Lab #2: Basis Sets

Background

The Bohr model of an atom involves visualizing the electrons as fixed in "orbits", moving at a constant radius around the nucleus. During the early part of this century, serious chemical and physical errors were found in that model, and a new idea took its place. Electrons do not move in fixed orbits, with a constant radius, the theory says, but in random paths, only maintaining some semblance of organization. This theory fits with other quantum theory by saying that we cannot predict the behavior of an individual electron precisely, but we can know general properties about it, and we can know certain things about the behavior of a group of electrons. The form that electrons take around the nucleus is a sort of "cloud". That is, we cannot know the individual locations and movements of certain electrons, but we know where they will spend a percentage of their time. This is the same as saying that if we could take a snapshot of the atom, the cloud is the region where the electrons would appear in almost every one of the snapshots. This cloud is called an "orbital".

The orbital can be represented mathematically by a wave function. This is a mathematical abstraction which has no exact physical meaning. If the wave function is squared and multiplied by some factors, it represents the actual probability of the presence of the electron at a given place and time. However, examining the graph of the wave function can help us understand how electron clouds are handled computationally.

The orbital representations that we will be working with are called Slater type orbitals (STOs) and Gaussian type orbitals (GTOs). These two are about equally hard to compute for hydrogen, but the STOs increase in mathematical complexity too much to be useful once several electrons are introduced. GTOs are used as the next best approximation of the actual wave function. These approximations are used in *ab initio* and DFT methods to mathematically calculate the appearance of electron clouds and orbitals. However, once a molecule begins to be complex, (approximately more than 50 heavy atoms), even the GTO approximation is quite computationally expensive to be used.

The formulas for the STO wave function and the GTO wave function are shown below. Notice the similarities and differences in the two equations. Both are functions of the radius, squared in the case of the GTO equation. Both have constant terms with pi in the denominator.

$$GTO = \left(\frac{2\alpha}{\pi} \right)^{0.75} e^{-\alpha r^2} \qquad\qquad STO = \left(\frac{\zeta^3}{\pi} \right)^{0.5} e^{-\zeta r}$$

Procedure

To follow this study, you will need an Excel Spreadsheet. Please open one on your desktop now. This activity assumes you know how to construct a spreadsheet, enter values, labels and formulas, do fills, and construct graphs. Some of the instructions are

included in this Case Study, but if you are not comfortable with spreadsheets, you should ask the instructor to show you how to do the construction tasks.

Section 1
We will be modeling the simplest of atoms, hydrogen. As you know, the most common form of hydrogen has only one proton as its nucleus and a single electron in the orbital. However, even this basic form requires complex calculations for a realistic model! To model the electron cloud(s), several numerical constants are needed. The set of constants that are used for a given atom, with a given level of complexity in the mathematical representation, is called the basis set. The name of the basis set is often indicative of how it is constructed. For example, STO-3G is an approximation of a Slater type orbital using three Gaussian functions in the approximation. Gaussian functions are similar in shape to the bell curve, or normal distribution, which you have seen. A number of these curves are combined, or superimposed, to create another, more precise, approximation. You will investigate how the Gaussian functions are computed, combined, and how the number of Gaussians affects the accuracy of the combined model.

We will start by constructing a Slater Type Orbital (STO) for hydrogen. The function for this is shown above where ζ has the value of 1.24 and r is radius, or distance from the nucleus.

Start your spreadsheet by putting this constant in a cell somewhere around the upper left hand corner. I put the value in Cell B1, with the label "xi" in Cell A1. Notice what cell it is in, because you will have to refer to it in your equations.

Now we need to give the equations a list of radii to use in calculating the wave function. Leave some cells at the top, and put a label in the left most column, "Radius". I put the label Radius in Cell A6. We want to model the equations from 0 to 6 angstroms away from the nucleus (nucleus=0, and units are in angstroms). So put a 0 in the cell below Radius. We want use steps of 0.01 units in the list of radii.

To avoid typing in all these numbers, we're going to use a series command in Excel. Highlight the 0 and enough cells below it to contain all the values we will have for radius (my spreadsheet went from Row 7 to Row 607). Now go to Fill, but instead of using Down or Sideways, click on Series. The series command will ask for a step size. Make that 0.01, and click OK.

Next to that list, we are going to generate values for the STO wave function. So label it something clever like "STO" and put the formula in the first cell, making sure to refer to the ζ value and the radius by cell name in the appropriate places. Be careful of your parentheses; use lots of them, but make sure that they all match up properly! To help with this, Excel will color code the parentheses.

You should get a value in the first cell which starts out "0.779036". If you don't, go back and examine your formula more closely. Fill the formula down the column.

Now that we have this set of numbers, let's put it into a graph. Highlight the lists "Radius" and "STO", including the titles if you want. Now click on the button which has a bar graph and a wand in the toolbar. This will ask you to click on the already highlighted area. Follow the steps in this to create a "XY scatter" (fifth type of chart), and use the labels appropriately. Note the shape of this curve; this is a basic STO wave function.

Now we need to create a wave function for a single Gaussian Type Orbital, using the function above. The value of α (alpha) for a simple Gaussian is 0.4166. Put the GTO orbital in the column next to the STO. The first value of the GTO (nucleus=0) is 0.36957. If your value isn't correct, check your formula, particularly the use of parentheses.

Create a new graph that plots STO and GTO on the y-axis as a function of radius on the x-axis.

Questions: Assuming that the STO wave function is "correct", what do you notice about the GTO wave function?

How does it compare to the STO wave function?

Section 2
You should have observed that the GTO is significantly in error with the STO orbital, especially near the nucleus where one would expect the wave function to be the most accurate. For this next part, you will create an approximation to the STO wave function by combining three GTO orbitals. This basis set is known as an STO-3G basis set, since it is constructed by adding together three GTOs.

The next task is to create three new GTO wave functions. Each of these GTOs has its own value for α. You need to go find these values. Using the Gaussian Basis Set Order Form which can be found at:

http://www.emsl.pnl.gov/forms/basisform.html

"order up" the data for the STO-3G basis set for hydrogen. A sample screenshot is shown at the top of the next page. Notice that I have the element in the form box, and you need to select the STO-3G Basis set. You can choose whatever code format you want, I tend to choose Gaussian94 because I've used Gaussian in the past.

With the Gaussian94 option, you will get two columns of numbers. The column on the left gives the alpha values. The column on the right gives the contraction coefficients, which are normalization terms that account for some degree of electron shielding. Using the value for each of the three alphas, build three GTO wave functions.

No single one of these three GTOs is an approximation on its own; they must be combined. The method of combining them is called "Linear Combination of Atomic Orbitals" (LCAO). The other list of numbers in the basis set gives the coefficients for adding up the three Gaussians. They are used in the following equation:

$$LCAO = c_1 GTO_1 + c_2 GTO_2 + c_3 GTO_3$$

Create another column next to the three GTOs, and label it "STO-3G". Put the equation, referring to the appropriate constants, in the first cell, and fill the column. The first few rows of your spreadsheet might look like this:

Radius	STO	GTO	g1	g2	g3	STO-3G
0	0.779036	0.36957241	1.794441832	0.500326	0.187735	0.628247
0.01	0.769436	0.369557013	1.793827296	0.500295	0.187732	0.628134
0.02	0.759954	0.369510829	1.79198495	0.500202	0.187723	0.627795

To see if the new STO-3G approximation is a better approximation of the STO wave function, plot STO, GTO, and STO-3G on a graph as a function of radius. There is no need to plot GTO1, GTO2, or GTO3.