

# Lecture 40

## (3-D Potentials & Hydrogen Atoms)

Physics 2310-01 Spring 2020

Douglas Fields

# Schrödinger's Wave Equation

- What if our potential depends on more than one coordinate?
- For instance, instead of a 1-D infinite potential well, what if we have a complete 3-dimensional box?

$$V(x, y, z) = 0 \begin{cases} 0 \leq x \leq a \\ 0 \leq y \leq b \\ 0 \leq z \leq c \end{cases}$$

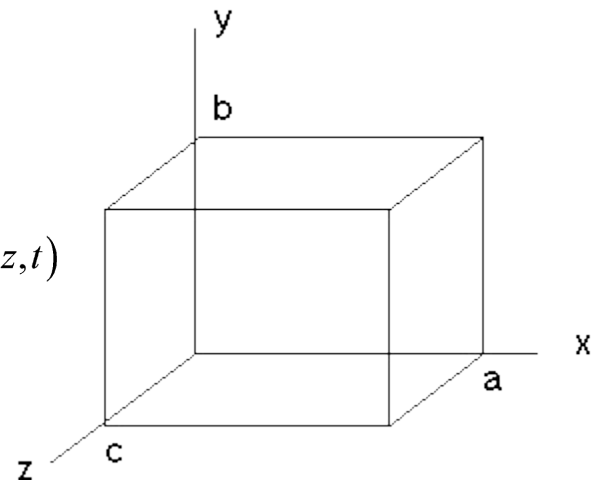
$$V(x, y, z) = \infty \quad \text{otherwise}$$

- Let's start with our complete time-dependent Schrödinger's equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V \Psi$$

- And write it out explicitly in Cartesian coordinates:

$$i\hbar \frac{\partial \Psi(x, y, z, t)}{\partial t} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi(x, y, z, t) + V(x, y, z) \Psi(x, y, z, t)$$



# Time Independent Schrödinger's Wave Equation

- And we do what we did before, assuming that the solution can be written as a product of the space and time parts:

$$\Psi(x, y, z, t) = \psi(x, y, z) e^{-iEt/\hbar}$$

- To get the 3-D time independent Schrödinger's equation

$$i\hbar \frac{\partial}{\partial t} (\psi(x, y, z) e^{-iEt/\hbar}) = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) e^{-iEt/\hbar} + V(x, y, z) \psi(x, y, z) e^{-iEt/\hbar} \Rightarrow$$

$$E\psi(x, y, z) e^{-iEt/\hbar} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) e^{-iEt/\hbar} + V(x, y, z) \psi(x, y, z) e^{-iEt/\hbar} \Rightarrow$$

$$E\psi(x, y, z) = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) + V(x, y, z) \psi(x, y, z)$$

# Separation of Variables

- Now, the equation may look like a monster to solve, but it turns out that there is a nice method to approach such a problem, called separation of variables.
- First, let's assume that the solution can be written as a product of functions of a single variable:

$$\psi(x, y, z) = X(x)Y(y)Z(z)$$

- And plugging this into the time independent wave equations gives us:

$$EX(x)Y(y)Z(z) = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) X(x)Y(y)Z(z) + V(x, y, z)X(x)Y(y)Z(z) \Rightarrow$$

$$EX(x)Y(y)Z(z) = -\frac{\hbar^2}{2m} \left( Y(y)Z(z) \frac{\partial^2 X(x)}{\partial x^2} + X(x)Z(z) \frac{\partial^2 Y(y)}{\partial y^2} + X(x)Y(y) \frac{\partial^2 Z(z)}{\partial z^2} \right) + V(x, y, z)X(x)Y(y)Z(z) \Rightarrow$$

$$E = -\frac{\hbar^2}{2m} \left( \frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} + \frac{1}{Y(y)} \frac{\partial^2 Y(y)}{\partial y^2} + \frac{1}{Z(z)} \frac{\partial^2 Z(z)}{\partial z^2} \right) + V(x, y, z)$$

- Now, in the case where  $V=0$  (inside our 3-D box), we are left with an equation that is independent of any spatial variables on the left-hand side ( $E$  is a constant), and has three terms on the right, each just dependent on one of the spatial variables.

