**Lab 3. Extrapolation techniques for accurate thermochemistry**

*Due date: April 2, 2020*

In this lab you will calculate the bond dissociation energy (BDE) in F2 molecule. In order to obtain the accurate value of dissociation energy, you will employ a large basis set and an accurate correlated method (CCSD(T)). You will also learn how to perform basis set extrapolations and how to use correlation energy additivity scheme.

**Lab procedure**

1. Optimize geometry of F2 molecule at the MP2/cc-pVDZ level and calculate the zero-point vibrational energy (ZPE). Write down the equilibrium geometry and ZPE in kcal/mol (look in the VIBRATIONAL ANALYSIS section).

2. Using the found optimal geometry of F2 molecule, calculate the HF, MP2, and CCSD(T) [coupled cluster with single and double excitations and perturbative triple corrections method] energies in a series of the cc-pVDZ, cc-pVTZ, and cc-pVQZ bases. Write down all these energies. Write down the number of basis functions in each basis.

**Hint:** the HF and MP2 energies will be printed in the CCSD(T) calculations as well, so you do not need to do separate calculations for HF and MP2. The CCSD(T) calculation may be invoked by providing the line:

METHOD CCSD(T)

**Hint:** you can use @@@ separator to run all of these calculations from the same input

file.

3. Repeat step 2 for F atom. Do not forget to change multiplicity accordingly.

Write down all obtained HF, MP2, and CCSD(T) energies.

**Lab report**

1. Estimate the basis set limits of the HF energies (i.e., complete basis set (CBS) HF

energies) for F2 and F by using the following formula:

EHFX = EHFCBS + B exp(-AX),

where A and B are constants to be determined, E**x** is the HF energy in cc-pV***X***Z basis, and ECBS is the sought-for energy in the complete basis set. This extrapolation scheme requires 3 bases; use the 2-, 3-, and 4-zeta bases to obtain the CBS values (i.e., X=2, 3, 4).

2. Estimate the MP2 and CCSD(T) ***correlation energy*** basis set limits

(i.e., E(MP2)-E(HF), and E(CCSD(T))-E(HF)) by the following formula:

EcorrX = EcorrCBS + CX-3 ,

where C is the coefficient, E**X** and ECBS are the correlation energies in the cc-pV***X***Z basis and in the CBS limit. This is two-point scheme, you need two basis sets to obtain CBS energies. Calculate the MP2 and CCSD(T) CBS *correlation* energies using X=2,3 and X=3,4.

Calculate the MP2 and CCSD(T) ***total energy*** CBS limits, which are sums of the HF CBS energies and the correlation CBS energies. Note that you will have two different values of the CBS energies. You can refer to them as CBS(2,3) and CBS (3,4). That is, in this step you calculate MP2/CBS(2,3), MP2/CBS(3,4), CCSD(T)/CBS(2,3), CCSD(T)/CBS(3,4) energies of F2 and F.

3. Calculate the bond dissociation energies (Ediss = E(F2)-2E(F)) by HF, MP2, and CCSD(T) in different basis sets. Calculate CBS-estimated bond dissociation energies as a difference between CBS energies of F2 and F:

EdissCBS = ECBS(F2) -2ECBS(F).

Use kcal/mol units for reporting bond dissociation energies.

Plot HF, MP2, and CCSD(T) bond dissociation energies versus the size of the basis set (E

vs X graph). Show CBS(2,3) and CBS(3,4) values on this graph.

Find an experimental value of BDE in F2. Add the experimental BDE to the plot; compare it with calculated BDEs.

**Attention**: when comparing experimental and computational BDEs, you need to account for ZPE energy. You may either shift experimental BDE energy by (computed) ZPE or include ZPE in all computational values of BDEs.

4. Analyze and discuss your results using following questions as a guideline. Assume that ***the targeted accuracy in prediction of BDE is 1 kcal/mol.***

a) Compare convergence of HF, MP2, and CCSD(T) wrt basis set. Why do the HF

energies converge faster than the correlated method energies?

b) Compare MP2 CBS extrapolations with X=2,3 and X=3,4. What is the energy difference between two extrapolations? Is X=2,3 extrapolation reliable, i.e., is the difference between X=2,3 and X=3,4 extrapolations less than the targeted accuracy of 1 kcal/mol?

c) Do the same analysis for CCSD(T) extrapolation schemes.

c) Discuss the ***accuracy and reliability*** of HF, MP2, and CCSD(T) in CBS for predicting BDE. What can you say about accuracy and reliability of HF, MP2, and CCSD(T) energies in the cc-pVTZ basis?

d) Use the energy additivity scheme for MP2 and CCSD(T) energies:

Ebig (CCSD(T)) = Esmall(CCSD(T)) + [Ebig(MP2) - Esmall(MP2)],

where Ebig and Esmall are energies in bigger and smaller basis sets.

Use cc-pVTZ and cc-pVQZ bases in this formula and compare the exact CCSD(T)/cc-pVQZ total energies of F2 and F with the ones obtained by the formula.

Calculate BDEs based on this extrapolation. What is the error in BDE produced by this formula?

e) What is the estimated CCSD(T)/CBS BDE value if CCSD(T)/cc-pVQZ value is estimated by the above energy additivity formula? How different is this BDE from the calculated CCSD(T)/CBS(3,4) BDE and from experiment?

f) Based on your results, what is ***the computationally cheapest way*** to achieve the ***targeted accuracy*** (i.e., 1 kcal/mol) in predicting BDE of F2? (Let’s assume that electronic structure calculations are the time-limiting step, rather than your calculations in Excel/Python.)