

Introduction to joint density-functional theory (JDFT)

The BEAST collaboration

3rd Annual BEAST Workshop, 2024

August 22, 2024

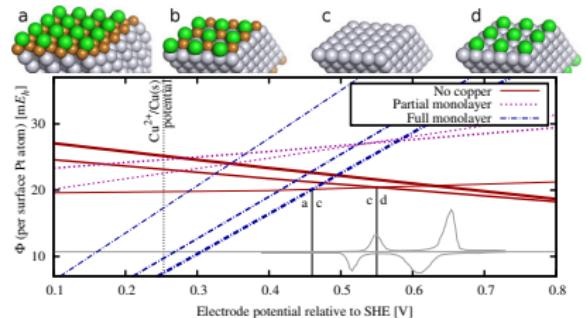
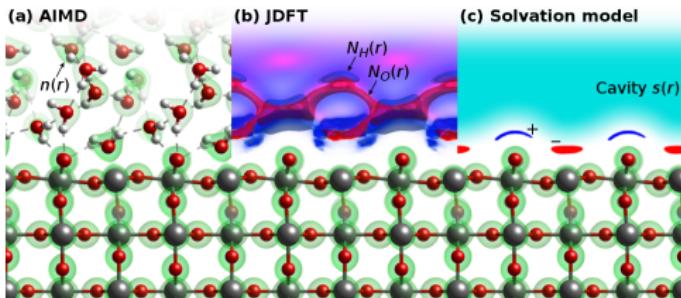


Office of Science

Award # DE-SC0022247



Outline



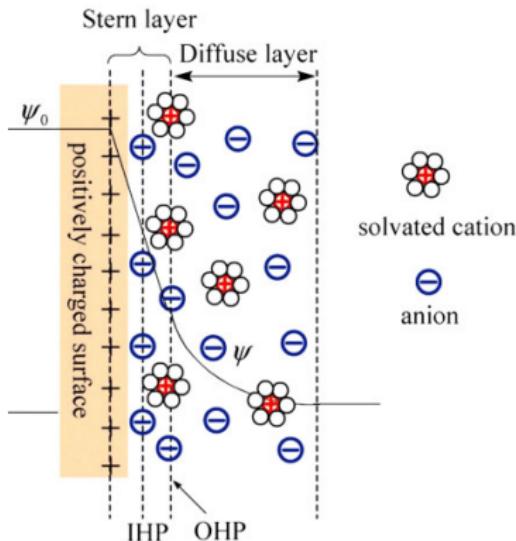
- ▶ The electrochemical interface
- ▶ Computational methods & challenges
- ▶ Solvated grand-canonical DFT
- ▶ Impact of charge state and solvation
- ▶ Future challenges

JDFT calculations in practice with JDFTx

The JDFTx collaboration
J. Am. Chem. Soc., 2011
August 21, 2021



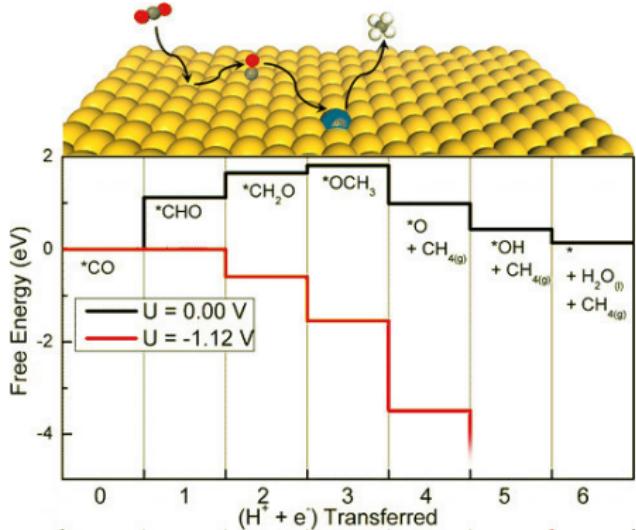
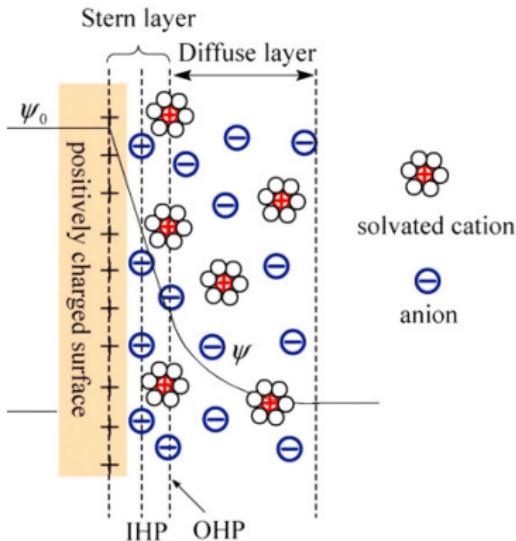
The electrochemical interface



- ▶ Gouy-Chapman-Stern model: double layer and diffuse ions



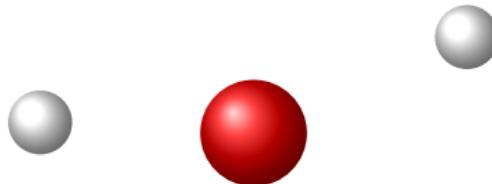
The electrochemical interface



- ▶ Gouy-Chapman-Stern model: double layer and diffuse ions
- ▶ Typical first-principles calculation:
 - ▶ No / minimal treatment of solvent and electrolytes
 - ▶ Proton-coupled electron transfer (PCET) steps only
 - ▶ Fixed charge + 'computational hydrogen electrode' (CHE)



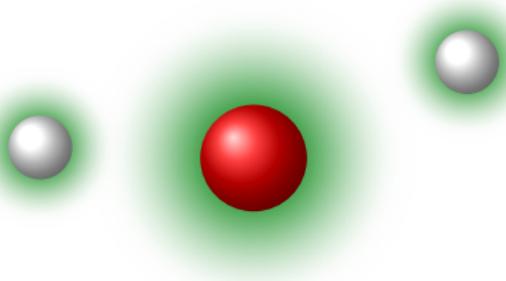
Ab initio electronic structure: goal



► Given nuclear positions



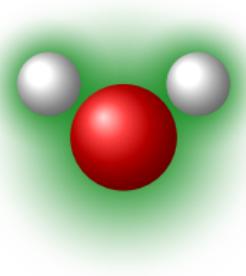
Ab initio electronic structure: goal



- ▶ Given nuclear positions
- ▶ Compute electronic wavefunctions,
energy and forces



Ab initio electronic structure: goal



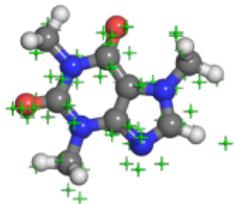
- ▶ Given nuclear positions
- ▶ Compute electronic wavefunctions, energy and forces
- ▶ Optimize/update nuclear positions to obtain structure/dynamics



Ab initio electronic structure: methods

- Solve N -electron Schrödinger's equation in terms of $\psi(r_1, r_2, \dots, r_N)$

$$E = \min_{\psi} \left\langle \psi \left| \sum_i \left(\underbrace{-\frac{\hbar^2 \nabla_i^2}{2m_e}}_{\text{Kinetic}} + \underbrace{\sum_{j < i} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{e^- - e^-} + \underbrace{\sum_j \frac{-Z_j e^2}{|\vec{r}_i - \vec{R}_j|}}_{e^- - \text{nuclear}} \right) \right| \psi \right\rangle \right.$$



