Atomic-Scale Modelling of Charge Transport Across Interfaces

Kurt Stokbro, QuantumWise A/S

Outline

QuantumWise

Density Functional Theory

Quantum Transport

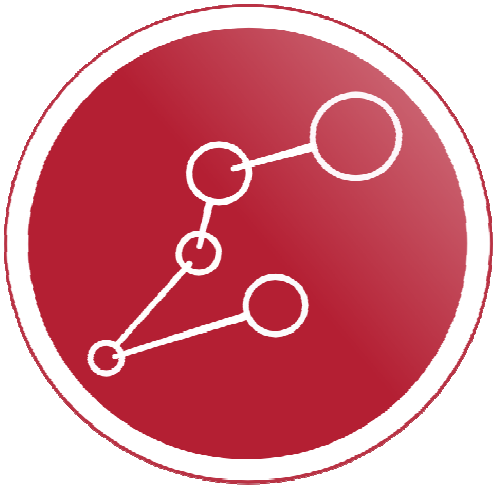
Simulation of Interfaces

Simulation of Batteries

Company background

- We love science/physics - and in particular atomic scale simulations
- Help customers be more successful in atomic-scale modelling
- Internal development of quantum-mechanical simulation engines combined with community codes in certain areas
- Founded 2008, with Headquarter in Copenhagen, Denmark
- 30 FTEs; majority has a PhD (+3-5/year)
- Sales reps in USA, Singapore, Japan
- Resellers in India, China, Taiwan, Korea, …
- Profitable with 30% growth rate – no external capital

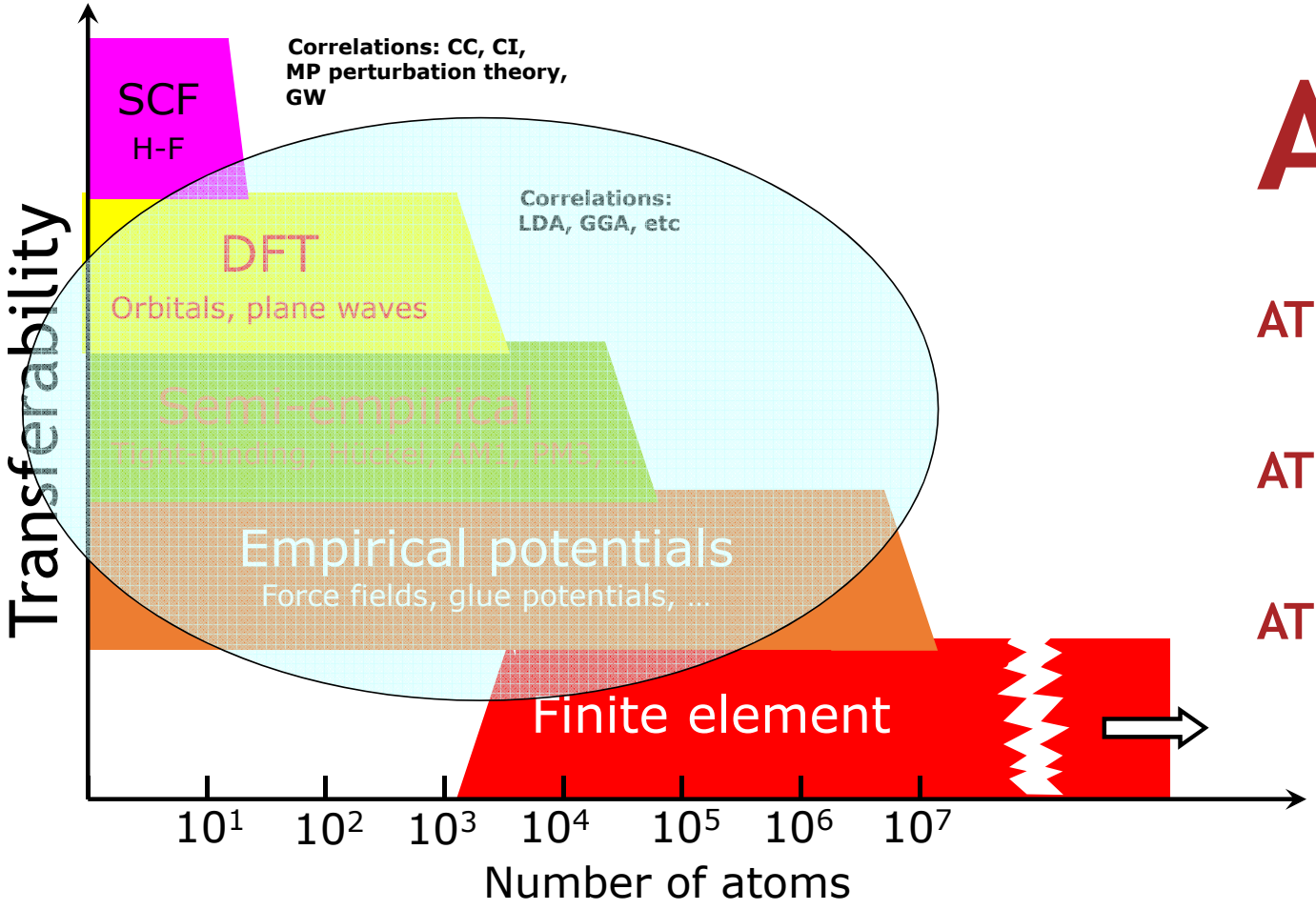
QuantumWise



BØRSEN. GAZELLE 2015

- More than 300 users worldwide
- Rapidly expanding number of academic and industrial users

Atomistix ToolKit (ATK)



ATK

FHI-aims (full potential)
Abinit (Plane Waves)

ATK-DFT (LCAO)

ATK-SE

ATK-Classical

Macro scale

Python interface to atomic-scale simulations

Geometry

Molecule
Bulk
Surface configuration
Device

Geometry →

Calculators

DFT
SemiEmpirical
Classical

Energy
Forces
Stress →

Dynamics

Geometry Optimization
Molecular Dynamics
(NVE, NVT, NPT)
Genetic structure finder
Nudged Elastic Bands
Adaptive Kinetic Monte-Carlo

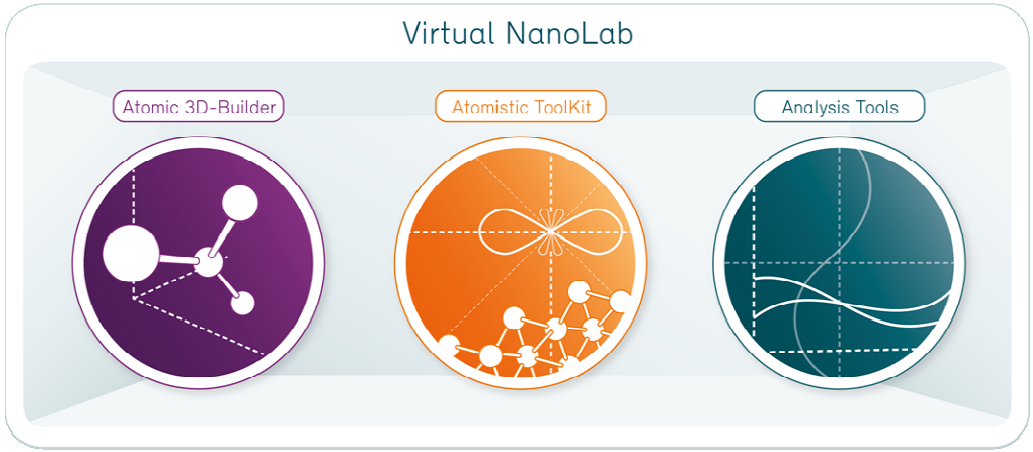
Band structure
DOS
Complex band structure
Effective band structure
Effective mass
Piezoelectric properties
Optical properties
ELF
Bloch states
Total energy
Electron density
Potential

Forces, stress
Local stress/atoms
Dynamical matrix
Elastic constants
Phonon spectrum/DOS

Deformation potential
Mobility
Inelastic current

Transmission spectrum
I-V curve
Local/device DOS
Transmission eigenstates
Transmission pathways
Current density
Spin transfer torque

Virtual NanoLab with the Atomistix ToolKit (ATK)



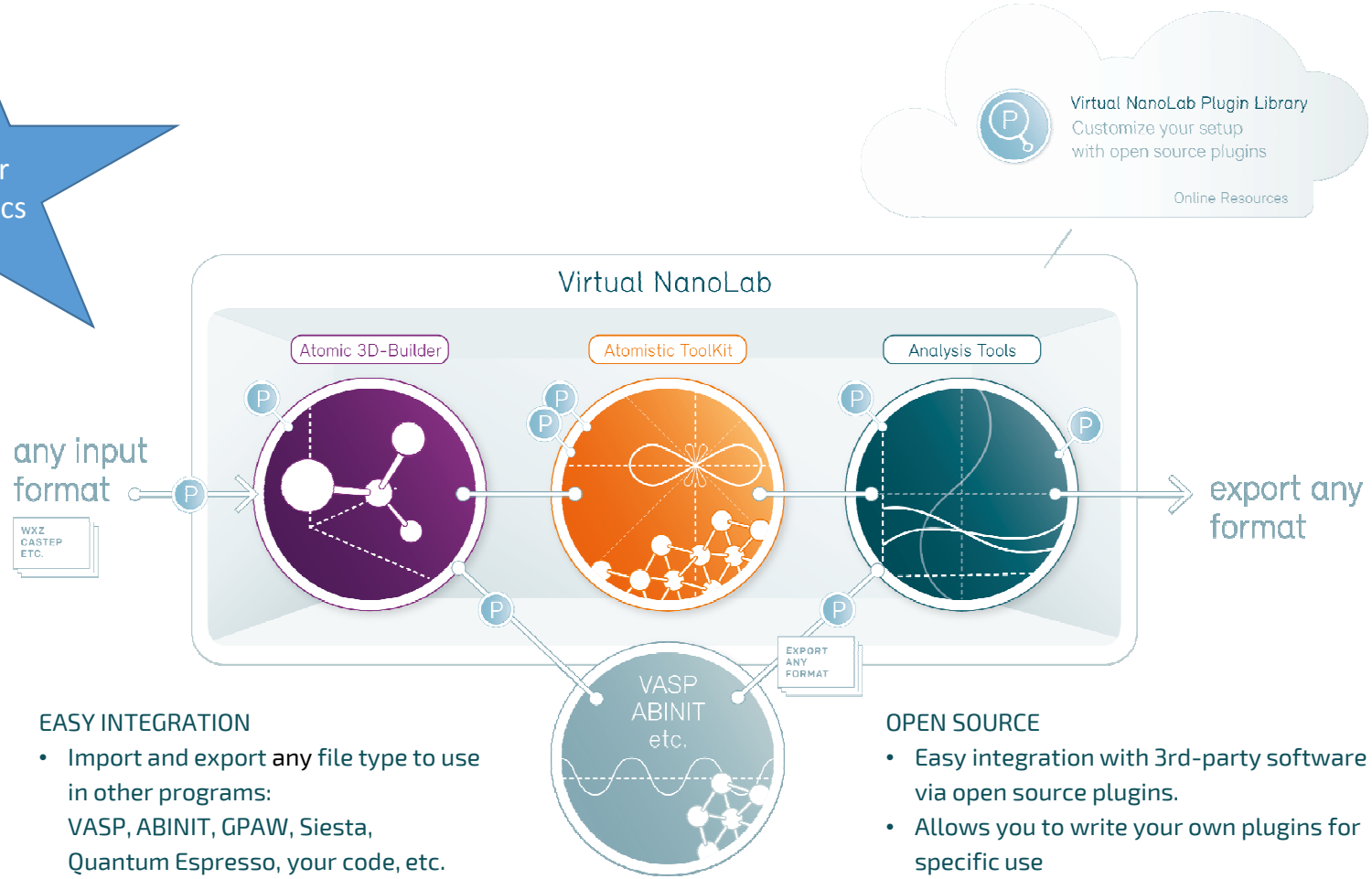
Build
Interfaces
Nanotubes
Nanosheets
Nanopribbons
Molecules
Crystals by symmetry
Cleave surfaces
Polycrystals

Methods
DFT
Semi-Empirical
Classical potentials
(Abinit)
(FHI-Aims)
Non-Equilibrium Green's Functions (NEGF) formalism

Analyze results
3D visualizations, isosurfaces
Manipulate 3D grids
Band structure, density of states
MD trajectory analysis
Analyze and visualize your data
Produce movies and animated GIFs

Virtual NanoLab, GUI for ATK and other simulators

Free for academics



EASY INTEGRATION

- Import and export any file type to use in other programs:
  VASP, ABINIT, GPAW, Siesta,
  Quantum Espresso, your code, etc.

