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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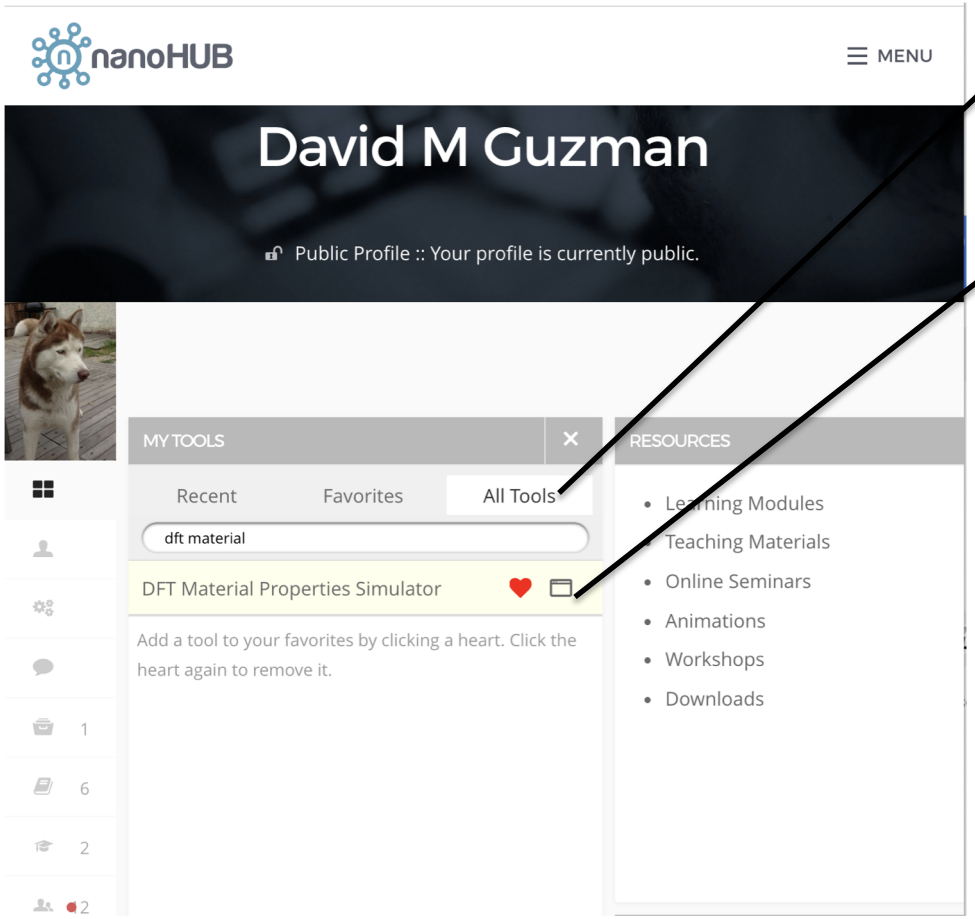
Launch the DFTMatProp tool in nanoHUB

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



- From *All Tools* find: **DFT material**
- Launch tool by clicking on: 

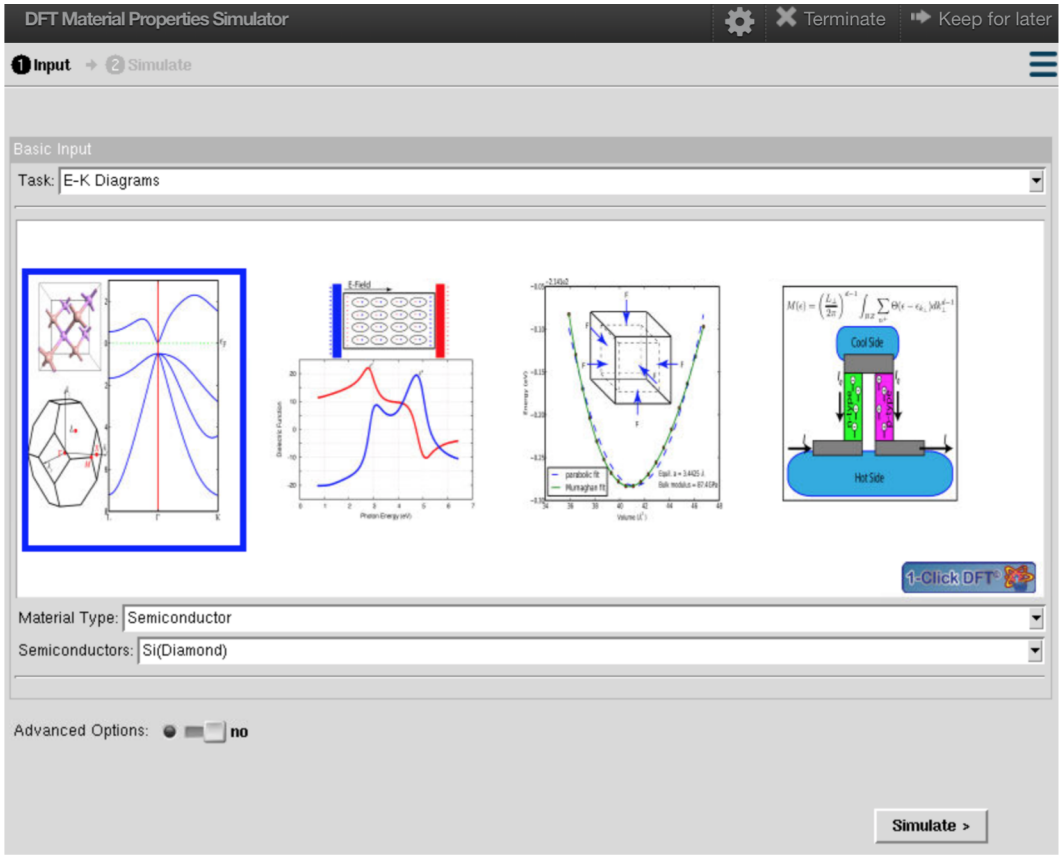
Electronic structure and binding in Si

- 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

Step 1: Basic Input

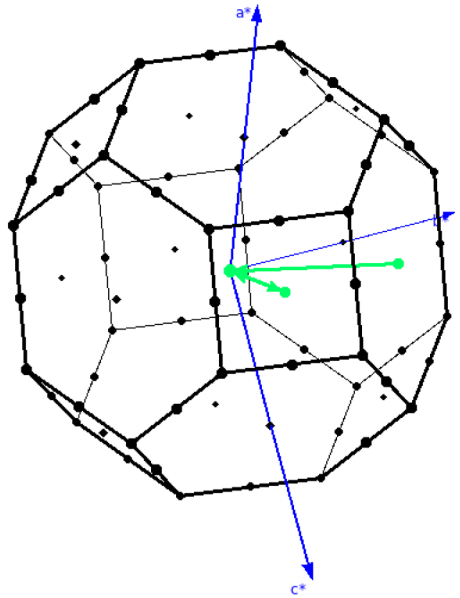
- select "E-K Diagram" from task menu
- then "Semiconductor" from material type
- followed by "Si(Diamond)" in semiconductors.
- Finally switch to "yes" the advanced options

Electronic structure of Si perfect crystal



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)

