

# The Quantum Mechanical Treatment of the Hydrogen Atom

## Motivation:

Hydrogen atom orbitals and energy levels form the basis of an understanding of larger molecules.

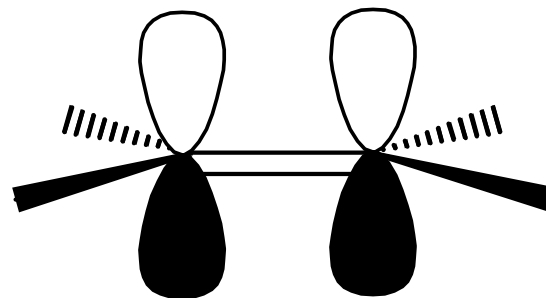
In fact, the results of the quantum mechanical treatment of the hydrogen atom permeate through our modern description of chemistry.

*covalent bonding*

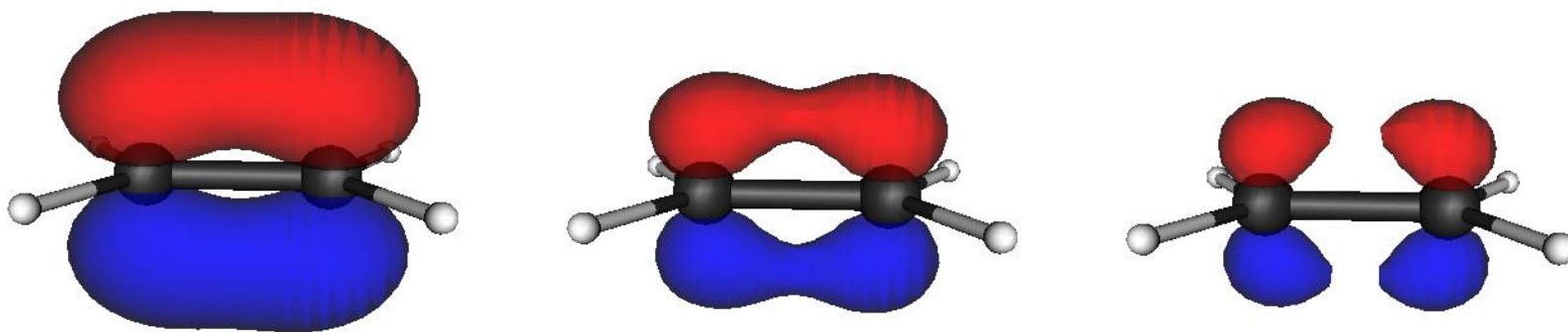
*molecular orbitals*

*hybridization*

For example, we often speak of the  $\pi$ -bond in a C-C double bond as a result of the interaction between two p orbitals on each carbon.

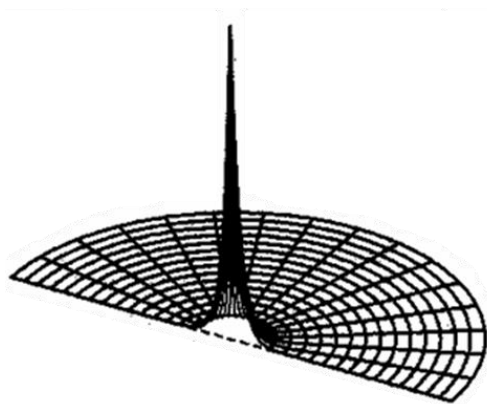


The orbitals we so often speak of come from the quantum mechanical treatment of the hydrogen atom.

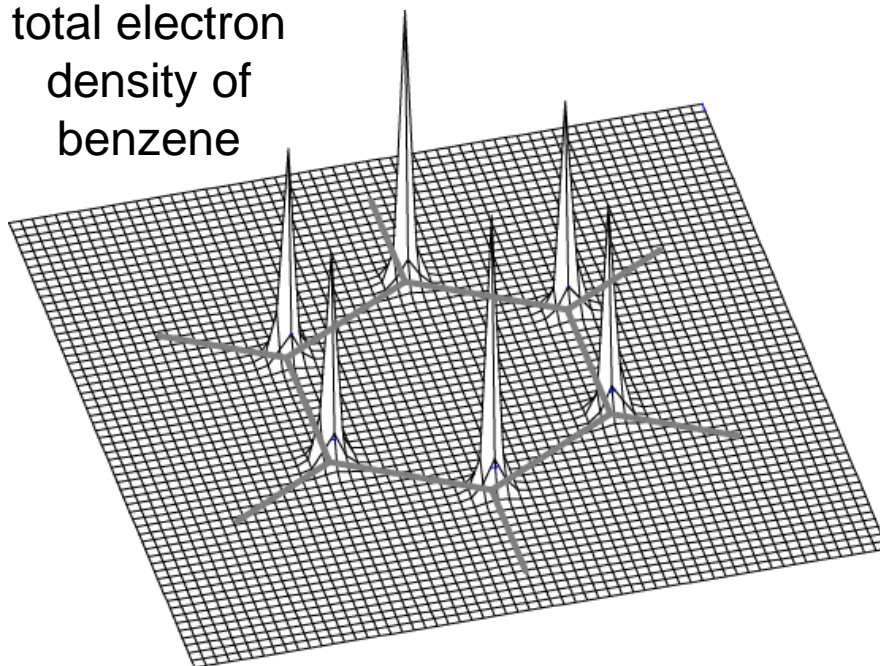


3-D plot of the  $\pi$ -bonding orbital in ethylene from a quantum chemical calculation.

*H atom ground state  
electron density*

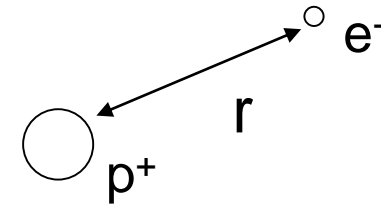


total electron  
density of  
benzene



# The Hydrogen Atom – The Physical Model

The hydrogen atom is a two-particle system consisting of a proton and an electron.



We will treat the proton and electron as point masses that interact via Coulomb's Law given by (in SI units):

$$V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$

*How does this potential compare to harmonic oscillator?*

$r$  is the distance between the electron and nucleus.

$e$  is the charge of the electron:

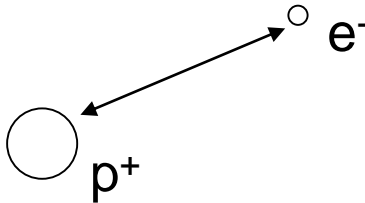
$$e = 1.602 \times 10^{-19} \text{ C}$$

$\epsilon_0$  is the vacuum permittivity constant and in SI units has a value of:

$$\epsilon_0 = 8.854188 \times 10^{-12} \text{ C}^2 \cdot \text{s}^2 \cdot \text{kg}^{-1} \cdot \text{m}^{-3}$$



The quantum mechanical Hamiltonian for this system is:

$$\hat{H} = -\frac{\hbar^2}{2m_p} \nabla_p^2 - \frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$


The diagram shows a large circle labeled p+ and a smaller circle labeled e-. An arrow points from the p+ circle to the e- circle, representing the distance r between the two particles.

This is a two-particle system, and just like the Harmonic Oscillator and Rigid Rotor problem, we can separate the Hamiltonian into a center of mass coordinate and a relative coordinate system:

$$\hat{H}_{total} = \hat{H}_{CM} + \hat{H}_{int}$$

$$\hat{H}_{CM} = -\frac{\hbar^2}{2(m_p + m_e)} \nabla_{CM}^2 \quad \text{translational motion of the center of mass}$$

$$\hat{H}_{int} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \quad \text{relative or internal motion}$$

where  $\mu$  is the reduced mass

$$\mu = \frac{m_e m_p}{m_e + m_p}$$

$$\hat{H}_{total} = -\frac{\hbar^2}{2(m_p + m_e)} \nabla_{CM}^2 - \frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$
$$= \hat{H}_{CM} + \hat{H}_{int}$$

This Hamiltonian is **separable**, with the solution of the center of mass Hamiltonian being that of the free particle, we have previously examined.

We want to find the wave functions that govern the **internal motion** of the system.

$$\hat{H}_{int}\psi = E\psi$$

These solutions are the hydrogen atom wave functions that we are interested in.

The Hamiltonian operator for the internal energy of the hydrogen atom is:

$$\hat{H}_{\text{int}} = \hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$

kinetic energy of  
internal motion

potential energy,  
Coulomb's law.

In many textbooks, you will often see the hydrogen-atom Hamiltonian written with  $m_e$ , the mass of the electron, instead of  $\mu$ .

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$

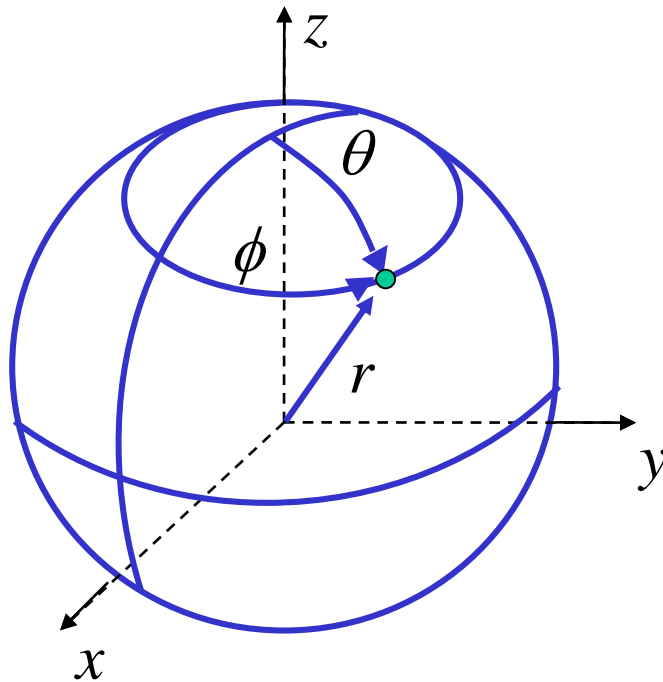
**Who is correct? Are these other textbooks incorrect?**



$$\mu = \frac{m_e m_p}{m_e + m_p}$$

## Schrödinger's equations for the H atom is Best Solved in Polar Spherical Coordinates

This problem has the same spherical symmetry as the 3-D rigid rotor, so this suggests that it would be easier to solve our problem in polar spherical coordinates.



$$\psi \rightarrow \psi(r, \theta, \phi)$$

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

***What do we need to do to convert our Hamiltonian into polar spherical coordinates?***

$$0 \leq r < \infty$$

$$0 \leq \theta \leq \pi$$

$$0 \leq \phi \leq 2\pi$$

# Polar Spherical Coordinates

The **Laplacian operator** in polar spherical coordinates is:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

*(there is no need to memorize the above, but you should know how to work with it and what it means)*

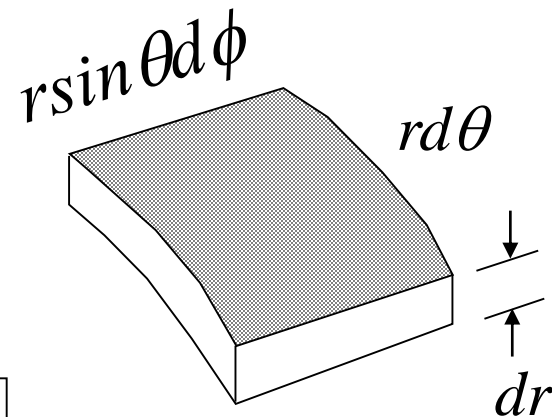
## The Integration Element

In Cartesian coordinates the integration over all space involves the following integration element:

$$d\tau = dx \, dy \, dz$$

The equivalent integration element in polar spherical coordinates is given by:

$$d\tau = r^2 \sin \theta \, dr \, d\theta \, d\phi$$





$$\hat{H}\psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$$

In polar spherical coordinates the Schrodinger equation becomes:

$$\left( -\frac{\hbar^2}{2\mu} \left( \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) - \frac{e^2}{4\pi\epsilon_0 r} \right) \psi = E\psi$$

Unlike the rigid rotor,  **$r$  is not fixed** because the electron is free to move closer or farther away from the nucleus.

Therefore, we cannot simplify the Laplacian further. This is unfortunately the Schrödinger equation we have to work with!

The **Hamiltonian is not separable**, but if we multiply both sides of the SE by  $2\mu r^2$ , it becomes pseudo-separable.

$$-\hbar^2 \left( \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \psi + \underbrace{\left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)}_{\text{depends only on } \phi \text{ and } \theta} \psi \right) - \frac{2\mu r^2 e^2}{4\pi\epsilon_0} \frac{1}{r} \psi = 2\mu r^2 E \psi$$

*depends only on  $\phi$  and  $\theta$*

The above is pseudo-separable, so we can collect angular components ( $\theta$  and  $\phi$ ) on one side and radial components on the other side.

