Applications of Calculus II

Applications of Polar Coordinates in Chemistry

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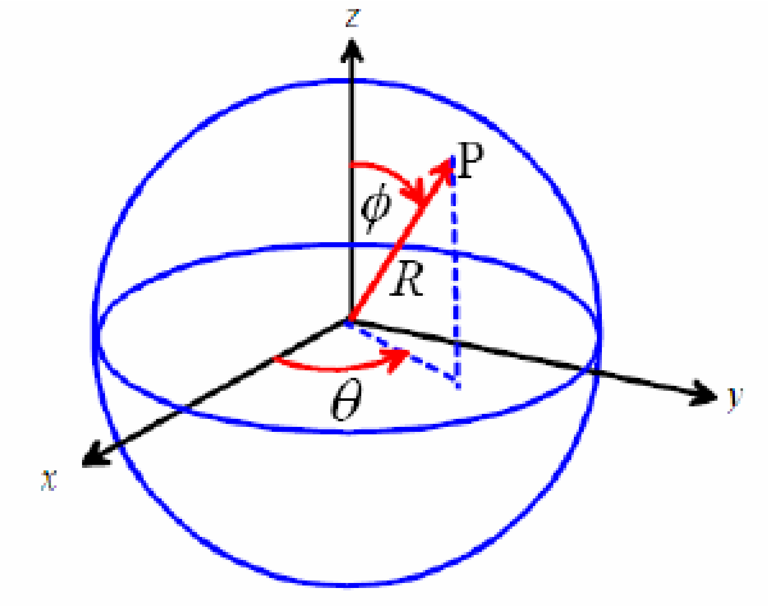
Spherical Polar Coordinates



$x = r\cos\theta \; ; \; y = r\sin\theta \; ; \; z = r\cos\varphi$

The Schrödinger Equation in Spherical Polar Coordinates

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right)+\frac{1}{r^2 \sin\varphi}\frac{\partial}{\partial \varphi}\left(\sin\varphi\frac{\partial \psi}{\partial \varphi}\right)+\frac{1}{r^2 \sin^2\varphi}\frac{\partial^2 \psi}{\partial \theta^2}+\frac{8\pi^2 m}{h^2}(E+V)\psi = 0$$

Solving the Schrödinger Equation

- To solve the equation we write the wave function Ψ, which is a function of r, θ and φ as the product of three functions R(r), Θ(θ) and Φ(φ)

Manipulation of the Schrödinger Equation

- Substitution into the Schrödinger Equation and division by RΘΦ gives:

$$\frac{1}{r^2 R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{1}{r^2\sin\varphi\Phi}\frac{d}{d\varphi}\left(\sin\theta\frac{d\Phi}{d\varphi}\right)+\frac{1}{r^2\sin^2\varphi}\left(\frac{1}{\Theta}\frac{d^2\theta}{d\theta^2}\right)+\frac{8\pi^2 m}{h^2}(E+V)\psi=0$$

Polar Coordinates in Chemistry

- Before we continue with the solution to the Schrödinger Equation let's see what you remember from last week's class meeting

Back to the Schrödinger Equation

- Spherical Polar Coordinates:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right)+\frac{1}{r^2\sin\varphi}\frac{\partial}{\partial \varphi}\left(\sin\varphi\frac{\partial \psi}{\partial \varphi}\right)+\frac{1}{r^2\sin^2\varphi}\frac{\partial^2\psi}{\partial \theta^2}+\frac{8\pi^2 m}{h^2}(E+V)\psi=0$$

- After substitution of R(r), Θ(θ) and Φ(φ) and division by RΘΦ:

$$\frac{1}{r^2 R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{1}{r^2\sin\varphi\Phi}\frac{d}{d\varphi}\left(\sin\theta\frac{d\Phi}{d\varphi}\right)+\frac{1}{r^2\sin^2\varphi}\left(\frac{1}{\Theta}\frac{d^2\theta}{d\theta^2}\right)+\frac{8\pi^2 m}{h^2}(E+V)\psi=0$$

Boundary Conditions

- Once we have divided the Schrödinger Equation into functions of Φ and φ; Θ and θ; and R and r we integrate the differential equations.
- However there are certain "Boundary" conditions that must be followed.
  - That is all integration constants can only take on integer values.