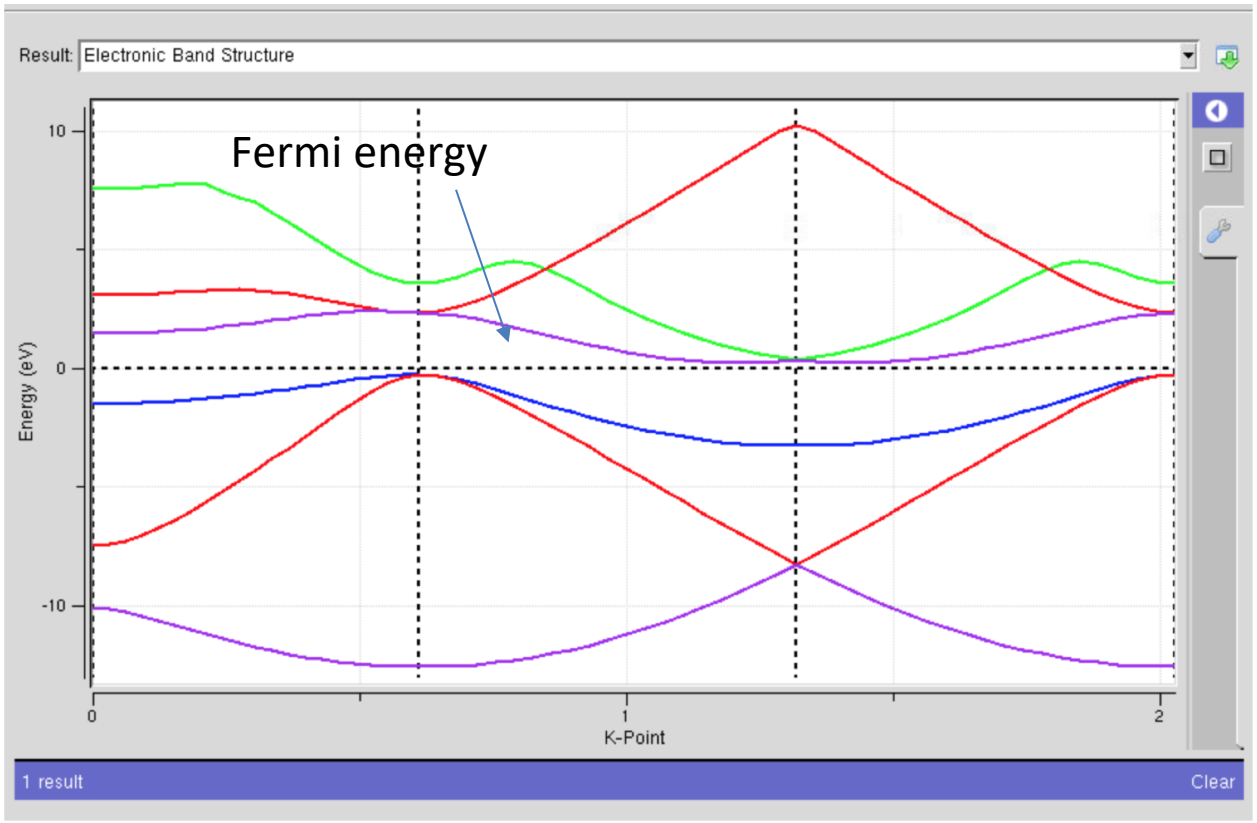
$$K_{path} = L - \Gamma - X - \Gamma$$

Explore the electronic band structure of Si

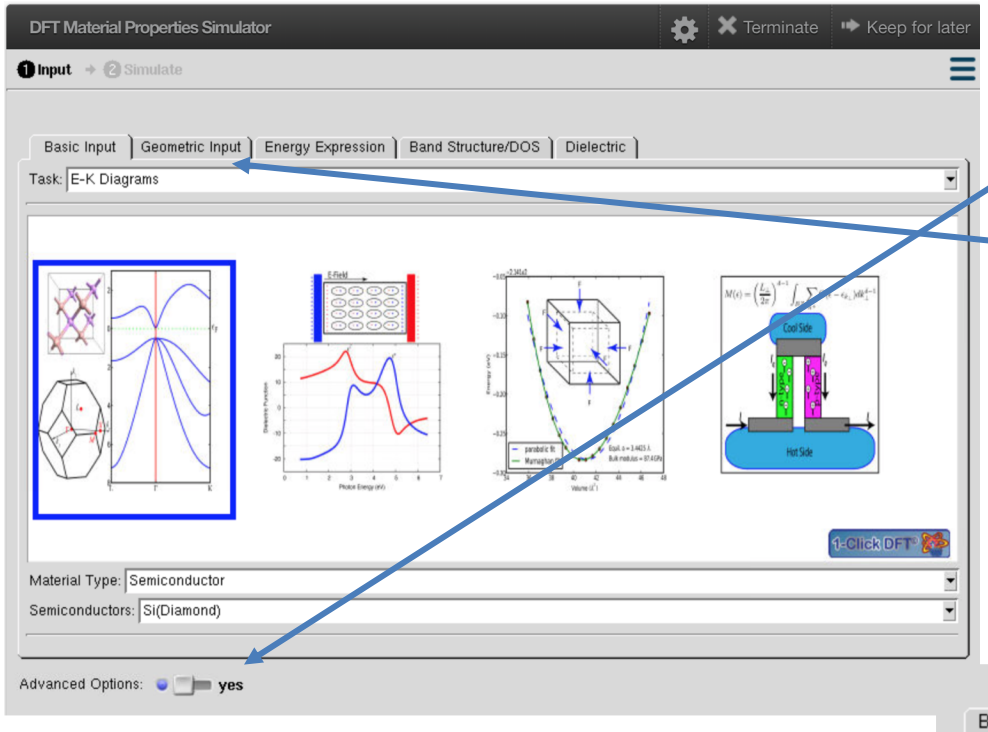
Assignment

- 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)



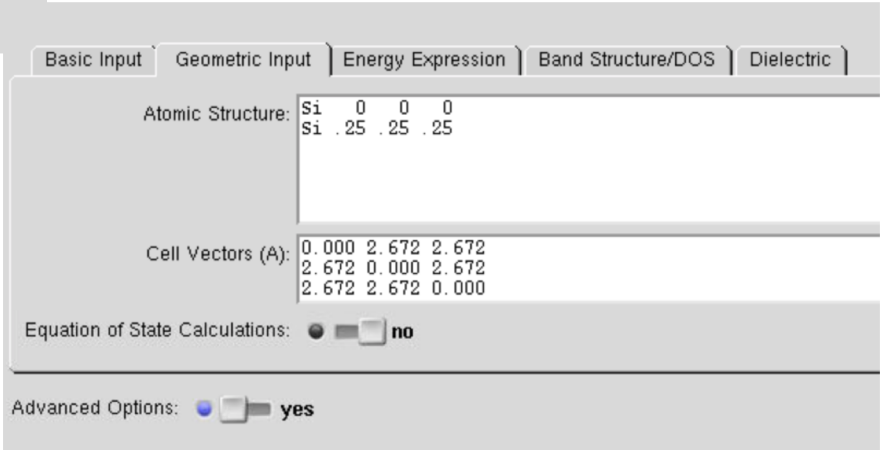
Electronic structure of an isolated Si atom



