Introduction to joint density-functional theory (JDFT)

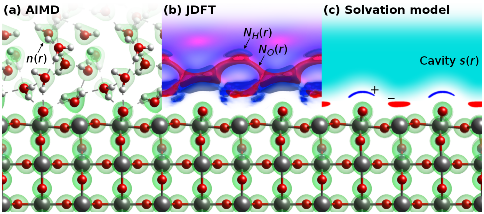
The BEAST collaboration

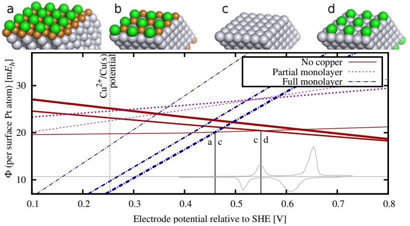
2nd Annual BEAST Workshop, 2023

August 17, 2023

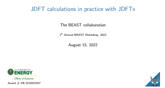
U.S. DEPARTMENT OF ENERGY
Office of Science
Award # DE-SC0022247

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

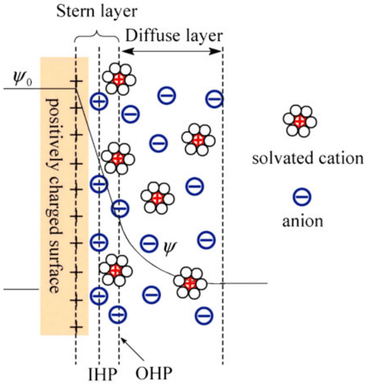
The BEAST collaboration

1^{st} Annual BEAST Workshop, 2022

August 15, 2022

Award # DE-SC0022247

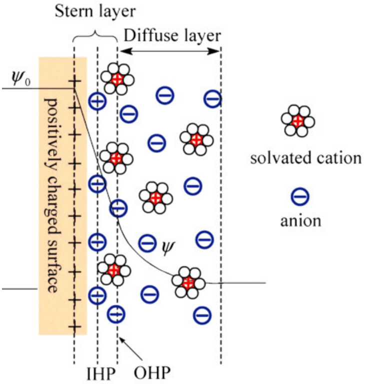
The electrochemical interface

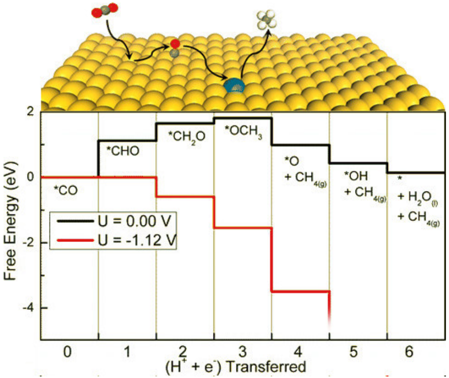


- Gouy-Chapman-Stern model: double layer and diffuse ions

LL Zhang and XS Zhao, *Chem. Soc. Rev.* **38**, 2520 (2009)

The electrochemical interface

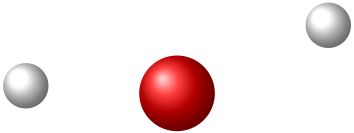




- Gouy-Chapman-Stern model: double layer and diffuse ions
- Typical first-principles calculation:
  - No / minimal treatment of solvent and electrolytes
  - Proton-coupled electron transfer (PCET) steps only
  - Fixed charge + ‘computational hydrogen electrode’ (CHE)

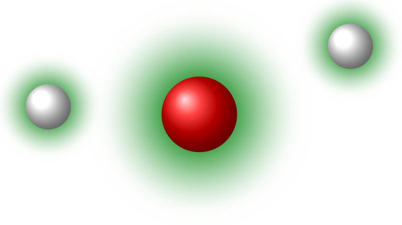
LL Zhang and XS Zhao, *Chem. Soc. Rev.* **38**, 2520 (2009)
MJ Cheng et al., *ACS Catal.* **6**, 7769 (2016)

