FYSMENA 4111 Project 2020

The deadline for submitting the project report is **Friday 27. November**. The report should be delivered as a single pdf file via the Canvas page. It is possible for two persons to collaborate on a project and submit a common report.

There will also be a mini-"conference" where all the projects are presented to the other students **on Wednesday 2. December**; all students should then give a presentation about the project. You are expected to listen to the other students and ask questions.

The task in this project is to use VASP to perform DFT calculations on a chosen material, and to write a report about the results.

Note that the computational resources are limited, and that some of the computations needed for your report may take a while to finish. It is thus strongly advised to start working on the computational part of the project as soon as possible. You will for most of the projects below need to increase the resource allocation for the jobs to finish. You will probably have to increase both the number of CPUs and the maximum allowed computational time in jobfile, e.g.:

```
#SBATCH --nodes=1 --ntasks-per-node=16
#SBATCH --time=03:00:00
```

The NPAR parameter in INCAR should be changed accordingly; it should be as close to sqrt(ntasks) as possible (e.g. NPAR = 4 in the example above).

Mind that a limited number of CPUs can be used for FYS-MENA4111 simultaneously; you should thus expect some extra time waiting for others in the course when running intensively.

It is up to you to choose what to calculate and what to include in the report. The following is a short list of properties that may be natural to calculate and present:
- Convergence of numerical parameters
- Relaxed crystal structure
- Calculated total and relative energies
- Density of states (DOS and LDOS)
- Band gaps
- Band structure
- Spatial electronic structure; 3D plot of the charge density

The report typically consists of the following parts:
- Short introduction on the material
- Briefly about the method; choice of parameters, cutoff, etc.
- Presentation of the most important results
- Discussion of how the results can be interpreted, e.g. compared to experiments or previous calculations from the literature.
- Conclusions and summary

Remember to save pictures etc. for the report and presentation while you perform your calculations.

Possible projects are defined on the following pages.

1   Self-defined project

It is possible to define your own project based on interest or the topic of your master thesis. This has to be agreed with Ole Martin in advance, to ensure that the tasks are realistic and will not require too large computational resources.

You are expected to perform similar tasks as those described on p. 1. In addition you will have to get hold of atomistic structures (POSCAR) yourself. This can e.g. be done via you supervisor or through online databases. Ask Ole Martin if you need help with this.

One option is the International Crystal Structure Database (ICSD): https://icsd.fiz-karlsruhe.de/ , which is a database of experimental structures. UiO has site license on the database, so you need to be on campus or use the Programkiosk (http://view.uio.no) to get access throug your UiO IP address.

Another option is the Materials Project database: https://materialsproject.org/ . This is a non-profit database generated by research groups in USA, using VASP calculations. All known crystalline inorganic compounds are represented in the database, in addition to a large and growing amount of hypothetical compounds. You have to register to get access, but there is no spam or commercial activity resulting from this.

The structures from those databases are typically available as CIF files (*.cif). They can be converted to POSCAR files with the cif2pos.py script:

```
$ cif2pos.py filename.py
```

2 Nanostructured silicon

We have already looked quite detailed at silicon in the datalab. We have seen how reduced dimensionality can significantly change the electronic properties of Si. You are in this project supposed to check the size dependence. Use the models created in the datalab, and increase/reduce the number of atoms constituting the model. As an example, calculate the properties of a Si slab with 2, 4, 6, and 8 layers. Remember to add hydrogen saturating the dangling bonds. This can be done efficiently with ASE, similar to the Vibrations lab.

You could also look at the dielectric function of Si. You do this by adding the tag

```
LOPTICS = .TRUE.
```

