Molecular Orbital (MO) Calculations

By Dr. J. Mihalick 1998; revised: J. Mihalick 2/07; J. Gutow 2/00, 2/01, 9/05, 2/09, 2/10, 1/11, 2/13

Prelab Assignment:

1. Review: Atkins & dePaula 9th ed. 10.7-10.8 (QM computations); 17.1 (dipole moments).
2. You will be given a list of assigned molecules. In your notebook draw a Lewis diagrams of each molecule.
3. Write the ground state electronic configuration of each atom.
4. Sketch the atomic orbitals which are occupied by valence electrons.
5. Find the experimental equilibrium geometry(bond lengths and angles), vibrational frequencies, and dipole moments and copy them into your notebook (See my "Useful Links"-> "Properties of Substances" page. The NIST sites "Spectral and Physical Properties..." and "Computational Chemistry ..." are a good place to start).

Introduction

The electronic structure of a molecule determines much of its reactivity. If a description of the most probable locations of electrons and their energies is available, one may be able to predict useful properties such as the molecular dipole moment, polarizability, vibrational frequencies, probability of absorption of visible light, and tendency to donate electrons in a reaction.

The wavefunctions for electrons in molecules are known as molecular orbitals. We can only find exact eigenfunctions and eigenvalues for a single atom with one electron (H, He^+, Li^{2+}). The potential energy part of the Hamiltonian operator becomes more complicated for systems with more than two charged particles (one electron and one nucleus), and no analytical solutions have been found for the eigenvalue problem.

The variational principle allows us to approximate true wavefunctions with sums (linear combinations) of trial wavefunctions. We write the wavefunction as

$$\Psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + \ldots \tag{1}$$

where ψ_i is a trial wavefunction and c_i is its contribution to Ψ. The problem is to find the set of coefficients which produces the lowest energy for the electron (bound electrons have negative potential energies, so we look for the most negative value). Since the trial wavefunctions are not eigenfunctions of the Hamiltonian, the expectation value of the energy is calculated.

$$\langle \hat{H} \rangle = \langle E \rangle = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} \quad , \tag{2}$$

where the denominator in equation 2 ensures normalization. Each of the "basis set" wavefunctions used to form the trial wavefunction is normalized, but the total wavefunction must still be normalized, putting additional constraints on the values of the coefficients. The larger the basis set, the more accurate the energy prediction will be. Since the potential energy of the system depends on the position of all other electrons and nuclei (generating the self-consistent field), an accurate molecular geometry is also necessary for a correct prediction of electronic energy. In a geometry optimization calculation, one searches for the best geometry by trying different arrangements of atoms until the energy of the system is minimized.

Electronic structure calculations have traditionally been done by physical chemists and chemical physicists with advanced degrees. The first calculations were done with pencil and paper, but computers were necessary for the calculation of properties of most interesting molecules. Computers allow us to use large basis sets, improving the predictions of geometries and energies, but there are still time and memory costs associated with a large computation. With the reduction in price of computers, many non-specialists have the opportunity to do electronic structure calculations. Software packages are marketed to the chemical industry as a tool for saving money and limiting waste by avoiding reactions that won't work. The modern programs also have excellent graphics capabilities, allowing us to view three dimensional representations of molecules and/or molecular orbitals.

This laboratory experiment is designed to teach you to be skeptical of computer output, to understand the approximations used in the various methods, and to compare different levels of theory for consistency of predictions.

You will use the computer program GAMESS[1] to do these calculations. The software includes several methods for doing calculations.

Molecular Mechanics is part of another software package you will use called Jmol. You will use this for initial guesses of the molecular structure. Molecular mechanics uses classical, not quantum, mechanics. It treats molecules as collections of classical harmonic oscillators. Average force constants for different types of bonds are derived from vibrational and rotational spectroscopy. The program adjusts atom positions to minimize the stress on the molecule. The best results will be generated for molecules similar in composition to those used to develop the average force constants (usually organic molecules). Since the calculation depends on the number of atoms, rather than the number of electrons, it can be used for large systems, including biochemicals and solvated molecules. This is a useful method for predicting molecular geometry (bond lengths and angles) and qualitative information about relative energies of different molecular conformations.

