

Online simulations via nanoHUB: Binding and electronic structure of Si

In this tutorial:

- Use density functional theory calculations to explore:
 - How the electronic structure of Si develops
 - Understand binding in the Si crystal

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Launch the [DFTMatProp](#) tool in nanoHUB

From your *My HUB* page launch DFT calculations with Quantum Espresso

nanoHUB MENU

David M Guzman

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MY TOOLS

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dft material

DFT Material Properties Simulator

RESOURCES

- Learning Modules
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• From *All Tools* find:
DFT material

• Launch tool by clicking
on: 

DFT Material Properties Simulator

1 Input Simulate

Basic Input

Task: E-K Diagrams

Material Type: Semiconductor

Semiconductors: Si(Diamond)

Advanced Options: no

Simulate >

Electronic structure and binding in Si

- DFT calculations using the DFTMatProp tool in nanoHUB
- Explain the formation of the band structure in Si starting from the simple electronic structure of a Si atom

DFT Material Properties Simulator

1 Input → 2 Simulate

Basic Input | Geometric Input | Energy Expression | Band Structure/DOS | Dielectric

Task: E-K Diagrams

Material Type: Semiconductor

Semiconductors: Si(Diamond)

Advanced Options: yes

Simulate >

Step 1: Basic Input

- select “E-K Diagram” from task menu
- then “Semiconductor” from material type
- followed by “Si(Diamond)” in semiconductors.
- Finally switch to “yes” the advanced options

Electronic structure of Si perfect crystal

DFT Material Properties Simulator

1 Input → 2 Simulate

Basic Input

Task: E-K Diagrams

Material Type: Semiconductor

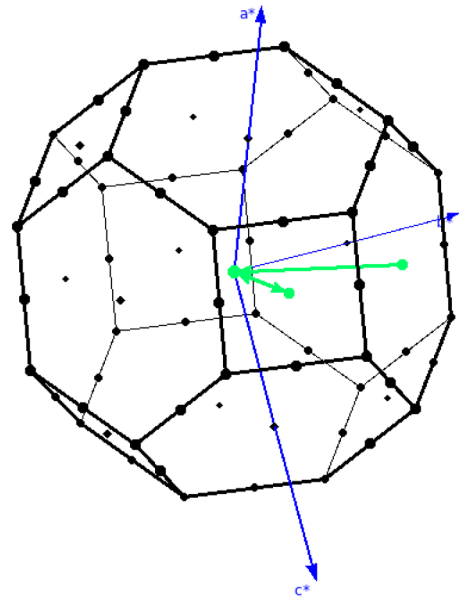
Semiconductors: Si(Diamond)

Advanced Options: no

Simulate >

Run the default E-k diagram simulation (select semiconductor and Si)

Reciprocal space



Band structure will be shown along the following path (tat contains the valence band maxima and conduction band minima)

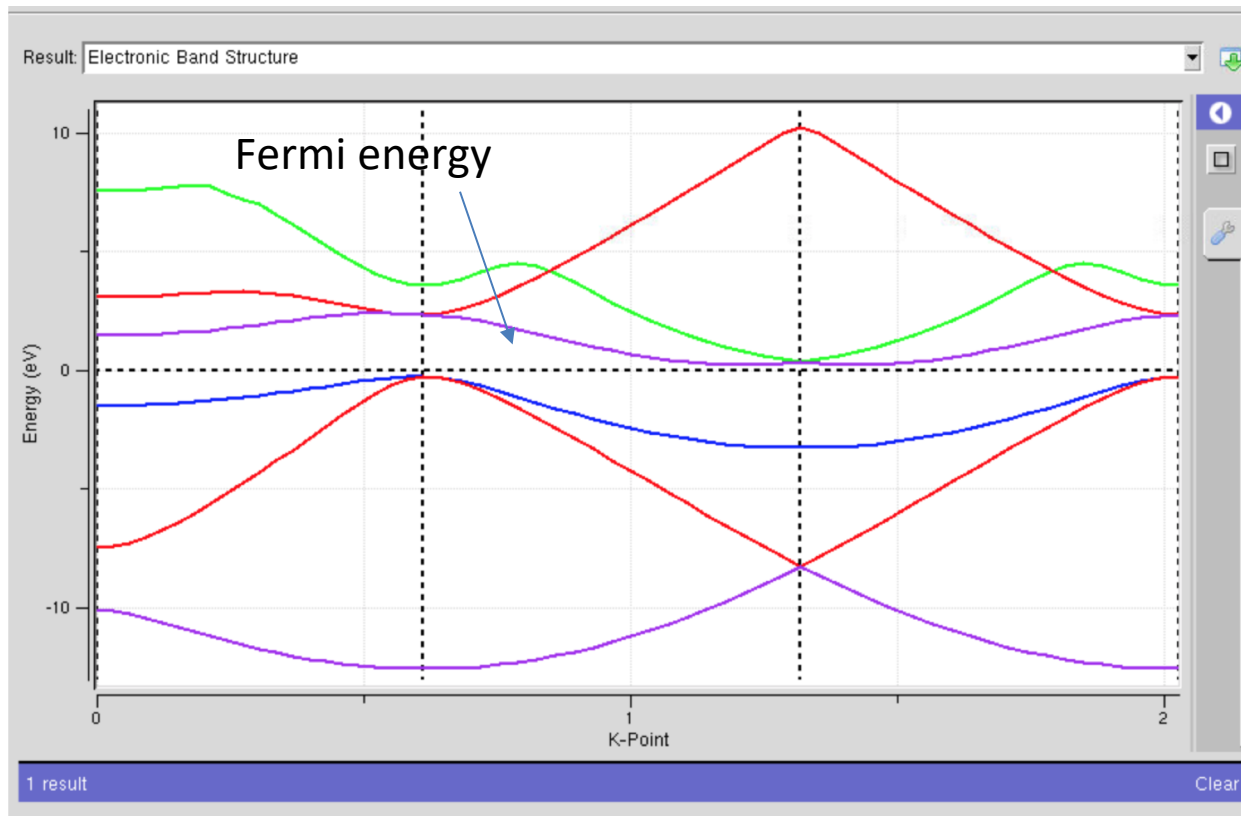
$$K_{path} = L - \Gamma - X - \Gamma$$

Explore the electronic band structure of Si

Assignment

- Identify the valence band maximum and conduction band minima
- Is Si direct or indirect band gap semiconductor?

