

# Doing your own MO calculations with HyperChem

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This note is intended to give you a tiny introduction to doing simple *ab initio* MO calculations in HyperChem. If you're serious about doing *ab initio* calculations, you'll need a lot more than this document provides, but this will get you off the ground if you just want to play around.

**The first time you run HyperChem** on a University computer, you need to go through the following procedure: Open up Windows Explorer, then navigate to

OSDisk (C:) $\rightarrow$ UofL $\rightarrow$ Hyper80 $\rightarrow$ Program

In this folder, you will find a program called `NewUser80.exe`. Run this program. You should be all set to go.

1. If you're going to look at interesting molecules, it may be necessary to turn **on** the following two options:
  - **Build $\rightarrow$ Allow Arbitrary Valence**  
This allows you to build molecules that don't satisfy the usual Lewis rules.
  - **Build $\rightarrow$ Explicit Hydrogens**  
This prevents HyperChem from adding hydrogens to complete octets.(Turning these options off is particularly useful for organic compounds. Then you only need to put in the non-hydrogen atoms, and HyperChem will use hydrogens to complete the octets, saving a lot of drawing time.)
2. Click on **Display $\rightarrow$ Labels**, then select **Symbol** under **Name**. This will show the symbol of the elements in your molecule, which is often helpful when you're drawing.
3. Now draw the molecule. Here are a few hints as to how to do that:
  - Click on the Drawing tool (the first button to the left).
  - Click on **Build $\rightarrow$ Default Element**. This will bring up a periodic table from which you can choose the element you want to put on the canvas. You can go back to this periodic table to select other elements as you're drawing.
  - Click on the canvas. This will place an atom.
  - If you want to add an atom bonded to another atom, click and drag from the first atom to the position where you want the second atom.
  - If you want to make a bond between two atoms, click and drag from one atom to another.

- You don't need to get the right bond order to do an *ab initio* calculation because all the program really cares about is the number of nuclei and the number of electrons, which are fixed by the atoms you put in and the total charge of the molecule. In theory, you don't even need to draw bonds. However, it helps HyperChem generate a better initial structure in the **Model Build** step below if you do know the bond order ahead of time. To increase the order of a bond, left-click on it. To decrease the order of a bond, right-click on it. (If you right-click too many times, you will delete the bond as well as any terminal atoms that were attached to it.)
  - If you put in an atom of the wrong kind, go back to the periodic table, select the atom you want, and then click on the atom you want to change.
4. Now click on **Build**→**Model Build**. This takes your crude drawing and cleans it up, correcting your bond lengths and bond angles to realistic starting values.
  5. Click on **Setup**→**Ab Initio**. Here, you will choose a basis set. The larger the basis set, the more accurate the calculation, but also the longer it takes to complete the calculation. For simple experimentation, the minimal or small basis sets are good enough.
    - Before you leave this dialog box, click on the **Options** button. This is possibly the trickiest part of the setup. You need to set the charge and spin multiplicity and choose the spin pairing option.
      - The charge is straightforward (zero for a neutral molecule, 1 for a singly charged cation, -1 for a singly charged anion, etc.).
      - The spin multiplicity is  $n_u + 1$ , where  $n_u$  is the number of unpaired spins in the electron configuration. The problem is that we often need to know the result of the MO calculation before we can figure out the multiplicity. I don't have much advice to give you other than to look at your orbital occupancy when you're done. The result should satisfy the usual rules for orbital occupancy. If not, it's usually because you got the multiplicity wrong.
      - If the multiplicity is 1 (no unpaired electrons), set the **Spin Pairing** to RHF. Otherwise, set the **Spin Pairing** to UHF. (You may need to select UHF before you can set the multiplicity.) UHF calculations are harder to interpret, so as a rule I wouldn't use these if the multiplicity is 1.
  6. Now click on **Compute**→**Geometry Optimization**. This will do two things: (a) Compute the electronic wavefunction, and (b) find the equilibrium (minimum energy) geometry. This is done by calculating the forces (derivatives of the effective potential energy) and moving the nuclei in the directions indicated by the forces until all the forces are close to zero (equilibrium). Every time the geometry is adjusted, the program has to go back and recalculate the electronic wavefunction,<sup>1</sup> so this takes a little time.
  7. To view the MO energy diagram and orbital occupancy, click on **Compute**→**Orbitals**. Tick the **Labels** box, which will show the orbital occupancy. Select an orbital you want to plot by clicking on its energy level. (The selected energy level will be red.) You can play with the plotting options if you like, and either click **Plot** or **OK** when you want to see the results.
  8. If, after doing a geometry optimization, you lose the ability to view the orbitals, just click on **Compute**→**Single Point**. This just recalculates the electronic wavefunction, and is very fast.

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<sup>1</sup>In fact, it's worse than that, because calculating the forces requires that we move the nuclei a little bit and see how the effective potential energy has changed. In other words, we have to do several electronic wavefunction calculations at every step.