OPEN SOURCE

- Easy integration with 3rd-party software via open source plugins.
- Allows you to write your own plugins for specific use

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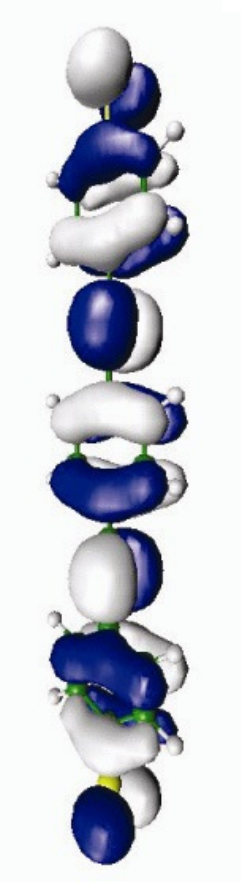
The Schrödinger equation



Kinetic energy

Potential energy between ions

Electrostatic energy from other electrons!

$$H = -\sum_i \frac{\hbar^2 \nabla_i^2}{2m} - \sum_{i,I} \frac{Z_I e^2}{|R_I - r_i|} + \sum_{i<j} \frac{e^2}{|r_j - r_i|}$$

$$H\,\psi(r_1,\ldots,r_n) = E_0\,\psi(r_1,\ldots,r_n)$$

In DFT we only need to solve a one-electron Schrödinger equation

$$\left[-\frac{\hbar^2\nabla^2}{2m} + V_{eff}[n(r)]\right]\psi_\alpha(r) = \varepsilon_\alpha\,\psi_\alpha(r)$$

1. The Kohn-Sham functional

$$H = -\sum_i \frac{\hbar^2 \nabla_i^2}{2m} - \sum_{i,I} \frac{Z_I e^2}{|R_I - r_i|} + \sum_{i<j} \frac{e^2}{|r_j - r_i|}$$

1. The Kohn-Sham functional

The ground state energy can be found by minimizing the Kohn-Sham functional with respect to the density.

Kinetic energy of non interacting electron gas with density *n*

Electrostatic energy from the ions

Average repulsion from the other electrons, called the Hartree energy

All the missing terms

$$E_{KS}[n] = T[n] - e^2 \sum_I \int \frac{Z_I\, n(r)}{|R_I - r|} dr + \frac{1}{2} e^2 \iint \frac{n(r) n(r')}{|r - r'|} dr dr' + E_{XC}[n]$$

$$H = -\sum_i \frac{\hbar^2 \nabla_i^2}{2m} - \sum_{i,I} \frac{Z_I e^2}{|R_I - r_i|} + \sum_{i<j} \frac{e^2}{|r_j - r_i|}$$

2. The Kohn-Sham equations

Calculate the kinetic energy of a non-interaction electron gas with effective potential $V_{eff}(r)$

$$H_{1el} = -\frac{\hbar^2\nabla^2}{2m} + V_{eff}(r)$$

$$H_{1el}\,\psi_\alpha(r) = \varepsilon_\alpha\,\psi_\alpha(r)$$

$$n(r) = \sum_{\alpha\in occ} |\psi_\alpha|^2$$

Must be the same as the density of the interacting electron gas

$$T = \sum_{\alpha\in occ} \left\langle \psi_\alpha \left| -\frac{\hbar^2\nabla^2}{2m} \right| \psi_\alpha \right\rangle$$

How to find $V_{eff}(r)$ such that the density is similar to the interacting electron gas?

2. The Kohn-Sham equations

Because the Kohn-Sham functional is variational, we have for the ground state density

$$\frac{\delta E_{KS}[n]}{\delta n} = 0$$

Because the Kohn-Sham functional is variational, we have for the ground state density

$$\frac{\delta E_{KS}[n]}{\delta n} = 0 \Rightarrow V_{eff}(r) = -e^2 \sum_I \frac{Z_I}{|R_I - r|} + e^2 \int \frac{n(r')}{|r - r'|} dr' + \frac{\delta E_{XC}[n]}{\delta n}$$

2. The Kohn-Sham equations

Ion potential

Hartree pot.

XC potential

$$\frac{\delta E_{KS}[n]}{\delta n} = 0 \Rightarrow V_{eff}(r) = -e^2 \sum_I \frac{Z_I}{|R_I - r|} + e^2 \int \frac{n(r')}{|r - r'|} dr' + \frac{\delta E_{XC}[n]}{\delta n}$$

Thus, $V_{eff}(r)$ is a functional of *n(r)*

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + V_{eff}[n(r)] \right] \psi_\alpha(r) = \varepsilon_\alpha \psi_\alpha(r)$$

$$n(r) = \sum_{\alpha \in occ} |\psi_\alpha|^2$$

Selfconsistent equations

The Kohn-Sham orbitals are often interpretated as real electrons and ε_α are to a good approximation the electron energies

The Local Density Approximation, LDA

$$E_{XC}[n] = \int \varepsilon_{xc}(n(r))dr$$

Perdew-Zunger, PRB 23, 5048 (1981)

The Generalized Gradient Approximation, GGA

$$E_{XC}[n] = \int \varepsilon_{xc}(n(r), \nabla n(r))dr$$

Perdew-Burke-Enzenhofer, PRL 77, 3865 (1996)

Meta-GGA functionals

$$E_{XC}[n] = \int \varepsilon_{xc}(n(r), \nabla n(r), \tau)dr$$

Becke-Johnson *J. Chem. Phys.*, 124, 221101 (2006)

Hybrid functionals

$$E_{XC}[n] = \alpha E_X + (1-\alpha)E_X[n] + E_C[n]$$

B3LYP J. Phys. Chem. 98, 11623 (1994)

Summary DFT

- Select an exchange-correlation functional
- Perform a selfconsistent calculation of the density
- Get total energy, bandstructure, etc.

Summary: https://www.youtube.com/watch?v=Fnr_1AShksE
Youtube search quantumwisetv DFT three

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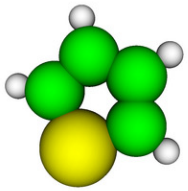
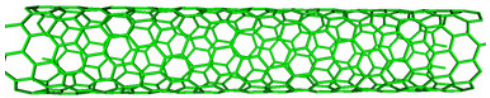
Electronic transport in nanostructures

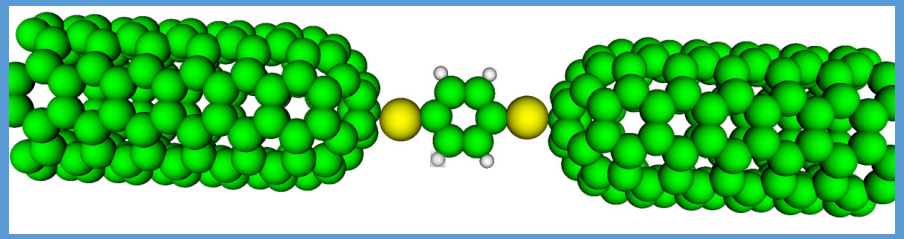
Traditional quantum-based software can model either

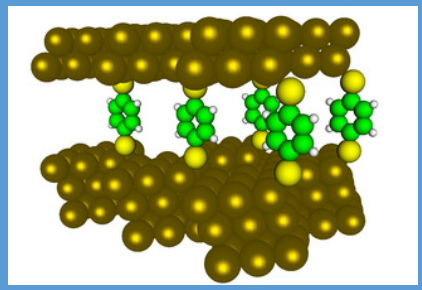
isolated molecules or periodic systems





Devices are more complex; need to model nanostructures combining molecules with periodic systems and macroscopic elements

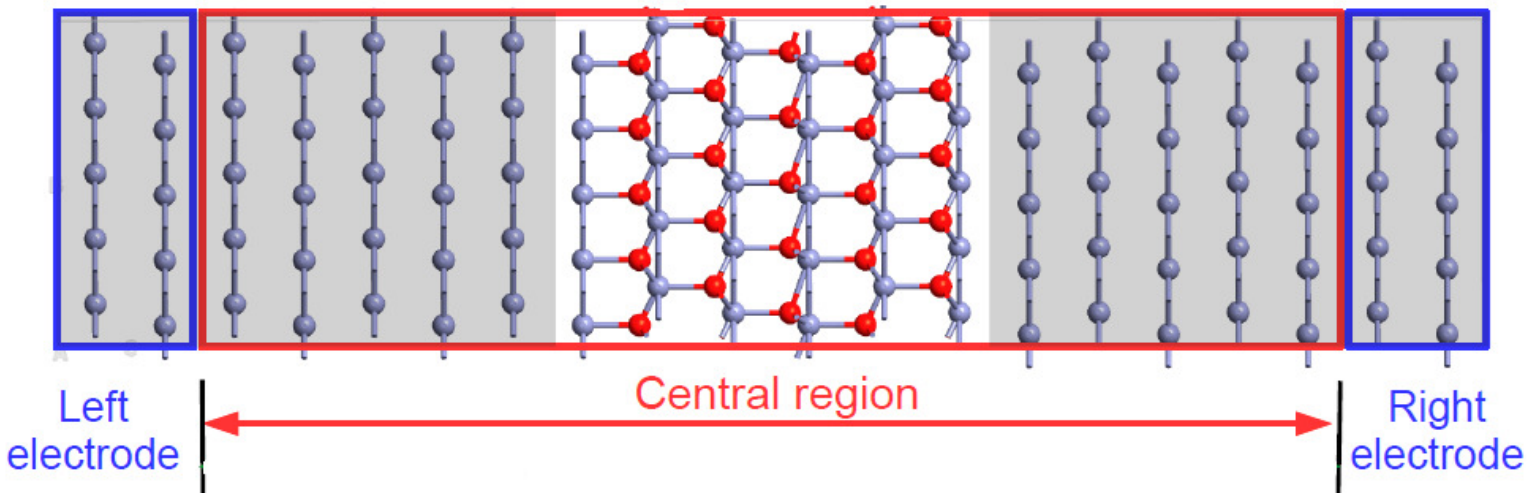




This enables simulations of electrical properties of complex nanoscale components and systems like transistors or gate stacks

M. Brandbyge, J.-L. Mozos, P. Ordejon, J. Taylor, K. Stokbro, Phys. Rev. B. **65**, 165401 (2002).

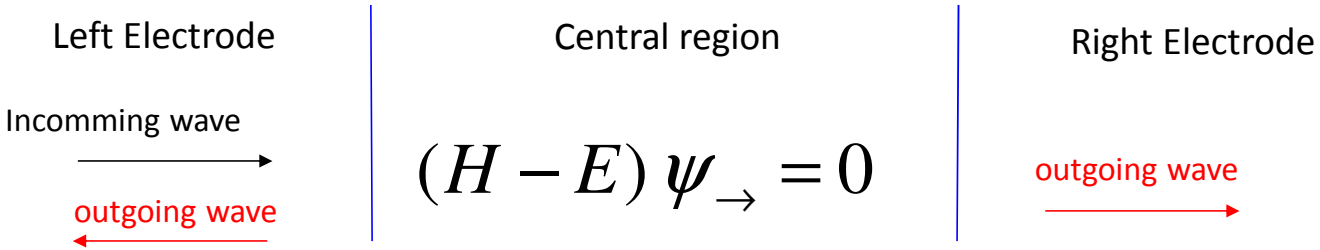
NEGF transport methodology



- The system is divided into 3 regions: left, central, right regions
- Properties of left and right regions are calculated using PBC
- The electron density of the central region is donated by the electrode reservoirs, i.e. open boundary conditions
- The electro-static potential of the central region is obtained from the density and using the electrode boundary conditions

