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

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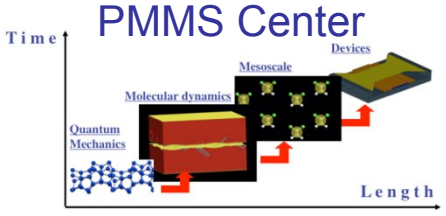
Based on Purdue MSE270 lectures by Alejandro Strachan

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# Learning module on: Bonding and band structure in Si

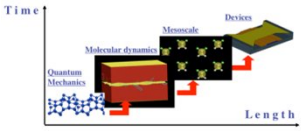
**Learning Objectives**:

•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

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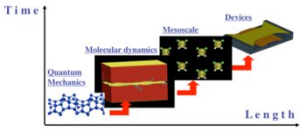
# Outline

- 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

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# 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

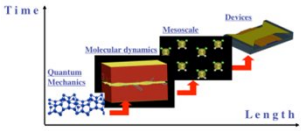
$$H = -\frac{\hbar^2}{2m}\nabla^2 + U(r,t)$$

*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.

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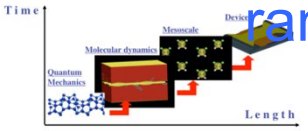
# Introduction to DFT

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)
  - Khon 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

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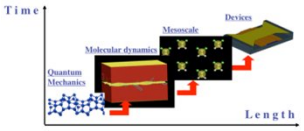
# Further Resources on DFT

- 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”

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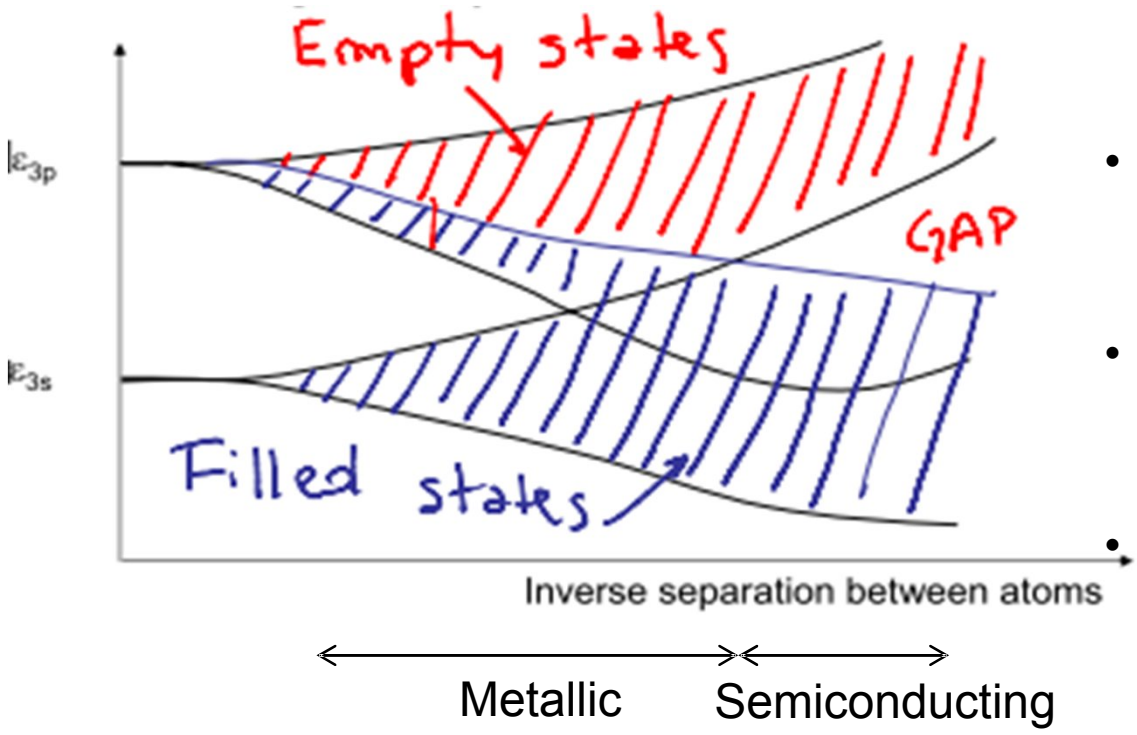
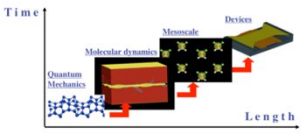
# Correlations in Atomic and Electronic Structure

