

# Introduction to joint density-functional theory (JDFT)

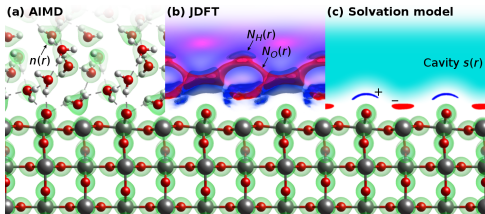
The BEAST collaboration

3<sup>rd</sup> Annual BEAST Workshop, 2024

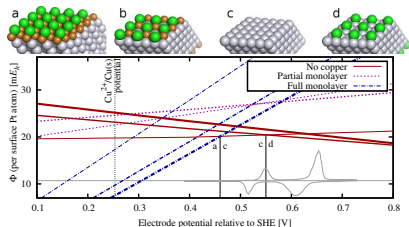
August 22, 2024



# Outline



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

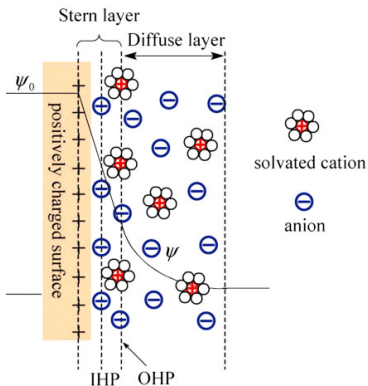


JDFT calculations in practice with JDFTx

The MESSY collaboration  
 TU Braunschweig  
 August 17, 2023



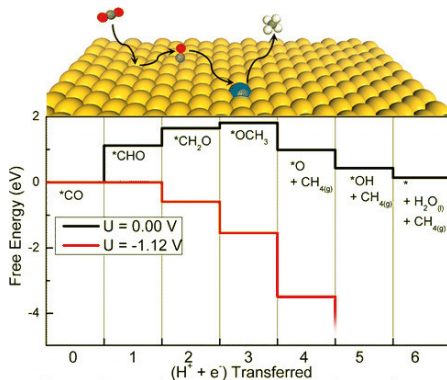
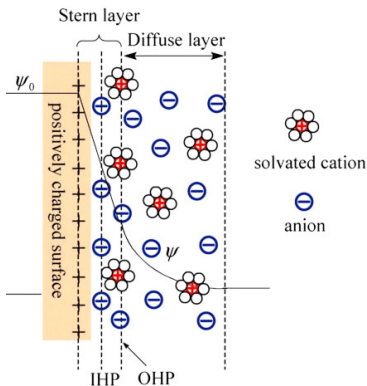
# The electrochemical interface



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



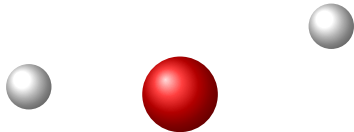
# The electrochemical interface



- ▶ 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)



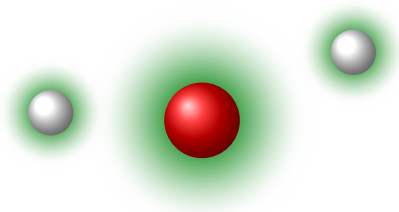
# *Ab initio* electronic structure: goal



▶ Given nuclear positions



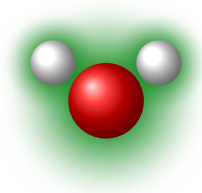
## *Ab initio* electronic structure: goal



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



## *Ab initio* electronic structure: goal



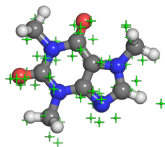
- ▶ Given nuclear positions
- ▶ Compute electronic wavefunctions, energy and forces
- ▶ Optimize/update nuclear positions to obtain structure/dynamics



