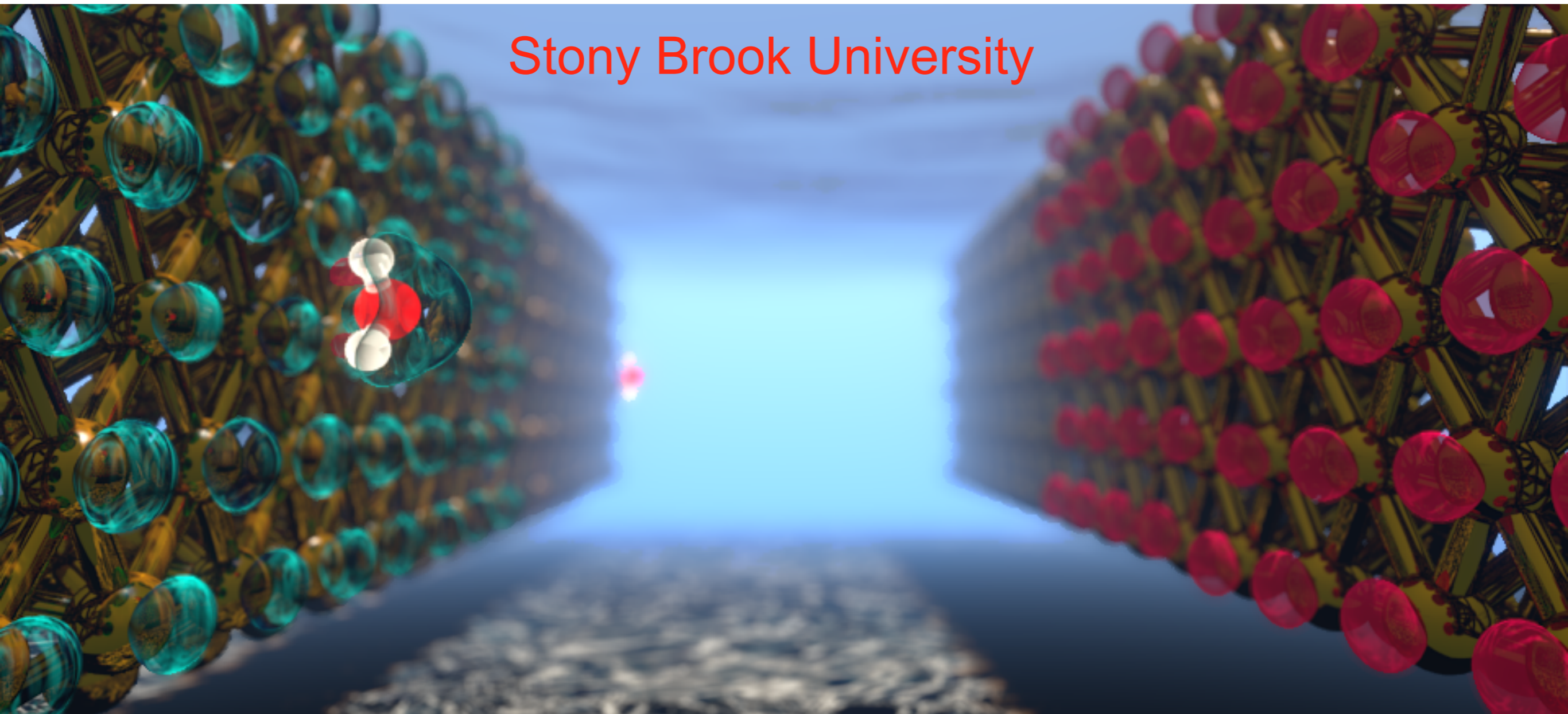


Understanding Water/Solid Functional Interfaces for Photocatalysis and Electrochemical Applications

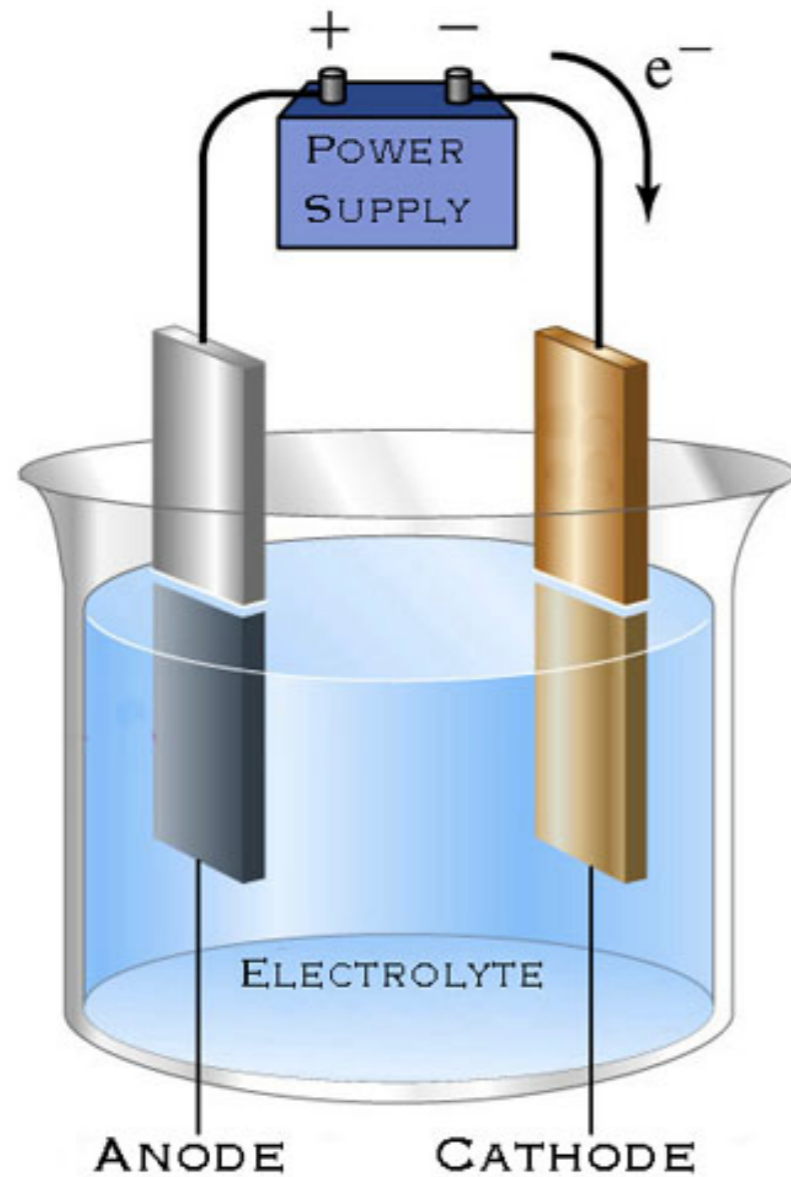
Marivi Fernandez-Serra

Stony Brook University



Motivation

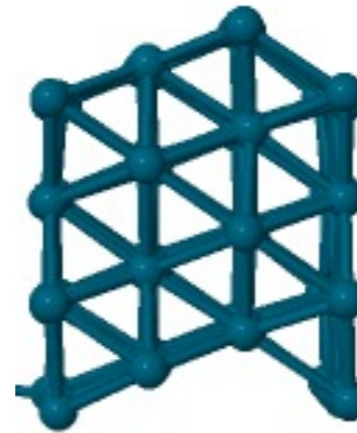
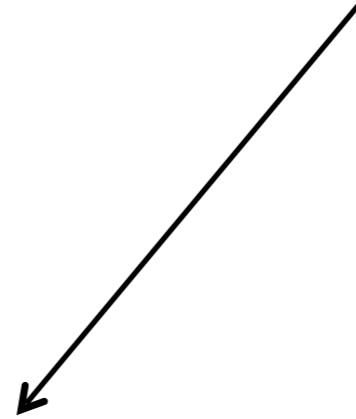
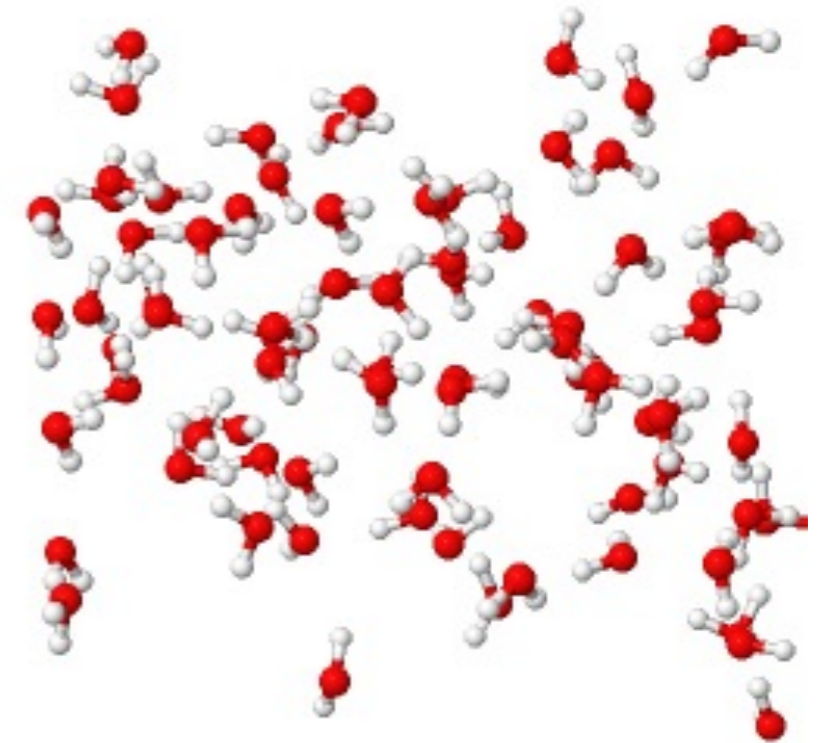
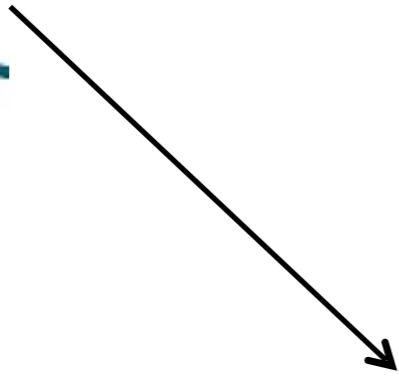
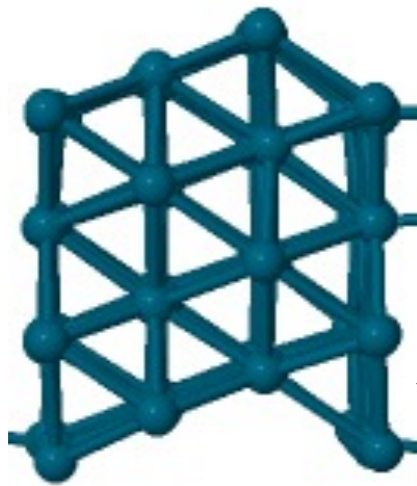
- **Electrochemistry (electrolysis)**



- Correspondence between the macroscopic voltage and the microscopic interfacial charge distribution in electrochemical fuel cells.
- What is the actual structure of the electrochemical double layer?
- How V modifies it?

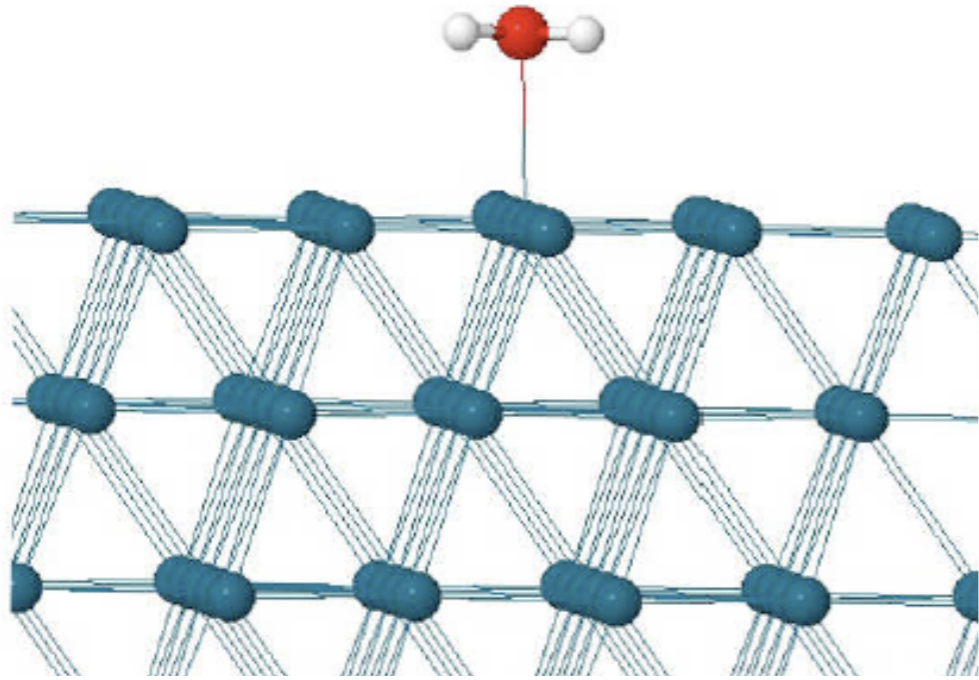
Exact H_2 evolution mechanism?
Volmer+Tafel Steps?

