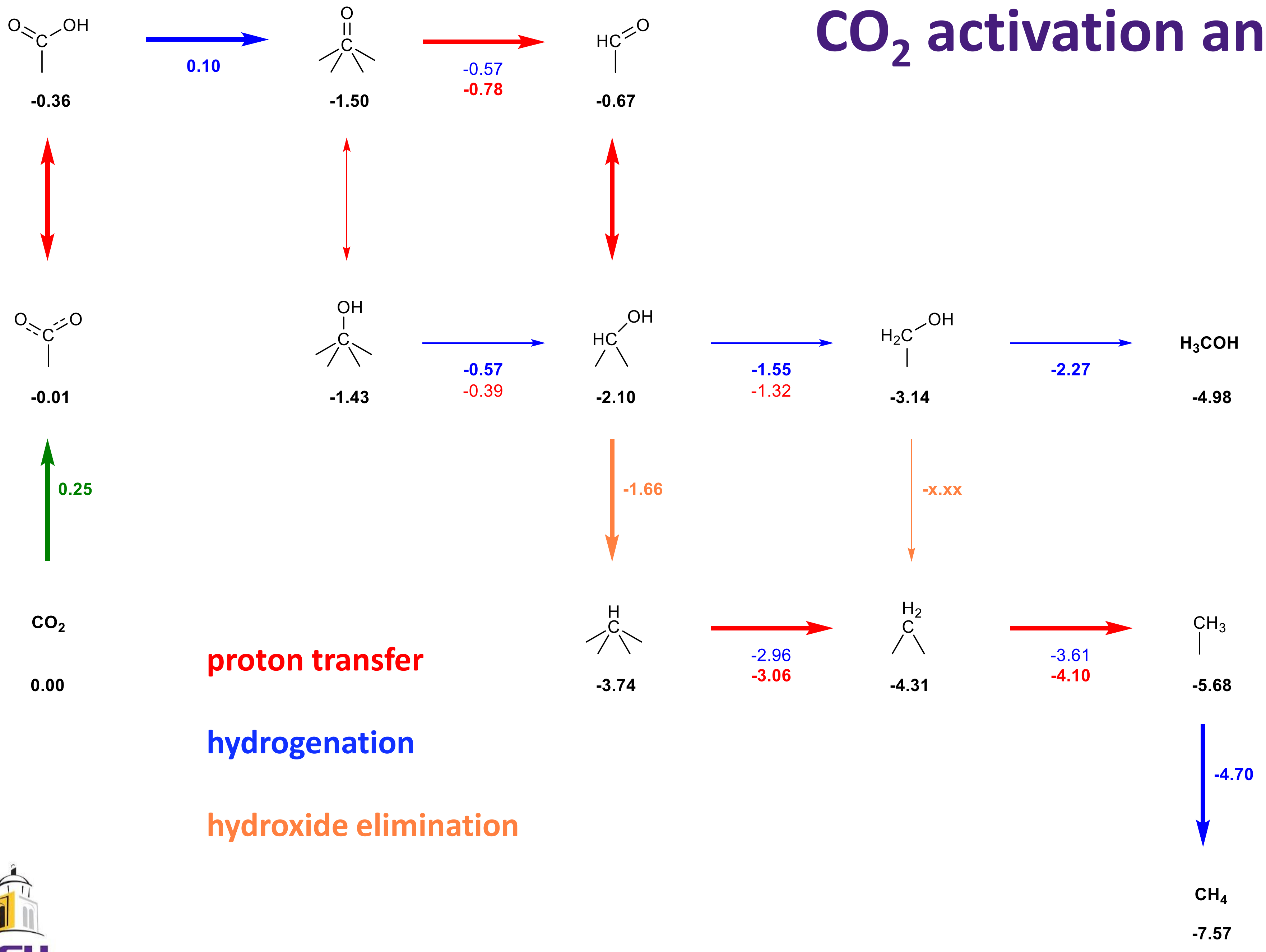
Ethylene

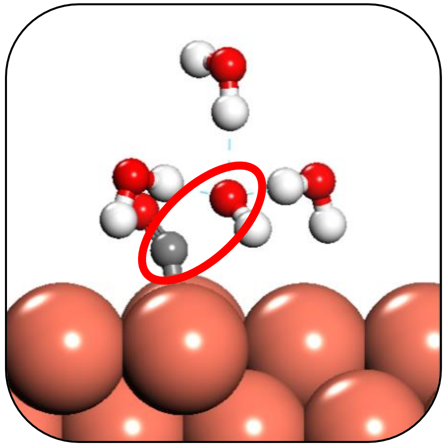
Ethanol

Acetate

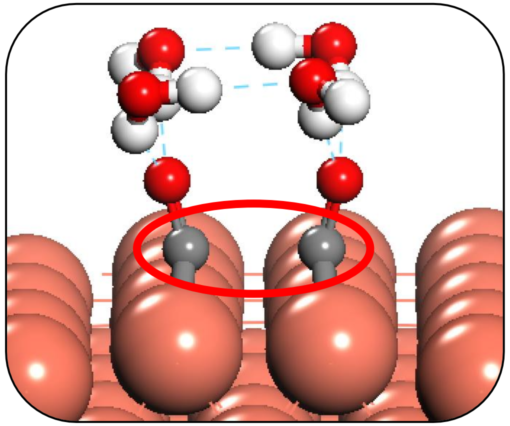
Increasing CO coverage

CO_2 activation and C_1 pathways

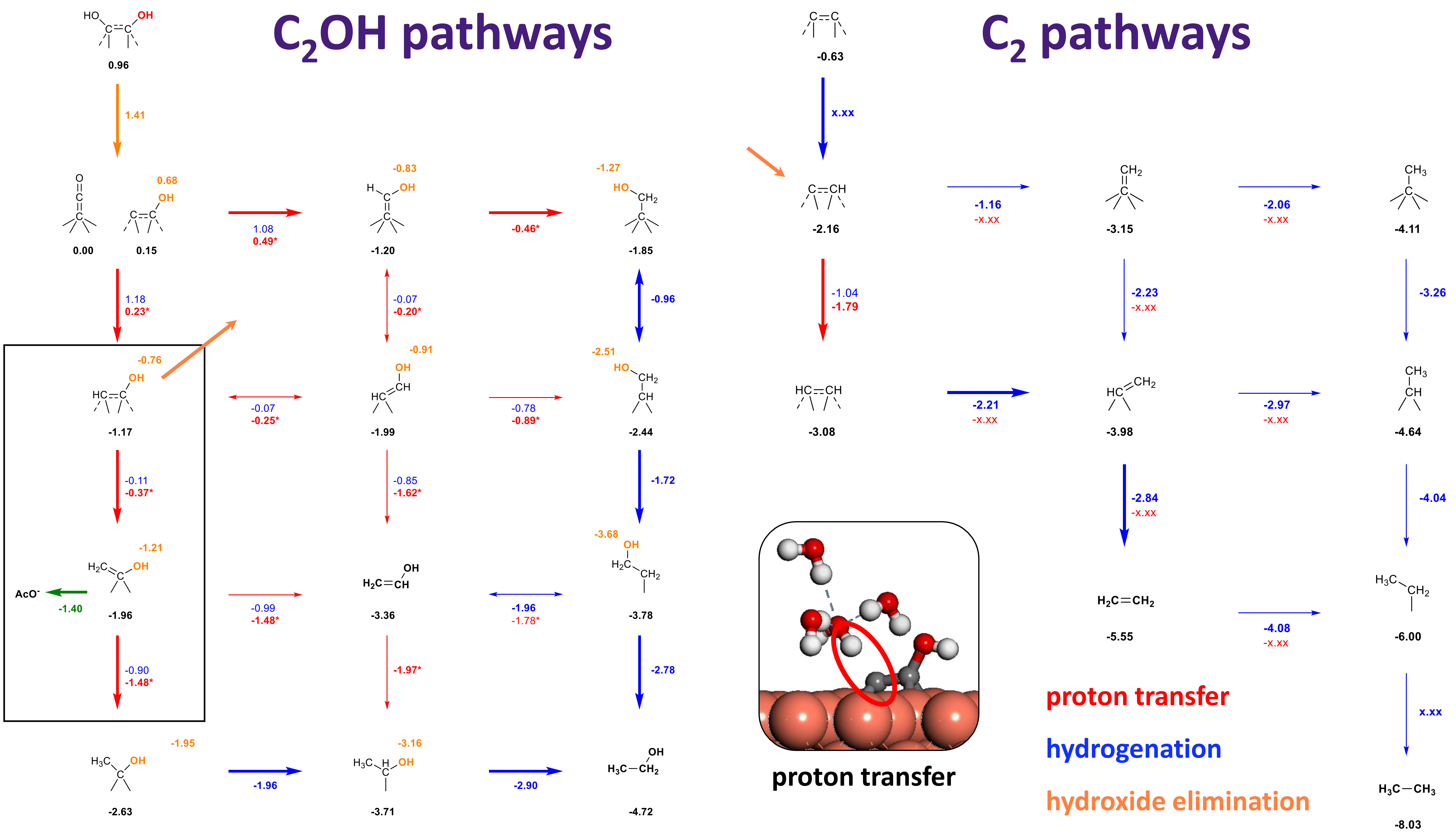




OH^- elimination



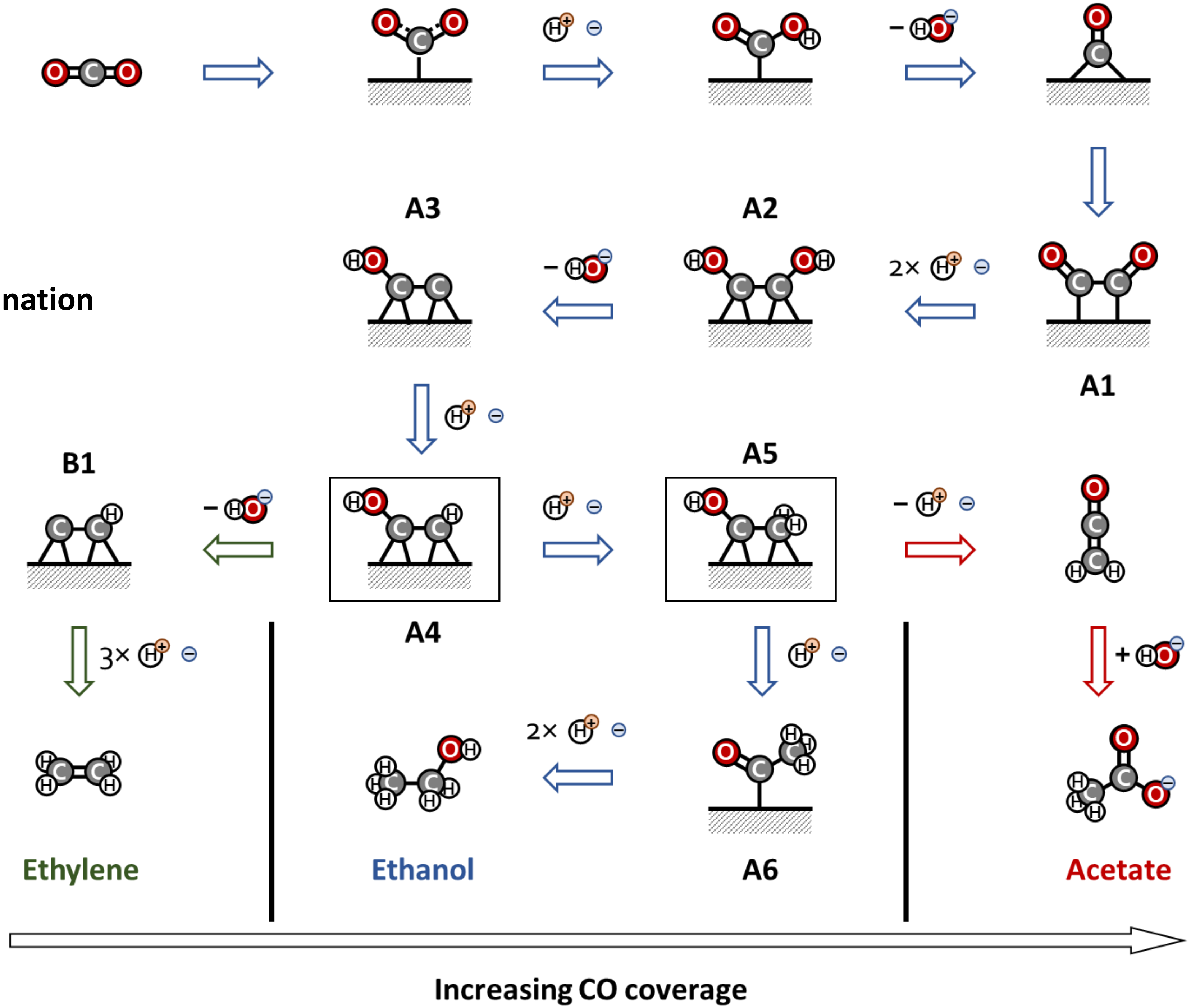
CO dimerization



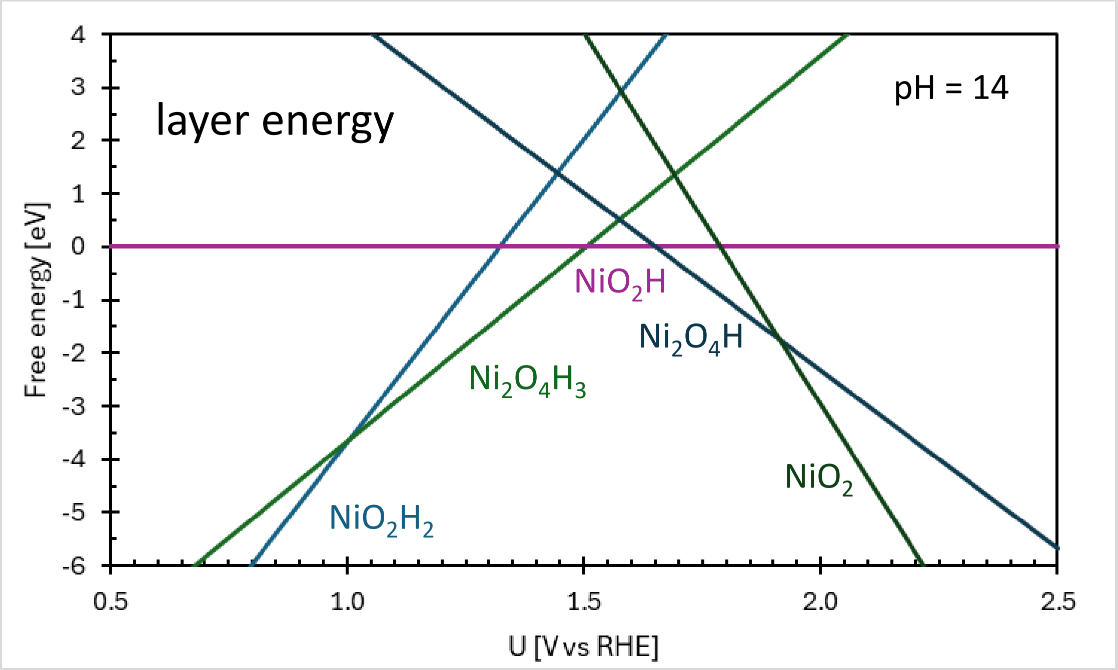
C_2OH pathways
C_2 pathways
0.96
1.41
0.00
0.68
0.15
1.08
0.49*
-0.83
-1.20
-0.46*
-1.27
-1.85
1.18
0.23*
-0.07
-0.20*
-0.96
-0.76
-1.17
-0.07
-0.25*
-0.91
-1.99
-0.78
-0.89*
-2.51
-2.44
-0.11
-0.37*
-0.85
-1.62*
-1.72
-1.21
AcO⁻
-1.40
-1.96
-0.99
-1.48*
-3.36
-1.96
-1.78*
-3.68
-3.78
-0.90
-1.48*
-1.97*
-2.78
-1.95
-2.63
-1.96
-3.16
-3.71
-2.90
-4.72
-0.63
x.xx
-2.16
-1.16
-x.xx
-3.15
-2.06
-x.xx
-4.11
-1.04
-1.79
-2.23
-x.xx
-3.26
-3.08
-2.21
-x.xx
-3.98
-2.97
-x.xx
-4.64
-2.84
-x.xx
-4.04
-5.55
-4.08
-x.xx
-6.00
x.xx
-8.03
proton transfer
proton transfer
hydrogenation
hydroxide elimination