Ab initio electronic structure: goal



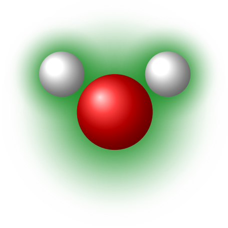
- Given nuclear positions

Ab initio electronic structure: goal



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

Ab initio electronic structure: goal

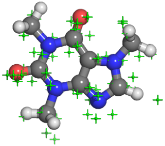


- Given nuclear positions
- Compute electronic wavefunctions, energy and forces
- Optimize/update nuclear positions to obtain structure/dynamics

Ab initio electronic structure: methods

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

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



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

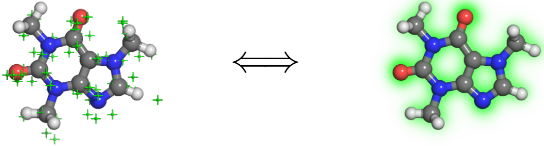
Ab initio electronic structure: methods

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

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

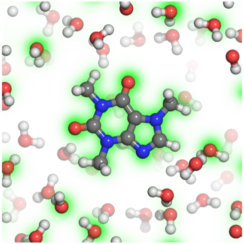
- Hohenberg-Kohn theorem: optimize functional of electron density $n(\vec{r})$

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



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

Electronic structure of a solute in liquid



$\sim$ 15 min[1]

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

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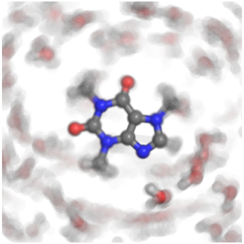
[1] Typical timings using JDFTx on a single NVIDIA K20 GPU

Electronic structure of a solute in liquid

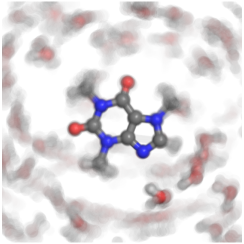


$\sim 10\ \text{min} \times 10^3$ steps

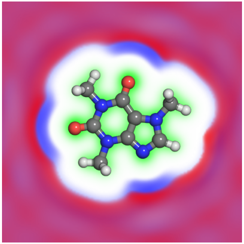
$$\underbrace{F_{\text{HK}}[n]}_{\text{Electrons}}$$

- Molecular dynamics / Monte Carlo sampling of liquid configurations

Electronic structure of a solute in liquid



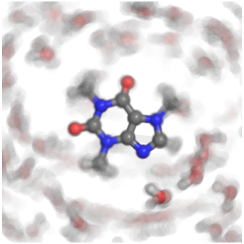
$\sim$ 10 min$\times 10^3$ steps



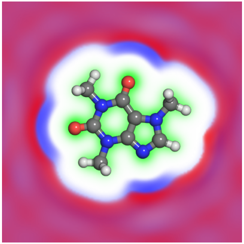
$$\underbrace{F_{\text{HK}}[n]}_{\text{Electrons}}$$

- 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



$\sim$ 10 min$\times 10^3$ steps



$\sim$ 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[1,2]

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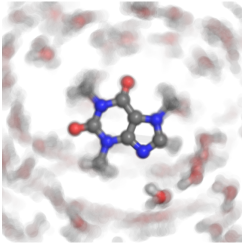
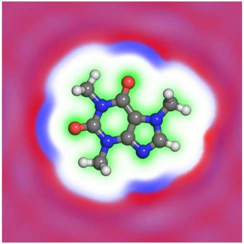
[1] R. Sundararaman and T.A. Arias, *Comp. Phys. Comm.* **185**, 818 (2014)

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

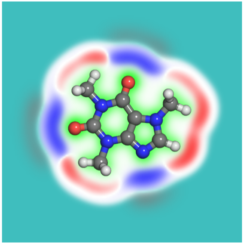
Electronic structure of a solute in liquid



