

Orbital Graphing

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Prerequisites: This worksheet is appropriate for use in Junior-Senior level physical chemistry classes. To use the document you should have some familiarity with Mathcad. In addition, it is recommended that you study the sections of a physical chemistry textbook that relate to the solution of the Schrodinger equation for the hydrogen atom. This document requires Mathcad 2001i Professional or later.

Goal: This document is designed to allow students to interactively explore the hydrogen-like atomic orbitals. The first part focuses on the atomic orbitals and how linear combinations of solutions to the Schrodinger equation are used to depict the familiar p and d orbitals. The second part of the document allows students to use linear combinations of atomic orbitals to construct and explore hybrid orbitals.

Performance Objectives: After completing the work described in this document you should be able to:

1. use Mathcad to graph 3-D mathematical functions that represent atomic orbitals
2. describe the shape of atomic orbitals
3. explain how the familiar pictures of p and d orbitals are obtained from solutions to the Schrodinger equation for the hydrogen atom
4. construct hybrid orbitals from atomic orbitals
5. visualize the angular parts of hybrid orbitals

Introduction: These exercises will introduce you to the graphical representations of hydrogen-like atomic orbitals. Specifically, we will primarily consider the angular part of atomic orbitals. Once you are familiar with graphing the angular parts of atomic orbitals, you will see how Mathcad can be used to display the angular parts of hybrid orbitals. Hybrid orbitals are molecular orbitals formed by linear combinations of atomic orbitals. Some introductory material is presented, and then the exercises begin. Questions for the student to answer are written in **maroon**.

Note: Similar Mathcad documents can be found on the CD-ROM *Explorations in Physical Chemistry: A Resource for Users of Mathcad*, by P. Atkins and J. dePaula, or in *A Mathcad Primer for Physical Chemistry*, by M. P. Cady and A. Trapp.

Part 1, Angular Parts of Atomic Orbitals

First, we must define some parameters. The commands below set up an array of angles for use in graphing.

numpts := 50

m := 0 .. numpts n := 0 .. numpts

$\phi_m := \frac{2 \cdot \pi \cdot m}{\text{numpts}}$ $\theta_n := \frac{\pi \cdot n}{\text{numpts}}$ This sets ϕ to range from 0 to 2π in 50 steps, and θ ranges from 0 to π in 50 steps.

Now in order to graph the angular parts of the orbitals, we can use Mathcad's ability to make 3D plots with arrays of (X,Y,Z) data. We set an array of X, Y, and Z data points and Mathcad will plot them for us. Now, how do we determine the proper X, Y, and Z points for a given orbital? First, the angular part of an orbital is expressed in terms of angles θ and ϕ . To get (X,Y,Z) we must convert from spherical coordinates to Cartesian coordinates. Remember that the conversions are: $x = r \sin\theta \cos\phi$, $y = r \sin\theta \sin\phi$, and $z = r \cos\theta$. θ and ϕ are the angles defined above. So, what is r? Recall that the orbitals are wavefunctions, and the probability of finding the electron is proportional to $|\psi|^2$. We want our graphs to convey the probability of finding the electron, so we will let $r = |\psi|^2$. Or, more precisely, we will take the angular part of $|\psi|^2$. This will create surfaces of constant probability, similar to pictures of orbitals in your textbook.

The simplest orbital is an s orbital.

What does the angular part of an s orbital look like?

Look in your textbook and find the angular part of a 1s orbital. Make sure it is only the angular part and does not include the radial part! Write the result in after this text.

If you found it, you wrote in $\sqrt{\frac{1}{4\pi}}$. We're going to take this, square it, and use it to plot an s orbital. Ready?

Here is x. $X_{m,n} := \left(\sqrt{\frac{1}{4\pi}}\right)^2 \cdot \sin(\theta_n) \cdot \cos(\phi_m)$ Use the left bracket key to get the m and n subscripts (array subscripts).