Practical for $N \sim 10$, heroic for $N \sim 100$



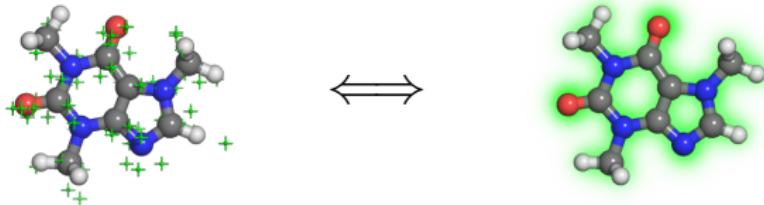
Ab initio electronic structure: methods

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- Hohenberg-Kohn theorem: optimize functional of electron density $n(\vec{r})$

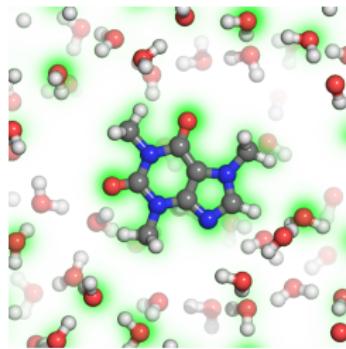
$$E = \min_n \left[F_{HK}[n] + \int d\vec{r} n(\vec{r}) \sum_j \frac{-Z_j e^2}{|\vec{r} - \vec{R}_j|} \right]$$



Practical for $N \sim 1000$, heroic for $N \sim 10^6$



Electronic structure of a solute in liquid



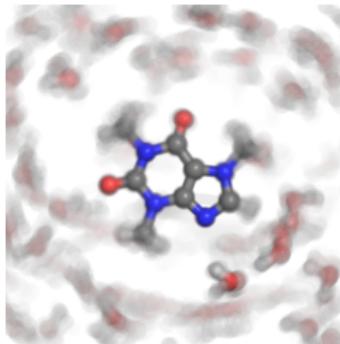
$\sim 15 \text{ min}^1$

$$\underbrace{F_{HK}[n]}_{\text{Electrons}}$$

¹Typical timings using JDFTx on a single NVIDIA K20 GPU



Electronic structure of a solute in liquid



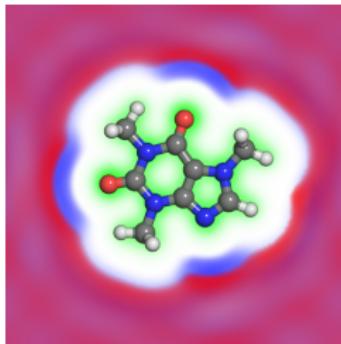
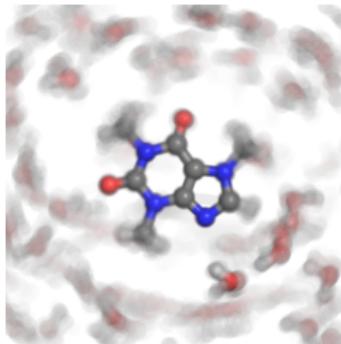
$\sim 10 \text{ min} \times 10^3 \text{ steps}$

$$\underbrace{F_{HK}[n]}_{\text{Electrons}}$$

- ▶ Molecular dynamics / Monte Carlo sampling of liquid configurations



Electronic structure of a solute in liquid



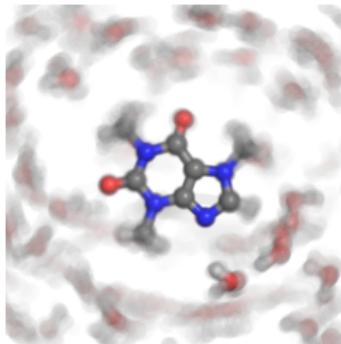
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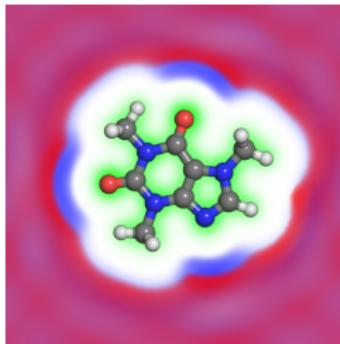
- ▶ Molecular dynamics / Monte Carlo sampling of liquid configurations
- ▶ Describe liquid in terms of equilibrium densities ($N_O(\vec{r})$, $N_H(\vec{r})$ for water)



Electronic structure of a solute in liquid



$\sim 10 \text{ min} \times 10^3 \text{ steps}$



$\sim 5 \text{ min}$

$$\Phi_{\text{JDFT}}[n, \{N_\alpha\}] = \underbrace{F_{\text{HK}}[n]}_{\text{Electrons}} + \underbrace{\Phi_{\text{CDFT}}[\{N_\alpha\}]}_{\text{Liquid}} + \underbrace{\Delta\Phi[n, \{N_\alpha\}]}_{\text{Coupling}}$$

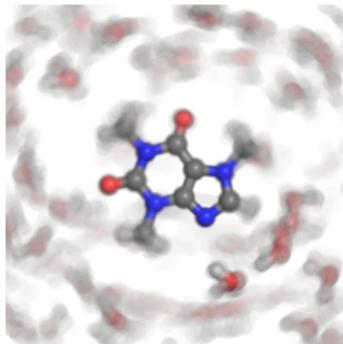
- ▶ Molecular dynamics / Monte Carlo sampling of liquid configurations
- ▶ Describe liquid in terms of equilibrium densities ($N_O(\vec{r})$, $N_H(\vec{r})$ for water)
- ▶ Joint density-functional theory: free energy functional for liquid^{1,2}

¹R. Sundararaman and T.A. Arias, *Comp. Phys. Comm.* **185**, 818 (2014)

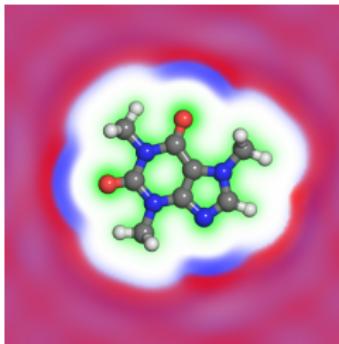
²R. Sundararaman, K. L.-Weaver and T.A. Arias, *J Chem Phys* **140**, 144504 (2014)



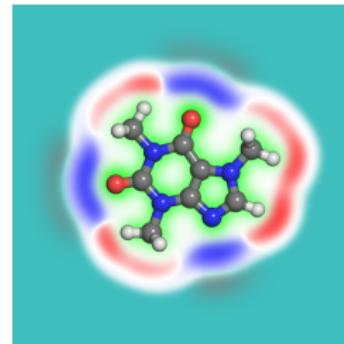
Electronic structure of a solute in liquid



$\sim 10 \text{ min} \times 10^3 \text{ steps}$



$\sim 5 \text{ min}$



$\sim 30 \text{ s}$

$$\Phi_{\text{JDFT}}[n, \{N_\alpha\}] = \underbrace{F_{\text{HK}}[n]}_{\text{Electrons}} + \underbrace{\Phi_{\text{CDFT}}[\{N_\alpha\}]}_{\text{Liquid}} + \underbrace{\Delta\Phi[n, \{N_\alpha\}]}_{\text{Coupling}}$$

