

Molecular Modeling and Electronic Structure Calculations with QC-Lab

Molecular Modeling and Electronic Structure Calculations

George Schatz, Baudilio Tejerina, Shelby Hatch and Jennifer Roden

Department of Chemistry, Northwestern University, Evanston, Illinois
60208-3113

[QC Lab module.pdf](#) (275 KB, uploaded by 3 years 5 months ago)

This laboratory is designed to use the program GAMESS (General Atomic Molecular Electronic Structure System, developed in Gordon research group at Iowa State) through a website called [nanoHUB](#) to determine the geometric and electronic properties of numerous small molecules. GAMESS uses *ab initio* and semi-empirical calculations to determine these properties. *Ab initio* (“from first principles”) calculations solve the Schrödinger equation using the exact computational expression for the energy of the electrons.¹ The particular *ab initio* method that we will use for this lab is called Hartree-Fock (HF). HF uses an approximate wavefunction to solve Schrödinger, so the resulting molecular properties are approximate, but for many applications the accuracy is adequate for interpreting experiments. Semi-empirical calculations use an approximate energy expression for the electrons, but solve for the exact wavefunction associated with this expression. Usually the energy expression uses empirical parameters (found experimentally) to match molecular properties, but the resulting properties are still approximations to the correct values. The semi-empirical method that we used in this lab is called PM3. This stands for “parameterized model 3,” which was the third (and best) method that the original authors of the method developed.

The underlying theory for GAMESS will be described in the lecture. In brief, GAMESS self-consistently solves the Schrödinger equation. The self-consistent method is an iterative approach that minimizes the energy by adjusting the wave functions of the molecules. Further information can be obtained from the GAMESS user guide ([GAMESS Manual](#)).

Pre-Lab Information

GAMESS is located in the QC-Lab tool on the nanoHUB website. To access this tool you must first create a user account (see Appendix A for directions).

Make sure to include the results that you obtain (bond distances, bond angles, energy values, and charge per atom) in your lab notebooks.

The units on these results should be the same as the units used in GAMESS (distances in Angstroms (Å), angles in degrees, energy in Hartrees).

The results should be presented neatly, preferably in a tabular form with some experimental

data obtained from literature also recorded. Literature values can be located through the National Institute of Standards and Technology (NIST) Computational Chemistry Comparison and Benchmark Database (CCCBDB) at <http://srdata.nist.gov/cccbdb/default.htm>.

It is important to note that calculated energy values cannot be directly compared to experimental energy values.²

PROBLEM 1: Warm-up and Practice

In this problem, the properties of three small linear molecules (CO, H₂, and N₂) will be calculated using a semi-empirical and an ab initio method. The calculation for CO will be shown in full detail and the remaining two molecules (H₂ and N₂) will be left for the reader to perform individually.

Carbon Monoxide Walk through:

1. (In lab notebook) Determine the input coordinates.

—A Draw the Lewis Dot structure to determine basic bonding and lone pairs, :C__=__O:

—B Redraw the molecule using the appropriate Valence Shell Electron Pair Repulsion (VSEPR) model to determine basic structure. *Linear*

—C Place molecule on Cartesian coordinates using the average bond lengths given in the textbook.

—i Make x-axis the bonding axis:

C	0.0	0.0	0.0
O	1.12	0.0	0.0

—ii Reassign the origin of the coordinates in order to achieve the highest symmetry possible. This will reduce number of calculations and speed up the process (trivial for small linear molecules but helpful for larger non-linear molecules).