# Ab initio electronic structure: methods

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

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



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





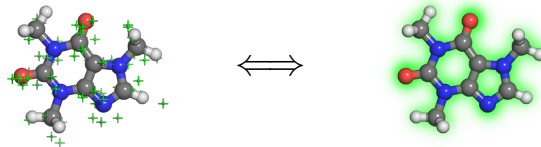
# Ab initio electronic structure: methods

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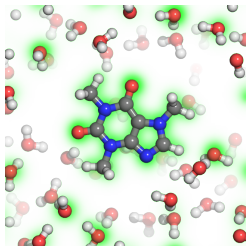
$$E = \min_{\psi} \left\langle \psi \left| \sum_i \left( \underbrace{-\frac{\hbar^2 \nabla_i^2}{2m_e}}_{\text{Kinetic}} + \underbrace{\sum_{j < i} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{e^- - e^-} + \underbrace{\sum_j \frac{-Z_j e^2}{|\vec{r}_i - \vec{R}_j|}}_{e^- - \text{nuclear}} \right) \right| \psi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

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

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



# Electronic structure of a solute in liquid



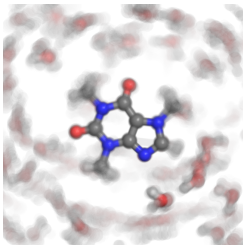
$\sim 15 \text{ min}^1$

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

<sup>1</sup>Typical timings using JDFTx on a single NVIDIA K20 GPU



# Electronic structure of a solute in liquid



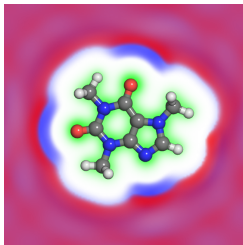
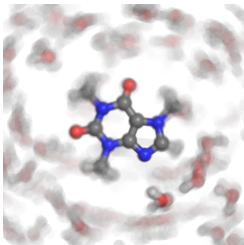
$\sim 10 \text{ min} \times 10^3 \text{ steps}$

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

- ▶ Molecular dynamics / Monte Carlo sampling of liquid configurations



# Electronic structure of a solute in liquid



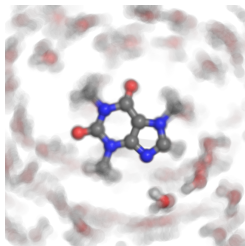
$\sim 10 \text{ min} \times 10^3 \text{ steps}$

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

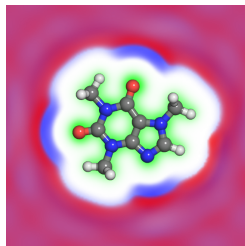
- ▶ Molecular dynamics / Monte Carlo sampling of liquid configurations
- ▶ Describe liquid in terms of equilibrium densities ( $N_O(\vec{r})$ ,  $N_H(\vec{r})$  for water)



# Electronic structure of a solute in liquid



~ 10 min  $\times 10^3$  steps



~ 5 min

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

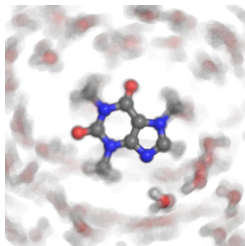
- ▶ Molecular dynamics / Monte Carlo sampling of liquid configurations
- ▶ Describe liquid in terms of equilibrium densities ( $N_O(\vec{r})$ ,  $N_H(\vec{r})$  for water)
- ▶ Joint density-functional theory: free energy functional for liquid<sup>1,2</sup>

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

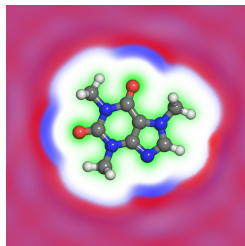
<sup>2</sup>R. Sundararaman, K. L.-Weaver and T.A. Arias, *J Chem Phys* **140**, 144504 (2014)



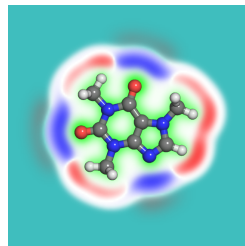
# Electronic structure of a solute in liquid