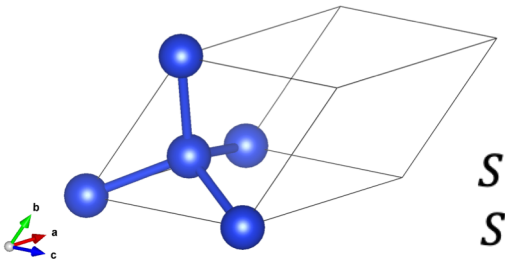
Advanced options

Geometric inputs

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



Primitive cell

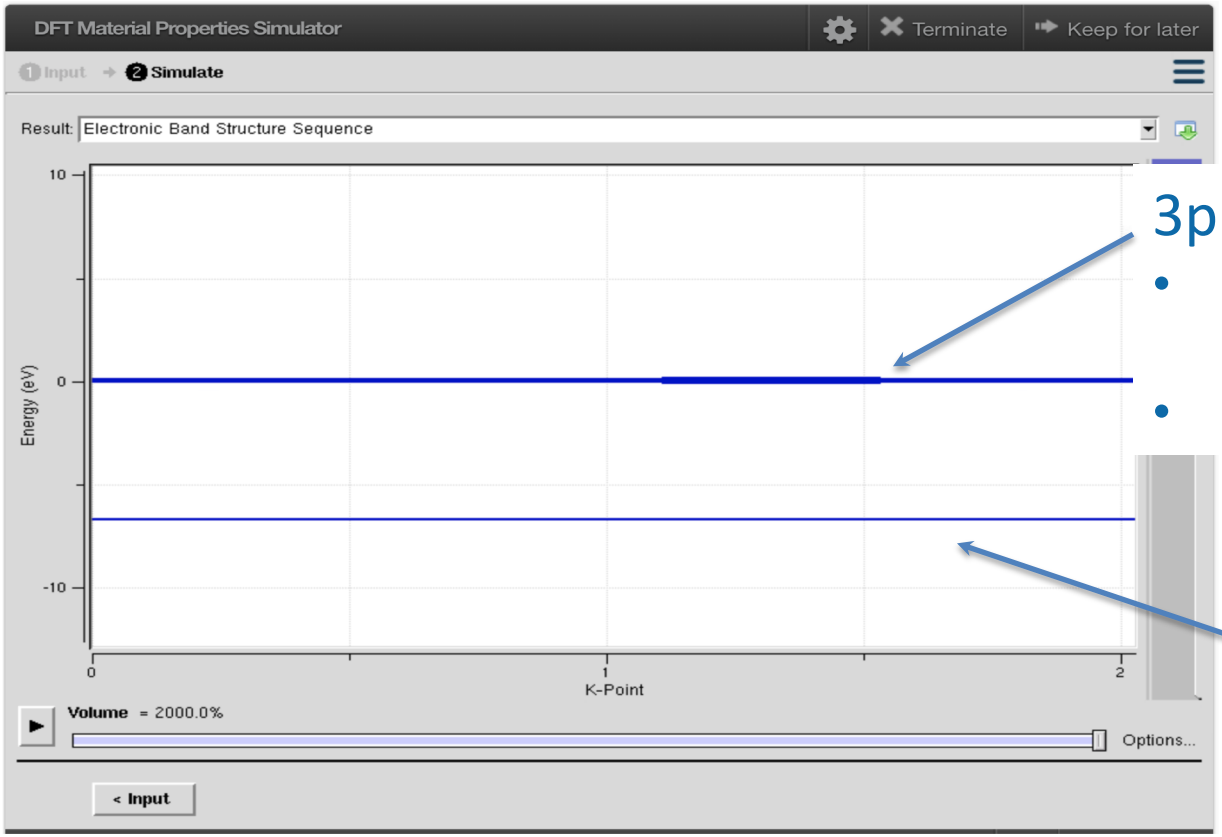


$$\vec{a} = a_0(0, ½, ½)$$
$$\vec{b} = a_0(½, 0, ½)$$
$$\vec{c} = a_0(½, ½, 0)$$

$$Si_1: 0.00, 0.00, 0.00$$
$$Si_2: 0.25, 0.25\ 0.25$$

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

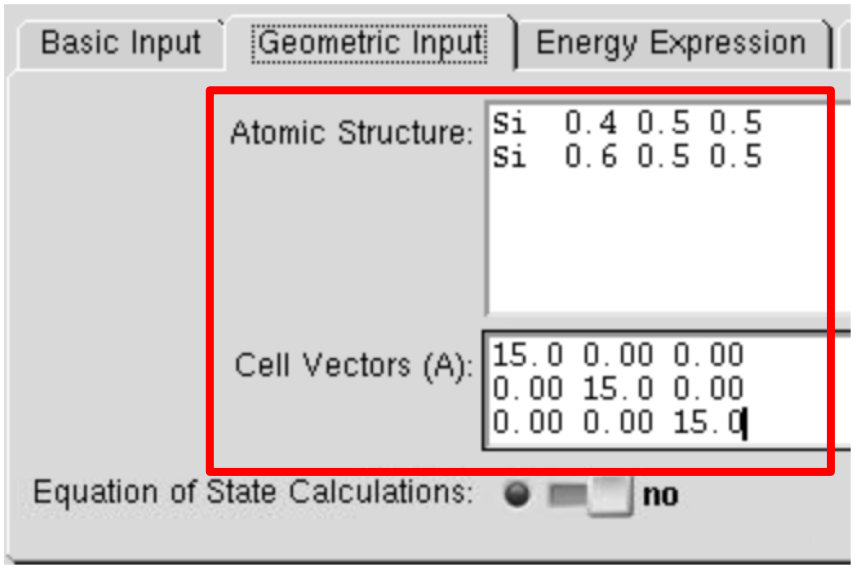
Now let us look at the electronic properties of silicon molecule. In the following we will start with a guess for the separation between Si atoms, compute the GGA predicted bonding distance, and compute the electronic structure of such system. To get started launch a new DFTMAtProp window.

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

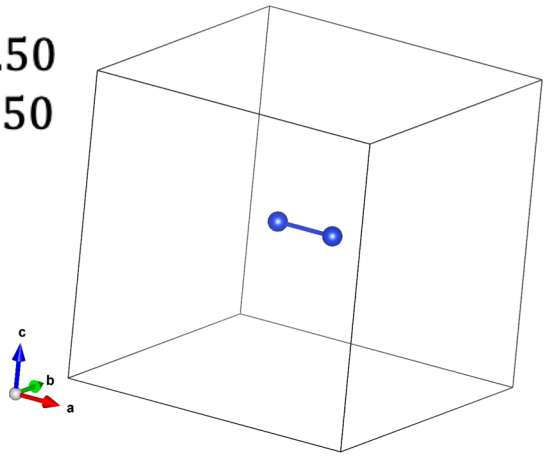
Electronic structure of silicon molecule Si_2

Step 2: Geometric input
Change the atomic structure and cell vectors fields as follows:



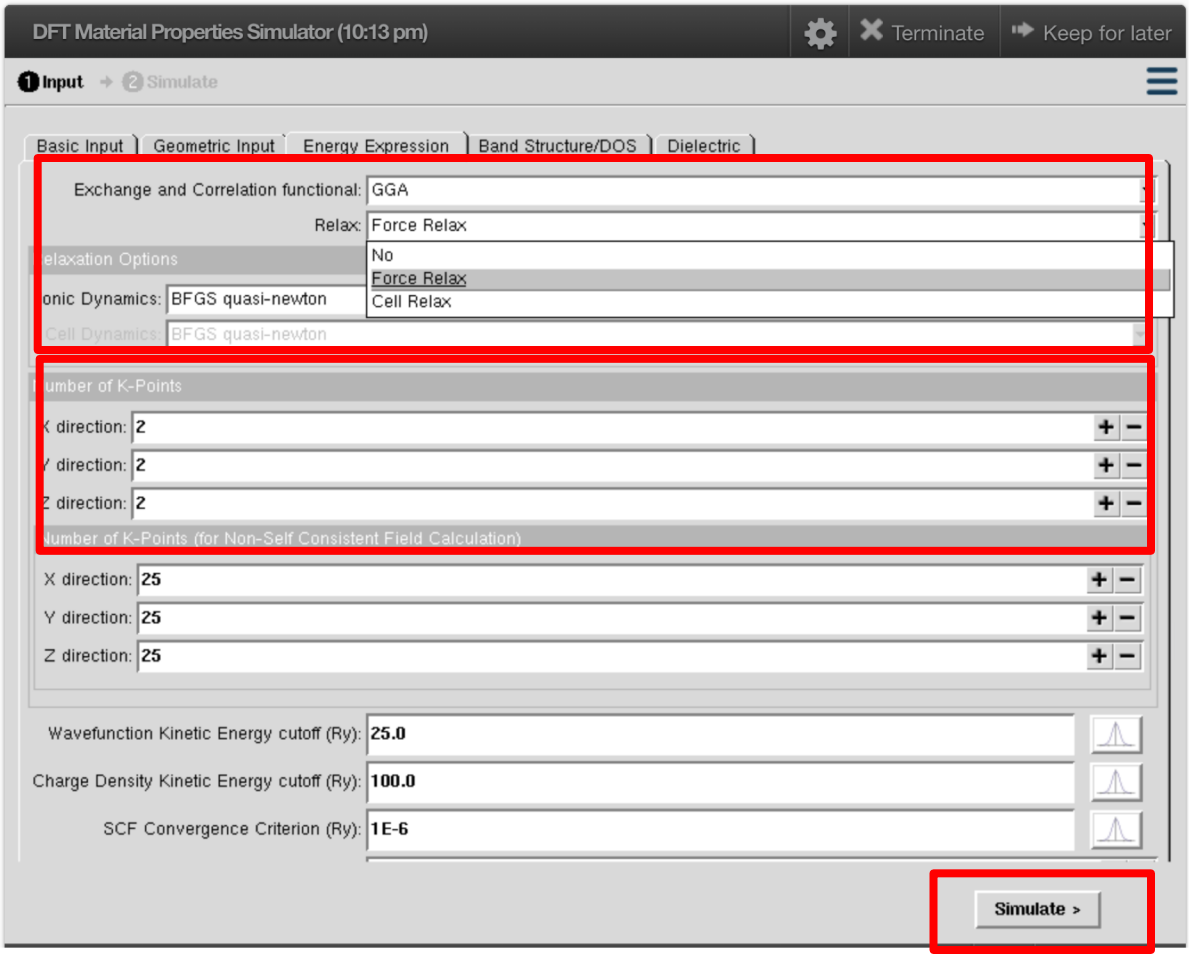
Si_2 molecule:
To model a molecule in a code that implements DFT based on plane waves and periodic boundaries, we need to increase the size of the simulation box to avoid interactions with adjacent images

$$Si_1: 0.40, 0.50, 0.50$$
$$Si_2: 0.60, 0.50\ 0.50$$
$$\vec{a} = a_0(1,0,0)$$
$$\vec{b} = a_0(0,1,0)$$
$$\vec{c} = a_0(0,0,1)$$
With $a_0 = 15Å$



The molecule is located in the middle of the simulation box and the atoms are initially separated by 3Å

