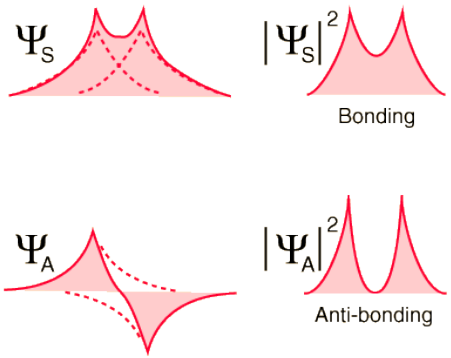
TranSIESTA: Advanced Applications in Electrochemistry and Spintronics

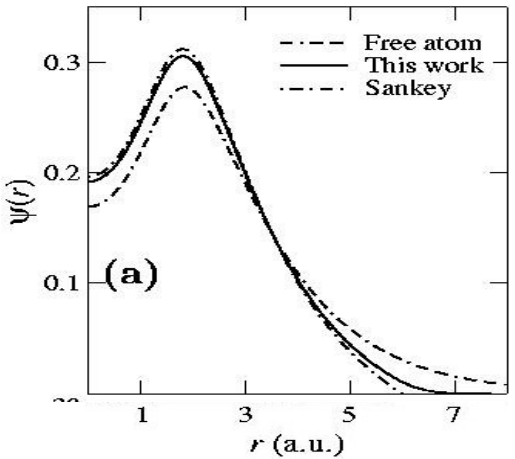
Pablo Ordejón
Catalan Institute of Nanoscience and Nanotechnology – ICN2
Barcelona - Spain

DFT with atomic orbitals



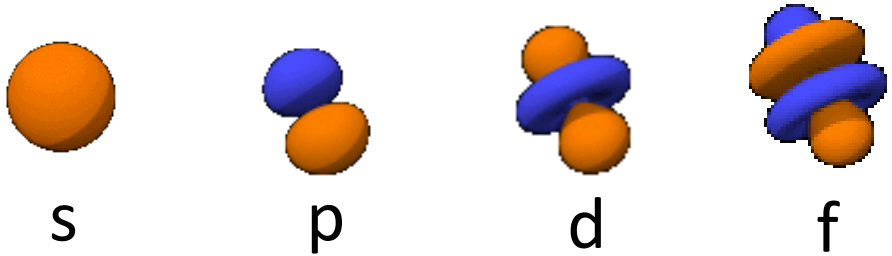
LCAO: $\psi_n(r) = \sum_\mu c_{n\mu} \phi_\mu(r)$

(pseudo)atomic orbitals
- **Short ranged**
- **Arbitrarily complete**



$\phi_\mu(\vec{r}) = \varphi_\mu(|r|) Y_{lm}(\theta,\varphi)$

Spherical harmonics

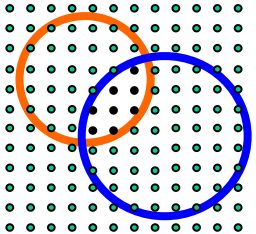


Scaling vs system size

1. Hamiltonian Building:

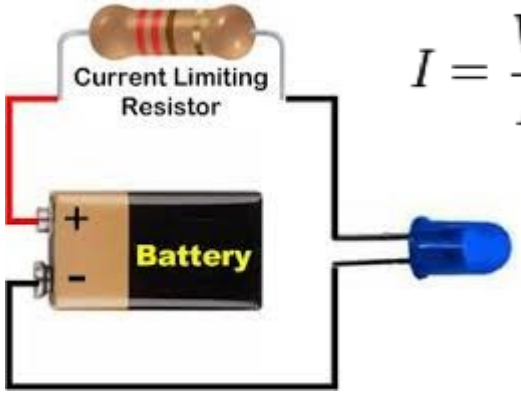
   Always O(N)
   Load Balancing for **real-space grid operations**
   (inhomogeneous systems)

$$\hat{h}_{\mu\nu} = \left\langle \varphi_\mu \middle| \hat{h} \middle| \varphi_\nu \right\rangle$$

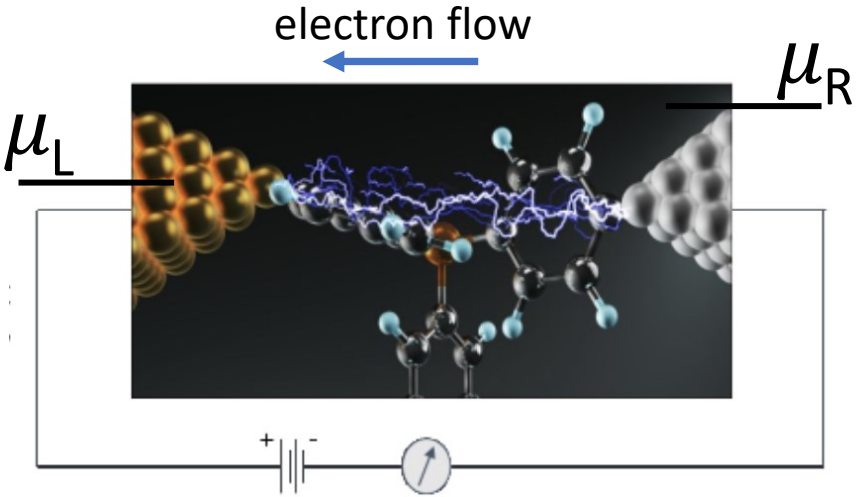


2. Hamiltonian Solvers: obtaining the charge density from the Hamiltonian
   - Standard parallel diagonalization libraries – **SCALAPACK** $O(N^3)$
   - New diagonalizers: **ELPA, MRRR** $O(N^3)$
   - **PEXSI method** – massive parallelization and reduced scaling: $O(N, N^{3/2}, N^2)$ for 1, 2 and 3D
   - O(N) method based on **localized occupied orbitals** (Ordejón et al; Mauri et al)
   - O(N) method (**Fermi Operator Expansion**), porting the CheSS library from the BigDFT project to SIESTA.

Challenge: Electronic Transport at the Nanoscale



$$I = \frac{V}{R}$$



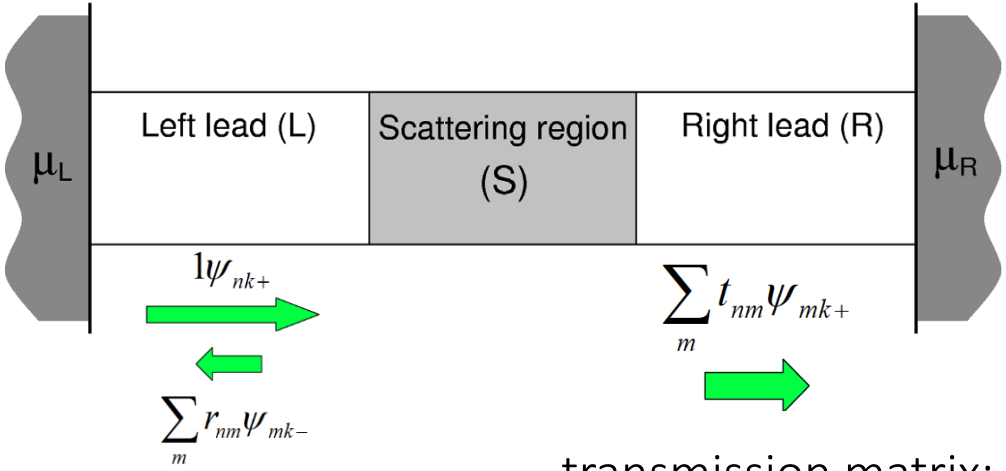
Molecular Electronics

Nanoelectronics
(devices with nanometric features)

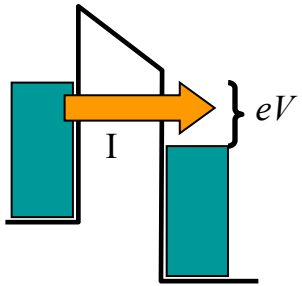
- Open systems (intensive quantities)
- Non-Periodic
- Semi-infinite electrodes

- Out of equilibrium:
  - Chemical potential is not unique
  - Net electronic current flowing

Landauer formulation of electronic transport



transmission matrix: $T(\varepsilon) = Tr\,[t^{+}t]\,(\varepsilon)$

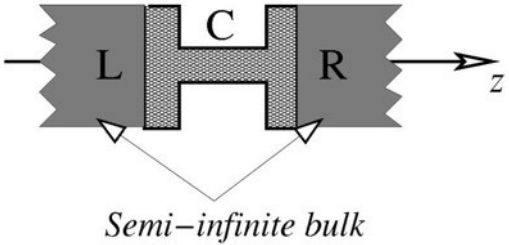


$$I = \frac{2e}{h}\int d\varepsilon \left(f_L(\varepsilon) - f_R(\varepsilon)\right) T(\varepsilon)$$

LANDAUER - BÜTTIKER

Transmission from Green's functions: $\mathbf{t}(\varepsilon) = [\mathbf{\Gamma}_R(\varepsilon)]^{1/2}\mathbf{G}(\varepsilon)[\mathbf{\Gamma}_L(\varepsilon)]^{1/2}$

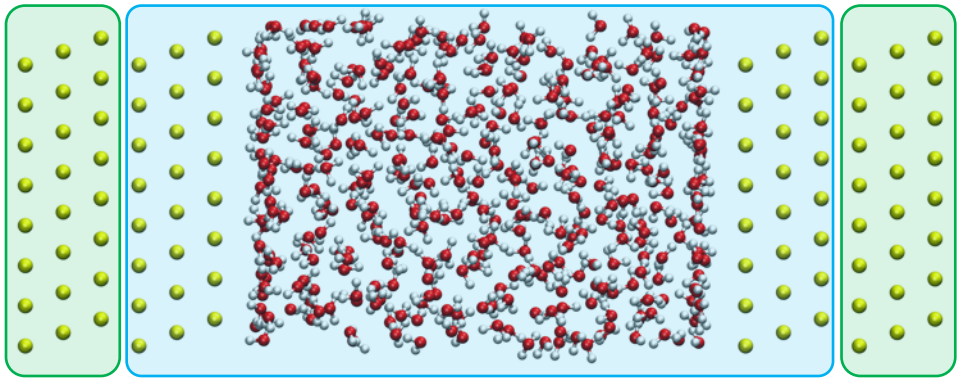
Green's function formalism - TranSIESTA



Green's function

$$G(z) = [z - H]^{-1} \quad (z = \varepsilon + i\eta) \qquad \rho(\varepsilon) = -\frac{1}{\pi} Im\,[G(z)] \quad (\eta \to 0^{+})$$

$$G(z) = [z - H - \Sigma_L(z) - \Sigma_R(z)]^{-1}$$

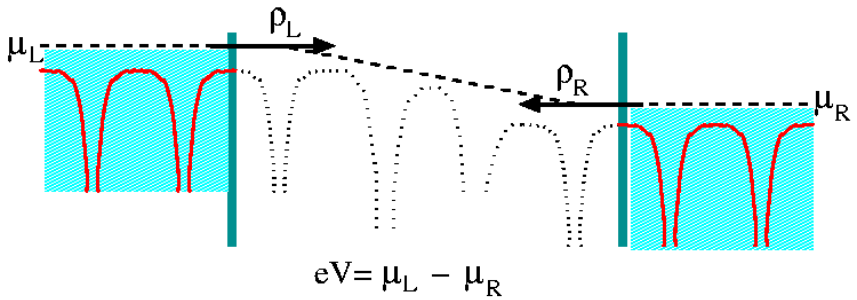


- All screening must happen within the contact region C (L and R are bulk-like)
- Green's Functions are computed in the simulation cell "L+C+R", connected to semi-infinite bulk electrodes (self-energies **Σ**).