M. Brandbyge, J.-L. Mozos, P. Ordejon, J. Taylor, K. Stokbro, Phys. Rev. B. **65**, 165401 (2002).

Open boundary conditions

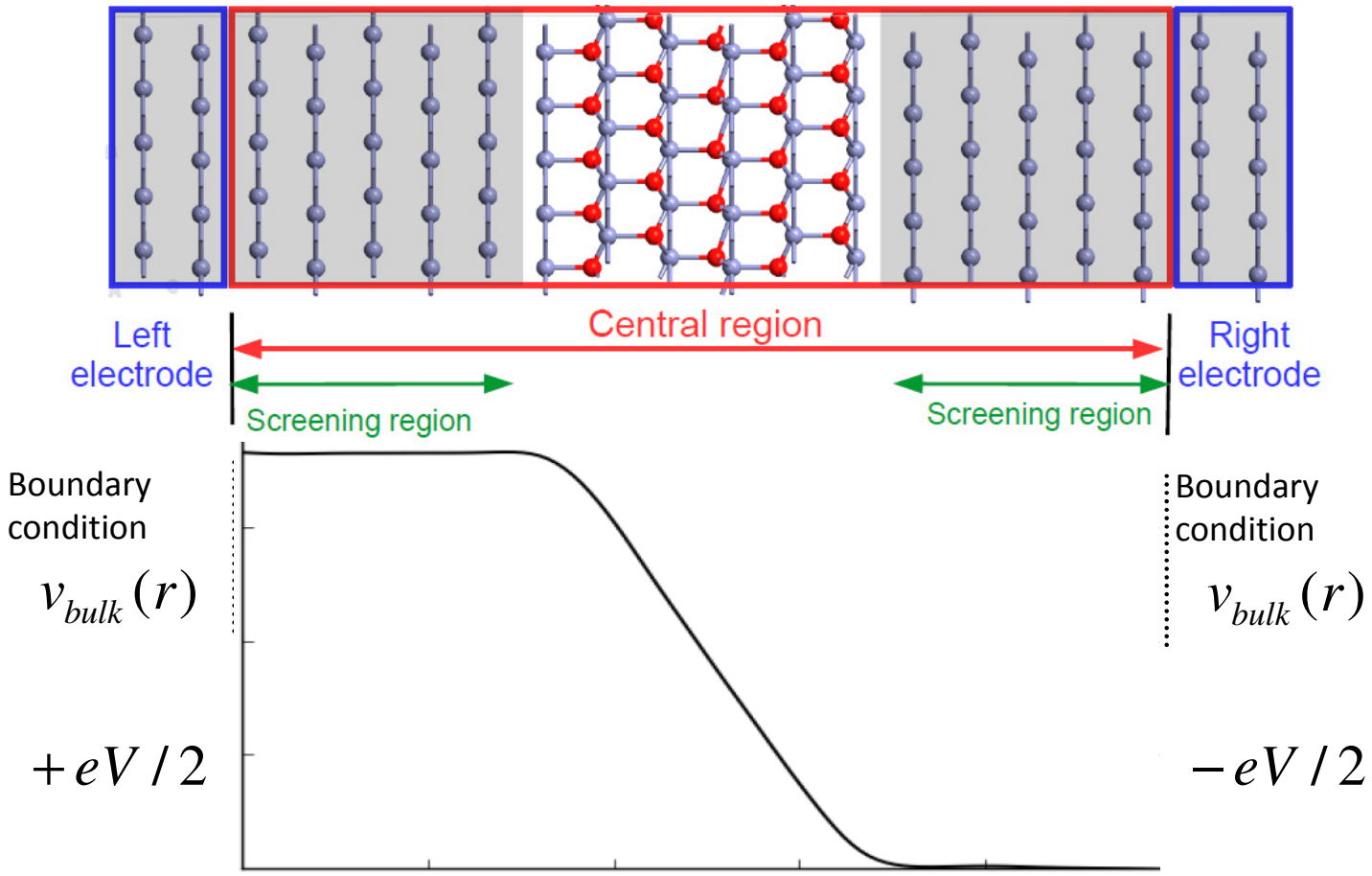


$$n(r)=\int_{-\infty}^{L}\left|\psi_{\rightarrow}(E,r)\right|^2 dE+\int_{-\infty}^{R}\left|\psi_{\leftarrow}(E,r)\right|^2 dE$$

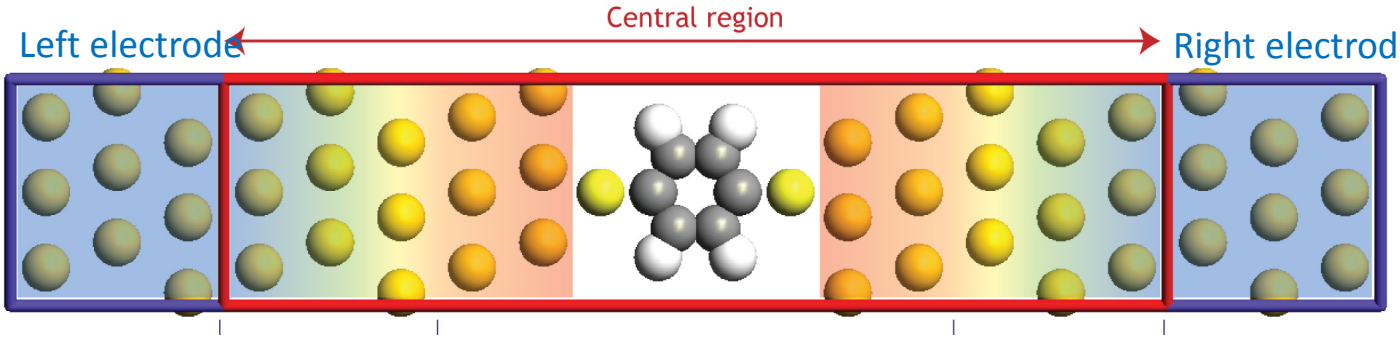
- For efficiency calculate n(r) using NEGF with complex contour integration

M. Brandbyge, J.-L. Mozos, P. Ordejon, J. Taylor, K. Stokbro, Phys. Rev. B. **65**, 165401 (2002).

Solving for the electro-statics



Self-consistent solution



Poisson solver

- Multigrid, FFT2D,

Non Equilibrium density

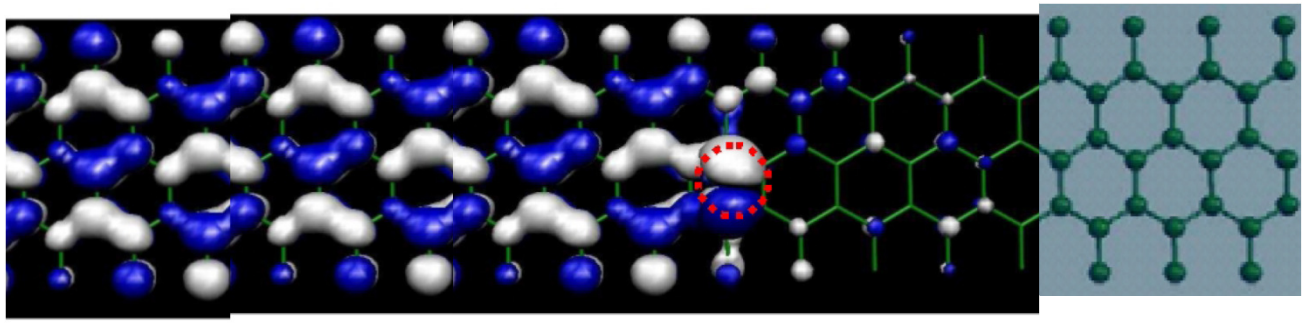
- Description of semi-infinite electrodes via self-energies
- Non-equilibrium electron distribution using NEGF

D

H

M. Brandbyge, J.-L. Mozos, P. Ordejón, J. Taylor, K. Stokbro, Physical Review **B 65**, 165401 (2002)

Electron transmission coefficients from Kohn-Sham Hamiltonian



Propagation of wave function in nanoscale structure,

Calculation of transmission amplitudes **t**

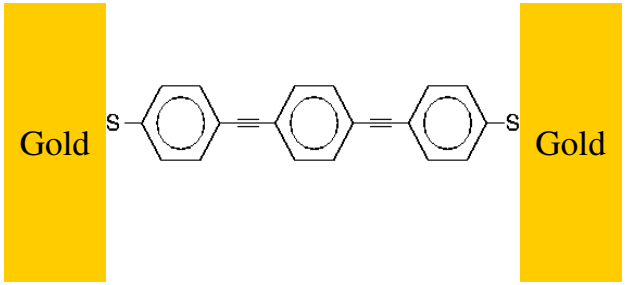
Calculation of current,

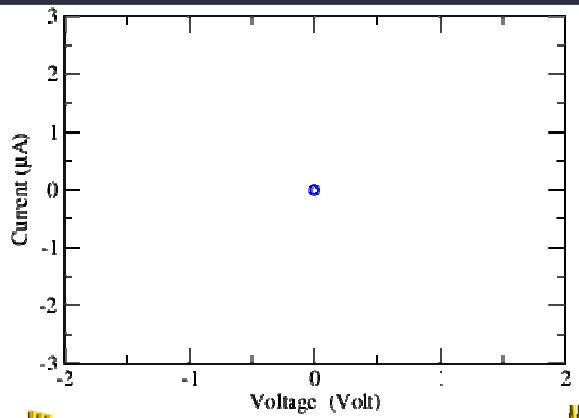
$$I = \frac{2e^2}{h} \int dE (f_R(E) - f_L(E)) T_{\text{tot}}(E)$$

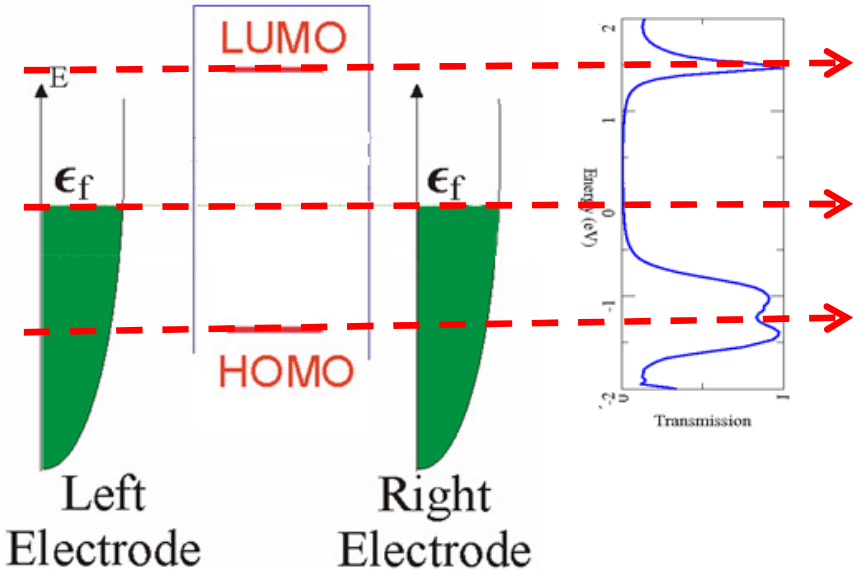
$T_{\text{tot}}(E)$: Total Quantum Transmission

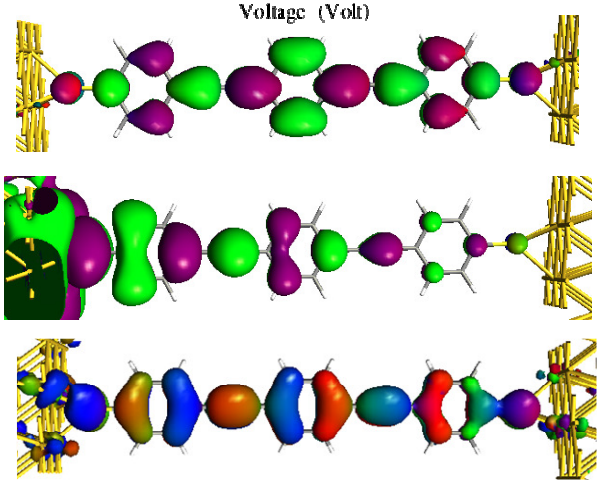
$$T_{\text{tot}}(E) = \text{Tr}[\mathbf{t}^\dagger \mathbf{t}](E)$$

