

# MOST IMPORTANT SCIENCE TABLE

ALSO A BRIEF HISTORY OF CHEMISTRY

HYD

Periodic Table  
of the Elements

1	2																	3	4	5	6	7	8	9	10
1 H	2 He																	3 B	4 C	5 N	6 O	7 F	8 Ne		
3 Li	4 Be																	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar		
11 Na	12 Mg	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr						
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe								
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn								
87 Fr	88 Ra	89 Ac	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt	110	111	112	113													

\* Lanthanide Series

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

\* Actinide Series

90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

For Hydrogen-like atoms  $H = -\frac{1}{2} \nabla^2 - \frac{Z}{r}$

$$H \Psi(r, \theta, \varphi) = E_{nl} \Psi(r, \theta, \varphi); \Psi = R_{nl}(r) Y_l^m(\theta, \varphi)$$

# ATOMIC HYDROGEN

Atomic No. 1,  $1s^1$ , Atomic Radius 78pm

## History of HYD

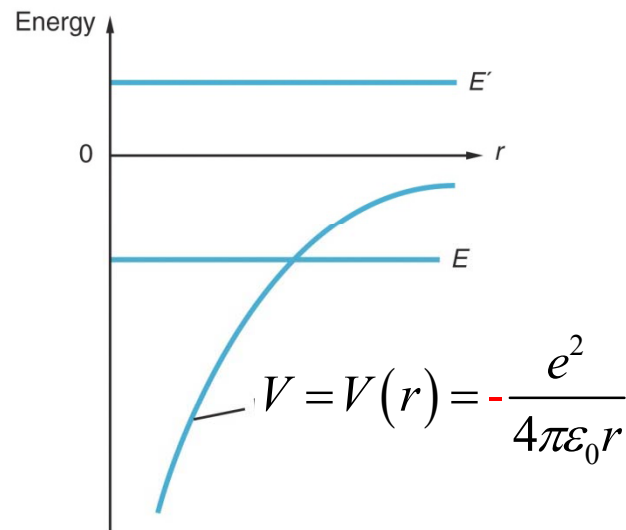
(Gr. *hydro*: water, and *genes*: forming)

Hydrogen was prepared many years before it was recognized as a distinct substance by Cavendish in 1776. Named by Lavoisier, hydrogen is the most abundant of all elements in the universe. Hydrogen is estimated to make up more than 90% of all the atoms -- **three quarters of the mass of the universe!** This element is found in the stars, and plays an important part in powering the universe through both the proton-proton reaction and carbon-nitrogen cycle. Stellar hydrogen fusion processes release massive amounts of energy by combining hydrogens to form Helium. The heavier elements were originally **made from hydrogen atoms** or from other elements that were originally made from hydrogen atoms.

***CARRIER OF ENERGY IN THE UNIVERSE***

# Hydrogen Atom

Atom is a *3D object*, and the electron motion is three-dimensional. We'll start with the simplest case - a hydrogen atom. An electron and a proton (nucleus) are bound by the central-symmetric Coulomb interaction. Because  $m_p \gg m_e$ , we neglect the proton motion (the reduced mass is very close to  $m_e$ , the center of mass of this system is  $\sim 2000$  times closer to the proton than to the electron). Thus, we can treat this problem as the motion of an electron in the 3D central-symmetric Coulomb potential.



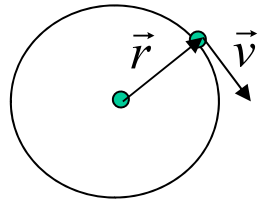
Three dimensions – we expect that the motion will be characterized with *three quantum numbers* (in fact, there will be the fourth one, the electron spin, which corresponds to the “internal degree of freedom” for an electron; the spin will be added later “by hand”, it is not described by the non-relativistic quantum mechanics).

$E < 0$  – bound motion, discrete spectrum,

$E > 0$  – unbound motion, continuous spectrum

The task: solve the  $t$ -independent S.Eq. for  $E < 0$ , find the energy eigenvalues (the spectrum) and eigenfunctions (stationary states).

# Orbital Motion in Classical Mechanics

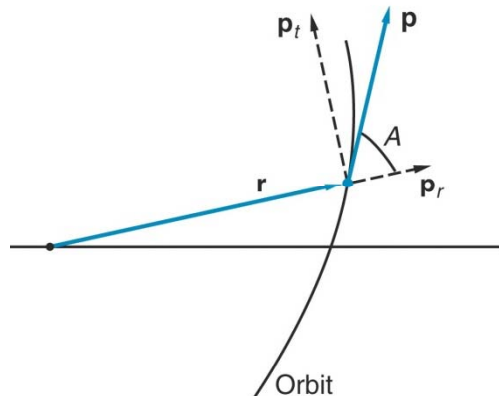


We consider the case of a *central* force: the force is directed along the line that connects the electron and proton or, in our Figure, the electron and the coordinate origin.

Coulomb interaction is responsible for acceleration:

$$\vec{F} = -\frac{e^2}{4\pi\epsilon_0 r^3} \vec{r} = -\frac{mv^2}{r^2} \vec{r} \quad \left( F = \frac{mv^2}{r} \right) \quad \text{Kinetic energy: } K = \frac{mv^2}{2} = \frac{p^2}{2m} = \frac{(p_r^2 + p_t^2)}{2m}$$

$p_r$  and  $p_t$  – the *radial* and *tangential* components of the momentum



The angular momentum  $\vec{L} = \vec{r} \times \vec{p}$   $\vec{L} = \vec{r} \times \vec{p} = \vec{r} \times (\vec{p}_r + \vec{p}_t) = \vec{r} \times \vec{p}_t$

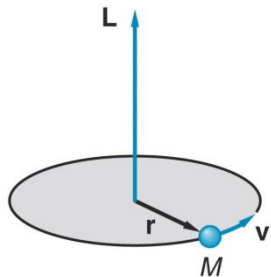
$$K = \frac{(p_r^2 + p_t^2)}{2m} = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2} \quad \text{For a circular motion: } K = \frac{L^2}{2mr^2}$$

In general, a non-zero torque leads to the time dependence of  $L$ :  $\vec{\tau} = \frac{d\vec{L}}{dt}$

In the field of a *central* force, the torque is *zero*, and the angular momentum about the center is *conserved*:

$$\vec{\tau} = \frac{d\vec{L}}{dt} = \vec{r} \times \frac{d\vec{p}}{dt} = \vec{r} \times \vec{F} = 0$$

( $\vec{r}$  is antiparallel to  $\vec{F}$ )



This makes  $L$  especially useful for analyzing the central force motion.

# Quantum-Mechanical Approach


As usual, we start with the time-dependent Schrödinger Equation (but now it is 3D case):

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

$$V(x, y, z) = -\frac{e^2}{4\pi\epsilon_0 \sqrt{x^2 + y^2 + z^2}} = -\frac{e^2}{4\pi\epsilon_0 r} \quad \text{- potential energy of Coulomb interaction between electron and proton}$$

$$i\hbar \frac{\partial \Psi(x, y, z, t)}{\partial t} = \hat{H} \Psi(x, y, z, t) \quad \hat{H} \equiv \underbrace{-\frac{\hbar^2}{2m} \left( \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \right)}_{K \text{ operator}} + \underbrace{V(x, y, z)}_{V \text{ operator}}$$

$\hat{p} = \frac{\hbar}{i} \left( \frac{d}{dx} + \frac{d}{dy} + \frac{d}{dz} \right) = \frac{\hbar}{i} \nabla$   
 Laplacian  $\nabla^2$



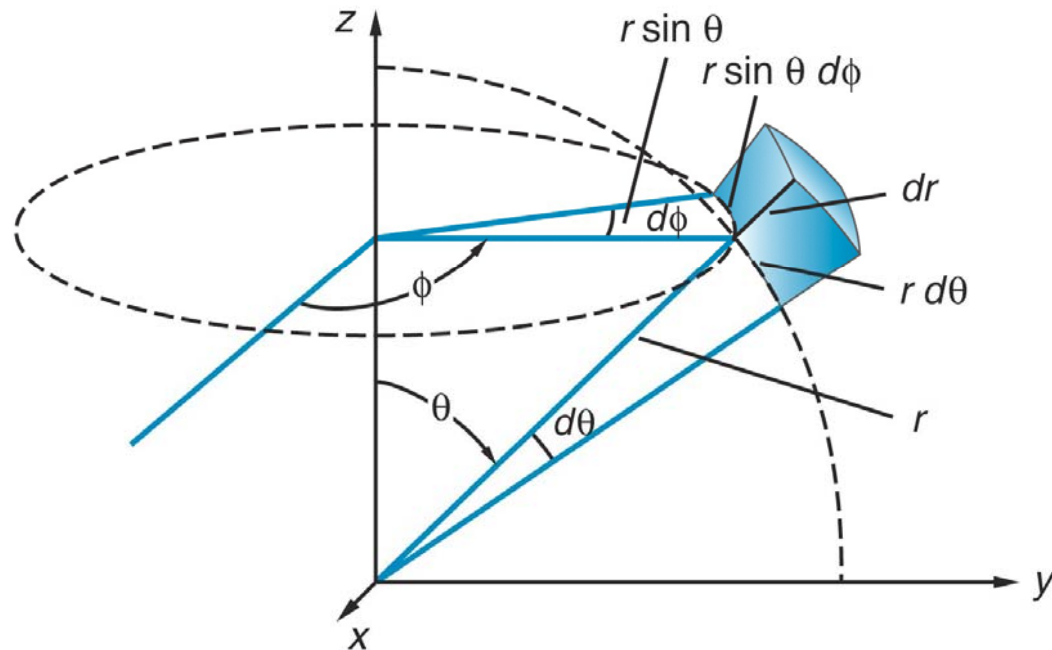
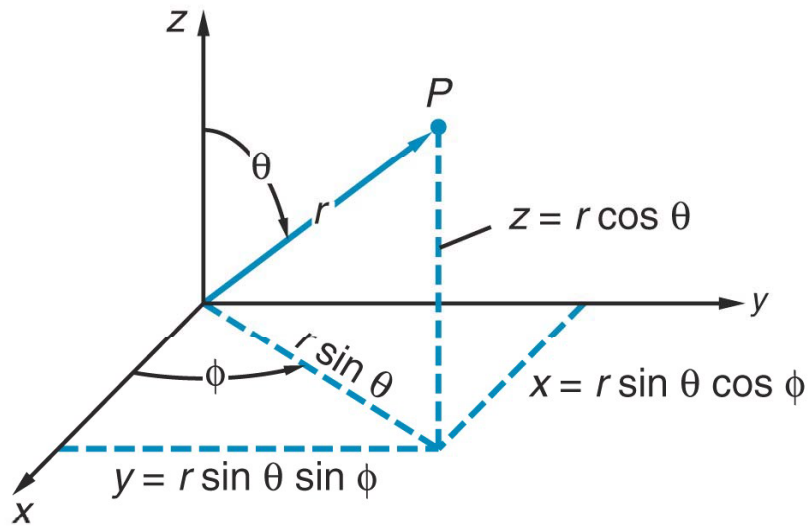
The potential is *time-independent*, thus we can separate time and space variables:

$$i\hbar \frac{dT(t)}{dt} = ET(t) \quad \hat{H}\psi(x, y, z) = E\psi(x, y, z) \quad \Rightarrow \quad \Psi(x, t) = \psi_E(x) \exp\left(\frac{-iEt}{\hbar}\right)$$

