

CHEM-596 Practice Session 2: Density Functional Theory Calculations using Q-Chem

Name: _____

Due: March 2, 2023 (11:59 pm)

In this practice, you will use IQmol to set up density functional theory (DFT) calculations for Q-Chem. You will use those calculations to investigate (i) the intermolecular interaction between two water molecules and (ii) the ring strain of cycloalkanes.

You will need to **complete the tables and short-answer questions on this handout** and also generate the requested files for submission. Please refer to the **Assignment page** on Canvas for detailed submission guidelines. **Note:** for this practice, **8 points** are associated with the completion of this handout and the rest **2 points** are for attendance.

Exercise 1: The interaction between two water molecules

In this exercise, you will

- Compare the accuracy of different density functionals in predicting the water dimer interaction energy
- Compare the H-bond strengths in H₂O, NH₃, and HF dimers
- Assess the effectiveness of counterpoise corrections for BSSE when used with different basis sets
- Generate the potential energy curve for the dissociation of water dimer

Note: Energy minimization or geometry optimization should NOT be performed in this exercise.

Your first task is to calculate the interaction energy between two water molecules at the equilibrium geometry of water dimer (provided) using the functionals listed in Table 1 and the def2-TZVPD basis. Steps to follow:

- Open “water_dimer_eq.xyz” and go straight to “Q-Chem Setup”. Set “Method” to “Omega-B97X-V” (which is ω B97X-V), and then manually specify “BASIS = def2-TZVPD” in the generated input. Remember to change “Convergence” (SCF_CONVERGENCE) to 8.
- Submit the calculation and record the energy given by the output as the first dimer result in Table 1. Then repeat the same procedure for the rest of functionals: for M06-2X, you only need to change the “Method” to “M06-2X”; for B3LYP-D3(BJ) and B3LYP-D3(0), you should first select “B3LYP” as the “Method”, and then go to “Advanced → DFT → Dispersion Correction” and set the Model to “DFT-D3(BJ)” and “DFT-D3(0)”, respectively in those two calculations.
- Now you need to calculate the energy of each monomer using all 4 functionals. To speed up the process, here we take advantage of the feature of running Q-Chem jobs *sequentially*. Re-select ‘water_dimer_eq.xyz’ under “Model View” and go to “Q-Chem Setup” again. Click “Reset” on the right bottom of the control panel to clean things up. You should then delete the last 3 rows of coordinates under the \$molecule section (which corresponds to the 2nd monomer), and then set up the 1st calculation (ω B97X-V/def2-TZVPD) the same as above. After doing that, **click the green “+” button** next to “Edit”. You will see “Job 2” is now after “Job Section” and that a new input shows up which is separated from the original input (now faded) by “@@@”. You can now set up the “Method” for the 2nd job and then

Table 1: Evaluation of the water dimer interaction energy using different functionals. All energies should be reported in a.u. (with 6 digits after decimal point) except for the last column. **(1 pt)**

| Functional | dimer | monomer 1 | monomer 2 | ΔE (kcal/mol) |
|-----------------|-------|-----------|-----------|-----------------------|
| ω B97X-V | | | | |
| M06-2X | | | | |
| B3LYP-D3(BJ) | | | | |
| B3LYP-D3(0) | | | | |

add the 3rd and 4th jobs in the same way. When the job finishes, you will see **4 numbers** under “Geometries”, which corresponds to the results of 4 different functionals.

- Repeat the above for the 2nd water monomer (now delete the first 3 rows of XYZ coordinates under the \$molecule section) and report all the monomer energies in Table 1. You can now evaluate the intermolecular interaction energy (ΔE_{int}) as:

$$\Delta E_{\text{int}} = E(\text{dimer}) - E(\text{monomer 1}) - E(\text{monomer 2}) \quad (1)$$

Note: 1 a.u. (hartree) = 627.5095 kcal/mol

Questions:

1. Which functional yields the lowest energy for the water dimer? Does that imply that this functional is of the best accuracy? Why or why not? **(0.25 pt)**
2. The reference value for the water dimer interaction (given by high-level wavefunction theory) is -5.08 kcal/mol. Compared to this reference, which functional performs the best with the def2-TZVPD basis? What are the absolute (in kcal/mol) and relative (in %) errors? **(0.25 pt)**
3. Which flavor of “-D3” correction gives more accurate interaction energy when paired with the B3LYP functional? If we compare the electron density produced by B3LYP-D3(0) and B3LYP-D3(BJ), would you expect to see any difference? Why or why not? **(0.25 pt)**
4. The M06-2X functional is *not* dispersion-corrected. Based on the result in Table 1, do you expect that adding dispersion correction will improve its accuracy? Why or why not? **(0.25 pt)**

Now we compare the strength of the hydrogen bond in water dimer to those in the HF dimer and NH_3 dimer: with the given equilibrium structures (“HF_dimer_eq.xyz” and “NH3_dimer_eq.xyz”), calculate the interaction energies for these two dimer complexes at the ω B97X-V level and report the results in Table 2. How does the hydrogen bond strength in these two systems compare to that in water dimer? **(0.25 pt)**

