Lab 1:

O-H Bond Strengths

In this first computer exercise, you will use two different quantum chemical methods to calculate the O-H bond strength in three different molecules. The main purpose of this exercise is for you to get familiar with the software used in this course. You will also start to learn which kind of questions that can be answered by quantum chemical calculations.

Methods:
In this excersise you will use two different methods:

1. Hartree-Fock (HF)
2. Density Functional Theory (DFT), using the B3LYP functional

Hartree-Fock (HF) theory is the simplest *ab initio* approach and the basis for most post-HF methodology. DFT methods are based on the one-to-one correspondence between the electron density and the energy; the B3LYP functional is one modern general purpose DFT-based method that we will use.

In your calculations, you need to specify a set of known functions, the basis set, which are used to expand the unknown wavefunction and solve the Schrödinger equation approximately. We will use the Def2-SVP basis set, which is of double-zeta quality, and includes polarization functions on all atoms.

Bond Strength:
The R-H bond strength (where R is a chemical group) is defined as the energy difference between R-H and R + H (at infinite separation). In order to determine the bond strength, you will need to optimize the structures of R-H and R, and perform a single-point calculation on H.

You will compute the O-H bond strengths in the following molecules:

Water $\qquad$ H_2O
Methanol $\qquad$ CH_3OH
Vinyl alcohol $\qquad$ CH_2CHOH

For example, for water, you will need to perform the following calculations:
H_2O $\quad$ with HF/Def2-SVP and with B3LYP/Def2-SVP
·OH $\quad$ with HF/Def2-SVP and with B3LYP/Def2-SVP
·H $\quad$ with HF/Def2-SVP and with B3LYP/Def2-SVP

Fermionic particles, such as electrons, have a spin quantum number $S = \pm\frac{1}{2}$. The orbitals in water methanol and vinyl alcohol are all doubly occupied with equal numbers of spin up and spin down electrons, resulting in a total spin of zero ($S = 0$). This situation is called a closed shell *singlet*, where "singlet" stands for the multiplicity of the electronic state. Multiplicity is calculated as: $2S+1$ and is equal to 1 for closed shell states. In contrast, R and H are radicals,

and carry one unpaired electron each (S = ½). Make sure you calculate and enter the right multiplicity for each molecule.

Instructions on How to Use ORCA:
In this exercise, we will build each molecule 'manually' by writing down a z-matrix directly into the input file. Below is an example input for geometry optimization of fluoroamine, NH_2F:

```
#Geometry optimization NH2F
! HF opt def2-SVP

* int 0 1
N 0 0 0  0 0   0
H 1 0 0  1 0   0
H 1 2 0  1 105 0
F 1 2 3  1.4 105 120
*
```

To run a single point energy calculation one should simply remove the 'opt' keyword in the input. To instead run a DFT calculation "HF" would be replaced by "B3LYP Grid4" in the example above. Use Windows explorer to handle files, and to use notepad to edit the input and read the output. To submit a calculation with ORCA in Windows you need to use the command prompt (this is easier in Linux or on a Mac). To find the command prompt in Windows search for cmd.exe in the start menu. Open the terminal if you are working in Linux or Mac.

Selected commands for Windows command prompt:

Create a directory:	mkdir
Show contents of directory:	dir
Show address of directory:	cd
Move from one directory to another:	cd address_newDir
Move to parent folder:	cd ..
Copy a file from file1 to a new file file2:	copy file1 file2
Copy a file from another directory to current directory:	copy address_otherDir/filename .
(. Marks your current directory)	
Rename/move a file:	move file1 file2
Delete a file:	del file
Print lines from file containing a specific string:	find "text" filename

Selected commands for Linux/Mac terminal (if you're using your own laptop):

|	
Create a directory:	mkdir
Show contents of directory:	ls
Show address of directory:	pwd
Move from one directory to another:	cd address_newDir
Move to parent folder:	cd
Copy a file from file1 to a new file file2:	cp file1 file2
Copy a file from another directory to current directory:	cp address_otherDir/filename .
(. Marks your current directory)	
Rename/move a file:	mv file1 file2
Delete a file:	rm file

Print lines from file containing a specific string: grep "text" filename

Before you run a calculation you need to navigate to the folder with your saved input file. Then start your job by writing: orca input.inp > input.out

Analyze Your Results:
Did the optimization proceed as it should? Check energy and forces in the name.out file. If the optimization was successful there will be a line containing the string "HURRAY" close to the end of the file. The optimized structure is written into a file with ending .xyz.