- solution of the *t*-independent S. Eq. gives us the eigenfunctions (the orthogonal basis  $\psi_i$ ) and eigenvalues (spectrum  $E_i$ ) of the Hamiltonian. Eigenfunctions correspond to the *stationary* states with a well-defined energy.

# Spherical Polar Coordinates

The Coulomb potential has *central symmetry* ( $U(r)$  depends on neither  $\theta$  nor  $\phi$ ). It's to our advantage to use *spherical polar coordinates* (this will allow us to separate variables).



$$r = \sqrt{x^2 + y^2 + z^2}$$

- distance from origin to point P

$$\theta = \cos^{-1} \frac{z}{\sqrt{x^2 + y^2 + z^2}}$$

- zenith angle

$$\phi = \tan^{-1} \frac{y}{x}$$

- azimuth angle

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

- a (small) volume element used for integration (no relation to the torque  $\tau$ )

## t-independent Schrödinger Equation in Polar Coordinates

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

$$\frac{\partial^2 \psi(x, y, z)}{\partial x^2} + \frac{\partial^2 \psi(x, y, z)}{\partial y^2} + \frac{\partial^2 \psi(x, y, z)}{\partial z^2}$$

$$\underbrace{\left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \frac{\partial \psi(r, \theta, \phi)}{\partial r} \right] + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left[ \sin \theta \frac{\partial \psi(r, \theta, \phi)}{\partial \theta} \right] + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi(r, \theta, \phi)}{\partial \phi^2} \right]}_{\text{Laplacian in polar coordinates}}$$

$$+ \frac{2m}{\hbar^2} [E - V(r, \theta, \phi)] \psi(r, \theta, \phi) = 0$$

After multiplying by  $r^2 \sin \theta$

$$\sin^2 \theta \frac{\partial}{\partial r} \left[ r^2 \frac{\partial \psi}{\partial r} \right] + \sin \theta \frac{\partial}{\partial \theta} \left[ \sin \theta \frac{\partial \psi}{\partial \theta} \right] + \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} r^2 \sin^2 \theta \left[ E + \frac{e^2}{4\pi\epsilon_0 r} \right] \psi = 0$$

# Separation of Variables

$$\sin^2 \theta \frac{\partial}{\partial r} \left[ r^2 \frac{\partial \psi}{\partial r} \right] + \sin \theta \frac{\partial}{\partial \theta} \left[ \sin \theta \frac{\partial \psi}{\partial \theta} \right] + \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} r^2 \sin^2 \theta \left[ E + \frac{e^2}{4\pi\epsilon_0 r} \right] \psi = 0$$

For a spherically-symmetric potentials ( $V=V(r)$ ), one can separate the variables by using a trial function

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

$$\frac{\sin^2 \theta}{R} \frac{d}{dr} \left[ r^2 \frac{dR}{dr} \right] + \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left[ \sin \theta \frac{d\Theta}{d\theta} \right] + \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} + \frac{2m}{\hbar^2} r^2 \sin^2 \theta \left[ E + \frac{e^2}{4\pi\epsilon_0 r} \right] = 0$$

To show that the variables are separable, let's rewrite:

$$\frac{\sin^2 \theta}{R} \frac{d}{dr} \left[ r^2 \frac{dR}{dr} \right] + \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left[ \sin \theta \frac{d\Theta}{d\theta} \right] + \frac{2m}{\hbar^2} r^2 \sin^2 \theta \left[ E + \frac{e^2}{4\pi\epsilon_0 r} \right] = -\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2}$$

Since the left and right sides depends on different variables, both parts should be equal to the *same* constant:

$$-\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = m_l^2$$

Divide by  $\sin^2 \theta$  and regroup:

$$\frac{1}{R} \frac{d}{dr} \left[ r^2 \frac{dR}{dr} \right] + \frac{2m}{\hbar^2} r^2 \left[ E + \frac{e^2}{4\pi\epsilon_0 r} \right] = \frac{m_l^2}{\sin^2 \theta} - \frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left[ \sin \theta \frac{d\Theta}{d\theta} \right]$$

## Separation of Variables (cont'd)

Thus

$$\frac{1}{R} \frac{d}{dr} \left[ r^2 \frac{dR}{dr} \right] + \frac{2m}{\hbar^2} r^2 \left[ E + \frac{e^2}{4\pi\epsilon_0 r} \right] = l(l+1)$$

Equation for  $R(r)$

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

Equation for  $\Theta(\theta)$

$$-\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = m_l^2$$

Equation for  $\Phi(\phi)$

Or, in a more conventional form:

$$\frac{1}{r^2} \frac{d}{dr} \left[ r^2 \frac{dR}{dr} \right] + \left[ \frac{2m}{\hbar^2} \left( E + \frac{e^2}{4\pi\epsilon_0 r} \right) - \frac{l(l+1)}{r^2} \right] R = 0$$

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

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

The initial equation in 3 polar coordinates has been separated into three one dimensional equations.

$$\frac{d^2\Phi}{d\varphi^2} = -m^2\Phi$$

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

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) - \frac{\ell(\ell+1)}{r^2} R + \frac{2\mu}{\hbar^2} \{E - V(r)\} R = 0$$

**Solve  $\Phi$  equation. Find it is good for only certain values of  $m$ . (0,+1,..+ $\ell$ )**

**Solve  $\Theta$  equation. Find it is good for only certain values of  $\beta=\ell(\ell+1)$ ;  $\ell=0,1,2\dots$ ]**

**Solve  $R$  equation. Find it is good for only certain values of  $E$ . Quantization with**

**Principal quantum number “n” ;  $n=1,2,3,\dots$ ;  $\ell=n-1$  ]**

**Since  $\beta = \ell(\ell + 1)$  , we have**

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left[ -\frac{\ell(\ell + 1)}{r^2} + \frac{2\mu}{\hbar^2} (E - V(r)) \right] R = 0$$

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

**The potential only enters into the  $R(r)$  equation.  $Z$  is the charge on the nucleus. One for H atom. Two for  $\text{He}^+$ , etc.**

**Make the substitutions**

$$\alpha^2 = -\frac{2\mu E}{\hbar^2}$$

$$\lambda = \frac{\mu Ze^2}{4\pi\epsilon_0 \hbar^2 \alpha}$$

**Introduce the new independent variable**

$$\rho = 2\alpha r \quad \rho \text{ is the the distance variable in units of } 2\alpha.$$

**Making the substitutions and with**

$$S(\rho) = R(r)$$

**yields**

$$\frac{1}{\rho^2} \frac{d}{d\rho} \left( \rho^2 \frac{dS}{d\rho} \right) + \left( -\frac{1}{4} - \frac{\ell(\ell+1)}{\rho^2} + \frac{\lambda}{\rho} \right) S = 0 \quad 0 \leq \rho \leq \infty$$

**To solve - look at solution for large  $\rho$ ,  $r \rightarrow \infty$  (like H. O.).**

**Consider the first term in the equation above.**

$$\frac{1}{\rho^2} \left( \frac{d}{d\rho} \left( \rho^2 \frac{dS}{d\rho} \right) \right) = \frac{1}{\rho^2} \left( \rho^2 \frac{d^2 S}{d\rho^2} + 2\rho \frac{dS}{d\rho} \right)$$

$$= \frac{d^2 S}{d\rho^2} + \frac{2}{\rho} \frac{dS}{d\rho}$$

**This term goes to zero as  $r \rightarrow \infty$**

**The terms in the full equation divided by  $\rho$  and  $\rho^2$  also go to zero as  $r \rightarrow \infty$  .**

Then, as  $r \rightarrow \infty$

$$\frac{d^2 S}{d\rho^2} = \frac{1}{4} S.$$

The solutions are

$$S = e^{-\rho/2}$$

$$S = e^{+\rho/2}$$

This blows up as  $r \rightarrow \infty$   
Not acceptable wavefunction.

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The full solution is

$$S(\rho) = e^{-\rho/2} F(\rho)$$

Substituting in the original equation, dividing by  $e^{-\rho/2}$  and rearranging gives

$$F'' + \left( \frac{2}{\rho} - 1 \right) F' + \left( \frac{\lambda}{\rho} - \frac{\ell(\ell+1)}{\rho^2} - \frac{1}{\rho} \right) F = 0 \quad 0 \leq \rho \leq \infty$$

The underlined terms blow up at  $\rho = 0$ . Regular point.

Singularity at  $\rho = 0$  - regular point,  
to remove, substitute

$$F(\rho) = \rho^\ell L(\rho)$$

**Gives**

$$\rho L'' + (2(\ell + 1) - \rho)L' + (\lambda - \ell - 1)L = 0.$$

Equation for  $L$ . Find  $L$ , get  $F$ . Know  $F$ , have  $S(\rho) = R(r)$ .

**Solve using polynomial method.**



$$a_{\nu+1} = \frac{-(\lambda - \ell - 1 - \nu)a_{\nu}}{[2(\nu + 1)(\ell + 1) + \nu(\nu + 1)]}$$

Provides solution to differential equation,  
but not good wavefunction if infinite  
number of terms.