Table 2: Interaction energies for the HF dimer and NH₃ dimer calculated at the ω B97X-V/def2-TZVPD level (0.5 pt)

| Species | monomer 1 | monomer 2 | dimer | ΔE (kcal/mol) |
|-----------------------|-----------|-----------|-------|-----------------------|
| HF dimer | | | | |
| NH ₃ dimer | | | | |

With basis sets that are smaller than def2-TZVPD, counterpoise (CP) corrections for BSSE needs to be applied to obtain accurate results. As shown in **lecture 7**, Q-Chem offers a convenient job control option for that purpose with “JOBTYPE = BSSE”. Follow the procedure below to set up interaction energy calculations with CP correction using ω B97X-V and 3 different basis sets: 6-31+G(d), def2-SVPD (need to be manually specified), and pc-2:

- Reopen “water_dimer_eq.xyz” using IQmol. For “BSSE” calculations, we need to specify fragments (each fragment corresponds to a monomer) in the \$molecule section: after specifying the charge and multiplicity for the whole molecule, each fragment should start with “--” and then each fragment’s charge and multiplicity need to be specified. For our water dimer system, the “\$molecule” section should look like:

```

$molecule
0 1
--
0 1
O -1.5185926 -0.1196873 0.0000000
H -1.9230771 0.7490524 0.0000000
H -0.5658786 0.0425227 0.0000000
--
0 1
O 1.3920081 0.1083319 0.0000000
H 1.7517321 -0.3484272 0.7639214
H 1.7517321 -0.3484272 -0.7639214
$end

```

- Under “Calculate”, select “BSSE Correction”. The functional and basis set can be set as before (note: 6-31+G(d) \equiv 6-31+G*). Remember to change “SCF_CONVERGENCE” to 8 and set “GUI = 0”.
- Submit the job to the server. Once finished, open the output file using IQmol (expand the job under Model View and then expand “Files”). Find the number of basis functions first (by searching for “basis functions” in the output) and then scroll down to the bottom. The numbers under “E(CP-CORR)” are CP-corrected monomer energies, which should be reported in Table 3 and so is the energy of the “Complex” (dimer). The final interaction energies can still be calculated using Eq. (1) whereas the monomer energies should be replaced by CP-corrected ones.

Table 3: Evaluation of water dimer interaction energies using smaller basis sets and counterpoise corrections for BSSE (0.75 pt)

| Basis set | #Basis (dimer) | monomer 1 | monomer 2 | dimer | ΔE (kcal/mol) |
|-----------|----------------|-----------|-----------|-------|-----------------------|
| 6-31+G(d) | | | | | |
| def2-SVPD | | | | | |
| pc-2 | | | | | |

Questions:

1. Which basis set yields the best agreement with the reference value (-5.08 kcal/mol) after being CP-corrected? **(0.25 pt)**
2. Which basis set contains the largest number of basis functions? Does it give the best (lowest) variational energy for the monomers and the dimer here? **(0.25 pt)**

As the final task in Exercise 1, we are going to generate the potential energy curve for the dissociation of the water dimer at the ω B97X-D/6-31+G(d) level (note: in reality you should consider using a larger basis like def2-TZVPD for this). This can be done with the following steps:

- Reopen “water_dimer.eq.xyz”. Under the “Select Mode” (the magic wand) click the two oxygen atoms on each water molecules. Then select “Build \rightarrow Set Geometric Constraint”. A small window should pop up.
- Select “Scan”, and then set the starting and ending distances to 2.7 and 3.6 Å, respectively; set the number of points to 10 so that the increment will be 0.1 Å. Click “Apply”. You should see a purple line connecting two O atoms with a little “disk” in the middle.

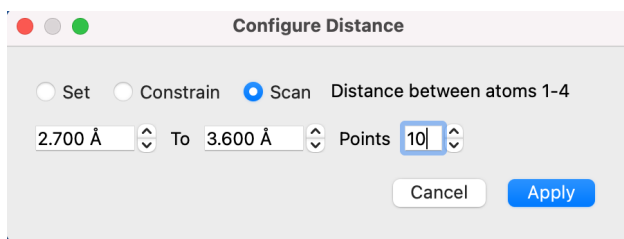


Figure 1: Setup of the O \cdots O distance scan

- Now go to “Q-Chem Setup”. Q-Chem has a job type called “PES scan” that is specifically designed for this type of task. Select that under “Calculate”. Now you should see a small section appear in the generated input:

```
$scan
stre 1 4 2.700 3.600 0.100
$end
```

This indicates the scan for the distance (“stretch”) between atoms 1 and 4 from 2.7 to 3.6 Å with an increment of 0.1 Å.

