Surface Studies with Combined Free Energy Functionals of Electronic and Liquid Densities

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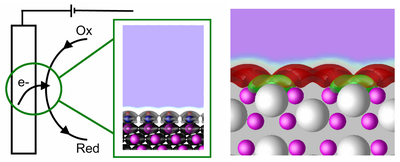
Free Energy Functionals for Solvated Surfaces

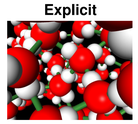
Solvated Surfaces: Potential Applications



Catalysis — Surface Stability

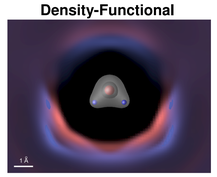
Which Solvation Theory is Appropriate?

Explicit



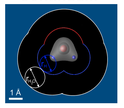
High Cost:
- Many Electrons
- Thermodynamic Sampling

Density-Functional



- Includes full *ab-initio* description of solute
- No explicit solvent molecules
- Does not require phase space sampling
- Reproduces properties of bulk liquid

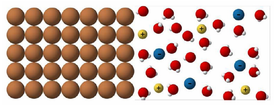
Continuum



Low Reliability:
- Highly parametrized
- No shell structure
- Cavitation incorrect

Joint Density-Functional Theory (JDFT)

Rigorous description of electronic systems in complex environments:[1]



Solute — $n(r)$: Solute electron density

Solvent — $N_\alpha(r)$: Liquid atomic site densities (α=O,H,ionic species)

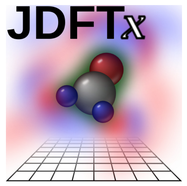
Thermodynamic Equilibrium Free Energy:

$$A = \min_{n,\{N_\alpha\}} \left(A[n,\{N_\alpha\}] \right)$$

$$A[n,\{N_\alpha\}] = \tilde{\Omega}[\{N_\alpha\}] + F_{HK}[n] + \Delta A[n,\{N_\alpha\}]$$

- $\tilde{\Omega}[\{N_\alpha\}]$: Liquid functional minimized over solvent electronic degrees of freedom
- $F_{HK}[n]$: Electronic DFT Functional for solute
- $\Delta A[n,\{N_\alpha\}]$: Coupling between liquid and solute

Open Source Software:



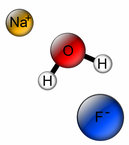
http://jdftx.sourceforge.net

[1] S.A. Petrosyan et al, *Physical Review* **B**, 205105 (May 2007)

Liquid Functional $\tilde{\Omega}[\{N_\alpha\}]$

$$\tilde{\Omega} = \Omega_{NI}[P_\Omega] + \int (V_\alpha - \mu)\cdot N_\alpha + F_{ex}[\{N_\alpha\}]$$

Ideal gas of:
- Water molecules[2,3] (α=O,H)
- Sodium ions (α=Na$^+$)
- Fluorine ions (α=F$^-$)



in **external potentials** $V_\alpha = \frac{\partial \Delta A}{\partial N_\alpha}$.

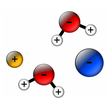
Excess Functional:

$F_{ex}[\{N_\alpha\}] =$

$\Phi_{TZ}[\{N_\alpha\}]$ — Mixture of Hard Spheres[4]

$+\int N_O A_{VW_{att}}(N_O \otimes w_{LJ})$ — Isotropic Attraction[5]

$+\int N_\alpha Z_\alpha K Z_\beta N_\beta$ — Long Range Coulomb



[2] J. Lischner, T. A. Arias, J Phys. Chem. B, 114, 1946 (2010).
[3] R. Sundararaman, K. Letchworth-Weaver, T.A. Arias. http://arxiv.org/abs/1112.1442 (2011).
[4] P. Tarazona, Phys. Rev. Lett. **84**, 694 (2000).
[5] C.A. Jeffrey, P.H. Austin, J. Chem Phys **110**, 484 (1999).

Coupling Functional $\Delta A[n,\{N_\alpha\}]$

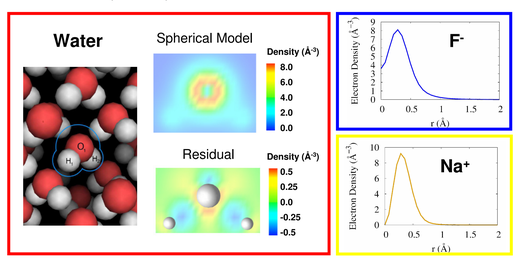
Density-Only DFT: Thomas-Fermi-LDA approximation:[6,7]

ΔA= G[ ]–G[ ]–G[ ]

$$G[n_s(r)] = \underbrace{\frac{3}{10}(3\pi)^{2/3}\int n_s(r)^{5/3} d^3r}_{\text{Kinetic Energy (Thomas-Fermi Approx.)}} + \underbrace{\frac{1}{2}\iint \frac{\rho_s(r)\rho_s(r')}{|r-r'|} d^3r\, d^3r'}_{\text{Mean Field Coulomb ("Hartree")}} + \underbrace{\int n_s(r)\varepsilon_{LDA}[n_s(r)] d^3r}_{\text{Exchange \& Correlation (Local Density Approx.)}}$$

