Excercise 1: **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

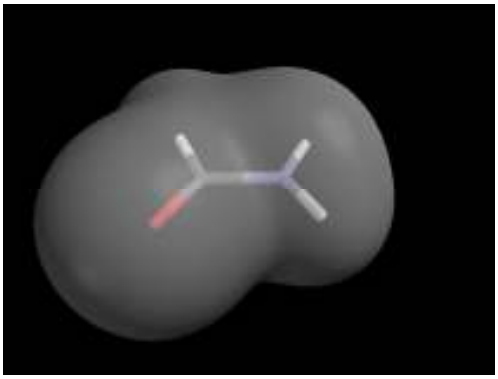
Gaussian writes the size of the basis set ("*xx* basis functions") and the number of two-electron integrals ("*xxx* integrals produced for a total of *xxx*") (the last one) in the output file. **How does the number of integrals grow as a function of the number of basis functions (i.e. number of integrals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

Exercise 2: 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*.



Formamide

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

备注：

由于机房没有 Gaussian 程序，所以以上作业中的运算过程已由助教跑好。所有的输入文件和输出文件都放在文件夹 exercise1 中。同学们依据里面的文件完成以上作业。