Quantum Numbers

- The integration constants are called "Quantum Numbers" and are designated by n, l, and m_l
  - n is the principal quantum number
    - $n = 1, 2, 3, \ldots \infty$
  - l is the angular momentum quantum number
    - $l = 0, 1, 2, \ldots (n - 1)$
  - m_l is the magnetic quantum number
    - $m_l = -l, \ldots 0 \ldots +l$

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Ψ and Ψ^2

- The wave functions, Ψ, which are solutions to the Schrödinger Equation are called orbitals
- Ψ^2 gives information about the region in space where the probability of finding the electron is greatest

Orbitals

- Orbitals are designated by certain letters. For example:

  $l = 0$ is called an “s” orbital

  $l = 1$ is called an “p” orbital

  $l = 2$ is called an “d” orbital

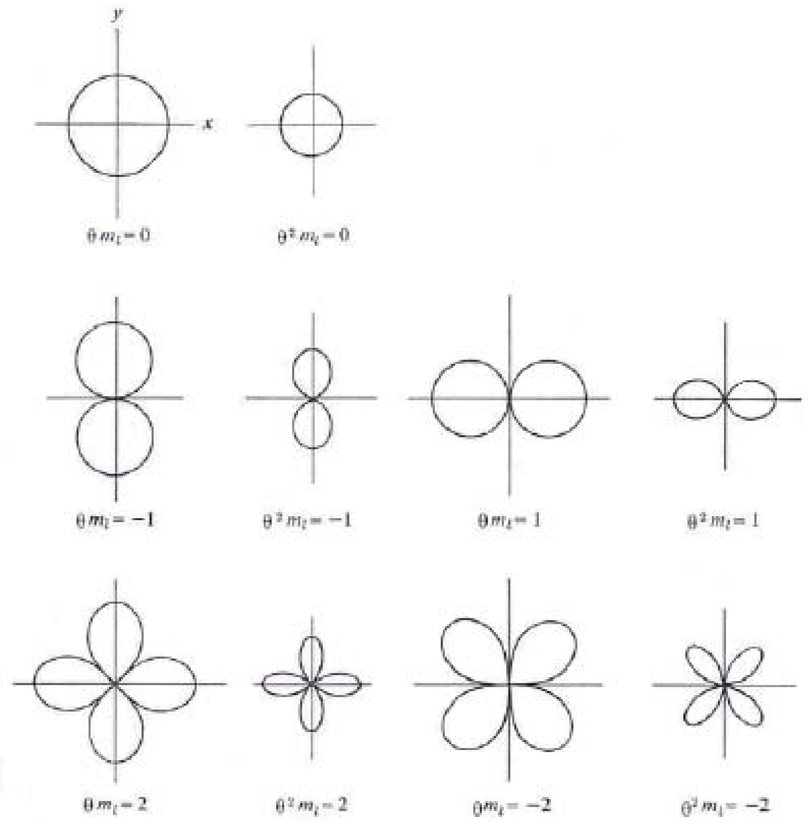
  $l = 3$ is called an “f” orbital

Solutions to Θ

- Let's take a look at solutions to the "Θ" part of the Schrödinger wave equation.

Value of m_l	Function
0	$\Theta_0 = \frac{1}{\sqrt{2\pi}}$
1	$\Theta_1 = \frac{1}{\sqrt{\pi}}\cos\theta$
-1	$\Theta_{-1} = \frac{1}{\sqrt{\pi}}\sin\theta$
2	$\Theta_2 = \frac{\cos(2\theta)}{\sqrt{\pi}}$
-1	$\Theta_{-2} = \frac{\sin(2\theta)}{\sqrt{\pi}}$

Plane Polar Plots of θ and θ^2



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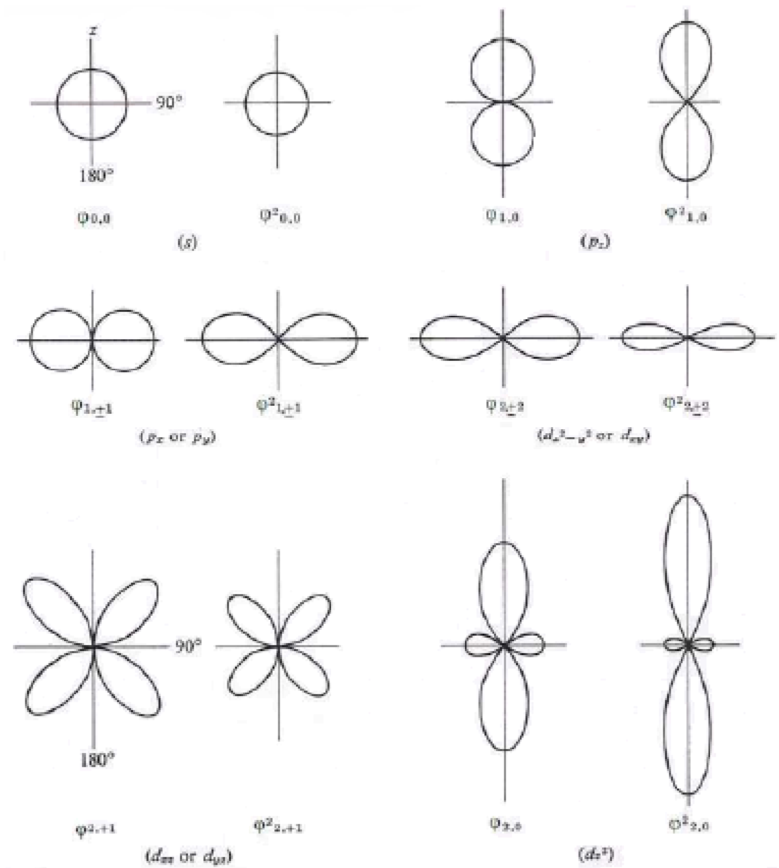
Solutions to Φ

