

sp³d⁰ Hybrid Orbitals and Molecular Geometry

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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. The MathCad document "Orbital Graphing" would familiarize the students with the use of MathCad to visualize orbitals. Completion of this document would be useful but not necessary for successful completion of this document. It is available at the [MathCad in Physical Chemistry](#) web page. (Double click on the link to access it.) Also, review the molecular geometries of VSEPR theory from general chemistry. This document requires Mathcad 2000 Professional or later.

Goal: This document is designed to allow students to interactively explore the sp³d⁰ hybrid orbitals that give rise to the following molecular geometries: octahedral, trigonal bipyramidal, square planar, and square pyramidal. The linear combinations of solutions to the Schrodinger equation are used to construct hybrid orbitals from s, p, and d 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 the angular parts of hybrid orbitals
2. describe the shapes of the angular parts of hybrid orbitals and relate them to molecular geometries

Introduction: These exercises will introduce you to the graphical representations of complex hybrid orbitals. Specifically, we will primarily consider the angular part of these orbitals. Once you are familiar with graphing these orbitals, you will see how MathCad can be used to visualize these hybrid orbitals and the resulting molecular geometries. Some introductory material is presented, and then the exercises begin. Questions for the student to answer are written in maroon. Answers for instructors are provided in bold and should be deleted before the document is used.

Part 1, Graphing the Angular Parts of Hybrid Orbitals: sp³d

You are probably familiar with sp, sp², and sp³ hybrid orbitals. These orbitals are useful in understanding the geometry of many small molecules. However, they are useful only if the central atom has 4 or fewer electron pairs around it. For larger atoms, including Cl, Br, Xe, and others, more than 4 electron pairs might be around the central atom within a molecule, so more orbitals are involved in the hybridization process. Specifically, the d orbitals are now utilized. Linear combinations of s, p, and d orbitals produce hybrid orbitals whose geometry determines the shape of the molecular compound. In these exercises, you will generate the hybrid orbitals and be able to see the shapes of the angular parts of those orbitals.

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

```
numpnts := 50
m := 0, numpnts      n := 0, numpnts
phi_m :=  $\frac{2 \pi m}{numpnts}$       theta_n :=  $\frac{\pi n}{numpnts}$       This sets theta range from 0 to 2pi in 50 steps, and phi ranges from 0 to 2pi in 50 steps.
```

Now in order to graph 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 theta and phi. To get (X,Y,Z) we must project the functions in spherical coordinates to the Cartesian axes. Remember that the conversions from spherical to Cartesian coordinates are: $x = r \sin\theta \cos\phi$, $y = r \sin\theta \sin\phi$, and $z = r \cos\theta$. theta and phi are the angles defined above. To project the functions on to the Cartesian axes, we will therefore define $X = |y|^2 \sin^2 \cos\phi$, $Y = |y|^2 \sin^2 \sin\phi$, and $Z = |y|^2 \cos^2$. Below, we will choose a value of r that is useful for viewing the angular part of the orbitals.

Remember that the orbitals are wavefunctions, and the probability of finding the electron is proportional to |y|^2. Our graphs will convey the probability of finding the electron for a particular value of r. This is different than the graphs in your textbook. Those typically show surfaces of constant probability, that is, the boundary of the region in which the probability of finding the electron is 90% (or, depending on the book, 95%). Creating the pictures for the textbook is rather difficult, because that requires determining the values of r (different for each orbital) for which the probability of finding the electron between 0 and r is 0.90 (or 0.95). A simpler approach, the one taken here, is to choose a particular value of r and graph the functions at that value. This has the benefit of showing the shapes of the orbitals without the tedious work of solving for a value of r that gives a 90% probability inside.

The hybrid orbitals are formed from atomic orbitals generated by the solution of the Schrodinger equation for the H atom. These can be found in your textbook. The variable $\sigma = r/a_0$, r is distance from nucleus, a_0 is the Bohr radius, 52.9 pm) determines approximately what "slice" of the orbital we observe. These orbitals are best viewed from about $\sigma = 12$. Also, keep in mind as you perform these exercises that we are graphing the angular part of $|\psi|^2$. Because we have chosen a specific value of σ (θ) and graphed the functions at that value, most radial information, such as radial nodes, are not apparent in these graphs. With that in mind, the relevant atomic orbitals are defined here.

