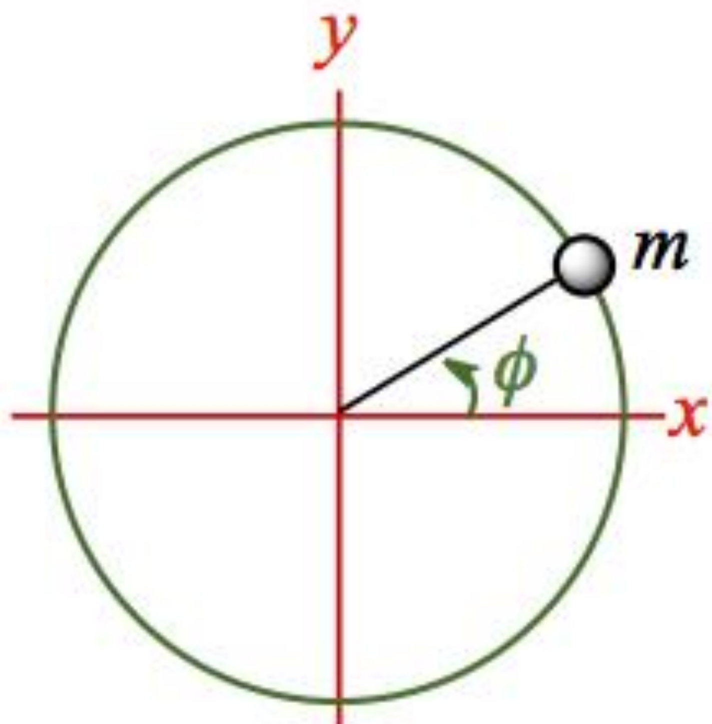
Quantum Mechanics

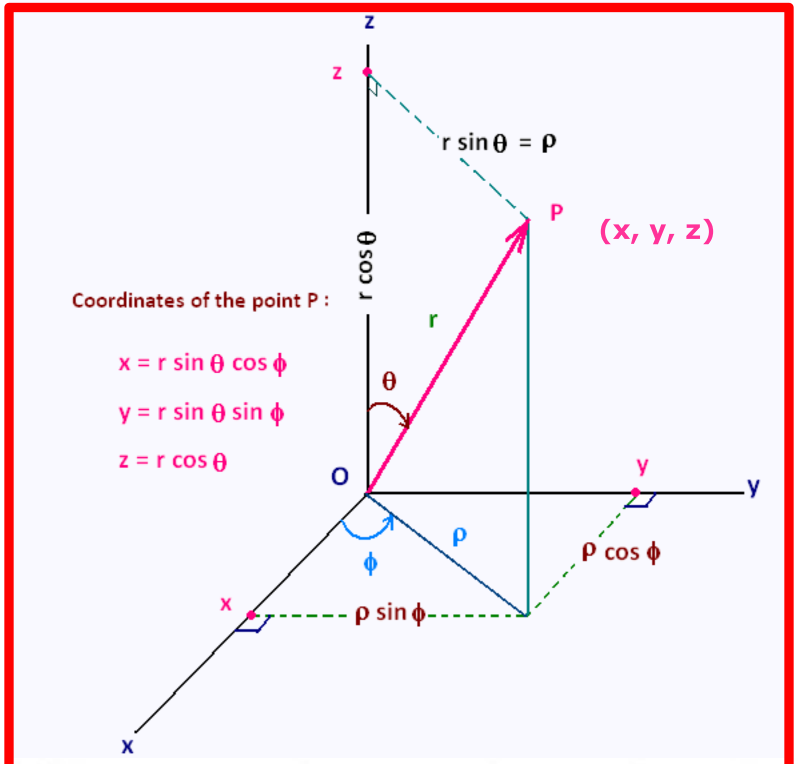
Course Outline

The course will examine the fundamental ideas as a series of postulates of quantum mechanics and apply these to some simple systems such as particle in a box, particle on a ring, rigid rotor, one-dimensional simple harmonic oscillator and to the simplest chemical system-hydrogen atom. This also would attempt to predict and compare the results with spectral properties of different systems.

Particle on a ring



Spherical Co-ordinate System



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

$$V = \int_0^a r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi = \left(\frac{a^3}{3}\right)(2)(2\pi) = \frac{4\pi a^3}{3}$$

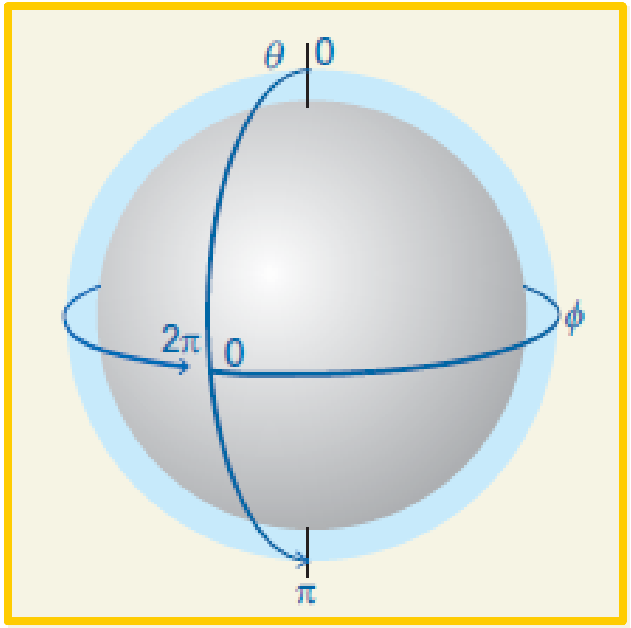
$$dV = r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi = 4\pi r^2 dr$$

This quantity is the volume of a spherical shell of radius r and thickness dr

The factor $4\pi r^2$ represents the surface area of the spherical shell and dr is its thickness.