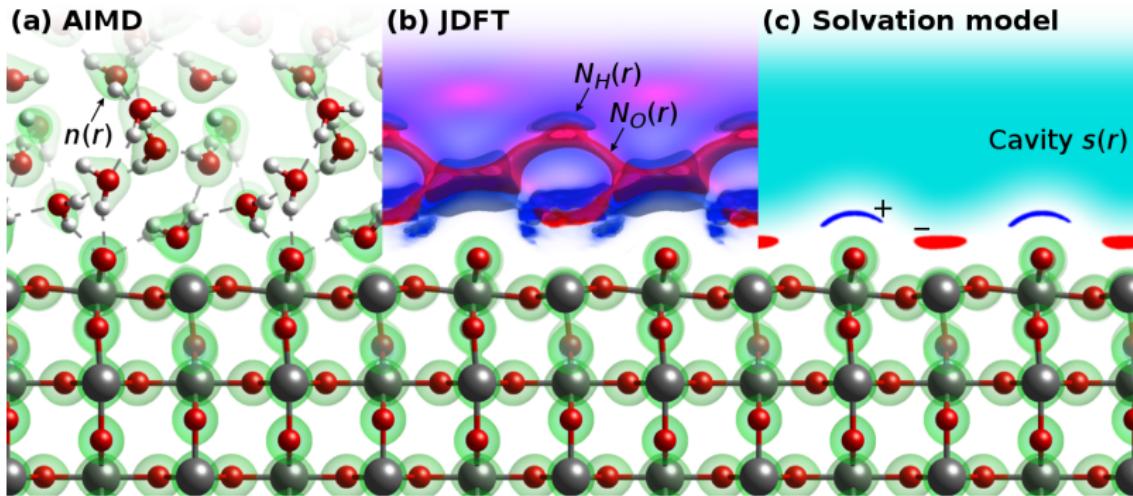
- ▶ Molecular dynamics / Monte Carlo sampling of liquid configurations
- ▶ Describe liquid in terms of equilibrium densities ($N_O(\vec{r})$, $N_H(\vec{r})$ for water)
- ▶ Joint density-functional theory: free energy functional for liquid
- ▶ Basis for non-empirical continuum solvation methods^{1,2}

¹R. Sundararaman and W.A. Goddard, *J. Chem. Phys.* **142**, 064107 (2015)

²R. Sundararaman, K. L.-Weaver et al., *J. Chem. Phys.* **142**, 054102 (2015)



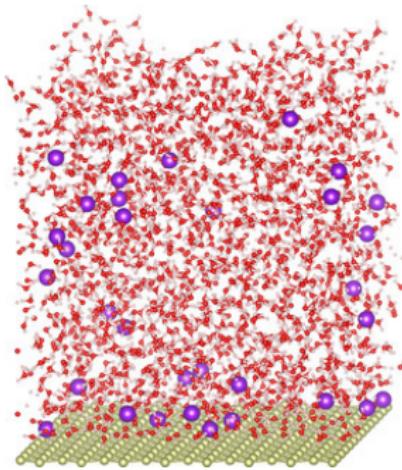
Solid-liquid interface example



- ▶ Comparison of techniques shown for rutile $\text{TiO}_2(110)$ aqueous interface:
 - ▶ Explicit: require dynamics, $\sim 10^4 \times$ as expensive
 - ▶ Structured implicit: free energy from equilibrium liquid densities
 - ▶ Continuum implicit: electrostatic model + corrections
- ▶ Most work to date: continuum implicit models
- ▶ Future: structured implicit models (JDFT, RISM)



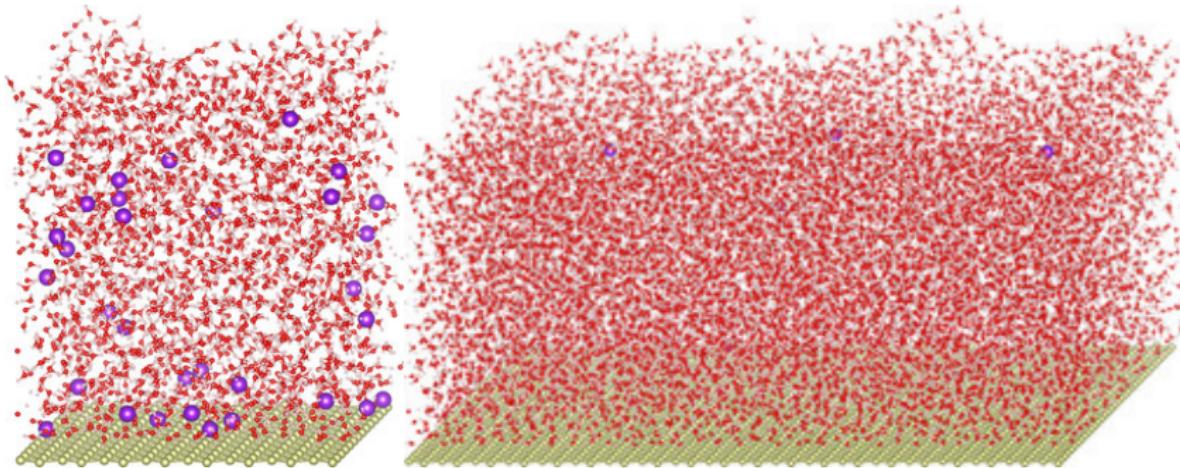
Electrolytes: further complications



- ▶ Large unit cells for statistically meaningful number of ions
- ▶ Example 1: 1M aqueous KOH with 32 ion pairs \Rightarrow 1800 H₂O



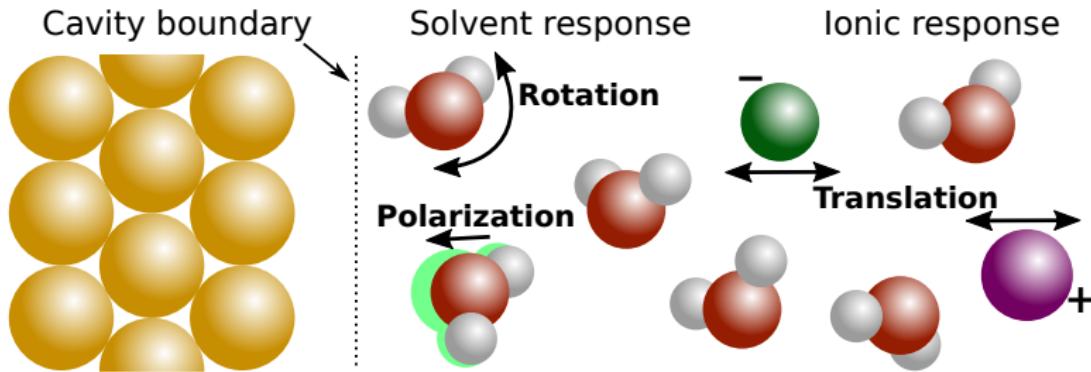
Electrolytes: further complications



- ▶ Large unit cells for statistically meaningful number of ions
- ▶ Example 1: 1M aqueous KOH with 32 ion pairs \Rightarrow 1800 H₂O
- ▶ Example 2: 0.03M aqueous KOH with 6 ion pairs \Rightarrow 11000 H₂O
- ▶ Additionally, large time scales for ion diffusion and equilibration
- ▶ AIMD not yet practical at these scales: need continuum solvation