$$\sigma = 12$$

$$\Psi_{1s} = \frac{1}{81\sqrt{3}\pi} (27 - 18\sigma + 2\sigma^2) e^{-\frac{\sigma}{3}}$$

$$\Psi_{3p_{z,m=0}} = \frac{\sqrt{2}}{81\sqrt{\pi}} \sigma (6 - \sigma) e^{-\frac{\sigma}{3}} \cos(\theta_0)$$

$$\Psi_{3p_{y,m=0}} = \frac{\sqrt{2}}{81\sqrt{\pi}} \sigma (6 - \sigma) e^{-\frac{\sigma}{3}} \sin(\theta_0) \cos(\phi_0)$$

$$\Psi_{3p_{x,m=0}} = \frac{\sqrt{2}}{81\sqrt{\pi}} \sigma (6 - \sigma) e^{-\frac{\sigma}{3}} \sin(\theta_0) \sin(\phi_0)$$

$$\Psi_{3d_{z^2,m=0}} = \frac{1}{81\sqrt{6}\pi} \sigma^2 e^{-\frac{\sigma}{3}} [3(\cos(\theta_0))^2 - 1]$$

$$\Psi_{3d_{xy,m=0}} = \frac{1}{81\sqrt{2}\pi} \sigma^2 e^{-\frac{\sigma}{3}} (\sin(\theta_0))^2 \cos(2\phi_0)$$

We will now start by graphing the angular parts of orbitals that arise from sp^3 hybridization.

Recalling that sp^3 hybrid orbitals arise from $s+p+p+p$, how many sp^3 orbitals are formed in the hybridization?
Answer: 4

Based on your answer to the previous question, how many hybrid orbitals are formed in sp^3 hybridization?
Answer: 5

The normalized wavefunctions for the sp³d hybrid orbitals are given here. In the next section we will see how to determine these wavefunctions. For now, we will accept them as given so that we can learn how to graph them.

$$\Psi_{1\ m,0} = \frac{1}{\sqrt{3}} \Psi_{3s\ m,0} + \frac{1}{\sqrt{6}} \Psi_{3p\ m,0} + \frac{1}{\sqrt{2}} \Psi_{3d\ m,0}$$

$$\Psi_{2\ m,0} = \frac{1}{\sqrt{3}} \Psi_{3s\ m,0} + \frac{1}{\sqrt{6}} \Psi_{3p\ m,0} - \frac{1}{\sqrt{2}} \Psi_{3d\ m,0}$$

$$\Psi_{3\ m,0} = \frac{1}{\sqrt{3}} \Psi_{3s\ m,0} - \frac{2}{\sqrt{6}} \Psi_{3p\ m,0}$$

$$\Psi_{4\ m,0} = \frac{1}{\sqrt{2}} \Psi_{3p\ m,0} + \frac{1}{\sqrt{2}} \Psi_{3d\ m,0}$$

$$\Psi_{5\ m,0} = \frac{1}{\sqrt{2}} \Psi_{3p\ m,0} - \frac{1}{\sqrt{2}} \Psi_{3d\ m,0}$$

To graph these, we need to project the square of the wavefunction on the Cartesian coordinates, as described above. To square the wavefunction, we must multiply it by its complex conjugate. To do that in MathCad, select the function and type the double quote (Shift+"). It should give you a line over the function, as shown here:

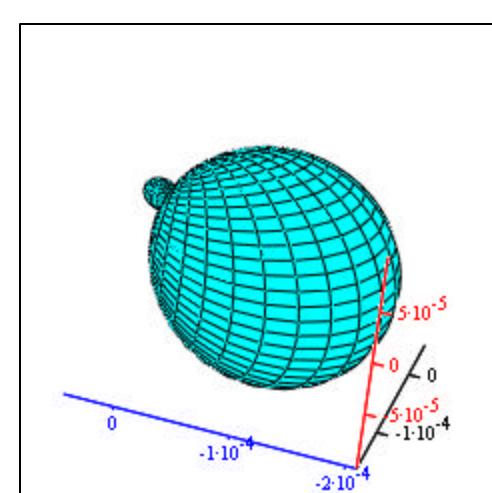
$$\overline{\Psi_{1\ m,0}}$$

So the x, y, and z-coordinates of the Psi1 hybrid orbital will be:

$$X_{1\ m,0} = \left(\overline{\Psi_{1\ m,0}} \right) \sin(\theta_a) \cos(\phi_a) \quad Y_{1\ m,0} = \left(\overline{\Psi_{1\ m,0}} \right) \sin(\theta_a) \sin(\phi_a)$$

$$Z_{1\ m,0} = \left(\overline{\Psi_{1\ m,0}} \right) \cos(\theta_a)$$

To introduce you to the graphing process, we'll graph this one by itself. Go to the Insert menu and select Surface Plot (Ctrl+Z). In the placeholder, type (X,Y,Z) .