$\sim$ 10 min$\times 10^3$ steps



$\sim$ 5 min



$\sim$ 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[1,2]

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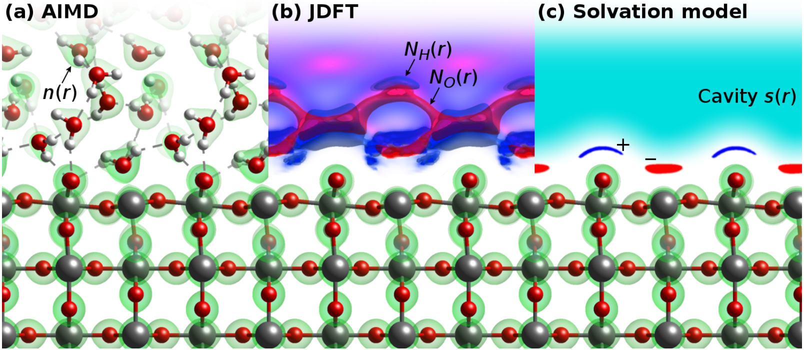
[1] R. Sundararaman and W.A. Goddard, *J. Chem. Phys.* **142**, 064107 (2015)

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

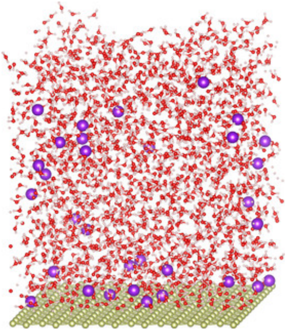
Solid-liquid interface example



- Comparison of techniques shown for rutile $TiO_2(110)$ 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)

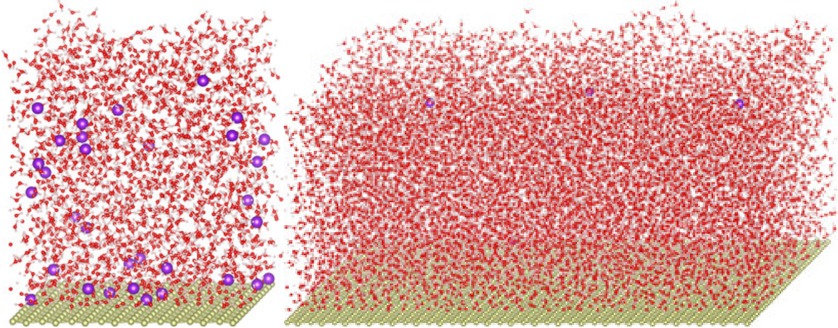
R. Sundararaman and T. A. Arias, chapter in
'Atomic-Scale Modelling of Electrochemical Systems' (Wiley, 2021)

Electrolytes: further complications



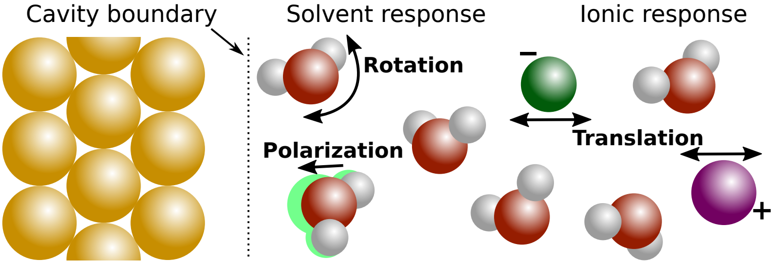
- Large unit cells for statistically meaningful number of ions
- Example 1: 1M aqueous KOH with 32 ion pairs ⇒ 1800 H_2O