Collecting sides gives:

*radial dependence  
(depends on  $r$ )*

*angular dependence  
(depends on  $\phi$  and  $\theta$ )*

$$\hbar^2 \frac{\partial}{\partial r} r^2 \frac{\partial \psi}{\partial r} + \left( \frac{2\mu r^2 e^2}{4\pi\epsilon_0} \frac{1}{r} + 2\mu r^2 E \right) \psi = -\hbar^2 \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \psi$$

This suggests that we can write our total hydrogen atom wave function as a product of a radial and angular functions.

## The Hydrogen Atom Wave Function can be Written as a Product of Radial and Angular Components

$$\psi(r, \theta, \phi) = R(r) \cdot A(\theta, \phi)$$

Using this form of the wave function and substituting into the last equation on the previous slide and rearranging gives:

$$\frac{1}{R} \left( \hbar^2 \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{2\mu r^2 e^2}{4\pi\epsilon_0} \frac{1}{r} + 2\mu r^2 E \right) R = -\frac{\hbar^2}{A} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) A$$

Because the lhs depends only on the variable  $r$ , and the rhs depends only on the angular variables  $\theta$  and  $\phi$ , each side must be equal to a constant.

$$\frac{1}{R(r)} \left( \hbar^2 \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{2\mu r^2 e^2}{4\pi\epsilon_0} \frac{1}{r} + 2\mu r^2 E \right) R(r) = \lambda = lhs$$

$$rhs = \lambda = -\frac{\hbar^2}{A(\theta, \phi)} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) A(\theta, \phi)$$

# The Angular Part of the Hydrogen Atom Wave Function

Let's first examine the angular part of the hydrogen atom Schrödinger equation:

$$\lambda = -\frac{\hbar^2}{A(\theta, \phi)} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) A(\theta, \phi)$$

Multiplying both sides by  $A$  gives:

$$\underbrace{-\hbar^2 \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)}_{\hat{L}^2} A(\theta, \phi) = \lambda A(\theta, \phi)$$

The above is simply an eigenvalue equation, where the operator is the  $L^2$  operator.

$$\hat{L}^2 A(\theta, \phi) = \lambda A(\theta, \phi)$$

***Haven't we already solved these already? What is  $A$ ?***

# Spherical Harmonics Make up the Angular Component of the Total Hydrogen Atom Wave Function

The spherical harmonics are eigenfunctions of the  $L^2$  operator, recall:

$$\hat{L}^2 Y_{\ell m}(\theta, \phi) = \hbar^2 \ell(\ell + 1) \cdot Y_{\ell m}(\theta, \phi) \quad \begin{array}{l} \ell = 0, 1, 2, \dots \\ m = 0, \pm 1, \pm 2, \dots, \pm \ell \end{array}$$

Comparing the above and our angular Schrödinger equation

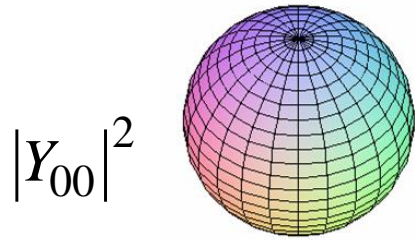
$$\hat{L}^2 A(\theta, \phi) = \lambda A(\theta, \phi)$$

tells us that:

$$A(\theta, \phi) = Y_{\ell m}(\theta, \phi) \quad \lambda = \hbar^2 \ell(\ell + 1)$$

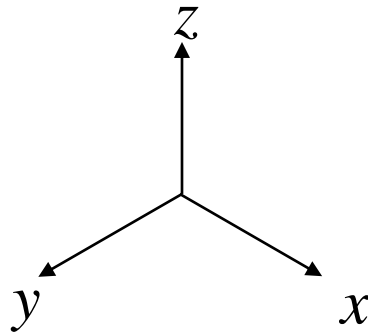
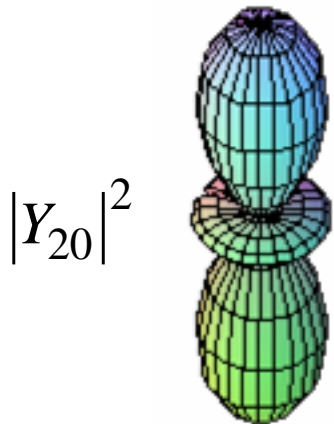
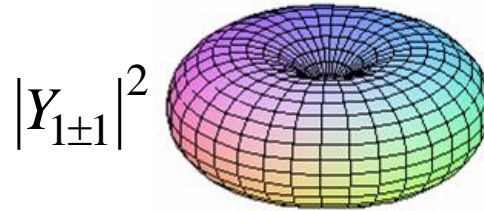
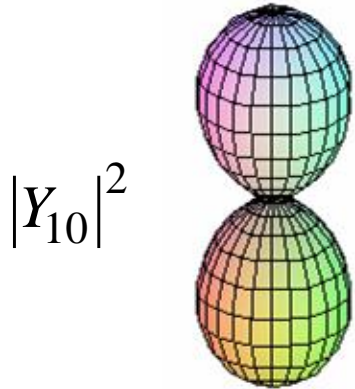
So the angular component of the total wave function of the hydrogen atom are the spherical harmonics:

$$\psi(r, \theta, \phi) = R(r) Y_{\ell, m}(\theta, \phi)$$



This is why the angular plots of the spherical harmonics looked like our familiar s, p and d orbitals.

Some of them don't, like the donut below (to be discussed shortly).



*We have solved for the angular part of the total hydrogen atom wave function, now we need to solve for the radial component.*

## Solving for the Radial Component of the H-Atom Wave Function

From a few slides back, we had an expression for the radial wave function  $R(r)$ ,

$$\frac{1}{R(r)} \left( \hbar^2 \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{2\mu r^2 e^2}{4\pi\epsilon_0} \frac{1}{r} + 2\mu r^2 E \right) R(r) = \lambda$$

From the solution of the angular part, we know that rearranging

equation and dividing through by  $2\mu r^2$  gives:

$$\left( -\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{\hbar^2 \ell(\ell+1)}{2\mu} \frac{1}{r^2} \right) R(r) = ER(r)$$

$\lambda = \hbar^2 \ell(\ell+1)$

This is known as the **radial Schrödinger equation** for the hydrogen atom. This is the only new equation we have to solve for to get our total wave function for the hydrogen atom.

Again, we will not explicitly solve this equation. The solutions will simply be presented and analyzed.

# Radial Wave Functions of the Hydrogen Atom

The solution of the radial Schrödinger equation gives what the radial wave function that depends on a new **quantum number,  $n$** .

$$R_{nl}(r) \quad \begin{array}{l} n = 1, 2, 3... \\ \ell = 0, 1, 2...n-1 \end{array}$$

Notice the new restriction on the quantum number  $\ell$  (why?) and that that radial wave function does not depend on the quantum number  $m$ .

The general form of the radial wave function is:

$$R_{nl}(r) = \left( \begin{array}{c} \text{normalization} \\ \text{constant} \end{array} \right) \left( \begin{array}{c} \text{exponential decay} \\ \text{function:} \\ e^{-r/na_o} \end{array} \right) \left( \begin{array}{c} \text{polynomial} \\ \text{in } r \end{array} \right)$$

All hydrogen atom wave functions decay exponentially away from the nucleus.



# Normalized Radial Functions of the Hydrogen Atom

$$R_{nl}(r) \quad \begin{array}{l} n = 1, 2, 3 \dots \\ \ell = 0, 1, 2 \dots n-1 \end{array}$$

$n = 1$

$$R_{10} = 2 \left( \frac{1}{a_0} \right)^{3/2} e^{-r/a_0}$$

$$\text{Bohr radius } a_0 = \epsilon_0 h^2 / \pi \mu e^2 \\ = 0.0529 \text{ nm}$$

$n = 2$

$$R_{20} = \frac{1}{\sqrt{2}} \left( \frac{1}{a_0} \right)^{3/2} \left( 1 - \frac{r}{2a_0} \right) e^{-r/2a_0}$$

$$R_{21} = \frac{1}{2\sqrt{6}} \left( \frac{1}{a_0} \right)^{5/2} r e^{-r/2a_0}$$

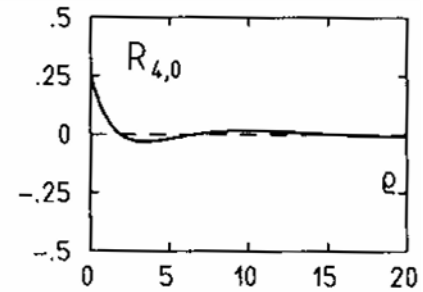
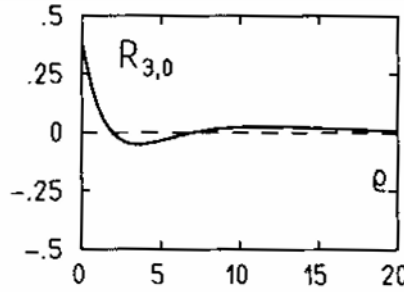
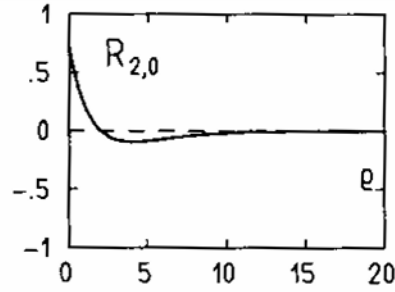
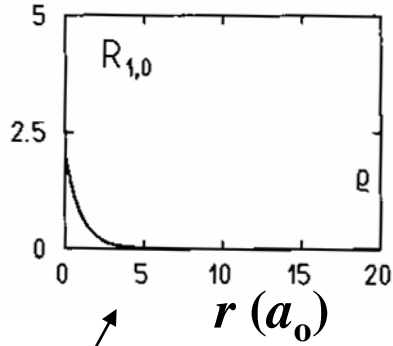
$n = 3$

$$R_{30} = \frac{2}{3\sqrt{3}} \left( \frac{1}{a_0} \right)^{3/2} \left( 1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2} \right) e^{-r/3a_0}$$

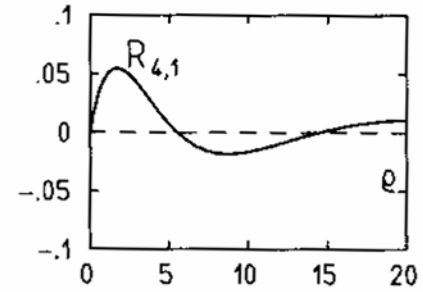
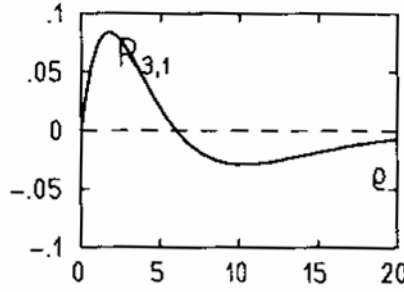
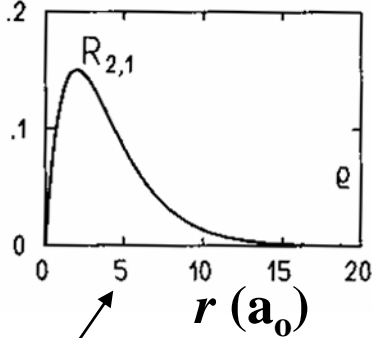
$$R_{32} = \frac{4}{81\sqrt{30}} \left( \frac{1}{a_0} \right)^{7/2} r^2 e^{-r/3a_0}$$

$$R_{31} = \frac{8}{27\sqrt{6}} \left( \frac{1}{a_0} \right)^{3/2} \left( \frac{r}{a_0} - \frac{r^2}{6a_0^2} \right) e^{-r/3a_0}$$