MOPAC[2] is a semi-empirical method. It uses empirical data to provide estimates of the values for two electron overlap integrals needed for calculating <**H**>. It offers four choices of Hamiltonians called MNDO (moderate neglect of differential overlap), MNDO/3, AM1 and PM3. Each is restricted to certain elements, primarily nonmetals of the second and third periods. The parametrization is derived from experimentally determined enthalpies of formation, ground state geometries, dipole moments, and ionization potentials (this gives very good geometries). These calculations are significantly faster than complete *ab initio* calculations.

Ab initio is the best level of theory. All integrals are calculated. There are still approximations since the self-consistent field model and a finite sized basis set are used. The smallest basis set is called MINI (it will give quick, approximate results). A low level of calculation is the 6-21G gaussian basis set. There are many other available basis sets, but in order of increasing size the basis sets you will use are: 6-21G, 6-31G, DZV (double zeta valence). For large molecules we also have the capability of doing density functional calculations (DFT). This is a different way of laying out the integrals and doing the calculations that is more efficient for large numbers of electrons. Also available are core potentials for doing calculations with relativistic corrections for heavy atoms. These calculations may take a long time to run. The software can calculate geometries, vibrational frequencies, electronic transition frequencies, dipole moments and many other properties.

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[1] M.W.Schmidt, K.K.Baldridge, J.A.Boatz, S.T.Elbert, M.S.Gordon, J.H.Jensen, S.Koseki, N.Matsunaga, K.A.Nguyen, S.J.Su, T.L.Windus, M.Dupuis, J.A.Montgomery *J.Comput.Chem.* **14**, 1347-1363(1993).

[2] (MOPAC 6) M. J. S. Dewar *J. Mol Struct.* **100**, 41(1983); M.J.S. Dewar, E.G. Zoebisch, E. F. Healy, J. J. P. Stewart *J. Am. Chem. Soc.* **107**, 3902(1985).

Assignment: You will have three weeks to run the calculations on your three assigned molecules and produce a web poster (report) with the following information.

For each molecule:

1. Results of your geometry optimizations using different levels of theory. This section should contain diagrams of the optimized geometry using MOPAC, three levels of *ab initio* theory and a comparison with the experimental geometry. At a minimum provide a live display of your best optimized geometry and discuss how it was chosen as the "best".
2. Live displays of the HOMO and LUMO orbitals (use your best *ab initio* results).
3. Live displays of the molecular electrostatic potential mapped on to the molecular surface using your best calculation.
4. Live displays of “partial atomic charges” (use your best *ab initio* results).
5. Dipole moment from "best" calculation and the experiment value. Note if a lower quality calculation gives an answer closer to the experimental value.

Additionally for your diatomic molecule:

1. A valence energy level diagram for your diatomic molecule similar to the diagrams shown in Atkins & dePaula 9th ed. figure 10.33. In addition to the energy level ordering each level should be flanked by a static image of the corresponding molecular orbital and should be identified as bonding, anti-bonding or non-bonding. Use your best *ab* initio results.
2. A plot of the potential energy of bond stretching at different levels of theory and a discussion of how the results vary with the basis set size.
3. Calculated vibrational frequency.

Additionally for your smallest polar molecule:

1. A table of dipole moments at each level of theory and the experimental value.
2. A discussion of how the dipole moment results vary with choice of basis set and what characteristic of the basis appears to be most important for getting good dipole moments.

Additionally for your small polyatomic and your aromatic compounds:

1. Either a copy of or link to an IR vibrational spectrum.
2. Try to identify the primary motions associated with each of the peaks in the experimental vibrational spectrum.
3. Provide animations of each of these modes as well.

Additionally for your aromatic compound:

1. Table of predicted significant UV-Vis absorption peak positions and the experimental peak positions.
2. A discussion of how the predicted UV-Vis peak positions compare with the experimental values.

The web site should also include the following sections of a traditional lab report:

1. Title, author list and a brief abstract.
2. An introduction summarizing the kinds of calculations that will be reported and on what molecules.
3. A conclusion, discussing when you think computational results can be useful and when you think they are not useful.
4. References to all sources of information you used including references to the software used for calculation and manipulation of the data.

