

Quantum Chemistry with Ghemical: A Guide

To give you a break from the “classroom/lecture” environment, and allow you to explore the world of computational chemistry, we'll next do calculations on some very simple multielectron systems that cannot be solved with a paper & pencil! We'll need a computer. In fact, you will possibly be able to use your own laptop .

These problems will explore the atomic and molecular orbitals of polyelectronic atoms, diatomic molecules, and some small molecules. We will solve these problems using **Ghemical**, a free, open-source quantum chemistry software package. This software is available for Windows and MAC/OS, but in these operating systems it does not come with the quantum mechanical “engine” that allows us to do the calculations here. In fact, most serious computational chemistry is done on supercomputers, and as a result most of the software is available most readily on the Unix operating system. We will use Linux, a flavor of Unix. What's that? You don't use Linux?

Fortunately, we can make most PC computers run Linux temporarily by using a Linux LiveCD (it's actually a DVD). This is a special DVD that can be used to start up the computer, *instead of using the hard disk on the computer*. No changes are made to the computer's hard drive, nothing is installed on the computer at all. We'll be using a “flavor” of Linux called Linux Mint 13, and you'll be given a LiveCD with all the software on it. (Yes, you may keep it if you wish, both the software and Linux Mint itself are completely free and open-source.) **You don't have to use your own computer-- the University PCs will run Linux from the LiveCD.**

Starting Linux from the LiveCD:

1. If the PC is off, turn on the PC, and immediately open the CD drive. Don't wait for Windows to load. If Windows is already running, see step 2.
2. Insert the DVD into the drive, and close it. If Windows was already running, restart the computer.
3. The computer should begin to read the DVD and you should see a screen saying “Starting Linux Mint”. Starting Linux from the CD may take a few minutes, wait until you see the “Maya” desktop and have a mouse cursor. **Congratulations, you're running Linux Mint.** See the following pages for instructions in using the Ghemical software.
4. If Windows has already started to load by the time you get the DVD in the drive, wait until Windows starts up, leaving the DVD in the drive. Once Windows has started, ask the computer to “Restart”. This time, the DVD should get recognized. Go to step 3 above.
5. If Windows keeps starting even with the DVD in the drive, then the computer is not set to boot from the DVD drive. Ask your instructor for help, unless you know how to use the BIOS boot setup menu....

Exiting Linux and the LiveCD:

1. Exit any app(s) you have open, though this isn't absolutely critical. **All the work you have done in Linux, and all settings you have made, will be lost when you exit Linux** because Linux is not using your computer's disk at all-- only the memory, which will be cleared when you leave Linux, leaving your computer exactly as it was before you inserted the DVD.
2. Click the “gear” icon in the very lower left of the Linux Mint desktop.
3. Select “Quit”
4. Select “Shutdown” if you want to power off your computer. Select “Restart” if you want to leave the computer on, but go back to your normal operating system.
5. When prompted, remove the Linux LiveCD from the drive, and press enter.
6. That's it. The computer will either power down, or start up again in its “normal” operating system, depending on what you requested.

Exploring Linux Mint 13

If you're curious you can feel free to explore Linux Mint. It operates similarly to MAC/OS and Windows (in fact MAC/OS is built on Unix, so it's a sister OS to Linux). You will find the Firefox browser, and you may find that Linux has correctly configured your internet connection automatically. Yes, it's legit, and people use it as their main computer environment. But as you work with Linux, there are two things you should know:

Scary Warning Number 1:

Don't click on the "Install to Hard Drive" icon, unless you plan on actually replacing your operating system with Linux! If you accidentally click this, you'll be given more warnings and a chance to bail out, (and it's possible to have two operating systems on one computer) but it's best not to do this unless you really, really know what you are doing. If you do want to install Linux, get a more up-to-date version, as Mint 13 "Maya" has been replaced by another more up-to-date version.

