Hands on Density-Functional Theory

0. **Getting started.** All calculations will be performed on the qm3 cluster, where one node with 20 processors is reserved for each participant. Familiarize yourself with the environment.

   (a) First, log in to the qm3 cluster. The `ssh` option `-X` can be used to redirect interactive plots, graphical text editors, etc. to the local machine.

   ```
   [user@pool ~]$ ssh -X qm3grk@qm3-login.bccms.uni-bremen.de
   ```

   (b) Next, log in to the compute node assigned to you.

   ```
   [qm3grk@login ~]$ ssh -X nodeXXX
   ```

   (c) You can monitor the activity of the node using the command `top`. Within `top`, pressing 1 will list all 20 processors. To leave `top`, press q.

   ```
   [qm3grk@nodeXXX ~]$ top
   ```

   (d) All calculations must be run in the `scratch` filesystem. Go to the `scratch` directory for the tutorial.

   ```
   [qm3grk@nodeXXX ~]$ cd /scratch/qm3grk
   ```

   (e) To not interfere with other participants, create a separate directory for your calculations.

   ```
   [qm3grk@nodeXXX qm3grk]$ mkdir userXXX
   [qm3grk@nodeXXX qm3grk]$ cd userXXX
   ```

   (f) To be able to run `vasp`, load the necessary modules.

   ```
   [qm3grk@nodeXXX userXXX]$ module load intel/2016
   [qm3grk@nodeXXX userXXX]$ module load openmpi/2.0
   [qm3grk@nodeXXX userXXX]$ module load vasp/5.3.5
   ```

   (g) Since plotting is not possible on the compute nodes, it is convenient to open a session on the login node in a separate tab (`Ctrl-Shift-T`). In the new tab, repeat step 0a and test if the redirection of plots is working. Create a test plot script with the editor of your choice (e.g. `vi`, `emacs`, `gedit`).

   ```
   [qm3grk@login ~]$ cd /scratch/qm3grk/userXXX
   [qm3grk@login userXXX]$ vi plot.py
   ```

   For example, plot a simple cosine using `matplotlib`.

   ```
   #!/usr/bin/env python
   import numpy as np
   import matplotlib.pyplot as plt
   x = np.linspace(0, 2 * np.pi)
   y = np.cos(x)
   plt.plot(x, y)
   plt.show()
   ```

   Run the Python script. It should open in a new window. Try to zoom in.

   ```
   [qm3grk@login userXXX]$ python plot.py
   ```

   Tip: To cancel a running calculation, type `Ctrl-C`. To log out, type `Ctrl-D`.

   Warning: Please do not run heavy calculations (`mpirun`) on the login node.

   Warning: Please do not use the home directory for any input or output ($\sim$ or `/home1/qm3grk/`). Instead, use the `scratch` filesystem (`/scratch/qm3grk/`).

1. **Hydrogen atom.** Calculate the total energy and the Kohn–Sham energies of the hydrogen atom.

   The essential input files for vasp are INCAR with general parameters, POSCAR with the atomic positions, KPOINTS with the wave-vector specifications, and POTCAR with pseudopotentials for all atoms involved. Useful documentation can be found at https://www.vasp.at/wiki.

   (a) Create a new directory for this exercise and prepare the INCAR.

   ```
   [qm3grk@nodeXXX userXXX]$ mkdir 1_H_atom && cd 1_H_atom
   [qm3grk@nodeXXX 1_H_atom]$ vi INCAR
   ```

   A very basic INCAR file could look like this:

   ```
   SYSTEM = H atom ! description
   ISMEAR = 0       ! smearing type
    SIGMA = 0.1     ! smearing width (eV)
    NCORE = 4       ! number of cores per orbital
   NBANDS = 15      ! number of bands
   ```

   (b) Add a POSCAR to the same directory.

   ```
   H atom          ! description
   1               ! length unit (AA)
   10.0  0.0  0.0 ! 1st lattice vector
    0.0 10.0  0.0 ! 2nd lattice vector
    0.0  0.0 10.0 ! 3rd lattice vector
   H               ! atom symbols
   1               ! atom counts
   Cartesian       ! coordinate basis
   0.0 0.0 0.0     ! coordinates of 1st atom
   ```

   (c) Add a KPOINTS file too.

   ```
   Automatic uniform mesh ! description
   0                       ! number of k points (or automatic)
   Gamma point included    ! shift mesh?
   1 1 1                   ! number of k points per dimension
   ```

   (d) Finaly, copy the POTCAR file for hydrogen.

   ```
   [qm3grk@nodeXXX 1_H_atom]$ cp /scratch/qm3grk/POTCARS/H/POTCAR .
   ```

   (e) Now, run vasp in the same directory.

   ```
   [qm3grk@nodeXXX 1_H_atom]$ mpirun vasp-mpi
   ```

   This will use all processors available in parallel. With ls, verify that many output files have been created. The main output file is OUTCAR. Familiarize yourself with its content. Search for the final occurrence of the total energy (TOTEN), which still excludes the atomic energy (EATOM). Below, you will find the Fermi level or chemical potential (E-fermi) and the Kohn-Sham eigenvalues for all k points. Alternatively, the Fermi level can be read from the 4th value of the 6th line of the DOSCAR and the the Kohn-Sham eigenvalues are listed in the file EIGENVAL.

