

# A Brief introduction to GAMESS-US.\*

## I. EXPLORING THE CONVERGENCY TOWARD THE BASIS SET LIMIT

In this exercise we will investigate the basis set convergency properties of some electronic structure methods, in particular HF, MP2 and DFT. We will chose the simple molecule of water, H<sub>2</sub>O, as an example. Every electronic structure method requires in input atomic coordinates. There are two choices:

- Cartesian coordinates:

for each atom in the molecule write a line containing the atomic symbol, and the three cartesian coordinates, in some specified unit. For the water molecule an input structure is as follows (in Bohr units):

```
O    0.0000000000    0.0000000000   -0.1174995771
H   -1.5152607127    0.0000000000    0.9324015387
H    1.5152607127    0.0000000000    0.9324015387
```

Note that usually molecular point group symmetry is used,  $C_{2v}$  in the case of water.

- Z matrix

A completely equivalent way to provide information on the molecular structure is through the specification of the so-called Z-matrix. The Z matrix construction is trivial for simple molecules like water, where it looks like the following:

```
O
H  1  rOH
H  1  rOH  2  aHOH
```

```
rOH=.9755117251752355
aHOH=110.565
```

In the example we numbered the atoms such that the Oxygen is atom number 1, and the two Hydrogens are number 2 and 3 (the order does not matter). The first atom (O atom) is placed at the origin of our reference system. The second atom (H) is placed on the  $z$  axis at a distance equal to a O–H bond length (0.975 Å). The specification of the position of the third atom requires instead the specification of a bond length, in the example above with the Oxygen (atom number 1), and an angle with the Oxygen and the first Hydrogen atom. The use of variables in the definition of the Z matrix, as in the example above, is usually permitted.

All subsequent atoms need a distance, and angle and a torsional angle (in this sequence) for a complete specification of the molecule. For example in the case of ethylene, a perfectly valid Z matrix would be:

```
C
C  1  rcc
H  1  rch  2  ahch
H  2  rch  1  ahch  3  180.0
H  1  rch  2  ahch  4  0.0
H  2  rch  1  ahch  5  180.0
```

```
rcc=1.34
rch=1.10
ahch=120.0
```

Sometimes it is also necessary to include so called "dummy" atoms, in order to resolve situations of linearity, as for example in the case of acetylene:

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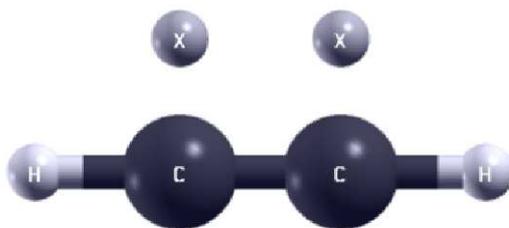


FIG. 1: Numbering scheme and placement of dummy atoms for acetylene.

```
H
C 1 HC
X 2 XL 1 A1
C 2 CC 3 A1 1 D1
X 3 XL 2 A1 3 D2
H 4 HC 5 A1 2 D1
```

```
HC = 1.08
XL = 1.0
CC = 1.2
A1 = 90.0
D1 = 180.0
D2 = 0.0
```

Dummy atoms have usually the special symbol X, and their coordinates are frozen in geometry optimizations.

#### Exercise I

Write the Z matrix for methane. Methane ( $\text{CH}_4$ ) has 4 Hydrogen atoms arranged at the vertex of a tetrahedral. The H-C-H angles have a value of 109.4710 degrees and the C-H bond lengths are of 1.089000 Angstroms.

We are now ready to start our calculations. We present below an input file for a SCF energy calculation on water:

```
$CONTRL
  SCFTYP=RHF
  RUNTYP=ENERGY
  COORD=ZMT
  NZVAR=0
  UNITS=BOHR
$END
$SYSTEM TIMLIM=1 $END
$BASIS
  GBASIS=ACCD
$END
$GUESS
  GUESS=HUCKEL
$END
$DATA
Water ground-state C_2v geometry...RHF/aug-cc-pVDZ
Cnv 2

0
H 1 rOH
H 1 rOH 2 aHOH

rOH=.9755117251752355
aHOH=110.565
```

```
$END
$SCF
  CONV=1.0d-10
$END
```

The input consists of keywords arranged into groups. Below is a list of the more important ones:

- **\$CONTRL**: specify fundamental job options, such as the type of the SCF calculation (restricted HF in this case), the type of calculation (single-point energy), the type of coordinates (cartesian or Z matrix) and the units (Bohrs)
- **\$SYSTEM**: provide information for the computer operation, such as the time limit of the job (1 minute in the example above). This is not necessary.
- **\$STATPT**: Controls the search for stationary points.
- **\$BASIS**: Information on the basis set. The keyword *GBASIS* is used to specify the gaussian basis set (aug-cc-pVDZ in the example above).

We will use the following one-electron basis:

1. *GBASIS=STO NGAUSS=3*: STO-3G minimal basis;
  2. *GBASIS=CCD*: cc-pVDZ correlation consistent basis set;
  3. *GBASIS=ACCD*: aug-cc-pVDZ correlation consistent basis set with one set of diffuse functions;
  4. *GBASIS=CCT*: cc-pVTZ correlation consistent basis set;
  5. *GBASIS=ACCT*: aug-cc-pVTZ correlation consistent basis set with one set of diffuse functions;
  6. *GBASIS=CCQ*: cc-pVQDZ correlation consistent basis set
- **\$GUESS**: Specify a starting guess for the HF density matrix. The usual choice is to start with molecular orbitals from a Hückel type of calculation.
  - **\$DATA**: Here is a block with the molecule specification, such as the symmetry point-group ( $C_{2v}$  for water), the order of the highest rotation axis (2, since there is a  $C_2$  rotation axis), the Z matrix.
  - **\$SCF**: Inside are keywords that control the SCF iterations, such as convergency thresholds for the elements of the density matrix.