I-V Characteristics of a molecule

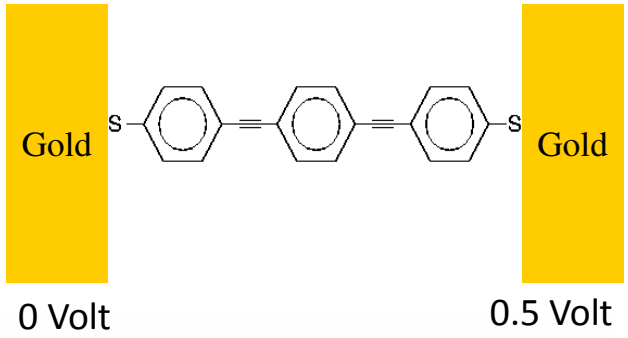


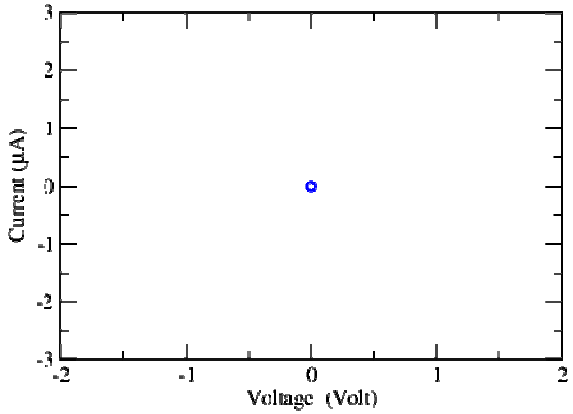


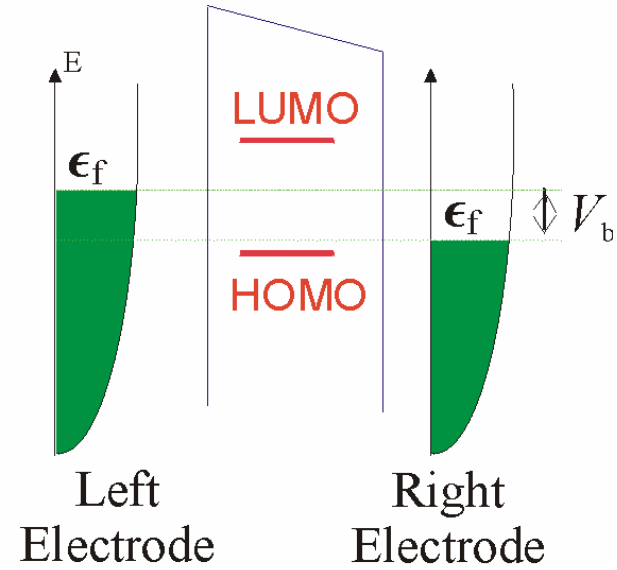




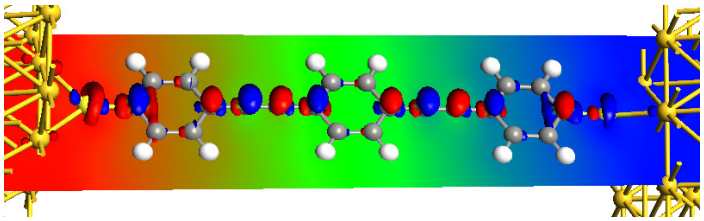
Apply bias

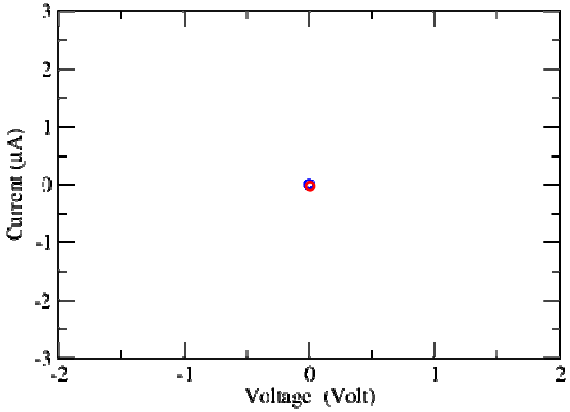

Gold
S
S
Gold
0 Volt
0.5 Volt


Current (μA)
Voltage (Volt)
3
2
1
0
-1
-2
-3
-2
-1
0
1
2


E
LUMO
ϵ_f
ϵ_f
V_b
HOMO
Left Electrode
Right Electrode

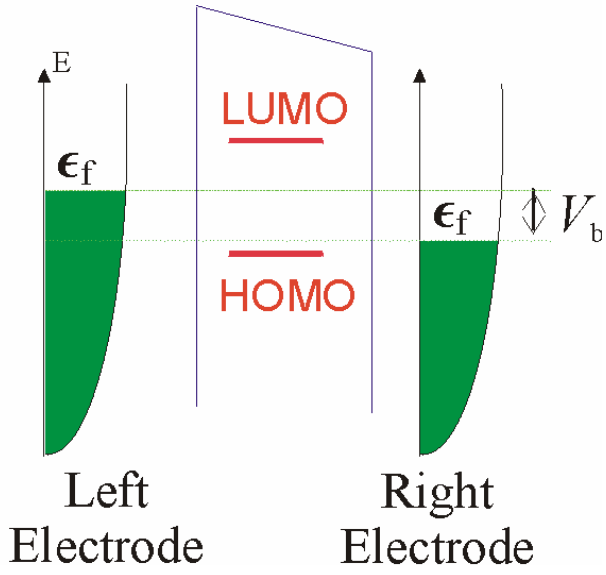
Apply bias

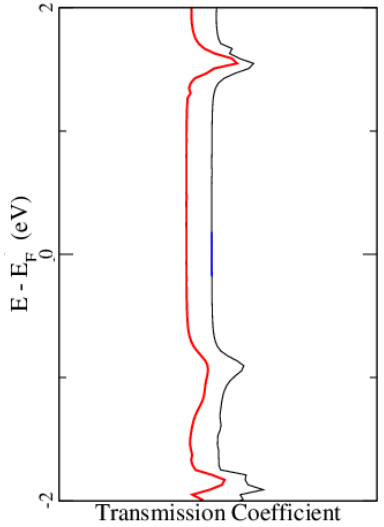




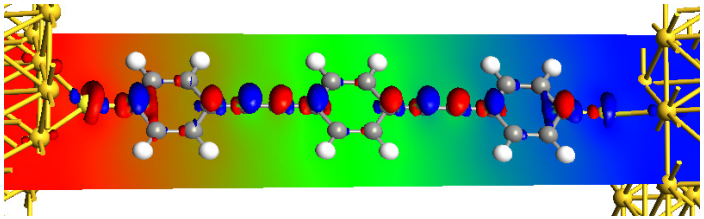
0 Volt

0.5 Volt



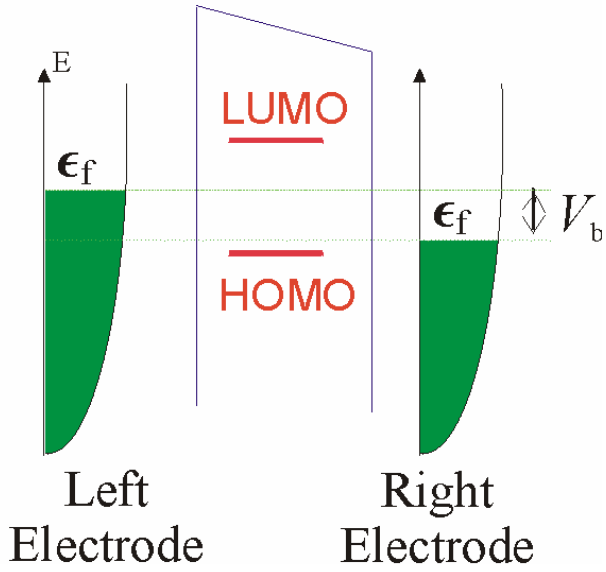


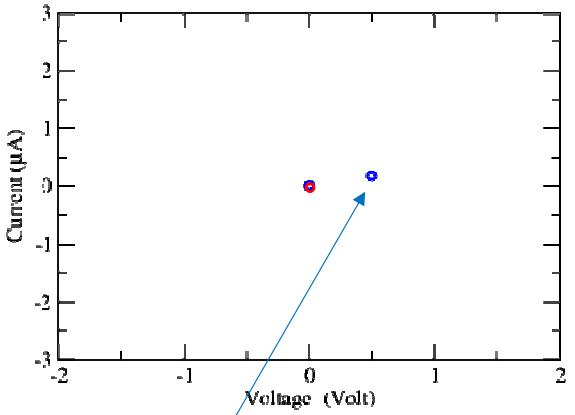
Apply bias

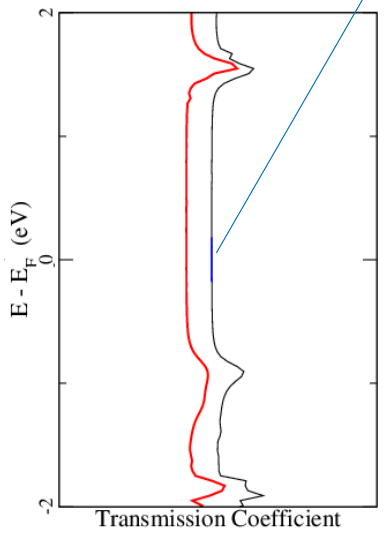


0 Volt

0.5 Volt







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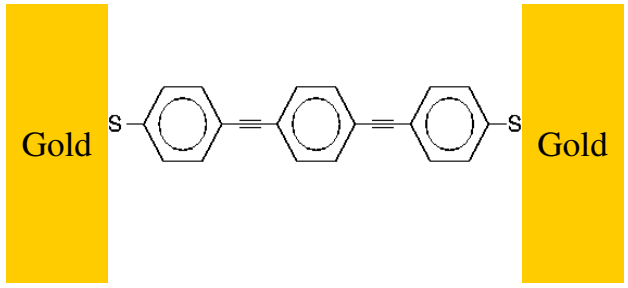
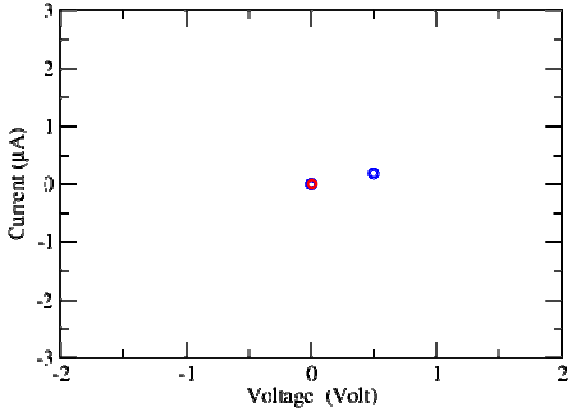
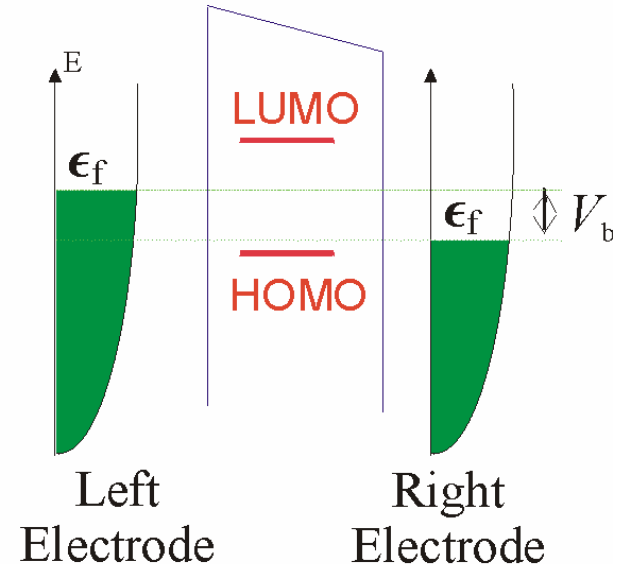
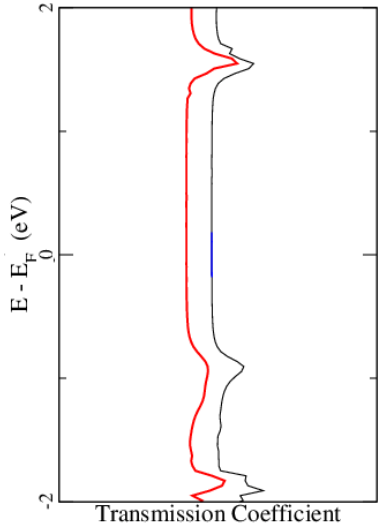


