Visualization of Atomic Orbitals

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Introductory Readings

Where are the electrons in an atom? There are a number of **models** that look to describe the location and behavior of electrons in atoms. It is important to know this information, as it helps chemists to make statements and predictions about how atoms will react with other atoms to form molecules. The model one chooses will oftentimes influence the types of statements one can make about the behavior – that is, the reactivity – of an atom or group of atoms.

One model, the **Bohr model**, describes electrons as small billiard balls, rotating around the positively charged nucleus, much in the way that planets orbit around the Sun. The placement and motion of electrons are found in fixed and quantifiable levels called **orbits**, or, in older terminology, **shells.** There are specific numbers of electrons that can be found in each orbit – 2 for the first orbit, 8 for the second, and so forth. The Bohr model is very useful for predicting the behaviors of a number of atomic properties. Unfortunately, it also has some significant problems as a model for atomic structure.
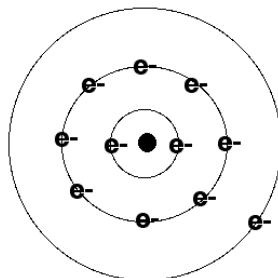
In this investigation, we plan to explore what these atomic **orbitals** look like, what orbitals do electrons occupy for each of these, and what the energies of these orbitals might be.

The main equation that is solved using molecular orbital (MO) theory is the Schrödinger equation:

$$H\Psi = E\Psi$$

This simple looking equation is anything but simple. The "H" is a very complicated **operator**. This operator, known as the "Hamiltonian" operator, calculates information about the

Models - a description of some physical object or behavior in nature. Models are often mathematical, describing the behavior of some event.

Bohr model - states that no two electrons in an atom can have the same set of four quantum numbers.

Orbits- where electrons are believed to be located in the Bohr model. Orbits have a fixed amount of energy, and are identified with the principle quantum number "n" (n=1,2,3,etc)

Shells – another name for orbits.

Orbitals – mathematical descriptions of where electrons <u>might</u> be located. Orbitals are different types (s, p, d, f) and have distinct shapes

Operator – **a** mathematical process. Common operators are plus, minus, multiplication, and square root.

"Hamiltonian" operator, calculates information about the electrons in an atom or molecule. There are four types of data that are determined by the Hamiltonian operator (NOTE: for purposes of this reading, this discussion is being presented very simplistically – the mathematics behind the Schrödinger equation and the Hamiltonian are <u>quite</u> complicated):

1. The kinetic energy (KE) of the electrons
2. The repulsive force between electrons
3. The repulsive force between nuclei (for molecules)
4. The attractive force between electrons and nuclei

The value "Ψ" represents the **wavefunction**, a mathematical entity that can be <u>correlated</u> with the probability of finding an electron somewhere in the atom or molecule. The value "E" represents the energy of the atom or molecule. From this energy value, we can determine a wide variety of other properties and characteristics of the atom or molecule.

Note that the value "Ψ" reappears on the right-hand side of the equation. This is because this version of the Schrödinger equation is an **eigenfunction**, a special type of mathematical equation. The value generated for E is known as an **eigenvalue**. For purposes of this lab, the mathematical mechanics are not important.

In this activity, we wish to determine the location and energy of each electron in a particular orbital. By now you should be familiar with the "s, p, d, f" notation of orbitals. Each of these orbitals represents the probability of there being an electron in that location. For "s" orbitals, there can be no more than two (2) electrons in the orbital. The s orbital has a spherical shape. For "p" orbitals, of which there are three (p_x, p_y, and p_z), can hold up to six (6) electrons, two in each of the three orbitals. These orbitals look like figure of 8 balloons. Lastly, "d" orbitals have five types, for a total of 10 electrons. The shape of these five orbitals is something you have to see to understand!

What, then, do these orbitals really look like, and can we solve Schrödinger's equation to find the energy and orbital type of each of the electrons? It is likely that you are familiar with **electron configuration** notation. For example, carbon, with 6 electrons, has the electron configuration of:

$$1s^2 2s^2 2p^2$$
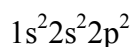
Wavefunction – a mathematical description of the electrons in atoms and molecules. Analogous to orbital.