## 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 (partially 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

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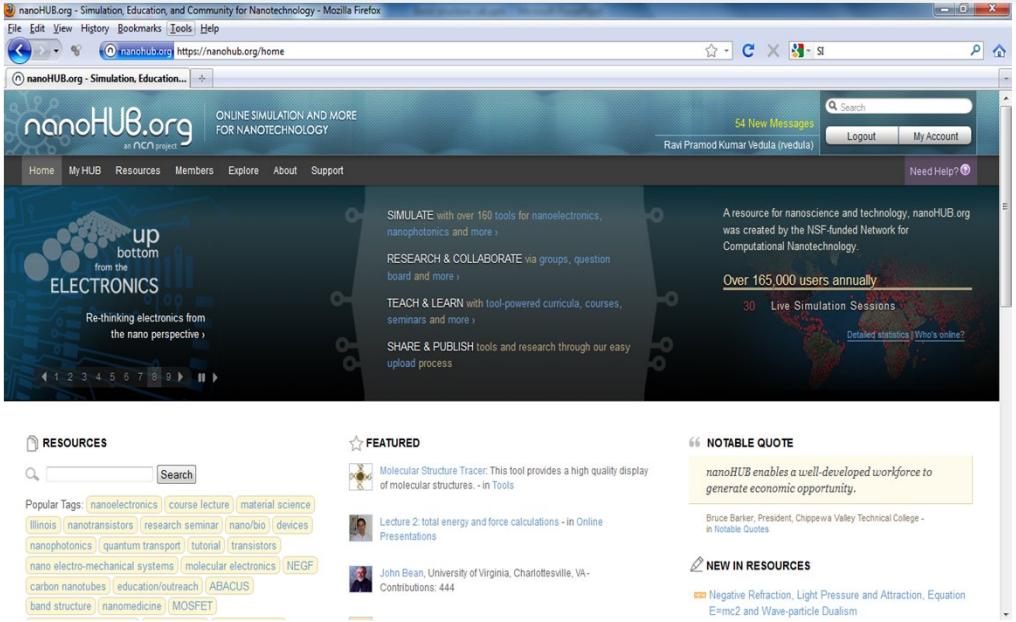
# Running DFT **calculations: nanoHUB tools**

Tools @ nanHUB.org:

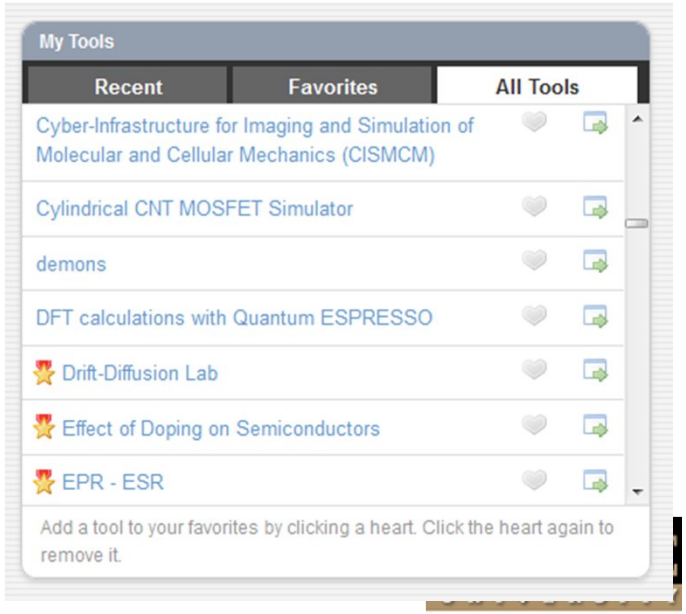
***DFT calculations with Quantum ESPRESSO***