- Solutions of the Φ part of the Schrödinger Equation

l	m_l	Function
0	0	$\Phi = \frac{1}{\sqrt{\pi}}$
1	0	$\Phi = \frac{\sqrt{6}}{2}\cos\varphi$
1	+1, -1	$\Phi = \frac{\sqrt{3}}{2}\sin\varphi$
2	0	$\Phi = \frac{\sqrt{10}}{4}\left(3\cos^2\varphi - 1\right)$
2	+1, -1	$\Phi = \frac{\sqrt{15}}{2}\sin\varphi\cos\varphi$
2	+2, -2	$\Phi = \frac{\sqrt{15}}{4}\sin^2\varphi$

Plane Polar Plot of φ and $φ^2$



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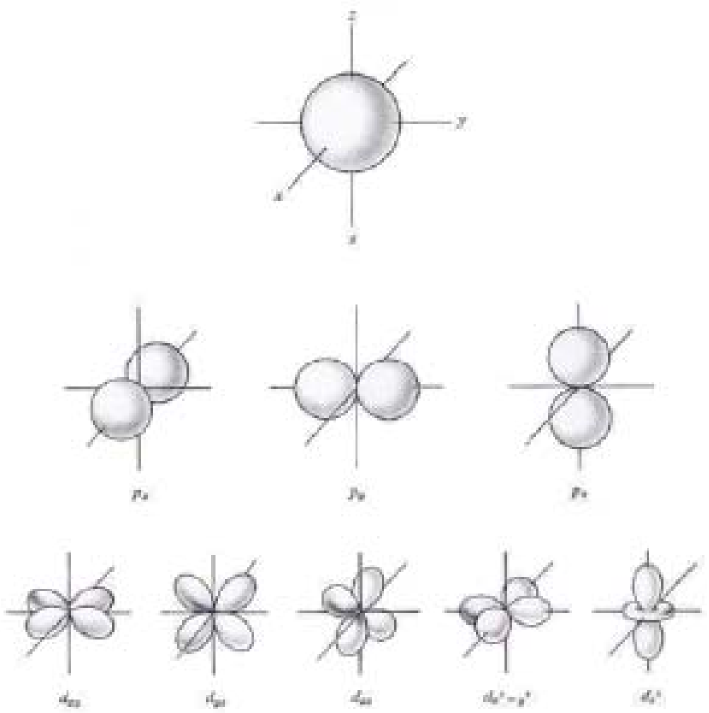
Plot of $[\Theta(\theta)\Phi(\varphi)]^2$

- Let's use both θ and φ in 3-dimensions and plot $[\Theta(\theta)\Phi(\varphi)]^2$



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Radial Portion of the Schrödinger Equation

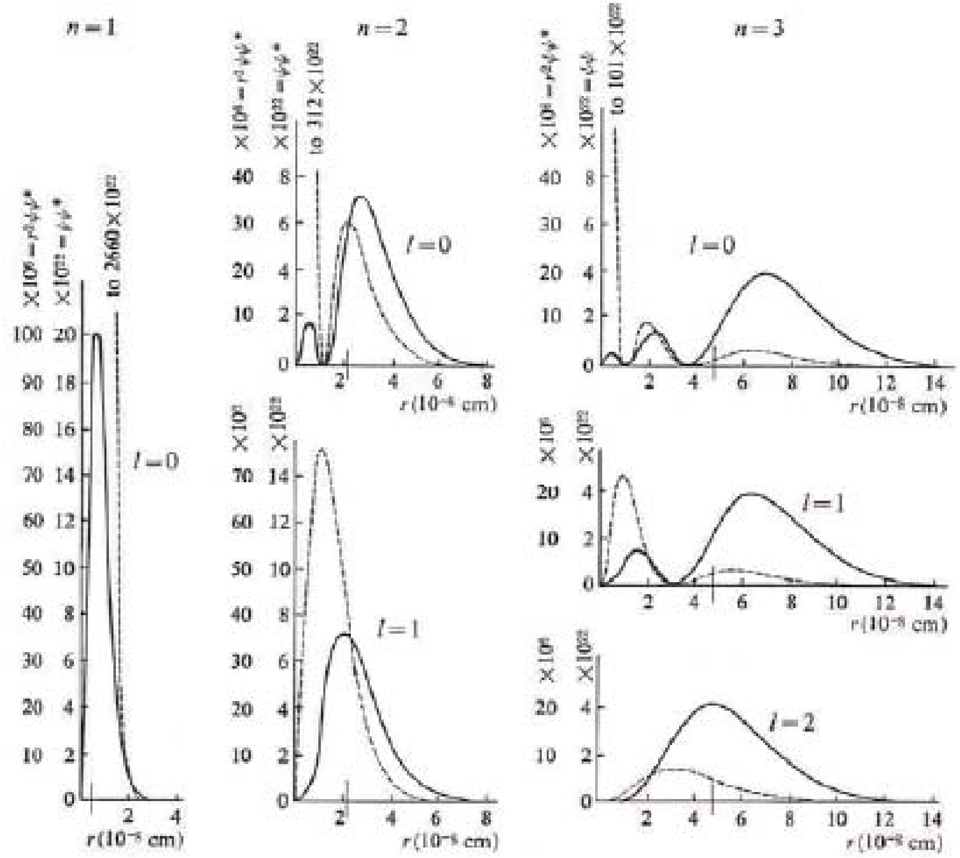
- Let's now look at the radial part of the Schrödinger Equation R(r).
- R(r) depends only on the "*n*" and "*l*" values and has an exponential term e^{-r/na_0} where a_0 = 0.529Å and a pre-exponential term involving a polynomial of the (*n*-1) degree