C	-0.56	0.0	0.0
O	0.56	0.0	0.0

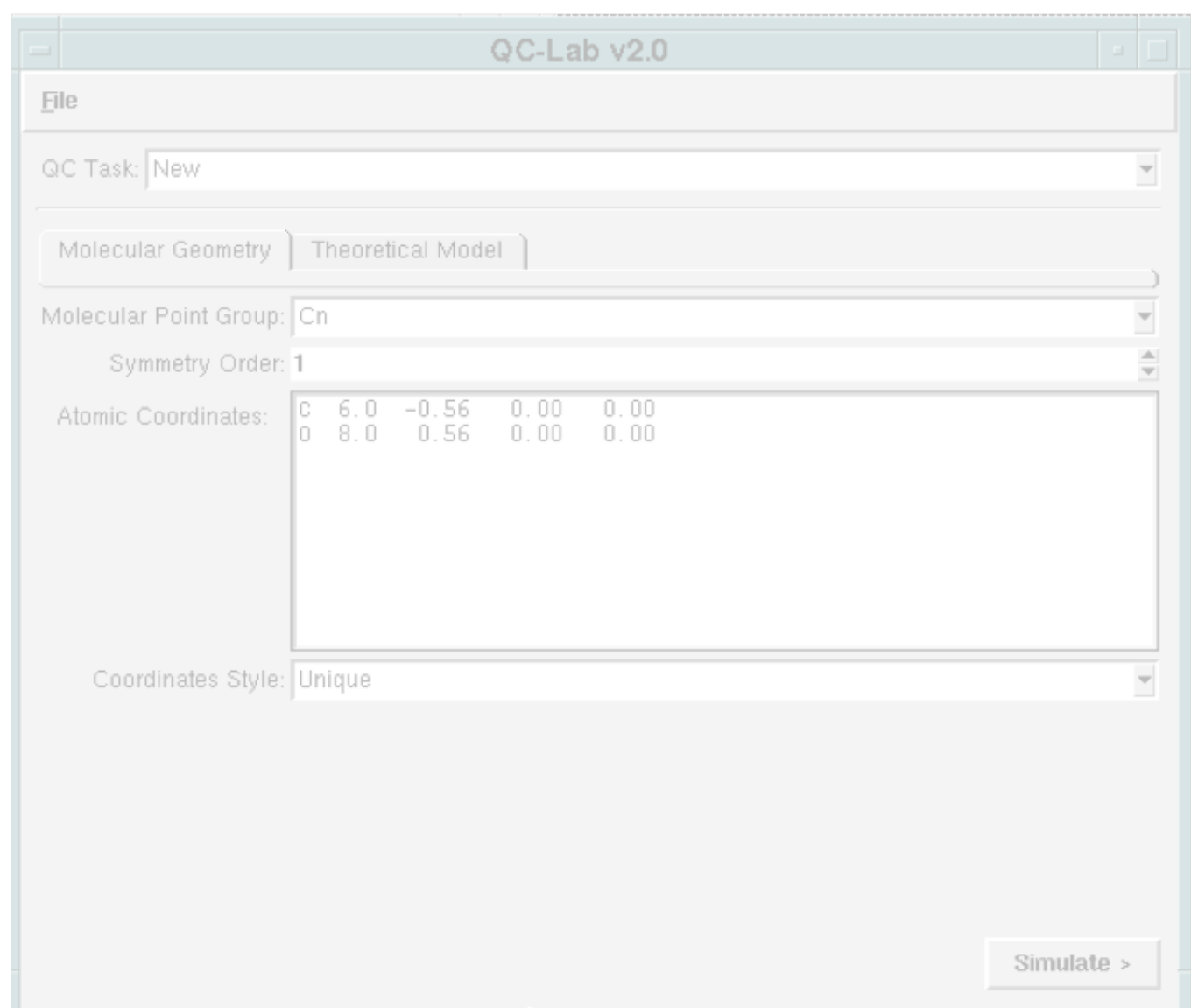
—D Be sure to show all of your work in your notebook.

2. (In Nanohub) Perform semi-empirical calculations.

—**A** After setting up a nanoHUB account and launching the QC-lab tool, select new from the 'QC task' pull-down menu.

—**B** Delete the text in the atomic coordinates box and enter the input coordinates (X, Y, Z) that you determined, being sure to first put the atomic symbol and atomic number. Be sure to note the syntax (spacing, using the decimal, etc.) See screenshot on next page.