Need to break off after the  $n'$  term by taking

$$\lambda - \ell - 1 - n' = 0$$

or

$$\lambda = n \quad \text{with} \quad n = n' + \ell + 1 \quad n \text{ is an integer.}$$

integers

$n'$   $\longrightarrow$  radial quantum number

$n$   $\longrightarrow$  total quantum number

$n = 1$       s orbital       $n' = 0, l = 0$

$n = 2$       s, p orbitals       $n' = 1, l = 0$  or  $n' = 0, l = 1$

$n = 3$       s, p, d orbitals       $n' = 2, l = 0$  or  $n' = 1, l = 1$  or  $n' = 0, l = 2$

**Thus,**

$$R(r) = e^{-\rho/2} \rho^\ell L(\rho)$$

**with**

$$L(\rho)$$

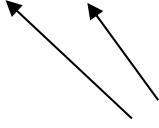
**defined by the recursion relation,**

**and**

$$\lambda = n$$

$$n = n' + \ell + 1$$

**integers**



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

$$\lambda = \frac{\mu Z e^2}{4\pi\epsilon_0 \hbar^2 \alpha}$$

$$\alpha^2 = -\frac{2\mu E}{\hbar^2}$$

$$n^2 = \lambda^2 = -\frac{\mu Z^2 e^4}{32\pi^2 \epsilon_0^2 \hbar^2 E}$$

$$E_n = -\frac{\mu Z^2 e^4}{8\epsilon_0^2 \hbar^2 n^2}$$

**Energy levels of the hydrogen atom.**

**Z is the nuclear charge. 1 for H; 2 for He<sup>+</sup>, etc.**

$$a_0 = \frac{\epsilon_0 h^2}{\pi \mu e^2} \quad a_0 = 5.29 \times 10^{-11} \text{ m}$$

**Bohr radius - characteristic length in H atom problem.**

**In terms of Bohr radius**

$$E_n = -\frac{Z^2 e^2}{8\pi\epsilon_0 a_0 n^2}$$

**Lowest energy, 1s, ground state energy, -13.6 eV.**

**Rydberg constant**

$$R_H = 109,677 \text{ cm}^{-1}$$

$$E_n = -\frac{Z^2}{n^2} R_H h c$$

$$R_\infty = \frac{m_e e^4}{8\epsilon_0^2 h^3 c}$$

**Rydberg constant if proton had infinite mass.  
Replace  $\mu$  with  $m_e$ .  $R_\infty = 109,737 \text{ cm}^{-1}$ .**

**Have solved three one-dimensional equations to get**

$$\Phi_m(\varphi) \quad \Theta_{\ell m}(\theta) \quad R_{n\ell}(r)$$

**The total wavefunction is**

$$\Psi_{n\ell m}(\varphi, \theta, r) = \Phi_m(\varphi) \Theta_{\ell m}(\theta) R_{n\ell}(r)$$

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

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

$$m = \ell, \ell - 1, \dots, -\ell$$

- First few radial wave functions  $R_{n\ell}$

# Hydrogen Atom Radial Wave Functions

**Table 7.1 Hydrogen Atom Radial Wave Functions**

$n$	$\ell$	$R_{n\ell}(r)$
1	0	$\frac{2}{(a_0)^{3/2}} e^{-r/a_0}$
2	0	$\left(2 - \frac{r}{a_0}\right) \frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\frac{r}{a_0} \frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\frac{1}{(a_0)^{3/2}} \frac{2}{81\sqrt{3}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{6}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$
3	2	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{30}} \frac{r^2}{a_0^2} e^{-r/3a_0}$

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- Subscripts on  $R$  specify the values of  $n$  and  $\ell$ .

# Solution of the Angular and Azimuthal Equations

- The solutions for Eq (7.8) are  $e^{im_\ell\phi}$  or  $e^{-im_\ell\phi}$
- Solutions to the angular and azimuthal equations are linked because both have  $m_\ell$ .
- Group these solutions together into functions.

$$Y(\theta, \phi) = f(\theta)g(\phi) \text{ ---- spherical harmonics}$$

# Normalized Spherical Harmonics

**Table 7.2** Normalized Spherical Harmonics  $Y_{\ell m_{\ell}}(\theta, \phi)$

$\ell$	$m_{\ell}$	$Y_{\ell m_{\ell}}$
0	0	$\frac{1}{2\sqrt{\pi}}$
1	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}} \cos \theta$
1	$\pm 1$	$\mp \frac{1}{2}\sqrt{\frac{3}{2\pi}} \sin \theta e^{\pm i\phi}$
2	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}} (3 \cos^2 \theta - 1)$
2	$\pm 1$	$\mp \frac{1}{2}\sqrt{\frac{15}{2\pi}} \sin \theta \cos \theta e^{\pm i\phi}$
2	$\pm 2$	$\frac{1}{4}\sqrt{\frac{15}{2\pi}} \sin^2 \theta e^{\pm 2i\phi}$
3	0	$\frac{1}{4}\sqrt{\frac{7}{\pi}} (5 \cos^3 \theta - 3 \cos \theta)$
3	$\pm 1$	$\mp \frac{1}{8}\sqrt{\frac{21}{\pi}} \sin \theta (5 \cos^2 \theta - 1) e^{\pm i\phi}$
3	$\pm 2$	$\frac{1}{4}\sqrt{\frac{105}{2\pi}} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$
3	$\pm 3$	$\mp \frac{1}{8}\sqrt{\frac{35}{\pi}} \sin^3 \theta e^{\pm 3i\phi}$

# Solution of the Angular and Azimuthal Equations

- The radial wave function  $R$  and the spherical harmonics  $Y$  determine the probability density for the various quantum states. The total wave function  $\psi(r, \theta, \phi)$  depends on  $n$ ,  $\ell$ , and  $m_\ell$ . The wave function becomes

$$\psi_{nlm_\ell}(r, \theta, \phi) = R_{nl}(r)Y_{\ell m_\ell}(\theta, \phi)$$

# Principal Quantum Number $n$

- It results from the solution of  $R(r)$ . Because  $R(r)$  includes the potential energy  $V(r)$ .

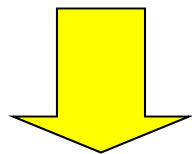
The result for this quantized energy is

$$E_n = \frac{-\mu}{2} \left( \frac{e^2}{4\pi\epsilon_0\hbar} \right)^2 \frac{1}{n^2} = -\frac{E_0}{n^2}$$

- The negative means the energy  $E$  indicates that the electron and proton are bound together.

# Orbital Angular Momentum Quantum Number $\ell$

- It is associated with the  $R(r)$  and  $f(\theta)$  parts of the wave function.
- Classically, the orbital angular momentum  $\vec{L} = \vec{r} \times \vec{p}$  with  $L = m v_{\text{orbital}} r$ .
- $\ell$  is related to  $L$  by  $L = \sqrt{\ell(\ell + 1)}\hbar$ .
- In an  $\ell = 0$  state,  $L = \sqrt{0(1)}\hbar = 0$



It disagrees with Bohr's semiclassical "planetary" model of electrons orbiting a nucleus  $L = n\hbar$ .

# Orbital Angular Momentum Quantum Number $\ell$

- A certain energy level is **degenerate** with respect to  $\ell$  when the energy is independent of  $\ell$ .
- Use letter names for the various  $\ell$  values.

– $\ell =$	0	1	2	3	4	5 ...
– Letter =	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>	<i>h ...</i>
- Atomic states are referred to by their  $n$  and  $\ell$ .
- A state with  $n = 2$  and  $\ell = 1$  is called a  $2p$  state.
- The boundary conditions require  $n > \ell$ .

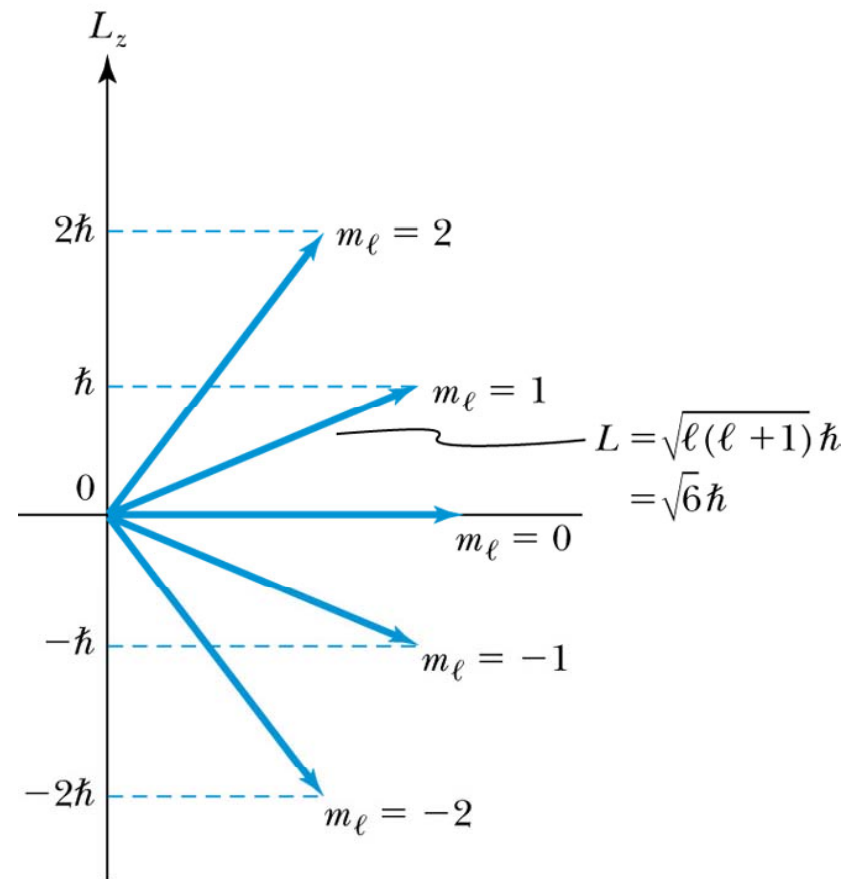
# Magnetic Quantum Number $m_\ell$

- The angle  $\phi$  is a measure of the rotation about the z axis.
- The solution for  $g(\phi)$  specifies that  $m_\ell$  is an integer and related to the z component of  $L$ .  $L_z = m_\ell \hbar$

- The relationship of  $L$ ,  $L_z$ ,  $\ell$ , and  $m_\ell$  for  $\ell = 2$ .