(Note that DFT tends to underestimate band gaps)



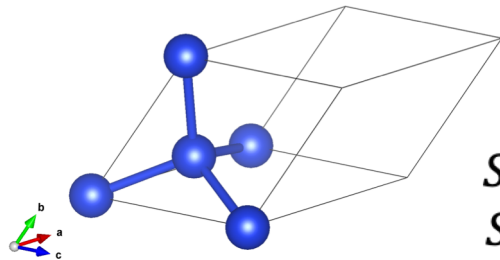
Electronic structure of an isolated Si atom

Advanced options

Geometric inputs

Make lattice parameter 20Å
(with such large lattice parameter
atoms do not see each other)

Primitive cell



$$\vec{a} = a_0(0, \frac{1}{2}, \frac{1}{2})$$

$$\vec{b} = a_0(\frac{1}{2}, 0, \frac{1}{2})$$

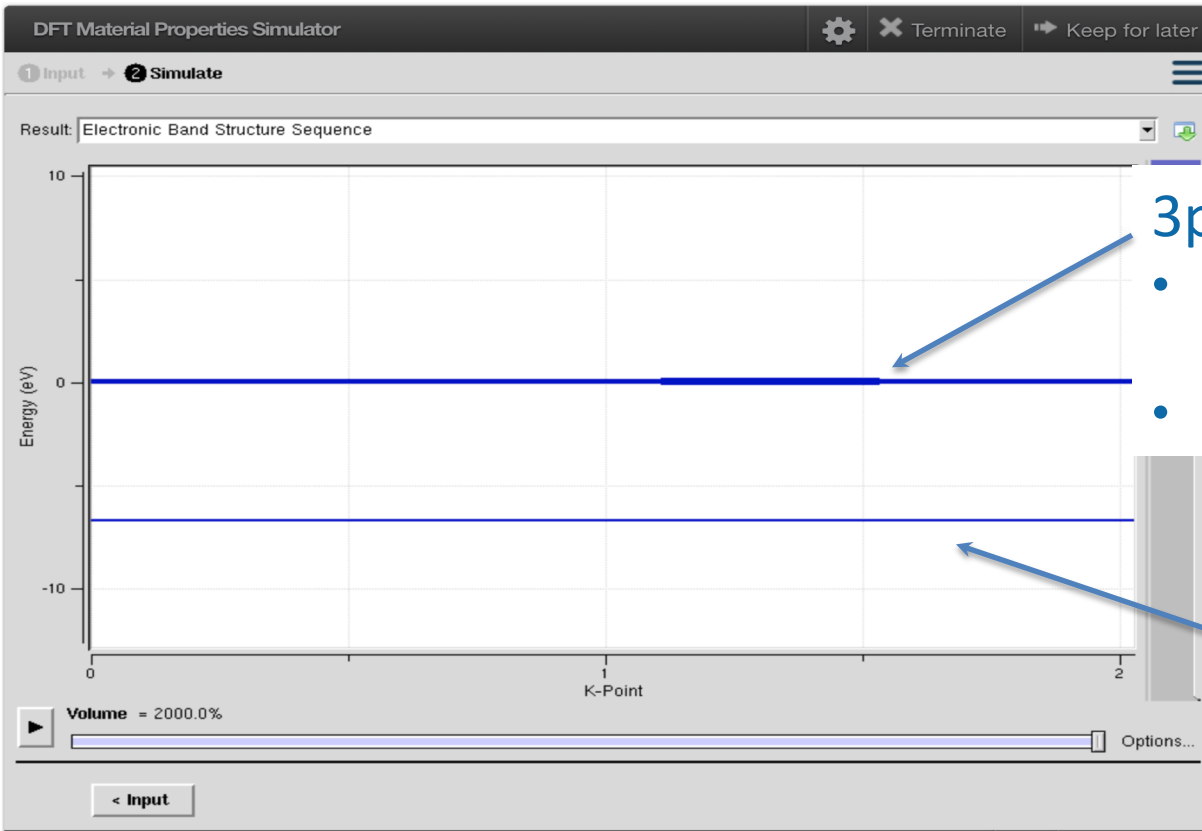
$$\vec{c} = a_0(\frac{1}{2}, \frac{1}{2}, 0)$$

$$Si_1: 0.00, 0.00, 0.00$$

$$Si_2: 0.25, 0.25, 0.25$$

Electronic structure of Si isolated atoms and crystal

Analyze the band structure of the 2 isolated silicon atoms



3p states

- Three from each atom in the simulation
- Six total states

3s states

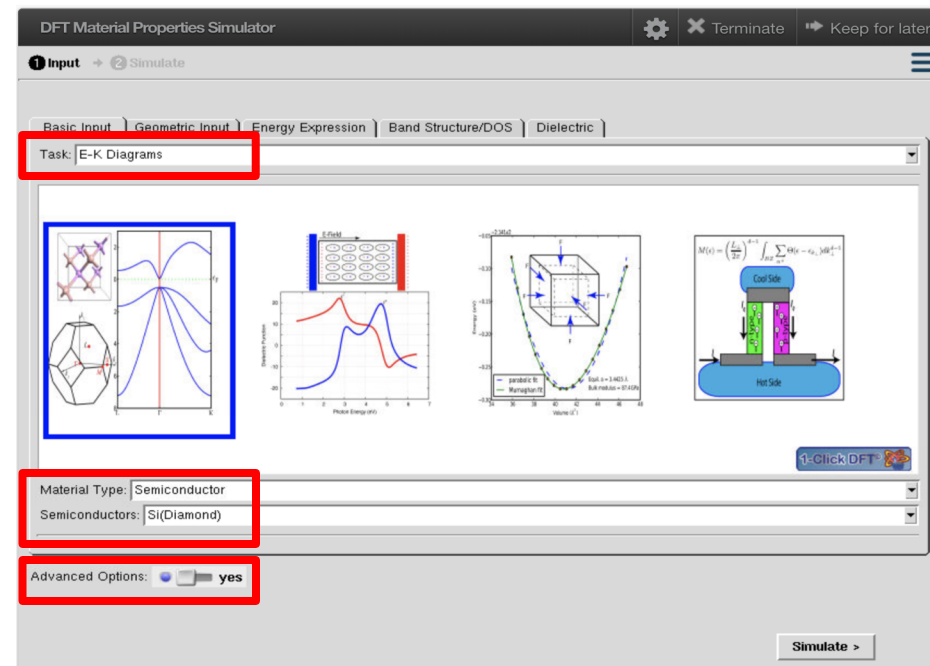
- One from each atom
- Two total states

NOTICE: No dispersion, i.e. no k-dependence

- Non-interacting atoms
- k determines how WF varies from unit cell to unit cell – does not affect the energy as atoms are far way

Electronic structure of silicon molecule Si_2

Now let us look at the electronic properties of silicon molecule. In the following we will start with a guess for the separation between Si atoms, compute the GGA predicted bonding distance, and compute the electronic structure of such system. To get started launch a new DFTMATProp window.



Step 1: Basic Input

- select “E-K Diagram” from task menu
- then “Semiconductor” from material type
- followed by “Si(Diamond)” in semiconductors.
- Finally switch to “yes” the advanced options

Electronic structure of silicon molecule Si_2

DFT Material Properties Simulator (10:13 pm) [Settings] [Terminate] [Keep for later]

1 Input → 2 Simulate

Basic Input | Geometric Input | **Energy Expression** | Band Structure/DOS | Dielectric

Exchange and Correlation functional: GGA

Relax: Force Relax

Relaxation Options: No, Force Relax, Cell Relax

Electronic Dynamics: BFGS quasi-newton

Cell Dynamics: BFGS quasi-newton

Number of K-Points

K direction: 2 + -

Y direction: 2 + -

Z direction: 2 + -

Number of K-Points (for Non-Self Consistent Field Calculation)

