First principles molecular dynamics simulation of electrochemical reactions: application and extension of the effective screening medium method

Energy materials simulation group, Nanosystem research institute, National Institute of Advanced Industrial Science and Technology (AIST)

Collaborators

Fuel cell

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- Tamio Ikeshoji (Tohoku U.)
- Yoshitada Morikawa (Osaka U.)
- Yasuharu Okamoto (NEC)
- Osamu Sugino (U. of Tokyo)
- Yumin Qian (AIST)
- Nicephore Bonnet (AIST)

Lithium ion battery

- Tsukuru Ohwaki (NISSAN)
- Tetsuya Morishita (AIST)
- Akinori Tezuka (AIST)

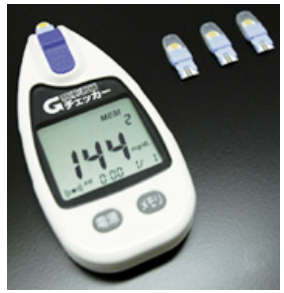
Photoelectrochemical cell, Super capacitor

- Tadashi Ogitsu (LLNL)
- Brando Wood (LLNL)
- David Prendergast (LBNL)

Outline

- Introduction
  - Application of electrochemical device
  - What is the target of our simulation?
- Method
  - History of the theoretical simulation on the electrochemical interface
  - What is the ESM method?
- Application
  - How to apply bias potential to metal/water interface
  - Model of the electrochemical system
  - Electrochemical reactions
- Extension
  - Limitation of the current ESM method
  - Smooth ESM & Constant bias potential MD simulation
- Summary

Applied electrochemistry



Battery
- Manganese dry cell
- Lead battery
- NiCd, NiH secondary battery
- Fuel cell
- Lithium secondary battery

Capacitor
- Electrolytic condenser
- Double layer condenser
- Supercapacitor

Photovoltaic cell
- c-Si, a-Si solar cell
- Dye sensitized solar cell
- photoelectrochemical hydrogen production

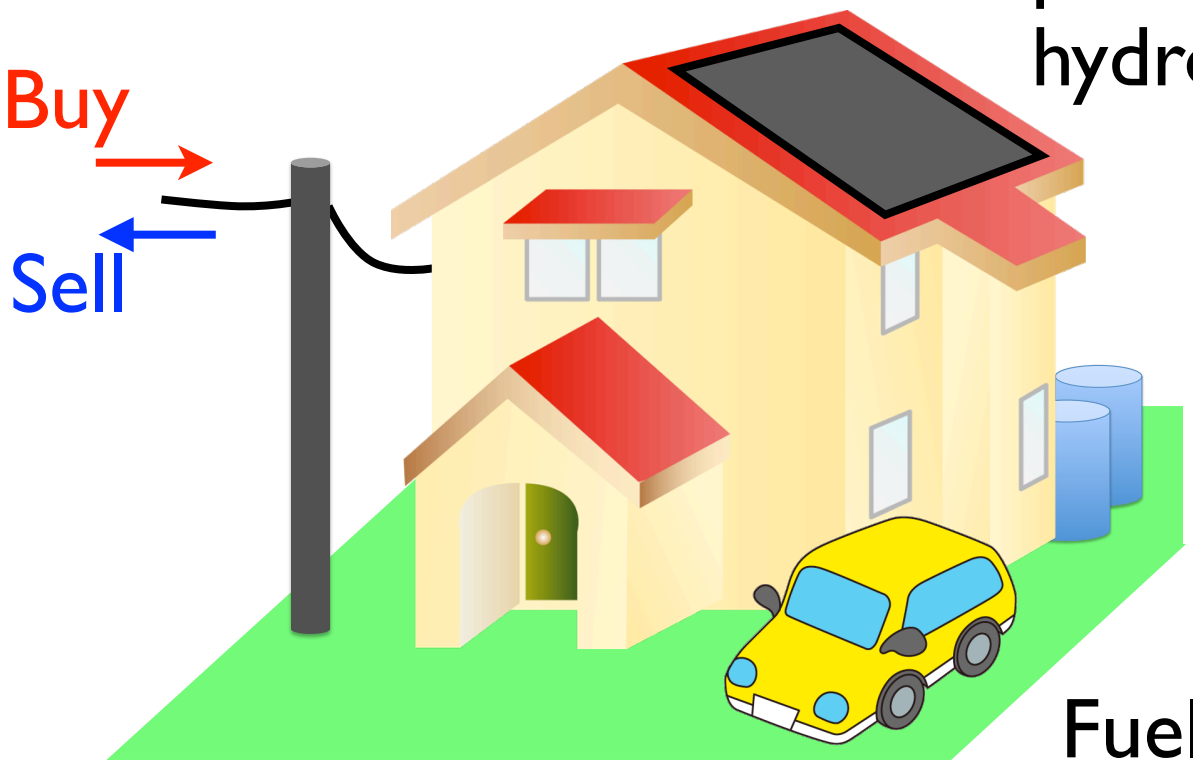
Sensor
- pH meter
- ion selective concentration meter
- glucose, etc. (using enzyme)
- gas (oxygen, etc.)

Electroplating

Cathodic protection
- $Fe \rightarrow Fe_2O_3$

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

Energy harvesting & storage



photovoltaic cell/
hydrogen production

Li-ion battery
Capacitor
Hydrogen storage

Fuel cell/Electric vehicle

Electrochemical reactions at electrode/electrolyte interface play an important role in renewable energy society.

Goal of our study

- Develop a new calculation method to simulate electrochemical systems.
- Try to understand microscopic detail of the electrochemical reaction.
- Propose or predict high efficiency, durable and cheap catalysts or electrode materials for the fuel cell or energy storage devices.

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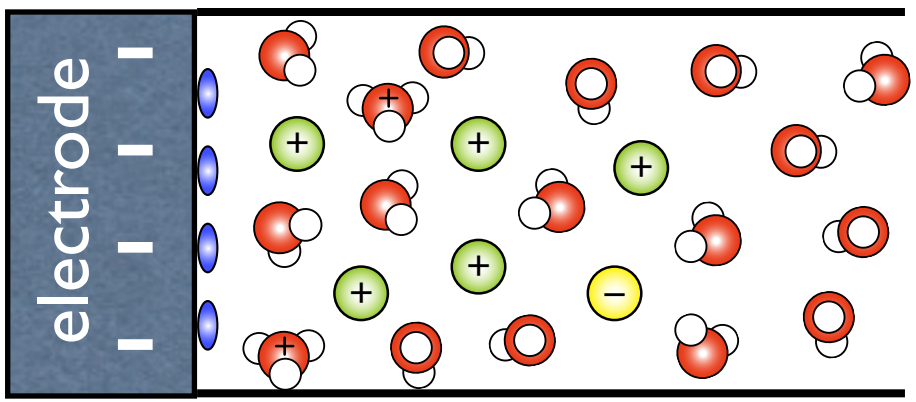
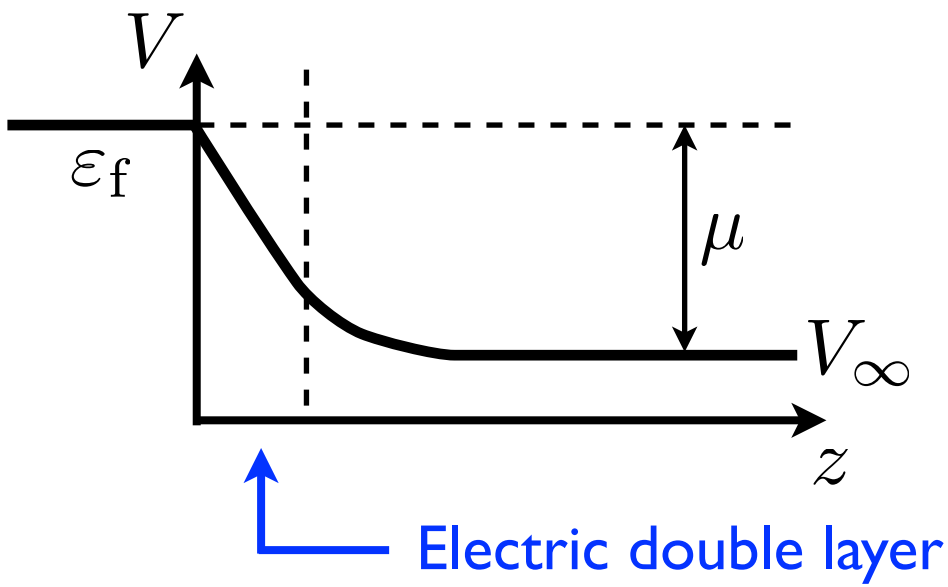
Electrode/electrolyte interface

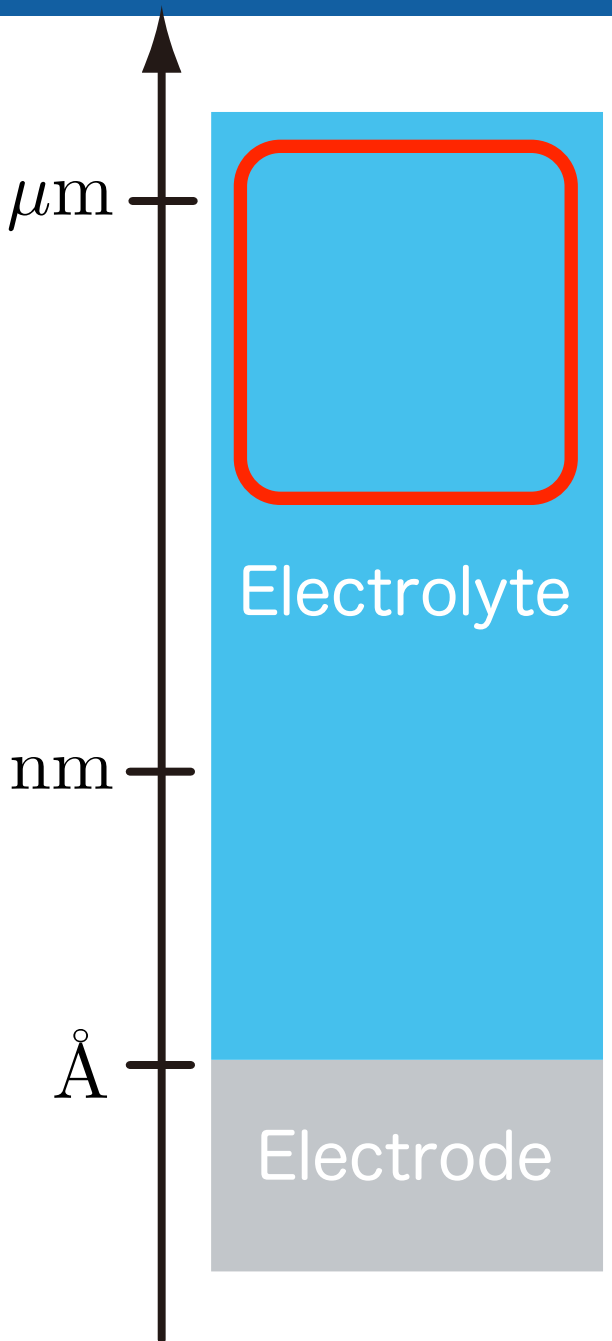
Things to be considered:

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





Hierarchical structure of interface



Gouy-Chapman model (1910~)

Water: continuum $(\epsilon_r \sim 80)$

Ion: point charge/Boltzman distribution

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Water: continuum $(\epsilon_r \sim 80)$

Ion: point charge/Boltzmann distribution

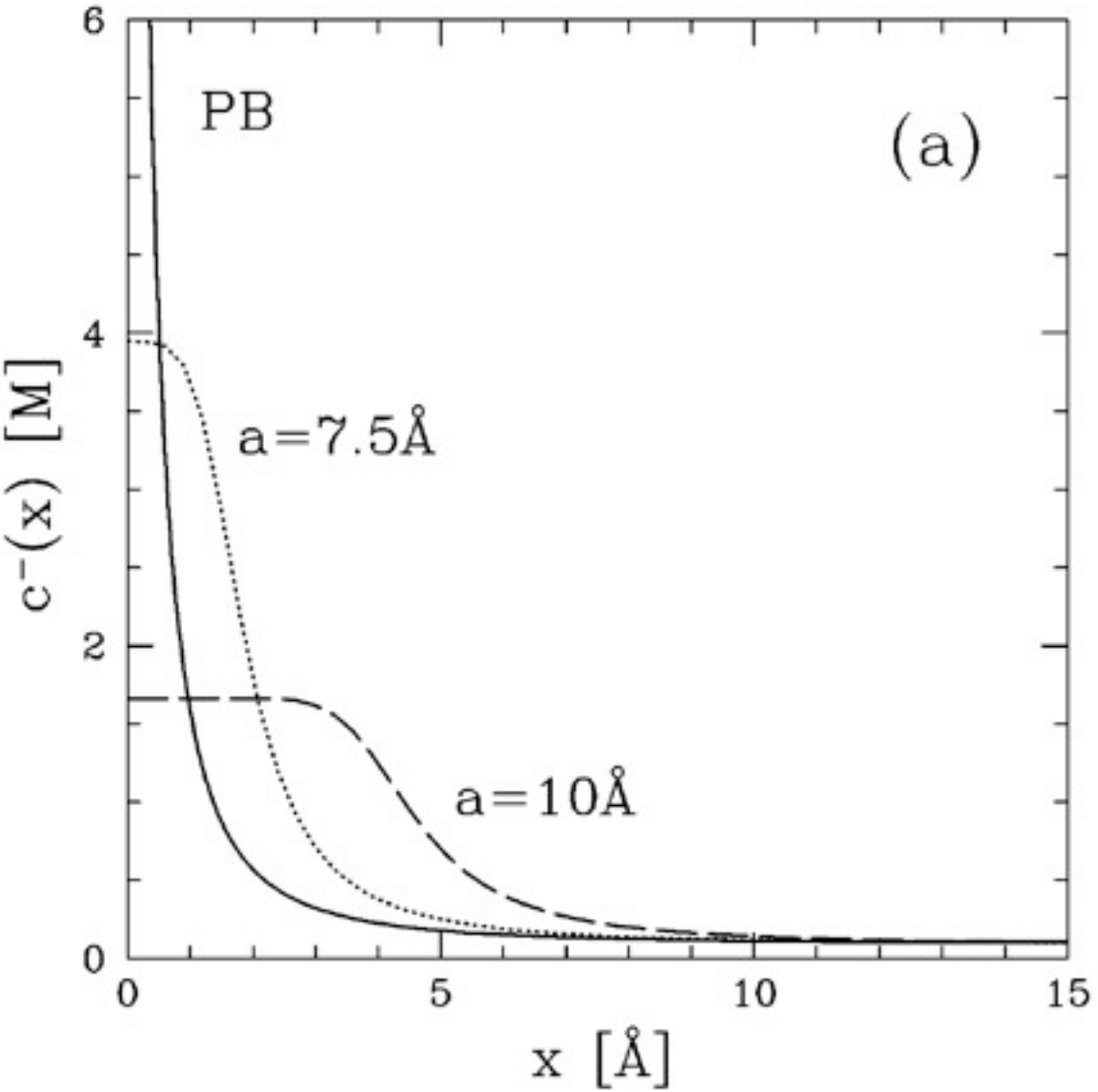
Modified Poisson-Boltzmannn model (1924~)

Water: continuum

Ion: point chg. + volume effect/
Boltzmann dist.

Electrode: wall, atom

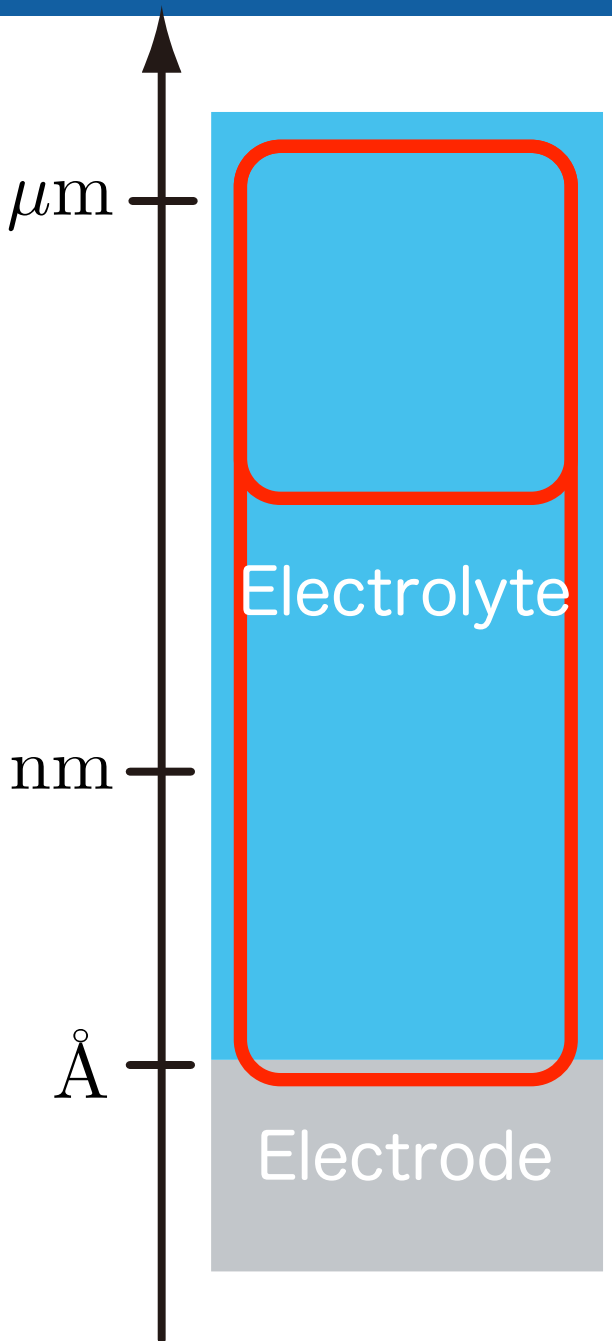
Poisson Boltzmann distribution



a: ion size

I. Brukhov, et.al. PRL '97

Hierarchical structure of interface



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Water: continuum$(\epsilon_r \sim 80)$
Ion: point chg./Boltzmann dist.

Modified Poisson-Boltzmann model (1920~)
Water: continuum
ion: point chg.+excluded volume/
Boltzmann distribution
Electrode: wall

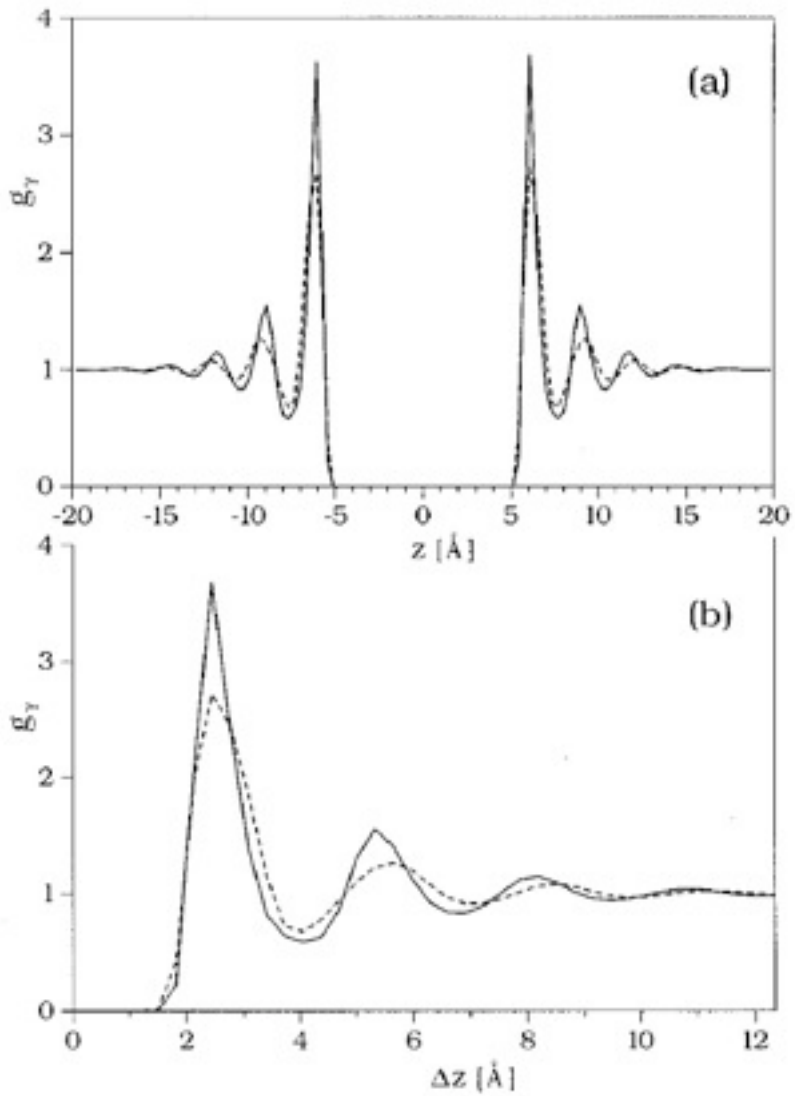
Integral equation+DFT (1980~)