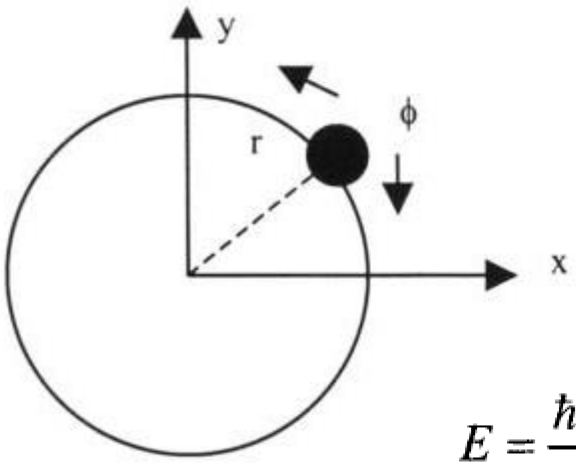
Spherical Co-ordinate System

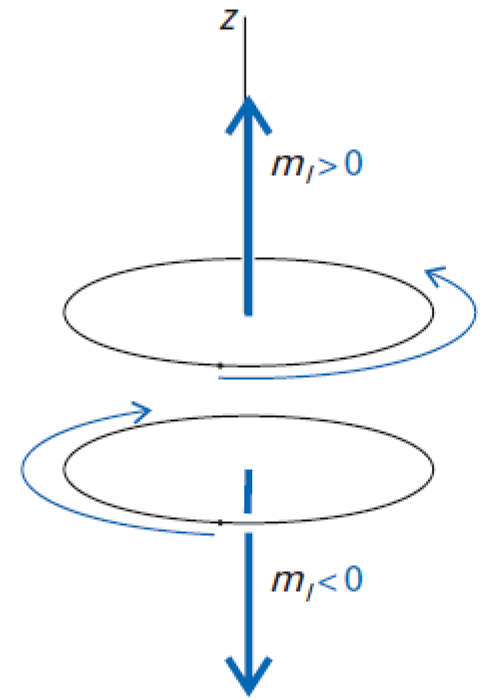
$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$ *Laplacian operator*



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

Particle on a ring

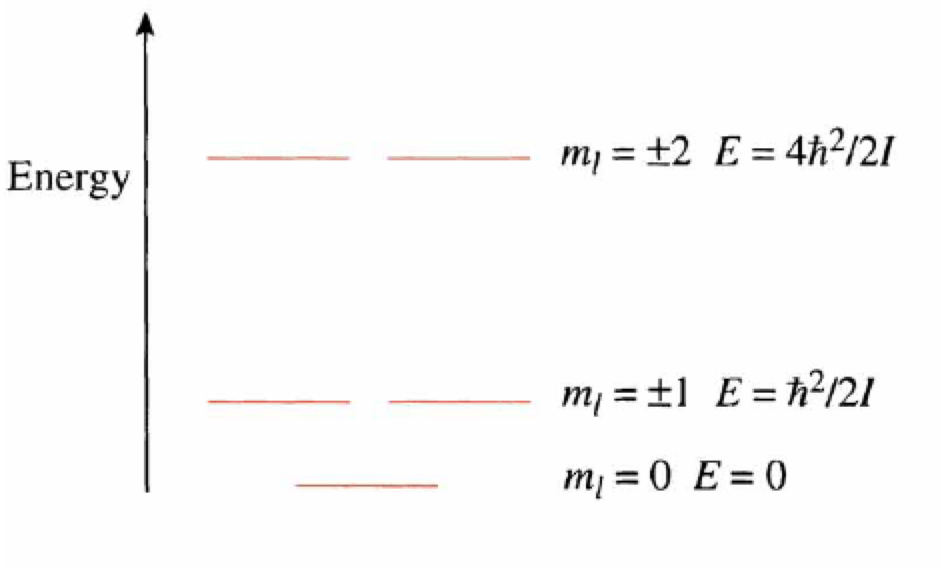




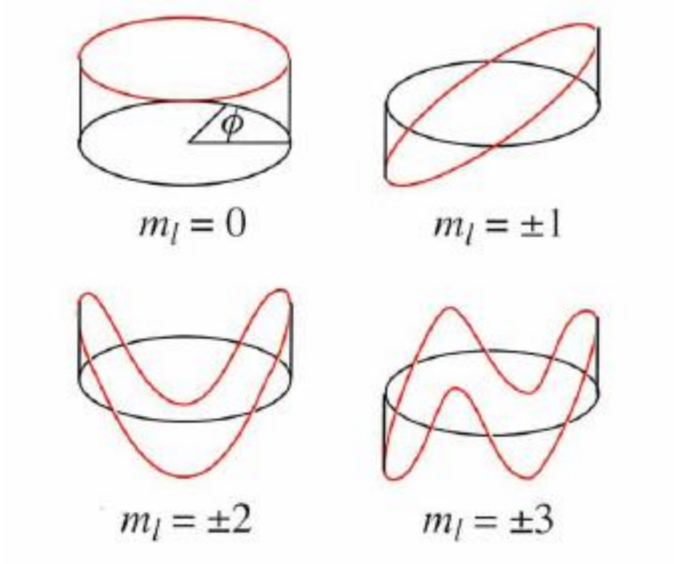
$$E = \frac{\hbar^2 m_l^2}{2I} \quad m_l = 0, \pm 1, \pm 2, \pm 3, .$$

$$L = m_l \hbar \quad m_l = 0, \pm 1, \pm 2, \pm 3, \ldots$$

Particle on a ring



The energy levels for a particle moving in a circle



The real (cosine) parts of the wave function for a particle moving in a circle

Angular Momentum

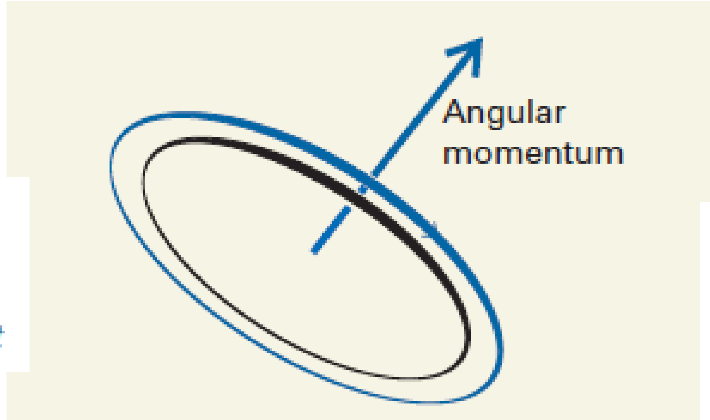
$$\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z$$

$$\mathbf{v} \equiv \frac{d\mathbf{r}}{dt} = \mathbf{i}\frac{dx}{dt} + \mathbf{j}\frac{dy}{dt} + \mathbf{k}\frac{dz}{dt}$$

$$v_x = dx/dt, \quad v_y = dy/dt, \quad v_z = dz/dt$$

$$\boxed{\mathbf{p} \equiv m\mathbf{v}}$$

$$p_x = mv_x, \quad p_y = mv_y, \quad p_z = mv_z$$



$$\boxed{\mathbf{L} \equiv \mathbf{r} \times \mathbf{p}}$$

$$\mathbf{L} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

The basic ideas of the vector representation of angular momentum: the magnitude of the angular momentum is represented by the length of the vector, and the orientation of the motion in space by the orientation of the vector (using the right-hand screw rule).

