Homework 3
Lectures 4: Electronic Structure Models
(CBE 60547)

Prof. William F. Schneider

Due: 02/12/2015

Here is an example input deck for a HFS/6-31G calculation on NH_3. This is a good starting template for the calculations below. You can also construct an input deck in Avogadro. Refer to the GAMESS manual for more information.

```
!   File created by the GAMESS Input Deck Generator Plugin for Avogadro
 $BASIS GBASIS=N31 NGAUSS=6 $END
 $CONTRL RUNTYP=ENERGY DFTTYP=SLATER $END

 $DATA
Title
C1
N     7.0    -1.03363     0.80618     0.00000
H     1.0    -0.01363     0.80618     0.00000
H     1.0    -1.37362     1.64340    -0.47314
H     1.0    -1.37363     0.79732     0.96162
 $END
```

1 GAMESS vs. FDA

Using `GAMESS`, perform a DFT/Hartree-Fock-Slater (`DFTTYP=SLATER`) calculation on an Ar atom using the 6-31G basis set.

(a) How many primitive Gaussians are included in this calculation? How many total basis functions? How do they divide between s, p, and d?

(b) How many SCF iterations does the calculation take to converge?

(c) What is the final calculated HFS/6-31G energy of the atom?

(d) What are the identities (1s, 2p, etc.) and energies of the occupied atomic orbitals?

(e) Compare your computed total energy and atomic orbital energies with those you got from Homework 2 using the fda code for Ar.

2 The Generalized Gradient Approximation

The generalized gradient approximation (GGA) is an improvement on Hartree-Fock-Slater that gives a nice balance between accuracy and computational expense. Using `GAMESS`, perform a single point calculation (`RUNTYP=ENERGY`) on the bent triatomic SO_2 using the GGA (`DFTTYP=PBE`) and PC1 basis set (`GBASIS=PC1`, `ISPHER=1`; no `NGAUSS` flag needed). Guess appropriate bond lengths and angle. Be sure to report your input file for your calculation.

(a) What is the spin multiplicity of SO_2? (Recall, the spin multiplicity is 2S +1, where S = 1/2 for one unpaired electron, S = 1 for two unpaired electrons, and so on).

(b) How many basis functions are in this calculation?

(c) How many SCF cycles does it take to converge?

(d) What SCF algorithm does the code use?

(e) What is the final total energy of the molecule?

(f) How many occupied orbitals does the molecule have? What are the energies of the HOMO and LUMO?

(g) What is the final dipole moment?

(h) What are the Mulliken gross charges on the S and O atoms?

(i) Plot out the electrostatic potential of SO_2. Which end of the molecule is electrophilic and which is nucleophilic?

3 Geometry Optimization of SO_2

(a) Do a series of calculations in which you vary the S–O distances and O–S–O angle over a regular grid of values. Approximate the combination of values that give the lowest energy.

(b) A geometry optimization (`RUNTYP=OPTIMIZE`) is a faster way to find the optimal geometry of a molecule. Perform a geometry optimization on SO_2 using the same computational model as above. What are the optimal S–O distances and O–S–O angle?

4 Other Molecules

Oxygen makes bonds with lots of things. Fill out the table below by doing an appropriate set of calculations:

AO_2	A-O (Å)	O-A-O (°)	Spin Multiplicity	Dipole Moment (eÅ)	Mulliken Charge
CO_2					
NO_2					
SiO_2					
SO_2					