in INCAR. You find the real and imaginary parts of the dielectric function in OUTCAR; search for IMAGINARY.
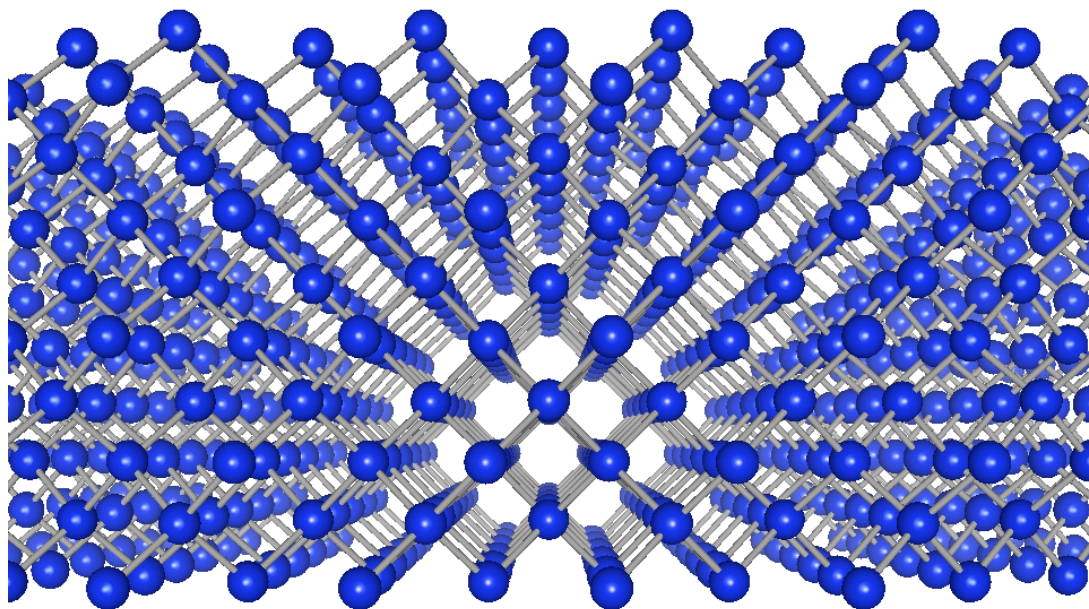
A 10-layer slab of Si seen from the side. Hydrogen terminating the dangling bonds has not been added yet.

3   Phase transformations of bulk Si

You have seen in chapter 2.5 of Sholl and Steckel that it is possible to predict pressure induced phase transformations with DFT. The basis for this is calculations of the total energy as a function of volume, similar to what was done in Fig. 2.4 for Cu and in Datalab 3 for Pt.

The aim of this project is to go further by introducing the Gibbs free energy according to Eqs. 2.10 and 2.11 in Sholl and Steckel. This will give you a possibility to predict phase changes as a function of pressure, schematically illustrated in Fig. 2.5.

In addition to the diamond structure of Si (which was used for all previous calculations on Si in the datalab), six different high-pressure candidate structures have been made available. They are placed in the folder /cluster/projects/nn9989k/fm4111/project/phase-change/ at saga. Both the original cif files (with information about the space groups, authors, etc.) and POSCAR files (with the same name as the cif files, only with a .pos suffix) can be found in this directory.

You should make separate directories for all (or some) of the structures and perform volume-energy calculations similar to those performed in Datalab 3. Remember to change the names to POSCAR in all the cases.
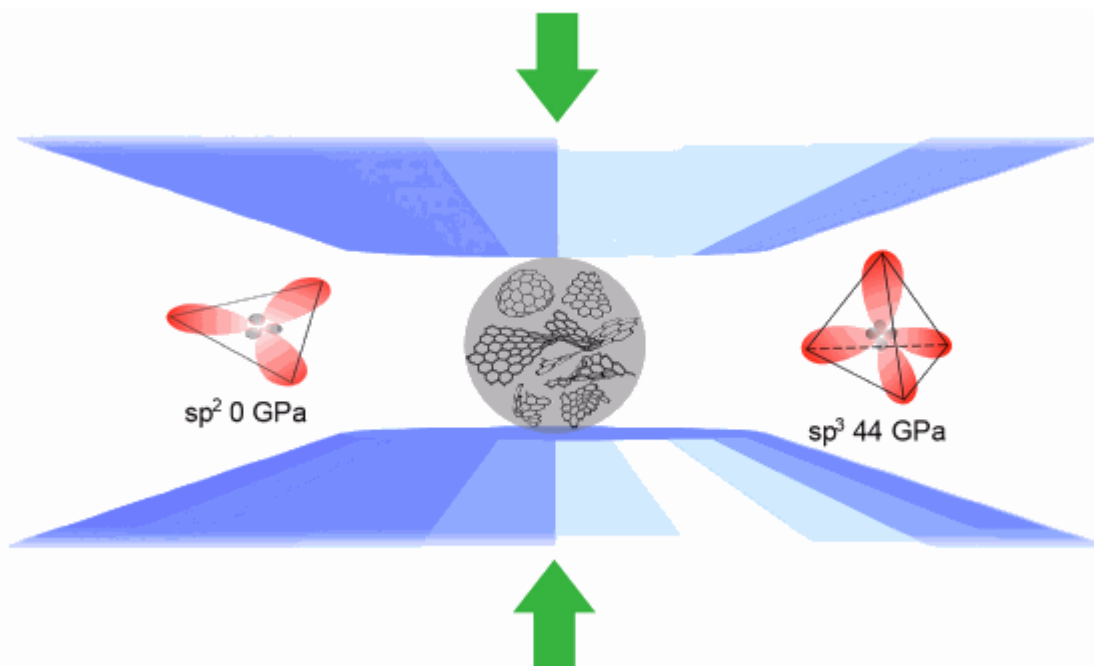
High pressure experiments with e.g. a diamond anvil cell can give information about high-pressure phases. The figure shows how carbon can be transformed; we will look into how silicon can change phase at higher temperatures.