Water/Solid interface

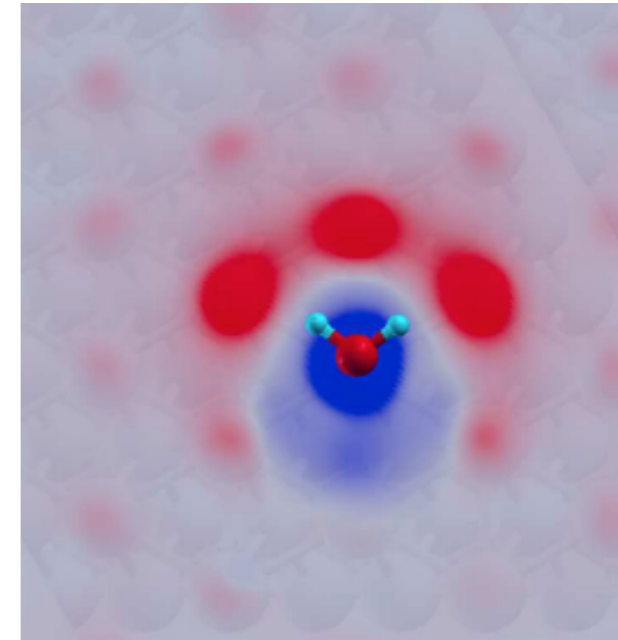


- **Structure of water at the interface**
- **Charge transfer**
- **Correct description of the water and metal**

Water/Metal (Pd) interaction



- 1 H₂O: flat (DFT)



- Metal screens water and creates image charge.
- Interaction may be compared to a H-bond
- Electrostatically not most stable

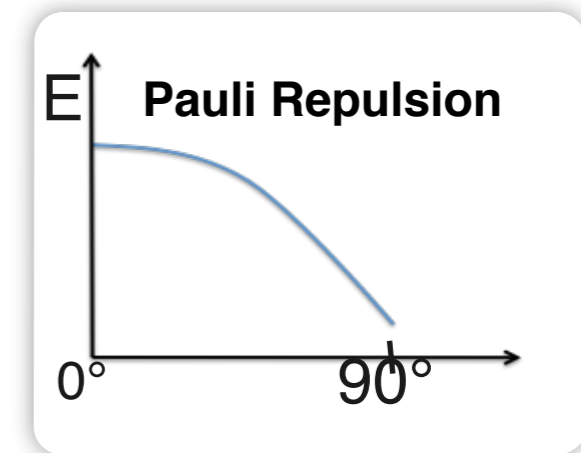
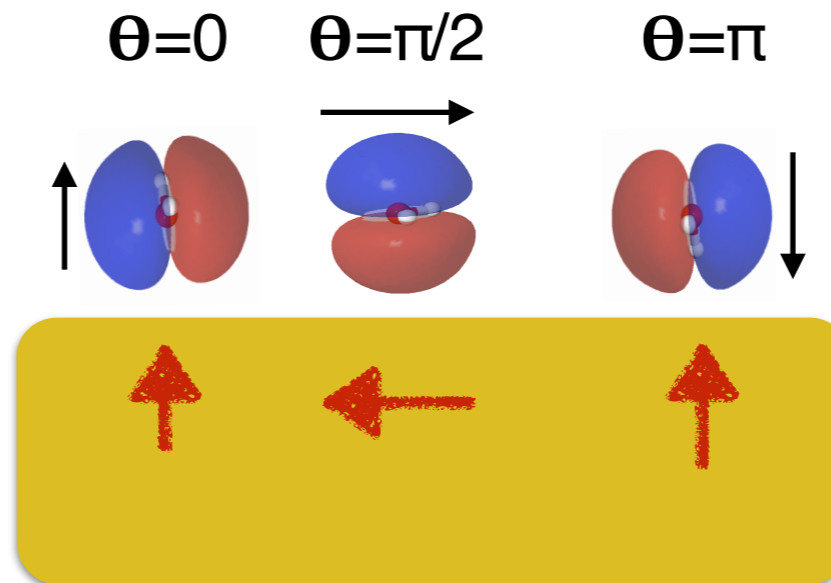
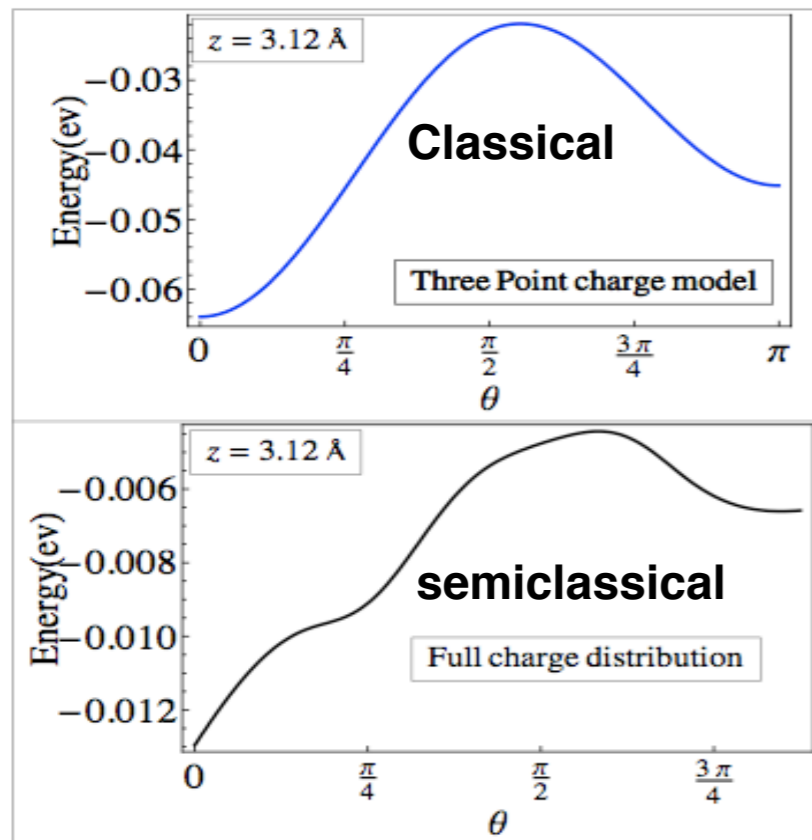
A. Michaelides *et. al.*, PRL 90, 216102 (2003)

A. Poissier *et. al.*, PCCP 13, 3375 (2011)

Water/Metal interaction

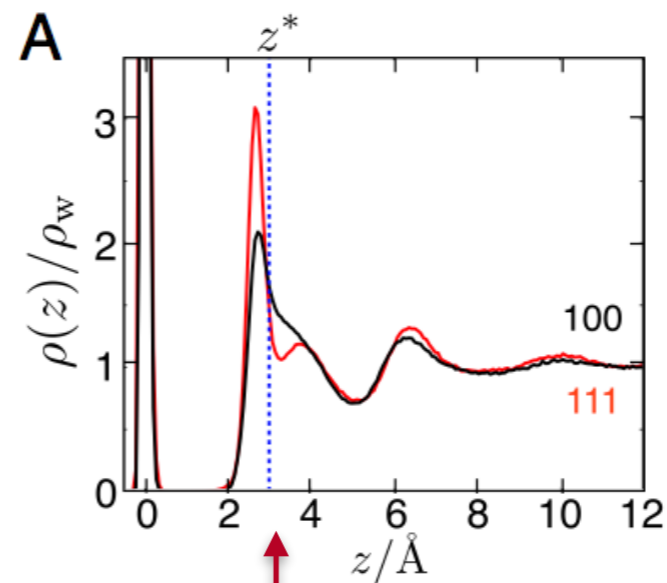
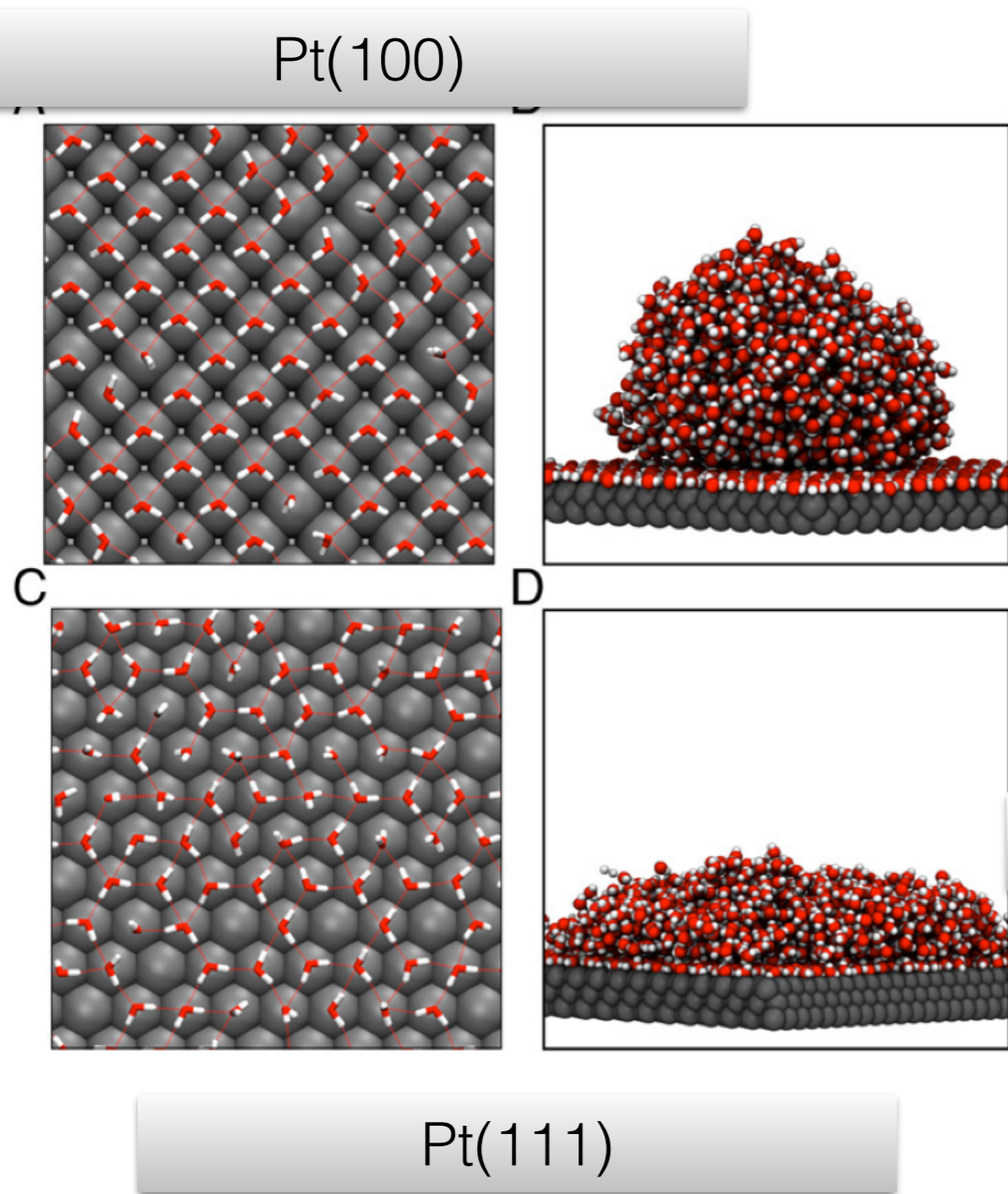
- Classical electrostatics does not explain the adsorption of water molecules on metallic surfaces.
- **Quantum mechanics, i.e charge transfer and Pauli repulsion** is needed to understand the binding

$$U_{ir}(z, \theta) = \frac{-1}{8\pi\epsilon_0} \iint \frac{\rho_{total}(\vec{r}, R_i(z, \theta))\rho_{image}(\vec{r}', R_i(z, \theta))}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}'$$

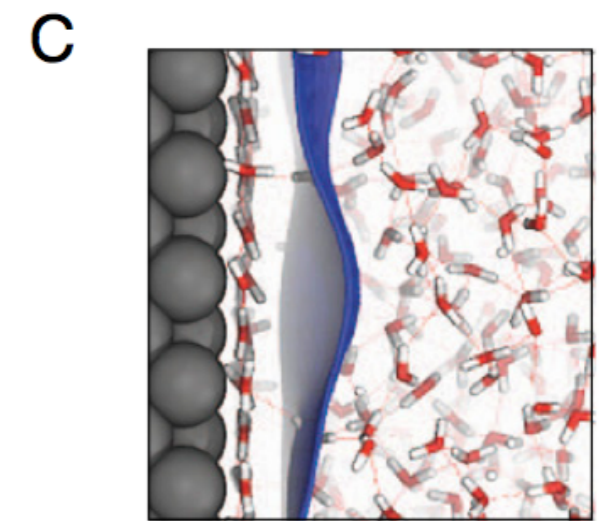


ab initio or Classical force field?