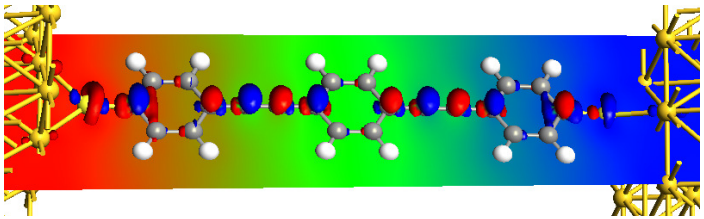
0 Volt 1.0 Volt

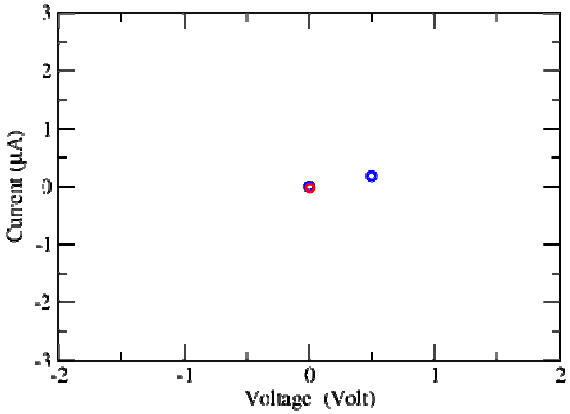






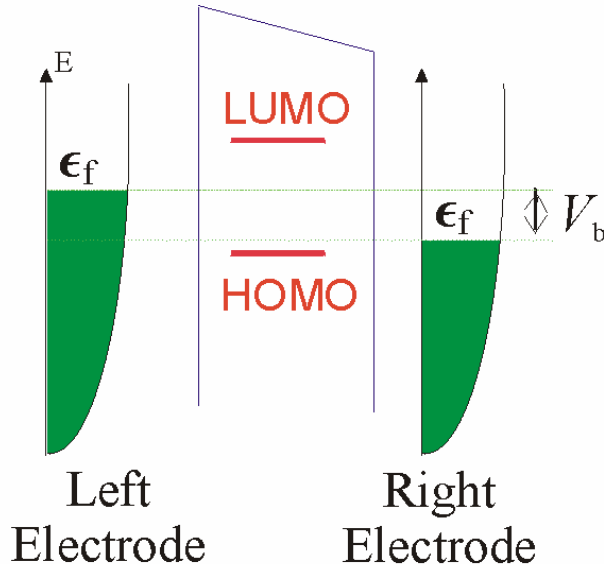
Apply bias

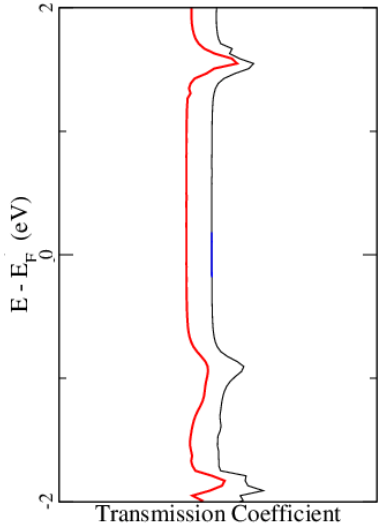




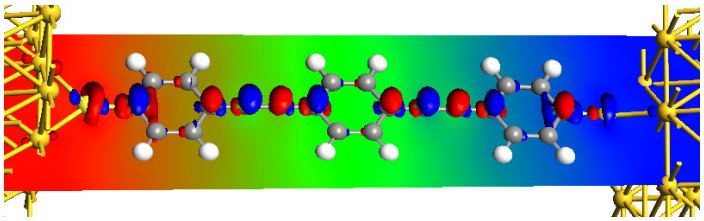
0 Volt

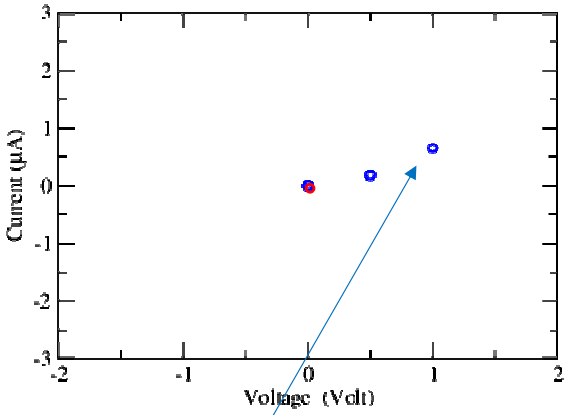
1.0 Volt





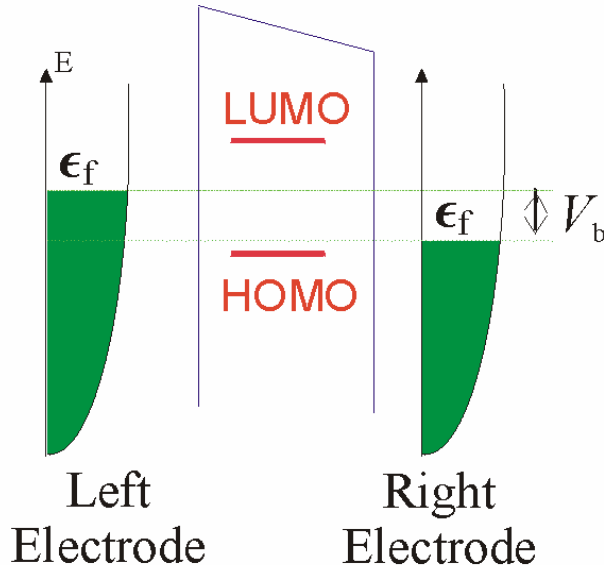
Apply bias

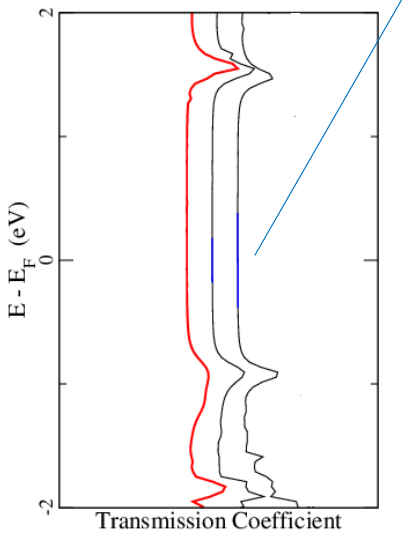




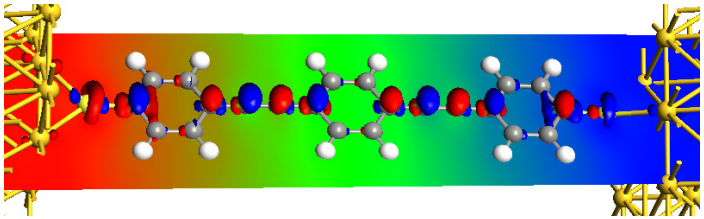
0 Volt

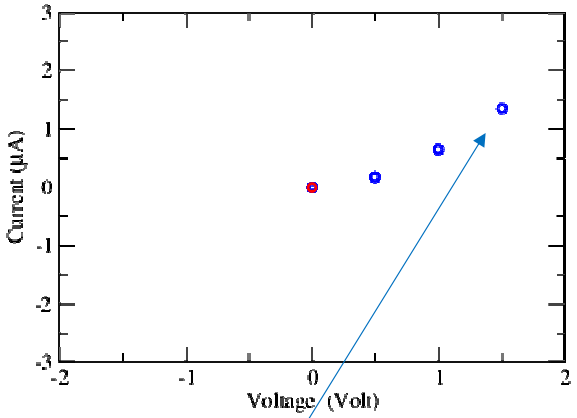
1.0 Volt





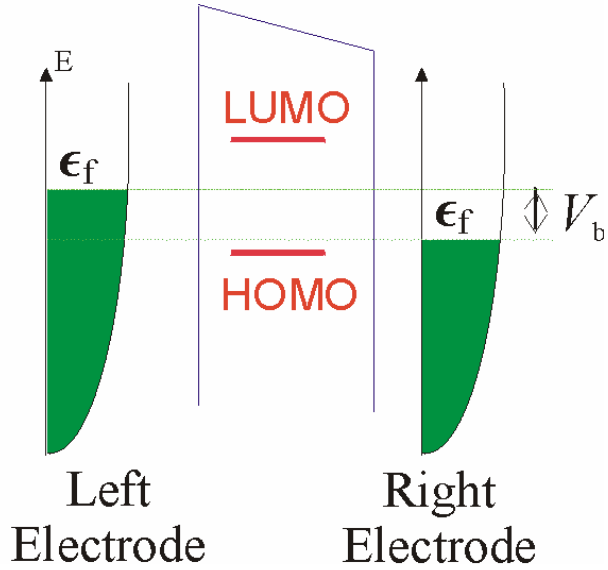
Apply bias

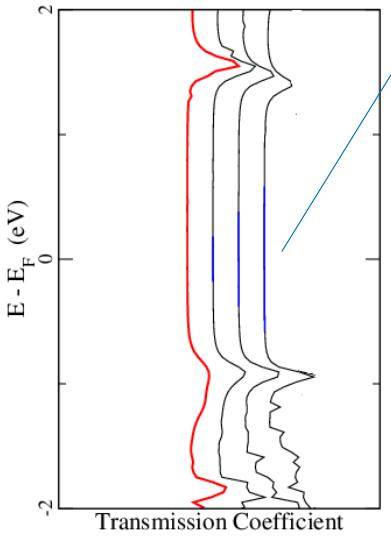




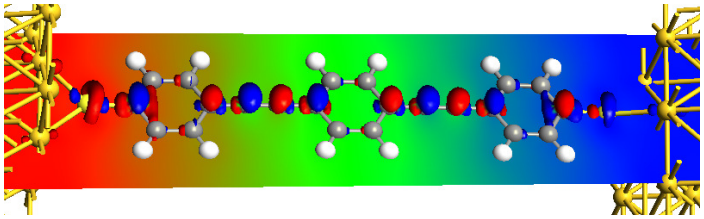
0 Volt

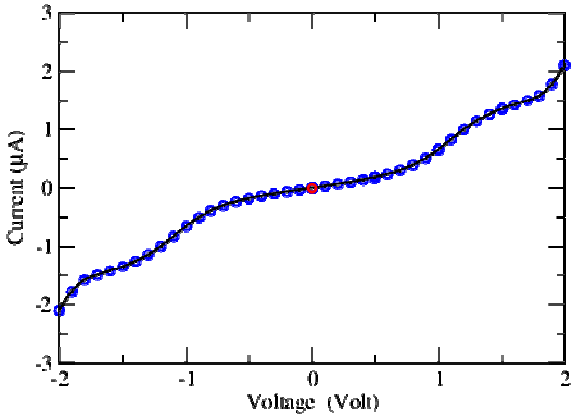
1.5 Volt

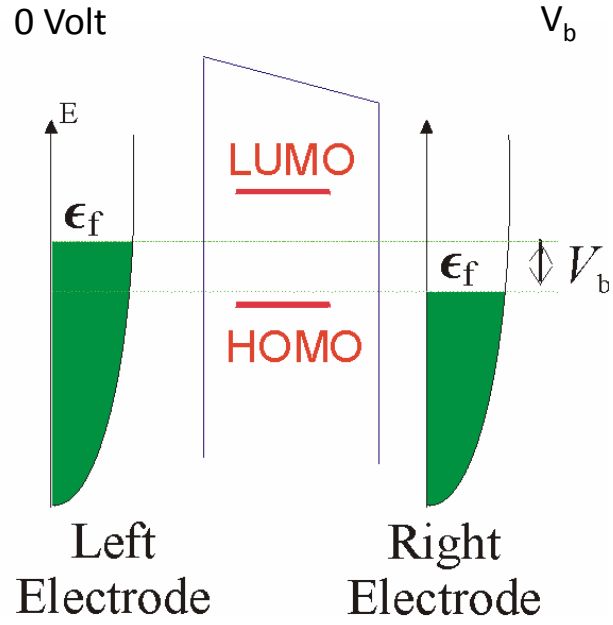


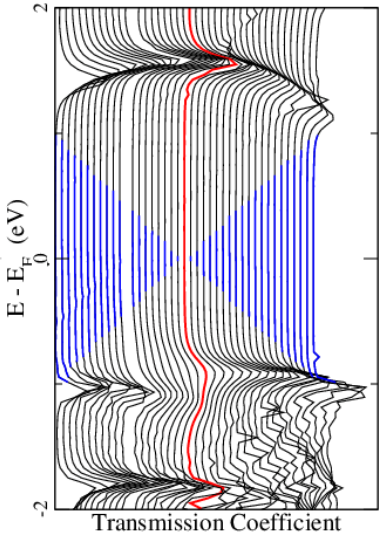


Apply bias

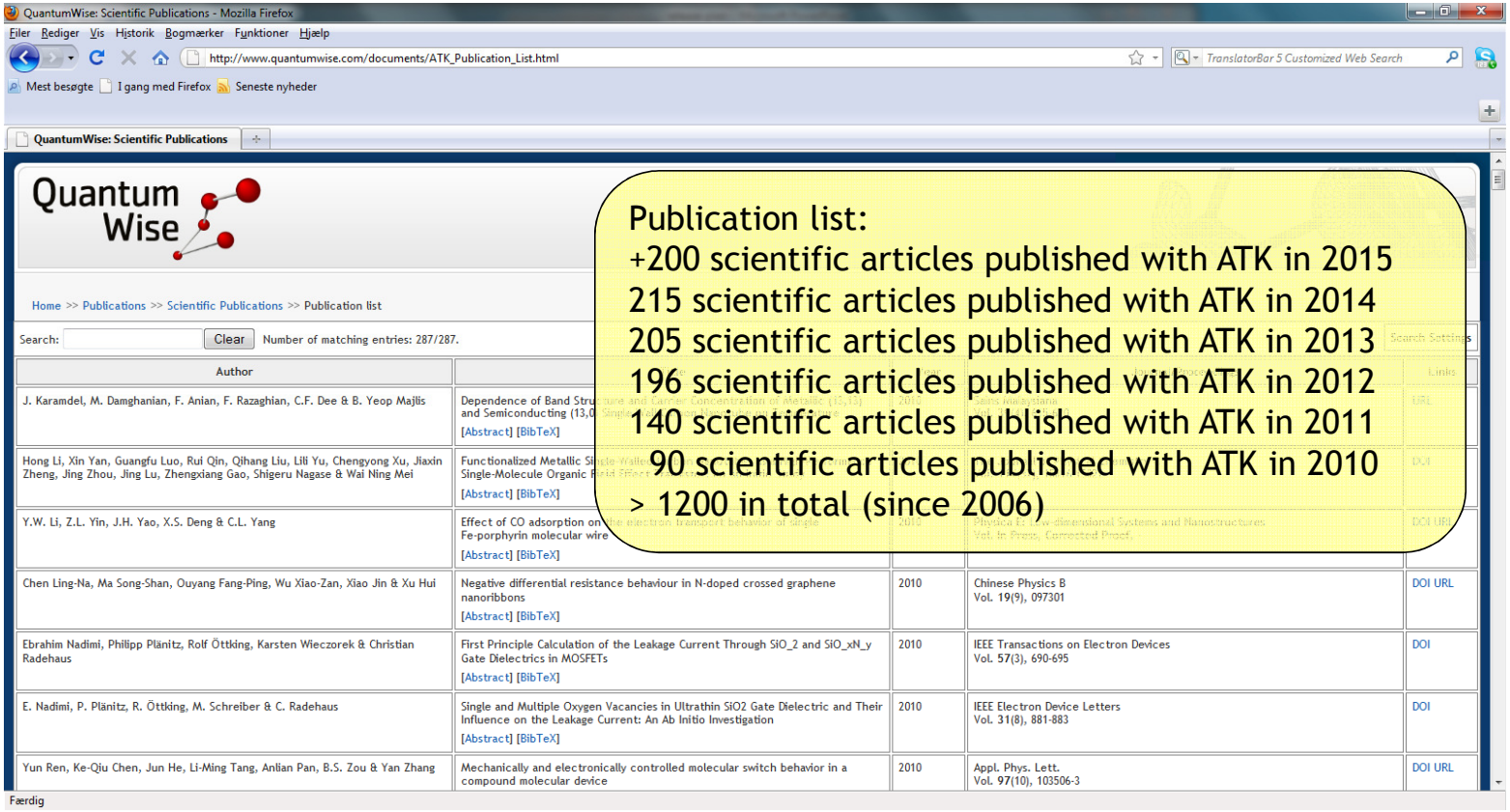



Current (μA)
Voltage (Volt)
3
2
1
0
-1
-2
-3
-2
-1
0
1
2


0 Volt
V_b
E
LUMO
ϵ_f
ϵ_f
V_b
HOMO
Left Electrode
Right Electrode


E - E_F (eV)
2
0
-2
Transmission Coefficient

http://quantumwise.com/documents/ATK_Publication_List.html



Publication list:
+200 scientific articles published with ATK in 2015
215 scientific articles published with ATK in 2014
205 scientific articles published with ATK in 2013
196 scientific articles published with ATK in 2012
140 scientific articles published with ATK in 2011
90 scientific articles published with ATK in 2010
> 1200 in total (since 2006)