4   Silicon carbide as a solar cell material

Silicon carbide is an abundant and easily available material that is used in a lot of mundane applications. However, it can also be used in power electronics due to its high band gap and high degree of stability. It has recently also been suggested that it can be used as the active part of an intermediate band solar cell material. The take-home message is that the theoretical efficiency of an intermediate band solar cell is almost twice as high as that of a normal, single gap solar cell. It requires very high doping levels, so that an impurity band in the band gap transforms into an intermediate band with high mobility and long charge carrier lifetimes, similar to an ordinary conduction band.

The purpose of this project is to investigate how doping changes the band structure of SiC. We will use the cubic polytype 3C-SiC, which has the smallest band gap and most beneficial optoelectronic properties for a solar cell material. The conventional unit cell can be found here: /cluster/projects/nn9989k/fm4111/project/SiC/. The most promising dopant is B. Possible ingredients include:

- Change the unit cell size
- Vary the formal charge of the dopant, using the tag NELECT in INCAR
- Plot the DOS with and without dopant
- Change to other dopants
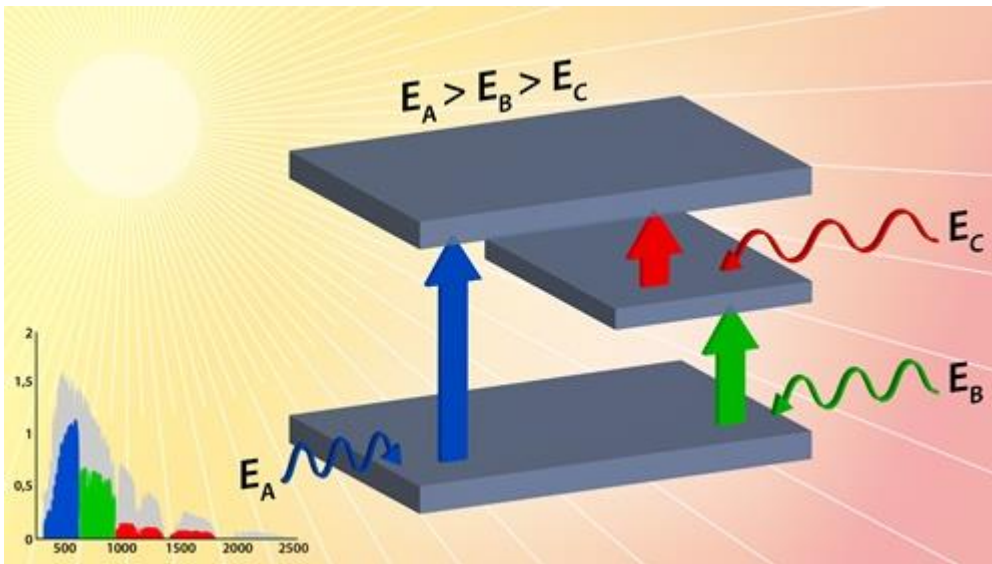
An intermediate band solar cell can absorb light with three different band gaps, increasing the theoretical efficiency to above 60%. This project will investigate the feasibility to achieve this in heavily doped SiC.
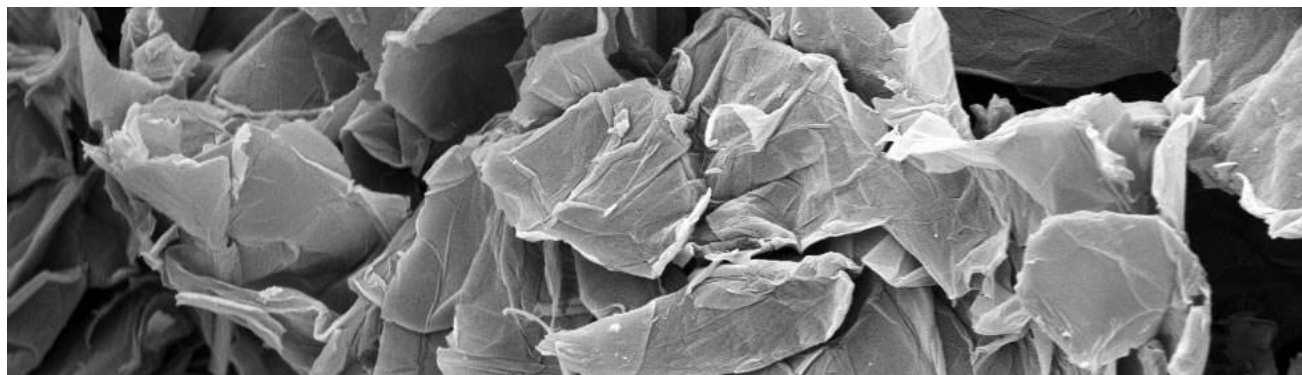
5   Graphene oxide