# Separation of Variables

- So each term must also be equal to a constant:

$$E = -\frac{\hbar^2}{2m} \left( \frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} + \frac{1}{Y(y)} \frac{\partial^2 Y(y)}{\partial y^2} + \frac{1}{Z(z)} \frac{\partial^2 Z(z)}{\partial z^2} \right) \Rightarrow$$

$$E_x = -\frac{\hbar^2}{2m} \frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2}$$

$$E_y = -\frac{\hbar^2}{2m} \frac{1}{Y(y)} \frac{\partial^2 Y(y)}{\partial y^2}$$

$$E_z = -\frac{\hbar^2}{2m} \frac{1}{Z(z)} \frac{\partial^2 Z(z)}{\partial z^2}$$

- And we recognize each of these as just the 1-D time-independent wave equation for the infinite square well, so we also know the solutions:

$$X(x) = A \sin \frac{n_x \pi x}{a}, \quad E_x = \frac{n_x^2 \pi^2 \hbar^2}{2ma^2}$$

$$Y(y) = B \sin \frac{n_y \pi y}{b}, \quad E_y = \frac{n_y^2 \pi^2 \hbar^2}{2mb^2}$$

$$Z(z) = C \sin \frac{n_z \pi z}{c}, \quad E_z = \frac{n_z^2 \pi^2 \hbar^2}{2mc^2}$$

# Separation of Variables

- Remember that to get the total wave function, we have to put it all back together:

$$\Psi(x, y, z, t) = \psi(x, y, z) e^{-iEt/\hbar}$$

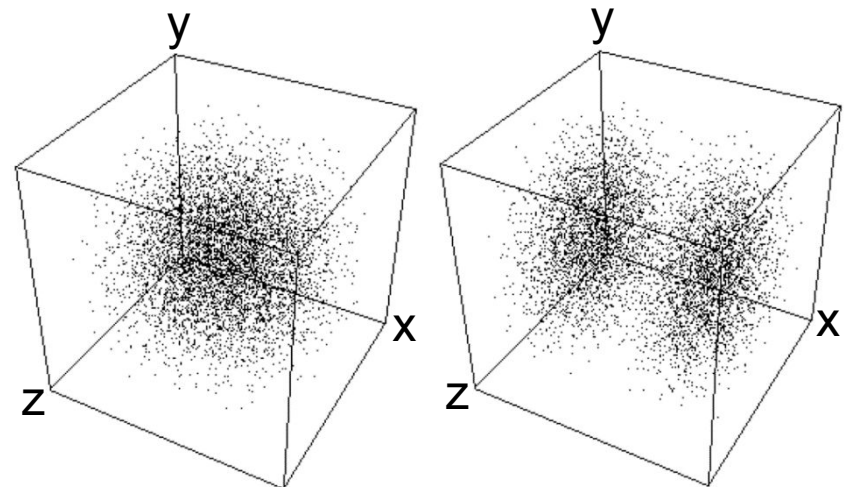
$$\Psi(x, y, z, t) = X(x)Y(y)Z(z) e^{-iEt/\hbar}$$

$$\Psi(x, y, z, t) = D \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c} e^{-iEt/\hbar}$$

- And the total energy is given by:

$$E = E_x + E_y + E_z$$

$$E = \frac{n_x^2 \pi^2 \hbar^2}{2ma^2} + \frac{n_y^2 \pi^2 \hbar^2}{2mb^2} + \frac{n_z^2 \pi^2 \hbar^2}{2mc^2}$$



$$n_x = 1, n_y = 1, n_z = 1$$

$$n_x = 2, n_y = 1, n_z = 1$$

# Symmetry and Degeneracy

- Now, let's look at what happens when we make the box symmetric...