Outline

QuantumWise

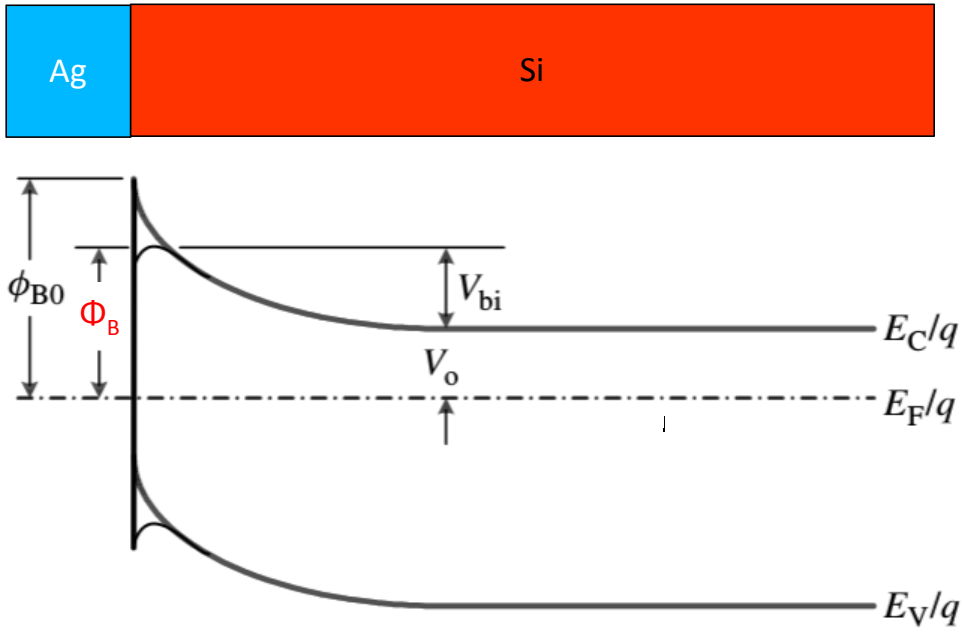
Density Functional Theory

Quantum Transport

Simulation of Interfaces

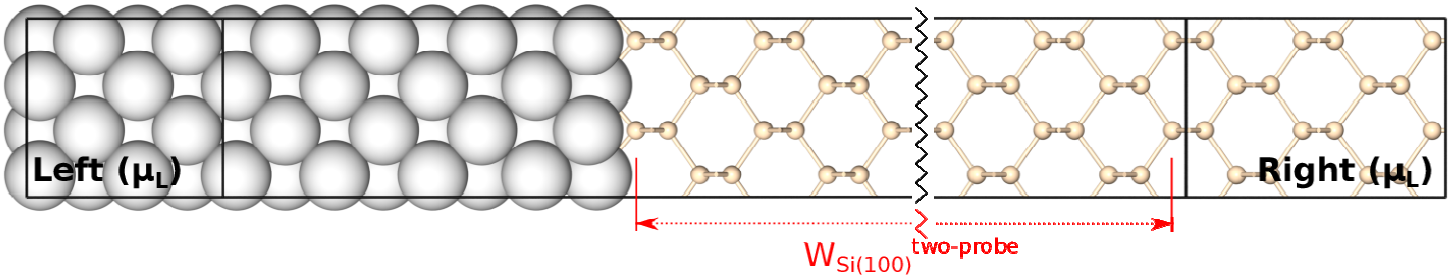
Simulation of Batteries

Metal-Semiconductor Schottky contact



Φ_{B0}= Ideal barrier height
Φ_B = Effective barrier height
V_{bi} = build in potential
V_0 = potential (E_F-E_V)

Model Ag(100)/Si(100) investigated using DFT+NEGF



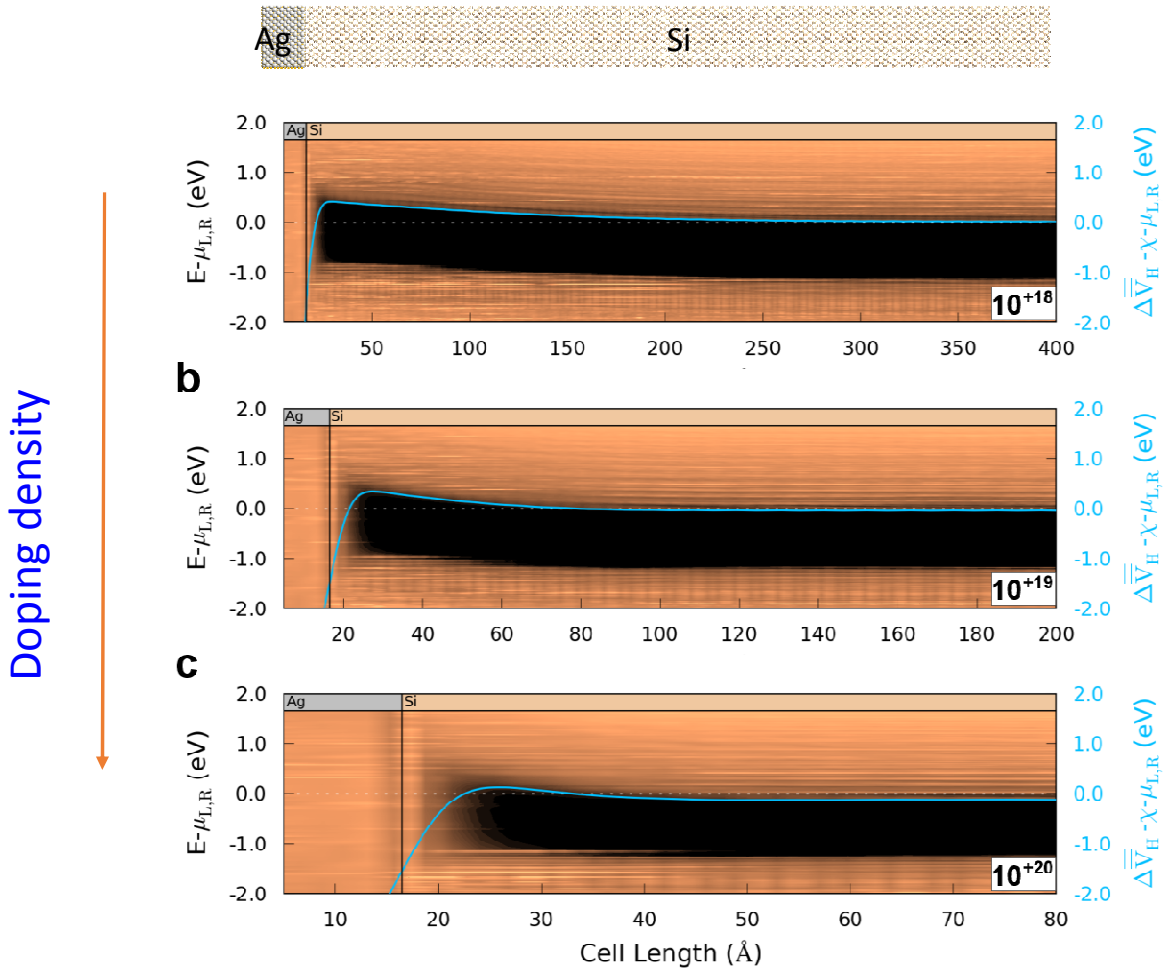
- **DFT+NEGF formalism***: exact representation of the non-periodic interface
- **Meta-GGA functional****: correctly accounts for the silicon band gap (E_g = 1.17 eV)
- **Effective doping** of the silicon side using localized charges on the Si atoms

Stradi et. al. Phys. Rev. B **93,** 155302 (2016)

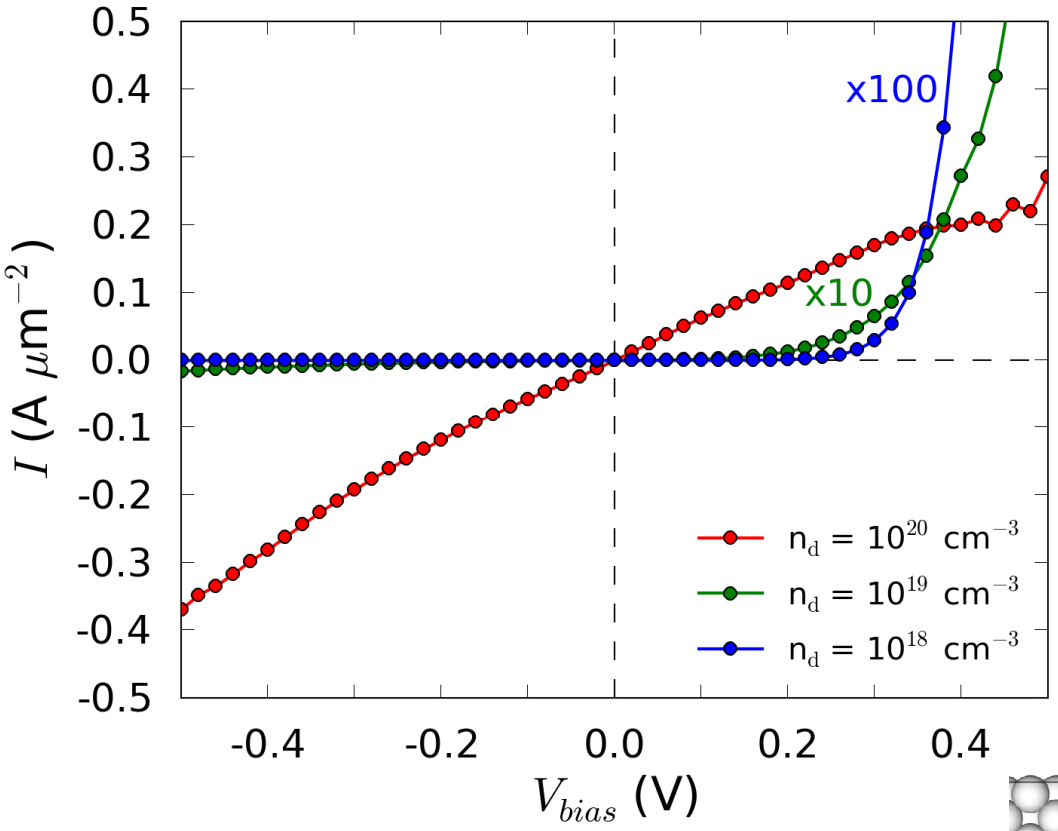
*Brandbyge et al. *Phys. Rev. B* **65**, 165401 (2002)

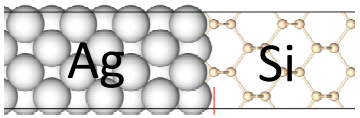
** Tran, Blaha *Phys. Rev. Lett.***102**, 226401 (2009)