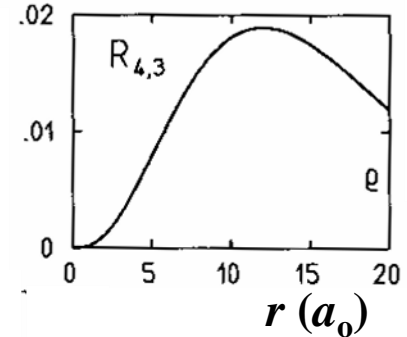
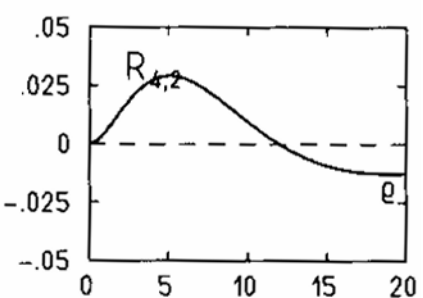
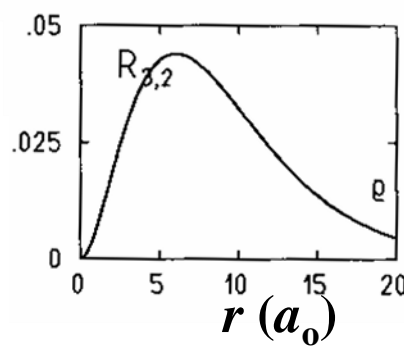
# Plots of Radial Wave Functions



$$R_{10} = 2 \left( \frac{1}{a_0} \right)^{3/2} e^{-r/a_0}$$



$$R_{21} = \frac{1}{2\sqrt{6}} \left( \frac{1}{a_0} \right)^{5/2} r e^{-r/2a_0}$$



The radial wave functions are plotted as a function of  $r$  in units of

**Bohr radii**  $a_0 = (\epsilon_0 h^2) / (\pi \mu e^2)$

## The Energy of the Hydrogen Atom

$$\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) R(r) + \left( \underset{\uparrow}{E} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} - \frac{\hbar^2 \ell(\ell+1)}{2\mu} \frac{1}{r^2} \right) R(r) = 0$$

The energy of the hydrogen atom can be derived by solving the radial Schrödinger equation. It is given by:

$$E = -\frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{n^2} = -\frac{e^2}{8\pi\epsilon_0 a_0} \frac{1}{n^2} \quad n = 1, 2, 3\dots$$

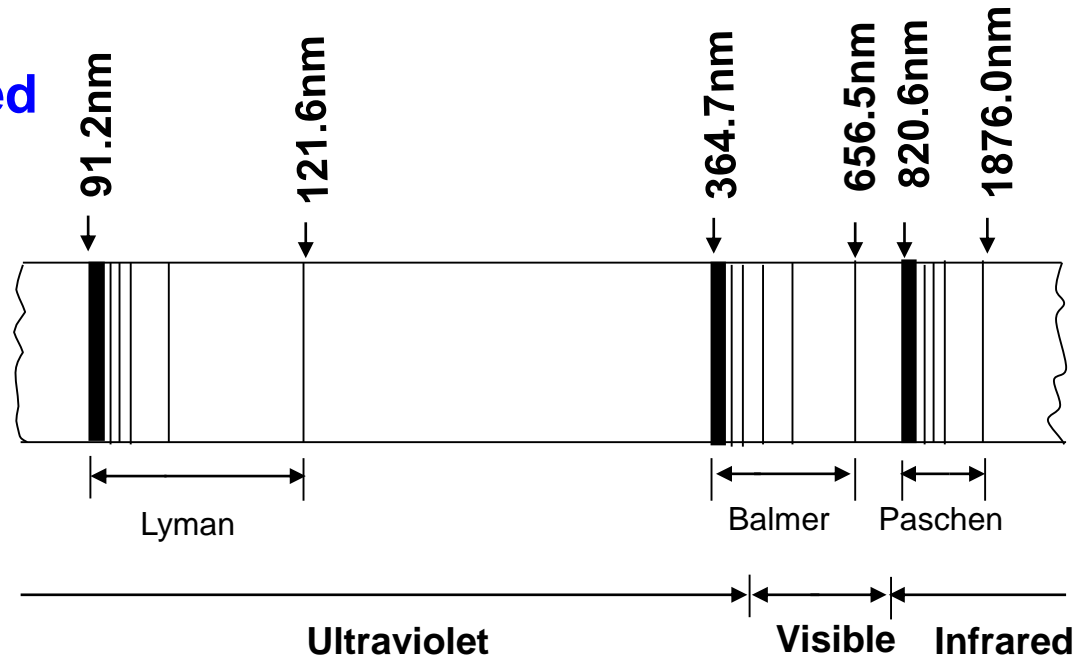
The total energy of the hydrogen atom depends only on the quantum number  $n$ , and not on the other two quantum numbers,  $\ell$  and  $m$ .

NOTE that  **$E$  is the total energy** (kinetic + electrical potential energy) of the hydrogen atom, not just the 'radial energy'.

## Experimental Verification of the Hydrogen-Atom Solution

One of the most powerful experimental verifications of the quantum mechanical description of the hydrogen atom involves the emission spectra of hydrogen atoms. Selection rule for H-atom electronic transitions:

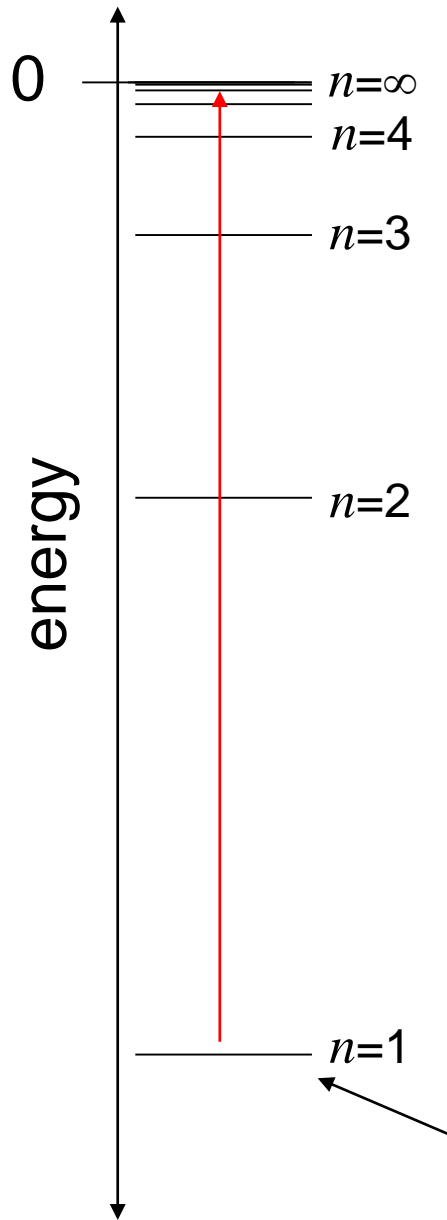
$\Delta n$  unrestricted



The energy levels are essentially in exact agreement with the discrete line spectra of atomic hydrogen.

$$\Delta E_{n_1, n_2} = -\frac{e^2}{8\pi\epsilon_0 a_0} \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

# The Ground State Energy and the Ionization Energy



The numerical value of the ground state energy (**13.59670 eV**) is given by:

$$E_1 = -\frac{e^2}{8\pi\epsilon_0 a_0} \frac{1}{1^2} = -1311.9 \text{ kJ/mol}$$

The ionization energy is the energy required to remove an electron from the ground state of an atom.

Experimentally, the hydrogen atom ionization energy is  $-1311.9 \text{ kJ/mol}$ .

This is another powerful way the quantum mechanical description of the hydrogen atom can be confirmed experimentally.

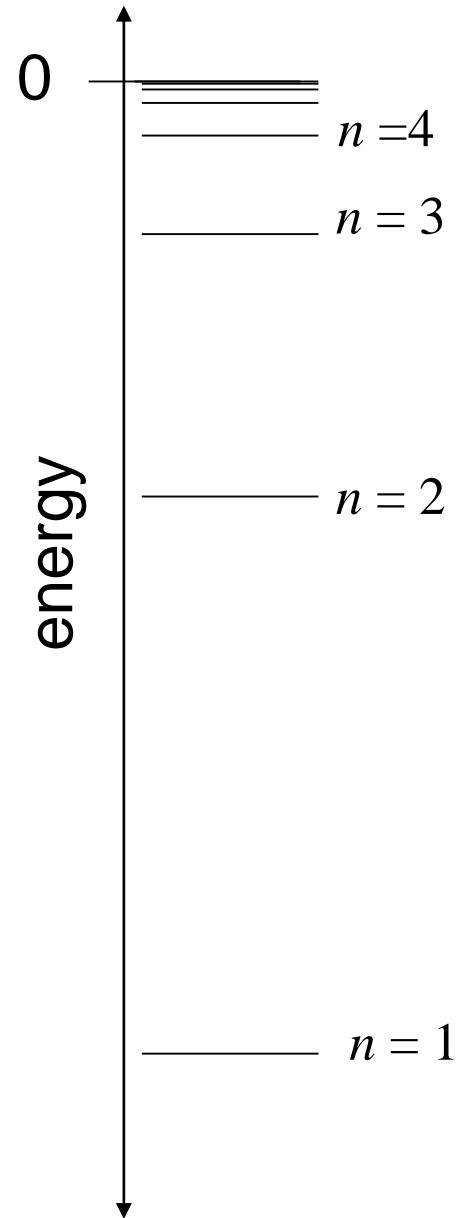
$-1311.9 \text{ kJ/mol}$

$$E = -\frac{e^2}{8\pi\epsilon_0 a_0} \frac{1}{n^2} \quad n = 1, 2, 3\dots$$

The hydrogen atom energy levels are depicted to the right.

Notice that the energies are all **negative**, and as  $n$  increases, the energy tends to zero.

***Does this make sense?***



# Lagoon Nebula using the VLT (very large telescope) in Chile





## Trifid Nebula

**Red:** H alpha  
( $n = 3$  to  $n = 2$ )

**Blue:** scattered  
light

**Dark brown:**  
dust



# Rosette Nebula using the VLT



# Total Wave Functions for “Hydrogen-Like” Atoms

(One-Electron Systems: H, He<sup>+</sup>, Li<sup>2+</sup>, Be<sup>3+</sup>, ...)

The total wave function of the hydrogen atom is **the product of the radial wave function  $R(r)$  and the spherical harmonic  $Y_{nl}(\phi, \theta)$ :**

$$\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r)Y_{\ell m}(\theta, \phi)$$

$$n = 1, 2, 3 \dots$$

$$\ell = 0, 1, 2 \dots (n - 1)$$

$$m = 0, \pm 1, \pm 2 \dots \pm \ell$$

Notice that there are three distinct quantum numbers that characterize the state of a hydrogen atom.

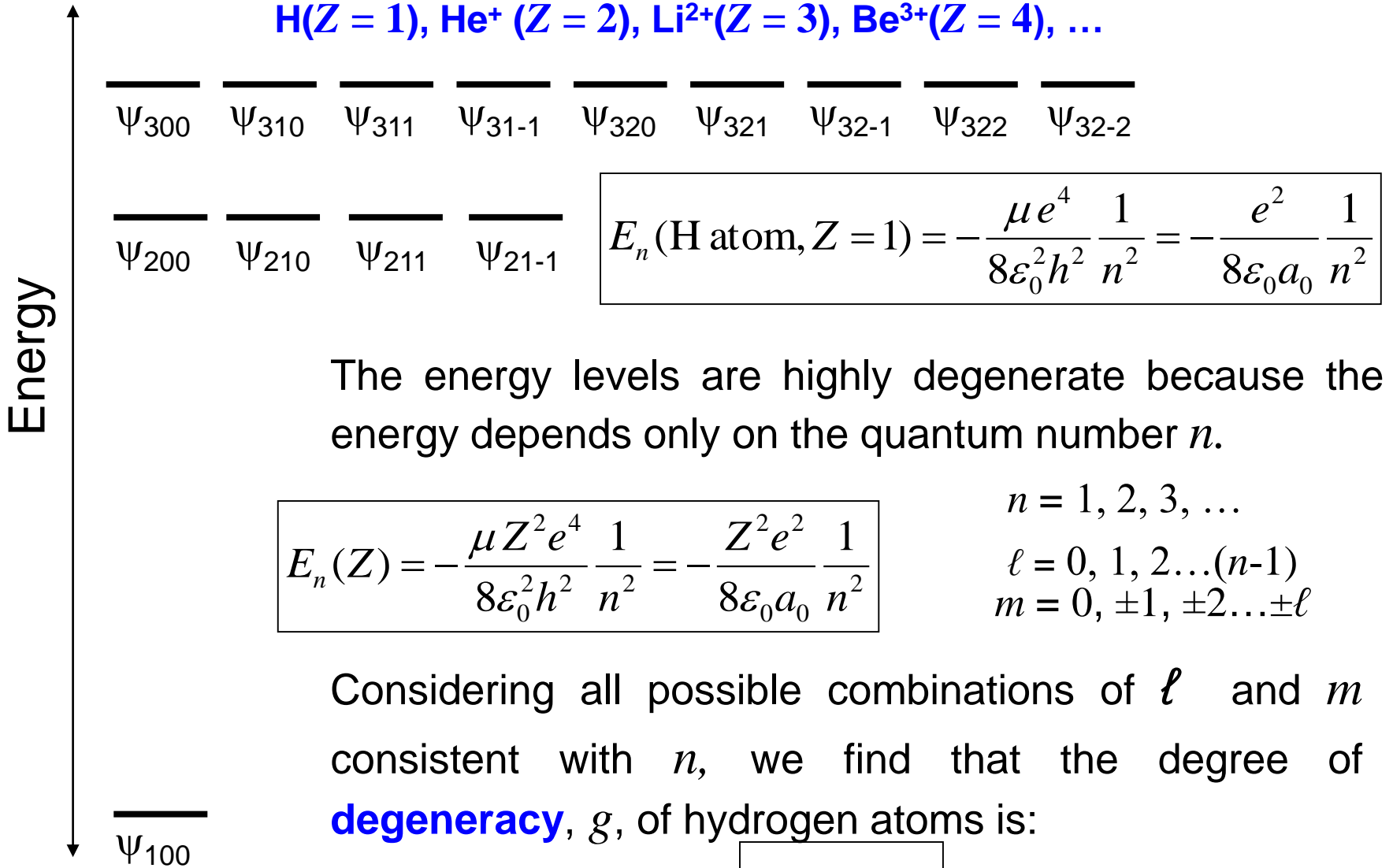
We, therefore label the total wave function with these three quantum numbers,  $n$ ,  $\ell$  and  $m$ , usually in this order.

