ACM3, Exercise 3

Hand in your report latest on 2007-12-12.

This exercise tests mostly the part of the course related to the Hartree-Fock and DFT methods, and the basis sets. The parts related to scripting may be of use as well. The exercise consists of following parts:

1. Run energy calculations for hydrogen atom with HF and few DFT methods. Use basis sets of different quality: SZ, DZ, TZ, QZ.
2. Optimize geometry of hydrogen molecule "manually" – propose a time-effective method.
3. Optimize geometry of hydrogen molecule "automatically".
4. Most important point: Write a report!

The input files specified below are Dalton-specific. Full Dalton manual can be found at `http://www.theochem.kth.se/dalton/dalton20manual.pdf`

Other programs use a different input syntax, please consult appropriate user manuals.

1 Running dalton at theochem computers

2 Single atom energy calculations

The goal of this part is to study the basis set dependence of the Hartree-Fock and density functional energies on the basis set. Use following Dalton input:

```
BASIS
3-21G
H atom  (first comment line).
(Second comment line).
Atomtypes=1
Atoms=1 Charge=1
H1   0   0   0
**DALTON INPUT
.RUN WAVE
**WAVE FUNCTION
.HF
**END OF INPUT
```

For the purpose of this exercise, three lines are important. Second line (`3-21G` in this case) specifies the basis set to be used in the calculation. Line 7 specifies the coordinates of the hydrogen atom: $(0, 0, 0)$. Finally, line number 11 specifies the wave function type, in this case Hartree-Fock. Save this file to eg. `exercise3.dal` (extension is important). Run dalton as follows:

```
/pkg/dalton/2.0/bin/dalton exercise3
```

The output will be saved to `exercise3.out` file. You can extract the final energy using

```
awk '/Final.*energy/' exercise3.out
```

1. Extend this command to extract not the entire line but the energy value only.

2. Run the same calculation using `cc-pVDZ`, `cc-pVTZ`, `cc-pVQZ`, `cc-pV5Z`, `aug-cc-pVDZ` basis sets, and extract the final energies. Look at the coefficients of these basis sets in `/pkg/dalton/basis` directory, and explain the dependence of the final energy on the size and *type* of the basis set. Classify these basis sets (polarization, x-zeta, diffuse, etc). Can a convergence with the basis size be observed? If so, how fast is it? How does it compare to the exact solution of 0.5 Hartree?

3. Run the same set of calculations on the DFT level, replacing `.HF` with following two-line sequence:

   ```
   .DFT
   PBE
   ```

   Is the energy converging with the respect to the basis set size?

4. How does the DFT energies compare to the exact solution of 0.5 Hartree?

3 "Manual" geometry optimization

Use the following molecule specification:

```
BASIS
3-21G
H2 molecule  (first comment line).
(Second comment line).
```

```
Atomtypes=1
Atoms=2 Charge=1
H1   0   0   0
H1   0   0   1.2
```

The remaining part of the input file is the same. This molecule input defines a H_2 molecule with the distance between atoms set to 1.2 a.u.

The molecular geometry can be optimized by performing few calculations around the expected minimum (which internuclear distance for hydrogen molecule do you expect?) and then fitting a polynomial to computed points. You can try for example internuclear distances 1.2, 1.3, 1.4, 1.5. Is the potential energy curve in this region parabolic? Write down your actions step by step, describing carefully your studies.

Report following for HF wave function and `3-21G`, `cc-pVDZ` and `cc-pVTZ` basis sets.

1. Find the polynomial (report the method you used to find it and the found coefficients) that fits to the computed data, and its minimum.

2. Have you found this exercise tiresome? Is there any way to make it more automatic? How? Would it involve any tradeoffs?

4 Automatic geometry optimization

Dalton can optimize the molecular geometry automatically. Replace `.RUN WAVE` keyword in the input file with `.OPTIMIZE` to do that.

1. Run the geometry optimization for `cc-pVDZ` basis set. What method Dalton (or your favourite program) use? How does the final result compare to the one you obtained in the previous "manual" part of this exercise in terms of accuracy and computational effort?