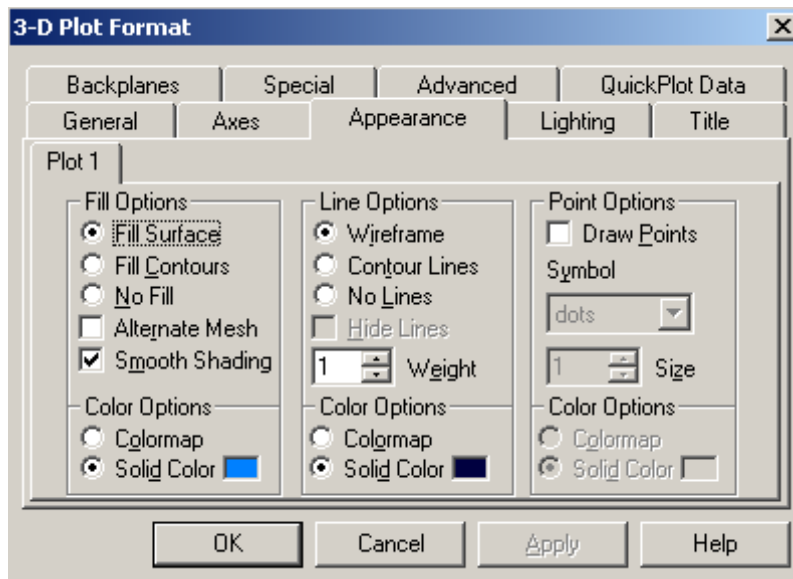
So the square of the angular part, $\left(\sqrt{\frac{1}{4\pi}}\right)^2$ is r, and sin and cos of the angles convert to Cartesian coordinates.

Now, here is y. $Y_{m,n} := \left(\sqrt{\frac{1}{4\pi}}\right)^2 \cdot \sin(\theta_n) \cdot \sin(\phi_m)$

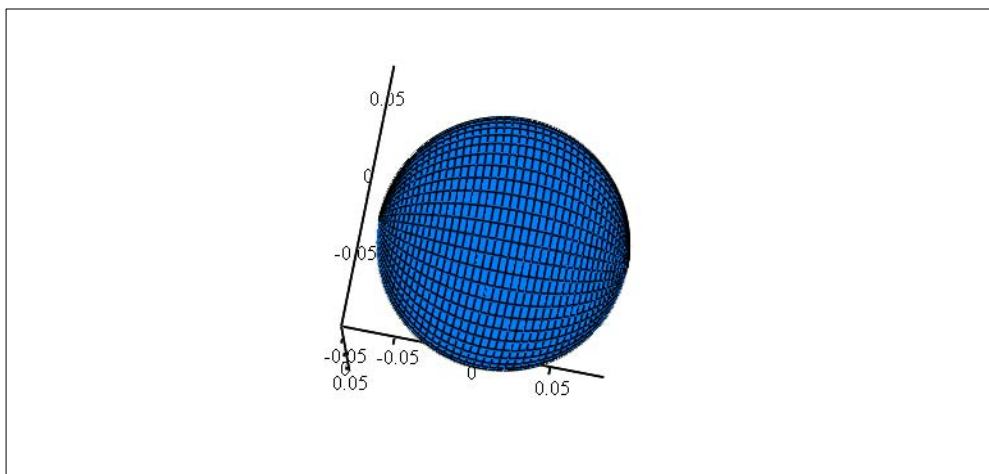
Do you follow this?

Finally, $z_{m,n} := \left(\sqrt{\frac{1}{4\pi}}\right)^2 \cdot \cos(\theta_n)$

Now we can insert a graph. Under the Insert menu, select graph and select Surface Plot. Below the plot area is a small box. Put (X,Y,Z) there, (be sure that X,Y,Z are in parentheses) and Mathcad does the rest!



The appearance of the orbital can be improved with some formatting. Right click in the graph and set the Appearance features as they are in the dialogue box above. Specifically, under Fill Options, select Fill Surface and select a Solid Color other than white or black. Blue is used in this example, but you may use your favorite color!



(X, Y, Z)

You can right click on the graph and change various properties of the display. **Make sure to select Equal Scales** so that the graph has the proper perspective.

Does it look like an s orbital? Describe its shape in your own words below.

Try changing the variable numpnts above. What does the display look like if you make numpnts small?

What does the display look like if you make numpnts large?

Do you notice the computer slowing down if numpnts is large, especially when you try to look at the orbital from different angles? What value of numpnts is a good compromise between display quality and computer speed?

Now let's plot the angular parts of p orbitals. What is the orbital angular momentum quantum number (l) of a p orbital?

