

# **Atomic-Scale Modelling of Charge Transport Across Interfaces**

**Kurt Stokbro, QuantumWise A/S**

Kurt Stokbro



# Outline



QuantumWise

Density Functional Theory

Quantum Transport

Simulation of Interfaces

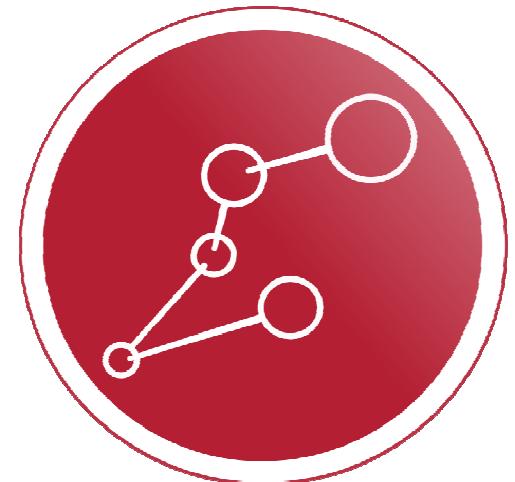
Simulation of Batteries

## Company background

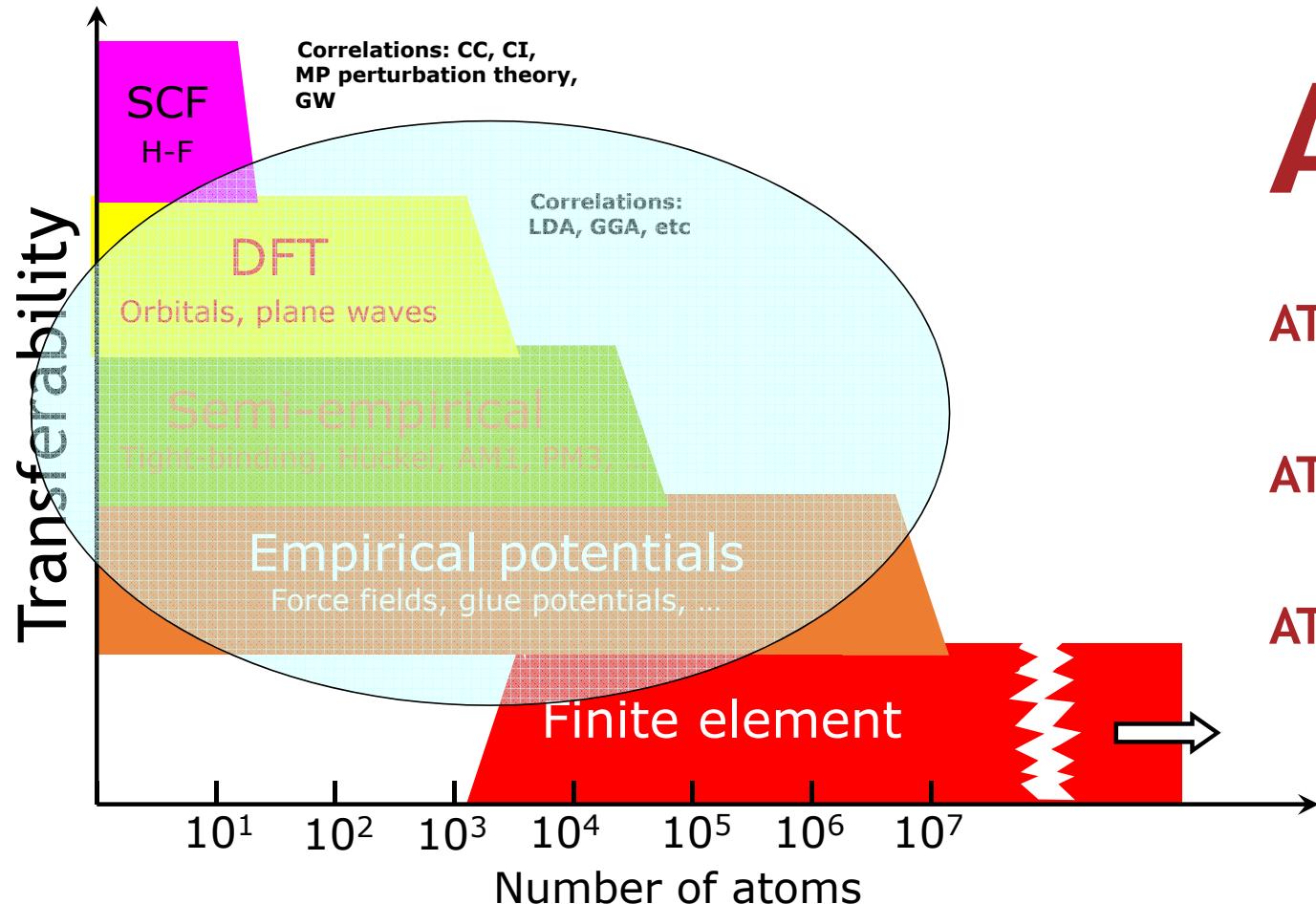


- We love science/physics - and in particular atomic scale simulations
- Help customers be more successful in atomic-scale modelling
- Internal development of quantum-mechanical simulation engines combined with community codes in certain areas
- Founded 2008, with Headquarter in Copenhagen, Denmark
- 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



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



**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

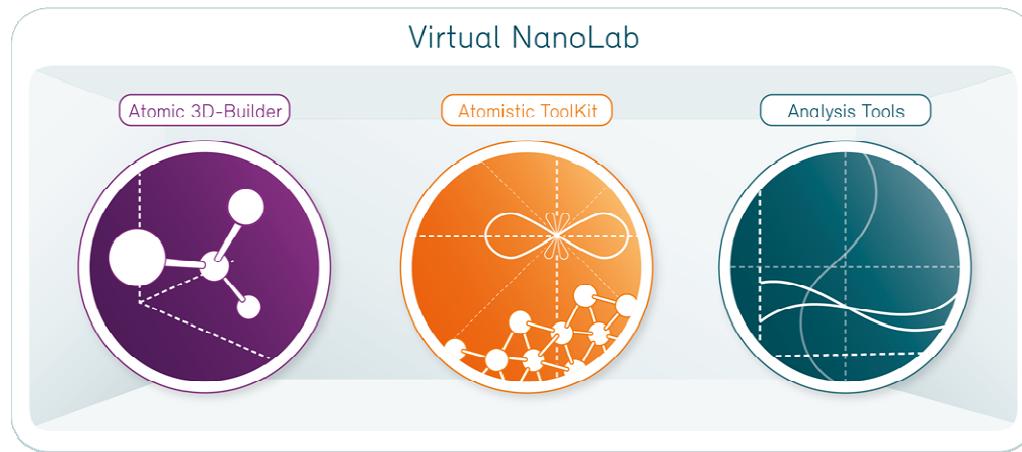
Band structure  
DOS  
Complex band structure  
Effective band structure  
Effective mass  
Piezoelectric properties  
Optical properties  
ELF  
Bloch states  
Total energy  
Electron density  
Potential

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)

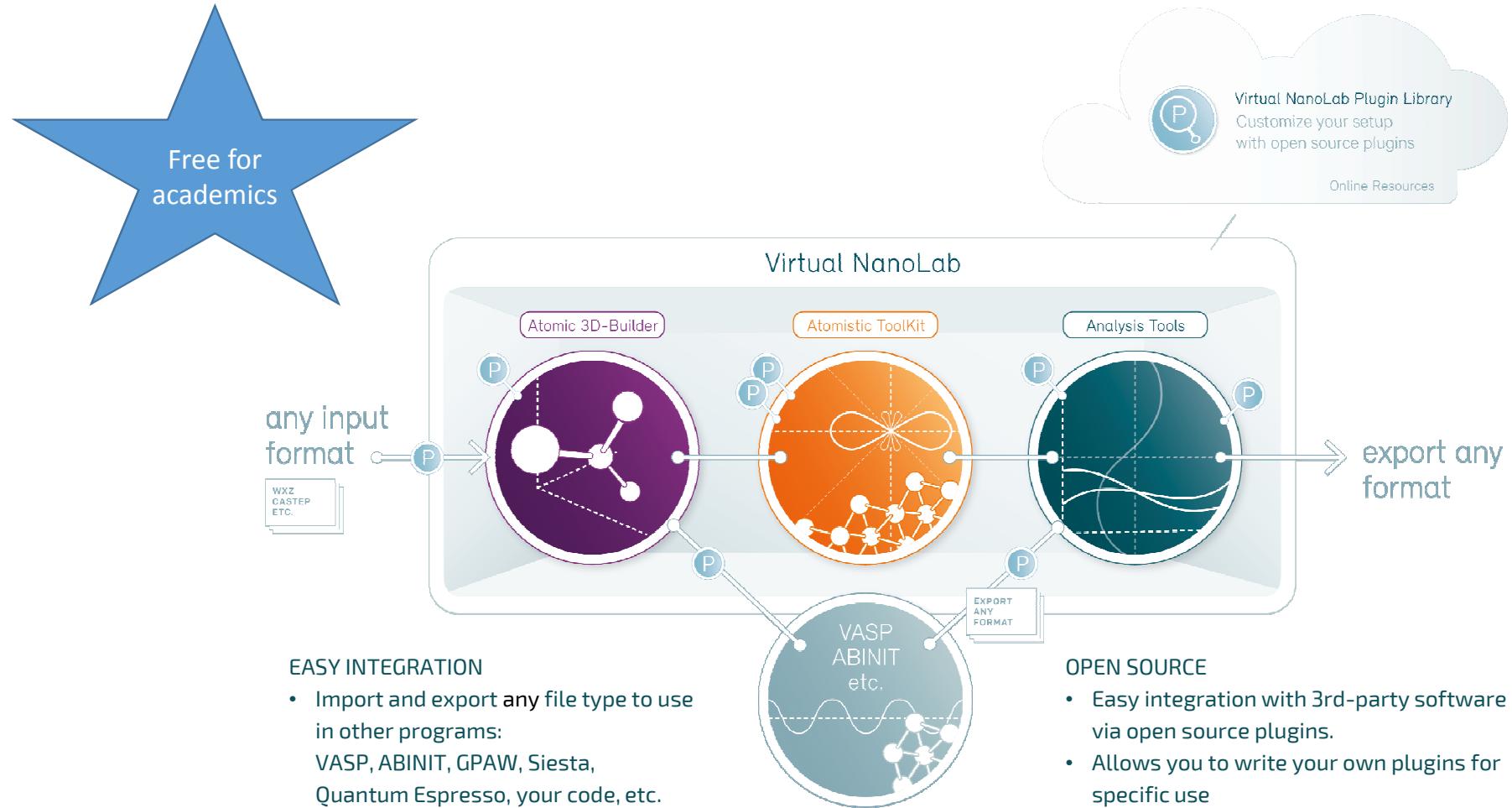


**Build**  
Interfaces  
Nanotubes  
Nanosheets  
Nanopatterns  
Molecules  
Crystals by symmetry  
Cleave surfaces  
Polycrystals

**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



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QuantumWise

**Density Functional Theory**

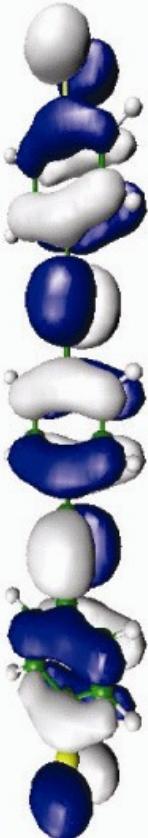
Quantum Transport

Simulation of Interfaces

Simulation of Batteries



# The Schrödinger equation



Kinetic energy

Potential energy  
between ions

Electrostatic  
energy from  
other electrons!