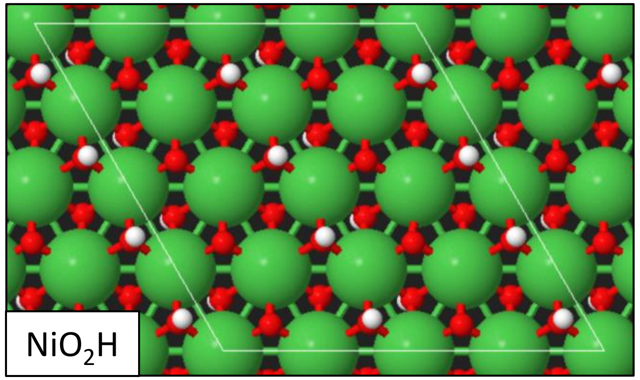
Selectivity determining steps

CO coverage suppresses OH elimination relative to C-H bond formation

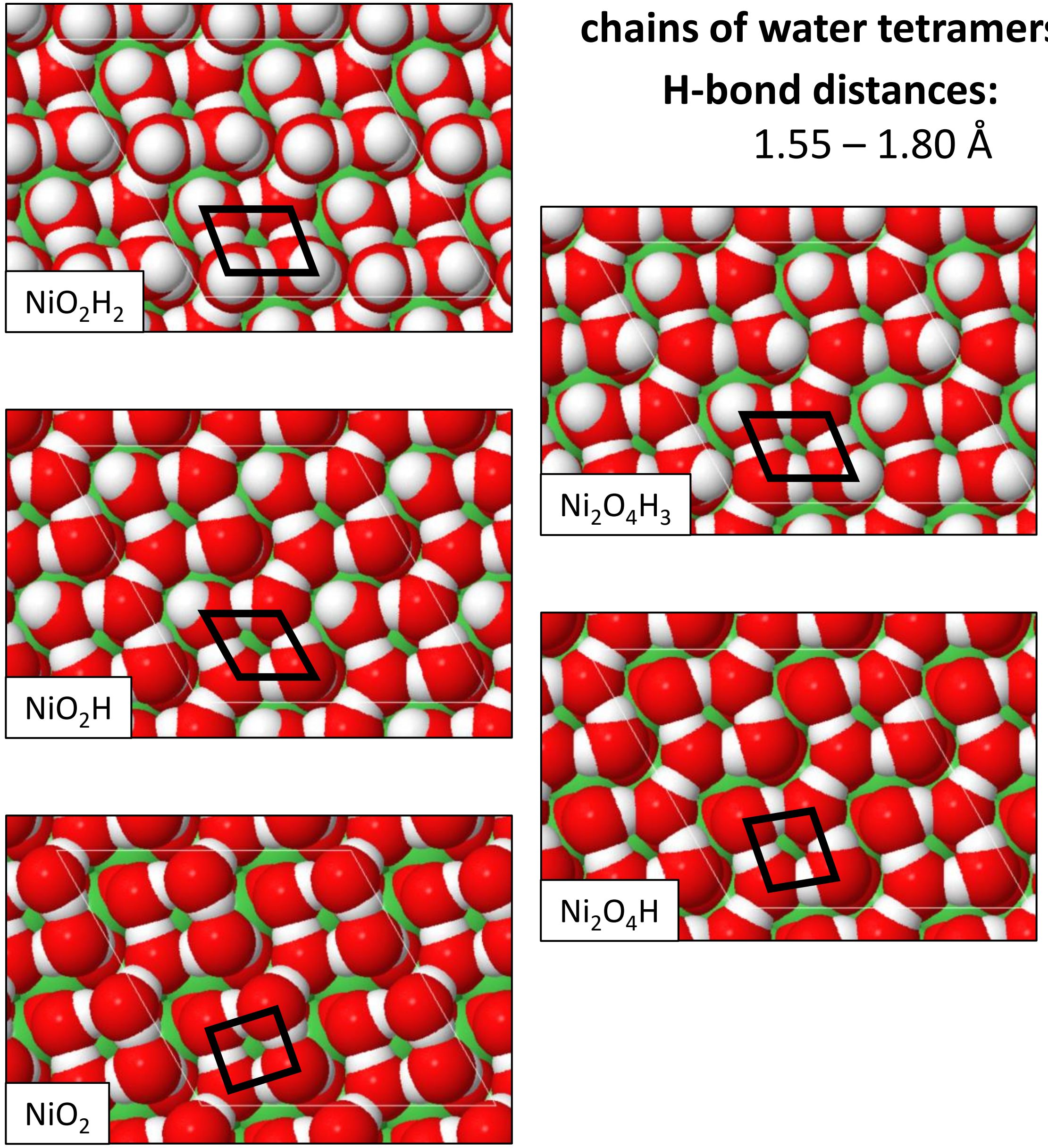


Thermodynamics of layered oxyhydroxides (NiO_xH_y)





explicit water

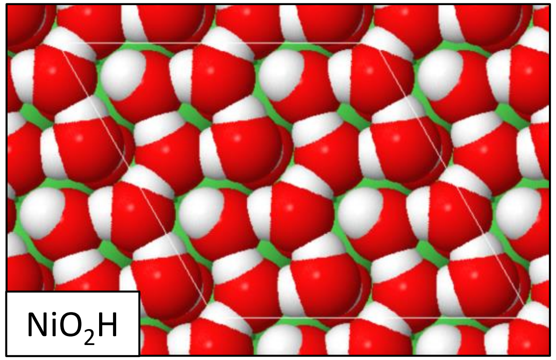


chains of water tetramers

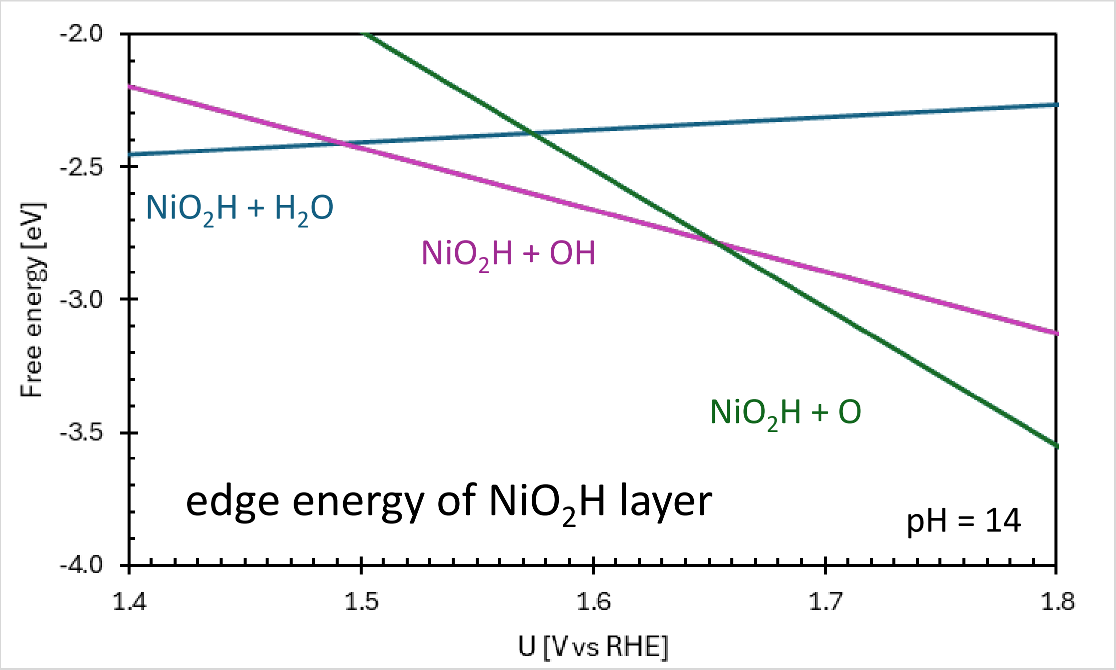
H-bond distances:

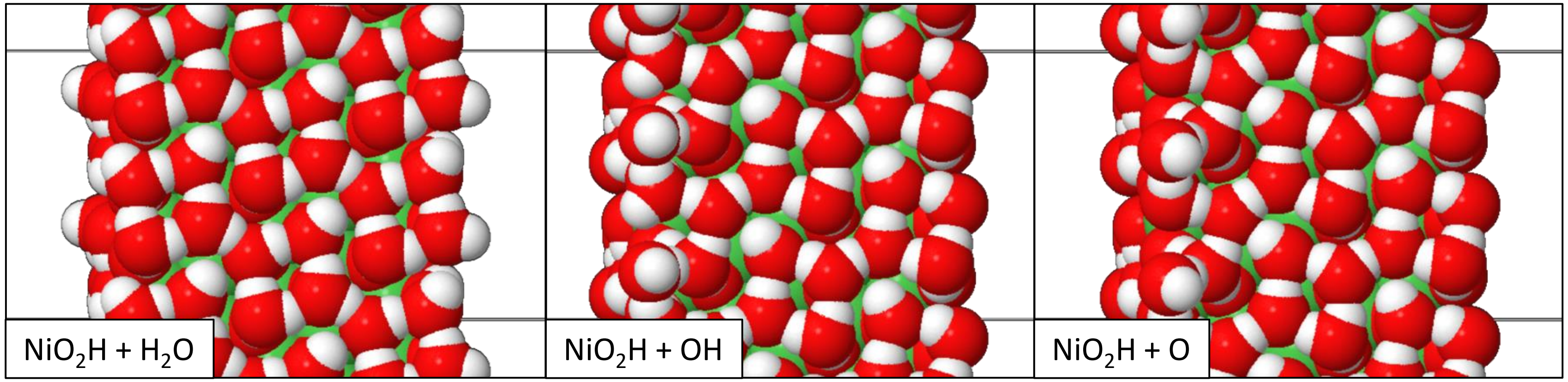
1.55 – 1.80 Å

Thermodynamics of layered oxyhydroxides (NiO_xH_y)