X direction: 25 + -

Y direction: 25 + -

Z direction: 25 + -

Wavefunction Kinetic Energy cutoff (Ry): 25.0

Charge Density Kinetic Energy cutoff (Ry): 100.0

SCF Convergence Criterion (Ry): 1E-6

Simulate >

Step 3: Energy Expression

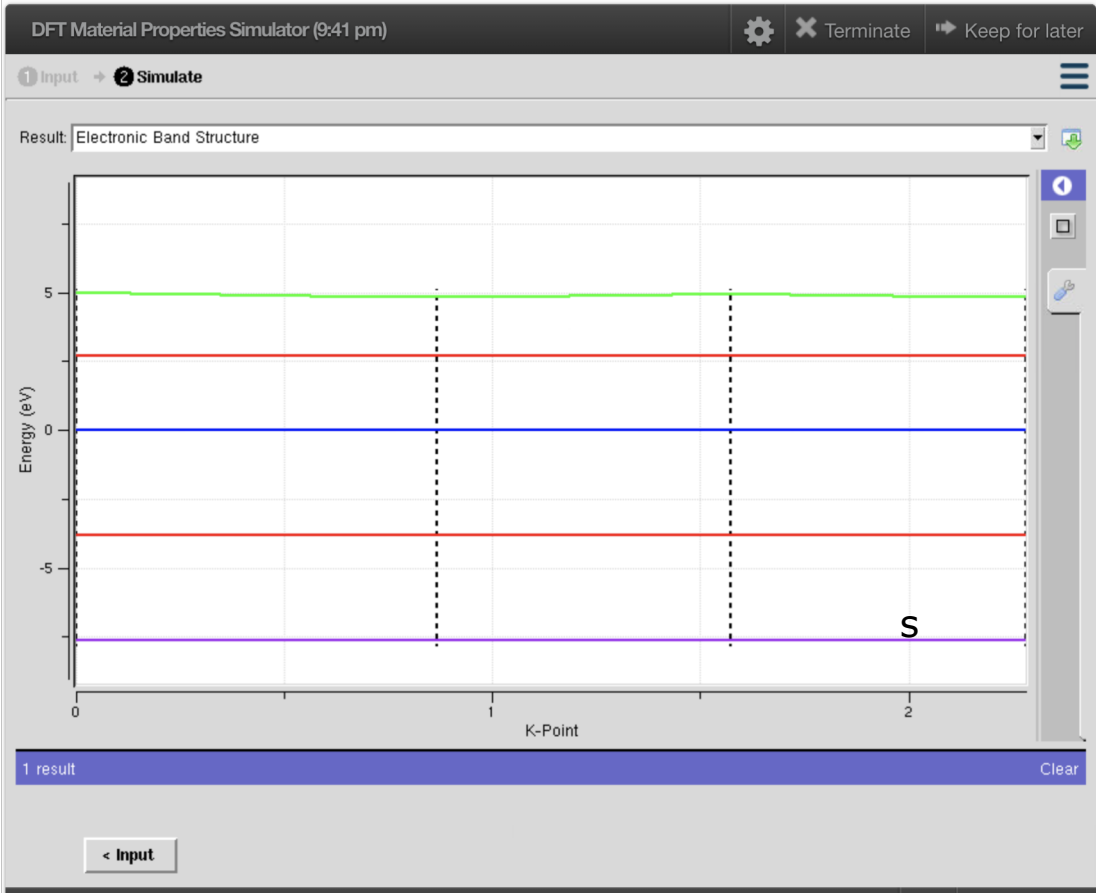
Change the **Relax** field to “**Force Relax**”

Change **Number of K-Points** to “**2 2 2**”

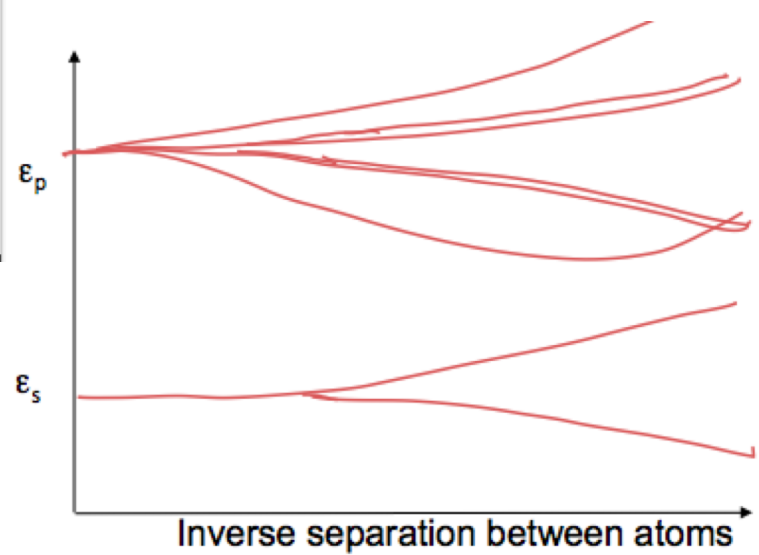
Leave the defaults for the rest of the field.

Step 4: **CLICK SIMULATE**

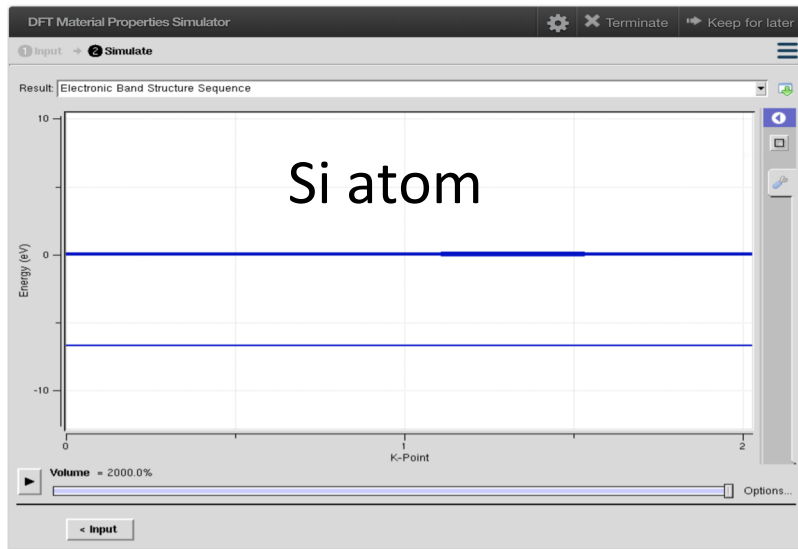
Electronic structure of silicon molecule Si_2