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

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

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

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

# 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  $V_{eff}(r)$

$$\left. \begin{aligned} H_{1el} &= -\frac{\hbar^2 \nabla^2}{2m} + V_{eff}(r) \\ H_{1el} \psi_\alpha(r) &= \epsilon_\alpha \psi_\alpha(r) \end{aligned} \right\} n(r) = \sum_{\alpha \in occ} |\psi_\alpha|^2$$

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

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

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

## 2. The Kohn-Sham equations



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

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

## 2. The Kohn-Sham equations



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

Ion potential

Hartree pot.

XC potential

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

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

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



Selfconsistent  
equations

The Kohn-Sham orbitals are often interpreted as real electrons and  $\epsilon_\alpha$  are to a good approximation the electron energies

### 3. Exchange-correlation functionals



#### The Local Density Approximation, LDA

$$E_{XC}[n] = \int \mathcal{E}_{xc}(n(r)) dr \quad \text{Perdew-Zunger, PRB 23, 5048 (1981)}$$

#### The Generalized Gradient Approximation, GGA

$$E_{XC}[n] = \int \mathcal{E}_{xc}(n(r), \nabla n(r)) dr \quad \text{Perdew-Burke-Enzenhofer, PRL 77, 3865 (1996)}$$

#### Meta-GGA functionals

$$E_{XC}[n] = \int \mathcal{E}_{xc}(n(r), \nabla n(r), \tau) dr \quad \begin{matrix} \text{Becke-Johnson} \\ J. Chem. Phys., 124, 221101 (2006) \end{matrix}$$

#### Hybrid functionals

$$E_{XC}[n] = \alpha E_X + (1 - \alpha) E_X[n] + E_C[n] \quad \begin{matrix} \text{B3LYP J. Phys. Chem. 98,} \\ 11623 (1994) \end{matrix}$$

## 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](https://www.youtube.com/watch?v=Fnr_1AShksE)  
Youtube search quantumwisetv DFT three

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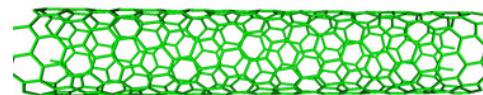
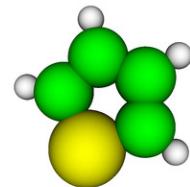
Simulation of Batteries



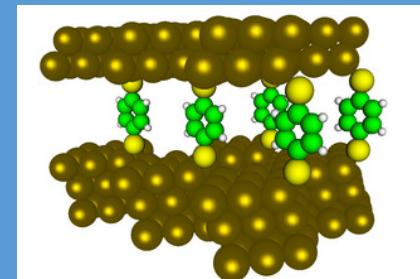
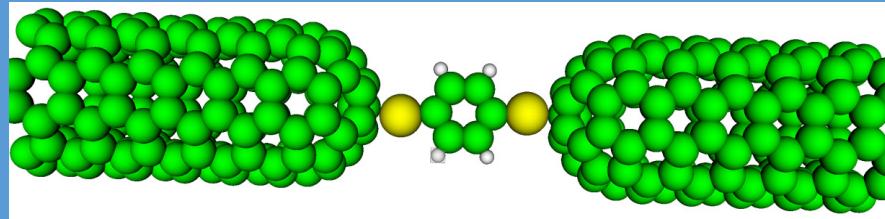
# Electronic transport in nanostructures



Traditional quantum-based software can model either  
isolated molecules or periodic systems



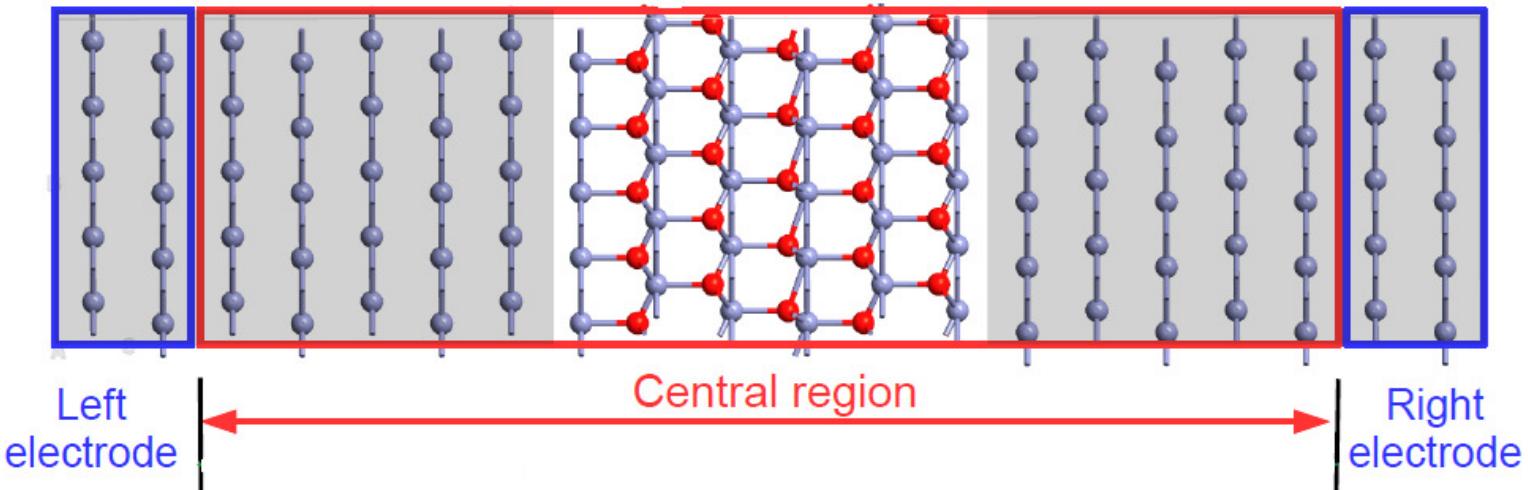
Devices are more complex; need to model nanostructures combining molecules with periodic systems and macroscopic elements



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).

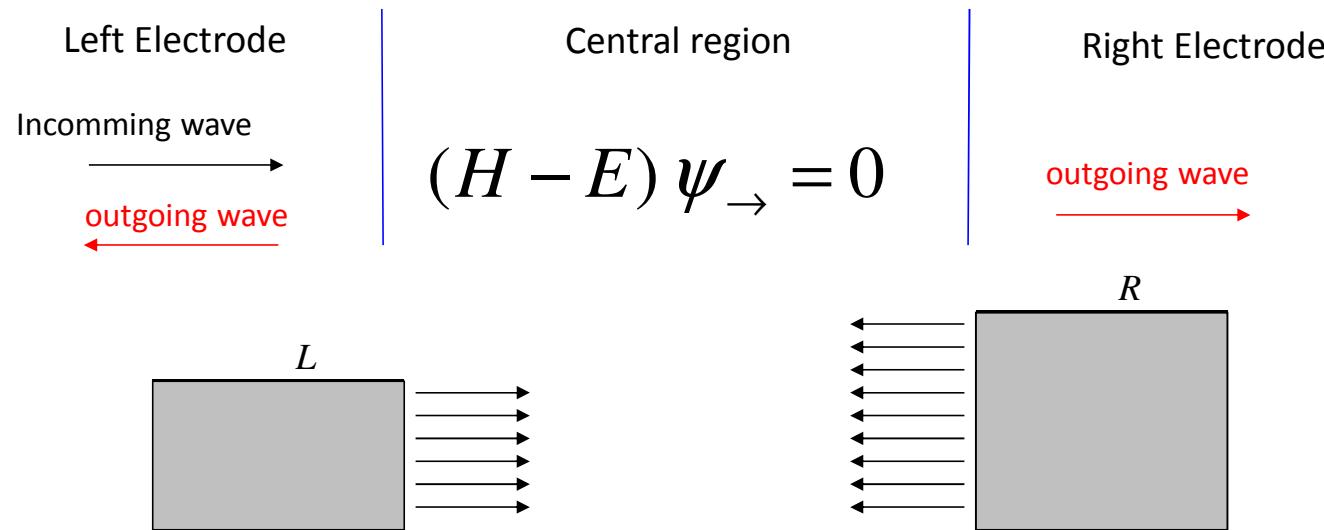
## NEGF transport methodology



- ❖ 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

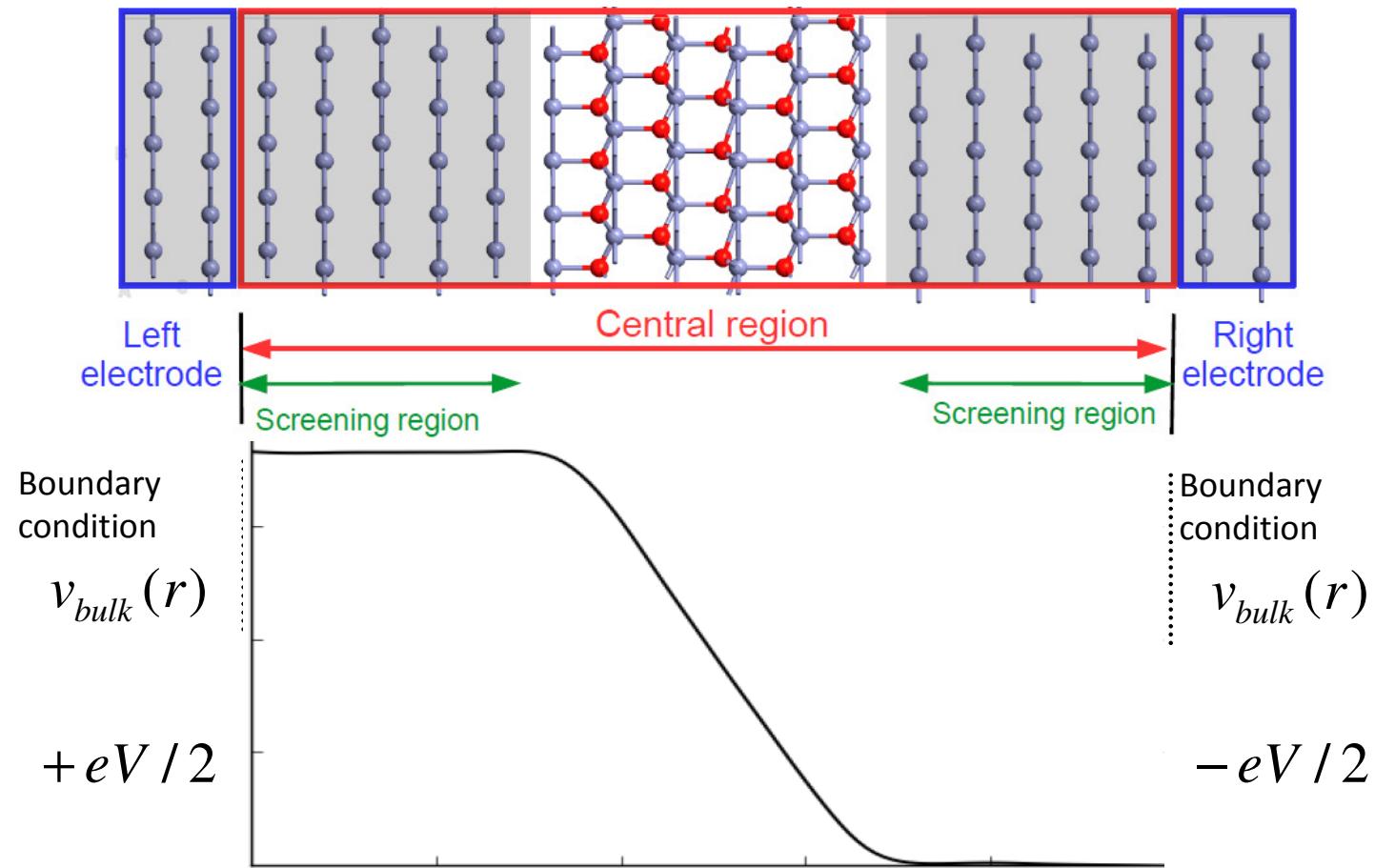


$$n(r) = \int_{-\infty}^L |\psi_{\rightarrow}(E, r)|^2 dE + \int_{-\infty}^R |\psi_{\leftarrow}(E, r)|^2 dE$$

