

Lab 02. Energy point calculations (HF,DFT)

1 SCF energy

Create an input for SCF calculation for CH_4 molecule. Use STO-3G basis set.

Find the following information in the output:

- the total and nuclear repulsion energy,
- the number of occupied orbitals and the SCF orbital energies,
- the number of basis functions used in the calculation, and
- the bond distances.

Modify the input to use the cc-pVDZ basis set. Run the calculation and compare the Koopman energy difference to that for the STO-3G basis.

2 UHF/DFT calculation CH4

Files SCF.energy UHF.CH4plus.input, DFT.energy.CH4plus.input

Identify keywords related to specification of occupation numbers.

Now run the calculation and identify in the output,

- a) the total charge,
- b) S, and S(S+1), and
- c) the dipole moment.

Modify the input to perform DFT calculation. Run the job with LDA, BLYP and B3LYP functional. Compare the "correlation" energy.

3 RI/CD calculations

Modify the input for RHF calculation of CH_4 , and use ANO-RCC-VDZP basis set.

Repeat the calculation three time. Once without any further modification (conventional two-electron integrals) and twice using the two options for Cholesky Decomposition (RICD and MEDIUM). Note that the RIDC option is a Gateway input and the MEDIUM option is a Seward input.

Compare the differences in energies obtained with conventional integrals, and with RI/CD integrals. Compare the timing and the size of the files in WorkDir.

4 Interaction between two molecules

The goal of this exercise is to compute density difference between two interacting molecules.

Using GV build CH_3OH molecule, and place a water molecule nearby. Save the resulting XYZ file as methanol_water.xyz

Make two additional copies of this XYZ file (methanol.xyz and water.xyz) and modify them, substituting some atomic labels to X. E.g. file methanol.xyz should contain 'real' atomic labels for atoms in methanol, and 'X' as atomic labels for atoms in water.

Create three inputs (to run GATEWAY, SEWARD, SCF, GRID IT). Place keyword Group=C1 (or NOMOVE) to GATEWAY input (to prevent molecule from shifting from the origin), and keyword TOTAL to GRID IT (to compute total density).

Run three calculations and save resulting grid files. Visualize the density difference with GV:

```
molcas gv -a 1.0 water.grid methanol.grid -out summ.grid
molcas gv -a -1.0 complex.grid summ.grid
```

To change the iso-surface value: press F4, and type e.g. 0.0001

5 Potential energy curve

Compute $E_{RHF}(R)$ and $E_{UHF}(R)$ for hydrogen molecule.

Computation of UHF wavefunction of H2 molecule with different inter-atomic distances requires some non obvious moments. First, we should make the calculation with a symmetry, which allows UHF solution, and also we should introduce some difference between alpha and beta orbitals. In addition to that we might face a problem with convergence, especially in a region where RHF wavefunction transforms into UHF. To avoid convergence problems we should use relatively large basis set, and switch off some convergence acceleration.

We can use EMIL commands to create a single input for this exercise. A template looks like:

```

>>export INIT=0.6
>>foreach LOOP in ( 1 .. 300 )
>>eval DIST=$INIT+$LOOP/50
&GATEWAY
coord
2
H 0 0 0
H $DIST 0 0
basis=ANO-S-VDZ
group=c1
&seward
&scf
UHF
scramble=0.2
NODIIS
>>enddo

```

You may modify the number of steps, and the increment in the loop.

You can use script ee (extract energy) to extract energies from the output file, and create ee.geo.molden file (to be visualized with GV).

At what distance the difference between RHF and UHF solutions becomes essential?