Laboratory 4
Gaussian 03
Introduction

Lesson	Information covered	Time to complete
Gaussian Input file	Creating simple input file for Gaussian 03. Z-matrix format	45 minutes
Geometry Optimization of simple molecules in Gaussian 03	Geometry optimization and vibrational analysis using B3LYP method and 6-311G(d,p) basis set. Introduction to GaussView 3.09 and Molden 4.2 visualization program	45 minutes
Creating Z-matrix for Vanillin, optimizing geometry	Geometry optimization and vibrational analysis using B3LYP method and 6-31G(d,p) basis set for vanillin molecule	45 minutes

Creating input for Gaussian 03

You can find on line manual for Gaussian 03 on
www.gaussian.com. Tech Support, Manual.

Gaussian 03 input consists of a series of lines in an ASCII text file. The basic structure of a Gaussian input file includes several different sections:
Link 0 Commands: Locate and name scratch files (not blank line terminated).
Route section (♯ lines): Specify desired calculation type, model chemistry and other options (blank line terminated).
Title section: Brief description of the calculation (blank line terminated).
Molecule specification: Specify molecular system to be studied (blank line terminated).
Optional additional sections: Additional input needed for specific job types (usually blank line terminated).

Many Gaussian 03 jobs will include only the second, third, and fourth sections. Here is an example of such a file, which requests a single point energy calculation on water:

```
♯ B3LYP/6-31G(d,p)                Route section

                water energy              Title section
0 1                          Charge and multiplicity
O -0.464 0.177 0.0             Molecule specification (xyz, z-matrix)
H -0.464 1.137 0.0
H 0.441 -0.143 0.0
```

Using Internal Coordinates

Each line of a Z-matrix gives the internal coordinates for one of the atoms within the molecule. The most-used Z-matrix format uses the following syntax:

Element-label, atom 1, bond-length, atom 2, bond-angle, atom 3, dihedral-angle

Although these examples use commas to separate items within a line, any valid separator may be used. Element-label is a character string consisting of either the chemical symbol for the atom or its atomic number. If the elemental symbol is used, it may be optionally followed by other alphanumeric characters to create an identifying label for that atom. A common practice is to follow the element name with a secondary identifying integer: C1, C2, etc.

Atom1, atom2, atom3 are the labels for previously-specified atoms and are used to define the current atoms' position. Alternatively, the other atoms' line numbers within the molecule specification section may be used for the values of variables, where the charge and spin multiplicity line is line 0.

The position of the current atom is then specified by giving the length of the bond joining it to atom1, the angle formed by this bond and the bond joining atom1 and atom2, and the dihedral (torsion) angle formed by the plane containing atom1, atom2 and atom3 with the plane containing the current atom, atom1 and atom2. Note that bond angles must be in the range $0^o <$ angle $< 180^o$. Dihedral angles may take on any value.

As an initial example, consider hydrogen peroxide. A Z-matrix for this structure would be:

```
H
O 1 0.9
O 2 1.4 1 105.0
H 3 0.9 2 105.0 1 120.0
```

The first line of the Z-matrix simply specifies a hydrogen. The next line lists an oxygen

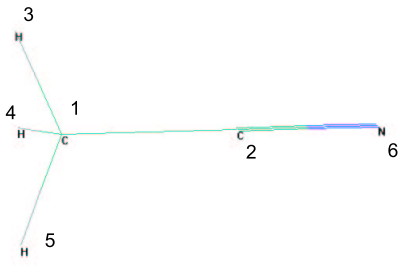
atom and specifies the internuclear distance between it and the hydrogen as 0.9 Angstroms. The third line defines another oxygen with an O-O distance of 1.4 Angstroms (i.e., from atom 2, the other oxygen) and having an O-O-H angle (with atoms 2 and 1) of 105 degrees. The fourth and final line is the only one for which all three internal coordinates need be given. It defines the other hydrogen as bonded to the second oxygen with an H-O distance of 0.9 Angstroms, an H-O-O angle of 105 degrees and a H-O-O-H dihedral angle of 120 degrees.