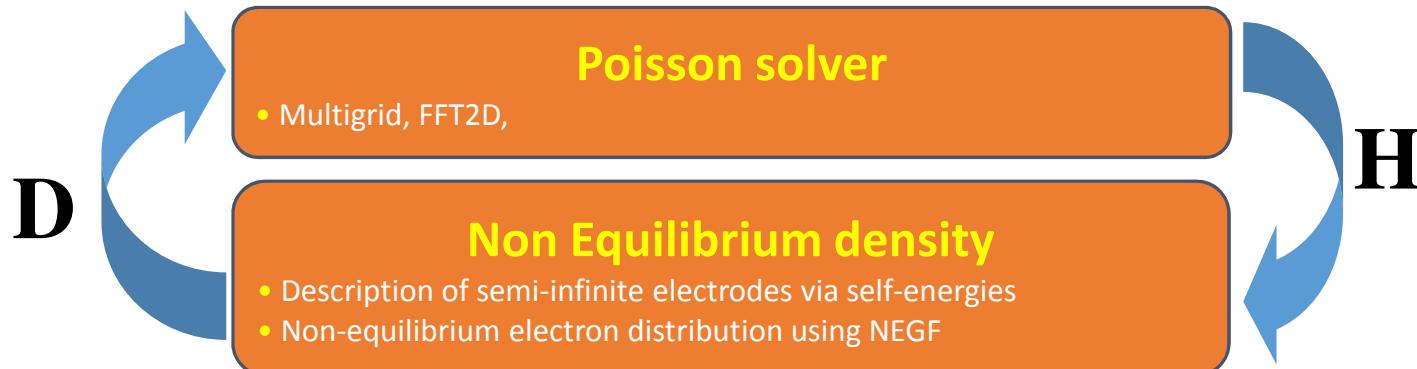
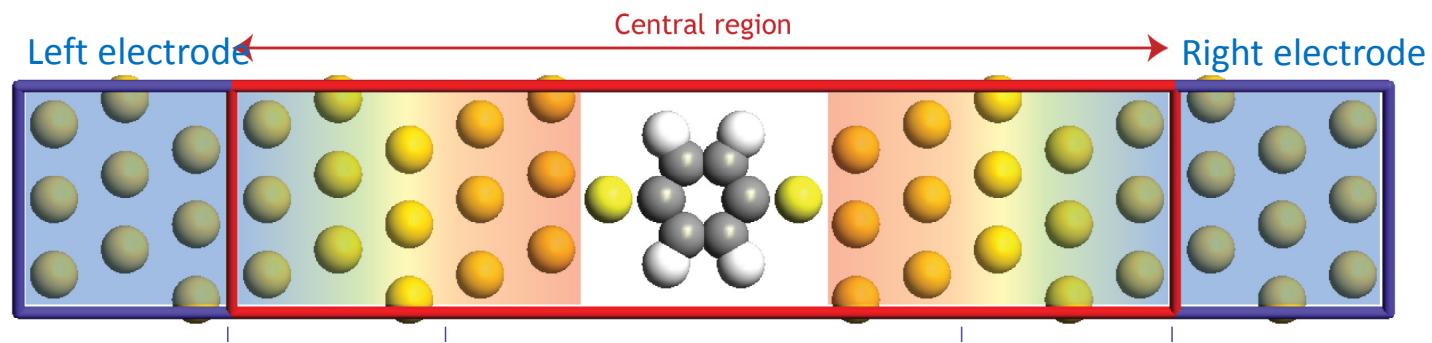
- ❖ For efficiency calculate  $n(r)$  using NEGF with complex contour integration

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

## Solving for the electro-statics

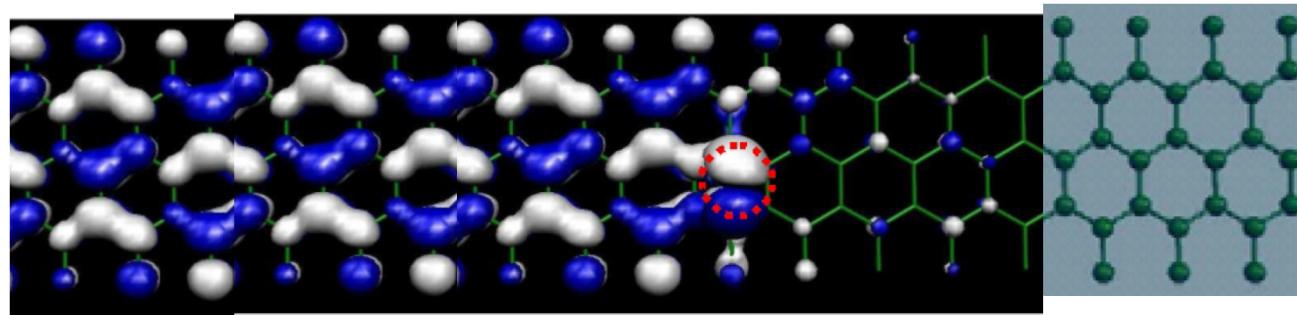


# Self-consistent solution



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  $\mathbf{t}$

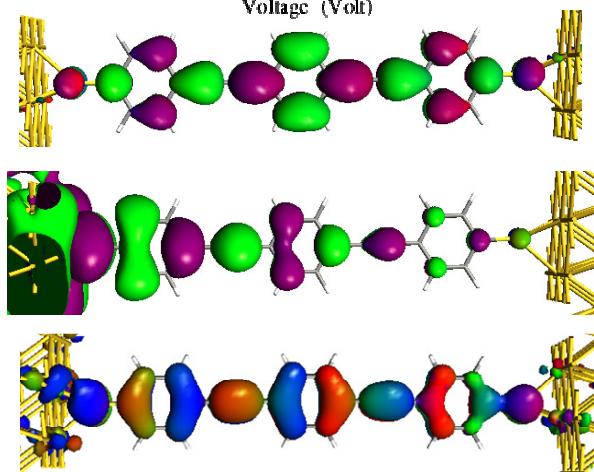
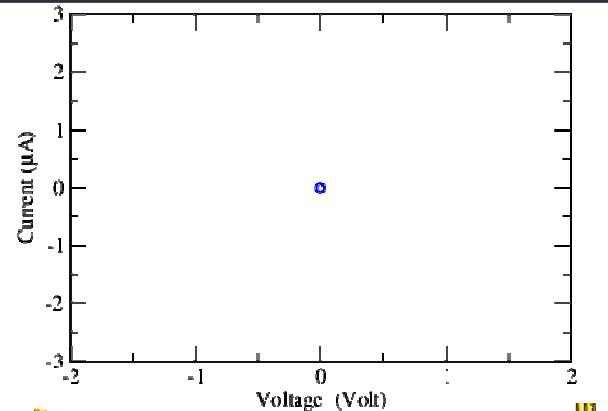
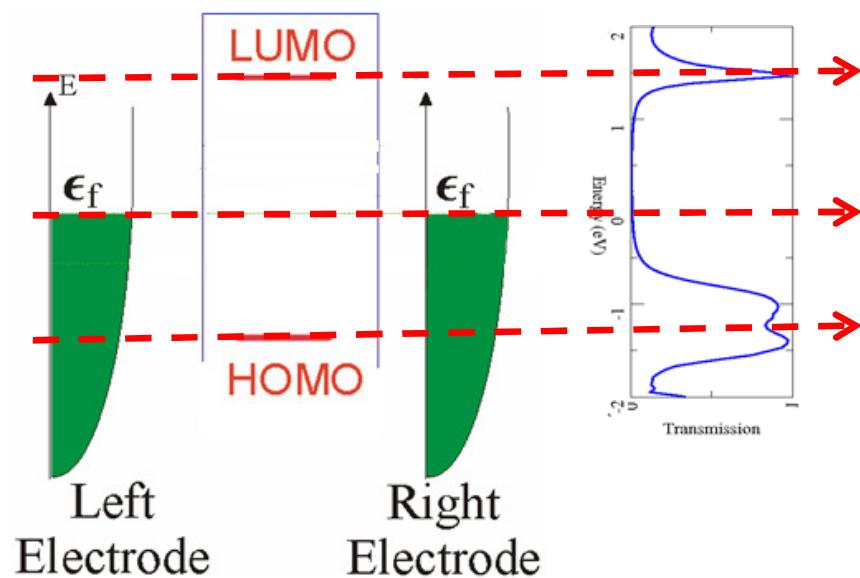
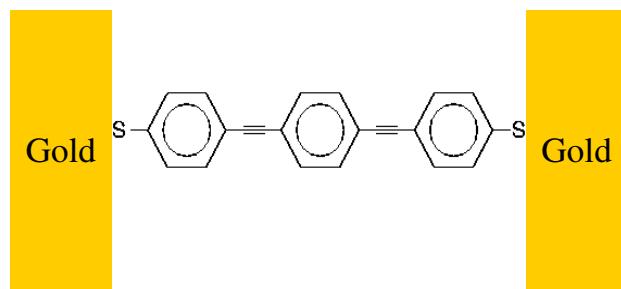
Calculation of current,

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

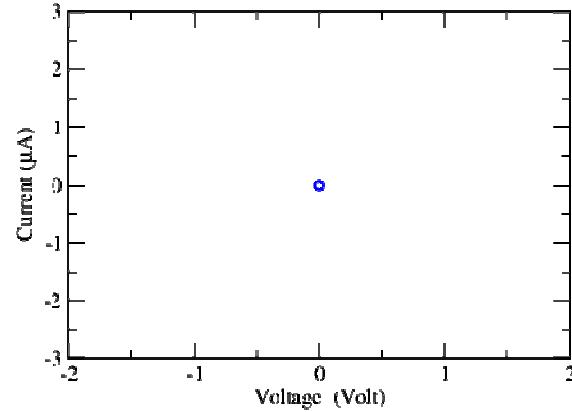
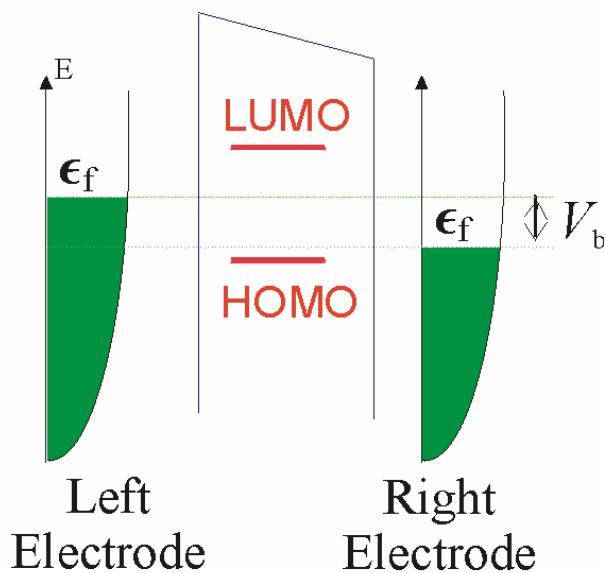
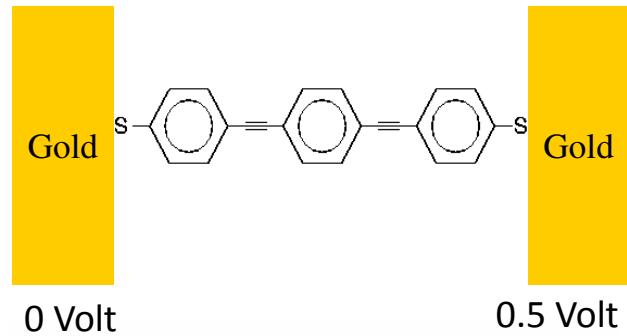
$T_{\text{tot}}(E)$ : Total Quantum Transmission