4200–4205 | PNAS | March 12, 2013 | vol. 110 | no. 11



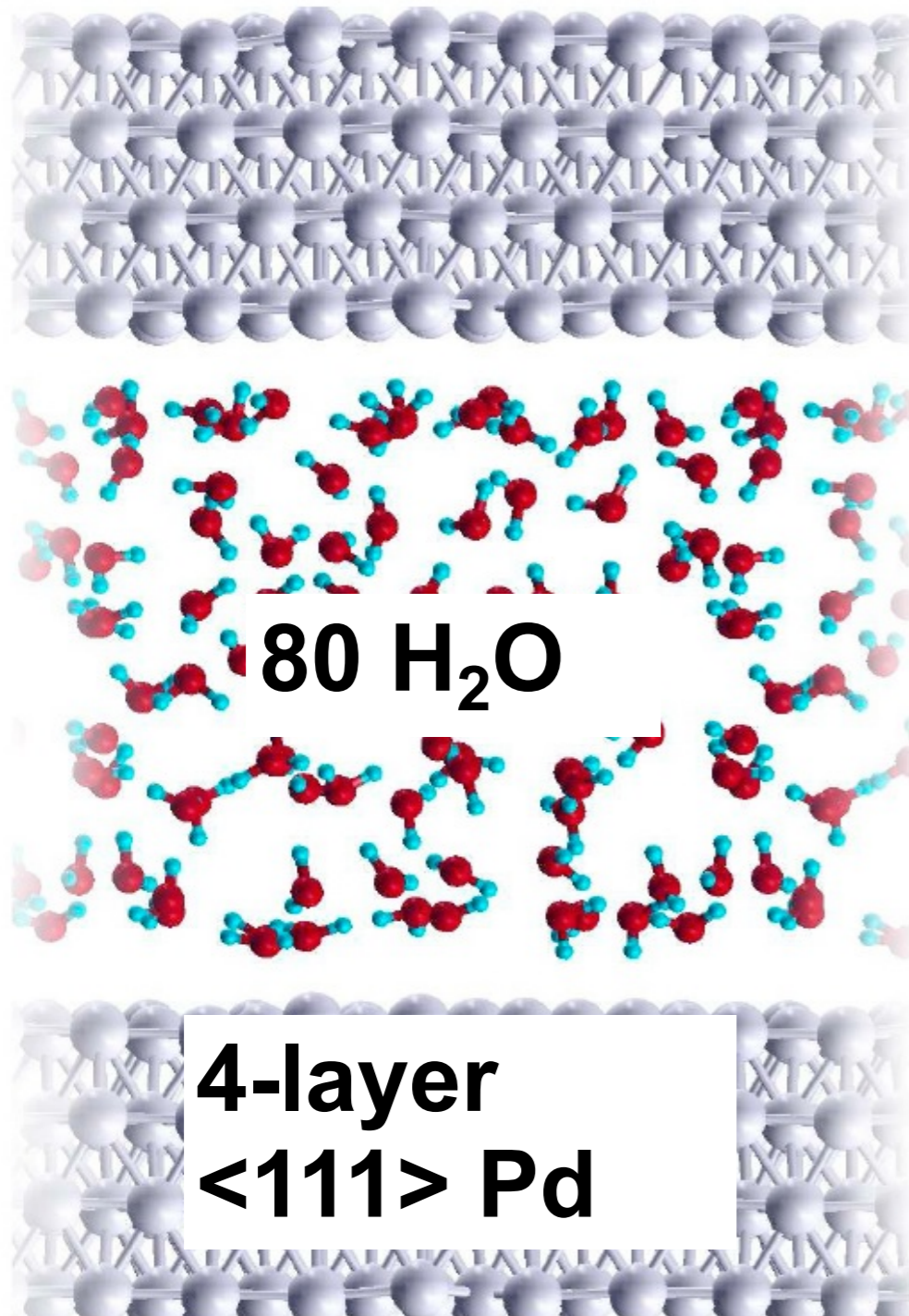
Flat molecules



Hydrophobic layer

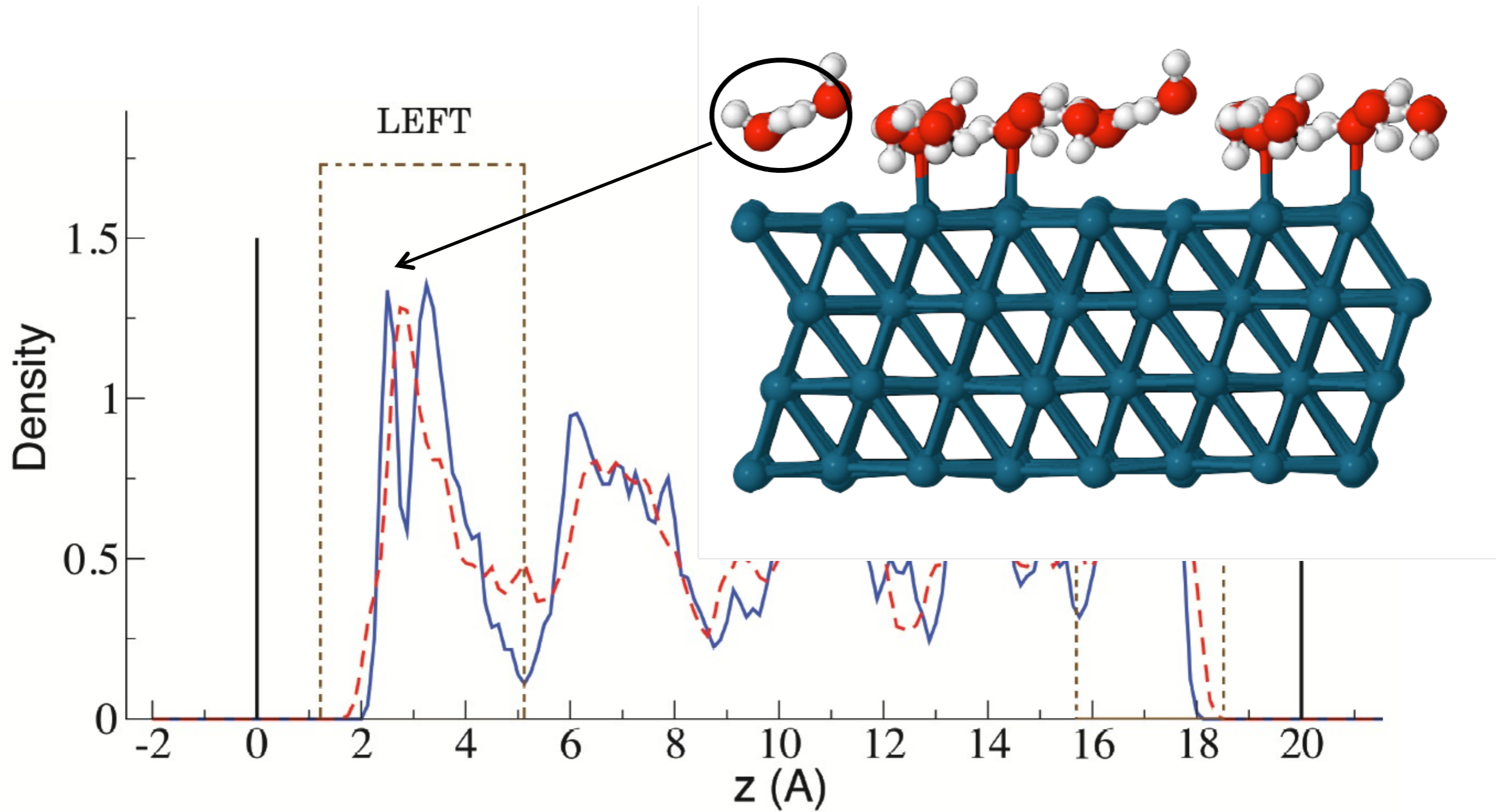
Siepmann-Sprink water-Metal force field
SPC/E (rigid, point charges) model for water
polarizable metal
Model fitted to reproduce H₂O/Pt monolayer
adsorption (geometry and energetics)

Ab initio Molecular Dynamics



- DFT – PBE GGA;
- DFT – vdW-DF^{PBE}
- Troullier-Martins pseudopotential;
- **SIESTA code;**
- >30 ps
- T = 300 K
- Unit cell: 9.75 x 16.85 x 25.97 Å
- Water density = 0.97 g/cm³
- Net Charge: +1|e| and -1|e|

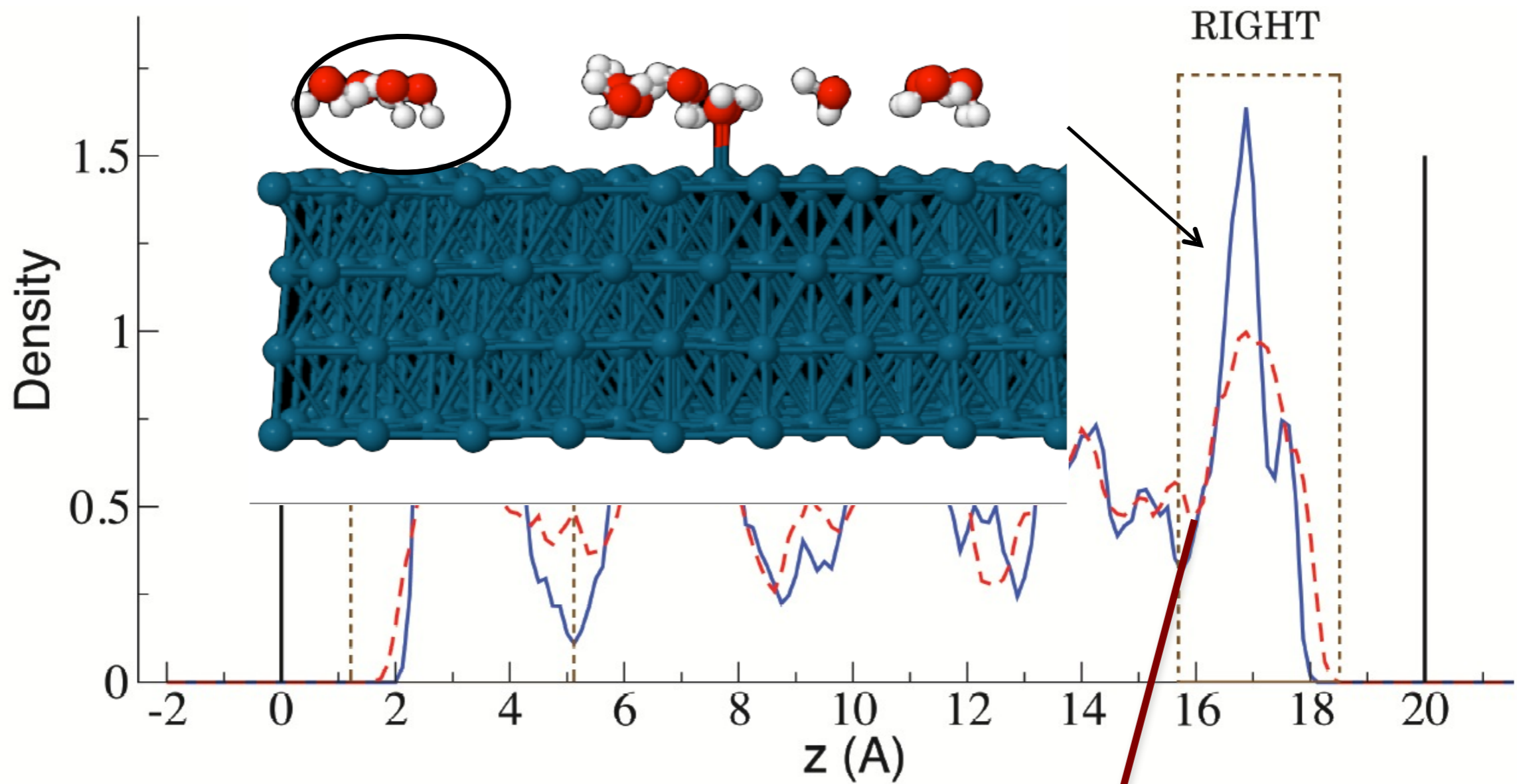
Z-density Pd/H₂O



PBE

Pedroza, Poissier, Fernandez-Serra, JCP 2015

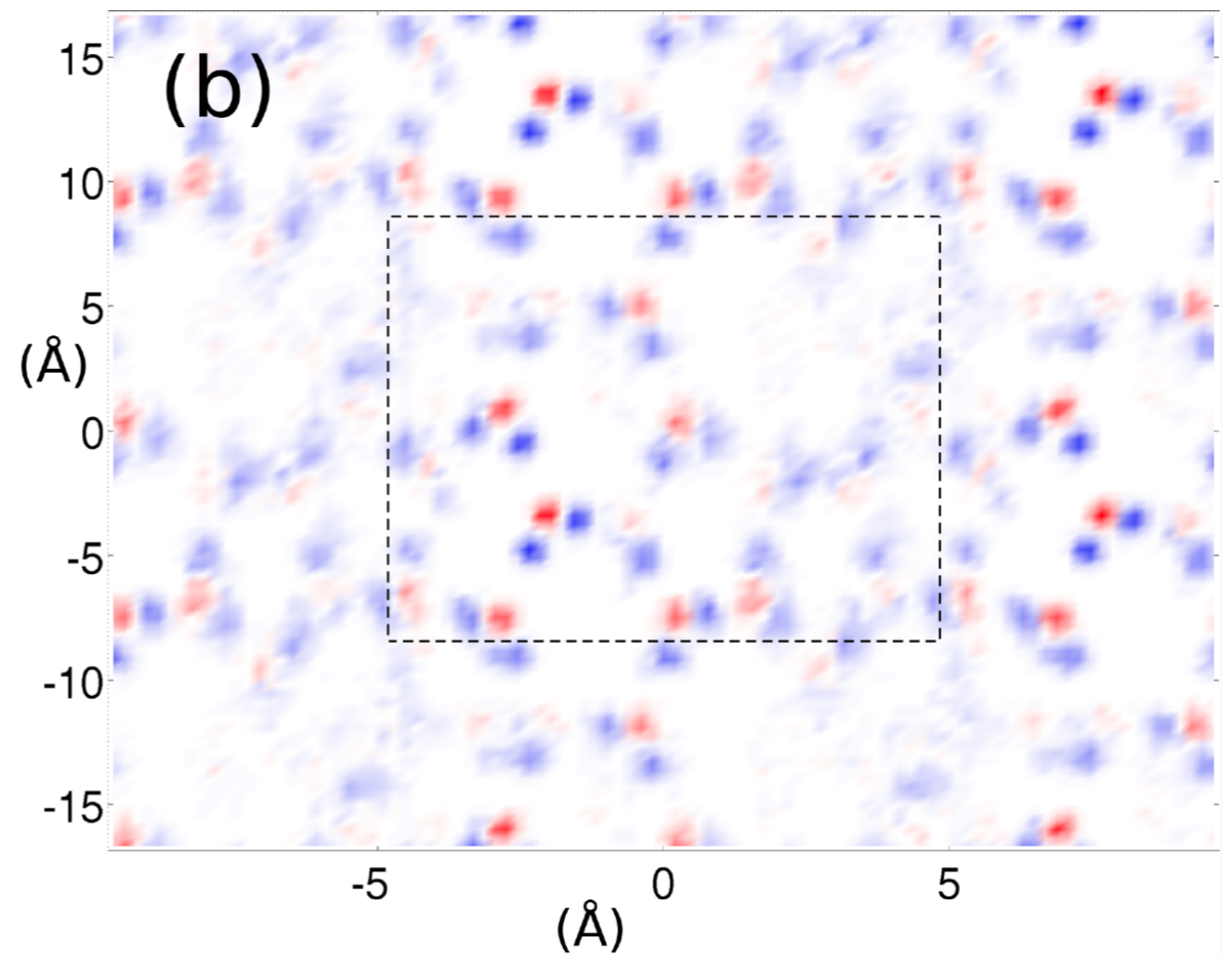
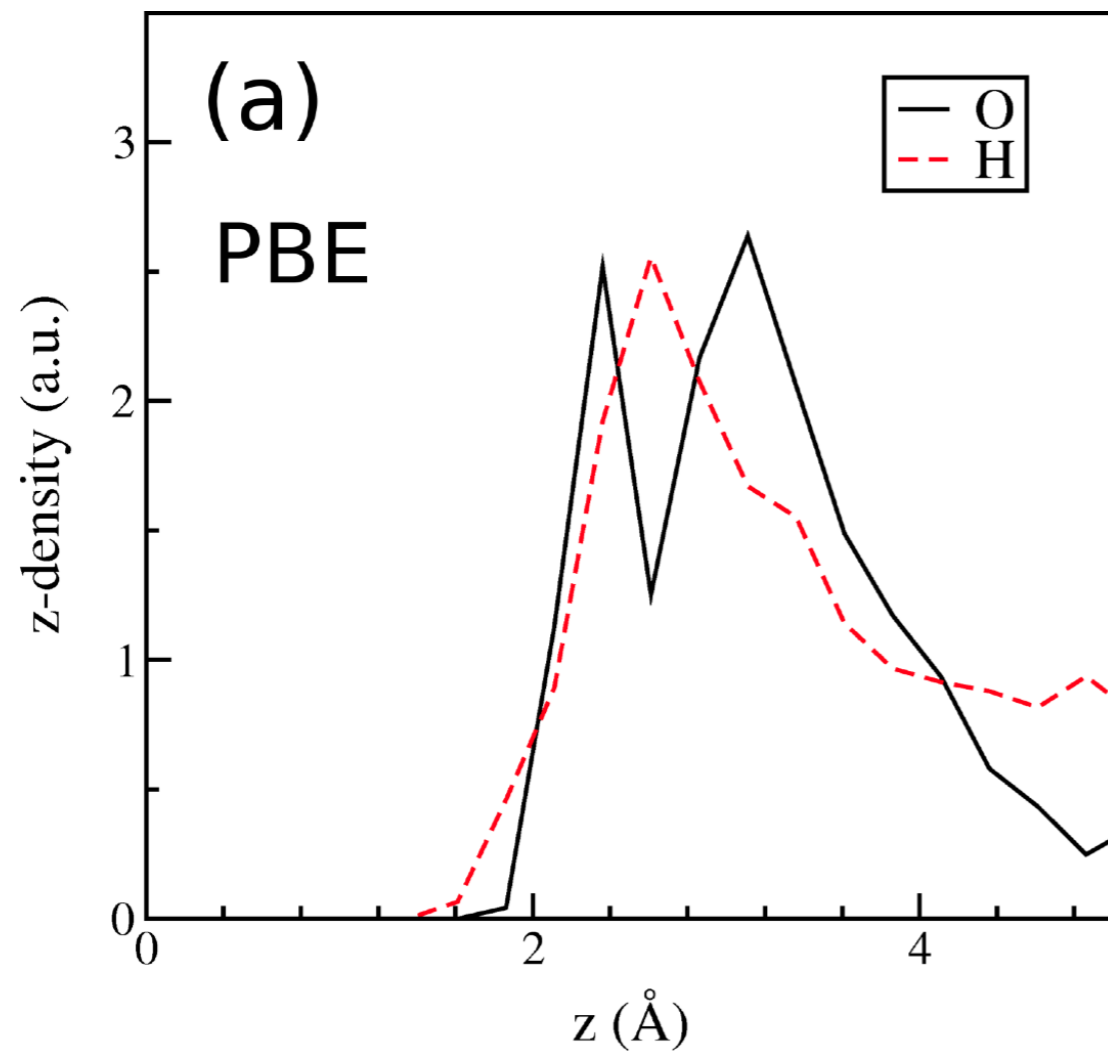
Z-density Pd/H₂O