Not-Very-Scary Warning Number 2:

You will probably figure out all kinds of things you can configure and set (your Internet settings, desktops you like, bookmarking webpages, etc.). Feel free, BUT: Everything you set, change, save, etc. while you are using the LiveCD WILL ONLY BE STORED IN MEMORY (because Linux is not using your hard disk) and so when you restart Linux you will have to configure all of this all over again. If you want to permanently set stuff, you'll have to actually install Linux. (See Warning #1 though!)

Starting the Ghemical Software

We will be using the Ghemical software for our quantum chemistry calculations. Here's how to get it started (it's pre-installed on your DVD):

1. Right-click anywhere on the desktop.
2. Pick "Open in Terminal".
3. At the prompt that appears, type **ghemical** and press "enter".
4. You should be greeted by a new window. Click the "+" sign in the upper right corner of the window to "maximize" the window on your display.
5. Below the ghemical window is a "toolbar" similar to those in MAC/OS and Windows. Right click on the toolbar and pick "Add to Panel...".
6. Scroll down on the list that appears, and click on "System Monitor". Click "add", then "close". You should have a little scrolling bar graph in your desktop panel now. This indicates how "busy" your computer is. This "applet" will come in handy as you are using the ghemical software, because when the software is busy computing, it will seem as if nothing is happening. The bar graph will assure you that your computer is working on the problem.

Exiting the Ghemical Software

1. You will probably figure this out for yourself! But here's the low-down: Click the "x" in the upper right corner of the Ghemical window. It should close, and leave you with only the terminal window you opened when you started it.
2. Type `exit` at the prompt and press enter. (Or click "x" in the terminal window's upper right corner).
3. That's it.
4. If you're done, see the section above on "Exiting Linux".

Drawing Molecules:

Got Ghemical? Good. Before you can compute anything, you have to draw it. It's fun, and three dimensional.

1. Left-Click on the "pencil". That's the "draw a molecule tool".
2. The third icon from the right in the top bar? That's supposed to be a periodic table. Left-Click it, and you can pick what element you want to draw.
3. Left-Click once in the black drawing window to drop an atom of that element on the desktop.
4. To draw an atom and bond it to another atom:
 - o Pick the element you want to add from the periodic table.
 - o Pick the bond order you want (single, double, triple, or conjugated) by left-clicking the bond order button in the toolbar.
 - o Left-Click on the atom you want to bond the new atom TO, and then while holding the left mouse button, drag to where you want the new atom to go. Let go of the left mouse button to finish adding the new atom.
 - o The eraser gets rid of atoms you didn't mean to draw. What else?

Drawing Hints:

- Usually, computational chemists do not draw in the Hydrogens on their molecules by hand. To add these, right click on the black background anywhere, choose "Build", "Hydrogens", "Add". Usually the computer gets this right, but you can use the eraser and pencil to fix things up.
- Don't worry about making the molecule look right. Bond lengths, bond angles, etc. All of this will get fixed up by the computer. Just connect everything the right way, no matter how lopsided your rings are, etc.

Viewing What You Drew:

- The various toolbar icons let you do a lot with viewing your molecule. The twisty arrow icons and the magnifying glass convert your mouse to translate, rotate, or zoom your molecule. (Switch to rotate, and use your left mouse button to spin your molecule-- if you let off the mouse button while spinning it, it will keep on spinning forever, pretty fun!)
- Right-click the black background select "Render", and then "Render Mode". You can change the way the molecule appears. But for what we will be doing the Ball and Stick (default) rendering is probably best.

Another Warning Before We Get Started:

- It is entirely possible to "crash" Ghemical. Usually what happens is that it just disappears (sometimes the terminal window, too). It's OK. Welcome to the world of scientific software. There will be some things you just can't "do" without crashing. It won't hurt anything. Just restart ghemical and don't do that thing again. At least not quite in the same way....

Printing Your Molecules:

- There may be a "Take Screenshot" app under your Menu/Accessories buttons (lower left corner of the Linux Desktop). You MAY be able to save these to a network drive or USB. If not, there's always your cell phone camera. Or ask your instructor for help. All you have to do for the course is write down your results, though.

There. I drew my molecule. Now What?

Now the fun begins. Here is a tour of what you may want to do. What you actually do is up to you and what the problem calls for. Best to go in this order at first, you'll see why. Later you'll know where you can change up the steps.

