Theory and computation of electrocatalytic thermodynamics and kinetics: The grand canonical approach

Marko M. Melander

Computational Catalysis Department of Chemistry University of Jyväskylä marko.m.melander@jyu.fi

#### 20.11.2019



### Electrocatalysis?

- 2 The grand canonical approach: Thermodynamics
- 3 Grand canonical kinetics
- Why is this stuff presented at an ASE workshop?

## Why electrochemistry and electrocatalysis?



## Controlling redox reaction thermodynamics and kinetics with the Figure from Zhi Wei Seh et.al. Science 13 Jan 2017: Vol. 355, Issue 6321, eaad4998

Marko M. Melander

GC approach to electrocatalysis

## The electrochemical interface and experiments

• Experiments probe chemistry at electrochemical, electrified solid-liquid interface



- The thermodynamic state is unambiguously determined by the independent thermodynamic variables: T, V, and P/c (Helmholtz/Gibbs) or T, V, and μ (Landau or Grand canonical) → Thermodynamics and kinetics as a function of the electrode potential in the presence of electrolytes
- Quantum mechanics, thermodynamics, rate theory ...

Marko M. Melander

GC approach to electrocatalysis

## Motivation and need: Electrocatalytic reactions

- Important reactions especially for energy conversion and storage: ORR, OER, HER, CO2RR...= PCET Reactions
- Depending on the reaction and catalyst, both coupled and decoupled processes possible



- Rate and thermodynamics depend on the electrode potential
- Goal: Theory and computational methods to study PCET reactions at fixed potentials including tunneling, non-adiabaticity, pH... → extend common DFT and rate theory

#### Electrocatalysis?

2 The grand canonical approach: Thermodynamics

#### 3 Grand canonical kinetics

Why is this stuff presented at an ASE workshop?

## DFT thermodynamics for electrons and nuclei

- Normal DFT:  $U(S, V, N)[\rho]$ , energy operator  $\hat{E} = \hat{H}$
- Thermal DFT: Legendre transform to Helmholtz  $\rightarrow A(T, V, N)[\hat{\rho}]$ , a thermal ensemble of states using density operator  $\hat{\rho}$ ,  $\hat{E} = \hat{H} T\hat{S}$
- Thermal GC-DFT: Further Legendre transform to open systems with fixed chemical potentials: Ω(T, V, μ)[ρ̂<sub>GC</sub>], Ê = Ĥ - TŜ - μÑ
- Multicomponent DFT: treat both electron and nuclear densities for a fully quantum theory, *E*[*ρ*(**r**), {*N*(**R**)}]
- By minimizing the energy functional one obtains thermodynamic quantities
- Note: In experiments only independent thermodynamic variables can be controlled, not (local) temperature, surface charges, concentrations/pH, coverages etc. → only controllable parameters should be included in the theoretical treatment

## GCE for electrochemistry

- For large enough systems all ensembles are equally useful but for simulating small systems the choice of ensemble is critical
- In an electrochemical setup both the electronic and nuclear/ionic chemical potentials are fixed
- Practical solution: Fix electron and electrolyte chemical potentials to mimic experiments at fixed electrode potential and electrolyte concentration
- Free energy from a single calculation!
- General description for thermodynamics and kinetics



## Grand canonical electron/electrolyte DFT

General framework: Multicomponent grand canonical DFT<sup>1</sup>

$$\Omega(T, V, \tilde{\mu}_{\pm}, \tilde{\mu}_n) \equiv \operatorname{Tr}\left[\hat{\rho}\hat{\Omega}\right] \equiv \Omega[\hat{\rho}]$$
$$= \sum_{i} p_i \left[\beta \ln p_i + \langle \Psi_i | \hat{H}_{tot} - \mu_{\pm}^{N}(\hat{N}_{+} + \hat{N}_{-}) - \tilde{\mu}_n \hat{N}_n | \Psi_i \rangle\right]$$

$$\hat{\Omega} = \hat{H}_{tot} - T\hat{S}_{Nn} - \sum_{i} \tilde{\mu}_{i}\hat{N}_{i}$$
$$\hat{\rho}^{GC} = \frac{\exp\left[-\beta(\hat{H}_{tot} - \sum_{i} \tilde{\mu}_{i}\hat{N}_{i})\right]}{\operatorname{Tr}\left[\exp\left[-\beta(\hat{H}_{tot} - \sum_{i} \tilde{\mu}_{i}\hat{N}_{i})\right]\right]}$$

• Fully quantum nuclear and electronic densities, nonadiabatic effects...