- Set the “Method” to “Omega-B97X-D” and “Basis” to “6-31+G*”. Remember to set the SCF_CONVERGENCE to 8 and “GUI” to 0. Submit the calculation.
- After the calculation is done and copied back, expand it under “Model View” and then double-click on “Scan Geometries”. You should see a sketch plot of the potential energy curve. Right-click on the plot and save the image, **which will need to be submitted.** **(0.25 pt)**

Question: Under which O \cdots O distance does the water dimer have the most favorable energy? Is it in good agreement with the O \cdots O distance in the initial equilibrium structure (“water_dimer.eq.xyz”)? **(0.25 pt)**

Note: Before you start Exercise 2, you may want to clean up the list under “Calculation \rightarrow Job Monitor”, and then restart IQmol.

Exercise 2: Quantifying ring strain in cycloalkanes

In this exercise, you will use a low-cost DFT method PBEh-3c [*J. Chem. Phys.* **143**, 054107 (2015)] to predict the ring strain in cycloalkanes C_nH_{2n} with $n = 3-8$. The cyclic alkanes can be considered as rings of CH_2 groups. If there is no ring strain, then the energy of a cycloalkane C_nH_{2n} should simply be n times the energy of a CH_2 group in an *infinitely long straight chain alkane*. We thus define the ring strain as the following:

$$E_{RS} = E[C_nH_{2n}] - nE[CH_2] \quad (2)$$

where E_{RS} is the ring-strain energy, $E[C_nH_{2n}]$ is the energy of a cycloalkane with n carbon atoms (e.g., $n = 3$ for cyclopropane, $n = 4$ for cyclobutane, etc.), and $E[CH_2]$ is the energy of a CH_2 group in an infinite straight chain alkane.

Let's determine the value of $E[CH_2]$ first with the following procedure:

1. Draw the propane molecule using IQmol with the procedure as you constructed benzene in our last practice (Build the carbon skeleton → Add hydrogens → click the “E↓” button to minimize the energy)
2. We are now going to perform a PBEh-3c calculation directly with this structure *without* further geometry optimization. Open “Q-Chem Setup”. Make sure that you are calculating “Energy”. The PBEh-3c method is not supported by IQmol yet so you need to specify that manually on the generated input: “METHOD = PBEh-3c”, “BASIS = def2-mSVP” (note that PBEh-3c should only be used with this special basis), and then remember to set “Convergence” to 8.
3. Submit the calculation to the server. When it is done, report the energy in the 2nd column (“ $E(\text{chain})$ ”) of Table 4.

Repeat steps 1–3 for straight chain alkanes with $n = 4-8$ and then further evaluate the results for the 3rd column: $E(n) = E(\text{chain})/n$ (you may want to calculate them using **Excel**). (0.5 pt)

Table 4: Determination of the ring strain in cycloalkanes. The ring-strain energy (E_{RS}) should be reported in kcal/mol with 2 digits after decimal point, and the rest are in a.u. (6 digits required).

| n | $E(\text{chain})$ (a.u.) | $E(\text{chain})/n$ (a.u.) | $E(\text{cyclo})$ (a.u.) | E_{RS} (kcal/mol) |
|-----|--------------------------|----------------------------|--------------------------|---------------------|
| 3 | | | | |
| 4 | | | | |
| 5 | | | | |
| 6 | | | | |
| 7 | | | | |
| 8 | | | | |

In order to obtain the value of $E(n)$ at $n \rightarrow \infty$, which will be the value of $E[CH_2]$ that we need, we can assume that $E(n)$ depends on n as:

$$E(n) = a + b/n \quad (3)$$

You can obtain the parameters a and b from *least-square fitting*. An easy way to do so is to use Excel to generate a scatter plot of $E(n)$ vs. $1/n$, and then use the “Add Trendline” feature. Make sure to display the fitted equation and the R^2 value on the chart. If you did so, change the title of that plot to “ $E(n)$ vs. $1/n$ ” in Excel and then save the figure, **which needs to be submitted with your report (0.25 pt)**. You can use other software to do the least-square fitting and a plot *showing the original data and fitted line* is needed. Report the values of fitted parameters a and b as well as the R^2 value below (0.5 pt):

Based on the R^2 value you obtained, does Eq. (3) do a good job in describing the relationship between $E(n)$ and n ? **(0.25 pt)**

Regardless your answer to the previous question, we will proceed by using the value of the fitted parameter a for $E[\text{CH}_2]$. Now, repeat the steps 1–3 above for cycloalkanes with $n = 3$ –8. Report your results in the 4th column of Table 4 **(0.5 pt)** and then calculate the values of ring-strain energy E_{RS} for each of the cycloalkanes based on Eq. (2) **(0.5 pt)**.

Using Excel or other software, **generate a plot of E_{RS} vs. the number of carbon atoms (which also needs to be submitted)**. **(0.25 pt)** Discuss the trend you observe on this plot **(0.25 pt)** and rationalize the results based on what you learned in organic chemistry classes **(0.5 pt)**.

Hint: you can check the typical C–C–C bond angles in each cycloalkane using IQmol and compare them to the ideal bond angle for sp^3 carbon.