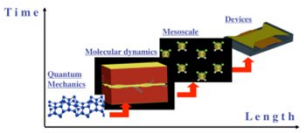
***nanoMATERIALS SeqQuest DFT***

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*



# Running DFT calculations : Step 1

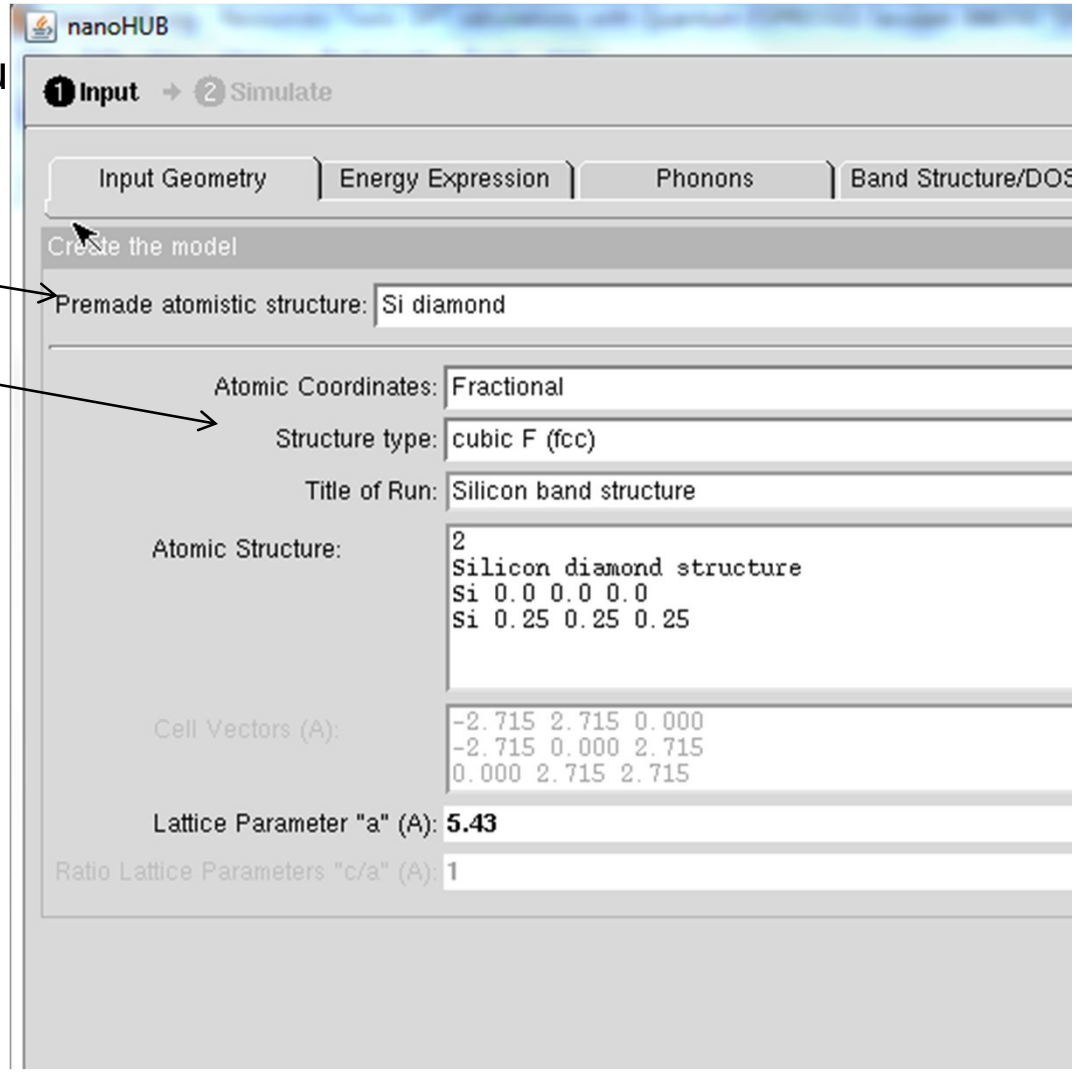
Select a premade model from menu
Click on Si diamond
All the necessary parameters are loaded by default