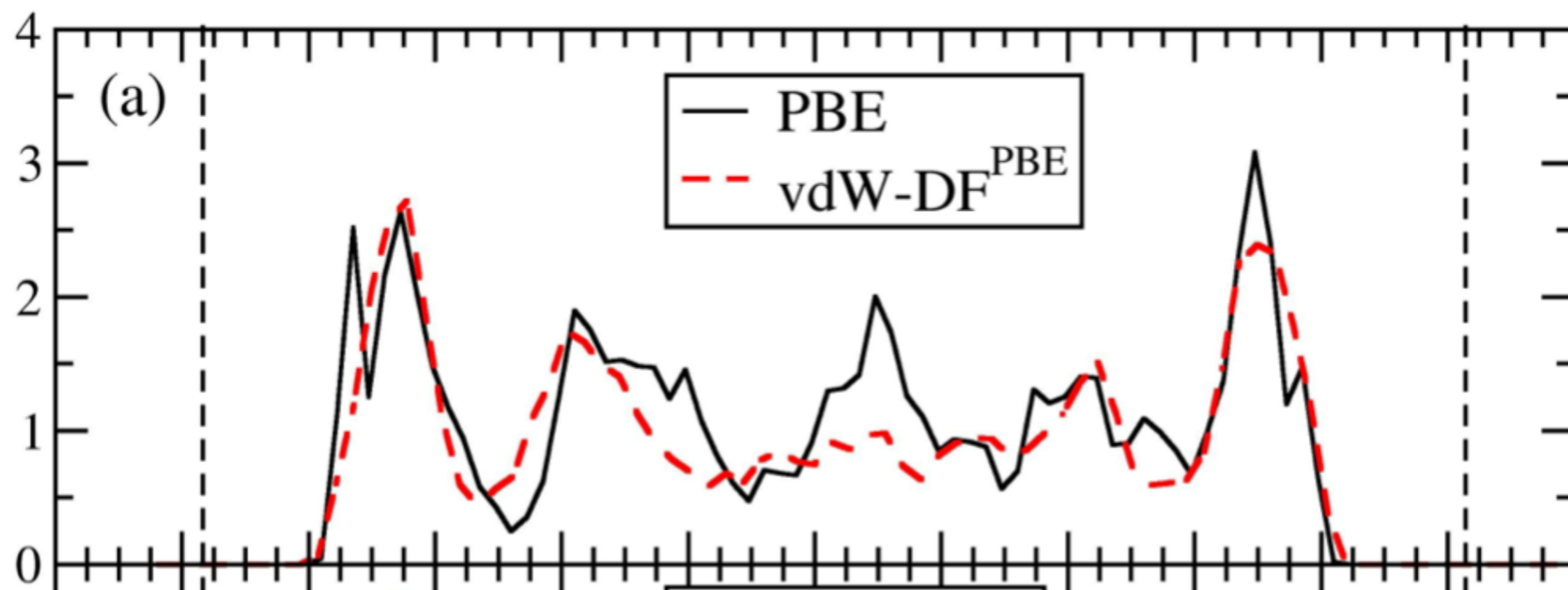
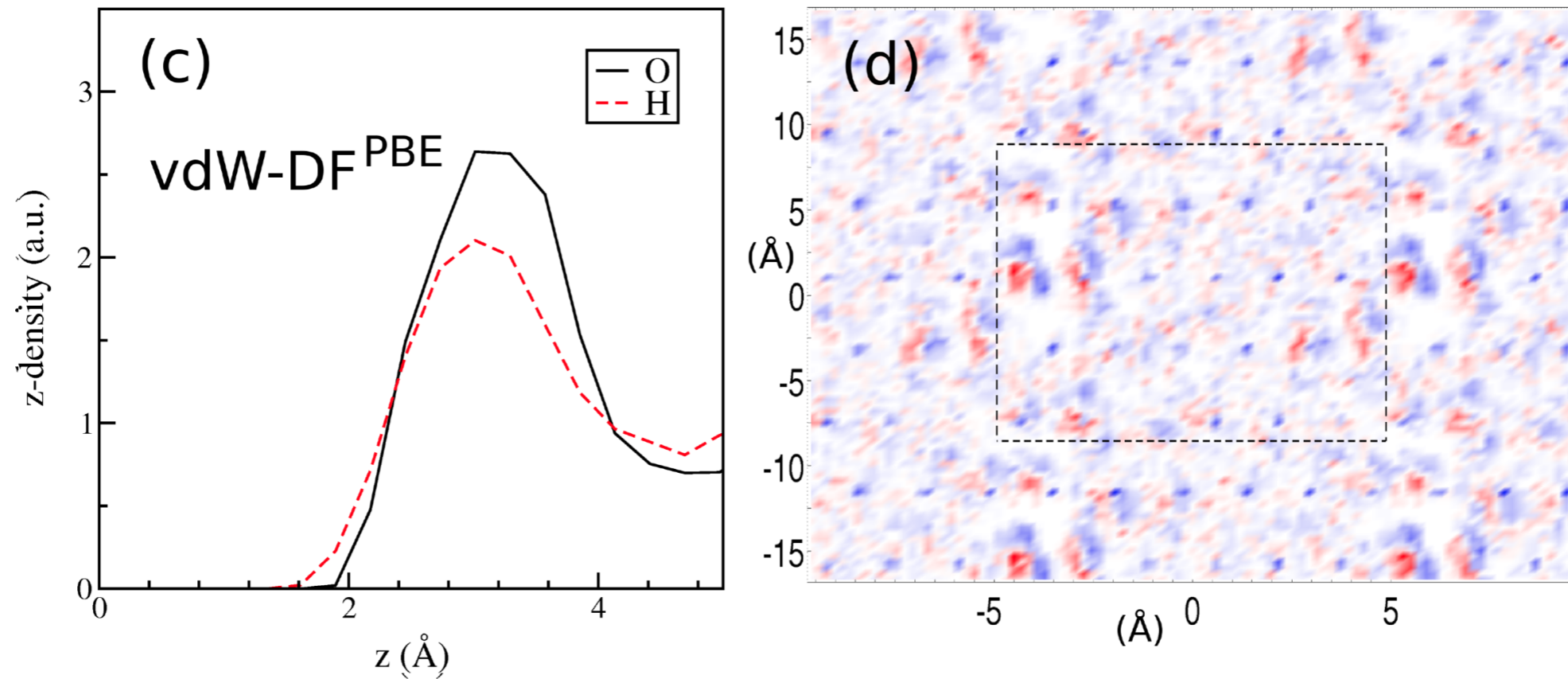
PBE

More down molecules

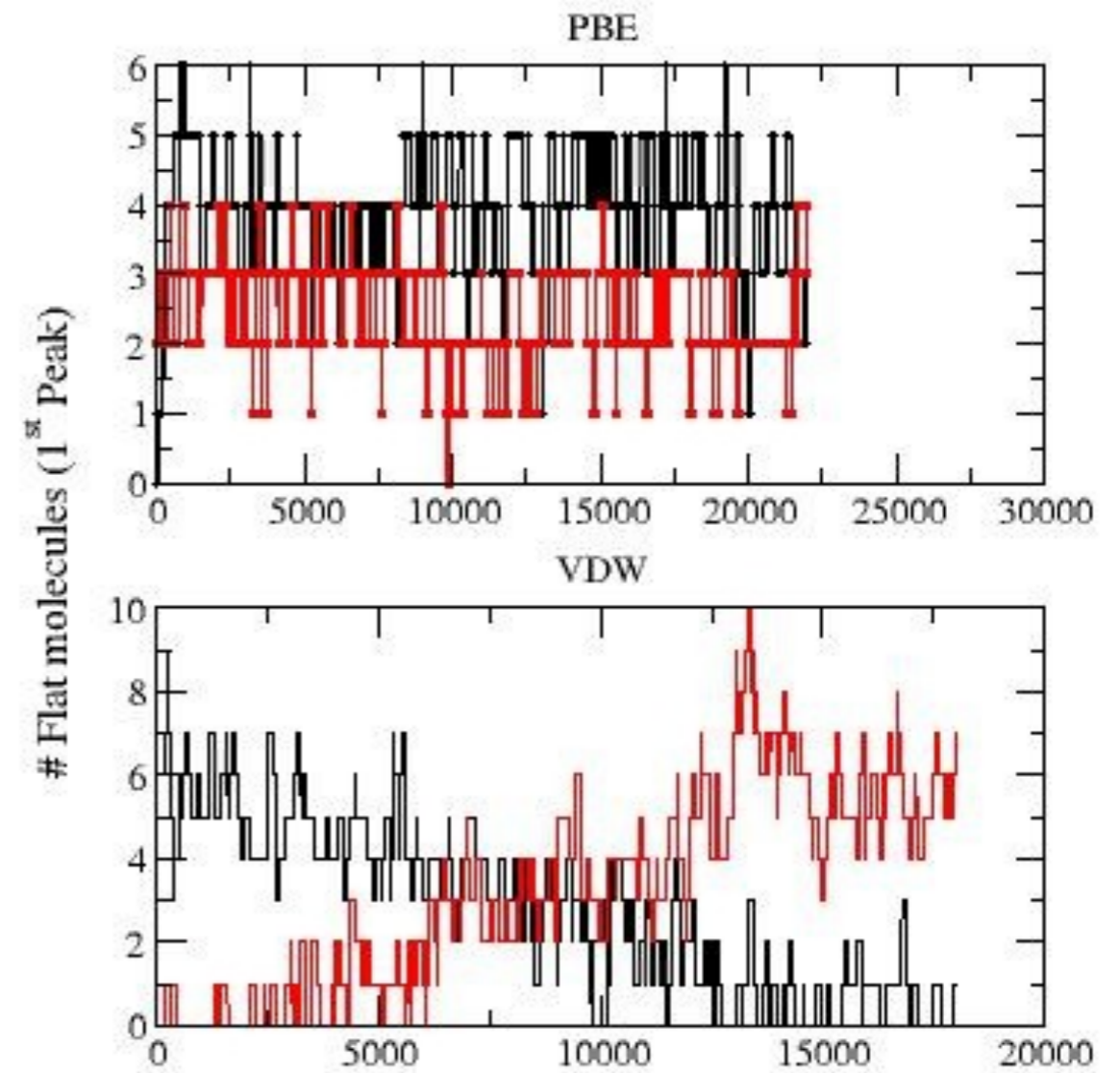
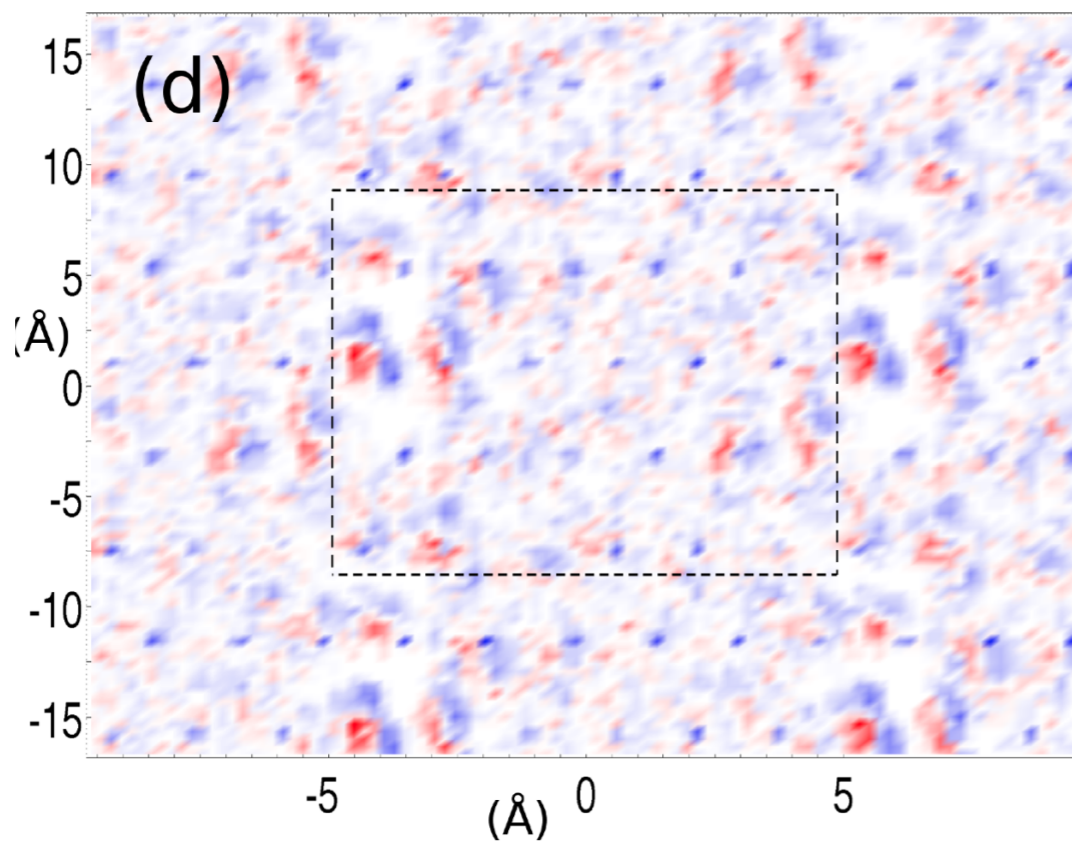
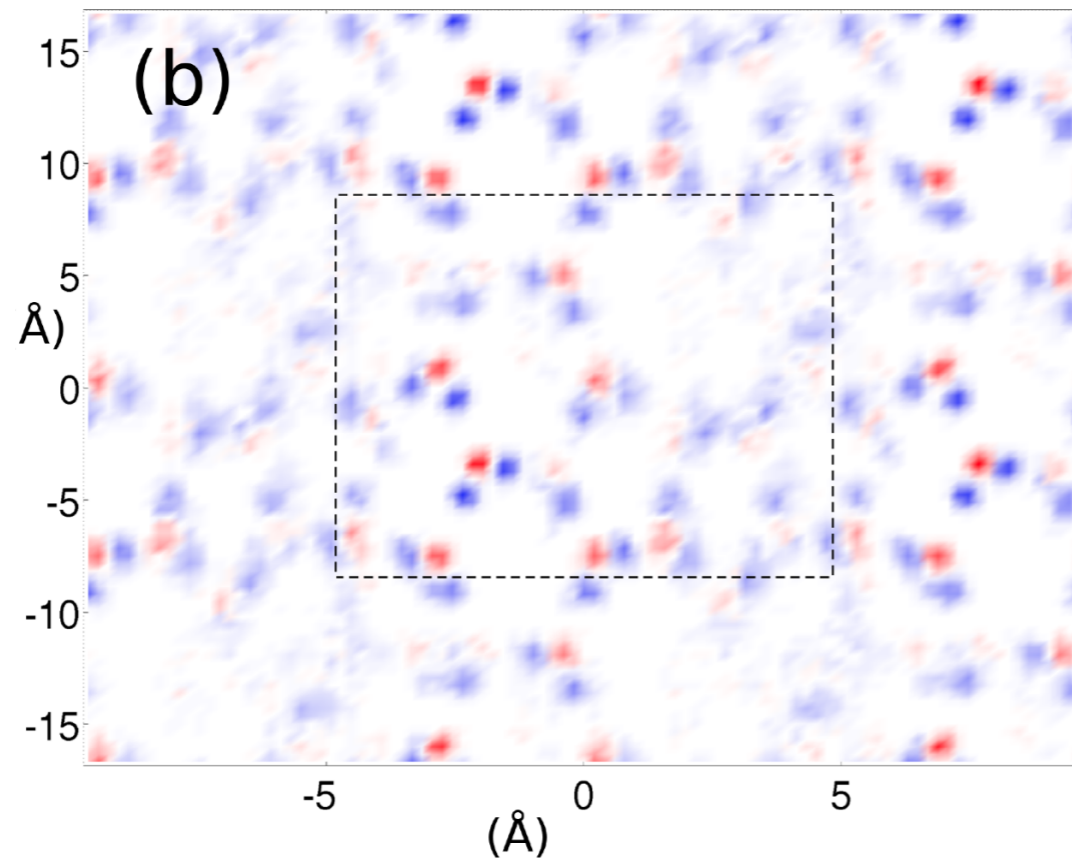
Z-density Pd/H₂O