Rough Positioning of Atoms:

Your molecule is probably misshapen because a mouse is not a precision drawing instrument. We'll first make a very rough fix to the positions of the atoms.

1. Click on the "MM" toolbar button.
2. It should say Tripos 5.2, under the "all MM" tab. This means use an approximate (classical) method called "molecular mechanics" to roughly position the atoms. If not, click the "all MM" tab, and select Tripos 5.2.
3. Click OK to close the window.
4. Right click on the black background and select Compute.
5. Choose Energy. (Ignore the numbers that get displayed....)
6. Right click the black background again and select Compute again.
7. Choose Geometry Optimization...
8. Click OK to accept the defaults.
9. Your molecule should look a lot closer to the "correct" geometry now. Conjugated bonds may sometimes fail with MM optimization, in this case use MOPAC7/MNDO as described in the next section.

Fine Positioning of Atoms (if energies are not critical, you can skip this step):

Now that your molecule is close, if you wish, you can "fine tune" it using Quantum Mechanics. This will use the potential energy fields to move the nuclei of the atoms into roughly correct positions, using a very approximate (and old-school) semiempirical quantum mechanical model called MOPAC7/MNDO.

1. Click the "MM" toolbar button.
2. Click the "all QM" tab (all quantum mechanics)
3. Click on the pull down selector and pick MOPAC7/MNDO (first on the list).
4. Click OK to close the "MM" dialog window.
5. Right click on the black background and select Compute.
6. Choose Energy. (Ignore the numbers that get displayed....)
7. Right click the black background again and select Compute again.
8. Choose Geometry Optimization...
9. Click OK to accept the defaults.
10. Your molecule is now tweaked well enough to go on to more sophisticated calculations.

Molecular Geometry (Bond Lengths & Angles):

If you wish to measure the bond distances, now that your molecule's nuclei have been positioned fairly well, you can click on the measurement tool (it looks like two arrows pointing between dots). Then left-click on two atoms for which you wish to measure the intermolecular distance (bond length). The distance (in nanometers) will be displayed in the text window just below the chemical drawing window. For polyatomics with at least three atoms, selecting three atoms will give you a bond angle in degrees.

Hartree-Fock Orbital Energies

Now that your molecule has a geometry, you may wish to compute the ground-state and orbital energies using Hartree-Fock methods (discussed in class). Here are the steps:

- 1. Pick a basis set.** You'll remember that this is the number and type of functions that are used to represent the individual atomic orbitals (AO). If you're working with a single atom (in which case all the stuff about geometry above was pretty much unnecessary!) then the AOs are as far as your calculations will go. If you're working with a molecule, then the AOs will themselves form the basis set for your molecular orbitals (MOs). But either way, you have to start with a basis set. To pick your basis set:
 - Click on the MM icon to set up your computational engine.
 - Click the "all QM" tab (but it should be selected already).
 - Click on the "Select the Engine Class" button, and pick one of the **eng1_qm_mpqc** options. These begin with STO-3G (Slater-Type Orbital, 3 Gaussians) and become increasingly more sophisticated as you go down the list. See the lecture notes for descriptions of each, but here are some guidelines:
 - The more gaussians, the more precise. The fewer gaussians, the faster the computations and the less likely you are to run out of memory (and crash Gchemical) with big molecules. So STO-3G is less precise than STO-6G.
 - The STO-type basis sets work best with spherically symmetric orbitals. They do more poorly when your molecule has more pi bonds than sigma bonds.
 - The split-valence basis sets (everything including and after 3-21G) are named using three numbers like (x-yzG) where x is the number of gaussians used to model the core electrons, y is the number of gaussians used to model the inner valence electrons (like the 2s electrons in C, and z is the number of gaussians used to model the outer valence electrons. Again the more gaussians, the slower the calculations, but the better the results.
 - The basis sets with a * include more "d" orbital character, which allows electron density to move farther from the nucleus. This is often useful with really highly polar bonds, as in HF, etc.
- 2. Select the Total Charge on the atom or molecule you are working with.** If this isn't right, of course the number of electrons in your atom or molecule will be completely wrong.
- 3. Ignore the Spin Multiplicity window** (it's grayed out anyway). **In this version of Gchemical, we are not allowed to have any unpaired electrons.** This is an issue for some paramagnetic molecules like O₂ but they will not be included in our problems.
- 4. Click OK** to close the Setup Window.
- 5. Right-click on the black background, select Compute, and then select Energy.** This is necessary to complete the Hartree-Fock calculations.
- 6. About the "kJ per mole" number** in the text window: This number is not a standard energy of formation, but the energy change in going from neutral ATOMS (not elements in their standard state) to the finished molecule you drew. You *can* approximate ΔH for a reaction using these numbers, but you must calculate all products' and reactants' energies in Gchemical using the same basis set in each case. Solvation energies are of course not included since your molecule is in a vacuum.
- 7. Look in the Terminal Window** (this is why we opened it in the first place).
- 8. The Hartree-Fock Self-Consistent Field energy is shown as the "total scf energy" in the terminal window.** The units of energy are Hartrees (Ha). 1 Ha = 27.211 eV.