For this value of l , what values can the magnetic quantum number, m , have? In general, what does m signify?

For a given value of n , there are three p orbitals, each having a different value of m . The p orbital corresponding to $m=0$ is the p_z orbital, because it points along the z axis. Let's make a graph of it here. **Look in your textbook and find the angular part of the wavefunction for a p_z orbital. Write it here.**

This is our wavefunction, so define $\psi_{m,n}$ as this function. Use the colon to make the definition equals sign, and use the left bracket to give the array subscripts.

$$\psi_{m,n} := \sqrt{\frac{3}{4\pi}} \cdot \cos(\theta_n)$$

Now we define X, Y, and Z for plotting. Remember that we use ψ^2 , and because ψ could be complex, ψ^2 is ψ times its complex conjugate. Mathcad can handle complex conjugates in the following manner. We have defined $\psi_{m,n}$. To get the complex conjugate of $\psi_{m,n}$, type it in, select it, and type a double quote, " , the key right next to the Enter key. If you did it correctly, Mathcad put a horizontal bar over $\psi_{m,n}$, as shown below.

$$\overline{\psi_{m,n}}$$

Now we can define $\psi_{m,n}$ for each wavefunction that we want to plot and use the same definitions for X, Y, and Z throughout the document. (Gotta love that cut and paste!)

For p_z , you already defined $\psi_{m,n}$ above. **Define X, Y, and Z as shown above for the angular part of the p_z orbital. Use the colon to make the define-equals.**

Graph the angular part of this orbital.

The orientation of orbitals with angular momentum ($l > 0$) is important. In order to quickly see the orbital orientation color code the x,y, and z axes. **Make the z-axis red, the y-axis blue and the x-axis black using the format dialogue box and the axes tab.** Also make sure that you right-click in the graph and select "Equal Scales."

What does the angular part of this orbital look like? Describe it in your own words.

Along which axis does it point?

Now let's graph the angular parts of a p_x orbital and a p_y orbital. The angular parts associated with the other (non- p_z) orbitals are found in the list of Spherical Harmonics, $Y_{1,+1}$ and $Y_{1,-1}$, in your textbook. We will define them Ppos (for $m=+1$) and Pneg (for $m=-1$): (An imaginary number is entered in Mathcad by typing "1i".)

$$P_{\text{pos}_{n,m}} := \sqrt{\frac{3}{8\pi}} \sin(\theta_n) \cdot e^{i \cdot \phi_m}$$

$$P_{\text{neg}_{n,m}} := \sqrt{\frac{3}{8\pi}} \sin(\theta_n) \cdot e^{-i \cdot \phi_m}$$

Instructor Note: It is helpful to remind the students that if two wavefunctions have the same eigenvalue (in this case energy), then any linear combination of those wavefunctions will also have the same eigenvalue. This means that the p orbitals created as linear combinations have the same energy value.

Define the first wavefunction and display it.

$$\psi_{m,n} := P_{\text{pos}_{n,m}}$$

Make the z-axis red, the y-axis blue and the x-axis black using the format dialogue box and the axes tab. Also right-click in the graph and select "Equal Scales."

Does it look like a familiar p orbital? Describe its shape in your own words.

Repeat the process for the other angular part of a p orbital given above. Define the wave function and graph it.

$$\psi_{m,n} := P_{\text{neg}_{n,m}}$$

Make the z-axis red, the y-axis blue and the x-axis black using the format dialogue box and the axes tab. Also right-click in the graph and select "Equal Scales."

Does it look like a familiar p orbital? Does it look any different than the previously graphed wavefunction?

The familiar p_x and p_y orbitals are not given by the solutions to the Schrodinger equation given above. Rather, they are *linear combinations* of the the above functions. Let's define:

$$\psi_{m,n} := \frac{1}{\sqrt{2}} \cdot (P_{\text{pos}_{n,m}} + P_{\text{neg}_{n,m}})$$

Graph the angular part of this orbital.

Make the z-axis red, the y-axis blue and the x-axis black using the format dialogue box and the axes tab. Also right-click in the graph and select "Equal Scales."

Is this a more familiar shape? Along which axis does it point?

Repeat the process for the "minus" linear combination.

$$\psi_{m,n} := \frac{1}{\sqrt{2}} \cdot (P_{\text{pos}_{n,m}} - P_{\text{neg}_{n,m}})$$

Make the z-axis red, the y-axis blue and the x-axis black using the format dialogue box and the axes tab. Also right-click in the graph and select "Equal Scales."