How to handle non-equilibrium distributions

How to compute the density if the chemical potential is not unique?

Non-equilibrium Green's Functions (Keldish formalism):



$$D_{\mu\nu} = \int_{-\infty}^{\infty} d\varepsilon \left[\rho^{L}_{\mu\nu}(\varepsilon)\, n_F(\varepsilon - \mu_L) + \rho^{R}_{\mu\nu}(\varepsilon)\, n_F(\varepsilon - \mu_R) \right]$$

$$\rho^{L}_{\mu\nu}(\varepsilon) = \frac{1}{\pi}[\mathbf{G}(\varepsilon)\boldsymbol{\Gamma}_L(\varepsilon)\mathbf{G}^{\dagger}(\varepsilon)]_{\mu\nu}$$

$$\boldsymbol{\Gamma}_L(z) \equiv i[\boldsymbol{\Sigma}_L(\varepsilon) - \boldsymbol{\Sigma}_L(\varepsilon)^{\dagger}]/2$$

TranSIESTA

First principles (DFT): **TranSIESTA**

- Semi-infinite electrodes through Self-Energies
- Non-Equillibrium Green's Functions for finite voltage
- Conductance through Landauer formulation

Brandbyge, Mozos, Ordejon, Taylor, Stokbro PRB 65, 165401 (2002)

Papior, Lorente, Frederiksen, García, Brandbyge, Comp. Phys. Comm. 212, 8 (2017)

- Accelerated Green's function solvers (linear scaling with contact length)
- Improved parallelization
- Multiterminal devices; Gate voltages; ....

Spin Transport **Electrochemistry**

Spintronics with TranSIESTA

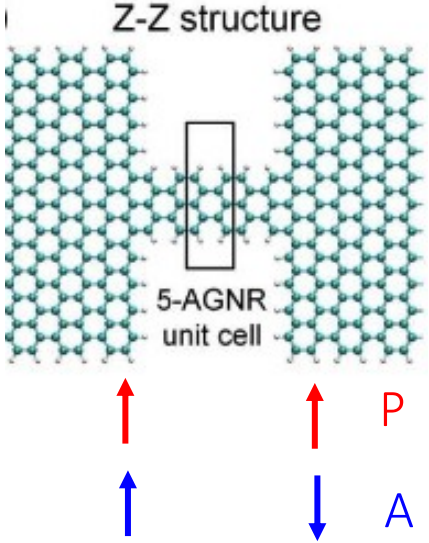
- Spin-polarized DFT
  - Collinear spin directions: common magnetization direction through space
  - No Spin-orbit coupling

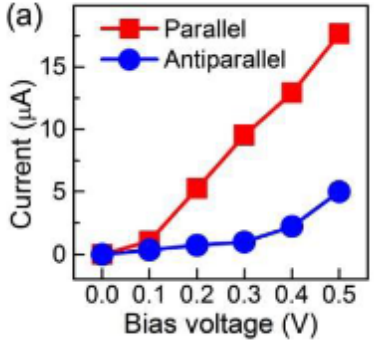
No spin

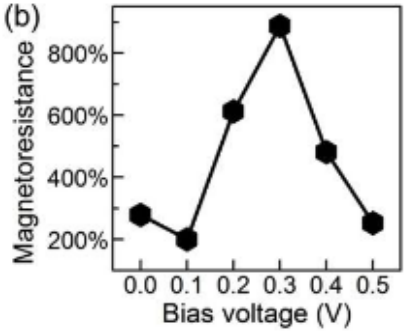
H

Spin polarized

$(H^{\uparrow}, H^{\downarrow})$



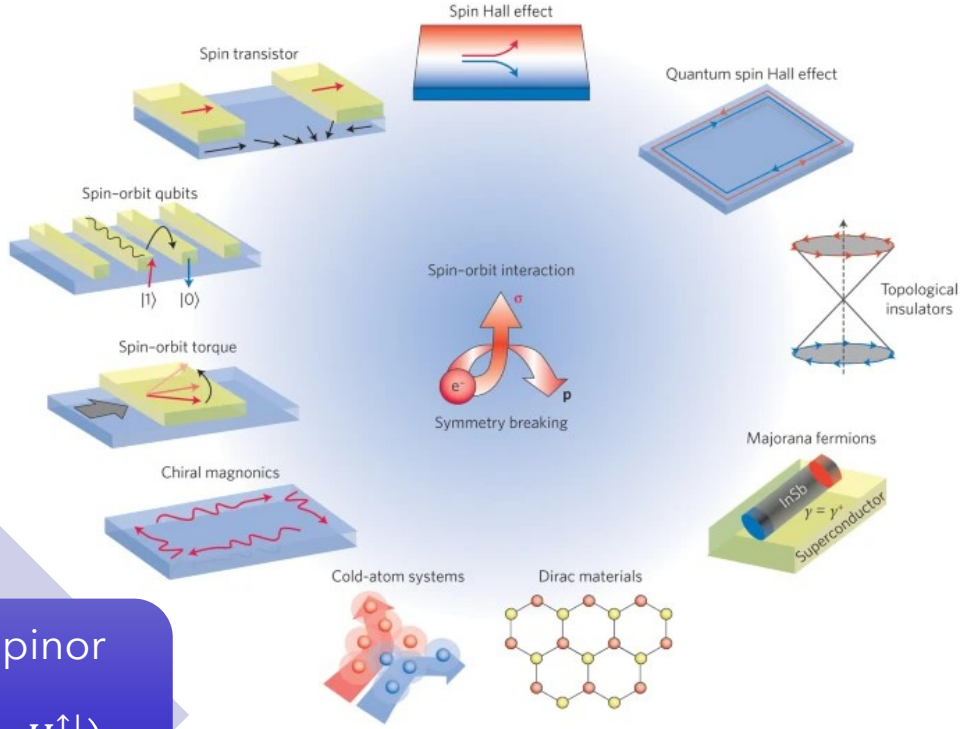




S. Li, Y.-W. Son, Su Ying Quek,
Appl. Phys. Lett. 105, 242413 (2014)

- **Non-Collinear magnetism**
- **Spin-Orbit Coupling**

→ require spinor description



Manchon, *Nature Mater* **14** (2015).

No spin

H

Spin polarized

$(H^{\uparrow}, H^{\downarrow})$

Full Spinor

$$\begin{pmatrix} H^{\uparrow\uparrow} & H^{\uparrow\downarrow} \\ H^{\downarrow\uparrow} & H^{\downarrow\downarrow} \end{pmatrix}$$

Non-eq. Green's Functions with spinors

Non-eq. Green's Function (NEGF)

$$\mathbf{G}_{\mathbf{k}}(z) = \left(z\,\mathbf{S}_{\mathbf{k}} - \mathbf{H}_{\mathbf{k}}^{\mathrm{DFT}} - \sum_{\mathbf{e}} \boldsymbol{\Sigma}_{\mathbf{e},\mathbf{k}}(z) \right)^{-1} \longrightarrow \begin{pmatrix} \mathbf{G}_{\mathbf{k}}^{\uparrow\uparrow} & \mathbf{G}_{\mathbf{k}}^{\uparrow\downarrow} \\ \mathbf{G}_{\mathbf{k}}^{\downarrow\uparrow} & \mathbf{G}_{\mathbf{k}}^{\downarrow\downarrow} \end{pmatrix} = \left(z \begin{pmatrix} \mathbf{S}_{\mathbf{k}} & \mathbf{0} \\ \mathbf{0} & \mathbf{S}_{\mathbf{k}} \end{pmatrix} - \begin{pmatrix} \mathbf{H}_{\mathbf{k}}^{\uparrow\uparrow} & \mathbf{H}_{\mathbf{k}}^{\uparrow\downarrow} \\ \mathbf{H}_{\mathbf{k}}^{\downarrow\uparrow} & \mathbf{H}_{\mathbf{k}}^{\downarrow\downarrow} \end{pmatrix} - \sum_{\mathbf{e}} \begin{pmatrix} \boldsymbol{\Sigma}_{\mathbf{e},\mathbf{k}}^{\uparrow\uparrow} & \boldsymbol{\Sigma}_{\mathbf{e},\mathbf{k}}^{\uparrow\downarrow} \\ \boldsymbol{\Sigma}_{\mathbf{e},\mathbf{k}}^{\downarrow\uparrow} & \boldsymbol{\Sigma}_{\mathbf{e},\mathbf{k}}^{\downarrow\downarrow} \end{pmatrix} \right)^{-1}$$

Spectral function

$$\boldsymbol{\mathcal{A}}_{\mathbf{e},\mathbf{k}}(z) = \mathbf{G}_{\mathbf{k}}(z)\boldsymbol{\Gamma}_{\mathbf{e},\mathbf{k}}(z)\mathbf{G}_{\mathbf{k}}^{\dagger}(z) \longrightarrow \begin{pmatrix} \boldsymbol{\mathcal{A}}_{\mathbf{e},\mathbf{k}}^{\uparrow\uparrow} & \boldsymbol{\mathcal{A}}_{\mathbf{e},\mathbf{k}}^{\uparrow\downarrow} \\ \boldsymbol{\mathcal{A}}_{\mathbf{e},\mathbf{k}}^{\downarrow\uparrow} & \boldsymbol{\mathcal{A}}_{\mathbf{e},\mathbf{k}}^{\downarrow\downarrow} \end{pmatrix} = \begin{pmatrix} \mathbf{G}_{\mathbf{k}}^{\uparrow\uparrow} & \mathbf{G}_{\mathbf{k}}^{\uparrow\downarrow} \\ \mathbf{G}_{\mathbf{k}}^{\downarrow\uparrow} & \mathbf{G}_{\mathbf{k}}^{\downarrow\downarrow} \end{pmatrix} \begin{pmatrix} \boldsymbol{\Gamma}_{\mathbf{e},\mathbf{k}}^{\uparrow\uparrow} & \boldsymbol{\Gamma}_{\mathbf{e},\mathbf{k}}^{\uparrow\downarrow} \\ \boldsymbol{\Gamma}_{\mathbf{e},\mathbf{k}}^{\downarrow\uparrow} & \boldsymbol{\Gamma}_{\mathbf{e},\mathbf{k}}^{\downarrow\downarrow} \end{pmatrix} \begin{pmatrix} \mathbf{G}_{\mathbf{k}}^{\uparrow\uparrow} & \mathbf{G}_{\mathbf{k}}^{\uparrow\downarrow} \\ \mathbf{G}_{\mathbf{k}}^{\downarrow\uparrow} & \mathbf{G}_{\mathbf{k}}^{\downarrow\downarrow} \end{pmatrix}^{\dagger}$$

