

Introduction to Ab Initio Quantum Chemical Computation

Purpose:

1. To become acquainted with basic concepts of ab initio quantum chemistry computations.
2. To learn how to use the program Gaussian09W (abbreviated G09W, where W stands for Microsoft Windows version) a program for building molecules and computing properties to the point that further self-teaching is possible if desired. We will use the graphical interface program, GaussView, for conveniently preparing input to G09W and for analyzing results. GaussView is *unnecessary*, but quite handy.

Note: The instructors will walk you through much of this material.

Specific Objectives:

1. Create an input file for water. Compute its equilibrium energy and structure, and examine its molecular orbitals. **(Exercise A)**
2. Compute the geometry and energy of a pair of H-bonded waters. **(Exercise B)**
3. Compare the effect of method and basis set on the computed vibrational frequencies and normal modes of N₂O. Relate these to CO₂. **(Exercise C)**
4. Examine MOs of benzene, and vibrational modes of benzene and benzene-d₁. **(Exercise D)**

Report

The lab report will simply consist of doing the four Exercises A-D, and turning them in by next lab period.

Background

Some background from the Gaussian web site:

<http://www.gaussian.com/>

GaussView5 links:

<https://www.d.umn.edu/~psiders/courses/chem5650/gaussviewtutorial/tutorial.html>

<https://www.mtholyoke.edu/courses/jwijngaa/PS/Gaussview2.pdf>

Gaussian09 link: www.molcalx.com.cn/wp-content/uploads/2015/01/Gaussian09W_tutorial.pdf

Hardcopy References (in the Lab):

1. GaussView reference.
2. Gaussian09 user reference
3. Gaussian 09W reference
4. Exploring Chemistry with Electronic Structure Methods, 2nd edition
by J.B. Foresman and A. Frisch

Gaussian 09W can be used to model many properties:

- Energies using a wide variety of methods, including Hartree-Fock, Density Functional Theory, MP2, Coupled Cluster, and high accuracy methods like G3, CBS-QB3 and W1U.
- Geometries of equilibrium structures and transition states (optimized in redundant internal coordinates for speed), including QST2 transition structure searching.
- Vibrational spectra, including IR, non-resonant and pre-resonance Raman intensities, anharmonic vibrational analysis and vibration-rotation coupling.
- Magnetic properties, including NMR chemical shifts and spin-spin coupling constants.
- Spectra of chiral molecules: optical rotations, VCD and ROA.
- G tensors and other contributions to hyper-fine spectra.

Gaussian 09W can be used to study compounds and reactions under a wide range of conditions:

- In the gas phase and in solution.
- In the solid state, using the Periodic Boundary Conditions facility.
- Excited states can be studied with several methods: CASSCF and RASSCF, Time Dependent DFT and SAC-CI.
- The Atom Centered Density Matrix Propagation (ADMP) method can be used to perform quantum molecular dynamics simulations in order to study reaction paths and product state distributions.

Brief Description of Principles (see Appendix A of ref. 4)

Ab initio calculations solve the Schrödinger equation for a system of nuclei and electrons by use of the *variation principle*, which states that the "best" wavefunction for the ground state is the one that has the lowest energy when the "shape" of the wavefunction is varied. The *basis set* of atomic orbitals (AOs) chosen is one key to increasing accuracy, because the more AOs used, the more finely the wavefunction can be varied to give the lowest energy.

A list of common basis sets and methods are listed on p. 102 of ref. (4) and a truncated version is provided below

A common simple basis is 3-21G. The G stands for Gaussian functions (*not* the company Gaussian Inc., which produces the program). The first number is the number of Gaussians used to make the inner shell AOs. The 21 means that *two* different sized AOs are used for each of the

basis valence shell AOs (for carbon, two different 2s, two different 2px, 2py, and 2pz, etc.). One will be made from 2 Gaussians and other with only 1.

The second main key to accuracy is the level of *electron correlation* that is included.

