Computational Chemistry Experiment

[*Developed by Lisa M. Pérez, Laboratory for Molecular Simulation, Texas A&M University*]

Objectives

- To examine the bonding (bond lengths and bond orders) of diatomic molecules using Molecular Orbital (MO) Theory.
- Learn to use the Quantum Mechanical software Gaussian 09 via the Ampac Graphical User Interface (AGUI).

Prior Reading

- *Chemical Principles: The Quest for Insight*, 7th ed., by Peter Atkins, Loretta Jones, and Leroy Laverman, W.H. Freeman & Co., New York (2016), Topics 2G.1 – 2G.3; pp. 127 - 135.

OR

- *Chemistry & Chemical Reactivity*, 9th ed., by John C. Kotz, Paul M. Treichel, John R. Townsend, and David A. Treichel, Cengage Learning, Stamford, CT (2015), Section 9-3, pp. 354-365.

The Gaussian 09 suite of programs, provide state-of-the-art capabilities for electronic structure calculations. Starting from the fundamental laws of quantum mechanics, Gaussian 09 predicts the energies, molecular structures, vibrational frequencies and molecular properties of molecules and reactions in a wide variety of chemical environments. The Ampac Graphical User Interface (AGUI) allows users to build their molecular systems and set up and run Gaussian 09 calculations.

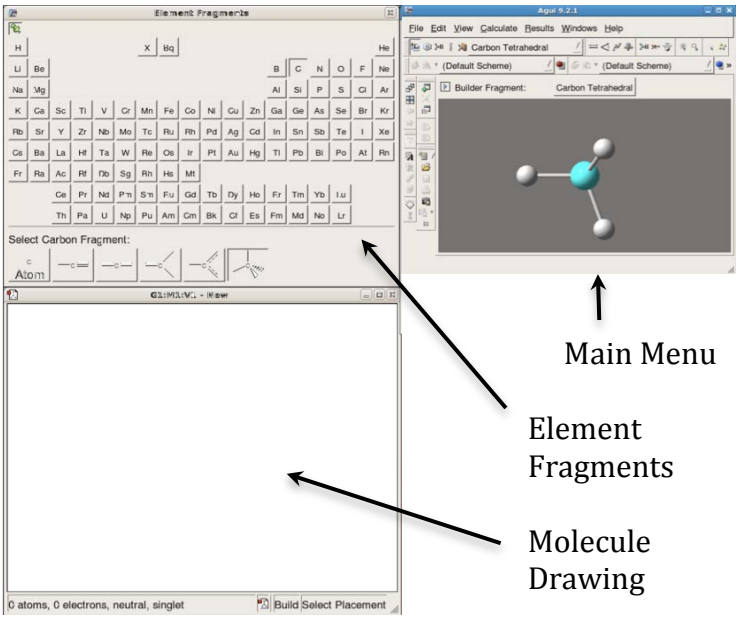
Experimental Section

Procedure

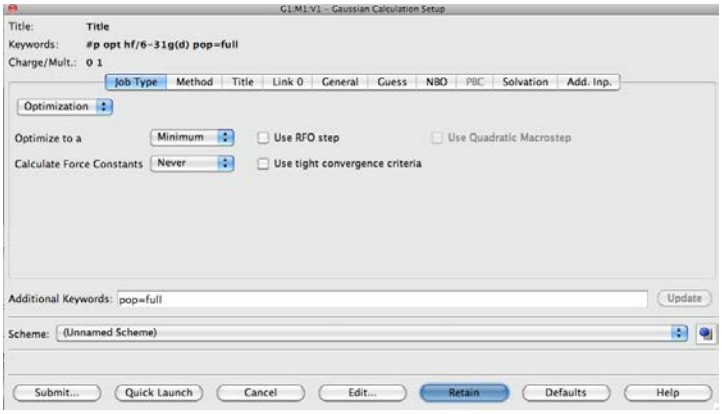
Part A: Tutorial for AGUI and Gaussian 09

Estimated time to complete the experiment: 1/2 hour.
Experimental Steps: (1) Use the Ampac Graphical User Interface (AGUI) program to draw the molecules H_2 and then (2) run a Hartree-Fock (HF) geometry optimization with the 6-31G(d) basis set using the Gaussian 09 program. (3) Use AGUI to visualize the geometry, Molecular Orbitals (MOs) and MO diagrams. (4) Measure the optimized H-H bond distance.