Continuum solvation ingredients

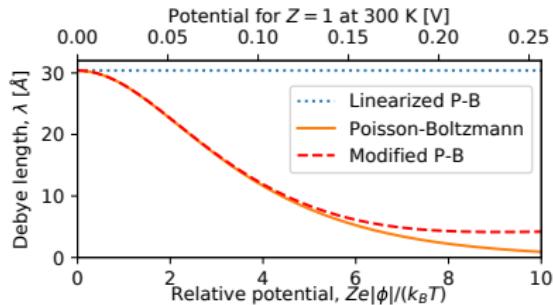


- ▶ **Response:** *how the solvent and electrolyte create a charge density*
- ▶ **Cavity:** *where they can create this charge density*
- ▶ Beyond electrostatic pieces: free energy to form cavity, repulsion, dispersion etc.: less critical for electrochemistry (will skip discussion here)



Continuum solvation: electric response

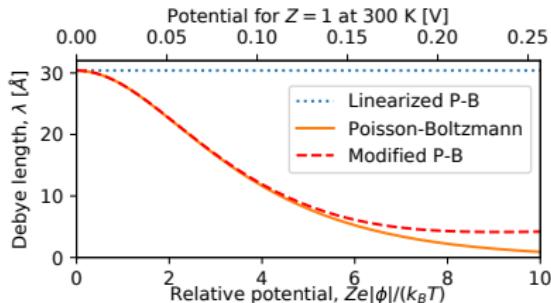
Ionic response



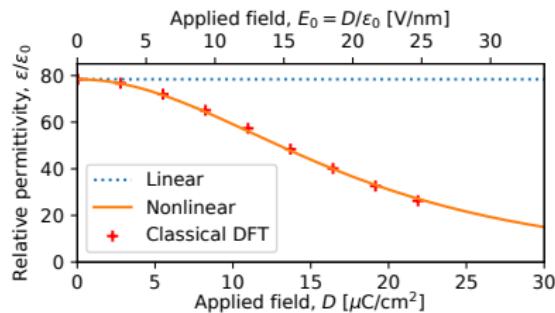
- ▶ Charge density induced in solvent/electrolyte due to interactions with solute/electrode
- ▶ Contributions in a multipole expansion:
 - ▶ **Monopole ($l = 0$)**: overall movement of charged ions; nonlinearity due to Boltzmann statistics of ions \Rightarrow (modified) Poisson-Boltzmann theory

Continuum solvation: electric response

Ionic response

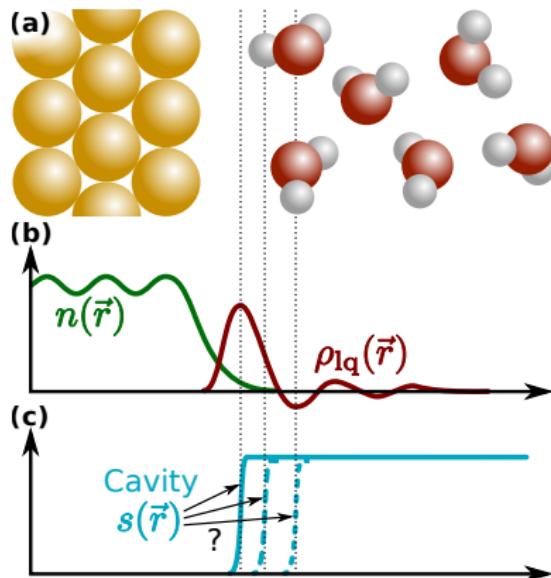


Dielectric response



- ▶ Charge density induced in solvent/electrolyte due to interactions with solute/electrode
- ▶ Contributions in a multipole expansion:
 - ▶ **Monopole ($l = 0$)**: overall movement of charged ions; nonlinearity due to Boltzmann statistics of ions \Rightarrow (modified) Poisson-Boltzmann theory
 - ▶ **Dipole ($l = 1$)**: dipole rotation and induced dipoles in molecules (and ions); nonlinearity due to saturation in dipole alignment with field
- ▶ Nonlinearity of *both responses* critical in electrochemical charge distribution

Response location: cavity



- ▶ Regardless of approximation level, reproduce *where* ρ_{Lq} appears
- ▶ Not exactly center of solvent molecules, not nearest atom
- ▶ Should correlate with atom sizes, or with electron density (overlaps)



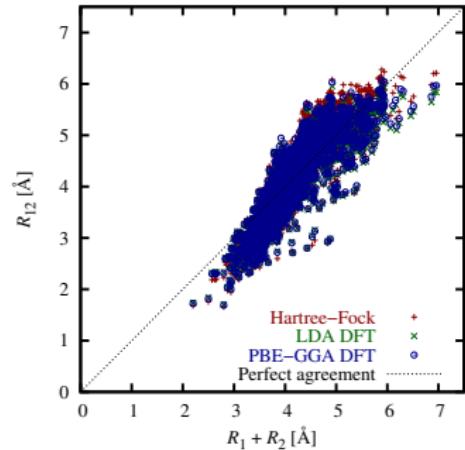
Minimally-empirical nonlocal solvation models

- ▶ Drastic approximation: point charges / dipoles at molecular scale; compensated by solvation energy fit



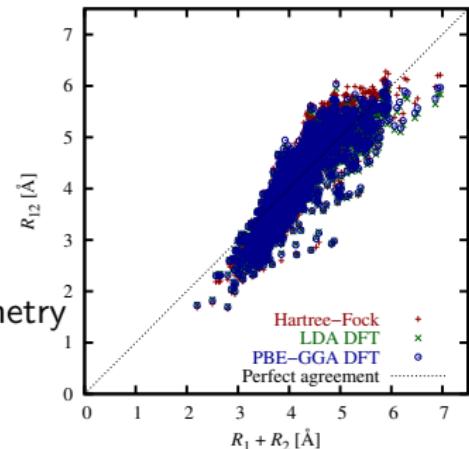
Minimally-empirical nonlocal solvation models

- ▶ Drastic approximation: point charges / dipoles at molecular scale; compensated by solvation energy fit
- ▶ Spherically-averaged liquid susceptibility ansatz (SaLSA)
 - ▶ Directly treat *non-local* solvent response \Rightarrow cavity-size corresponds physically to solute-solvent atom separation
 - ▶ Cavity from overlap of solute and solvent electron densities, correlated to electron density overlap of all pairs of atoms
 - ▶ *No fit to solvation energies* for cavity size