~ 10 min  $\times 10^3$  steps



~ 5 min



~ 30 s

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

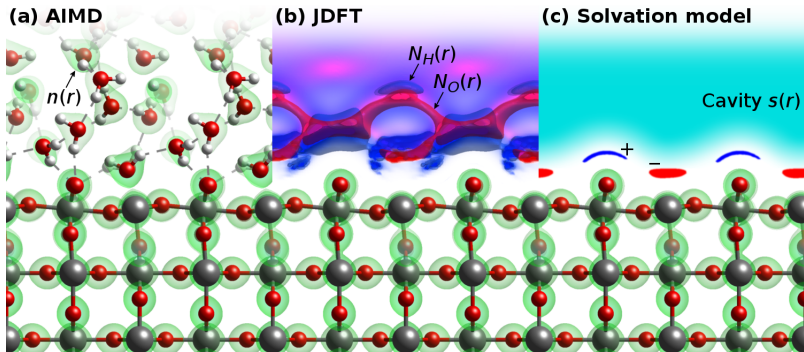
- ▶ Molecular dynamics / Monte Carlo sampling of liquid configurations
- ▶ Describe liquid in terms of equilibrium densities ( $N_O(\vec{r})$ ,  $N_H(\vec{r})$  for water)
- ▶ Joint density-functional theory: free energy functional for liquid
- ▶ Basis for non-empirical continuum solvation methods<sup>1,2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

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

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



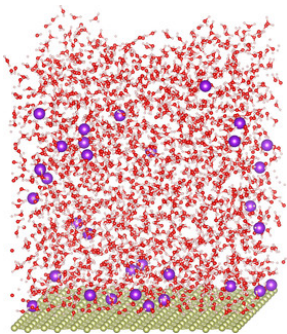
# Solid-liquid interface example



- ▶ 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

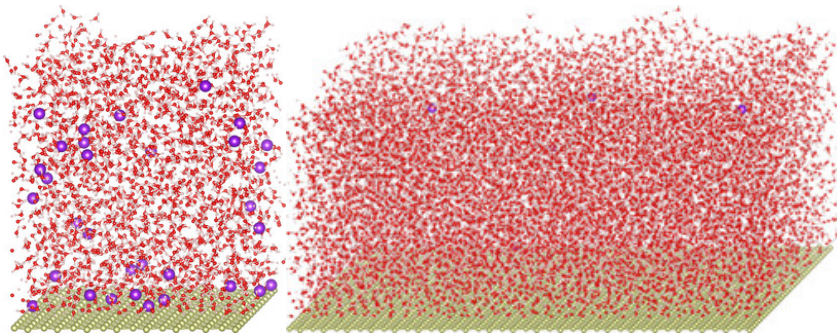


- ▶ Large unit cells for statistically meaningful number of ions
- ▶ Example 1: 1M aqueous KOH with 32 ion pairs  $\Rightarrow$  1800 H<sub>2</sub>O





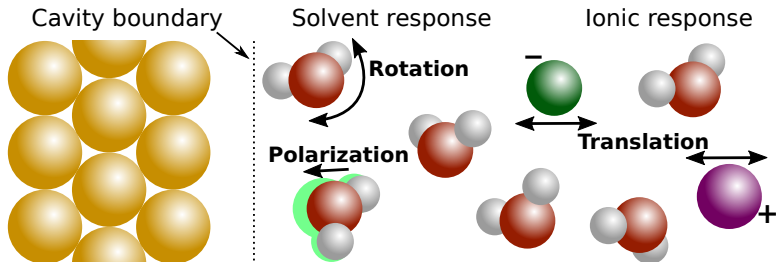
## Electrolytes: further complications



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



# Continuum solvation ingredients

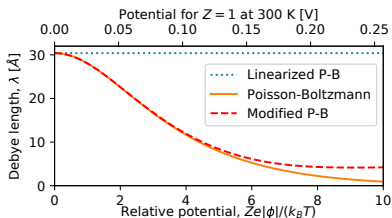


- ▶ **Response:** *how* the solvent and electrolyte create a charge density
- ▶ **Cavity:** *where* they can create this charge density
- ▶ Beyond electrostatic pieces: free energy to form cavity, repulsion, dispersion etc.: less critical for electrochemistry (will skip discussion here)