9. Other useful information in the terminal window after an energy calculation is:
- The number of Gaussians in the basis set is shown as **n(basis) = xxx** where xxx is a number. This is good measure of how sophisticated the calculation was. The more gaussians, the more sophisticated.
 - The line saying **HOMO is n A = m** is telling you that the Highest Occupied MO is number (n) and that its energy is equal to m (units are Hartrees = 27.211 eV) Koopman's Theorem states that this energy is pretty close to the first ionization energy.
 - The line saying **LUMO is n A = m** is telling you that the Lowest Unoccupied MO is number (n) and that its energy is equal to m (units are Hartrees again). The LUMO *would* be the first excited state, except that it is usually too high because of the Hartree Fock assumptions described in lecture.

Orbital Energy Diagrams:

Now that you've calculated H-F energies, Ghemical will draw a nice energy level diagram for you if you follow the procedure below.

1. Right click on the background of the drawing window.
2. Select Render.
3. Select Views
4. Select Create
5. Select Energy Level Diagram.
6. You will need to use the Pan and Zoom tools to actually zoom in on the energy levels. The yellow arrows are supposed to be electrons with their spins. The numbers by each level are the energies in Hartrees. Remember that Ghemical will not handle unpaired electrons, so if your molecule or atom should have had unpaired spins, it will lie to you.
7. Notice that the lowest energy MO is numbered zero, and the energies increase from there.
8. Notice that the Highest Occupied Molecular Orbital (HOMO) should have a number that corresponds to the (n) displayed in the terminal window as described above. The LUMO also...
9. If you want to plot a particular MO, note its number for the steps that follow.

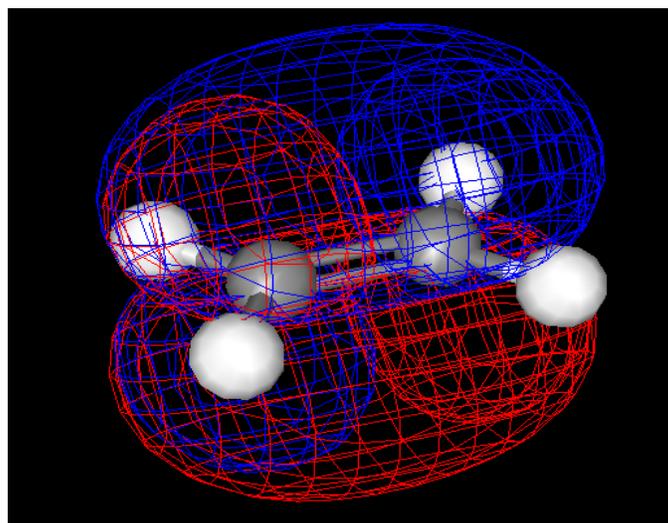


Illustration 1: MO Surfaces for Ethene

Plotting Orbital Surfaces, ESP Surfaces, and Electron Density Surfaces :