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

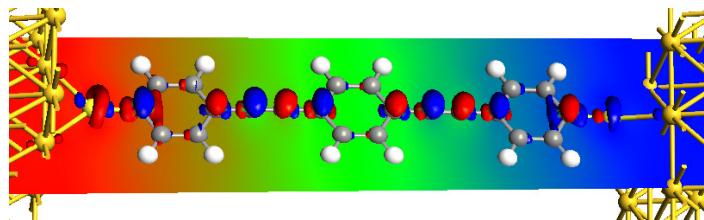
# I-V Characteristics of a molecule



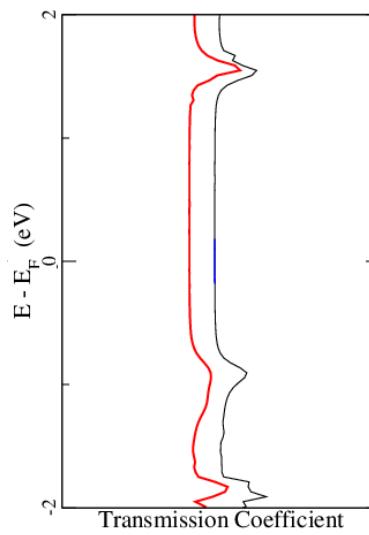
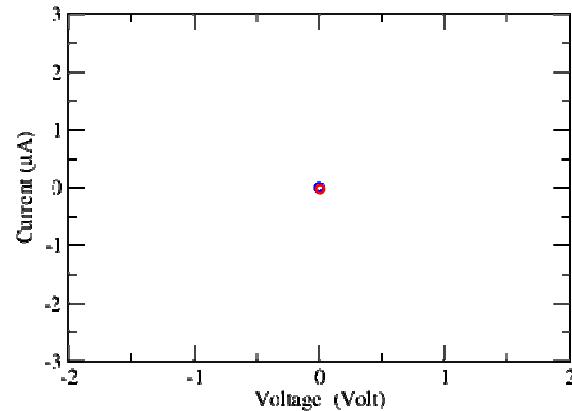
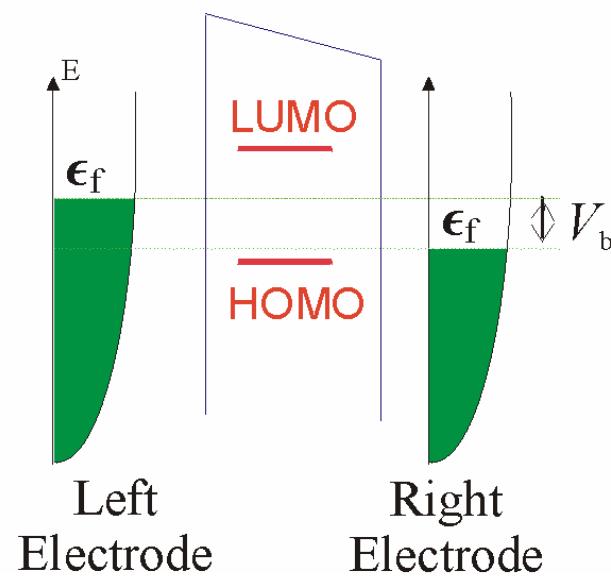
## Apply bias



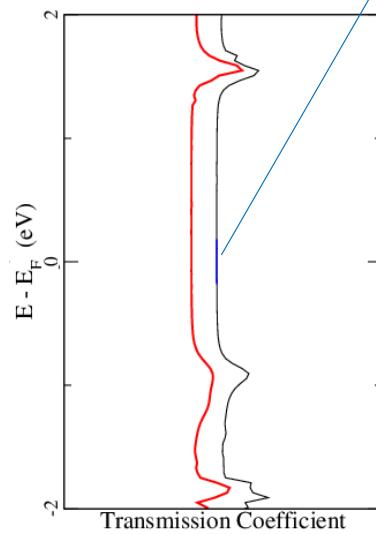
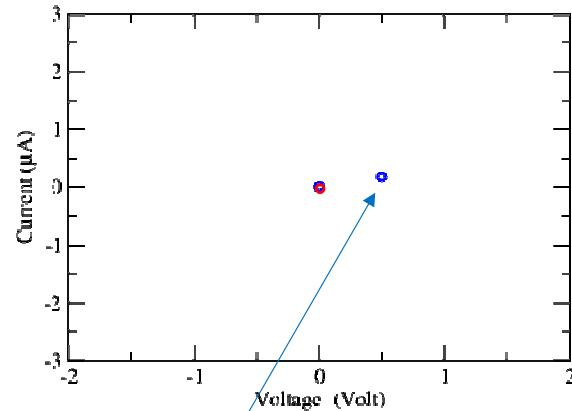
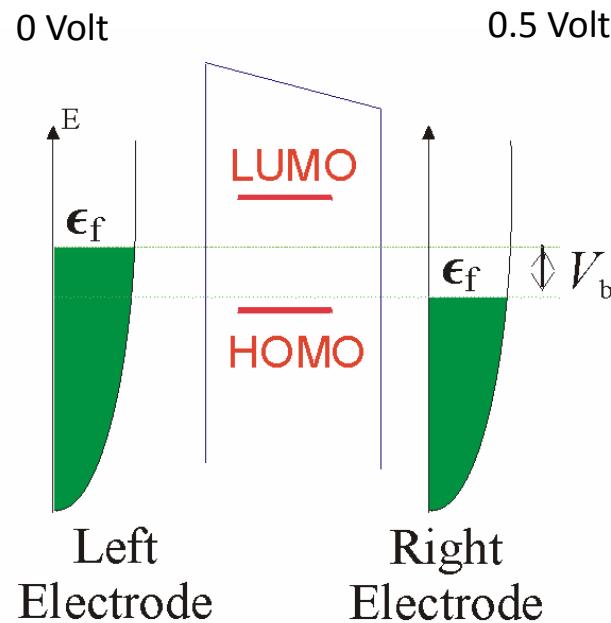
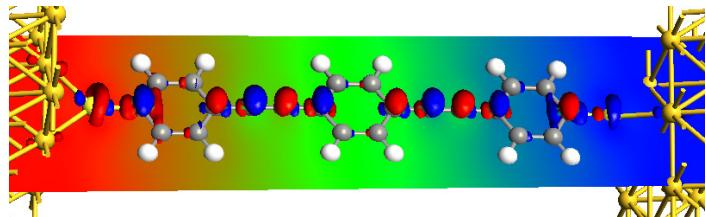
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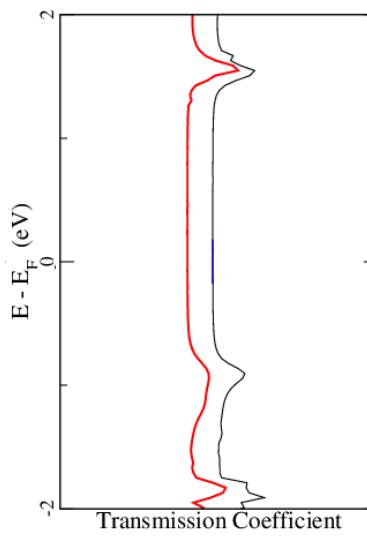
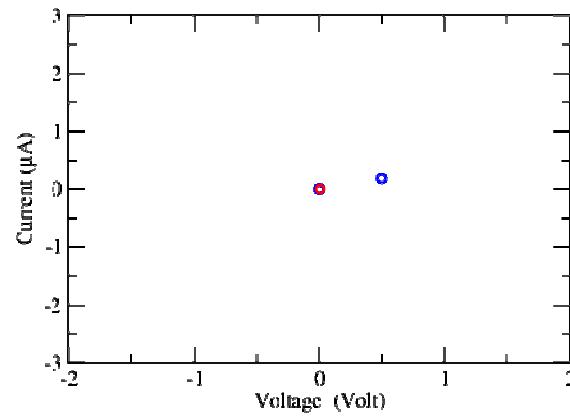
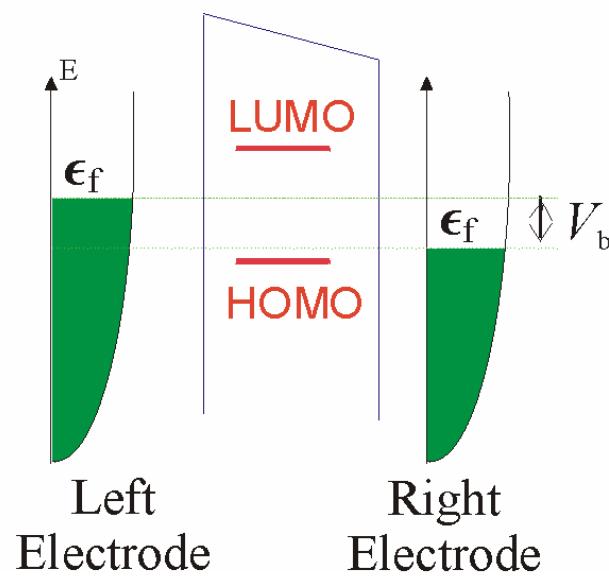
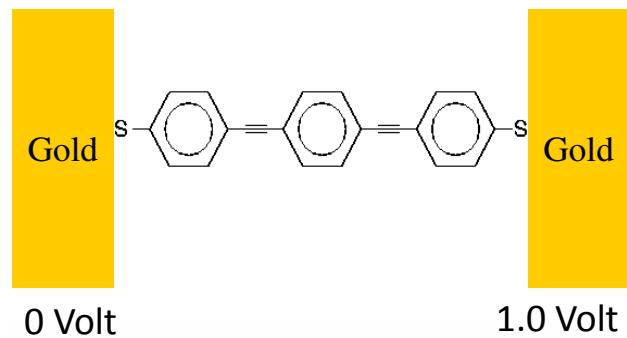
0 Volt