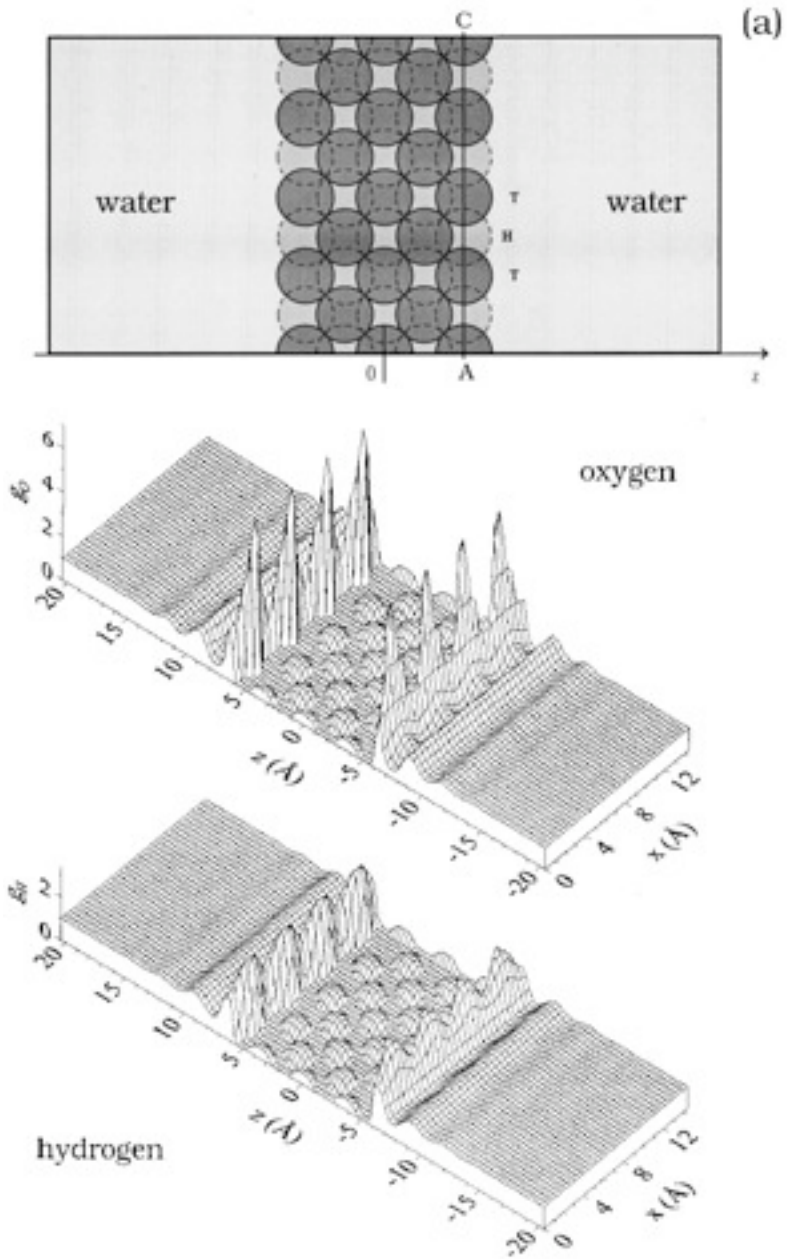
Orstein-Zernike eq.+
- HNC approximation
- RHNC approximation
- RISM
- 3D RISM

Water/ion : sphere, sphere+di(multi)pole, molecule

Electrode: wall, jellium, atom (pseudo potential)

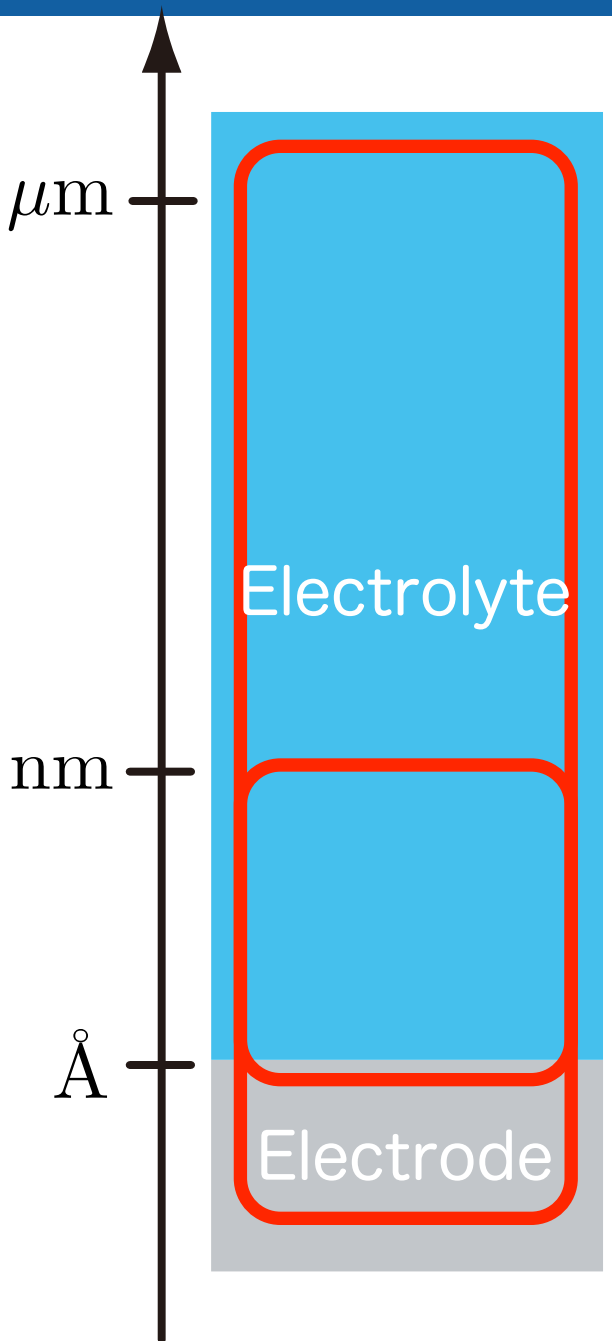
3D RISM+DFT [Cu(100)/water]





A. Kovalenko, et.al. JCP (1999)

Hierarchical structure of interface



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DFT+Molecular dynamics (1995~)

Water, ion, metal: pseudo potential

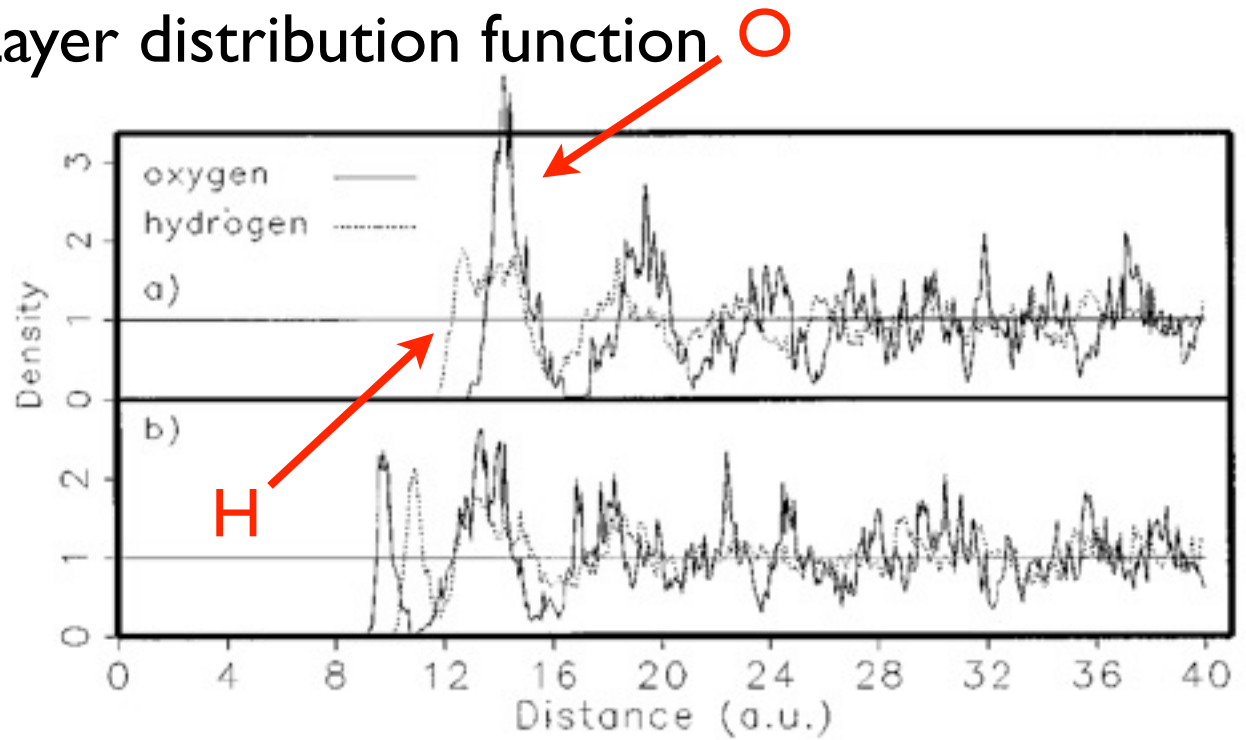
Potential : model potential, ab-initio

Bias potential : surface charge

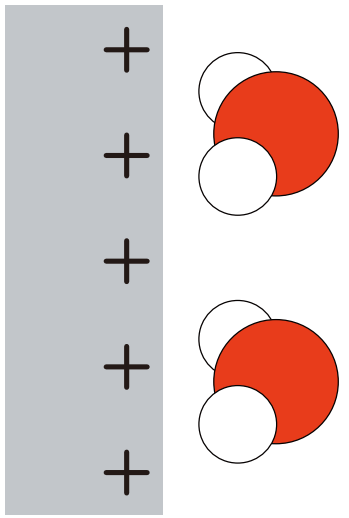
Car-Parrinello MD [Cu(100)/water]

180 Cu atoms & 245 water molecules

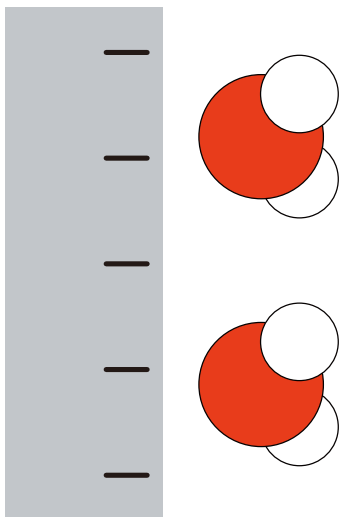
Layer distribution function



oxygen-up



oxygen-down



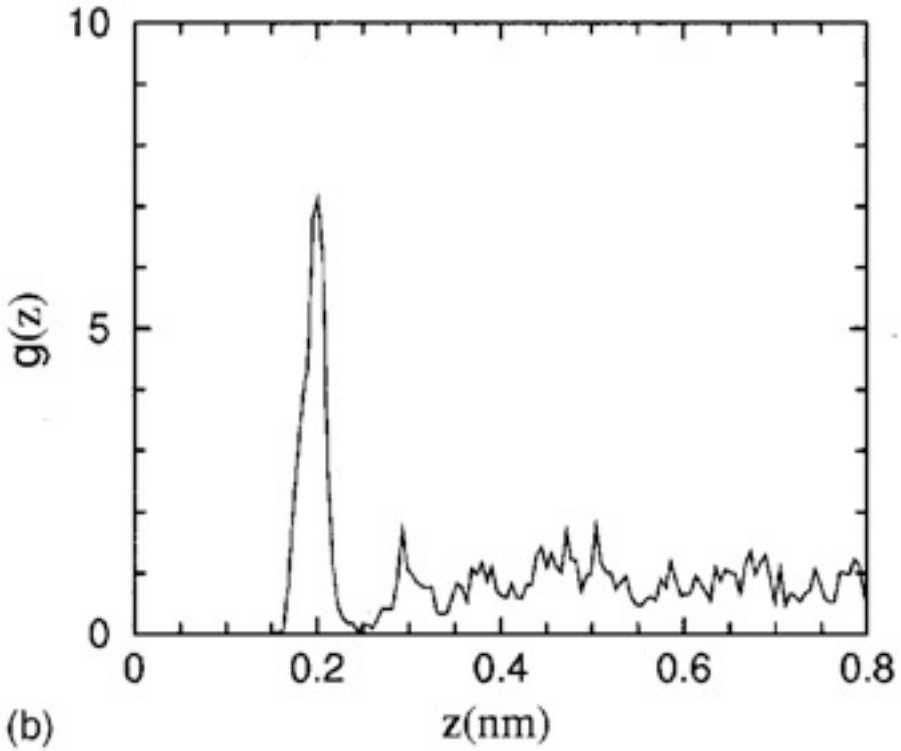
No full DFT (charge on water molecules are fixed)

D.L. Price, et. al. JCP (1995)

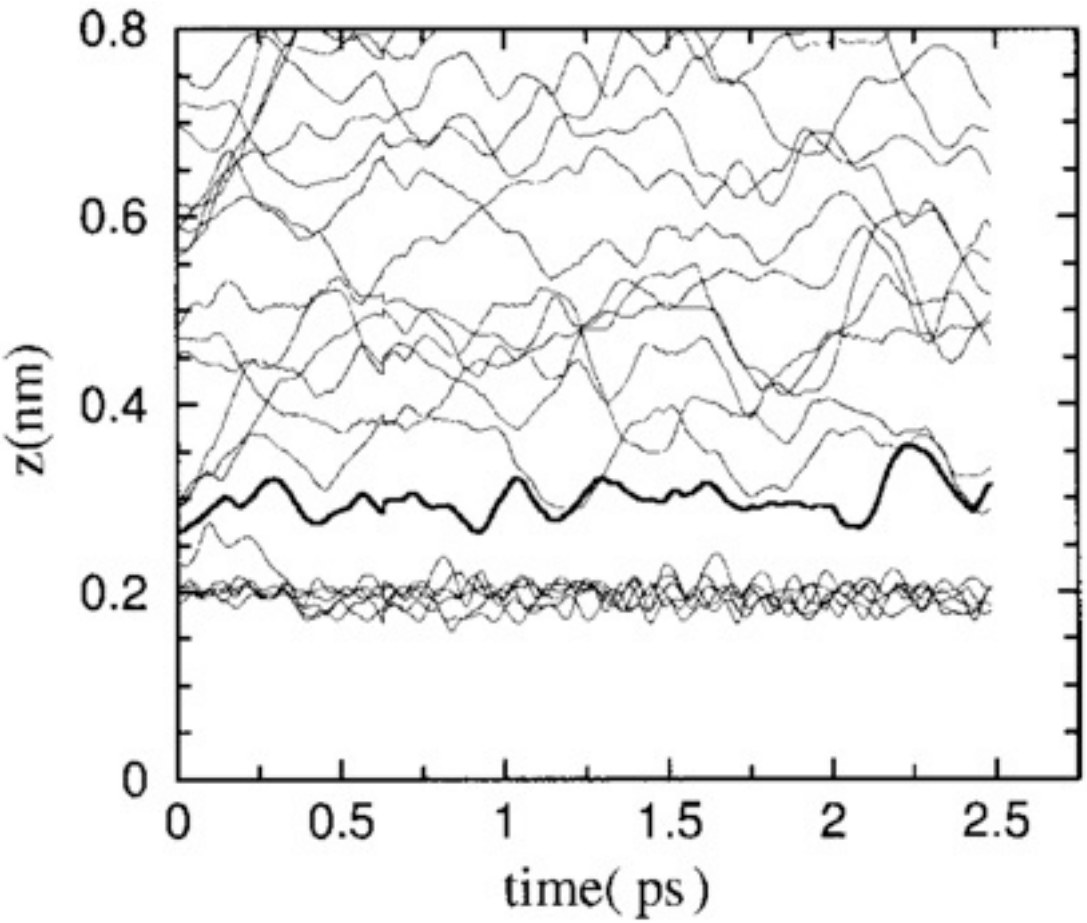
Car-Parrinello MD [Cu(100)/water]

63 Cu atoms & 24 water molecules

Layer distribution function

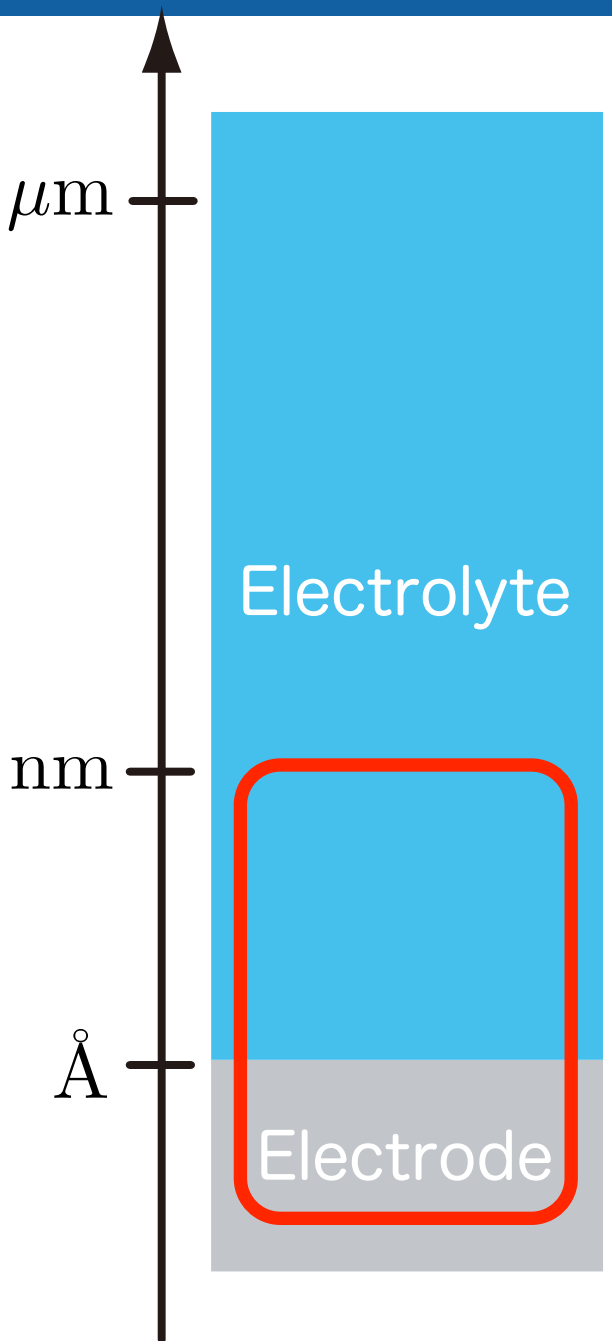


Pt-O distance



S. Izvekov, et. al. JCP (2001)

Hierarchical structure of interface



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Electrode: wall, jellium, atom (pseudo potential)

DFT+Molecular dynamics (1995~)

Water, ion, metal: pseudo potential

Potential : model potential, ab-initio

Bias potential : surface charge

We need to develop a new method
- ✓FPMD (with out model potential)
- ✓bias potential

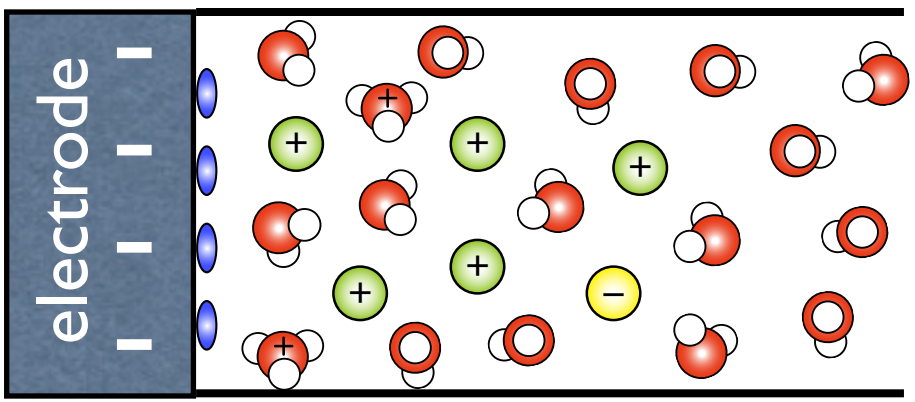
Electrode/electrolyte interface

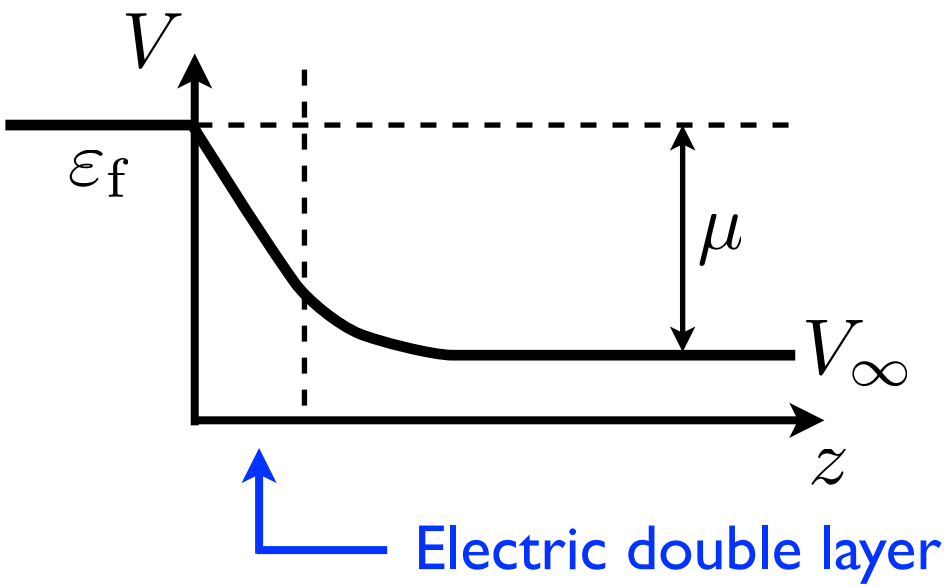
Things to be considered:

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

⇩

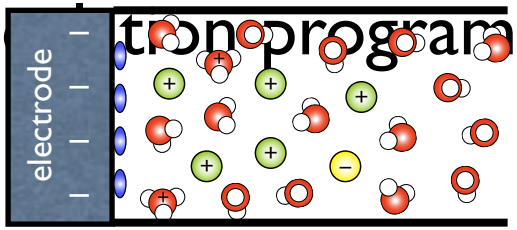
First-principles molecular dynamics simulation with a bias potential.