Electronic structure of silicon molecule Si_2



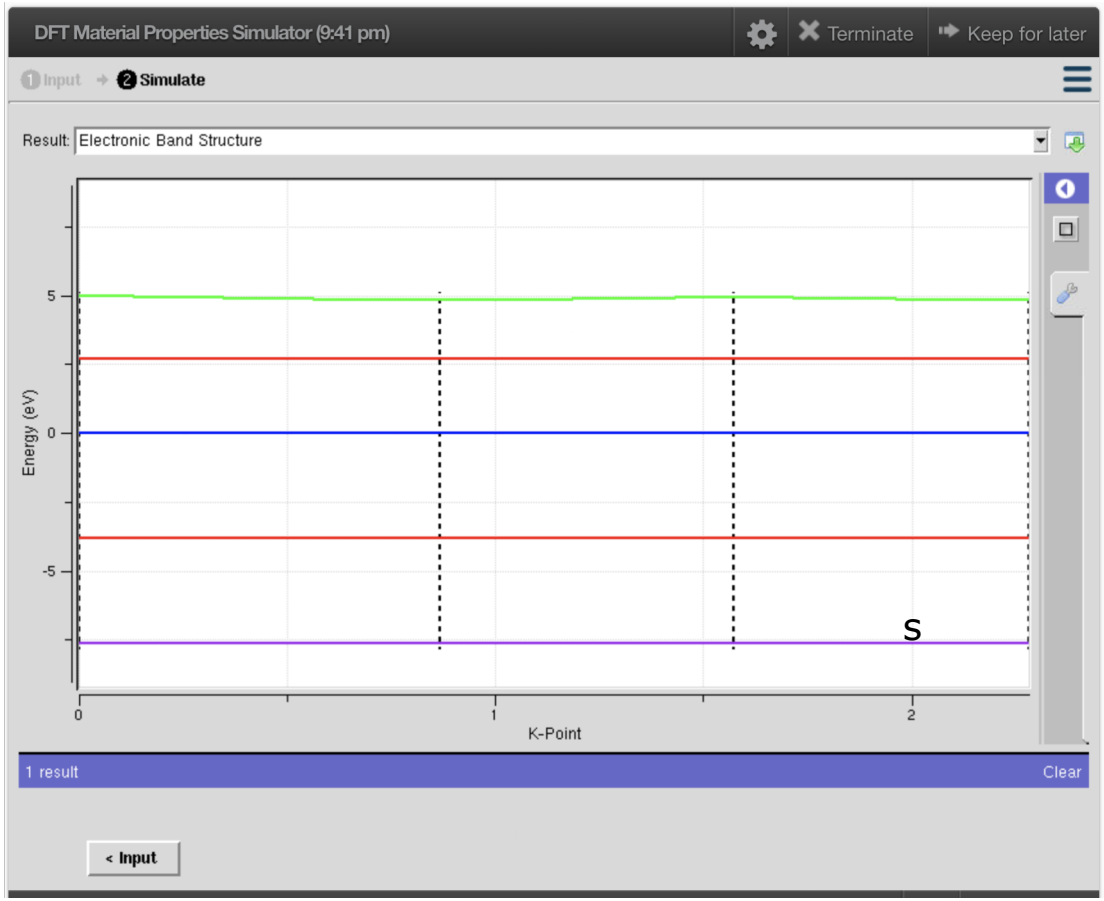
Step 3: Energy Expression
Change the Relax field to "Force Relax"

Change Number of K-Points to "2 2 2"

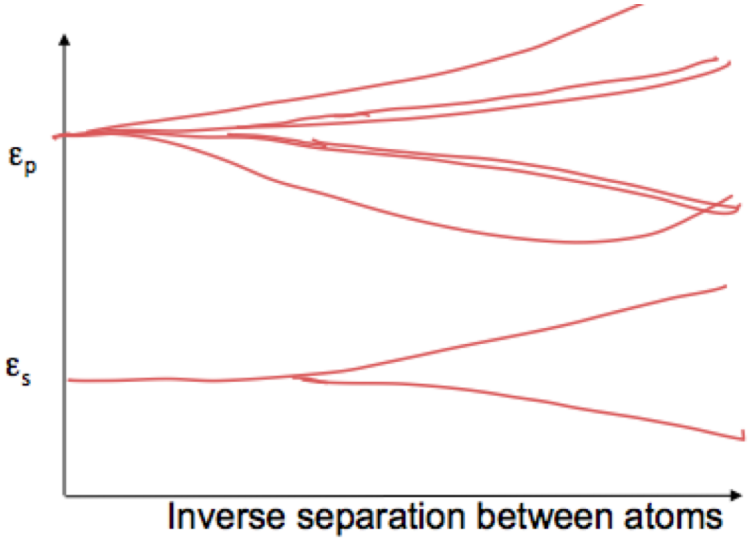
Leave the defaults for the rest of the field.

Step 4: CLICK SIMULATE

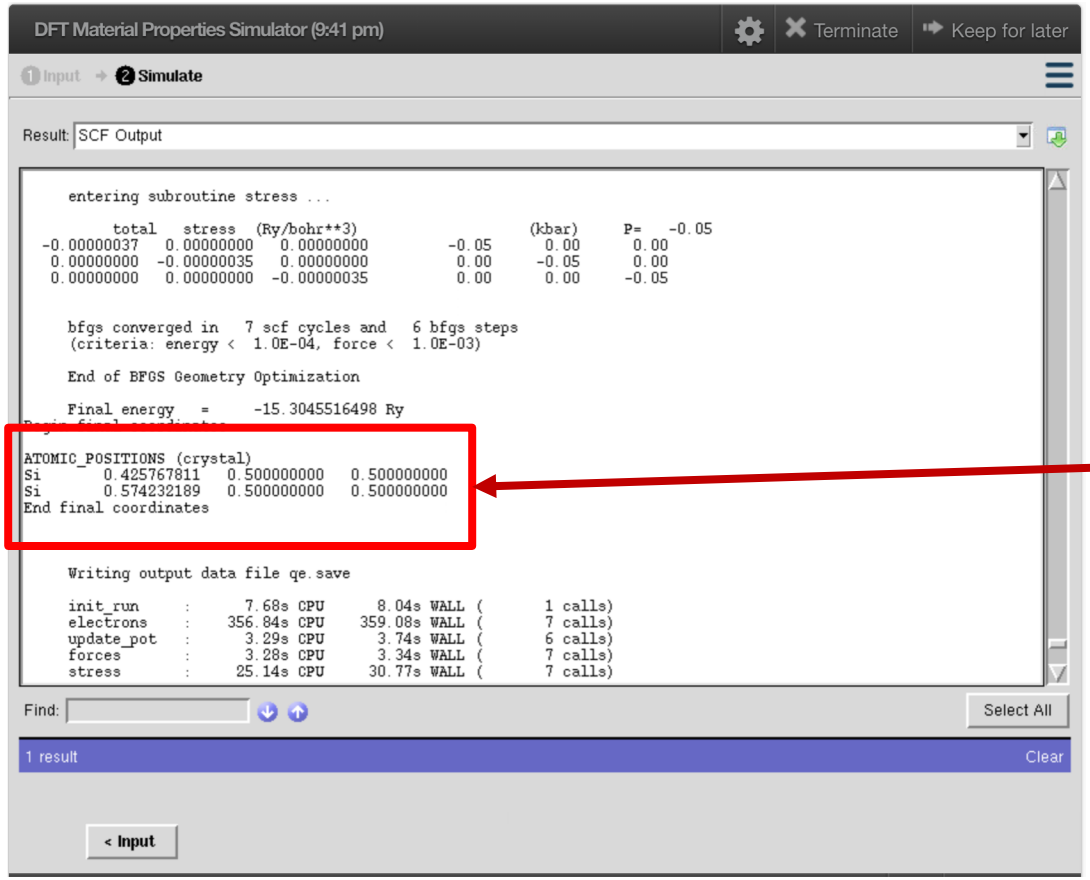
Electronic structure of silicon molecule Si_2



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

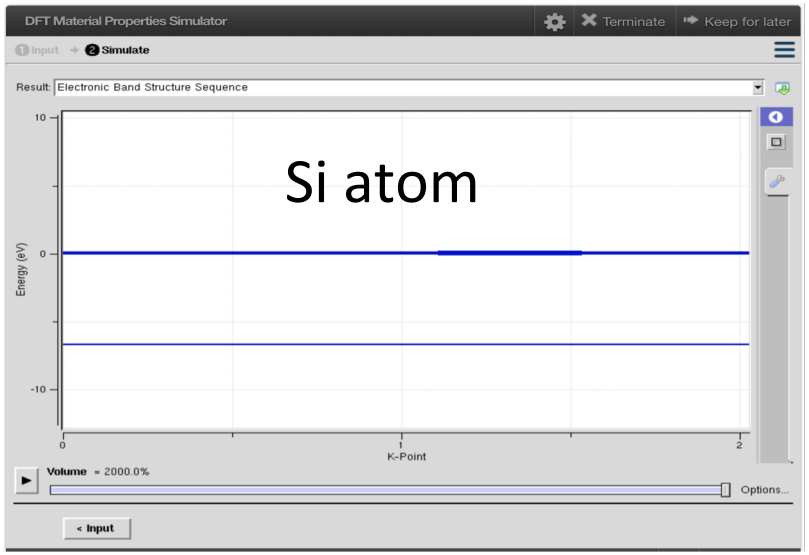


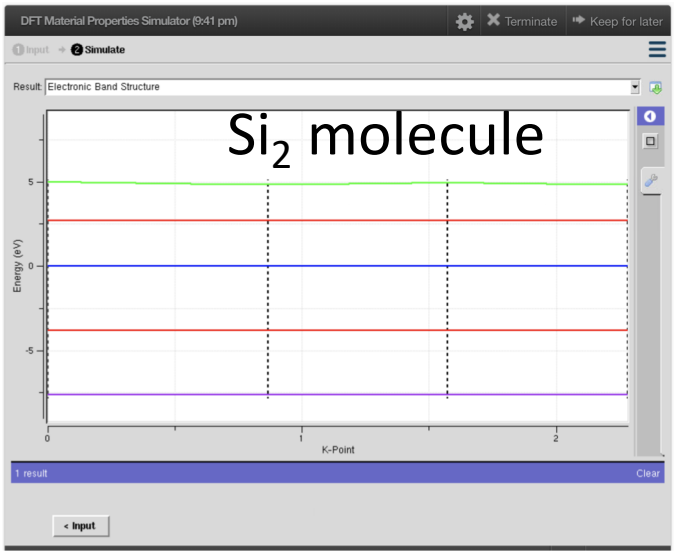
Electronic structure of silicon molecule Si_2