- $L = \sqrt{\ell(\ell + 1)}\hbar = \sqrt{6}\hbar$  is fixed because  $L_z$  is quantized.

- Only certain orientations of  $\vec{L}$  are possible and this is called **space quantization**.



# Magnetic Quantum Number $m_\ell$

- Quantum mechanics allows  $\vec{L}$  to be quantized along only one direction in space. Because of the relation  $L^2 = L_x^2 + L_y^2 + L_z^2$  the knowledge of a second component would imply a knowledge of the third component because we know  $\vec{L}$ .

- We expect the average of the angular momentum components squared to be  
$$\langle L_x^2 \rangle = \langle L_y^2 \rangle = \langle L_z^2 \rangle$$

$$\langle L^2 \rangle = 3 \langle L_z^2 \rangle = \frac{3}{2\ell + 1} \sum_{m_\ell = -\ell}^{\ell} m_\ell^2 \hbar^2 = \ell(\ell + 1) \hbar^2$$

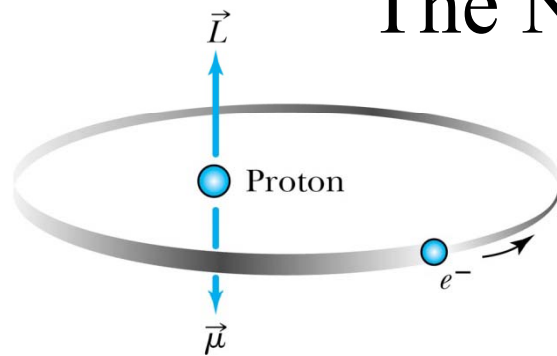
## 7.4: Magnetic Effects on Atomic Spectra—The Normal Zeeman Effect

- The Dutch physicist Pieter Zeeman showed the spectral lines emitted by atoms in a magnetic field split into multiple energy levels. It is called the **Zeeman effect**.

### **Anomalous Zeeman effect:**

- A spectral line is split into three lines.
- Consider the atom to behave like a small magnet.
- Think of an electron as an orbiting circular current loop of  $I = dq / dt$  around the nucleus.
- The current loop has a magnetic moment  $\mu = IA$  and the period  $T =$
- $\vec{\mu} = -\frac{e}{2m} \vec{L}$  where  $L = mvr$  is the magnitude of the orbital angular momentum.

## The Normal Zeeman Effect



- Since there is no magnetic field to align them,  $\vec{\mu}$  point in random directions. The dipole has a potential energy

$$V_B = -\vec{\mu} \cdot \vec{B}$$

- The angular momentum is aligned with the magnetic moment, and the torque between  $\vec{\mu}$  and  $\vec{B}$  causes a precession of  $\vec{\mu}$ .

$$\mu_z = \frac{e\hbar}{2m} m_\ell = -\mu_B m_\ell$$

Where  $\mu_B = e\hbar / 2m$  is called a **Bohr magneton**.

- $\vec{\mu}$  cannot align exactly in the z direction and has only certain allowed quantized orientations.

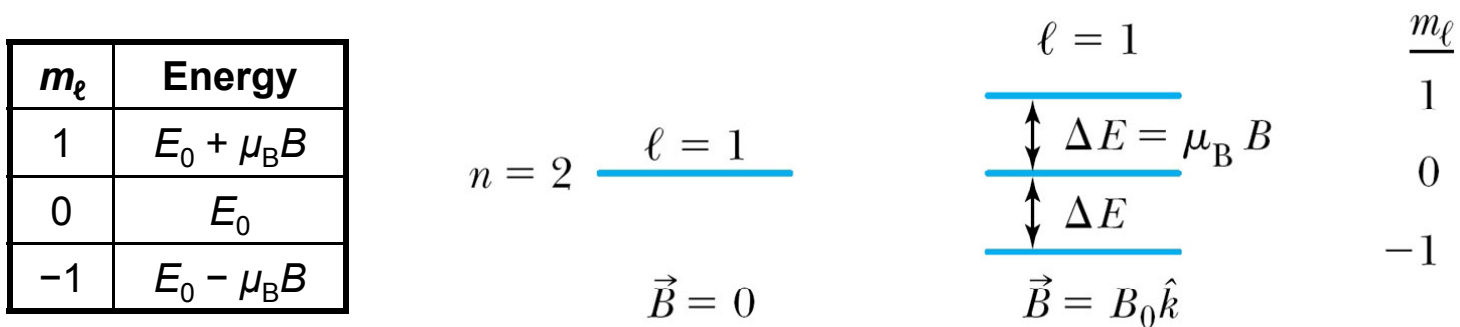
$$\vec{\mu} = -\mu_B \vec{L} / \hbar$$

# The Normal Zeeman Effect

- The potential energy is quantized due to the magnetic quantum number  $m_\ell$ .

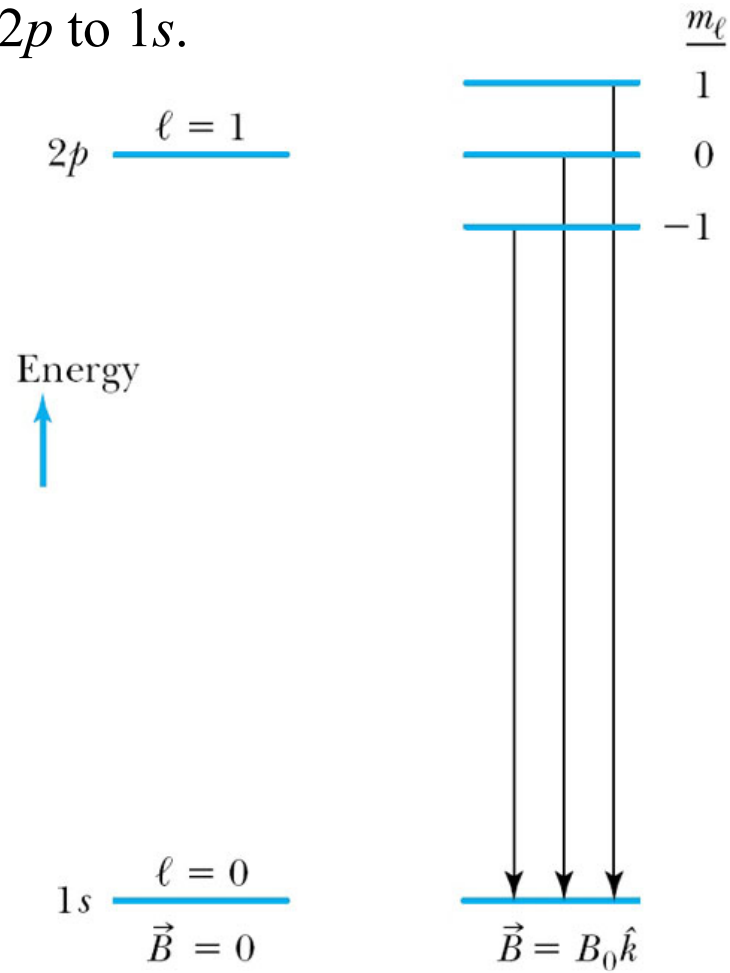
$$V_B = -\mu_z B = +\mu_B m_\ell B$$

- When a magnetic field is applied, the  $2p$  level of atomic hydrogen is split into three different energy states with energy difference of  $\Delta E = \mu_B B \Delta m_\ell$ .



# The Normal Zeeman Effect

- A transition from  $2p$  to  $1s$ .



# Probability Distribution Functions

- The differential volume element in spherical polar coordinates is

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

Therefore,

$$P(r) \, dr = r^2 R^* (r) R(r) \, dr \int_0^\pi |f(\theta)|^2 \sin \theta \, d\theta \int_0^{2\pi} |g(\phi)|^2 \, d\phi$$

- We are only interested in the radial dependence.

$$P(r) \, dr = r^2 |R(r)|^2 \, dr$$

- The radial probability density is  $P(r) = r^2 |R(r)|^2$  and it depends only on  $n$  and  $l$ .

# Ground State ( $n = 1, l = 0, m_l = 0$ )

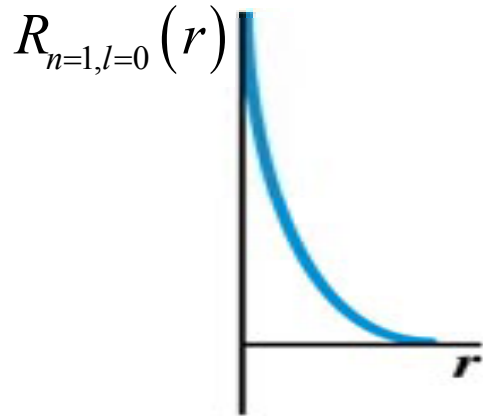
For all s-states ( $l=0$ ), the angular momentum is zero, and the radial equation is reduced to

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \frac{2m}{\hbar^2} [E - U(r)] R = 0$$

$$R_{10} = \frac{2}{\sqrt{a_0^3}} e^{-r/a_0}$$

The ground state ( $n = 1, l = 0, m_l = 0$ ):

$$\Psi_{1,0,0}(r, \theta, \phi, t) = R_{n=1, l=0}(r) \Theta_{l=0, m_l=0}(\theta) \Phi_{m_l=0}(\phi) e^{-iE_1 t}$$



$$= \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} e^{-iE_1 t}$$

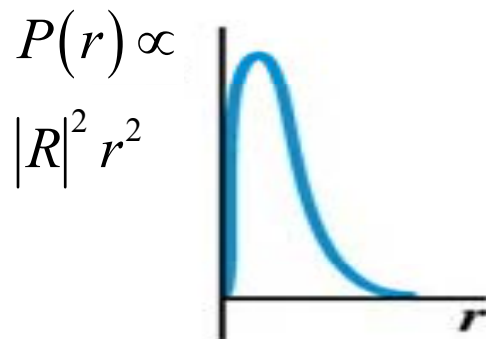
$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$$

