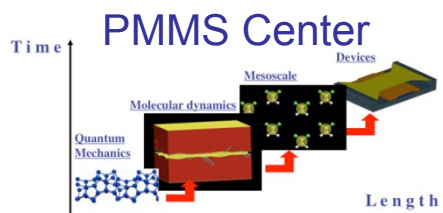


nanoHUB.org learning module: Prelab lecture on bonding and band structure in Si

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Based on Purdue MSE270 lectures by Alejandro Strachan



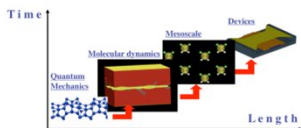
Learning module on: Bonding and band structure in Si

Learning Objectives:

- Understand how the band structure of a semiconductor develops from the electronic states of the atoms
- Understand cohesion energy in the crystal

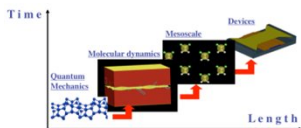
Approach:

- This is hand-on learning module where students will run online electronic structure calculations in nanoHUB.org at the DFT level to explore bonding and band structures



Outline

- DFT
 - Basic Quantum Mechanics
 - Introduction to DFT
 - Relevant resources for further learning
- Lab problem
 - Correlation between atomic and electronic structure in bulk-Si
 - Formation of electronic bands
 - Bonding and anti-bonding states
- Running first Simulations
 - Setting up the input
 - Running the simulation
 - Viewing the results
- Links to hands-on activities



Basic Quantum Mechanics Background

- Solving the time independent Schrodinger equation forms the basis for solving any electronic structure problem.

$$H\psi(r) = E\psi(r)$$

where H is Hamiltonian operator defined by

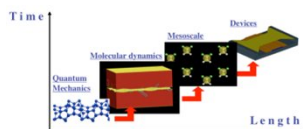
$$H = -\frac{\hbar^2}{2m}\nabla^2 + U(r,t)$$

Eigenvalue problem: Many functions $\psi_m(r)$ satisfy the time independent Schrodinger Eqn. with energy eigenvalues E_m

- Hamiltonian for a multi-atom system

$$H = \sum_{i=1}^N \frac{-\hbar^2}{2M_i} \vec{\nabla}_{R_i}^2 + \sum_{i=1}^n \frac{-\hbar^2}{2m_e} \vec{\nabla}_{r_i}^2 - \sum_{i,j}^{n,N} \frac{Z_i e^2}{|r_i - R_j|} + \sum_{i<j}^n \frac{e^2}{|r_i - r_j|}$$

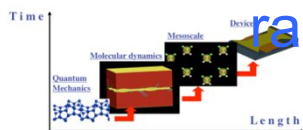
- DFT methods solve the Schrodinger equation within certain approximations.



Introduction to DFT

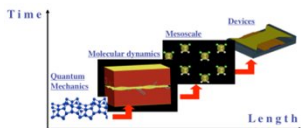
We would now like to learn about bonding and bandstructure in semiconductors. The equations become impossible to solve with paper and pencil so we will use research-grade simulation tools to do this

- Solving the Schrodinger equations exactly for systems involving many electrons is computationally VERY intensive
- We will use Density Functional Theory (DFT) that provides a good balance between accuracy and computational accuracy
- A few words about DFT
 - Pierre Hohenberg and Walter Kohn show that the ground state wavefunction of a system is a functional of the electron density (1964)
 - Kohn and Lu Sham propose equations to solve the DFT equations (1965)
 - During the 1980's and 1990's several accurate "functionals" were developed that allow accurate calculations for a wide range of materials



