有効遮蔽媒質法の応用と拡張：より現実的な電気化学系の記述に向けて

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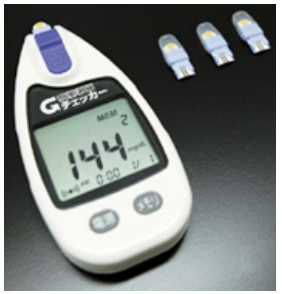
常行班：第一原理分子動力学法、熱物理とダイナミクス

2011/10/07　東大工学部

Outline

- Introduction
  - Examples of application of electrochemistry
  - Why do we need the effective screening medium method?
- Method
  - What is the ESM method?
  - How to apply bias potential to metal/water interface
- Application
  - Model of the electrochemical system
  - Electrochemical reactions (a few steps in the electrolysis of water)
- Extension
  - Limitation of the current ESM method
  - Toward more realistic modeling
- Summary

Applied electrochemistry



Battery
- Manganese dry cell
- Lead battery
- NiCd, NiH secondary battery
- Fuel cell
- Lithium secondary battery
  - primary: only dischargeable
  - secondary: chargable

Capacitor
- Electrolytic condenser
- Double layer condenser

Photovoltaic cell
- c-Si, a-Si solar cell
- Dye sensitized solar cell

Sensor
- pH meter
- ion selective concentration meter
- glucose, etc. (using enzyme)
- gas (oxygen, etc.)

Separator
- DNA, protein (using electromigration)

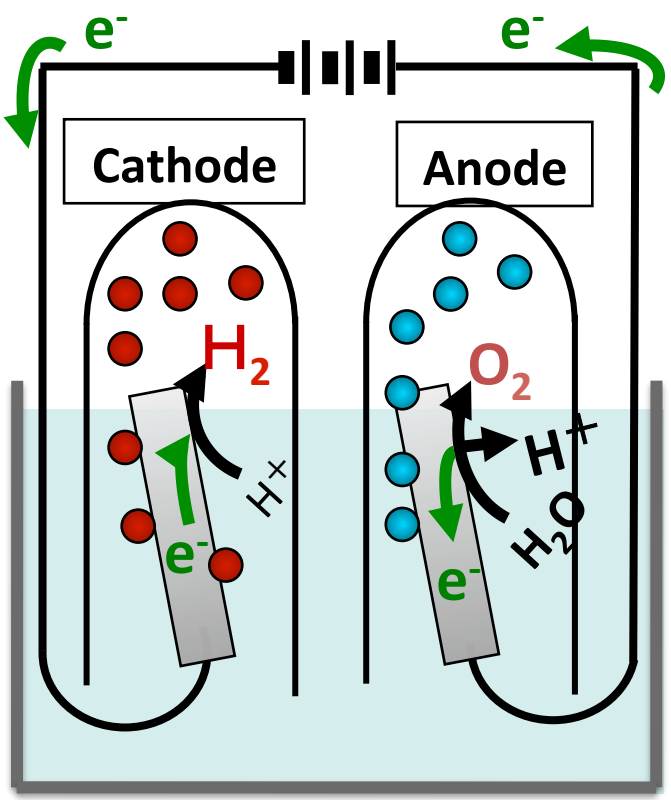
Electroplating

Cathodic protection

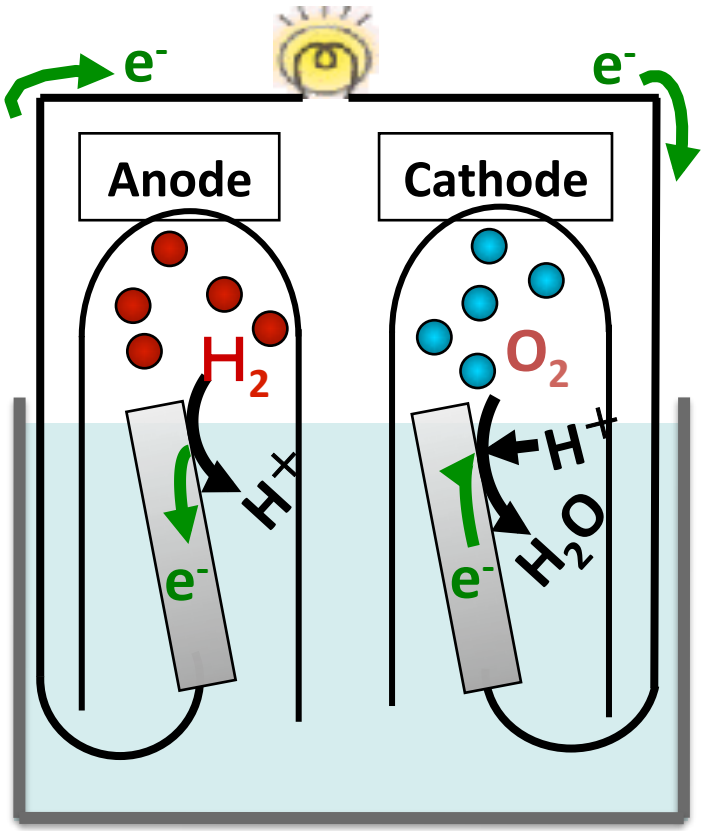
Electrolysis
- Aluminum, Copper, etc.
- Water, salt, etc.
- Organic chemicals
- tetraethyl lead

Electrolysis vs. Fuel cell

Electrolysis of water



Hydrogen fuel cell



Cathode: $2\mathrm{H}^+ + 2e^- \rightarrow \mathrm{H}_2$ $\quad\quad$ $\mathrm{O}_2 + 4\mathrm{H}^+ + 4e^- \rightarrow 2\mathrm{H}_2\mathrm{O}$

Anode: $2\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{O}_2 + 4\mathrm{H}^+ + 4e^-$ $\quad\quad$ $\mathrm{H}_2 \rightarrow 2\mathrm{H}^+ + 2e^-$

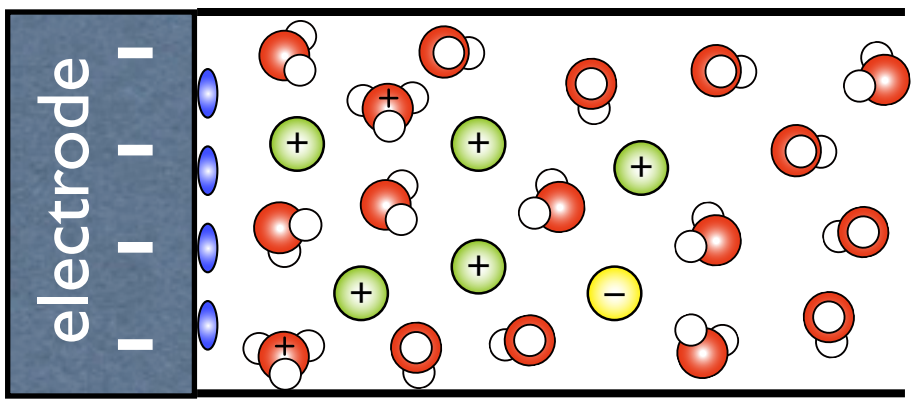
Goal of our study

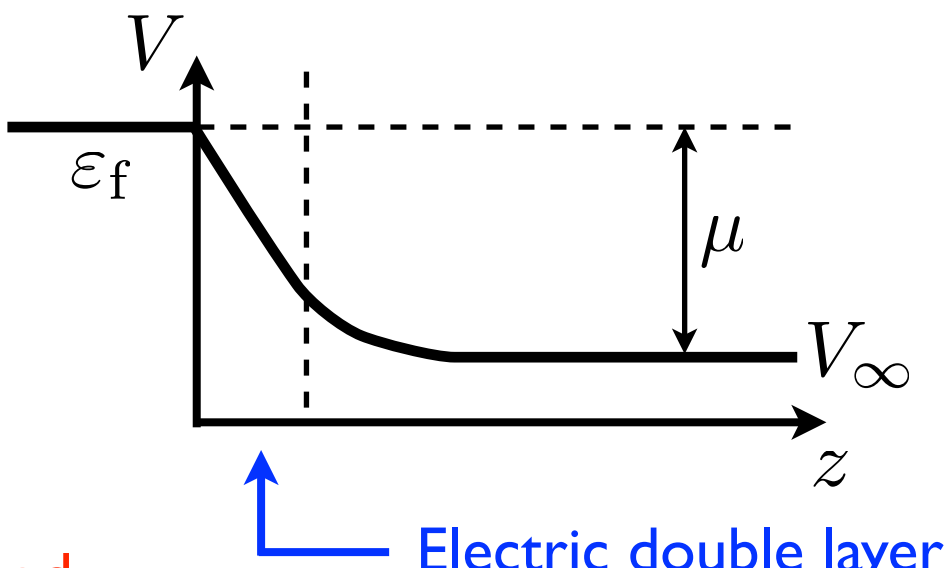
- Develop a new calculation method to simulate electrochemical systems.
- Reproduce electrochemical reactions on an electrode/electrolyte interface
- Calculate the free energy difference and activation energy of electrochemical reactions.
- Design or predict high efficiency, durable and cheap catalysts for the fuel cell or electrolysis of water.

Electrode/electrolyte interface

Things to be considered:

- Ion distribution
- Screening effect of water
- Interaction btw water & metal
- Electronic structure
- Bias potential
- Electric double layer



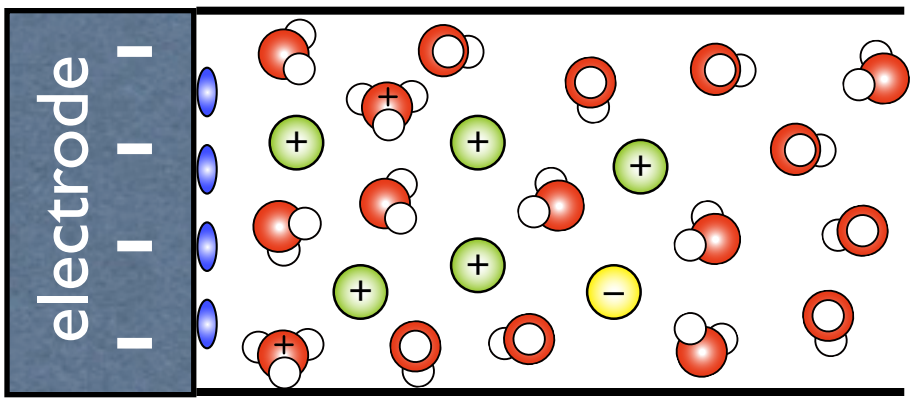


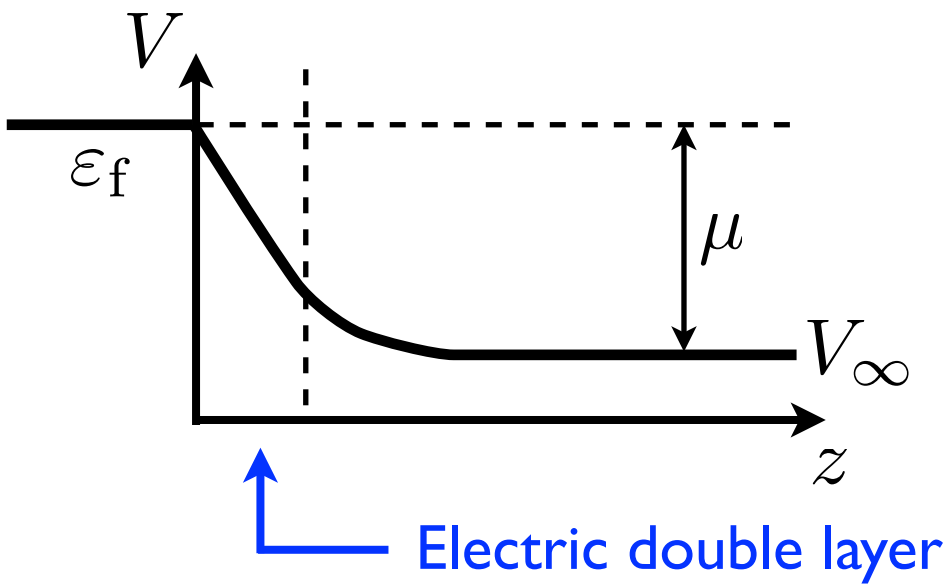
Effective Screening Medium (ESM) method

M.O. and O. Sugino, PRB 73, 115407 (2006)