(X,Y,Z)

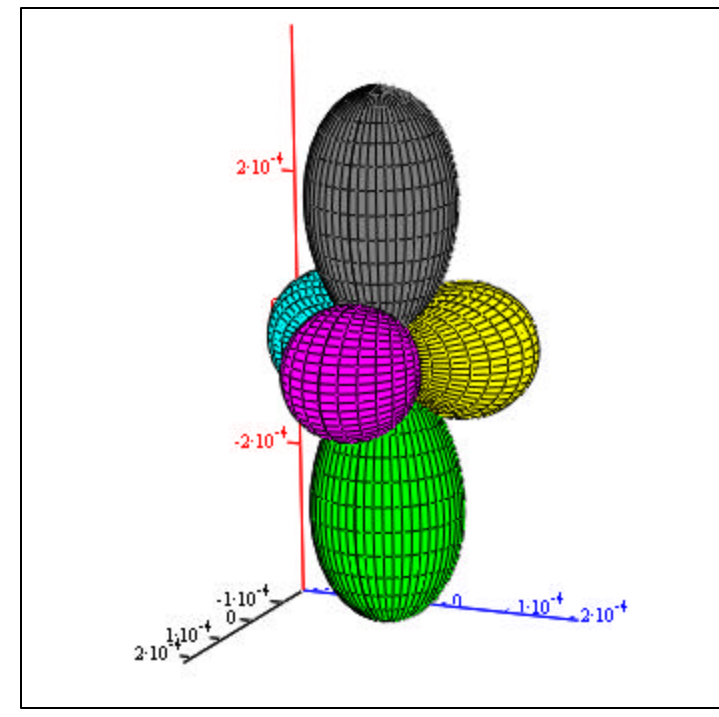
Make sure that you right-click in the graph and select "Equal Scales". Also, double-click on the graph, click on the Axes tab, and set the x-axis color black, the y-axis color blue, and the z-axis color red. Finally, under the Appearance tab, click on Solid Color and set it to the color of your choice.

Noting the colors of the axes, in which direction does the angular part of this hybrid orbital point?
Answer: on a 45-degree angle between the x and y axes

It would be difficult to plot each angular part separately and then try to visualize how they result in a particular geometrical arrangement. Fortunately, MathCad can graph multiple functions in the same graph. First, we need to define all of the x, y, and z-coordinates for all of the hybrids.

$$\begin{aligned}
X2_{m,n} &= \left[\text{Psi2}_{m,n} \right] \left(\overline{\text{Psi2}_{m,n}} \right)^{\wedge} \sin(\theta_d) \cos(\theta_n) & Y2_{m,n} &= \left[\text{Psi2}_{m,n} \right] \left(\overline{\text{Psi2}_{m,n}} \right)^{\wedge} \sin(\theta_d) \sin(\theta_n) \\
Z2_{m,n} &= \left[\text{Psi2}_{m,n} \right] \left(\overline{\text{Psi2}_{m,n}} \right)^{\wedge} \cos(\theta_d) \\
X3_{m,n} &= \left[\text{Psi3}_{m,n} \right] \left(\overline{\text{Psi3}_{m,n}} \right)^{\wedge} \sin(\theta_d) \cos(\theta_n) & Y3_{m,n} &= \left[\text{Psi3}_{m,n} \right] \left(\overline{\text{Psi3}_{m,n}} \right)^{\wedge} \sin(\theta_d) \sin(\theta_n) \\
Z3_{m,n} &= \left[\text{Psi3}_{m,n} \right] \left(\overline{\text{Psi3}_{m,n}} \right)^{\wedge} \cos(\theta_d) \\
X4_{m,n} &= \left[\text{Psi4}_{m,n} \right] \left(\overline{\text{Psi4}_{m,n}} \right)^{\wedge} \sin(\theta_d) \cos(\theta_n) & Y4_{m,n} &= \left[\text{Psi4}_{m,n} \right] \left(\overline{\text{Psi4}_{m,n}} \right)^{\wedge} \sin(\theta_d) \sin(\theta_n) \\
Z4_{m,n} &= \left[\text{Psi4}_{m,n} \right] \left(\overline{\text{Psi4}_{m,n}} \right)^{\wedge} \cos(\theta_d) \\
X5_{m,n} &= \left[\text{Psi5}_{m,n} \right] \left(\overline{\text{Psi5}_{m,n}} \right)^{\wedge} \sin(\theta_d) \cos(\theta_n) & Y5_{m,n} &= \left[\text{Psi5}_{m,n} \right] \left(\overline{\text{Psi5}_{m,n}} \right)^{\wedge} \sin(\theta_d) \sin(\theta_n) \\
Z5_{m,n} &= \left[\text{Psi5}_{m,n} \right] \left(\overline{\text{Psi5}_{m,n}} \right)^{\wedge} \cos(\theta_d)
\end{aligned}$$

Once all of the coordinates have been calculated, we can insert a graph. Multiple plots are created by separating the groups of coordinates by commas.