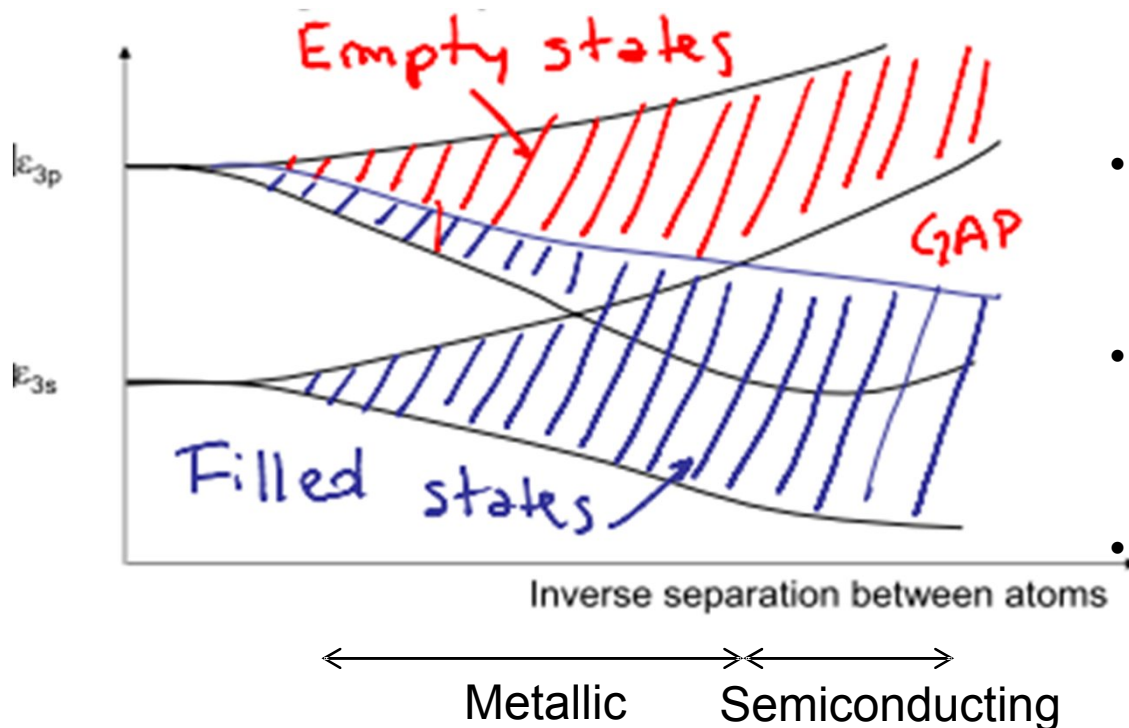
Further Resources on DFT

- Want to learn more about DFT?
 - Rev. Mod. Phys. 64, 1045-1097 (1992)
 - Online book: “The ABC of DFT”
<http://dft.uci.edu/materials/bookABCDFT/gamma/g1.pdf>
 - Take MSE597G “Modeling and simulations of materials”

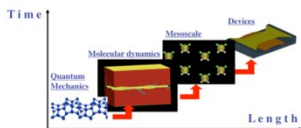


Correlations in Atomic and Electronic Structure

Imagine Si atoms to form a fcc lattice at different interatomic distances. How do the energy levels look conceptually?



- As Si atoms are brought closer, the atomic energy levels broaden into bands.
- 3s levels are always fully occupied. 3p levels are partially occupied (1/3)
- For larger lattice parameters, Si is observed to be metallic (partial occupation of bands)
- This shows that the atomic arrangement and electronic structure are strongly correlated.



Lab Exercise: Can you show similar behavior using DFT calculations done on Si

Running DFT calculations: nanoHUB tools

Tools @ nanHUB.org:

DFT calculations with Quantum ESPRESSO

nanoMATERIALS SeqQuest DFT

General Purpose tools for DFT simulations

Step1: Go to nanoHUB web portal nanohub.org

Step2: Create an account

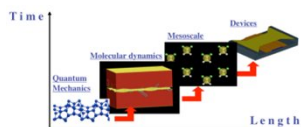
Step3: Login

Step4: Click on “All Tools” and select:

DFT calculations with Quantum ESPRESSO

nanoHUB.org - Simulation, Education, and Community for Nanotechnology - Mozilla Firefox
https://nanohub.org/home
nanoHUB.org ONLINE SIMULATION AND MORE FOR NANOTECHNOLOGY
54 New Messages
Rawl Pramod Kumar Vedula (vedula) Logout My Account
Home My HUB Resources Members Explore About Support
Need Help?
UP from the bottom ELECTRONICS
Re-thinking electronics from the nano perspective
SIMULATE with over 160 tools for nanoelectronics, nanophotonics and more
RESEARCH & COLLABORATE via groups, question board and more
TEACH & LEARN with tool-powered curricula, courses, seminars and more
SHARE & PUBLISH tools and research through our easy upload process
Over 165,000 users annually
30 Live Simulation Sessions
Detailed statistics Who's online?
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nanophotonics quantum transport tutorial transistors
nano electro-mechanical systems molecular electronics NEGF
carbon nanotubes education/outreach ABACUS
band structure nanomedicine MOSFET
FEATURED
Molecular Structure Tracer: This tool provides a high quality display of molecular structures. - in Tools
Lecture 2: total energy and force calculations - in Online Presentations
John Bean, University of Virginia, Charlottesville, VA - Contributions: 444
NOTABLE QUOTE
nanoHUB enables a well-developed workforce to generate economic opportunity.
Bruce Barker, President, Chippewa Valley Technical College - in Notable Quotes
NEW IN RESOURCES
Negative Refraction, Light Pressure and Attraction, Equation $E=mc^2$ and Wave-particle Dualism

My Tools
Recent Favorites All Tools
Cyber-Infrastructure for Imaging and Simulation of Molecular and Cellular Mechanics (CISMCM)
Cylindrical CNT MOSFET Simulator
demons
DFT calculations with Quantum ESPRESSO
Drift-Diffusion Lab
Effect of Doping on Semiconductors
EPR - ESR
Add a tool to your favorites by clicking a heart. Click the heart again to remove it.



Running DFT calculations : Step 1

Select a premade model from menu
Click on [Si diamond](#)
All the necessary parameters are loaded by default

Select Structure type

Some possible operations

Input the atom coordinates for the unit cell

Modify the lattice parameters

nanoHUB

1 Input → 2 Simulate

Input Geometry | Energy Expression | Phonons | Band Structure/DOS

Create the model

Premade atomistic structure: Si diamond

Atomic Coordinates: Fractional

Structure type: cubic F (fcc)

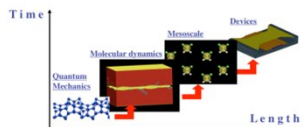
Title of Run: Silicon band structure

Atomic Structure: 2
Silicon diamond structure
Si 0.0 0.0 0.0
Si 0.25 0.25 0.25

Cell Vectors (A):
-2.715 2.715 0.000
-2.715 0.000 2.715
0.000 2.715 2.715

Lattice Parameter "a" (A): 5.43

Ratio Lattice Parameters "c/a" (A): 1



Running DFT calculations : Step 2

Energy Expression:

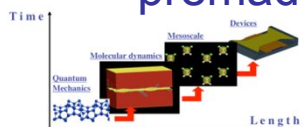
Exchange and Correlation functional approximation: LDA/GGA

K-grid spacing(indicates the number of integrals in reciprocal space)

Number of bands: 8 (4 Valence bands and 4 Conduction Bands)

Kinectic Energy Cutoffs: determine the size of the basis set used for calculations

All the optimized values for Si are loaded by default when Si diamond premade structure is selected.