Angular Momentum Components

$$\hat{L}_x = y\hat{P}_z - z\hat{P}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \qquad \hat{L}_x = -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_y = z\hat{P}_x - x\hat{P}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \qquad \hat{L}_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_z = x\hat{P}_y - y\hat{P}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \qquad \hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

Since the rotation of particle on a ring is confined to the x-y plane, the only nonzero component of the angular momentum of the particle is along the z-axis

Angular Momentum of particle on a ring is quantised

A Since the circumference of the circular path has to be equal to an integral number of wavelengths, we can write:

$$2\pi r = m_l \lambda$$

where the wavelength is taken to be negative when the particle is moving in a clockwise direction. When this equation is combined with the de Broglie relation, $p = h/\lambda$, the following expression is obtained for the magnitude of the linear momentum at any instant:

$$p = \frac{m_l h}{2\pi r}$$

L is equal to mvr, and so to pr. Hence:

$$L = \frac{m_l h}{2\pi} = m_l \hbar$$

Since the rotation is confined to the x-y plane, the only nonzero component of the angular momentum of the particle is along the z-axis

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi} \qquad \hat{L}_z = \frac{\hbar}{i}\left(\frac{d}{d\phi}\right).$$

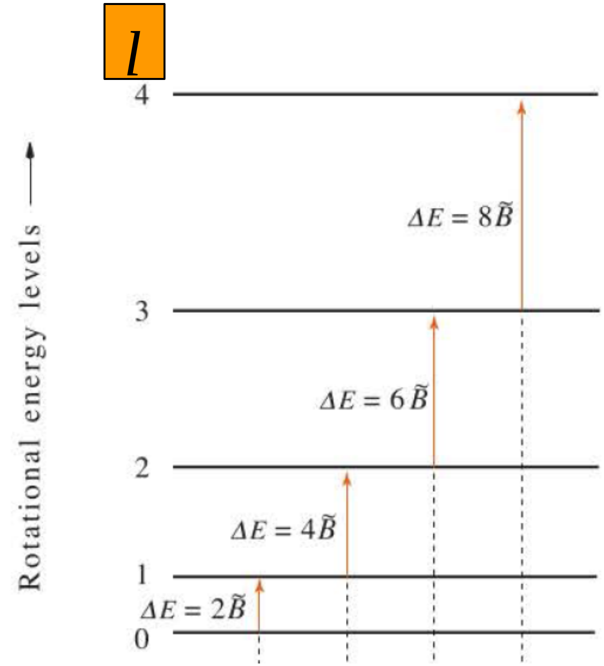
The angular momentum expectation value, is determined as follows:

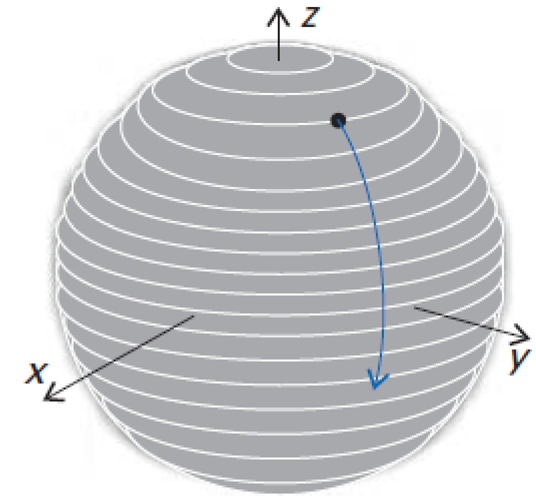
$$< L_z >= \langle\psi(\phi)|\hat{L}_z|\psi(\phi)\rangle$$

$$= \int_0^{2\pi}\left[\left(\sqrt{\frac{1}{2\pi}}e^{-im_l\phi}\right)\frac{\hbar}{i}\left(\frac{d}{d\phi}\right)\left(\sqrt{\frac{1}{2\pi}}e^{im_l\phi}\right)\right]d\phi = m_l\hbar.$$

