

CHEM-596 Practice Session 1: Building molecules using IQmol; Hartree-Fock energy calculations; Basis set convergence

Name: _____

Due: Feb. 16, 2023 (11:59 pm)

In this practice, you are expected to learn how to use IQmol and Q-Chem (the quantum chemistry package on the back end) to build molecules and run basic quantum chemistry calculations using Hartree-Fock theory and DFT. You will also learn how to look into the results of Q-Chem calculations using IQmol.

You will need to **complete the tables and short-answer questions on this handout** as well as other tasks such as **generating graphics or other files** using IQmol based on the instructions. Please refer to the **Assignment page on Canvas** for detailed submission guidelines.

Exercise 1: Hartree-Fock calculation for a hand-crafted benzene

In this exercise, you will build a benzene molecule from scratch using IQmol and calculate its energy using HF/6-31G(d); you will then compare it with (i) the HF energy of the built-in structure of benzene in IQmol and (ii) the optimized structure of benzene at the HF/6-31G(d) level. First, let's build a benzene molecule with the following steps:

- Open IQmol. You should already be in the “Build” mode. Now just click anywhere on the Viewer (the part with a blue background), you should see a carbon atom appear (shown as a grey sphere).
- Click on the C atom and drag your mouse towards any random direction. You should see another C atom appear which forms a single bond with the original C atom. Keep doing that until 6 carbon atoms are added that form a hexagon. (Don't worry about how crappy it looks)
- To ensure that the correct number of H atoms are added, we need to change 3 of the C–C bonds to C=C (otherwise two H atoms will be added to each C). To create a double bond, you just need to drag between two C atoms one more time. After adding 3 C=C bonds (alternating with the C–C bonds), click “Add Hydrogens” (the icon on the left of “↓E”): each C atom should get one H added.
- To provide a more reasonable starting structure for your calculations, IQmol can perform an initial optimization of the hand-crafted structure using the molecular mechanical (MM) force fields built in. To do that, simply click the “Minimize Energy” (“↓E”) button on the toolbar.

Completing the above procedure should give you a decent-looking structure of the benzene molecule. Now you can start setting up your first HF calculation:

- Click “Calculation → Q-Chem Setup”, leave the job type (the drop-down menu of “Calculate”) and “Method” *unchanged* since a HF energy calculation is just what we need
- Change the “Basis” to “6-31G*” (which is equivalent to 6-31+G(d)) and set “Convergence” to 8 (corresponding to keyword SCF_CONVERGENCE = 8)
- The job control panel should look like in Fig. 1. Now click “Submit” (make sure that the name of server is “Q-Chem”). You will be asked to give a name to your job, for which you can put something like “benzene_handdraw”. The job will then be executed by the remote server at Q-Chem.

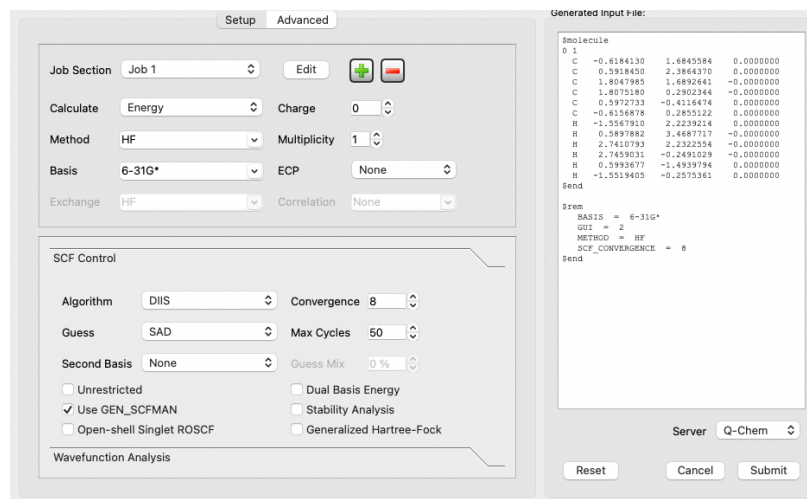


Figure 1: Job setup for benzene HF/6-31G(d) calculation

Once the job finishes, IQmol will ask you to copy it back from the remote server. It is recommended that you assign a specific directory on your computer for these jobs and then create a separate folder for each of the calculations so that things won't get accidentally overwritten. You are now asked to **report the obtained HF energy in Table 1**. To find that out, you can simply expand the job that just finished ("benzene_handdraw") under the Model View (the column on the left), and then further expand "Geometries": there should be one number under that which is the (single-point) HF energy you need.