# Continuum solvation: electric response

## Ionic response

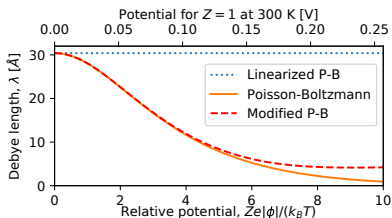


- ▶ Charge density induced in solvent/electrolyte due to interactions with solute/electrode
- ▶ Contributions in a multipole expansion:
  - ▶ **Monopole** ( $l = 0$ ): overall movement of charged ions; nonlinearity due to Boltzmann statistics of ions  $\Rightarrow$  (modified) Poisson-Boltzmann theory

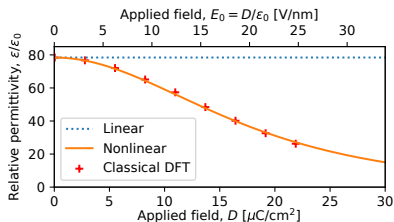


# Continuum solvation: electric response

## Ionic response



## Dielectric response



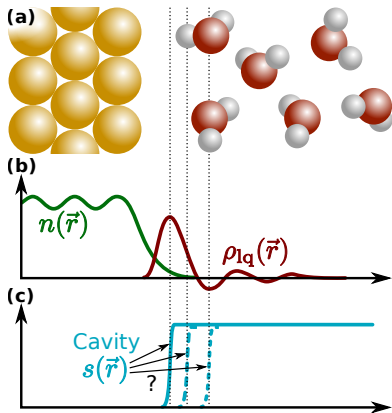
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- ▶ Contributions in a multipole expansion:
  - ▶ **Monopole ( $l = 0$ ):** overall movement of charged ions; nonlinearity due to Boltzmann statistics of ions  $\Rightarrow$  (modified) Poisson-Boltzmann theory
  - ▶ **Dipole ( $l = 1$ ):** dipole 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

R. Sundararaman, K. L.-Weaver and K. Schwarz, *JCP* **148**, 144105 (2018)

K. Schwarz and R. Sundararaman, *Surf. Sci. Rep.* **75**, 100492 (2020)



# Response location: cavity



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



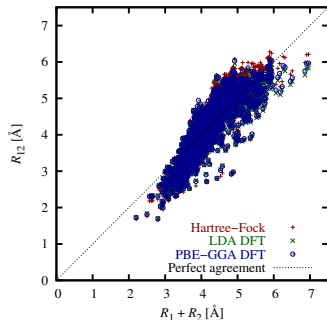
## Minimally-empirical nonlocal solvation models

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



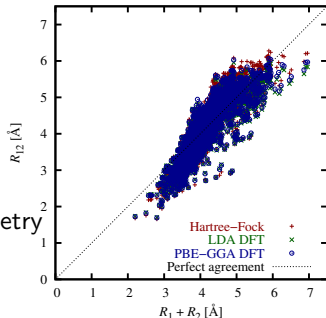
# Minimally-empirical nonlocal solvation models