Guide for the calculations: Some of the necessary computations will take the computer significant amounts of time; thus the order you do things in is important. Use this outline of what you should try to accomplish in lab each week as a guide. Specific instructions for getting each of these pieces of data from the software are provided in the instructions for each piece of software that follow this list.

Week 1:

1. Learn how to use WxMacMolPlt to build molecules. Use the instructions found at: http://www.scl.ameslab.gov/MacMolPlt/Manual_pages/builder.html. This link is also available in the laboratory section of the class web site. Before starting make the following menu selection so you can see your atoms: *>View>Display Style>Ball and Stick*. A good molecule to practice on is making ethane in both the staggered and eclipsed formation. You will have to pay attention to how you rotate a functional group about a bond in the "Modifying Subgroups" section. Also try converting your ethane to ethylene by deleting all the hydrogens (in the *Builder* menu) and then right-clicking on the carbons to change their coordination number to three. Then you can add the hydrogens back in.
2. Using wxMacMolPlt build your molecules. Take advantage of the prototypes available in the *Builder Tools*. Save each molecule in a directory with an informative name. Make sure to add the appropriate extension to the filename, <name>.cml.
3. Open each .cml file in Jmol. Perform a molecular mechanics optimization on the structure. Save the new coordinate results as .xyz files. See the specific instructions for Jmol, below.
4. Use wxMacMolPlt and the molecular mechanics geometries (.xyz files) to generate AM1 & PM3 geometry optimization input files (.inp) for the GAMESS computation package. Use GamessQ to submit these to the GAMESS package.
5. When the calculations finish: Use the *View Logs* item in the *Jobs menu* of GamessQ to check the end of the log files of each calculation; if the calculation worked, save the results in each molecule's directory (save to folder) using the *Jobs menu* or the pop-up you get from right-clicking. Use informative names that tell you something about the level of theory.
6. Open the result files (.log) for each calculation that worked in wxMacMolPlot and make sure that the geometry optimization completed (see below for details, but under default conditions it should stop before 20 steps are completed).
7. For your diatomic molecules optimize the geometry at each level of theory. You can generate all the input files at once using wxMacMolPlt from your AM1 or PM3 results (.log files) and queue them at the same time.
8. While the diatomic calculations are running generate the geometry optimization .inp files for the lowest levels for your polyatomic and aromatic compounds from your AM1 or PM3 results and add them to the calculation queue. These will take longer to run. Keep checking to see when they finish, so that you can start the next level of calculation as quickly as possible. You will generate the input files for higher levels of theory using the results from the previous lower level.
9. While waiting for the polyatomic and aromatic calculations check that the diatomic calculations worked by looking at the .log file in GamessQ and in wxMacMolPlt as in steps 5 & 6.
10. Use Jmol to view the molecular orbitals (MOs) from your diatomic calculations See the "Displaying Orbitals" in the "Make a Web Page: 1. Familiarize yourself with Jmol" section of the tutorial at: http://www.uwosh.edu/faculty_staff/gutow/Jmol_Web_Page_Maker/Export_to_web_tutorial.shtml. The tutorial is also linked from the class lab page. Don't forget that the optimized geometry is in the last frame. How do the MOs compare with your mental picture of Sigma and Pi bonds?
11. As soon as the lowest calculation for the polyatomic or aromatic compound finishes, check that it ran properly (just like steps 5 & 6) and then use the results to generate an input file for the 2nd

larger basis set. Add the new .inp file to the calculation queue. Keep checking for this to complete so that you can start the 3rd and last optimization.

12. When the 2nd larger basis set calculation completes, check that it ran properly (like steps 5 & 6) and use the results to generate an input file for a geometry optimization using the largest basis set. Add this new .inp file to the calculation queue.
13. While waiting for calculations to complete use Jmol to compare the geometries from completed calculations with the experimental ones you found. See the "Make and Show Measurements" in the "Familiarize yourself with Jmol" section of the tutorial.
14. Using wxMacMolPlt and the optimized geometry results from your largest basis set for each molecule, generate .inp files for vibrational frequency calculations. Add them to the calculation queue. If they don't complete before you leave you can check them and store the results the next day.
15. If time allows start on activities listed in week 2.