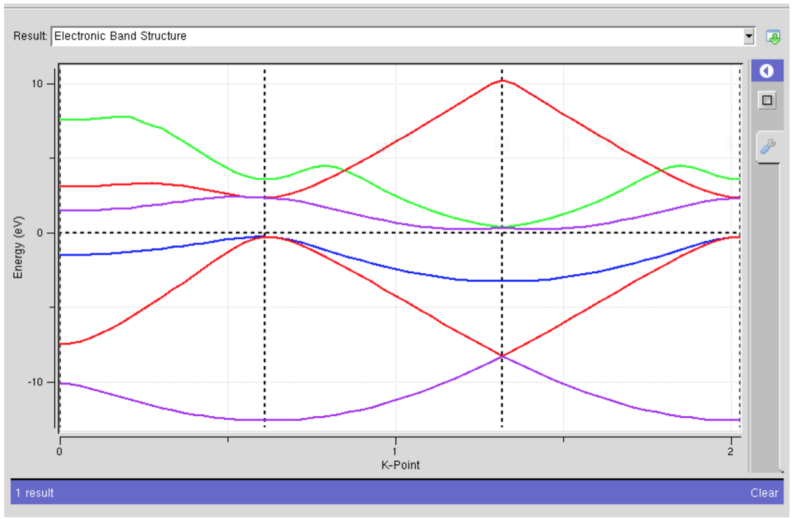
What is the final separation between silicon atoms?

From single atom and molecule to crystal





Si crystal



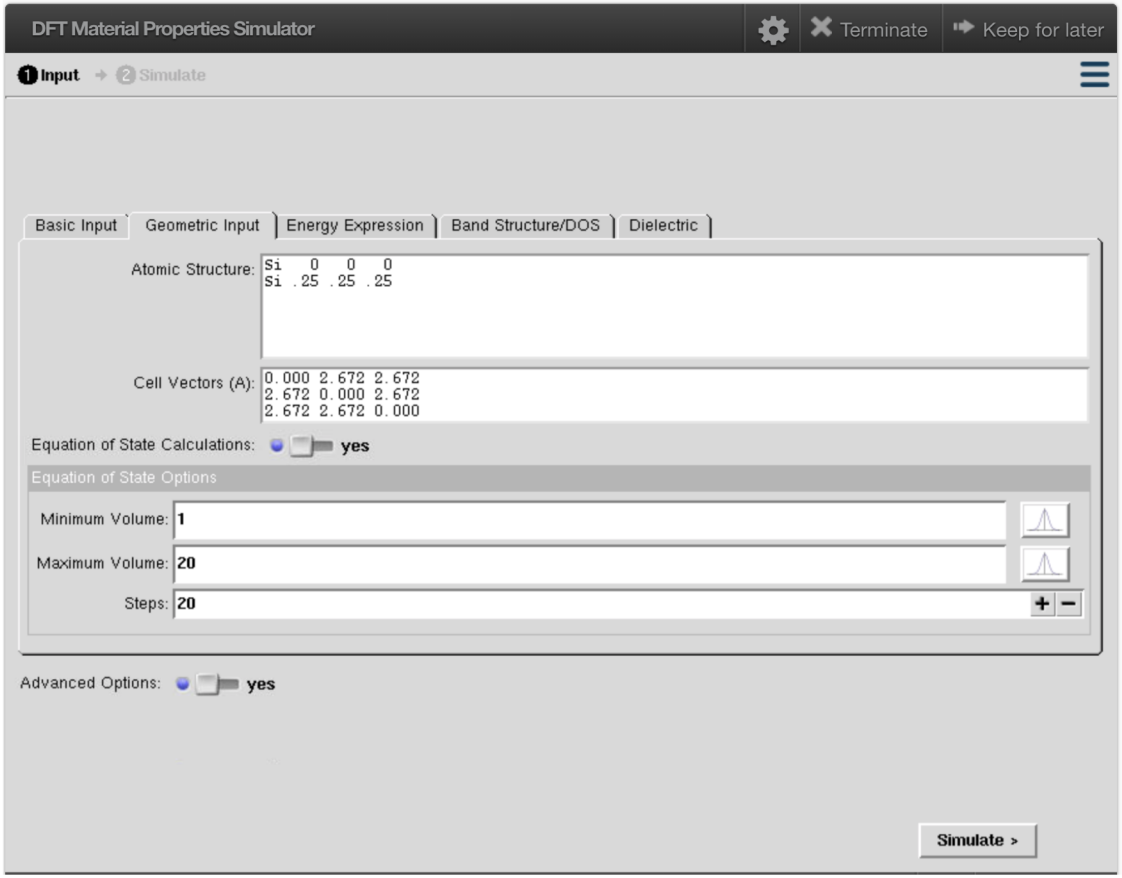
- To better understand the band structure of Si we will perform a series of simulations with varying lattice parameters
- From a large lattice parameter with isolated atoms to the equilibrium lattice parameter of the crystal

Electronic structure vs. lattice parameter

Geometric input

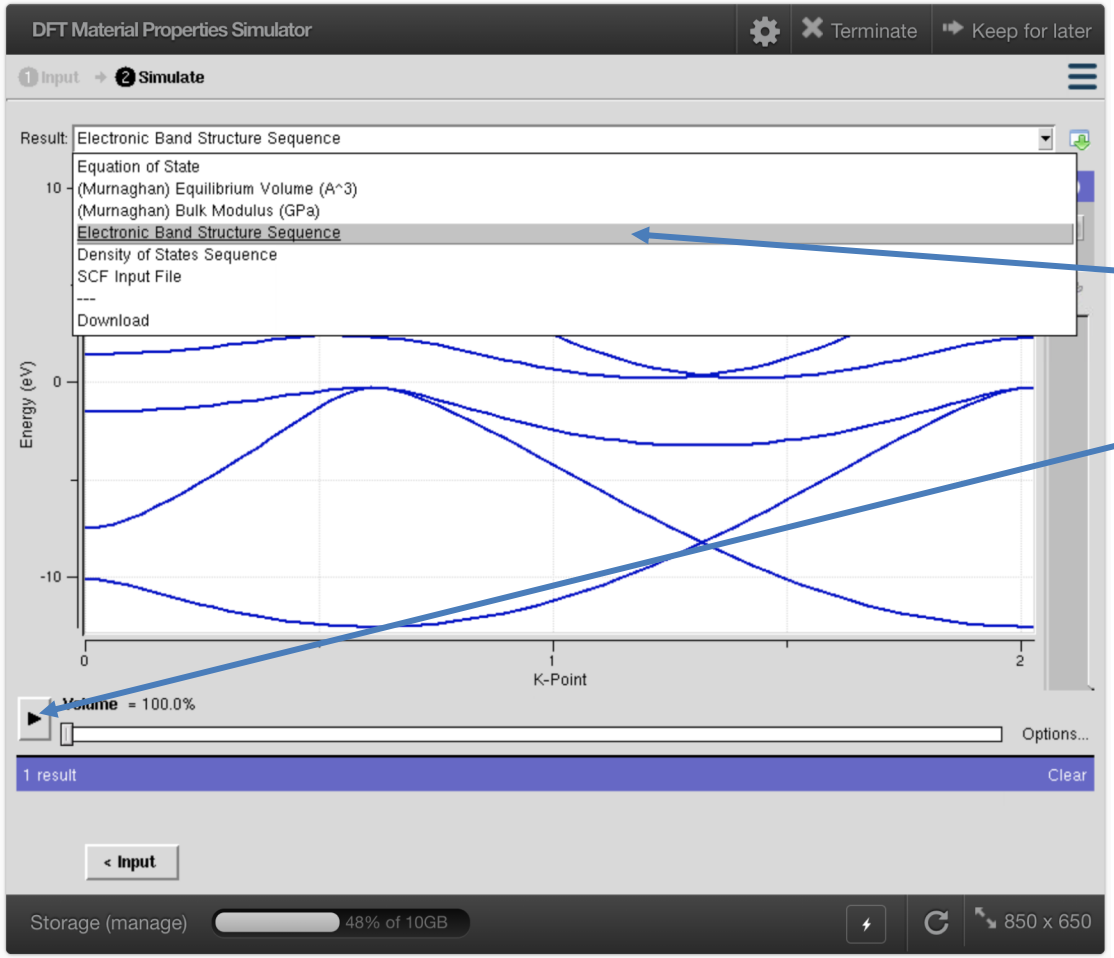
Switch the EOS calculation to YES and change minimum volume to 1, maximum volume to 20, and steps to 20