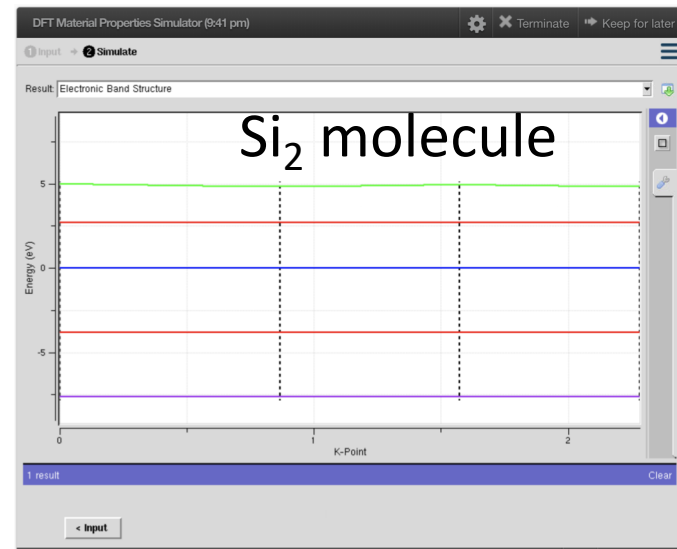
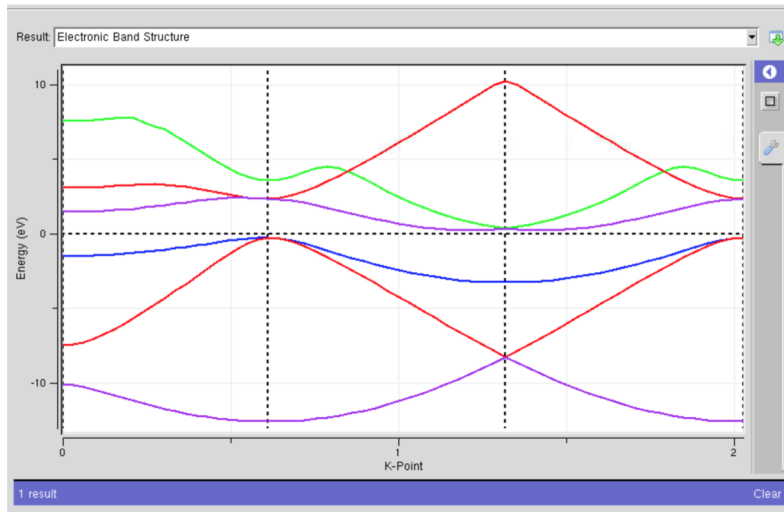
Remember bonding and anti-bonding curves with s and p states



From single atom and molecule to crystal



Si crystal



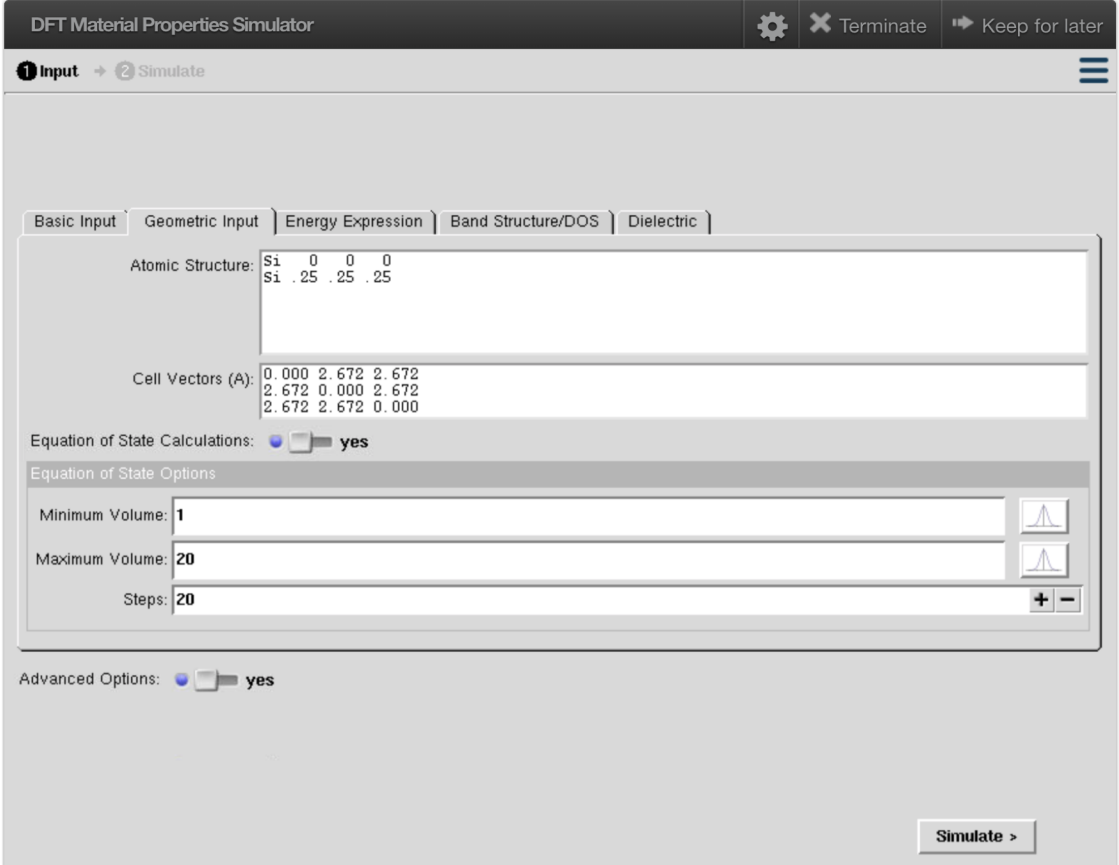
- To better understand the band structure of Si we will perform a series of simulations with varying lattice parameters
- From a large lattice parameter with isolated atoms to the equilibrium lattice parameter of the crystal

Electronic structure vs. lattice parameter

Geometric input

Switch the **EOS calculation** to **YES** and change **minimum volume** to **1**, **maximum volume** to **20**, and **steps** to **20**

Remember to set the lattice parameters back to the original value or re-start the tool



The screenshot shows the DFT Material Properties Simulator interface. The title bar reads "DFT Material Properties Simulator" and includes buttons for "Terminate" and "Keep for later". The main window has a progress indicator showing "1 Input" and "2 Simulate". The "Geometric Input" tab is selected, displaying the following fields:

- Atomic Structure:** A table with two rows: Si (0, 0, 0) and Si (.25, .25, .25).
- Cell Vectors (A):** A table with three rows: (0.000, 2.672, 2.672), (2.672, 0.000, 2.672), and (2.672, 2.672, 0.000).
- Equation of State Calculations:** A radio button set with "yes" selected.
- Equation of State Options:** Three input fields: "Minimum Volume: 1", "Maximum Volume: 20", and "Steps: 20".
- Advanced Options:** A radio button set with "yes" selected.