1. Login to the Linux machine with the username: **training** and the password: **lms4linux**
2. Open up a terminal window by clicking the right mouse button on the background and selecting terminal from the pop-up menu.
3. Once a terminal window is open, open the AGUI program by typing: **agui** at the prompt. You should now see 3 new windows: Main Menu window, Element Fragments, and the Drawing window.
4. Draw molecular hydrogen (H_2). Selecting H from the periodic table and the Hydrogen Terminal fragment (—H) from the Select Hydrogen Fragment section. Left-click in the blank Molecule Drawing window and molecule hydrogen should appear.
5. Setup your calculation. Left-click on "Calculate" from the main menu and select "Gaussian Calculation Setup" from the dropdown menu.
   a. In the new window, make sure in the "Job Type" tab "Optimization" is selected.

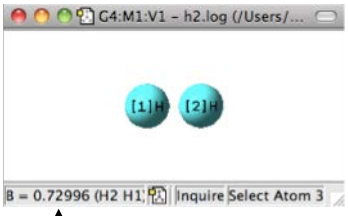


b. In the "Method" tab select the Ground State/Hartree-Fock/Restricted method and the 6-31G(d) Basis Set. For H_2, the charge should be 0, and the Spin should be a singlet (no unpaired electrons).



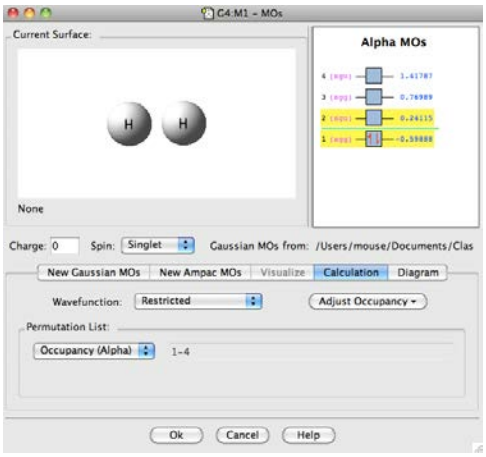
c. Click the "Submit" button to run the calculation. You will get a popup window stating that you need to save a Gaussian input file first. Click Save and name the file h2.com. Click ok in the next pop-up window to start the calculation.

6. Visualize the results:
   a. When the job is finished, you will get a pop-up window with the title Gaussian Job Completed and the option to open the h2.chk or h2.log file. If it is not already, highlight the h2.log file and click ok.
   b. Measure the bond distance: Click on the inquire button in the main menu window. Click on one of the hydrogen atoms and then click on the other. In the lower left hand corner of the drawing window, you will see the bond distance listed in Ångstroms. Note that AGUI does not draw a bond between the hydrogen atoms. The bonding shown in AGUI is not always accurate because AGUI determines bonding by incorporating Van der Waals radii and atom distance only and in the case of H_2 it erroneously does not draw a bond.

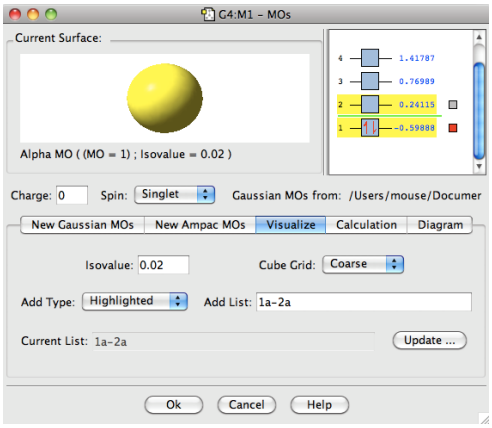


H-H bond distance

   c. Visualize the Molecular Orbital diagram: Right-click in the h2.log molecule window and left-click on the edit/MOs… menu. This will bring up a new window illustrating the MO diagram for H_2 with the MO notation listed. Do not worry about the g and u notation. Molecular Orbital 1 (MO 1) is the Highest Occupied Molecular Orbital (HOMO) with a calculated energy of -0.59888 hartrees (atomic units) and a symmetry of σ_g (listed as sgg). The arrows in the blue box of MO 1 represent the electron pair in the HOMO. Orbital 2 is the Lowest Unoccupied Molecular Orbital (LUMO) with a calculated energy of 0.24115 hartrees and a symmetry of σ_u (sgu). The blue box of MO 2 is empty because it is unoccupied. Note that the MO diagram is not drawn to scale.