- Let  $a=b=c=L$ :

$$E = E_x + E_y + E_z$$

$$E = \frac{n_x^2 \pi^2 \hbar^2}{2mL^2} + \frac{n_y^2 \pi^2 \hbar^2}{2mL^2} + \frac{n_z^2 \pi^2 \hbar^2}{2mL^2}$$

$$E = \left( n_x^2 + n_y^2 + n_z^2 \right) \frac{\pi^2 \hbar^2}{2mL^2}$$

- Note: The energy can be the same for states with different sets of quantum numbers!
- This is called **degeneracy** – more than one state has the same energy – and is a direct result of symmetry.
- For each degree of symmetry, there will be a corresponding degree of degeneracy.
- For instance, in the above case there is symmetry in 3-D, and we will find the same energy in groups of 3 states, i.e., (2,1,1) and (1,2,1) and (1,1,2).
- If one of the sides of the box was a different length, then there would only be 2-fold degeneracy.

# The Coulomb Potential

- OK, so let's now investigate a more interesting potential than just a 3-D box.
- Let's look at the Coulomb potential, the potential between two fundamental charges, e:

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

- Wait, but why look at the Coulomb potential?
- Because this is the potential that an electron feels due to a proton in the Hydrogen atom!
- Because of the spherical symmetry of the Coulomb potential, we can use a similar method to write the wave function as a product of three terms:

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

- Which, as before gives us three separate differential equations to solve.
- However, because the potential isn't zero, and because of the spherical symmetry, the equations are no longer as straightforward as the infinite 3-D box.



# The Hydrogen Atom

$$-\frac{\hbar^2}{2mr^2} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \left( \frac{\hbar^2 l(l+1)}{2mr^2} + V(r) \right) R(r) = ER(r)$$

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + \left( l(l+1) - \frac{m_l^2}{\sin^2 \theta} \right) \Theta(\theta) = 0$$

$$\frac{d^2 \Phi(\phi)}{d\phi^2} + m_l^2 \Phi(\phi) = 0$$

- See, not so bad...

# The Hydrogen Atom

- The solution looks foreboding, but, in fact, it's not as bad as it looks.

$$\psi_{nlm_l}(r, \theta, \varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) Y_l^{m_l}(\theta, \varphi)$$