Electrolytes: further complications



- Large unit cells for statistically meaningful number of ions
- Example 1: 1M aqueous KOH with 32 ion pairs ⇒ 1800 H_2O
- Example 2: 0.03M aqueous KOH with 6 ion pairs ⇒ 11000 H_2O
- Additionally, large time scales for ion diffusion and equilibration
- AIMD not yet practical at these scales: need continuum solvation

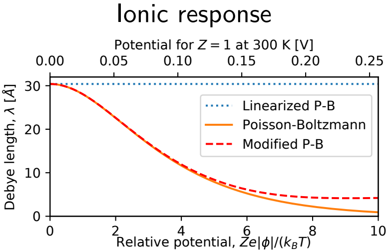
Continuum solvation ingredients



- **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)

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

Continuum solvation: electric 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 ⇒ (modified) Poisson-Boltzmann theory

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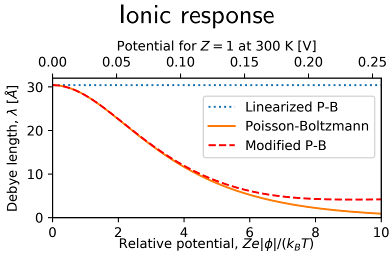
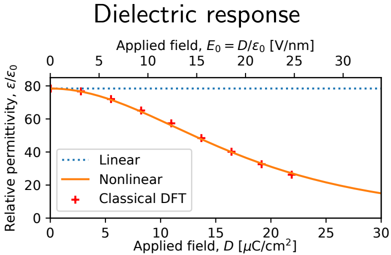
R. Sundararaman, K. L.-Weaver and K. Schwarz, *JCP* **148**, 144105 (2018)
K. Schwarz and R. Sundararaman, *Surf. Sci. Rep.* **75**, 100492 (2020)

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

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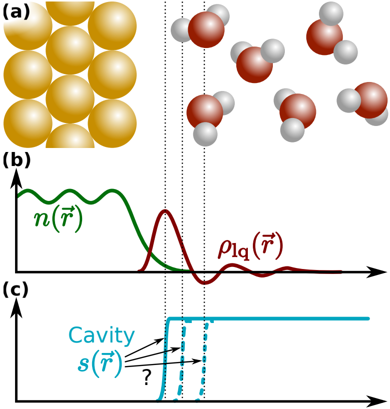
R. Sundararaman, K. L.-Weaver and K. Schwarz, *JCP* **148**, 144105 (2018)
K. Schwarz and R. Sundararaman, *Surf. Sci. Rep.* **75**, 100492 (2020)

Response location: cavity



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

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

Minimally-empirical nonlocal solvation models

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

Minimally-empirical nonlocal solvation models

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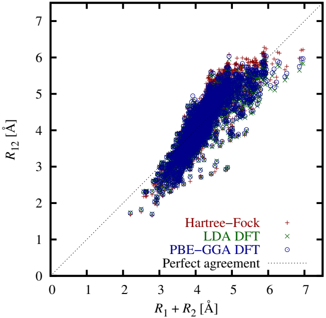
- Spherically-averaged liquid susceptibility ansatz (SaLSA)
  - Directly treat *non-local* solvent response ⇒ cavity-size corresponds physically to solute-solvent atom separation
  - Cavity from overlap of solute and solvent electron densities, correlated to electron density overlap of all pairs of atoms
  - *No fit to solvation energies* for cavity size



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

Minimally-empirical nonlocal solvation models

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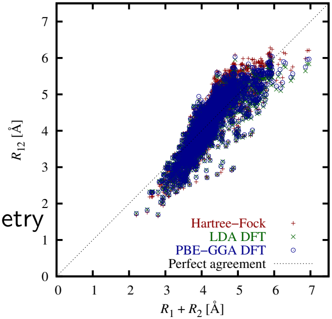
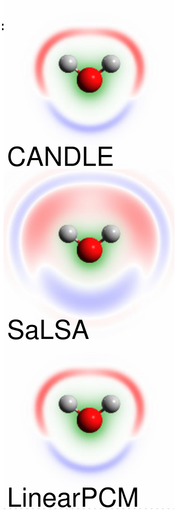