Graphene is currently one of the most hyped materials due to its very promising properties for electronic, optoelectronic and other devices. It is a very simple material, consisting of only a single sheet of carbon atoms. In practice, it will usually be attached to a substrate, but in this project we will leave it surrounded by vacuum. The smallest unit cell only contains 2 carbon atoms; you will find this here: /cluster/projects/nn9989k/fm4111/project/graphene/.

One way to treat graphene is as graphene oxide - this delays agglomeration and makes it possible to keep it in a solution. It is possible to reduce this oxide into something close to graphene, but some oxygen often remains. The purpose of this project is to investigate the interaction of oxygen with graphene; which sites are preferred and how strong is the binding.

You should in this project first check for convergence of relevant parameters. The electronic structure is especially important, particularly with respect to the k-point density. Then try out different adsorption sites for oxygen, similar to how you tested adsorption of hydrogen on Pt in Lab 6. Other possible topics include:

- Test if different potentials give different results. You can e.g. try LDA, GGA, and one of the hybrid functionals HSE or PBE0.
- Check how the electronic properties change as a result of the oxygen coverage.
- Check if the zero point energy changes the relative stability of the oxygen adsorption sites.
- Plot and compare the band structure of pure graphene and graphene oxide
- Test how the unit cell size (number of C atoms) influences the results, and from this quantify the interaction between neighbour oxygen atoms.

Graphene oxide is a commercial material with many possible future applications. This picture was taken from a Norwegian company selling graphene oxide.
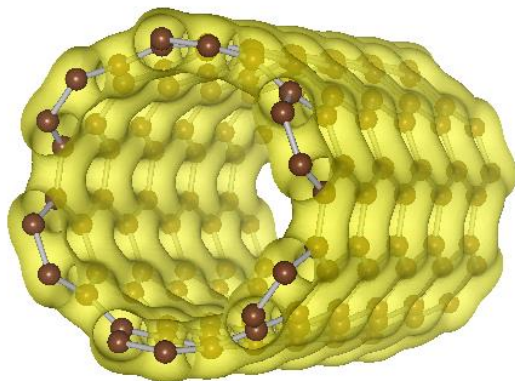
6   Carbon nanotubes

These have been among the most popular nanostructures for many years. You can find a lot of information about them on the internet, and there are also a few resources where you can generate coordinates for nanotubes. You will find two starting structures at /cluster/projects/nn9989k/fm4111/project/nanotubes. It is straightforward to build more nanotubes using ASE: https://wiki.fysik.dtu.dk/ase/ase/build/build.html?highlight=tube#ase.build.nanotube

The m and n indexes determine the type of nanotube. $m = 0$ gives a zigzag termination of the tube, while $m = n$ gives an armchair. Other combinations give chiral nanotubes.

You should in this project at least compare a zigzag and an armchair structure. The $(n,m) = (6,6)$ and (10,0) structures are located in the /cluster/projects/nn9989k/fm4111/project/nanotubes folder. A possible chiral nanotube is (8,4). Hint: it is particularly challenging to obtain properly converged bandgaps with respect to the **k** point density, so pay attention to this.

The charge density of a carbon nanotube, calculated with VASP. This is an armchair structure, with its particular electronic properties.