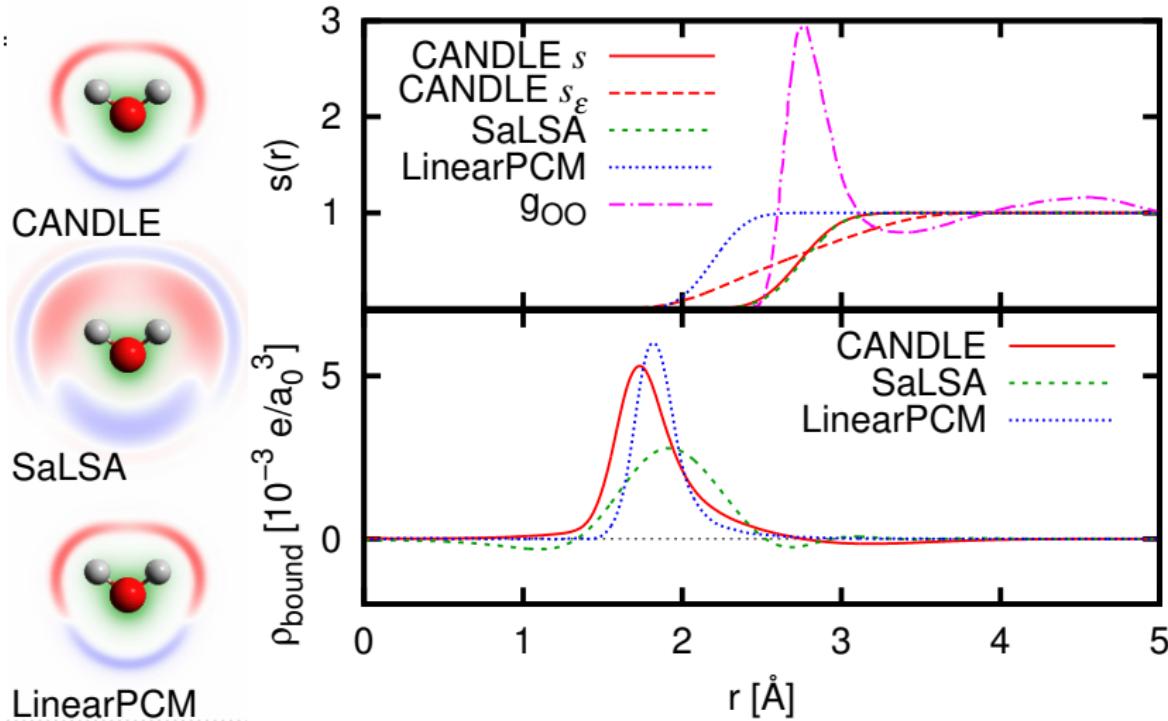


Minimally-empirical nonlocal solvation models

- ▶ Drastic approximation: point charges / dipoles at molecular scale; compensated by solvation energy fit
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 - ▶ Directly treat *non-local* solvent response ⇒ cavity-size corresponds physically to solute-solvent atom separation
 - ▶ Cavity from overlap of solute and solvent electron densities, correlated to electron density overlap of all pairs of atoms
 - ▶ *No fit to solvation energies* for cavity size
- ▶ CANDLE: solvation model with charge asymmetry
 - ▶ Charge-Asymmetric: +/- charges solvated differently in most polar solvents
 - ▶ Nonlocally-Determined: using SaLSA cavity definition for transferability
 - ▶ Local-Electric: replace non-local response with displaced local response (for improved computational efficiency, ease of implementation)



Solvation model cavity and charge comparison



SaLSA: R Sundararaman, K Schwarz, K L-Weaver, TA Arias, *JCP* **142**, 054102 (2015)

CANDLE: R. Sundararaman and W.A. Goddard III, *JCP* **142**, 064107 (2015)

LinearPCM = VASPsol, SCCS



Solvation energy comparison

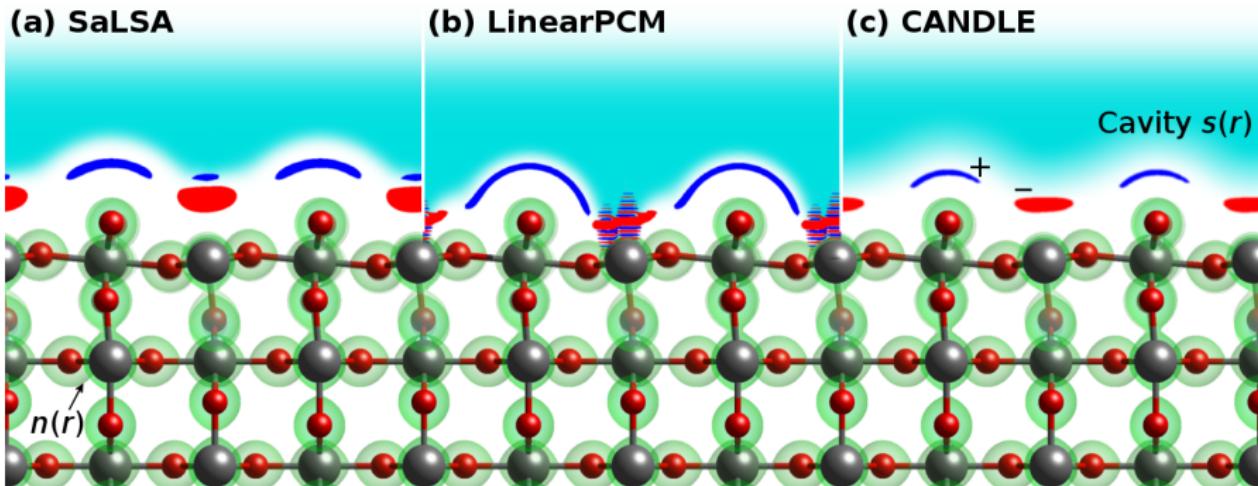
- ▶ Same set of solutes consisting of
 - ▶ 240 neutral organics
 - ▶ 51 organic cations
 - ▶ 55 organic anions

| MAE [kcal/mol] | Neutrals | Cations | Anions | All |
|----------------------|----------|---------|--------|-------------|
| IEF-PCM (Gaussian03) | | 4.00 | 10.2 | |
| IEF-PCM (Gaussian09) | | 11.9 | 15.0 | |
| Original SCCS (QE) | 1.20 | 2.55 | 17.4 | 3.97 |
| Original SCCS' (QE) | 1.28 | 2.66 | 16.9 | 3.97 |
| Cation fit SCCS (QE) | | 2.26 | | |
| Anion fit SCCS (QE) | | | 5.54 | |
| SaLSA (JDFTx) | 1.36 | 3.20 | 19.7 | 4.55 |
| CANDLE (JDFTx) | 1.26 | 2.64 | 3.54 | 1.84 |

- ▶ CANDLE: uniform accuracy for neutral, differently charged solutes
- ▶ Near chemical accuracy of 1 kcal/mol ($\sim 1.7 k_B T$ at 300 K)



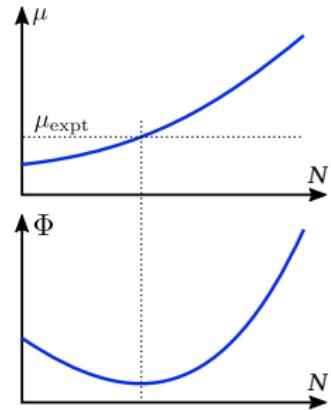
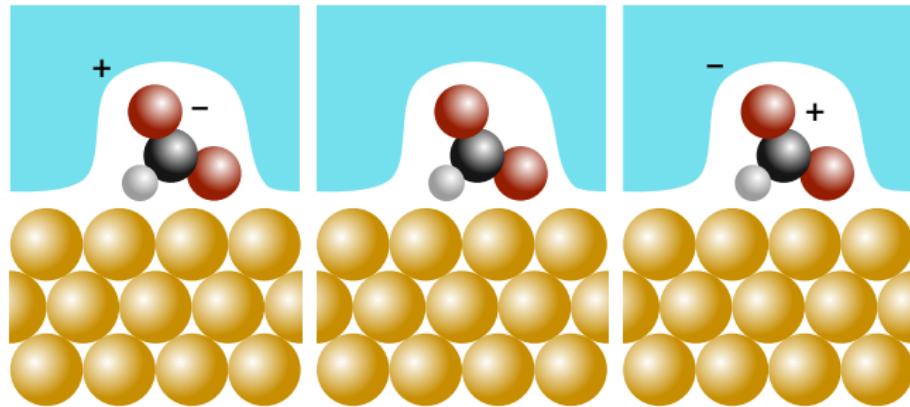
Solvation models at rutile TiO₂ aqueous interface