Solutions for R

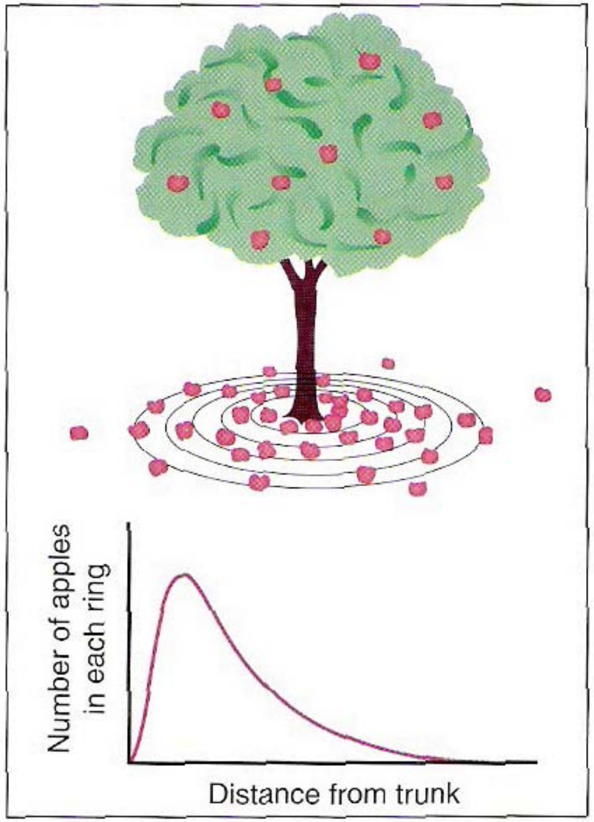
- Solutions of R for $n = 1$, $l = 0$; $n = 2$, $l = 0$; and $n = 2$, $l = 1$

n	l	Function
1	0	$R = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$
2	0	$R = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$
2	1	$R = \frac{1}{4\sqrt{6\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}$

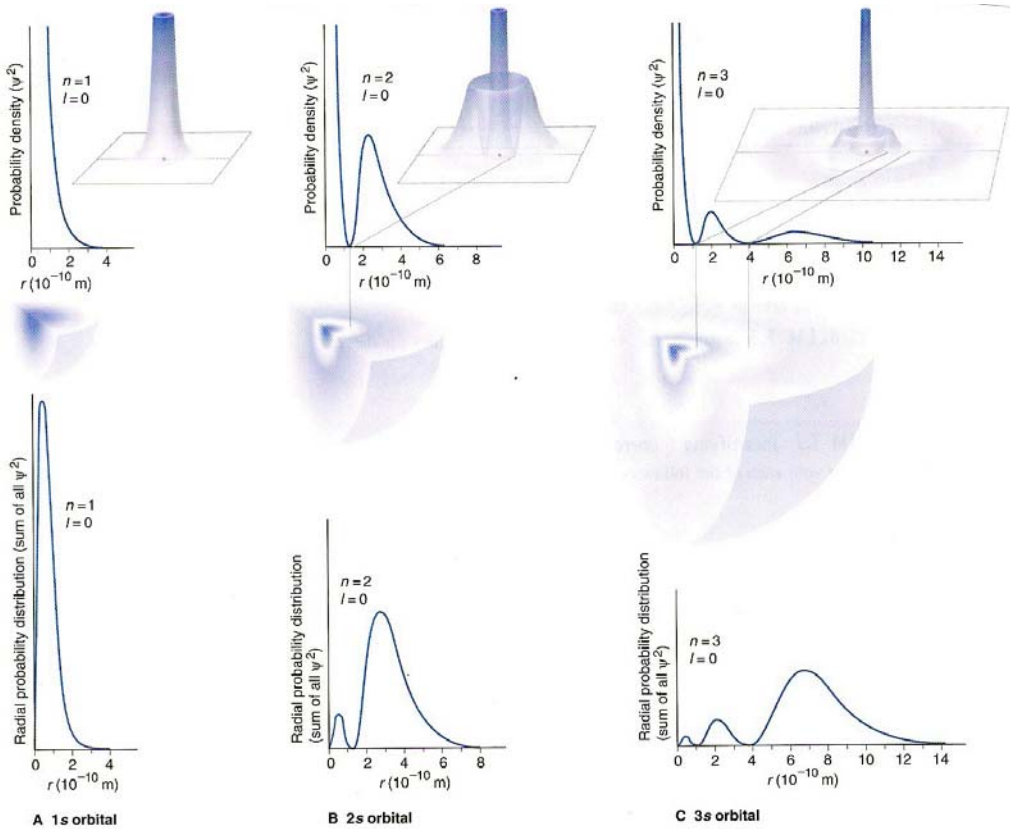
Plot of the Radial Probability Distribution Function