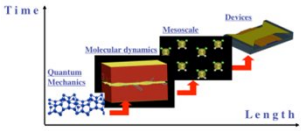
Select Structure type

Some possible operations

Input the atom coordinates for the unit cell

Modify the lattice parameters

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# Running DFT calculations : Step 2

Energy Expression:

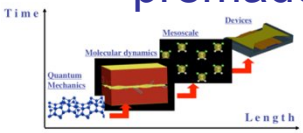
Exchange and Correlation functional approximation: LDA/GGA

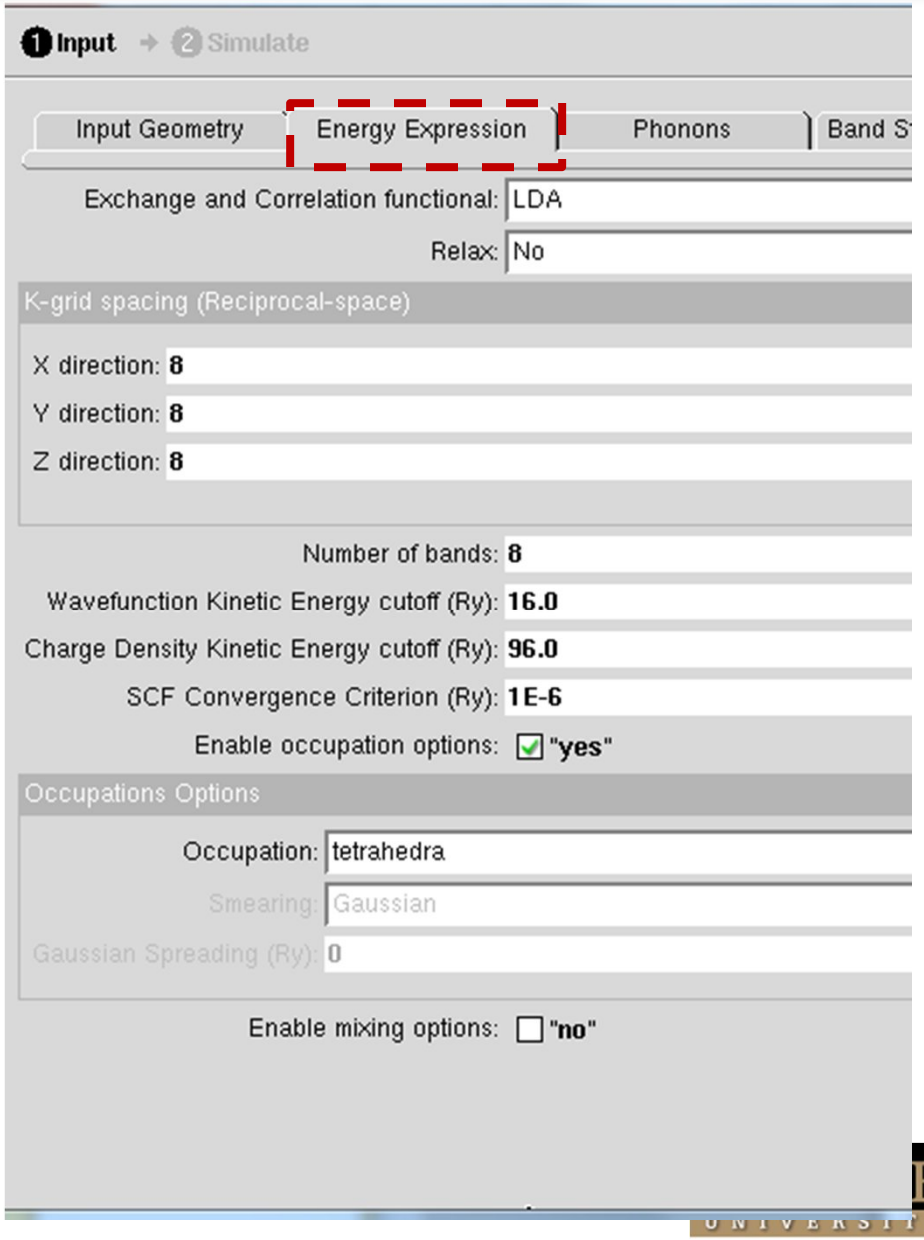
K-grid spacing(indicates the number of integrals in reciprocal space)

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.