- ▶ Example: Rutile TiO₂(110) - water interface
- ▶ SaLSA shows minimal secondary structure
- ▶ Local-cavity models models go where *no solvent has gone before*
- ▶ CANDLE: simple response, stable cavity (borrowed from SaLSA)



First-principles scheme for electrochemistry

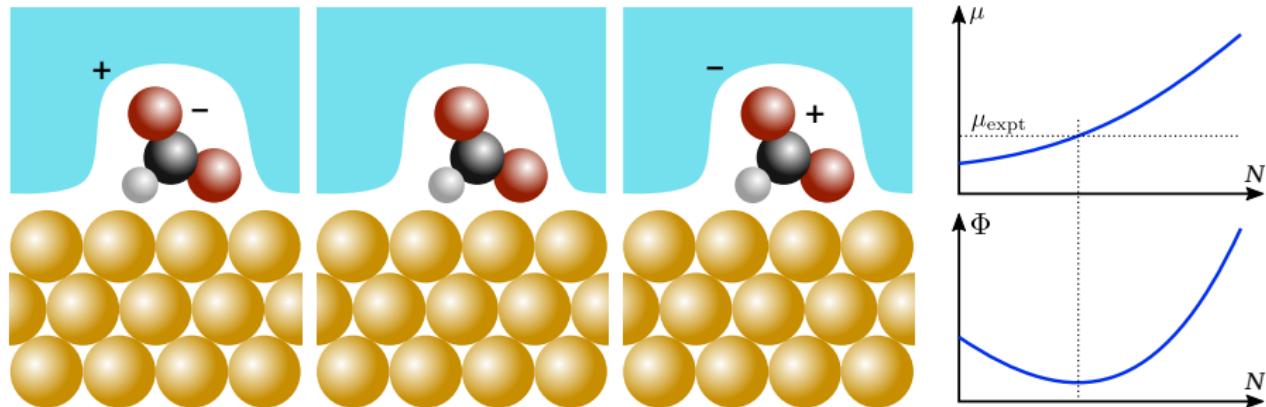


- ▶ Continuum solvation models with electrolyte \Rightarrow compensate charge on electrode + adsorbate \Rightarrow net unit cell neutral
- ▶ Electron chemical potential μ relatable to electrode potential³

³K L-Weaver and TA Arias, PRB **86**, 075140 (2012)



First-principles scheme for electrochemistry



- ▶ Continuum solvation models with electrolyte \Rightarrow compensate charge on electrode + adsorbate \Rightarrow net unit cell neutral
- ▶ Electron chemical potential μ relatable to electrode potential³
- ▶ Need sequence of calculations with varying electron number N
- ▶ Find electron number appropriate for μ corresponding to experiment
- ▶ Grand free energy Φ minimum at the correct N

³K L-Weaver and TA Arias, PRB **86**, 075140 (2012)



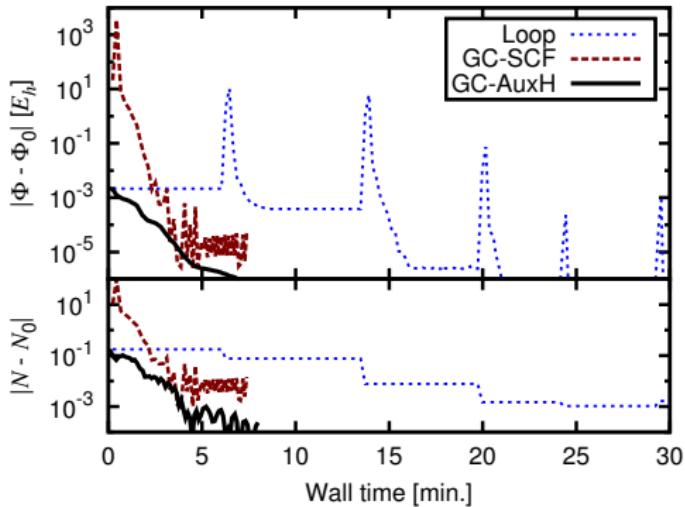
Grand-canonical DFT

- ▶ At given electrochemical potential, solute in some non-neutral charge state
- ▶ Original: perform DFT calculations with varying charge to find equilibrium



Grand-canonical DFT

- ▶ At given electrochemical potential, solute in some non-neutral charge state
- ▶ Original: perform DFT calculations with varying charge to find equilibrium
- ▶ Now: directly perform DFT at fixed electrochemical potential⁴
- ▶ Convenient and more efficient than fixed-charge DFT



- ▶ **GC-SCF:** update Kerker preconditioner and metric in self-consistent field iteration: support change in charge between cycles
- ▶ **GC-AuxH:** variational minimization of grand free energy: analytically continued functional of wave functions and subspace Hamiltonian

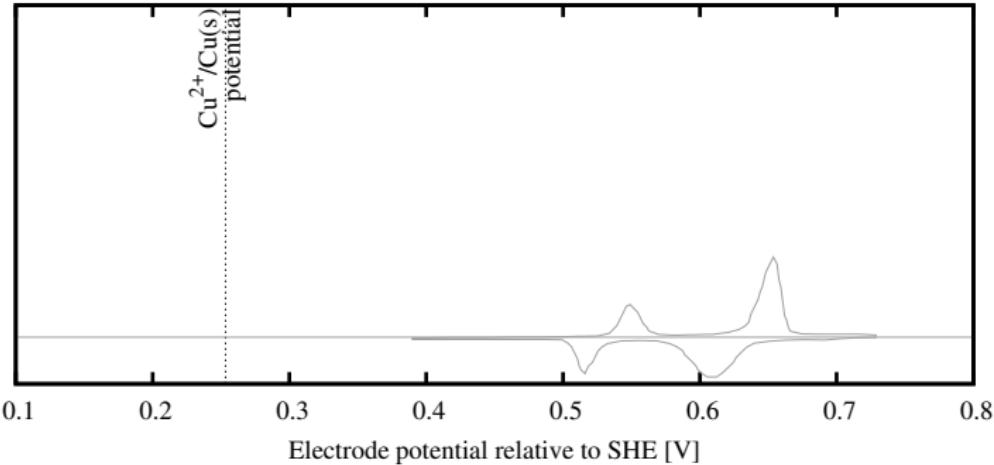
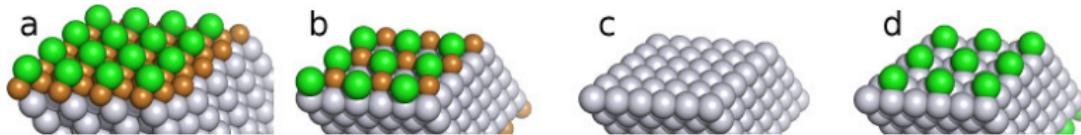
⁴R. Sundararaman, WA Goddard and TA Arias, *JCP* **146**, 114104 (2017)

Key advances

- ▶ Minimally-empirical solvation models for electrochemical interfaces
 - ▶ Solvation models stabilize charged surface configurations
 - ▶ Grand-canonical DFT determines correct charge at experimental potential
-
- ▶ CANDLE + GC-DFT increasingly adopted in first-principles electrocatalyst design for water-splitting, CO₂RR, ammonia synthesis etc.
 - ▶ Next: showcase effect with one example