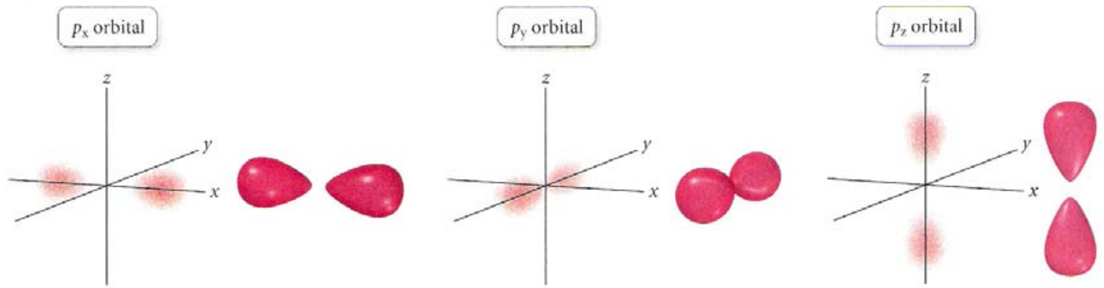
Radial Probability Distribution of Apples

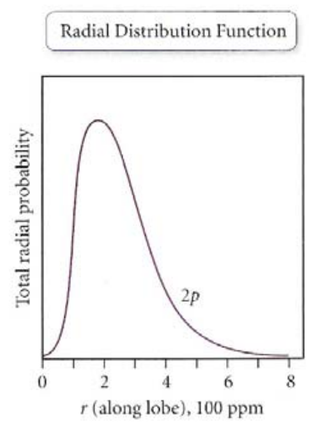


Another Way of Looking at the Radial Distribution Function



The 2p Orbitals





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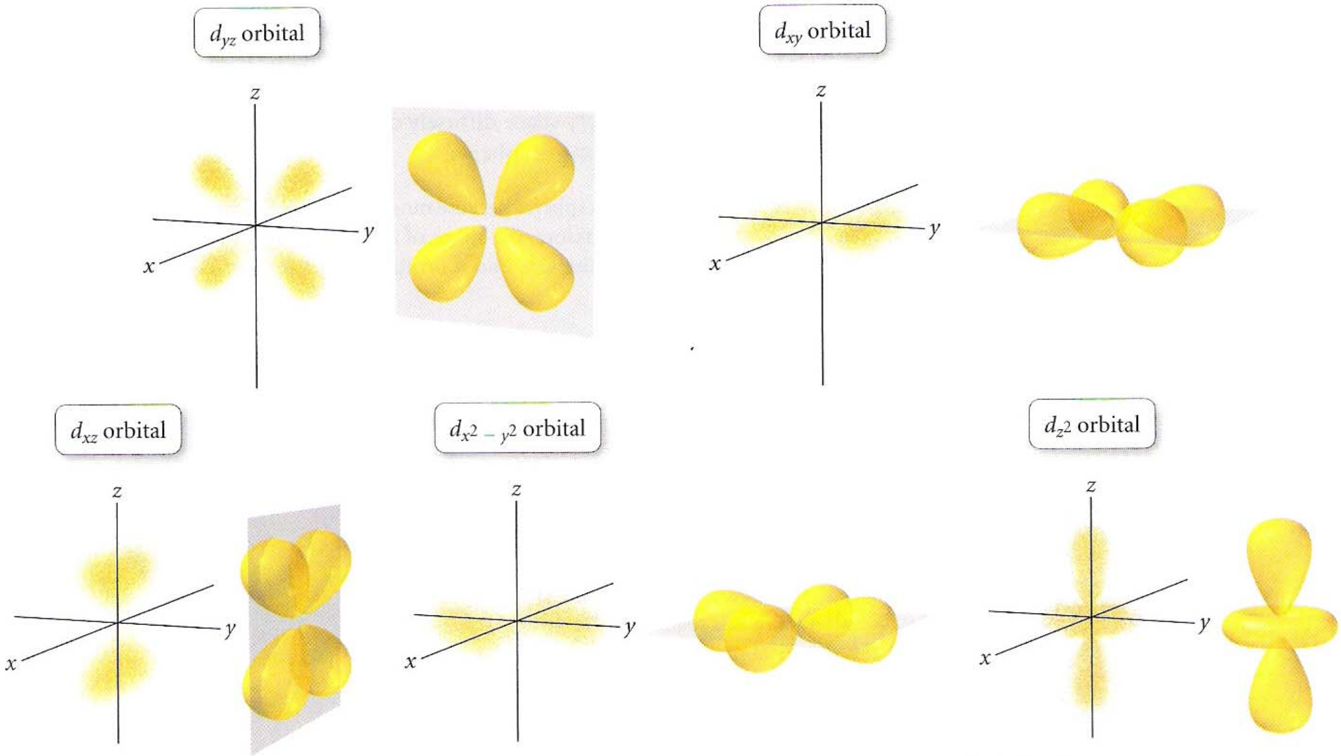
The 3-D Orbitals