(X1, Y1, Z1), (X2, Y2, Z2), (X3, Y3, Z3), (X4, Y4, Z4), (X5, Y5, Z5)

Here the x-axis is black, the y-axis is blue, and the z-axis is red. Each individual angular part has been given a unique color to distinguish it from the others.

In which direction do each angular part of these hybrid orbitals point? If there was an atom at the center, and each lobe were involved in a bond, what would the molecular geometry be? (An example of a molecule with this geometry is PF_5 .)

Answer: two point in +z and -z directions, the others are in the xy plane, 120 degrees from each neighbor; geometry would be trigonal bipyramidal

For this set of orbitals, what would the molecular geometry be if four lobes were involved in bonding and one lobe contained a lone pair of electrons instead of a bonding pair? (An example of a molecule with this geometry is SF_4 .)

Answer: see-saw

For this set of orbitals, what would the molecular geometry be if three lobes were involved in bonding and two lobes contained lone pair of electrons instead of a bonding pair? (An example of a molecule with this geometry is ClF_3 .)

Answer: t-shaped

For this set of orbitals, what would the molecular geometry be if two lobes were involved in bonding and three lobes contained a lone pair of electrons instead of a bonding pair? (An example of a molecule with this geometry is I_2 .)

Answer: linear

Part , Graphing the Angular Parts of Hybrid Orbitals: sp³d²

In the previous section, we were given the wavefunctions for the hybrid orbitals. Determining these wavefunctions is not difficult, especially with the aid of MathCad. Here, we will learn how to determine those wavefunctions using normalization and orthogonality.

sp³d² hybrid orbitals result in an octahedral geometry, with orbitals pointing along the x, y, and z axes. The atomic orbitals involved, then, are the 3s, 3p_x, 3p_y, 3d_{z²}, and 3d_{x²-y²}. The hybrid orbitals will have two that point along the z axis: one in the +z direction and one in the -z direction. Clearly, the only two orbitals that point in these directions are the 3p_z and the 3d_{z²}. Thus, the hybrids along the z axis must be linear combinations of only these two atomic orbitals. Specifically, $\psi_1 = a\psi_{3p_z} + b\psi_{3d_{z^2}}$ and, since the other hybrid must be equivalent to the first but point in the opposite direction, $\psi_2 = -a\psi_{3p_z} + b\psi_{3d_{z^2}}$. Because ψ_1 and ψ_2 must be

normalized, we have $a^2 + b^2 = 1$. Also, because they must be orthogonal, we have

$-a^2 + b^2 = 0$, or $a^2 = b^2$. This gives $2a^2 = 1$, or $a = b = \frac{1}{\sqrt{2}}$. These orbitals are defined here:

$$\Psi_{11,m,n} = \frac{1}{\sqrt{2}} \Psi_{3p_{m,n}} + \frac{1}{\sqrt{2}} \Psi_{3d_{z^2,m,n}}$$

$$\Psi_{21,m,n} = \frac{1}{\sqrt{2}} \Psi_{3p_{m,n}} - \frac{1}{\sqrt{2}} \Psi_{3d_{z^2,m,n}}$$

$$X_{1,m,n} = \left(\Psi_{11,m,n} \right) \left(\overline{\Psi_{11,m,n}} \right) \sin(\theta_n) \cos(\theta_n) \quad Y_{1,m,n} = \left(\Psi_{11,m,n} \right) \left(\overline{\Psi_{11,m,n}} \right) \sin(\theta_n) \sin(\theta_n)$$

$$Z_{1,m,n} = \left(\Psi_{11,m,n} \right) \left(\overline{\Psi_{11,m,n}} \right) \cos(\theta_n)$$

$$X_{2,m,n} = \left(\Psi_{21,m,n} \right) \left(\overline{\Psi_{21,m,n}} \right) \sin(\theta_n) \cos(\theta_n) \quad Y_{2,m,n} = \left(\Psi_{21,m,n} \right) \left(\overline{\Psi_{21,m,n}} \right) \sin(\theta_n) \sin(\theta_n)$$

$$Z_{2,m,n} = \left(\Psi_{21,m,n} \right) \left(\overline{\Psi_{21,m,n}} \right) \cos(\theta_n)$$