Underpotential deposition of Cu on Pt(111)



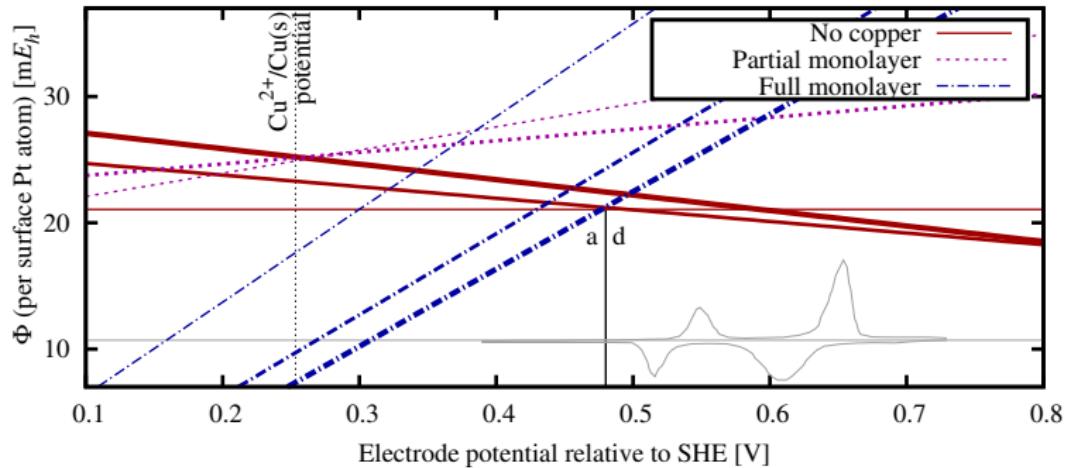
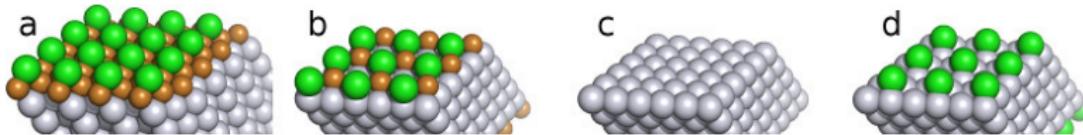
- ▶ Identity of second voltammetric peak in presence of Cl^-

Markovic et al., *Surf. Sci.* **335**, 91 (1995)

Bludau et al., *Surf. Sci.* **402**, 786 (1998)



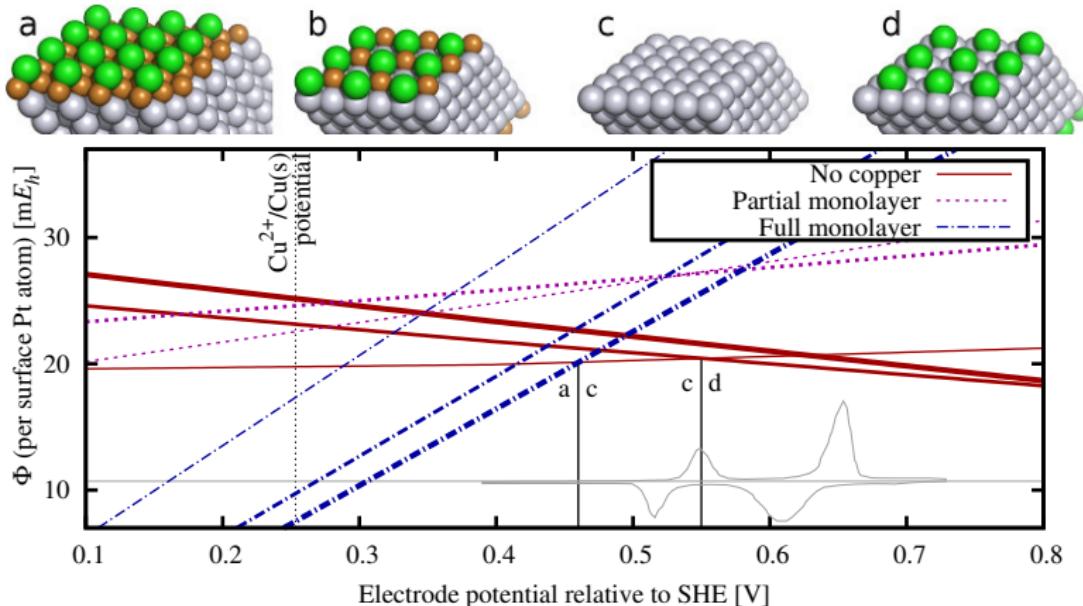
Underpotential deposition of Cu on Pt(111)



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Underpotential deposition of Cu on Pt(111)

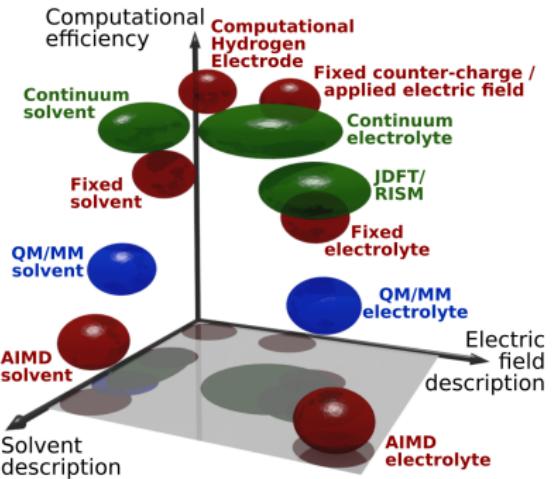


- ▶ Identity of second voltammetric peak in presence of Cl⁻
- ▶ Neutral vacuum DFT calculations predict only one transition
- ▶ Fixed-potential CANDLE calculations predict Cl-desorption peak
- ▶ Peak positions with accuracy ~ 0.05 eV



Electrochemical solvation summary

- ▶ Large spread in detail of charge and solvation effects in electrochemical predictions
- ▶ Most solvation model problems: limitation of local models
- ▶ Nonlocal-cavity models eg. CANDLE accurate for high-charge systems
- ▶ Grand-canonical DFT conveniently captures changing charge states for reaction modeling

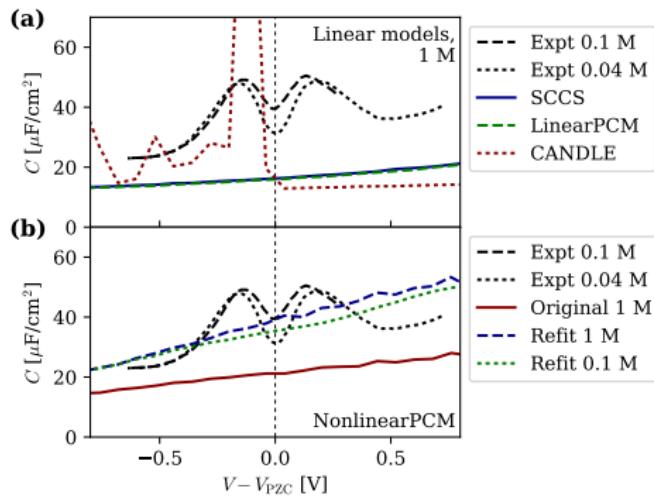


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- ▶ **Book chapter:** 'Joint and grand-canonical density-functional theory' in 'Atomic-Scale Modelling of Electrochemical Systems' (Wiley, 2021)
 - ▶ **Review article:** 'The electrochemical double layer in first-principles calculations', *Surf. Sci. Rep.* **75**, 100492 (2020)
 - ▶ **Review article:** 'Improving the Accuracy of Atomistic Simulations of the Electrochemical Interface,' *Chem. Rev.* **122**, 10651 (2022)



First-principles electrochemistry: beyond continuum?