d. Visualize the Molecular Orbitals (MOs):
   i. Click on the New Gaussian MOs Tab
   ii. The checkpoint File: section should already list h2.chk, therefore, you should only need to click on the Load button.
   iii. Click on the Visualize Tab
   iv. Click on the Update … button to calculate MO surfaces for the highlighted orbitals in the MO diagram (HOMO and LUMO in this example). To highlight other orbitals, hold down the shift key and click on the MO number of interest.
   v. When the surface calculation is finished, you should see a surface appear in the Current Surface section. You can change the MO being displayed by clicking on the small gray box to the right of each orbital in the MO diagram. The MO being displayed has a red box.
   vi. When done click "OK" to close the window.



7. Shutdown AGUI (File/Exit).

Part B: Investigate the Bonding in N_2 and O_2 using AGUI and Gaussian 09

Estimated time to complete the experiment: 1 hour.
Experimental Steps: (1) Use the Ampac Graphical User Interface (AGUI) program to draw the molecules N_2 and O_2 and then (2) run Hartree-Fock (HF) geometry optimizations with the 6-31G(d) basis set using the Gaussian 09 program. (3) Use AGUI to visualize the geometry, Molecular Orbitals (MOs) and MO diagrams. (4) Determine bond distances and bond orders of each molecule.

1. Using the detailed instructions in the tutorial for AGUI and Gaussian 09, run a HF/6-31G(d) calculation on N_2, N_2^+, and N_2^- and visualize the results. When setting up the N_2^+ calculation choose the Restricted-Open Hartree-Fock method, use a charge of 1 and a doublet spin (1 unpaired electron) and for N_2^-, a charge of -1 and a doublet spin. Use the filenames: n2.com, n2plus.com, and n2minus.com (Linux filenames should only consist of standard alpha numerics (A-Z, a-z, 0-9), underscore (_), and period (.).
   a. Record the N-N bond lengths of N_2, N_2^+, and N_2^-.
   b. Record the MO energy diagram (approximately to scale) for N_2, and the schematic representation of the occupied MOs and the LUMO. If you would like to see the degeneracy in the MO diagram, click on the Diagram tab in the Edit/MOs window and change the Degeneracy Threshold from 0 to 0.001

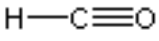
2. Run a HF/6-31G(d) calculation on O_2, O_2^+, and O_2^- and visualize the results. When setting up the calculation for O_2 make sure to choose the Restricted-Open Hartree-Fock method with a charge of 0 and a triplet spin (2 unpaired electron). For the O_2^+ calculation, use a charge of +1 and a doublet spin, and for O_2^-, use a charge of -1 and a doublet spin. Use the filenames: o2.com, o2plus.com, and o2minus.com
   a. Record the O-O bond length of O_2, O_2^+, and O_2^-.
   b. Record the MO energy diagram (approximately to scale) for O_2, and the schematic representation of the occupied MOs, including the 2 Singly Occupied Molecular Orbitals (SOMOs). Again, if you would like to see the degeneracy in the MO diagram, click on the Diagram tab in the Edit/MOs window and change the Degeneracy Threshold from 0 to 0.001

Part C: Investigate the Bonding in carbon monoxide and nitric oxide using AGUI and Gaussian 09

Estimated time to complete the experiment: 1 hour.
Experimental Steps: (1) Use the Ampac Graphical User Interface (AGUI) program to draw the molecules carbon monoxide and nitric oxide and then (2) run Hartree-Fock (HF) geometry optimizations with the 6-31G(d) basis set using the Gaussian 09 program. (3) Use AGUI to visualize the geometry, Molecular Orbitals (MOs) and MO diagrams. (4) Determine bond distances and bond orders of each molecule.