Week 2:

1. Continue any calculations not completed last week.
2. Extract the dipole moment from the .log files. You will probably have to open them in TextEditor or Console and search for “Debye”, the units on the dipole. Make sure to keep track of which level of theory gave which values.
3. For your smallest polar molecule try to generate better dipole moments by redoing your geometry optimizations (use the results at each level as the starting point), with diffuse functions. See below for instructions.
4. Generate the potential energy surface versus bond length for your diatomic molecule. Use your best *ab initio* results as the starting point and do the calculation at the 6-21G, 6-31G and DZV level.
5. Use the optimized results at each of the three levels of *ab* initio theory to generate .inp files to calculate UV-Vis spectra of your aromatic compound. Add these to the calculation queue. These are some of the longest calculations you will be doing.
6. When the potential energy versus bond-length calculations finish extract the potential energy surfaces from you files using the Igor tool provided by your instructor.
7. While calculations are running learn how to use Jmol and a Web editor to make web pages with live 3-D molecules. Work your way through the Jmol tutorial that you looked at pieces of last week.
8. Use Jmol to visualize the molecular vibrations and compare the calculated transition energies with those observed in experimental spectra.
9. Begin developing your web site. To make it easier to set things up create a folder for your web site and save the web page in that folder with all the images you wish to include in this folder. Images should be saved as .png files when possible.
10. If time allows work on things listed for week 3.

Week 3:

1. If you have any calculations left to do, get them running as soon as possible.
2. Complete the Jmol development of your web site. Although it would be nice, you do not have to get all your written work in before the end of class. You can work on this like a normal report outside of class.

Software Instructions

MacMolPlt[3]:

Drawing molecules and generating starting points for MOPAC and ab initio calculations.

Drawing molecules:

1. It is easiest if you set the display to Ball and Stick using the menu selection: *>View>Display Style>Ball and Stick.*
2. If the toolbar is not showing at the top of the drawing window turn it on by typing ⌘I.
3. If the build tools window is not open use ⌘T to open it.
4. Select the atom or prototype you want to add and click in the window where you want it to appear. More details available at the wxMacMolPlt web site: http://www.scl.ameslab.gov/MacMolPlt/Manual_pages/builder.html.
5. Save the molecule when done as a .cml file.

Setting up a geometry optimization:

1. If starting from a previous calculation locate the geometry you want to start with. This is also how you check if an optimization worked.
   a. Open the .log file in wxMacMolPlt.
   b. From the *Subwindow* menu select *Energy Plot.*
   c. If the number of energy points is equal to the step limit (default is 20), the geometry optimization **failed to converge** and should be run again starting from the best geometry found.
   d. Click on the dot of lowest energy (usually the last). This will take you to the lowest energy geometry found, which you will use as your starting point.
2. Bulding the input file:
   a. Make sure you are looking at the geometry from which you want to start your search (step 1).
   b. From the *Subwindow* menu select *Input Builder*. Select categories from the list at left.
      1) *Basis*: in order of increasing basis size select from 6-21G, 6-31G and DZV.
      2) *Control*: set the *Run Type* to *Optimization*; set *SCF Type* to *RHF* for molecules with all paired electrons (most) and *UHF* for molecules with some unpaired electrons (some molecules with an even number of electrons still have unpaired electrons); set *Exe. Type* to *Normal Run*; check the *Molecule Charge*.
      3) *Data*: set *Coord. Type* to *Unique cartesian* and pick an informative *Title.*
      4) *System*: default values are fine.
      5) *MO Guess*: set *Initial Guess* to *Hückel*.
      6) *Summary*: read through to make sure everything seems correct.
   c. When everything is the way you want it click on *Write File*. Store the file in a unique folder with your molecule's name and give the file a descriptive name, (e.g. acetone_321G_geo_opt.inp). The extension must be **.**inp and the name of the file cannot contain any spaces**.**

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[3] Bode, B. M. and Gordon, M. S. *J. Mol. Graphics Mod.*, **16**, 133-138(1998).