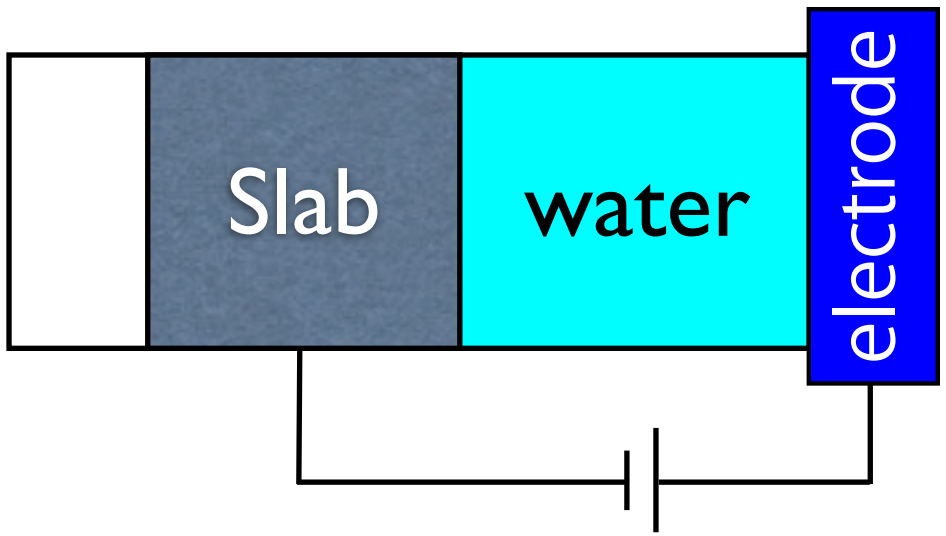
Effective screening medium method

M.O. and O. Sugino, PRB 73, 115407 (2006)





Slab model

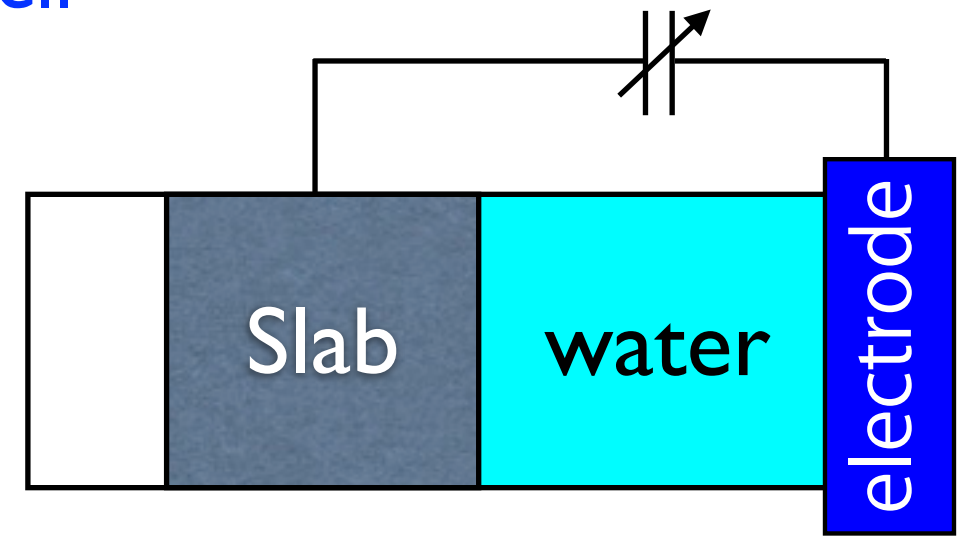


- A slab model for an electrode
- Put water molecules
- Introduce a counter electrode with an imaginary battery

ESM method

M.O. and O. Sugino, PRB 73, 115407 (2006)

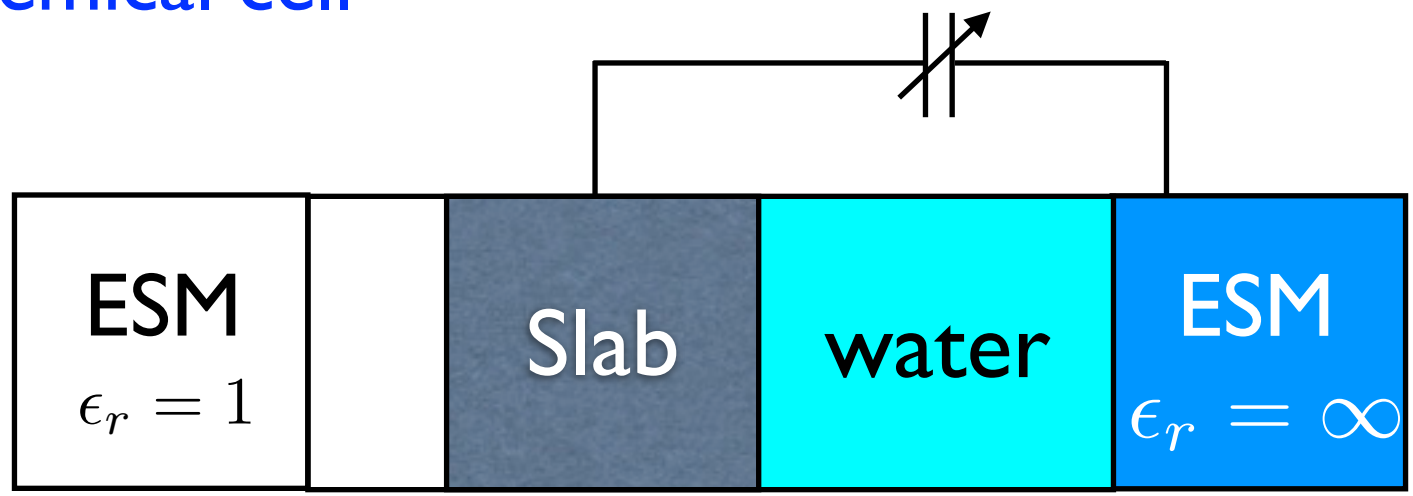
Electrochemical cell



ESM method

M.O. and O. Sugino, PRB 73, 115407 (2006)

Electrochemical cell



conventional formalism:

Solved PE with PBC

$$\epsilon(\boldsymbol{r}) = 1$$

$$V(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r} \frac{\rho_{\mathrm{tot}}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}$$

ESM formalism:

Model dependent BCs

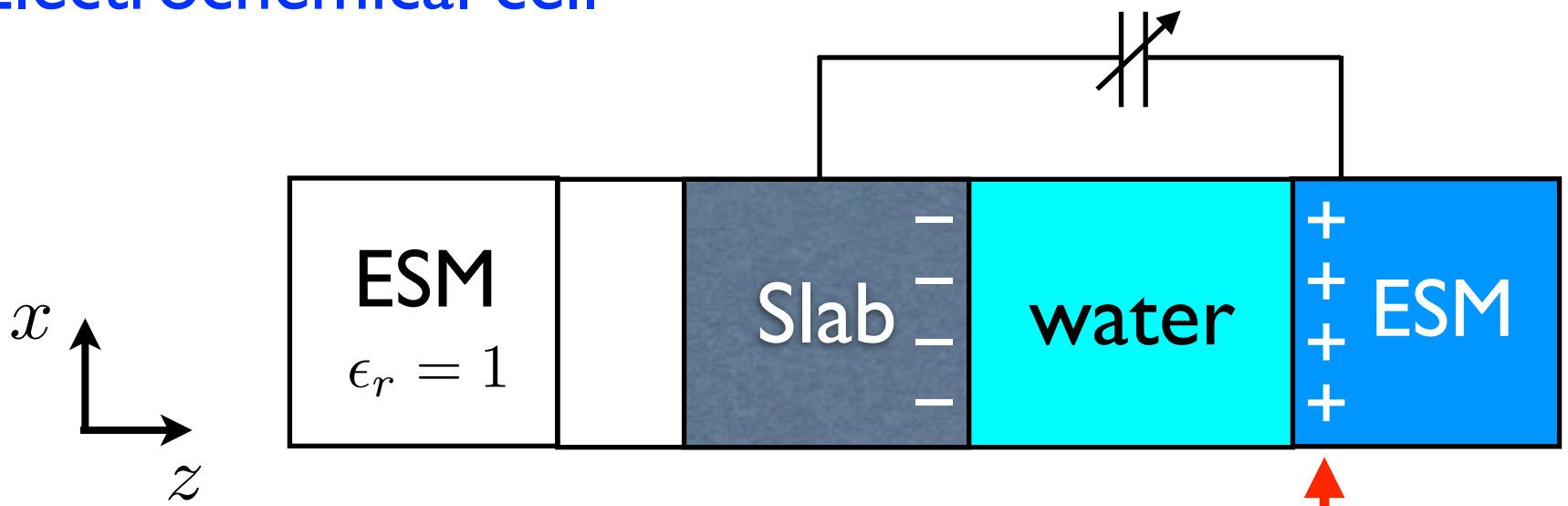
$\epsilon(\boldsymbol{r})$: model dependent

$$V(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r} G(\boldsymbol{r}, \boldsymbol{r}') \rho_{\mathrm{tot}}(\boldsymbol{r}')$$

ESM method

M.O. and O. Sugino, PRB 73, 115407 (2006)