Brief Overview of Methods

Some common choices of methods are listed below in order of increasing CPU time:

1) Hartree-Fock (self consistent field): pretend the electrons are clouds instead of particles that dodge each other because of their immense repulsion. This is the "no correlation" base line. Each electron occupies a molecular orbital (MO) that is affected by the other electrons only by the average electric field of the other electrons combined.

Example: HF/3-21g

2) Configuration Interaction (CI): CIS, CISD, CISDT, etc.

For excited states and creating electron correlation.

Example CIS/3-21g (a first approximation for describing excited states)

3) MP2, MP4: include CI by Moeller-Plesset perturbation theory

Example MP2/6-31G(d) Note: better basis sets are necessary to capitalize on better electron correlation techniques.

4) Density Functional Theory: B3LYP, etc. Here the *density*, i.e., the square of the wavefunction, is directly varied instead of the wavefunction. This has become the method of choice because of the combination of speed and accuracy. (considerable electron correlation is incorporated efficiently)

Example: B3LYP/6-31g(d)

A Short Glossary

Input File. (.gjf or .com extension) gjf means gaussian job file

General: specify only the **atom atomic numbers or symbols**, their **coordinates**, the **charge**, and how the electrons are coupled, i.e. **spin multiplicity** (see below). (Note that one does not indicate bonds or where the electrons reside; that comes from the quantum mechanics. The program applies the variation principle by varying the electron density and atom positions to reach the lowest energy it can with a particular method and basis set of atomic orbitals)

The essential ingredients of this file come in the following order: the **route section** (or “**route card**”) begins with #, and contains the method/basis (e.g., hf/6-31g) and other key words (separated by any number of spaces, in any order, case insensitive (non-ambiguous abbreviations are allowed). The route section may contain any number of lines, terminated by a blank line.

Following the route section comes a **title** of any number of lines followed by a blank line.

Next is the **net charge and multiplicity**. (multiplicity = degeneracy of the total electron spin state = $2S + 1$. Total **ANY** angular momentum squared = $S(S+1)(h/2\pi)^2$. For a singlet state (closed shell ground state is always singlet) $S=0$, $2S+1 = 1$. For a doublet, $S=1/2$, i.e., (1 unpaired electron), $2S + 1 = 2$; and for triplet, $S=1$, $2S+1 = 3$ (2 unpaired electrons with z component electron spin quantum numbers, $m_s = -1, 0, 1$).

Next is a list of **atom symbols or atomic numbers and coordinates** given as either a set of x,y,z values or by a **Z-matrix**. Important: numerical coordinates **must have decimal points**, with spaces between. Exact positioning does not matter.

The list of atoms and coordinates **must end with a blank line**.

Example input file for H₂O: h2o-1.gjf

```
%chk=mydirectory/h2o-1.chk  
# hf/3-21g opt pop=full
```

```
title information
```

```
0 1  
o 0. 0. 0.  
h 1. 0. 0.  
h 0. 0. 0.
```

blank lines mark the different sections of input

Output File (.out or .log extension) This is perhaps most challenging to read at first, but one soon learns how to find the few things you want out of what can be several thousand lines of output.)

Checkpoint File (.chk if binary or .fchk if converted to ascii)

This is optional, but necessary if you want to visualize the MOs, vibrational modes, etc. It is requested by a line such as %chk=directory/filename.chk coming **before the route card**. This contains all information generated, in a compact form (but not readable). It can be used as the starting point for a restart or succeeding calculation. It can be converted to a readable format with formchk.

Some Useful Information:

Energy units are atomic units (or *Hartrees*). 1 a.u. is the potential energy of 1 proton when 1 bohr radius (atomic unit of distance) from another proton. The average *potential* energy of the H atom is therefore -1.000 a.u. and the total kinetic energy is therefore (from the *virial theorem*) +0.5 a.u., and the total E is -0.5 a.u. **1 Hartree = 627.51 kcal/mol or 2625.5 kJ/mol.**

Recall that chemical accuracy is about 1 kcal/mol (a change of **1.4 kcal/mol = 5.7 kJ/mol = 0.0022 a.u.** in Gibbs free energy means a **10-fold change in equilibrium constant**, or a 10-fold change in calculated rate, if we are calculating an activation energy).