cleave edge



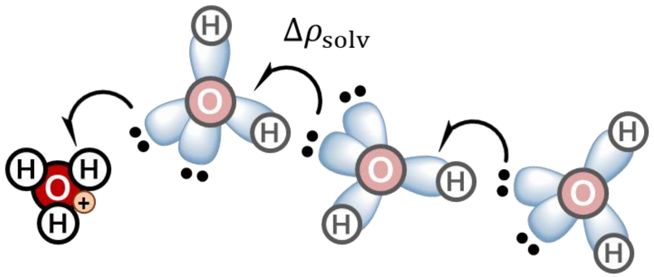


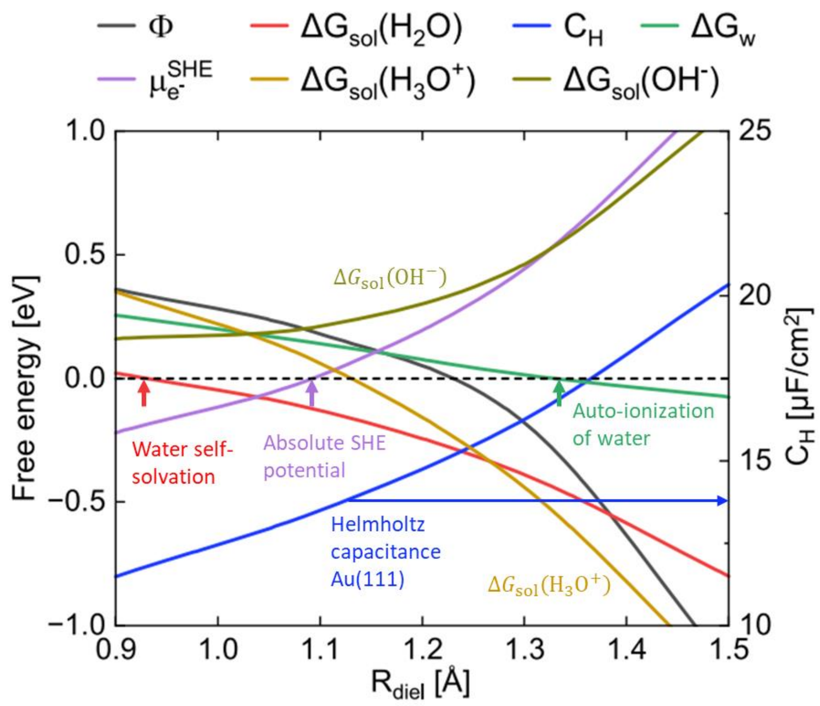
The Future

The Implicit Quantum Electrolyte

Water is more than just a dielectric

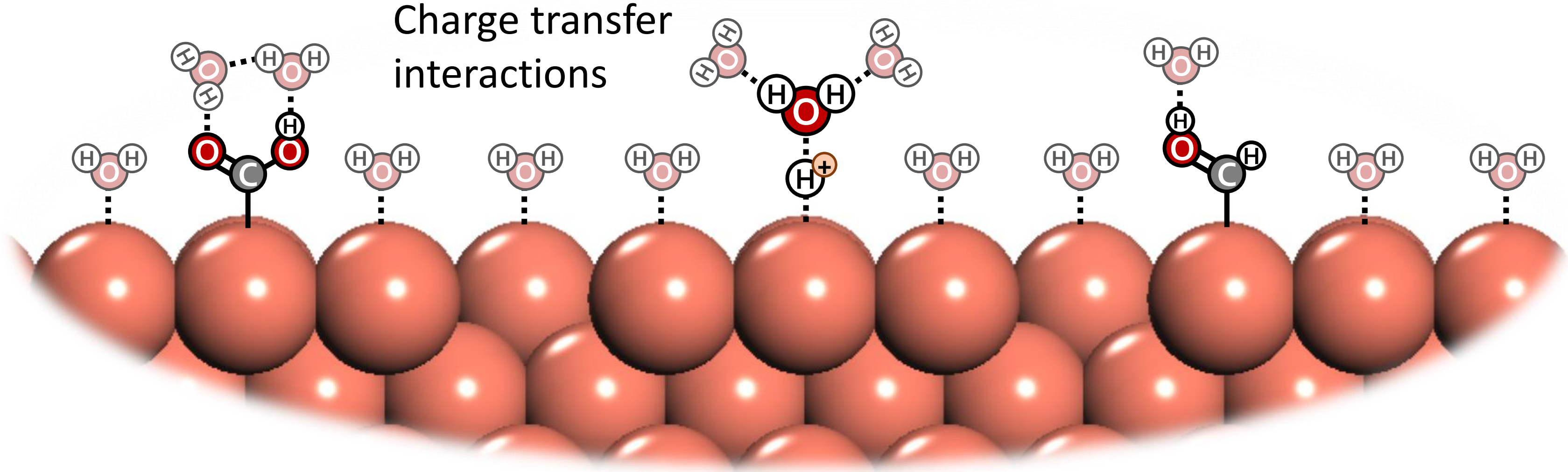
Charge transfer through H-bond networks

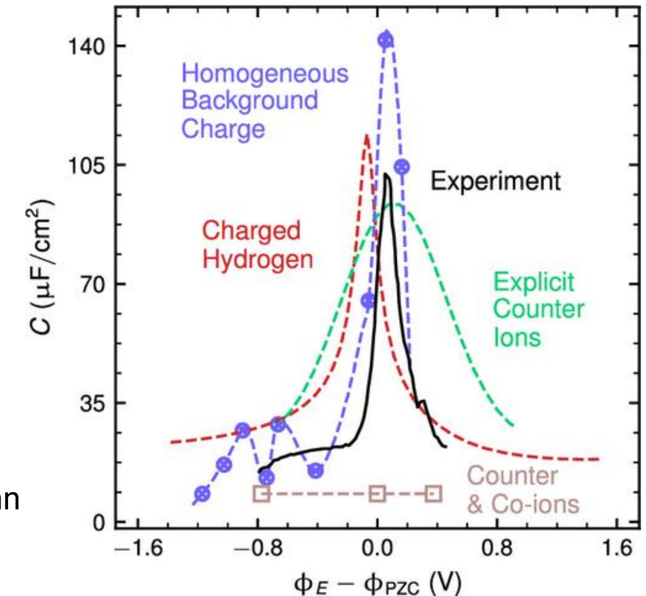




Hydrogen bonding

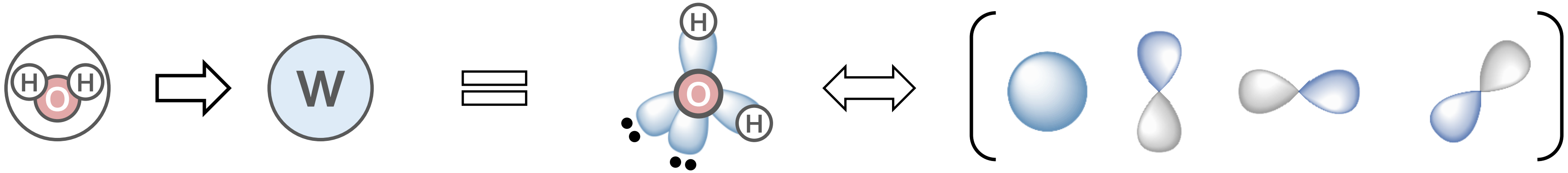
Charge transfer interactions





Lang Li, Karsten Reuter, and Nicolas G. Hörmann
ACS Electrochemistry **2025** *1* (2), 186-194