Electrochemical cell



bare coulomb part

$$\nabla[\epsilon(\boldsymbol{r})\nabla]V(\boldsymbol{r}) = -4\pi\rho_{\mathrm{tot}}(\boldsymbol{r})$$

$$G(g_{\parallel}, z, z') = \frac{4\pi}{2g_{\parallel}} \mathrm{e}^{-g_{\parallel}|z-z'|}$$

Image charge part

$$-\frac{4\pi}{2g_{\parallel}} \mathrm{e}^{-g_{\parallel}(2z_1-z-z')}$$

$$\begin{cases} V(g_{\parallel}, z_1) = 0 \\ \partial_z V(g_{\parallel}, z \to -\infty) = 0 \end{cases}$$

$$g_{\parallel} = (g_x, g_y)$$

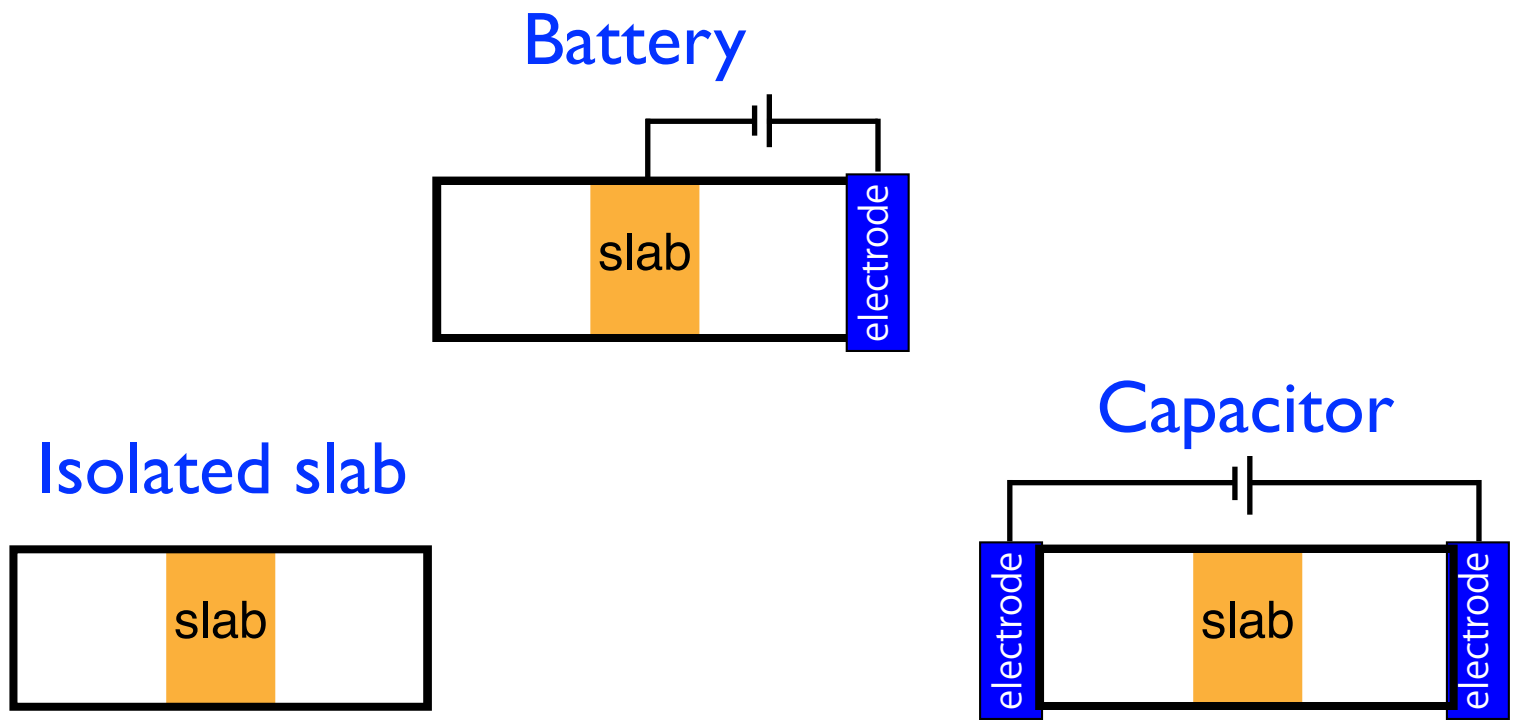
$$V(g_{\parallel}, z) = \int \mathrm{d}z G(g_{\parallel}, z, z')\rho_{\mathrm{tot}}(g_{\parallel}, z')$$

Advantages of the ESM method

- Various boundary conditions are applicable.
- We do not need any correction or modification of the coulomb interaction.
- Easy to implement without additional calculation costs.
- SIESTA, PWscf, OpenMX are available.

Advantages of the ESM method

- Various boundary conditions are applicable.



Implementation of the ESM

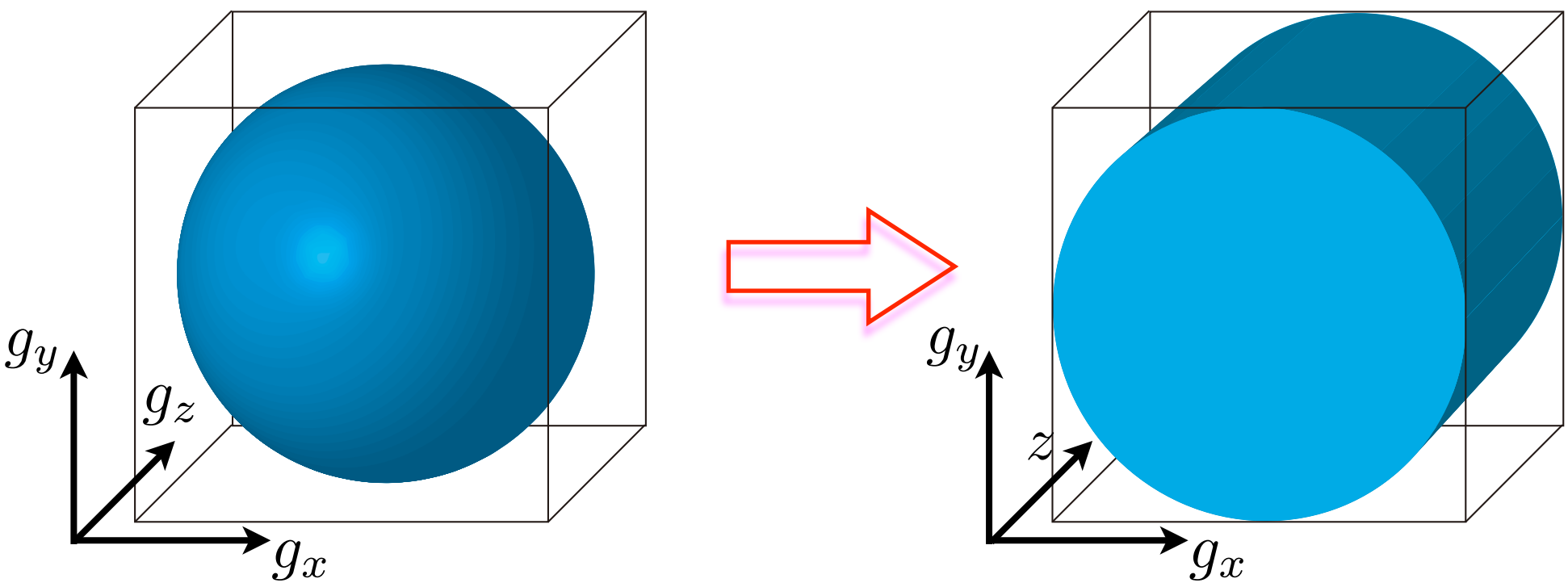
M.O. and O. Sugino, PRB 73, 115407 (2006)

Only the electrostatic parts are modified:

- Ewald energy & force (each MD step)
- Local (long-rang) part (each MD step)
- Hartree potential (each SCF step)

Conventional g-component

g-component in ESM method



Electrolysis of water

$$2H_2O \rightarrow 2H_2 + O_2$$

HER

$H_3O^+ + e^- \rightarrow H_2O + H_{ad}$

$H_{ad} + H_{ad} \rightarrow H_2$

or

$H_3O^+ + H_{ad} + e^- \rightarrow H_2O + H_2$

OER

$H_2O \rightarrow (H_2O)_{ad}$

$(H_2O)_{ad} \rightarrow (OH)_{ad} + H_3O^+ + e^-$

$(OH)_{ad} + (OH)_{ad} \rightarrow O_{ad} + H_2O$

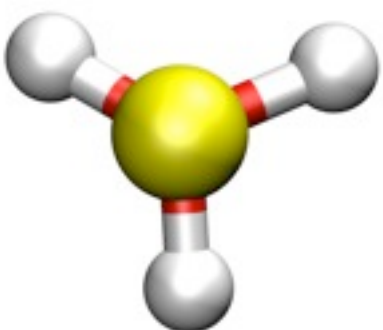
$O_{ad} + O_{ad} \rightarrow O_2$

Direct simulation

Constrained dynamics (Blue-moon ensemble)

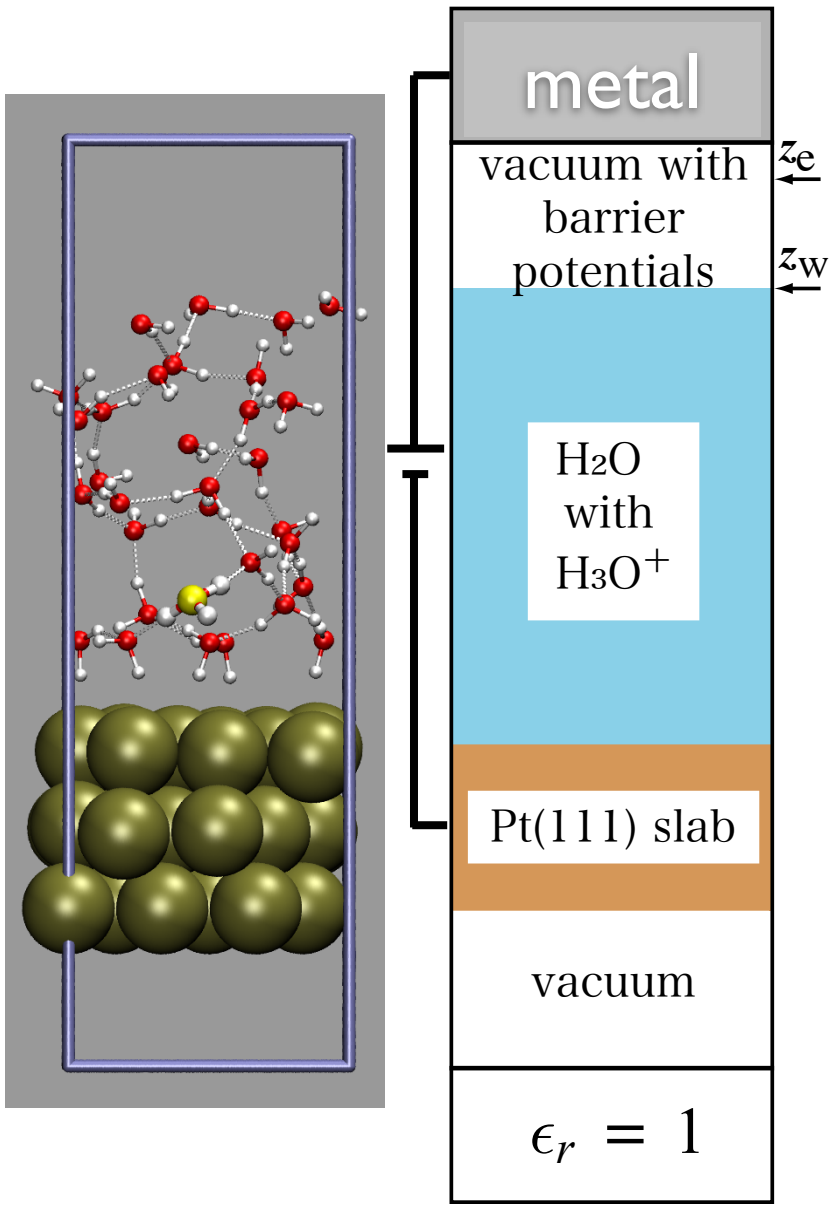
Simulation condition

- 32 water molecules
- 36 Pt atoms (3-layers)
- GGA-PBE
- Plane wave - Ultrasoft pp
- Temperature: 80℃
- Bias potential (−/+)