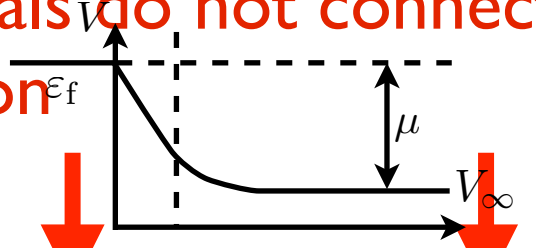


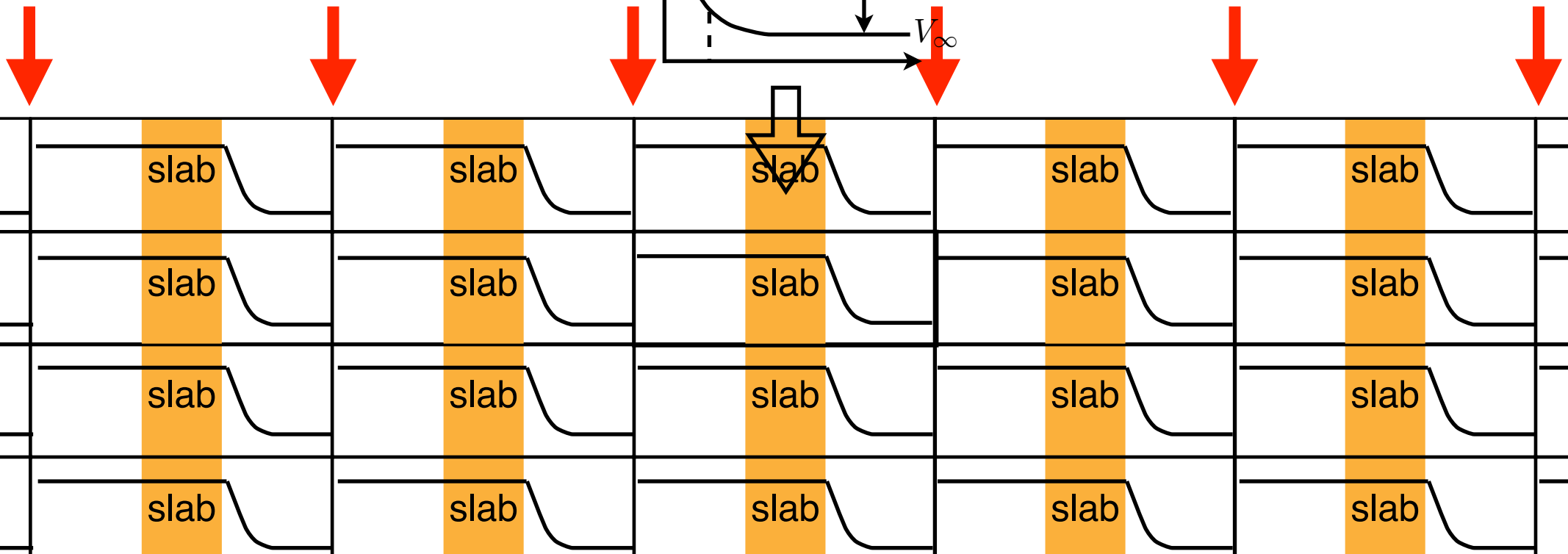
Why conventional DFT does now work?

Conventional DFT calculation program uses periodic boundary condition.



Electrostatic potentials do not connect to each other at the cell edge region





Idea of the method

Total energy functional

$$E[\rho] = T[\rho] + E_{\mathrm{xc}}[\rho] + \frac{1}{2}\iint d\boldsymbol{r}d\boldsymbol{r}'\frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \int d\boldsymbol{r} v_{\mathrm{ext}}(\boldsymbol{r})\rho(\boldsymbol{r}) + E_{\mathrm{ion}}$$

V ➠ variable

$$E[\rho_{\mathrm{e}}, V] = T[\rho_{\mathrm{e}}] + E_{\mathrm{xc}}[\rho_{\mathrm{e}}] + \int d\boldsymbol{r}\left[+\frac{\epsilon(\boldsymbol{r})}{8\pi}|\nabla V(\boldsymbol{r})|^2 + \rho_{\mathrm{tot}}(\boldsymbol{r})V(\boldsymbol{r})\right]$$

$\frac{\delta E}{\delta V} = 0$ → Poisson equation

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

conventional

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

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

ESM

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

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

$\frac{\delta E}{\delta \rho_{\mathrm{e}}} = 0$ → Kohn-Sham equation

$$\left[-\frac{1}{2}\nabla^2 + V(\boldsymbol{r}) + \hat{V}_{\mathrm{NL}} + V_{\mathrm{xc}}(\boldsymbol{r})\right]\psi_i(\boldsymbol{r}) = \varepsilon_i\psi_i(\boldsymbol{r})$$

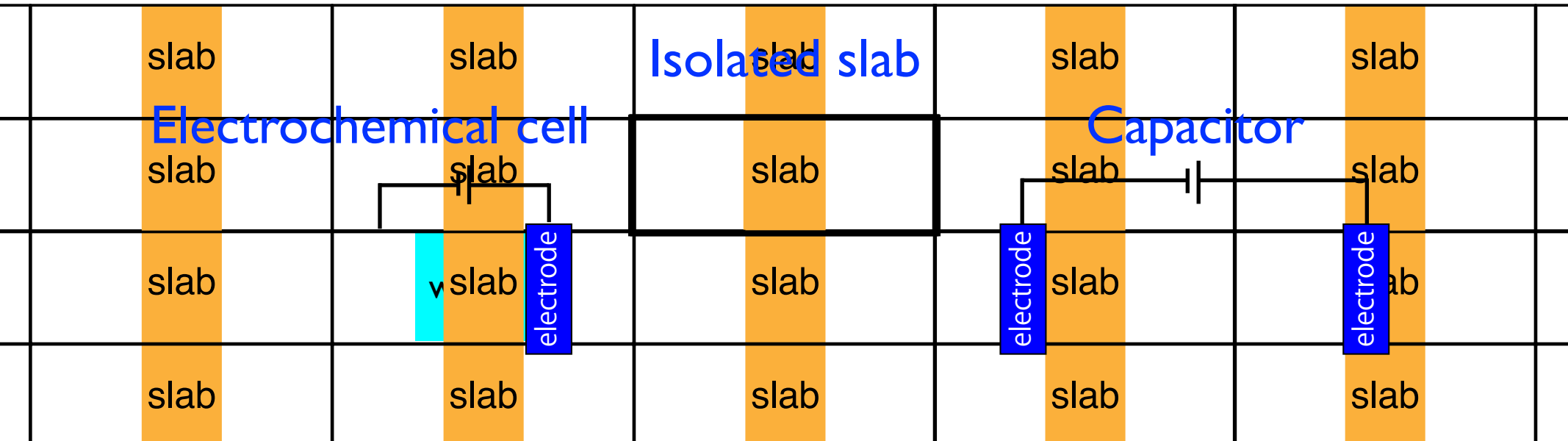
Effective screening medium method

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

electrostatic pot. ⟷ charge density (Poisson eq.)

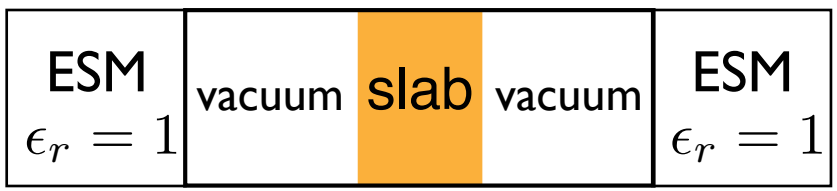
ESM method:

- Remove PBC along z-direction
- Impose model dependent boundary condition

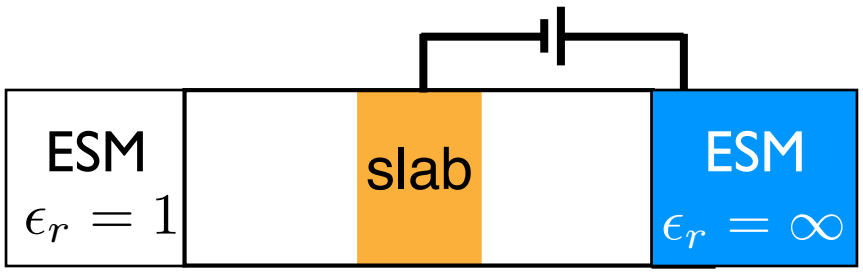


Effective screening medium method

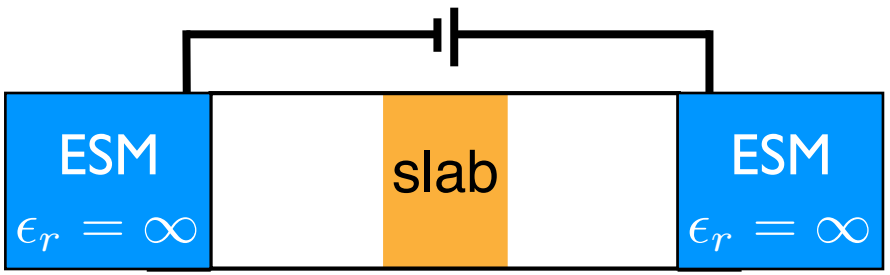
(i) Slab model (standard model)



(ii)STM, Capacitor, electrochemical cell



(iii) nanostructure in capacitor



- Poisson equation:

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

- Model dependent boundary condition
- ESM is characterized only by permittivity constant (ϵ_r)
- Solve the PE using the Green's function technique

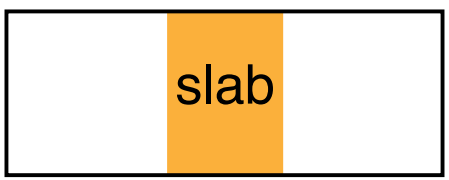
M.O. and O. Sugino, PRB 73, 115407 (2006)

Effective screening medium method

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

(i)

$$\partial_z V(g_\parallel, z)\big|_{z=\pm\infty} = 0, \quad \epsilon(z) = 1$$

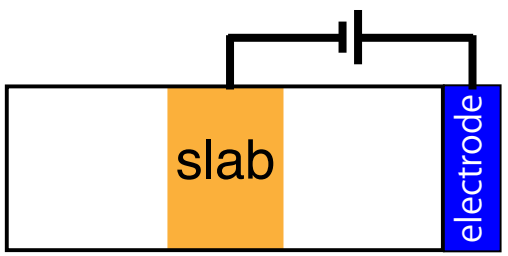


neutral surface, polarized surface...

(ii)

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

$$\epsilon(z) = \begin{cases} 1 & \text{if} \quad z \geq z_1 \\ \infty & \text{if} \quad z \leq z_1 \end{cases}$$

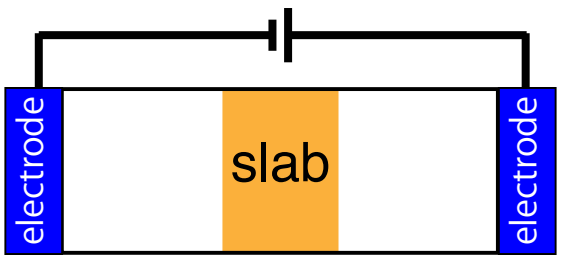


STM, gate electrode...

(iii)

$$\begin{cases} V(g_\parallel, z_1) = 0 \\ V(g_\parallel, -z_1) = V_0 \end{cases}$$

$$\epsilon(z) = \infty \quad \text{if} \quad |z| \geq z_1$$



nano-structure in capacitor, zigzag pot.

Effective screening medium method

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

How to solve the poisson equation?

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

Laue representation

$$[\partial_z\{\epsilon(z)\partial\} - \epsilon(z)g_{||}^2]V(\boldsymbol{g}_{||}, z) = -4\pi\rho(\boldsymbol{g}_{||}, z)$$

$$[\partial_z\{\epsilon(z)\partial\} - \epsilon(z)g_{||}^2]G(\boldsymbol{g}_{||}, z, z') = -4\pi\delta(\boldsymbol{g}_{||}, z - z')$$

We can get Green's function analytically with each boundary conditions.

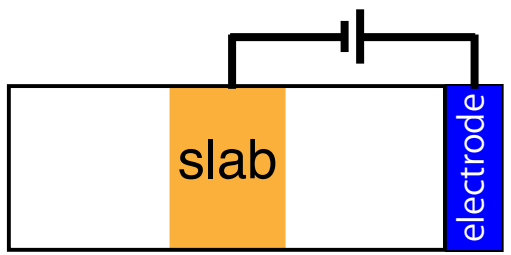
Effective screening medium method

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

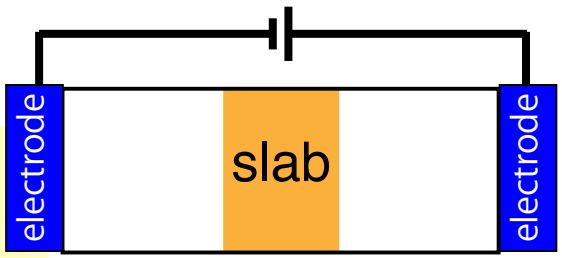
Green's functions in real space

bare coulomb part
image charge part

$$G^{(\mathrm{i})}(r_\parallel - r'_\parallel, z, z') = \frac{1}{\sqrt{(|r_\parallel - r'_\parallel|^2 + (z - z')^2}}$$



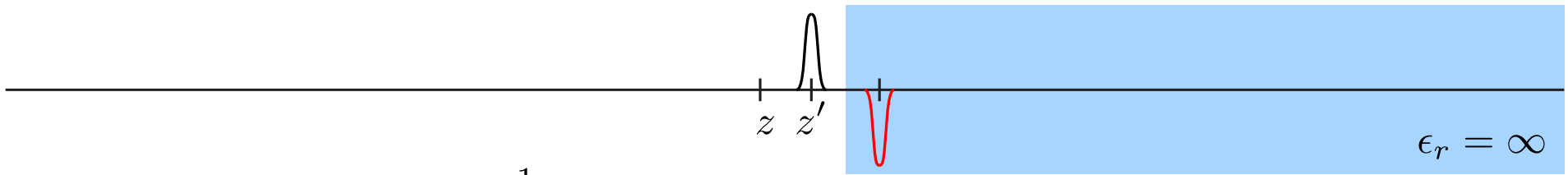
$$G^{(\mathrm{ii})}(r_\parallel - r'_\parallel, z, z') = \frac{1}{\sqrt{(|r_\parallel - r'_\parallel|^2 + (z - z')^2}} + \frac{1}{\sqrt{|r_\parallel - r'_\parallel|^2 + (2z_1 - z - z')^2}}$$



$$G^{(\mathrm{iii})}(r_\parallel - r'_\parallel, z, z') = \frac{1}{\sqrt{(|r_\parallel - r'_\parallel|^2 + (z - z')^2}}$$
$$+ \sum_{m=0}^{\infty} \left[\frac{1}{\sqrt{|r_\parallel - r'_\parallel|^2 + (z - z' + (4m+4)z_1))^2}} + \frac{1}{\sqrt{|r_\parallel - r'_\parallel|^2 - (-z + z' + (4m+4)z_1))^2}} \right]$$
$$- \sum_{m=0}^{\infty} \left[\frac{1}{\sqrt{|r_\parallel - r'_\parallel|^2 + (z + z' + (4m+4)z_1))^2}} + \frac{1}{\sqrt{|r_\parallel - r'_\parallel|^2 - (-z - z' + (4m+4)z_1))^2}} \right]$$

Series of mirror images

$$G^{(\mathrm{ii})}(r_\parallel - r'_\parallel, z, z') = \frac{1}{\sqrt{(|r_\parallel - r'_\parallel|^2 + (z - z')^2}} + \frac{1}{\sqrt{|r_\parallel - r'_\parallel|^2 + (2z_1 - z - z')^2}}$$



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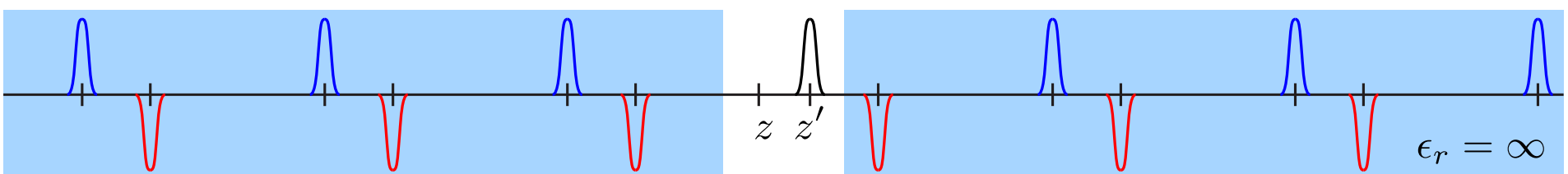
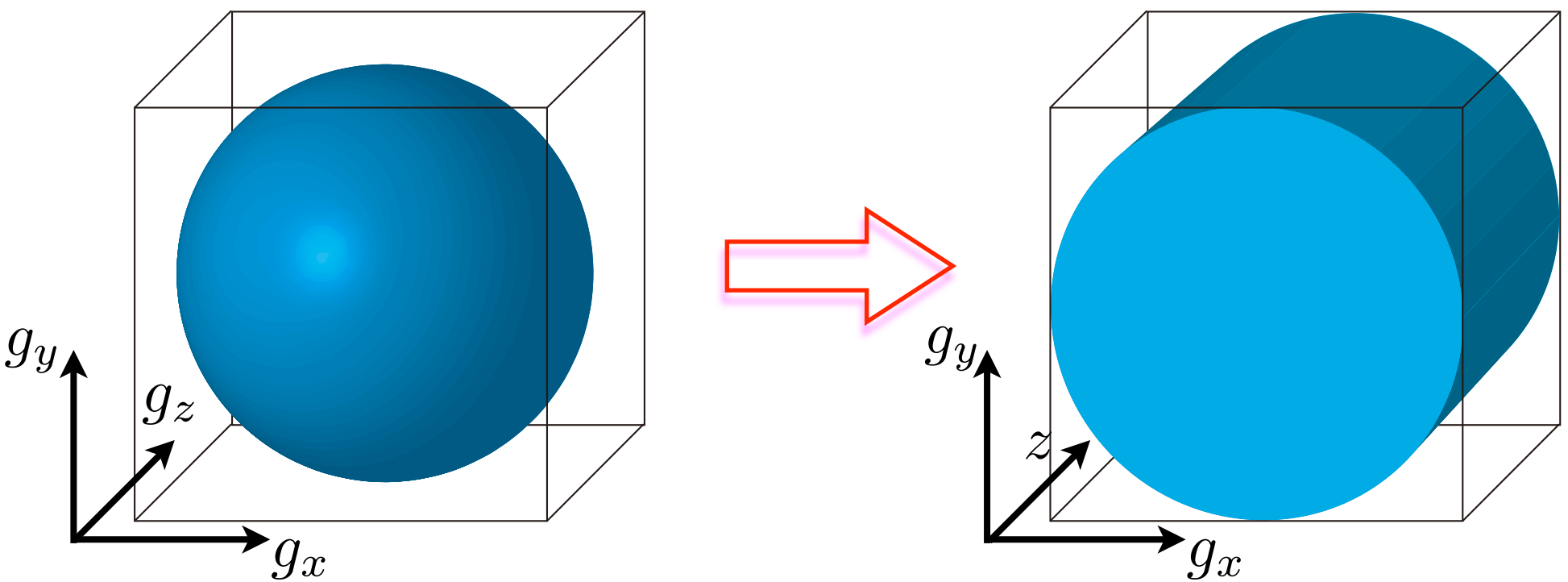


Effective screening medium method

- Various boundary conditions (battery, FET, STM...)
- Easy to implement "state of the art" DFT programs
- Calculation cost for ESM part is negligible
- No dipole (or more higher order) correction for polar surface

Conventional g-component

g-component in ESM method



Implementation

$$V_{\mathrm{hart}}(r) = \int dr' G(r,r')\rho_{\mathrm{e}}(r')$$

$$V_{\mathrm{hart}}(r) = \int_{-z_1}^{z_1} dz' G(g_\parallel, z, z')\rho_{\mathrm{e}}(g_\parallel, z')$$

$$= \sum_{g_z} \rho_{\mathrm{e}}(g_\parallel, g_z) \int_{-z_1}^{z_1} dz' G^{(\mathrm{iii})}(g_\parallel, z, z') \mathrm{e}^{\mathrm{i}g_z z'}$$

$$= \sum_{g_z} \frac{4\pi}{g_\parallel^2 + g_z^2} \rho_{\mathrm{e}}(g_\parallel, g_z) \mathrm{e}^{\mathrm{i}g_z z}$$

$$+ \frac{4\pi \sinh(g_\parallel(z - z_1))}{\sinh(2g_\parallel z_1)} \sum_{g_z} \frac{\mathrm{e}^{-\mathrm{i}g_z z_1}}{g_\parallel^2 + g_z^2} \rho_{\mathrm{e}}(g_\parallel, g_z)$$

$$- \frac{4\pi \sinh(g_\parallel(z - z_1))}{\sinh(2g_\parallel z_1)} \sum_{g_z} \frac{\mathrm{e}^{\mathrm{i}g_z z_1}}{g_\parallel^2 + g_z^2} \rho_{\mathrm{e}}(g_\parallel, g_z)$$

conventional

$$V(G) = \sum_G \frac{4\pi}{G^2} \rho_{\mathrm{e}}(G)$$

g_x, g_y, g_z

g_x, g_y

g_z

z

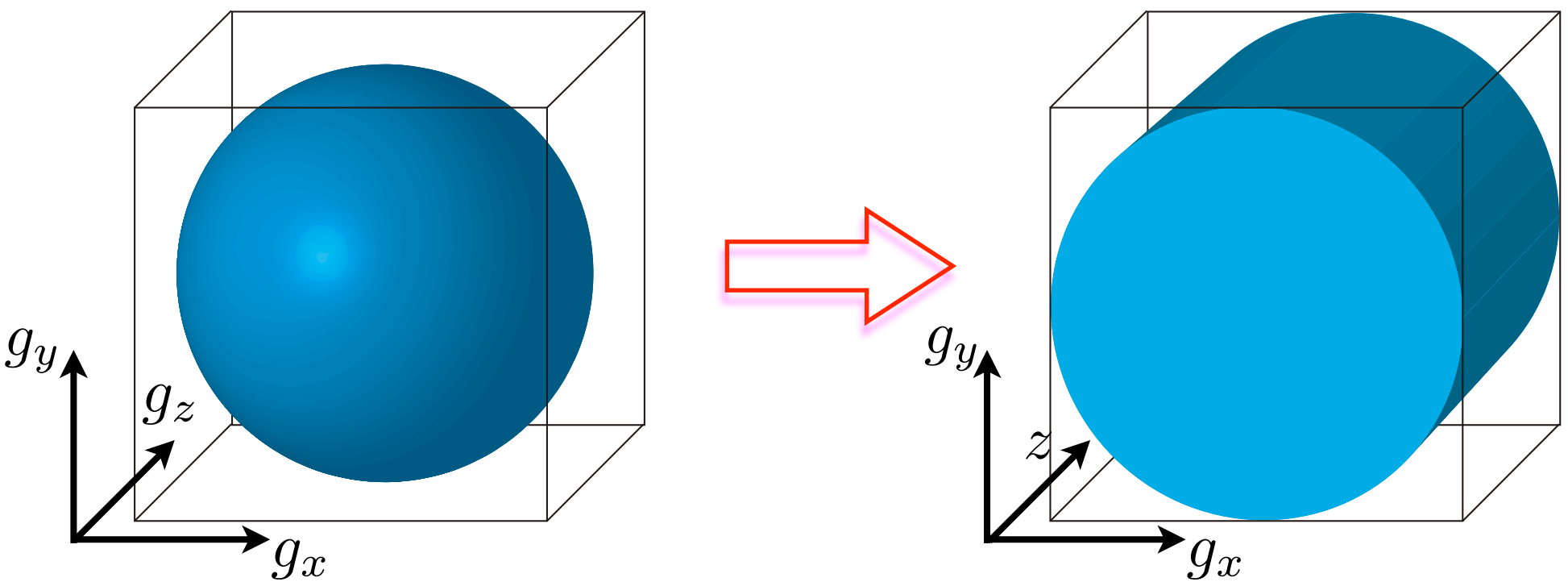
independent g_z loop

Effective screening medium method

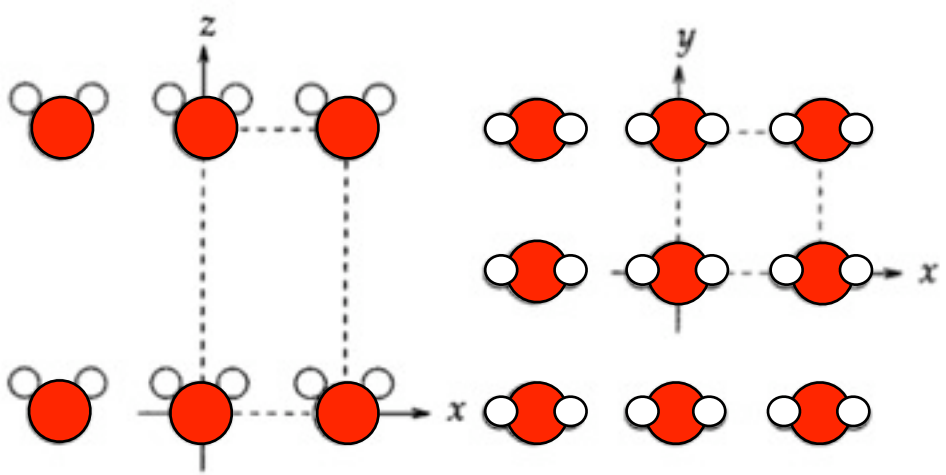
- Various boundary conditions (battery, FET, STM...)
- Easy to implement "state of the art" DFT programs
- Calculation cost for ESM part is negligible
- No dipole (or more higher order) correction for polar surface