$$\psi_{100} \rightarrow n = 1, \ell = 0, m = 0$$

$$\psi_{32-1} \rightarrow n = 3, \ell = 2, m = -1$$

# Degeneracies of the Hydrogen-Like Atom States

H ( $Z = 1$ ), He<sup>+</sup> ( $Z = 2$ ), Li<sup>2+</sup> ( $Z = 3$ ), Be<sup>3+</sup> ( $Z = 4$ ), ...



# Complete Hydrogen Atom Wave Functions

wave functions  $\Psi_{nlm}(r, \theta, \phi)$   
for  $n = 1, 2,$  and  $3$

**$n = 1, \ell = 0$**

$$\psi_{100} = \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_o} \right)^{3/2} e^{-r/a_o}$$

**$n = 3, \ell = 0$**

$$\psi_{300} = \frac{1}{81\sqrt{3\pi}} \left( \frac{1}{a_o} \right)^{3/2} \left( 27 - \frac{18r}{a_o} + 2 \left( \frac{r}{a_o} \right)^2 \right) e^{-r/3a_o}$$

**$n = 3, \ell = 1$**

$$\psi_{310} = \frac{1}{81} \left( \frac{2}{\pi} \right)^{1/2} \left( \frac{1}{a_o} \right)^{3/2} \left( \frac{6r}{a_o} - \left( \frac{r}{a_o} \right)^2 \right) e^{-r/3a_o} \cos \theta$$

$$\psi_{31\pm 1} = \frac{1}{81\sqrt{\pi}} \left( \frac{1}{a_o} \right)^{3/2} \left( \frac{6r}{a_o} - \left( \frac{r}{a_o} \right)^2 \right) e^{-r/3a_o} \sin \theta e^{\pm i\theta}$$

**$n = 2, \ell = 0$**

$$\psi_{200} = \frac{1}{4\sqrt{2\pi}} \left( \frac{1}{a_o} \right)^{3/2} \left( 2 - \frac{r}{a_o} \right) e^{-r/2a_o}$$

**$n = 3, \ell = 2$**

$$\psi_{320} = \frac{1}{81\sqrt{6\pi}} \left( \frac{1}{a_o} \right)^{7/2} r^2 e^{-r/3a_o} (3\cos^2 \theta - 1)$$

$$\psi_{32\pm 1} = \frac{1}{81\sqrt{\pi}} \left( \frac{1}{a_o} \right)^{7/2} r^2 e^{-r/3a_o} \sin \theta \cos \theta e^{\pm i\phi}$$

$$\psi_{32\pm 2} = \frac{1}{162\sqrt{\pi}} \left( \frac{1}{a_o} \right)^{7/2} r^2 e^{-r/3a_o} \sin^2 \theta e^{\pm 2i\phi}$$

**$n = 2, \ell = 1$**

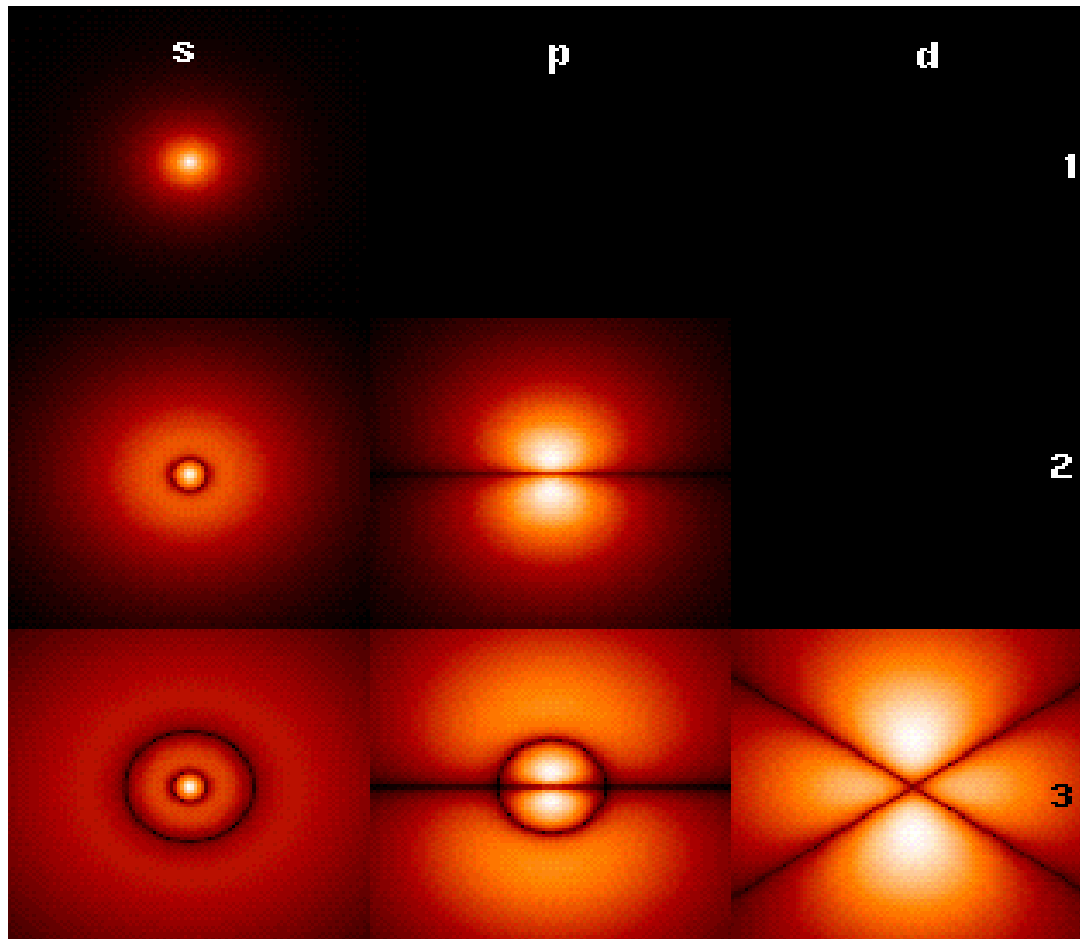
$$\psi_{210} = \frac{1}{4\sqrt{2\pi}} \left( \frac{1}{a_o} \right)^{5/2} r e^{-r/2a_o} \cos \theta$$

$$\psi_{21\pm 1} = \frac{1}{8\sqrt{\pi}} \left( \frac{1}{a_o} \right)^{5/2} r e^{-r/2a_o} \sin \theta e^{\pm i\phi}$$

# Probability distribution functions

$$\Psi_{nlm}^*(r, \theta, \phi) \Psi_{nlm}(r, \theta, \phi) r^2 \sin \theta dr d\theta d\phi$$

for  $n = 1, 2, 3$



Show that the hydrogen atom wave function  $\Psi_{100}$  is normalized.



Show that the hydrogen atom wave function  $\Psi_{100}$  is orthogonal to the  $\Psi_{211}$  wave function.

$$\psi_{100} = \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{3/2} e^{-r/a_0}$$



$$\psi_{211} = \frac{1}{8\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{5/2} r e^{-r/2a_0} \sin \theta e^{+i\phi}$$

# The One-Electron Wave Function

The hydrogen atom wave functions were derived by considering the two-body (proton + electron) system as an effective “one-body” system.

Due to the large mass difference of the proton and electron, the hydrogen atom Hamiltonian and wave functions essentially describe the motion of the electron.

*Why?*



## A One-Electron Wave Function is Called an **Orbital**

The hydrogen atom wave functions are often called orbitals, a term frequently used in chemistry. Formally an orbital has the following definition:

An **orbital** is the wave function describing a single electron. In other words, an orbital is a one-electron wave function.

# What do Hydrogen Atom Wave Functions 'Look' Like?

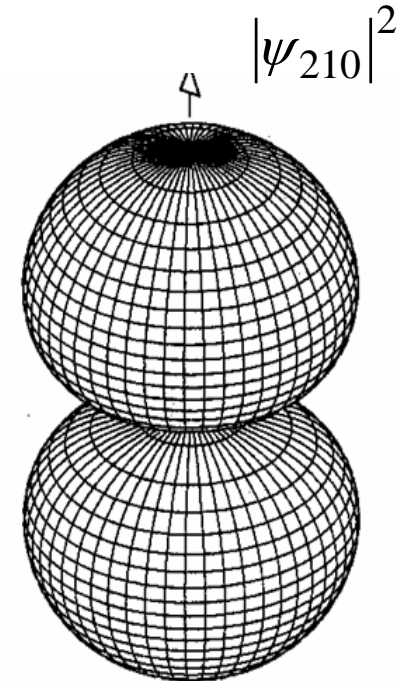
The hydrogen atom wave functions are 3-dimensional functions of space. In other words, associated with every point in space, is a value of that wave function. There are many different ways to visualize wave functions.

## 3D-Isosurface Plots

When a chemist thinks of a 3-D representation of an orbital, such as a  $\psi_{210}$  or  $2p_z$  orbital, they usually have a 3-D isosurface plot in mind.

Shown to the right is the **isosurface plot** of the density of the  $\psi_{210}$  orbital:

An isosurface plot is 3-dimensional surface of which the function **has the same value**. Thus, associated with each isosurface plot, should be a value of that surface.

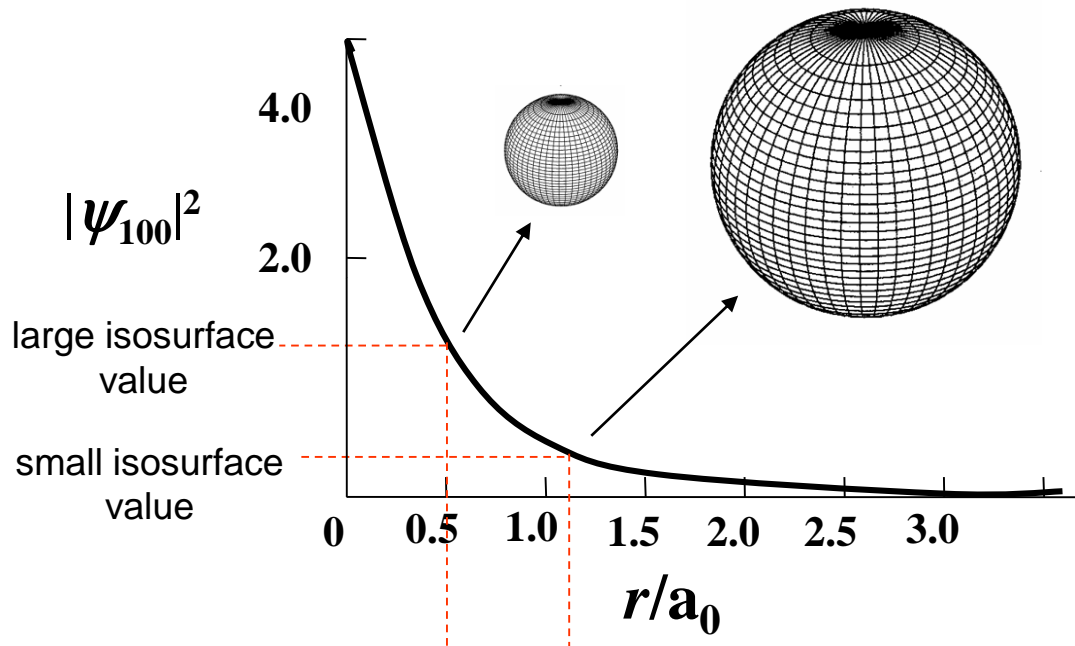


$$\rho = 0.02 \text{ a.u.}$$



# The size of an Orbital in an Isosurface plot is Arbitrary

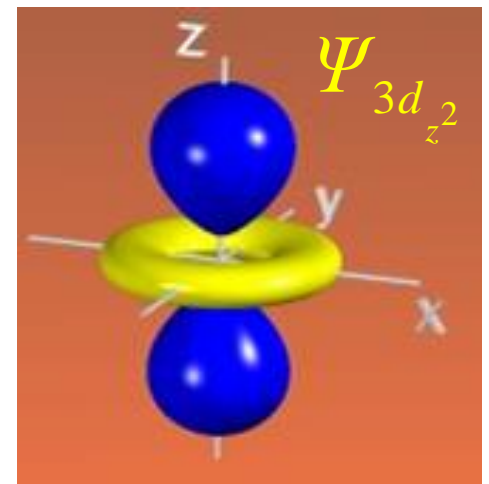
How 'big' the orbitals are when we visualize them depends on what isosurface value we choose.