To determine the normalization constants for the other orbitals, we realize that the orbitals will lie in the xy plane. Thus, they will be linear combinations of the $3s$, $3p_x$, $3p_y$, and $3d_{x^2-y^2}$ orbitals. Because the x and y directions are similar (an orbital pointing along the x axis will look the same as an orbital pointing along the y axis), the expressions for the hybrid orbitals will be similar. Specifically,

$$\begin{aligned} \text{Pa3} &= a^* \text{Pa3s} + b^* \text{Pa3px} + c^* \text{Pa3py} + d^* \text{Pa3dx}^2\text{-y}^2 \text{ (Points along } +x \text{ direction)} \\ \text{Pa4} &= a^* \text{Pa3s} + f^* \text{Pa3px} + g^* \text{Pa3py} + h^* \text{Pa3dx}^2\text{-y}^2 \text{ (Points along } +y \text{ direction)} \\ \text{Pa5} &= a^* \text{Pa3s} + b^* \text{Pa3px} + c^* \text{Pa3py} + d^* \text{Pa3dx}^2\text{-y}^2 \text{ (Points along } +x \text{ direction)} \\ \text{Pa6} &= a^* \text{Pa3s} + f^* \text{Pa3px} + g^* \text{Pa3py} + h^* \text{Pa3dx}^2\text{-y}^2 \text{ (Points along } -y \text{ direction)} \end{aligned}$$

These wavefunctions must be normalized and orthogonal. To satisfy normalization,

$$\int \text{Pa3}^* \text{Pa3} dt = 1. \text{ That expands to:}$$

$$a^2 \int \text{Pa3s}^* \text{Pa3s} dt + b^2 \int \text{Pa3px}^* \text{Pa3px} dt + c^2 \int \text{Pa3py}^* \text{Pa3py} dt +$$

$$d^2 \int \text{Pa3dx}^2\text{-y}^2 \text{Pa3dx}^2\text{-y}^2 dt + \text{cross terms} = 1$$

Because the atomic orbitals are orthonormal, the integrals shown here are equal to 1, and the cross term integrals are zero. Thus $a^2 + b^2 + c^2 + d^2 = 1$. We get three more equations similar to this by normalizing Pa4. We also get four equations by making sure the Pa3 are orthogonal. We thus have seven unknowns and eight simultaneous equations. MathCad can help us find the unknowns in a system of simultaneous equations. First, we have to give MathCad guesses as to what the values might be. We know that all the values will be less than 1. We also know that because the $3s$ orbital is spherically symmetric, it will contribute an equal portion to each hybrid orbital. Thus, $4a^2 = 1$, or $a = \frac{1}{\sqrt{4}}$. We give MathCad guesses for the values of the unknowns and then set up a solve block. In the solve block, we provide the equations and then tell MathCad to find the values. You can put constraints on the values that MathCad finds; for instance here I have limited $a > 0$.

$$a = \frac{1}{2} \quad b = \frac{1}{4} \quad c = \frac{1}{4} \quad d = \frac{1}{4} \quad f = \frac{-1}{2} \quad g = \frac{1}{4} \quad h = \frac{1}{4}$$

Given

$$a^2 + b^2 + c^2 + d^2 = 1$$

$$a^2 + f^2 + g^2 + h^2 = 1$$

$$a^2 - b^2 + c^2 + d^2 = 0$$

$$a^2 + b f + c g + d h = 0$$

$$a^2 + b f - c g + d h = 0$$

$$a^2 - bf + cg + dh = 0$$

$$a^2 - bf - cg + dh = 0 \quad a > 0$$

$$a^2 + f^2 - g^2 + h^2 = 0$$

$$\text{Find}(a, b, c, d, f, g, h) = \begin{pmatrix} 0.5 \\ 0.7071 \\ -1.6379 \times 10^{-10} \\ 0.5 \\ 2.6694 \times 10^{-10} \\ 0.7071 \\ -0.5 \end{pmatrix}$$