Conventional g-component

g-component in ESM method



Dipole correction

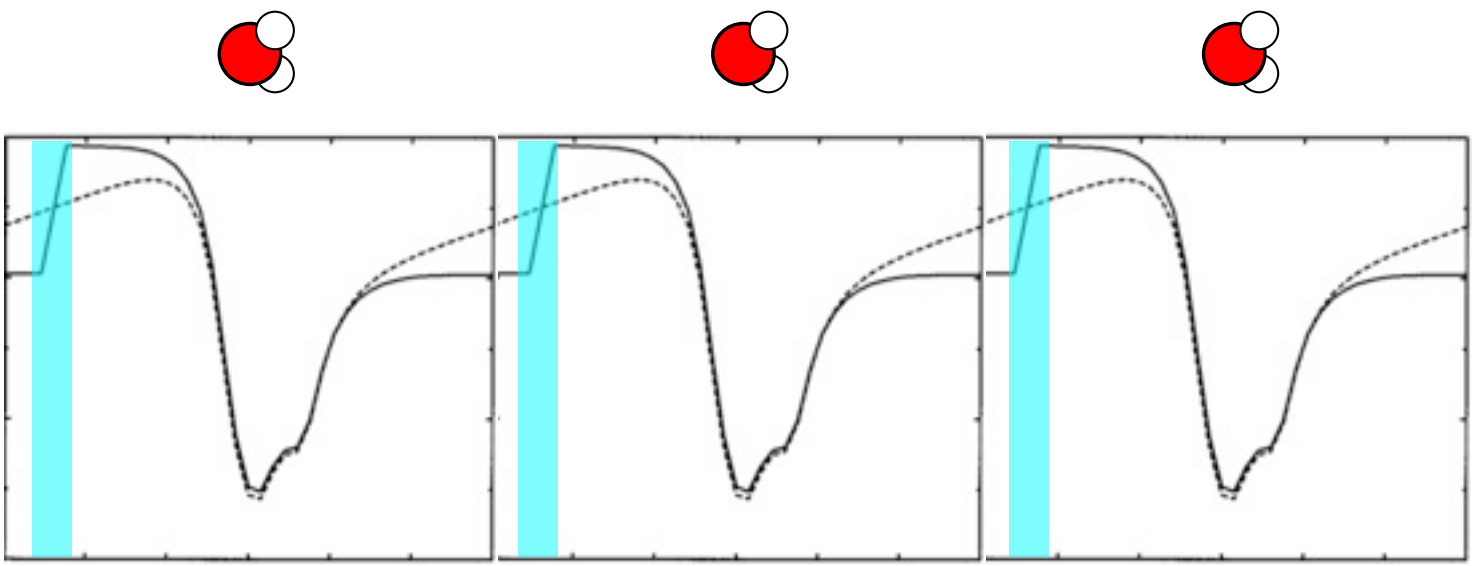


L. Bengtsson, PRB **59**, 12301 (1999)

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

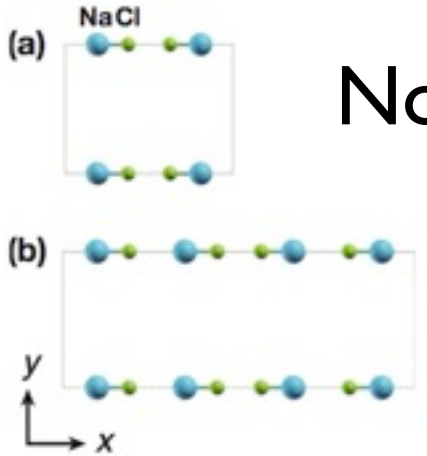
$$g_{\parallel} \rightarrow 0 \text{ term}$$

dipole layer

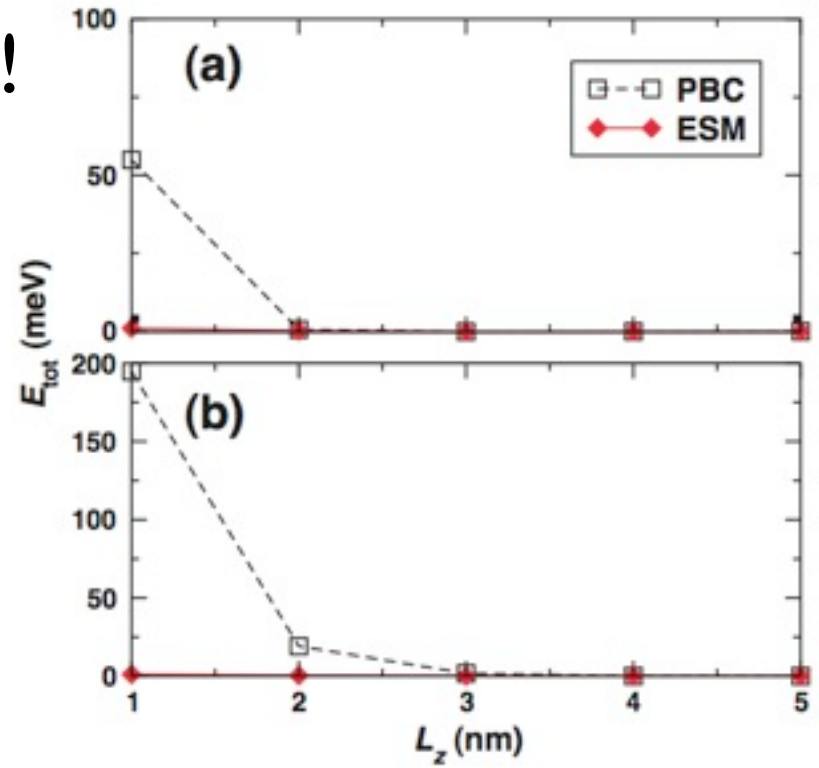


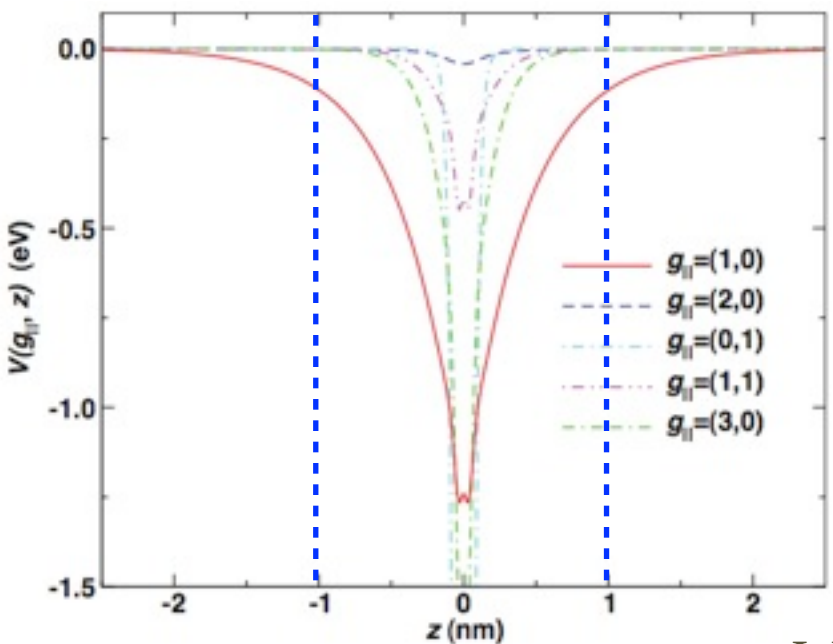
Only dipole contribution can be corrected, but...

Multipole interaction between slab



No dipole moment!





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

$$g_{\parallel} = (1,0) \text{ term}$$

quadrupole term give an error.

I. Hamada, M.O. O. Sugino, and Y. Morikawa, PRB **80**, 165411 (2009)

Effective screening medium method

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- Easy to implement "state of the art" DFT programs
- Calculation cost for ESM part is negligible
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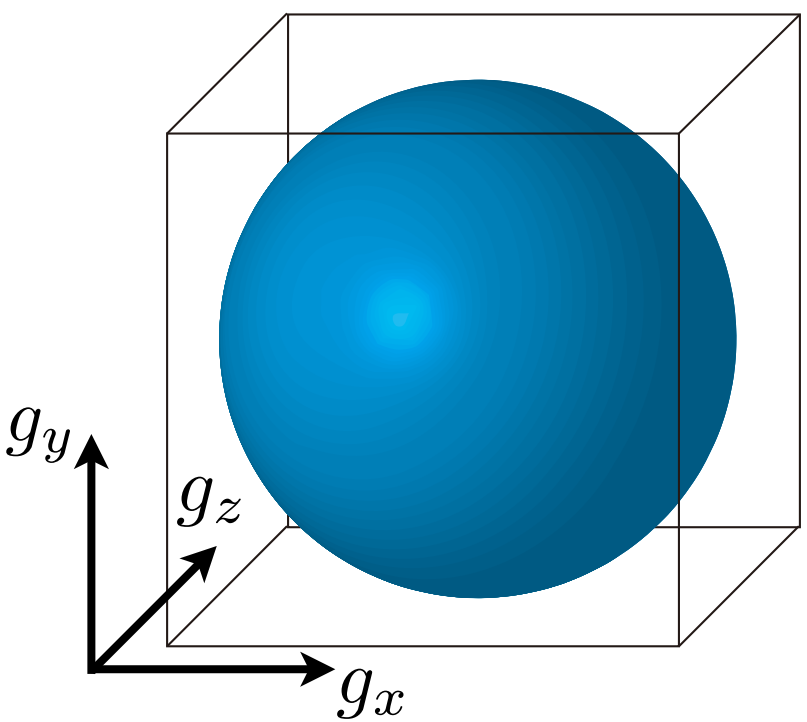
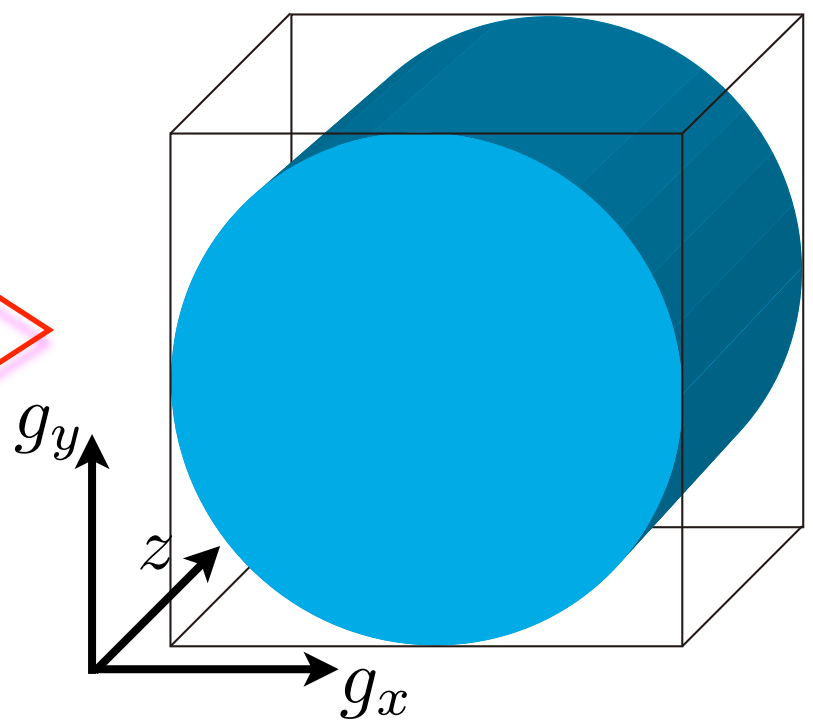


g-component in ESM method



ESM ready programs

- TAPP
- STATE
- PWSCF

} Plane wave + Pseudopotential

- OpenMX
- SIESTA

} Localized basis + Pseudopotential

- QBOX?

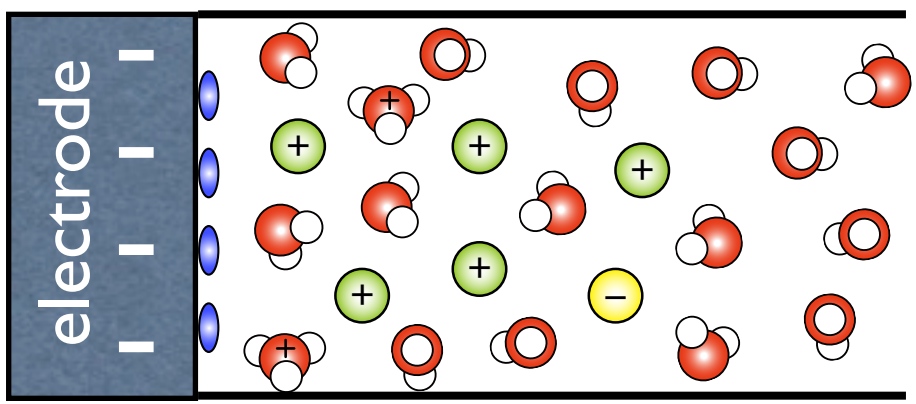
http://sugino.issp.u-tokyo.ac.jp/esm/

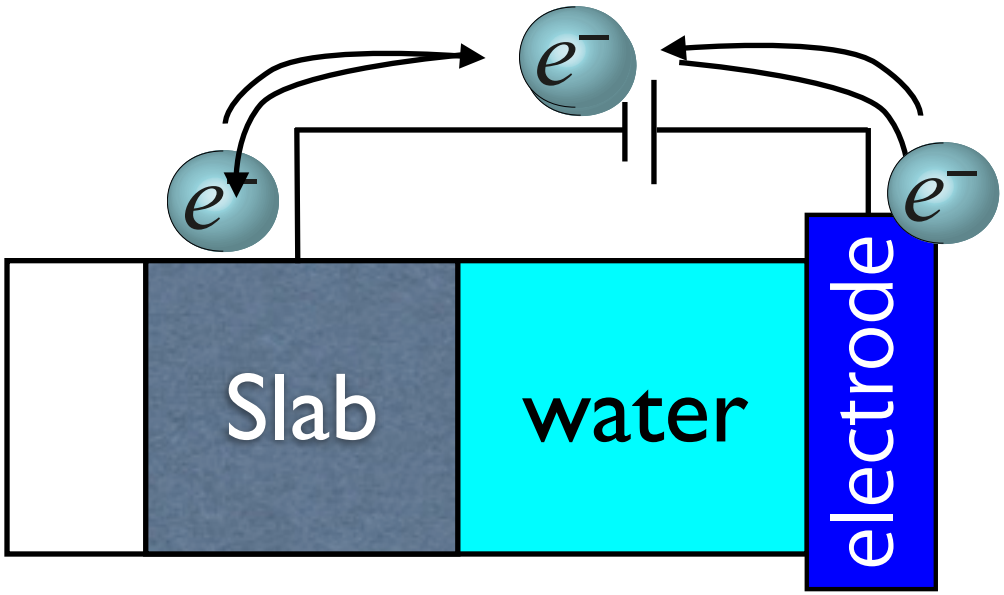
Outline

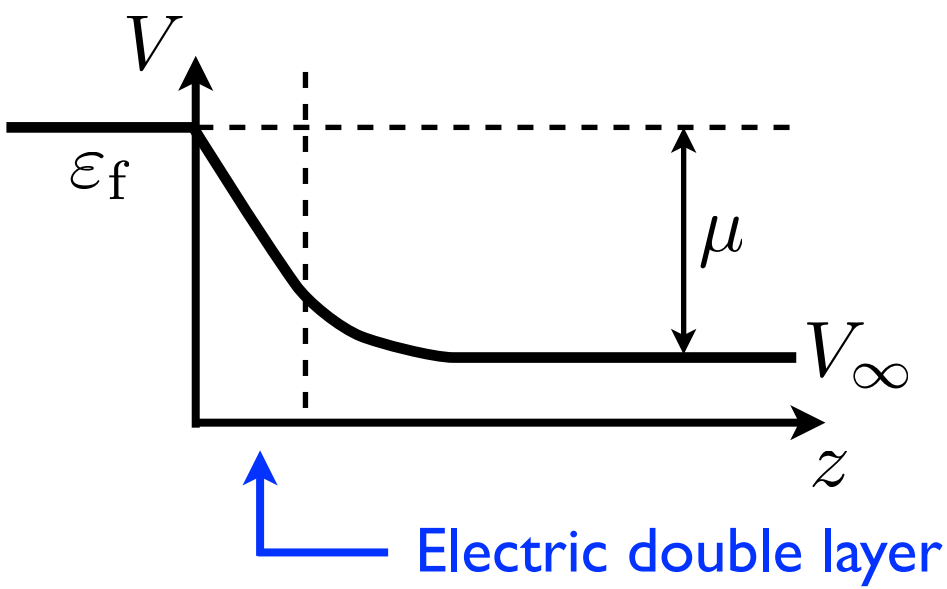
- Introduction
  - Application of electrochemical device
  - What is the target of our simulation?
- Method
  - History of the electrochemical interface in theoretical simulation
  - What is the ESM method?
- Application
  - How to apply bias potential to metal/water interface
  - Model of the electrochemical system
  - Electrochemical reactions (a few steps in the electrolysis of water)
- Extension
  - Limitation of the current ESM method
  - Smooth ESM & Constant bias potential MD simulation
- Summary

Effective screening medium method

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



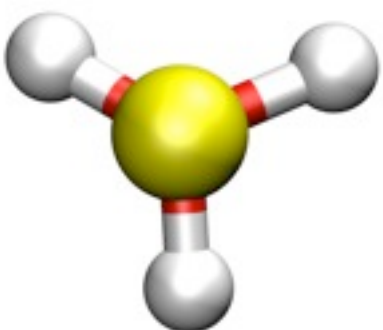




- A slab model for an electrode
- Introduce a counter electrode with an imaginary battery
- Adding/removing an electron from slab electrode → bias potential

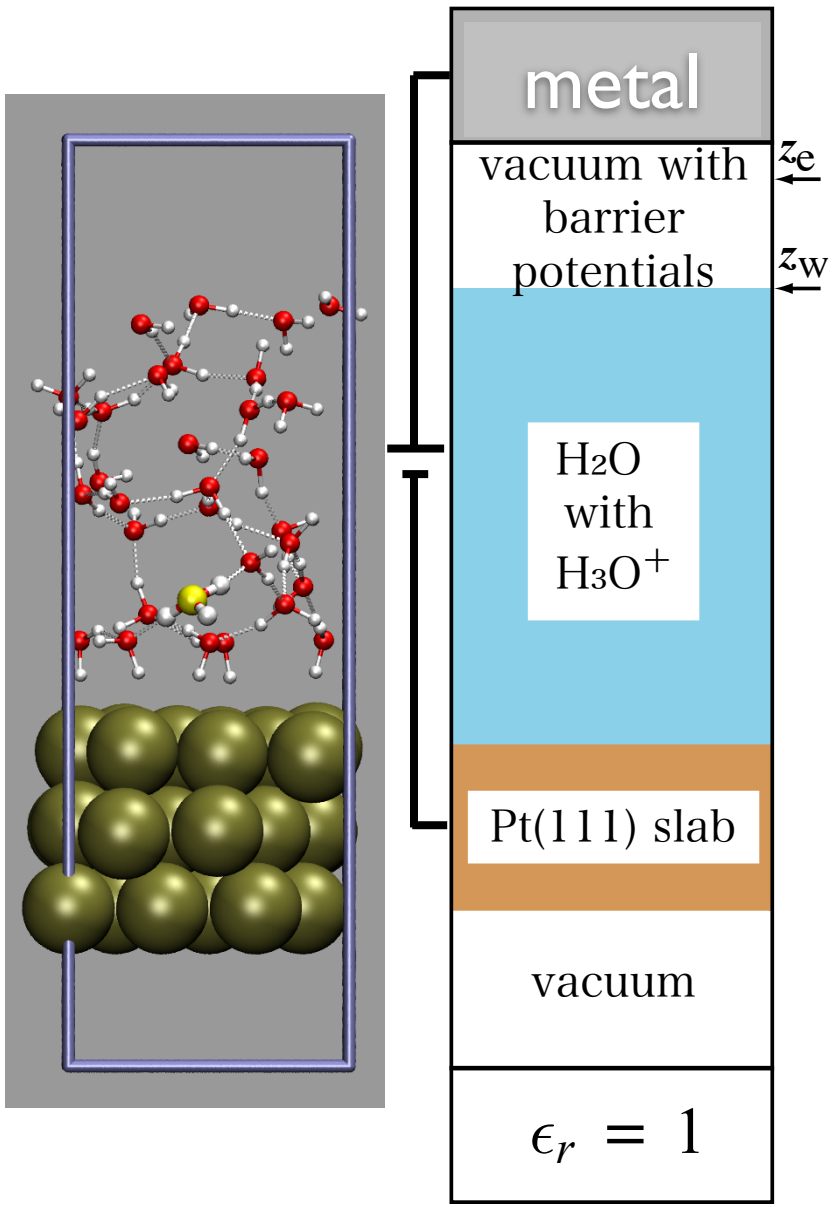
Simulation condition

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



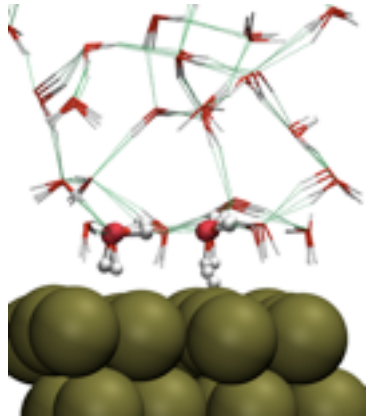
H_3O^+

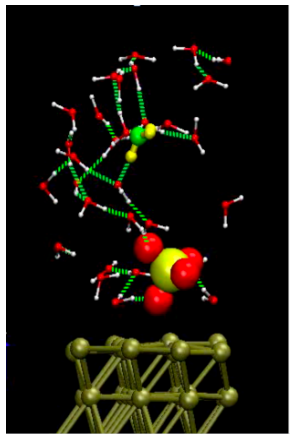
OH^-

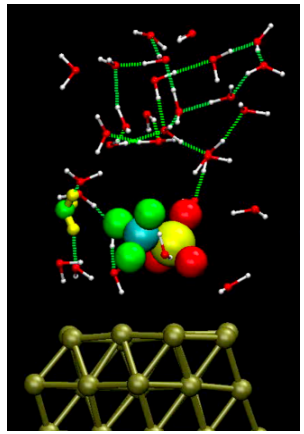


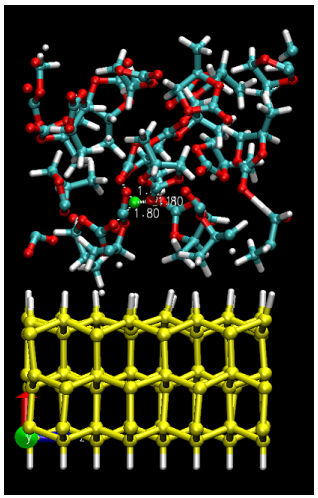
Application of the ESM

- Pt/water interface
  - Hydrogen adsorption reaction
  - Water splitting and formation
  - Pitted pt surface
  - HSO_4, CF_3SO_4
- Si/propylene carbonate (PC)
  - Solvation and desolvation of Li
  - Formation mechanism of solid electrolyte interface (SEI).