How vdW interactions modify the picture?

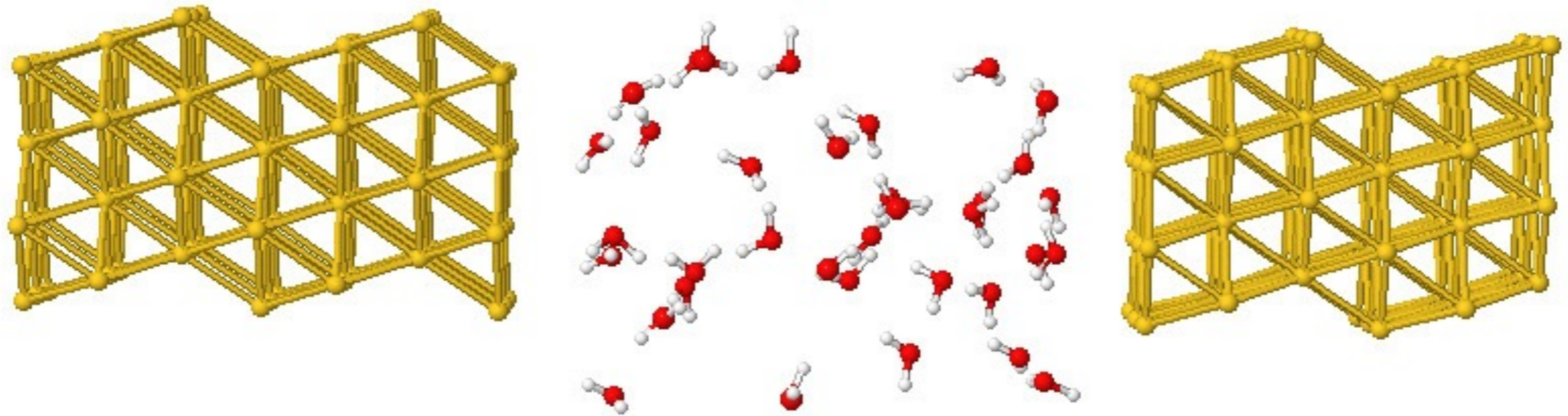


2D order Pd/H₂O



Fluctuation of domains

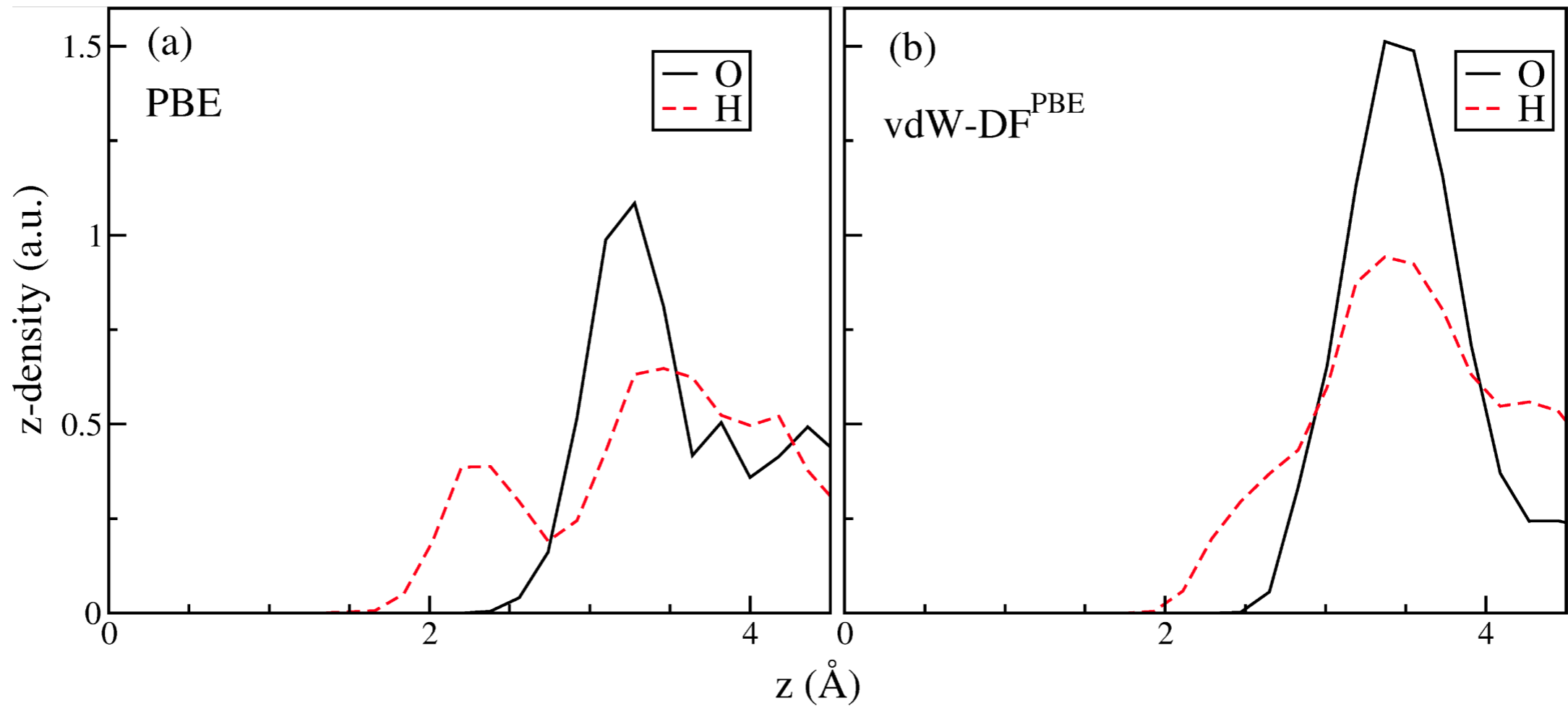
Au(111)



No charge Transfer Effects
Similar to Pt (Siepmann-Sprink model)

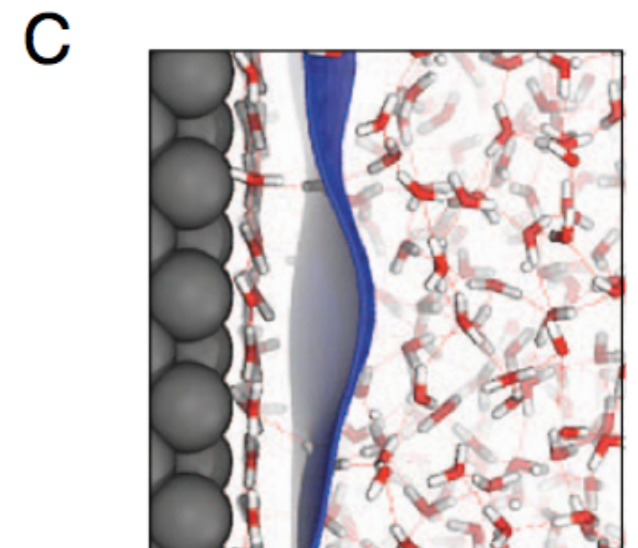
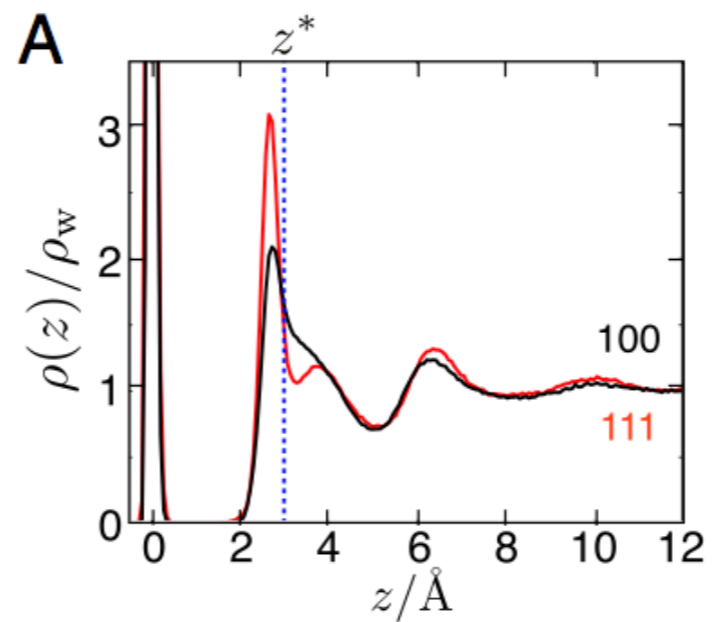
Z-density Au/H₂O

48 Au + 37 H₂O

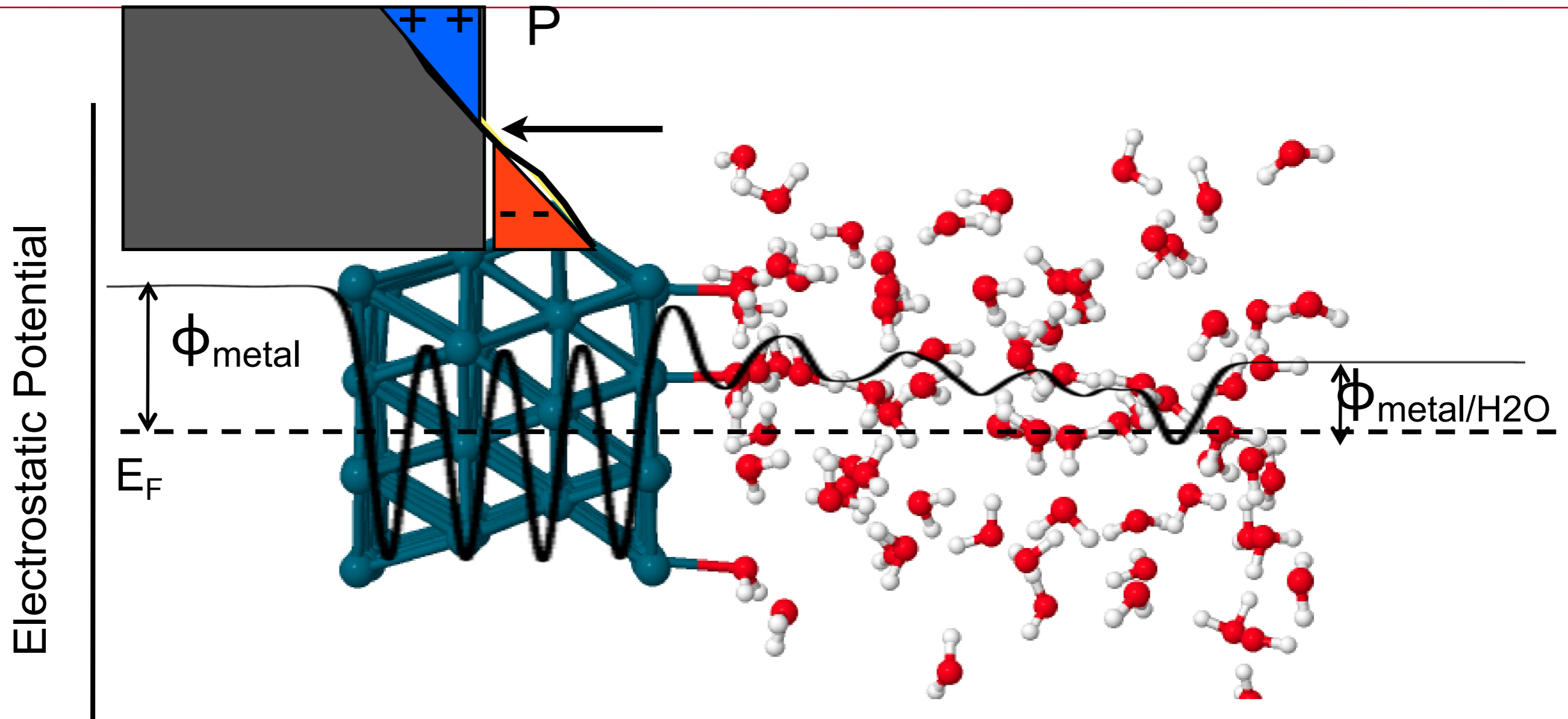


Limmer et al.

