

Computational Chemistry Homework 3

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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.

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

Input file of GAMESS for 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
```

Let's look at the log file. We used 13 primitive Gaussians.

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

NUMBER OF CARTESIAN GAUSSIAN BASIS FUNCTIONS = 13

Because we used 6-31G Basis set, 6 gaussian functions are used for core shells and 3 and 1 gaussian functions are used for inner and outer regions of valance shells. See table 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

1.2 How many SCF iterations does the calculation take to converge?

Let's look at the log file again. 12 iterations are required to reach convergence.

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

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

1.3 What is the final calculated HFS/6-31G energy of the atom?

The final HFS/6-31G energy: -524.452 Hartree.

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

E_FDA values are from HW2.

Orbital	E _{GAMESS} (Hartree)	E _{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	

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

The total energy from FDA is -526.8275 Hartree. Compared to HFSs/6-31G energy (-254.425 Hartree), FDA shows slightly lower total energy.

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.

2.1 What is the spin multiplicity of SO₂? (Recall, the spin multiplicity is $2S + 1$, where $S = 1/2$ for one unpaired electron, $S = 1$ for two unpaired electrons, and so on).

The spin multiplicity for SO₂ is $2 * 0 + 1 = 1$.

2.2 How many basis functions are in this calculation?

Let's look at the log file. We used 49 primitive Gaussians.

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

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

2.3 How many SCF cycles does it take to converge?

It takes 22 SCF cycles to converge.

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

```
E(R-PBE)= -548.2342329889 E(NUC)= 109.8468077125 22 ITERS
```

2.4 What SCF algorithm does the code use?

The code uses the DIIS algorithm.

See log file. we can see "DIIS = T"

2.5 What is the final total energy of the molecule?

The final total energy is -548.234 Hartree

```
1 grep "TOTAL ENERGY = " S02/S02.log
```

```
TOTAL ENERGY =      -548.2342329889
```

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

There are 16 occupied orbitals.

```
1 grep "NUMBER OF OCCUPIED" S02/S02.log
```

```
NUMBER OF OCCUPIED ORBITALS (ALPHA) = 16
NUMBER OF OCCUPIED ORBITALS (BETA   ) = 16
```

HOMO: -0.2826 Hartree (16th)

LUMO: -0.1472 Hartree (17th)

2.7 What is the final dipole moment?

The final dipole moment is 1.453 debyes

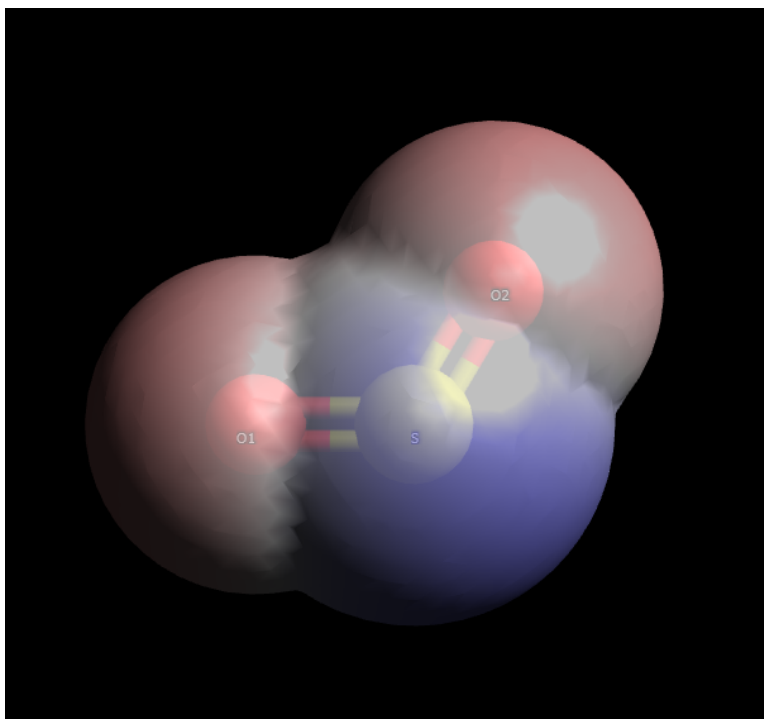
2.8 What are the Mulliken gross charges on the S and O atoms?

The Mulliken charges are tabulated below.

ATOM	CHARGE
S	0.570174
O	-0.296290
O	-0.273884

2.9 Plot out the electrostatic potential of SO₂. Which end of the molecule is electrophilic and which is nucleophilic?

The electrostatic potential can be plotted by using Avogadro.



3 Geometry Optimization of SO_2

3.1 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.

Molecular energies were calculated using Gaussian B3LYP functional and 6-31G(d) basis set:

Energy (Ha)	1.35(Å)	1.45(Å)	1.50(Å)	1.55(Å)	1.65(Å)
105°	-548.531	-548.574	-548.574	-548.565	-548.529
115°	-548.548	-548.586	-548.584	-548.573	-548.535
120°	-548.550	-548.587	-548.585	-548.573	-548.534
125°	-548.549	-548.585	-548.583	-548.571	-548.532
135°	-548.538	-548.574	-548.572	-548.561	-548.523

As shown in the table, the combination of values that give the lowest energy is S–O distance = 1.45 Å and O–S–O angle = 120°.

3.2 A geometry optimization 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?

Geometry optimization was done using Gaussian B3LYP functional and 6-31G(d) basis set (`./S02.txt`): the optimal S–O distances are 1.46 Å and O–S–O angle is 119°. We got pretty close results using the rough scan.

4 Other Molecules

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

Geometry optimization was done using Gaussian B3LYP functional and 6-31G(d) basis set:

AO ₂	A-O (Å)	O-A-O (°)	Spin Multiplicity	Dipole Moment (eÅ)	Mulliken Charge
CO ₂ ./C02.txt	1.169	180	1	0	C: 0.72, O: -0.36
NO ₂ ./N02.txt	1.203	133.84	2	0.32	N: 0.48, O: -0.24
SiO ₂ ./Si02.txt	1.520	180	1	0	Si: 0.95, O: -0.48
SO ₂ ./S02.txt	1.463	119.08	1	1.78	S: 0.82, O: -0.41