Single point calculation: A "single point" calculation just calculates the energy and wavefunction at the geometry given in the input and then stops.

(geometry) **optimization:** using the key word, **opt** tells the program to compute the forces on the atoms at completion of a single point calculation, and then move the atoms a small amount downhill in energy according to those forces, do another single point calculation, follow the forces iteratively until the forces are effectively negligible (i.e., the system has reached a **local minimum** in energy. (Note: if you want the **global minimum**, it is up to you to locate the correct starting point that will lead there.) If the geometry is such that the energy is at a local maximum or local minimum, there will be no force and the atoms will not move to a lower energy.

Procedures

General

1. Click on the GaussView icon to run GaussView, the graphical interface which *facilitates* setting up the input file and the viewing of results. GaussView is **completely unnecessary** for obtaining the results from G09, which is *completely independent* of GaussView. The input files can be generated using any text editor, and the numerical output can be read in the editor. NOTE: the .gjf or .com file **MUST be a txt file, but must end with extension = .gjf** (a .txt, or .doc file cannot will not run)

2. Generate the molecule graphically on the screen in the (rough) form you want for starting

coordinates. This is done using a combination of icons  and **save**. (z-matrix is the default but you can select Cartesian coordinates by checking the box when you save the file.)

Click on **Results on menu bar** or the **View File icon**,  and view the file. Edit the file to complete the input details.

On your desktop or under programs, click on the **G09W icon** to start G09W. In its File menu, **open** the input file you just made. You may make any further modifications at this point if needed. When it is ready you should save the file; then click the **Run** button.

View the results in the .out file in Notepad by simply clicking the magnifying glass icon  in the upper right corner, or go back to GaussView and open the .out file (or .chk file if viewing MOs is desired). Analyze the structure, vibrations, MOs, etc.

Specific tasks:

A. Energy, geometry, and molecular orbitals of the water molecule

1. Run GaussView
2. Click the **element** button and select O
3. Select the --O-- fragment from the submenu and click the blank window. (**control-z** will undo and **control-y** will redo)
4. Save the file as h2o1 (it will actually end up as h2o1.gjf (Gaussian Job File))
5. View the file and make it conform to the example given for h2o above.

Note: often the default is set to include the “geom = connectivity” keyword. Then the last section of the input gives for each atom the atoms connected to it and the bond order of the connection bond. **This in no way influences the calculation** and can be deleted (or not); it is primarily used for graphical viewing and by the “clean” command, and for renumbering if you open an existing .gjf file as a starting point for a new calculation.

6. Save the file again following any changes.

Run Gaussian09W (G09W) as follows:

7. *open* the input file you just saved using the *file* menu
8. at this point you can again edit and save the input if needed.
9. hit the run button. This calculation should take only a few seconds.

To view the molecular orbitals :

10. in GaussView, open h2o1.chk. (file open select .chk as the file type)
11. Click on the MO editor button (red & green orbital), select the filled orbitals, click on *visualize* and click the *update* button. After a few seconds, the MOs are displayed. Clicking the box beside the energy level will display that MO.
12. **view the h2o1.out file** (recall, GaussView is not really necessary)

The .out (.log) file is easy to read—if you know what to look for. Most of the output will not be of interest. We will have a **guided tour** of the log file in class, but here are some tips on how to find key information using the “find” command *control-f* in your editor:

a. search for **scf done** to see the HF-SCF energies at each stage of an optimization. Notice how the values get more negative at each stage of the optimization. When the improvement becomes smaller than a certain value, the optimization ceases, and the **stationary point found** will be printed.

b. search for **predicted change in energy** to observe the progress toward reaching optimization criteria.

c. to view the MO energies (eigenvalues) and MOs (eigenvectors = atomic orbital coefficients), search for “**molec**” to find Molecular Orbital Coefficients:

Try to imagine how each MO would look from these coefficients.