$$\text{with, } \rho = \frac{2r}{na_0} \quad \text{and, } n = 1, 2, 3, \dots$$

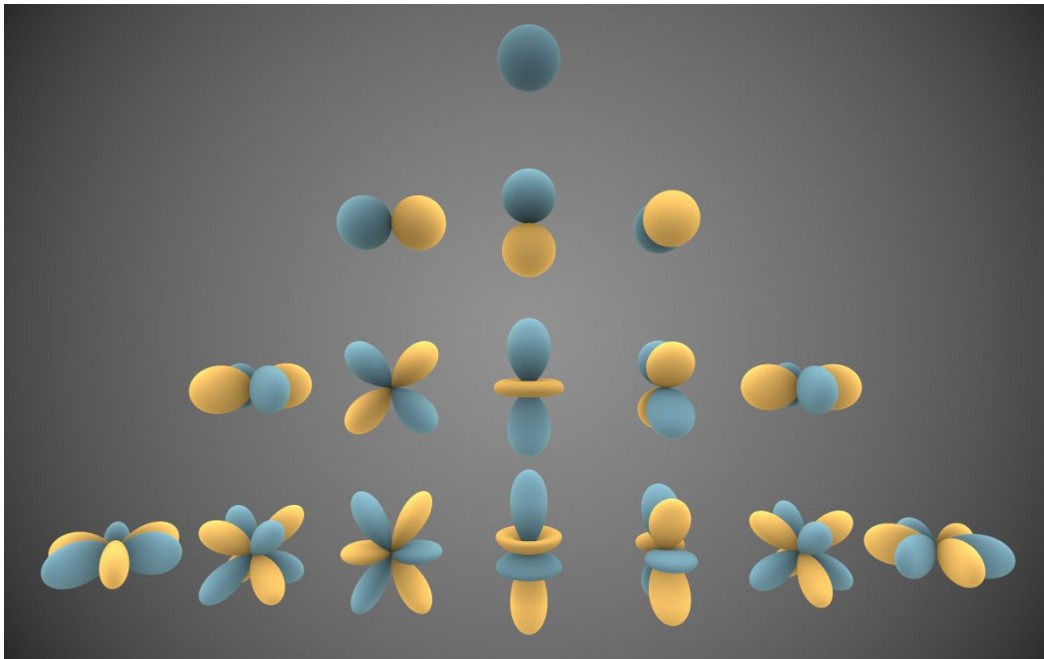
$$l = 0, 1, 2, \dots, n-1$$

$$m_l = -l, \dots, l$$

- The normalization constant.
- The r-dependence is just an exponential multiplied by a specific type of polynomial called a generalized Laguerre polynomial.
- The  $\theta$ -dependence is just a special polynomial in  $\sin\theta$  and  $\cos\theta$ .
- And the  $\varphi$ -dependence is just  $e^{im_l\varphi}$ .
- The theta and phi parts together are known as the Spherical Harmonics, and are found in solutions to many spherically symmetric problems in physics.

# Spherical Harmonics

$$\psi_{nlm_l}(r, \theta, \varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) Y_l^{m_l}(\theta, \varphi)$$



$l = 0$

$l = 1$

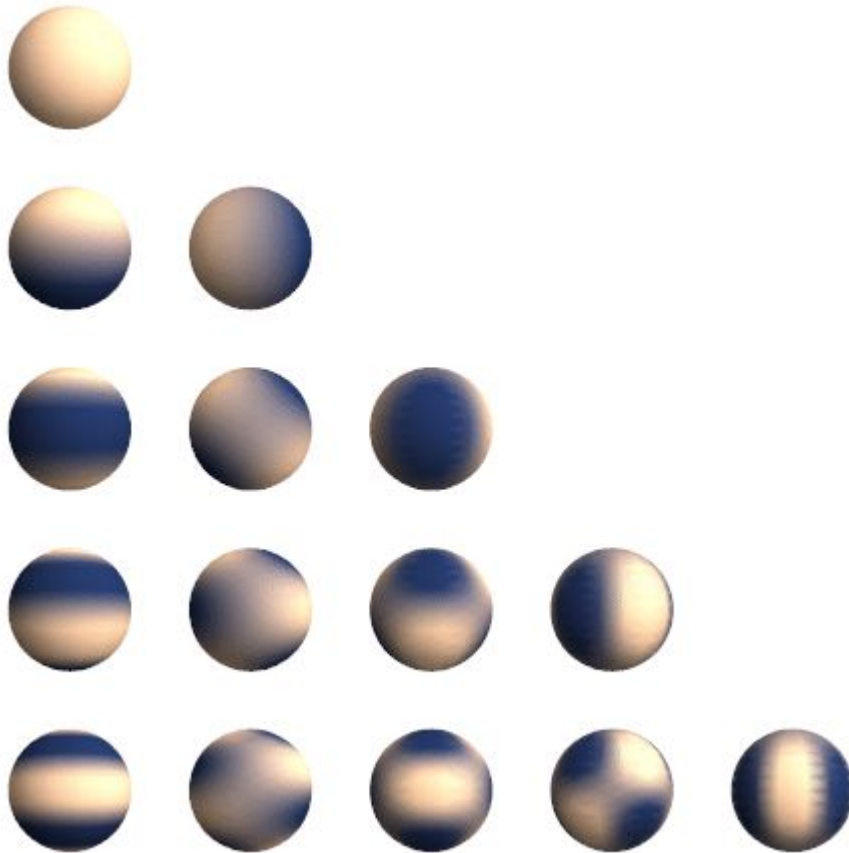
$l = 2$

$l = 3$

Visual representations of the first few real spherical harmonics. Blue portions represent regions where the function is positive, and yellow portions represent where it is negative. The distance of the surface from the origin indicates the value of  $Y_l^{m_l}$  in angular direction  $(\theta, \varphi)$ .

# Spherical Harmonics

$$\psi_{nlm_l}(r, \theta, \varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) Y_l^{m_l}(\theta, \varphi)$$



$l = 0$

$l = 1$

$l = 2$

$l = 3$

$l = 4$

Real (Laplace) spherical harmonics  $Y_l^{m_l}(\theta, \varphi)$  for  $l = 0, \dots, 4$  (top to bottom) and  $m = 0, \dots, l$  (left to right). Zonal, sectoral, and tesseral harmonics are depicted along the left-most column, the main diagonal, and elsewhere, respectively. (The negative order harmonics  $Y_l^{-m_l}(\theta, \varphi)$  would be shown rotated about the  $z$  axis by  $90^\circ$  with respect to the positive order ones.)