H_3O^+

OH^-



Simulation model

system	Q_{ESM}(e/cell)	component	on surface	in water	
A3	-0.7	$H_{65}O_{32}$	H_3O^+		
A2	0.35	$H_{65}O_{32}$	H_3O^+		HER
A1	0.0	$H_{65}O_{32}$	H_3O^+		
B	0.0	$H_{64}O_{32}$			PZC
C1	0.0	$H_{63}O_{32}$	OH		
C2a	0.35	$H_{63}O_{32}$	OH		OER
C2b	0.35	$H_{63}O_{32}$	2OH	H_3O^+	
C3	0.7	$H_{63}O_{32}$	2OH	H_3O^+	

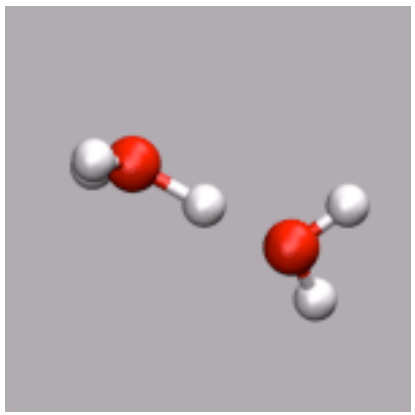
HER

O. Sugino, et al., Surf. Sci. 601, 5237 (2007)
M. Otani et al., J. Phys. Soc. Jpn. 77, 024802 (2008)
M. Otani, et al., Phys. Chem. Chem. Phys. 10, 1609 (2008)

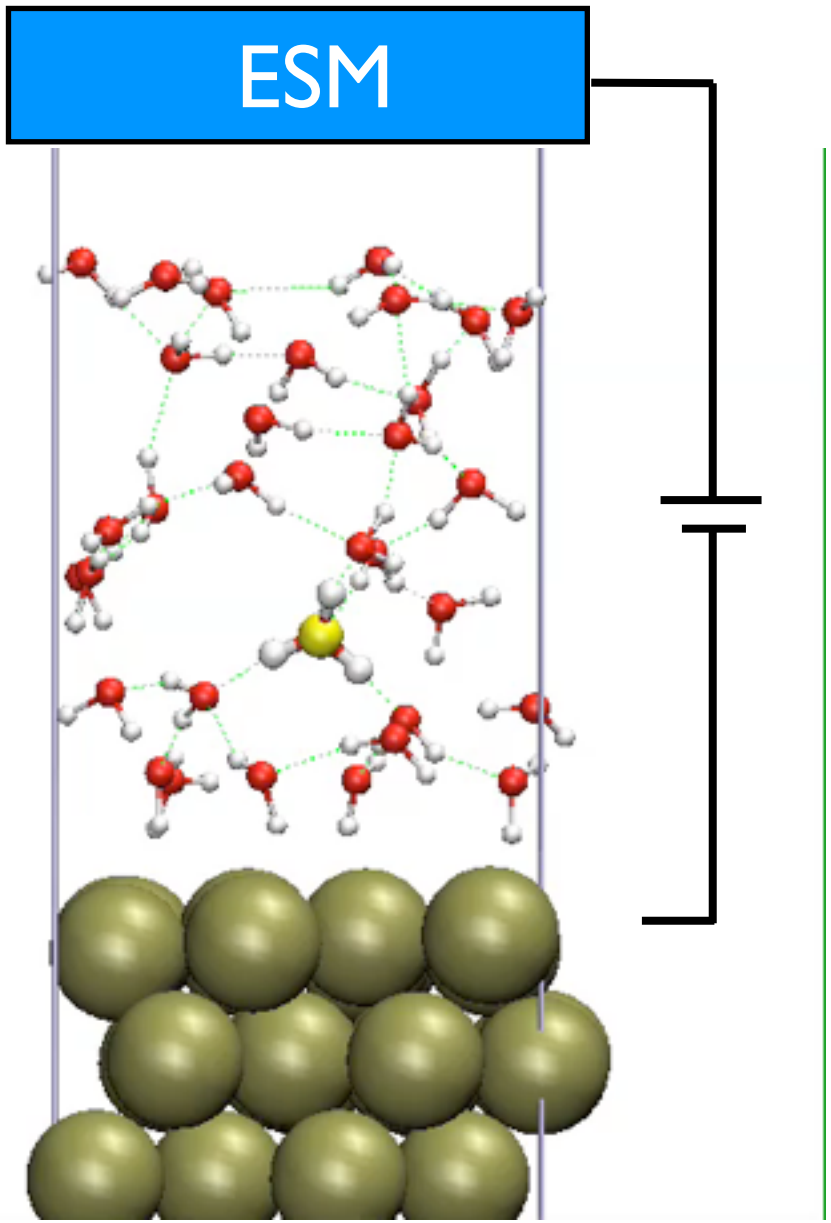
OER

T. Ikeshoji, et al., Phys. Chem. Chem. Phys. in press

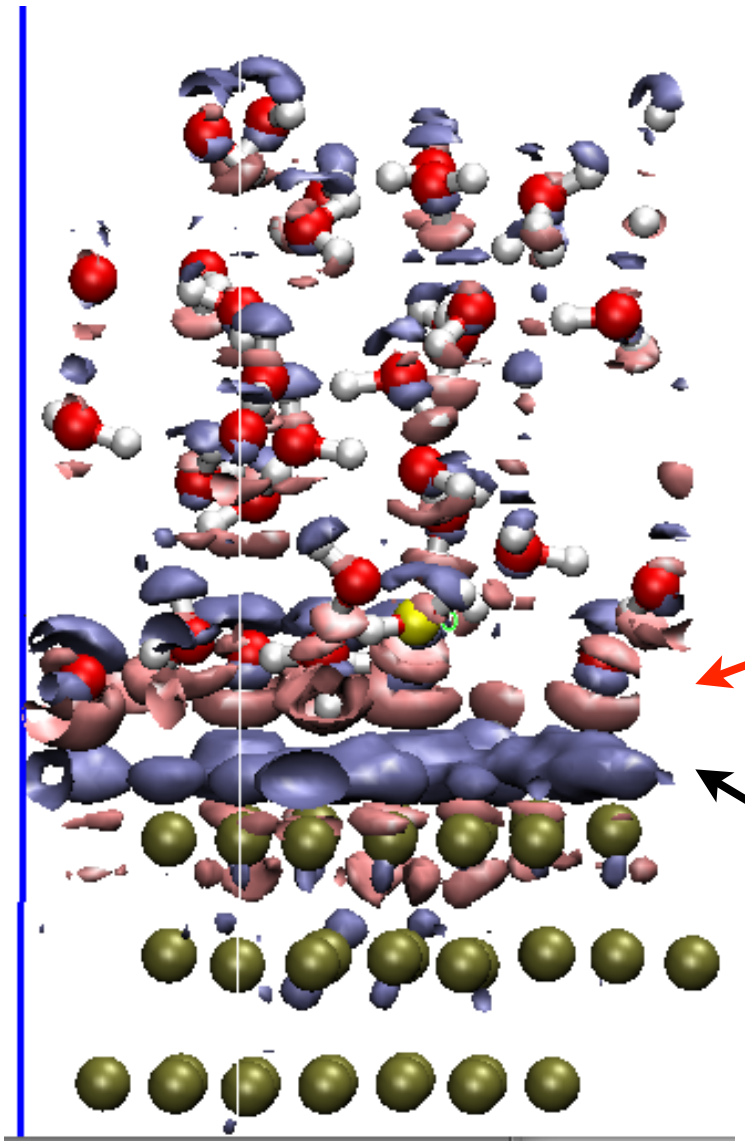
MD simulations with bias potential



Grotthuss mechanism



Charge redistribution



$$\Delta\rho = \rho(\text{charged}) - \rho(\text{neutral})$$

polarization of water

Large charge redistribution occurs at the interface

Accumulated charge on metal surface

Electrolysis of water

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HER

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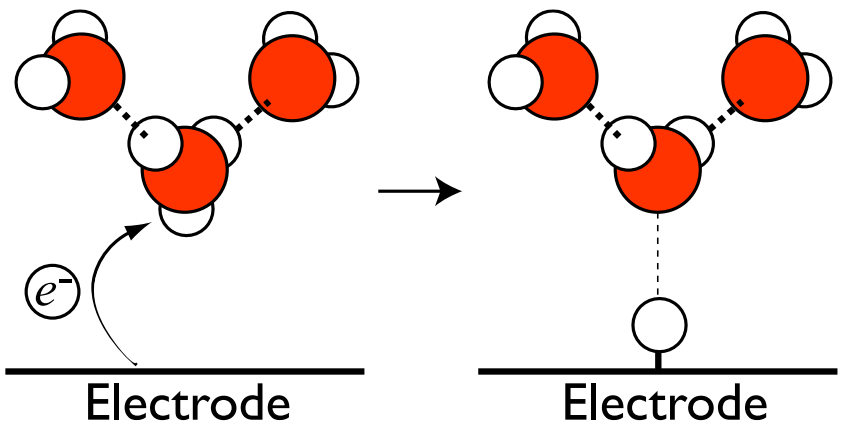
Direct simulation

Constrained dynamics (Blue-moon ensemble)