7   Hydrogen on a platinum surface

Platinum is a very important catalyst, particularly in fuel cells. The task in this project is to study the interaction of hydrogen with a Pt surface, similar to the Vibrations lab. You can find a python script generating a larger Pt slab at /cluster/projects/nn9989k/fm4111/project/platinum.

In order to find the most stable site for a hydrogen atom on this surface, you should try the four different high-symmetry sites indicated in the figure. This is very similar to how hydrogen atoms were positioned above Cu in the Vibrations lab, only with a larger surface unit cell. This time report the adsorption energy, which is defined as

$$E_{ads} = E(\text{slab with hydrogen}) - E(\text{slab}) - \tfrac{1}{2}\,E(H_2).$$

Make sure that you compare the same number of atoms of each species. The energy of hydrogen gas $E(H_2)$ can be calculated by embedding a H_2 molecule in vacuum (like the cluster in the Surface lab). For the most stable site, you should check how E_{ads} varies with the coverage θ. The POSCAR file you start with has a surface unit cell of 2×2, thus the coverage is $\theta = 0.25$ for one hydrogen atom. You can add more adsorbates with the python script by uncommenting the lines adding adsorbates with an offset.
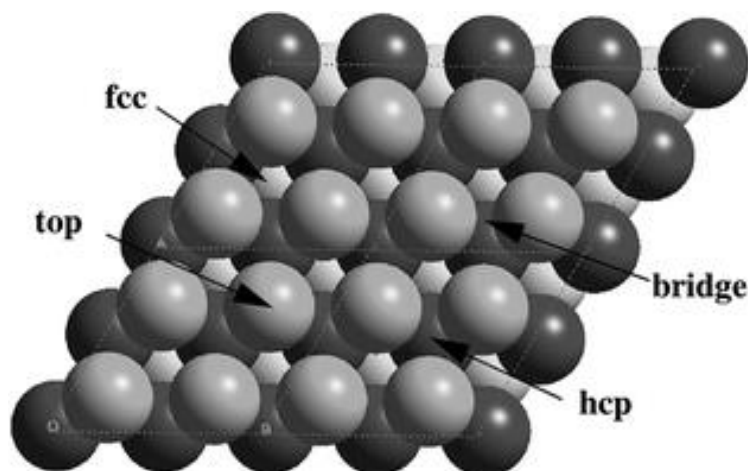
The Pt(111)-surface seen from above, with the four high-symmetry sites ontop, bridge, fcc og hcp marked with arrows. Atoms in the second layer are dark, the others are light.

8 Optical properties of titanium dioxide

Titanium dioxide (TiO_2) is a very useful and versatile material, being used in everything from painting and toothpaste to self-cleaning windows and advanced solar cells. An interesting problem is to investigate the difference in optical properties between bulk and thin-film TiO_2.

The task in this project is to make use of rutile, which is the most common structure of TiO_2 in nature. You can find a POSCAR of bulk rutile at /cluster/projects/nn9989k/fm4111/project/tio2. Create one or more slab models of rutile and compare the electronic structure and DOS of the different geometric structures. Also calculate the dielectric function. You do this by adding the tag

```
LOPTICS = .TRUE.
```

in INCAR. You find the real and imaginary parts of the dielectric function in OUTCAR; search for IMAGINARY.
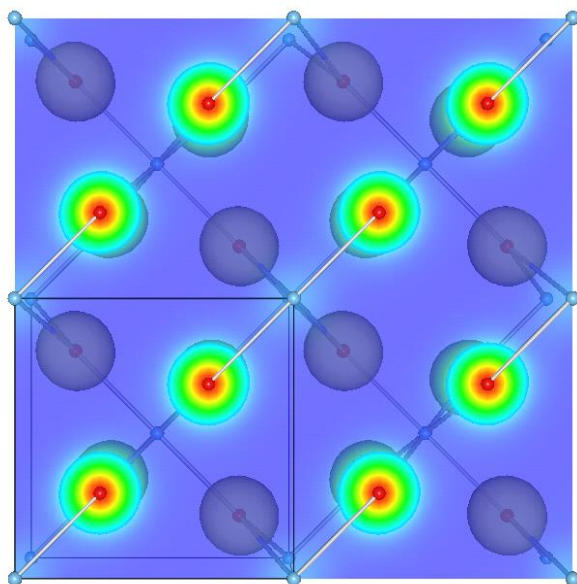
Contour plot of the electronic density of rutile. The unit cell is outlined.