—**C** Leave the 'Molecular Point Group,' 'Symmetry Order,' and 'Coordinate Style' at the default setting (C_n , 1, unique).³

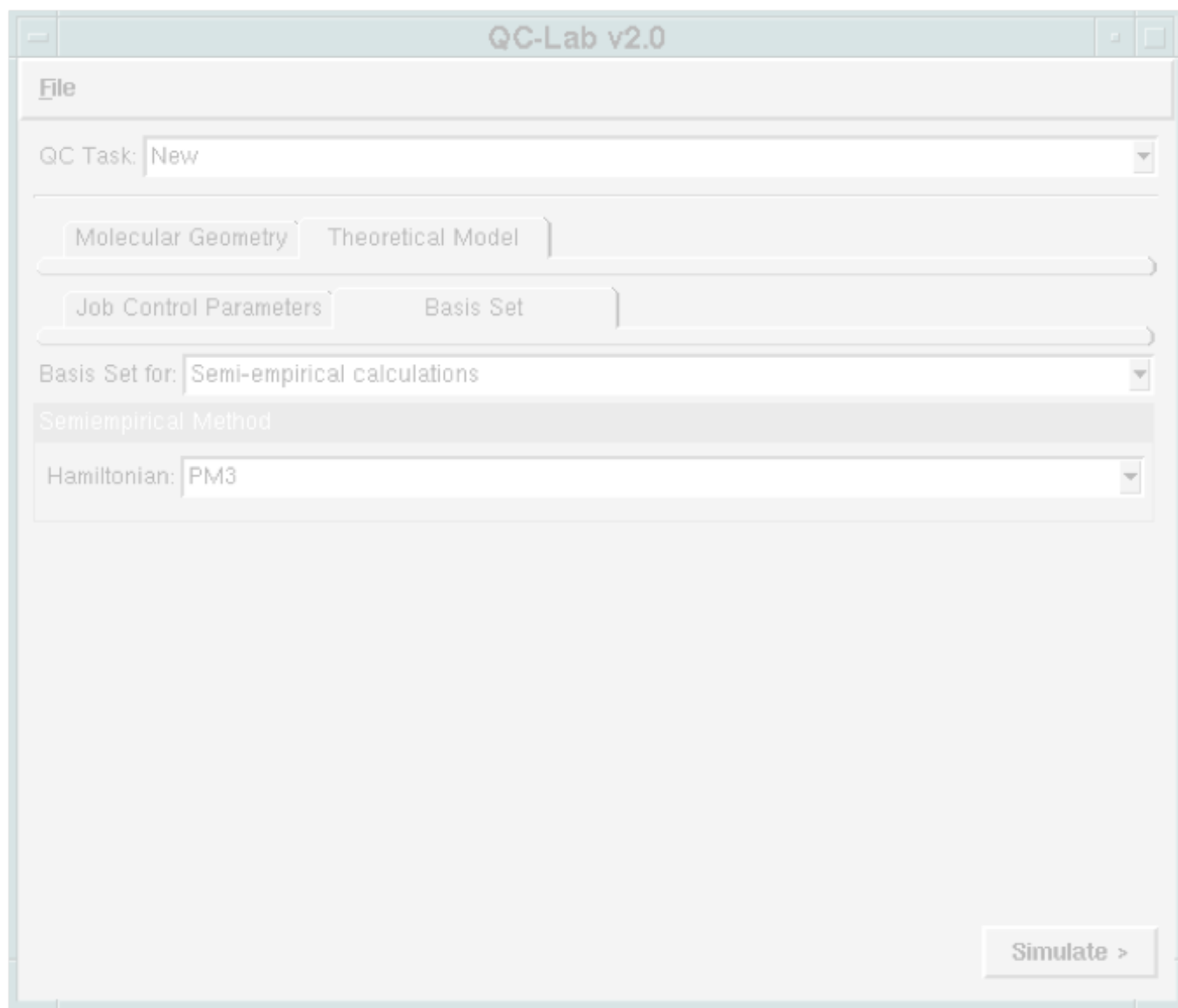


—**D** Click on the 'Theoretical Model' tab (circled in previous image).