Appendix: Z-matrix input file

```
%chk=h2o1.chk
# hf/3-21g opt pop=reg nosym

water

0 1
O
H          1          B1
H          1          B2      2          A1

      B1          0.96000000
      B2          0.96000000
      A1          109.50000006
```

The 3 lines following the charge and multiplicity (0 1) comprise what is called a Z-matrix, which is a way of entering the positions of the atoms using bond lengths, angles, and dihedral angles. In this case the bond lengths (B1, B2) and bond angle (A1) are included in the Z-matrix as variables instead of numbers. When this is done, the initial values are specified following a blank line.

Exercise A

1. Make rough freehand drawings of the filled MOs
2. Classify each as sigma or pi, primarily bonding, non-bonding, or antibonding, and core or valence. (bonding orbitals have electron density in the bonds, and antibonding MOs have nodes in the bonds.)

B. Finding the geometry of the water dimer and the H-bond energy.

1. In GaussView, open a new window and place two waters in the window. By holding the alt and shift keys down, click one of the molecules with the left mouse button and drag it to position the two O atoms roughly 3 Angstroms apart. Check the distance with the **Modify bond** button. Doing the same, but using the Alt key only, allows you to rotate one of the molecules so that its H is pointing *roughly* to the O of the other molecule. Don't make it too perfect.
2. Save the file as dimer after editing the route line to read as it did for the h2o1 file. Here it is nice to add the **nosym** keyword so that your input geometry is maintained. Otherwise Gaussian

will change the output geometry to its “standard orientation”, making the molecules appear to jump around as you visualize successive stages of optimization.

3. Run Gaussian09. It will take about 1 minute to run and will not usually reach a true minimum before reaching the maximum number of iterations. (If so, there will be an error message, but it just means the program gave up; *if it did finish gracefully, that might mean it got stuck in a symmetrical conformation. In that case, you will have to use a different starting geometry and start again.*) Even if it exits with the error, the energy and structure will be very close to the energy minimum for the basis set used).

4. Open the dimer.out file in GaussView with the “**Read Intermediate Geometries**” box **checked**. Then click the green circle to start a movie of the optimization steps. Click the X to stop it. Click on the step boxes to see individual steps.

6. View the dimer.out file and record the final energy given in Hartrees (also known as atomic units).

Exercise B:

1. Draw a rough picture and describe the structure of the water dimer.
2. Calculate the energy required to break the H-bond in kcal/mol from twice the energy of H₂O minus – the energy of the dimer. Compare to the observed energy of ~5 kcal/mole.

C. Normal vibrational modes and frequencies for N₂O: Effect of basis set and electron correlation.

1. Using Notepad make an input file, n2osto3g.gjf, for N₂O, this time manually entering Cartesian coordinates by editing one of your existing .gjf files.
 - a. delete all the lines of the Z-matrix or coordinates, i.e., all below the charge and multiplicity line: 0 1
 - b. type the following to create a **perfectly linear** NNO molecule: (otherwise the program will crash trying to get to the linear state because some trigonometry functions will blow up)
n 0. 0. 0.
n 1. 0. 0.
o 2. 0. 0.
 - c. make sure you leave at least one blank line following the Cartesian coordinates
 - d. make the route: # hf/sto-3g opt freq pop=reg
 - e. add the %chk line with the n2osto3g.chk name and destination directory path
2. after running G09W, open the **.out** file in GaussView and click on vibrations in the results menu.
3. run another job, n2ob3, differing from this one only in replacing hf/sto-3g with

B3LYP/6-311++G(d,p) ; this combines a large, versatile basis set with quite good correlation (from the B3LYP method). The ++ adds some larger atomic orbitals, and d,p means that d orbitals are included for the used for the heavy atoms and p orbitals are included for H atoms, when present. This allows for orbital distortions due to the bonding in the molecules.