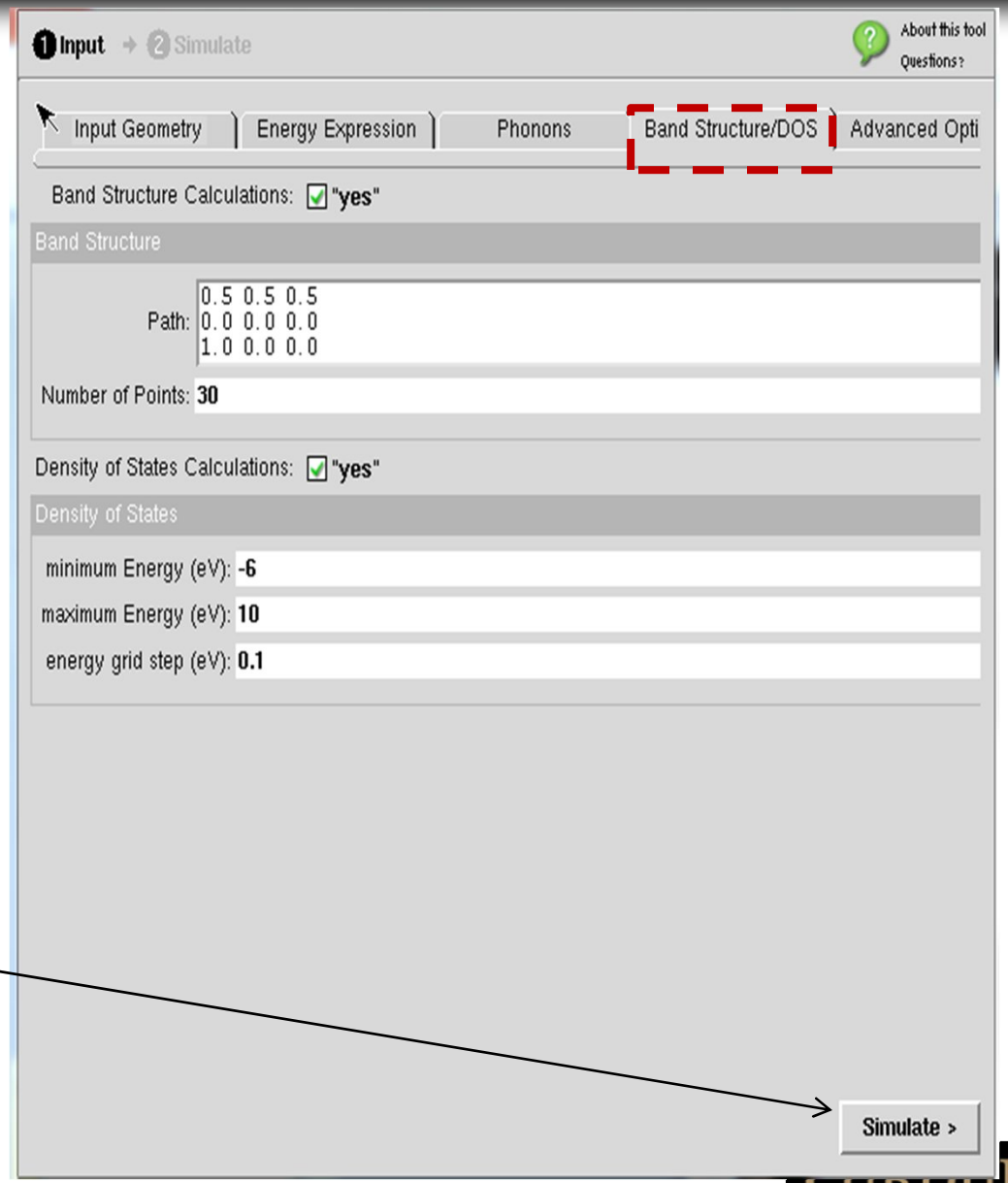
# Running DFT calculations : Step 3

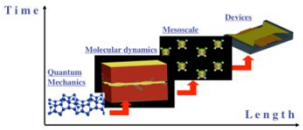