Capacitance for Ag(100) surfaces in non-adsorbing aqueous electrolyte

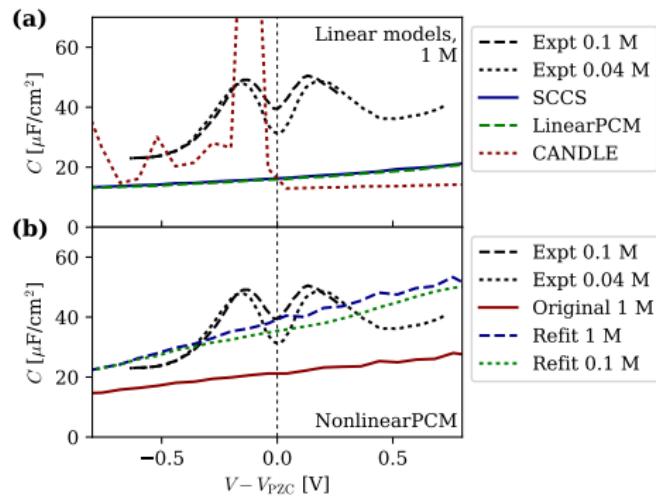


- ▶ Most models underestimate capacitance by 50%
- ▶ Can reparametrize, but still misses qualitative features
- ▶ CANDLE cavity asymmetry
⇒ spikes in capacitance (but charge remains reasonable)



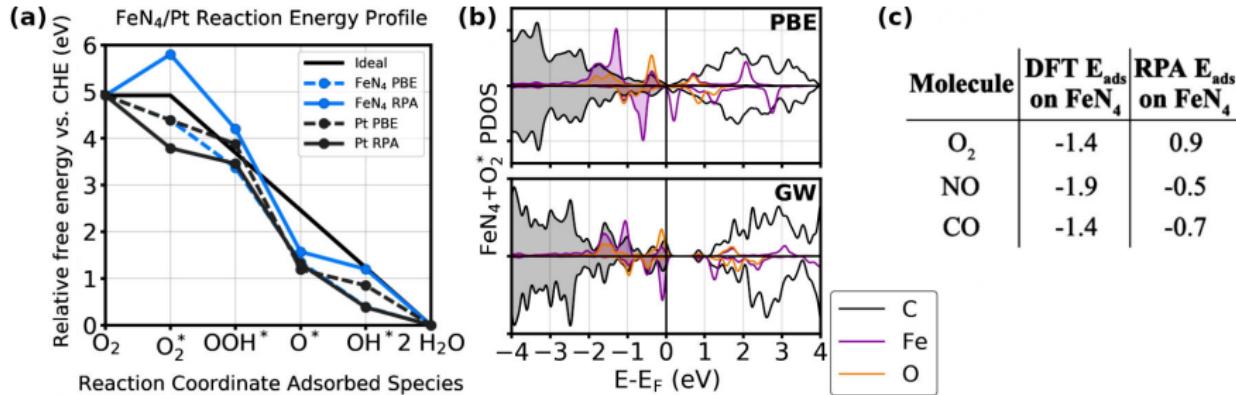
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- ▶ Most models underestimate capacitance by 50%
- ▶ Can reparametrize, but still misses qualitative features
- ▶ CANDLE cavity asymmetry ⇒ spikes in capacitance (but charge remains reasonable)
- ▶ Continuum models still miss double-layer structure
- ▶ Future: liquid structure models (classical DFT / RISM) beyond the cavity approximation

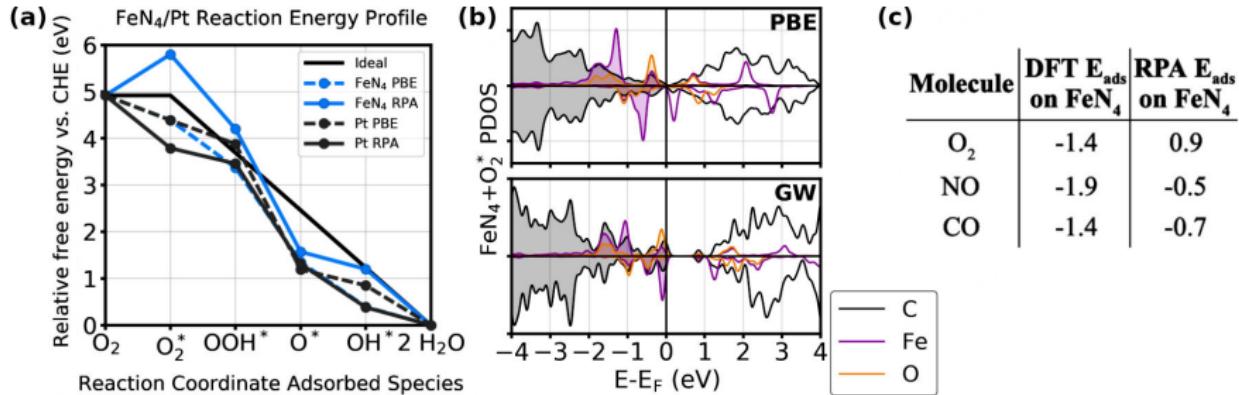
First-principles electrochemistry: beyond DFT?



- ▶ Charge states are key \Rightarrow need solvation and grand-canonical methods
- ▶ Is DFT accurate enough to capture the correct charge state?



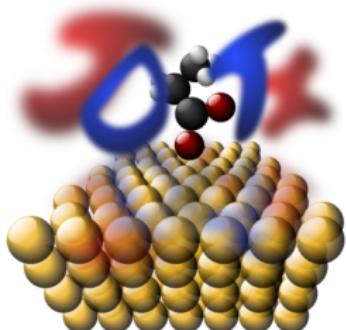
First-principles electrochemistry: beyond DFT?



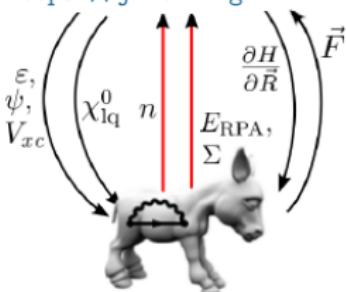
- ▶ Charge states are key \Rightarrow need solvation and grand-canonical methods
- ▶ Is DFT accurate enough to capture the correct charge state?
- ▶ Often, no: e.g. O₂ binding on FeN₄ and Pt OER catalysts
- ▶ Over 1 eV errors in binding energy $\Rightarrow 10^{16} \times$ in rates!
- ▶ Need solvated and grand-canonical beyond-DFT methods such as RPA
- ▶ This is critical to computationally optimize the active site



Hence, BEAST



<https://jdftx.org>



<https://berkeleygw.org>

First-principles for electrochemistry typically:

- ▶ Ignore electrolyte entirely, or use overly simplistic implicit models, and
- ▶ Use DFT, which can be inaccurate for electronic structure of interfaces.

To address, this BEAST aims to:

- ▶ Make accurate solvation methods readily available to the electrochemistry community, and
- ▶ Couple them with many-body methods such as RPA for accuracy beyond the DFT level.

