计算物理 作业二

<u>Excercise 1:</u> Illustration of the convergence of the dissociation energy for H_2 toward HF limit.

In this exercise, *basis* indicates one of the following basis sets: STO-3G, cc-pVDZ, cc-pVTZ, cc-pVQZ or cc-pV5Z. Z-Matrix coordinates are used to represent the atom positions.

a) First look at how the HF energy for the H atom (charge=0, multipicity=2) converges towards the exact value of -0.50 au. when the basis set is increased. Perform five single point energy calculations with the above five kinds of basis sets separately. **The keywords are: #P UHF/*basis* SCF=TIGHT.**

Read Gaussian mannual, *Gaussian 03 Input,* of the *Gaussian 03 User's Reference* to understand the structure of Gaussian input files. An example input file for STO-3G basis set *H_STO-3G.com* may look like (Pay attention to the blank lines):

```
#T UHF/STO-3G SCF=TIGHT

Unrestricted Hartree-Fock single point energy of H atom with STO-3G basis set

0 2
H

```

to get the Gaussian 98 output log file. Search for the line including "SCF Done:" in the log file to get the energy. Search the line including "Job cpu time:" t**o get the calculation time. Compile a table with columns *Basis set, Energy* and *CPU time.* What is your conclusion about theses basis sets?**

b) Next, perform a series of calculations for the H_2 molecule (charge=0, multiplicity=1) with an H-H distance of 0.74 Å using the **keywords: #P RHF/basis SCF=CONVENTIONAL.** An example file for the STO-3G basis is:

```
#P RHF/STO-3G SCF=CONVENTIONAL

Restricted Hartree-Fock single point
```

energy of H2 molecule with STO-3G basis set
0 1
H1
H2 H1 0.74

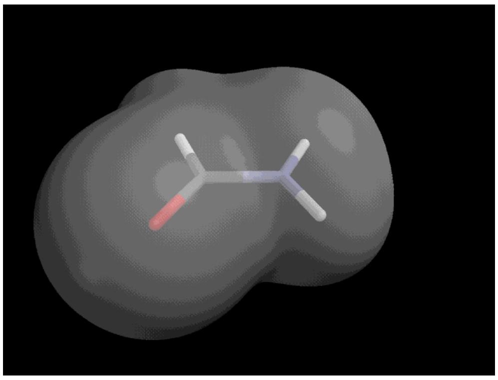
Gaussian writes the size of the basis set ("*xx* basis functions") and the number of two-electron integrals ("*xxx* integrals produced for a total of *xxx*") (the last one) in the output file. **How does the number of integrals grow as a function of the number of basis functions (i.e. number of integrals ~ (number of basis functions)^n)?** Theoretically in the large basis set limit *n*=4.

Calculate how the dissociation energy dE = (2 E(H)-E(H_2)) converges as a function of the basis set size. Compare with the experimental value of 0.17442 au. Why is the HF limiting value too low? Compile a table with columns *Bais set*, *# Functions*, *# Integrals*, *CPU time*, *E(H)*, *E(H2)*, *dE* to show your result data. **How does the CPU time scale with the number of functions in the basis set?**

Why do we use UHF for the H atom but RHF for the H_2 molecule? What is ROHF?

<u>Exercise 2</u>: Visualizing Gaussian output with Molden

On the computers in our computer lab there is no graphical user interface (GUI) for *Gaussian*. Other X-Window applications can be used to prepare the input molecular or visualize the results stored in *Gaussian* output files. In this exercise we will optimize the structure of formamide (HCONH2) using *Gaussian*.



Prepare a formamide molecule in *Gaussian View* and optimize the structure with the HF base set. Export this structure to a Gaussian format file. Copy this file to your working directory.

Open your log file with *Molden*. Click *Movie* to see the procedures of optimization. Click *Norm. Mode* and choose different frequencies to see the vibration of atoms and bonds.

Click on *Dens. Mode*. Click *PlotPlane* and type in *nptsx=60, nptsy=60,nptsz=60,edge=15.0*, which means setting the 3-dimensional grid to 60x60x60 with a total size of 15.0. Click on the *Space* and set the contour level to be 0.10. Click on 3D, 3D-X to see different representations of the orbital. Click on the button at the right side of *Space* button and choose *OpenGL* to see a nice 3D representation. Click on *Orbital* to see different orbitals. Click on *Homo* to see the HOMO (Highest Occupied Molecular Orbital) and *Lumo* to see the LUMO (Lowest Unoccupied Molecular Orbital).

Print out the OpenGL representations of HOMO and LUMO by changing the background color of the OpenGL window to white (click the right mouse button on the window to get the menu) and capture the screen as a PortScript file (the file will be named *moldenogl.ps*).