   (f) Which value of the total energy do you expect? Is this reproduced by the calculation?

   (g) Compare the Kohn–Sham eigenvalues to the exact energy levels $-$Rydberg$/n^2$. Do the results agree? Can we expect this?

   (h) So far, we assumed that all states are spin-degenerate. Allow for spin polarization by setting ISPIN = 2 in the INCAR and repeat the calculation. How do the results of exercises 1f and 1g change?

2. **Hydrogen molecule.** Calculate the total energy of the hydrogen molecule for different bond lengths.

The input files remain largely identical. Since we are not interested in high-energy Kohn–Sham eigenvalues, we can remove NBANDS from the INCAR. Also, spin-polarization (ISPIN) should be disregarded. In the POSCAR, the number of atom changes and we need another line with an atomic position.

Tip: Is is convenient to use a separate subdirectory for each bond length.

Tip: In bash, a loop over different distances could look like this:

```
for d in `seq 0.30 0.05 2.00`
do
        echo $d
done
```

Tip: If seq uses German decimal commas, you can fix this by letting d=${d/,/.}.

Tip: With sed, certain text in a file can be replaced in-place.

```
sed -i s/DIST/$d/ POSCAR
```

(a) Plot the total energy as a funtion of the bond length.

(b) What is the equilibrium bond length?

(c) What is the dissociation energy?

3. **Hydrogen chain.** Calculate the total energy and the band structure of a linear chain of hydrogen atoms for different lattice constants.

Now, we again have only one atom in the unit cell. However, one axis of the unit cell is shortened such that neighboring atoms are coupled in this direction. Along the corresponding reciprocal lattice vector, a single k point is no longer sufficient. For example, if your chain is oriented along the first Bravais lattice vector, your automatic k-point mesh should be $n_k \times 1 \times 1$, where n_k is the number of k points. In real space, n_k corresponds to the length of the chain, i.e., to the number of unit cells, into which the complex wave function must fit.

Once you obtained a self-consitent charge density, you can perform another, non-self-consistent calculation to increase the k resolution for the band-structure plot. vasp can be instructed to reuse an existing CHGCAR by setting LORBIT = 11 in the INCAR. To plot the bands on the interval $k_x \in [-\pi/a, \pi/a]$ with the lattice constant a, you can use a different variant of the file KPOINTS:

```
k-point path   ! description
100            ! number of points along line segement
Line           ! mode
Reciprocal     ! coordinate basis
-0.5 0.0 0.0 1 ! coordinates of 1st vertex
+0.5 0.0 0.0 1 ! coordinates of 2nd vertex
```

Tip: It is convenient to use different subdirectories for different lattice constants as well as for the self-consistent and the non-self-consistent calculation.

(a) What is the equilibrium lattice constant?

(b) Compare the band structure, in particular the band lowest in energy, to the dispersion of the tight-binding chain with nearest-neighbor coupling?

(c) How does the lowest-energy band change as a function of the lattice constant? Is there an intuitive explanation for this?

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4. **Silicon.** Calculate the lattice constant and the band structure of silicon in the diamond structure.

   A possible choice for the Bravais lattice vectors is

   $$\boldsymbol{a}_1 = \frac{a}{2}\begin{bmatrix}0\\1\\1\end{bmatrix}, \qquad\qquad \boldsymbol{a}_2 = \frac{a}{2}\begin{bmatrix}1\\0\\1\end{bmatrix}, \qquad\qquad \boldsymbol{a}_3 = \frac{a}{2}\begin{bmatrix}1\\1\\0\end{bmatrix}.$$

   There are two atoms in the unit cell, whose positions read $\boldsymbol{r}_1 = 0$ and $\boldsymbol{r}_2 = (\boldsymbol{a}_1 + \boldsymbol{a}_2 + \boldsymbol{a}_3)/4$.

   Make sure to use a sufficienty dense $n \times n \times n$ $\boldsymbol{k}$-point mesh for the self-consistent calculation. An appropriate KPOINTS file for the non-self-consistent calculation is given below.

   ```
   k-point path  ! description
   50            ! number of points along line segment
   Line          ! mode
   Reciprocal    ! coordinate basis
   0.5 0.5 0.5 1 ! L
   0.0 0.0 0.0 1 ! Γ

   0.0 0.0 0.0 1 ! Γ (again)
   0.0 0.5 0.5 1 ! X
   ```

   (a) Compare the lattice constant to the experimental value.

   (b) Compare the band gap to the experimental value.

5. **Germanium.** Repeat exercise 4 for germanium in the diamond structure.

   (a) What is different here?

Tip: If a vasp-mpi process keeps running in the background (visible in top), you can stop it with killall vasp-mpi. Be careful, this will kill all processes of this name on the node.

Tip: If you need inspiration, you can find examplary solutions for all exercises in the directory /scratch/qm3grk/Solutions.