Along which axis does it point?

Now graph the angular part of the d_{z^2} orbital. Use your textbook to find the appropriate function.

Make the z-axis red, the y-axis blue and the x-axis black using the format dialogue box and the axes tab. Also right-click in the graph and select "Equal Scales."

Along which axis does the angular part of this orbital point?

Next you will graph the angular parts (spherical harmonics) of $l=2$ and $m=-1$, and of $l=2$ and $m=1$. Before you do that, answer these questions: What do you expect for the appearance of these angular parts? What do you expect to be similar and different about these angular parts?

Make the z-axis red, the y-axis blue and the x-axis black using the format dialogue box and the axes tab. Also right-click in the graph and select "Equal Scales."

Make the z-axis red, the y-axis blue and the x-axis black using the format dialogue box and the axes tab. Also right-click in the graph and select "Equal Scales."

Do these look like the angular parts of any d orbitals you have seen?

Finally, graph the "plus" linear combination of these two functions ($l=2, m=-1$ and $l=2, m=1$).

Make the z-axis red, the y-axis blue and the x-axis black using the format dialogue box and the axes tab. Also right-click in the graph and select "Equal Scales."

Is this shape more familiar to you? In which plane is it centered?

This orbital is typically named d_{xz} . It has a total angular momentum ($l=2$) consistent with the two angular nodes. From the spherical harmonics used to construct this orbital, $Y_{2,+1}$ and $Y_{2,-1}$, we see that the angular momentum about the z-axis is $|m| = 1$. The angular momentum about the z-axis can also be observed by viewing the orbital looking along the z-axis.

Orient the angular part of the d_{zx} orbital to view along the z-axis.

Looking along the z-axis of the d_{zx} orbital, only one angular node is observed. This indicates one unit of angular momentum about the z-axis for this orbital. **Now orient the angular part of the d_{zz} orbital (scroll back up to its graph) so that you are looking down the z-axis. What is the orbital angular momentum about the z-axis?**

Below is given a linear combination of spherical harmonics that produces a familiar angular part of a d-orbital. Plot this so that you can determine the angular momentum about the z-axis. Give its familiar name.

$$\psi_{m,n} := \frac{1}{\sqrt{2}} \left[\sqrt{\frac{15}{32 \cdot \pi}} \cdot (\sin(\theta_n))^2 \cdot e^{2i \cdot \phi_m} - \sqrt{\frac{15}{32 \cdot \pi}} \cdot (\sin(\theta_n))^2 \cdot e^{-2i \cdot \phi_m} \right]$$

Have you ever wondered what the angular parts of f orbitals look like? [Double-click on this link to see!](#)

Summary Questions

- 1. How do the angular parts of the orbitals graphed here help you visualize the electrons in atoms?**
- 2. What is the benefit of using orbitals that are linear combinations of the solutions to the Schrodinger equation?**

Part 2, Hybrid Orbitals

We can use the same process to graph the angular parts of hybrid orbitals. Hybrid orbitals are a linear combination of atomic orbitals. The simplest hybrid orbital is an sp hybrid, which is a combination of an s orbital and a p orbital. You are familiar with hybrids involving s and p atomic orbitals, and we will graph some here. For hybrid orbitals, we must also include the radial part of the wavefunction, because for a given n, the s and p orbitals do not have the same radial function. For example, 2s and 2p orbitals have different radial parts of their wavefunctions.

We will first examine sp hybrid orbitals made by combining 2s and 2p orbitals. The radial

wavefunction for a 2s orbital is $\psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} (2 - \sigma) e^{-\frac{\sigma}{2}}$. $\sigma = \frac{Z \cdot r}{a_0}$, where Z is the

atomic number and a_0 is the Bohr radius, 52.9177 pm. These constants will only affect the apparent size of the orbitals and not their shape, so we will simplify matters for ourselves and set them equal to 1. Similarly, the radial part of the wavefunctions for a 2p orbital is