<sup>&</sup>lt;sup>1</sup>M. Melander, M. Kuisma, T. Christensen, K. Honkala, J. Chem. Phys. 150, 041706 (2019)

## Practical electron/electrolyte grand canonical DFT

- A systematic coarse-graining can be performed to obtain
  - Quantum dynamics (GC-PIMD, GC-RPMD)
  - Dynamics with classical nuclei (GC-AIMD)
  - Selected nuclei treated with QM: The NEO-DFT approach
  - Classical electrolyte with well-defined ions and solvent (QM/MM or classical DFT with atom/molecular densities)
  - Continuum models (dielectric + mPB)

Implemented modified Poisson-Boltzmann models in GPAW.

$$\begin{split} \Omega &= -\frac{1}{2} \sum_{i} \langle \psi_{i} | \nabla^{2} | \psi_{i} \rangle + \int d\mathbf{r} \epsilon_{xc}[n(\mathbf{r})] n(\mathbf{r}) \\ &+ \frac{1}{2} \int d\mathbf{r} \phi(\mathbf{r})[n(\mathbf{r}) + \rho_{\pm}(\mathbf{r}) - N(\mathbf{r})] - \int d\mathbf{r} \tilde{\mu}_{n} n(\mathbf{r}) \\ &- \int d\mathbf{r} \mu_{\pm} \rho_{\pm}(\mathbf{r}) - TS_{ions} + G_{chem} \end{split}$$

 General electron/ion Kohn-Sham-Mermin in dielectric electrolyte environment

## Grand canonical Electronic DFT: Potentiostat

- Extended Lagrangian for fixed potential calculations, similar to thermostats or barostats
- Fictitious dynamics for the number of electrons

$$\dot{n}_e = rac{P_{n_e}}{M_e}$$
 and  $\dot{P}_{n_e} = F_e = U - U_0$ 

- Both  $n_e$  and U fluctuate around their (set) equilibrium values  $\rightarrow$  proper ensemble averaging
- Available ASE thanks to Mikael Kuisma



Bonnet, PRL 109, 266101 (2012)

## Grand canonical Electronic DFT: Iterative

 Naive implementation is easy but efficient recycling of wave functions / density is needed for real situations



(Stolen from G. Kastlunger, J. Phys. Chem. C 2018, 122, 24, 12771)

## Simple GC-DFT calculator

1 2

3 4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

```
class GCDFT (Calculator) :
    implemented_properties = ['energy', 'forces', 'grand_energy']
    def init (self, calc, atoms, charge = None, U=0., Uref = -4.44,
        new calculation = False, optimizer setups = { 'method': 'secant', 'maxstep':0.2,
        'tolerance':0.01, 'steps':20, 'minimum':-4, 'maximum':4, 'initial step':0.01}):
        < INITIALIZE CALCULATOR AND SET REFERENCE OUANTITIES >
    def calculate(self, atoms, properties, system changes):
        def fdgc(c):
        ''' Finite-difference grand canonical calculator. Takes charge (c) and returns
        difference from chosen potential '''
            self.calc.set(charge = c)
            self.atoms.set calculator(self.calc)
            self.E = self.atoms.get potential energy()
            self.Ef = self.calc.get fermi level()
            dII = -self Ef - self IIref - self II
            return du
        if self.opt['method'] == 'secant':
            self.opt charge = self.secant(fdgc)
        else: ...
    def secant(self, f):
        self.dU0 = self.U0 - self.U
        while abs(self.dU1) > self.opt['tolerance'] and iteration_counter < self.opt['steps</pre>
            denominator = float(self.dU1 - self.dU0) / (self.c1 - self.c0)
            c = self.c1 - float(self.dU1)/denominator
       self.c0 = copy.copy(self.c1)
        self c1 = c
       self.charge step = self.c1 - self.c0
       self.dU0 = self.dU1.copy()
       self.dU1 = f(self.c1)
```

## Handling charged slabs: The electrostatics

- The GC-EDFT calculations lead to partly periodic charged systems
- Also one needs the absolute electrode potential at various charge states: one point should be the same for all situations
- Depends on the DFT code but Dirichlet boundary conditions (fixed value) for Poisson equation is a good
- Charged systems either neutralized with Poisson-Boltzmann or jellium or use "metallic or tin-foil" boundary conditions