- the Bohr radius

$$a_0 \approx 0.53 \text{ \AA} = 0.053 \text{ nm}$$

- recall that we got this estimate from the uncertainty principle

$$P(r) d\tau = |R\Theta\Phi|^2 d\tau \quad d\tau = r^2 \sin\theta dr d\theta d\phi$$



The probability of finding an electron in a spherical shell between  $r$  and  $r+dr$  from the nucleus (§6.7):

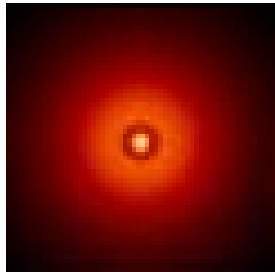
$$P(r) dr = |R|^2 r^2 dr \int_0^\pi |\Theta|^2 \sin\theta d\theta \int_0^{2\pi} |\Phi|^2 d\phi = \underline{|R|^2 r^2 dr}$$

$r^2 dr$  captures the volume of the shell

# Other $\ell = 0$ States (s-states)

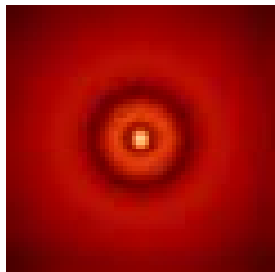
For all s-states, the angular momentum is zero:

$$n = 1, 2, 3, \dots \quad l = 0 \quad m_l = 0$$



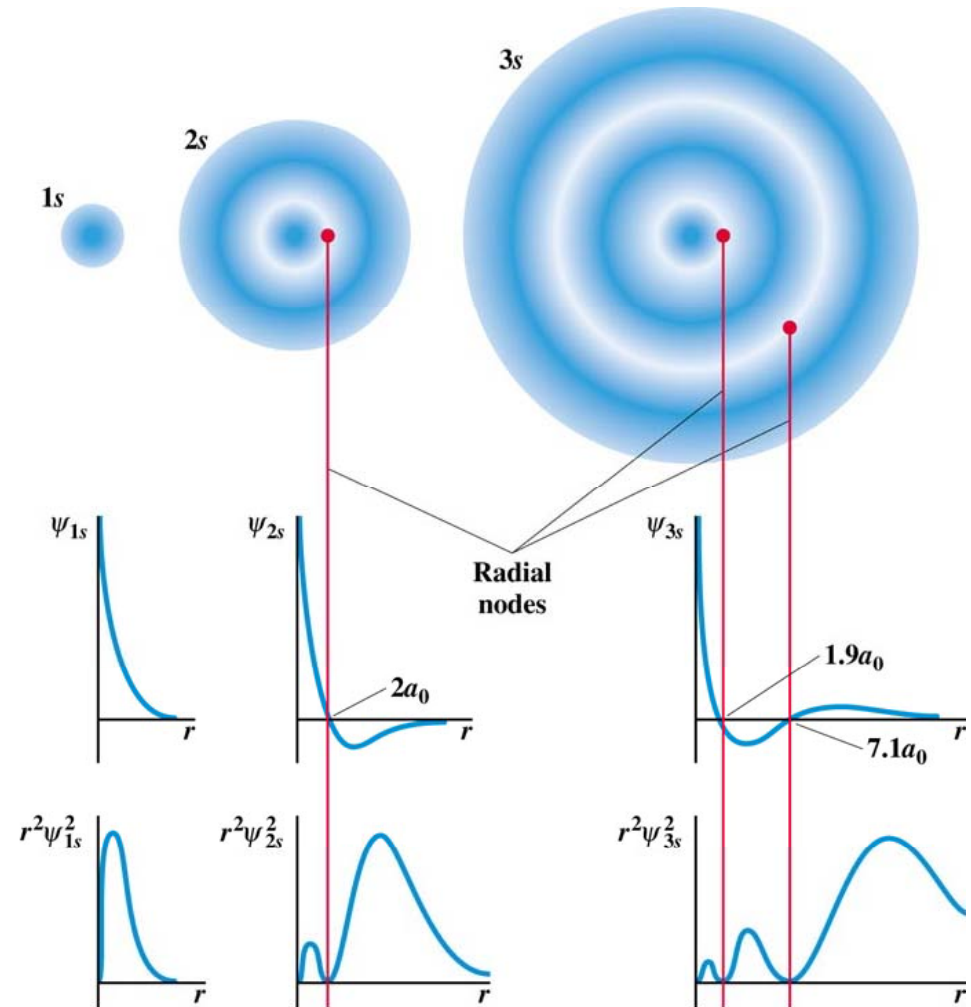
$n=2$

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



$n=3$

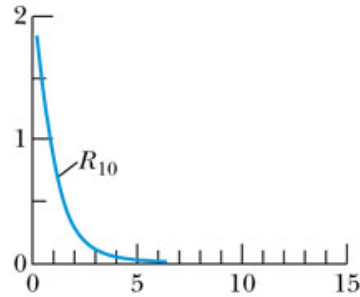
$$R_{30} = \frac{2}{3\sqrt{3}a_0^3} \left( 1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2} \right) e^{-r/3a_0}$$



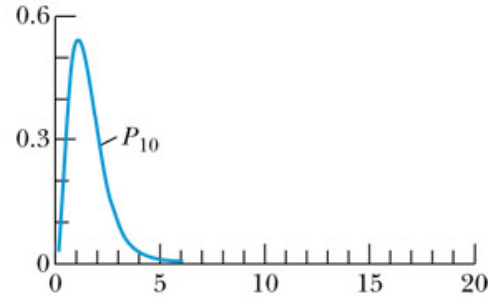
“Boundary” sphere:  $r_{1s} = 1.4 \text{ \AA}$ ,  $r_{2s} = 3.3 \text{ \AA}$ ,  $r_{3s} = 10 \text{ \AA}$

# Probability Distribution Functions

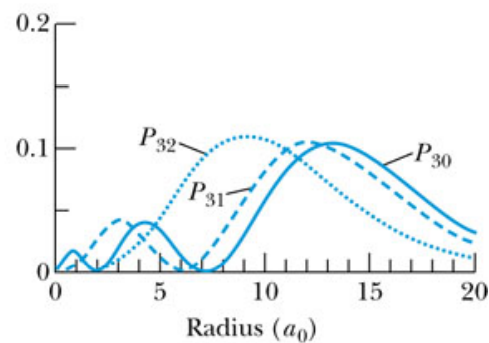
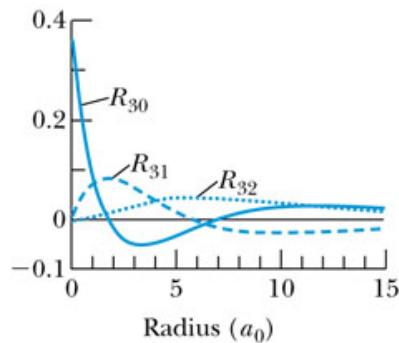
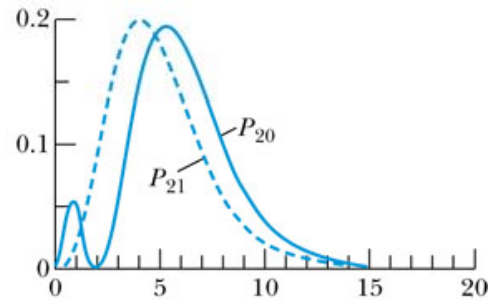
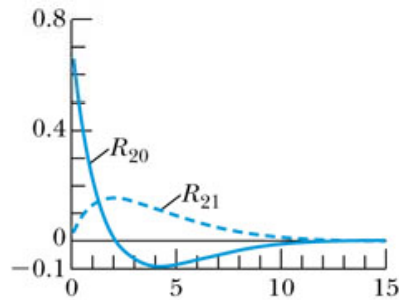
Radial wave functions ( $R_{n\ell}$ )



Radial probability distribution ( $P_{n\ell}$ )



- $R(r)$  and  $P(r)$  for the lowest-lying states of the hydrogen atom.



(a)

(b)

## The 2s Hydrogen orbital

$$\psi_{2s} = B(2 - r/a_0)e^{-r/2a_0}$$

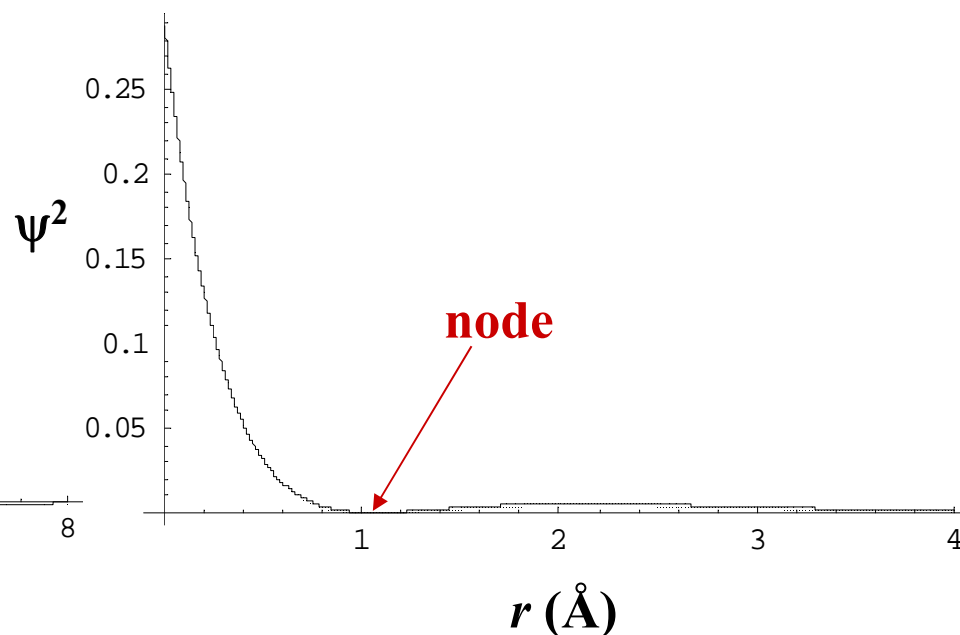
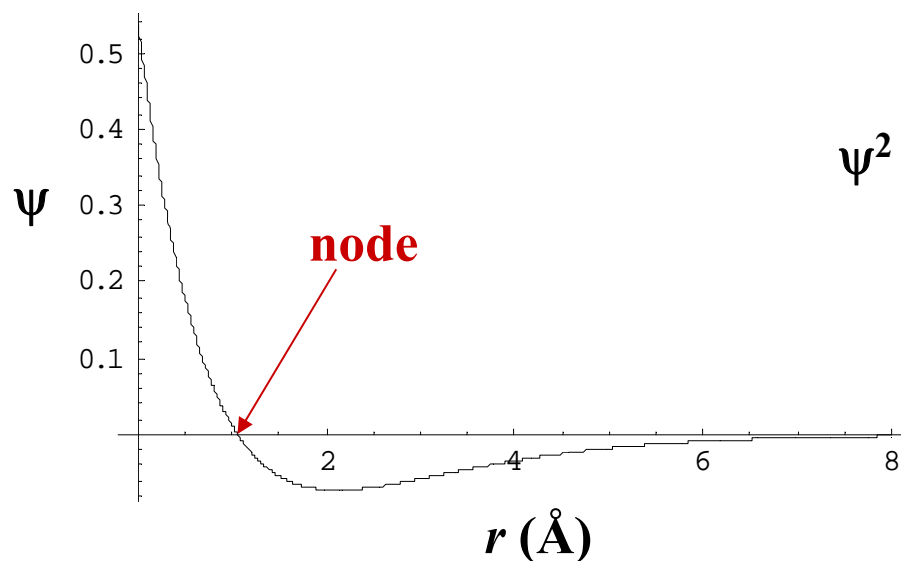
$$B = \frac{1}{4\sqrt{2\pi a_0^3}}$$