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



Electronic structure vs. lattice parameter

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

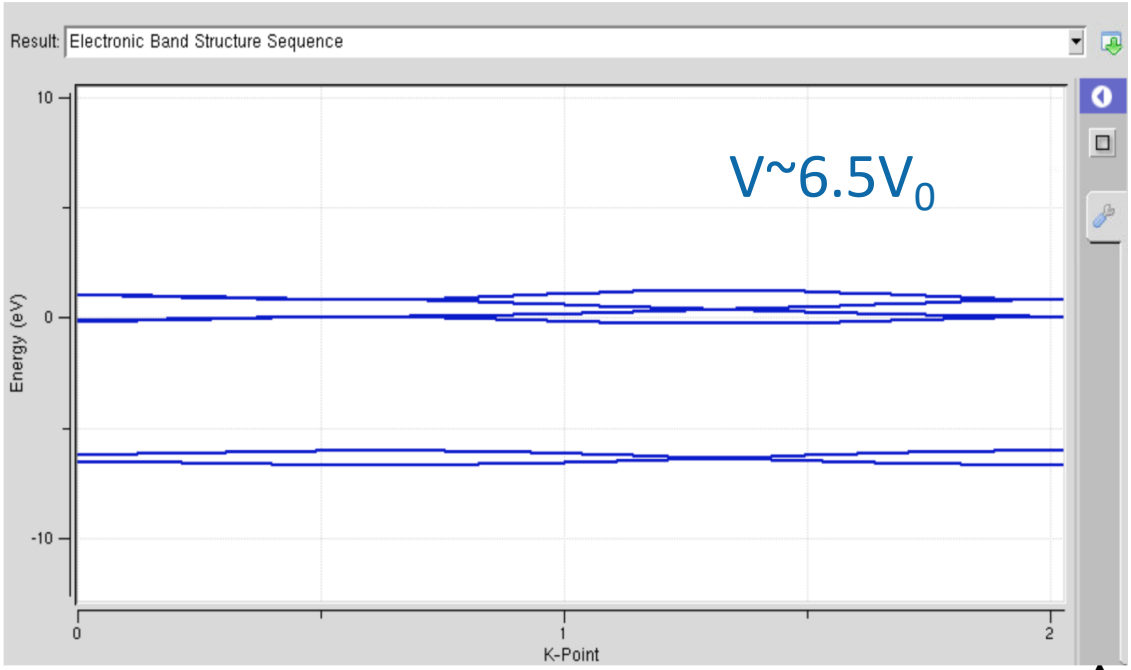


Once the all simulations are done, change the view to "Electronic Band Structure Sequence"

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

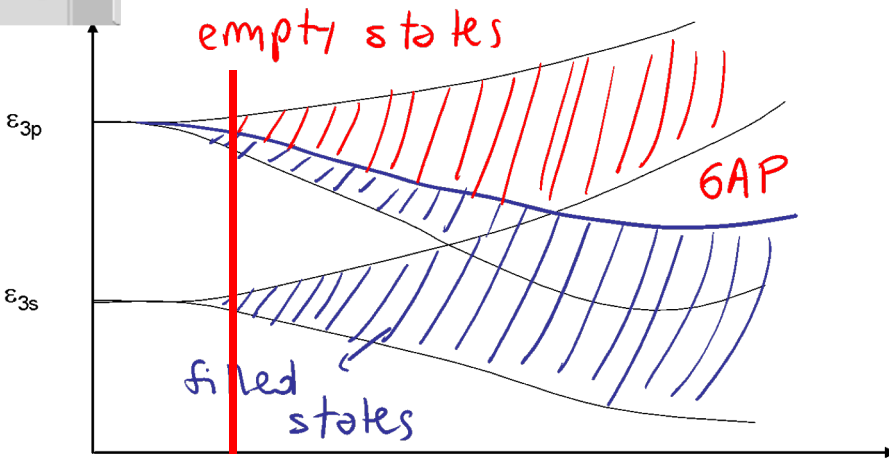
Electronic structure of Si isolated atoms and crystal

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



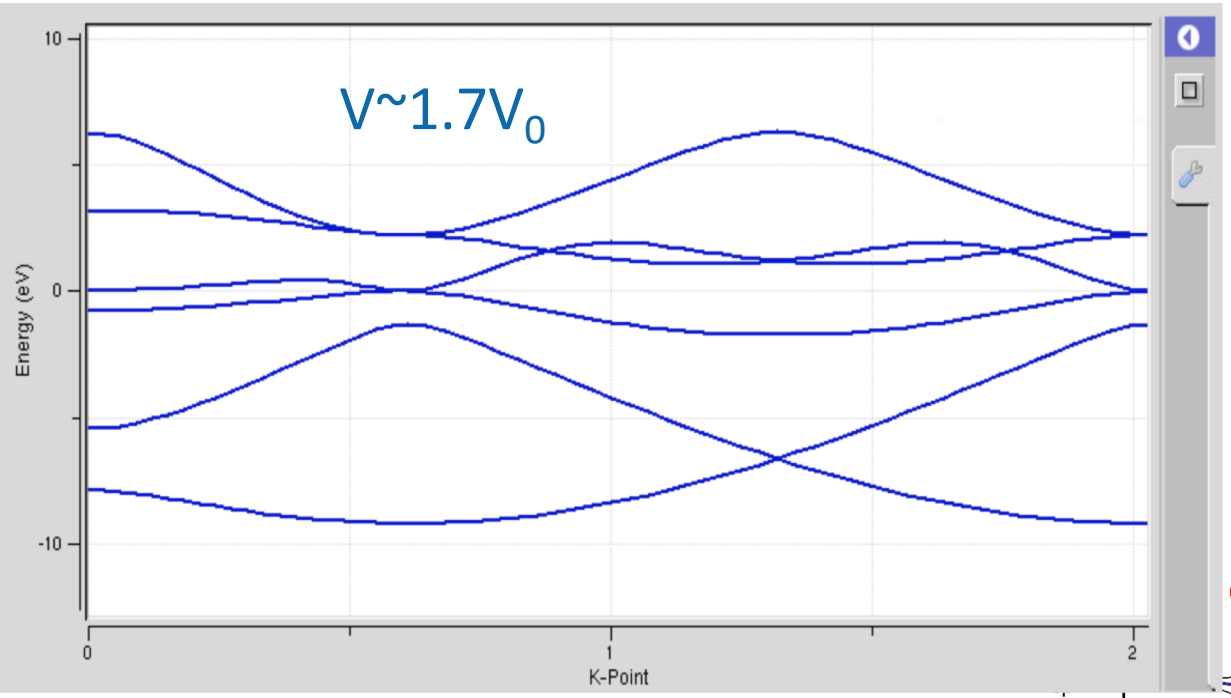
p-states (1/3 filled)
Bonding/antibonding + dispersion

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



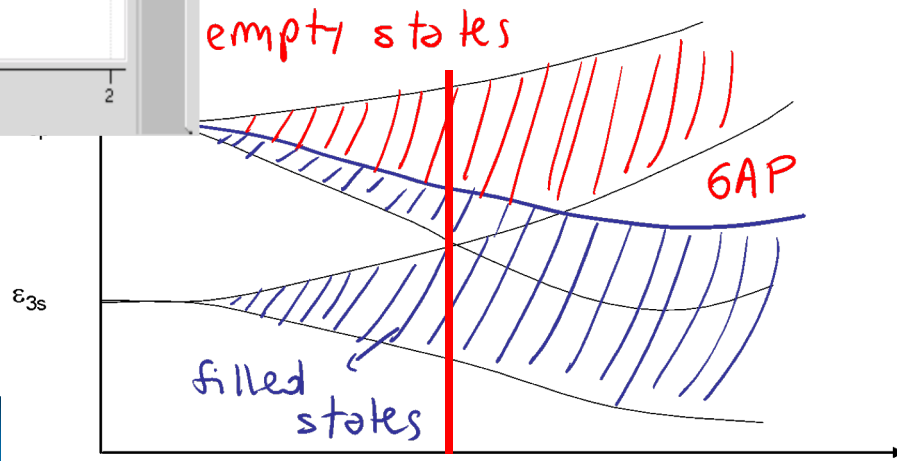
Electronic structure of Si isolated atoms and crystal