Also, compare the geometry of the formamide molecule obtained from the optimizations carried out in *Gaussian and experiment*.The data of experiment such as :

- C-O bond length: 1.193 Angstroem
- C-N bond length: 1.376 Angstroem
- C-H bond length: 1.102 Angstroem
- H-C-O angle: 122.97 degrees
- H-C-N angle: 113.23 degrees
- N-C-O angle: 123.80 degrees

unit of energies : 1 a.u. = 627.509541 kcal/mol = 2625.49992 kJ/mol

Excercise 3: H-H Bond Dissociation of H_2 Molecule with Different Methods

Use *Gaussian* to do a PES (Potential Energy Surface) scan for the dissociation of a H_2 molecule. That is, do a sequence of single point energy calculations with different bond lengths. CCSD/cc-pVQZ should be used (**find the last "E(CORR)=" of each step**), which also generates the results of SCF (RHF), MP2 and MP3 (locate the word "Summary"). T**he acronym refers to *Coupled Clusters with Singles and Doubles*** which is a method similar to CISD. **The keywords are *#T CCSD/cc-pVQZ Scan Test.*** Please read the *Gaussian03 user's reference* for using the **keyword *Scan***. Do the scan in the range of H-H bond lengths between [0.24Å, 1.14Å] with a step size of 0.1Å and in the range [1.14Å, 5.74Å] with the step size of 0.5Å.

Do it again with UHF. **Add the keyword *Guess=Mix* t**o destroy alpha-beta and spatial symmetries, otherwise the result is exactly the same as RHF. Plot your data from RHF, UHF, MP2, MP3 and CCSD in one picture. Print out both the data file and the plot. Explain the differences among the curves. You can use *xmgr* to plot the data. Prepare your data file such that the first column contains the H-H distance and all other columns contain the energies obtained with the different methods. The first line of the file may look like this:

```
0.2400 -0.32380 -0.23028  -0.35752 -0.36182  -0.36287513586D+00
```

After you have prepared the data file, run the command

```
$xmgr -nxy <data_file>
```

to plot it.

Exercise 4: Elimination Transition State Optimization

The purpose of this exercise is to show you that *Gaussian* can also deal with chemical reactions (It can not only predict the TS, but also follow reaction paths. T**he keyword *IRC*** can be used to do that). So no conclusion is required for this exercise. **Please print out the TS structure and explain the input file and output file**.

Predict the structure of the transition state for the following reaction:

$CH_3Br+Cl^- \text{->} CH_3Cl + Br^-$

What are the predicted Si-H and H-H bond lengths for the departing H atoms?

Exercise 5: Comparison of DFT with Ab Initio methods

Prepare a single water molecule with a program of your choice (for instance macromodel,gaussview). Then, minimize its energy using **HF, MP2** *ab initio* methods and with **DFT** using the BLYP, BPW91, B3LYP and B3PW91 functionals with the ***6-31g*** basis set. **Compile a table containing *Method, H-O bond length, H-O-H angle, Energy, Frequency 1, Frequency 2, Frequency 3* and *CPU Time*. Discuss your results**.

Exercise 6: Use DFT to solve a problematic system

Find the minimum energy structure of **a single FOOF** (fluorine peroxide) molecule using all of the methods of *Exercise 1* with the cc-pVDZ basis set (again, you need to construct an initial configuration of the molecule with some program, for instance macromodel,gaussview). **Compile a table including *Method, F-O bond length, O-O bond length* and *CPU Time.*** When you draw your conclusions, please note that results with larger basis sets or inclusion of more electron correlation clearly show that the good matching of MP2/cc-pVDZ values with the experimental values is accidental.

Exercise 7: User defined DFT models

Do a single point energy calculation with the cc-pVQZ basis set using CCSD, BLYP and B3LYP methods for the H_2 molecule with an H-H bond length of 0.74Å and 5.74Å separately. What can we learn from the results?

Gaussian 03 can lets us specify the parameters of a general DFT functional (refer to the *Gaussian 03 user's reference*). B3LYP is actually a functional based on BLYP with the parameters of *P1=1.0, P2=0.2, P3=0.72, P4=0.8, P5=0.81* and *P6=1.0*. Let's do the above calculations again with a user defined functional based on BLYP.

Question: you must point out the following parameters respond to what kind method of DFT

a) *P1=0.0* and *P2=1.0*.
b) *P5=P6=0.0*.
c) *P3=0.81* and *P4=0.72*.

Compare the energy values you get and explain the differences by considering the influences of exchange and correlation energies.