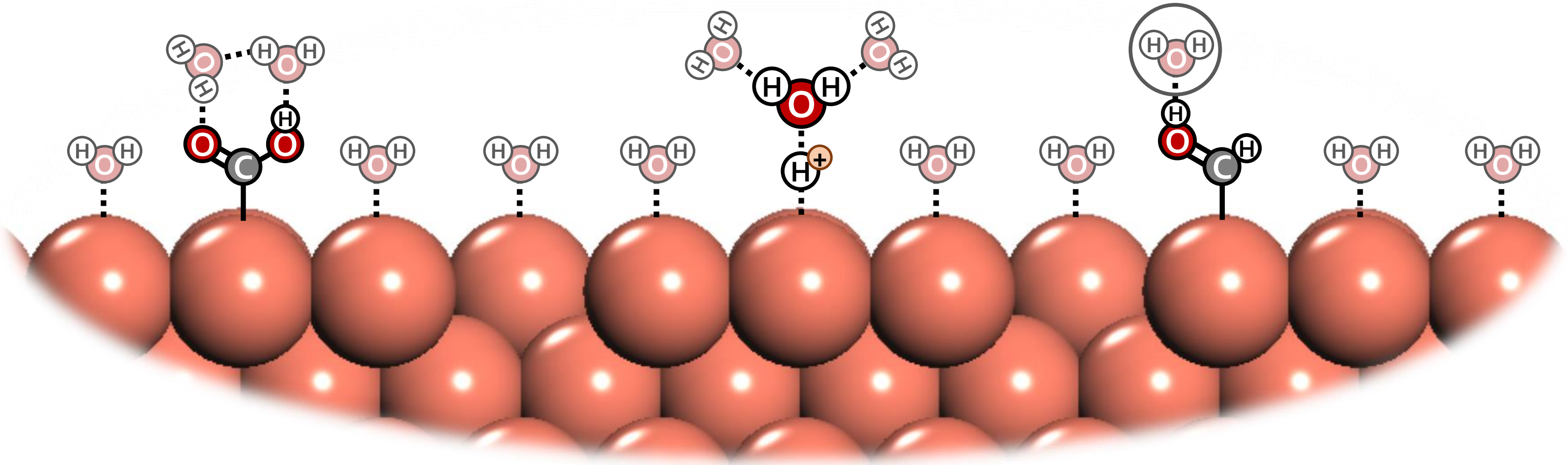
A tight binding model of water



“spherical” water

TB orbitals

Spherical harmonic basis



Analogous to “PAW” water

Single solvation site

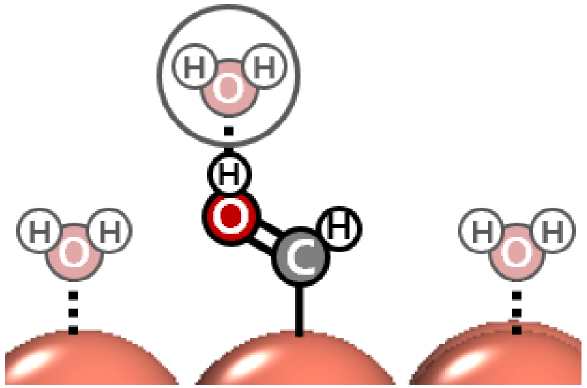
explicit

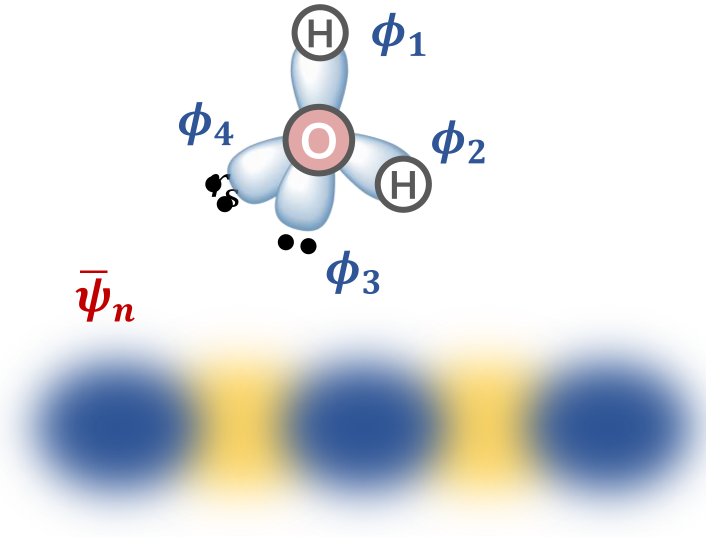
implicit TB

$$\psi_n(\mathbf{r}) = \frac{1}{\sqrt{1+A_n}}\left[\overline{\psi}_n(\mathbf{r}) + \sum_{\mu} c_{\mu n}\,\phi_\mu(\mathbf{r}-\mathbf{r}_s)\right]$$

On-site density matrix

$$P_{\mu\nu} = \sum_n \frac{f_n}{1+A_n}\, c^*_{\mu n}\, c_{\nu n}$$





$$n_{\mathrm{e}}^{(n)}(\mathbf{r}) = \frac{1}{1+A_n}\left[\overline{\psi}^*_n(\mathbf{r})\overline{\psi}_n(\mathbf{r}) + \sum_{\mu} c_{\mu n}\phi^*_\mu(\mathbf{r}-\mathbf{r}_s)\overline{\psi}_n(\mathbf{r}) + \text{c.c.} + \sum_{\mu,\nu} c^*_{\mu n}c_{\nu n}\phi^*_\mu(\mathbf{r}-\mathbf{r}_s)\phi_\nu(\mathbf{r}-\mathbf{r}_s)\right]$$

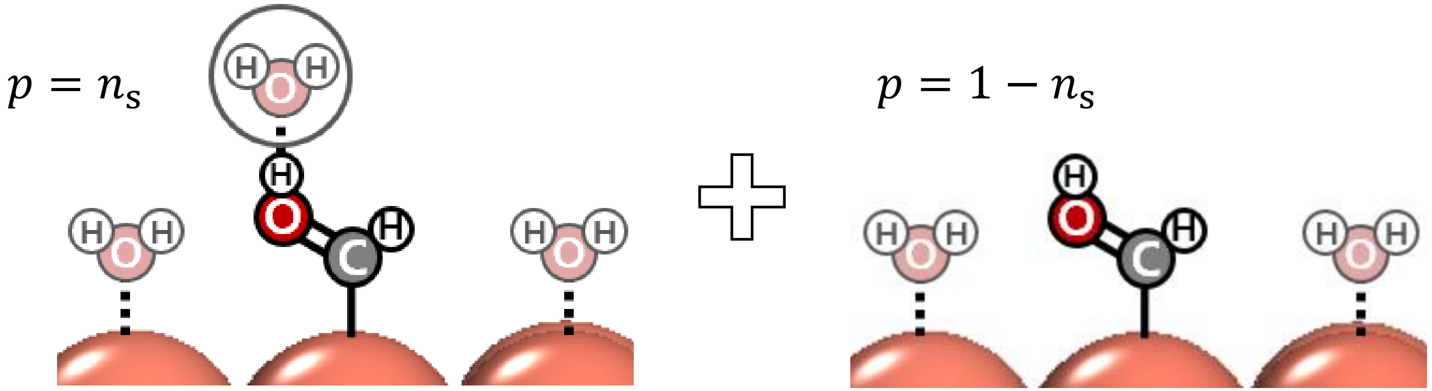
interference

$$\varepsilon^0_n = \frac{1}{1+A_n}\left[\langle\overline{\psi}_n|\widehat{H}^0_{\mathrm{KS}}|\overline{\psi}_n\rangle + \sum_{\mu} c_{\mu n}\langle\phi_\mu(\mathbf{r}-\mathbf{r}_s)|\widehat{H}^0_{\mathrm{KS}}|\overline{\psi}_n\rangle + \text{c.c.} + \sum_{\mu,\nu} c^*_{\mu n}c_{\nu n}\langle\phi_\mu(\mathbf{r}-\mathbf{r}_s)|\widehat{H}^0_{\mathrm{KS}}|\phi_\nu(\mathbf{r}-\mathbf{r}_s)\rangle\right]$$

$$E = \sum_n f_n\varepsilon^0_n + E_{\mathrm{H}}[\rho] + E_{\mathrm{xc}}[n_{\mathrm{e}}] - E_{\mathrm{H}}[\widetilde{\rho}] - E_{\mathrm{xc}}[\widetilde{n}_{\mathrm{e}}] + \sum_{\mu\nu} P_{\mu\nu}h^{\mathrm{s},0}_{\mu\nu} + \frac{1}{2}\sum_{\mu\nu\alpha\beta} P_{\mu\nu}W_{\mu\nu,\alpha\beta}P_{\alpha\beta}$$

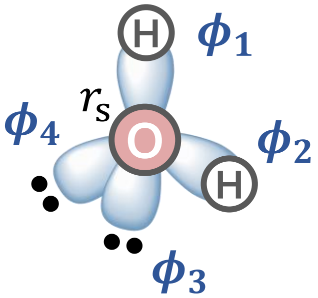
on-site correction

Single solvation site with statistical occupancy



$$P_{\mu\nu} = \sum_n \frac{f_n}{1 + n_s A_n} c^*_{\mu n}\, c_{\nu n}$$

$$n_{\mathrm{e}}^{(n)}(\mathbf{r}) = \frac{1}{1 + n_s A_n}\left[\overline{\psi}^*_n(\mathbf{r})\overline{\psi}_n(\mathbf{r}) + n_s \underbrace{\left[\sum_\mu c_{\mu n}\phi^*_\mu(\mathbf{r}-\mathbf{r}_s)\overline{\psi}_n(\mathbf{r}) + \mathrm{c.c.} + \sum_{\mu,\nu} c^*_{\mu n} c_{\nu n}\phi^*_\mu(\mathbf{r}-\mathbf{r}_s)\phi_\nu(\mathbf{r}-\mathbf{r}_s)\right]}_{\Delta n_{\mathrm{e}}^{(n)}(\mathbf{r})}\right]$$

