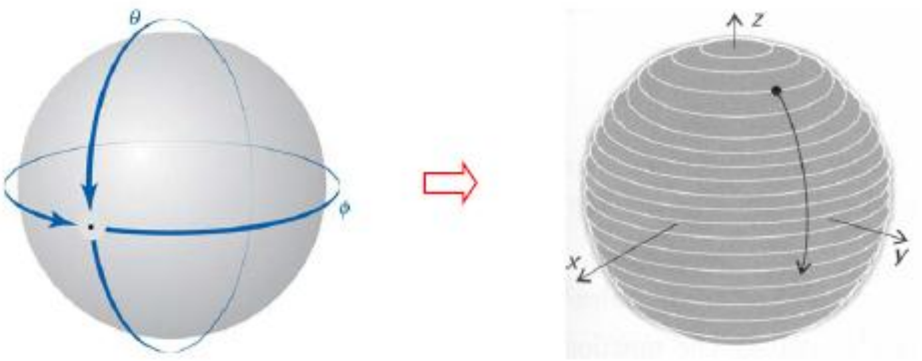
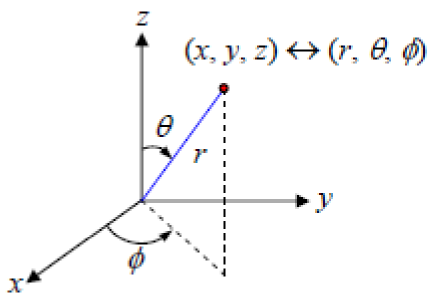
PARTICLE ON A SPHERE

- Particle can move anywhere on the surface of a sphere
- motion on a stack of rings with particle able to move between rings



- Acceptable wave function has to be single valued
- ⇒Wave function of particle has to interfere constructively around the "equator" and around the "poles"
- ⇒2 cyclic boundary conditions
- ⇒2 quantum numbers to describe state of system
- Spherical Polar Coordinates = most efficient way to describe position of particle on sphere



$$x = r\sin\theta\cos\phi \qquad y = r\sin\theta\sin\phi \qquad z = r\cos\theta$$

⟺

$$r = \sqrt{x^2 + y^2 + z^2} \qquad \theta = \cos^{-1}\left(\frac{z}{r}\right) \qquad \phi = \tan^{-1}\left(\frac{y}{x}\right)$$

- Particle constrained to sphere, V(x,y,z) = 0 on the sphere

$$\nabla^2\psi(\theta,\varphi) + \frac{2mr^2E}{\hbar^2}\psi(\theta,\varphi) = 0$$

- Use separation of variables:

$$\psi(\theta,\varphi) = \Theta(\theta)\Phi(\varphi)$$

- Solve SE in terms of each direction of rotation

❖ In case of angle = φ

$$\Phi_{m_l} = \frac{e^{im_l\varphi}}{\sqrt{2\pi}} \quad , \quad m_l = \pm\frac{\sqrt{2IE}}{\hbar} \quad , \ (m_l = 0, \pm1, \pm2, \dots)$$

❖ = Particle on a ring!

❖ In case of angle = θ

- Solutions are known as associated Legendre polynomials Θ_{m_l}

l	m	Θ_{lm}
0	0	$\sqrt{1/2}$
1	0	$\sqrt{3/2}\cos\theta$
1	±1	$\sqrt{3/4}\sin\theta$
2	0	$\sqrt{5/8}\,(3\cos^2\theta-1)$
2	±1	$\sqrt{15/4}\sin\theta\cos\theta$
2	±2	$\sqrt{15/16}\sin^2\theta$

❖ Acceptable solutions

❖ for a particle →wave functions specified by 2 quantum numbers restricted to values:

- $l = 0,1,2, \dots$ = angular momentum quantum number
- $m_l = l, l-1, \dots -l$ = magnetic quantum number