—**E** Leave the default ‘Job Control Parameters’ settings for now (Run, Geometry Optimization, Restricted Hartree-Fock Calculation, 0 and 1).⁴

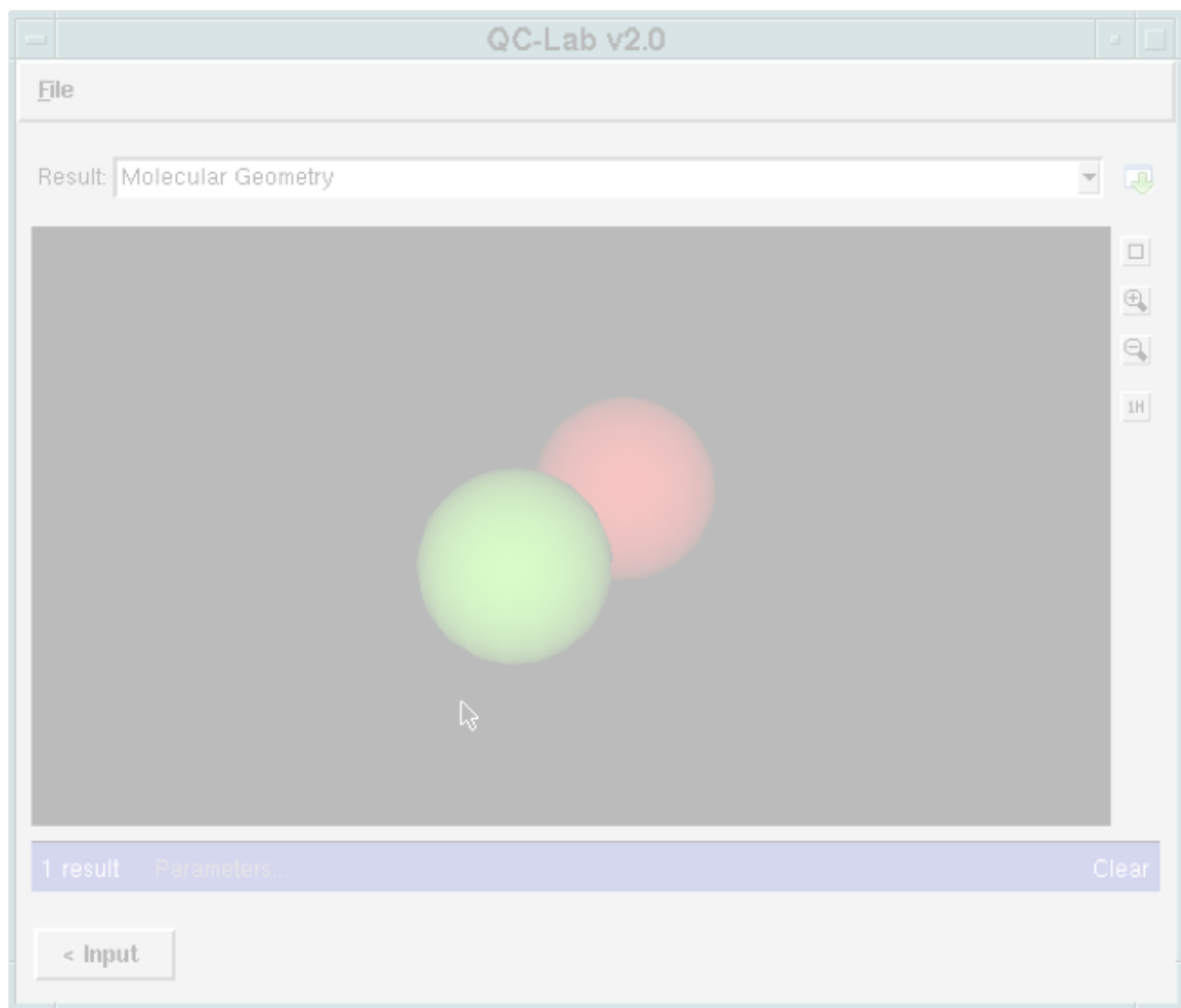
—**F** Under the ‘Basis Set’ tab, set the ‘Basis Set for’ pull down menu to ‘Semi-empirical calculations.’ This action will refresh your screen and bring you back to the ‘Job Control Parameters’ tab so click back into the ‘Basis Set’ tab (you might notice other tabs have vanished; this is okay).