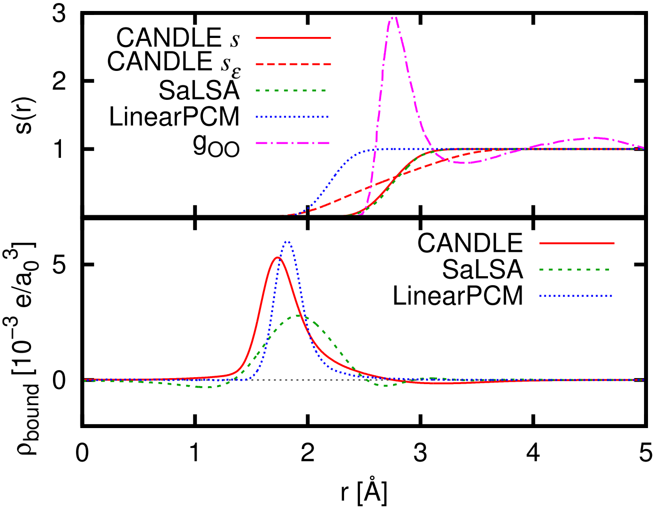
- CANDLE: solvation model with charge asymmetry
    - Charge-Asymmetric: +/- charges solvated differently in most polar solvents
    - Nonlocally-Determined: using SaLSA cavity definition for transferability
    - Local-Electric: replace non-local response with displaced local response (for improved computational efficiency, ease of implementation)

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

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

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

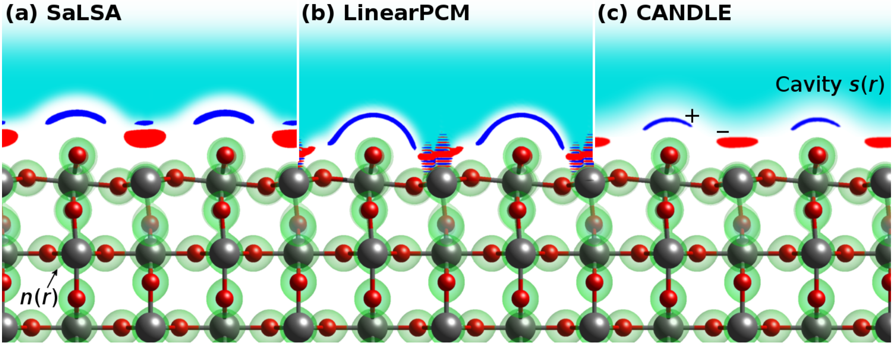
- Same set of solutes consisting of
  - 240 neutral organics
  - 51 organic cations
  - 55 organic anions

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)

SCCS and IEF-PCM results from Dupont et al., *JCP* **139**, 214110 (2013)

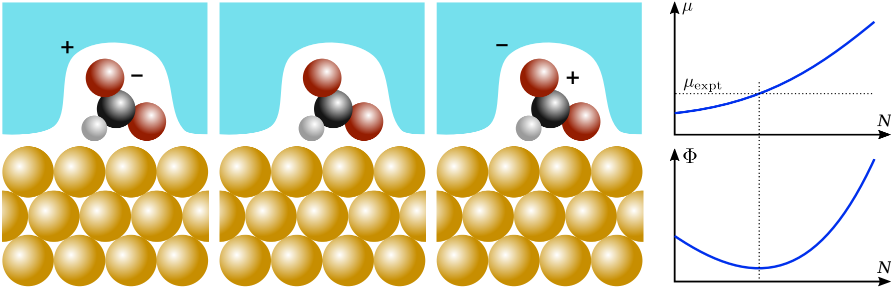
Solvation models at rutile TiO_2 aqueous interface



- Example: Rutile $TiO_2(110)$ - 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)