Band bending as function of doping



Calculated I-V characteristics





Outline

QuantumWise

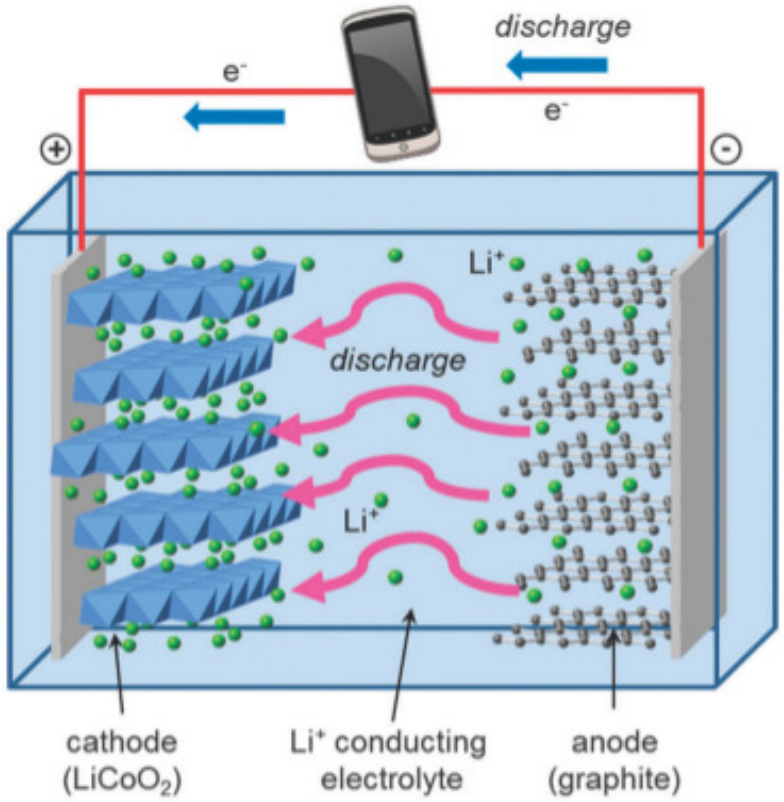
Density Functional Theory

Quantum Transport

Simulation of Interfaces

Simulation of Batteries

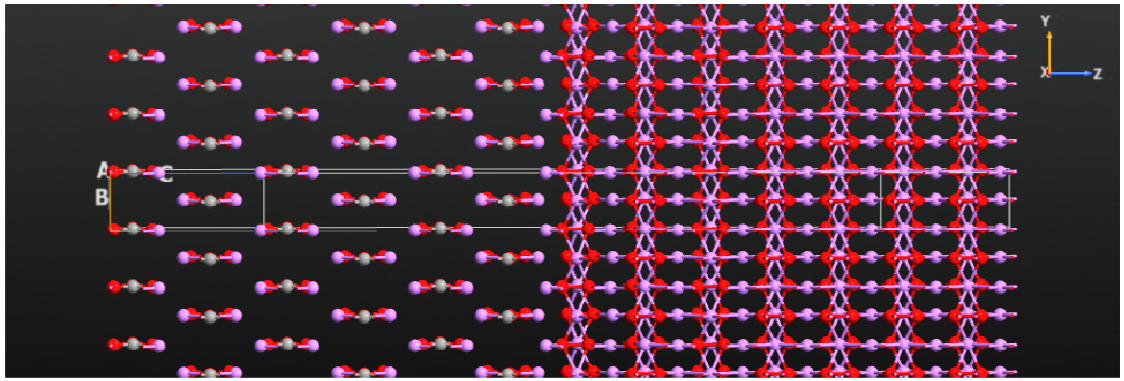
Operation of a Li ion battery



Electron transport across Li2O2/Li2CO3 interface

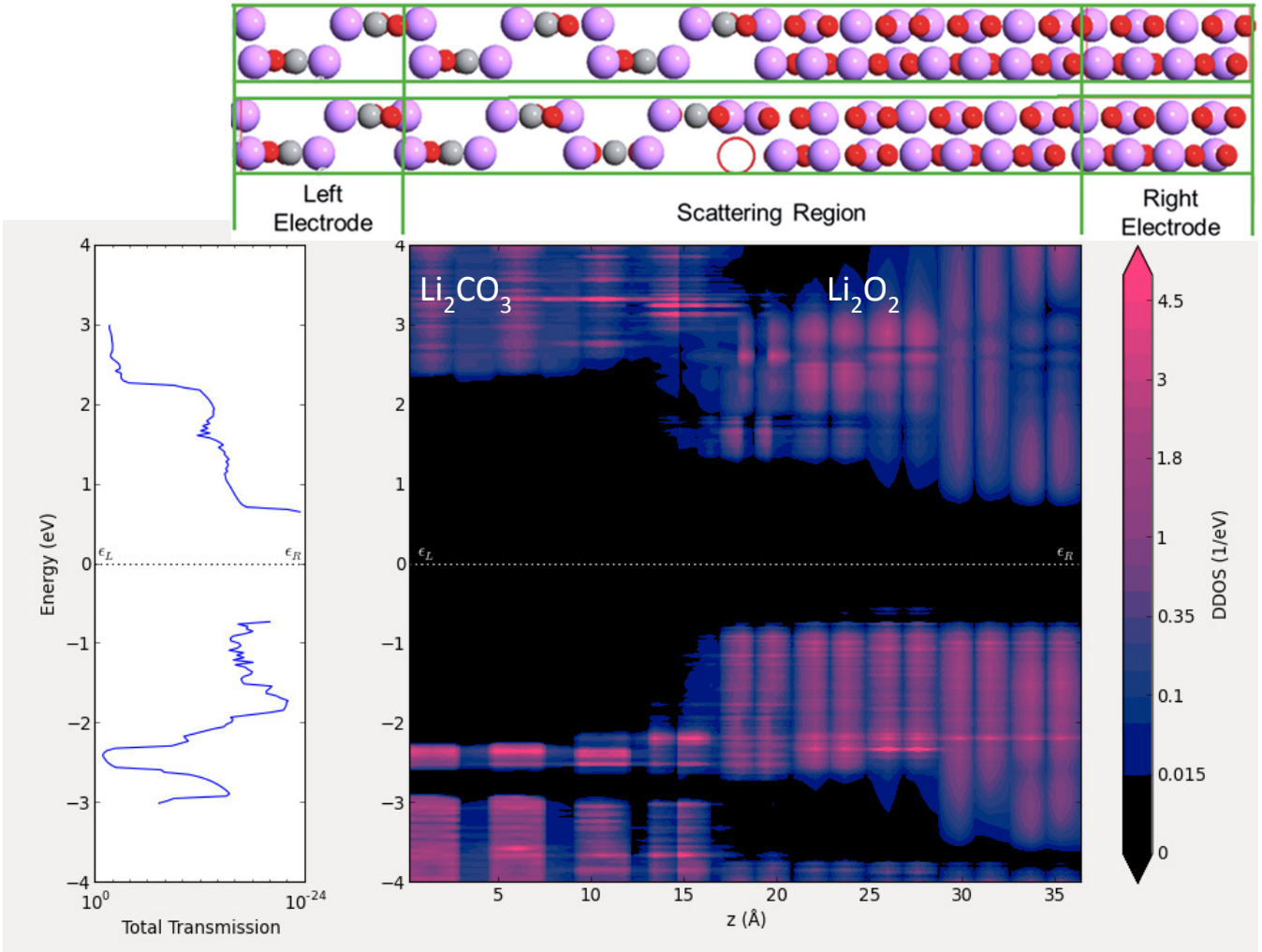
- Import/create Li_2O_2 and Li_2CO_3 bulk structures
- Cleave surfaces
- Create Li_2O_2/Li_2CO_3 interface
- Create device and optimize geometry
- Calculate electronic transport properties

Tutorial Tuesday
18-20

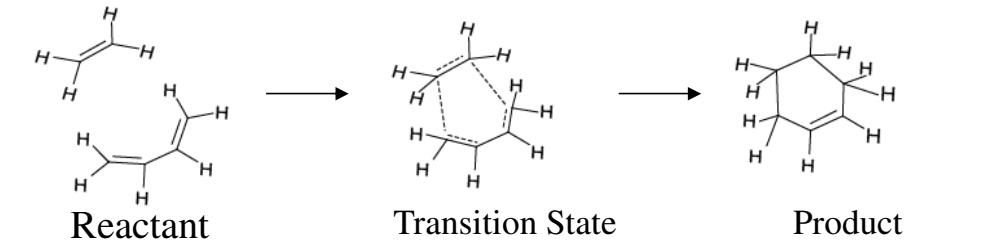


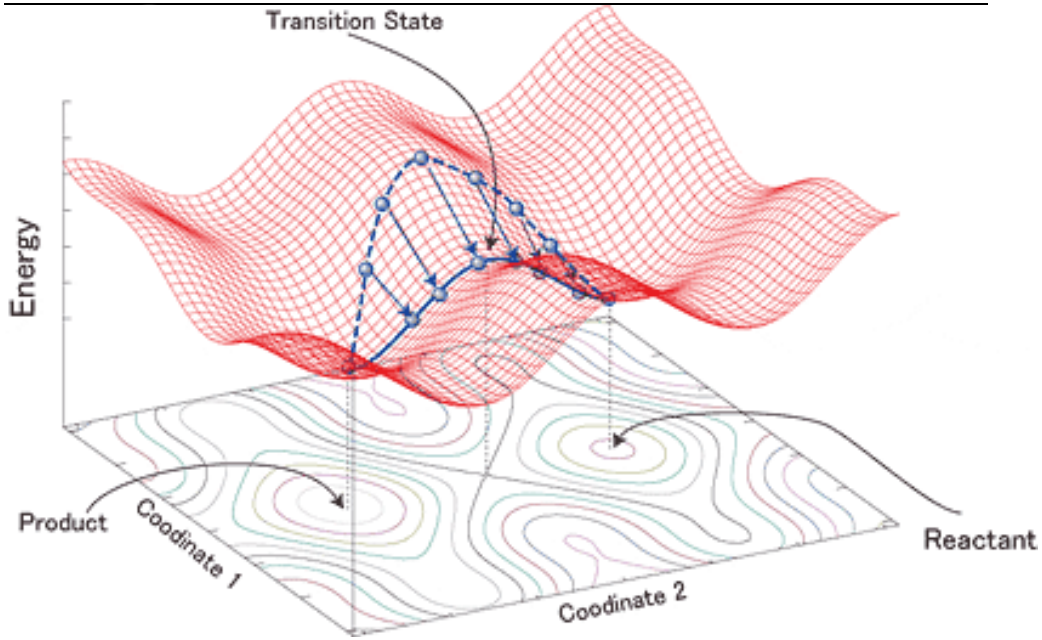
Yedilfana *et al.* JPCC (2015)