Setting up vibrational frequency calculations:

1. Vibrational frequencies calculations should start at the optimized geometry of the molecule.

2. Do the vibrational frequency calculation at the same level of theory as the optimization was done at.

3. Building the input file:

   a. Open the .log file in wxMacMolPlt and make sure that you are looking at the optimized geometry (usually the last frame, you can use the slider bar at the bottom of the window).

   b. From the *Subwindow* menu select *Input Builder*. Select categories from the scrolling list at left.

      1) *Basis*: should already contain the basis set that was used for the geometry optimization.

      2) *Control*: change *Run Type* to *Hessian*.

      3) *Hess. Options*: choose *Numeric* Method (vibrational analysis should be checked).

   c. When everything is the way you want it click on **Write File**. Store the file in a unique folder with your molecule's name and give the file a descriptive name, (e.g. acetone_321G_vib.inp). The extension must be **.inp.**

Improving dipole moments by adding diffuse functions:

1. Open the .log file for an optimized geometry calculation at the level of theory you wish to use in wxMacMolPlt. Make sure you are looking at the optimized geometry.

2. Building the input file:

   a. From the *Subwindow* menu select *Input Builder*. Select categories from the scrolling list at left.

      1) *Basis:* set the number of heavy and light atom polarization functions to something greater than zero. You probably want to run the calculation a number of times with different numbers of diffuse functions. If your molecule contains hydrogens select "Diffuse s-shells on hydrogens".

      2) *Control*: set the *Run Type* to *Optimization*; set *SCF Type* to *RHF* for molecules with all paired electrons (most) and *UHF* for molecules with some unpaired electrons (some molecules with an even number of electrons still have unpaired electrons); set *Exe. Type* to *Normal Run*; check the *Molecule Charge*.

      3) *Data*: set *Coord. Type* to *Unique cartesian*.

      4) *System*: default values are fine.

      5) *MO Guess*: set *Initial Guess* to *Huckel*.

      6) *Summary*: set the *Title* to something descriptive

   b. When everything is the way you want it click on *Write File*. Store the file in a unique folder with your molecule's name and give the file a descriptive name, (e.g. acetone_321G(d,p)_geo_opt.inp). The extension must be **.**inp**.**

2. After the calculation has run you can find the dipole moment by searching for "Debye" in the .log file.

Setting up potential energy versus bond length calculations:

1. Open the .log file for an optimized geometry calculation at the level of theory you wish to use in wxMacMolPlt. Make sure you are looking at the optimized geometry.

2. Building the input file:

   a. From the *Subwindow* menu select *Input Builder*. Select categories from the list at left.

      1) *Basis*: all settings should be the same as the calculation you opened.

      2) Control: set the Run Type to Surface. Everything else should be the same as for the file you opened.

      3) *Data*: same as for the file you opened.

      4) System: default values are fine.

      5) *MO Guess*: set *Initial Guess* to *Huckel*

      6) *Summary*: set the *Title* to something descriptive.

   b. When everything is the way you want it click on *Write File*.

3. Open each input file in a text editor (try TextEdit) and add some extra lines to the file.

   a. Add the following text to each .inp file just after the $CONTRL line

      $SURF IVEC1(1)=2,1 IGRP1=1 DISP1=0.1 ORIG1=-1.0 NDISP1=100 $END

      ***make sure that there is one blank space before the first $.

      ***for your information:

      IVEC1(1) = first atom, second atom (First atom is origin of translation vector)

      IGRP1 = atoms in group 1 that are to be translated (must include 2nd atom in IVEC1).

      DISP1 = step size for displacement

      ORIG1 = change from equilibrium geometry provided (make sure you don't subtract to much)

      NDISP1 = # of points (steps) to do

   b. Save the .inp file with an appropriate name.

4. Run the calculation using GamesQ

5. Use the IGOR macro provided to load the data in. You can then plot it using normal IGOR procedures.

Setting up UV-Vis transition energy calculations:

1. Using wxMacMolPlt write a .inp file of the best geometry for your molecules set up to do a *Single Point Energy* calculation (in the C*ontrol* section) at all the levels of theory you wish to do.