Charge density

$$\boldsymbol{\rho} = \frac{1}{2\pi} \iint_{BZ} \mathrm{d}\epsilon \mathrm{d}\mathbf{k} \sum_{i} \boldsymbol{\mathcal{A}}_{i,\mathbf{k}}(\epsilon + 0^{+}) \mathrm{n}_{\mathrm{F}}(\epsilon, \mu_i, T_i)\, e^{-i\mathbf{k}\cdot\mathbf{r}} \longrightarrow \begin{pmatrix} \boldsymbol{\rho}^{\uparrow\uparrow} & \boldsymbol{\rho}^{\uparrow\downarrow} \\ \boldsymbol{\rho}^{\downarrow\uparrow} & \boldsymbol{\rho}^{\downarrow\downarrow} \end{pmatrix} \quad \text{or} \quad \boldsymbol{\rho} \text{ and } \vec{\boldsymbol{m}}$$

Transmission Function for Spinors

Spin channel projected transmission

Conductivity
Current

$$T_{\boldsymbol{k}}^{\mathbf{e},\mathbf{e}'}(\epsilon,\vec{\boldsymbol{\sigma}}_n,\vec{\boldsymbol{\sigma}}_m)=\mathrm{Tr}\left\{\left\langle\vec{\boldsymbol{\sigma}}_m\right|\left(s_{\boldsymbol{k}}^{\mathbf{e},\mathbf{e}'}\right)^{\dagger}\left|\vec{\boldsymbol{\sigma}}_n\right\rangle\left\langle\vec{\boldsymbol{\sigma}}_n\right|s_{\boldsymbol{k}}^{\mathbf{e},\mathbf{e}'}\left|\vec{\boldsymbol{\sigma}}_m\right\rangle\right\}$$

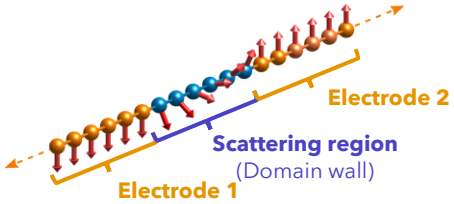
Transmission can be decomposed into different contributions, e.g.:

- $T_{\boldsymbol{k}}^{\mathbf{e},\mathbf{e}'}(\epsilon,\uparrow,\uparrow)$ spin-up transmission,
- $T_{\boldsymbol{k}}^{\mathbf{e},\mathbf{e}'}(\epsilon,\downarrow,\downarrow)$ spin-down transmission,
- $T_{\boldsymbol{k}}^{\mathbf{e},\mathbf{e}'}(\epsilon,\uparrow,\downarrow)$, $T_{\boldsymbol{k}}^{\mathbf{e},\mathbf{e}'}(\epsilon,\downarrow,\uparrow)$ spin-flip

Spin directions can be arbitrary and different for the two electrodes

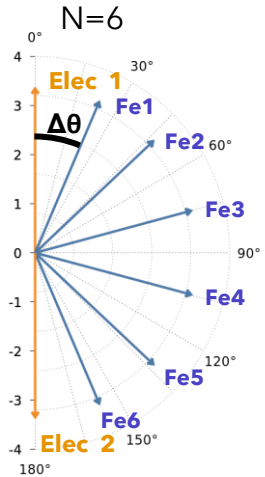
Test case: Domain Walls in Monatomic Fe Chain

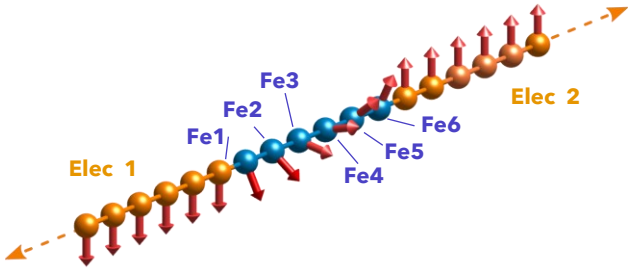
- Non-collinear spins
- Prediction of spin orientations
- Anisotropic magnetoresistance
- Spin channel projection



Bloch Domain Wall in Monatomic Chain

Domain wall length (α=180°)

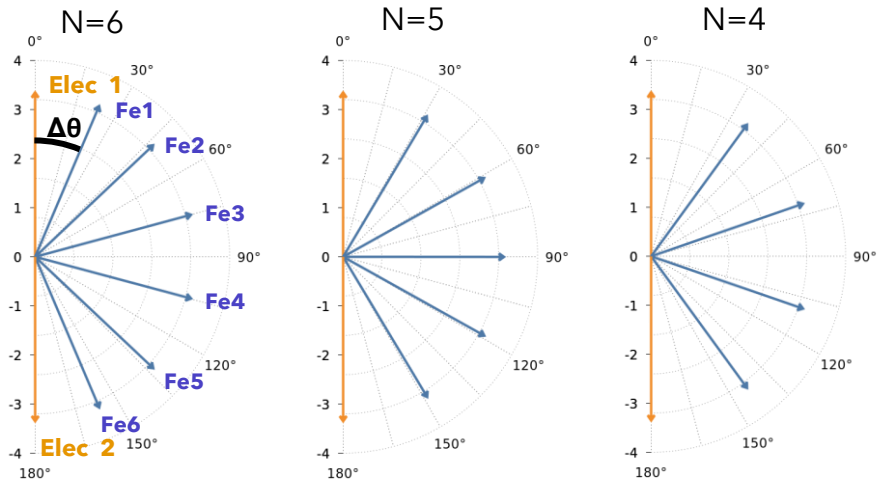




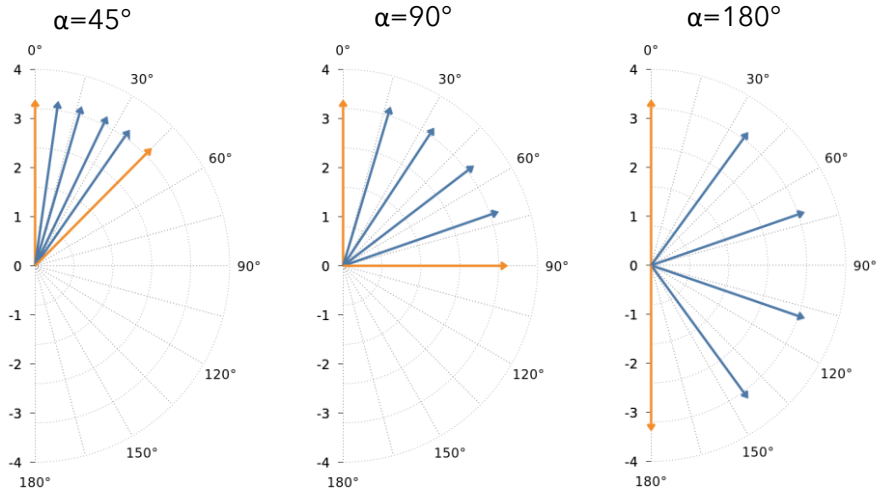
- All spin moments perpendicular to the chain axis
- Uniform change in spin direction along the domain wall

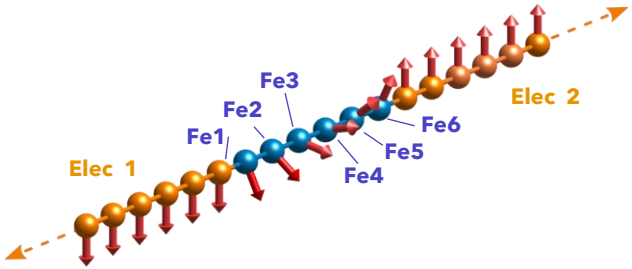
Bloch Domain Wall in Monatomic Chain

Domain wall length (α=180°)



Domain wall angle (N=4)

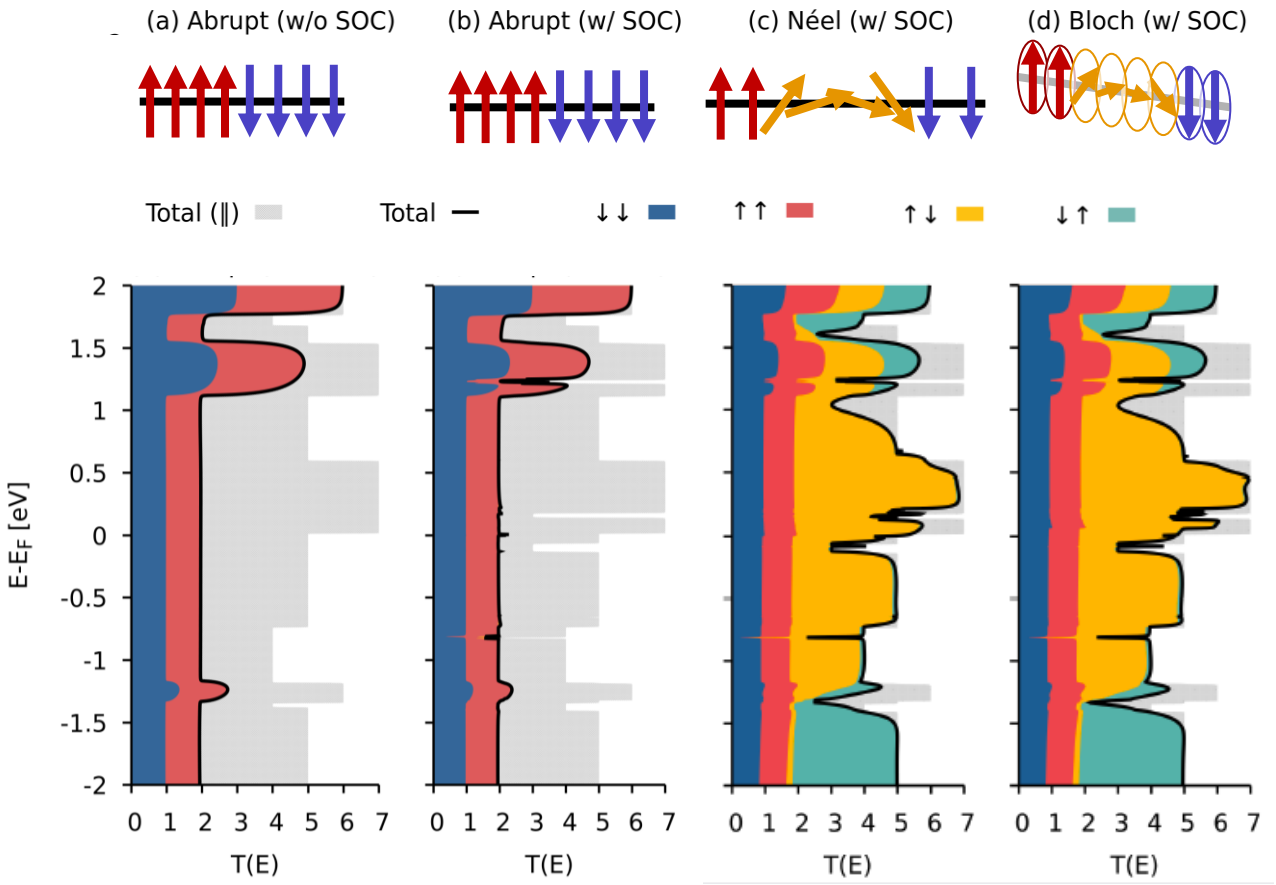




- All spin moments perpendicular to the chain axis
- Uniform change in spin direction along the domain wall