Particle on a sphere-Energy

$$E = l(l+1)\frac{\hbar^2}{2I} \quad l = 0, 1, 2, 3, \ldots$$



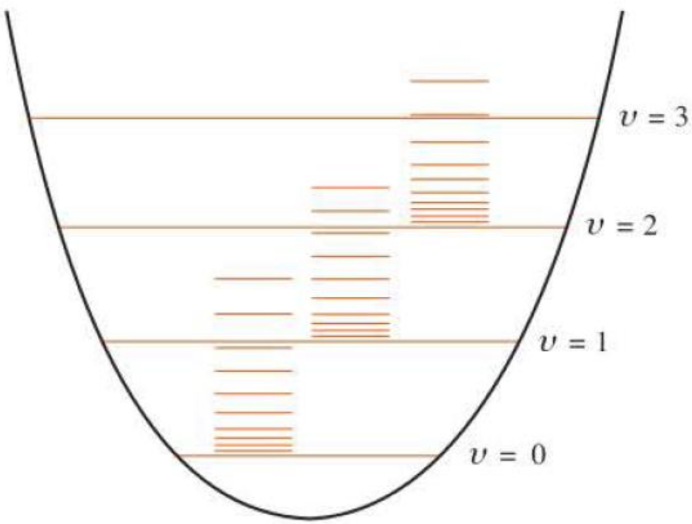


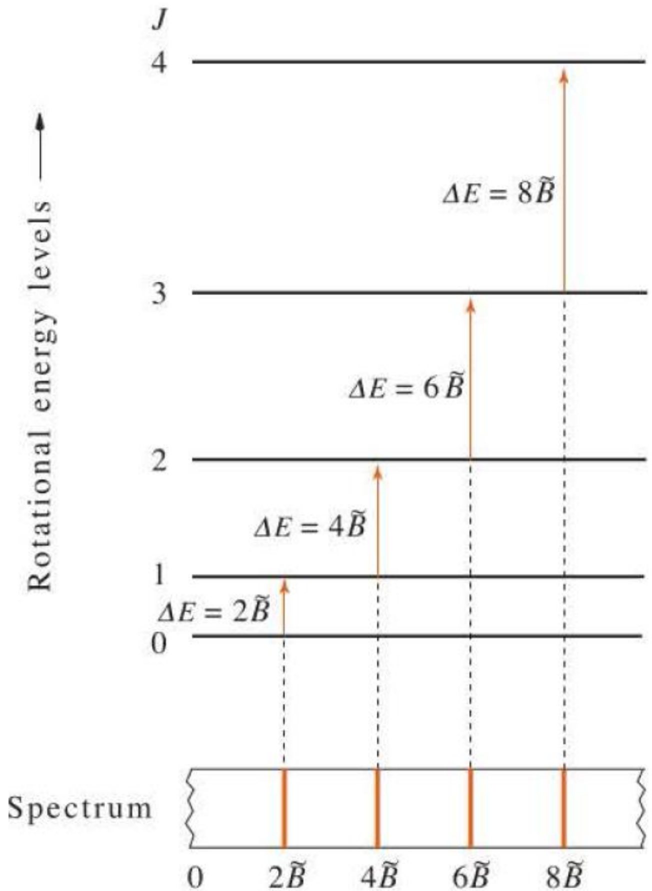
Because the energy is independent of the value of m_l, there will be $2l + 1$ states with the same energy, and the energy level is said to be **$(2l + 1)$-fold degenerate**

Particle on a sphere-Energy

$$\Delta E = E_{J+1} - E_J = \frac{\hbar^2}{2I}[(J+1)(J+2) - J(J+1)]$$

$$= \frac{\hbar^2}{I}(J+1) = \frac{h^2}{4\pi^2 I}(J+1) \qquad J = 0, 1, 2, \ldots$$





Spherical Harmonics

The product of the normalized associated Legendre polynomials along with the Particle-on-a-Ring functions are known as the ***spherical harmonics***

$$Y_{l,m}(\theta,\phi) = (-1)^m \left[\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} P_l^{|m|}(\cos\theta)\exp(im\phi)$$

for m<0 the factor $(-1)^m$ is omitted

The First Few Associated Legendre Functions $P_J^{|m|}(x)$

$$P_0^0(x) = 1$$
$$P_1^0(x) = x = \cos\theta$$
$$P_1^1(x) = (1-x^2)^{1/2} = \sin\theta$$
$$P_2^0(x) = \tfrac{1}{2}(3x^2-1) = \tfrac{1}{2}(3\cos^2\theta - 1)$$
$$P_2^1(x) = 3x(1-x^2)^{1/2} = 3\cos\theta\sin\theta$$
$$P_2^2(x) = 3(1-x^2) = 3\sin^2\theta$$
$$P_3^0(x) = \tfrac{1}{2}(5x^3-3x) = \tfrac{1}{2}(5\cos^3\theta - 3\cos\theta)$$
$$P_3^1(x) = \tfrac{3}{2}(5x^2-1)(1-x^2)^{1/2} = \tfrac{3}{2}(5\cos^2\theta - 1)\sin\theta$$
$$P_3^2(x) = 15x(1-x^2) = 15\cos\theta\sin^2\theta$$
$$P_3^3(x) = 15(1-x^2)^{3/2} = 15\sin^3\theta$$

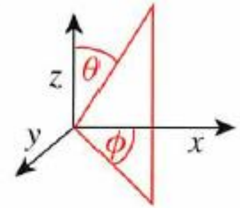
The First Few Spherical Harmonics, $Y_J^m(\theta,\phi)$ [a]

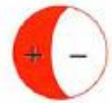
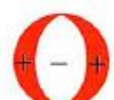
$$Y_0^0 = \frac{1}{(4\pi)^{1/2}} \qquad Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$$
$$Y_1^1 = -\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{i\phi} \qquad Y_1^{-1} = \left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{-i\phi}$$
$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta - 1) \qquad Y_2^1 = -\left(\frac{15}{8\pi}\right)^{1/2}\sin\theta\cos\theta e^{i\phi}$$
$$Y_2^{-1} = \left(\frac{15}{8\pi}\right)^{1/2}\sin\theta\cos\theta e^{-i\phi} \qquad Y_2^2 = \left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta e^{2i\phi}$$
$$Y_2^{-2} = \left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta e^{-2i\phi}$$

$$Y_{l,m}(\theta,\phi) = (-1)^m\left[\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(\cos\theta)\exp(im\phi)$$

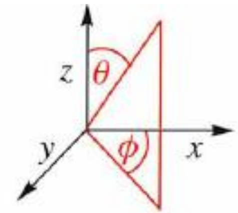
$$P_J^{|m|}(x) = (1-x^2)^{|m|/2}\frac{d^{|m|}}{dx^{|m|}}P_J(x)$$

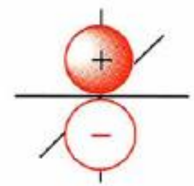
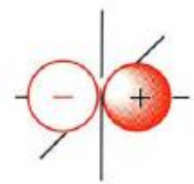
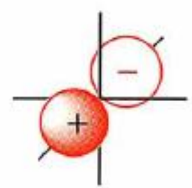
First nine spherical Harmonic wavefunctions