❖ Solution = Spherical Harmonics

$$Y_{l,m_l}(\theta,\varphi) = \frac{e^{im_l\varphi}}{\sqrt{2\pi}}\Theta_{m_l}(\theta)$$

l	m_l	Y_{l,m_l}
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
	±1	$\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{\pm i\varphi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta - 1)$
	±1	$\mp\left(\frac{15}{8\pi}\right)^{1/2}\cos\theta\sin\theta\, e^{\pm i\varphi}$
	±2	$\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta\, e^{\pm 2i\varphi}$
3	0	$\left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta - 3\cos\theta)$
	±1	$\mp\left(\frac{21}{64\pi}\right)^{1/2}(5\cos^2\theta - 1)\sin\theta\, e^{\pm i\varphi}$
	±2	$\left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta\, e^{\pm 2i\varphi}$
	±3	$\mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta\, e^{\pm 3i\varphi}$

❖ Energy

$$E_l = \frac{h^2}{8\pi^2 I}\, l(l+1) \qquad (l = 0,1,2,\ldots)$$

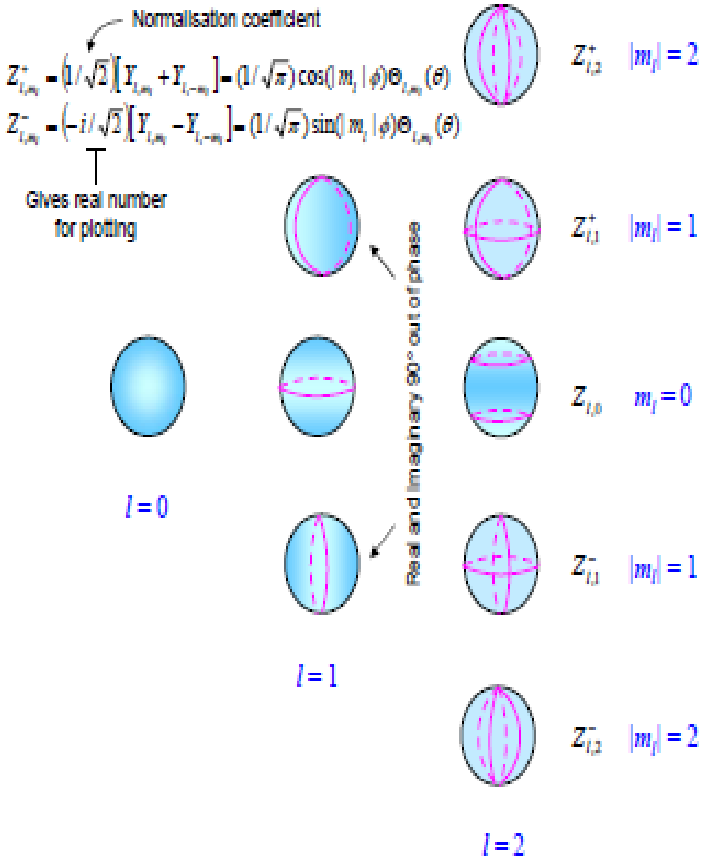
- Energy is quantized
- Energy depends on *l*
- Energy independent of m_l
- Degeneracy = 2*l* + 1