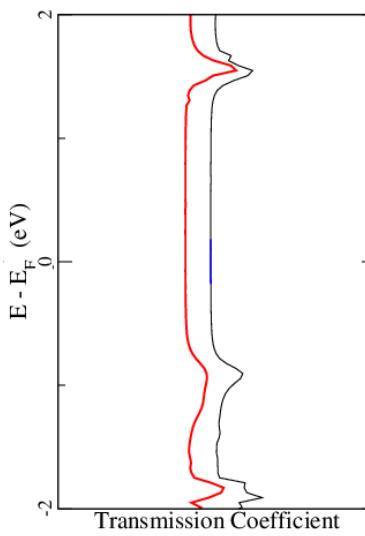
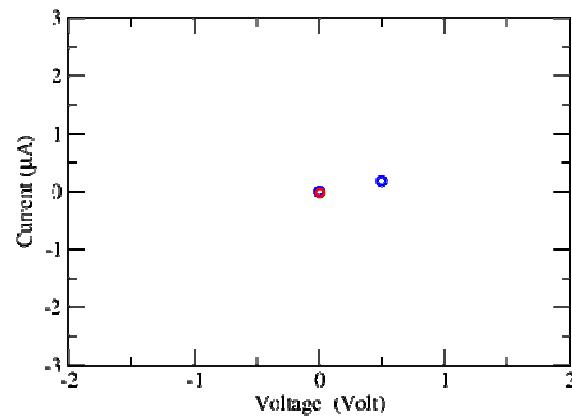
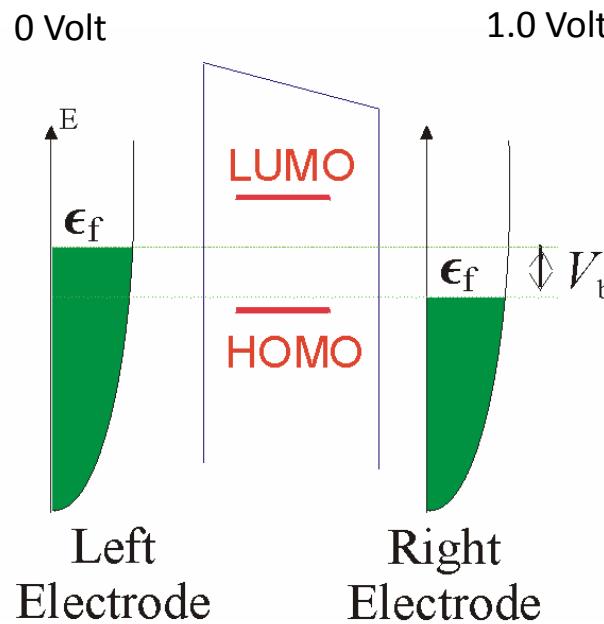
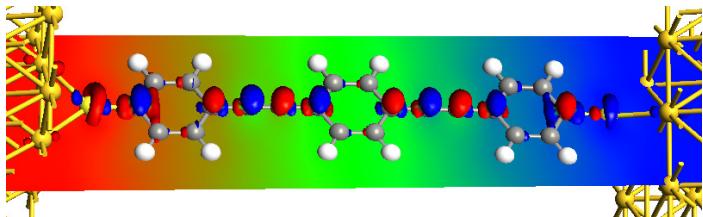
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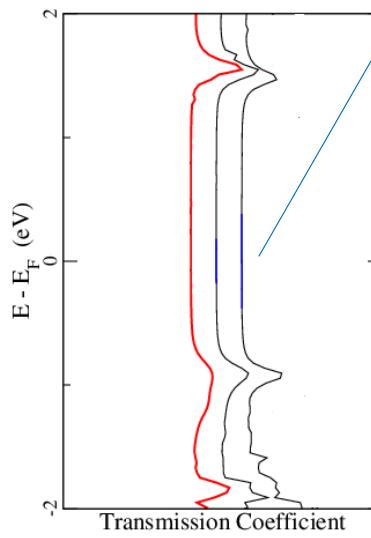
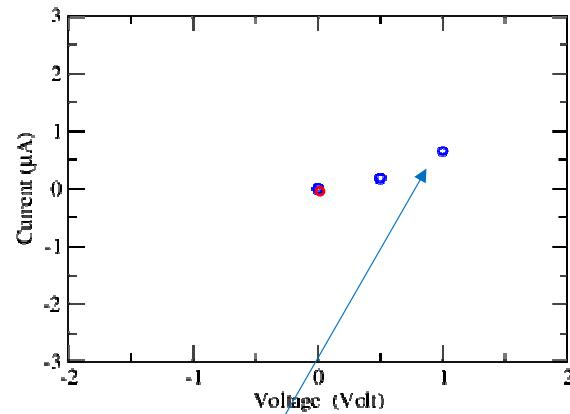
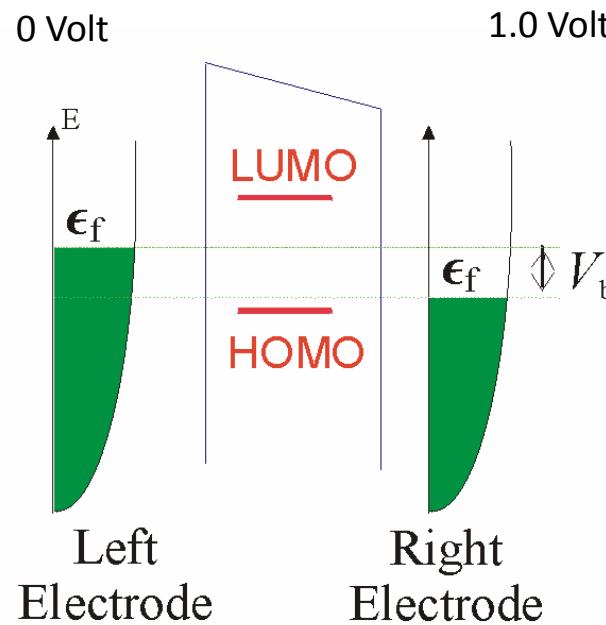
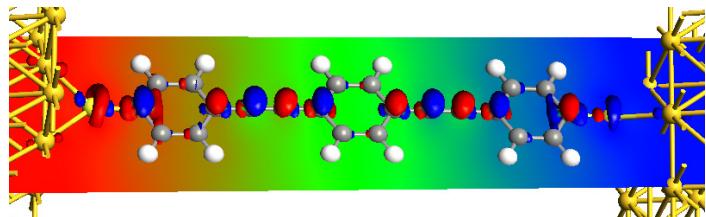
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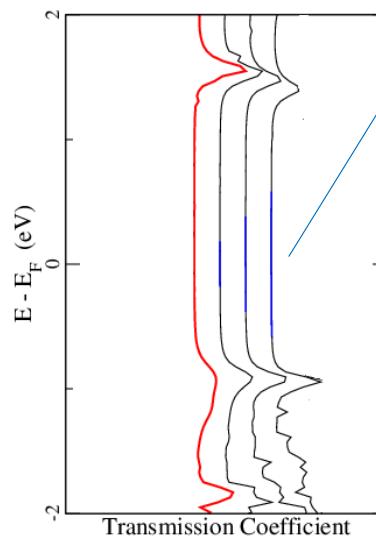
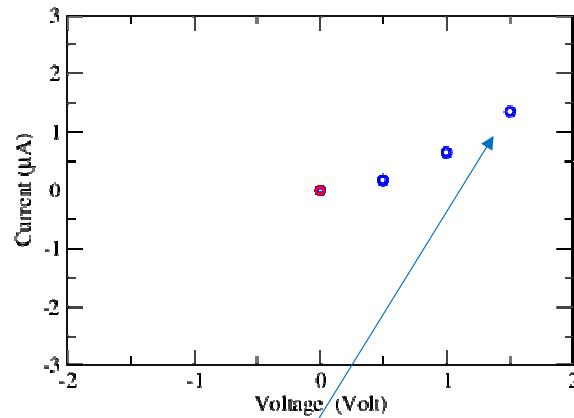
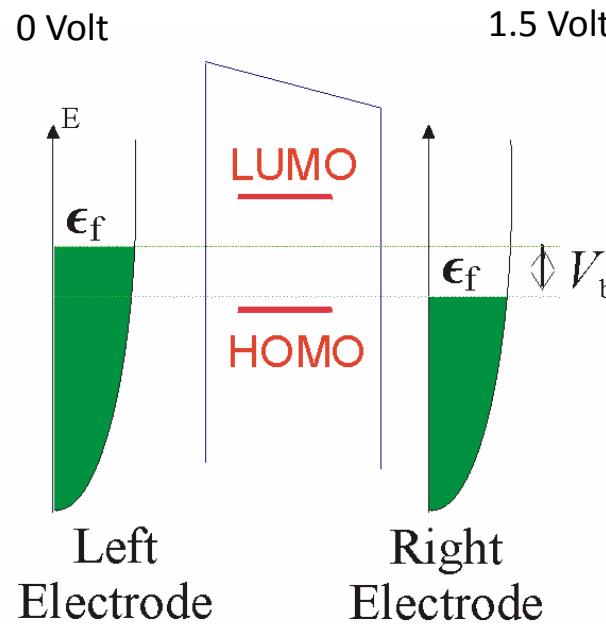
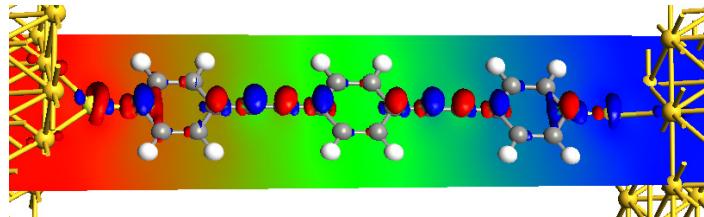
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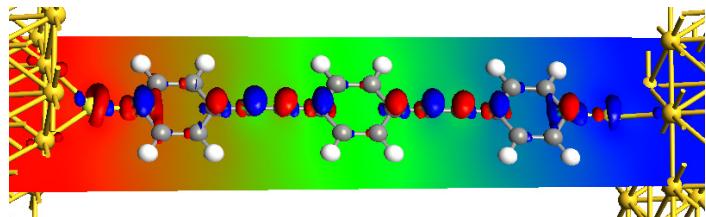
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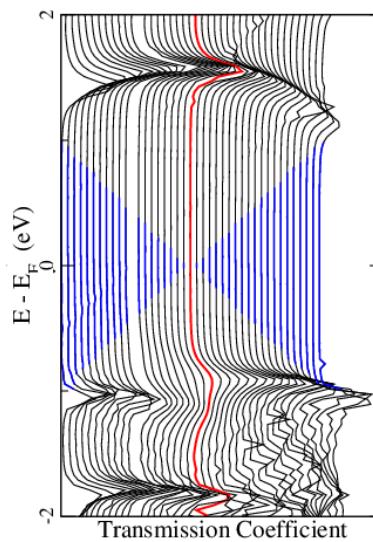
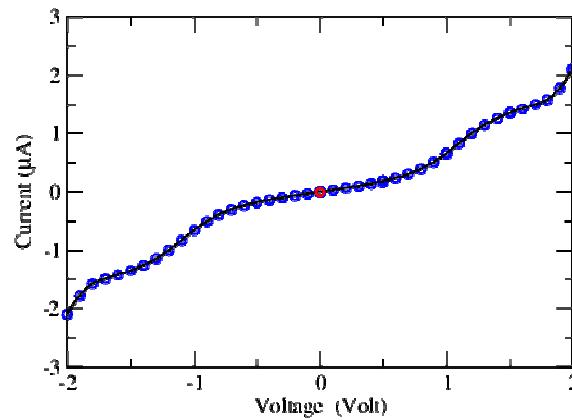
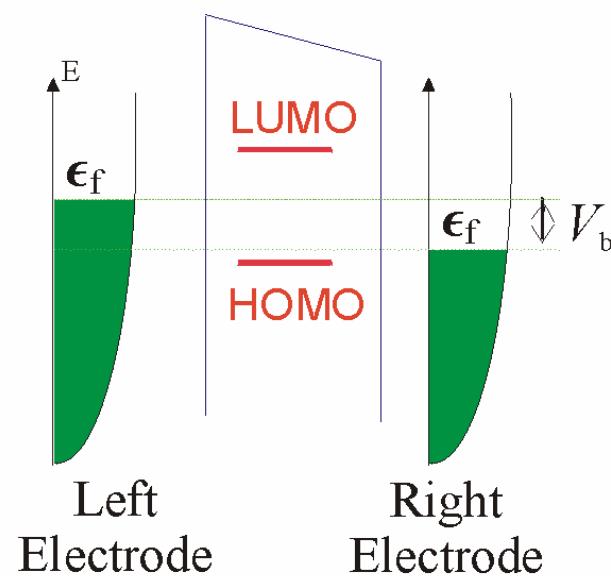
## Apply bias



## Apply bias



0 Volt                       $V_b$





QuantumWise: Scientific Publications - Mozilla Firefox  
Filér Rediger Vis Historik Bogmærker Funktioner Hjælp  
HTTP://WWW.QUANTUMWISE.COM/DOCUMENTS/ATK\_PUBLICATION\_LIST.HTML  
Mest besøgte I gang med Firefox Seneste nyheder