Solvent Electron Density: $n_{lq}[N_\alpha(r)] = \sum_\alpha \int n_\alpha(r-R) N_\alpha(R)\, d^3R$

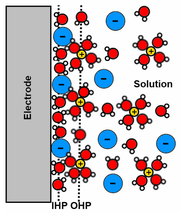
- $n_\alpha(r)$ are spherical models of site electron density for α = O, H[8] and ionic species.
- Determined by least squares fits to reference ab-initio calculations



[6] L.H. Thomas, Proc. Camb. Phil. Soc, **23**, 542–548 (1927)
[7] Hodak, Lu, Bernholc, J. Phys. Chem **128**, 104101 (2008)
[8] Kaminski et al, J. Phys. Chem. A **114**, 6082-6096 (2010)

Metal Surfaces in Aqueous Electrolyte

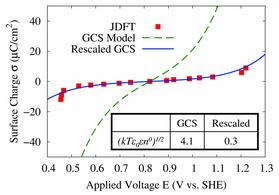
Gouy-Chapman-Stern Model



Conjecture of realistic electrolyte structure
Bockris, et al.

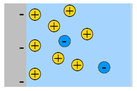
$$\sigma(E) = (8kT\varepsilon_0\varepsilon n^0)^{1/2}\sinh\left(\frac{e(E-E_{PZC})}{2kT}\right)$$

ε : dielectric constant, n^0 : ion number density



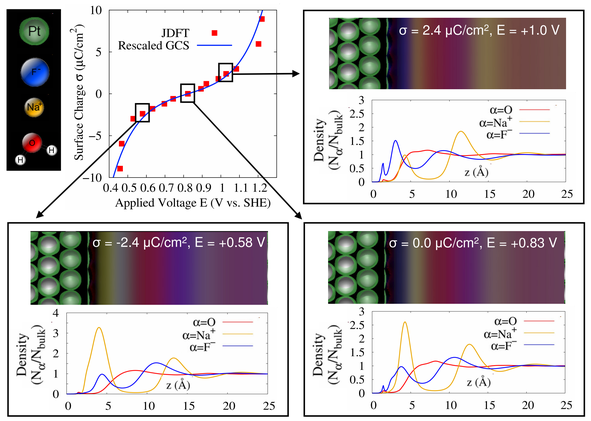
Guoy-Chapman-Stern Model Neglects:[9]

- Structure of the dielectric in first layer (ε).
- Saturation of the dielectric in strong fields (ε).
- Differences in anionic and cationic size (n^0).
- Ion-ion correlation (n^0).



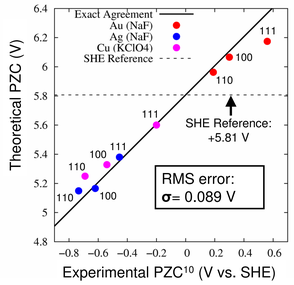
[9] Bard and Faulkner. Electrochemical Methods: Fundamentals and Applications.

Voltage-Dependent Structure



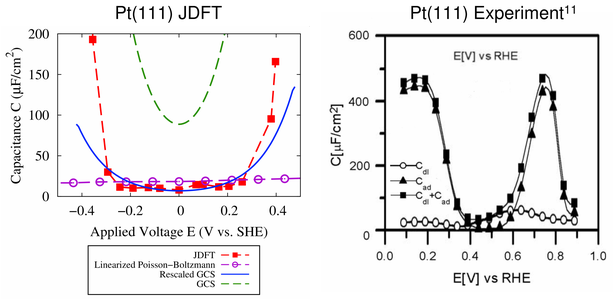
Potentials of Zero Charge

Single Crystalline Metallic Surfaces



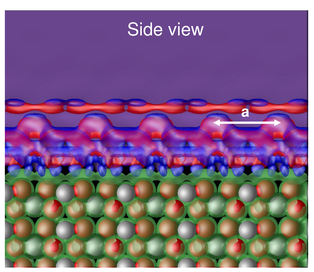
[10] S.Trasatti, Modern Aspects of Electrochemistry 33 (1999).

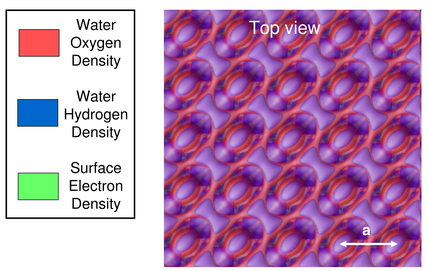
Double Layer and Adsorption Capacitance



[11] T. Pajkossy and D.M. Kolb, Electrochimica Acta 46, 3063 (2001)

Rutile TiO_2 (001) in Water

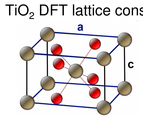




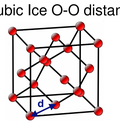
Potential of Zero Charge Shift (HOMO) from vacuum to solvated surface: ΔE_{PZC} = -1.2 V

Is ice forming at surface?

TiO_2 DFT lattice constant: a = 4.65 Å (Expt. 4.59 Å)



Cubic Ice O-O distance: d = 4.73 Å



Only 1% lattice mismatch!

Experiment: M.A. Henderson, Surf. Sci. 355 151 (1996)

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