Due to the exponential decay of all H-atom wave functions, the larger the isosurface value, the 'smaller' the orbital is depicted in an isosurface plot.

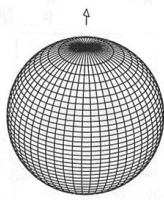
When wave functions are plotted, the color represents the sign of the wave function.

We will discuss complex-valued wave functions later.

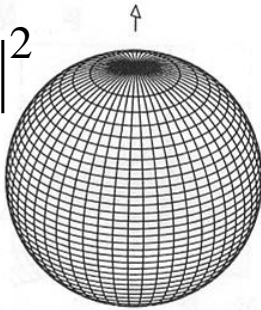


# Isosurface plots of the densities of the $n = 1, 2$ and 3 orbitals

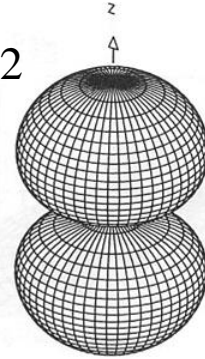
$$|\psi_{100}|^2$$



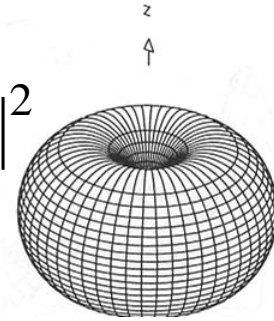
$$|\psi_{200}|^2$$



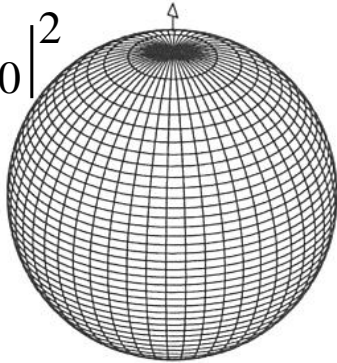
$$|\psi_{210}|^2$$



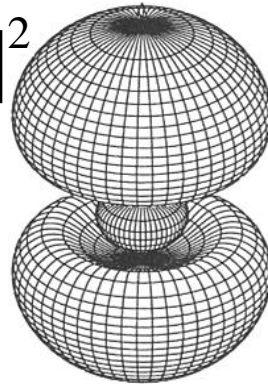
$$|\psi_{21\pm 1}|^2$$



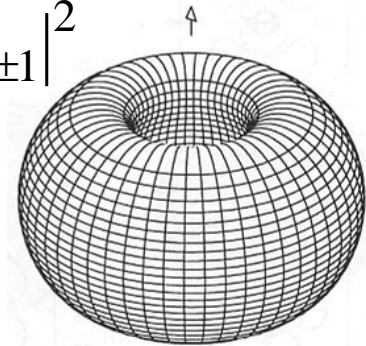
$$|\psi_{300}|^2$$



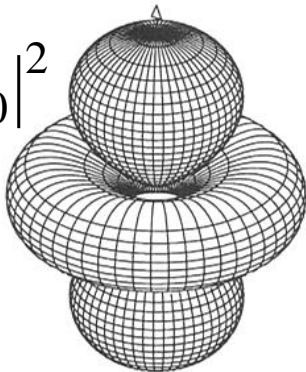
$$|\psi_{310}|^2$$



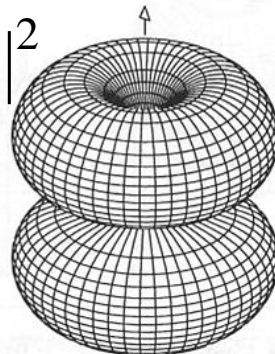
$$|\psi_{31\pm 1}|^2$$



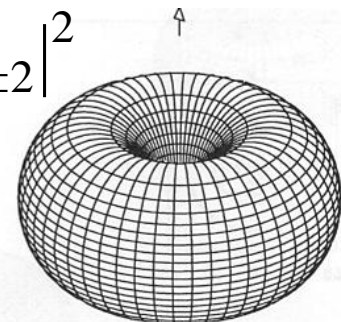
$$|\psi_{320}|^2$$



$$|\psi_{32\pm 1}|^2$$



$$|\psi_{32\pm 2}|^2$$



$z$

## Spectroscopic Designation of States

What about our familiar s, p and d orbitals? There is a relation between the quantum numbers  $\ell$  and the s, p, d labels we give the atomic orbitals.

|          |   |   |   |   |   |   |
|----------|---|---|---|---|---|---|
| $\ell =$ | 0 | 1 | 2 | 3 | 4 | 5 |
|          | s | p | d | f | g | h |

Ignoring the quantum number  $m$  for the time being, we have:

$$\psi_{1s} = \psi_{10} \quad n = 1, \ell = 0$$

$$\psi_{3s} = \psi_{30} \quad n = 3, \ell = 0$$

$$\psi_{2s} = \psi_{20} \quad n = 2, \ell = 0$$

$$\psi_{3p} = \psi_{31} \quad n = 3, \ell = 1$$

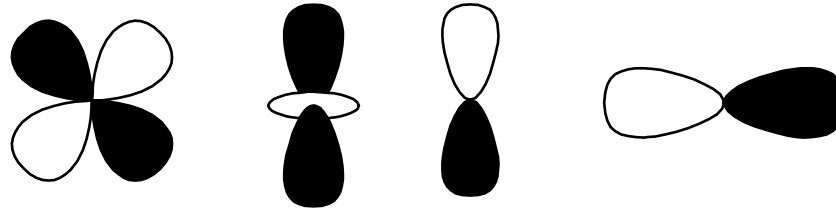
$$\psi_{2p} = \psi_{21} \quad n = 2, \ell = 1$$

$$\psi_{3d} = \psi_{32} \quad n = 3, \ell = 2$$

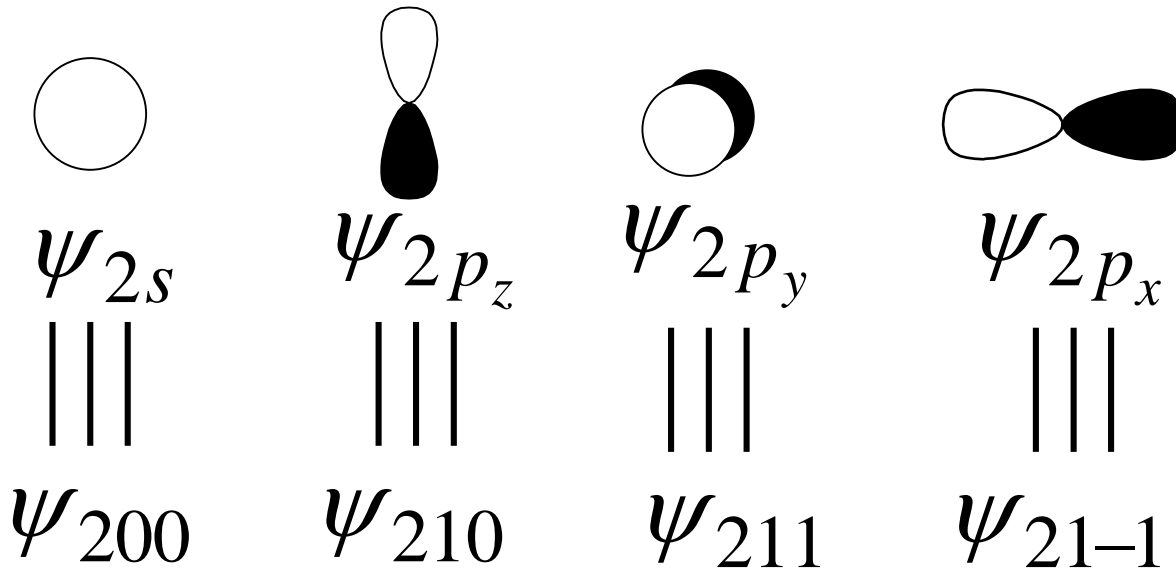
Notice that we are not specifying the  $x, y, z, x^2-y^2$  etc. states yet.

# Real and Directed Orbitals

In chemistry, we often speak about the  $s$ ,  $p_x$ ,  $p_y$ ,  $p_z$  and the five  $d$  orbitals,  $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$ ,  $d_{z^2}$  and  $d_{x^2-y^2}$ .



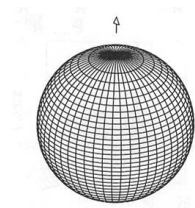
How are these orbitals, that we often use to explain chemical bonding, related to the atomic hydrogen orbitals? To illustrate this point, consider the  $n = 2$  states, where we would expect to have:



**Are they  
Equivalent?**

Consider the  $\psi_{200}$  wave function:

$$\psi_{200} = \frac{1}{4\sqrt{2\pi}} \left( \frac{1}{a_0} \right)^{3/2} \left( 2 - \frac{r}{a_0} \right) e^{-r/2a_0}$$



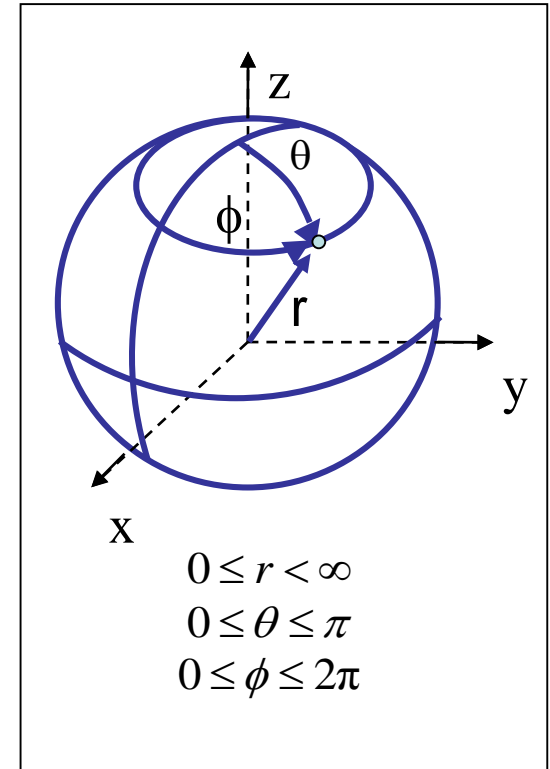
There is no angular dependence, meaning that this is a perfectly spherical function.

Indeed, the  $n = 2, \ell = 0, m = 0$  wave function is the familiar 2s orbital.

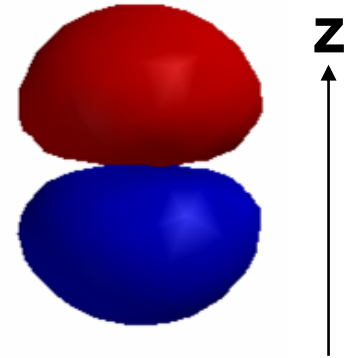
$$\psi_{200} \equiv \psi_{2s}$$

**What about the  $\psi_{210}$  wave function which is given as:**

$$\psi_{210} = \frac{1}{4\sqrt{2\pi}} \left( \frac{1}{a_0} \right)^{5/2} r e^{-r/2a_0} \cos \theta$$



An isosurface plot of the  $\psi_{210}$  wave function shown to the right shows that this is indeed our familiar  $2p_z$  orbital. (Here, positive is “red”, negative is “blue”.)



$$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}} \left( \frac{1}{a_o} \right)^{5/2} r e^{-r/2a_o} \cos \theta$$

$\boxed{z = r \cos \theta}$

**What about the  $\psi_{21+1}$  wave function? Is this one of the  $2p_x$  or  $2p_y$  orbitals?**

$$\psi_{21+1} = \frac{1}{8\sqrt{\pi}} \left( \frac{1}{a_o} \right)^{5/2} r e^{-r/2a_o} \sin \theta e^{+i\phi}$$

This is a complex function with both real and imaginary components, making it a bit difficult to plot.