## The absolute electrode potential?

There are no "absolute electrode potentials", only single electrode potentials

$$E(abs) = E(red) + K = \delta \phi_M^S - \mu_e^M + K$$

*K* is a constant depending on the reference scale and a Galvani potential difference  $\delta \phi_M^S$  between the electrode and solvent and  $\mu_e$  the chemical potential of electrons, i.e. the Fermi-level

- Different references need to be used for different models! For Poisson-Boltzmann the solvated "free electron",  $\mathcal{K} = \mu_e^S$  and  $E(abs)^{PB} = -\tilde{\mu}_e^M$ .
- On experimental scale:  $\Delta E(SHE) = E(abs)^{PB} + \Delta \chi_s E_{vac}^{SHE}$



#### Electrocatalysis?

2 The grand canonical approach: Thermodynamics

#### 3 Grand canonical kinetics

Why is this stuff presented at an ASE workshop?

## Theoretical framework<sup>3</sup>

- The theory is independent of the type of reaction: ET, PT, PCET, non-adiabatic, tunneling, adiabatic, solvent-controlled...
- For thermal reactions Miller's canonical rate theory<sup>2</sup> is extended to GCE

$$k(T, V, \mu)\Xi_{0} = \sum_{N} \exp[\beta \mu N] \int dE \exp[-\beta E] \underbrace{P(E)}_{\substack{\text{microcanonical}\\ \text{canonical}}}_{grandcanonical}$$

Miller's theory is generally valid for all thermal rate equations

<sup>&</sup>lt;sup>2</sup>W.H. Miller, J. Phys. Chem. A 102, 793 (1998)

<sup>&</sup>lt;sup>3</sup>M. M. Melander, submitted, preprint on ChemRxiv

# How is the GCE rate theory different from previous approaches?

- All rate theories derived the for canonical ensemble can be extended to GCE
- Does not rely on model Hamiltonians and can be used with whichever first principles method
- Electrode potential is self-consistently included to capture double-layer, electronic structre ... effects
- Non-adiabatic reactions do not rely on an orbital description or the DOS which are non-unitary:

$$k(E) \propto \int_{-\infty}^{\infty} d\epsilon |H_{ab}(\epsilon,\epsilon_0)|^2 f(\epsilon-E) imes \exp\left[-eta rac{(\lambda+e_0(E^0-E)-\epsilon_0)^2}{4\lambda}
ight]$$

For electron in  $b, \epsilon \to a, \epsilon_0$  and  $H_{ab}(\epsilon, \epsilon_0) = \langle \psi_a^{\epsilon_0} | \hat{H} | \psi_b^{\epsilon} \rangle$ 

## Adiabatic and non-adiabatic reactions

- Adiabatic: only the ground state electronic/vibronic potential energy surface is needed
- Non-adiabatic: transitions between ground and excited electronic/vibronic states
- Choice of the reaction coordinate lead to different theoretical and computational pictures: solvent/surrounding reorganization (Fermi-golden rule) or e.g. H-bond distances (NEB)?



## Electronically adiabatic reactions

 Assume classical nuclei and ignore re-crossing reactions: The GCE-TST

$$k(T, V, \mu) \equiv_I = \frac{k_B T}{h} \equiv^{\dagger} \rightarrow k(T, V, \mu) = \frac{k_B T}{h} \exp\left[-\beta \Delta \Omega^{\ddagger}\right]$$

At this limit normal tools such NEB and DIMER in ASE can be used directly

• Account for quantum nuclei but ignore back-propagating reactions: The GCE-TST with a correction

$$k(T, V, \mu) \equiv_I = \langle \kappa \rangle_{\mu} \frac{k_B T}{h} \equiv^{\dagger}$$

Effective crossing correction using on GC ground state: WKB-based approximations (analytical or numerical), (truncated) semi-classical TST ...

## Diabatic approach for adiabatic reactions

- Traditionally, (canonical) electrochemical rate equations are based on diabatic states: empirical valence bond theory (EVB)
- It turns out that GC-EVB can be established. In the simplest case, a Marcus-like rate is obtained

$$k = \frac{\kappa}{\sqrt{4k_BT\Lambda}} \exp\left[-\beta \frac{(\Delta\Omega_{FI} + \Lambda)^2}{4\Lambda}\right]$$



Fixed potential diabatic states using GC-constrained DFT<sup>4</sup>

<sup>4</sup>M. Melander et.al. JCTC. 2016, 12, 11, 5367

## Predictions from GC-EVB theory

 Generalized free energy relationships using BEP and Tafel slopes Tafel:

$$k(U) \propto \exp\{-\alpha \times (U - U_0)\}\exp\{-\Delta G^{\ddagger}(U_0)\}$$