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Molecules

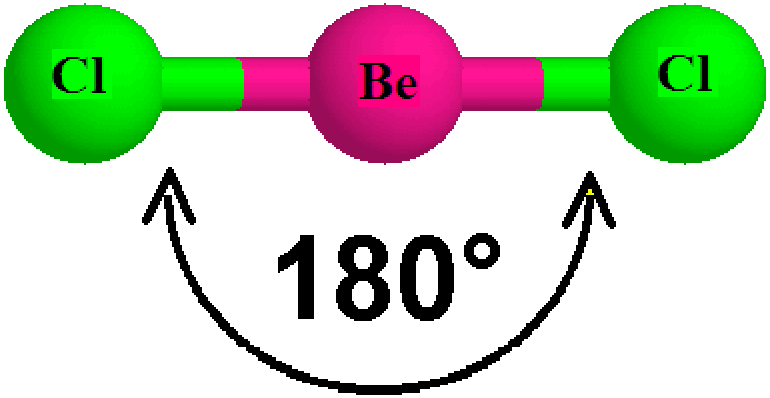
- Chemists are interested in more than just the shapes of atomic orbitals, we are interested in how the orbitals change shape in order to form MOLECULES

Molecular Shapes

- There are 5 basic shapes of molecules:
  - Linear
  - Trigonal Planar
  - Tetrahedral
  - Trigonal Bipyramid
  - Octahedral
- These shapes can be modified if lone pairs of electrons occupy one or more of the orbital positions

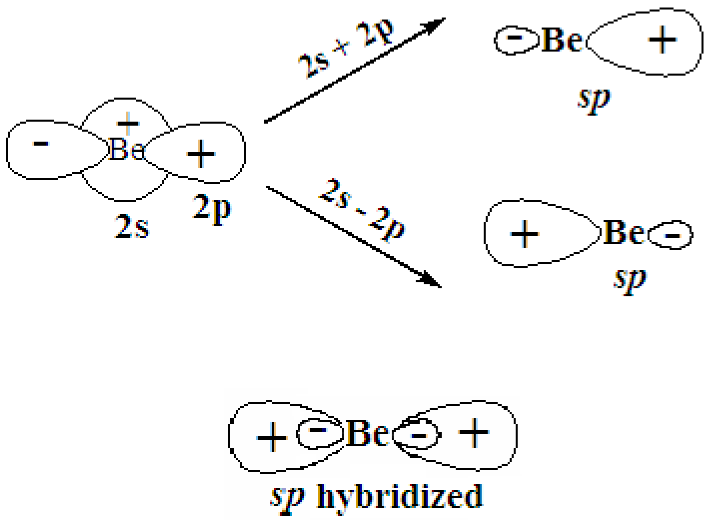
$BeCl_2$

- Let's construct with balloons the orbitals around the Be atom when it forms linear $BeCl_2$



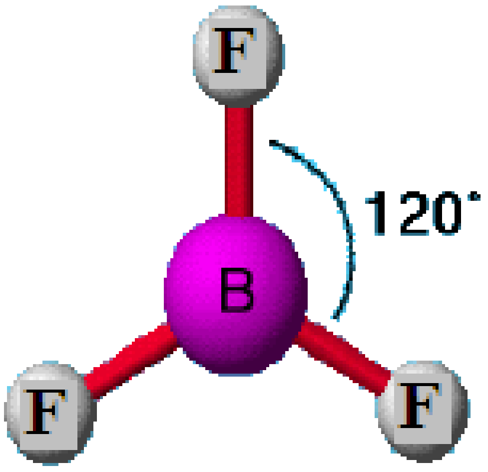
sp Hybridization

- How did the Be create these new orbitals
  - "Hybridization"