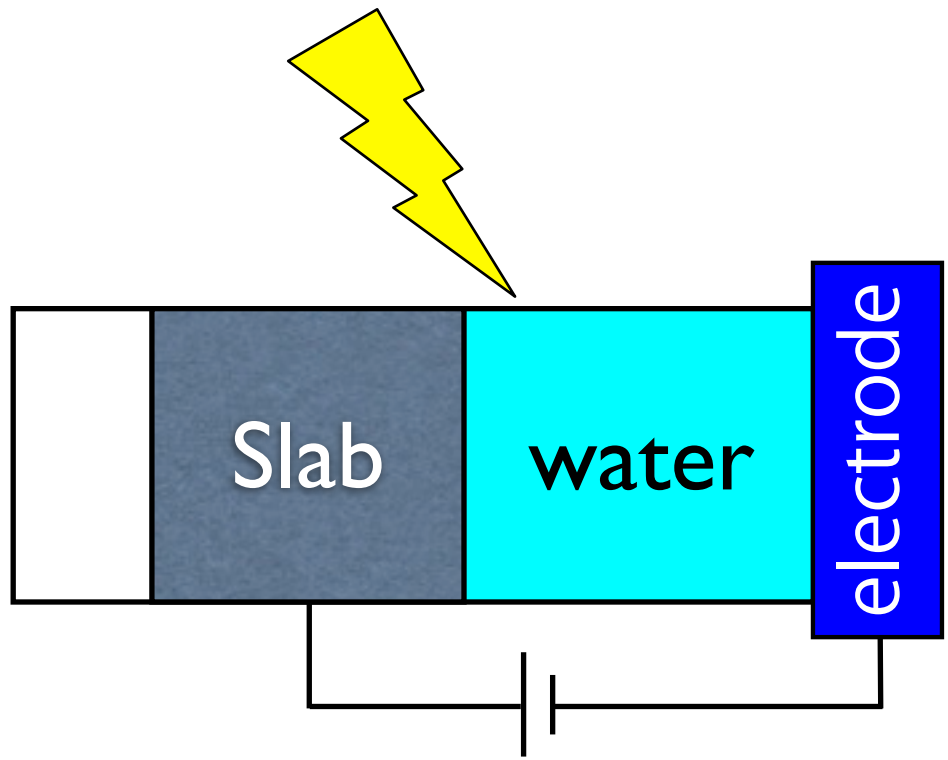




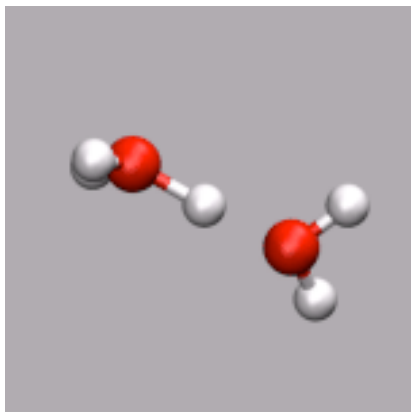




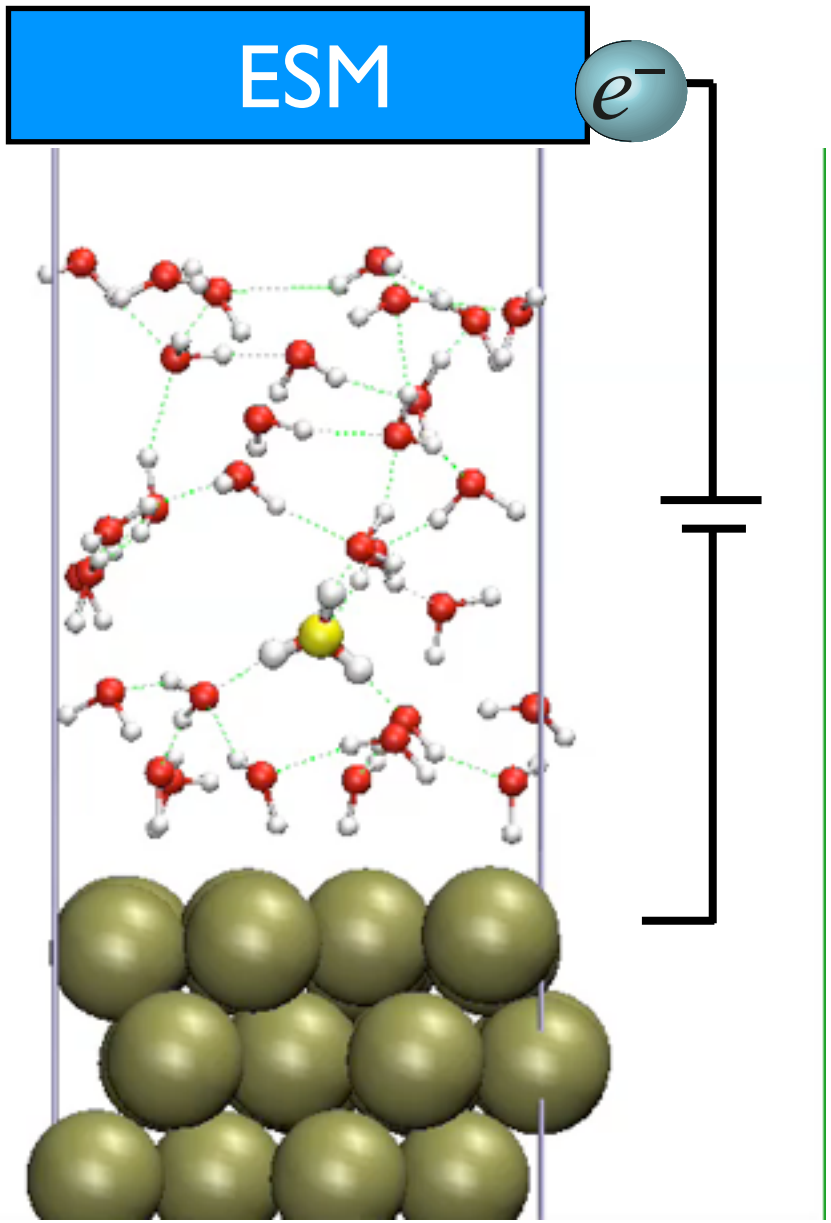
Impact of bias potential on vibration of water molecule and structure of water layer.



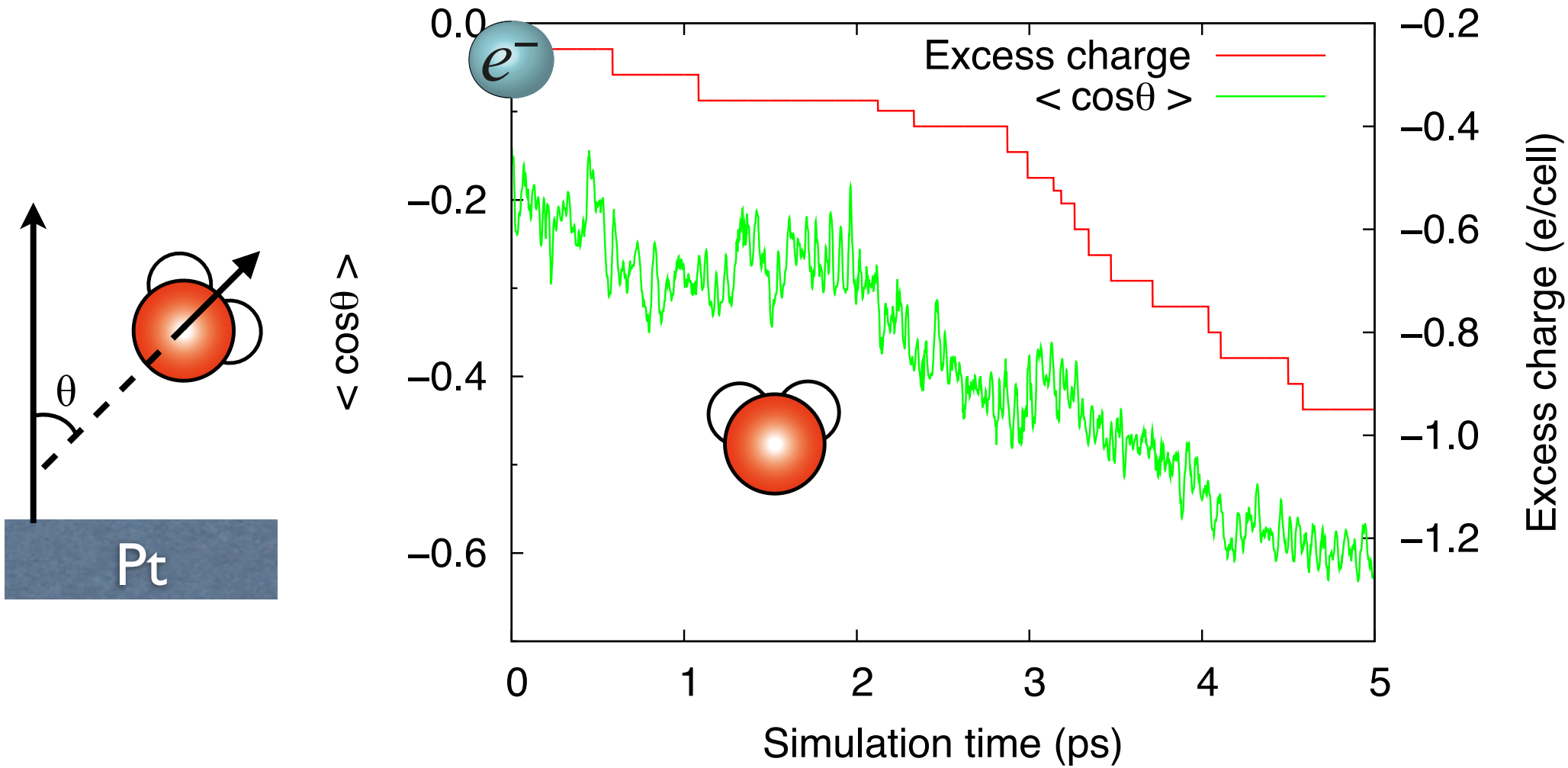
MD simulations with bias potential



Grotthuss mechanism



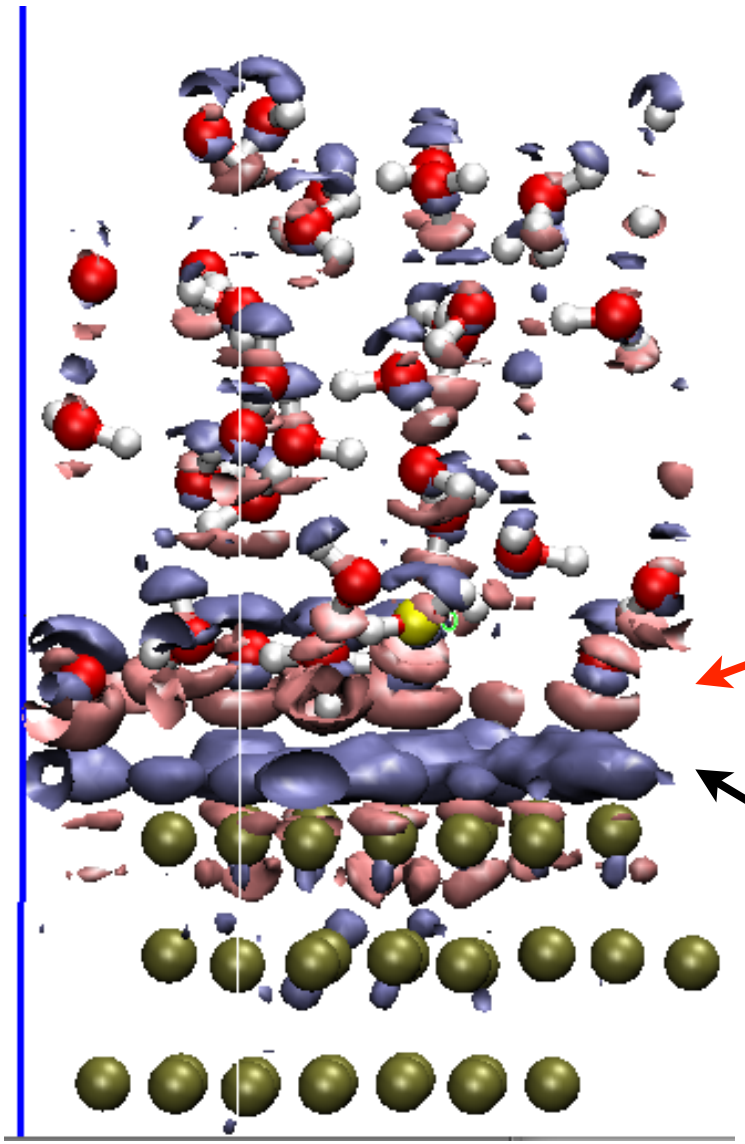
Rotation of water molecules



Increase surface charge (negative bias)

⇒ Screen external electric field

Charge redistribution



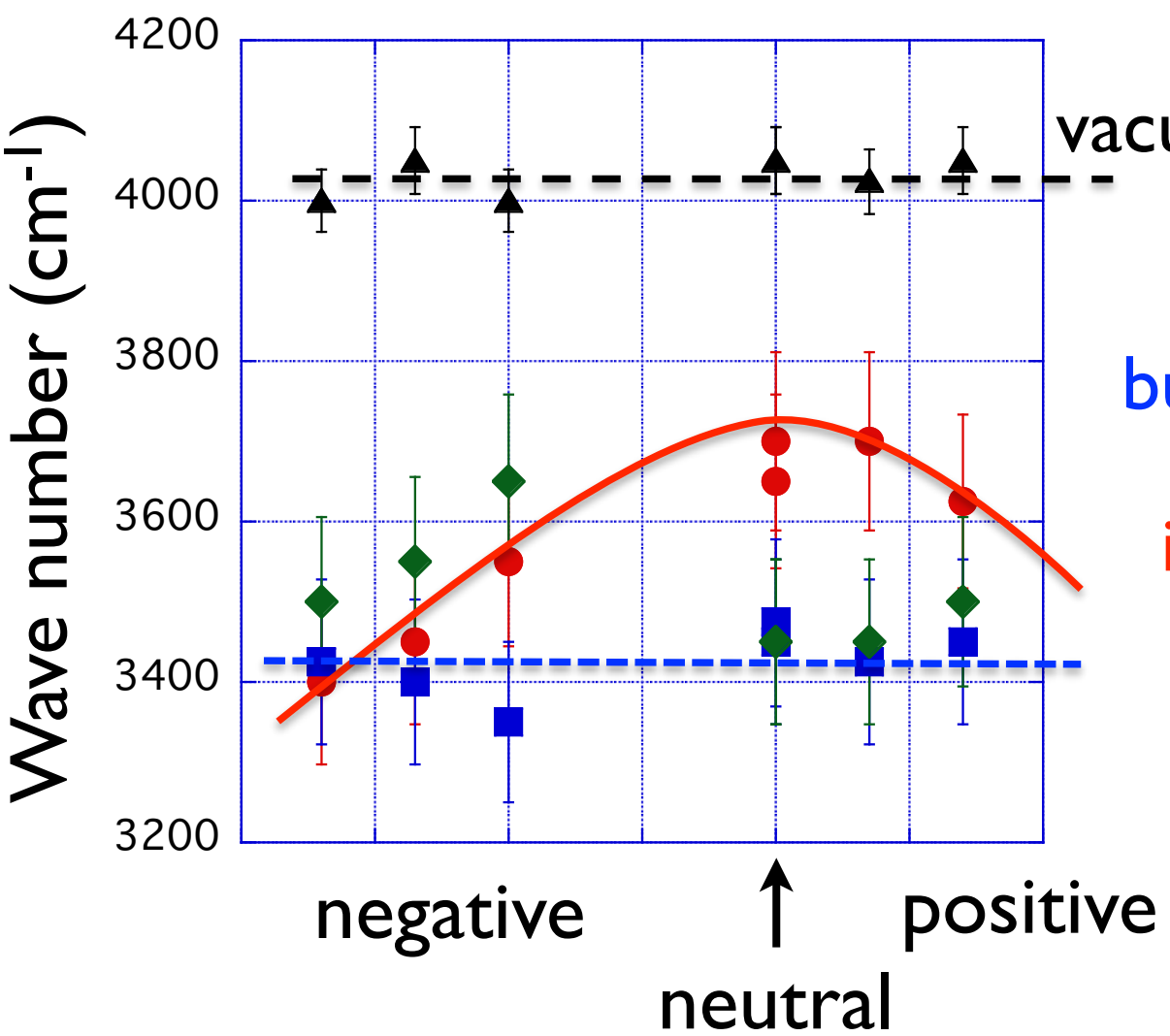
$$\Delta\rho = \rho(\text{charged}) - \rho(\text{neutral})$$

polarization of water

Large charge redistribution occurs at the interface

Accumulated charge on metal surface

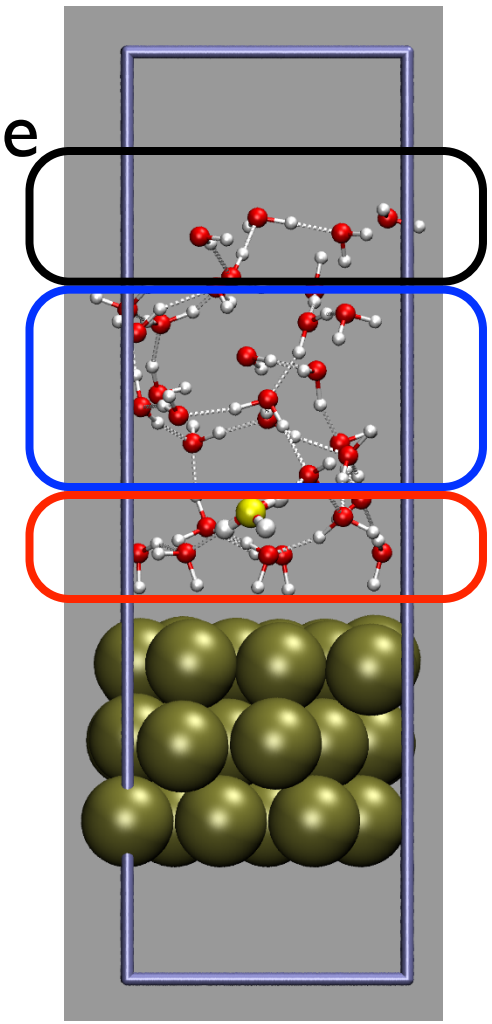
Vibration frequency (OH stretching)