Probability  
amplitude

When  $r = 2a_0$ , this term goes to zero.  $a_0 = 0.529$ , the Bohr radius  
There is a “node” in the wave function.

$$|\psi_{2s}|^2 = \left[ B(2 - r/a_0)e^{-r/2a_0} \right]^2$$

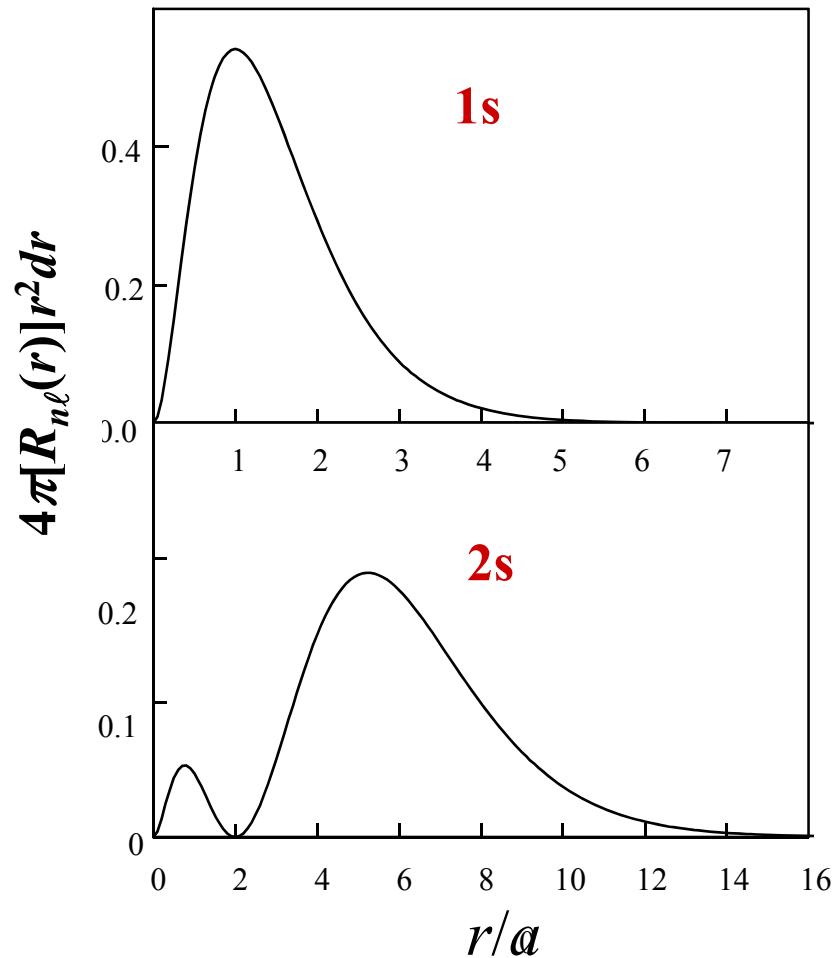
Absolute value of the wavefunction  
squared – probability distribution.



## Radial distribution function

$$D_{nl}(r) = 4\pi [R_{nl}(r)]^2 r^2 dr$$

Probability of finding electron distance  $r$  from the nucleus in a thin spherical shell.



## Example 20.2

a. Consider an excited state of the H atom with the electron in the  $2s$  orbital. Is the wave function that describes this state, an eigenfunction of the kinetic energy? Of the potential energy?

$$\psi_{200}(r) = \frac{1}{\sqrt{32\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

b. Calculate the average values of the kinetic and potential energies for an atom described by this wave function.

# Solution

a. We know that this function is an eigenfunction of the total energy operator because it is a solution of the Schrödinger equation. You can convince yourself that the total energy operator does not commute with either the kinetic energy operator or the potential energy operator by extending the discussion of Example Problem 20.1. Therefore, this wave function cannot be an eigenfunction of either of these operators.

# Solution

b. The average value of the kinetic energy is given by

$$\begin{aligned}\langle E_{kinetic} \rangle &= \int \psi^*(\tau) \hat{E}_{kinetic} \psi(\tau) d\tau \\ &= -\frac{h}{2\mu} \frac{1}{32\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0} \left( \frac{1}{r^2} \frac{d}{dr} \left[ r^2 \frac{d}{dr} \left\{ \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0} \right\} \right] \right) r^2 dr \\ &= -\frac{h}{2\mu} \frac{1}{8\pi a_0^3} \int_0^\infty \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0} \left( -\frac{e^{-r/2a_0}}{4a_0^3 r} \right) (16a_0^2 - 10a_0 r + r^2) r^2 dr \\ &= -\frac{h}{2\mu} \frac{1}{8\pi a_0^3} \left( \frac{9}{a_0^2} \int_0^\infty r^2 e^{-r/a_0} - \frac{8}{a_0} \int_0^\infty r e^{-r/a_0} - \frac{3}{a_0^3} \int_0^\infty r^3 e^{-r/a_0} + \frac{1}{4a_0^4} \int_0^\infty r^4 e^{-r/a_0} \right)\end{aligned}$$

# Solution

We use the standard integral,

$$\int_0^{\infty} x^n e^{-ax} dx = n! / a^{n+1} :$$

$$\langle E_{kinetic} \rangle = h^2 / 8\mu a_0^2$$

Using the relationship

$$\langle E_{kinetic} \rangle = \frac{e^2}{32\pi\epsilon_0 a_0} = -E, \text{ for } n = 2$$

# Solution

The average potential energy is given by

$$\begin{aligned}\langle E_{kinetic} \rangle &= \int \psi^* \hat{E}_{potential} \psi(\tau) d\tau \\ &= -\frac{e^2}{4\pi\epsilon_0} \frac{1}{32\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty \left[ \left( 2 - \frac{r}{a_0} \right) e^{-r/2a_0} \right] \left( \frac{1}{r} \right) \left[ \left( 2 - \frac{r}{a_0} \right) e^{-r/2a_0} \right] r^2 dr \\ &= -\frac{e^2}{4\pi\epsilon_0} \frac{1}{8\pi a_0^3} \left( 4 \int_0^\infty e^{-r/a_0} dr - \frac{4}{a_0} \int_0^\infty r^2 e^{-r/a_0} dr + \frac{1}{a_0^2} \int_0^\infty r^3 e^{-r/a_0} dr \right) \\ &= -\frac{e^2}{4\pi\epsilon_0} \frac{1}{8a_0^3} (2a_0^2) \\ &= -\frac{e^2}{16\pi\epsilon_0 a_0} = 2E_n \quad \text{for } n = 2\end{aligned}$$

# Solution

We see that

$$\langle E_{potential} \rangle = 2\langle E_{total} \rangle \text{ and } \langle E_{potential} \rangle = -2\langle E_{kinetic} \rangle$$

The relationship of the kinetic and potential energies is a specific example of the **virial theorem** and holds for any system in which the potential is Coulombic.

$$2\langle T \rangle = -n \langle V \rangle \quad V(\mathbf{r}) = \frac{1}{r^n}$$

# SHAPES OF HYDROGEN ATOM WAVE FUNCTIONS

**Have solved three one-dimensional equations to get**

$$\Phi_m(\varphi) \quad \Theta_{\ell m}(\theta) \quad R_{n\ell}(r)$$

**The total wavefunction is**

$$\Psi_{n\ell m}(\varphi, \theta, r) = \Phi_m(\varphi) \Theta_{\ell m}(\theta) R_{n\ell}(r)$$

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

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

$$m = \ell, \ell - 1 \dots -\ell$$

- First few radial wave functions  $R_{n\ell}$

# Hydrogen Atom Radial Wave Functions

**Table 7.1** Hydrogen Atom Radial Wave Functions

$n$	$\ell$	$R_{n\ell}(r)$
1	0	$\frac{2}{(a_0)^{3/2}} e^{-r/a_0}$
2	0	$\left(2 - \frac{r}{a_0}\right) \frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\frac{r}{a_0} \frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\frac{1}{(a_0)^{3/2}} \frac{2}{81\sqrt{3}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{6}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$
3	2	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{30}} \frac{r^2}{a_0^2} e^{-r/3a_0}$

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- Subscripts on  $R$  specify the values of  $n$  and  $\ell$ .