We know however that the square of the wave function is always positive, so let's try plotting this:

$$|\psi_{21+1}|^2$$



This means that:

$$|\psi_{211}|^2 = \frac{1}{64\pi} \left( \frac{1}{a_o} \right)^5 r^2 e^{-r/a_o} \sin^2 \theta$$

We will get the same result for the 21-1 orbital!

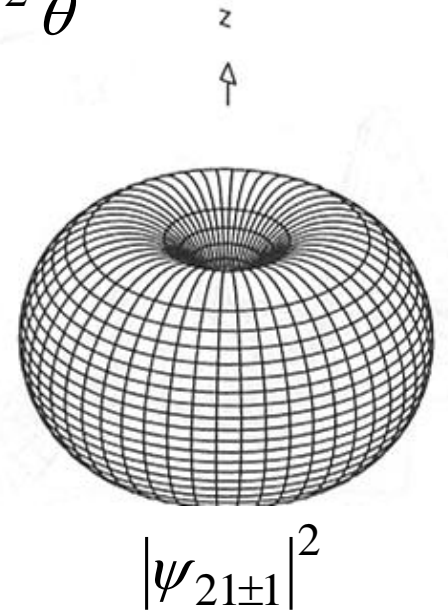
$$|\psi_{21-1}|^2 = \frac{1}{64\pi} \left( \frac{1}{a_o} \right)^5 r^2 e^{-r/a_o} \sin^2 \theta$$

When we plot this we get a donut isosurface plot!

**So what are all of the  $2p_x$ ,  $2p_y$ , and other orbitals we are familiar with?**

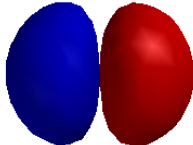
Are they donuts?

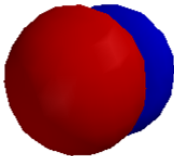
Are they complex?



# Real and Directed Orbitals are Linear Combinations of the Complex Set We have Derived

The orbitals we use in chemistry are **purely real functions** that are constructed as a linear combination of the wave functions we have derived.


$$\Psi_{2p_x} = \frac{1}{\sqrt{2}} (\Psi_{211} + \Psi_{21-1})$$


$$\Psi_{2p_y} = \frac{1}{i\sqrt{2}} (\Psi_{211} - \Psi_{21-1})$$

Show this for the  $2p_x$  orbital.



Show that the  $2p_x$  orbital as defined above is normalized.





# The Energies of the Real and Directed Orbitals

Do the real and directed orbitals still satisfy the Schrödinger equation for the hydrogen atom and what are their energies?

**Consider the  $2p_y$  orbital which is a linear combination of the  $211$  and  $21-1$  orbitals.**

$$\Psi_{2p_y} = \frac{1}{i\sqrt{2}} (\Psi_{211} - \Psi_{21-1})$$



Indeed, any linear combination of degenerate wave functions is also a solution to the Schrödinger equation with the same energy.

**Show this for the following linear combination:**

$$\Psi = A\Psi_{200} + B\Psi_{210} + C\Psi_{211}$$



## 2p<sub>x</sub> orbital directed along the x axis:

$$\begin{aligned}\psi_{2px} &= \frac{1}{\sqrt{2}} (\psi_{211} + \psi_{21-1}) \\ &= \frac{1}{8\sqrt{2\pi}} \frac{1}{a_0^{5/2}} r e^{-r/2a_0} (\sin \theta e^{i\phi} + \sin \theta e^{-i\phi}) \\ &= \frac{1}{8\sqrt{\pi}} \frac{1}{a_0^{5/2}} r e^{-r/2a_0} [\sin \theta (\cos \phi + i \sin \phi + \cos \phi - i \sin \phi)] \\ &= \frac{1}{4\sqrt{\pi}} \frac{1}{a_0^{5/2}} r e^{-r/2a_0} \sin \theta \cos \phi\end{aligned}$$

## 2p<sub>y</sub> orbital directed along the y axis:

$$\begin{aligned}\psi_{2p_y} &= \frac{1}{i\sqrt{2}} (\psi_{211} - \psi_{21-1}) \\ &= \frac{1}{8i\sqrt{2}\pi} \frac{1}{a_0^{5/2}} r e^{-r/2a_0} (\sin \theta e^{i\phi} - \sin \theta e^{-i\phi}) \\ &= \frac{1}{8i\sqrt{2}\pi} \frac{1}{a_0^{5/2}} r e^{-r/2a_0} [\sin \theta (\cos \phi + i \sin \phi - \cos \phi + i \sin \phi)] \\ &= \frac{1}{4\sqrt{\pi}} \frac{1}{a_0^{5/2}} r e^{-r/2a_0} \sin \theta \sin \phi\end{aligned}$$

## Is the $2p_x$ orbital normalized?

$$\begin{aligned}\int \psi_{2p_x}^* \psi_{2p_x} d\tau &= \int \left( \frac{\psi_{211} + \psi_{21-1}}{\sqrt{2}} \right)^* \frac{\psi_{211} + \psi_{21-1}}{\sqrt{2}} d\tau \\ &= \frac{1}{2} \int (\psi_{211} + \psi_{21-1})^* (\psi_{211} + \psi_{21-1}) d\tau \\ &= \frac{1}{2} \int (\psi_{211}^* \psi_{211} + \psi_{211}^* \psi_{21-1} + \psi_{21-1}^* \psi_{211} + \psi_{21-1}^* \psi_{21-1}) d\tau \\ &= \frac{1}{2} \int (\psi_{211}^* \psi_{211} + \psi_{21-1}^* \psi_{21-1}) d\tau \\ &= \frac{1}{2} (1 + 1) \\ &= 1\end{aligned}$$

Any linear combination of degenerate wave functions has the same energy.

$$\begin{aligned}\hat{H}\psi &= \hat{H}(A\psi_{200} + B\psi_{210} + C\psi_{211}) \\ &= \hat{H}A\psi_{200} + \hat{H}B\psi_{210} + \hat{H}C\psi_{211} \\ &= A\hat{H}\psi_{200} + B\hat{H}\psi_{210} + C\hat{H}\psi_{211} \\ &= AE_2\psi_{200} + BE_2\psi_{210} + CE_2\psi_{211} \\ &= E_2(A\psi_{200} + B\psi_{210} + C\psi_{211}) \\ &= E_2\psi\end{aligned}$$

## The Real and Directed d-Orbitals

The d-orbitals that we often use in transition metal chemistry are also normalized linear combinations of the complex functions we have derived.

What about the  $n = 3$ ,  $\ell = 2$ ,  $m = 0$  hydrogen atom orbital which is a purely real function?

$$\psi_{320} = \frac{1}{81\sqrt{6\pi}} \left( \frac{1}{a_0} \right)^{7/2} e^{-r/3a_0} \underbrace{(3r^2 \cos^2 \theta - r^2)}_{(3z^2 - r^2)}$$
$$z = r \cos \theta$$

So our familiar  $d_{z^2}$  orbital is shorthand for a  $3z^2 - r^2$  orbital.

The other d orbitals we are familiar with are linear combinations of the remaining four  $m = \pm 1$  and  $m = \pm 2$  functions.

## Linear combinations used to construct $nd$ orbitals:

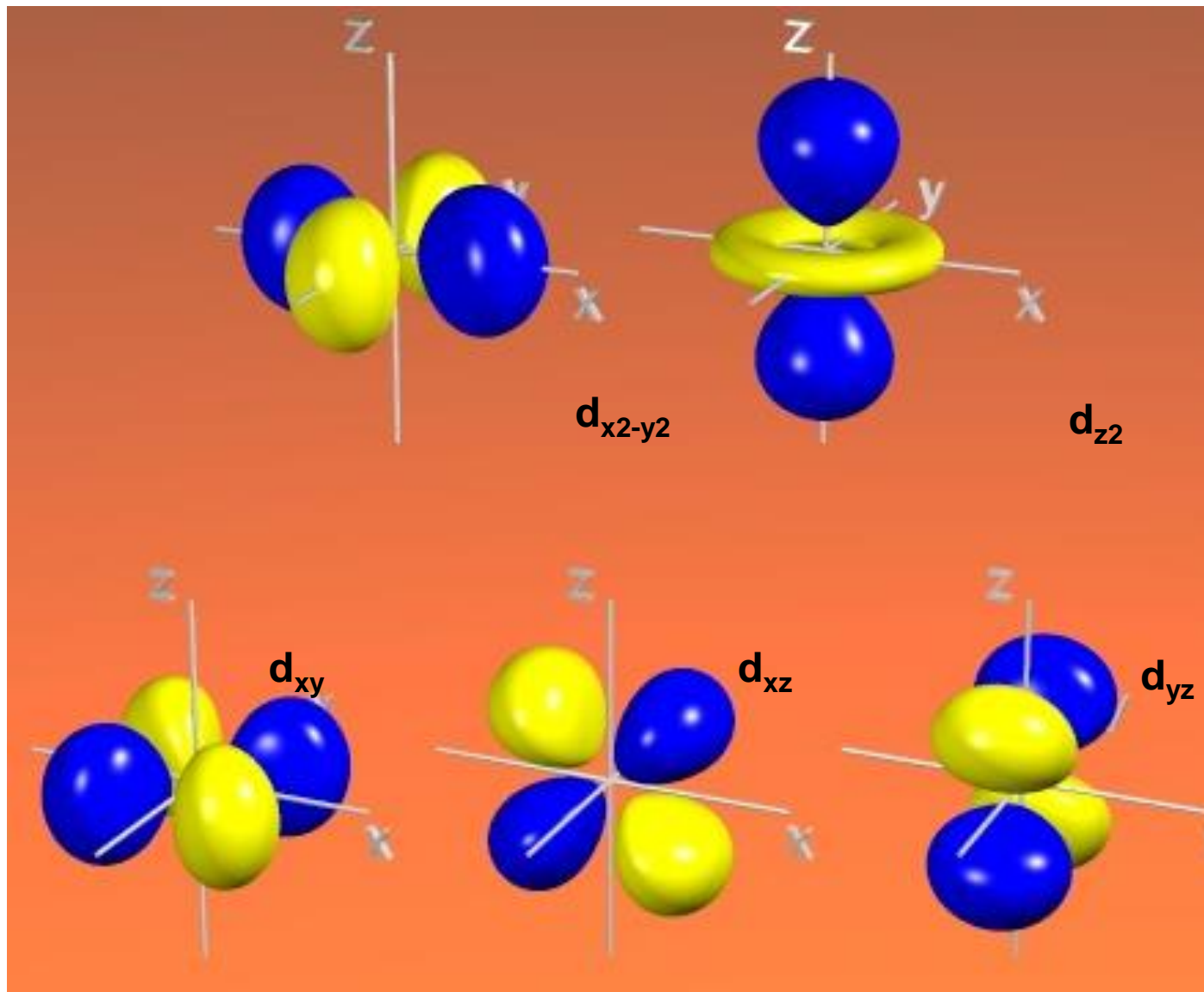
$$d_{nz^2} = \psi_{n20} = R_{n2}(r) \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$$

$$d_{nxz} = \frac{1}{\sqrt{2}} (\psi_{n21} + \psi_{n2-1}) = R_{n2}(r) \sqrt{\frac{15}{4\pi}} \sin \theta \cos \theta \cos \phi$$

$$d_{nyz} = \frac{1}{i\sqrt{2}} (\psi_{n21} - \psi_{n2-1}) = R_{n2}(r) \sqrt{\frac{15}{4\pi}} \sin \theta \cos \theta \sin \phi$$