vacuum surface region

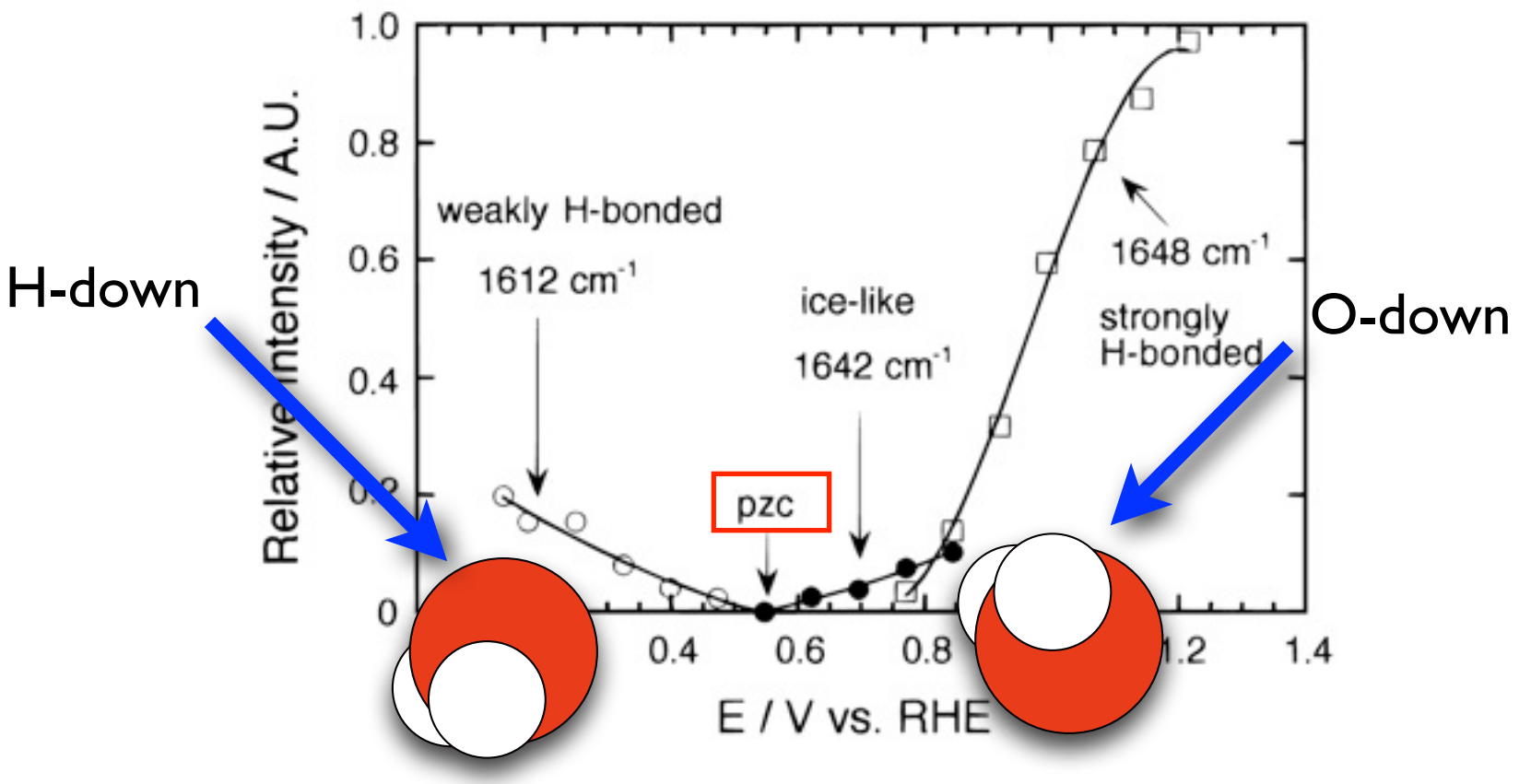
bulk region

interface region



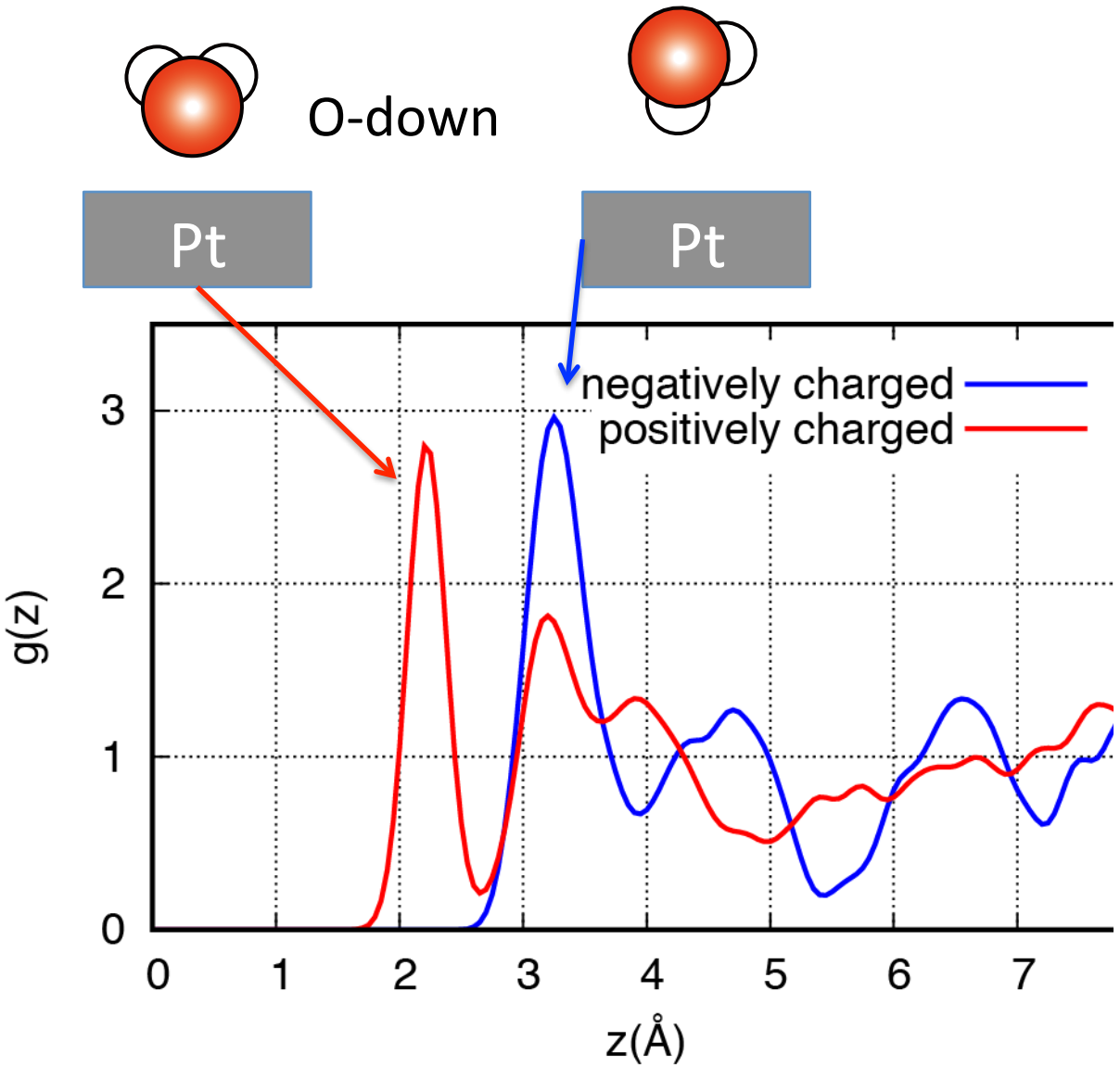
Orientation of water molecule at interface

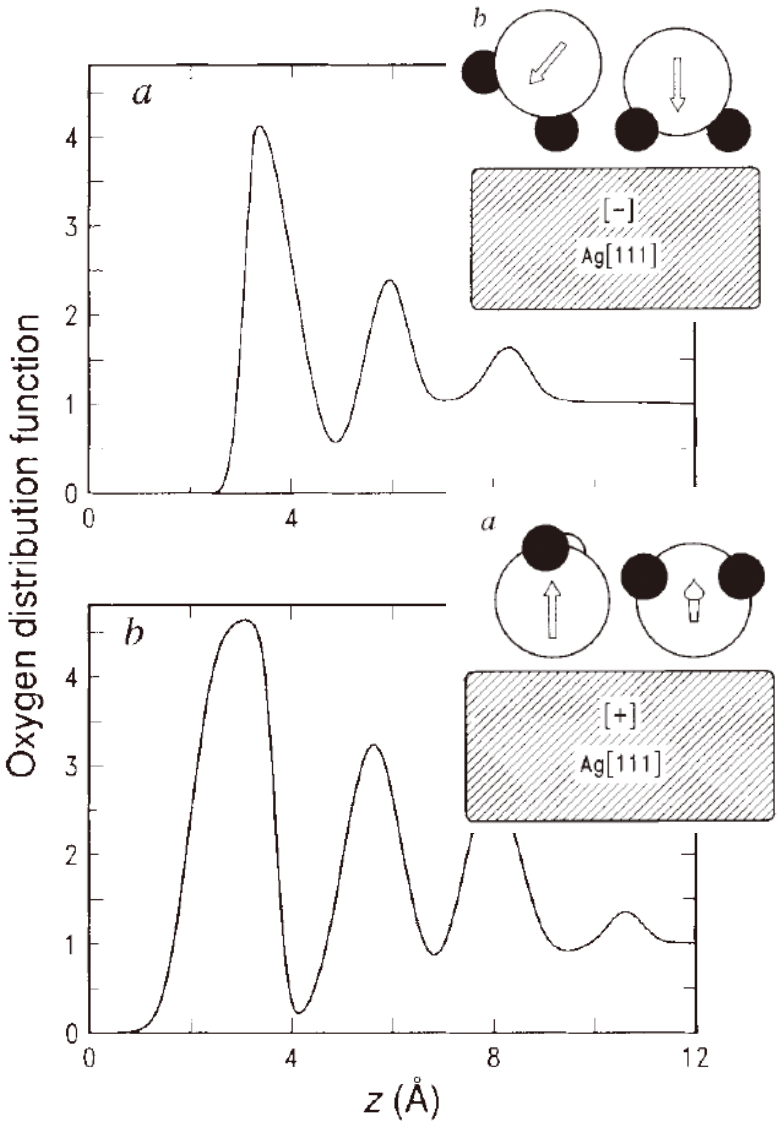
Surface enhanced infrared absorption spectroscopy (ATR-SEIRAS)
Au(111)/Water



K. Ataka, et.al. JPC (1996)

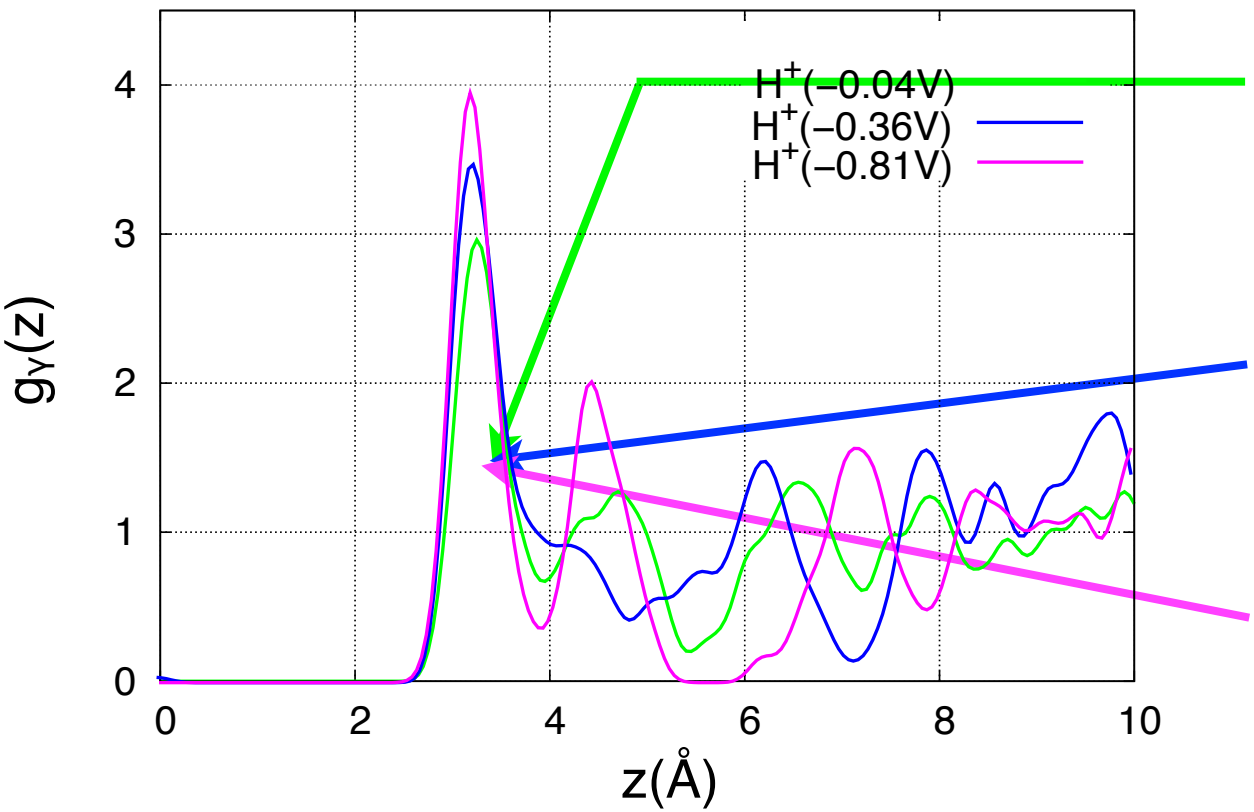
Orientation of water molecules





M.F. Toney, et.al. Nature (1994)

Density of water at interface



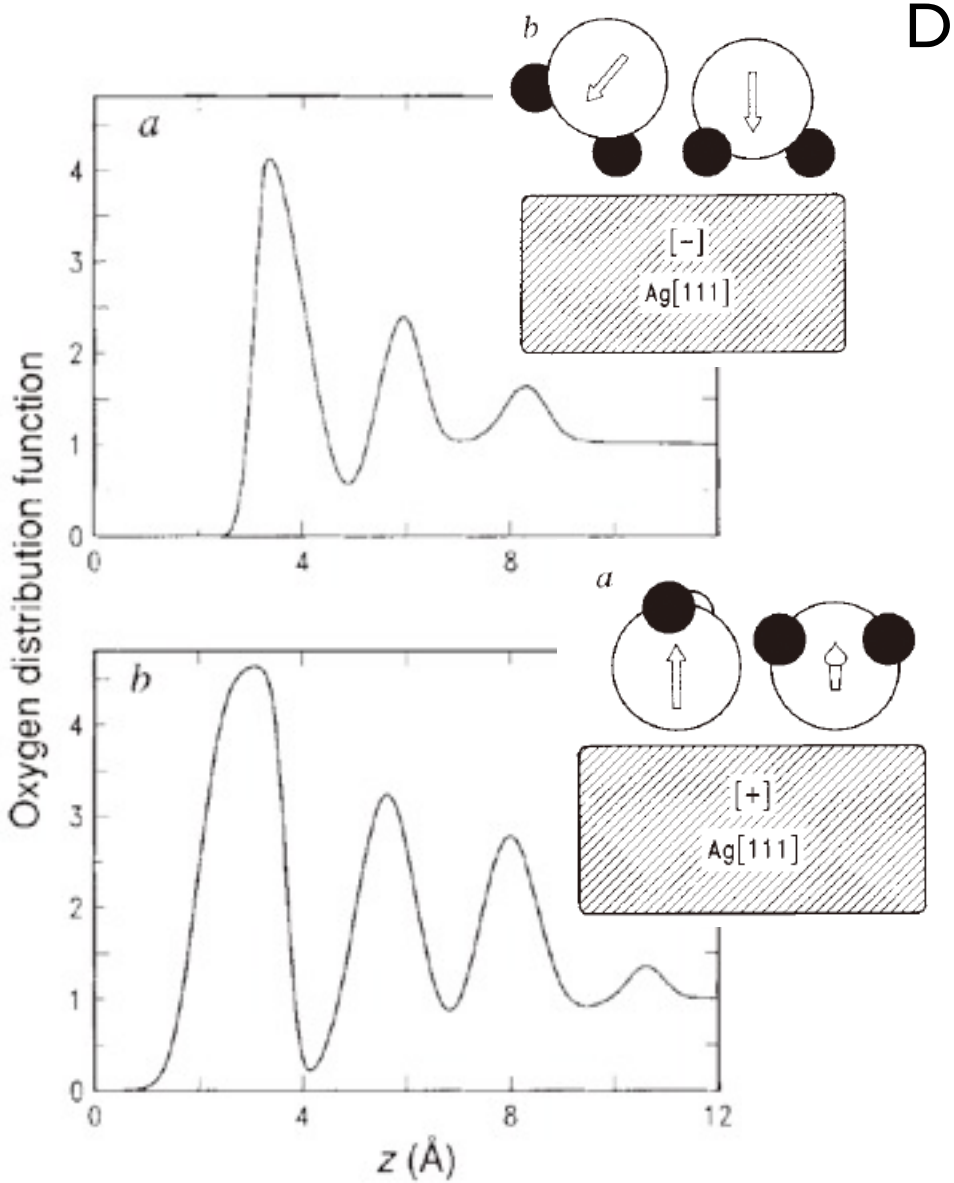
-0.04 V :
8.3 water molecules

-0.36 V :
8.5 water molecules

-0.81 V :
9.8 water molecules

Number of water molecules (density of water) increases as increasing the bias potential

Enhancement of water density



Distribution function [Ag(111)/Water]

V=-0.23 V vs. V_{pzc}

1.1 water mol. / Ag atom

Oxygen-up configuration

×1.4

bulk ~ 0.8 water mol. / Ag atom

×2.3

V=+0.52 V vs. V_{pzc}

1.8 water mol. / Ag atom

Oxygen-down configuration

M.F. Toney, et.al. Nature (1994)

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

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

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

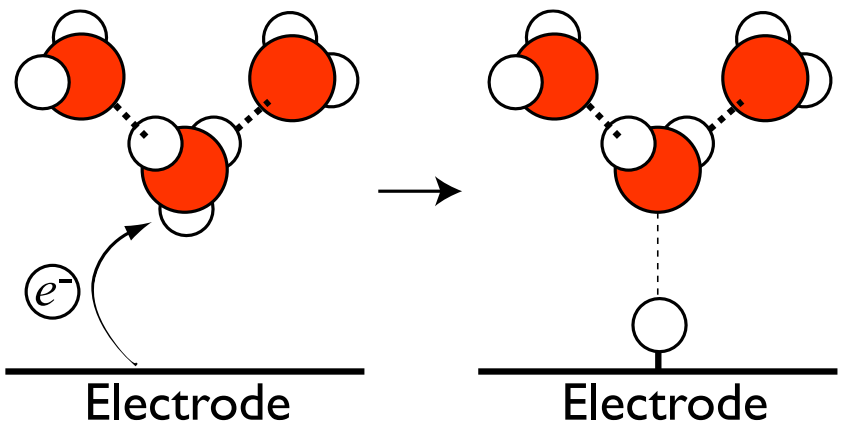
$(OH)_{ad} + (OH)_{ad} \rightarrow O_{ad} + H_2O$

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

Hydrogen evolution reaction

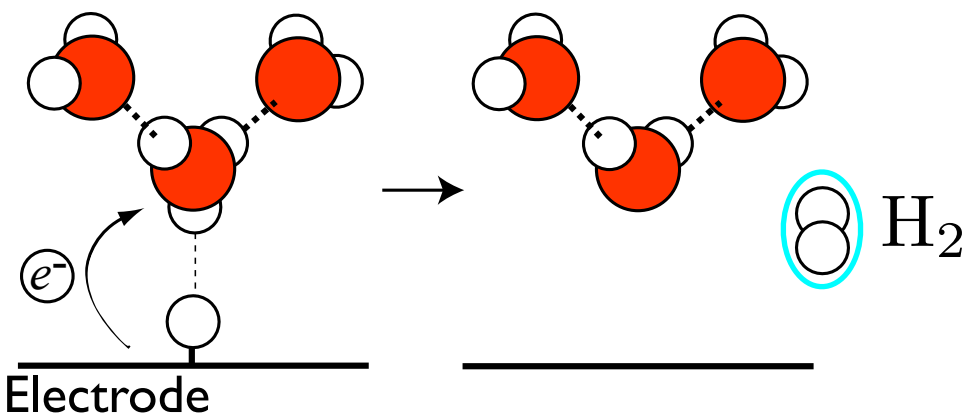
Hydrogen evolution $2\mathrm{H}^+ + 2e^- \rightarrow \mathrm{H}_2$

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

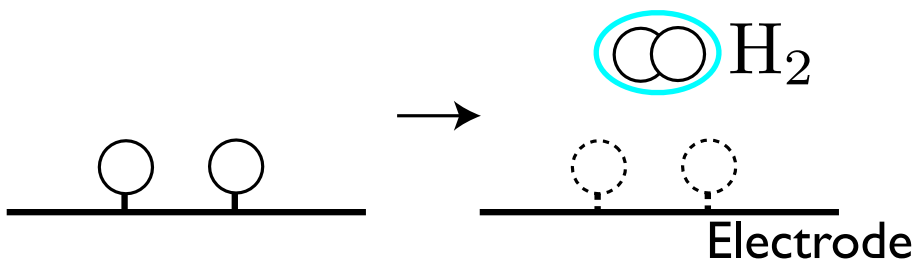


Heyrovsky step:

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



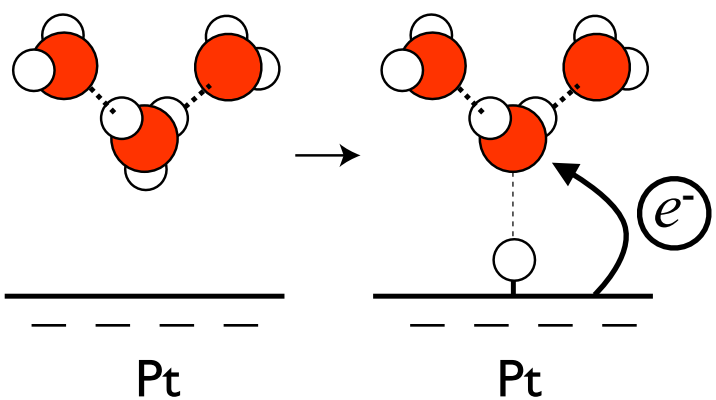
Tafel step: $\mathrm{H_{ad}} + \mathrm{H_{ad}} \rightarrow \mathrm{H_2}$