Simple picture: Pristine monatomic chain
→ Uniform magnetic coupling
→ **Uniform domain wall** ✓

Domain Wall Conductance – Iron Chain



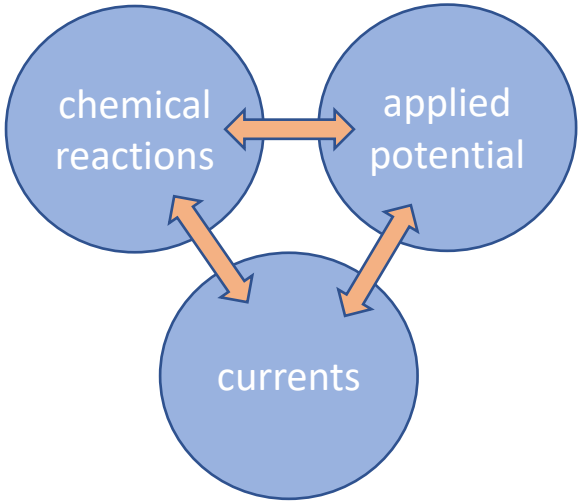
Abrupt domain wall

- No spin flips
- Small SOC effect

Smooth domain walls

- Significant spin flip
- Very similar for Néel and Bloch

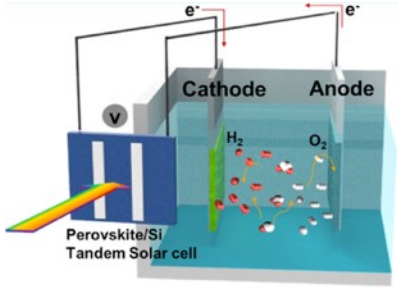
Understanding the electrified interface



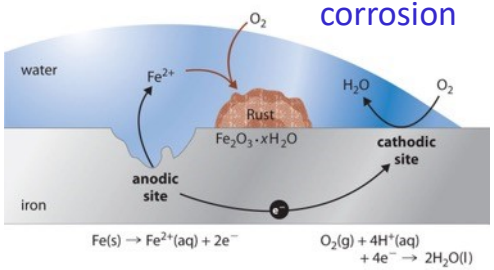
Electrochemical processes @ electrified interfaces at the atomic scale:

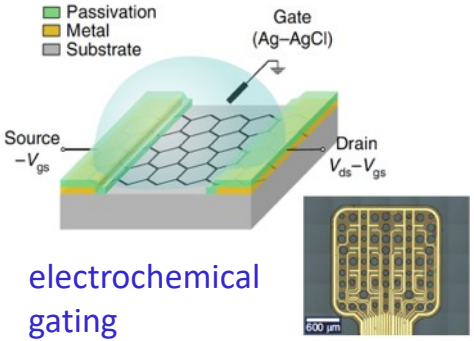
- deeper understanding
- accelerated discovery

water splitting

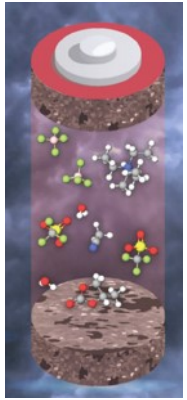


corrosion



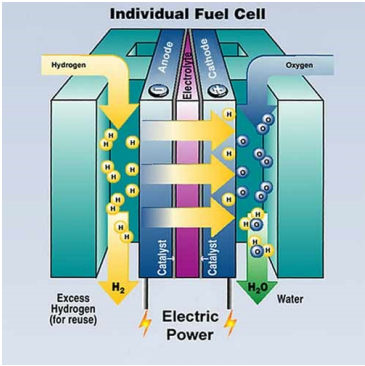


electrochemical gating

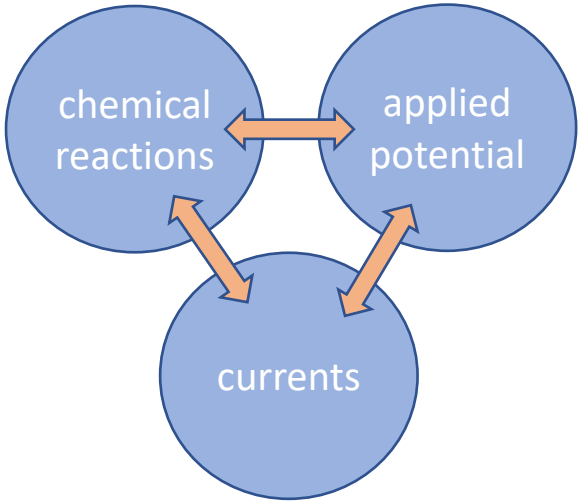


batteries
supercaps

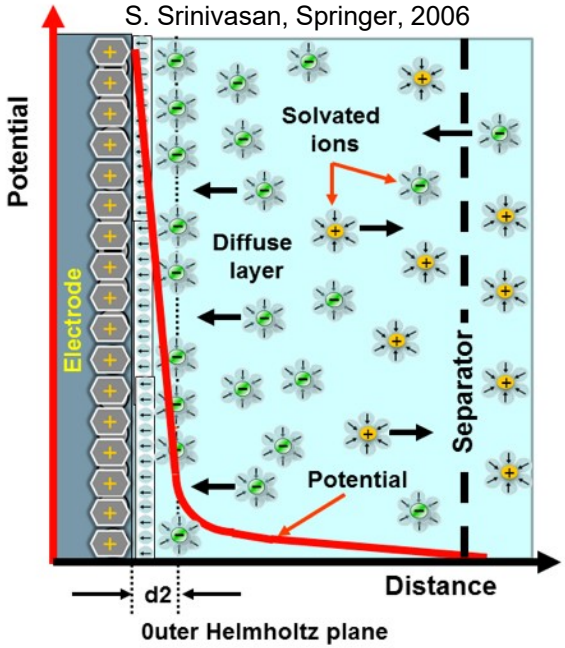
fuel cells



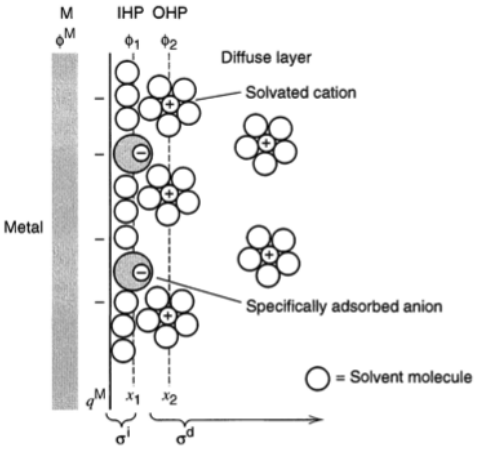
Understanding the electrified interface



S. Srinivasan, Springer, 2006



Bard and Faulkner, Wiley, 2001

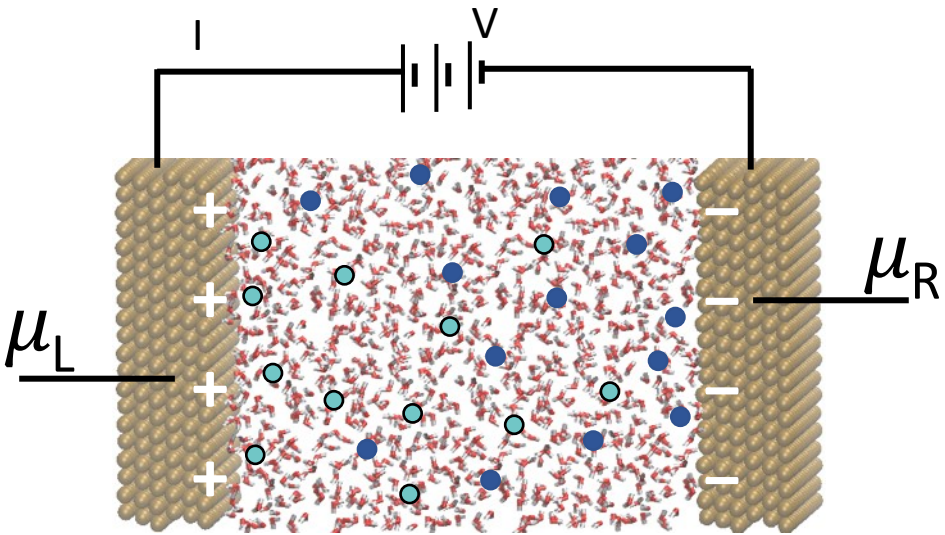


- Structure of the Double Layer
- Effect of the applied potential
- Currents (faradaic and non-faradaic)
- Chemical reactions

Challenges for first-principles modeling (DFT)

- Open systems (intensive quantities)
- Non-Periodic
- Semi-infinite electrodes

- Out of equilibrium:
  - Chemical potential is not unique
  - Flowing currents (ionic, electronic)
  - Electron transfer reactions (Faradaic)



Pedroza, Brandimarte, Rocha and Fernández-Serra
Chem. Sci. **9**, 62 (2018)

Proof-of-Concept Simulations

Au(111) electrodes + Water

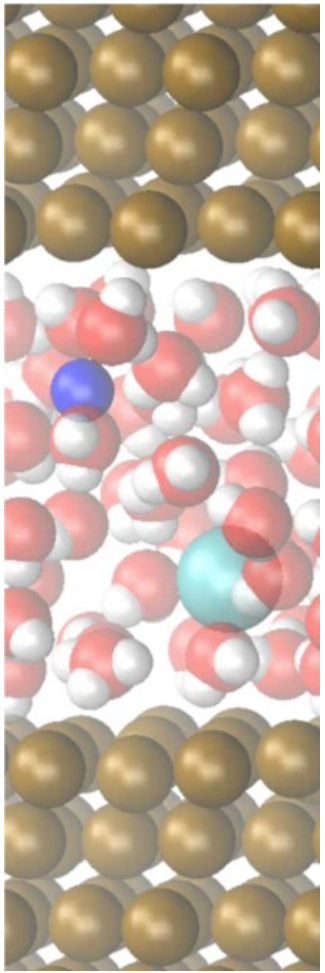
- pure H_2O
- H_2O with Na, Cl, and Na+Cl (at ~1.25 M)