Hydrogen evolution reaction

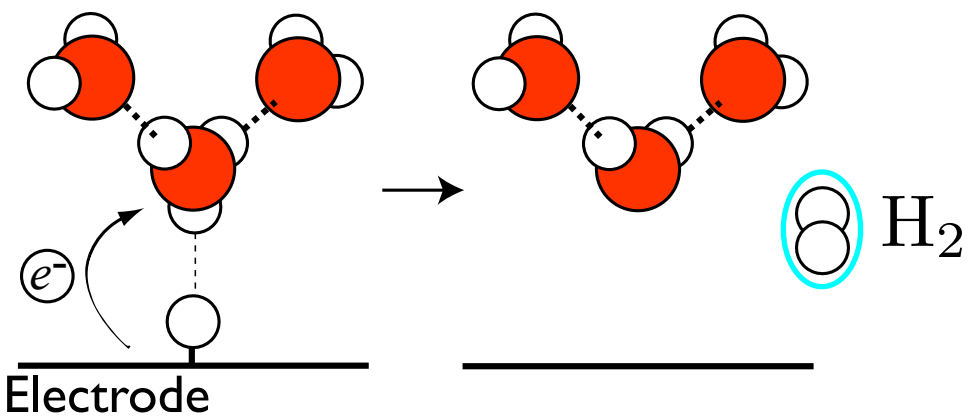
Hydrogen evolution $2\mathrm{H}^+ + 2e^- \rightarrow \mathrm{H}_2$

Volmer step: $\mathrm{H_3O^+} + e^- \rightarrow \mathrm{H_2O} + \mathrm{H_{ad}}$

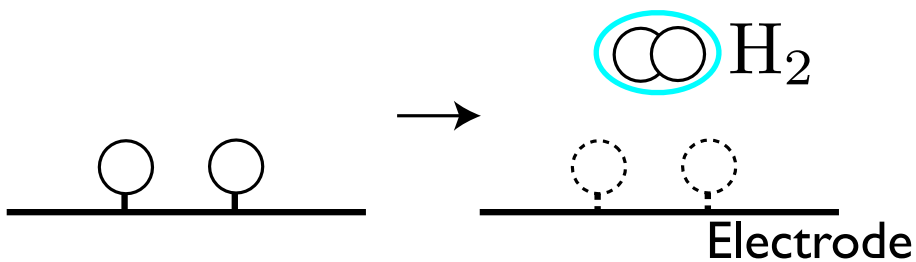


Heyrovsky step:

$\mathrm{H_3O^+} + \mathrm{H_{ad}} + e^- \rightarrow \mathrm{H_2O} + \mathrm{H_2}$



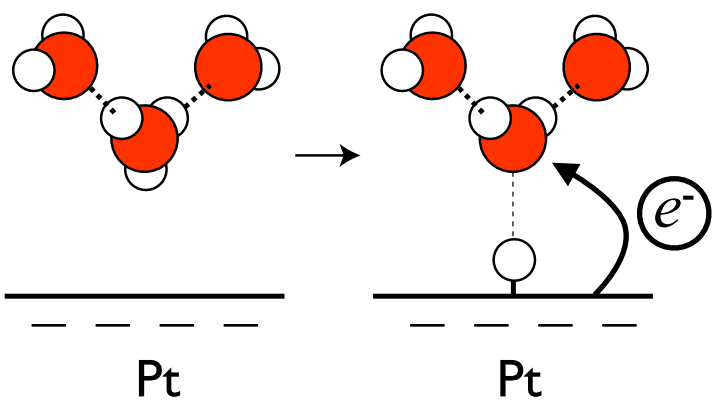
Tafel step: $\mathrm{H_{ad}} + \mathrm{H_{ad}} \rightarrow \mathrm{H_2}$

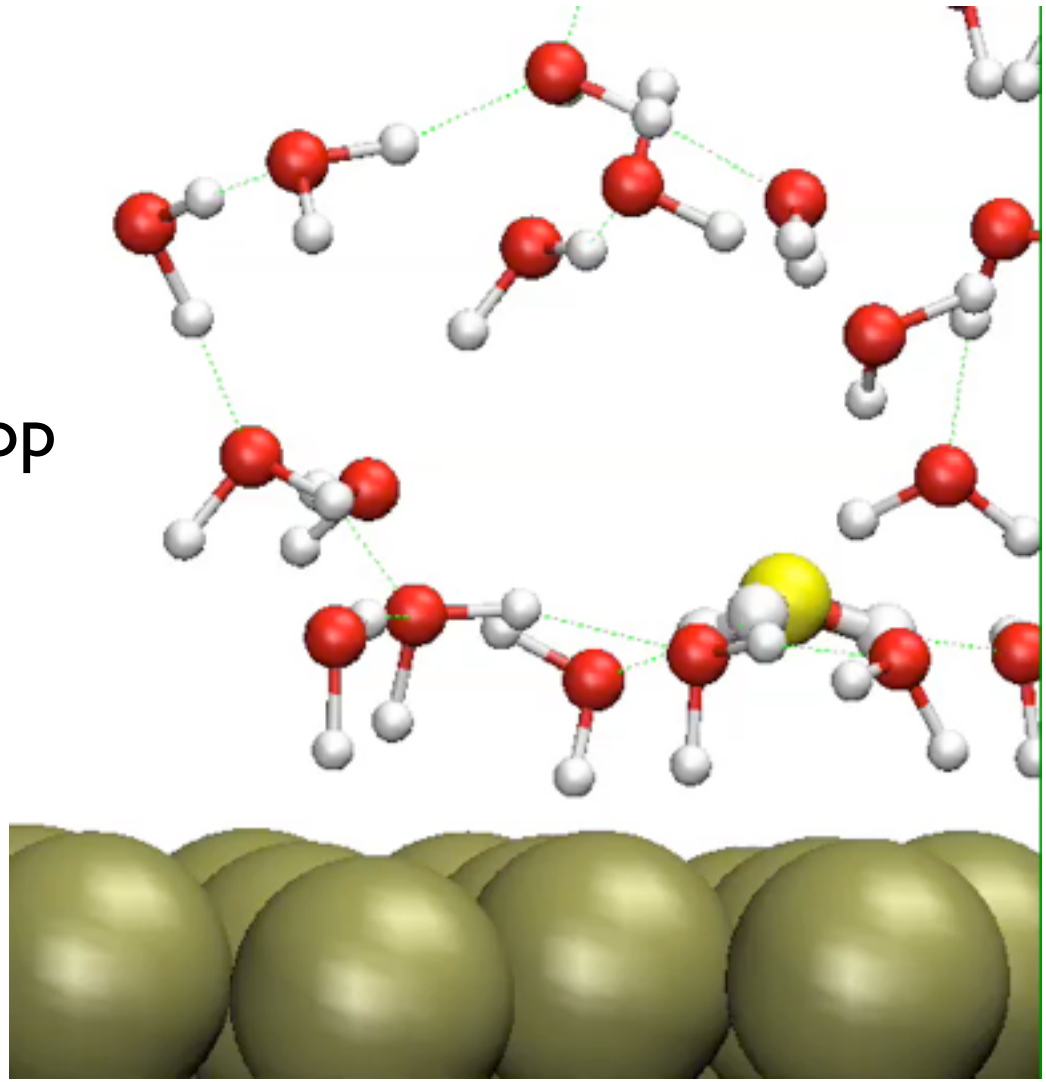


Electrochemical reaction (cathode)

Hydronium ion diffuses vis the Grotthus mechanism

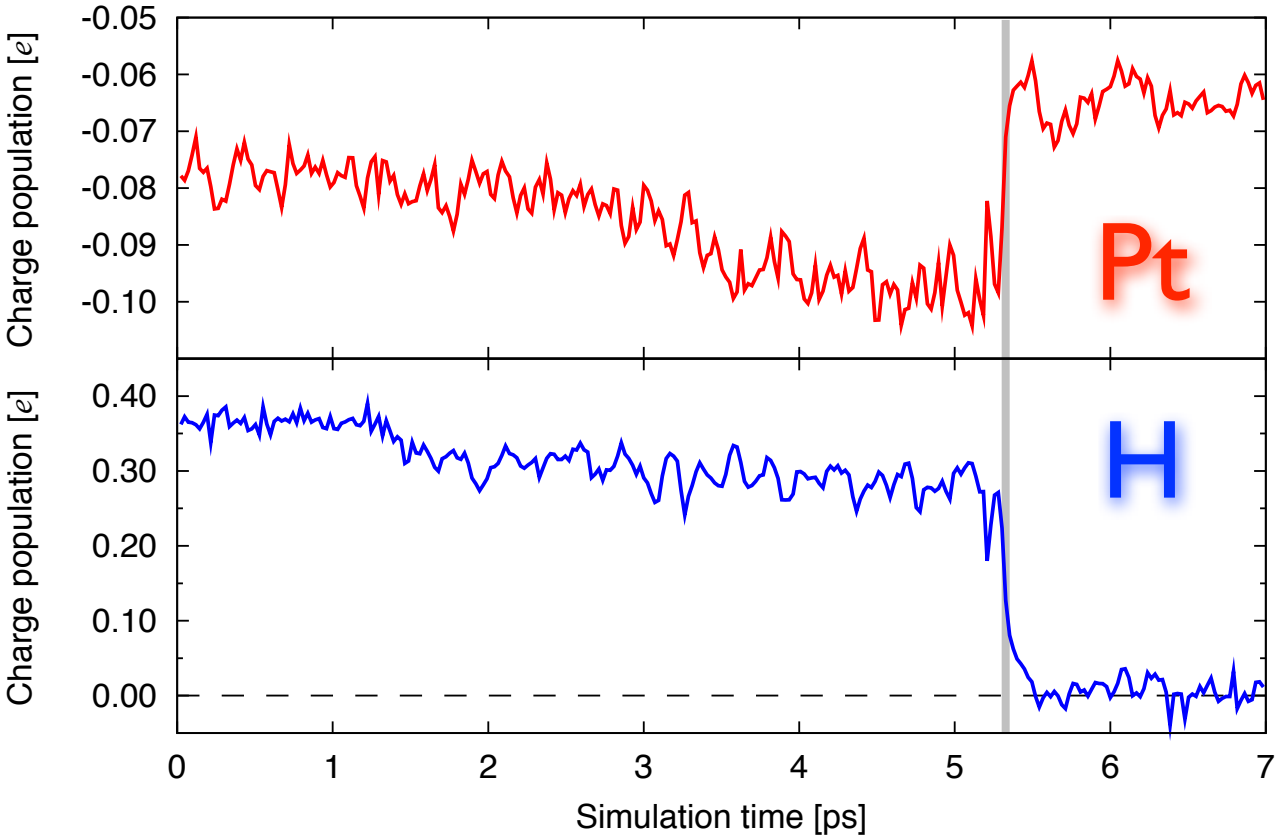
H atom is adsorbed on a top site of Pt surface.





