**Lab1. Electronic structure calculations: Basics**

*Due: September 12*

In this lab you will perform basic *ab initio* calculations in Q-Chem. You will learn how to create an input file for evaluation of basic properties of formaldehyde (CH2O) and analyze the information in the output. You will also learn how to compute the energy differences between different conformations of the same molecule (bent vs. linear water) and interaction energies between two molecules (water cluster).

Note: Your report need not be long and elaborate. Please be brief and concise. Electronic submission preferred (if possible sketch the orbitals and modes using your laptop/tablet). If not, paper submission is perfectly fine.

**Lab Procedure (Part A: computing energies of different conformations):**

1. Build a water molecule in IQmol. Minimize its energy with “Minimize Energy” option (this is a quick molecular mechanics optimization).
2. Perform geometry optimization of the molecule (choose "Geometry" instead of

"Energy" in Calculate menu) at the **HF/6-31G\*** level of theory. Note the final energy.

1. Build a linear water molecule using the text box available in IQmol (manually modify the generated input file section), perform geometry optimization and compute the final energy of the linear water molecule using the same level of theory.

Hint: Use Z-matrix coordinates as described below

$molecule

0 1

8

1 1 0.96

1 1 0.96 2 180.0

$end

**Lab Procedure (Part B: computing interaction energies):**

1. Compute the energies of two water clusters using the following given geometry at **HF/6-31G\*** level of theory.

O -0.089523 0.063946 0.086866

H 0.864783 0.058339 0.103755

H -0.329829 0.979459 0.078369

O 2.632273 -0.313504 -0.750376

H 3.268182 -0.937310 -0.431464

H 2.184198 -0.753305 -1.469059

Hint: Compute the energy of the first monomer **A** (first three atoms), then compute the energy of the second monomer **B** (last three atoms), followed by the energy of the dimer **AB** (all six atoms).

The total interaction energy Eint = E(AB) - E(A) - E(B).

**Lab Procedure (Part C: Fun with formaldehyde!):**

1. Build CH2O molecule in IQmol. Minimize its energy using “Minimize Energy” option.
2. Perform geometry optimization of the molecule (choose "Geometry" instead of

"Energy" in Calculate menu) at the **HF/6-31G\*** level of theory. Check how the geometry of the molecule changes during the optimization.

1. Perform vibrational frequency calculation of formaldehyde at equilibrium geometry at the same level of theory **HF/6-31G\*** (I suggest that you do not use “green plus” option in this lab and run all calculations separately).
2. Inspect vibrational modes of the molecule, practice these vibrational modes over the weekend.
3. Take a look at the molecular orbitals, electronic density, and electrostatic potential. Do you like the view? - yes! - you will have a lot of fun in this class ☺

**Lab report:**

• Bent vs. linear water

What is the total energy of the (optimized) bent water? What is the total energy of the (optimized) linear water? What are their relative energies? Express the relative energies in terms of kJ/mol, kcal/mol and in hartrees. Keeping in mind the boltzmann energy at room temperature (E = KBT), is the linear water conformation easily accessible at room temperature?

The following task in *italics* is not required for the scope of this lab report: *For those who are curious, you can repeat the same steps with planar and pyramidal ammonia (NH3) to see if the ‘umbrella inversion’ process is feasible at room temperature. Is tunnelling a factor in this inversion process?*

• Interaction energies of water clusters

What is the energy of monomers A, B and the dimer AB? What is the total interaction energy? Express this quantity in hartrees, kJ/mol and kcal/mol.

The following task in *italics* is not required for the scope of this lab report: *There is an easy trick to perform this entire simulation in one go. Check the last page of this document for a sample input. Don’t fret if you don’t understand what ‘BSSE’ means. You will learn in due course. Try running the simulation and check the last few lines of the output file.*

• Molecular orbitals of formaldehyde

Make a sketch (not a snapshot from IQmol) of ~8 occupied and ~4 virtual orbitals, provide their orbital energies (in Hartrees), and assign the character (i.e., bonding/antibonding/lone pair, sigma or pi, etc.) Indeed, the character is not always ambiguous, but do your best). Based on this analysis, write down electronic configuration of CH2O.

Hint: orbital energies are given in the output file

• Equilibrium geometry of formaldehyde

Present a geometry in such a way that **chemists** (not computer) could understand it: write down bond lengths and valence angles, not XYZ coordinates. Write down the nuclear repulsion and electronic energies in Hartrees ( **6 decimal digits**) (check the output file for these values).

• Harmonic vibrational frequencies of formaldehyde

Provide a sketch of each mode, write down its frequency and assignment (symmetric or asymmetric stretch, torsion, scissors, etc)

• Comparison to Experiment (properties of formaldehyde)

Compare your findings with available experimental data (geometry and frequencies). Are the calculated results accurate? How large are computational errors?

*Sample input file for a BSSE calculation:*

*$molecule*

*0 1*

*--*

*0 1*

*O -0.089523 0.063946 0.086866*

*H 0.864783 0.058339 0.103755*

*H -0.329829 0.979459 0.078369*

*--*

*0 1*

*O 2.632273 -0.313504 -0.750376*

*H 3.268182 -0.937310 -0.431464*

*H 2.184198 -0.753305 -1.469059*

*$end*

*$rem*

*JOBTYPE BSSE*

*METHOD HF*

*BASIS 6-31G*

*GUI 2*

*$end*