Start the Avogadro program, look at the optimized structures and measure bond distances and angles. To view an animation of the geometry optimization rename the name.trj (trajectory file) to name_trj.xyz and open it in Avogadro. Then under *Extensions* select *Animation*.
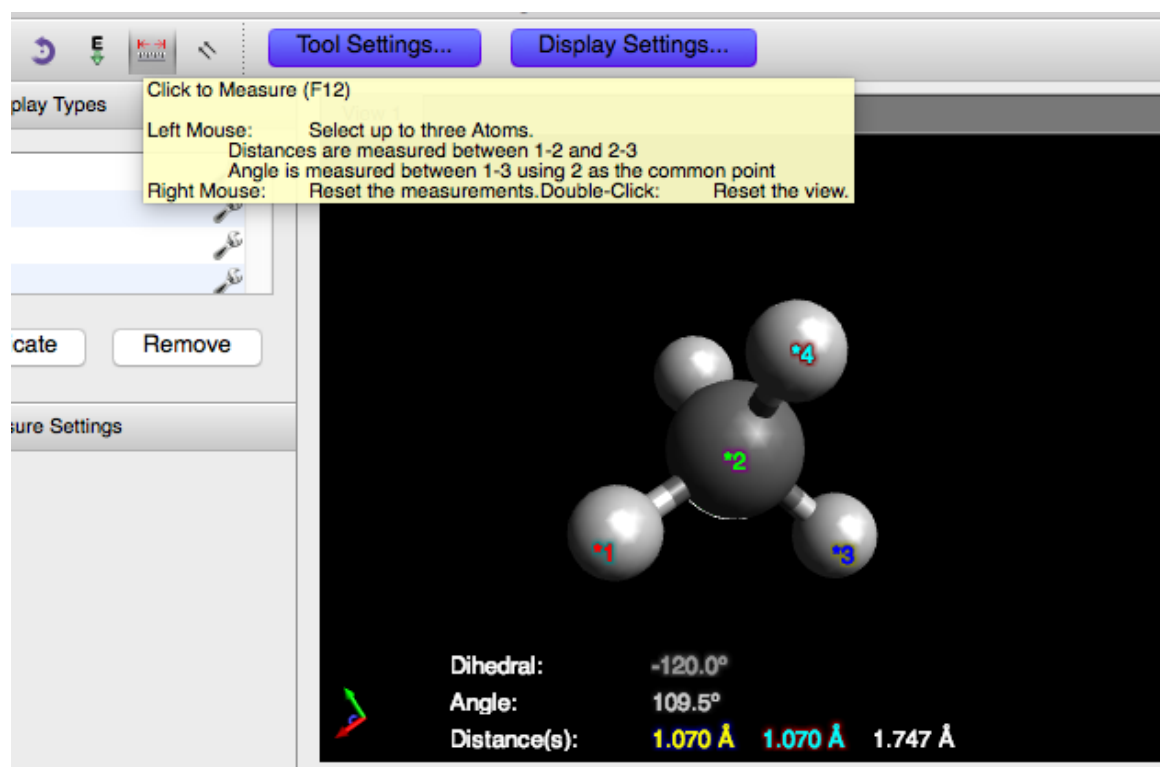
For both levels of theory:

- Write down the O-H bond distances (Å) and the H-O-R angles (degrees). Are the geometries reasonable? Compare O-H bond distances with experiment (see table 1 below).

- Calculate the O-H bond strengths from the computed total energies. Experimental OH bond strengths are 119 kcal/mol and 104.4 kcal/mol for H_2O and CH_3OH, respectively. Comment on the computed O-H bond strength in vinyl alcohol.