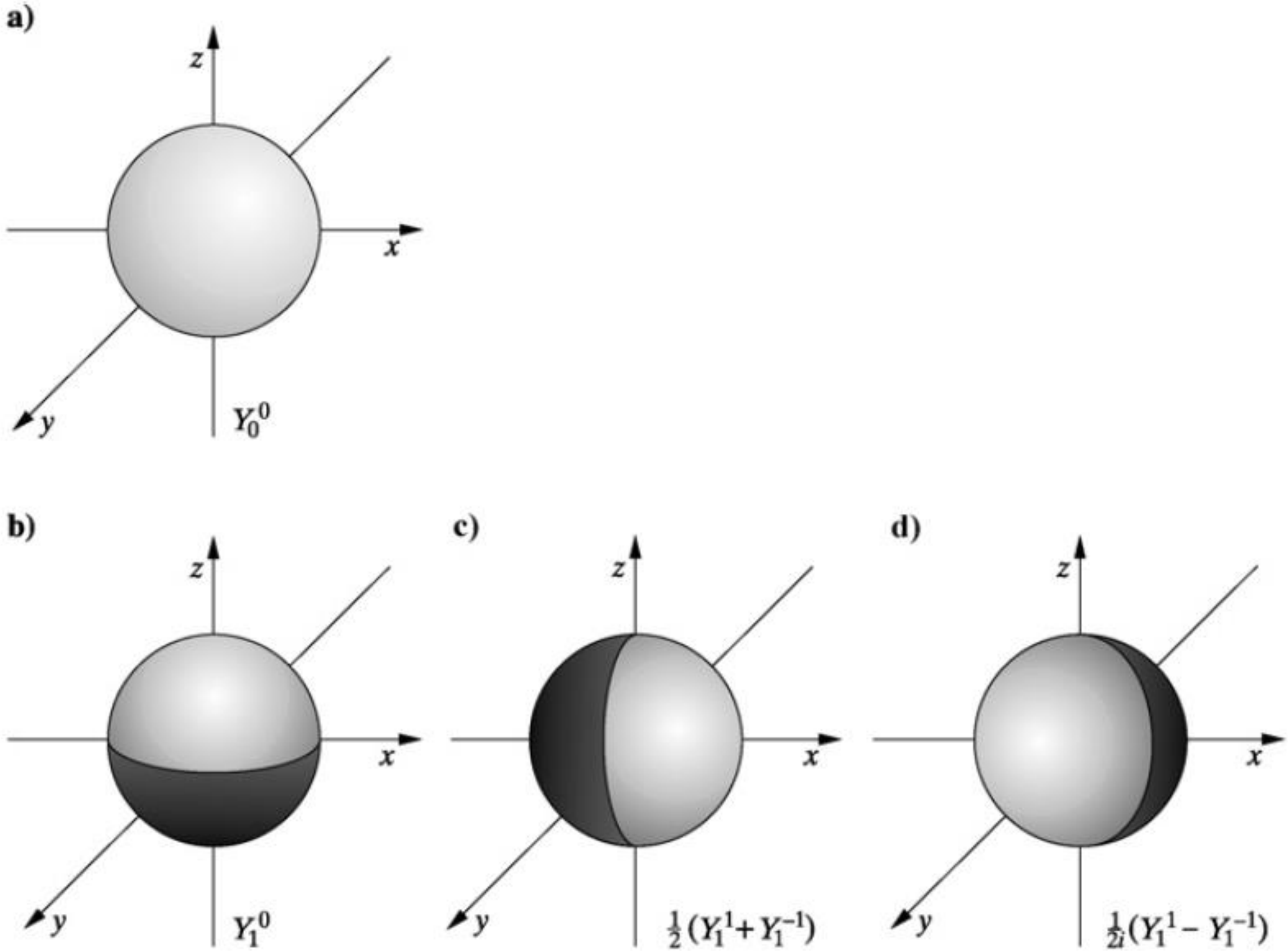


Quantum numbers l	m_l	ΘΦ (normalization constant omitted)	Sign of real part of wavefunction on surface of sphere
0	0	constant	
1	0	$\cos\theta$	
1	+1	$-\sin\theta\, e^{i\phi}$	
1	−1	$\sin\theta\, e^{-i\phi}$	
2	0	$3\cos^2\theta-1$	
2	+1	$-\cos\theta\sin\theta\, e^{i\phi}$	
2	−1	$\cos\theta\sin\theta\, e^{-i\phi}$	
2	+2	$\sin^2\theta\, e^{2i\phi}$	
2	−2	$\sin^2\theta\, e^{-2i\phi}$	

Polar Plots of spherical Harmonics



Quantum numbers l	m_l	ΘΦ (normalization constant omitted)	Polar plot of wavefunction
0	0	constant	
1	0	$\cos\theta$	
1	±1	$\sin\theta\cos\phi$	
1	±1	$\sin\theta\sin\phi$	



a)
z
x
y
Y_0^0
b)
z
x
y
Y_1^0
c)
z
x
y
$\frac{1}{2}(Y_1^1 + Y_1^{-1})$
d)
z
x
y
$\frac{1}{2i}(Y_1^1 - Y_1^{-1})$

Angular Momentum-Particle on a sphere

When the particle is confined to rotate in only two-dimensions (i.e. confined to rotate on a ring), the angular momentum is parallel to the z-axis and is fully determined by the value of m_l

In three-dimensional rotation, the angular momentum need not be parallel to the z-axis and may also have components in the x and y-axes.

Angular Momentum Components

$$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\hat{L}_x = -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \frac{\cos\phi}{\tan\theta}\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right),$$

$$\hat{L}_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \frac{\sin\phi}{\tan\theta}\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right).$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

$$\hat{L}^2 = \hat{L}_x{}^2 + \hat{L}_y{}^2 + \hat{L}_z{}^2$$

Spherical Harmonic wave functions are eigen functions of the square of the angular momentum

The square of the angular momentum, L^2, can be found from the angular momentum component operators. The square of the angular momentum is a scalar quantity as it represents the dot product of $\vec{L} \cdot \vec{L}$.

$$\hat{L}^2 = \hat{L}_x{}^2 + \hat{L}_y{}^2 + \hat{L}_z{}^2$$

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

$$\hat{L}^2 Y_{lm_l} = -\hbar^2\Lambda^2 Y_{lm_l} = \hbar^2 l(l+1)$$

$$\textit{magnitude of the angular momentum} = \hbar\sqrt{l(l+1)}$$

Spherical Harmonic wave functions are eigen functions of L_z

$$l_z Y_{lm_l} = \frac{\hbar}{i}\frac{\partial}{\partial\phi}\left(\Theta_{lm_l}\frac{e^{im_l\phi}}{\sqrt{2\pi}}\right) = m_l\hbar Y_{lm_l}$$

Thus,

$$\hat{L}^2 Y_l^m(\theta, \phi) = l(l+1)\hbar^2 Y_l^m(\theta, \phi), \quad l = 0, 1, 2, \ldots$$

$$\hat{L}_z Y_l^m(\theta, \phi) = m\hbar Y_l^m(\theta, \phi), \quad m = -l, -l+1, \ldots, l-1, l$$

Commutation Relationships

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$$

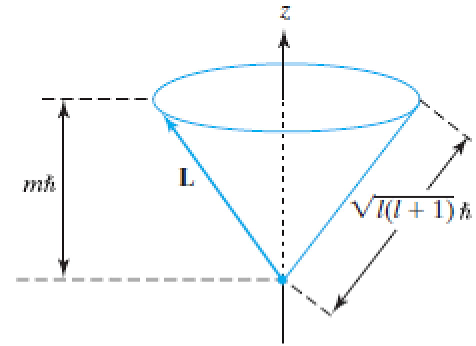
$$[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x$$