Au(111) surface: (3x4) supercell in-plane
2 layers for each electrode in simulation box
(attached to semi-infinite electrodes)

40 Water Molecules
~ 17Å between electrodes (~ 5 water layers)

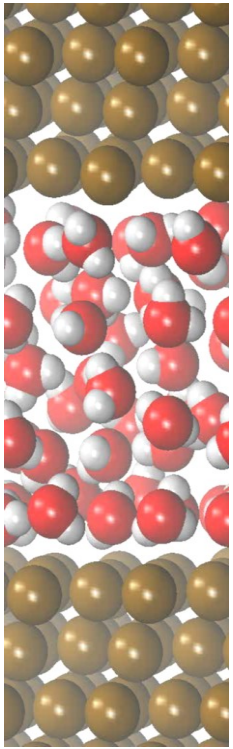
- DFT: VdW functional of Dion et al., PRL 92, 246401 (2004)
- Molecular Dynamics: 4ps; Beredsen thermostat (300K)
- Γ point in the surface plane
- 200 Ry real space mesh
- DZP basis

siesta

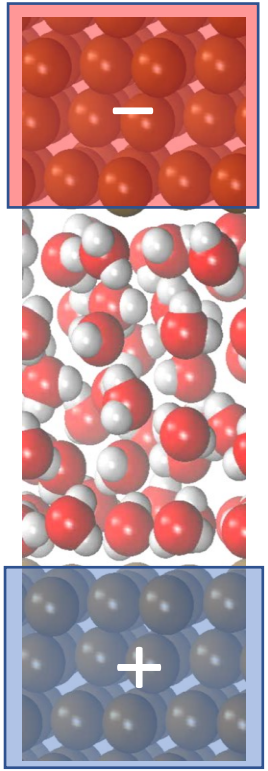


Water at zero and finite bias

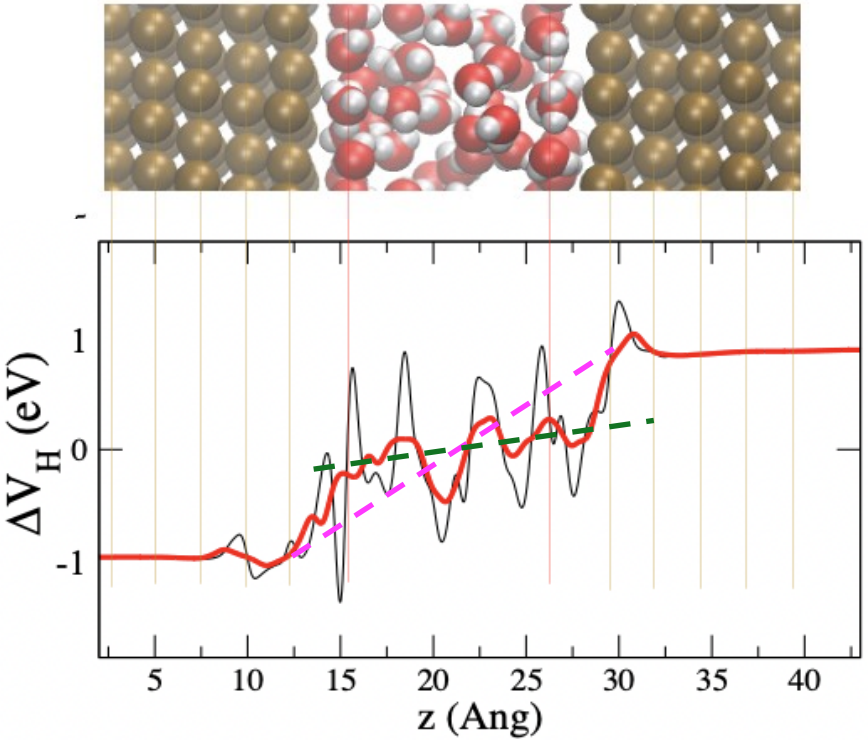
V = 0 V



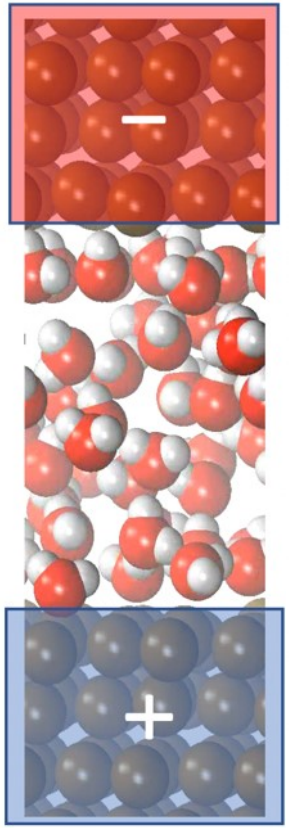
V = -2 V

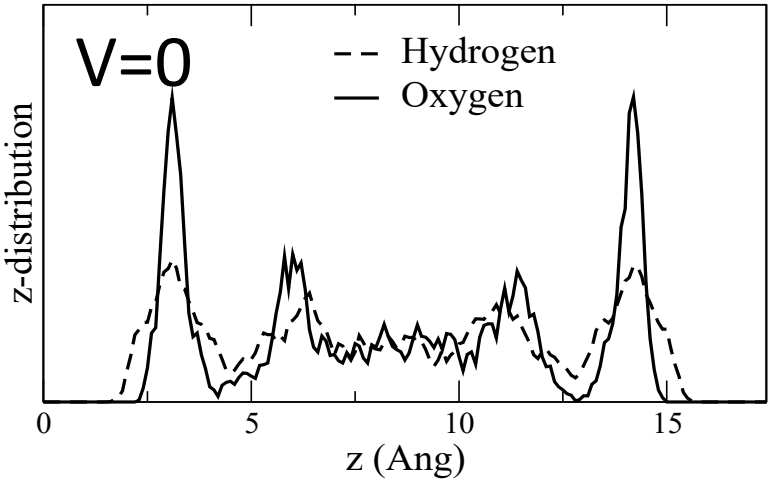


V = -2 V

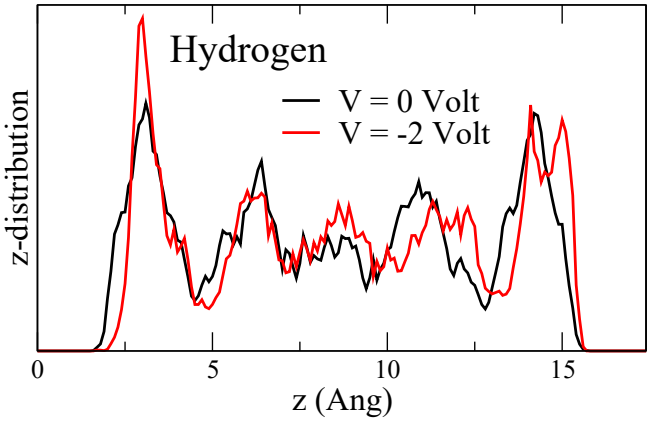


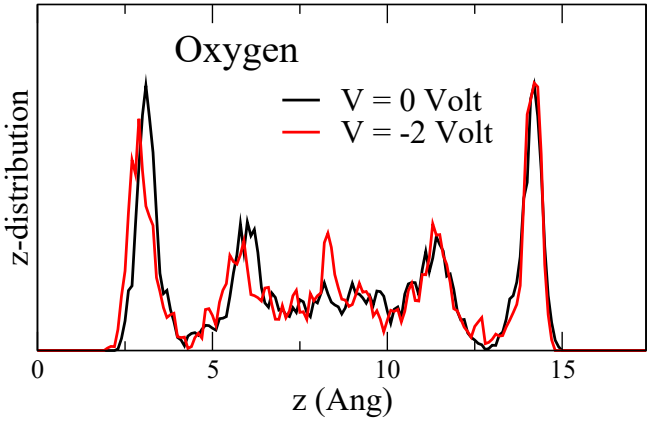
Water Structure



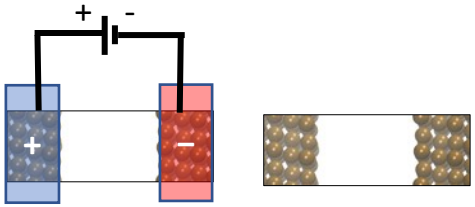


- Stronger layering induced by the bias
- Reorientation of water molecules: H towards negative; O towards positive electrode

