Homework 3 Lectures 4: Electronic Structure Models (CBE 60553)

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Here is an example input deck for a HFS/6-31G calculation on NH₃. 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 SO₂ 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 SO2. Which end of the molecule is electrophilic and which is nucleophilic?

3 Geometry Optimization of SO₂

- (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 SO₂ 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:

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AO<sub>2</sub> A-O (Å) O-A-O (°) Spin Multiplicity Dipole Moment (eÅ) Mulliken Charge

CO<sub>2</sub> NO<sub>2</sub>
SiO<sub>2</sub> SO<sub>2</sub>
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