## Band Structure Options

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

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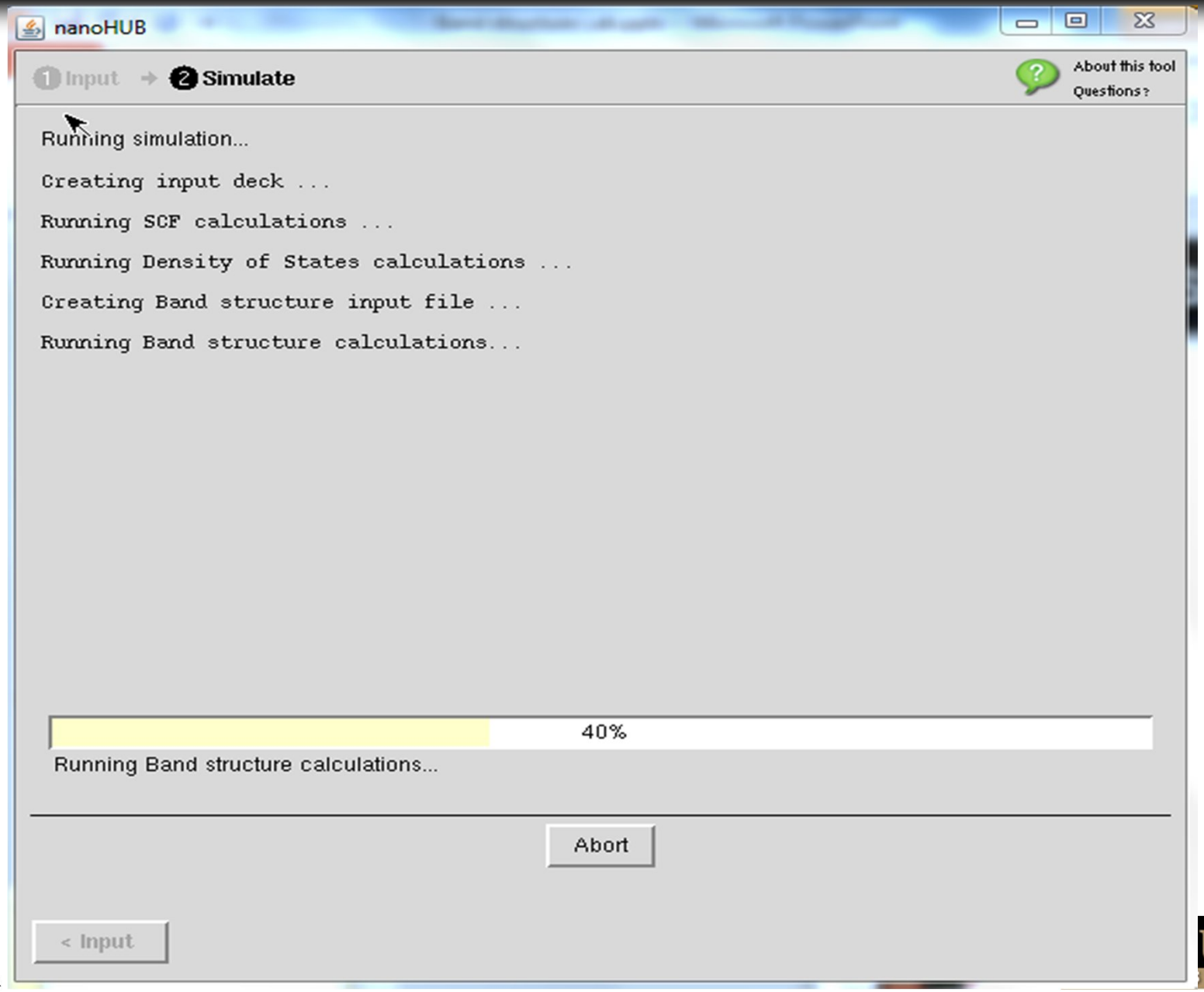
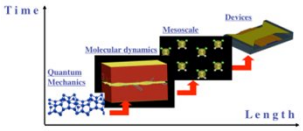
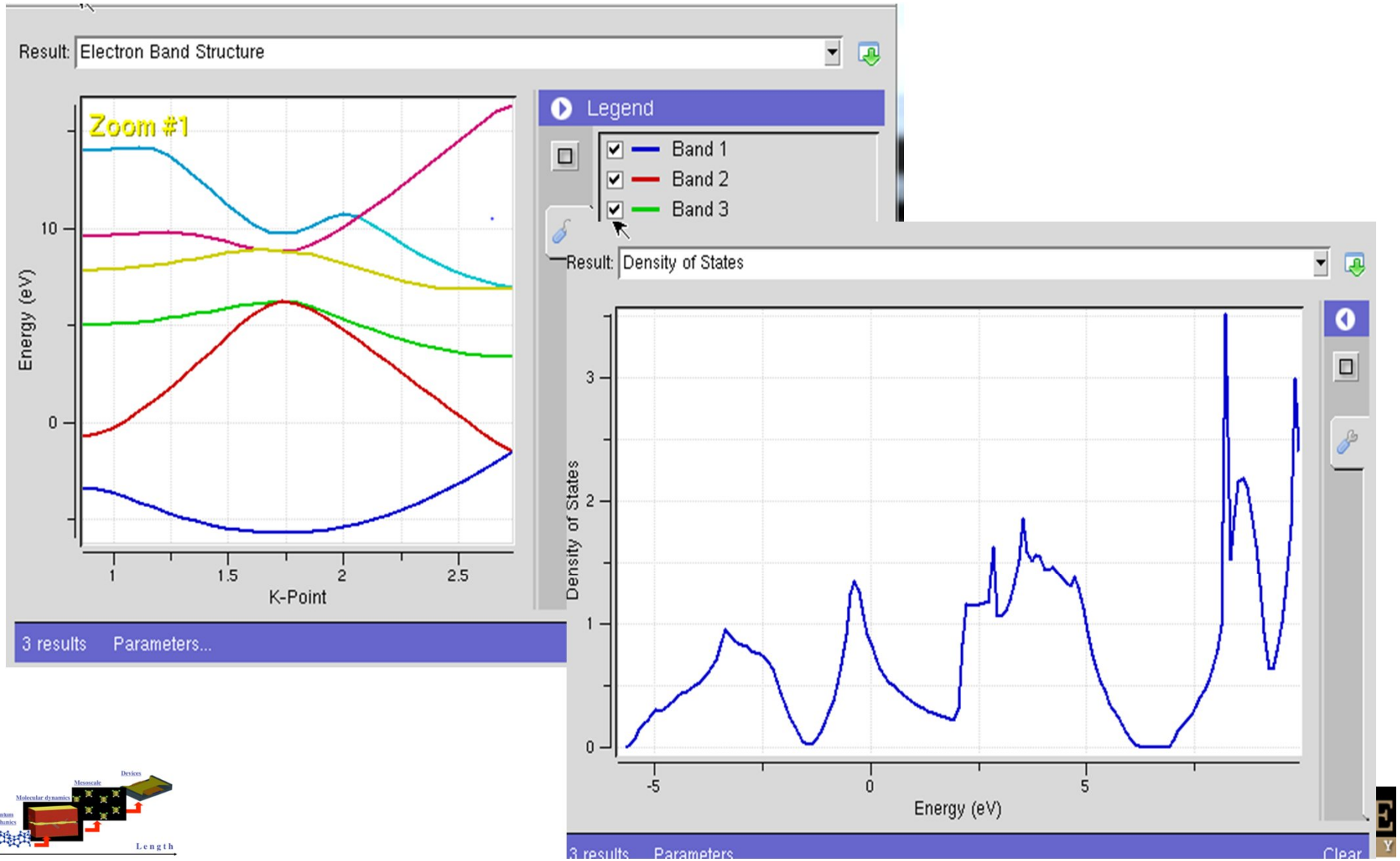
# Running the Simulation