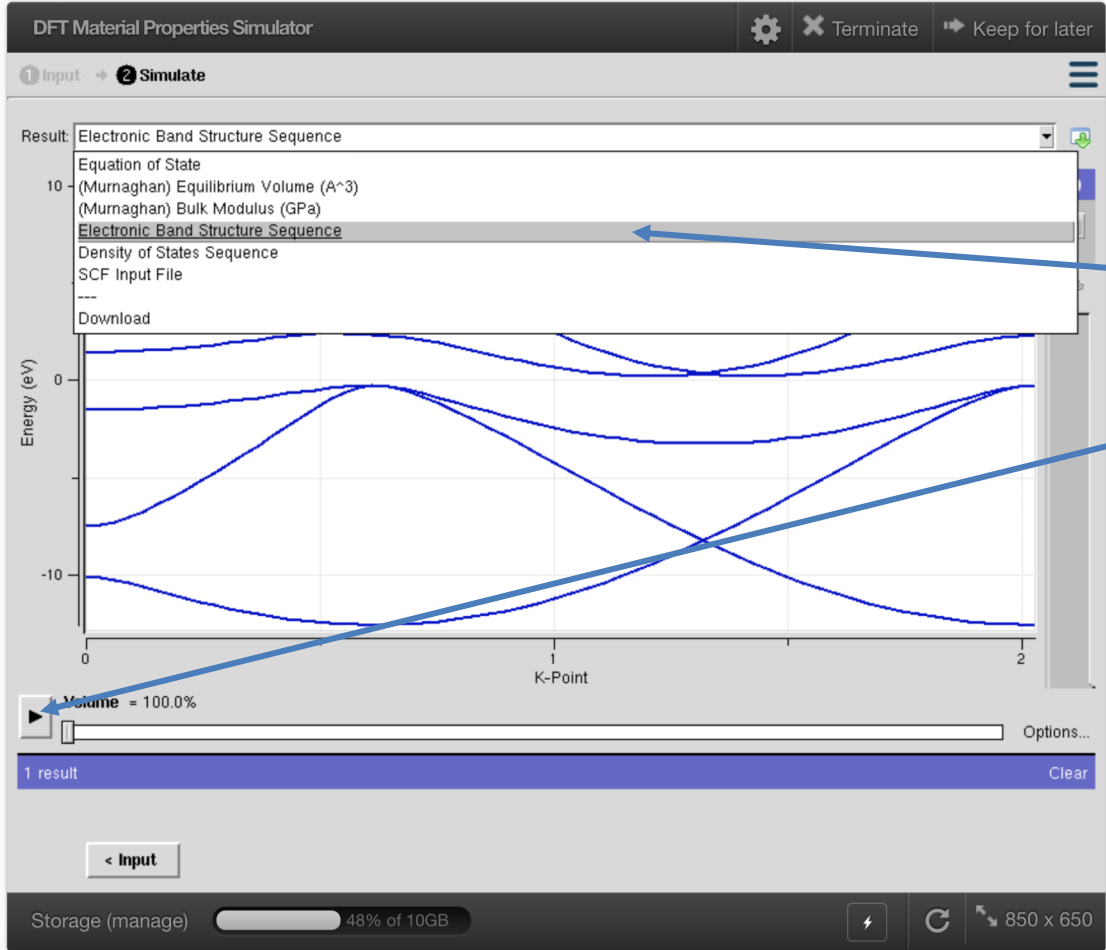
A "Simulate >" button is located at the bottom right of the interface.

Electronic structure vs. lattice parameter

The simulation will take several minutes since it will run 20 different calculations at different unit cell volumes.

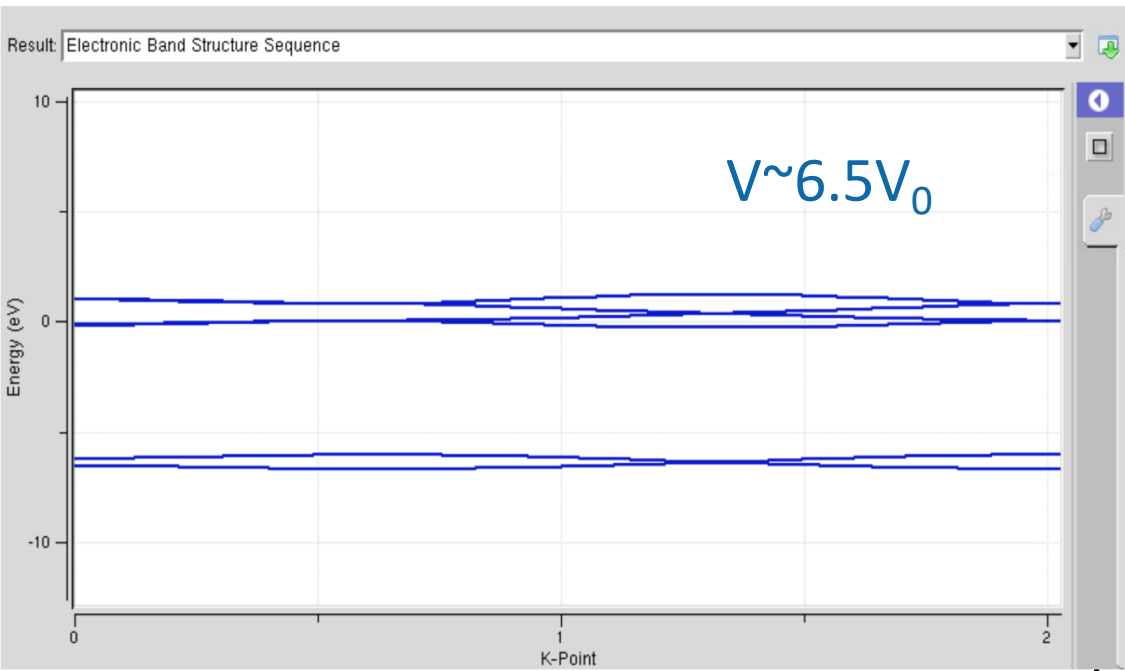
Once the all simulations are done, change the view to “**Electronic Band Structure Sequence**”

Click **Play** to see how the electronic structure of Silicon diamond changes when the volume is stretched from equilibrium (100%) to isolated Si atoms (2000%). See next slide?



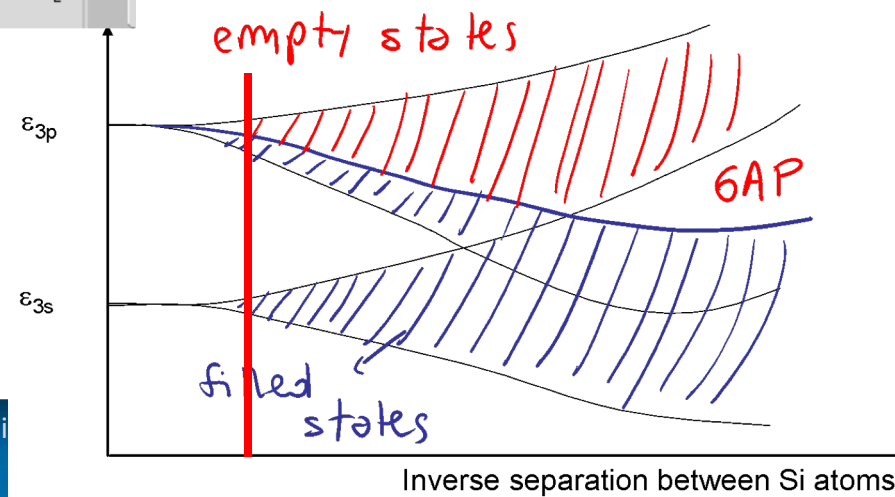
Electronic structure of Si isolated atoms and crystal