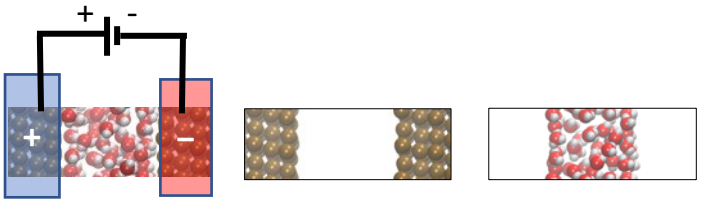




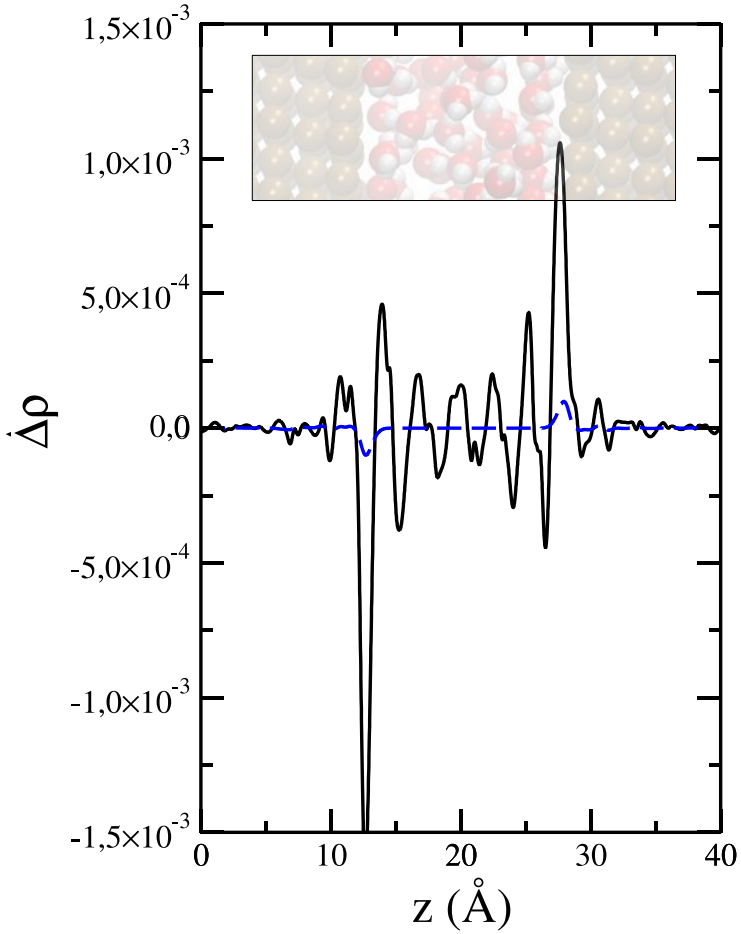
Bias and Surface Charges



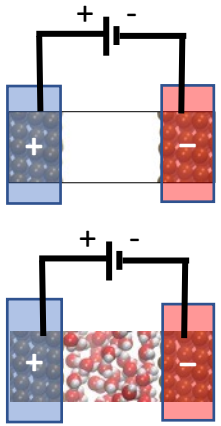
$$\Delta\rho = \rho^{V} - \rho^{V=0}$$



$$\Delta\rho = \rho^{V} - \rho_{Au} - \rho_{h2o}$$



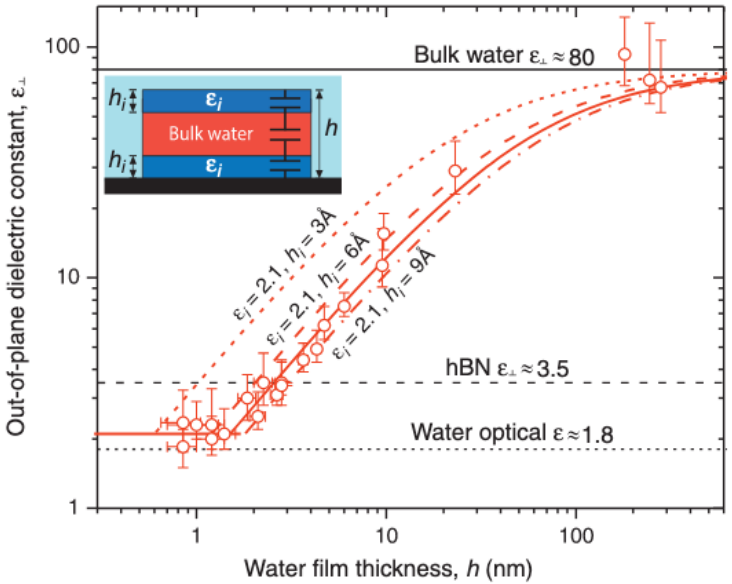
Capacitance and Permittivity



$$C = \frac{Q}{V} = \frac{\varepsilon A}{d}$$

$$\frac{Q}{Q_v} = \varepsilon$$

V=-0.25 → $\varepsilon \sim 13$



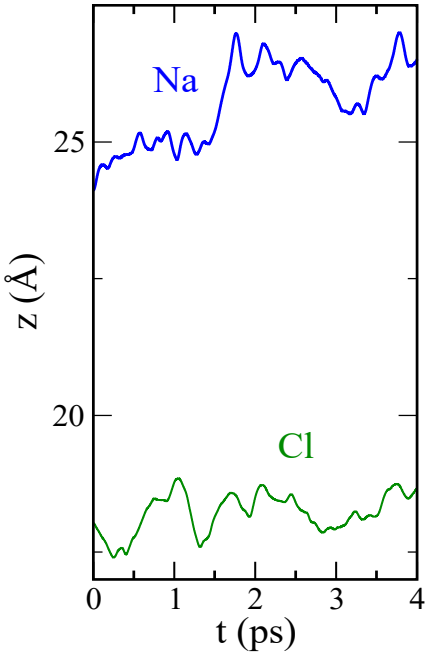
- Experimentally, for **bulk** water: $\varepsilon \approx 80$
- ε is much reduced for nano-confined water
- Experiment: water **nano-confined** in hBN slits:

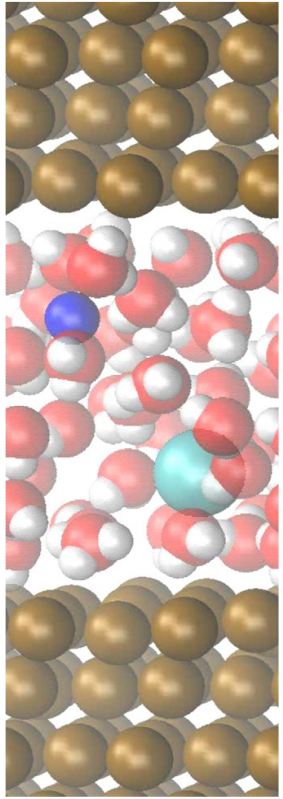
$$\varepsilon \sim 3 \text{ for } d \sim 17\text{Å}$$

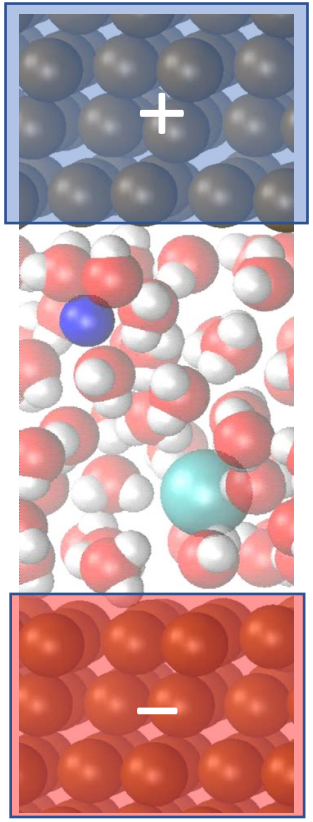
[see e.g. Fumagalli et al, Science **360**, 1339 (2018)]

Ionic species in solution: Cl + Na

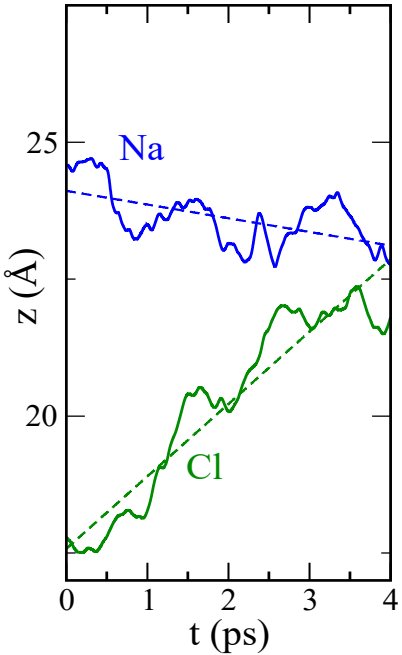
V = 0 V





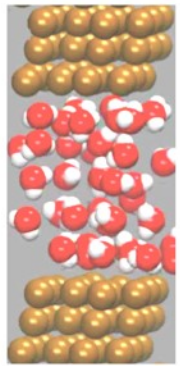


V = 1 V



Going to larger systems

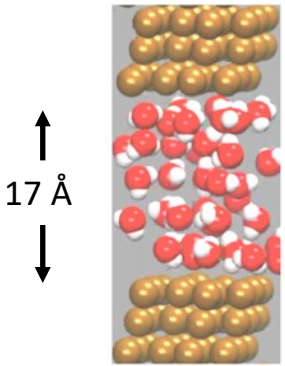
17 Å



40

12 / layer

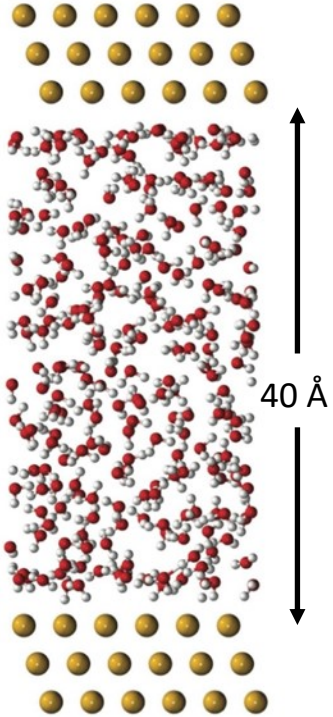
Going to larger systems



17 Å

40

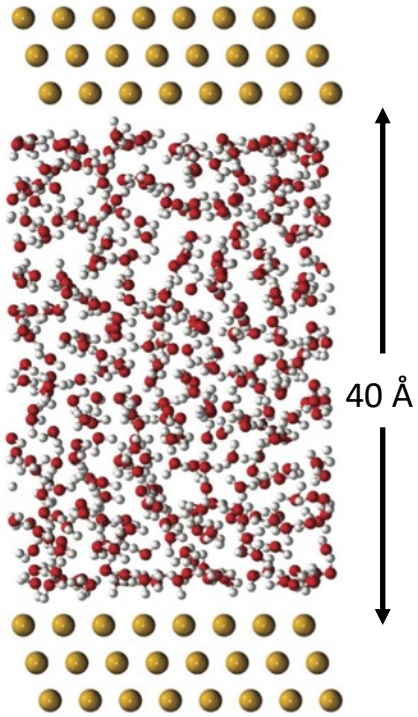
12 / layer



40 Å

236

30 / layer



40 Å

378

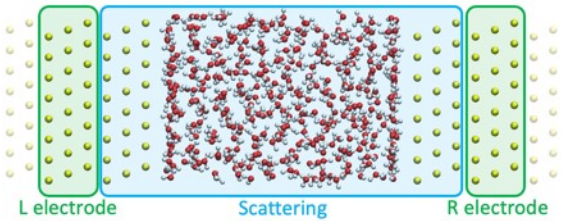
46 / layer

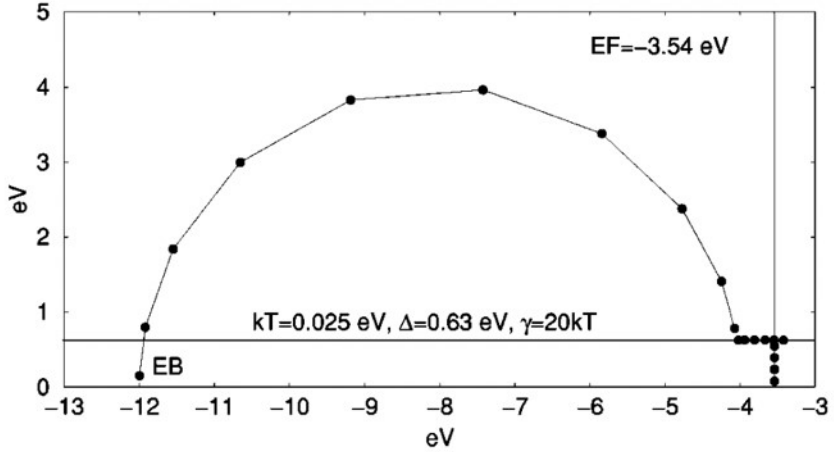
HPC: Parallelization

siesta

Green's function

$$G(z) = [z - H - \Sigma_L(z) - \Sigma_R(z)]^{-1} \quad (z = \varepsilon + i\eta)$$