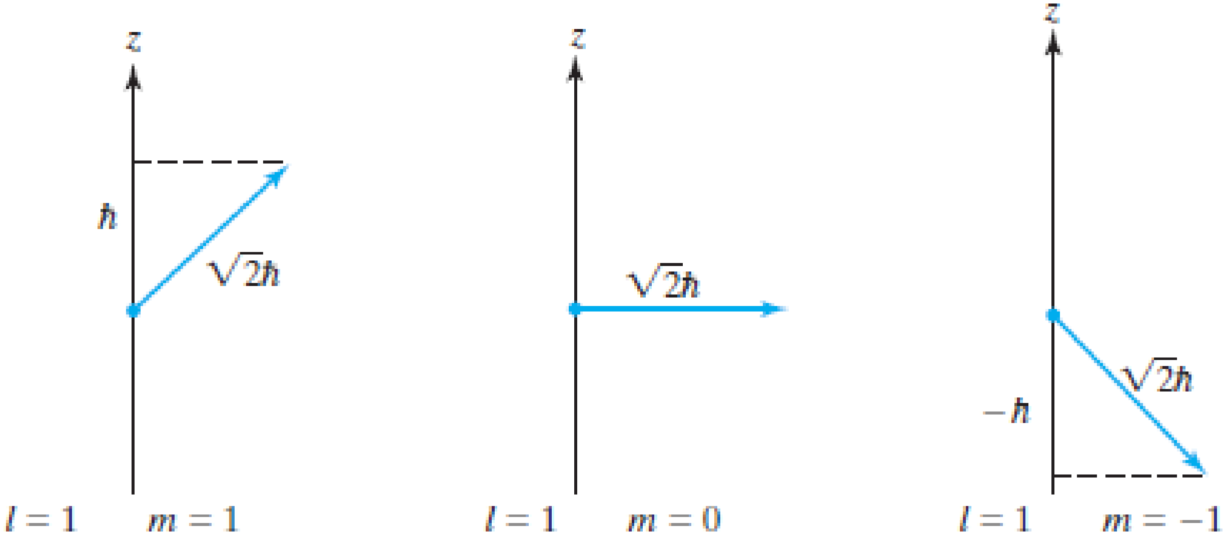
$$[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$$

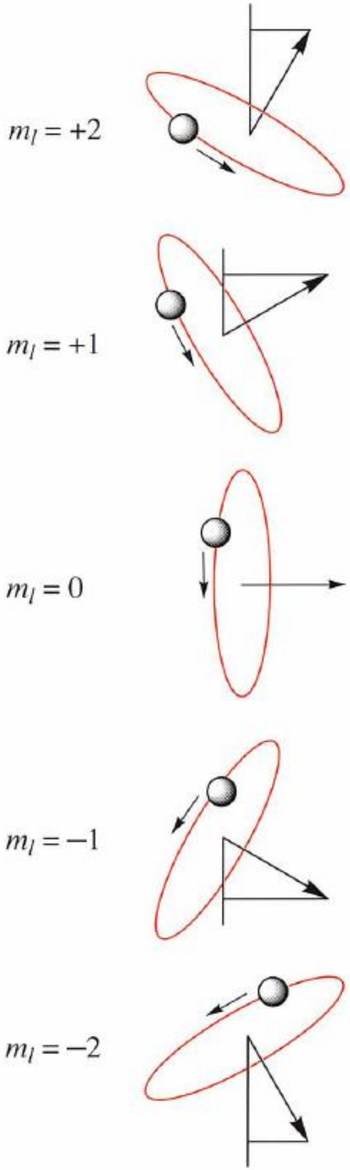
$$[\hat{L}^2, \hat{L}_x] = 0$$

$$[\hat{L}^2, \hat{L}_y] = 0, \quad [\hat{L}^2, \hat{L}_z] = 0$$

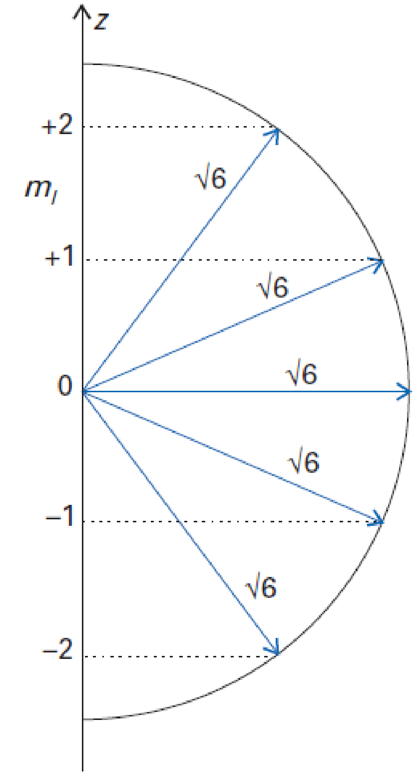
Orientations of L with respect to Z axis for l =1







Orientations of L with respect to Z axis for l =2



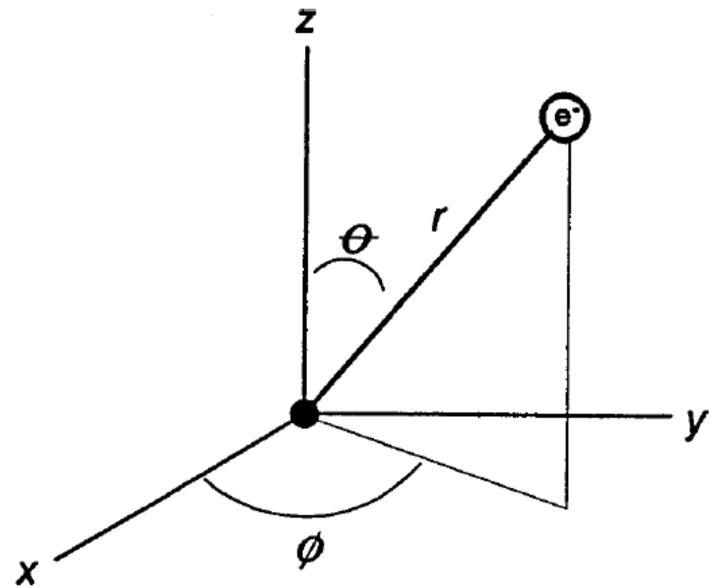
(2l+1)= 5 allowed orientations

Schrödinger's Solution to the Hydrogen Atom Problem

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_p}$$

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

$m_e + m_p \approx m_p$ and $\mu = m_e$



Schrödinger's Solution to the Hydrogen Atom Problem

$$H = T + V \qquad \hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{r}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\psi\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\psi + \frac{2\mu}{\hbar^2}\left(\frac{e^2}{r} + E\right)\psi = 0,$$