# The Hydrogen Atom

- Note that we now have three integers that represent particular states:

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

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

$$m_\ell = -\ell, \dots, \ell$$

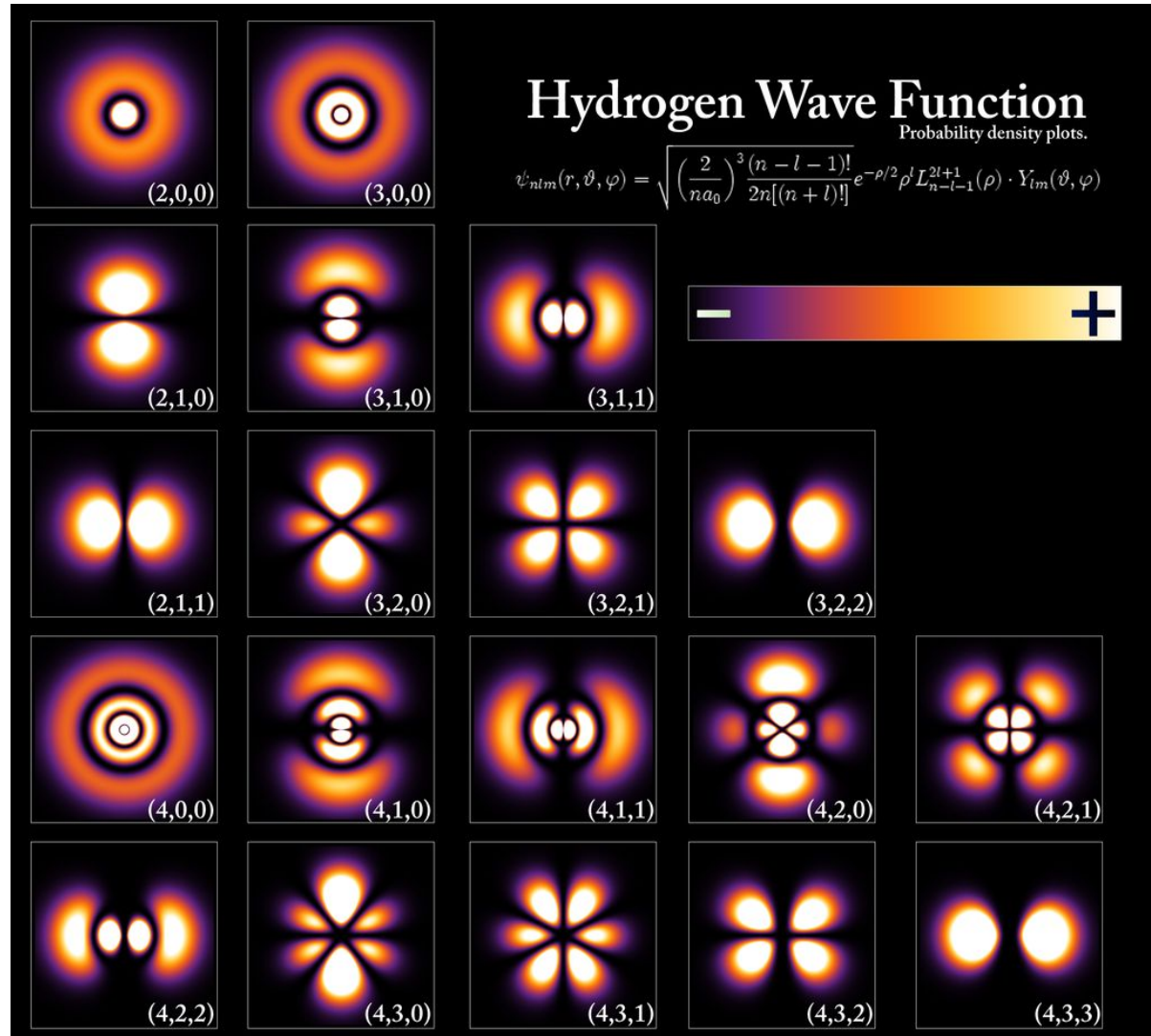
- We should have expected three quantum numbers, since we are in three dimensions (like  $n_x$ ,  $n_y$ , and  $n_z$  for the 3D box).
- Here,  $n$  represents the primary quantum number, and the energy of the states are given by:

$$E_n = -\frac{1}{(4\pi\epsilon_0)^2} \frac{me^4}{2n^2\hbar^2} = -\frac{13.6eV}{n^2}$$

- Recognize this?
- The fact that the Schrödinger's equation gives us the same energy states as Bohr's model (which were experimentally verified) is good verification that it is good model.
- In fact, we will find out that it tells us something about the atomic orbitals that is in disagreement with Bohr's model!

# Hydrogen Wave Functions

- The wave functions look like this, where we are looking at a cross-section of the 3-D wave functions, and color is used to show the amplitude of the wave function as a function of position.
- Note that these are the wave functions for a single electron in different states, depending on the quantum numbers  $n$ ,  $l$ , and  $m_l$ .

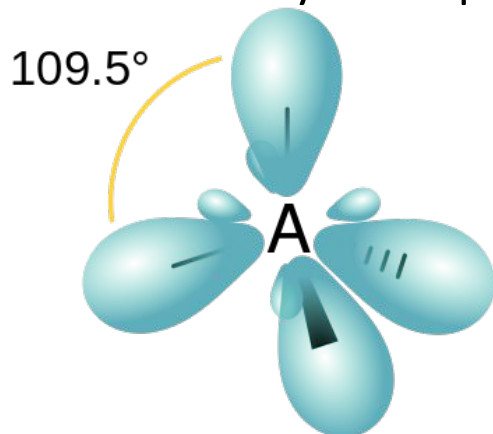


# Symmetry and Degeneracy (Again)

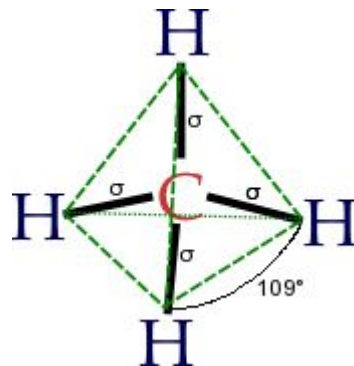
- Notice that the energy only depends on the quantum number  $n$ , so that there are several states that have the same energy.
- This is because the other two quantum numbers are associated with the angular dependence of the wavefunctions, and our potential, the Coulomb potential is independent of the angle!
- We will see later that we can break this symmetry (by adding an external electric or magnetic field) which will remove the degeneracies.

# Superposition of Degenerate States

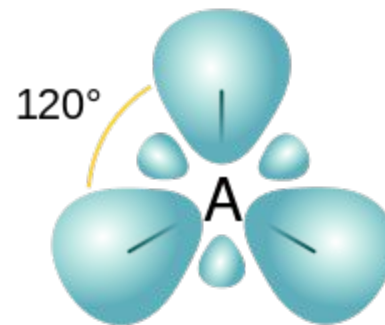
- The electron can be in any superposition of states, including states that have different energy.
- But if they have different energies, then the superposition state will have a probability distribution that changes with time.
  - This represents motion of the electron, and therefore radiation.
  - These superposition states won't be stable.
- However, if the states that are superimposed have the same energy, the probability distribution won't have any time dependence.
  - They will represent stable states.