- Write down the Mulliken spin population and the Mulliken charge on the oxygen atom. Briefly discuss observed trends. The mulliken spin population is the difference in population of alfa and beta spin electrons (for what molecules do you expect this to be relevant in this lab?)

Table 1. Experimental structural data for H_2O, CH_3OH, CH_2CHOH [*]

	H_2O	CH_3OH	CH_2CHOH
r_{OH} [Å]	0.958	0.956	0.96
a_{ROH} [Degrees]	104.47	108.87	108.3

[*] National Institute of Standards and Technology, Experimental Geometry data, http://cccbdb.nist.gov/expgeom1.asp, Accessed: 2017-10-18.

Use excel for data processing

Unit Conversion: 1 Hartree = 627.5 kcal/mol.

Choose the last energy in optimizaiton.

Present all relevant energies in the report in kcal/mol. The energies should be reported with one decimal accuracy.

If not explicitly asked for in the lab, the absolute energies do not need to be presented.

Double check that the correct multiplicity is used.

The optimized structure can be seen either through the .xyz file or the .trj file (last frame).

The reports should be named according to the following structure:
COURSECODE_LABNAME_Lastname-1_Lastname-2.pdf.

ORCA on laptop (an option for later):
If you wish to install ORCA and Avogadro on your own laptop in preparation for Lab 2 and 3, then you can find them here: https://cec.mpg.de/orcadownload/

Avogadro can be downloaded at https://sourceforge.net/projects/avogadro/ after registering. Local installations of ORCA and Avogadro onyour laptops are not necessary in order to do the labs, and we cannot support installation questions on your individual machines.

Energetic Extra Assignment 1
(to be included in individual labreport for higher grades):

Calculate the bond strengths of N_2 and F_2. Pay attention to the multiplicity of the ground state atoms. Discuss what your results say about the accuracy of the two used methods. What is the underlying reason for the difference in accuracy?

Experimental bond energies are 39.2 and 229.3 kcal/mol for F_2 and N_2, respectively.

Reminder: Criteria for higher (4 or 5) grades on individual lab report:

You do not need to present background theory on DFT or DFT functionals. But you do need to include a correct method description. Think of it this way: you are writing to another quantum chemist, who should be able to understand and reproduce what you have done. A quantum chemist who ideally should appreciate what you have found out. It is therefore very important to reflect and discuss your results.

Grade 4: A minimum of two out of three (2/3) energetic extra assignments performed and presented very well.

Grade 5: All energetic extra assignments performed and presented excellently.

Instructions on How to Use the Terminal

The terminal can be used to run programs and navigate between different folders of the computer. Orca is run through a terminal command as described above. The program Avogadro used for visualization of Orca output can also be opened from the terminal. These are a few steps to get you started.