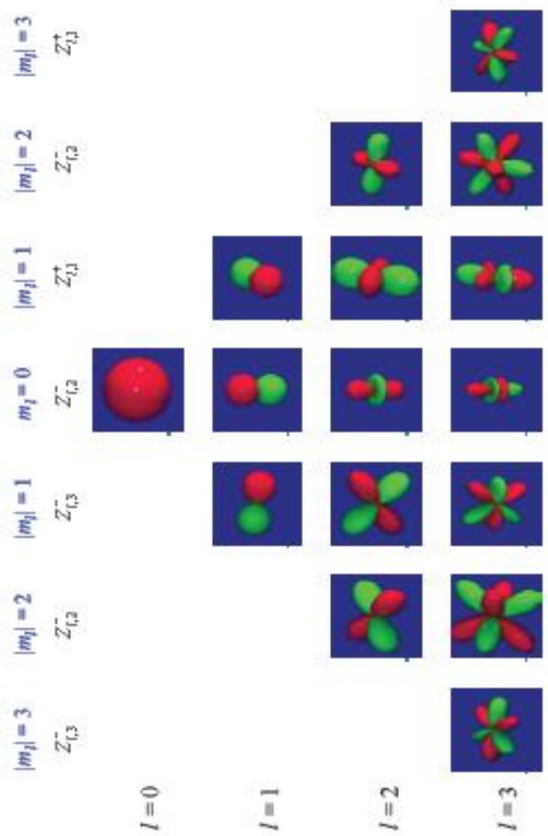
❖ If a wave function is complex (has real and imaginary components)

❖ to plot take linear combinations

❖ Fundamental principle:

- Any linear combination of degenerate eigen functions is also an eigen function

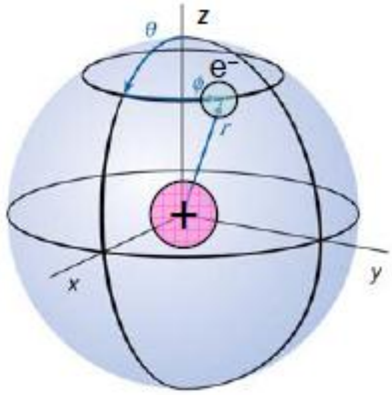




SOLVING THE HYDROGEN ATOM

☒ The hydrogen atom can be pictured as a proton fixed at the origin and an electron of reduced mass μ rotating around the proton in a sphere with radius r and the potential energy will be the Coulombic potential

$$V = \frac{e^2 Z}{(4\pi\varepsilon_0)r}$$



☒ The Schrödinger Equation for the Hydrogen Atom is

$$\nabla^2\psi + \frac{8\pi^2\mu}{h^2}(E - V)\psi = 0$$

$$\hat{\mathrm{H}}\psi = E\psi$$

$$\equiv \left[-\frac{h^2}{8\pi^2\mu}\nabla^2 - \frac{e^2 Z}{(4\pi\varepsilon_0)r}\right]\psi = E\psi$$

Kinetic Energy	Colombic Potential Energy	e^- and nucleus interaction

☒ Coulombic potential depends on *r* (not θ or φ)