Li2CO2/Li2O2 projected density of states



Calculation of reaction barrier using NEB

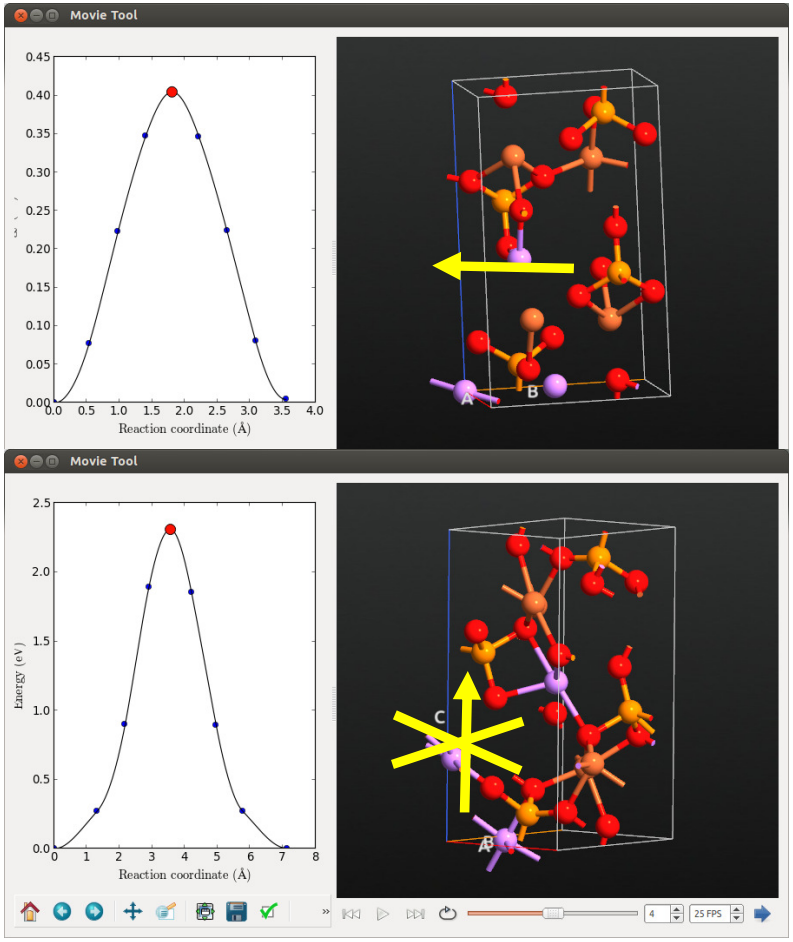




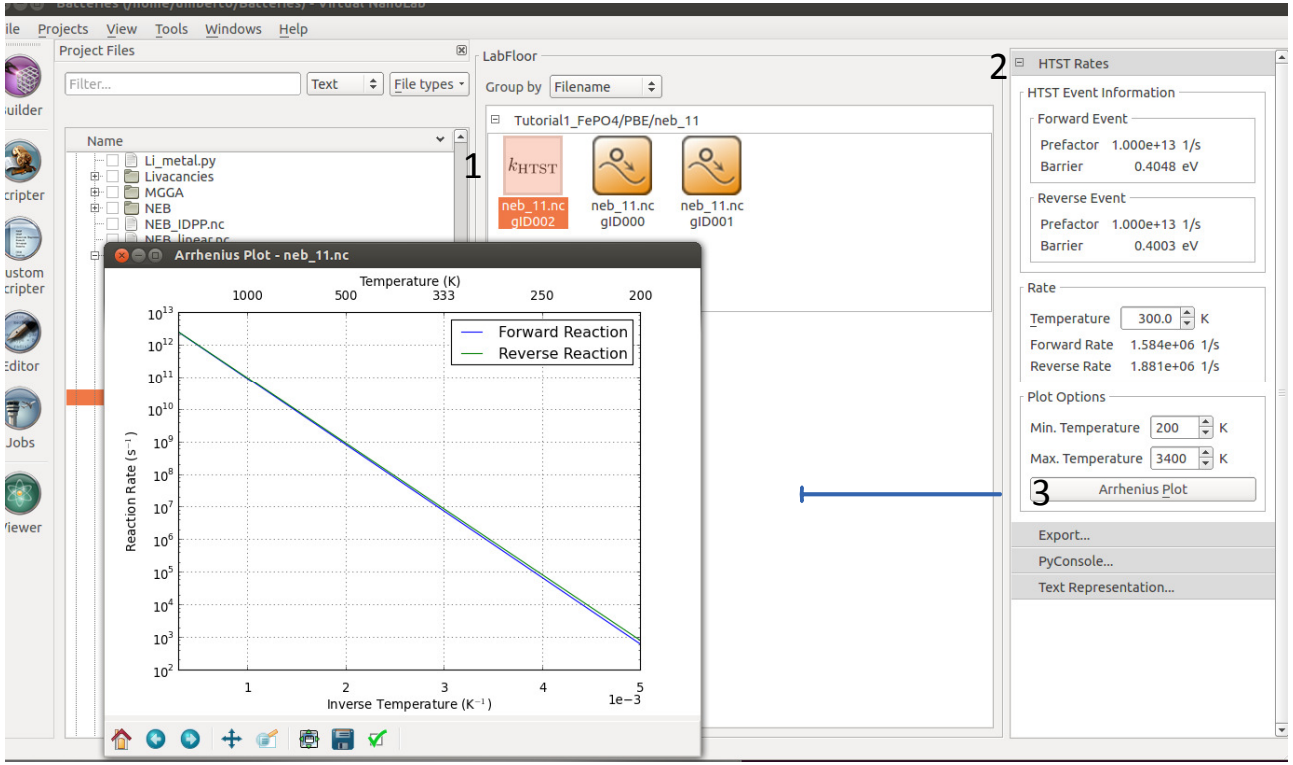
Li diffusion path

- Li diffusion along y axes:
- Barrier 0.41 eV

- Li diffusion along z axes:
- Barrier 2.31 eV



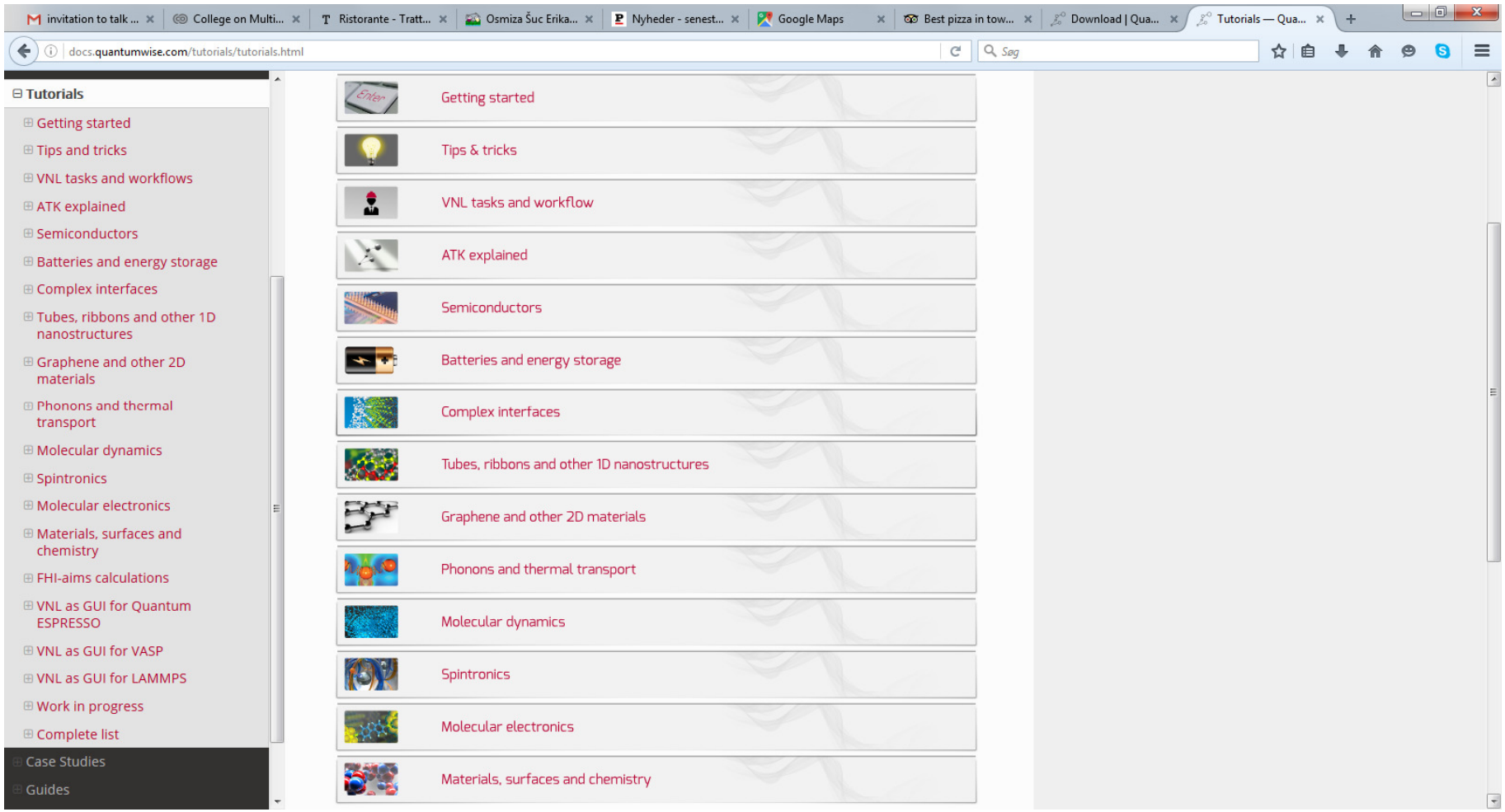
Calculate the reaction rates using harmonic transition state theory



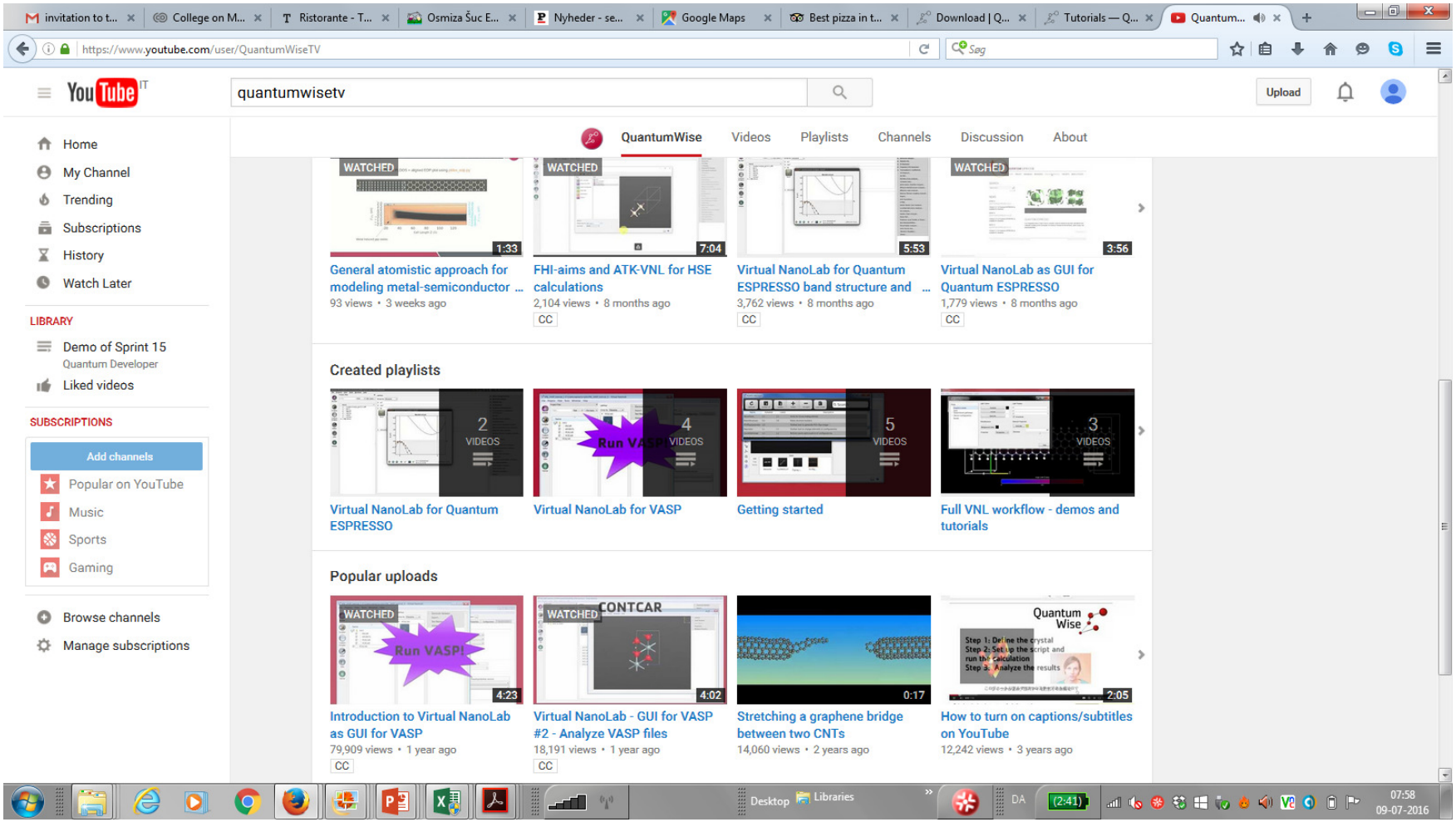
	Barrier	k_{HTST} @ 300 K
y direction	0.41 eV	1.6 10^{6} s^{-1}
z direction	2.31 eV	1.5 10^{-26} s^{-1}

See Tutorial: *Calculating Reaction Rates using Harmonic Transition State Theory*
http://docs.quantumwise.com/tutorials/neb_htst.html

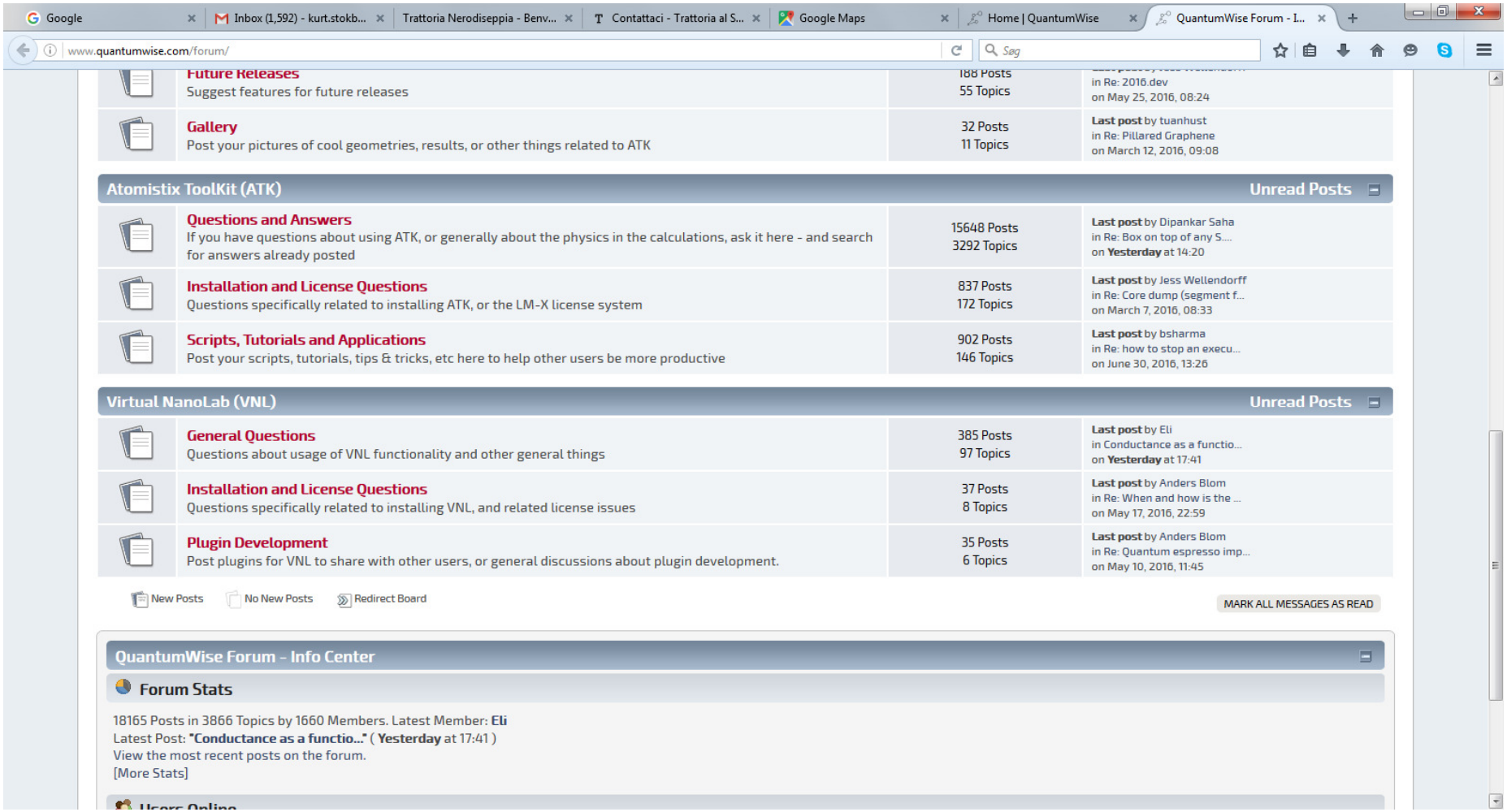
Tutorials available at QuantumWise



Youtube videos: QuantumWiseTV



Active forum with more than 1500 users



Thank You!