- ▶ 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



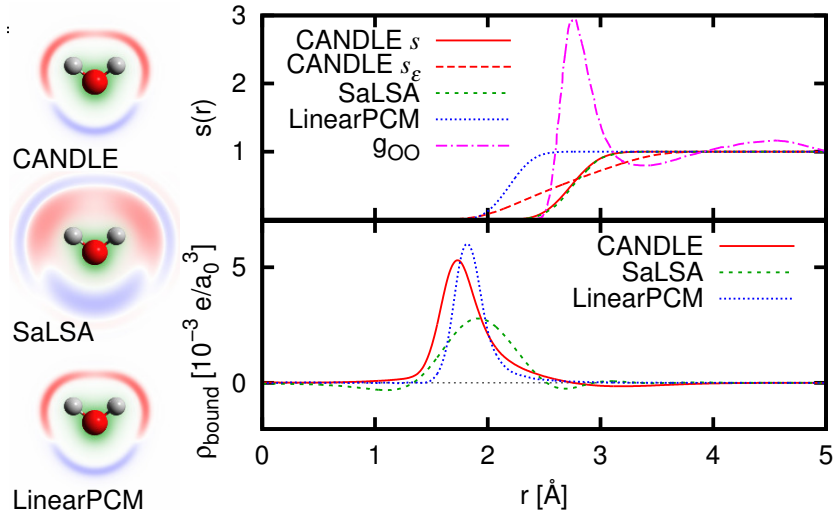
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  - ▶ Cavity from overlap of solute and solvent electron densities, correlated to electron density overlap of all pairs of atoms
  - ▶ *No fit to solvation energies* for cavity size
- ▶ CANDLE: solvation model with charge asymmetry
  - ▶ Charge-Asymmetric: +/- 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

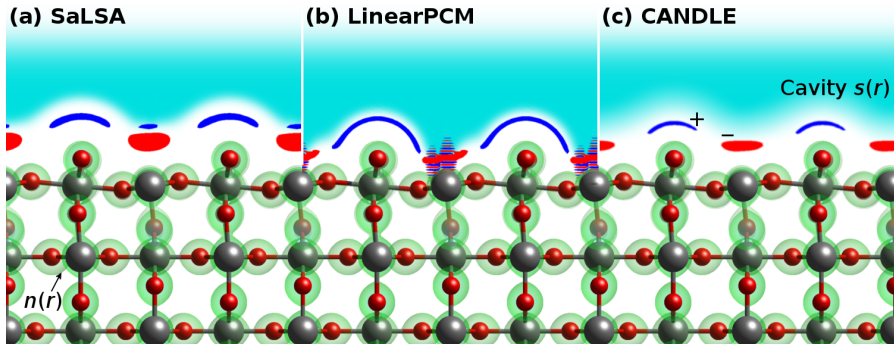
- ▶ Same set of solutes consisting of
  - ▶ 240 neutral organics
  - ▶ 51 organic cations
  - ▶ 55 organic anions

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 (JDFT <sub>x</sub> )	1.36	3.20	19.7	4.55
CANDLE (JDFT <sub>x</sub> )	1.26	2.64	3.54	<b>1.84</b>

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



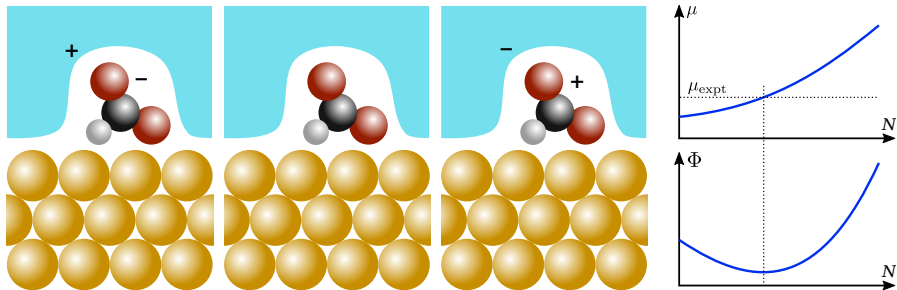
# Solvation models at rutile $\text{TiO}_2$ aqueous interface



- ▶ Example: Rutile  $\text{TiO}_2(110)$  - 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