Schrödinger's Solution to the Hydrogen Atom Problem

Φ

$$\frac{\partial^2 \Phi}{\partial \phi^2} + m^2 \Phi = 0.$$

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

Where m = 0, ±1, ± 2, ...

$$\psi(r, \theta, \phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} R(r) \Theta(\theta)$$

Schrödinger's Solution to the Hydrogen Atom Problem

θ

$$\frac{1}{\Theta \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)-\frac{m^2}{\sin^2\theta}=-\beta.$$

$$\Theta(\theta)=\sqrt{\frac{(2l+1)(l-|m_l|)!}{2(l+|m_l|)!}}P_l^{|m_l|}(\cos\theta)$$

Where $l = 0, 1, 2, \ldots$

$m_l = 0, \pm 1, \pm 2, \ldots$

$$P_J^{|m|}(x)=(1-x^2)^{|m|/2}\frac{d^{|m|}}{dx^{|m|}}P_J(x)$$

$m_l = 0$

The First Few Legendre Polynomials [a]

$x = \cos\theta$

$P_0(x) = 1$
$P_1(x) = x$
$P_2(x) = \frac{1}{2}(3x^2 - 1)$
$P_3(x) = \frac{1}{2}(5x^3 - 3x)$
$P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3)$

The First Few Associated Legendre Functions $P_J^{|m|}(x)$

$P_0^0(x) = 1$
$P_1^0(x) = x = \cos\theta$
$P_1^1(x) = (1 - x^2)^{1/2} = \sin\theta$
$P_2^0(x) = \frac{1}{2}(3x^2 - 1) = \frac{1}{2}(3\cos^2\theta - 1)$
$P_2^1(x) = 3x(1 - x^2)^{1/2} = 3\cos\theta\sin\theta$
$P_2^2(x) = 3(1 - x^2) = 3\sin^2\theta$

Angular part of the wave function

$$Y_{l,m}(\theta,\phi) = (-1)^m \left[\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(\cos\theta)\exp(im\phi)$$

ΦΘ

The First Few Spherical Harmonics, $Y_J^m(\theta, \phi)$ [a]

$Y_0^0 = \frac{1}{(4\pi)^{1/2}}$	$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$
$Y_1^1 = -\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi}$	$Y_1^{-1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{-i\phi}$
$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$	$Y_2^1 = -\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{i\phi}$
$Y_2^{-1} = \left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{-i\phi}$	$Y_2^2 = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{2i\phi}$
$Y_2^{-2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{-2i\phi}$	

Radial part of the wave function

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \left[\frac{8\pi^2\mu}{h^2}\left(E + \frac{e^2}{r}\right) - \frac{l(l+1)}{r^2}\right]R = 0$$

$$E = -\frac{2\pi^2\mu e^4}{n^2h^2}$$

$$n \geq l + 1$$

$$E = -\frac{2\pi^2\mu e^4}{n^2h^2} \qquad n = 1, 2, 3, \cdots$$

The R equation can be solved as follows:

1. Assume that E is negative (this restricts us to bound states), and note that $\beta = l(l+1)$ from the previous solving of the Θ equation.

2. Change variables for mathematical convenience.

3. Find the asymptotic solution pertaining to the large r limit, where the R equation becomes simplified.

4. Express the wavefunction as a product of the asymptotic solution and an unknown function. Express this unknown function as a power series and (after dealing with some singularities) obtain a recursion relation.

5. Note that the power series overpowers the asymptotic part of the solution unless the series is truncated. This leads to the requirement that n be an integer and hence that E be quantized. It also requires that $n > l$.

6. Recognize the truncated series to be associated Laguerre polynomials times ρ^l, where ρ is defined below.

Radial part of the wave function

$$R = r^{l} e^{r} U(r)$$

$$R(r) = -\sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} \left(\frac{2r}{na_0}\right)^l e^{-\frac{r}{na_0}} L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$$

The Hydrogen-like Radial Wave Functions, $R_{nl}(r)$, for $n = 1, 2,$ and 3 [a]

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

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

$$R_{21}(r) = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2} \rho e^{-\rho/2}$$

$$R_{30}(r) = \frac{2}{27}\left(\frac{Z}{3a_0}\right)^{3/2} (27 - 18\rho + 2\rho^2)e^{-\rho/3}$$

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

$$R_{32}(r) = \frac{4}{27\sqrt{10}}\left(\frac{Z}{3a_0}\right)^{3/2} \rho^2 e^{-\rho/3}$$

a. The quantity Z is the nuclear charge, and $\rho = Zr/a_0$, where a_0 is the Bohr radius. (0.529 A°)

Complete wave functions for the hydrogen-like species

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

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

$$\psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \rho e^{-\rho/2}\cos\theta$$

$$\psi_{21\pm1} = \pm\frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \rho e^{-\rho/2}\sin\theta e^{\pm i\phi}$$

$$\psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (27-18\rho+2\rho^2)e^{-\rho/3}$$

$$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \rho(6-\rho)e^{-\rho/3}\cos\theta$$

$$\psi_{31\pm1} = \pm\frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \rho(6-\rho)e^{-\rho/3}\sin\theta e^{\pm i\phi}$$