—**G** In the ‘Hamiltonian’ pull-down, select PM3.



—**H** Click the ‘Simulate’ button in the lower right.

—**I** After the job has finished running, an image of the molecule will appear in the window.



—**J** In order to obtain the necessary information, select the 'Output Log' from the 'Results' pull-down. The output contains all the results and information about the calculation.

—**K** The following key words can be found using the 'Find' feature to locate the desired information:

—**i.** LOCATED = the location in the output with the optimized coordinates and bond distances are printed

```
QC-Lab v2.0
File
Result: Output Log
1 c      6.0   0.0000017   0.0000000   0.0000000
2 o      8.0  -0.0000017   0.0000000   0.0000000

      MAXIMUM GRADIENT = 0.0000017   RMS GRADIENT = 0.0000010
1 ***** EQUILIBRIUM GEOMETRY LOCATED *****
COORDINATES OF ALL ATOMS ARE (ANGS)
  ATOM  CHARGE      X      Y      Z
-----
  C      6.0  -0.5673630369   0.0000000000   0.0000000000
  O      8.0   0.5673630369   0.0000000000   0.0000000000

      INTERNUCLEAR DISTANCES (ANGS.)
      -----
              C      O
1  C              0.0000000   1.1347261 *
2  O              1.1347261 *   0.0000000

* ... LESS THAN 3.000

Find: LOCATED line 1278 --93%--
1 result Parameters... Clear
< Input
```

—ii. Slightly above the word LOCATED will be a value for TOTAL WALL CLOCK TIME, NSERCH and ENERGY, which gives the time the calculation took, the number of steps taken by the computer to obtain an optimized geometry and the energy for the optimized structure.

```

QC-Lab v2.0
File
Result: Output Log
-----
      DX      DY      DZ      /D/ (DEBYE)
      0.185004  0.000000  0.000000  0.185004
..... END OF PROPERTY EVALUATION .....
ON NODE 0, STEP CPU TIME =      0.00 TOTAL CPU TIME =      0.1 (      0.0 MIN)
TOTAL WALL CLOCK TIME=      0.0 SECONDS, CPU UTILIZATION IS 100.00%

      NSERCH= 6      ENERGY=      -15.1193072

-----
GRADIENT (HARTREE/BOHR)
-----
      ATOM      ZNUC      DE/DX      DE/DY      DE/DZ
-----
      1  C          6.0      0.0000017  0.0000000  0.0000000
      2  O          8.0     -0.0000017  0.0000000  0.0000000

      MAXIMUM GRADIENT = 0.0000017      RMS GRADIENT = 0.0000010
1 ***** EQUILIBRIUM GEOMETRY LOCATED *****
COORDINATES OF ALL ATOMS ARE (ANGS)
      ATOM      CHARGE      X          Y          Z
-----

```

Find: LOCATED line 1278 --93%-- Select All

1 result Parameters... Clear

< Input

—iii. MOPAC CHARGES = this is located below the LOCATED and gives the charge for each atom.