$\psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \sigma e^{-\frac{\sigma}{2}}$ The variable σ determines approximately what "slice" of the orbital

we observe. These orbitals are best viewed from about $\sigma = 3$. The wavefunction for an sp hybrid orbital is $\psi_{sp} := \frac{1}{\sqrt{2}}(\psi_{2s} + \psi_{2pz})$. We define it in a similar manner to the way we defined the atomic orbitals above.

$$\sigma := 3 \quad \Psi_{2s_{m,n}} := \frac{1}{4\sqrt{2\pi}} \cdot (2 - \sigma) \cdot e^{-\frac{\sigma}{2}} \quad \Psi_{2pz_{m,n}} := \frac{1}{4\sqrt{2\pi}} \cdot \sigma \cdot e^{-\frac{\sigma}{2}} \cdot \cos(\theta_n)$$

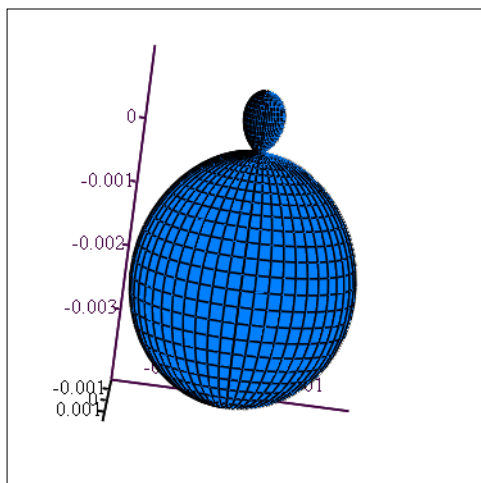
$$\Psi_{2px_{m,n}} := \frac{1}{4\sqrt{2\pi}} \cdot \sigma \cdot e^{-\frac{\sigma}{2}} \cdot \sin(\theta_n) \cdot \cos(\phi_m) \quad \Psi_{2py_{m,n}} := \frac{1}{4\sqrt{2\pi}} \cdot \sigma \cdot e^{-\frac{\sigma}{2}} \cdot \sin(\theta_n) \cdot \sin(\phi_m)$$

$$\psi_{m,n} := \frac{1}{\sqrt{2}} \cdot (\Psi_{2s_{m,n}} + \Psi_{2pz_{m,n}})$$

Now we can graph it.

$$X_{m,n} := (\psi_{m,n}) \cdot \sqrt{\psi_{m,n}} \cdot \sin(\theta_n) \cdot \cos(\phi_m) \quad Y_{m,n} := (\psi_{m,n}) \cdot \sqrt{\psi_{m,n}} \cdot \sin(\theta_n) \cdot \sin(\phi_m)$$

$$Z_{m,n} := (\psi_{m,n}) \cdot (\overline{\psi_{m,n}}) \cdot \cos(\theta_n)$$



Make the z-axis red, the y-axis blue and the x-axis black using the format dialogue box and the axes tab. Also right-click in the graph and select "Equal Scales."

(X, Y, Z)

Along which axis does the angular part of this orbital point? Additionally, in which direction, positive, or negative, does the larger lobe point?

Define and graph the "minus" combination. Along which axis does the angular part of this orbital point? Additionally, in which direction, positive, or negative, does the larger lobe point?

$$\sigma := 3$$

Now we can graph it.

Make the z-axis red, the y-axis blue and the x-axis black using the format dialogue box and the axes tab. Also right-click in the graph and select "Equal Scales."

One sp^2 hybrid orbital is $\frac{1}{\sqrt{3}}\psi_{2s} + \sqrt{\frac{2}{3}}\cdot\psi_{2pz}$ Define and graph the angular part of this orbital. Along which axis does it point?

$$\sigma := 3$$

Another sp^2 hybrid orbital is $\frac{1}{\sqrt{3}}\psi_{2s} - \frac{1}{\sqrt{6}}\psi_{2p_z} + \frac{1}{\sqrt{2}}\psi_{2p_x}$ Define and graph the angular part of this orbital. Along which axis does it point?

