

# Homework 3

## Lectures 4: Electronic Structure Models (CBE 60553)

Prof. William F. Schneider

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Here is an example input deck for a HFS/6-31G calculation on  $\text{NH}_3$ . 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.

- How many primitive Gaussians are included in this calculation? How many total basis functions? How do they divide between s, p, and d?
- How many SCF iterations does the calculation take to converge?
- What is the final calculated HFS/6-31G energy of the atom?
- What are the identities (1s, 2p, etc.) and energies of the occupied atomic orbitals?
- Compare your computed total energy and atomic orbital energies with those you got from Homework 2 using the fda code for Ar.

## 1.1 Solution

### 1.1.1 a)

This is an example input file for Ar. The resulting output files can be seen in ./Ar

```
$BASIS GBASIS=N31 NGAUSS=6 $END
$CONTRL RUNTYP=ENERGY DFTTYP=SLATER $END

$DATA
Title
C1
Ar    18.0    -3.86612    1.03789    0.00000
$END
```

By looking at the log file it seems we have 13 primitive Gaussians. Below is the shell command to produce this result.

---

```
1 grep "GAUSSIAN BASIS FUNCTIONS" Ar/Ar.log
```

---

NUMBER OF CARTESIAN GAUSSIAN BASIS FUNCTIONS = 13

We used the 6-31G basis set. The distribution of basis functions are listed below.

| Orbital | Basis Sets | Primitive gauss functions | Total gauss functions |
|---------|------------|---------------------------|-----------------------|
| 1s      | 1          | 6                         | 6                     |
| 2s      | 1          | 6                         | 6                     |
| 2p      | 3          | 6                         | 18                    |
| 3s      | 1          | 3                         | 3                     |
| 3p      | 3          | 3                         | 9                     |
| 3s+     | 1          | 1                         | 1                     |
| 3p+     | 3          | 1                         | 3                     |
| Total   | 13         |                           | 46                    |

### 1.1.2 b)

12 SCF iterations are required to reach convergence.

---

```
1 grep "ITER" Ar/Ar.dat
```

---

E(R-SLATER)= -524.4520526614, E(NUC)= 0.0000000000, 12 ITERS

### 1.1.3 c)

The final HFS/6-31G energy is -524.452 hartrees.

**Table 1:** GAMESS and FDA orbital energies

| Orbital | $E_{\text{GAMESS}}$ (hartree) | $E_{\text{FDA}}$ (hartree) |
|---------|-------------------------------|----------------------------|
| 1s      | -113.6768                     | -116.9366                  |
| 2s      | -10.7172                      | -11.6037                   |
| 2p      | -8.3677                       | -9.2721                    |
| 3s      | -0.8218                       | -1.1022                    |
| 3p      | -0.3222                       | -0.5735                    |
| 3s+     | 0.4316                        |                            |
| 3p+     | 0.5206                        |                            |

#### 1.1.4 d)

#### 1.1.5 e)

The FDA total energy is -526.8275 hartree, which means its a slightly better method for predicting the energy of Ar. The orbital energies are listed in 1.

## 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  $\text{SO}_2$  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  $\text{SO}_2$ ? (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  $\text{SO}_2$ . Which end of the molecule is electrophilic and which is nucleophilic?

### 2.1 Solution

INPUT File: [./S02/S02.inp](#) LOG File: [./S02/S02.log](#) DAT File: [./S02/S02.dat](#)

### 2.1.1 a)

The spin multiplicity for SO<sub>2</sub> is  $2 * 0 + 1 = 1$ .

### 2.1.2 b)

The number of basis functions in the calculation is 49.

---

```
1 grep "GAUSSIAN BASIS FUNCTIONS" ./S02/S02.log
```

---

```
NUMBER OF CARTESIAN GAUSSIAN BASIS FUNCTIONS =    49
```

### 2.1.3 c)

It takes 23 SCF cycles to converge.

---

```
1 grep ITER ./S02/S02.dat
```

---

```
E(R-PBE)=      -548.2499367382, E(NUC)=  109.8468077125,    23  ITERS
```

### 2.1.4 d)

The code uses the DIIS algorithm.

### 2.1.5 e)

The final total energy is -548.2499 hartrees

### 2.1.6 f)

There are 16 occupied orbitals.

---

```
1 grep OCCUPIED ./S02/S02.log
```

---

```
NUMBER OF OCCUPIED ORBITALS (ALPHA)          =    16
NUMBER OF OCCUPIED ORBITALS (BETA )          =    16
    16 ORBITALS ARE OCCUPIED (    7 CORE ORBITALS).
```

### 2.1.7 g)

The final dipole moment is 1.55 debyes

### 2.1.8 h)

## 3 Geometry Optimization of SO<sub>2</sub>

- (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<sub>2</sub> 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 <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>  |         |           |                   |                    |                 |