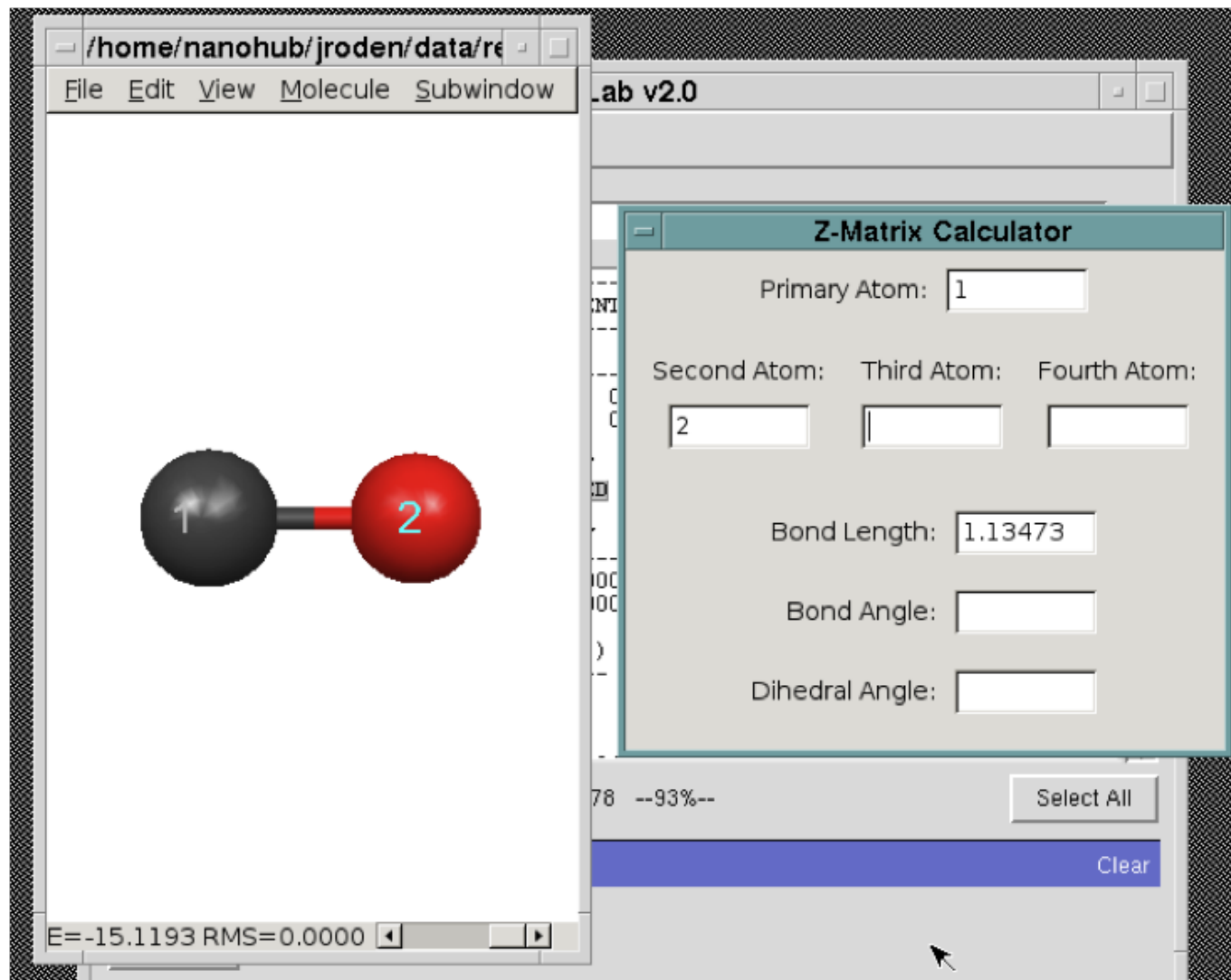
—L. In addition to searching the output file, results can also be obtained through [MacMolPlot](#). Clicking on the launchmolviewer tab at the bottom of the screen and using the pull down menu to select [MacMolPlot](#) will access this software.

—i. Select 'Open' from the 'File' menu to display all the jobs that were run in this session of QC-lab with the largest numbered file corresponding to the most recent calculation. Select the proper file and click open.