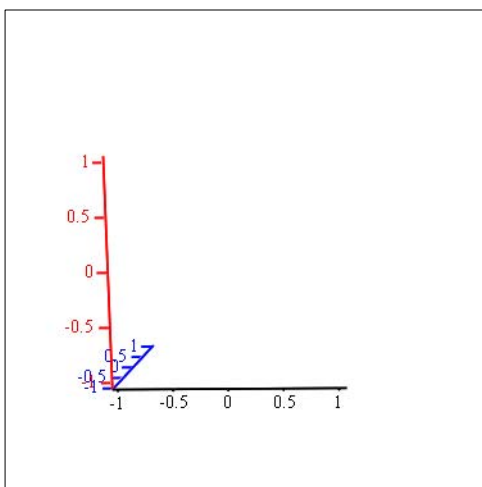
Earlier, we defined the p orbitals, so use them to create the hybrid orbital. Insert in the space immediately below the correct expression for this hybrid orbital $\psi_{m,n}$ and XX, YY, ZZ using the previous work as an example.

In order to be able to view the hybrid orbitals simultaneously side-by-side, we must use different labels for the x, y, and z coordinates of each hybrid. Label one set of coordinates X, Y, Z and the other set XX, YY, ZZ.

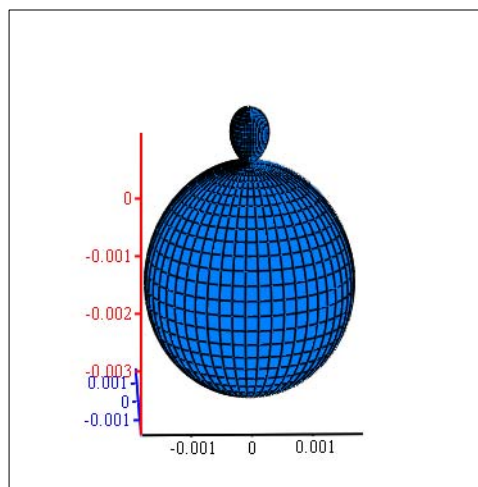
$$XX_{m,n} := \blacksquare$$

$$YY_{m,n} := \blacksquare$$

$$ZZ_{m,n} := \blacksquare$$



(XX, YY, ZZ)



(X, Y, Z)

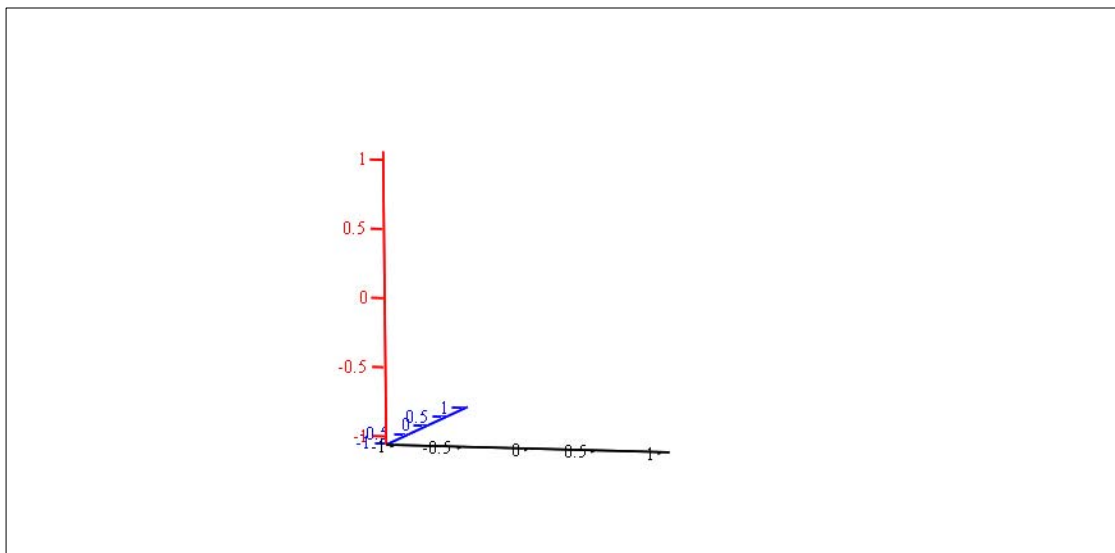
The final sp^2 hybrid is made from the linear combination: $\frac{1}{\sqrt{3}}\psi_{2s} - \frac{1}{\sqrt{6}}\psi_{2pz} - \frac{1}{\sqrt{2}}\psi_{2px}$

Plot the angular part of this hybrid orbital and display all three in the same graph. What is the bond angle that this set of angular parts creates?