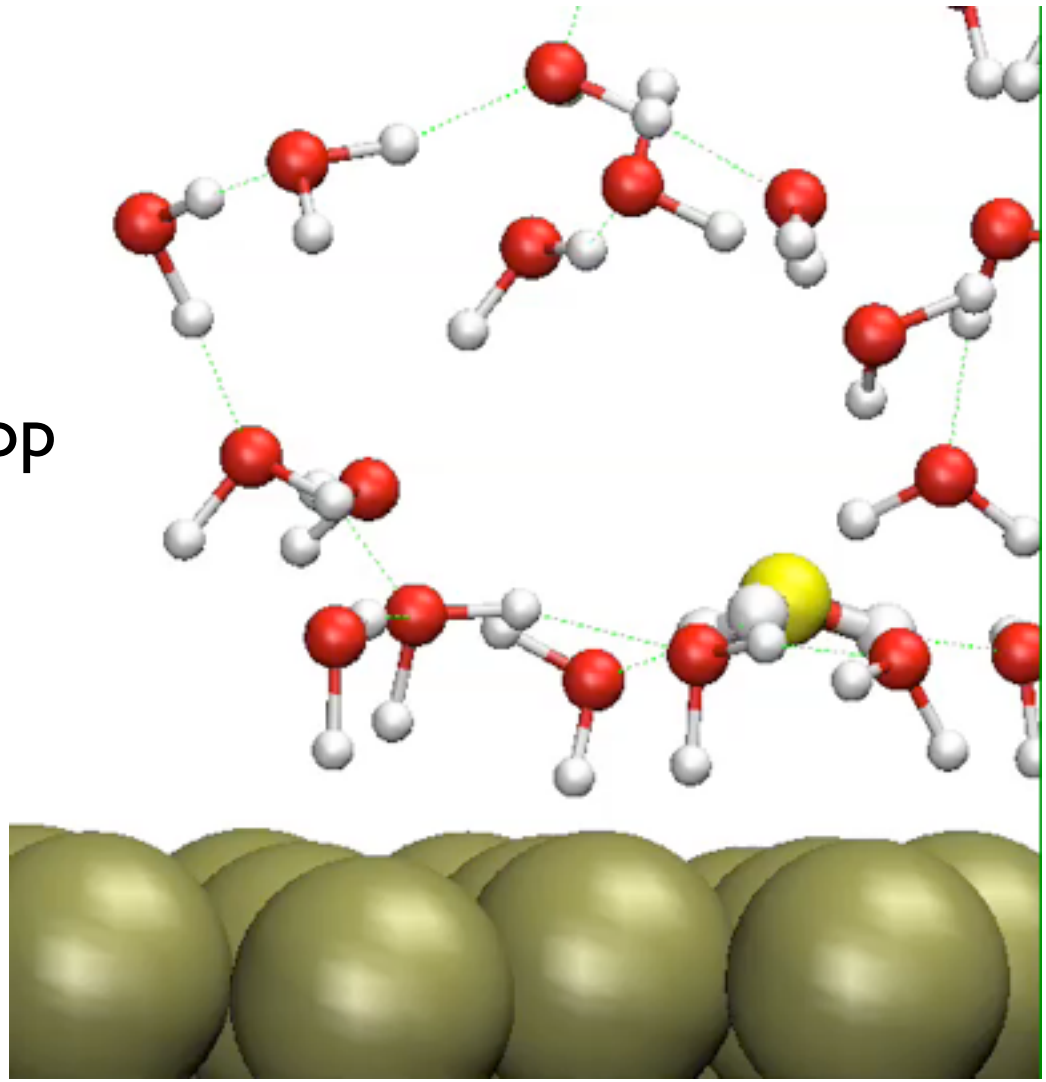


Electrochemical reaction (cathode)

Hydronium ion diffuses vis the Grotthus mechanism

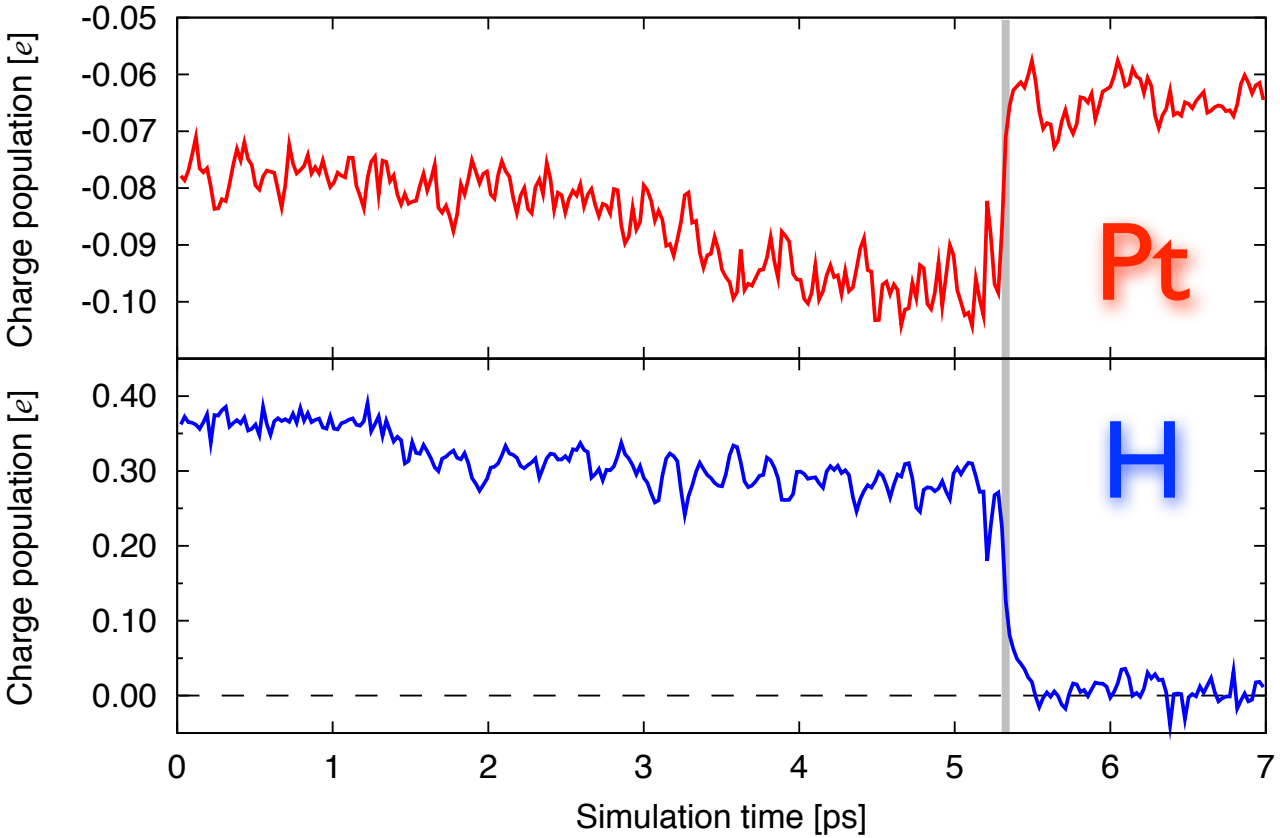
H atom is adsorbed on a top site of Pt surface.





Q=0.95 (e/cell)

Charge transfer

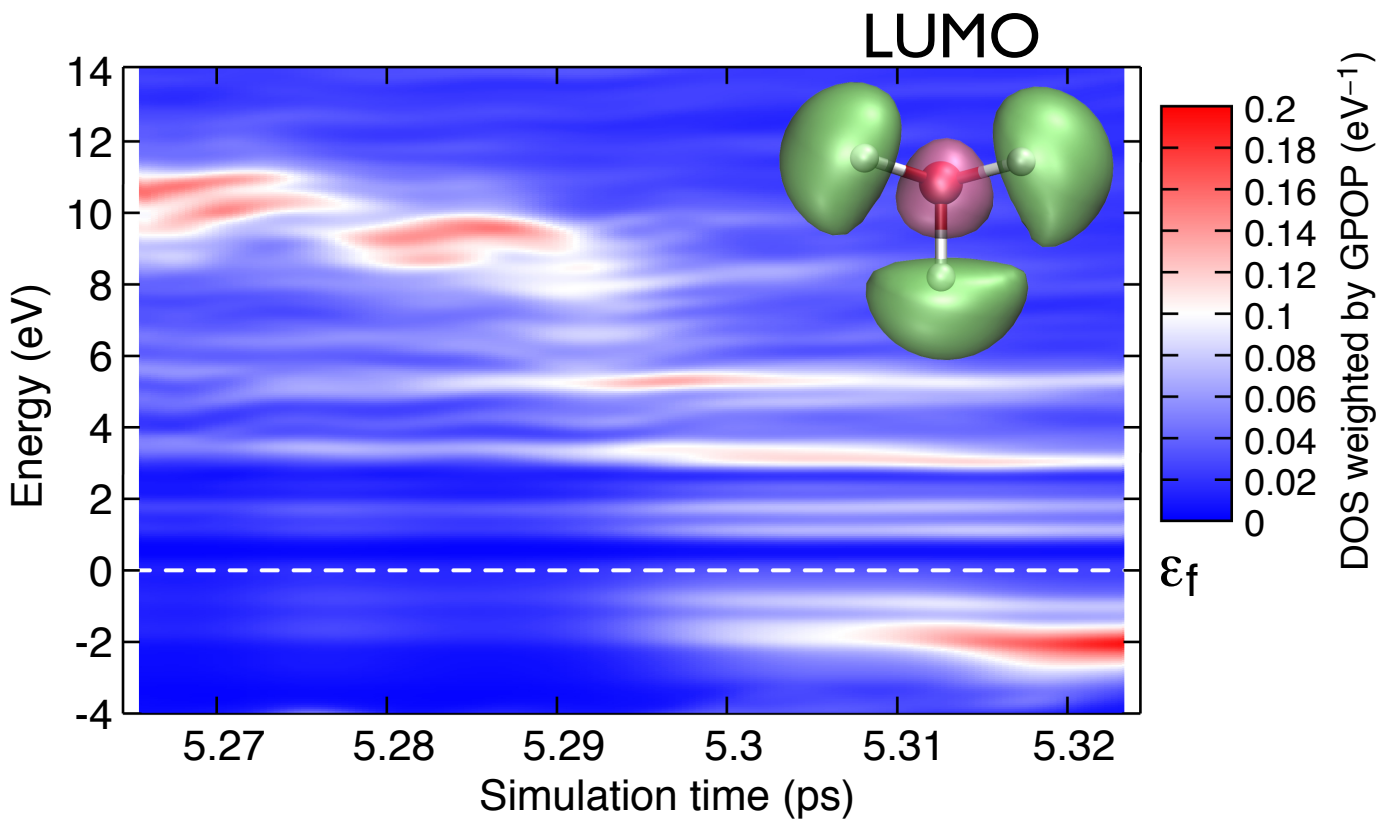


Charge population of top most Pt layer averaged by the number of Pt atoms

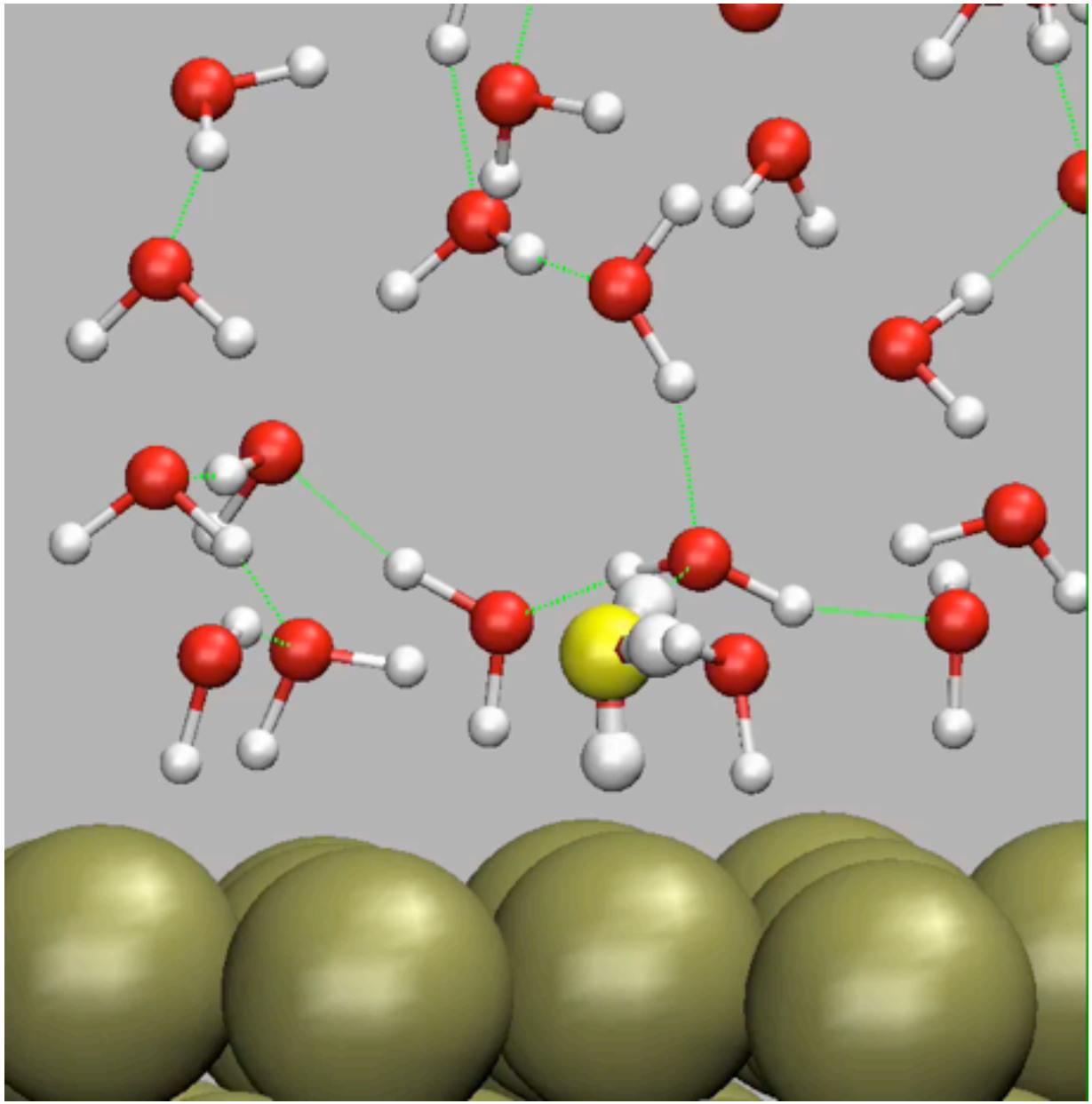
Charge population of the adsorbed hydrogen atom.

- 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



Reorganization of water molecule at interface



After the reaction, the water molecule goes upward.

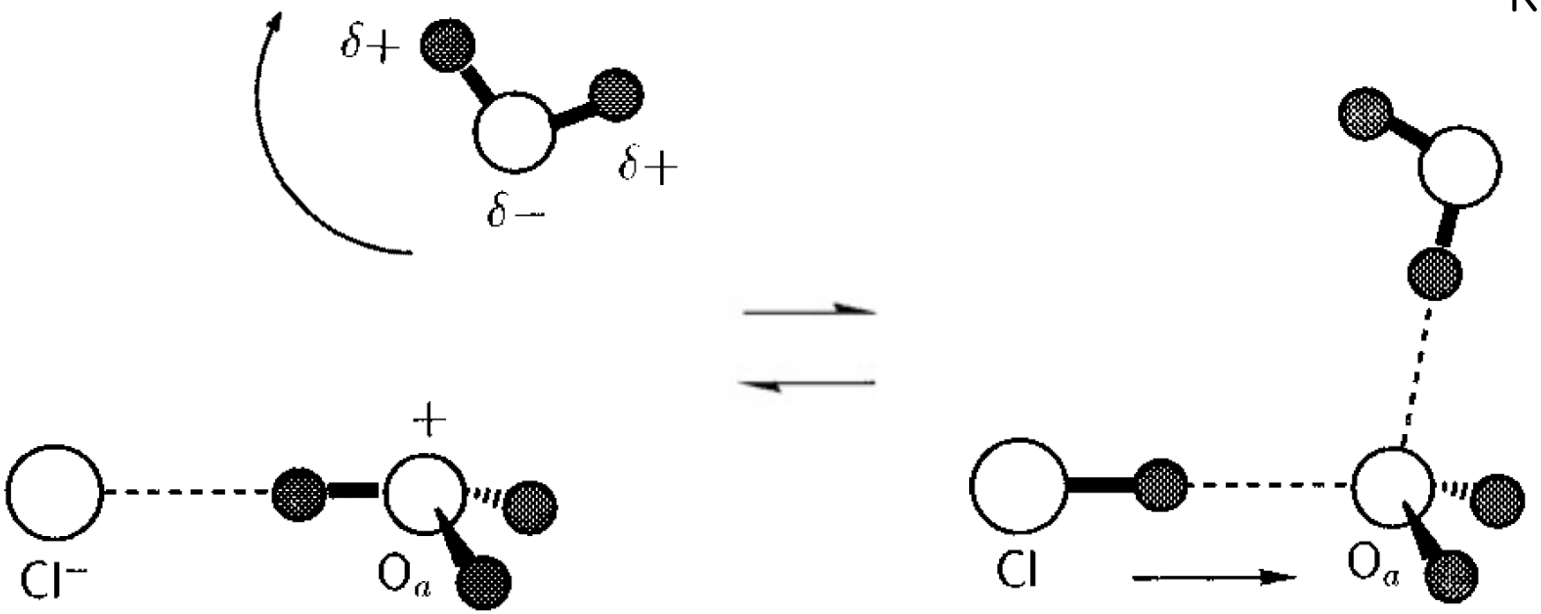
Rotate its molecular axis to have a H-down configuration.

Eventually, the water molecule comes back to the contact water layer with H-down configuration

Reorganization of water molecule in bulk

Usual picture of the reorganization motion of water after an electrochemical reaction.

K. Ando, 1997

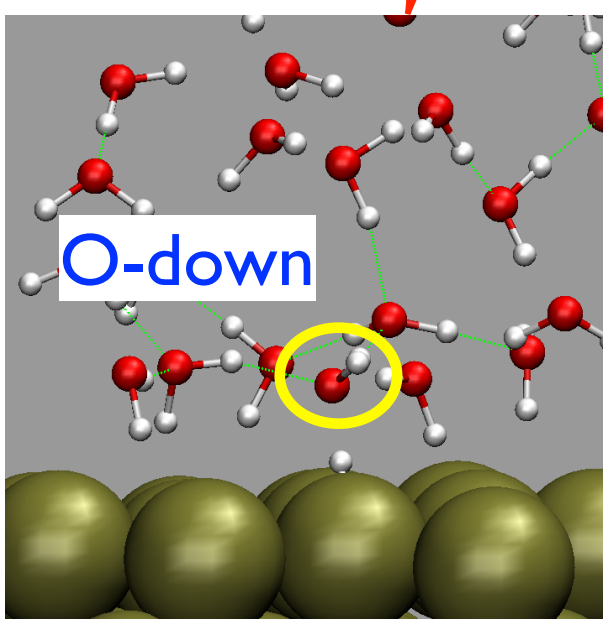


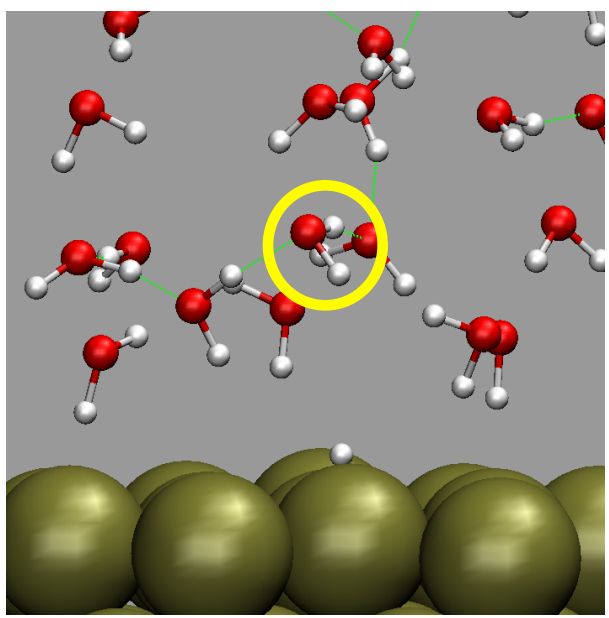
A water molecule belonging to the first hydration shell rotates its molecular axis to make a new hydrogen bond.