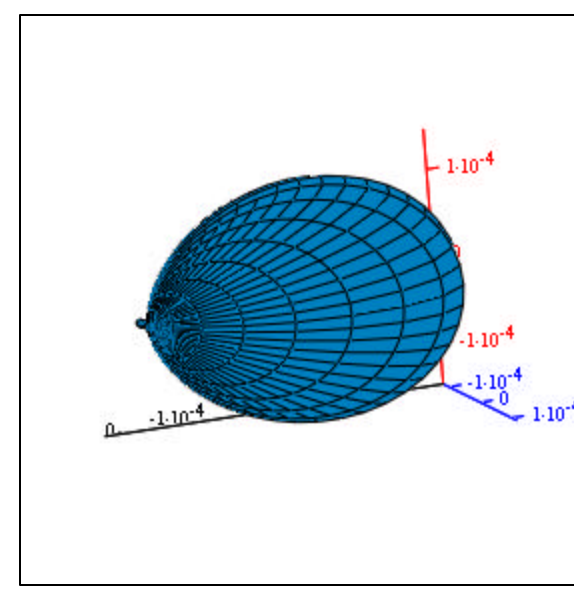
Here we see that $a = \frac{1}{2}$, $b = \frac{1}{2}$, $c = 0$, $d = \frac{1}{2}$, $f = 0$, $g = \frac{1}{\sqrt{2}}$ and $h = \frac{-1}{2}$.

Now we can define the wavefunctions for the hybrid orbitals in the xy plane.

$$\Psi_{1,0,0} = \frac{1}{\sqrt{4}} \Psi_{1,0,0} + \frac{1}{\sqrt{2}} \Psi_{1,0,0} + 0 \Psi_{1,0,0} + \frac{1}{\sqrt{4}} \Psi_{1,0,0}$$

$$X_{1,0,0} = \left(\frac{\Psi_{1,0,0}}{\sqrt{4}} \right) \left(\frac{\Psi_{1,0,0}}{\sqrt{2}} \right) \sin(\theta_a) \cos(\theta_b) \quad Y_{1,0,0} = \left(\frac{\Psi_{1,0,0}}{\sqrt{4}} \right) \left(\frac{\Psi_{1,0,0}}{\sqrt{2}} \right) \sin(\theta_a) \sin(\theta_b)$$

$$Z_{1,0,0} = \left(\frac{\Psi_{1,0,0}}{\sqrt{4}} \right) \cos(\theta_a)$$



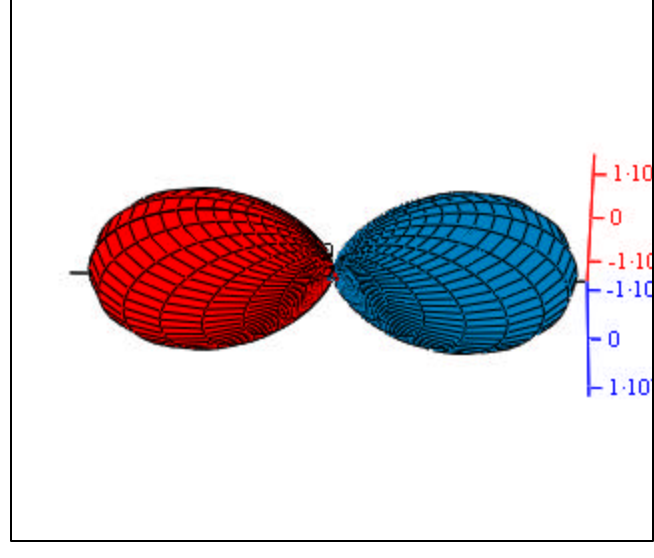
This is what one of the hybrid orbitals looks like by itself.

(X3, Y3, Z3)

$$\Psi_{m,1}^2 = \frac{1}{4} \Psi_{1s}^2 + \frac{1}{2} \Psi_{2p_{x,1}}^2 + 0 \Psi_{2p_{y,1}}^2 + \frac{1}{4} \Psi_{2p_{z,1}}^2$$

$$X_{m,0} = \left(\Psi_{1s,0}^2 \right)^{1/2} \sin(\theta_0) \cos(\phi_0) \quad Y_{m,0} = \left(\Psi_{1s,0}^2 \right)^{1/2} \sin(\theta_0) \sin(\phi_0)$$

$$Z_{m,0} = \left(\Psi_{1s,0}^2 \right)^{1/2} \cos(\theta_0)$$



(X3, Y3, Z3), (X5, Y5, Z5)

These are the angular parts of the orbitals Ψ_{33} and Ψ_{34} . In what directions do they point? Do these directions agree with the starting conditions when we defined Ψ_{33} and Ψ_{34} ?