This is a basic overview of a typical SCF input. For running an MP2 calculation you will need the following keyword in the **\$CONTRL** block:

```
MPLEVL=2.
```

The input for a DFT calculation is pretty similar to the one used in the SCF calculation. However we need to specify an exchange-correlation potential, with the keyword (in the **\$CONTRL** block):

```
DFTTYP=B3LYP
```

for the b3lyp exchange-correlation potential. Many choices are possible. See the online manual at <http://www.msg.chem.iastate.edu/gamess/documentation.html> for an up-to-date manual.

When using Coupled-Cluster methods (we will use CCSD(T)) you will need a keyword in the **\$CONTRL** block requesting a Coupled-Cluster (CC) calculation:

```
CCTYP=CCSD(T)
```

as well as a block for the control of the CC calculation:

```
$CCINP
  ICONV=9
$END
```

which sets the convergency threshold for the CC amplitudes to  $10^{-9}$ .

Once you have properly set up the input file, (*hf-accd.inp* for example) launch the job with the command:

```
rungms hf-accd.inp >& hf-accd.out &
```

### Exercise II

In this exercise you will examine the convergency of the total energy of the system when saturating the one electron basis. Run an HF, DFT (with b3lyp exchange-correlation potential) and MP2 calculation with the following basis sets: STO-3G, cc-pVDZ, aug-cc-pVDZ, cc-pVTZ, aug-cc-pVTZ, cc-pVQZ. Make a graph displaying the convergency behaviour. (When running the CC calculations with the bigger basis sets you may run out of memory on a small desktop computer).

## II. GEOMETRY OPTIMIZATION AND VIBRATIONAL ANALYSIS

In this section we will perform a geometry optimization and vibrational analysis for water. We chose the cc-pVTZ basis set and perform geometry optimization for HF, DFT (using b3lyp) and MP2. Note that a vibrational analysis, i.e. the calculation of vibrational frequencies and normal modes are meaningful only if performed after a geometry optimization employing the same chemistry model (basis set and electronic structure method). Note also that in general for better accuracy one should use tight convergency thresholds during the geometry optimization.

In order to perform a geometry optimization one need to add some keywords in the \$CONTRL block:

```
RUNTYP=OPTIMIZE
```

Note also that you need to use some keywords that control the location of the stationary points in the potential energy surface (PES). For this reason you should add yet another block:

```
$STATPT  
OPTTOL=1.0d-10  
$END
```

which sets the tolerance for the largest component of the energy gradient. A tighter threshold is needed for the subsequent vibrational analysis, which will provide us with harmonic frequencies, normal coordinates and infrared intensities in the double-harmonic approximation.

The vibrational analysis is performed on the optimized geometry with the following keyword:

```
RUNTYP=HESSIAN
```

Note also that you need to use some keywords that control the construction of the hessian matrix, which can be numerical or analytical (for electronic structure methods with analytic gradient and hessian). For variational methods gradients are usually calculated analytically, but sometimes the method lacks of analytic Hessians. In such a case the hessian is calculated with finite-difference methods from analytic gradients. When doing vibrational analysis you should add yet another block:

```
$FORCE  
METHOD= . . . .  
VIBANL= . T .  
$END
```

where *METHOD=ANALYTIC*, *METHOD=SEMINUM* for both RHF, DFT and MP2. When using Coupled-Cluster methods use *METHOD=FULLNUM*.

### Exercise III

Calculate the vibrational frequencies at the HF, DFT and MP2 level. Compare the results with the CCSD(T) geometry (O–H distance of 0.9595 Angstroms, bond angle of 103.598) and the following vibrational frequencies:

Mode	Symmetry	Frequency	IR Intensity
1	A1	3840.517	1.0453
2	A1	1668.493	1.0826
3	B2	3945.276	1.081

### Exercise IV

We will end the tutorial with a real-life example. We consider a system composed of a water molecule and the F<sup>-</sup> anion, which is weakly bound to the water molecule. Note that the system is closed-shell, but with a negative charge. You will complete a DFT b3lyp geometry optimization and vibrational analysis on the system. We will use a rather small double- $\zeta$  basis set with the keyword:

GBASIS=DZV

You should follow the steps:

- Construct the Z matrix. You will need a starting geometry. As a rule, the closer the starting guess to the final optimized structure, the faster (and safer) the convergence. You will use a CCSD(T) geometric structure, calculated with the aug-cc-pVTZ basis set (insert here data from article).
- Run an MP2 geometry optimization using the DZV basis set above.
- Perform a vibrational analysis.

The starting molecular structure looks like:

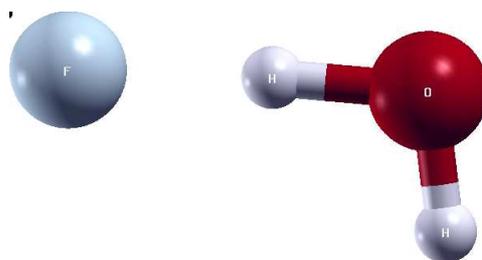


FIG. 2: CCSD(T) geometry of the  $F^- \dots H_2O$  complex.

Use the following starting geometry: the H–O–H angle is 101.9 degrees, the angle F–H–O is 177.1 degrees, the O–H bond non interacting with the fluorine is 0.961 Å while the second O–H bond is 1.056 Å.