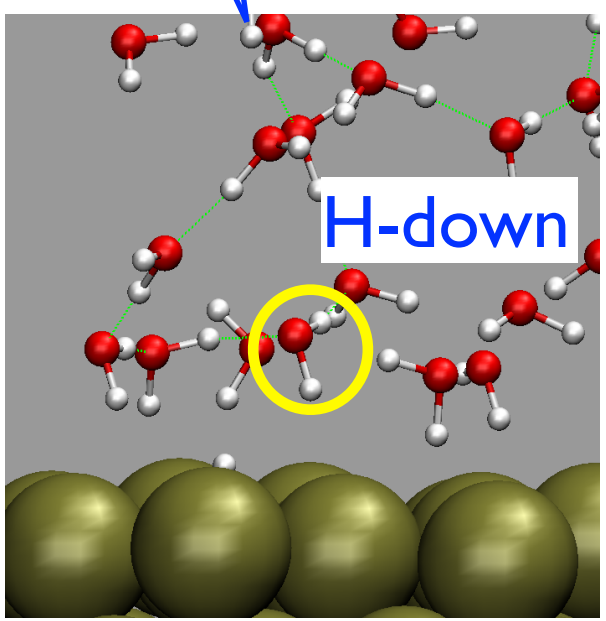
Reorganization of water molecule at interface

- Energetically unfavorable
- Can not contribute to sequential hydrogen adsorption

- Energetically favorable
- Can contribute to sequential hydrogen adsorption

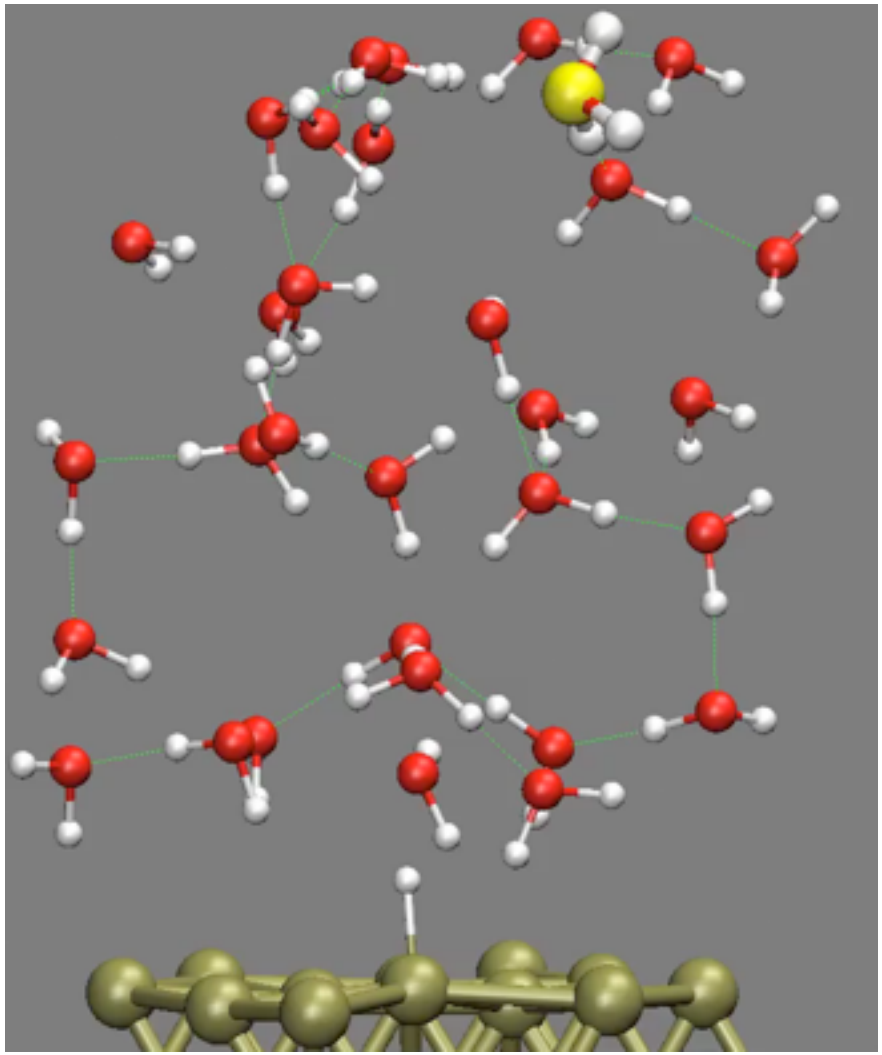


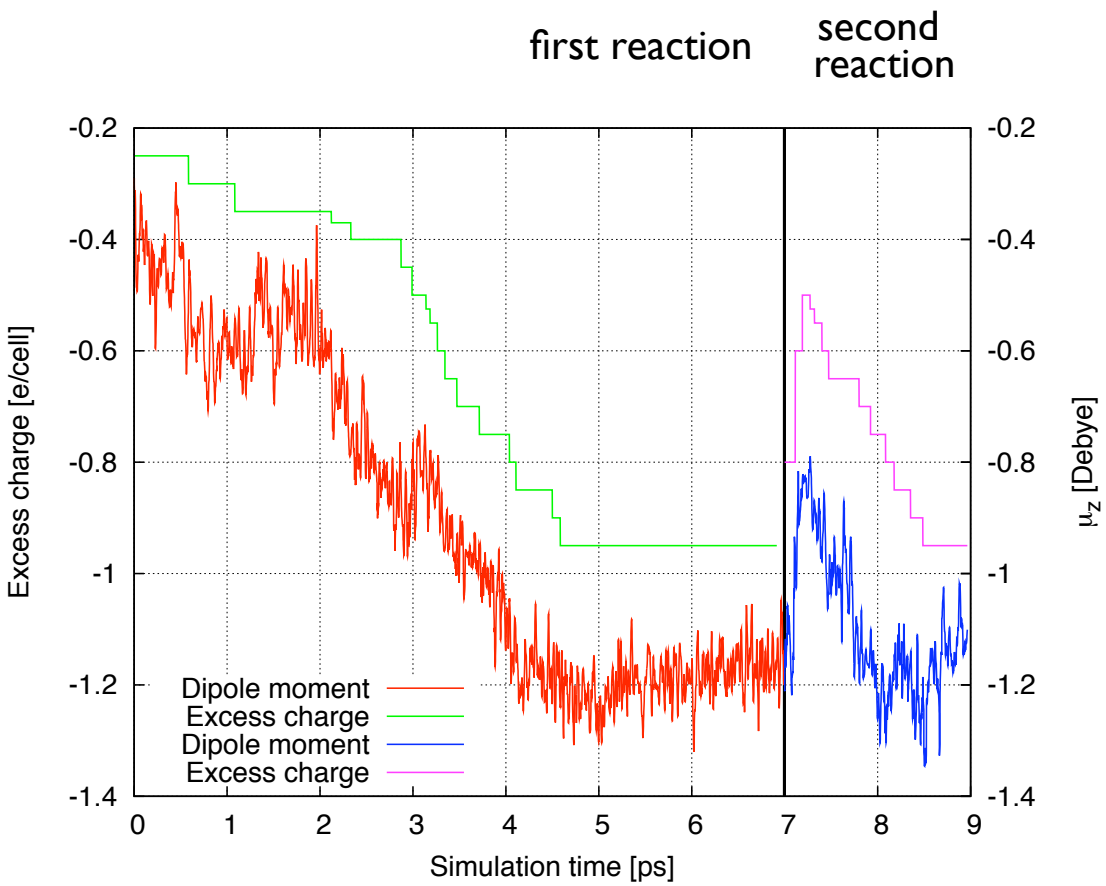




time

Sequential hydrogen adsorption





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

or

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

OER

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

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

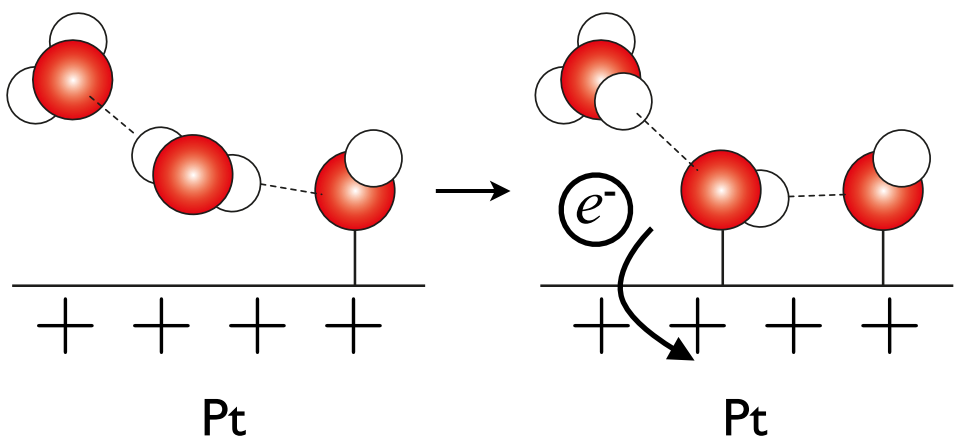
$(OH)_{ad} + (OH)_{ad} \rightarrow O_{ad} + H_2O$

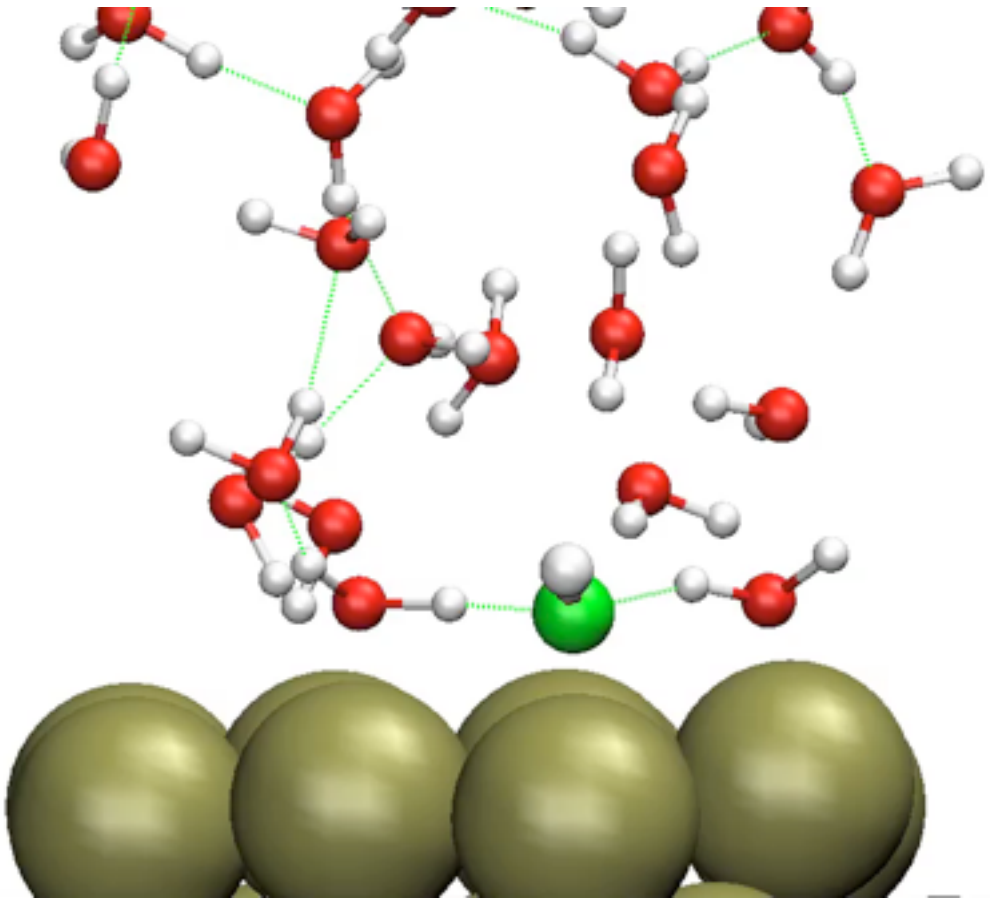
$O_{ad} + O_{ad} \rightarrow O_2$

Electrochemical reaction (anode)

Water dissociation:

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



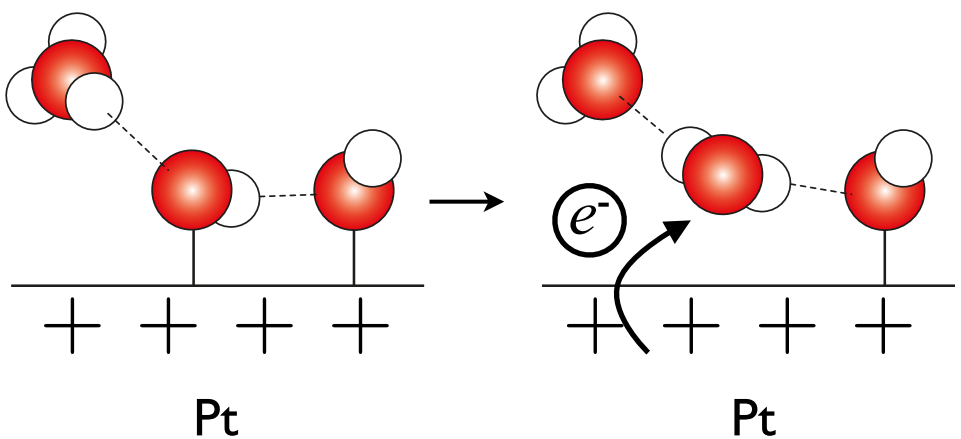


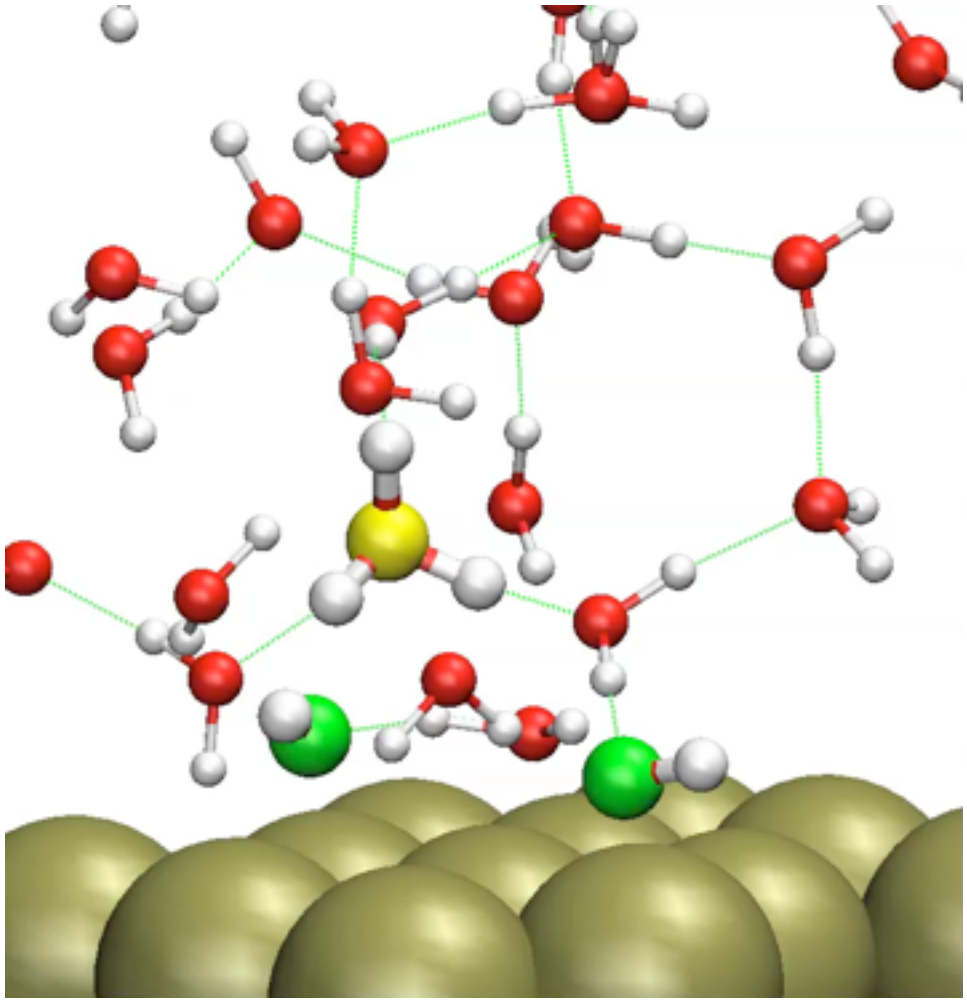
Q_{ESM}=-0.35 (e/cell)

Electrochemical reaction (anode)

Water formation:

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

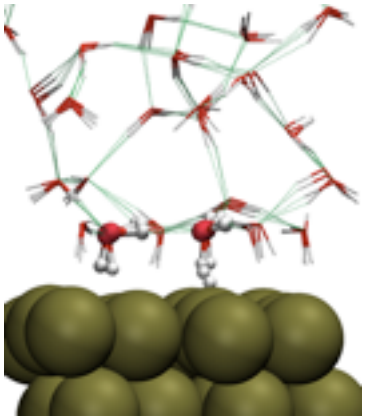


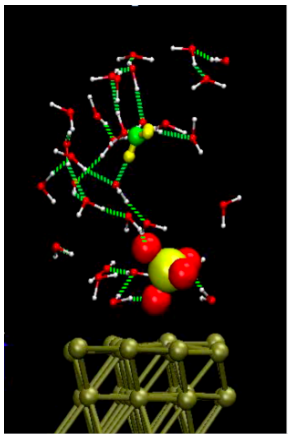


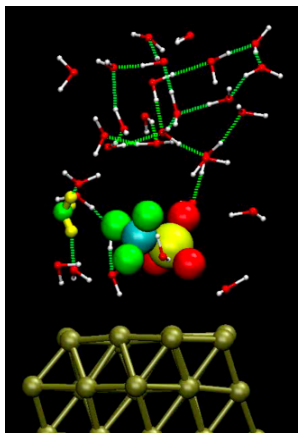
Q=-0.35 (e/cell)

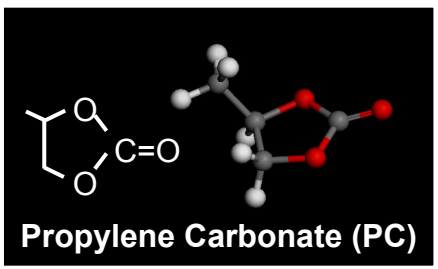
Application of the ESM

- Pt/water interface
  - Hydrogen adsorption reaction
  - Water splitting and formation
  - Pitted pt surface
  - HSO_4, CF_3SO_4
- Si/propylene carbonate (PC)
  - Solvation and desolvation of Li
  - Formation mechanism of solid electrolyte interface (SEI).

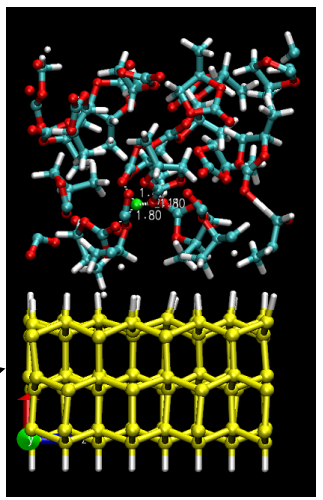




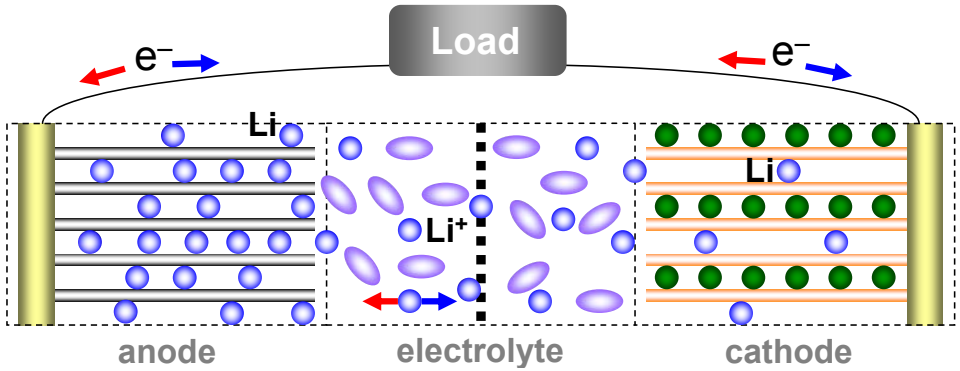


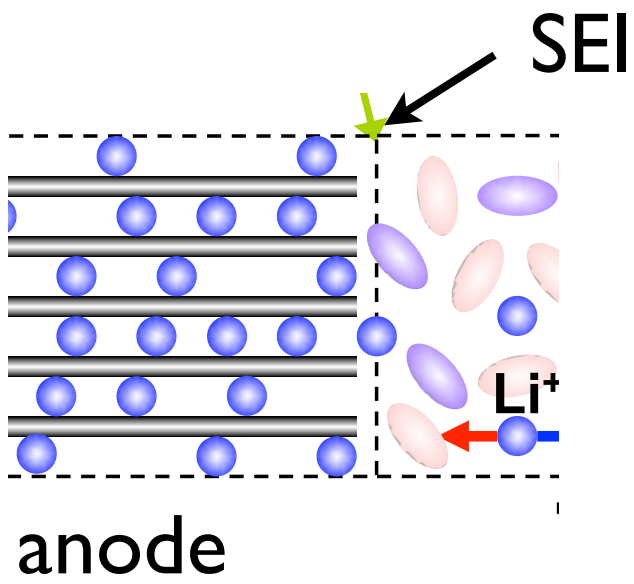


Si



Surface electrolyte interface (SEI)

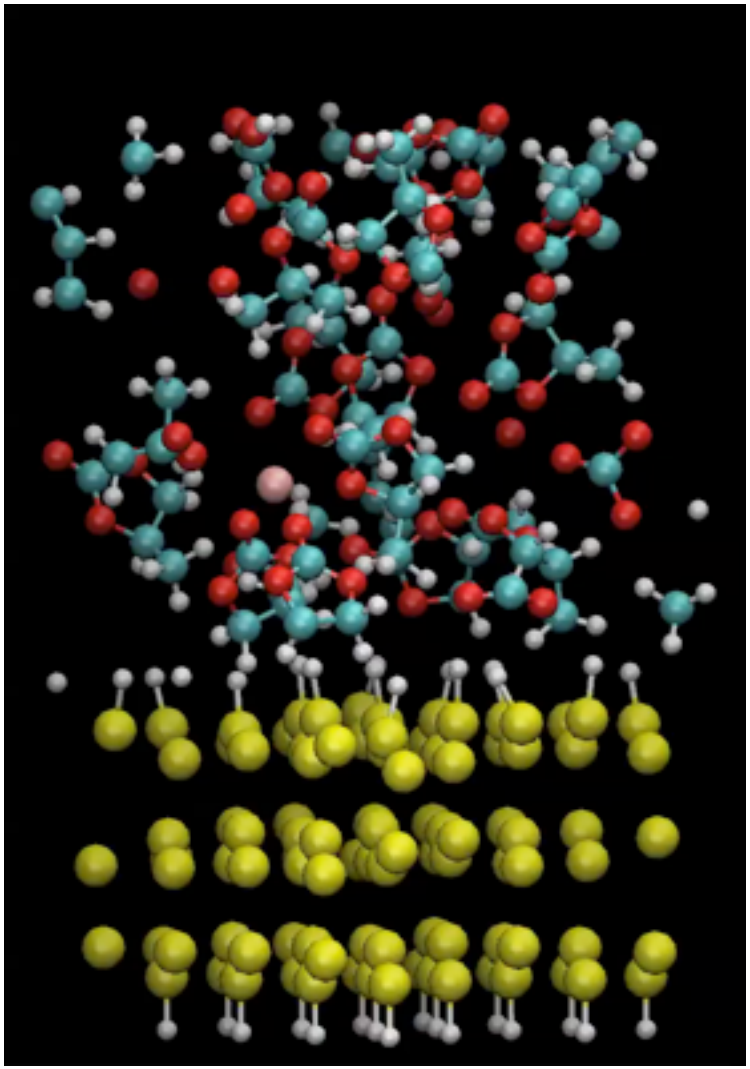




Purpose:

- Clarify the formation mechanism of the SEI
- Understand the solovation and desolvation of Li ion at the interface

Si-electrode for Li-ion battery



Li ion is solvated to PC

↓

desolvation

↓

Form a Li-Si bond

Summary

- Develop a new calculation method to simulate electrochemical systems.
- Reproduce electrochemical reactions on an electrode/electrolyte interface
- Constant bias potential is developed in the frame work of the first principles molecular dynamics with the ESM method.
- Next target is the constant bias simulation of the metal/water interface.