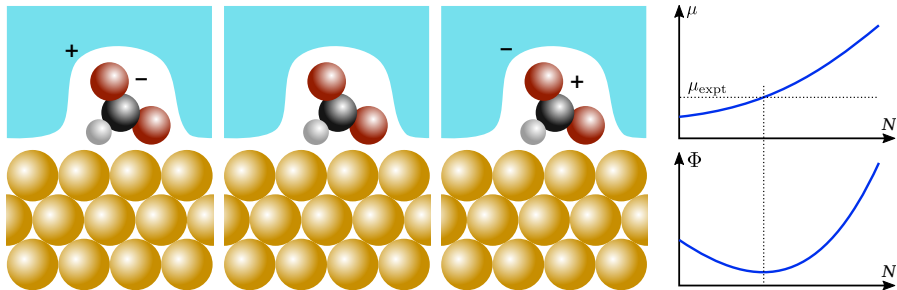


- ▶ Continuum solvation models with electrolyte  $\Rightarrow$  compensate charge on electrode + adsorbate  $\Rightarrow$  net unit cell neutral
- ▶ Electron chemical potential  $\mu$  relatable to electrode potential<sup>3</sup>

<sup>3</sup>K 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  $\mu$  relatable to electrode potential<sup>3</sup>
- ▶ Need sequence of calculations with varying electron number  $N$
- ▶ Find electron number appropriate for  $\mu$  corresponding to experiment
- ▶ Grand free energy  $\Phi$  minimum at the correct  $N$

<sup>3</sup>K 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

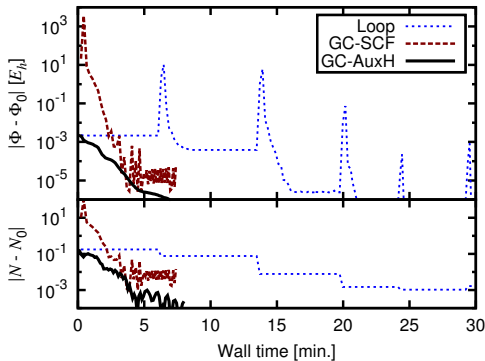
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<sup>4</sup>R. Sundararaman, WA Goddard and TA Arias, *JCP* **146**, 114104 (2017)



# 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 potential<sup>4</sup>
- ▶ 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

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



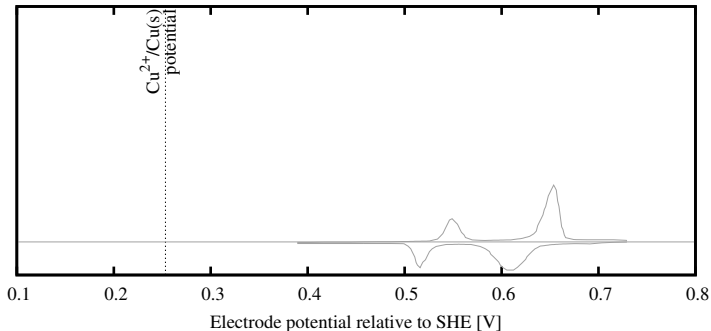
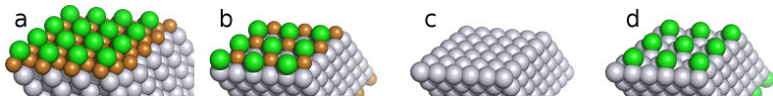
# Key advances

- ▶ 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, CO<sub>2</sub>RR, ammonia synthesis etc.
  - ▶ Next: showcase effect with one example





# Underpotential deposition of Cu on Pt(111)



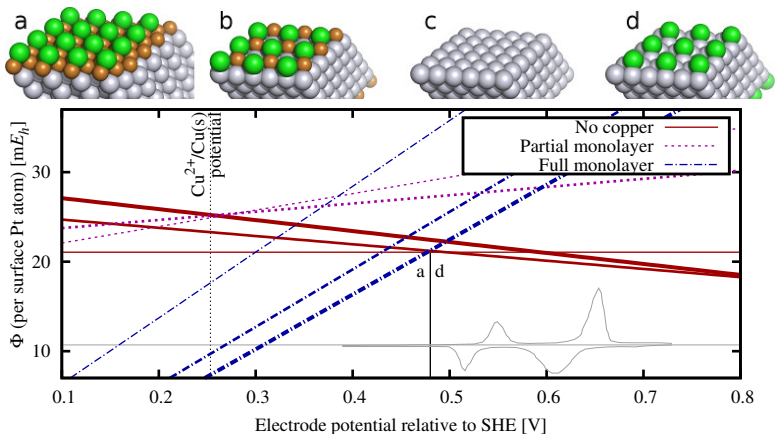
- Identity of second voltammetric peak in presence of  $\text{Cl}^-$

