Lab4

Objectives

- BSSE
- Understanding basis sets
- Thermochemistry

Basis set superposition error (BSSE)

Gaussian input file for water dimer:

```
%chk=water.chk
%nprocshared=2
# hf/3-21g counterpoise=2

Title Card Required

0 1 0 1 0 1
 O(Fragment=1)     -1.97619047   -1.11904760    0.00000000
 H(Fragment=1)     -1.01619047   -1.11904760    0.00000000
 H(Fragment=1)     -2.29664505   -0.21411177    0.00000000
 O(Fragment=2)      0.80952381   -0.38095238    0.00000000
 H(Fragment=2)      1.76952381   -0.38095238    0.00000000
 H(Fragment=2)      0.48906922    0.52398346    0.00000000
```

Basis set superposition error (BSSE)

$ grep A.U. water.log

```
SCF Done:  E(RHF) =  -151.183376551     A.U. after   10 cycles
SCF Done:  E(RHF) =  -75.5871648459     A.U. after    9 cycles
SCF Done:  E(RHF) =  -75.5908152208     A.U. after    9 cycles
SCF Done:  E(RHF) =  -75.5858099772     A.U. after   10 cycles
SCF Done:  E(RHF) =  -75.5858099773     A.U. after   10 cycles
```

```
grep -A 4 'Counterpoise ' water.log
Counterpoise corrected energy =    -151.177016439265
                  BSSE energy =       0.006360112084
             sum of fragments =    -151.171619954583
          complexation energy =      -7.38 kcal/mole (raw)
          complexation energy =      -3.39 kcal/mole (corrected)
```

Hands-on

1. Compute the BSSE for the water dimer
2. Determine the BSSE for the water dimer for several distances between the water molecules
3. Determine BSSE for the water dimer as a function of basis set size?

(Use HF method in all cases)

Hands-on

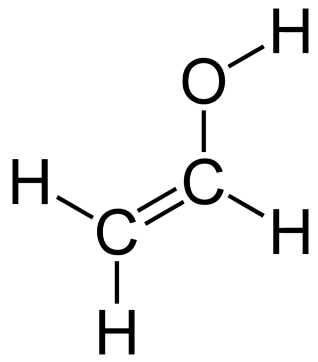
1. Compute the number of primitive gaussians for H2O and CH4 monomer for the following basis sets
   a. STO-3g
   b. 3-21g
   c. 6-31g
   d. 6-31g(d)
   e. 6-31g(d,p)
   f. 6-111g(d,p)

Vibrational spectroscopy

- Number of frequencies
- Visualization of normal modes using Jmol
- Number of imaginary frequencies
- IR intensities

Hands-on

- Find two isomers of vinyl alcohol and the transition state between them.



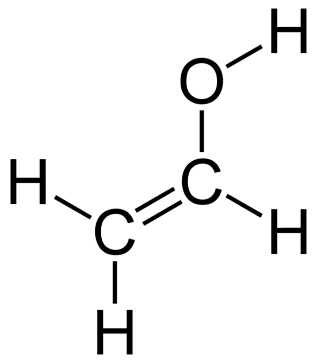
Thermochemistry

- Enthalpy and free energy

  https://gaussian.com/wp-content/uploads/dl/thermo.pdf

Hands-on

- Check the stability of vinyl alcohol isomers as a function of temperature



References

1. https://avogadro.cc/
2. https://gaussian.com/gaussian16/
3. https://gaussian.com/wp-content/uploads/dl/thermo.pdf