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



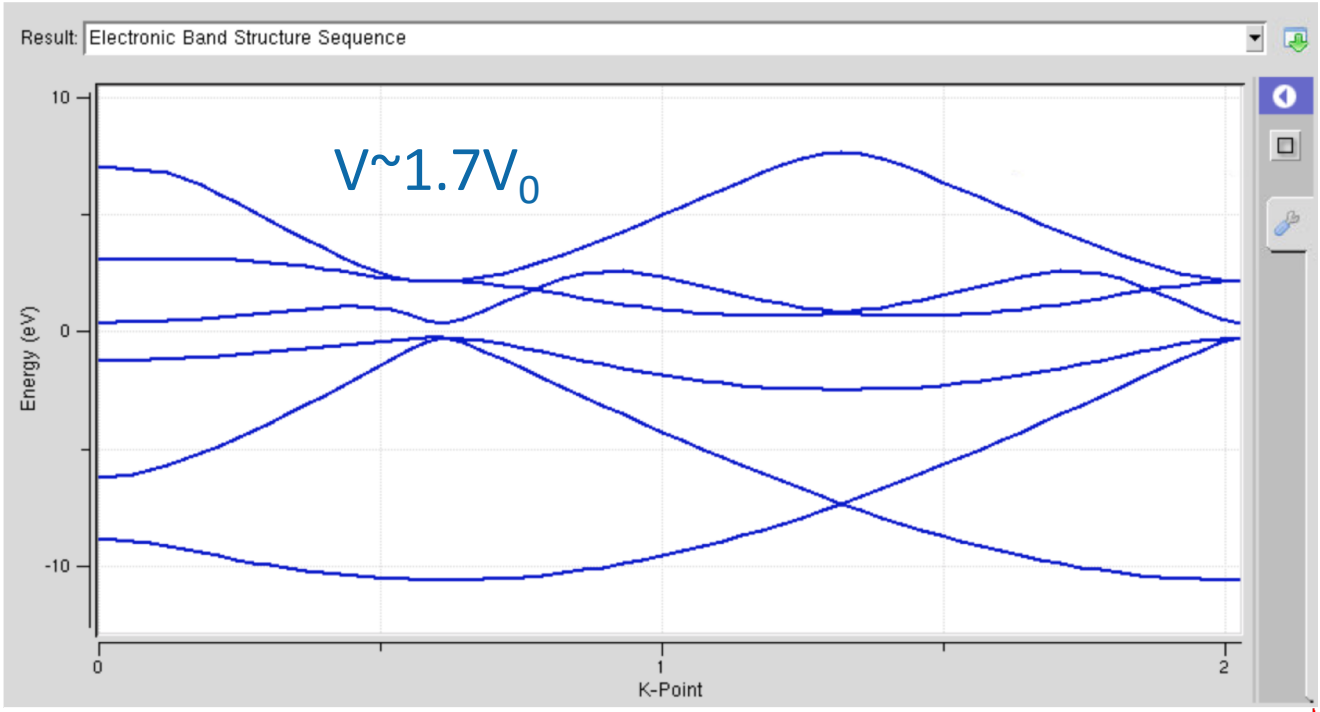
p-states
Bonding/antibonding + dispersion

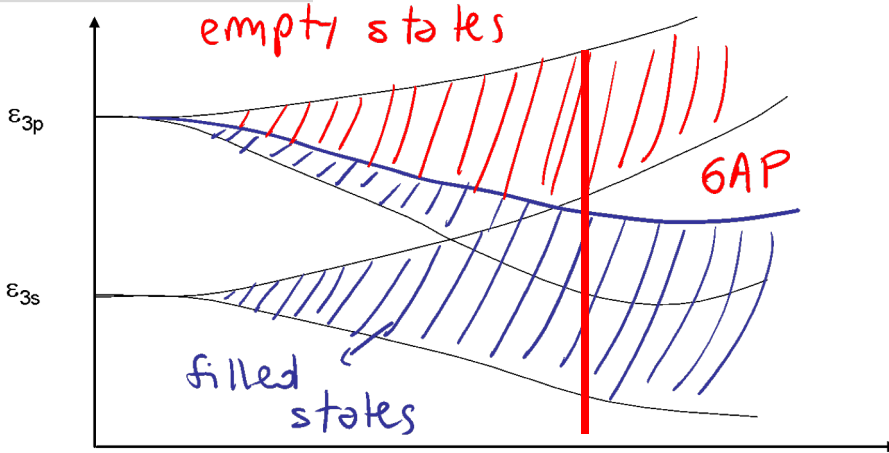
s-states
Bonding/antibonding + dispersion



Electronic structure of Si isolated atoms and crystal

A band gap opens up



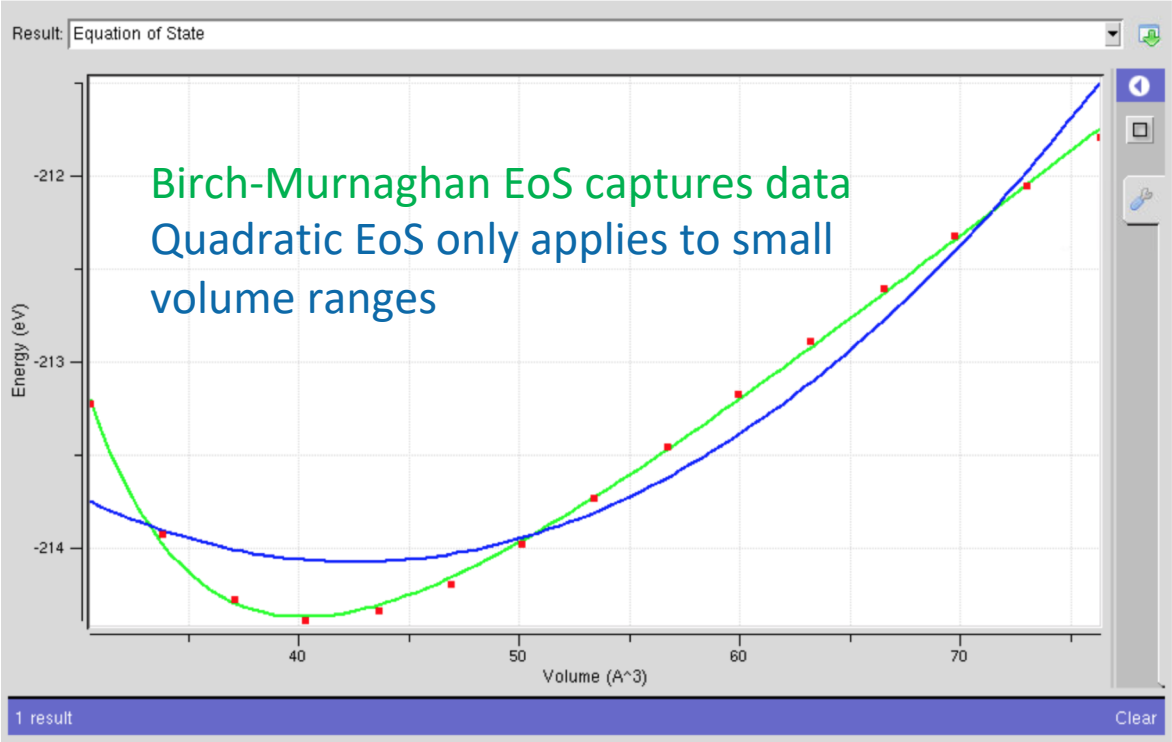


structure

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=0K in this case)

15 points form $0.8V_0$ to $2V_0$

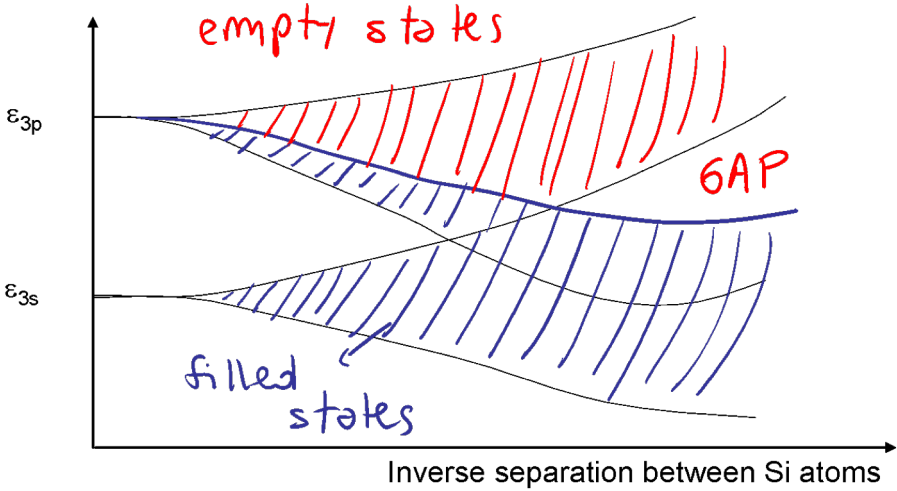


Additional Questions

- 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?