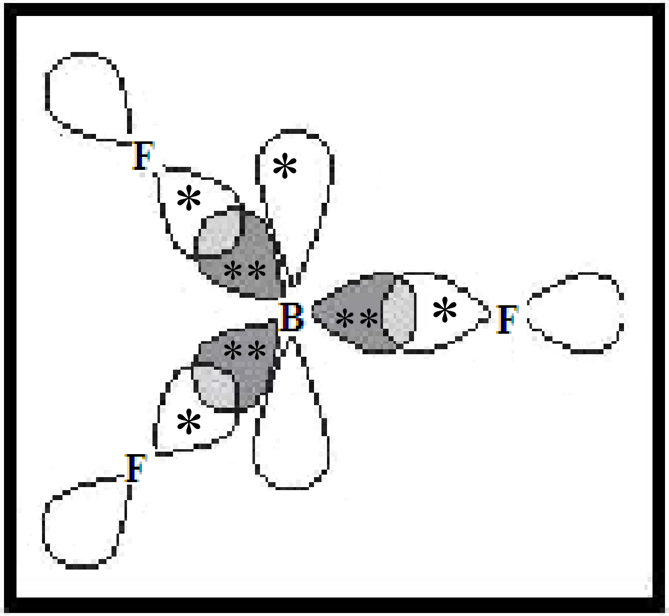
BF_3

- Construct with ballons the orbitals around the B atom when it forms BF_3



sp^2 Hybridization

- How did the B atom do this?



*p orbital
**sp^2 orbital

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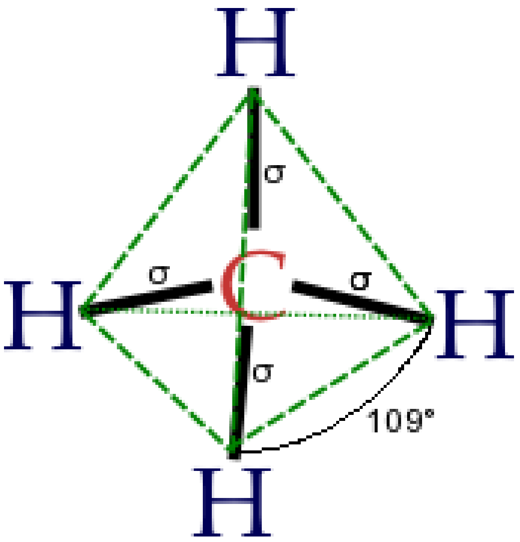
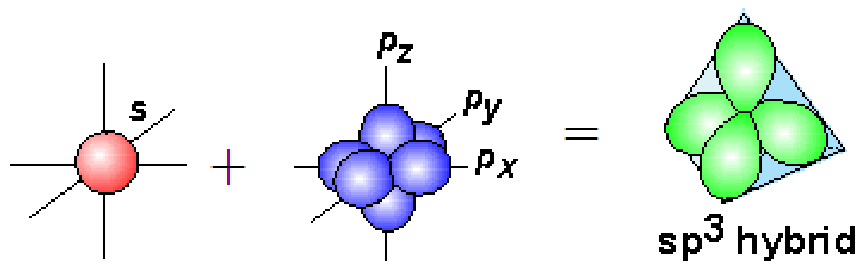
CH_4

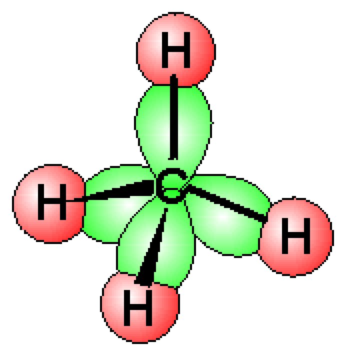
- Construct the orbital around C in CH_4
  - Tetrahedral geometry



sp^3 Hybridization

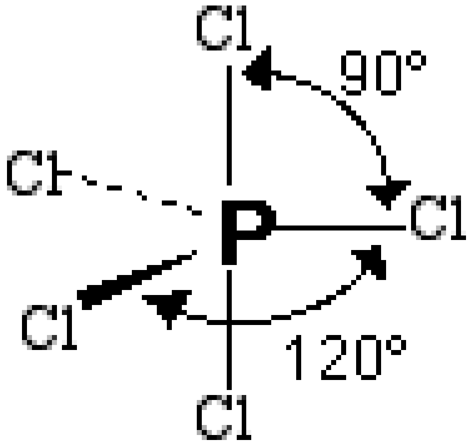
- How did the C atom do this?