Answer: **x** and **-x** directions; **yes**

$$\Psi_{4_{m,0}} = \frac{1}{\sqrt{4}} \Psi_{43_{m,0}} + 0 \Psi_{43_{m,0}} + \frac{1}{\sqrt{2}} \Psi_{43_{m,0}} - \frac{1}{\sqrt{4}} \Psi_{43_{m,0}}$$

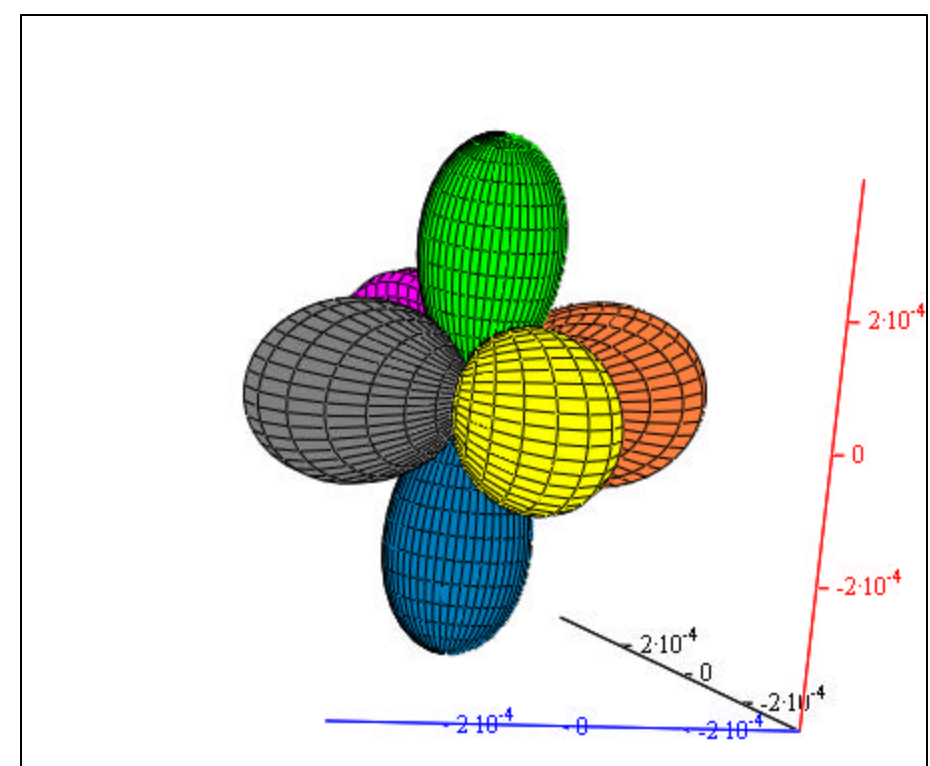
$$X_{4_{m,0}} = \left(\Psi_{4_{m,0}} \right) \left(\Psi_{4_{m,0}} \right) \sin(\theta) \cos(\theta_0) \quad Y_{4_{m,0}} = \left(\Psi_{4_{m,0}} \right) \left(\Psi_{4_{m,0}} \right) \sin(\theta) \sin(\theta_0)$$

$$Z_{4_{m,0}} = \left(\Psi_{4_{m,0}} \right) \left(\Psi_{4_{m,0}} \right) \cos(\theta_0)$$

$$\Psi_{6_{m,0}} = \frac{1}{\sqrt{4}} \Psi_{63_{m,0}} + 0 \Psi_{63_{m,0}} - \frac{1}{\sqrt{2}} \Psi_{63_{m,0}} - \frac{1}{\sqrt{4}} \Psi_{63_{m,0}}$$

$$X_{6_{m,0}} = \left(\Psi_{6_{m,0}} \right) \left(\Psi_{6_{m,0}} \right) \sin(\theta) \cos(\theta_0) \quad Y_{6_{m,0}} = \left(\Psi_{6_{m,0}} \right) \left(\Psi_{6_{m,0}} \right) \sin(\theta) \sin(\theta_0)$$

$$Z_{6_{m,0}} = \left(\Psi_{6_{m,0}} \right) \left(\Psi_{6_{m,0}} \right) \cos(\theta_0)$$