Variables may be used to specify some or all of the values within the Z-matrix. Here is another version of the previous Z-matrix:
H
O 1 r1
O 2 r2 1 a
H 3 r1 2 a 1 d
Variables:
r1 0.9
r2 1.4
a 105.0
d 120.0

Now Gaussian Input for optimization and vibration calculation looks:
♯ B3LYP/6-31G(d,p) Opt Freq

Optimization + harmonic frequency
0 1
H
O 1 r1
O 2 r2 1 a
H 3 r1 2 a 1 d
Variables:
r1 0.9
r2 1.4
a 105.0
d 120.0

Example (dummy atom):



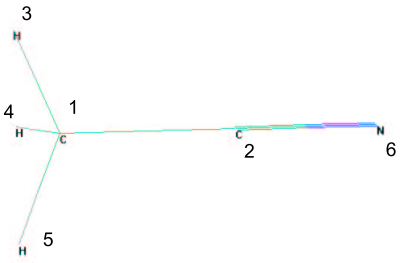
Atom numbering for methyl cyanide

Some important things to notice.
(1) Each atom must be specified in terms of atoms already defined, i.e. relative to atoms above.
(2) Each specification atom can only be used once in each line.
(3) The specification in terms of distance, angle and torsional angle has nothing to do with

the bonding in the molecule, e.g. the torsional angle for C4 in acetaldehyde is given to H3, but there is no bond between 02 and H3. A Z-matrix, however, is usually constructed so that the distances, angles and torsional angles follow the bonding. This makes it much easier to estimate reasonable values for the parameters.
(4) Distances should always be positive, and angles always in the range $0 - 180^{\diamond}$. Torsional angles may be taken in the range $-180 - 180^{\diamond}$, or $0 - 360^{\diamond}$.
(5) The symbolic variables show explicit which parameters are constrained to have the same values, i.e. H6 and H7 are symmetry equivalent and must therefore have the same distances and angles, and a sign difference in the torsional angle. Although the R4 and R5 (and A3 and A4) parameters have the same values initially, they will be different in the final optimized structure.
The limitation that the angles must be between $0^{\diamond}$ and $180^{\diamond}$ introduces a slight complication for linear arrays of atoms, like for example a cyano group.

Specification of the nitrogen in term of a distance to C2 and an angle to C1 does not allow a unique assignment of a torsional angle (it becomes undefined). There are two methods for solving this problem, one specifies N6 relative to C1 with a long distance:
C1
C2 1 R1
H3 1 R2 2 A1
H4 1 R2 2 A1 3 D1
H5 1 R2 2 A1 3 -D1
N6 1 R3 3 A2 2 D2
Variables: (can be blank line)
R1 = 1.50
R2 = 1.10
R3 = 2.70
A1 = 110.0
A2 = 110.0
D1 = 120.0
D2 = 0.0

Note that the variables imply that the molecule has C_{3v} symmetry. Alternatively, a Dummy Atom (X) may be introduced:



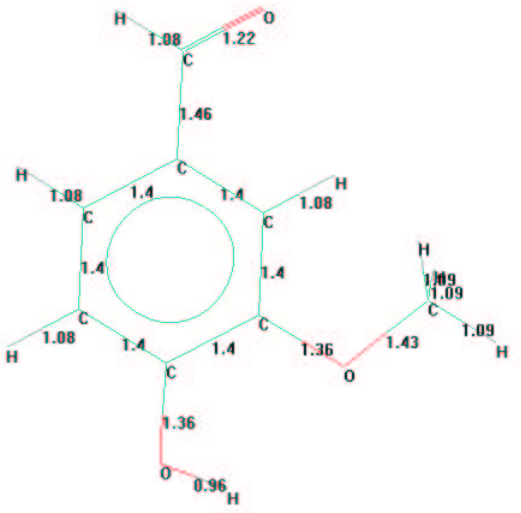
Atom numbering for methyl cyanide

C1
C2 1 R1
H3 1 R2 2 A1
H4 1 R2 2 A1 3 D1
H5 1 R2 2 A1 3 -D1
X6 2 R3 1 A2 3 D2
N7 2 R4 6 A3 1 D3
Variables: (can be blank line)
R1 = 1.50
R2 = 1.10
R3 = 1.00
R4 = 1.20
A1 = 110.0
A2 = 90.0
A3 = 90.0
D1 = 120.0
D2 = 0.0
D3 = 180.0

Write z-matrix for NH_3. Optimize geometry and perform vibrational analysis using B3LYP method and 6-31G(d,p) basis set. Compare obtained result (Gaussian vs. HyperChem).

Use GaussView 3.09 or molden (start from command line: *molden*) to visualize obtained results.

Creating Z-matrix for Vanillin, optimizing geometry



Vanillin - the flavour of vanilla icecream.

Vanillin is a single molecule, 4-hydroxy-3-methoxybenzaldehyde (much easier to call it Vanillin), whose structure is shown in the image. It's a white crystalline solid, which melts at 81°C. Vanilla planifola is an orchid which produces seed pods from which vanilla extracts are obtained

Based on previous examples build z-matrix for Vanillin molecule. Perform geometry optimization using B3LYP method and 6-31G(d,p) basis set. Do vibrational Analysis. Try to find some experimental data. Write down some geometrical parameters.