3. Using the detailed instructions in the tutorial for AGUI and Gaussian 09, run a HF/6-31G(d) calculation on CO, CO^+, and CO^- and visualize the results. To draw carbon monoxide, double-click on the R-Group Fragment button and select carbonyl ligand fragment button in the R-Group Fragment window. Left-click in the blank Molecule Drawing window and HCO should appear. To complete the drawing of carbon monoxide, you will need to delete the hydrogen and the dangling bond using the Delete atom tool. When setting up the carbon monoxide calculation, use a charge of 0 and a singlet spin (0 unpaired electron). Use the filename: co.com For the CO^+ calculation, use a charge of +1 and a doublet spin, and for CO^-, use a charge of -1 and a doublet spin. Use the filenames: coplus.com and cominus.com
   a. Record the C-O bond length of CO, CO^+, and CO^-.
   b. Record the MO energy diagram for CO and the schematic representation of the occupied MOs and the LUMO. If you would like to see the degeneracy in the MO diagram, click on the Diagram tab in the Edit/MOs window and change the Degeneracy Threshold from 0 to 0.001

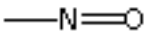
R-Group Fragment button



carbonyl ligand fragment


Delete atom

4. Using the detailed instructions in the tutorial for AGUI and Gaussian 09, run a HF/6-31G(d) calculation on NO, NO^+, and NO^- and visualize the results. To draw nitric oxide, use the nitroso fragment in the R-group templates and then delete the hydrogen and the dangling bond using the atom delete tool. When setting up the NO calculation, use a charge of 0 and a doublet spin (1 unpaired electron). Use the filename: no.com For the NO^+ calculation, use a charge of +1 and a singlet spin, and for NO^-, use a charge of -1 and a triplet spin. Use the filenames: noplus.com and nominus.com



nitroso fragment

   c. Record the N-O bond length of NO, NO^+, and NO^-.
   d. Record the MO energy diagram for NO and the schematic representation of the occupied MOs and the LUMO. If you would like to see the degeneracy in the MO diagram, click on the Diagram tab in the Edit/MOs window and change the Degeneracy Threshold from 0 to 0.001

Name _____ Section _____

Instructor _____ Date _____

PRELABORATORY REPORT SHEET – MOLECULAR MODELING EXPERIMENT

Objective

What programs will you be using to perform this experiment?

PRELABORATORY PROBLEMS – MOLECULAR MODELING EXPERIMENT – PAGE 2

1. Draw the MO energy diagram for N_2

2. Draw the MO energy diagram for O_2

PRELABORATORY PROBLEMS – MOLECULAR MODELING EXPERIMENT – PAGE 3

3. Draw the MO energy diagram for carbon monoxide.

4. Draw the MO energy diagram for nitric oxide.

Name _____ Section _____

Instructor _____ Date _____

DATA SHEET, MOLECULAR MODELING EXPERIMENT

Data Collection Table

1. Bond distance (Å)

N_2	_____
N_2^+	_____
N_2^-	_____
O_2	_____
O_2^+	_____
O_2^-	_____
CO	_____
CO^+	_____
CO^-	_____
NO	_____
NO^+	_____
NO^-	_____

2. Bond Order (Show Calculations)

N_2	_____
N_2^+	_____
N_2^-	_____
O_2	_____
O_2^+	_____
O_2^-	_____
CO	_____
CO^+	_____
CO^-	_____
NO	_____
NO^+	_____
NO^-	_____

Show calculations:

3. HF/6-31G(d) calculated MO energy diagram (approximately to scale) for N_2, and a schematic representation of the occupied MOs and the LUMO

4. Based on MO theory, explain the change in the bond distance when removing and adding an electron from N_2 (N_2^+ and N_2^-)

5. HF/6-31G(d) calculated MO energy diagram (approximately to scale) for O_2, and a schematic representation of the occupied MOs and the LUMO

6. Based on MO theory, explain the change in the bond distance when removing and adding an electron from O_2 (O_2^+ and O_2^-).

7. Was the bond length trend (increase or decrease) the same or different between N_2 and O_2 upon a change in charge? Explain why.

8. HF/6-31G(d) calculated MO energy diagram (approximately to scale) for CO, and a schematic representation of the occupied MO's and the LUMO

1. HF/6-31G(d) calculated MO energy diagram (approximately to scale) for NO, and a schematic representation of the occupied MOs and the LUMO

Name _____ Section _____

Instructor _____ Date _____

POSTLABORATORY PROBLEMS – MOLECULAR MODELING EXPERIMENT

1. Draw the MO diagram for CO

2. Based on the MO diagram, how many unpaired electrons are there in CO?

3. Will the CO bond distance increase or decrease when an electron is added (CO^-), when an electron is removed (CO^+)? Explain why.

4. Draw the MO diagram for NO

5. Based on the MO diagram, how many unpaired electrons are there in NO?

6. Will the NO bond distance increase or decrease when an electron is added (NO^-), when an electron is removed (NO^+)? Explain why.