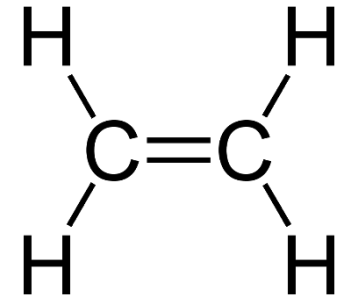
By Jfmelero - Own work, CC BY-SA 3.0, <https://commons.wikimedia.org/w/index.php?curid=17419806>



CC BY-SA 3.0, <https://commons.wikimedia.org/w/index.php?curid=540020>



By Jfmelero - Own work, CC BY-SA 3.0, <https://commons.wikimedia.org/w/index.php?curid=17419805>



Public Domain, <https://commons.wikimedia.org/w/index.php?curid=1507616>



# States

- A state of the electron is described by a specific wavefunction (or a specific combination of wavefunctions in the case of a superposition state).
- The wavefunction is the complete wavefunction:

$$\Psi(r, \theta, \phi, t) = \psi(r, \theta, \phi) e^{-iEt/\hbar}$$

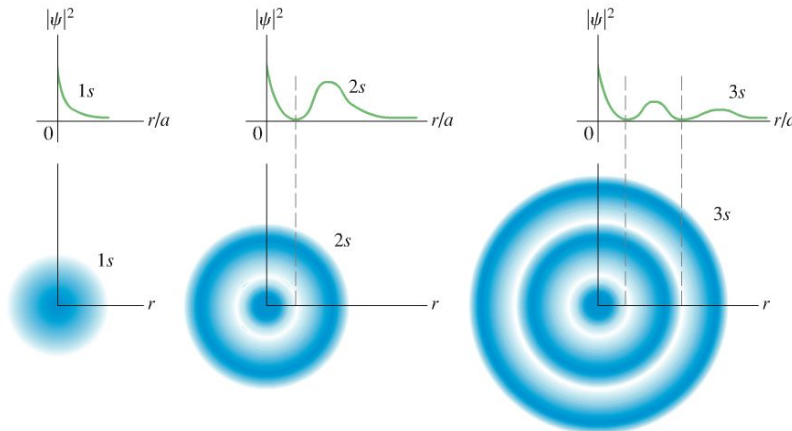
- And for states with determined energy (= eigenstates = stationary states), we solved the time independent 3D Schrodinger equation in spherical coordinates with the Coulomb potential to get:

$$\psi_{n\ell m_\ell}(r, \theta, \varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} e^{-\rho/2} \rho^\ell L_{n-\ell-1}^{2\ell+1}(\rho) Y_\ell^{m_\ell}(\theta, \varphi) \quad \text{with, } \rho = \frac{2r}{na_0}$$

$$E_n = -\frac{1}{(4\pi\epsilon_0)^2} \frac{me^4}{2n^2\hbar^2} = -\frac{13.6eV}{n^2}$$

$$\begin{aligned} n &= 1, 2, 3, \dots \\ \text{and, } \ell &= 0, 1, 2, \dots, n-1 \\ m_\ell &= -\ell, \dots, \ell \end{aligned}$$

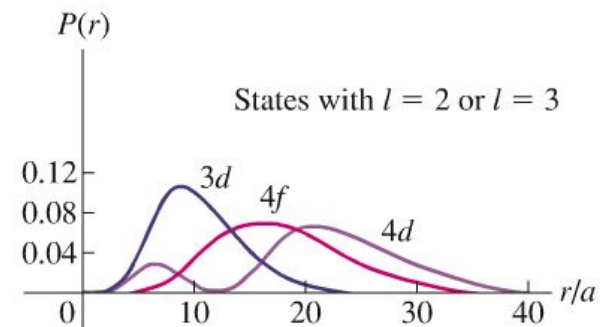
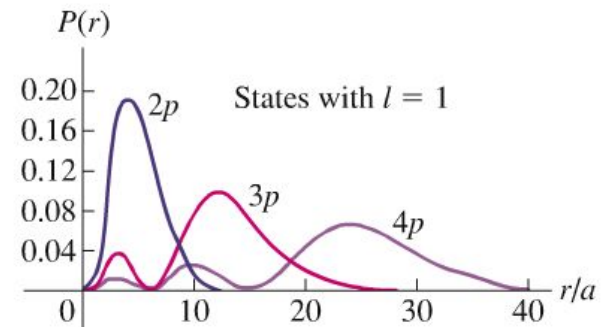
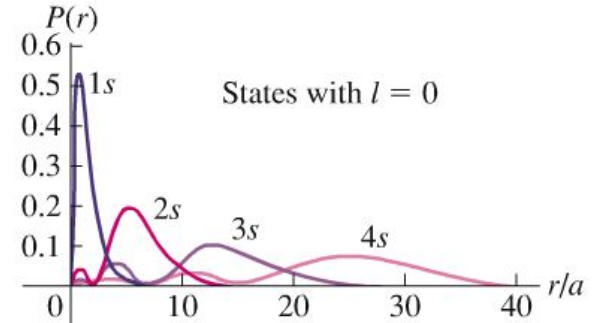
# Probability Distributions