Hybrid Parallelization Strategy:

- MPI: energies and k-points over processors (~100)

236
30 / layer

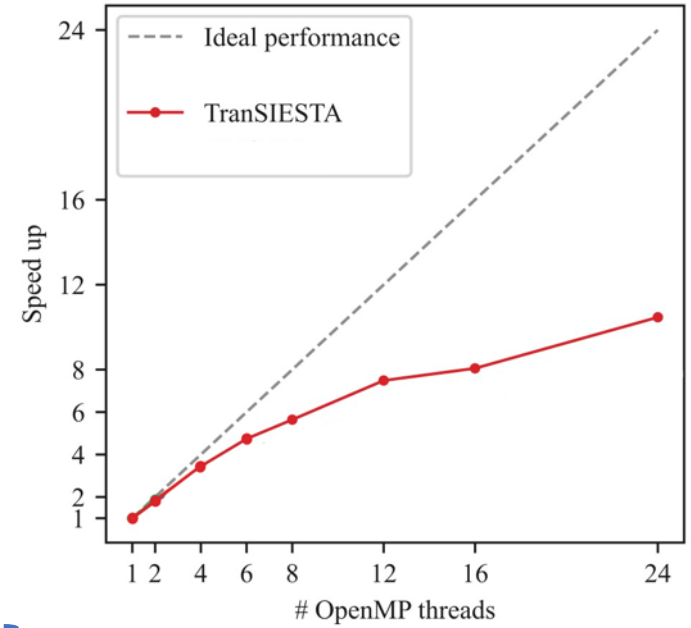
Inversion of matrices of size ~ 10.000 x 10.000

HPC: Parallelization

siesta

Green's function

$$G(z) = [z - H - \Sigma_L(z) - \Sigma_R(z)]^{-1} \quad (z = \varepsilon + i\eta)$$



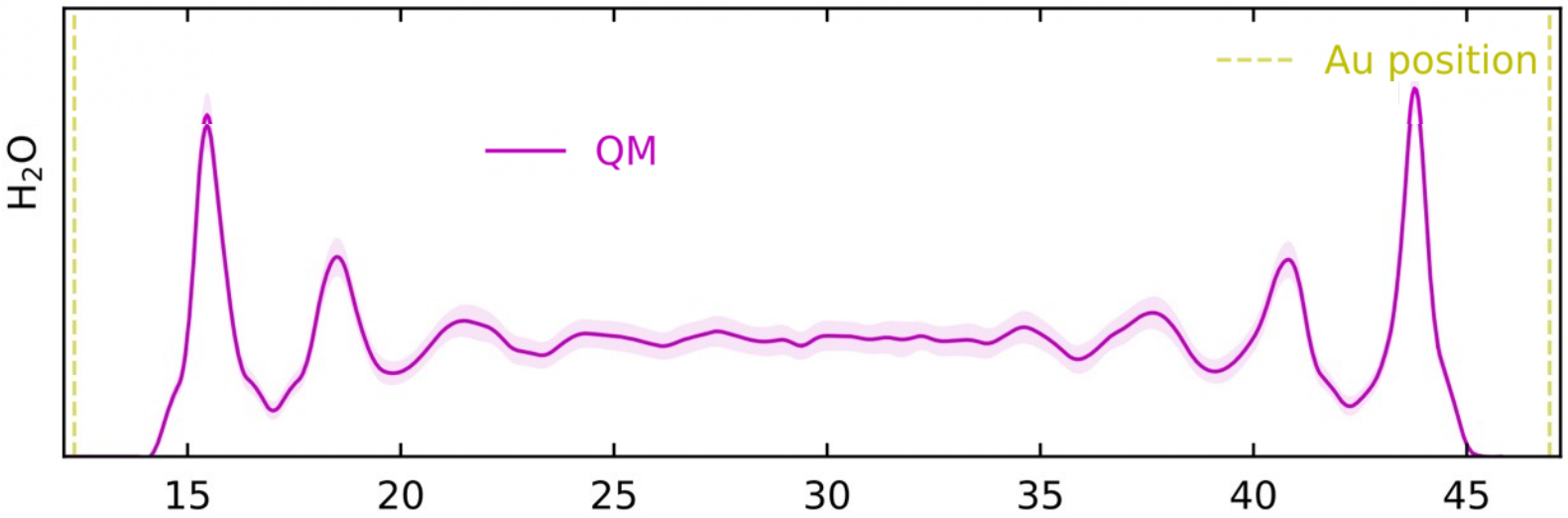
Hybrid Parallelization Strategy:

- MPI: energies and k-points over processors (~100)
- OpenMP (shared memory) throughout the code (4-12)

Parallel runs in 400 – 1.200 nodes

- MPI for distributed inversion (in progress) → **Massively Parallel runs in 4.000 – 40.000 nodes**

Going to larger systems



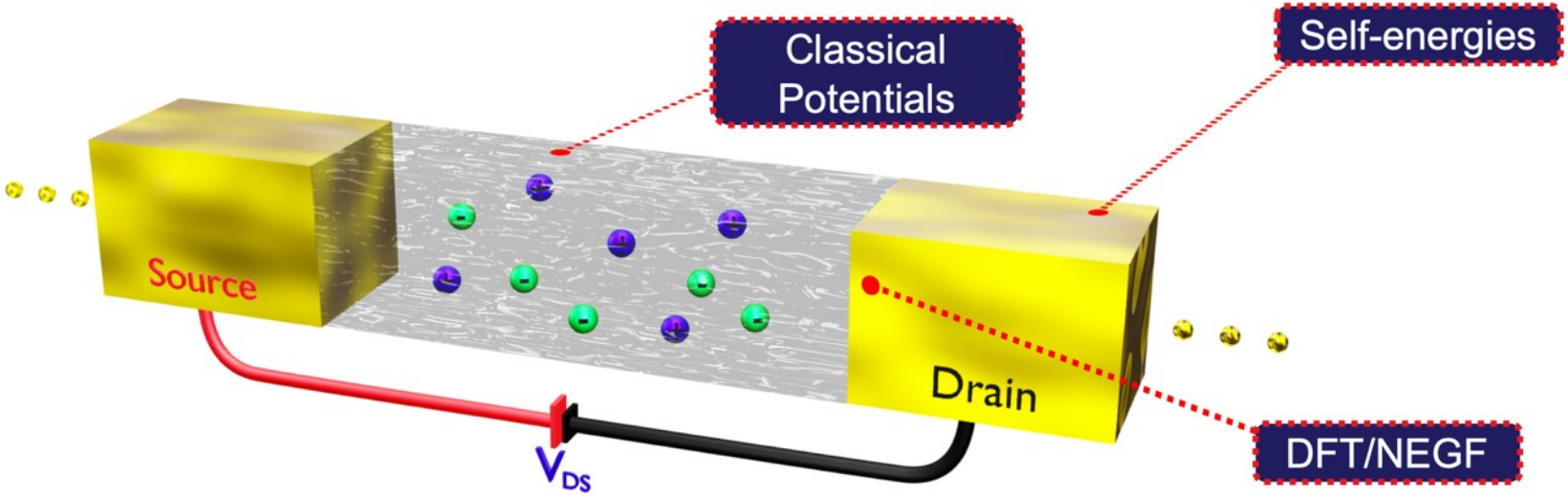
236

30 / layer

30 ps simulation

Going to larger systems: Hybrid QM/MM approach

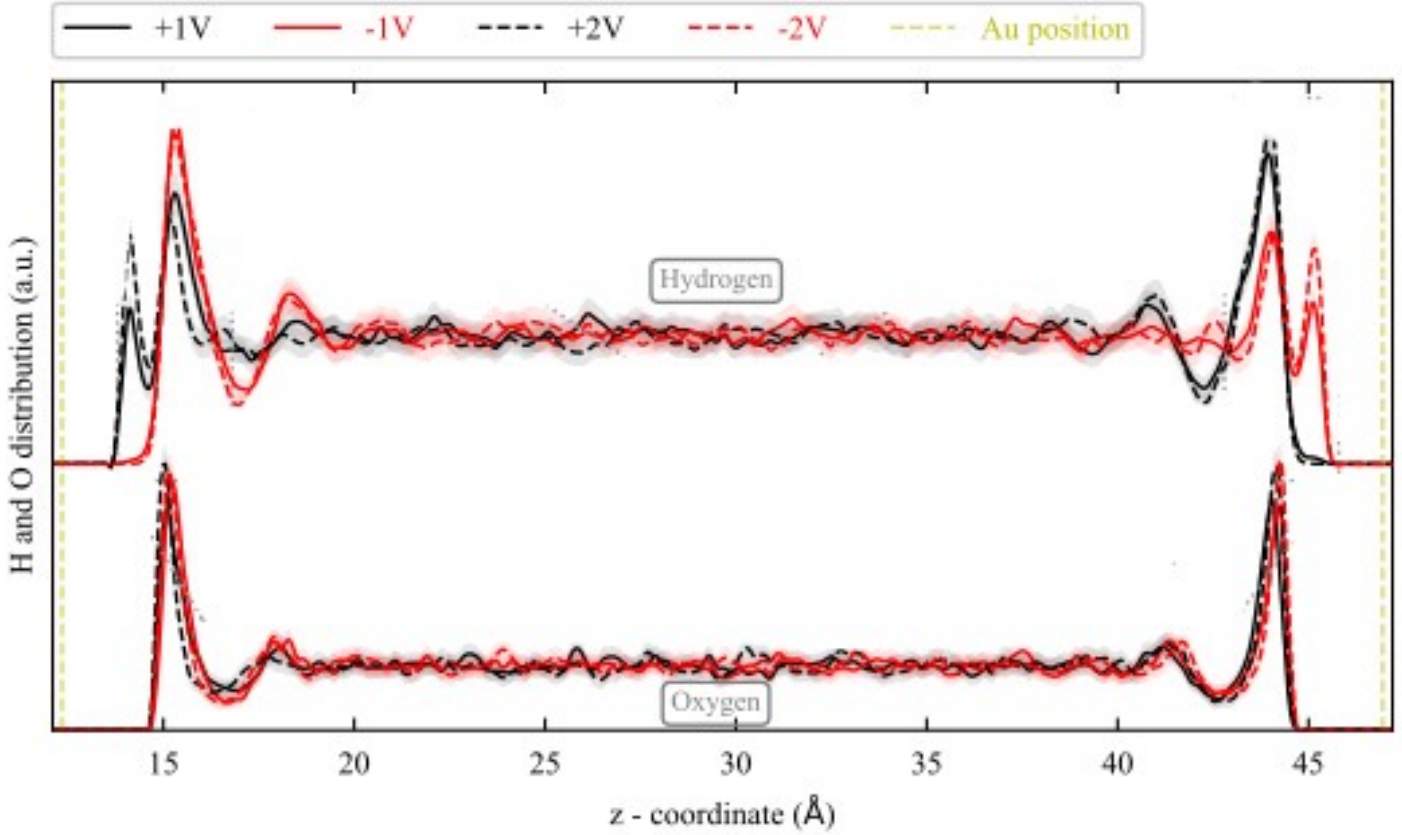
Sanz-Navarro et al., Theor. Chem. Acc., 128:825-833 (2011)
Crespo et al., J. Phys. Chem. B, 107, 13728-13736 (2003)