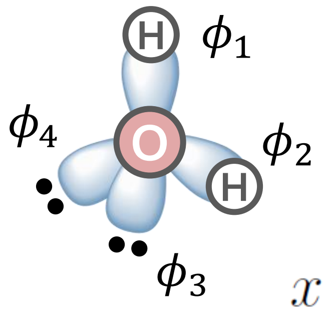


$$\varepsilon_n^0 = \frac{1}{1 + n_s A_n}\left[\langle\overline{\psi}_n|\widehat{H}^0_{\mathrm{KS}}|\overline{\psi}_n\rangle + n_s \underbrace{\left[\sum_\mu c_{\mu n}\langle\phi_\mu|\widehat{H}^0_{\mathrm{KS}}|\overline{\psi}_n\rangle + \mathrm{c.c.} + \sum_{\mu,\nu} c^*_{\mu n} c_{\nu n}\langle\phi_\mu|\widehat{H}^0_{\mathrm{KS}}|\phi_\nu\rangle\right]}_{\Delta\varepsilon_n^0}\right]$$

$\overline{\psi}_n$

$$E = \sum_n f_n \varepsilon_n^0 + E_{\mathrm{H}}[\rho] + E_{\mathrm{xc}}[n_{\mathrm{e}}] - E_{\mathrm{H}}[\widetilde{\rho}] - E_{\mathrm{xc}}[\widetilde{n}_{\mathrm{e}}] + n_s \underbrace{\left[\sum_{\mu\nu} P_{\mu\nu} h^{s,0}_{\mu\nu} + \frac{1}{2}\sum_{\mu\nu\alpha\beta} P_{\mu\nu} W_{\mu\nu,\alpha\beta} P_{\alpha\beta}\right]}_{E_{\mathrm{site}}}$$

A field of tight binding waters

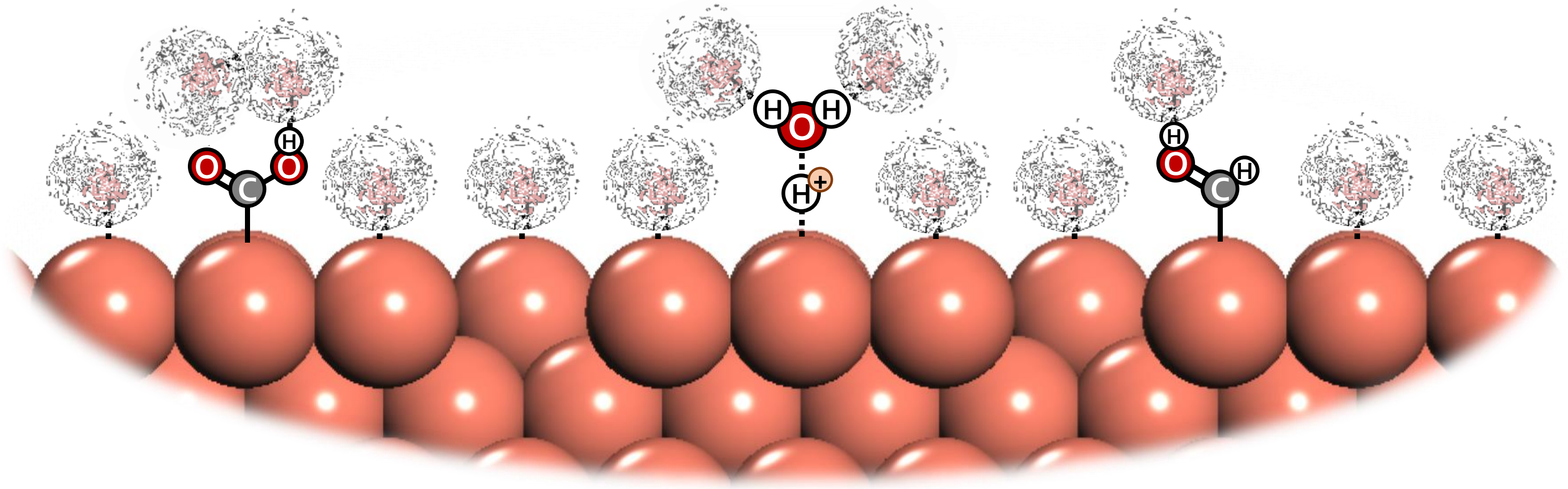


$$x = (\mathbf{r}_s, \omega)$$

$$n_{\mathrm{e}}^{(n)}(\mathbf{r}) = \frac{1}{1+A_n}\left[\boxed{\overline{\psi}_n^*(\mathbf{r})\overline{\psi}_n(\mathbf{r})} + \int d^6x\, \boxed{n_s(x)}\, \boxed{\Delta n_{\mathrm{e}}^{(n)}(\mathbf{r},x)}\right]$$

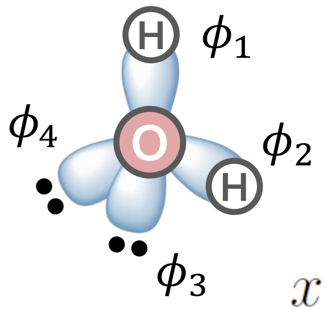
solvent density field

$$\varepsilon_n^0 = \frac{1}{1+A_n}\left[\boxed{\langle\overline{\psi}_n|\hat{H}_{\mathrm{KS}}^0|\overline{\psi}_n\rangle} + \int d^6x\, \boxed{n_s(x)}\, \boxed{\Delta\varepsilon_n(x)}\right]$$



Analogous to a field of PAW centers

A field of tight binding waters



combined
position +
orientation

$$x = (\mathbf{r}_s, \omega)$$

$$n_{\mathrm{e}}^{(n)}(\mathbf{r}) = \frac{1}{1+A_n}\left[\overline{\psi}_n^*(\mathbf{r})\overline{\psi}_n(\mathbf{r}) + \int d^6x\, n_s(x)\, \Delta n_{\mathrm{e}}^{(n)}(\mathbf{r}, x)\right]$$

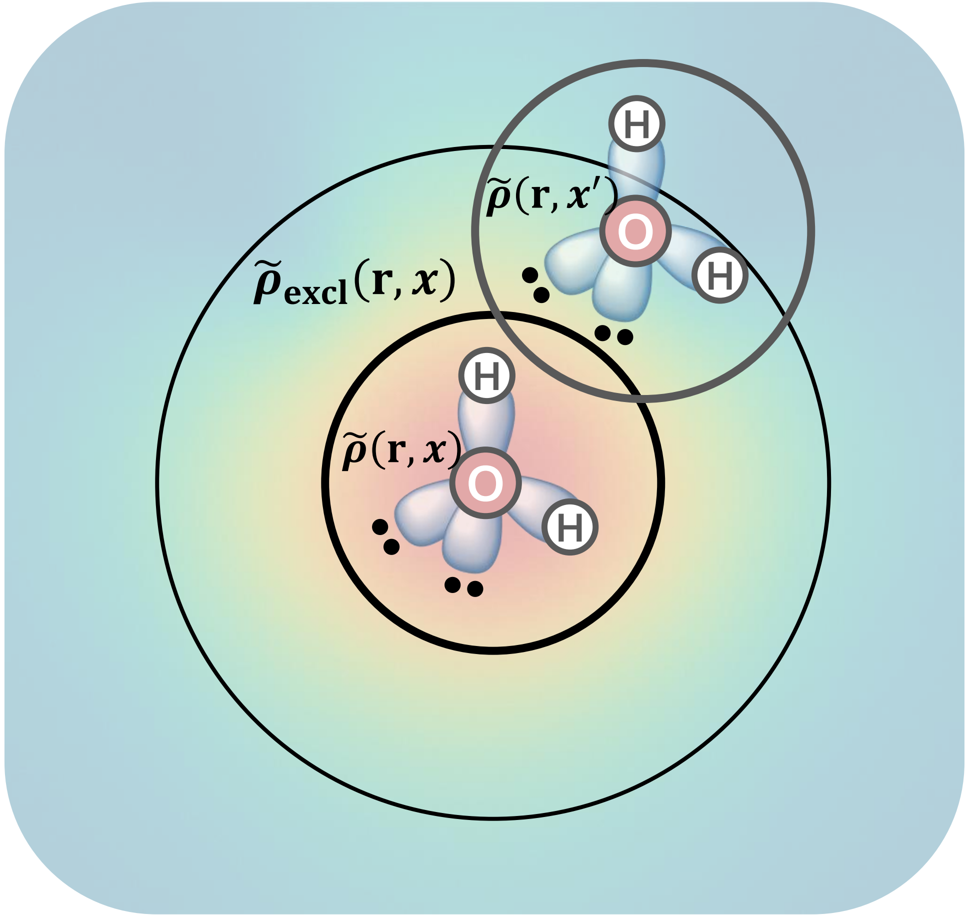
$$\varepsilon_n^0 = \frac{1}{1+A_n}\left[\langle\overline{\psi}_n|\widehat{H}_{\mathrm{KS}}^0|\overline{\psi}_n\rangle + \int d^6x\, n_s(x)\, \Delta\varepsilon_n(x)\right]$$