R. Sundararaman and T. A. Arias, chapter in
'Atomic-Scale Modelling of Electrochemical Systems' (Wiley, 2021)

First-principles scheme for electrochemistry



- Continuum solvation models with electrolyte ⇒ compensate charge on electrode + adsorbate ⇒ net unit cell neutral
- Electron chemical potential μ relatable to electrode potential[3]

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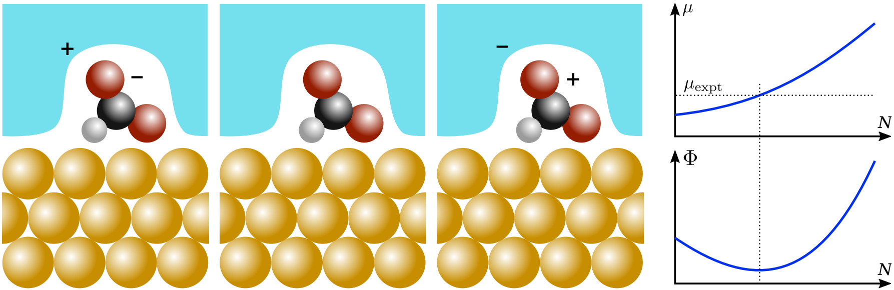
[3] K L-Weaver and TA Arias, *PRB* **86**, 075140 (2012)

First-principles scheme for electrochemistry



- Continuum solvation models with electrolyte ⇒ compensate charge on electrode + adsorbate ⇒ net unit cell neutral
- Electron chemical potential μ relatable to electrode potential[3]
- 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

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[3] 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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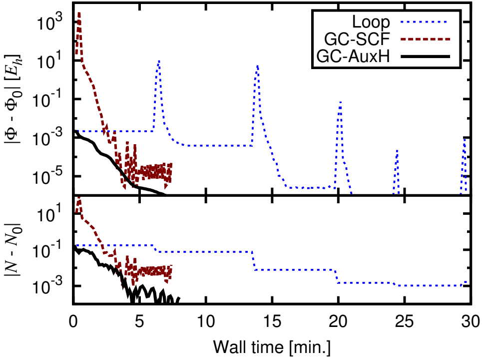
[4] R. Sundararaman, WA Goddard and TA Arias, *JCP* **146**, 114104 (2017)

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[4]
- 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

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[4] 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

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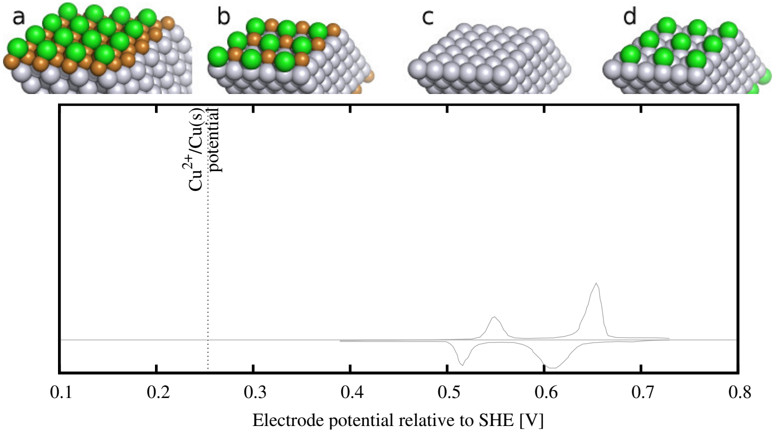
- CANDLE + GC-DFT increasingly adopted in first-principles electrocatalyst design for water-splitting, CO2RR, ammonia synthesis etc.
- Next: showcase effect with one example