1 Input → 2 Simulate

Input Geometry | **Energy Expression** | Phonons | Band S

Exchange and Correlation functional: LDA
Relax: No

K-grid spacing (Reciprocal-space)

X direction: 8
Y direction: 8
Z direction: 8

Number of bands: 8
Wavefunction Kinetic Energy cutoff (Ry): 16.0
Charge Density Kinetic Energy cutoff (Ry): 96.0
SCF Convergence Criterion (Ry): 1E-6
Enable occupation options: "yes"

Occupations Options

Occupation: tetrahedra
Smearing: Gaussian
Gaussian Spreading (Ry): 0

Enable mixing options: "no"

Running DFT calculations : Step 3

Band Structure Options

Path: Determines the path in k-space. For this simulation we will use L- Γ -X path (i.e. (0.5,0.5,0.5) to (0,0,0) to (1,0,0))

Number of points : Chooses the number of points along the path. The higher the number the smoother the curve

Simulate: Will submit your run – once finished (~5 min. in this example) the results will be displayed

1 Input → 2 Simulate ? About this tool
Questions?

Input Geometry | Energy Expression | Phonons | **Band Structure/DOS** | Advanced Opti

Band Structure Calculations: "yes"

Band Structure

Path:	0.5 0.5 0.5
	0.0 0.0 0.0
	1.0 0.0 0.0

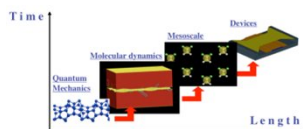
Number of Points: **30**

Density of States Calculations: "yes"