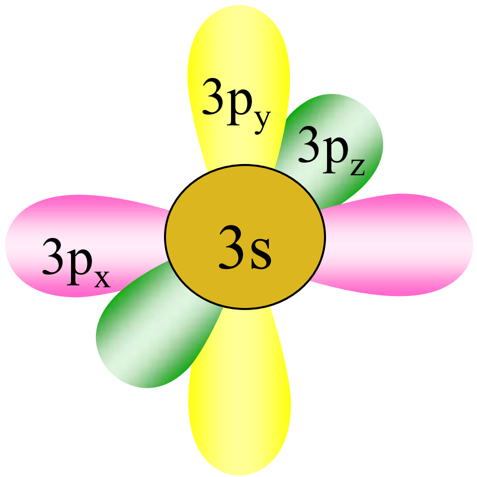
PCl_5

- Construct the orbital symmetry around the P atom in a molecule of PCl_5



$sp^3d_{z^2}$ Hybridization

- How did the P form these orbitals?



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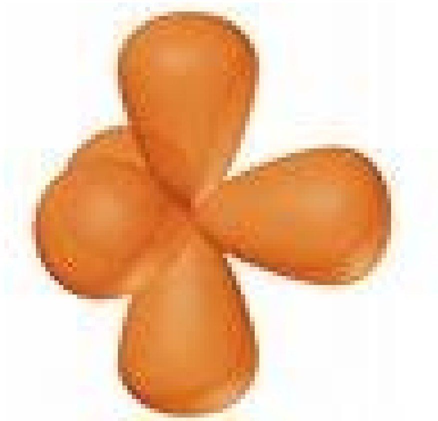
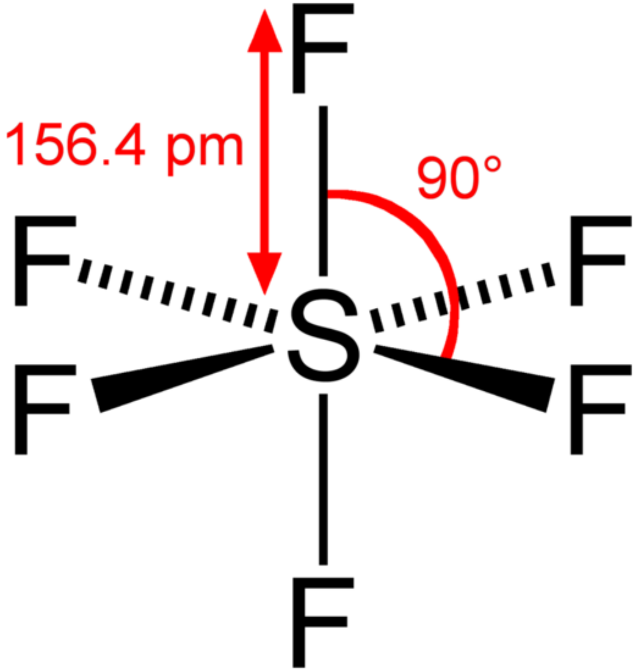


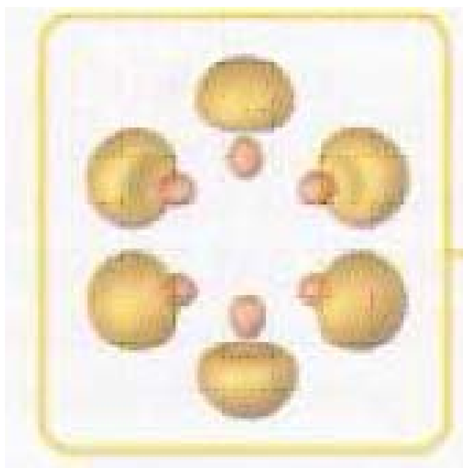
SF_6

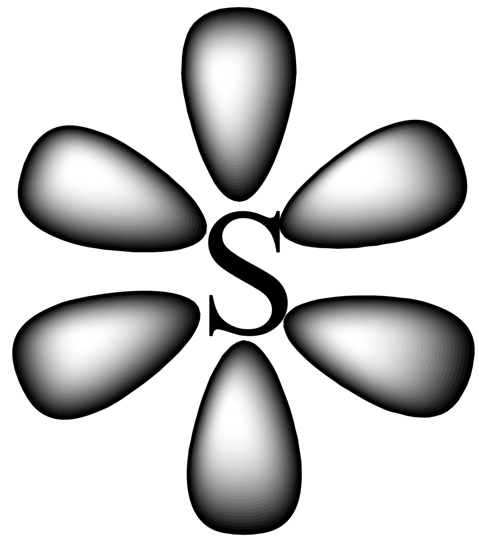
- Construct the orbital symmetry around the S atom in SF_6



$sp^3d_{x^2-y^2}d_{z^2}$ Hybridization

- How did the S do this?





The End

- You now know how chemists use polar coordinates