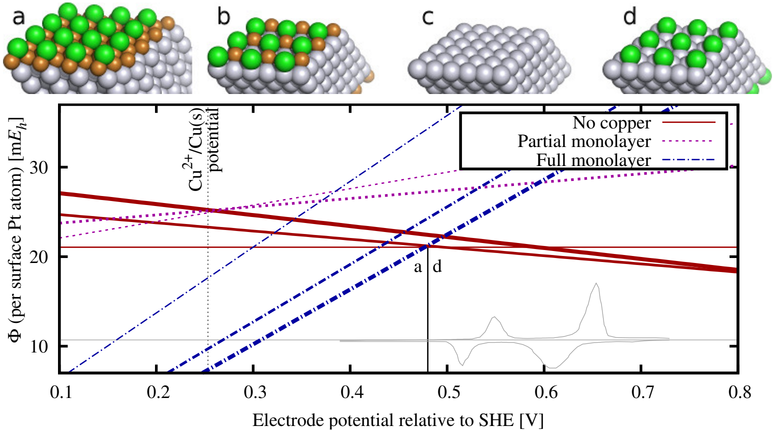
Underpotential deposition of Cu on Pt(111)



- 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)



- Identity of second voltammetric peak in presence of Cl$^-$
- Neutral vacuum DFT calculations predict only one transition

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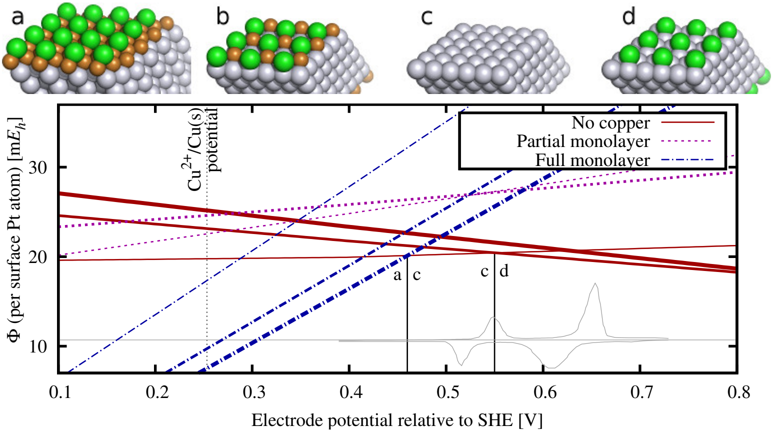
R. Sundararaman, WA Goddard and TA Arias, *JCP* **146**, 114104 (2017)

Underpotential deposition of Cu on Pt(111)

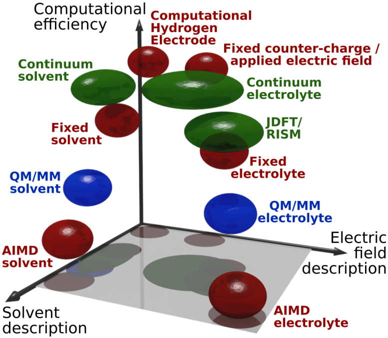


- Identity of second voltammetric peak in presence of Cl^-
- Neutral vacuum DFT calculations predict only one transition
- Fixed-potential CANDLE calculations predict Cl-desorption peak
- Peak positions with accuracy $\sim$ 0.05 eV

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

Electrochemical solvation summary

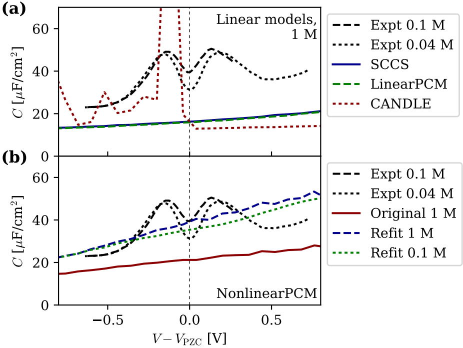
- Large spread in detail of charge and solvation effects in electrochemical predictions
- Most solvation model problems: limitation of local models
- Nonlocal-cavity models eg. CANDLE accurate for high-charge systems
- Grand-canonical DFT conveniently captures changing charge states for reaction modeling