This is one of the best things about Gchemical. You must have chosen a basis and computed the H-F energies, and you must know which orbital number you want to view. Then follow these steps:

1. Right-click on the black drawing background.
2. Select Set Current Orbital.
3. Click OK to acknowledge the annoying instruction box.
4. Replace the "X" in the window with the number of the orbital you want to plot, then press "Execute".
5. Right-click on the black drawing background.
6. Select Objects.
7. Select Molecular Orbital Surface, ESP Surface, or Electron Density Surface, as you wish.
8. Click Execute to accept the default values in the box.
9. You should now see the "system activity" bargraph in your Linux toolbar spike up, showing that the computer is busy. Gchemical will seem to have "hung" or "stuck" but it's actually busy computing. Wait.
10. In a few minutes, the orbital surface should appear, and the bar graph will drop to normal. You can now rotate, zoom, and view the requested surface.
11. To delete a surface when you are done, click the Project View tab on the main Gchemical window.
12. Right click the surface (at the bottom of the object list), and select "delete object".

Advanced users may want to alter the default MO surface rendering. A list of the "add surf2" parameters is given at the end of this guide.

Saving Files, etc:

The Linux Operating system on the LiveCD is not using your computer's hard drive at all, and so it has no place to really save anything. For this reason, Gchemical will "let" you save files, but they will disappear when you exit Linux. You *maybe* able to save files, though, if you plug in a USB drive to the computer while it is running Linux. The files may then be saved to the USB drive and recalled later in Gchemical for another work session.

All that is really saved, however, is the *nuclear positions* of the atoms in your molecule, and perhaps the calculation engines you have chosen (the basis functions, etc.). The orbitals themselves are not saved, and have to be recalculated each time you wish to plot them again. If you are able to use the Linux "screen shot" files (they are in the png format) then you may be able to export pictures of your orbitals to your USB drive once you have left Linux. See your instructor for questions on this.

Happy Computing!

There are many other functions in Gchemical that are not described here, and there are other free software programs that allow construction and modelling of very much larger molecules (DNA and proteins) both in Linux and in Windows. Your Linux LiveCD may contain two such programs: BallView and Avogadro. But if not, you can find Windows or MAC/OS versions of these also. They do not run quantum mechanical calculations, but instead use a simplified set of rules known as **Molecular Dynamics** to be able to compute the conformation and energies of macromolecules that would be far too large for quantum mechanical methods.

Now that you know the basics of Gchemical, you should be able to tackle the computational problems assigned in the class (if you get stuck, ask your instructor for help). The main goal of these problems is to give you a sense of what computational chemistry is all about, its limitations, and its uses. And also that it is much more interesting than sitting with a paper and pencil trying to solve math problems. Thanks to the work of many computational chemists (computing the basis sets for the elements and programming the variational methods that solve the LCAO-MO work), we can use software like Gchemical with very little need to remember calculus!

Appendix: Advanced Use of Gchemical “add surf2” parameters

Poking around in Gchemical's source code implies that the following parameters may be used to change the default rendering of MO surfaces. Notice that the “add MO Surface” dialog generates a command of the form:

```
add surf2 <vf1> <vf2> <cf1> <cf2> <sscale1> <sscale2> <cscale1> <cscale2> <dim> <res> <solid> <tp> <alpha>
```

several of these parameters are useful. Below are their defaults and what they mean.

- **vf1 = mo** always for molecular orbitals
- **vf2 = unity** always for molecular orbitals
- **cf1 = red** (color 1 for wavefunctions)
- **cf2 = blue** (color 2 for wavefunctions)
- **dim = 1.5** (increase this parameter if your MO surfaces are 'cut off' for large molecules)
- **res = 50** (resolution of MO surface grid, increase for fine grid but slow calculations!)
- **solid = 0** (setting this to 1 gives a solid surface instead of grid)
- **tp = 0** (setting this to 1 gives a transparent surface. Mostly useful with solid = 1)
- **alpha = 0.5** (sets the transparency of the surface if tp = 1. Alpha = 1.0 is opaque.)

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