You are now asked to run a second HF calculation, using the structure of benzene available in IQmol's library of molecular structures:

- Click "New Molecule" (the first button on the toolbar). You should see the Viewer get cleaned up and a new item "Untitled" appear under Model View
- Click "Add Fragment" (the button on the left of "Add Hydrogens"), then select "Molecules" → "Aromatics", under which you can find "Benzene". Select that and the click the "Select" button to close the window.
- Now you are under the "Build" mode. Click at a random place on the Viewer, you should see a benzene molecule show up. Use the same settings as above to run a HF/6-31G(d) energy calculation. **Report the obtained energy under "Benzene (built-in)" in Table 1.**

Finally we are going to evaluate the energy of the *optimized* structure of benzene at the HF/6-31G(d) level. You can just start from the structure you used for your second calculation. **The only change you need is to set the job type (the menu next to "Calculate") to "Geometry"**. While we haven't covered geometry optimization in lectures yet, you can understand it as an approach to finding the structure of *minimum energy*. Submit the geometry optimization job. Once finished, under "Geometries" you can find multiple energy values in a descending order, which shows the optimization procedure (you can double-click "Geometries" to see a plot of energies in each optimization cycle). **Report the the optimized energy (the last number) under "Benzene (optimized)" in Table 1.**

Table 1: Results of HF/6-31G(d) calculations for various structures of benzene (1 pt)

Structure	Benzene (manually built)	Benzene (built-in)	Benzene (optimized)
Energy (a.u.)			

Note: the energies should be reported with **6 digits** after the decimal point.

Follow-up questions & additional tasks:

1. Is your hand-crafted structure of benzene better or worse than the built-in structure in terms of how their energies compare to that of the optimized structure? **Provide a quantitative assessment. (0.25 pt)**
2. Using the calculation for hand-crafted benzene, visualize the HOMO and LUMO as 3D contour plots (**0.5 pt**). Steps to follow:
 - Select your first finished calculation under “Model View”, then double-click “Canonical Orbitals” under “Surfaces”. A window will pop up.
 - Set the range of orbitals to visualize from “Alpha 21 (HOMO)” to “Alpha 22 (LUMO)” (α and β orbitals are the same in this RHF calculation), and then click “Calculate”
 - The two orbitals will show up under “Canonical Orbitals” under Model View. Check them out by selecting one of them at a time. To save these 3D contour plots, select “File \rightarrow Save Picture”, and then you can save the images in the “.png” format (recommended).
 - The saved two images (HOMO and LUMO) need to be submitted

Exercise 2: Basis set convergence of HF energy for NH_3

In this exercise, we are going to investigate how the HF energy for the NH_3 molecule changes with increasingly large basis sets:

- Open the XYZ file `NH3.xyz` (which can be downloaded from Canvas) using IQmol (click **File \rightarrow Open** and then navigate to the directory where the .xyz file is stored). Set up a HF energy calculation with basis set “cc-pVDZ”. The “Convergence” parameter under “SCF Control” should be **set to 8 throughout this exercise**.
- Once the job is finished, report the obtained **HF energy**, the **total number of basis functions**, and the **time duration** (“wall time”) of the job in **Table 2**. The energy can be found under “Geometries”, while the latter two numbers will need to be retrieved from the Q-Chem output file: under the current job in Model View, expand “Files” and double-click the “.out” file. A window will pop up. You can simply search for keywords “basis functions” to find out the # of basis functions; and scrolling down to the bottom you will see a line starting with “Total job time”, from which you can find the wall time.
- Repeat the above with cc-pVTZ, cc-pVQZ, and cc-pV5Z basis sets and **complete Table 2**. Note: (i) cc-pV5Z is not available under the “Basis” dropdown menu so you need to edit the Generated input file manually (simply by typing); (ii) the calculation using cc-pV5Z will take a few minutes so please be patient.