Large lattice parameter ($V \sim 6.5V_0$) weak interactions



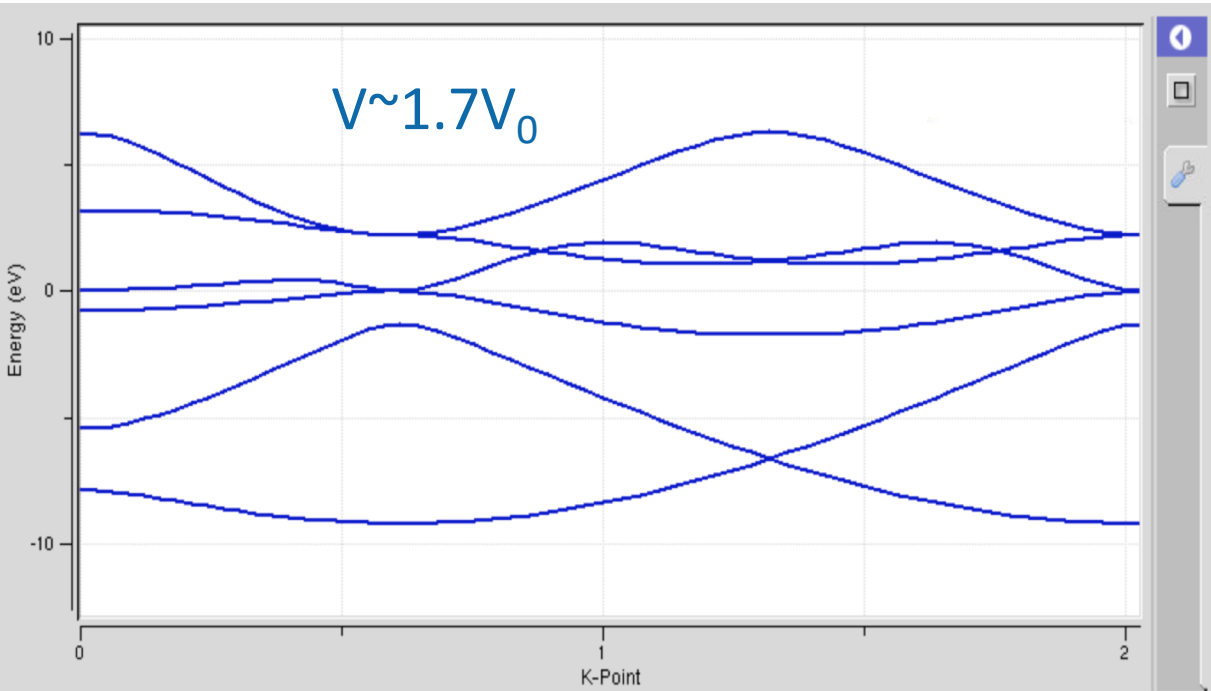
p-states (1/3 filled)
Bonding/antibonding + dispersion

s-states (all filled)
Bonding/antibonding + dispersion



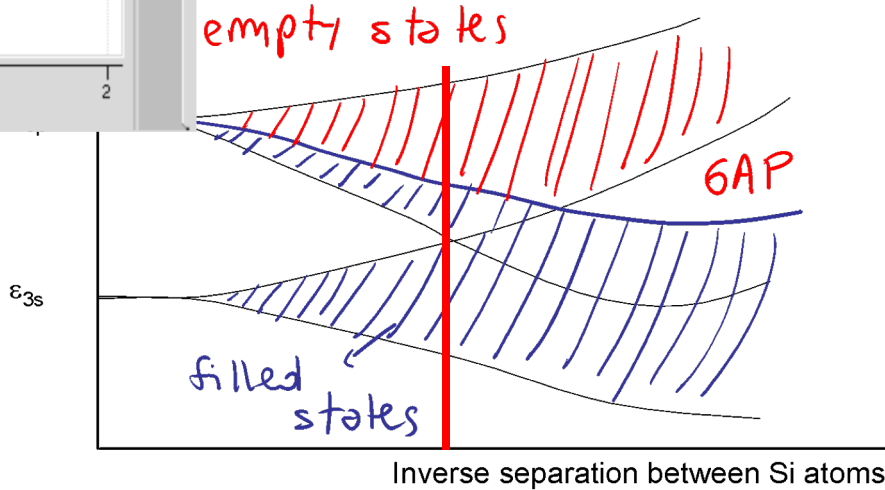
Electronic structure of Si isolated atoms and crystal

- s and p bands start to overlap in energy
- s/p splitting similar to bonding/antibonding splitting
- No gap



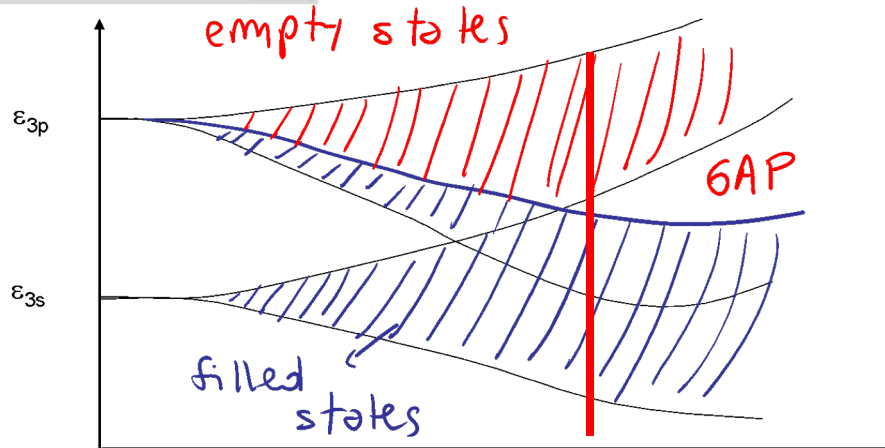
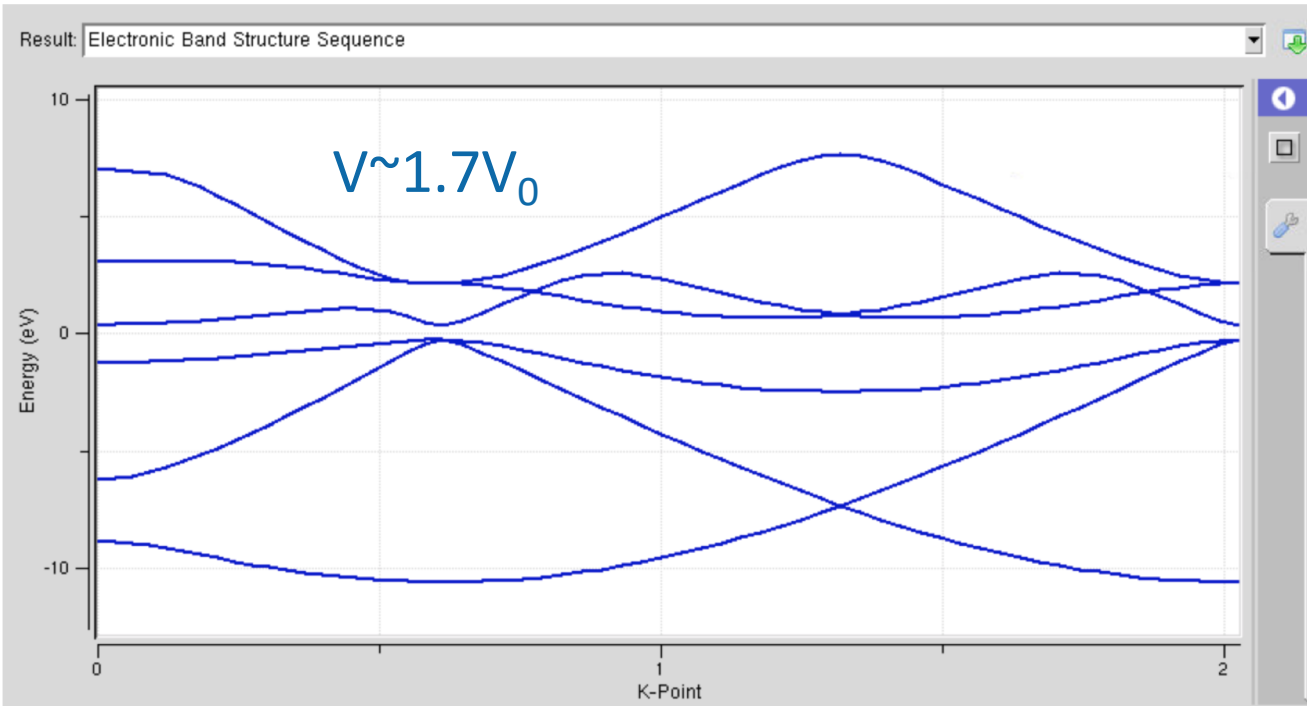
p-states
Bonding/antibonding + dispersion

