Using DFT to Simulate the Band Structure and Density of States of Crystalline Materials

In this activity you will use Density Functional Theory (DFT) in order to investigate properties of different materials. DFT is widely used in industry and in the academic research community because it is one of the computational methods that can (approximately) solve realistic quantum mechanical problems numerically. Here you will use it as a tool that provides you with band structures and densities of states for a given arrangement of atoms of a material.

To get started, open a web browser and go to [http://www.nanohub.org](http://www.nanohub.org). If you have no user account, create one (it is free) and then sign in. You can also sign in via Facebook or Google. Then select “Resources” and choose “Tools” from the drop-down menu. Select “DFT” in the left column, and then “DFT calculations with Quantum ESPRESSO” in the middle column:
Click “Launch Tool” in the right column and your screen should look like this:

First, go to the “Input Geometry” tab. Here you can see fields that determine what material and what arrangement of atoms you want to simulate. In the standard setting, which we’re going to use first, you can see that the tool will run for a silicon bulk crystal in the cubic fcc structure (“Structure Type”) and that the lattice parameter for this run is set to 5.43 Å (“Lattice Parameter”). You can also see the field “Atomic Structure”, where the atomic basis for silicon in the diamond structure is specified. Your screen should look like this:
Leave the input geometry unchanged for now, we will just study ideal silicon in the fcc structure. Click on the “Band Structure/DOS” tab and set the “Number of points” to something between 15 and 20. Also set the “energy grid step” to 0.05 eV. Larger numbers of points as well as smaller energy grid steps will most likely fail (since this is just a simple test). We still have to specify the path through the Brillouin zone for which we want to compute the band structure:
In order to know what to put there, go to the “Bilbao Crystallographic Server” ([http://www.cryst.ehu.es/](http://www.cryst.ehu.es/)) and select “KVEC” from the box “Space Groups Retrieval Tools”. You need to choose the right symmetry and we will do this via the space group number for fcc silicon: 227. (You can find this number, for instance, also in the MaterialsProject for many polymorphs of materials.)

**The k-vector types and Brillouin zones of the space groups**
Put 227 in the text box and hit enter, this brings up a table with many high-symmetry k-points. Before we select our path, click the word “Brillouin zone” right above the table to get a visual representation of the Brillouin zone and the labels for the high-symmetry points. Choose a closed path (starting and end point are identical) involving \( \Gamma, L, X, \) and \( W \). Now go back to the table on the previous page. Report the coordinates for the points on your path using the “Conventional basis”.

1. Include a figure of the Brillouin zone and highlight your path in your report.
2. Put the coordinates into the box “Path” in the right order and then hit “Simulate”. (Reminder: use the “conventional basis”)
3. Once the simulation is finished, select “Electron Band Structure” from “Results”. This shows your simulated band structure, report a plot of it! Determine (and report) the highest valence-band energy and the lowest conduction band energy and report at what k point they occur. What is the lowest direct and the lowest indirect band gap of silicon? What do you notice when you compare the band gap to experiment (cite your references)?
4. Select “Density of States” from “Results” and also report your density of states from this run.
5. Indicate what part of the DOS corresponds to filled (valence) states and what part corresponds to empty (conduction) states. Indicate also the band gap.
6. Using the DOS curve that you calculated, find the two largest peaks and indicate in the band structure what bands (energy region) those peaks are coming from. Hint: Hovering the mouse over the plot will provide you with the coordinates of points on the graph.
7. Using the values of \( E(\mathbf{k}) \) near the conduction band minimum and valence band maximum from your calculations, compute the effective mass of electrons and holes in the (100) direction. In order to do this successfully, remember that in the parabolic-band approximation the energy depends quadratically on the k vector. Pick a k vector in the (100) direction. (Note: Si has two kinds of holes.) Your description of the procedure for calculating this must be clear. Leave your answers in units of the free electron mass (it should be something times \( m_0 \)).
8. Now use the skills and knowledge you gained so far to find the material with the lowest electron mass and the one with the lowest hole mass from Si, GaP, GaAs, or GaN. (Hint: Adjust the elements and the lattice parameters in the input files to make sure you produce the correct results.) Are the lowest band gaps of these materials direct or indirect? Prove your answer using a band structure plot that you produced.