MM: Solvent, Ions in solution

QM: Metallic electrodes (screening; exchange of electros with electrolyte; external bias...)
Chemical species in the electrolyte which undergo chemical reactions

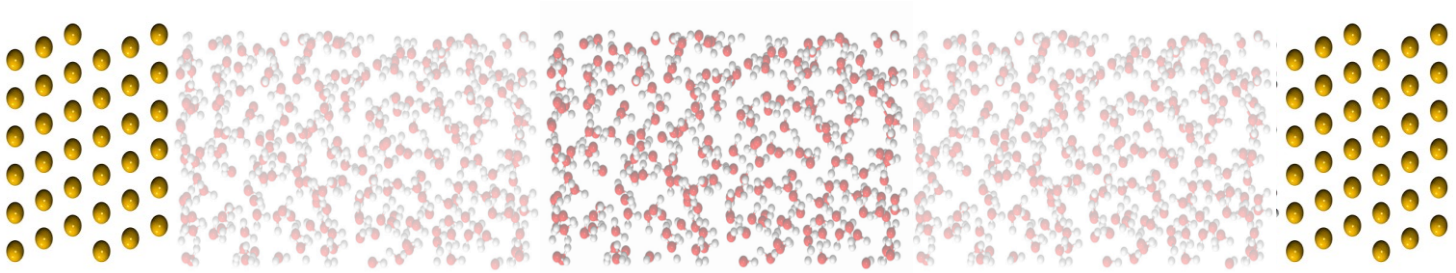
QM/MM: structure of water under bias



Scaling vs system size

Scaling: From 236 to 2360 H_2O molecules

$Au - (H_2O)_{236 \times n} - Au$ from n=1 to 10



n = 3

MareNostrum IV @ BSC
Intel Platinum 8160 @ 2.1 GHz

384 cores
96 MPI processes
4 openMP threads / MPI process

Barcelona Supercomputing Center
Centro Nacional de Supercomputación

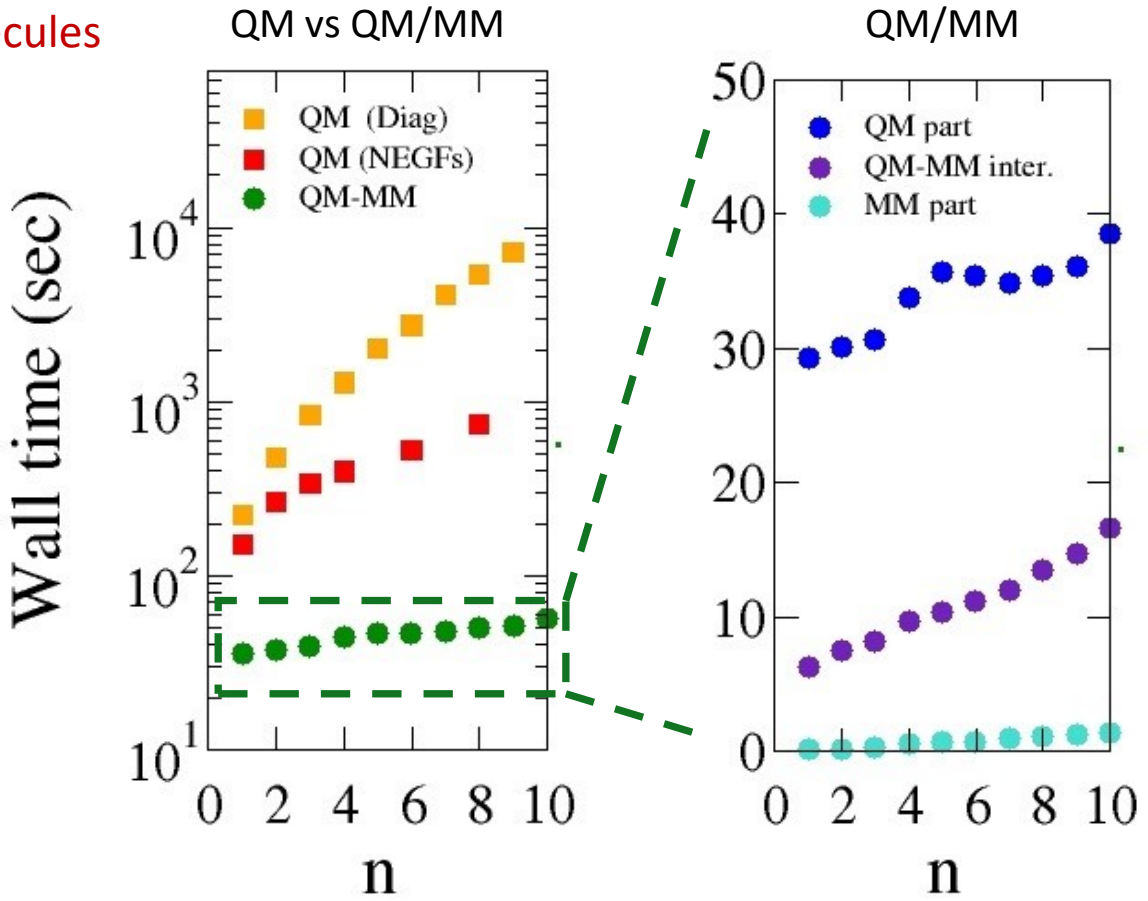
Scaling vs system size

Scaling: From 236 to 2360 H_2O molecules

$Au - (H_2O)_{236 \times n} - Au$

Wall time for 1 MD step

In 384 cores, for n=1:
QM/MM: 1ps / day
QM (NEGF): 0.1ps / day



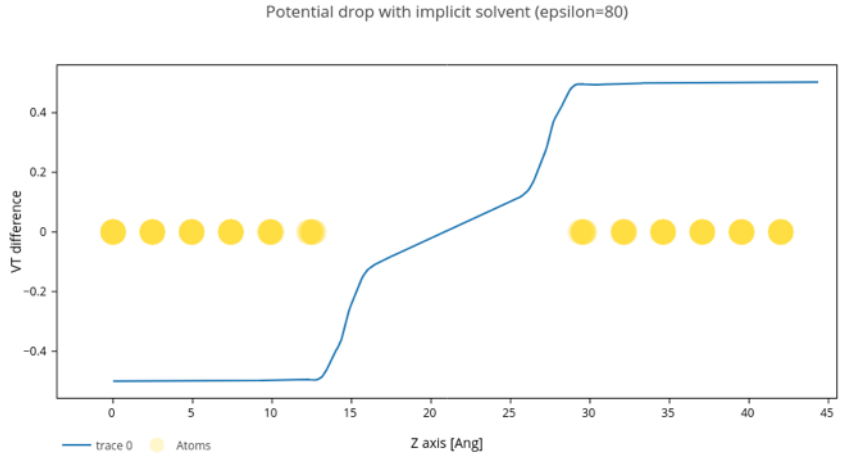
Going beyond - Continuum solvents

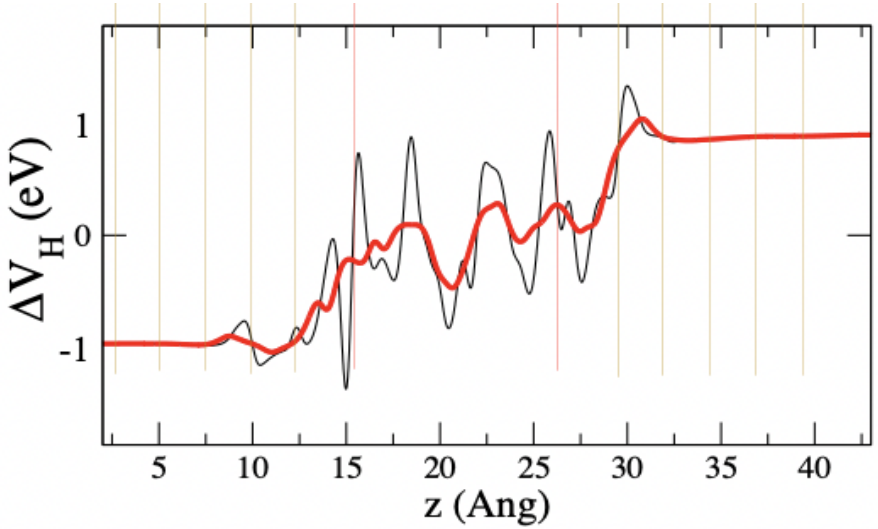
A generalized Poisson and Poisson-Boltzmann solver for electrostatic environments

G. Fisicaro ; L. Genovese; O. Andreussi; N. Marzari; S. Goedecker

J. Chem. Phys. 144, 014103 (2016)

- Dielectric medium - Generalized Poisson equation (neutral solvent)
- Poisson – Boltzmann equation (ionic solution)





Summary

- TranSIESTA for spintronics: Spin-orbit coupling and non-collinear spin states
- Analysis of the transmission in spin channels; spin flipping processes

- TranSIESTA for electrochemistry: a tool to study electrified solid / liquid interfaces from first principles
- Proof of concept: Water on Gold
- Combining QM with MM: speed-up and scale-up
- Efficient parallelization for hundreds of cores; near future - tens of thousands
- Further multiscale approaches (continuous solvents, Poisson-Boltzmann) in progress

Acknowledgements

Marivi Fernandez-Serra
Stony Brook

Pol Febrer
ICN2

Nils Wittemeier
ICN2

Ramón Cuadrado
(now at Univ. Southampton)

Ernane de Freitas
(RMIT / ICN2)

Federico Padron
ICN2

Nick Papior
(now at DTU)

Alberto García
ICMAB - Barcelona

Acknowledgements

Co-funded by the European Union

EuroHPC Joint Undertaking

Grant No 101093374 — MaX.

MAX DRIVING THE EXASCALE TRANSITION

MINISTERIO DE CIENCIA E INNOVACIÓN

Financiado por la Unión Europea NextGenerationEU

Plan de Recuperación, Transformación y Resiliencia

AGENCIA ESTATAL DE INVESTIGACIÓN

Grant PCI2022-134972-2 funded by MCIN/AEI/ 10.13039/501100011033 and by the European Union NextGenerationEU/PRTR.

GOBIERNO DE ESPAÑA MINISTERIO DE CIENCIA E INNOVACIÓN

EXCELENCIA SEVERO OCHOA

Grant No. SEV-2017-0706

Supercomputing resources at MareNostrum IV

RES RED ESPAÑOLA DE SUPERCOMPUTACIÓN

BSC Barcelona Supercomputing Center Centro Nacional de Supercomputación