PNAS, 110, 4200, (2013)



WORK FUNCTION CHANGE UPON SOLVATION

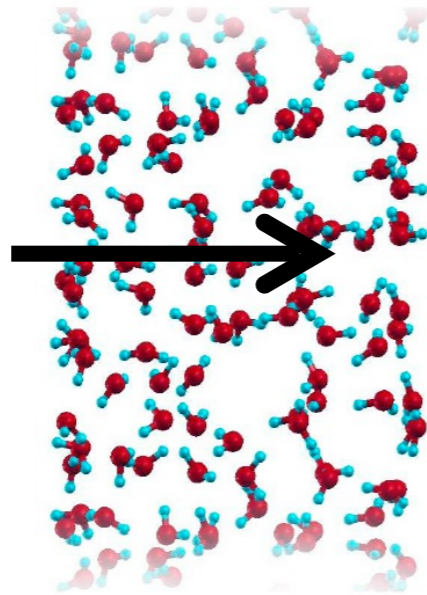


$$\Delta\phi = \phi_{\text{water}} + \phi_{\text{polarization}}^{\text{Water/metal}}$$

$$\phi_{\text{polarization}}^{\text{water/metal}} = \phi_{\text{image}}^{\text{metal}} + \phi_{\text{polarization}}^{\text{water}} + \phi_{\text{charge transfer}}^{\text{wat/met}}$$

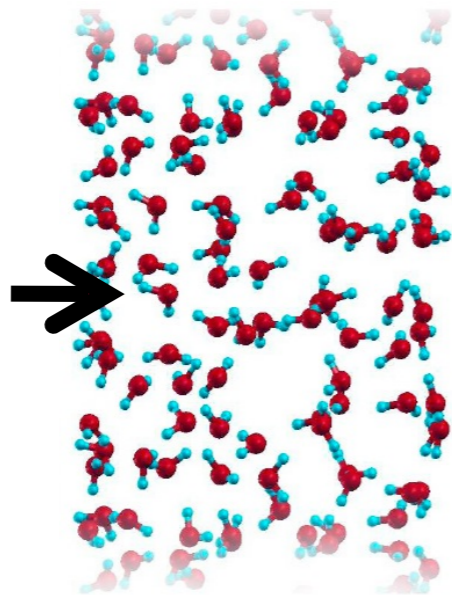
WORK FUNCTION CHANGE UPON SOLVATION

Pd (A)

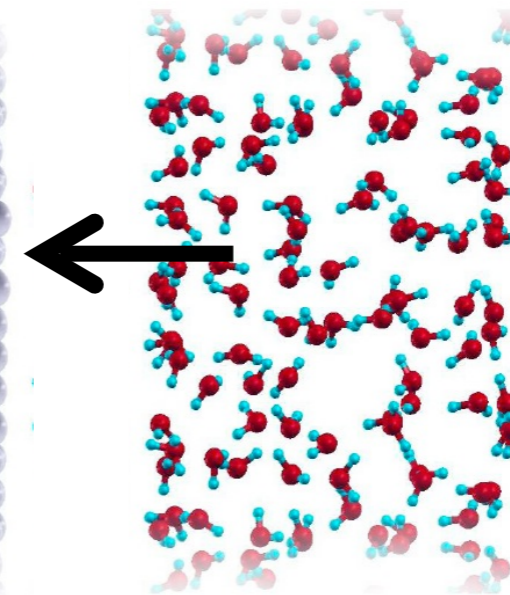
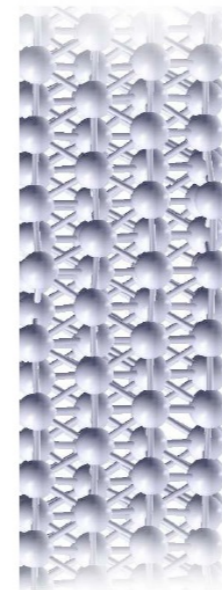


net dipole out

Au



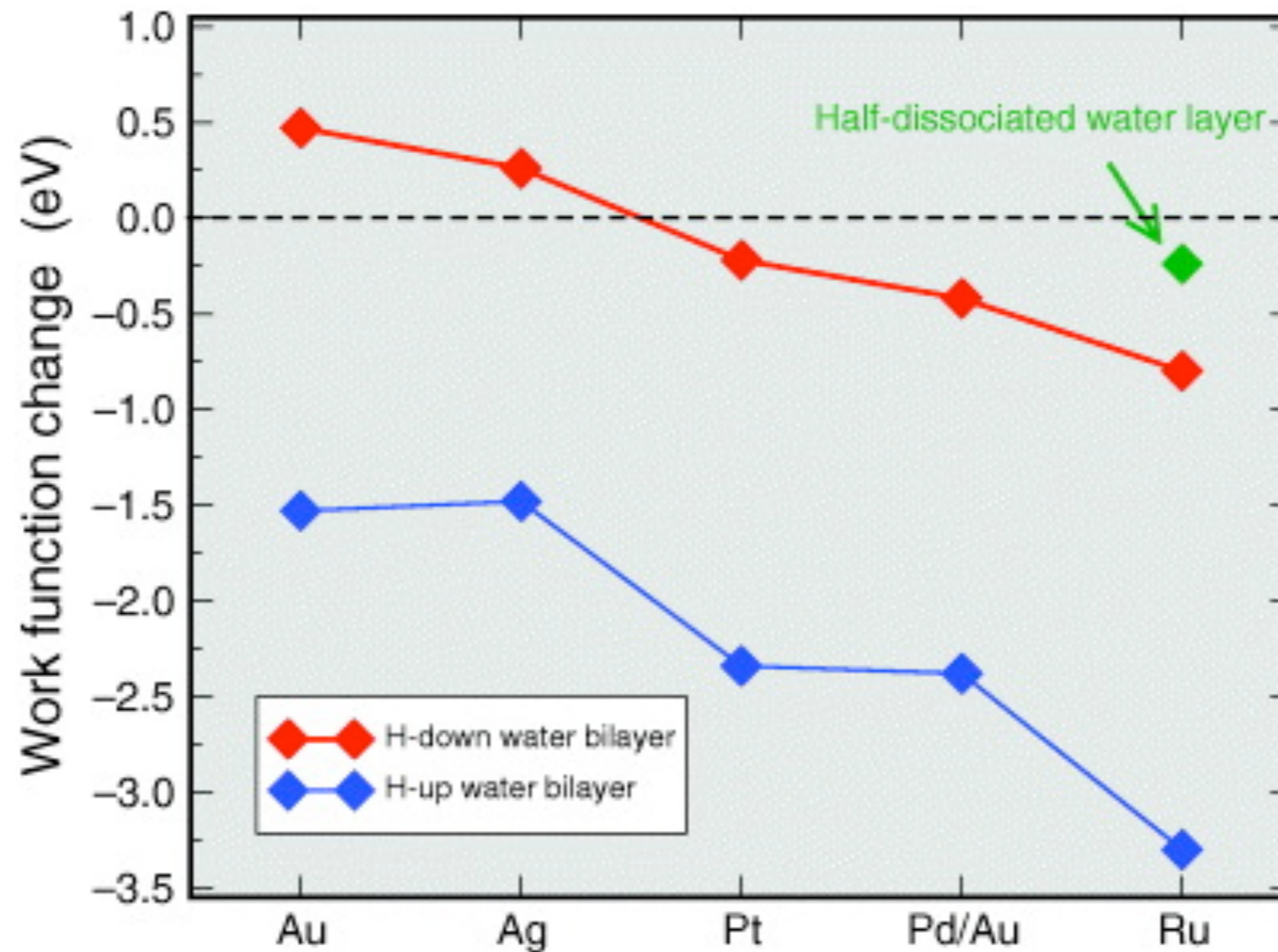
Pd (B)



net dipole in

Work function Change:
out : net decrease
in: net increase

Single bilayer H-up or H-down



Schnur and Gross
New J. Phys. 11 (2009) 125003

Work function change: ($\Phi_{\text{metal/water}} - \Phi_{\text{metal}}$)

TABLE I: Averaged delta work function ($\Phi_{\text{metal}/\text{H}_2\text{O}} - \Phi_{\text{metal}}$) (eV) obtained for the metal/water interfaces AIMD simulations.

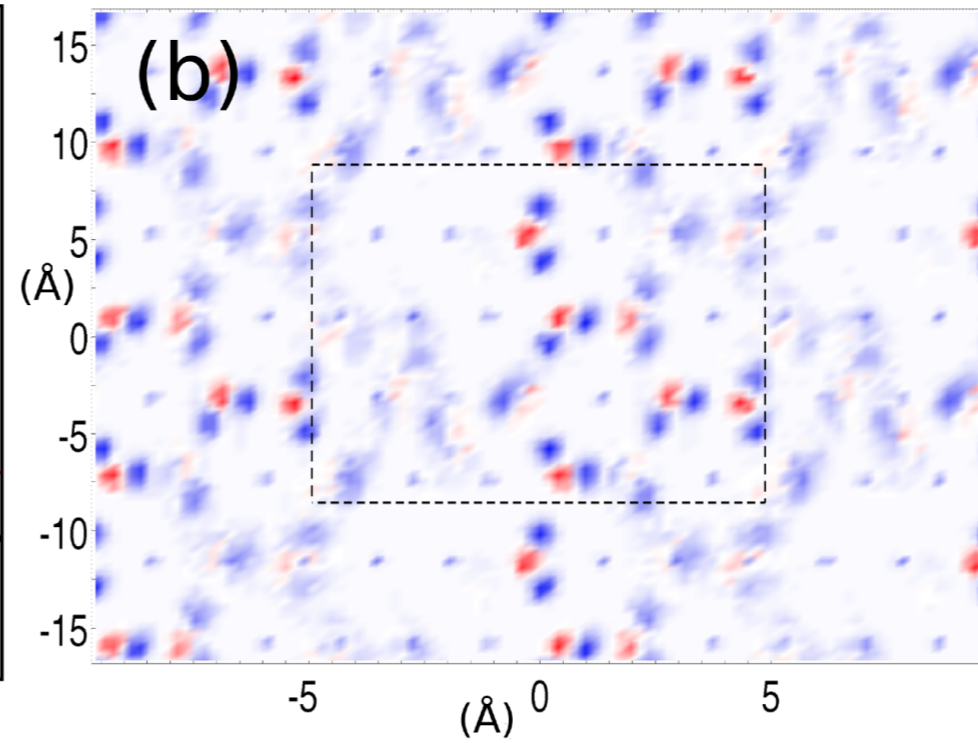
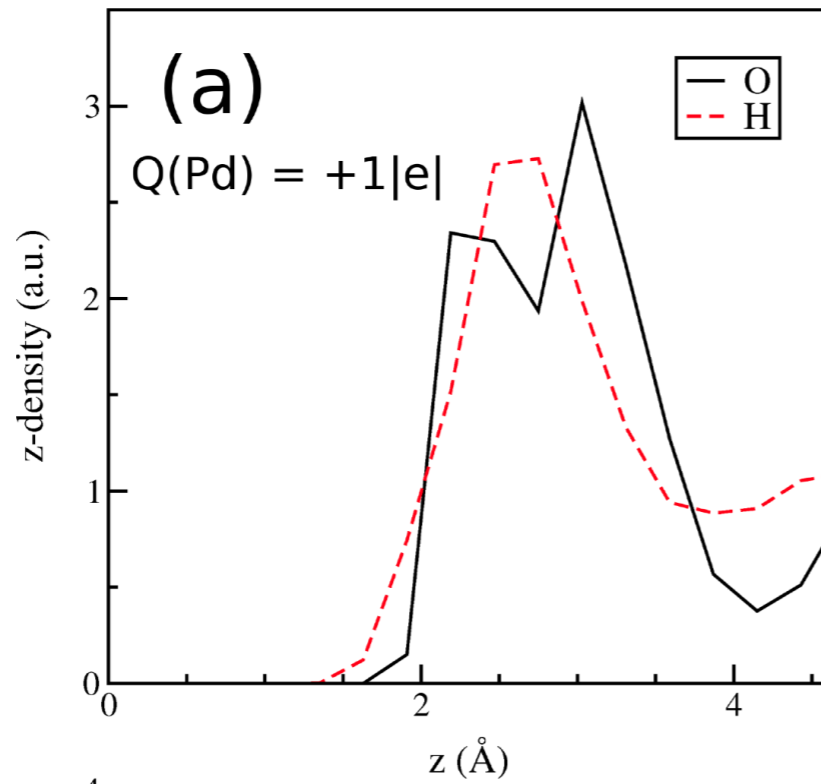
	PBE	vdW-DF ^{PBE}
Pd/H ₂ O	-1.95 ± 0.44	-1.15 ± 0.28
Au/H ₂ O	-0.32 ± 0.37	0.09 ± 0.39

	PBE (eV)	VDW (eV)	Exp (eV)
Pd	5.15 ± 0.01	5.40 ± 0.01	5.6
Au	4.58 ± 0.01	4.68 ± 0.02	4.52