- **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 $\Rightarrow$ 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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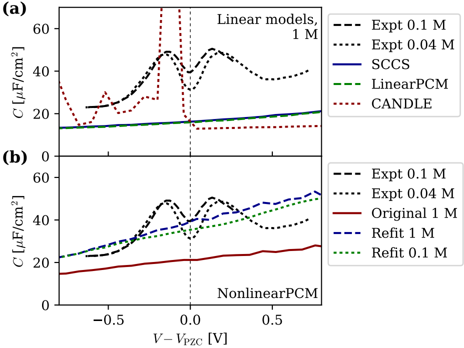

- Most models underestimate capacitance by 50%
- Can reparametrize, but still misses qualitative features
- CANDLE cavity asymmetry ⇒ spikes in capacitance (but charge remains reasonable)
- Continuum models still miss double-layer structure
- Future: liquid structure models (classical DFT / RISM) beyond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

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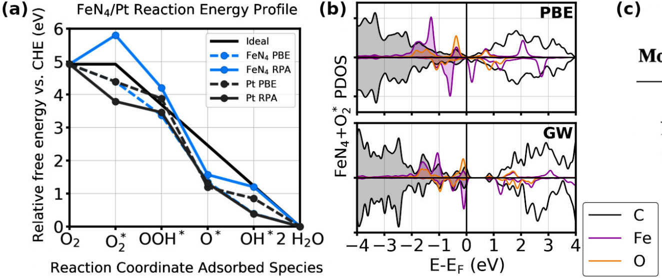
R. Sundararaman and K. Schwarz, *JCP* **146**, 084111 (2017)
R. Sundararaman, K. L.-Weaver and K. Schwarz, *JCP* **148**, 144105 (2018)

First-principles electrochemistry: beyond DFT?



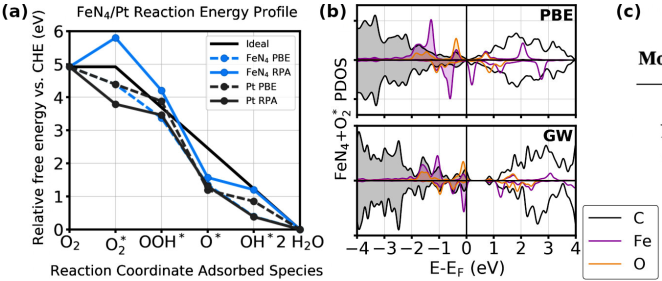
(c)

Molecule	DFT E_{ads} on FeN_4	RPA E_{ads} on FeN_4
O_2	-1.4	0.9
NO	-1.9	-0.5
CO	-1.4	-0.7

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

JM Clary, AM Holder, CB Musgrave and D Vigil-Fowler, *in preparation*

First-principles electrochemistry: beyond DFT?



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- Charge states are key ⇒ need solvation and grand-canonical methods
- Is DFT accurate enough to capture the correct charge state?
- Often, no: e.g. O_2 binding on FeN_4 and Pt OER catalysts
- Over 1 eV errors in binding energy ⇒ $10^{16}\times$ in rates!
- Need solvated and grand-canonical beyond-DFT methods such as RPA
- This is critical to computationally optimize the active site

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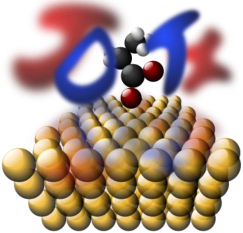
JM Clary, AM Holder, CB Musgrave and D Vigil-Fowler, *in preparation*

Hence, BEAST



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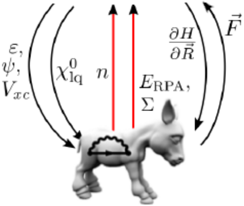

https://berkeleygw.org

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.