

# Lab 10

## Project

### 10.1 Overview

The point of this project is to put into practice what you have learnt over the course of the lab. The problem at hand should be representative of what might be encountered by a chemical researcher. Research of any type is kind of a four step process. The process is as follows

1. Decide what you are going to do.
2. Decide how you are going to do it.
3. Do it.
4. Tell people what you did through publications, conferences and so on.

I could be argued that there is a step between 2 and 3: “Get money to do it” but we’ll go with the four we have.

In this project step 1 will be assumed to have been dealt with. We are going to deal with steps 2 and the beginning of step 3. You will be allocated a problem and it will be your task to decide how you will tackle that problem using computational chemistry. You will then report back to the TA and the rest of the class

Having done that, you will then begin to put into place your plan before finally reporting to the TA what you have done and what progress you have made in your task, if any.

### 10.2 Description of What is to be done and When

At the beginning of the lab on November 30 you will receive a description of the chemical problem that you are to tackle. You then have until the lab on December 7 to decide what you are going to do. Before this lab the TA should receive a description of your plans. This description should be about 1 page. See the next section for more detail on what this description should include.

At the December 7 lab we will each describe to the rest of the class what our problem is and how we will tackle it. This presentation is pretty short (10 minutes at most) and can be as formal or informal as you want. Prepare a couple of pages for people to look at or just have a chat. It’s up to you.

Once you have decided what you will do and sent details of your plan to the TA, you should then start on your project. You are not expected to finish the project. What is

expected is that you will spend three or four hours over about a week running calculations. Once you have spent this time on your calculations, write a short report describing what you have done and why you did it. If you managed to get some results (not compulsory) describe what you learnt. The “what” part of this report should be very short. I can look at your inputs and outputs myself. The “why” part and, if you have them, results and analysis are more important. This process will be described in more detail in section 4. The report on your calculations is due December 14.

Note that if you can decide very quickly what you want to do you can write your description, send it to the TA and get onto the calculations immediately (ie before we meet on December 7). So you can get all finished a long time before December 14 if you want. You must send in your plan to the TA before you start however. That way he can stop any disasters from happening.

### 10.3 The Plan

When you are planning what you will do you should consider the following things:

- What exactly do you want to calculate? The barrier to a certain reaction? The structure of a certain molecule or molecules? The spectra of a certain molecule?
- What aspects of the property are important? The energy at the barrier? The structure at the barrier? The arrangement of atoms in a certain part of the molecule? A certain part of a spectrum? What approximate reaction coordinate will you use?
- Exactly what molecules are you going to examine? The real molecule? A model of the molecule? Several related molecules? One or a few molecules to represent a whole class of molecules?
- What other contributions might be important? Solvation? Relativity? Entropy?
- What technical details are important? What basis set will you use? What functional? Any other choice? Most of you are not really experienced in the ways of functionals and basis sets. See the last section for some ideas.

From your description of your plan another person who is knowledgeable about computational chemistry should be able to follow your plan without having to make any decisions themselves.

#### 10.3.1 What You Should Expect to be Able to Do

As part of your plan you should consider what computer resources you have at hand. We will assume that you have access to the kind of computer resources available in the Ziegler research group and that you have about 4-6 months to complete the project.

If you have a very big molecule (200 atoms or more) you will be limited to a mostly DZP or smaller basis set, you will not be able to run very many calculations and very few intensive calculations like frequencies or NMR.

If you are considering big molecules (about 50 to 150 atoms) and lots of calculations (ie transition state searches, different reactions, different molecules) your computational resources will probably limit you to a DZP basis set for the most part and you will not be able to run very many intensive calculations like frequencies or spectra.

If you have smaller molecules (under 50 atoms) and lots of calculations *or* larger molecules (50 to 150 atoms) with few calculations you might be able to go to a TZ2P basis set *or* run a larger number of intensive calculations.

If you have very small molecules (under 20 atoms) you can certainly use a TZ2P basis set and run lots of calculations and probably run a significant number of intensive calculations too.

If you have really small molecules (under 5 atoms) you can use whatever basis set you want and run just about any calculation you want and still hope to get it done in the required time.

If your molecules have symmetry then you will be able to run bigger calculations. For example, if you happen to be considering molecules with  $D_{4h}$  symmetry then you could probably run lots of TZ2P calculations involving spectra even if your molecules had around 50 atoms.

## 10.4 Basis Sets and Functionals

Over the course of the lab you will have picked up some ideas about what you can do with basis sets and functionals. Here's a few thoughts on basis sets.

- You don't need to use the same basis set type for all atoms in a molecule. It is a good idea to use a larger basis set for more important atoms (e.g. where the reaction is taking place) and a smaller basis set for other atoms.
- You don't need to use the same basis set for all calculations. Some types of calculation are less sensitive to the basis set than others. Geometries are less sensitive. So, you can optimize your geometry with one basis set and then perform a second calculation (e.g. to get the energy or the epr spectrum) at that geometry with a bigger basis set.
- Transition metal atoms and lanthanides and actinides generally need bigger basis sets. TZP a least. Particularly if they are important atoms.
- Spectra calculations (NMR, EPR, TDDFT) usually need somewhat bigger basis sets if possible.
- The TZ2P basis set is good for for most applications. QZ3P is only necessary for very small molecules.
- The DZP basis set is OK for most applications. DZ can be used for unimportant atoms if you must. SZ shouldn't be used except for very unimportant atoms.
- Diffuse functions are important for Rydberg states and also to describe anions. This is especially the case if the anion is in the gas phase or vacuum.

Here are some thoughts on functionals:

- Your main limitations on choice of functional is what ADF can and cannot do. ADF can do most things with LDA and the GGA. ADF can do most things with SAOP except geometries, frequencies and transition states. With hybrid functionals you can do many things but not as many as for GGAs.
- It's rare that you would choose to use LDA since usually a GGA will do a better job.
- There is not too much difference between GGAs. BLYP seems to be popular for organic molecules. BP is popular for inorganic molecules. Physicists like PBE. It is claimed that OLYP is very good.
- Hybrid functionals and especially B3LYP are often better than GGAs. This is especially the case for reaction barrier heights and spectra. For geometries B3LYP seems to be no better than GGAs. Thus you might calculate your transition state geometry with BP and calculate the energy at that geometry with B3LYP. Hybrids have been found to be less good for transition metal complexes.