Charged simulations

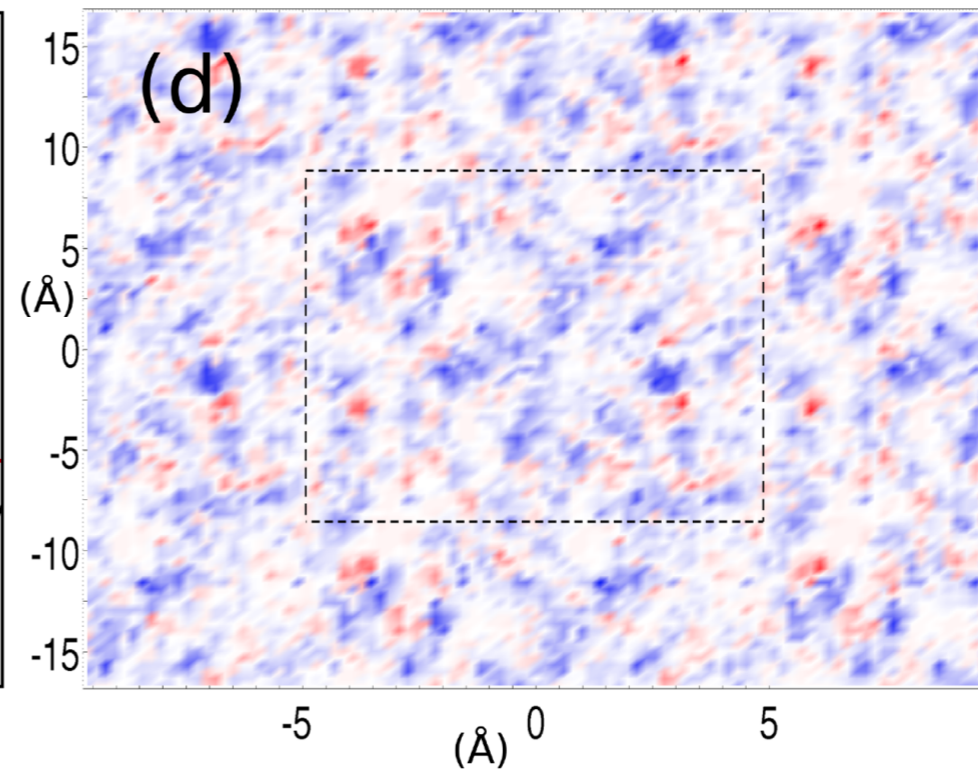
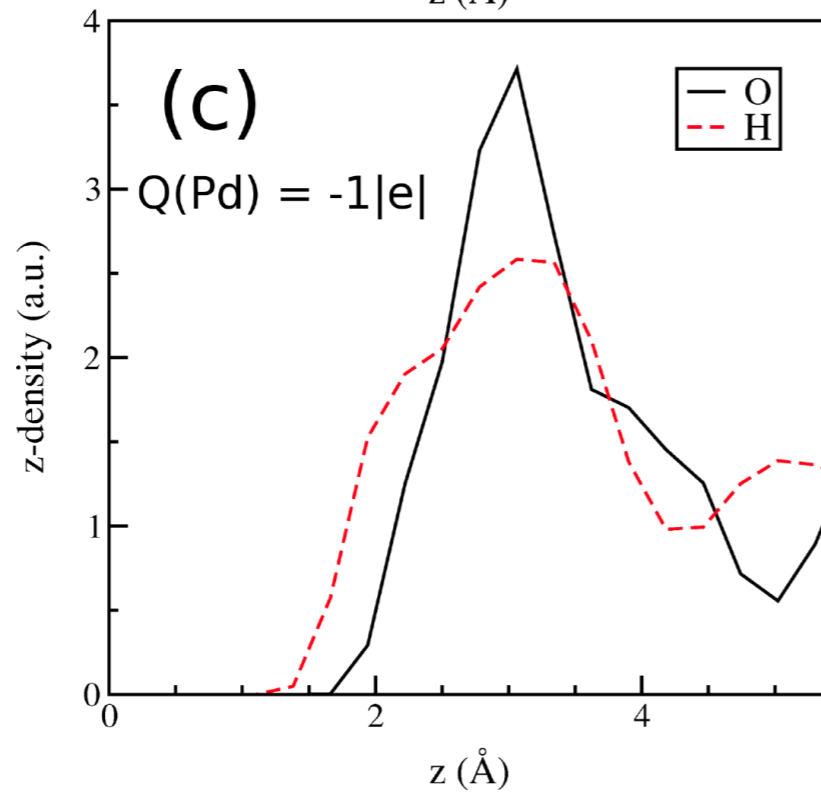
+ 1|e|

$V < 0$



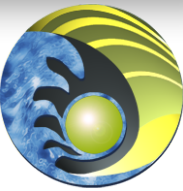
- 1|e|

$V > 0$

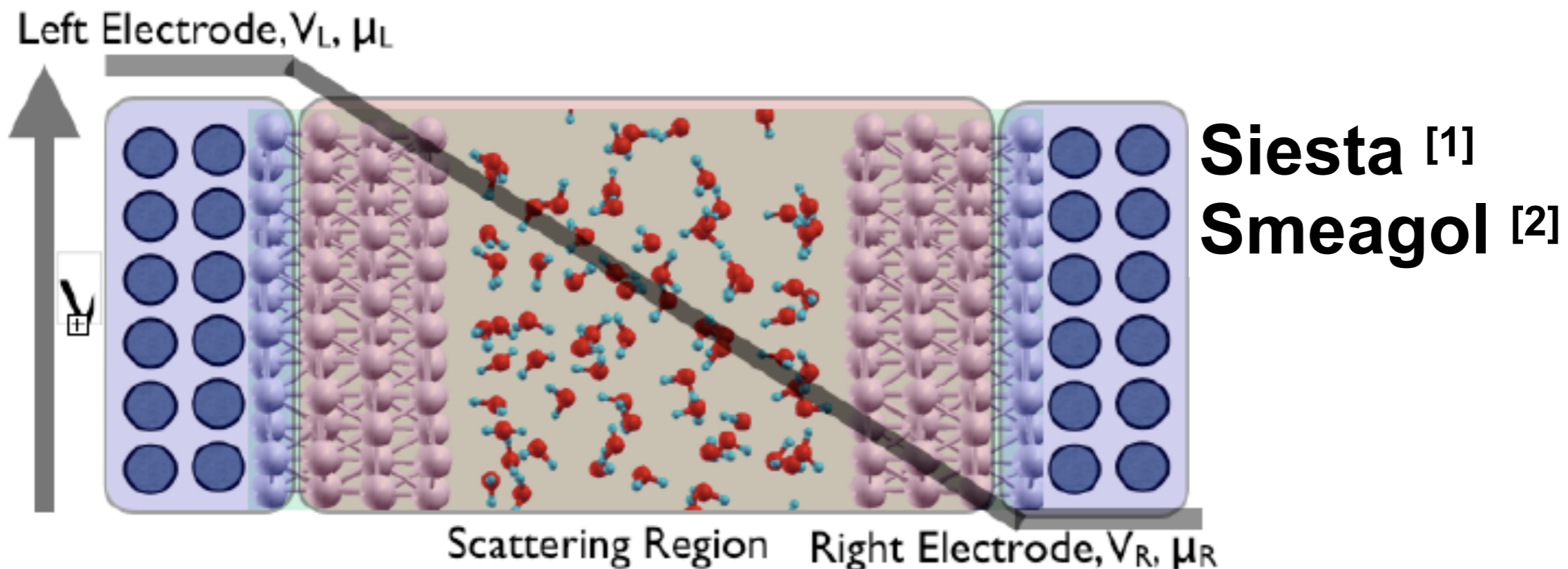




Molecular dynamics under bias potential



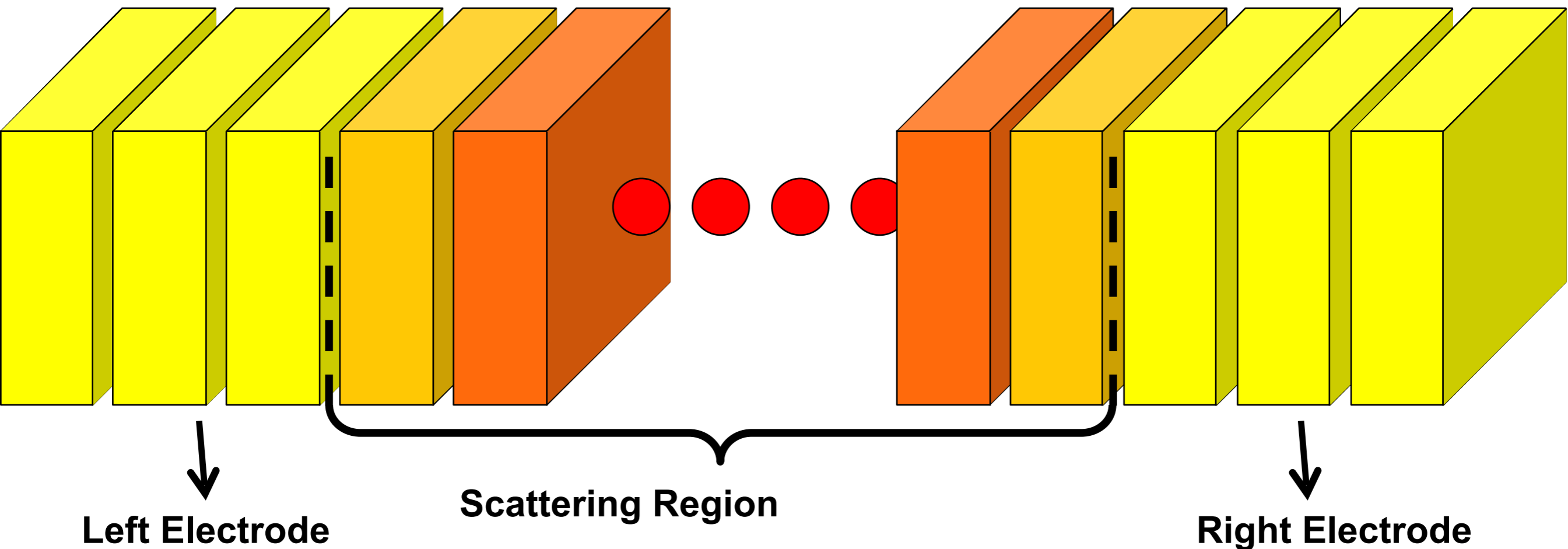
- Apply a bias at interface and connect the macroscopic voltage to the microscopic interfacial charge distribution: The electrochemical cell can be thought of as two metallic electrodes which act as charge reservoirs, with the two metal plates separated by a solution (mostly composed of water). This arrangement is analogous to the one encountered in simulations of electronic transport: a central scattering region coupled to electrodes



[1] J. M. Soler et al., J. Phys.: Condens Matter 14, 2745 (2002)

[2] A. R. Rocha et al., Phys. Rev. B 73, 085414 (2006);
Nature Materials 4, 335 (2005)

Transport Theory: NEGF + DFT



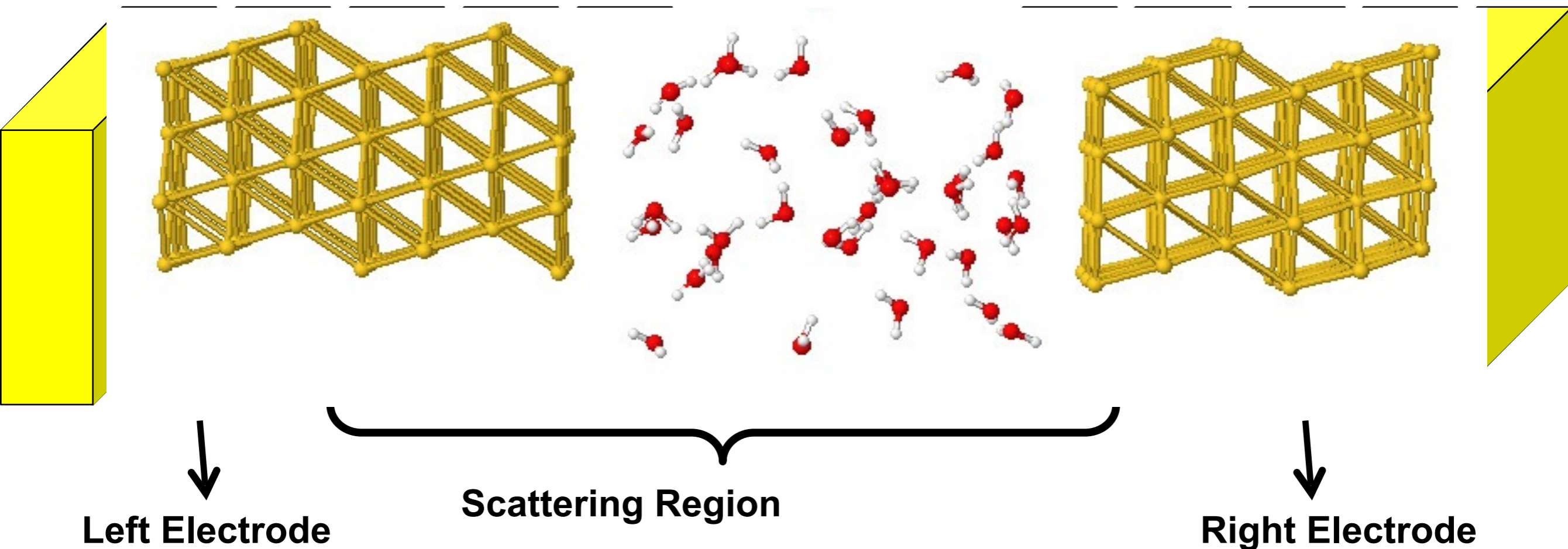
Smeagol (siesta)

A. R. Rocha et al., Phys. Rev. B 73, 085414 (2006);
Nature Materials 4, 335 (2005)

siesta



Transport Theory: NEGF + DFT



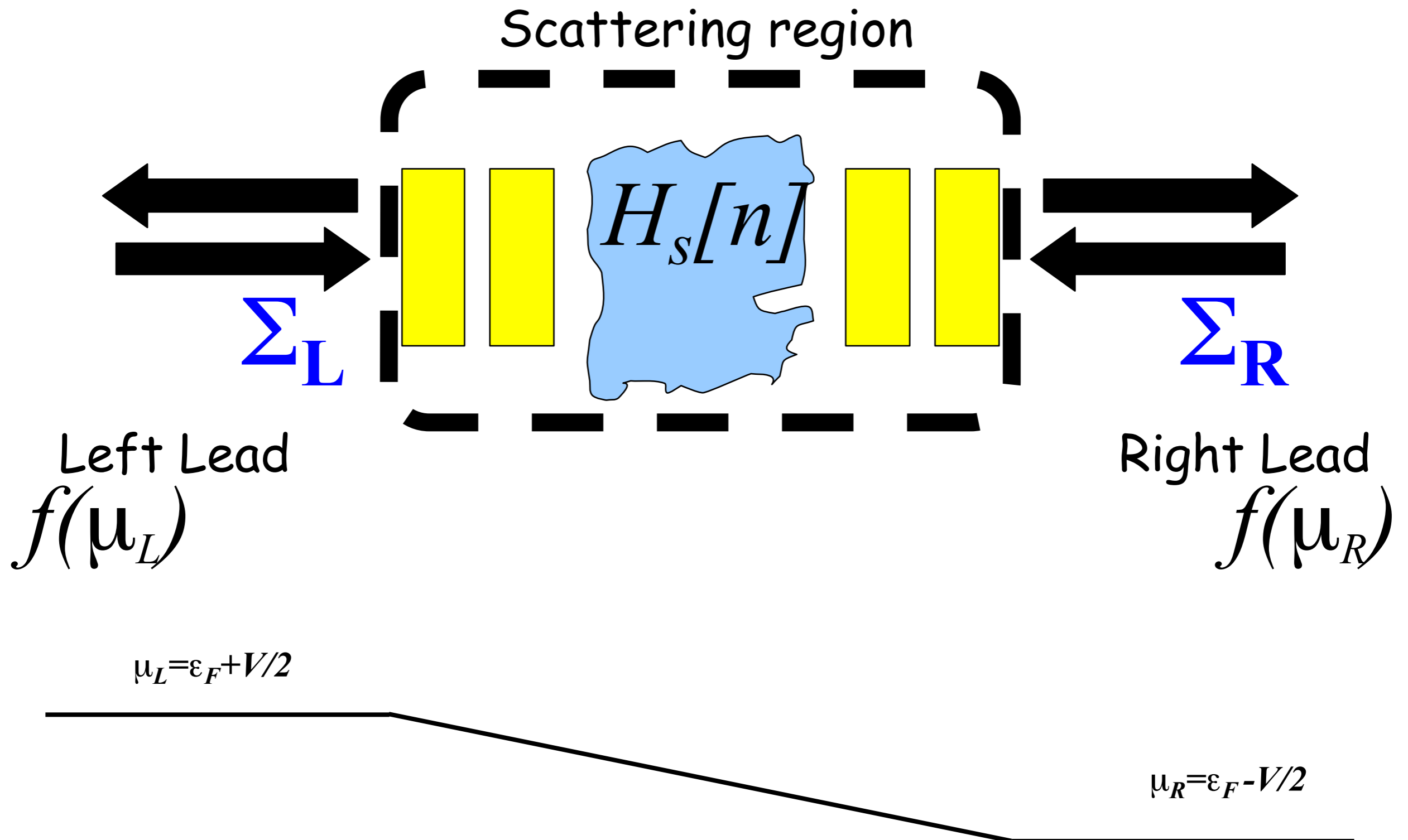
Smeagol (siesta)