TB coefficients promoted to fields

$$\Delta n_{\mathrm{e}}^{(n)}(\mathbf{r}, x) = \sum_\mu c_{\mu n}(x)\phi_\mu^*(x\circ\mathbf{r})\overline{\psi}_n(\mathbf{r}) + \text{c.c.} + \sum_{\mu,\nu} c_{\mu n}^*(x)c_{\nu n}(x)\phi_\mu^*(x\circ\mathbf{r})\phi_\nu(x\circ\mathbf{r})$$

$$\Delta\varepsilon_n(x) = \sum_\mu c_{\mu n}(x)\langle\phi_\mu(x\circ\mathbf{r})|\widehat{H}_{\mathrm{KS}}^0|\overline{\psi}_n\rangle + \text{c.c.} + \sum_{\mu,\nu} c_{\mu n}^*(x)c_{\nu n}(x)\langle\phi_\mu(x\circ\mathbf{r})|\widehat{H}_{\mathrm{KS}}^0|\phi_\nu(x\circ\mathbf{r})\rangle$$

Self interaction and correlation correction



$$\widetilde{\rho}(\mathbf{r},x) = \mathrm{e}\,\widetilde{n}_{\mathrm{e}}(\mathbf{r},x) + \rho_{\mathrm{mol}}(\mathbf{r}-\mathbf{r}_s)$$

$$\widetilde{\rho}_{\mathrm{excl}}(\mathbf{r},x) = \int d^6x'\, n_{\mathrm{s}}(x')\, w_{\mathrm{s}}(\mathbf{r}'_s - \mathbf{r}_s)\,\widetilde{\rho}(\mathbf{r},x')$$

$$E^{\mathrm{site}}_{\mathrm{corr}}(x) = \tfrac{1}{2}\int d^3\mathbf{r}\,\widetilde{\rho}(\mathbf{r},x)\, v_H\left[\widetilde{\rho}_{\mathrm{excl}}(\cdot,x)\right](\mathbf{r})$$

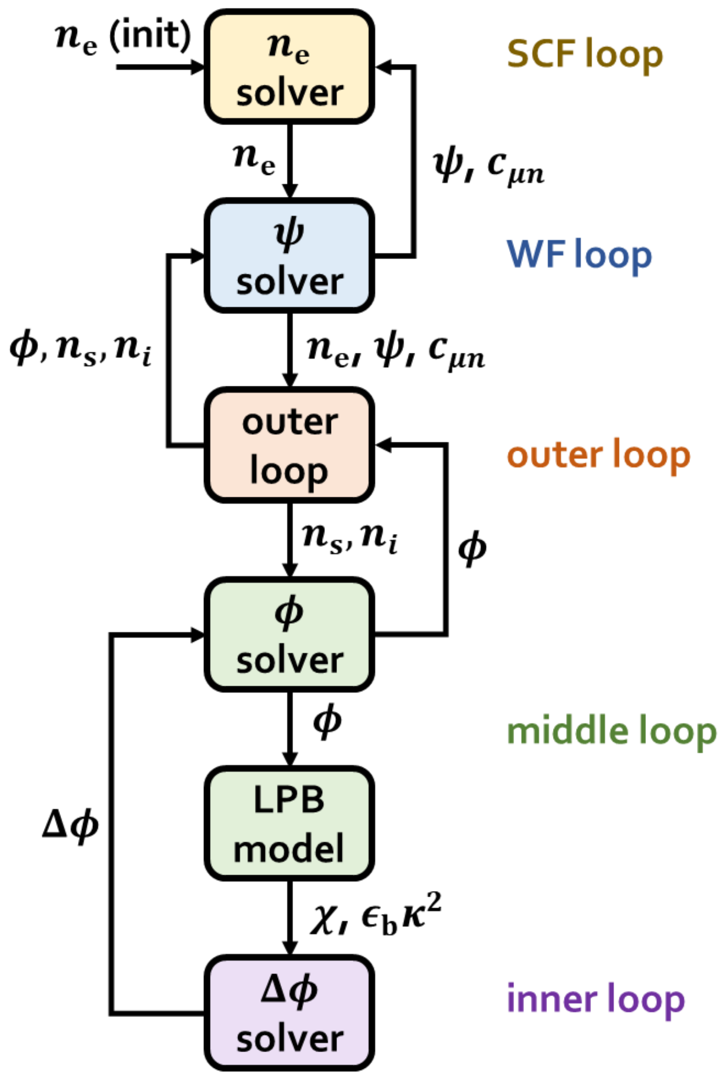
$\mathcal{F}_{\mathrm{ex}}$: Hard sphere excess free energy (e.g. White Bear Mark II)

$\mathcal{F}_{\mathrm{att}}$: Empirical attractive energy

$$\mathcal{F}_{\mathrm{solv}}[n_s] = \int d^6x\, n_s(x)\left[\ln\frac{n_s(x)}{n_s^b} - 1 + u_s((w_s * n_{\mathrm{e}})(x))\right]$$

$$\mathcal{F} = \sum_n f_n\varepsilon_n^0 + E_{\mathrm{H}}[\rho] + E_{\mathrm{xc}}[n_{\mathrm{e}}] - E_{\mathrm{xc}}[\widetilde{n}_{\mathrm{e}}] + \int d^6x\, n_s(x)\,[E_{\mathrm{site}}(x) - E^{\mathrm{corr}}_{\mathrm{site}}(x)] + \mathcal{F}_{\mathrm{solv}}[n_s] + \mathcal{F}_{\mathrm{ex}}[n_s] + \mathcal{F}_{\mathrm{att}}[n_s]$$

Implementation into an SCF cycle



Degrees of Freedom

$\bar{\psi}_n(\mathbf{r})$: explicit WFs

$c_{\mu n}(x)$: TB coefficients

$S(x)$: Solvent field

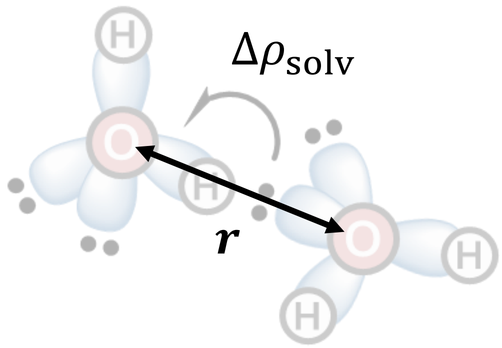
All terms in $\mathcal{F}$ can be computed in $O(N \log N)$ using convolutions

Separate out electrostatic effects by defining *excess potentials* $\boldsymbol{\Phi}_s(\mathbf{r}, \boldsymbol{\omega})$ and $\boldsymbol{\Phi}_i(\mathbf{r}, \boldsymbol{\omega})$

$$n_s(x) = n_s^b \exp\left(-\int d^3\boldsymbol{\omega}\, \Phi_s(\mathbf{r}, \boldsymbol{\omega})\right) \rho_{rot}\big(p_{mol}\hat{\mathbf{u}}(\boldsymbol{\omega}) \cdot \mathcal{E}(\mathbf{r}) + \Phi_s(\mathbf{r}, \boldsymbol{\omega})\big)$$

$$n_i(\mathbf{r}) = n_i^b \theta_i\big(z_i \phi(\mathbf{r}) + \Phi_i(\mathbf{r})\big)$$

Charge transfer through hydrogen bonding networks



correlation kernel

Pair density $$n_s^{(2)}(\mathbf{r},\mathbf{r}') = S(\mathbf{r})\,\kappa_b(|\mathbf{r}-\mathbf{r}'|)\,S(\mathbf{r}')$$

Solvent density $$n_s(\mathbf{r}) = \int d^3\mathbf{r}'\, n_s^{(2)}(\mathbf{r},\mathbf{r}') = S(\mathbf{r})\,(\kappa_b * S)(\mathbf{r})$$