Exercise C:

1. Open n2ob3.out in GaussView and compare the vibrational modes and frequencies to the sto-3g result, and compare the frequencies to experiment.
2. Modify the n2ob3 file to make co2ob3 for the CO₂ molecule, making sure it is exactly linear and the C is in the middle. Compare with the NNO vibrational modes.
3. Discuss any obvious differences in the vibrational behavior in the 3 cases, focusing in particular on the apparent difference in bond stretching force constants (single, double, triple bond) in the 3 cases.
4. Given that the center of mass does not change in the course of normal mode motion, why does the C move so much during the symmetric stretch compared to the middle N for NNO?

D. MOs and Normal Modes of Benzene and Benzene-d1

1. click on *Ring Fragment* and pick benzene
2. Save as benzene.gjf and run G09 after editing the route card to:
hf/3-21g opt freq pop=reg
3. In GaussView, open benzene.chk, and examine the 2 degenerate homos and lumos, and look at the vibrations.
4. You will note that the degenerate HOMO and LUMO MOs do not look symmetrical. Check the C-C bond lengths. Are they all exactly the same? Even if they were, because they are degenerate, any two linear combinations of a degenerate pair will still have the same energy and be legitimate MOs. (exactly as any two choices of directions for x and y axes can be used to describing two vectors)

Next, *we* will make "pretty" looking MOs by making sure all bonds are precisely the same length except for two C-H bonds para to one another:

5. Click on benzene, and then on clean (whisk broom icon). Under View, select label to see the atom numbers. Check to make sure all equivalent C-C and C-H bonds are exactly the same. Then make the C1-H7 and C4-H10 bond lengths = 1.08. (The others should be 1.07) The symmetry is now reduced to D_{2h}, (symmetrical for reflection in the plane that contains C1 and

C4 and is perpendicular to the ring plane). The MOs will not be changed significantly by such a small perturbation, but the degenerate ones will be symmetric about the axis containing the perturbed bonds. Save as benzene-D2h.gjf, and run a single point calculation by using the route card: # hf/3-21g pop=reg. Note the difference in the degenerate HOMOs and LUMOs.

5. Effect of deuteration: Benzene-d1: Open the file benzene.gjf and save it as benzene-d1.gjf. Make just one change: in the list of coordinates, replace the first H with H(iso=2). Now, that bond will be C-D. Save the file as benzene-d1.gjf and run it.

In GaussView, open benzene-d1.out

Exercise D.

1. Comment on the difference in appearance of the MOs for the two calculations in which the molecule was symmetrized and not symmetrized. Did this difference have any significant effect on the MO energies?

2. a. Compare the 6 C-H stretching normal modes of benzene and benzene-d1 and note the modes for which the frequencies changed significantly. What do you notice about these modes?

b. Particularly, there are pairs of double degenerate modes (modes with exactly the same frequency) just as for the HOMO and LUMO pairs pi MOs which have *exactly* the same MO energies. This is because of the D_{6h} (planar hexagon) symmetry of benzene.

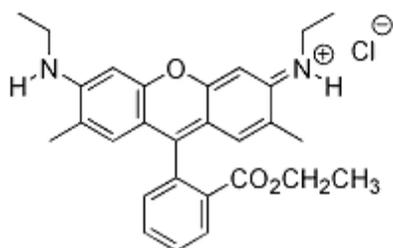
What always happens to the frequencies and modes of the degenerate pairs you examine.

c. Likewise, compare and contrast the two lowest frequency modes, and comment on the effect of the deuteration. What kind of vibrations are these and why do they have such low frequency?

Reference material for your possible future use (not part of this lab report):

E. Making a large, complex molecule input file

This is just to show what can be done with Gaussview.
You need not include the chloride ion.



Rhodamine 6G Laser dye

1. click on ***Ring Fragment*** and start with anthracene
2. Change the center C into O using the ***Element Fragment***.
- 2a Delete the H on the O using the delete atom button
3. Use ***Element Fragment*** to select the amino and click on the appropriate H atoms to add the amino. Use the ***Modify bond*** to make a partial double bond.
4. Use ***Modify dihedral*** to make the amino groups planar and the plane of the phenyl group twisted about 70degrees relative to the xanthene group if necessary after using the clean command.
5. Similarly, finish the structure.