QuantumWise: Scientific Publications

**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)**

Author	Title	Year	Journal	DOI URL
J. Karamdel, M. Damghanian, F. Anian, F. Razaghian, C.F. Dee & B. Yeop Majlis	Dependence of Band Structure and Semiconducting (13,0) Single-Walled Carbon Nanotube and Carrier Concentration of Metallic (15,15) Single-Walled Carbon Nanotube	2015	Sains Malaysiana	<a href="#">DOI</a>
Hong Li, Xin Yan, Guangfu Luo, Rui Qin, Qihang Liu, Lili Yu, Chengyong Xu, Jiaxin Zheng, Jing Zhou, Jing Lu, Zhengxiang Gao, Shigeru Nagase & Wai Ning Mei	Functionalized Metallic Single-Walled Carbon Nanotubes by Single-Molecule Organic Acid Effect	2015	Physica E: Low-dimensional Systems and Nanostructures	<a href="#">DOI</a>
Y.W. Li, Z.L. Yin, J.H. Yao, X.S. Deng & C.L. Yang	Effect of CO adsorption on the electron transport behavior of single Fe-porphyrin molecular wire	2015	Physica E: Low-dimensional Systems and Nanostructures	<a href="#">DOI</a>
Chen Ling-Na, Ma Song-Shan, Ouyang Fang-Ping, Wu Xiao-Zan, Xiao Jin & Xu Hui	Negative differential resistance behaviour in N-doped crossed graphene nanoribbons	2010	Chinese Physics B Vol. 19(9), 097301	<a href="#">DOI</a>
Ebrahim Nadimi, Philipp Plänitz, Rolf Öttking, Karsten Wieczorek & Christian Radehaus	First Principle Calculation of the Leakage Current Through SiO <sub>2</sub> and SiO <sub>x</sub> N <sub>y</sub> Gate Dielectrics in MOSFETs	2010	IEEE Transactions on Electron Devices Vol. 57(3), 690-695	<a href="#">DOI</a>
E. Nadimi, P. Plänitz, R. Öttking, M. Schreiber & C. Radehaus	Single and Multiple Oxygen Vacancies in Ultrathin SiO <sub>2</sub> Gate Dielectric and Their Influence on the Leakage Current: An Ab Initio Investigation	2010	IEEE Electron Device Letters Vol. 31(8), 881-883	<a href="#">DOI</a>
Yun Ren, Ke-Qiu Chen, Jun He, Li-Ming Tang, Anlian Pan, B.S. Zou & Yan Zhang	Mechanically and electronically controlled molecular switch behavior in a compound molecular device	2010	Appl. Phys. Lett. Vol. 97(10), 103506-3	<a href="#">DOI</a>

Færdig

# Outline

QuantumWise

Density Functional Theory

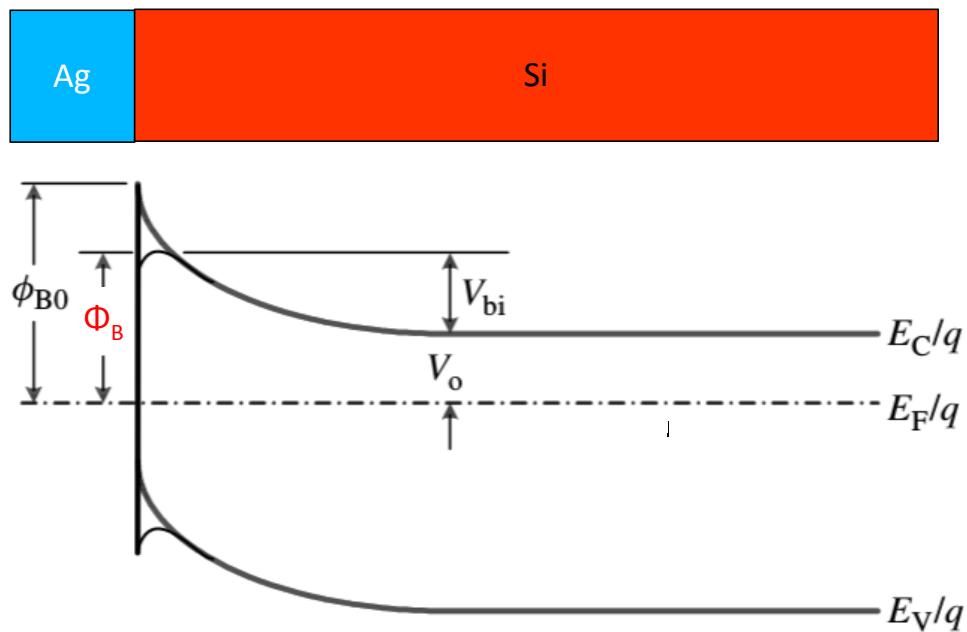
Quantum Transport

**Simulation of Interfaces**

Simulation of Batteries

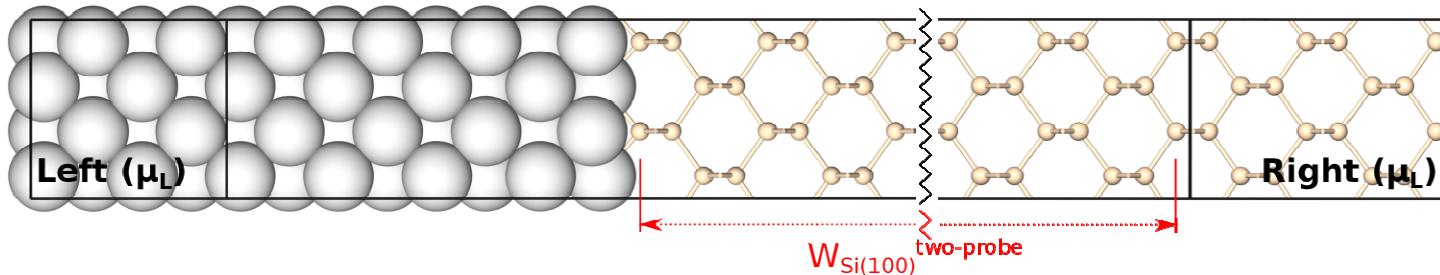


# Metal-Semiconductor Schottky contact



$\Phi_{B0}$  = Ideal barrier height  
 $\Phi_B$  = Effective barrier height  
 $V_{bi}$  = build in potential  
 $V_0$  = potential ( $E_F - E_V$ )

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



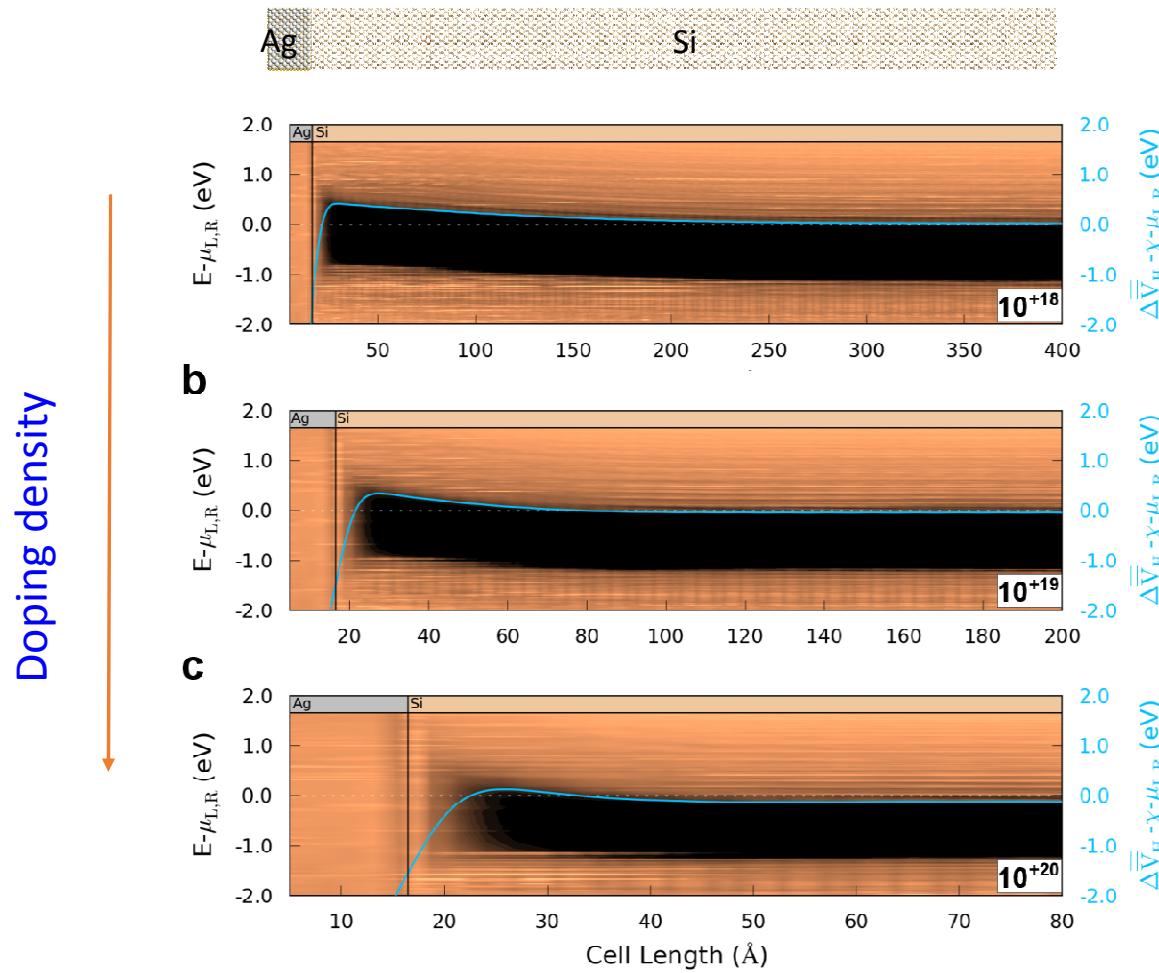
- **DFT+NEGF formalism\***: exact representation of the non-periodic interface
- **Meta-GGA functional\*\***: correctly accounts for the silicon band gap ( $E_g = 1.17 \text{ eV}$ )
- **Effective doping** of the silicon side using localized charges on the Si atoms

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

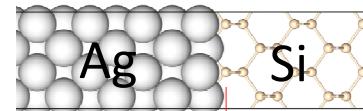
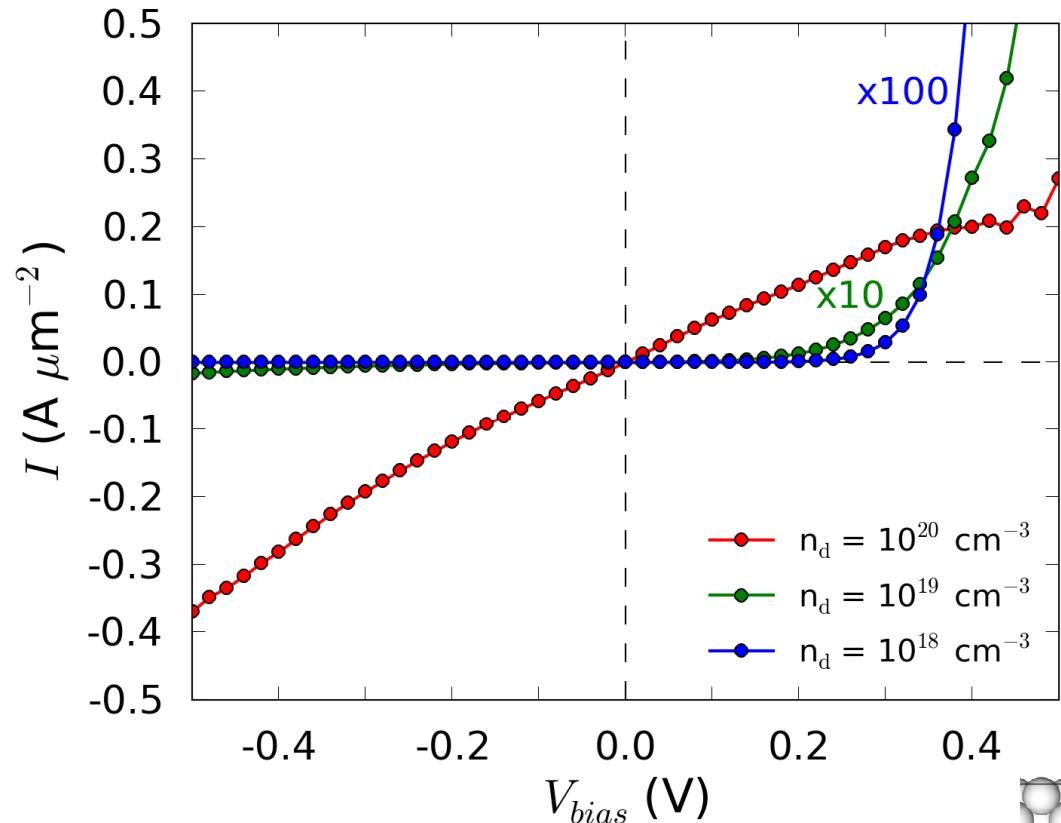
\*Brandbyge et al. *Phys. Rev. B* **65**, 165401 (2002)