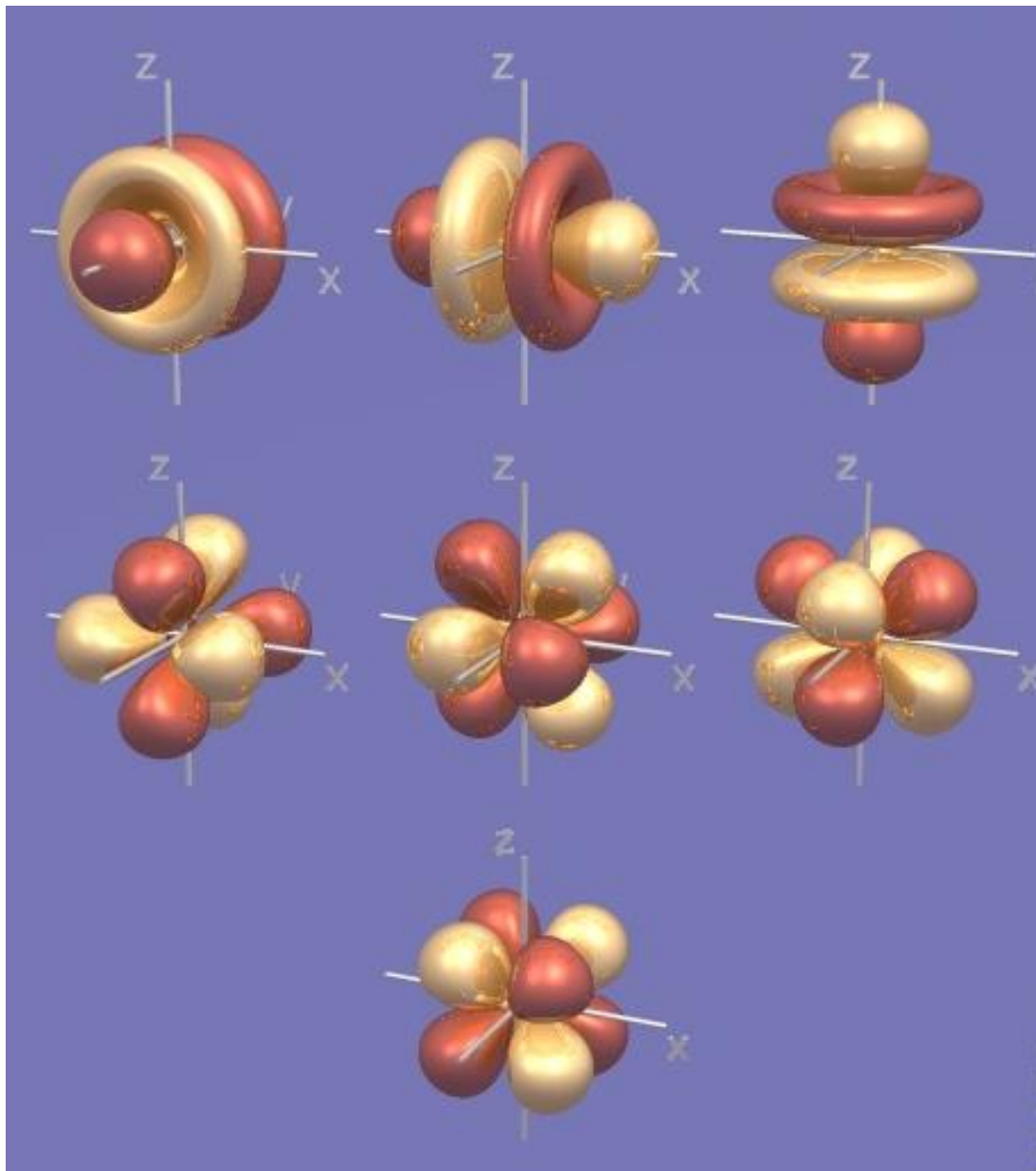
$$d_{n(x^2-y^2)} = \frac{1}{\sqrt{2}} (\psi_{n22} + \psi_{n2-2}) = R_{n2}(r) \sqrt{\frac{15}{16\pi}} \sin^2 \theta \cos 2\phi$$

$$d_{nxy} = \frac{1}{i\sqrt{2}} (\psi_{n22} - \psi_{n2-2}) = R_{n2}(r) \sqrt{\frac{15}{16\pi}} \sin^2 \theta \sin 2\phi$$



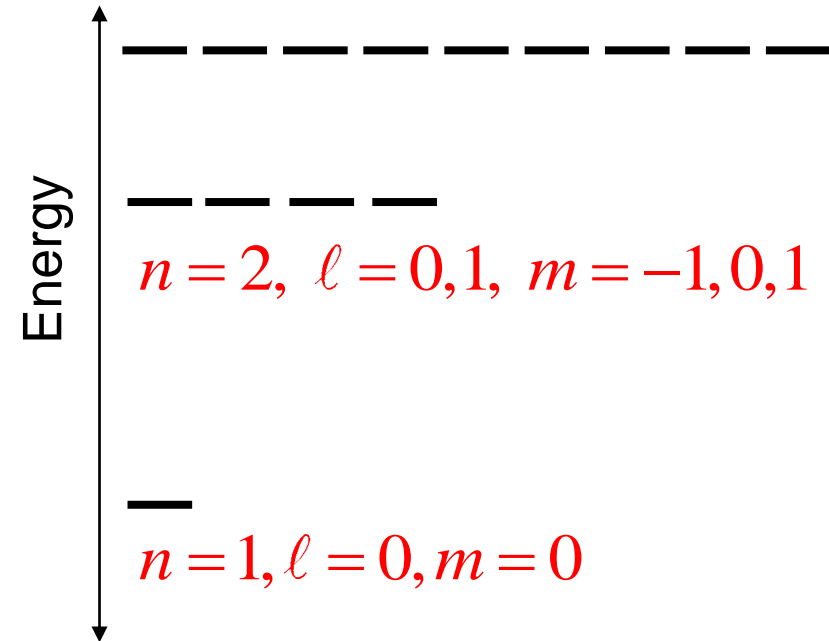
The familiar d-orbitals are the ‘real and directed’ d-orbitals. Here, “positive” is blue and “negative” is yellow.





The real and directed 4f orbitals

# Angular Momentum of the Hydrogen Atom



The hydrogen atom energy levels are  $n^2$ -fold degenerate.

$$g = n^2$$

***What is different about the states if the energies are the same?***

Each of the states has a different angular momentum. In other words, these states each have different values for  $L^2$  and  $L_z$ .

Recall that the total hydrogen atom wave function is a product of the radial wave function and the spherical harmonics.

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$$

The spherical harmonics are eigenfunctions of the  $L^2$  and  $L_z$  operators:

$$\hat{L}^2 Y_{\ell m}(\theta, \phi) = \hbar^2 \ell(\ell + 1) \cdot Y_{\ell m}(\theta, \phi)$$

$$\hat{L}_z Y_{\ell m}(\theta, \phi) = \hbar m \cdot Y_{\ell m}(\theta, \phi)$$

Because the  $L^2$  and  $L_z$  operators act only on  $\theta$  and  $\phi$ ,

$$\hat{L}^2 = -\hbar^2 \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \quad \hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

We know that the hydrogen atom wave functions are eigenfunctions of the  $L^2$  and  $L_z$  operators. Also, we know that each of the hydrogen atom states has a definite square of the angular momentum and  $z$ -component of the angular momentum.

**Show this**



## The Quantum Numbers $\ell$ and $m$ Define the Angular Momentum of the Hydrogen Atom State

The quantum number  $\ell$  defines the square of the magnitude of the angular momentum vector of the state:

$$|\vec{L}|^2 = \hbar^2 \ell(\ell + 1)$$

The quantum number  $m$  defines the  $z$ -component of the angular momentum vector of the state:

$$L_z = \hbar m$$

Because the angular momentum of the hydrogen atom is due to the angular motion of the electron, it is often referred to as the **orbital angular momentum**.

**Sketch the angular momentum vectors of the hydrogen atom in a 1s and 2p<sub>z</sub> orbitals.**



# The H-Atom Quantum Numbers have Common Names

***n*** The **principle quantum number**, specifies the energy of the hydrogen atom.

$$E = -\frac{e^2}{8\pi\epsilon_0 a_0} \frac{1}{n^2} \quad n = 1, 2, 3\dots$$

***l*** The **angular momentum quantum number**, (sometimes called the azimuthal quantum number), specifies the magnitude of the orbital angular momentum of the state.

$$|\vec{L}|^2 = \hbar^2 \ell(\ell + 1) \quad \ell = 0, 1, 2\dots(n-1)$$

***m*** The **magnetic momentum quantum number**, specifies the z-component of the angular momentum

$$L_z = \hbar m \quad m = 0, \pm 1, \pm 2\dots \pm \ell$$

# The Spatial and Nodal Structure of the Hydrogen Atom Orbitals

## Motivation

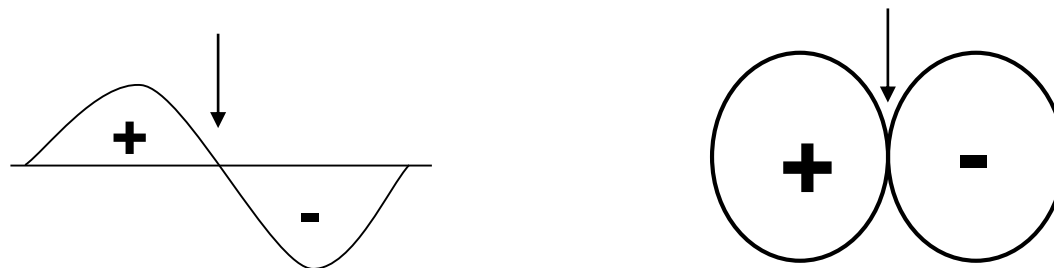
When using atomic orbitals to discuss molecular bonding, the spatial and nodal structure of the wave functions is important

For example, the overlap between orbitals on different atoms, either constructive, destructive or zero overlap, is highly dependent upon the nodal structure of the orbitals involved.

We will discuss this in terms of the purely real and directed orbitals. Recall both sets of orbitals are equivalent, and can be obtained from one another by rotation.

## Nodes of the Wave Function

Recall that nodes are where the wave function changes sign and has zero value.



## Radial and Angular Nodes

The number of nodes is determined by the quantum numbers  $n$  and  $\ell$ .  
The total number of nodes is given by:

$$\text{total number of nodes} = n - 1$$

So the ground state hydrogen atom wave function  $\psi_{100}$  has no nodes.

***Check this!***

The nodes can be categorized as radial and angular nodes arising from each component of the total hydrogen atom wave function,  $R$  and  $Y$ .

$$\text{number of radial nodes} = n - \ell - 1$$

$$\text{number of angular nodes} = \ell$$

# Angular Nodes

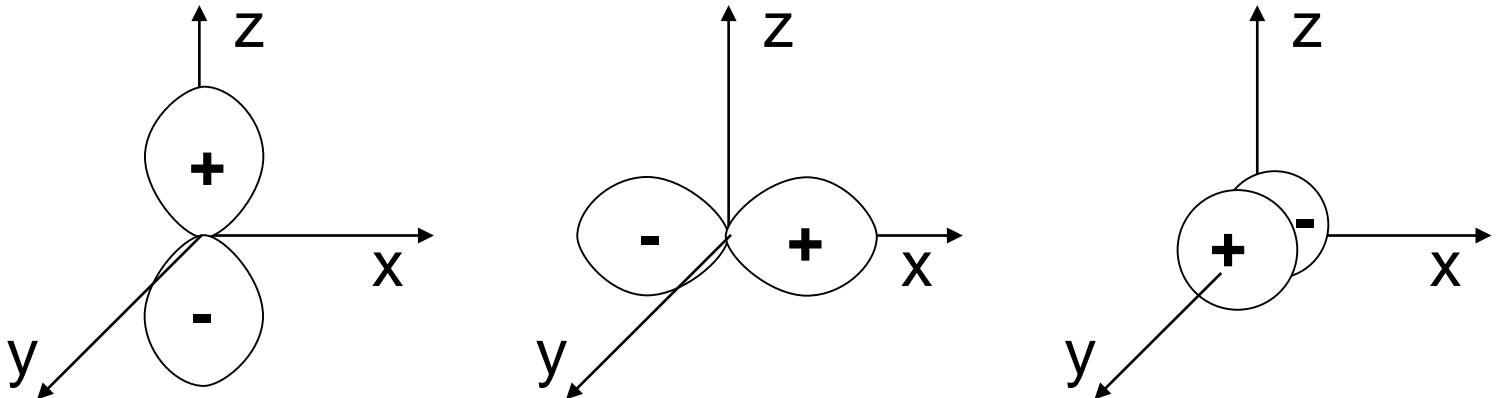
The real and directed orbitals have nodal planes (or equivalent) where the wave function changes sign. The number of angular nodes is given by the quantum number  $\ell$ .

## $\ell = 0$ , the 's' orbitals

The s orbitals have no angular dependence, and are spherical wave functions and therefore have no angular nodes.