1. Open the terminal window by typing "Terminal" in the search bar.
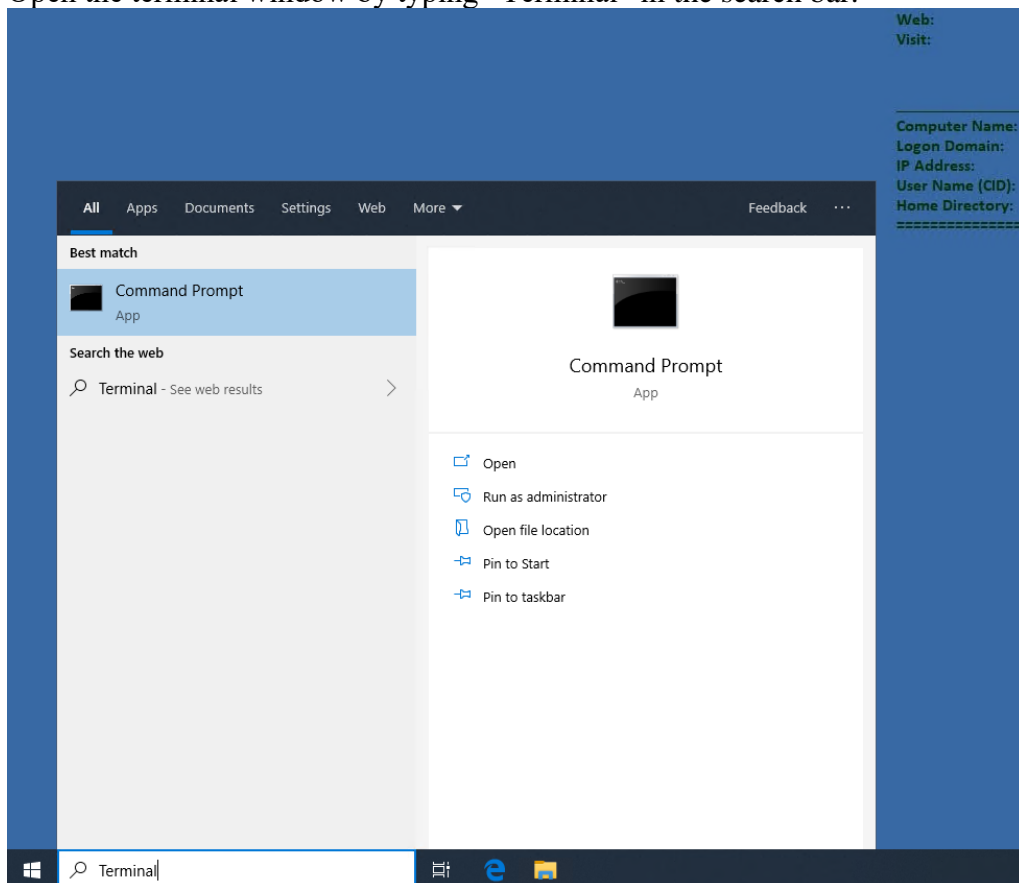
2. Navigate to your desired working directory using the "cd" command. Use "dir" to check your current location.
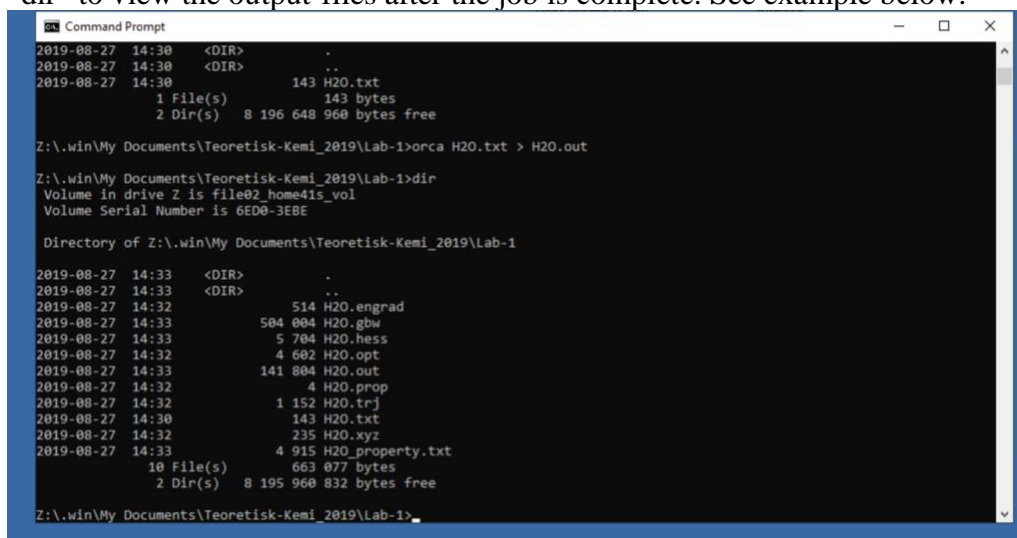
3. Run Orca by following the command syntax "orca input.inp > input.out". Use "dir" to view the output-files after the job is complete. See example below.

4. Open the various output-files with Avogadro. You can open Avogadro by typing "Avogadro" in the terminal or by searching for it via the taskbar.