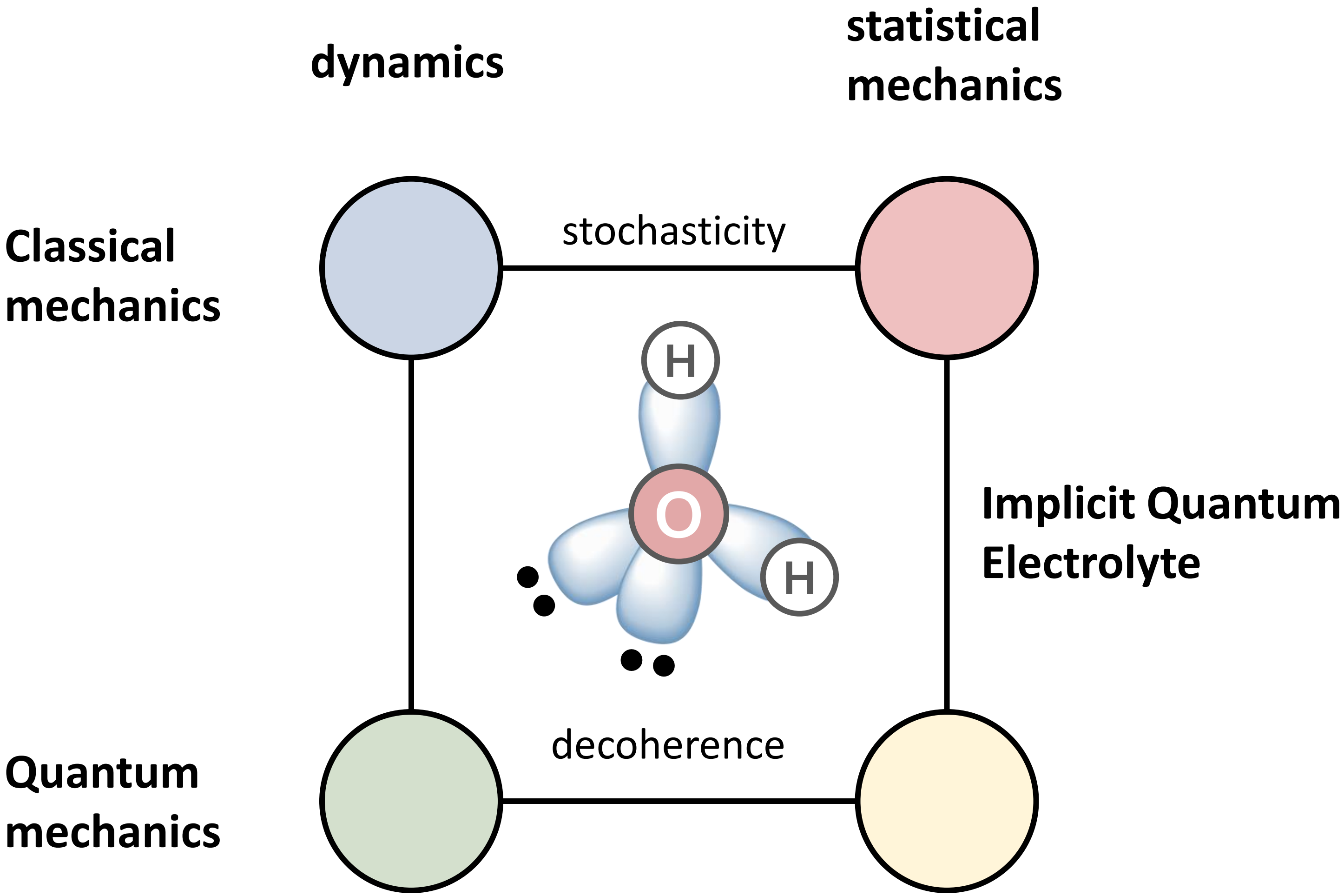
$$\Delta\rho_{\text{solv}}(\mathbf{r}) = \frac{1}{2}\sum_{\mu\to\nu}\int d^3\mathbf{r}'\,\kappa_b(|\mathbf{r}-\mathbf{r}'|)\,\Delta q\left(|\mathbf{r}-\mathbf{r}'|, \varepsilon_\nu(\mathbf{r}')-\varepsilon_\mu(\mathbf{r})\right)\,[\widetilde{n}_\nu(\mathbf{r}')-\widetilde{n}_\mu(\mathbf{r})]$$

$$\mathcal{F}[n_s, n_s^{(2)}] = k_B T\int d\mathbf{r}\, n_s(\mathbf{r})\left[\ln(n_s(\mathbf{r})\Lambda^3)-1\right] + \frac{1}{2}\int d\mathbf{r}\,d\mathbf{r}'\, n_s^{(2)}(\mathbf{r},\mathbf{r}')\,u(|\mathbf{r}-\mathbf{r}'|) + \mathcal{F}_{\text{ex}}[n_s]$$

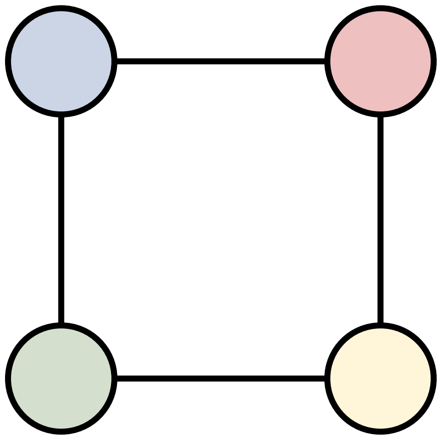
Outlook

Can We Unify Quantum and Statistical Mechanics?

Bridging the gap …



Bridging the gap …



Ornstein-Zernike eq

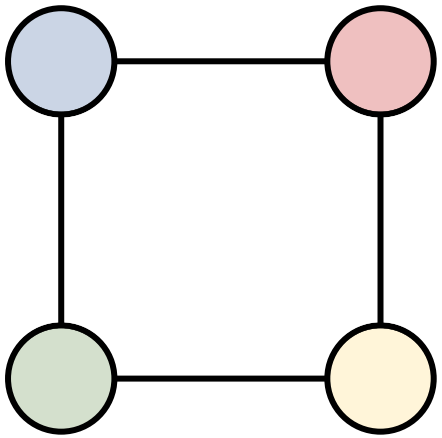
$$h(\mathbf{r}_1, \mathbf{r}_2) = c(\mathbf{r}_1, \mathbf{r}_2) + \int d\mathbf{r}_3 \, c(\mathbf{r}_1, \mathbf{r}_3) \, \rho(\mathbf{r}_3) \, h(\mathbf{r}_3, \mathbf{r}_2)$$

Coupled Clusters Doubles

$$0 = \langle ab||ij\rangle + \tfrac{1}{2}\sum_{cd}\langle ab||cd\rangle \, t_{ij}^{cd} + \tfrac{1}{2}\sum_{kl}\langle kl||ij\rangle \, t_{kl}^{ab} + P(ij)P(ab)\sum_{kc}\langle kb||cj\rangle \, t_{ik}^{ac}$$

$$+\tfrac{1}{4}\sum_{klcd}\langle kl||cd\rangle \left(t_{ik}^{ac}t_{jl}^{bd} - t_{il}^{ac}t_{jk}^{bd}\right) = 0$$

Bridging the gap …



Ornstein-Zernike eq

$$h(\mathbf{r}_1, \mathbf{r}_2) = c(\mathbf{r}_1, \mathbf{r}_2) + \int d\mathbf{r}_3 \, c(\mathbf{r}_1, \mathbf{r}_3) \, \rho(\mathbf{r}_3) \, h(\mathbf{r}_3, \mathbf{r}_2)$$

$$\boxed{\boldsymbol{h = c + c\rho h}}$$

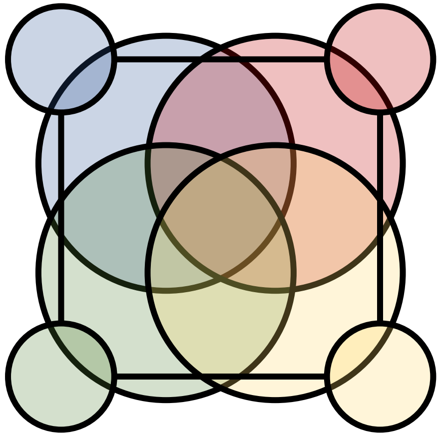
Coupled Clusters Doubles

$$0 = \langle ab||ij\rangle + \tfrac{1}{2}\sum_{cd}\langle ab||cd\rangle \, t_{ij}^{cd} + \tfrac{1}{2}\sum_{kl}\langle kl||ij\rangle \, t_{kl}^{ab} + P(ij)P(ab)\sum_{kc}\langle kb||cj\rangle \, t_{ik}^{ac}$$

$$+\tfrac{1}{4}\sum_{klcd}\langle kl||cd\rangle \left(t_{ik}^{ac}t_{jl}^{bd} - t_{il}^{ac}t_{jk}^{bd}\right) = 0$$

$$\boxed{\boldsymbol{T = V + VGT}}$$

… or the gap was never really there



Two manifestations of the same underlying structure

Theory	Dyson form	Object	Kernel
OZ (classical)	$h = c + c\,\rho\,h$	total correlation	direct correlation c
RPA (quantum linear response)	$\chi = \chi_0 + \chi_0 v \chi$	density response	Coulomb v
CCD (quantum wavefunction)	$T = V + VGT$	cluster amplitude	interaction V

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John Flake (LSU)

U.S. DEPARTMENT OF ENERGY | Office of Science

LSU High Performance Computing
Louisiana State University

An implicit electrolyte model for plane wave density functional theory exhibiting nonlinear response and a nonlocal cavity definition (JCP)

https://doi.org/10.1063/5.0176308

VASPsol++: A framework for implementing complex continuum fluid models in VASP density functional theory calculations

https://gitlab.com/cplaisance/vaspsol_pp
https://github.com/VASPsol/VASPsol