Q=0.95 (e/cell)

Charge transfer

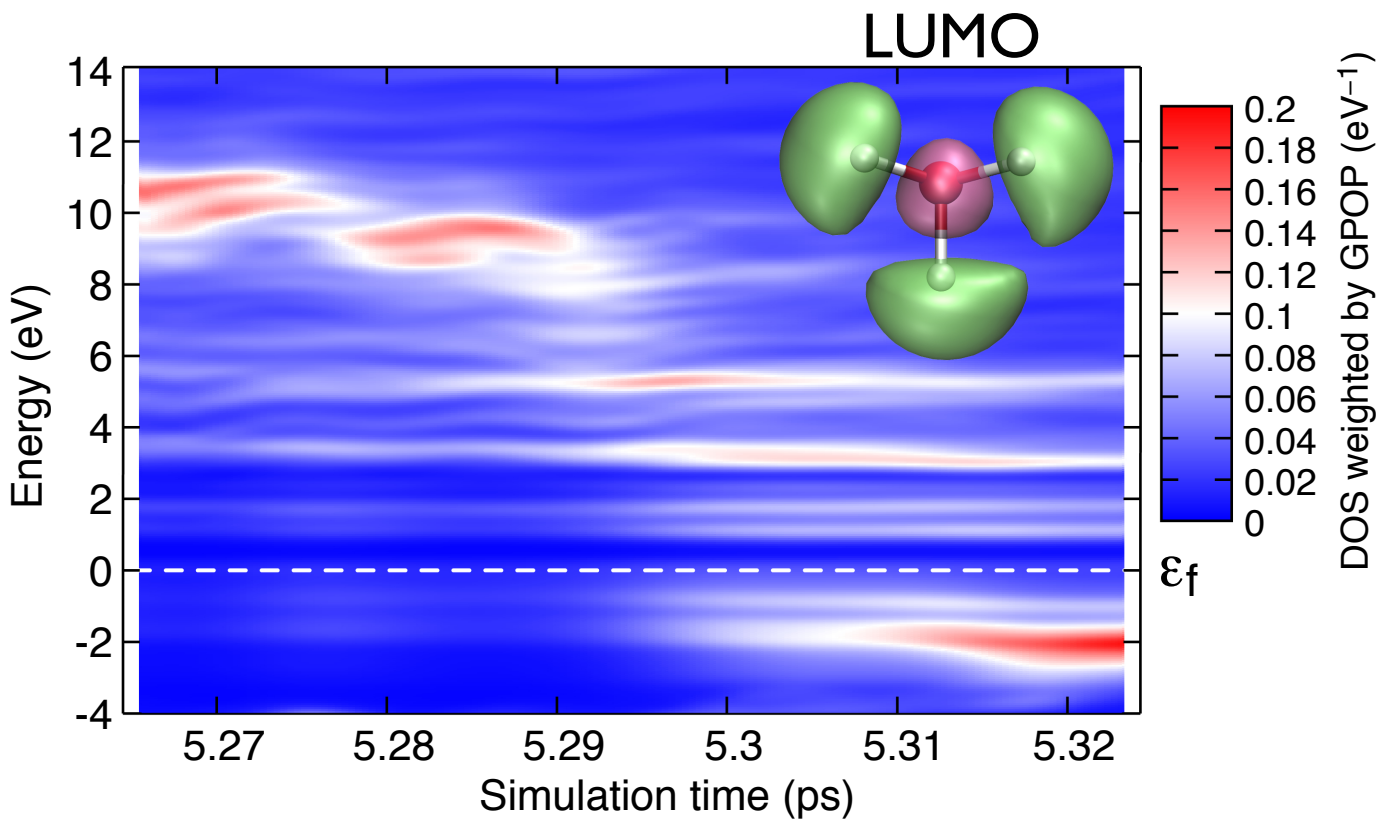


Charge population of top most Pt layer averaged by the number of Pt atoms

Charge population of the adsorbed hydrogen atom.

- Charge population of the Pt surface gradually decreases until the reaction and suddenly increases at the reaction.
- Charge population of the hydrogen atom slightly decreases before the reaction and suddenly decreases at adsorption

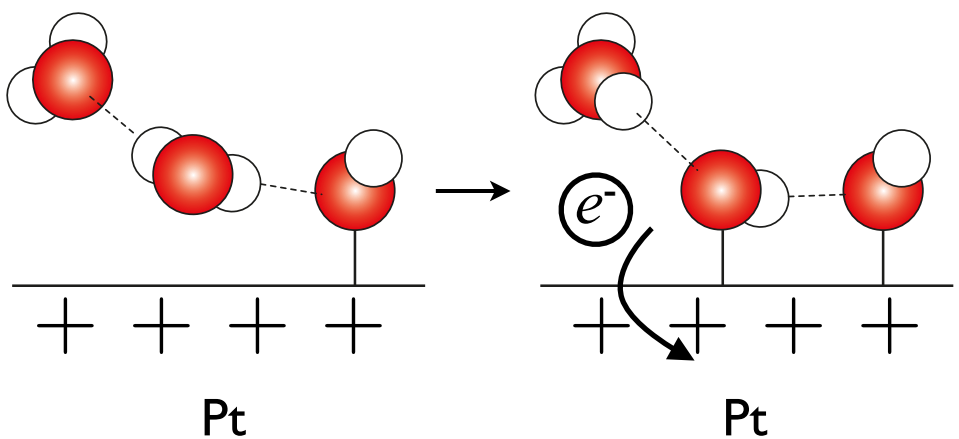
Electron transfer from Pt to water

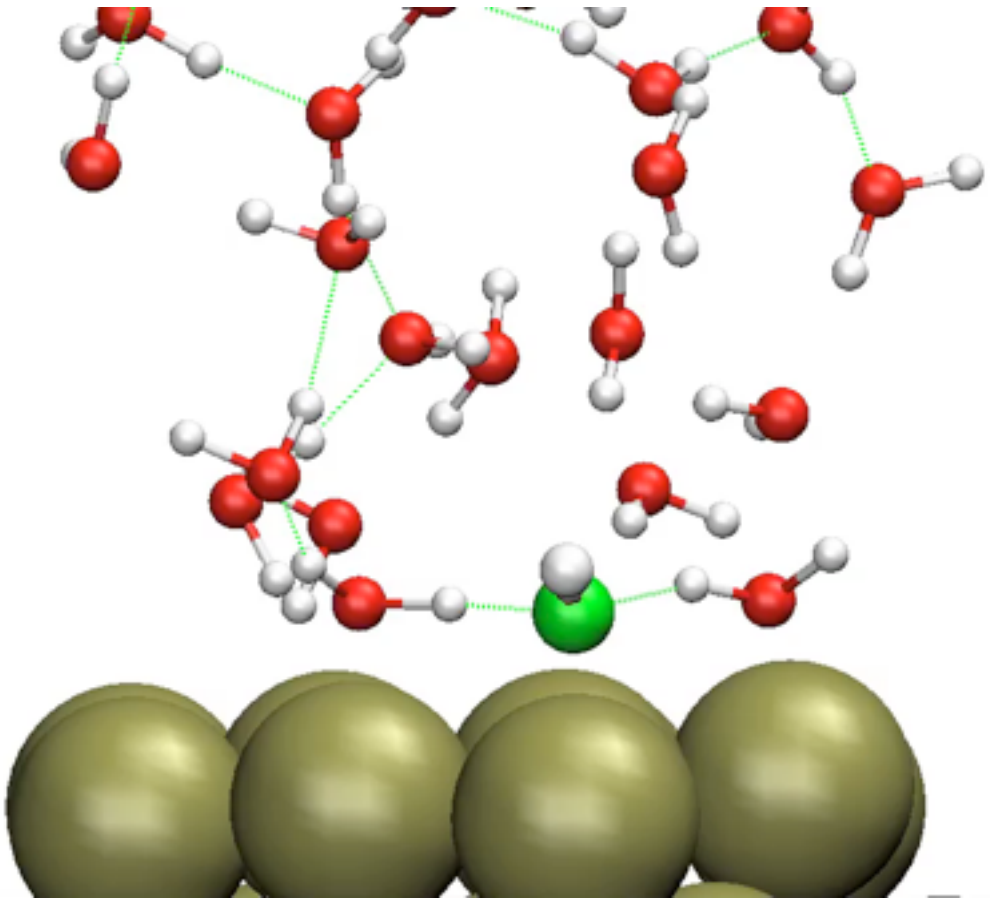


Electrochemical reaction (anode)

Water dissociation:

$$2H_2O + Pt \rightarrow Pt\text{-}OH^- + H_3O^+$$



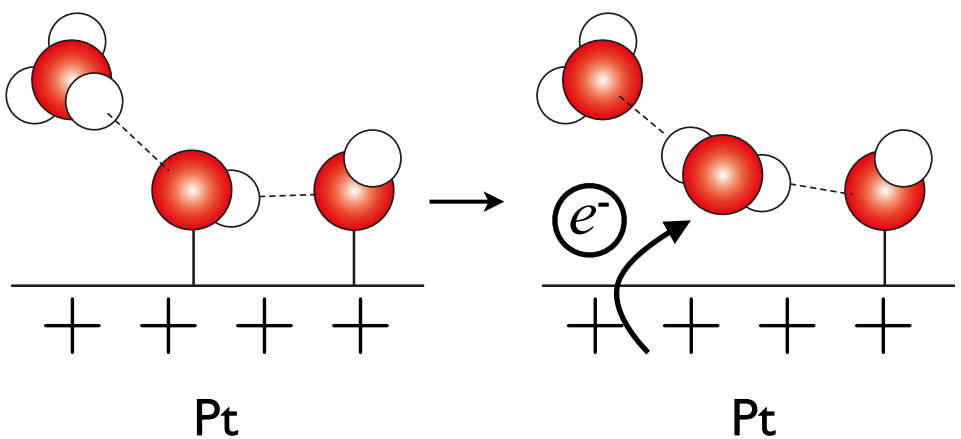


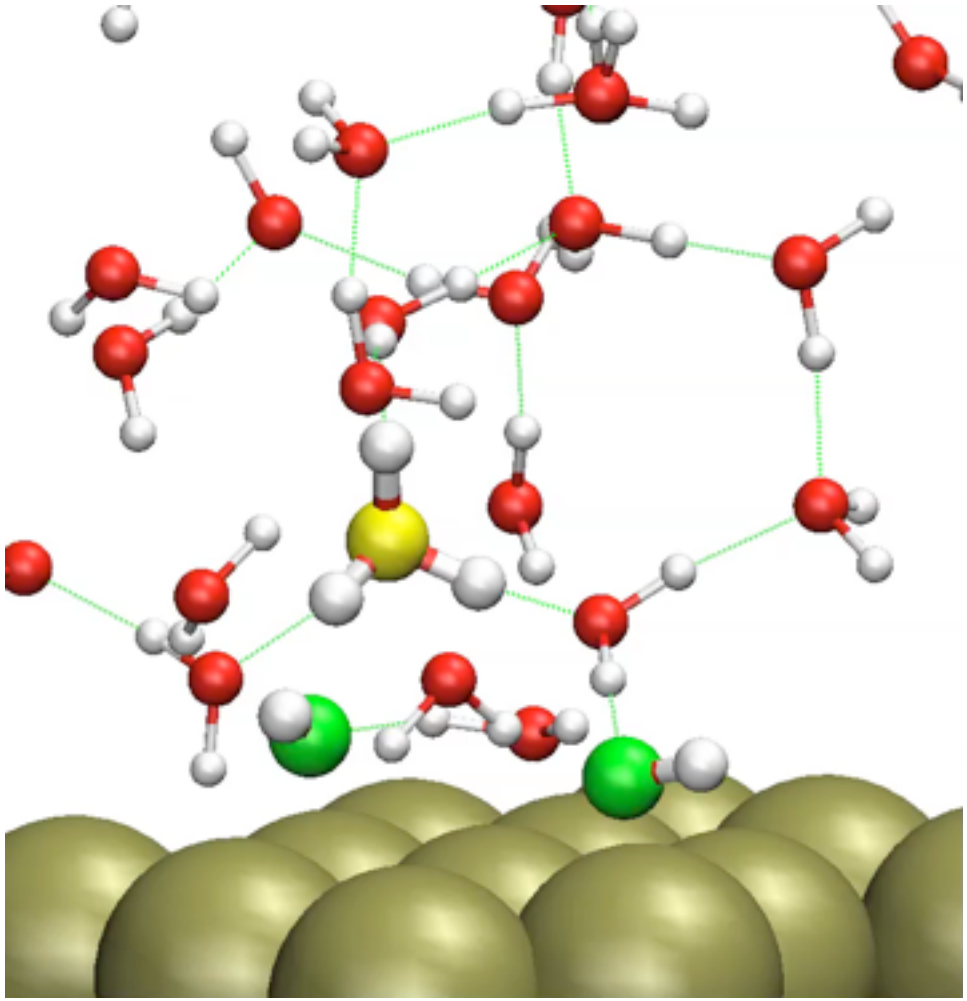
Q_{ESM}=-0.35 (e/cell)

Electrochemical reaction (anode)

Water formation:

$$\mathrm{Pt\text{-}OH^- + H_3O^+ \rightarrow 2H_2O + Pt}$$





Q=-0.35 (e/cell)

Reversible reaction of water splitting

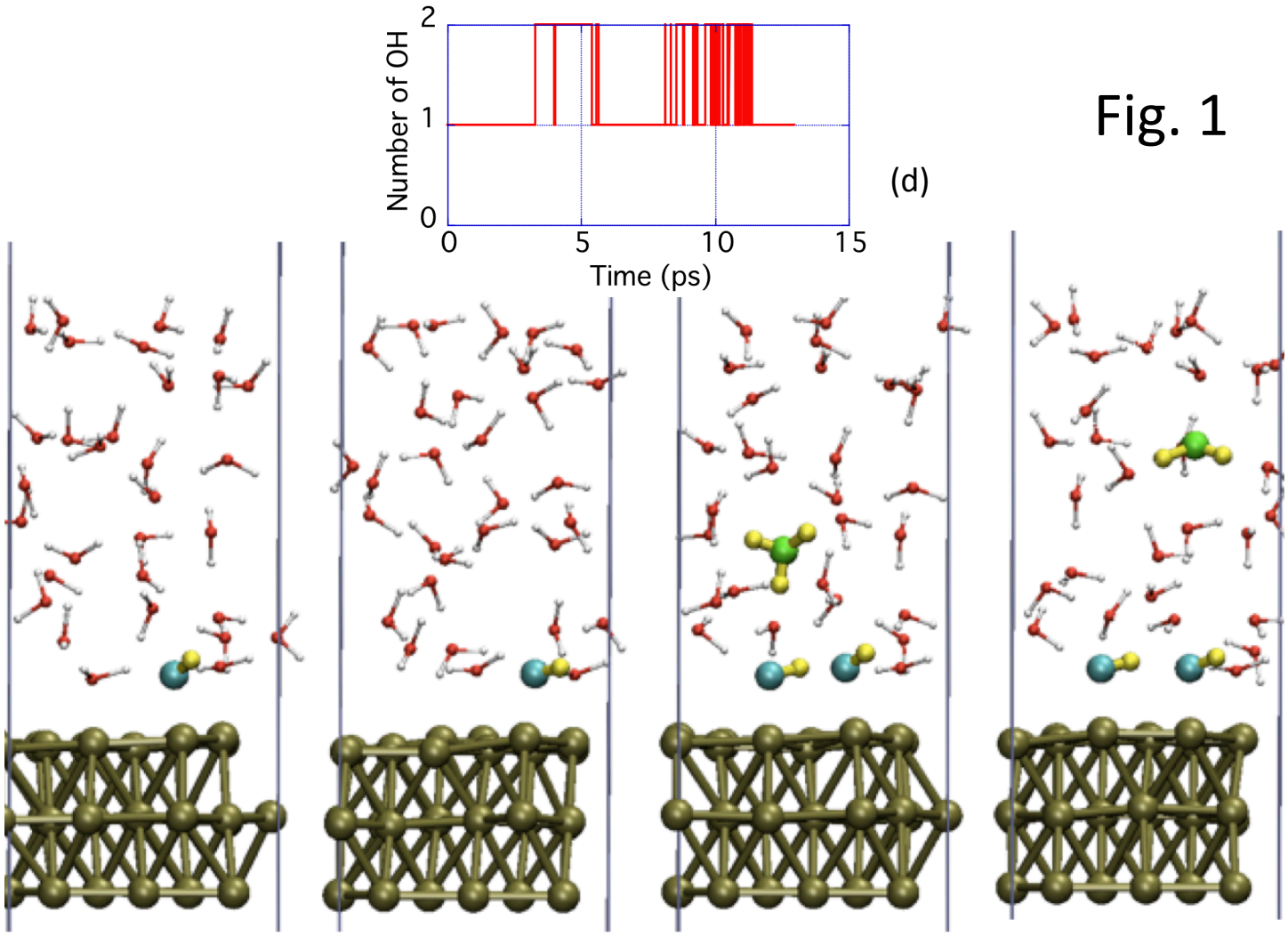
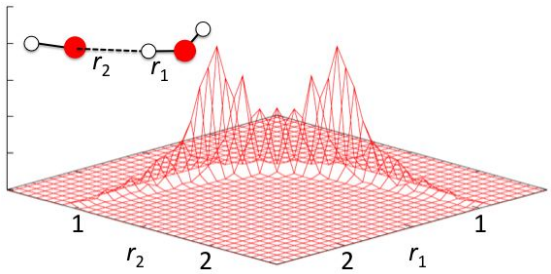


Fig. 1

Activation barrier hight & potential

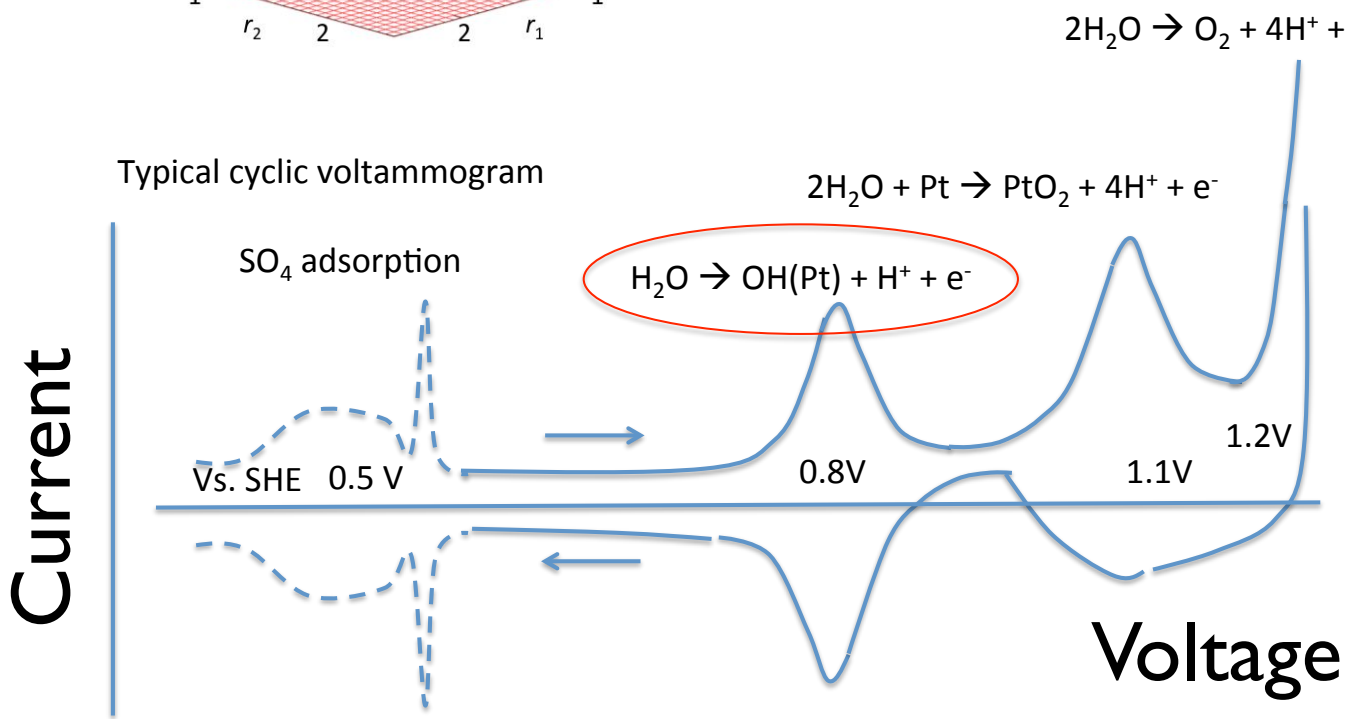
Density profile of OH distance



Activation barrier of water splitting

$$\Delta E = RT\Delta \log(\rho) = 0.02 \text{ eV}$$

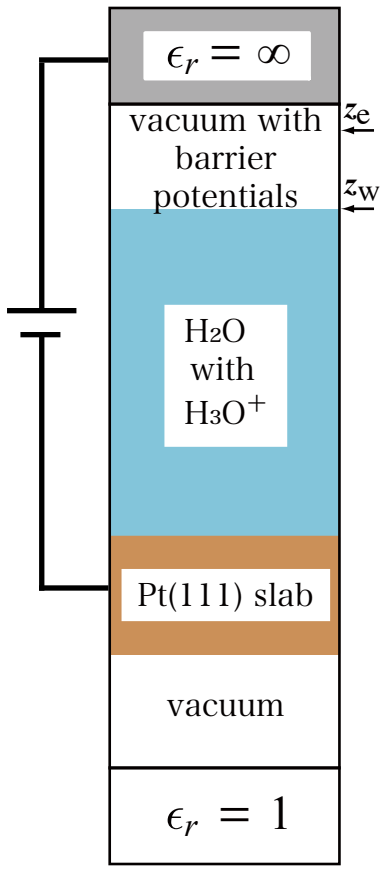
Typical cyclic voltammogram



electrode potential
= 0.6~0.7 V
(exp. = 0.7~0.8V)

What we have achieved are...