## $\ell = 1$ , the 'p' orbitals

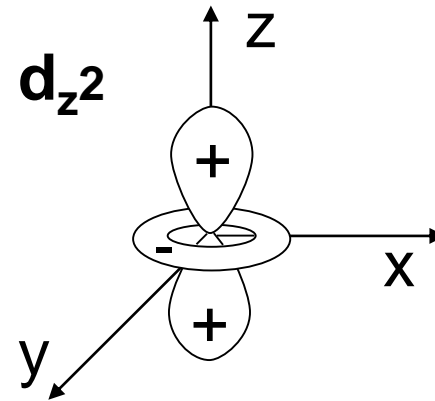
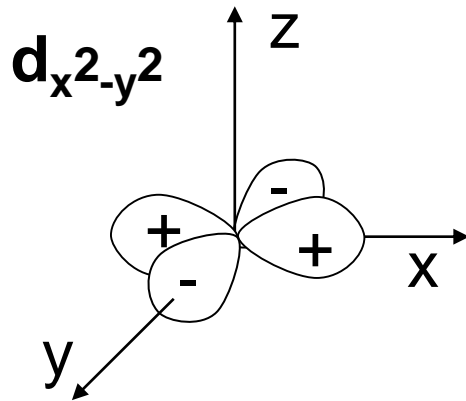
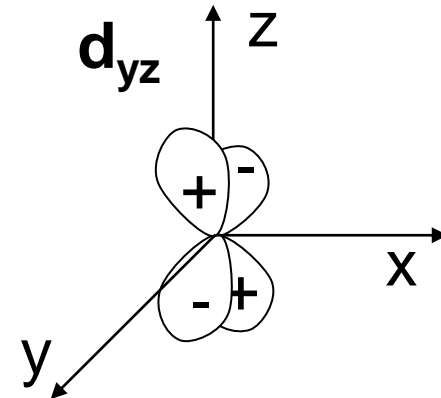
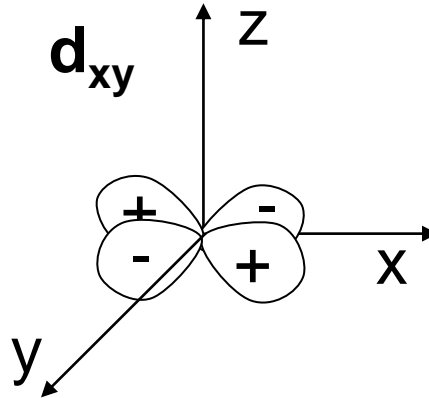
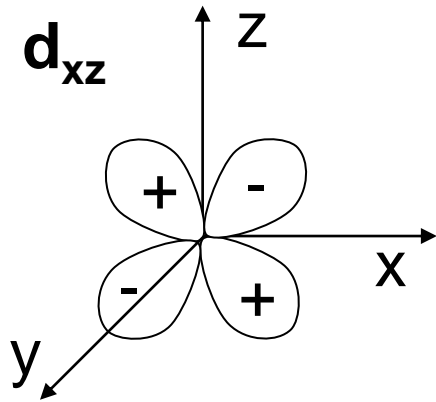
The p orbitals have **one** angular plane, each.





## $l = 2$ , the 'd' orbitals

The d orbitals have **two** angular planes each.



Where are the two angular nodes of the  $d_{z^2}$  orbital?

$$\psi_{320} = \psi_{3dz^2} = \frac{1}{81\sqrt{6\pi}} \left( \frac{1}{a_0} \right)^{7/2} r^2 e^{-r/3a_0} (3\cos^2\theta - 1)$$

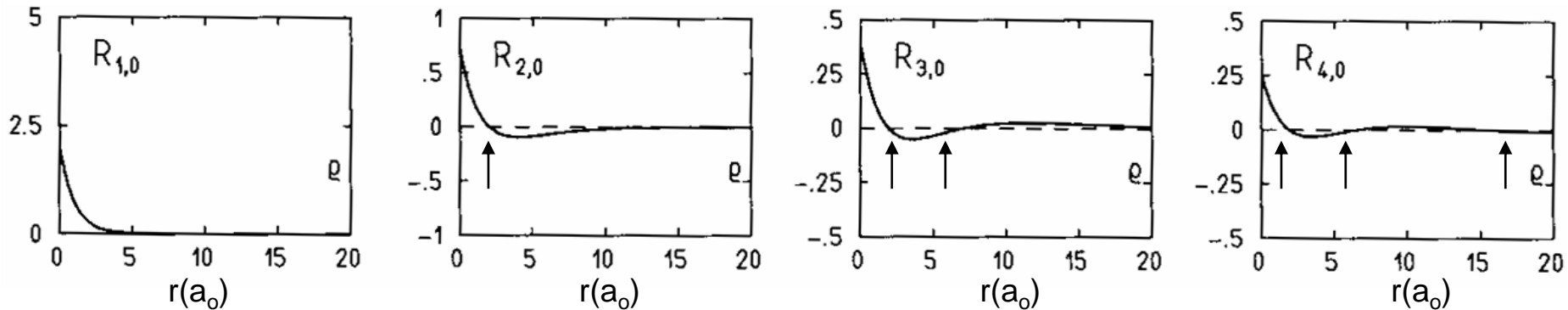


# Radial Nodes

Plots of the radial wave function show that the number of radial nodes is given by:

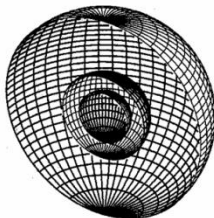
$$\text{number of radial nodes} = n - \ell - 1$$

Below are plotted the 1s, 2s, 3s and 4s radial wave functions.

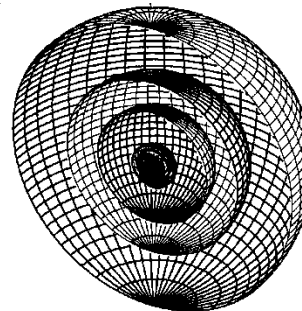


The radial nodes give isosurface plots of the electron density that are layered like an onion.

$$|\psi_{2s}|^2$$



$$|\psi_{3s}|^2$$



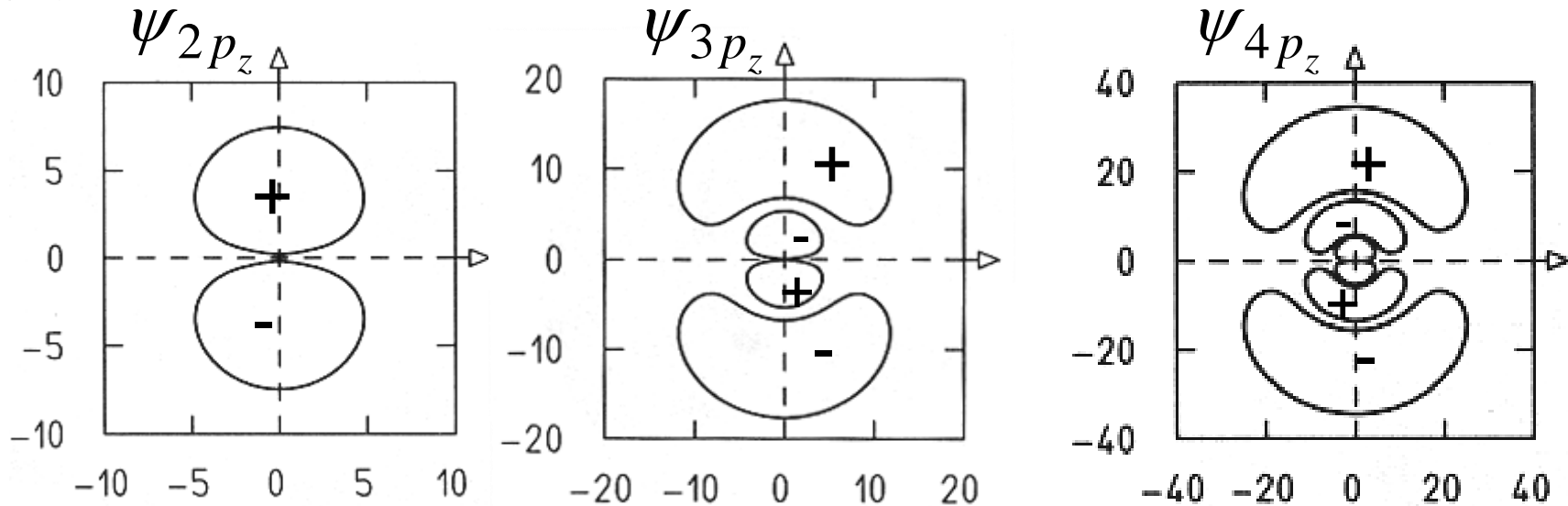
**Explain**



The nodes of the radial wave functions give the higher angular momentum wave functions a similar structure.

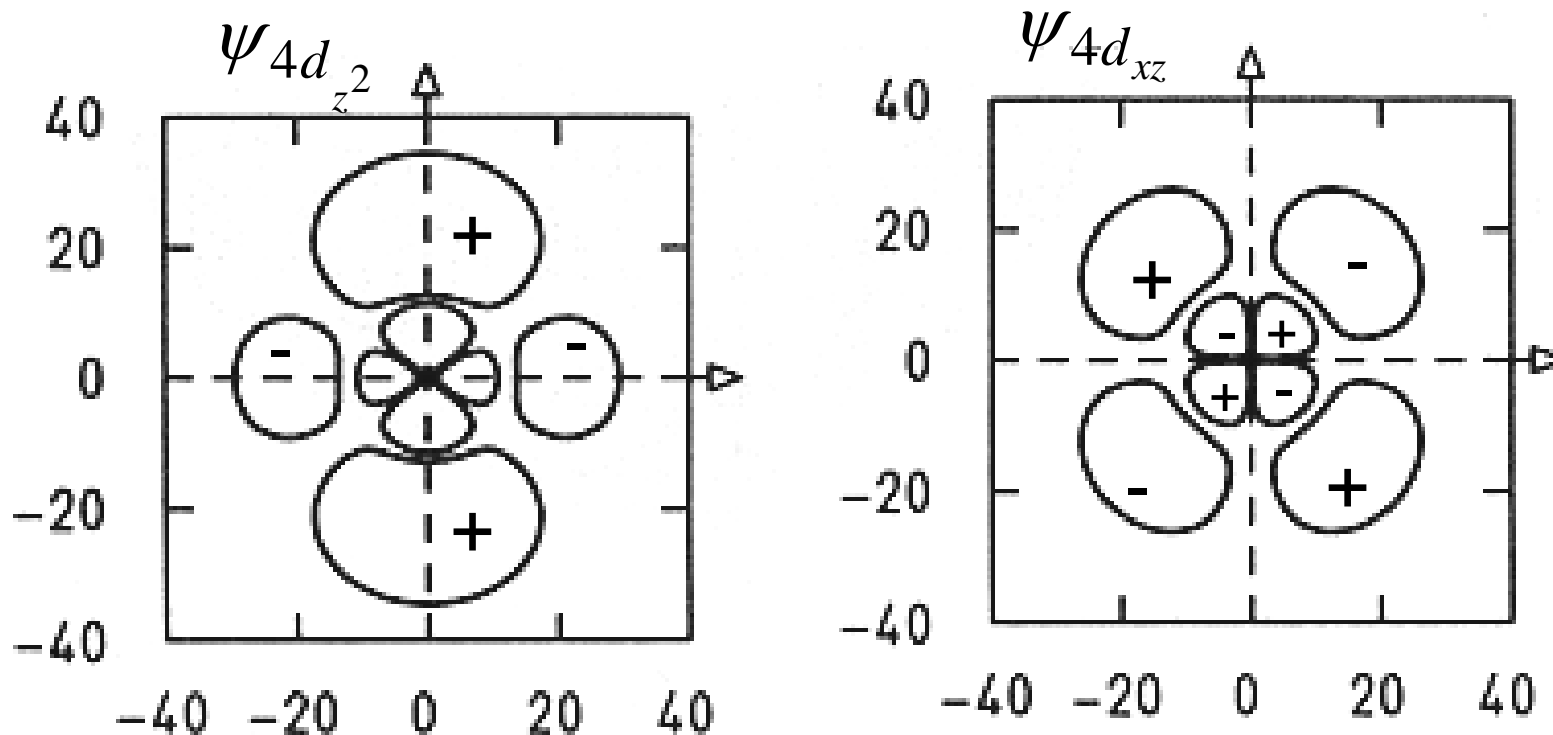


Sketched below are 2-D slices of the isosurface plots of the wave function.



Notice the alternation of the sign of the layers and the larger spatial extent as  $n$  varies from 2 to 4.

The same layered structure exists for the 4d and 5d orbitals!



The reason we don't sketch or represent the inner orbitals when discussing bonding is because it is only the outer 'layer' that participates in the interaction.