\*\* 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

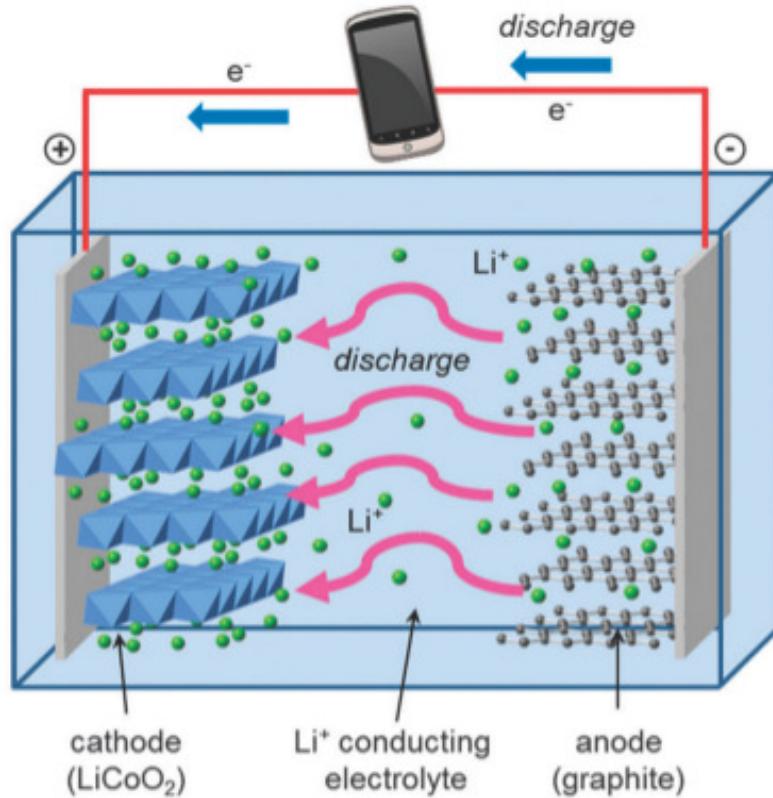
Simulation of Interfaces

**Simulation of Batteries**





## Operation of a Li ion battery

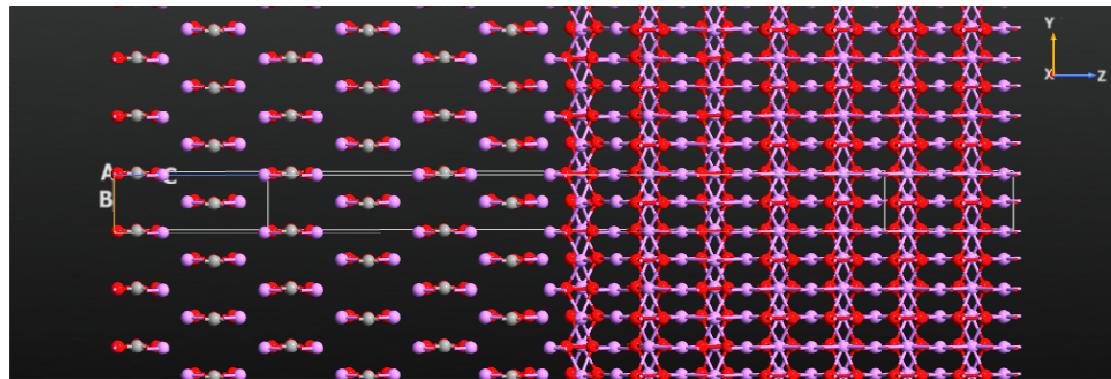


# Electron transport across Li<sub>2</sub>O<sub>2</sub>/Li<sub>2</sub>CO<sub>3</sub> interface



- ❖ Import/create Li<sub>2</sub>O<sub>2</sub> and Li<sub>2</sub>CO<sub>3</sub> bulk structures
- ❖ Cleave surfaces
- ❖ Create Li<sub>2</sub>O<sub>2</sub>/Li<sub>2</sub>CO<sub>3</sub> interface
- ❖ Create device and optimize geometry
- ❖ Calculate electronic transport properties

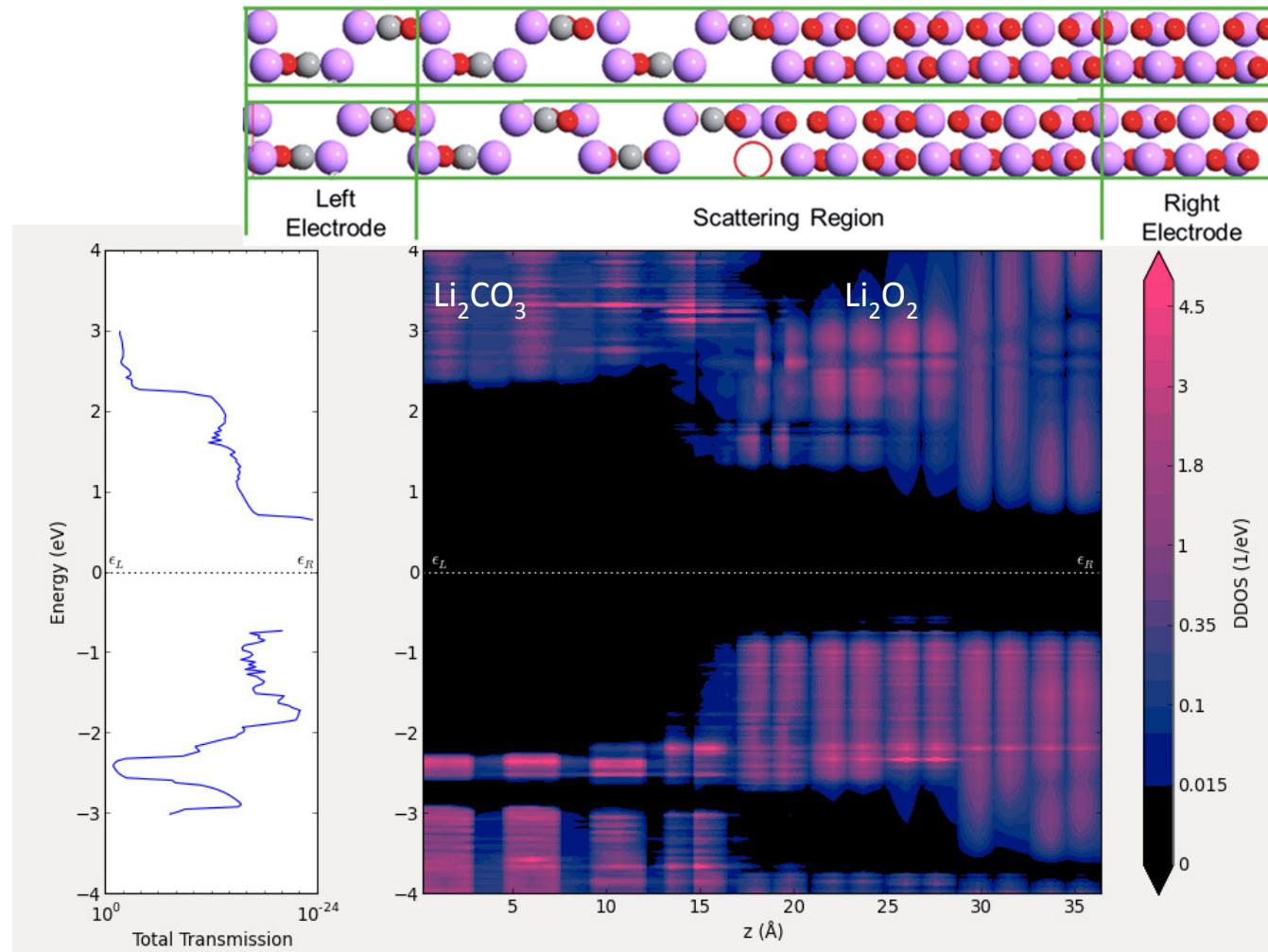
Tutorial Tuesday  
18-20



Yedilfana *et al.* JPCC (2015)