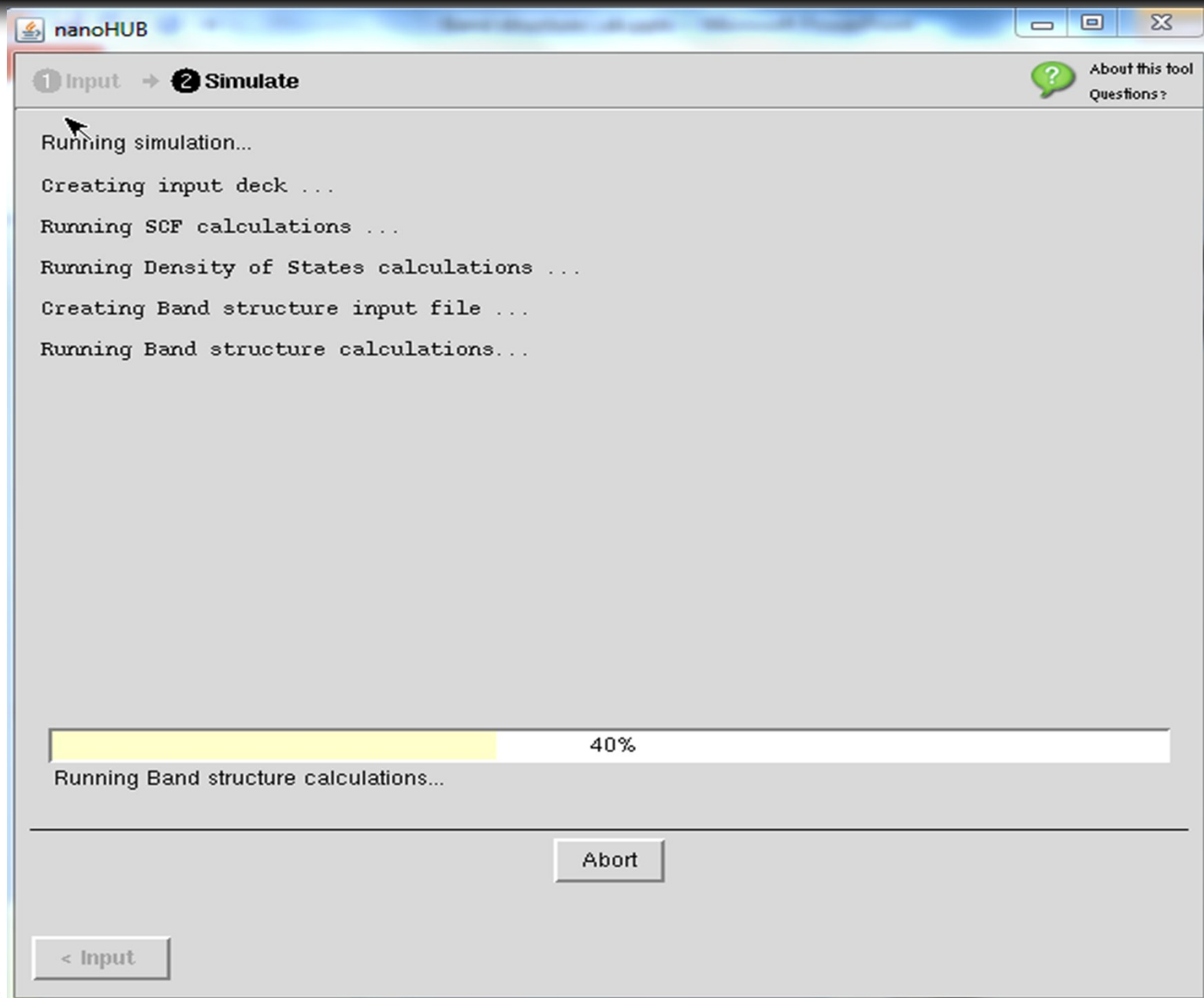
Density of States

minimum Energy (eV):	-6
maximum Energy (eV):	10
energy grid step (eV):	0.1

Simulate >



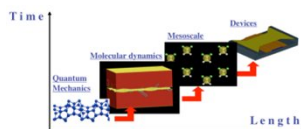
Running the Simulation



The screenshot shows the nanoHUB web interface during a simulation. The window title is "nanoHUB". At the top, there are two tabs: "1 Input" and "2 Simulate", with "2 Simulate" being the active tab. A green question mark icon and the text "About this tool Questions?" are located in the top right corner. The main content area displays a list of simulation steps in a monospaced font:

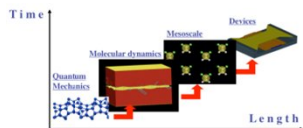
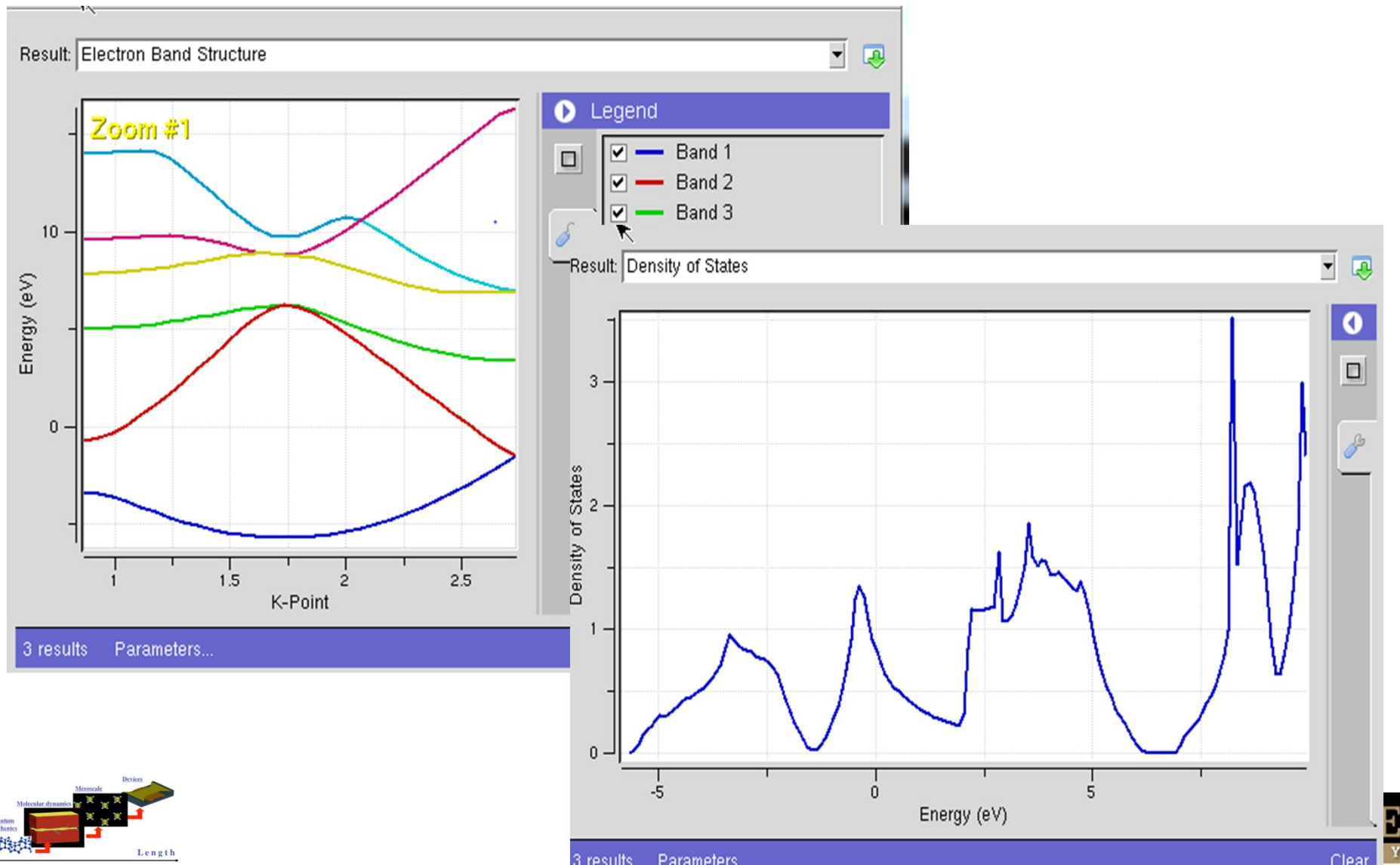
- Running simulation...
- Creating input deck ...
- Running SCF calculations ...
- Running Density of States calculations ...
- Creating Band structure input file ...
- Running Band structure calculations...