# Viewing the results

Select results to visualize



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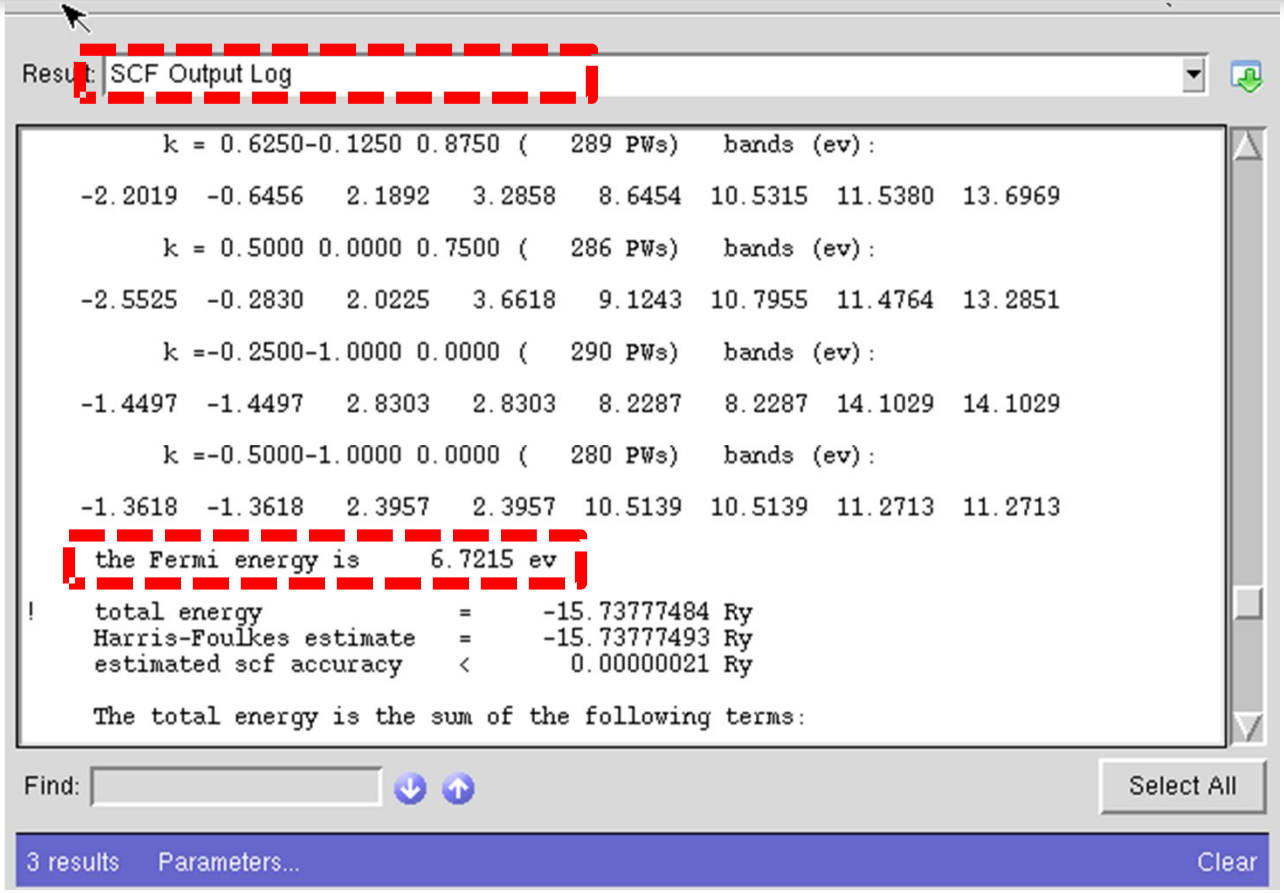
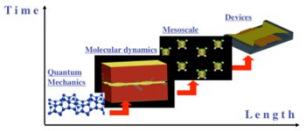



Fermi Energy : This is used to occupation statistics. All the energy levels below the fermi level are filled with 2 electrons and above the fermi level are empty.

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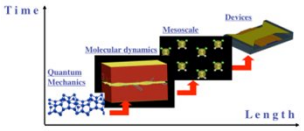
# A few Pointers on interpreting DFT simulations

- 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.

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