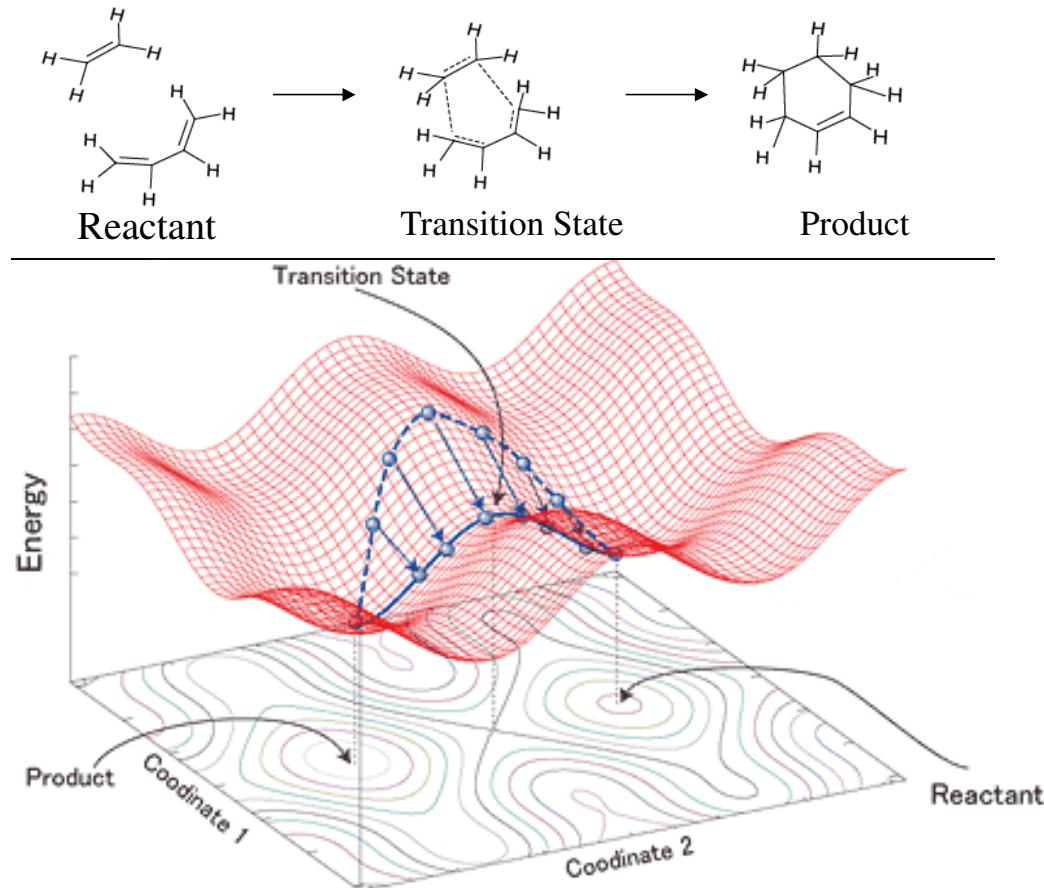


## Li<sub>2</sub>CO<sub>3</sub>/Li<sub>2</sub>O<sub>2</sub> projected density of states





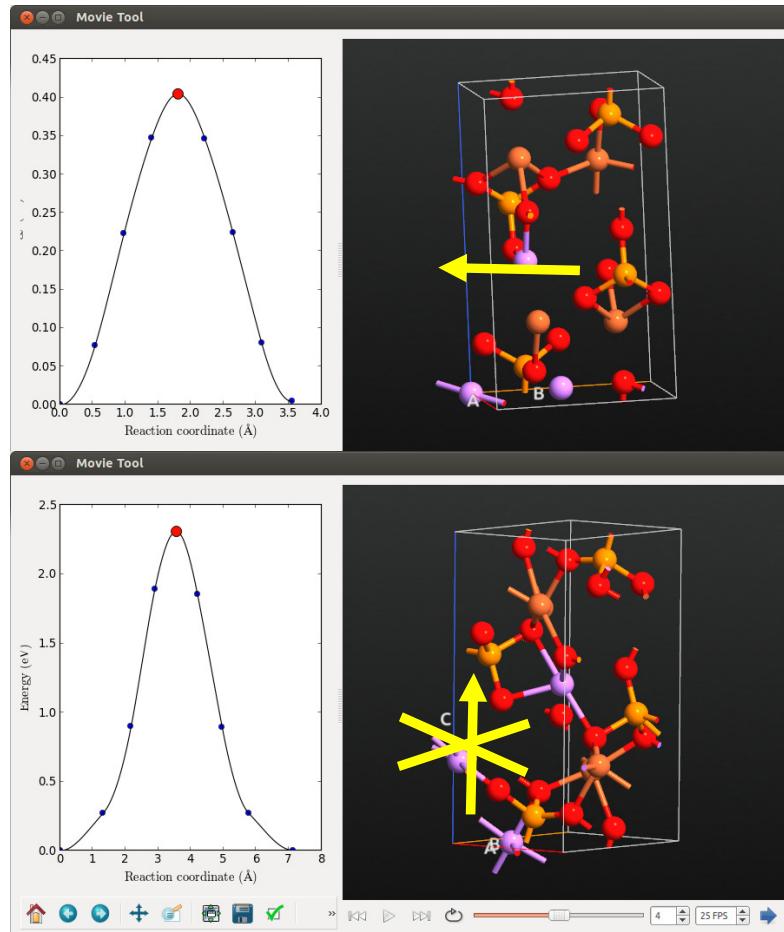
## Calculation of reaction barrier using NEB



# Li diffusion path

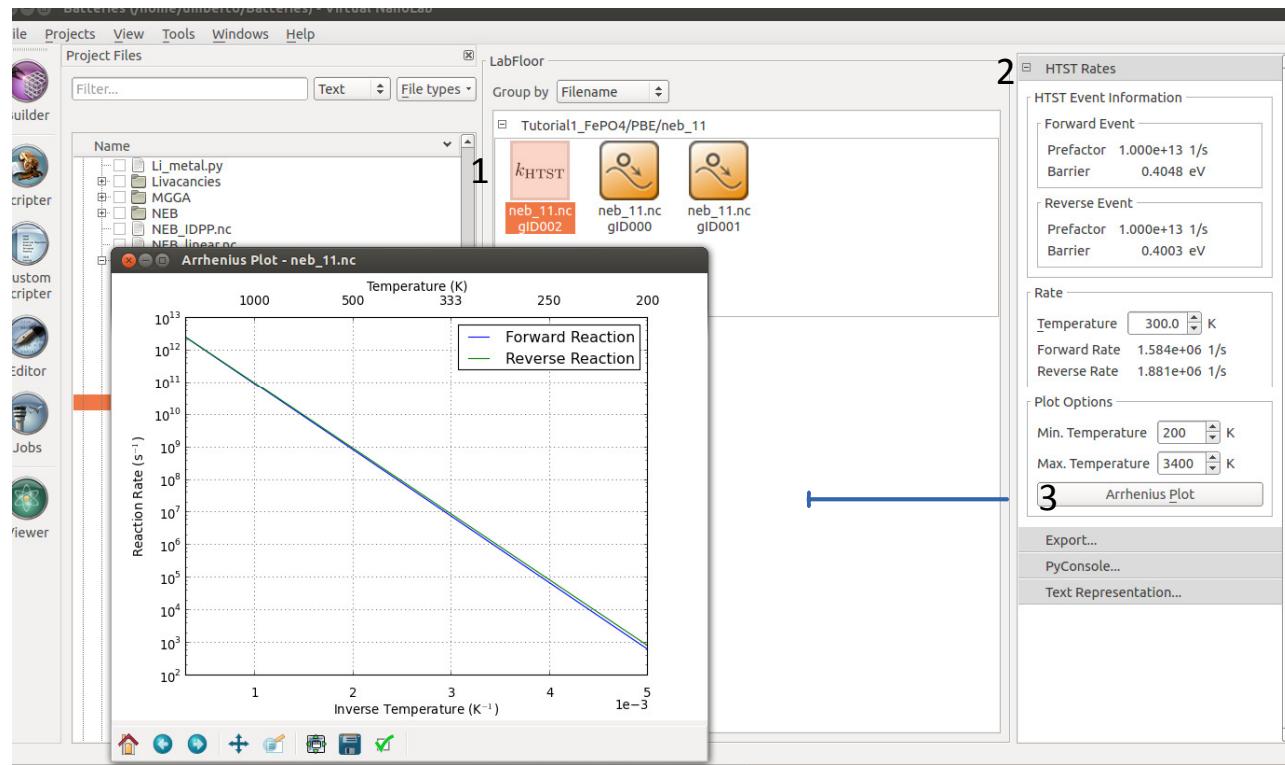


- ❖ Li diffusion along y axes:
- ❖ Barrier 0.41 eV



- ❖ Li diffusion along z axes:
- ❖ Barrier 2.31 eV

# Calculate the reaction rates using harmonic transition state theory



y direction  
z direction

Barrier	$k_{\text{HTST}} @ 300 \text{ K}$
0.41 eV	$1.6 \cdot 10^6 \text{ s}^{-1}$
2.31 eV	$1.5 \cdot 10^{-26} \text{ s}^{-1}$

See Tutorial: *Calculating Reaction Rates using Harmonic Transition State Theory*  
[http://docs.quantumwise.com/tutorials/neb\\_htst.html](http://docs.quantumwise.com/tutorials/neb_htst.html)



# Tutorials available at QuantumWise

The screenshot shows a web browser window with the URL [docs.quantumwise.com/tutorials/tutorials.html](http://docs.quantumwise.com/tutorials/tutorials.html). The page displays a sidebar menu on the left and a main content area on the right.

**Left Sidebar (Tutorials):**

- Getting started
- Tips and tricks
- VNL tasks and workflows
- ATK explained
- Semiconductors
- Batteries and energy storage
- Complex interfaces
- Tubes, ribbons and other 1D nanostructures
- Graphene and other 2D materials
- Phonons and thermal transport
- Molecular dynamics
- Spintronics
- Molecular electronics
- Materials, surfaces and chemistry
- FHI-aims calculations
- VNL as GUI for Quantum ESPRESSO
- VNL as GUI for VASP
- VNL as GUI for LAMMPS
- Work in progress
- Complete list
- Case Studies
- Guides

**Main Content Area:**

Icon	Title
	Getting started
	Tips & tricks
	VNL tasks and workflow
	ATK explained
	Semiconductors
	Complex interfaces
	Tubes, ribbons and other 1D nanostructures
	Graphene and other 2D materials
	Phonons and thermal transport
	Molecular dynamics
	Spintronics
	Molecular electronics
	Materials, surfaces and chemistry



# Youtube videos: QuantumWiseTV

The screenshot shows a web browser window displaying the QuantumWiseTV YouTube channel page. The URL in the address bar is <https://www.youtube.com/user/QuantumWiseTV>. The channel page features a navigation menu on the left with links to Home, My Channel, Trending, Subscriptions, History, Watch Later, Library, Subscriptions, and Manage subscriptions. The main content area displays several video thumbnails under sections like 'WATCHED' and 'Created playlists'. A large purple starburst graphic is overlaid on one of the video thumbnails in the 'Popular uploads' section.

**WATCHED** (4 videos)

- General atomicistic approach for modeling metal-semiconductor ... (1:33)
- FHI-aims and ATK-VNL for HSE calculations (7:04)
- Virtual NanoLab for Quantum ESPRESSO band structure and ... (5:53)
- Virtual NanoLab as GUI for Quantum ESPRESSO (3:56)

**Created playlists**

- Virtual NanoLab for Quantum ESPRESSO (2 VIDEOS)
- Virtual NanoLab for VASP (4 VIDEOS)
- Getting started (5 VIDEOS)
- Full VNL workflow - demos and tutorials (3 VIDEOS)

**Popular uploads**

- Introduction to Virtual NanoLab as GUI for VASP (4:23)
- Virtual NanoLab - GUI for VASP #2 - Analyze VASP files (4:02)
- Stretching a graphene bridge between two CNTs (0:17)
- How to turn on captions/subtitles on YouTube (2:05)

# Active forum with more than 1500 users



Google   |  Inbox (1,592) - kurt.stokb...   |  Trattoria Nerodisseppia - Benv...   |  Contattaci - Trattoria al S...   |  Google Maps   |  Home | QuantumWise   |  QuantumWise Forum - I...   |  +   |  X

www.quantumwise.com/forum/

**Future Releases**  
Suggest features for future releases

188 Posts  
55 Topics  
in Re: 2016.dev  
on May 25, 2016, 08:24

**Gallery**  
Post your pictures of cool geometries, results, or other things related to ATK

32 Posts  
11 Topics  
**Last post** by tuanhust  
in Re: Pillared Graphene  
on March 12, 2016, 09:08

**Atomistix ToolKit (ATK)**

**Questions and Answers**  
If you have questions about using ATK, or generally about the physics in the calculations, ask it here - and search for answers already posted

15648 Posts  
3292 Topics  
**Last post** by Dipankar Saha  
in Re: Box on top of any S....  
on **Yesterday** at 14:20

**Installation and License Questions**  
Questions specifically related to installing ATK, or the LM-X license system

837 Posts  
172 Topics  
**Last post** by Jess Wellendorff  
in Re: Core dump (segment f...  
on March 7, 2016, 08:33

**Scripts, Tutorials and Applications**  
Post your scripts, tutorials, tips & tricks, etc here to help other users be more productive

902 Posts  
146 Topics  
**Last post** by bsharma  
in Re: how to stop an execu...  
on June 30, 2016, 13:26

**Virtual NanoLab (VNL)**

**General Questions**  
Questions about usage of VNL functionality and other general things

385 Posts  
97 Topics  
**Last post** by Eli  
in Conductance as a functio...  
on **Yesterday** at 17:41

**Installation and License Questions**  
Questions specifically related to installing VNL, and related license issues

37 Posts  
8 Topics  
**Last post** by Anders Blom  
in Re: When and how is the ...  
on May 17, 2016, 22:59

**Plugin Development**  
Post plugins for VNL to share with other users, or general discussions about plugin development.

35 Posts  
6 Topics  
**Last post** by Anders Blom  
in Re: Quantum espresso imp...  
on May 10, 2016, 11:45

New Posts    No New Posts    Redirect Board    MARK ALL MESSAGES AS READ

**QuantumWise Forum - Info Center**

**Forum Stats**

18165 Posts in 3866 Topics by 1660 Members. Latest Member: Eli  
Latest Post: "Conductance as a functio..." ( **Yesterday** at 17:41 )  
View the most recent posts on the forum.  
[More Stats]

**Users Online**

Quantum  
Wise