A progress bar is shown below the list, with a yellow segment indicating 40% completion. Below the progress bar, the text "Running Band structure calculations..." is displayed. At the bottom of the interface, there is an "Abort" button and a "< Input" button.



Viewing the results

Select results to visualize



Viewing the results

```
Result: SCF Output Log

k = 0.6250-0.1250 0.8750 ( 289 PWs) bands (ev):
-2.2019 -0.6456 2.1892 3.2858 8.6454 10.5315 11.5380 13.6969

k = 0.5000 0.0000 0.7500 ( 286 PWs) bands (ev):
-2.5525 -0.2830 2.0225 3.6618 9.1243 10.7955 11.4764 13.2851

k = -0.2500-1.0000 0.0000 ( 290 PWs) bands (ev):
-1.4497 -1.4497 2.8303 2.8303 8.2287 8.2287 14.1029 14.1029

k = -0.5000-1.0000 0.0000 ( 280 PWs) bands (ev):
-1.3618 -1.3618 2.3957 2.3957 10.5139 10.5139 11.2713 11.2713

the Fermi energy is 6.7215 ev

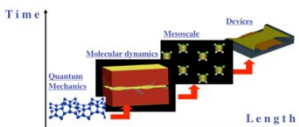
! total energy = -15.73777484 Ry
Harris-Foulkes estimate = -15.73777493 Ry
estimated scf accuracy < 0.00000021 Ry

The total energy is the sum of the following terms:
```

Find:

3 results Parameters...

Fermi Energy : This is used to occupation statistics. All the energy levels below the fermi level are filled with 2 electrons and above the fermi level are empty.



A few Pointers on interpreting DFT simulations

- Bandstructure predicted by DFT is representation of Kohn-Sham energy eigen values obtained. While these provide qualitative information, they are not the same as an actual bandstructure.
- All the major approximations used in the calculations are mentioned in the energy section
- For the simulations in this lab, all the optimized parameters can be used as default by selecting the premade Si diamond structure.