Eigenfunction – in mathematics, a special type of mathematics function in which the function being operated on is returned as part of the answer (multiplied by a constant known as the **eigenvalue**)

Electron configuration– a notational system used in chemistry to describe where each of the electrons is located in an atom. The notation includes the name of the orbital (s, p, d, f) and the number of electrons in that particular orbital.

A pictorial way of showing these electrons is:

$$
\begin{array}{ll}
\text{2p} & \uparrow \uparrow \underline{} \\
\\
\text{2s} & \uparrow\downarrow \\
\\
\text{1s} & \uparrow\downarrow
\end{array}
$$
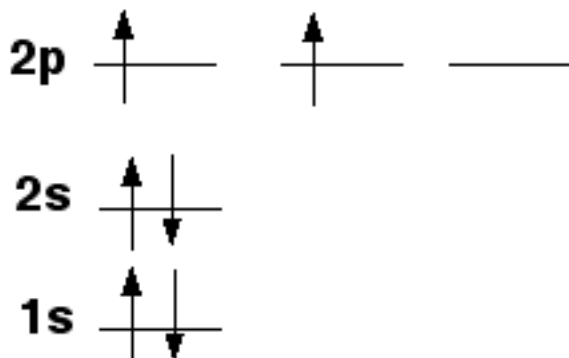
Notice that the two electrons (represented by arrows) are pointing in opposite directions. This notation is used in chemistry to convey the idea that electrons have spin, and paired electrons have opposite spin. In this lab, this will lead to the idea of "spin multiplicity", or simply **multiplicity**. The formula for multiplicity is:

$$M = 2S + 1$$

where M is multiplicity and S is the total spin. For carbon, the multiplicity is 3, otherwise known as a triplet. Why? The up arrows have a spin value of +1/2, and the down arrows have a spin value of −1/2. If you add the values of the spin, you should have S=1 (two "up" unpaired electrons). Putting 1 into the equation above should result in the value of 3, or a triplet.

At this point, you should have enough background to calculate and interpret the atomic orbitals for a number of elements.

Multiplicity – a value that describes the total spin of an atom or molecule.

Objectives of the Case Study

- To perform an atomic orbitals determination of a number of elements
- To visualize the atomic orbitals for those elements
- To determine the energy values (in units of Hartrees, where:

$$1 \text{ Hartree} = 627.15 \text{ kcal/mole})$$

Computational Approach

The following procedure will be used to generate the atomic orbitals for the following given element (or for those elements that you are instructed to determine by your teacher). The procedure for each of the atoms is the same. For each atom, you will need to determine the multiplicity of the atom prior to performing your calculation. This is best accomplished by drawing an atomic orbital diagram as we have done for carbon in the reading:

H, He, Li, Be, B, C, N, O, F, Ne, Na, Mg, Mn

Building the Atoms

1. Log into the chemistry server. (http://chemistry.ncssm.edu)
2. In the Job Manager, click on "New Job".
3. Once the molecular editor opens, click on "Open Editor" at the bottom of the window. The Java label should appear. On most machines, it will take Java a few minutes to open.
4. A drawing window should open. Under "Build", click on the [H] for [Hydrogen atom].
5. Click once in the drawing window. A [white, hydrogen atom] should appear. If more than one atom appears, select "File → New", then select "Tools → Build", then try again.
6. Under "File", click on "Close". This will close the editor window, and place your molecule in the Viewer window.
7. To move to the next step, click on the "next" arrow at the bottom right of the window.
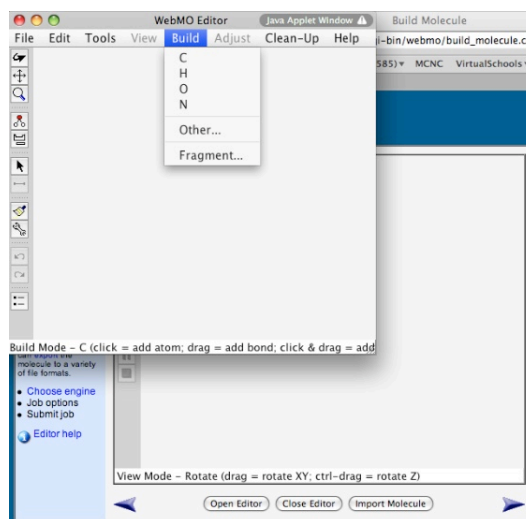
Configuring the Job

To prepare your molecule for calculation, follow these steps:

1. Choose the computational engine:→ Gaussian
2. In the Gaussian Job Option window you will need to choose the following options
   a. Job Name→ Leave as
   b. Calculation→Drop down menu, choose Molecular Orbital
   c. Theory→ Choose Hartree-Fock
   d. Basis Set→ Basic: 3-21G
   e. Charge→ 0
   f. Multiplicity→ Doublet (this value will be different for each atom)
3. Click the "next" arrow in bottom left hand corner; this should take you back to the job manger window. You should see your job running in the window or queued up either way you should start your next job. You should repeat steps 1 through 7 from the build section for the rest of the atoms listed above.
4. You can click on the word "Refresh" to see the progress of your calculation. This is particularly helpful if you are in the "queue".
5. Completing the chart below is a useful exercise prior to building and running your calculations.
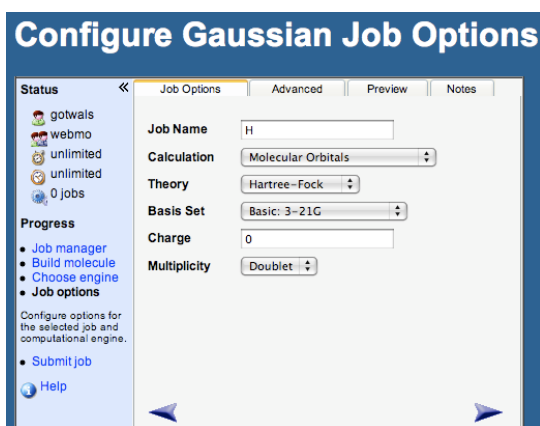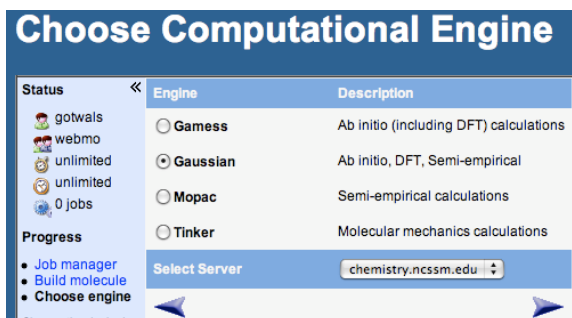
Element Name	Electron Configuration	Number of unpaired electrons (S=0.5)	Multiplicity (2S+1)
Hydrogen	$1s^1$	1	2(0.5)+1 = 2 (doublet)
Helium			
Lithium			
Beryllium			
Boron			
Carbon			
Nitrogen			
Oxygen			
Fluorine			
Neon			

Sodium			
Magnesium			
Manganese			
Phosphorus			
Zinc			

Data Analysis

Once your "job" is completed, follow this procedure:

1. To view the results of your completed job you may click on the name or the magnifying glass at the end of the job.
2. Scroll down and see a window label molecular orbitals. Notice in the window that you are given the number of orbitals, symmetry, occupancy (by electrons) and energy (more negative the number, the more tightly bound to the nucleus).
   a. For hydrogen, you should have a window that looks like the one in the picture. Notice that it shows four orbitals, labeled 1 through 4. Only Orbital 1 is occupied, with one electron (as is expected!).

The energy of the lone electron is –0.49620 Hartrees, or about –311 kcal/mole. The symmetry is listed as A_{1g}. This notation says that the shape of the orbital is symmetrical (B would be anti-symmetrical), and that it has been identified as "gerade", meaning that the value of the wavefunction is the same on each side of the atom. Ungerade, or "u" notation, would mean that the value of the wavefunction changes sign (positive to negative, or negative to positive) as one goes through the atom to the other side. Symmetry is a complicated topic, but it has usefulness in describing the structure of an atom or molecule.

3. In order to view orbitals, click on the magnifying glass to the right of the first orbital. Click "accept", "ok", "run", and/or "trust", depending on window that pops up. This should open up MOviewer, which allows you to see the orbitals. NOTE! MOViewer is a separate program, and should appear in your Taskbar (Windows) or Dock (Macintosh). To get back to MOViewer once it's open, click on the application icon in the appropriate location.

4. To visualize other orbitals, you can click on the MO number in the left-hand window of your MOViewer. You can zoom (size) the visualization by holding down the SHIFT key and holding/moving your mouse. Visualizations can be rotated with the mouse.