$XXX_{m,n} := \blacksquare$

$YYY_{m,n} := \blacksquare$

$ZZZ_{m,n} := \blacksquare$



(X, Y, Z), (XX, YY, ZZ), (XXX, YYY, **ZZZ**)

Mastery Exercise (optional)

Find the appropriate equations and define and graph the angular parts of the sp^3 hybrid orbitals.

Summary Questions

1. How do the angular parts of the hybrid orbitals graphed here help you understand bonding between atoms?
2. What is the difference between the linear combinations of this section and the linear combination in Part 1? In each example, do the orbitals involved in making the

linear combinations always have the same energy? Also, what can you say about the directions of the basic orbitals and their resulting linear combinations?

3. Mathcad color codes the orbitals in a purely mathematical fashion, indicating the magnitude of the the z-component of the orbital. How might a chemist prefer to have the orbitals colored?

Angular parts of f orbitals

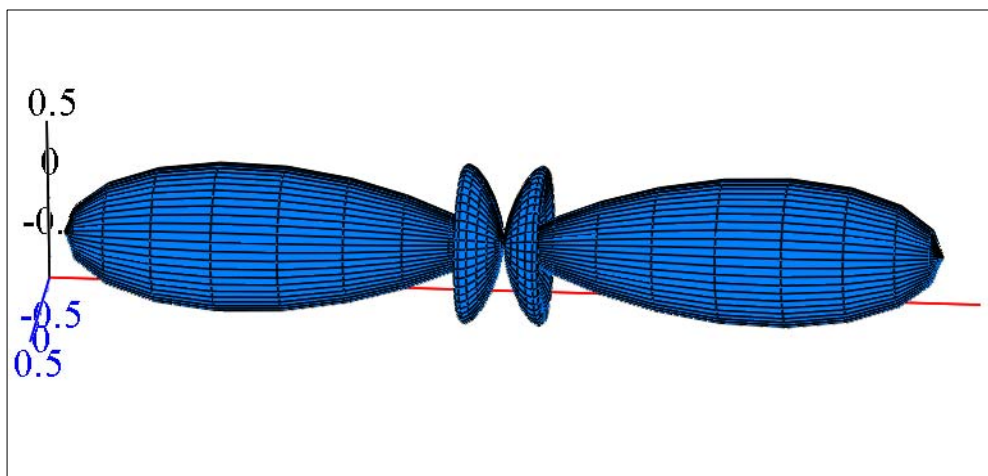
Double-click [here](#) to return to the document.

Here is a basic angular part of an f orbital:

$$\psi_{m,n} := \frac{3 \cdot \sqrt{14}}{4} \cdot \left[\left(\frac{5}{3} \right) \cdot (\cos(\theta_n))^3 - \cos(\theta_n) \right]$$

$$X_{m,n} := (\psi_{m,n}) \cdot (\overline{\psi_{m,n}}) \cdot \sin(\theta_n) \cdot \cos(\phi_m) \quad Y_{m,n} := (\psi_{m,n}) \cdot (\overline{\psi_{m,n}}) \cdot \sin(\theta_n) \cdot \sin(\phi_m)$$

$$Z_{m,n} := (\psi_{m,n}) \cdot (\overline{\psi_{m,n}}) \cdot \cos(\theta_n)$$



(X, Y, Z)

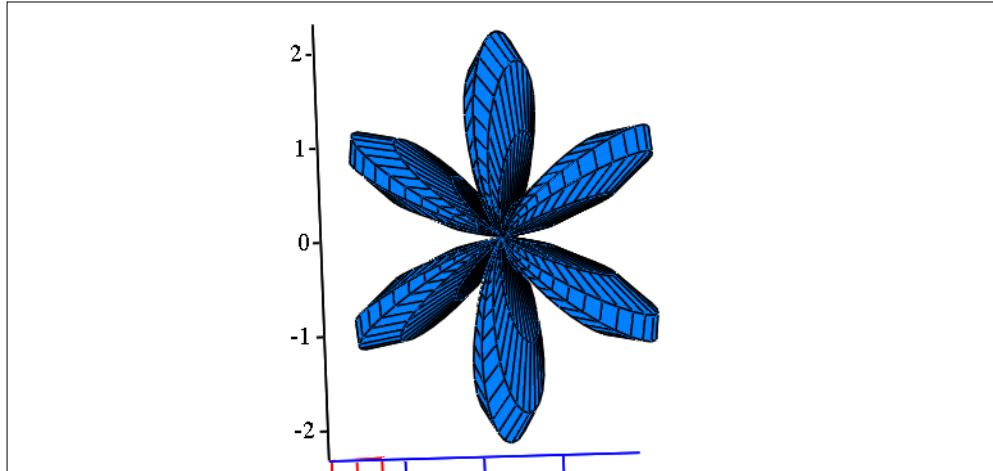
NEAT!! (What other angular part does this remind you of?)