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

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



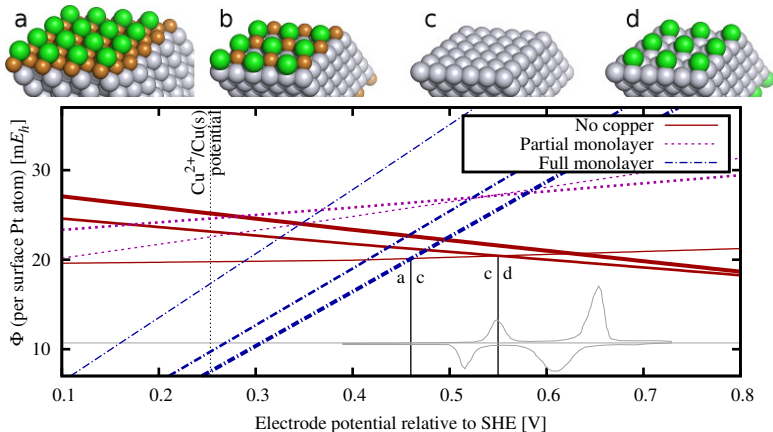
# Underpotential deposition of Cu on Pt(111)



- ▶ Identity of second voltammetric peak in presence of  $\text{Cl}^-$
- ▶ Neutral vacuum DFT calculations predict only one transition



# Underpotential deposition of Cu on Pt(111)

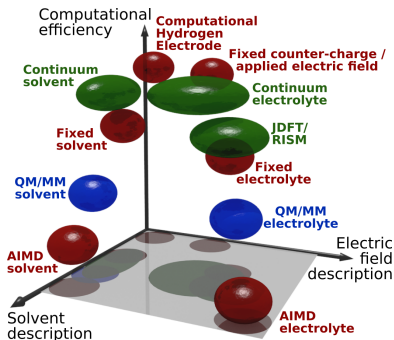


- ▶ Identity of second voltammetric peak in presence of  $\text{Cl}^-$
- ▶ Neutral vacuum DFT calculations predict only one transition
- ▶ Fixed-potential CANDLE calculations predict  $\text{Cl}$ -desorption peak
- ▶ Peak positions with accuracy  $\sim 0.05$  eV



# 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

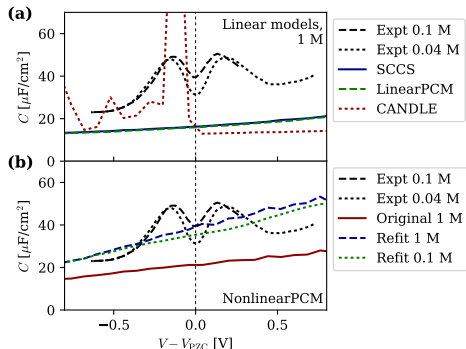


- ▶ **Book chapter:** 'Joint and grand-canonical density-functional theory' in 'Atomic-Scale Modelling of Electrochemical Systems' (Wiley, 2021)
- ▶ **Review article:** 'The electrochemical double layer in first-principles calculations', *Surf. Sci. Rep.* **75**, 100492 (2020)
- ▶ **Review article:** '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)