# Solution of the Angular and Azimuthal Equations

- The solutions for Eq (7.8) are  $e^{im_\ell\phi}$  or  $e^{-im_\ell\phi}$
- Solutions to the angular and azimuthal equations are linked because both have  $m_\ell$ .
- Group these solutions together into functions.

$$Y(\theta, \phi) = f(\theta)g(\phi) \text{ ---- spherical harmonics}$$

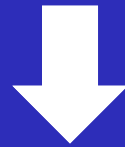
# Normalized Spherical Harmonics

**Table 7.2** Normalized Spherical Harmonics  $Y_{\ell m_{\ell}}(\theta, \phi)$

$\ell$	$m_{\ell}$	$Y_{\ell m_{\ell}}$
0	0	$\frac{1}{2\sqrt{\pi}}$
1	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}} \cos \theta$
1	$\pm 1$	$\mp \frac{1}{2}\sqrt{\frac{3}{2\pi}} \sin \theta e^{\pm i\phi}$
2	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}} (3 \cos^2 \theta - 1)$
2	$\pm 1$	$\mp \frac{1}{2}\sqrt{\frac{15}{2\pi}} \sin \theta \cos \theta e^{\pm i\phi}$
2	$\pm 2$	$\frac{1}{4}\sqrt{\frac{15}{2\pi}} \sin^2 \theta e^{\pm 2i\phi}$
3	0	$\frac{1}{4}\sqrt{\frac{7}{\pi}} (5 \cos^3 \theta - 3 \cos \theta)$
3	$\pm 1$	$\mp \frac{1}{8}\sqrt{\frac{21}{\pi}} \sin \theta (5 \cos^2 \theta - 1) e^{\pm i\phi}$
3	$\pm 2$	$\frac{1}{4}\sqrt{\frac{105}{2\pi}} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$
3	$\pm 3$	$\mp \frac{1}{8}\sqrt{\frac{35}{\pi}} \sin^3 \theta e^{\pm 3i\phi}$

Nodal Characteristics  
of

“Hydrogen Atom Wave Functions”



One Electron Wave Functions=ORBITALS



# Nodes of Hydrogenic wave functions

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

Total # of RADIAL NODES [ Spherical Surfaces ] =  $n - \ell - 1$

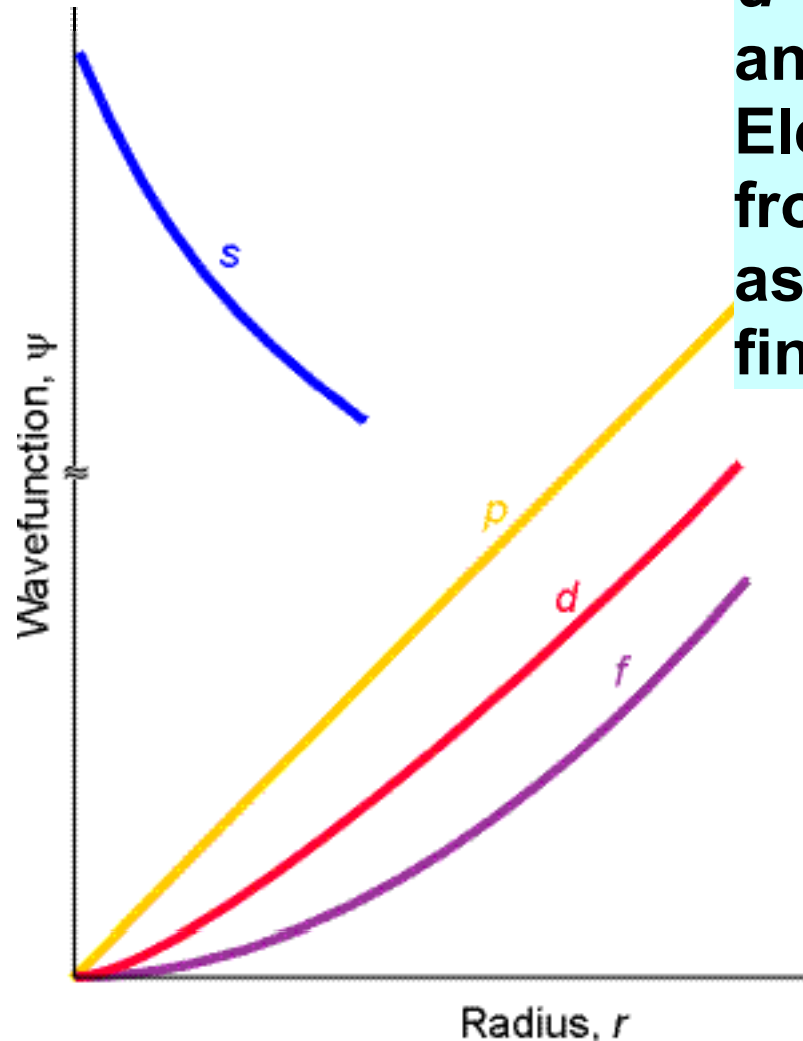
Total number of ANGULAR NODES [ Planes ] =  $\ell$

Total number of Nodes =  $n - 1$

## Orbitals of Hydrogenic Atom

## Wave Functions of Hydrogen

Close to the nucleus,  
 $p$  orbitals are proportional to  $r$ ,  
 $d$  orbitals are proportional to  $r^2$ ,  
and  $f$  orbitals are proportional to  $r^3$ .  
Electrons are progressively excluded  
from the neighbourhood of the nucleus  
as  $l$  increases. An  $s$  orbital has a  
finite, nonzero value at the nucleus.



## Orbital near nucleus

$$r^l \text{ as } r \rightarrow 0$$

The only radial node condition  
2s, 3p, 4d, 5f...orbital of Hydrogen atom

*The Only Radial Node*

*In the first excited state*

*of H – atom*

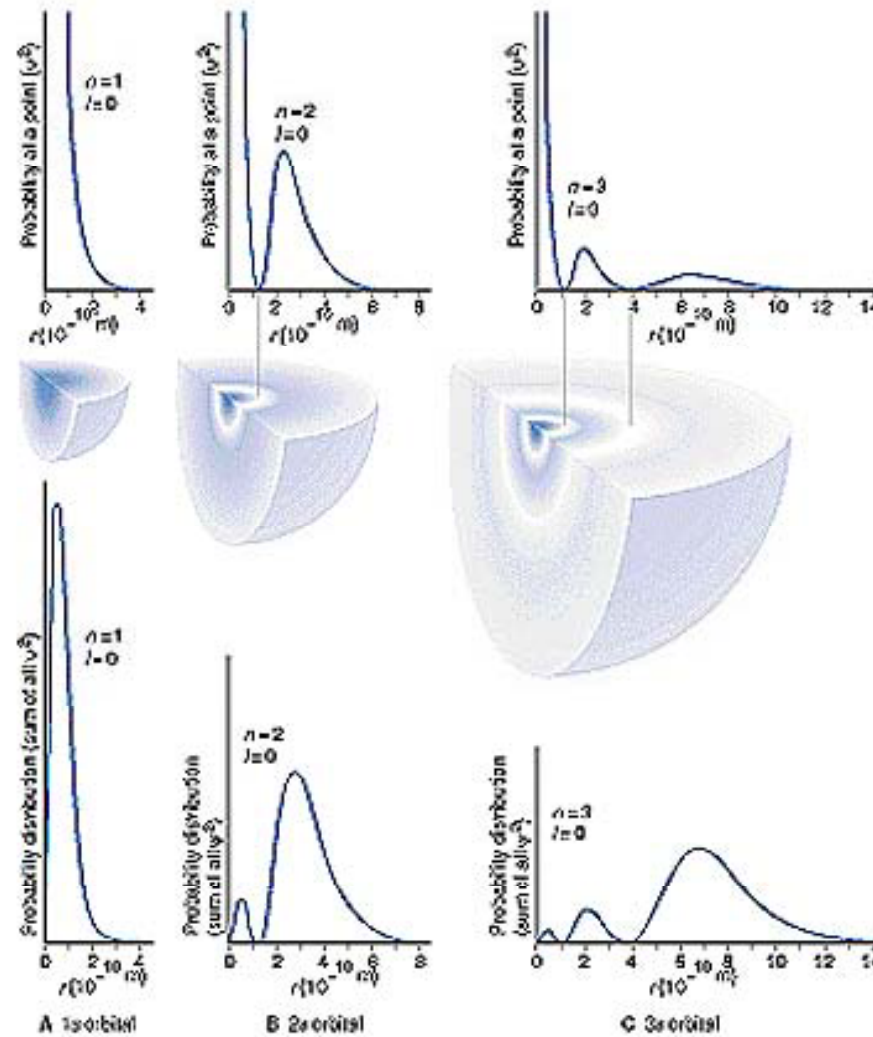
*for any given  $\ell$ , is given exactly*