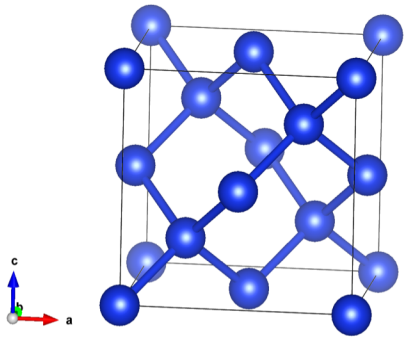
- Think about the development of the band structure in terms of the s and p picture in the figure below



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

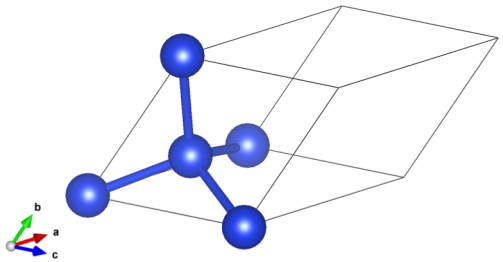
Conventional cell



$$\vec{a} = a_0(1,0,0)$$
$$\vec{b} = a_0(0,1,0)$$
$$\vec{c} = a_0(0,0,1)$$

$$Si_1: 0.00, 0.00, 0.00$$
$$Si_2: 0.25, 0.75\ 0.75$$
$$Si_3: 0.50, 0.00\ 0.50$$
$$Si_4: 0.00, 0.50\ 0.50$$
$$Si_5: 0.50, 0.50\ 0.00$$
$$Si_6: 0.75, 0.25\ 0.75$$
$$Si_7: 0.75, 0.75\ 0.25$$
$$Si_8: 0.25, 0.25\ 0.25$$

Primitive cell



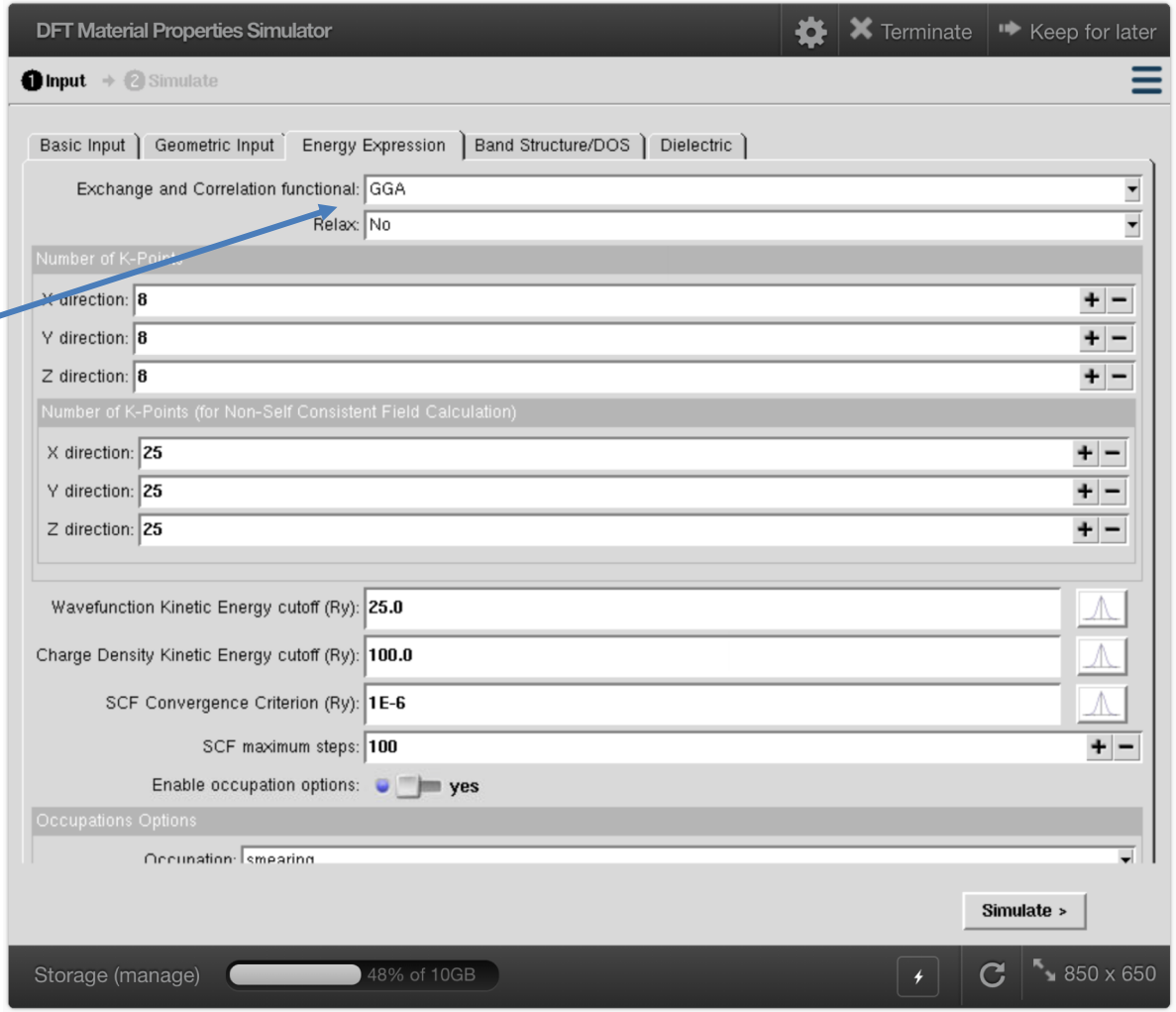
$$\vec{a} = a_0(0, ½, ½)$$
$$\vec{b} = a_0(½, 0, ½)$$
$$\vec{c} = a_0(½, ½, 0)$$

$$Si_1: 0.00, 0.00, 0.00$$
$$Si_2: 0.25, 0.25\ 0.25$$

Additional notes: exchange and correlation

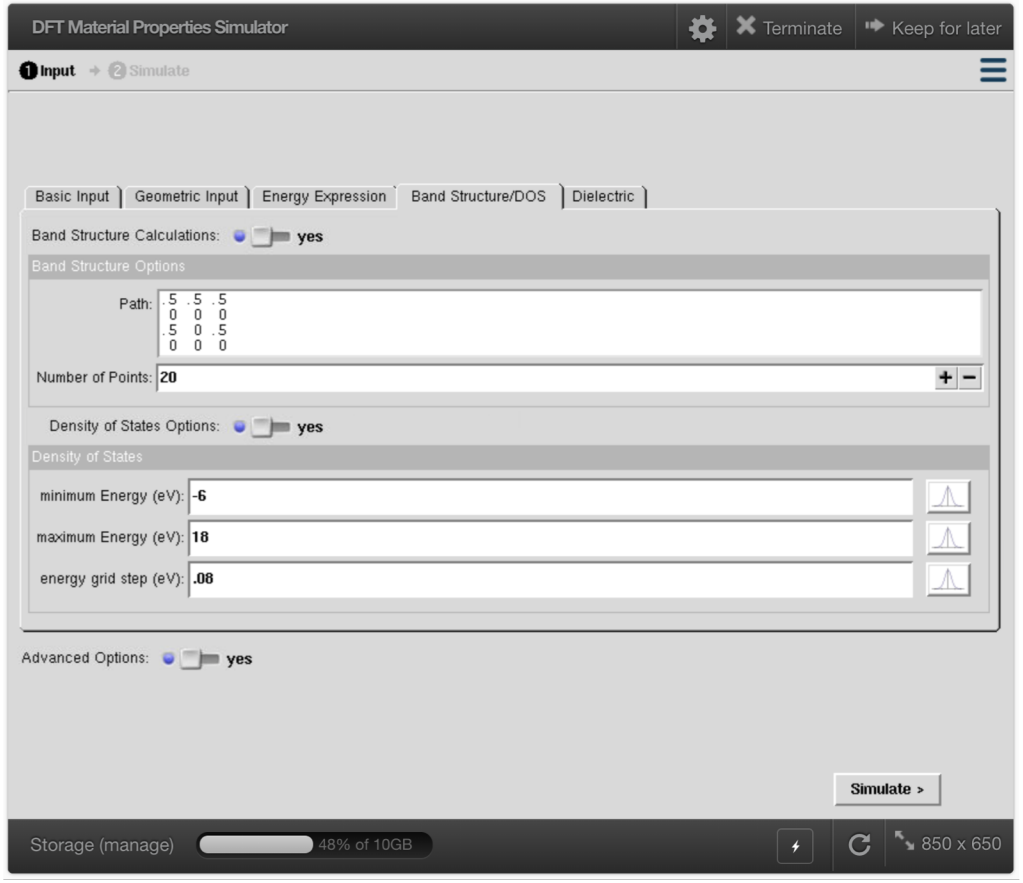
Energy Expression

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



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

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