☒ Use spherical-polar coordinates

☒ To solve the SE, use separation of variables

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

$$\psi(r,\theta,\varphi) = R(r)\mathrm{Y}(\theta,\varphi)$$

Radial Part

Angular Part
=Solution to particle on sphere
=Spherical Harmonics

☒ Solutions to the SE in terms of the radial and angular parameters

☒ Angular wave functions: same as particle on a sphere

☒ = spherical harmonics $\mathrm{Y}_{l,m_l}(\theta,\varphi)$

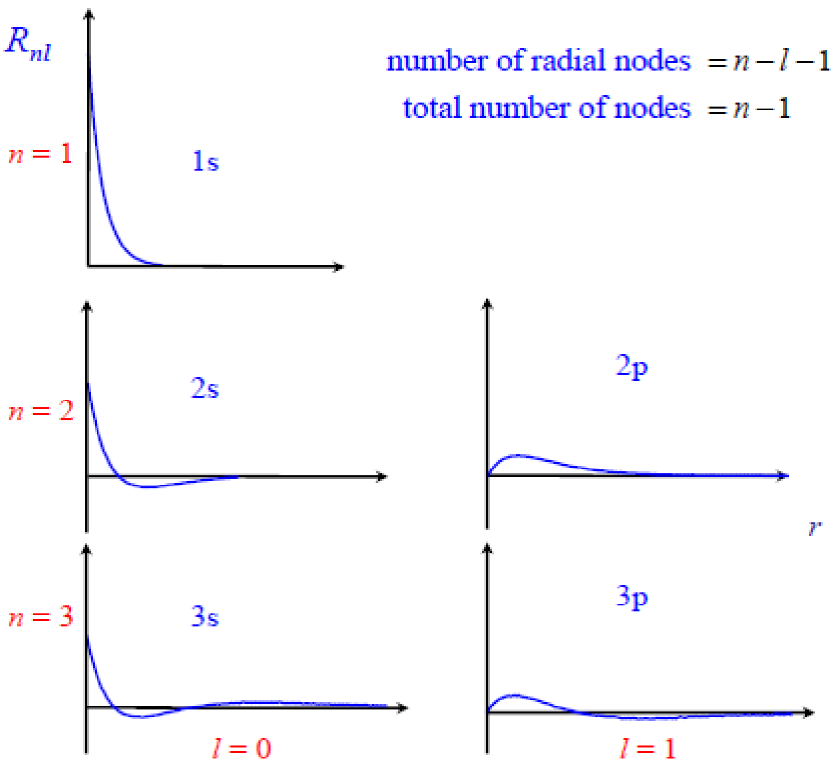
☒ Radial wave functions = $R_{n,l}(r)$

☒ $n = 1,2,3 \ldots$ & $l = 0,1,2, \ldots n-1$ & $m_l = l, l-1, \ldots -l$

Orbital	n	l	$R_{n,l}$
1s	1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho/2}$
2s	2	0	$\frac{1}{2(2)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2}(2-\frac{1}{2}\rho)e^{-\rho/4}$
2p	2	1	$\frac{1}{4(6)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2}\rho e^{-\rho/4}$
3s	3	0	$\frac{1}{9(3)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2}(6-2\rho+\frac{1}{9}\rho^2)e^{-\rho/6}$
3p	3	1	$\frac{1}{27(6)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2}(4-\frac{1}{3}\rho)\rho e^{-\rho/6}$
3d	3	2	$\frac{1}{81(30)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2}\rho^2 e^{-\rho/6}$

☒ H ATOM RADIAL WAVE FUNCTIONS

- Radial wave function = $R_{n,l}$ = how H atom wave function varies with distance of electron from nucleus
- Defined by 2 quantum numbers: n & l



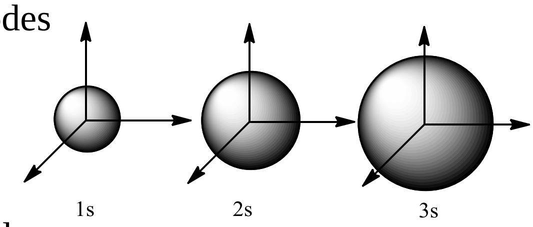
- Wave function passes through zero at a node
- For ψ with $l > 0$, $\psi = 0$ at $r = 0$
- But NOT radial node since r can't be negative
- ⇒ All nodes at nucleus are angular nodes

☒ H ATOM QUANTUM NUMBERS

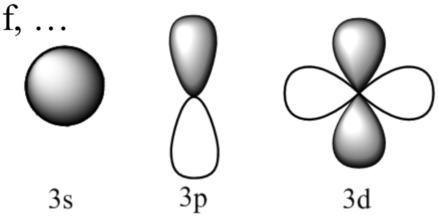
- Principle Quantum Number = n
  - ✓ Determines the energy:

$$E_n = -\frac{Z^2 e^4 \mu}{2n^2 \hbar^2 (4\pi\varepsilon_0)^2} = -\frac{Z^2 R}{n^2}$$

