Exercise 1: 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 2: 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 3: User defined DFT models

Do a single point energy calculations 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.

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 exercise3 中。同学们依据里面的文件完成以上作业。