$$r_{\text{only-node}} = (\ell + 1)(\ell + 2) \text{ a.u.}$$

# Radial Nodes $\rightarrow$ Spherical Surface(s) $\rightarrow n-\ell+1$

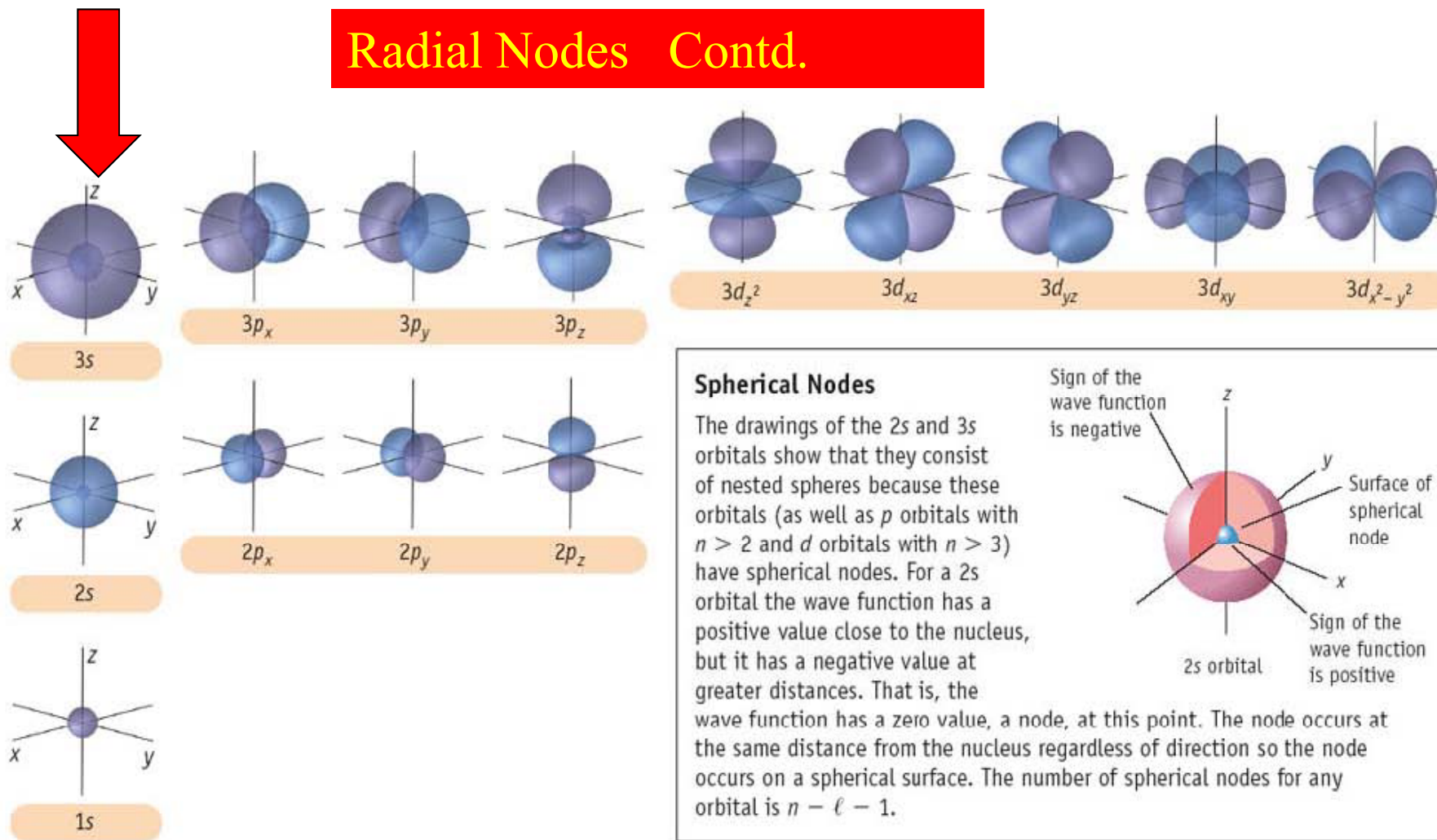
$$\psi\psi$$

$\ell=0;$   
1s, 2s, 3s

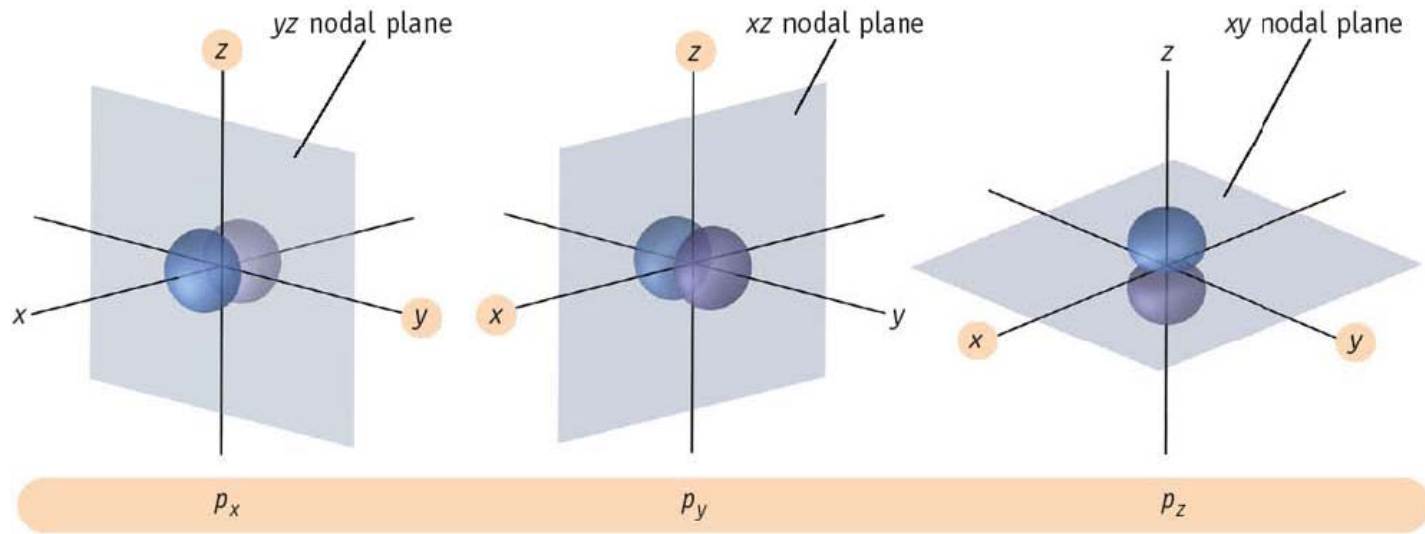


$$4\pi r^{**2} R(r)^{**2}$$

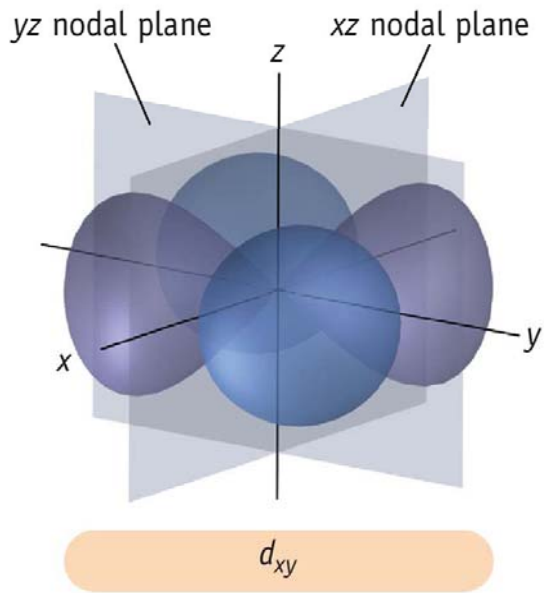
## Radial Nodes Contd.



# Angular Nodes $\rightarrow$ Planes $\rightarrow \ell$



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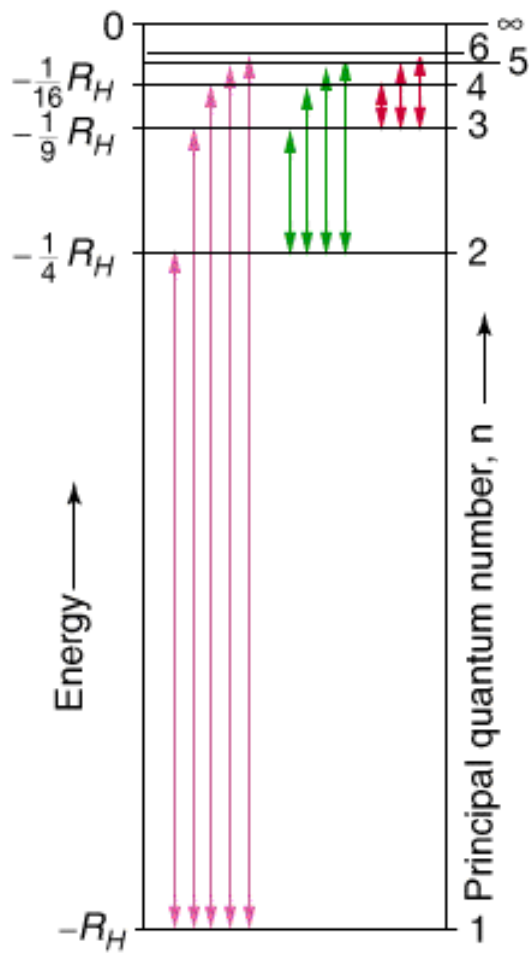
$$E_n = -Z^2 R_H / n^2$$

-1/32 a.u.

-1/18 a.u.

-1/8 a.u.

-0.5 a.u.



Degeneracy = n \* n



$$h\nu = \Delta E = E_{n_2} - E_{n_1} = -Z^2 R_H (1/n_2^2 - 1/n_1^2)$$

**The most probable value of  
moments of “ r “**

$$\langle r^n \rangle; n = 0, 1, 2, 3 \dots -1, -2, -3, \dots$$

# SPHERICALLY CONFINED HYDROGEN ATOM

## RADIAL EXPECTATION VALUES $\langle r^n \rangle$

$$\bar{r} = \frac{n}{2Z} \bar{\rho} = \frac{1}{2Z} [3n^2 - l(l+1)], \quad \bullet \quad \bullet \quad \bullet \quad (3.20)$$

$$\bar{r}^2 = \frac{n^2}{2Z^2} [5n^2 + 1 - 3l(l+1)], \quad \mathbf{3d} \quad \mathbf{3p} \quad \mathbf{3s} \quad (3.21)$$

$$\bar{r}^3 = \frac{n^2}{8Z^3} [35n^2(n^2 - 1) - 30n^2(l+2)(l-1) + 3(l+2)(l+1)l(l-1)], \quad (3.22)$$

$$\bar{r}^4 = \frac{n^4}{8Z^4} [63n^4 - 35n^2(2l^2 + 2l - 3) + 5l(l+1)(3l^2 + 3l - 10) + 12], \quad (3.23)$$

$$\bar{r}^{-1} = \frac{Z}{n^2}, \quad (3.24)$$

$$\bar{r}^{-2} = \frac{Z^2}{n^3(l + \frac{1}{2})}, \quad (3.25)$$

$$\bar{r}^{-3} = \frac{Z^3}{n^3(l+1)(l + \frac{1}{2})l}, \quad (3.26)$$

$$\bar{r}^{-4} = \frac{Z^4 \cdot \frac{1}{2} \cdot [3n^2 - l(l+1)]}{n^5(l + \frac{3}{2})(l+1)(l + \frac{1}{2})l(l - \frac{1}{2})}. \quad (3.27)$$