s-states
Bonding/antibonding + dispersion



Electronic structure of Si isolated atoms and crystal

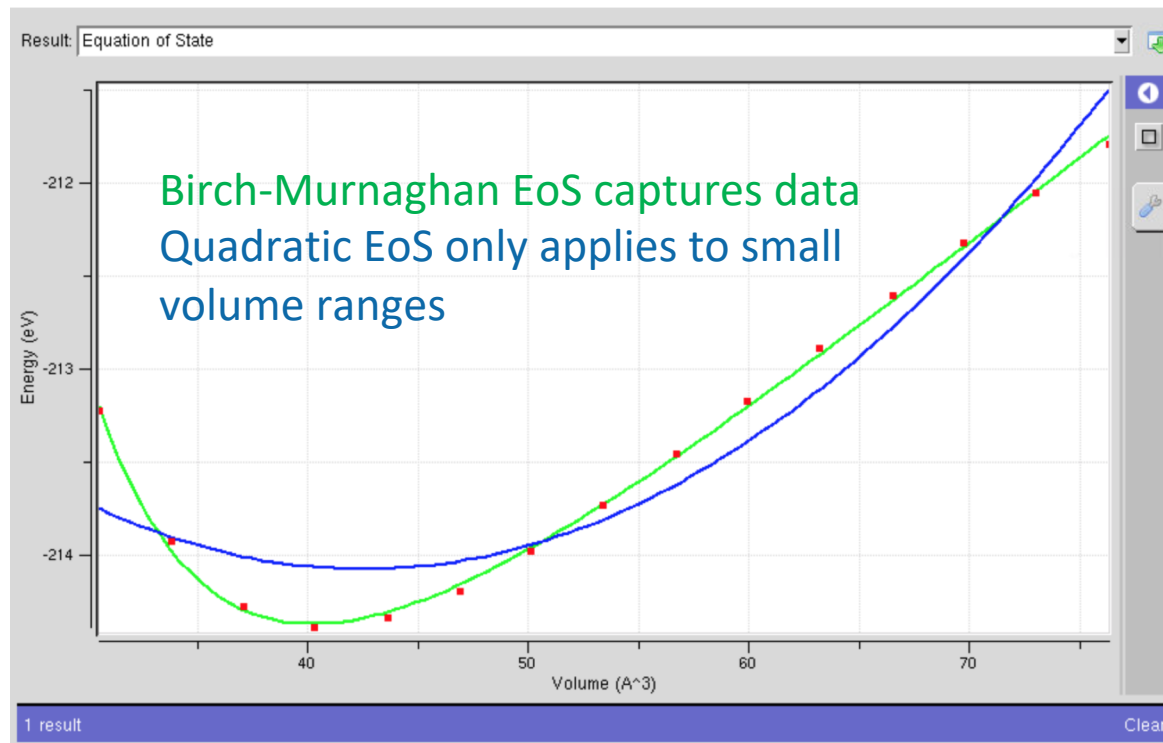
A band gap opens up



By-product: equation of state

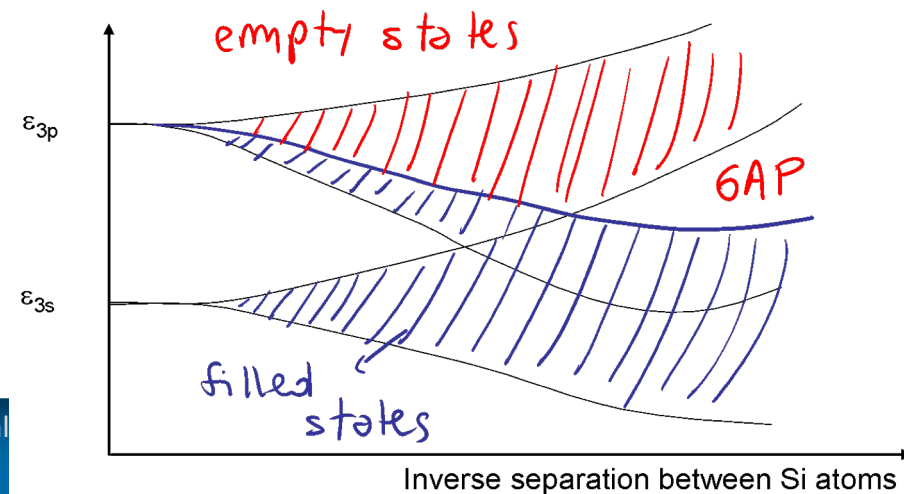
- The energy-volume relationship obtained is called equation of state
- From it, we can obtain the equilibrium volume (minimum energy) and bulk modulus of the system (at $T=0\text{K}$ in this case)

15 points from $0.8V_0$ to $2V_0$



Additional Questions

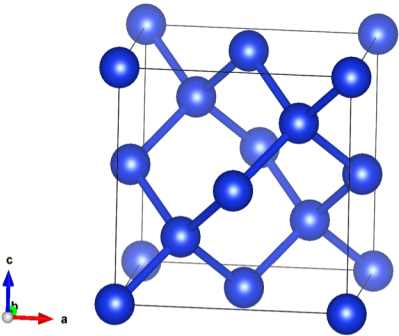
- Consider the Si_2 molecule. For each energy level in the band diagram plot, indicate its multiplicity (how many states have the same energy) and their electron occupation indicating electrons and their spin with arrows.
- At what lattice parameter does a band gap separating occupied and unoccupied states form?
- Think about the development of the band structure in terms of the s and p picture in the figure below



Additional notes: the diamond structure

Silicon crystalizes in the cubic $Fd-3m$ space group every Si atom is bonded to four equivalent Si atoms forming corner-sharing tetrahedra