Here is another one:

$$\psi_{m,n} := \frac{1}{\sqrt{2}} \cdot \left[\left[\frac{\sqrt{70}}{8} \cdot (\sin(\theta_n))^3 \cdot e^{3i \cdot \phi_m} \right] + \frac{\sqrt{70}}{8} \cdot (\sin(\theta_n))^3 \cdot e^{-3i \cdot \phi_m} \right]$$

$$X_{m,n} := (\psi_{m,n}) \cdot (\overline{\psi_{m,n}}) \cdot \sin(\theta_n) \cdot \cos(\phi_m) \quad Y_{m,n} := (\psi_{m,n}) \cdot (\overline{\psi_{m,n}}) \cdot \sin(\theta_n) \cdot \sin(\phi_m)$$

$$Z_{m,n} := (\psi_{m,n}) \cdot (\overline{\psi_{m,n}}) \cdot \cos(\theta_n)$$



(X, Y, Z)

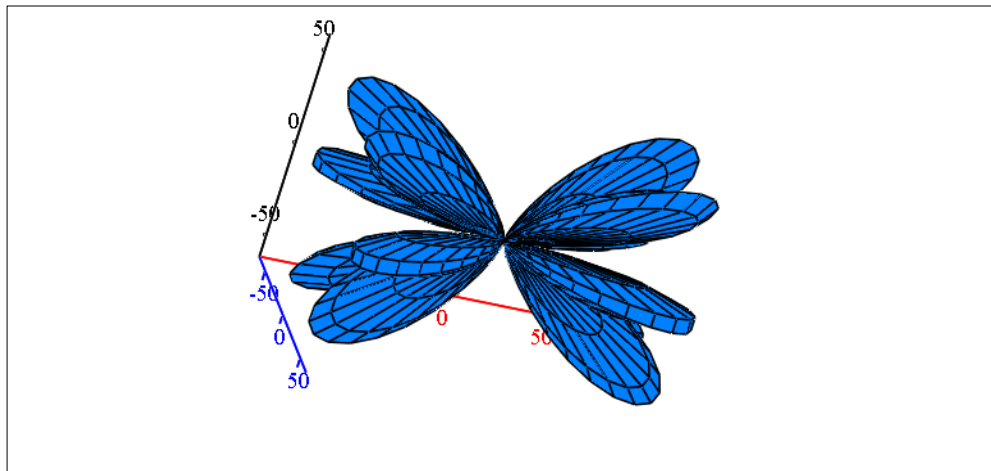
Isn't that cool?!

Here is the last one. If you're interested, look in your textbook for more formulas and try graphing your own!

$$\psi_{m,n} := \frac{1}{\sqrt{2}} \left[\frac{\sqrt{42}}{8} \cdot \sin(\theta_n) \cdot \left[(5 \cdot \cos(\theta_n))^2 - 1 \right] \cdot e^{3 \cdot (i \cdot \phi)_m} - \frac{\sqrt{42}}{8} \cdot \sin(\theta_n) \cdot \left[(5 \cdot \cos(\theta_n))^2 - 1 \right] \cdot e^{-3 \cdot (i \cdot \phi)_m} \right]$$

$$X_{m,n} := (\psi_{m,n}) \cdot (\overline{\psi_{m,n}}) \cdot \sin(\theta_n) \cdot \cos(\phi_m) \quad Y_{m,n} := (\psi_{m,n}) \cdot (\overline{\psi_{m,n}}) \cdot \sin(\theta_n) \cdot \sin(\phi_m)$$

$$Z_{m,n} := (\psi_{m,n}) \cdot (\overline{\psi_{m,n}}) \cdot \cos(\theta_n)$$



(X, Y, Z)

Double-click [here](#) to return to the document.