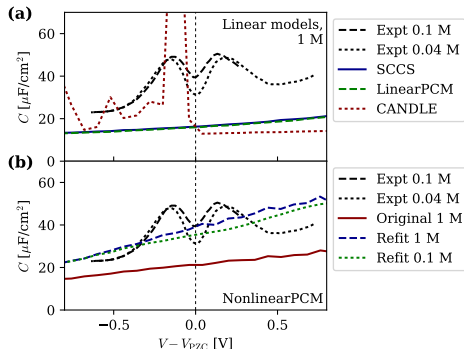
R. Sundararaman and K. Schwarz, *JCP* **146**, 084111 (2017)

R. Sundararaman, K. L.-Weaver and K. Schwarz, *JCP* **148**, 144105 (2018)



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



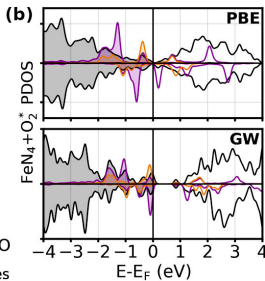
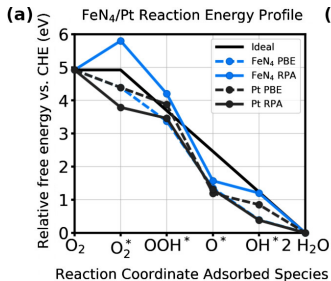
- ▶ Most models underestimate capacitance by 50%
- ▶ Can reparametrize, but still misses qualitative features
- ▶ CANDLE cavity asymmetry  $\Rightarrow$  spikes in capacitance (but charge remains reasonable)
- ▶ Continuum models still miss double-layer structure
- ▶ Future: liquid structure models (classical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

R. Sundararaman and K. Schwarz, *JCP* **146**, 084111 (2017)

R. Sundararaman, K. L.-Weaver and K. Schwarz, *JCP* **148**, 144105 (2018)



# First-principles electrochemistry: beyond DFT?



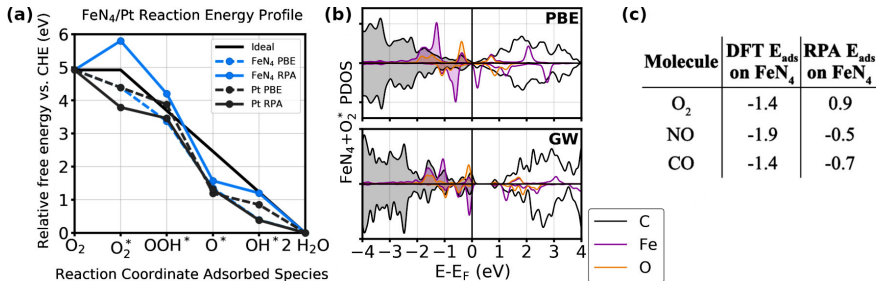
**(c)**

Molecule	DFT $E_{\text{ads}}$ on FeN <sub>4</sub>	RPA $E_{\text{ads}}$ on FeN <sub>4</sub>
O <sub>2</sub>	-1.4	0.9
NO	-1.9	-0.5
CO	-1.4	-0.7

- ▶ 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?

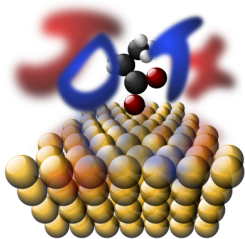


- ▶ Charge states are key  $\Rightarrow$  need solvation and grand-canonical methods
- ▶ Is DFT accurate enough to capture the correct charge state?
- ▶ Often, no: e.g. O<sub>2</sub> binding on FeN<sub>4</sub> and Pt OER catalysts
- ▶ Over 1 eV errors in binding energy  $\Rightarrow 10^{16} \times$  in rates!
- ▶ Need solvated and grand-canonical beyond-DFT methods such as RPA
- ▶ This is critical to computationally optimize the active site

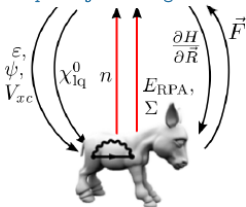




# Hence, BEAST



<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.