- ☑ direct simulation of electrochemical reactions
- ☑ potential dependence of interface structure and vibrational frequencies
- ☑ calculation of activation energies (using Blue-moon ensemble method)



Toward more realistic modeling...

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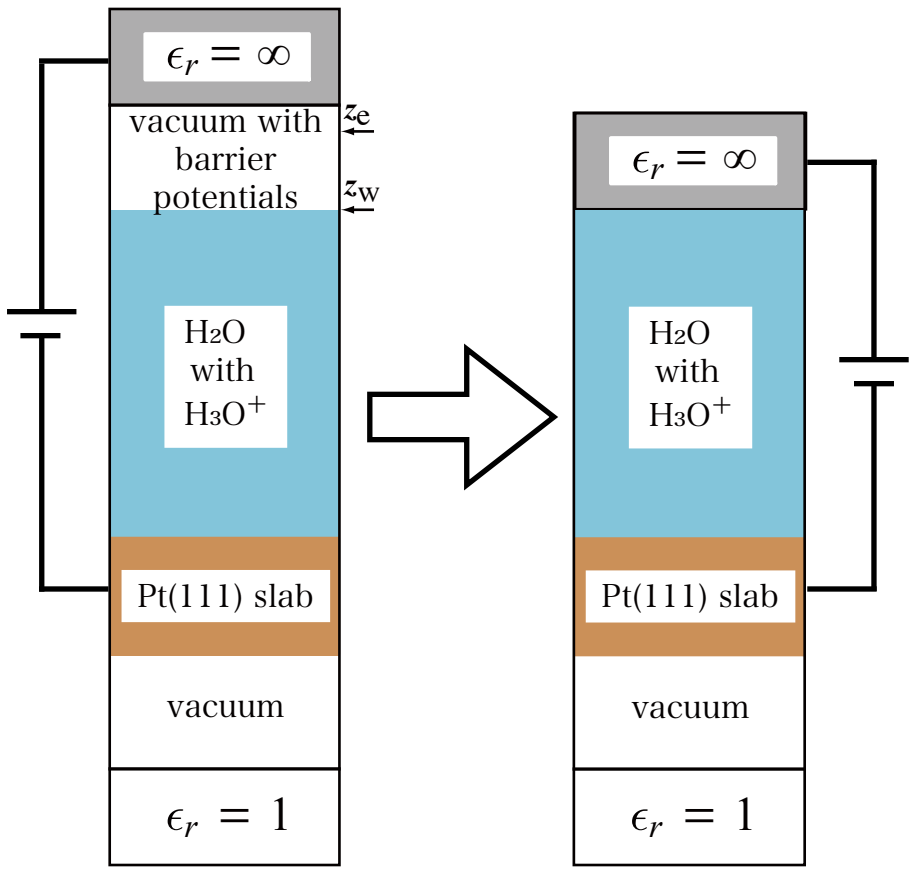
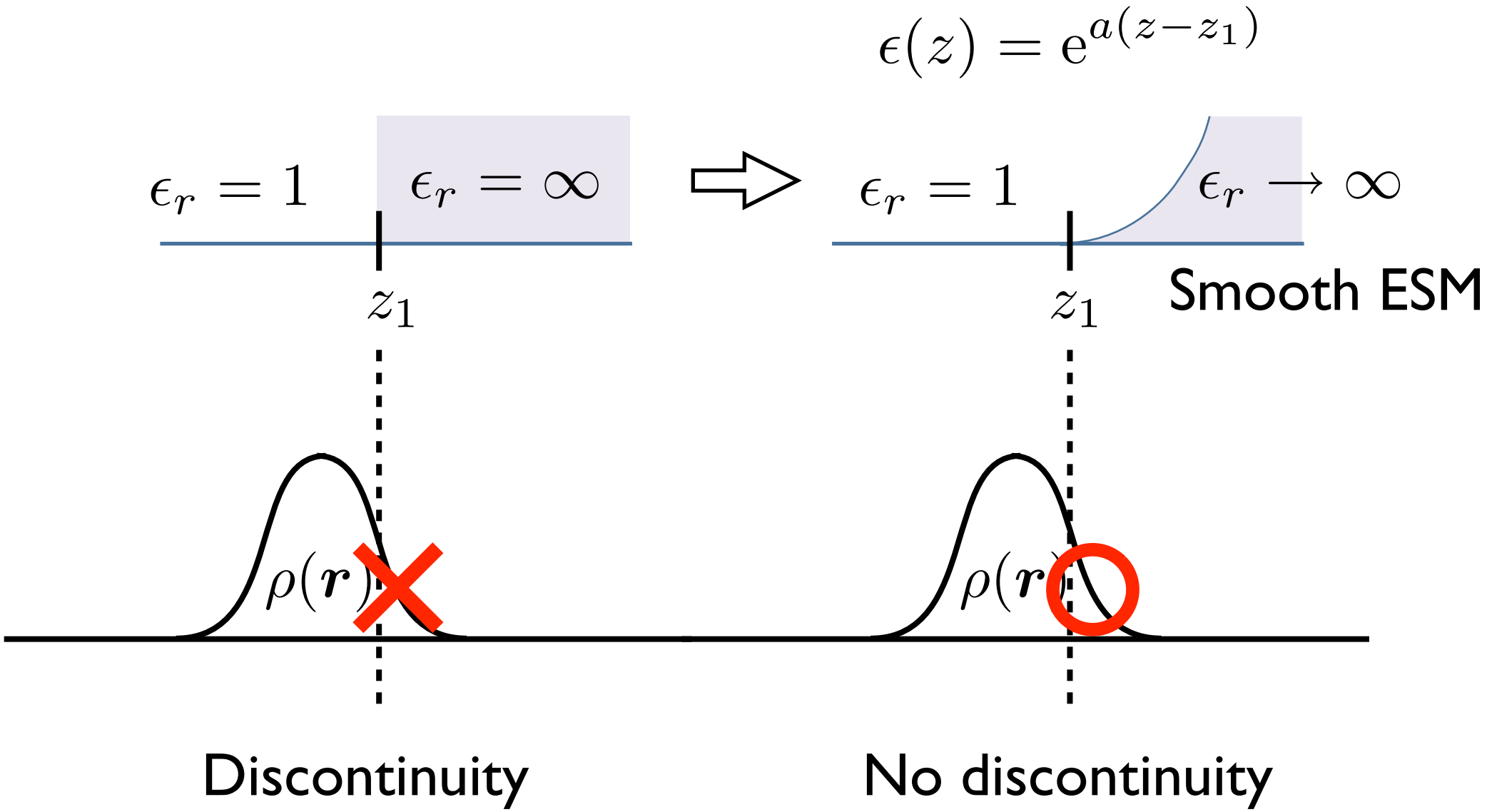
- ☑ direct simulation of electrochemical reactions
- ☑ potential dependence of interface structure and vibrational frequencies
- ☑ calculation of activation energies (using Blue-moon ensemble method)



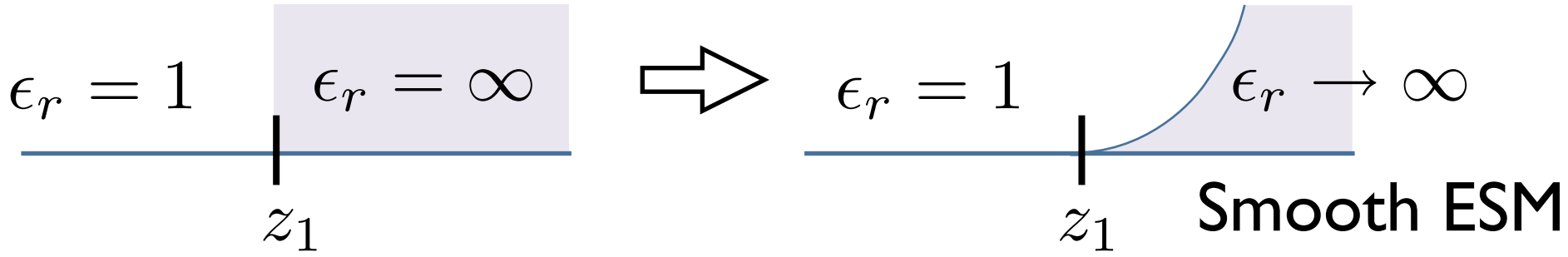
Toward more realistic modeling...

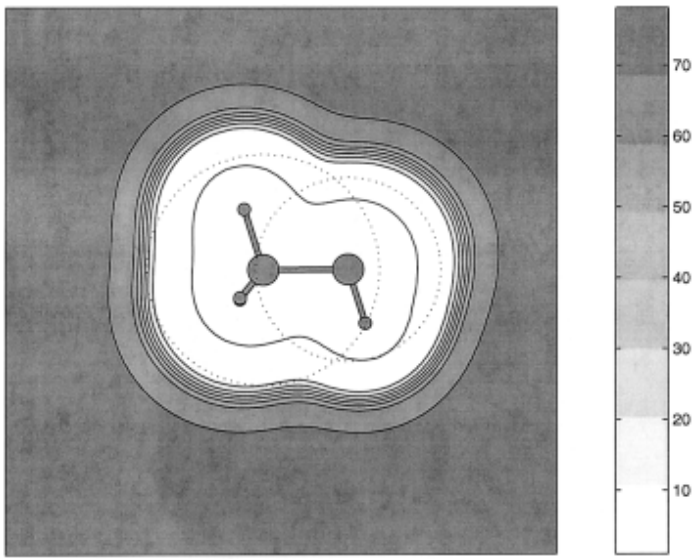
Toward more realistic modeling...



Smooth ESM

$$\epsilon(z) = \mathrm{e}^{a(z-z_1)}$$





Cavity model

$$\epsilon_\ell(\rho(\mathbf{r})) = 1 + \frac{\epsilon_\infty - 1}{2}\left(1 + \frac{1 - (\rho(\mathbf{r})/\rho_0)^{2\beta}}{1 + (\rho(\mathbf{r})/\rho_0)^{2\beta}}\right)$$

J-L Fattebert & F. Gygi, JCC(2001)

Summary

- Develop a new calculation method to simulate electrochemical systems.
- Reproduce electrochemical reactions on an electrode/electrolyte interface
- Calculate the free energy difference and activation energy of electrochemical reactions.
- Some new extensions are applied to the ESM method