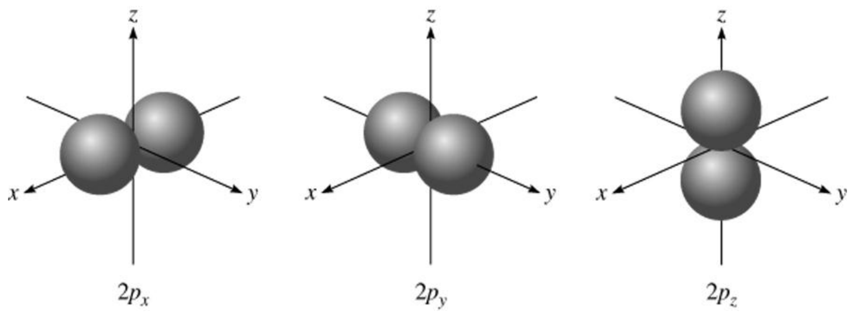
  - ✓ Same as Bohr atom
  - ✓ $n = 1,2,3 \ldots$
  - ✓ Total wave function has n – 1 nodes
  - ✓ Specifies the size of the orbital

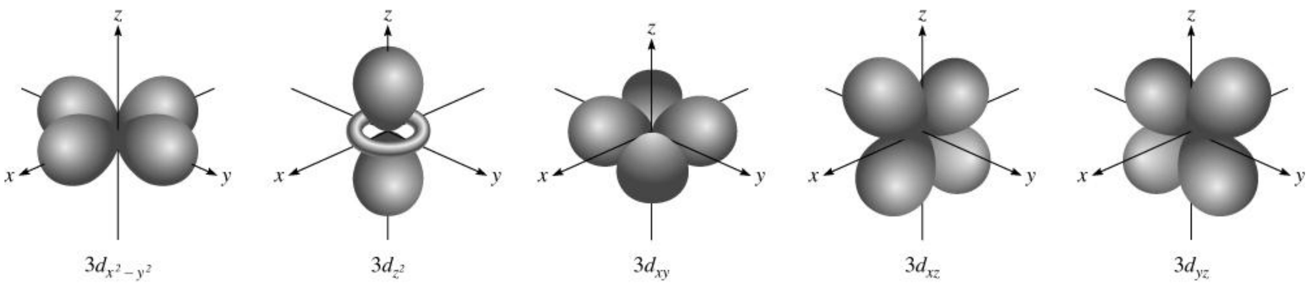


- Azimuthal quantum number = l
  - ✓ Determines the total orbital angular momentum
  - ✓ l restricted to values: $l = 0,\ 1,\ 2,\ 3, \ldots n-1$
  - ✓ Designated by letters: s, p, d, f, …
  - ✓ Specifies the shape of an orbital

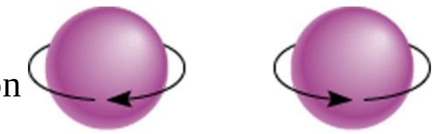


- Magnetic quantum number = m_l
  - ✓ Determines the z component of orbital angular momentum
  - ✓ Z component = $l_Z = m_l \hbar$
  - ✓ m_l restricted to values: $m_l = 0, \pm 1, \pm 2, \ldots, \pm l$
  - ✓ Specifies orientation of orbital in space





- Spin quantum number = m_s
  - ✓ Not predicted by this level of theory
  - ✓ Specifies the orientation of spin of electron
  - ✓ Takes only +1/2 (up) or -1/2 (down)



TOTAL ENERGY OF HYDROGEN ATOM

- The Schrödinger equation was solved exactly for the hydrogen atom giving an energy can be calculated from the following equation

$$E_n = -\frac{Z^2 e^4 \mu}{2n^2 \hbar^2 (4\pi\varepsilon_0)^2}$$

- Using the atomic units the total energy of the hydrogen atom will be

$$E_{Total} = -\frac{Z^2 e^4 \mu}{2n^2 \hbar^2 (4\pi\varepsilon_0)^2} = -E_h \frac{Z^2}{2} \frac{1}{n^2}$$

$$E_{Total} = -0.5\ E_h$$

Where

$$E_h(A.U.) = 27.211 eV$$

is called a Hartree