- The probability of finding an electron within a radial shell  $dr$  is just given by:

$$P(r)dr = |\psi|^2 dV = |\psi|^2 4\pi r^2 dr$$

- The factor  $dV$  goes to zero at  $r = 0$ , so that the probability distribution functions  $P(r)$ , (shown in the figure here) go to zero even though the wave functions do not (see above).
- Note that there are nodes in the distributions, but whenever  $\ell$  is maximum for a given  $n$ , there is a single peak at  $n^2 a_0$ , the same result given by the Bohr model.



# Angular Momentum Quantization

- So, what do the quantum numbers mean?
- The first,  $n$ , determines the average radial distance of the electron from the center of the nucleus, and is the primary driver of the electron's energy state.
- The second,  $\ell$ , determines the quantization of the orbital angular momentum:

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

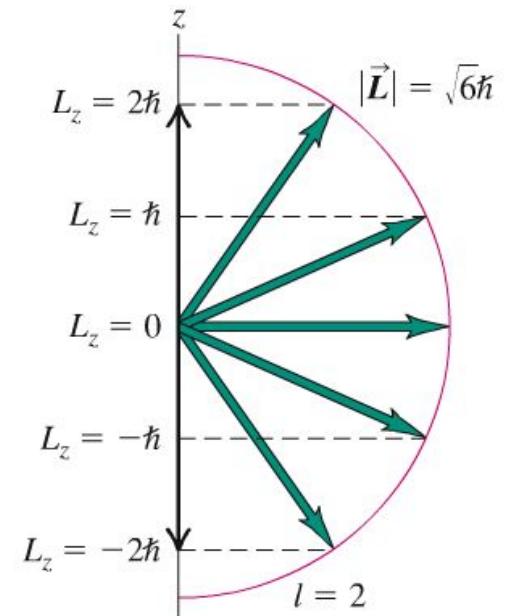
- Note that there are  $n$  different possibilities for the state of the orbital angular momentum for the  $n^{\text{th}}$  energy level.
- Also note that when  $\ell=0$ , the magnitude of the orbital angular momentum is zero – which is different from Bohr's model, where the electron is always orbiting around the nucleus.
- This means that for  $\ell=0$  states, the electron spends a small, but not insignificant amount of time **inside** the nucleus.

# Angular Momentum Quantization

- What about  $m_l$ ?
- The third quantum number defines the projection of the angular momentum  $L$  onto some axis (which we will denote by the z-axis).
- Note that in the absence of any “probe”, the potential is spherically symmetric, so we are free to define that in any direction.

$$L_z = m_l \hbar \quad m_l = 0, \pm 1, \pm 2 \dots \pm l$$

- For an  $l=2$  state,  $L_z$  can take on 5 values, as shown in the figure.



# Quantization and Mathematics

- The quantization of  $E$ ,  $L$  and  $L_z$  can be viewed as the result of the boundary conditions, normalization and periodicity of the wave functions.
- The condition that  $\Theta(\theta)$  does not go to infinity results in the quantum number  $\ell$ .
- The condition that  $\Phi(\phi)$  is periodic results in the quantum number  $m_\ell$ .
- But one can also view the particular quantization rules in terms of the uncertainty principle:
  - If any component of  $L$  could be equal to the magnitude, then we would have the electron orbiting in a plane such that  $p_z$  would be zero.
  - That absolute knowledge of one component of the momentum would require a complete uncertainty of its position in that coordinate.
  - Note that  $L_x$  and  $L_y$  are undetermined up to some value, leading to a definite and reasonable uncertainty on position.