A. R. Rocha et al., Phys. Rev. B 73, 085414 (2006);
Nature Materials 4, 335 (2005)

siesta

Smeagol
Non-equilibrium Electronic Transport

Transport Theory: NEGF + DFT





Metal – Water system

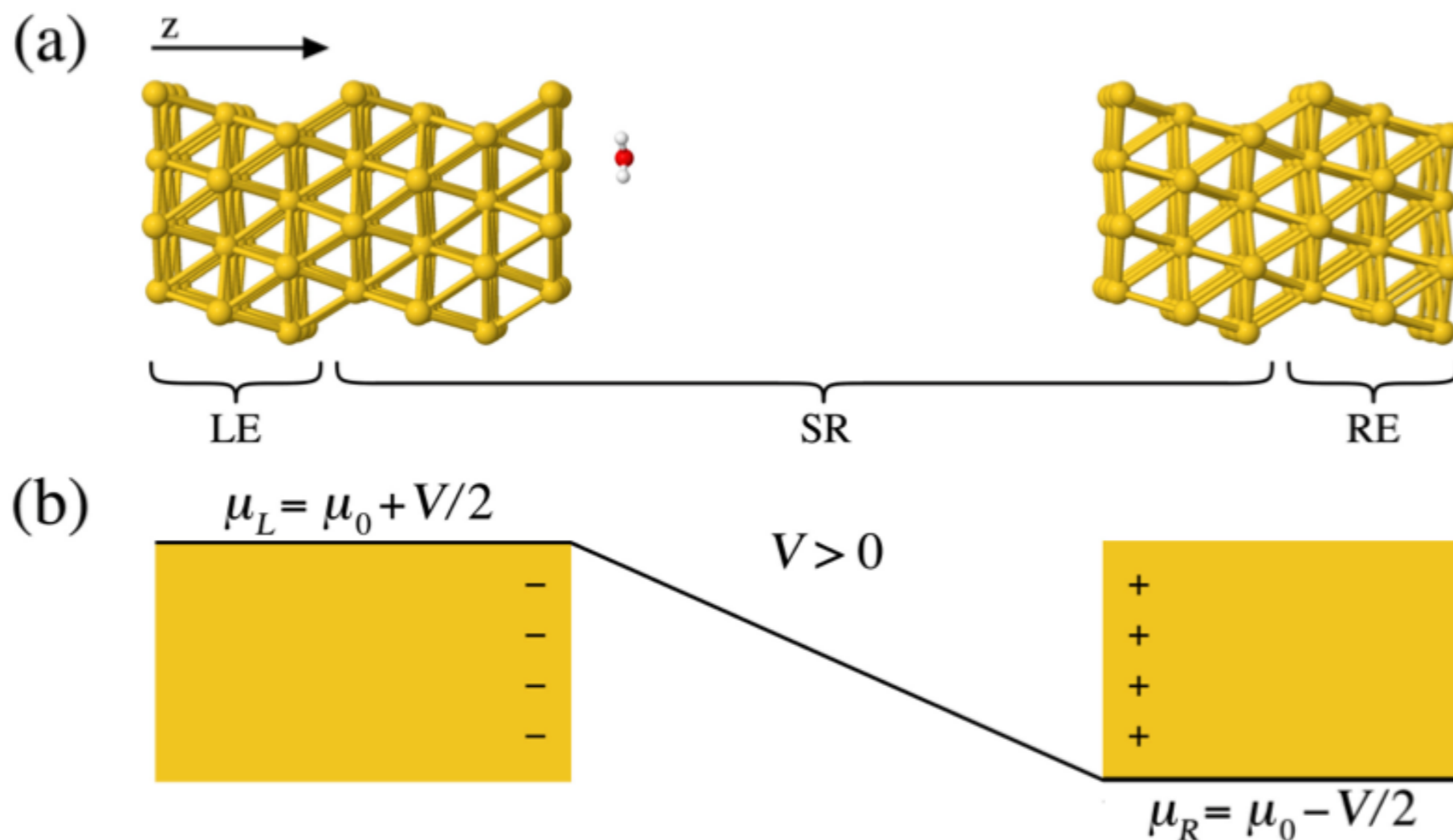
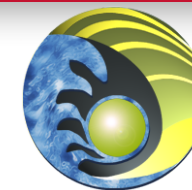


Fig. 1 (Color online) (a) Schematic view of the metal-water system used for the non-equilibrium calculations; the left (right) electrodes (LE/RE) and scattering region (SR) are indicated. (b) Sketch of the effect of a positive bias potential on a parallel plate capacitor; the corresponding charge accumulated in each plate as well as the bias ramp are shown.



Metal – Water system

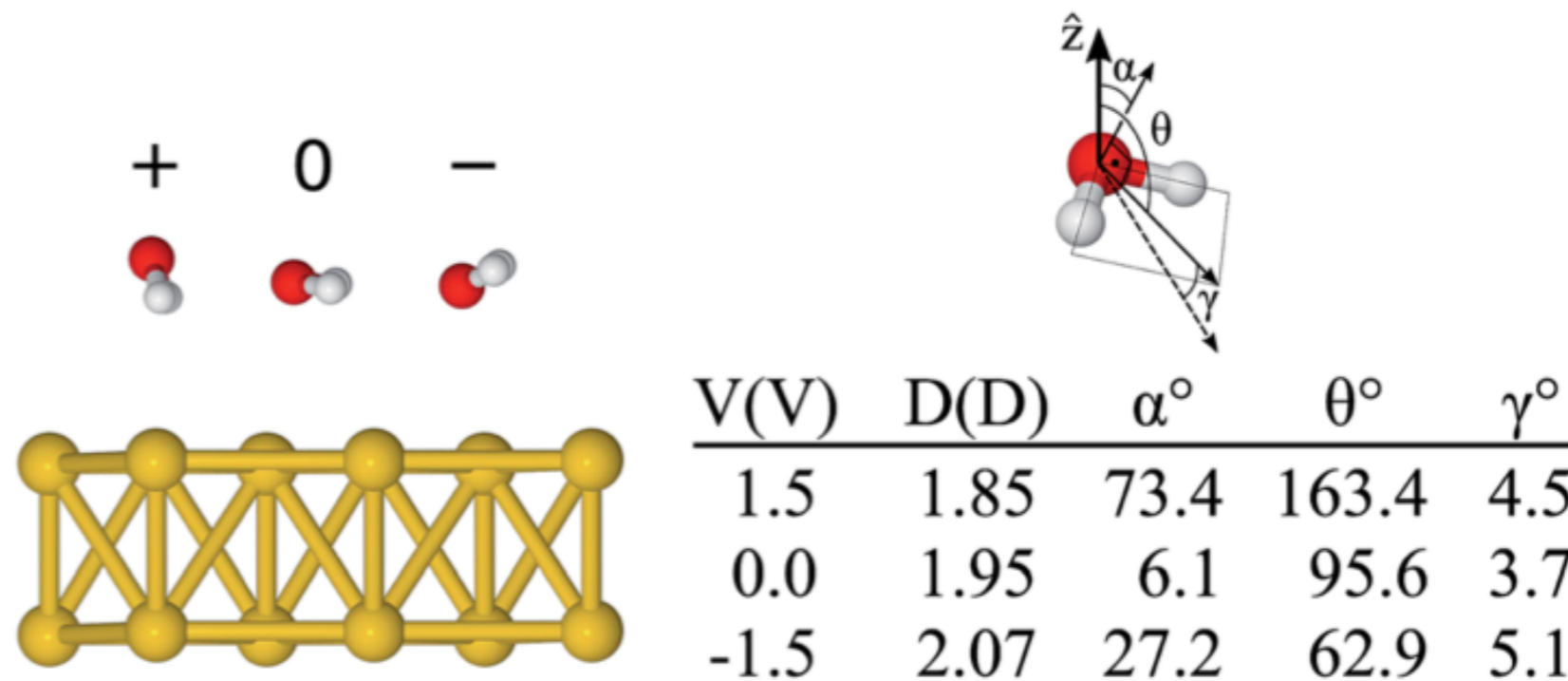
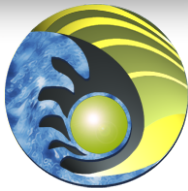


Fig. 4 Relaxed configurations of the water molecule on the Au surface for different bias voltages (+1.5 V \rightarrow +, 0 V, and -1.5 V \rightarrow -), the corresponding angles, and the estimated dipole moment (details in ESI†). The angle α is the angle between the molecular plane and the surface plane, θ is the angle between the isolated molecule dipole and the surface normal, and γ is the angle between the isolated molecule dipole and that calculated from the charge density of the combined Au + H₂O system.



Pauli repulsion- bias dependent

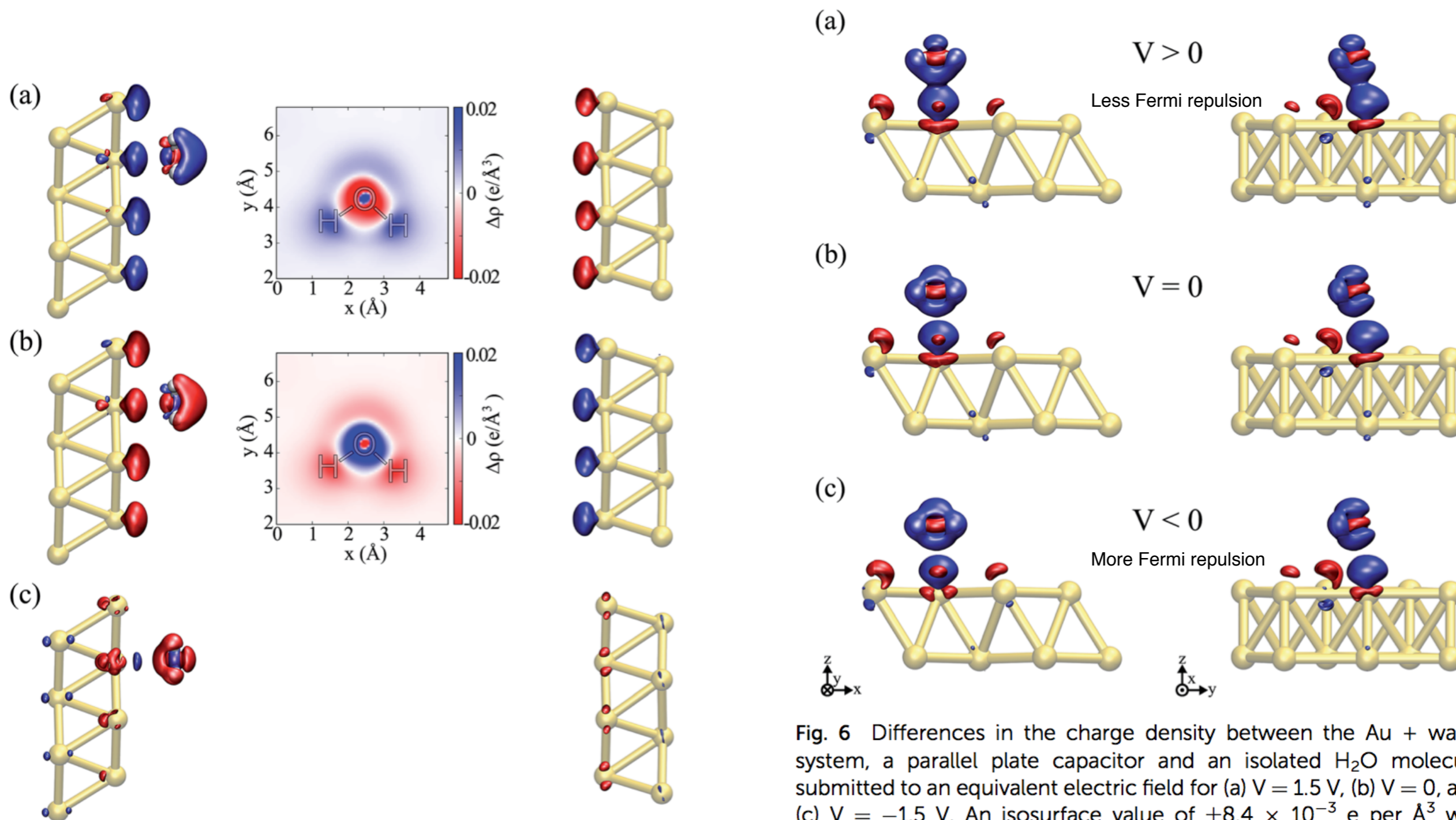


Fig. 6 Differences in the charge density between the Au + water system, a parallel plate capacitor and an isolated H₂O molecule submitted to an equivalent electric field for (a) $V = 1.5$ V, (b) $V = 0$, and (c) $V = -1.5$ V. An isosurface value of $\pm 8.4 \times 10^{-3}$ e per Å³ was considered in all of the plots, where red (blue) indicates an excess (deficiency) of electrons.

Conclusion



- Order of water at biased interfaces reflects two phases instabilities.
- DFT combined with NEGF can be used to describe water–metal systems under an external bias potent
- This framework allows for a description of a truly semi-infinite metallic electrode that sets a reference chemical potential that can be controlled by applying an external bias without adding/removing additional charge to the system.
- This methodology now allows one to properly calculate the forces and therefore perform relaxation or dynamics of water–metal systems out of equilibrium, simulating an electrochemical cell in the sense that ionic currents could be considered now.