General:

$$\alpha \propto \frac{\partial \ln k}{\partial U} = -\frac{\partial \ln k}{\partial \Delta \Omega} \frac{\partial \Delta \Omega}{\partial \tilde{\mu}_n} \frac{\partial \tilde{\mu}_n}{\partial U} = -\gamma \Delta \Omega'$$
$$\gamma = \frac{1}{2} \left[ 1 + \frac{\Delta \Omega}{\Lambda} \right] \quad \text{and} \quad \Delta \Omega' \sim \pm \text{constant}$$

The GC-EVB theory agrees nicely with GC-DFT results<sup>5</sup>



<sup>5</sup>Lindgren, Kastlunger, Peterson, arXiv:1903.09903

Marko M. Melander

GC approach to electrocatalysis

## GC-EVB in action: Volmer on Au at equilibrium



- Reorganization coordinate: Water rotates and diffuses from the surface
- Reorganization energy:  $\Lambda\approx 5.5$  eV, much larger than assumed for model Hamiltonian^6
- Effective coupling constant:  $\Omega_{\textit{IF}}\approx$  1.1 eV, much smaller than assumed for model Hamiltonian^6
- Smooth charge transfer and large coupling constant indicate electronic adiabaticity

<sup>&</sup>lt;sup>6</sup>Lam, Soudackov,Hammes-Schiffer, JPCL 2019, 10, 18, 5312

## Non-adiabatic reactions

- Sudden jumps in electronic states along the "reaction coordinate"
- Only jumps conserving the particle number are allowed
- The solvent/surrounding reorganize to enable electron/proton tunneling at a given energy
- Rate given by Fermi Golden Rule-like expression (for high-T, slow nuclei)

$$egin{aligned} &k_{GCE-NATST} pprox \sum_{N} p_{iN} rac{V_{N,if}^2}{\hbar\sqrt{4\pi k_B T \lambda}} \exp \left[ -rac{(\Delta E_{fi}^N + \lambda)^2}{4k_B T \lambda} 
ight] \ &pprox rac{\langle V_{if}^2 
angle_{\mu}}{\hbar\sqrt{4\pi k_B T \Lambda}} \exp \left[ -rac{(\Delta E_{fi}^\mu + \Lambda)^2}{4k_B T \Lambda} 
ight] \end{aligned}$$

- The latter form can be used for interpolating between adiabatic and non-adiabatic limits
- All quantities can be computed using (GC-)cDFT

## Non-adiabatic reactions: Why and when to bother?

- Small coupling constants and/or sudden changes in 1) charge or 2) dipole moment indicate non-adiabaticity<sup>7</sup>
- Volmer on Au: Model Hamiltonians indicate electronic adiabiticity and vibronic non-adiabaticity<sup>8</sup> and explain experiments<sup>9</sup>
- Non-adiabatic: Diabatic (Marcus)  $\approx$  adiabatic(NEB) barrier
- Long-distance electron transfer



<sup>7</sup>Sirjoosingh and Hammes-Schiffer, JPCA, 2011, 115, 2367

<sup>8</sup>Lam, Soudackov,Hammes-Schiffer, JPCL 2019, 10, 18, 5312

Sakaushi, Faraday Discuss., 2019

### Electrocatalysis?

2 The grand canonical approach: Thermodynamics

#### 3 Grand canonical kinetics

Why is this stuff presented at an ASE workshop?

- (Almost) any solid-state calculator supported by ASE can be used for performing electronically GC-DFT calculations
- Using ASE as the driver, both adiabatic and non-adiabatic calculations can be performed with a suitable DFT code
- Many of the standard minimum energy pathway and thermochemistry modules can be directly utilized
- Constant-potential molecular dynamics is straightforward
- Vibronic wave functions and overlaps needed for "reorganization energy" and matrix elements may be accessed from Huang-Rhys factors in ASE (NA-ET and PCET are kind of Franck-Condon transitions)

## Acknowledgements

- Thanks to Mikael Kuisma (JYU), Daniel Karlsson (JYU) and Thorbjørn Christensen (AU) on the mPB work
- Alexander Soudackov, Sharon Hammes-Schiffer, Zach Goldsmith, and Yang-Choi Lam at Yale on helping with the details of the rate theory formulation