—ii.' The molecule should appear in the window with the energy written in the bottom left corner.

—iii. The bond length (and angle) can be found by using the 'Z-Matrix Calculator' from the

'Subwindow' menu. The atoms will be numbered based on the order their coordinates were input (in this case C will be 1 and O will be 2). The assigned atom numbers can be displayed on the molecule image by selecting 'Atom Number' under the 'Atom Labels' menu in the 'View' pull-down.



—iv. Close out of the 'Z-Matrix Calculator' using the hyphen bar but DO NOT close the [MacMolPlot](#) window. Click back into the QC-Lab v2.0 window.

—v. Note: [MacMolPlot](#) cannot give you atomic charge information.

3. Perform Ab Initio Calculations

—A. In the QC-Lab v2.0 window, click on the 'INPUT' button in the bottom left corner.

—B. Click on the 'Molecular Geometry' tab and verify that your input geometry is the same as you entered for the semi-empirical calculation. Alternately, you can replace this input geometry

with your optimized geometry obtained using the semi-empirical method. That may reduce the number of steps (nserch) the computer will have to use. This is a common technique for more complex structures; however, is not necessary for simple structures.

—C. Click on the 'Theoretical Model' tab and select the 'Basis Set' tab. In the 'Basis set for' pull-down select 'All-electron calculation.' This will refresh your session and switch the screen back to the 'Job Control Parameters' tab; in addition it will add more tabs.

—D. Click on the 'Basis Set' tab again and select 6-31G from the 'Basis Set' pull down.

—E. Press the Simulate button.

—F. When your job has finished running, an image of the molecule will be present on the screen. The output log can be accessed in the same way it was in the semi-empirical calculation. However, you need to search for slightly different words using the 'Find' function.

—i. LOCATED = will take you to the region in the output where you can easily find the optimized coordinates, bond lengths, nserch, and total wall clock time.

—ii. TOTAL MULLIKEN = will give you the charge on the atoms, but be careful because the TOTAL MULLIKEN is printed off for each nserch and the only charge that matters is the one corresponding to the optimized geometry at the bottom of the output.

—G. You could also use the [MacMolPlot](#) GUI to process the results, keeping in mind that you cannot get atomic charge data from it.

H₂ and N₂ Practice:

Perform the same calculations (semi-empirical PM3 and ab initio 6-31G) except replace CO with H₂ and N₂. Report the same results.

Problem 1 Questions:

- 1.) What method of calculation compared the best with experimental results?
- 2.) Which method of calculation took a longer amount of time?
- 3.) Keeping 1 and 2 in mind, why would it be more beneficial to take the geometry generated from the semi-empirical calculation and set it as an input for the ab initio calculation?

1) The time-independent Schrödinger equation is $H\psi = E\psi$ where ψ is the wavefunction representing atomic/ electronic positions, E is the energy and H is the Hamiltonian, an operator which takes the wavefunction and finds the energy.

2) The calculated energy values are absolute energy values while the experimental values obtained are typically energy differences between states. Comparison between experimental

and computational energy values can be made. How?

3) These three selections have to do with taking advantage of symmetry to determine the input geometry with the different point groups dictating what symmetry operations (mirror of plane, rotation, inversion, etc.) need to be performed on a minimal number of input atoms to obtain the whole molecule. For water you would need to enter C_{nv} , 2, and unique with the input of one O and one H. The second H would be found through the performed symmetry operations.

4) These setting are very important in telling the software what calculations to run.

Execution Type	Tells the software to run the calculation or check the input
Run Type	Tells the software what type of calculation to run (geometry optimization = find 'lowest' energy geometry, Hessian = determines more information about the potential energy surface and can be used to find vibration information, single energy = finds energy of input geometry)
SCF Type	Provides computational details, to be discussed later
Molecular Charge	Indicates if the molecules in an ion (positively or negatively charged)
Spin Multiplicity	Gives the software information on how many electrons are spin up or spin down (which has to do with the number of unpaired electrons)