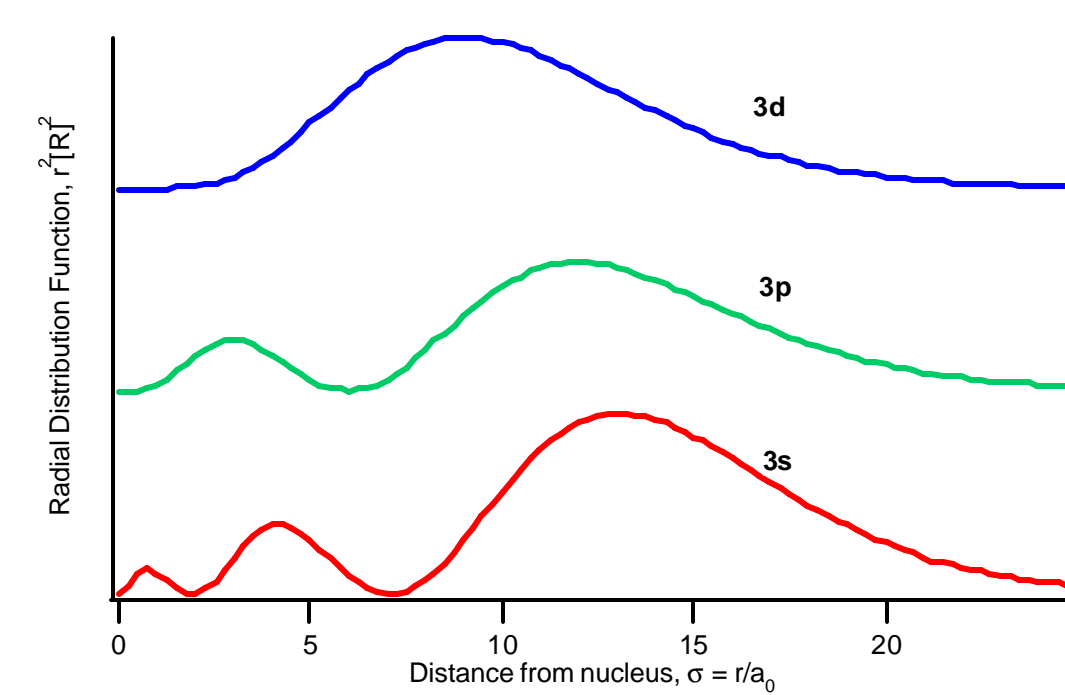


(X1, Y1, Z1), (X2, Y2, Z2), (X3, Y3, Z3), (X4, Y4, Z4), (X5, Y5, Z5), (X6, Y6, Z6)

The relative "sizes" of these orbitals might surprise you. However, the graph was done correctly. What did you expect the relative "sizes" to be?
Probable Answer: equal

To understand why the angular parts of the orbitals along the z axis appear smaller than those in the xy plane, we must re-examine the wavefunctions we are graphing. Recall at the beginning of this exercise, you were told that the parameter α (in/a₀) needed to be specified. When α is set equal to a number, the radial part of the wavefunction then is calculated to be some numerical value. We are graphing the square of the wavefunction, so this value is squared when MathCad calculates the plot. Do you follow so far?

Now, a 3p orbital is more diffuse than the 3d orbital. Look at the graph of the radial distribution functions of the hydrogen (or hydrogen-like) wavefunctions below. For a given value of α (12, on the x axis of the graph below), the square of the numerical value (y axis) for a 3p orbital is larger than that for a 3d orbital. The values for the 3s and 3p are about equal. This means that hybrid orbitals that contain significant fractions of 3s and 3p atomic orbitals will appear larger than those that contain significant components of 3d orbitals.



Let's look at the angular parts of the hybrid orbitals. Those that point along the z axis are one-half 3p_z and one-half 3d_{z²}. (The contribution of an atomic orbital to a hybrid orbital is found by squaring the appropriate coefficient.) For the angular parts of the orbitals that are in the xy plane, what fraction is 3s, what fraction is 3p, and what fraction is 3d?

Answer: orbitals in xy plane are 1/4 3s, 1/2 3p, and 1/4 3d

Use these fractions to explain why the angular parts of the hybrid orbitals in the xy plane appear larger than those along the z axis.

Answer: For the fractional composition above, the orbitals in the xy plane are 3/4 p and s, so they will appear large. The orbitals pointing along the z-axis are 1/2 p, so they appear somewhat smaller.

For this set of orbitals, what would the molecular geometry be if all six lobes were involved in bonding? (An example of a molecule with this geometry is SF₆.)

Answer: octahedral

For this set of orbitals, what is the molecular geometry if five lobes are involved in bonding and one lobe contains a lone pair of electrons instead of a bonding pair? (An example of a molecule with this geometry is BrF₅.)

Answer: square pyramidal

For this set of orbitals, what are the possible molecular geometries if four lobes are involved in bonding and two lobes contain lone pairs instead of a bonding pair? (An example of a molecule with this geometry is XeF₄.)

Answer: square planar or see-saw

Summary Questions

1. How do the angular parts of the hybrid orbitals graphed here help you understand bonding involving sp^{3d} hybrids?
2. What possible molecular geometries arise from sp^{3d} hybridization? From sp^{3d²} hybridization?
3. How are these graphical representations useful for understanding the shapes of molecules?