Follow-up questions & additional tasks:

1. Based on the HF energies you obtained using different basis sets, do you expect that the energy will eventually converge? Why or why not? (**0.25 pt**)
2. In our last lecture, we introduced that the computational cost of a HF calculation increases with the number of basis functions as $\mathcal{O}(n^4)$. Comparing the # of basis functions and timings for the cc-pVTZ and cc-pVQZ calculations, is the increase in computational cost (measured by the execution time of the program) steeper or less steep than the $\mathcal{O}(n^4)$ scaling? What about the comparison between cc-pVQZ and cc-pV5Z? (**0.5 pt**)

Table 2: Hartree-Fock energies for NH_3 using different basis sets (1.5 pts)

Basis set	Energy (a.u.)	# of basis functions	Timing (s)
cc-pVDZ			
cc-pVTZ			
cc-pVQZ			
cc-pV5Z			

Exercise 3: Ethane's rotational barrier and dissociation energy

In this exercise, you will calculate the **rotational barrier** and the **C–C dissociation energy of ethane** at the HF/cc-pVDZ level of theory. These two energetic quantities are defined as the follows:

$$\Delta E_b = E(\text{eclipsed}) - E(\text{staggered}) \quad (1)$$

$$\Delta E_d = 2E(\text{CH}_3) - E(\text{C}_2\text{H}_6) \quad (2)$$

Let's first obtain the energetically optimized structure of the *staggered* conformation with the following steps:

- Start with “New Molecule”, then load a staggered ethane structure into IQmol which can be easily done by selecting “Add Fragment → Molecules → Alkanes → Ethane”
- Submit a geometry optimization job (“Calculate → Geometry”) using HF/cc-pVDZ. Once the job is finished, report (i) **the optimized C–C bond length** and (ii) **the energy of the optimized structure** in **Table 3**. To obtain the bond length, you should first enter the “Select” mode by clicking the “magic wand” next to the red “X” on the toolbar. You can then click on the two carbon atoms: the bond length will show on the bottom left corner of the Viewer.
- Start over by clicking “New Molecule” and repeat the first step (load the ethane structure from IQmol's built-in library). We are now going to build the *eclipsed* structure from that. First, hit the key “T” on the keyboard, which will let IQmol show the index of each atom in the XYZ structure. Then under the **Select mode**, click atoms “1–2–5–8” (note: you must follow this order) and then select “Build → Set Geometric Constraint”. You will see a small window pop up which indicates that the torsion (dihedral) between atoms 1–2–5–8 is 180° . You can now change this number to 0° and click “Apply”. This change will generate an *eclipsed* conformation.
- Submit a geometry optimization job for the eclipsed conformation with the same settings. Report the equilibrium energy and C–C bond length in **Table 3**.

Table 3: Staggered and eclipsed ethane calculated at the HF/cc-pVDZ level (1 pts)

	staggered	eclipsed
C–C bond length (Å)		
Energy (a.u.)		

Based on the results in Table 3, calculate the rotational barrier (in kcal/mol, 1 a.u. = 627.5095 kcal/mol) of ethane using Eq. (1). (0.25 pt)

To evaluate the dissociation energy, we further need to obtain the optimized structure for $\cdot\text{CH}_3$. You can start over with another “New Molecule” and load an ethane. You can then select all atoms in one of the methyl groups and then click “Delete Selection” (the red “X”). You can then submit a geometry optimization job for the remaining part (the $\cdot\text{CH}_3$ radical) with the same settings, except that now the multiplicity is 2 (open-shell). **Report the energy of the optimized $\cdot\text{CH}_3$ below (0.25 pt):**

$$E(\cdot\text{CH}_3) =$$

Then, using Eq. (2) and the energy of the more stable *staggered* conformation, **calculate the bond dissociation energy**. Show your work below **(0.25 pt)**:

Follow-up questions & additional tasks:

1. Generate the XYZ coordinates of ethane in the staggered and eclipsed conformations. To do that, you need to select each of the geometry optimization jobs under Model View, and then click “File → Save as”, under which the default file type is `.xyz`. Name the two XYZ files as “`staggered.xyz`” and “`eclipsed.xyz`”, which need to be submitted. **(0.25 pt)**
2. If we take the barrier calculated using MP2 at the complete basis set limit, **2.78 kcal/mol**, as the reference, what are the *signed* absolute and relative (%) errors of HF/cc-pVDZ? **Show your work below (0.25 pt):**
3. The average bond energy for C–C is **347 kJ/mol** (1 kcal = 4.184 kJ). Compared to that, does HF/cc-pVDZ over- or underestimate the C–C bond energy? Answer this by calculating the signed absolute and relative errors. **Show your work below (0.25 pt):**
4. Based on the discussion of the main source of errors of HF theory in class, explain why the absolute error for ethane’s rotational barrier is much smaller than that for the dissociation energy of ethane’s C–C bond. **(0.5 pt)**