Conventional cell



$$\begin{aligned}\vec{a} &= a_0(1, 0, 0) \\ \vec{b} &= a_0(0, 1, 0) \\ \vec{c} &= a_0(0, 0, 1)\end{aligned}$$

$$Si_1: 0.00, 0.00, 0.00$$

$$Si_2: 0.25, 0.75, 0.75$$

$$Si_3: 0.50, 0.00, 0.50$$

$$Si_4: 0.00, 0.50, 0.50$$

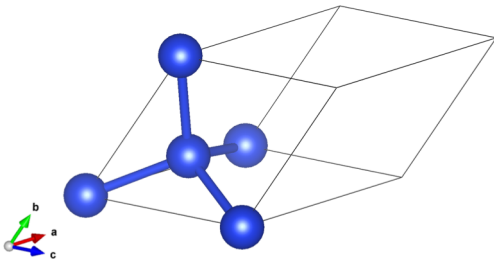
$$Si_5: 0.50, 0.50, 0.00$$

$$Si_6: 0.75, 0.25, 0.75$$

$$Si_7: 0.75, 0.75, 0.25$$

$$Si_8: 0.25, 0.25, 0.25$$

Primitive cell



$$\vec{a} = a_0(0, \frac{1}{2}, \frac{1}{2})$$

$$\vec{b} = a_0(\frac{1}{2}, 0, \frac{1}{2})$$

$$\vec{c} = a_0(\frac{1}{2}, \frac{1}{2}, 0)$$

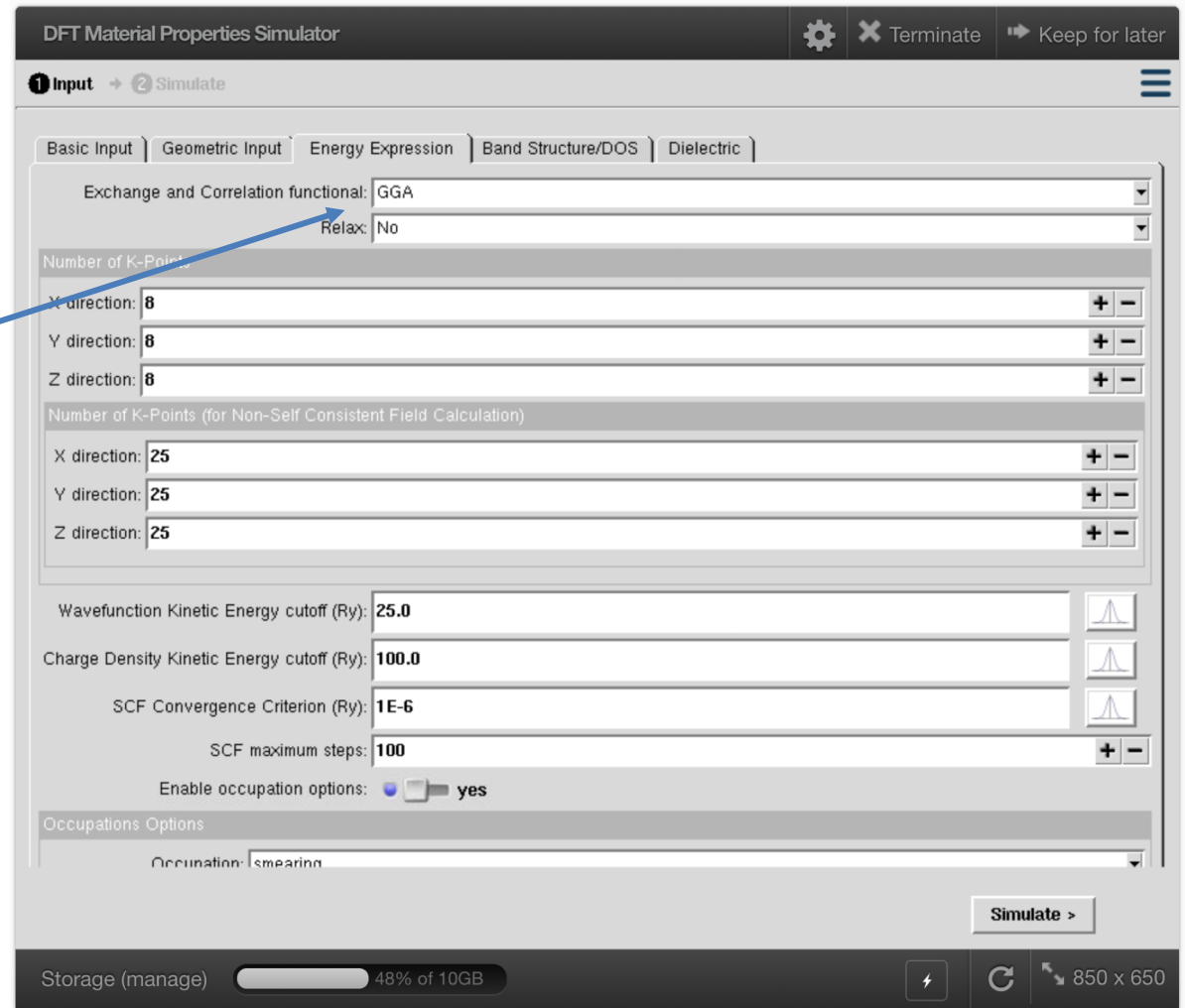
$$Si_1: 0.00, 0.00, 0.00$$

$$Si_2: 0.25, 0.25, 0.25$$

Additional notes: exchange and correlation

Energy Expression

You may explore the same results with LDA by changing the XC functional



The screenshot displays the 'DFT Material Properties Simulator' interface. The 'Energy Expression' tab is selected, showing the following settings:

- Exchange and Correlation functional: GGA
- Relax: No
- Number of K-Points:
 - X direction: 8
 - Y direction: 8
 - Z direction: 8
- Number of K-Points (for Non-Self Consistent Field Calculation):
 - X direction: 25
 - Y direction: 25
 - Z direction: 25
- Wavefunction Kinetic Energy cutoff (Ry): 25.0
- Charge Density Kinetic Energy cutoff (Ry): 100.0
- SCF Convergence Criterion (Ry): 1E-6
- SCF maximum steps: 100
- Enable occupation options: no yes
- Occupations Options: smearing

A blue arrow points from the text 'You may explore the same results with LDA by changing the XC functional' to the 'Exchange and Correlation functional' dropdown menu.

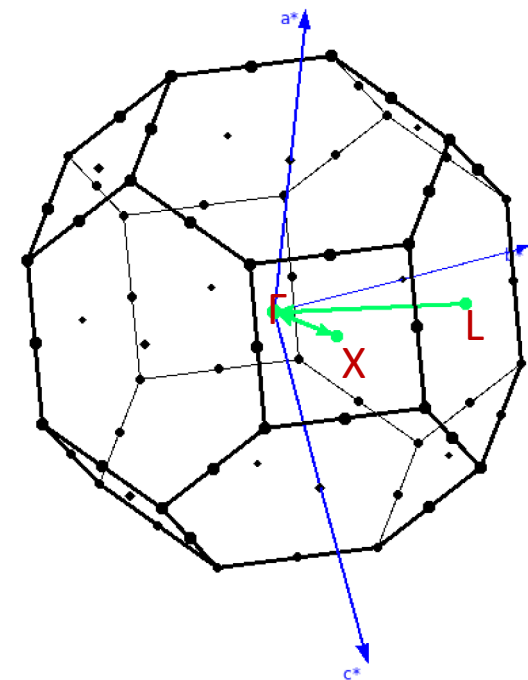
Additional notes: reciprocal space

Band Structure/DOS

Leave the defaults in all fields.

We selected a short K-path to plot the electron band dispersion which contains the valence band maxima and conduction band minima of Si diamond electronic structure

$$K_{path} = L - \Gamma - X - \Gamma$$



DFT Material Properties Simulator

1 Input + 2 Simulate

Basic Input | Geometric Input | Energy Expression | **Band Structure/DOS** | Dielectric

Band Structure Calculations: yes

Band Structure Options

Path: 5 .5 5
0 0 0
5 0 .5
0 0 0

Number of Points: 20

Density of States Options: yes

Density of States

minimum Energy (eV): -6

maximum Energy (eV): 18

energy grid step (eV): .06

Advanced Options: yes

Simulate >

Storage (manage) 48% of 10GB 850 x 650