2. Open each input file and add some extra lines to the file.a)

    a. Start by loading each .inp file into a text editor (try "TextEdit")

    b. Add the following text to the .inp file just after the $SYSTEM line:

    ```
     $CONTRL CITYP=CIS $END
     $CIS NSTATE=10 $END
    ```

    ***make sure that there is one blank space before the first $ on each line.

    ***Note that the keyword is $CONTRL not $CONTROL

    ***Note that you can set NSTATE > 10, but that is a lot of excited states to look at and probably unnecessary.

3. Save the .inp file.

4. Run the calculation using GamessQ.

5. Search for "CIS TRANSITION DIPOLE MOMENTS" in the .log file to find the beginning of the listing of transitions. You are interested in transitions from the ground state. The transition energy is given in many different units. Pick your favorite or convert to your favorite. The relative intensities of the transitions are given by the oscillator strength. If the program gives you a zero because of limited significant figures you can calculate their ratios yourself because oscillator strength is proportional to $^{k}|\mu_{fi}|^2$, where ^{k} is the frequency of the transition and μ_{fi} is the transition dipole between the initial and final state. Larger oscillator strength implies a stronger transition.

You can examine the results of calculations using wxMacMolPlt, but we will use **Jmol** to do this. Instructions for looking at orbitals and geometry in wxMacMolPlt may be found at: http://www.scl.ameslab.gov/MacMolPlt/MacMolPlt_Manual.html.

Jmol[4]:

Molecular mechanics, visualization of results, saving pictures and web page authoring.

Molecular mechanics geometry optimization:

1. Open the molecule file (probably a .cml created by wxMacMolPlt).
2. From the *File* menu open the *Console*. Move the console window so that you can see it and the molecule window.
3. Right-click in the molecule window to open the pop-up menu. Select *Optimize Structure* from the *Computation* submenu. In the console you will see a list of energy steps as the program adjusts the molecule's conformation.
4. Repeat step 3 until the optimization converges in less than 10 steps.
5. Save the optimized geometry as an .xyz file:
   a. Click on the *History* button in the console. This will display information about the file that was loaded.
   b. Select the full path name to the file (everything following "file:" until the next quotation mark. For example: "/User/Student/Documents/benzene/benzene.cml".
   c. Type <cntrl>C to copy this path.
   d. At the $ prompt type "write" followed by a quotation mark.
   e. Type <cntrl>V to past the path after the quotation mark.
   f. Backspace to change the .cml extension to .xyz.
   g. Close the quotation marks.
   h. Hit return. You should get a message saying the file was successfully written to the same directory as the .cml file.

Saving the Jmol view as a static image:

1. In the *File* menu select *Export Image...* from the *Export* submenu.
2. Navigate to the directory in which you want to save the image.
3. Set the image type to .png
4. Edit the filename (don't remove the extension, but make sure it matches the file type you chose).
5. Click on the *Save* button.

Instructions for visualizing results, labeling your molecules and making web pages are in the tutorial found at: http://www.uwosh.edu/faculty_staff/gutow/Jmol_Web_Page_Maker/Export_to_web_tutorial.shtml. The link is also available on the class web site.

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[4] The Jmol Development Team. http://www.jmol.org, accessed January 2011.

GamessQ:

Queuing up your calculations to run on your own computer.

Adding a computation to the queue:

1. Bring the GamessQ window to the front or start the program.
2. Click on the "+" button in the tool bar.
3. Navigate to the appropriate input file and click the *Open* button. This will add the calculation to the end of the queue. When the previous calculation completes it will start.

Checking the .log file to make sure the calculation ran properly:

1. Select the job you want to examine from the list.
2. Using either the pop-up or the *Jobs* menu select *View Logs*.
3. Scroll to the bottom of the .log file and look for a lines indicating:
    a. execution of gamess terminated normally;
    b. and that ddkick.x exited gracefully.
    c. If you do not already know how to deal with the error check with your instructor.

Saving the output:

1. Select the job you want to save from the list.
2. Using either the pop-up or the *Jobs* menu select *Save Output to Folder*.
3. Navigate to the folder you want the output saved in and click on the *Choose* button. This will write a .log file to this directory. The name will be derived from the .inp file name.