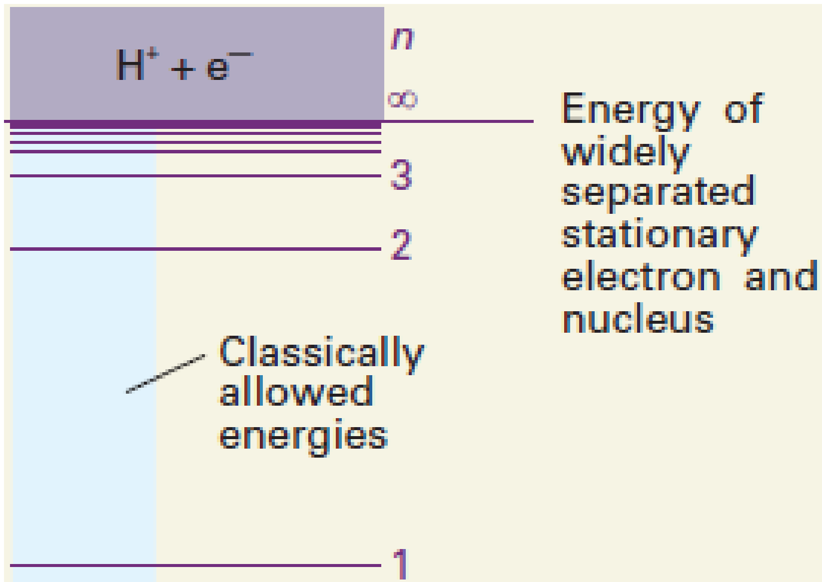
$$\psi_{320} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \rho^2 e^{-\rho/3}(3\cos^2\theta-1)$$

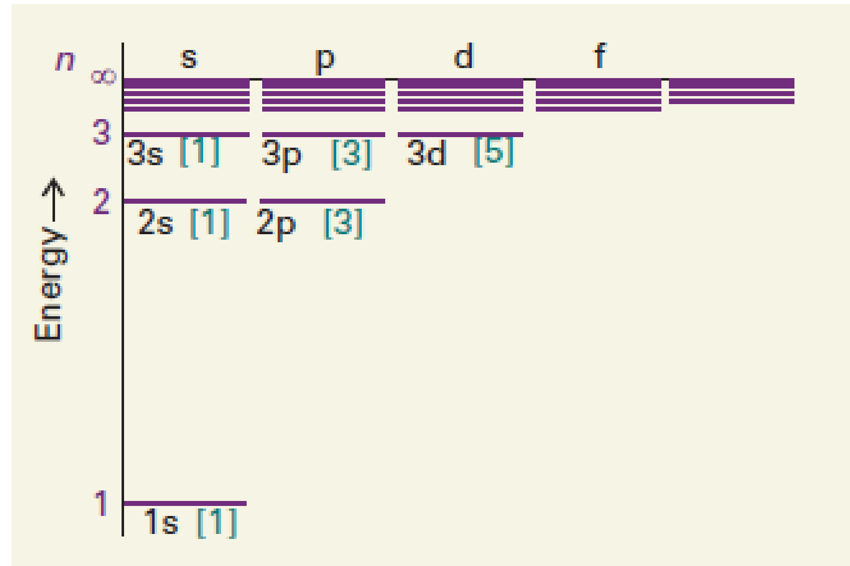
$$\psi_{32\pm1} = \pm\frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \rho^2 e^{-\rho/3}\sin\theta\cos\theta e^{\pm i\phi}$$

$$\psi_{32\pm2} = \frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \rho^2 e^{-\rho/3}\sin^2\theta e^{\pm 2i\phi}$$

a. The quantity Z is the nuclear charge, and $\rho = Zr/a_0$, where a_0 is the Bohr radius.

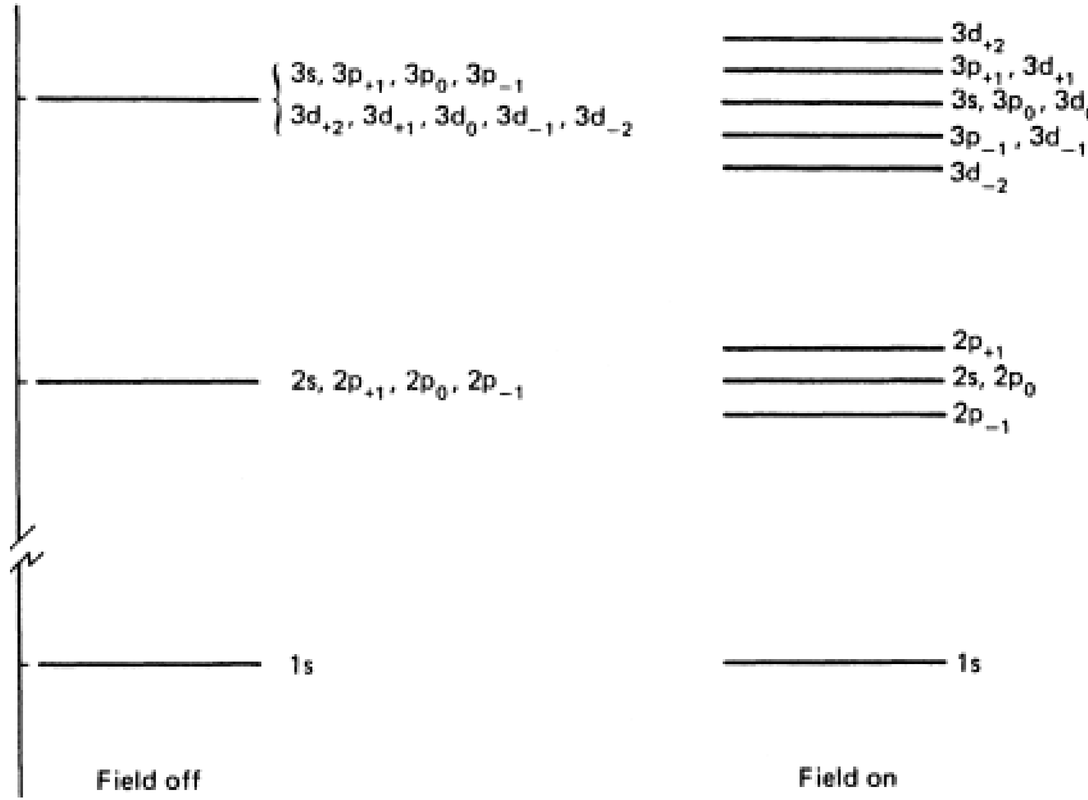
The energy levels of H-atom





The energy levels of hydrogenic systems depend on the principal quantum number 'n'. In hydrogenic atoms, all orbitals of a given shell have the same energy. In multi-electron systems, E depends on (n+ *l*)values

The energy levels of H-like system in the presence and absence of a magnetic field



Degeneracy = 2l + 1

Wave function(Ψ)

To visualize **orbitals**, useful to separate variables:

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

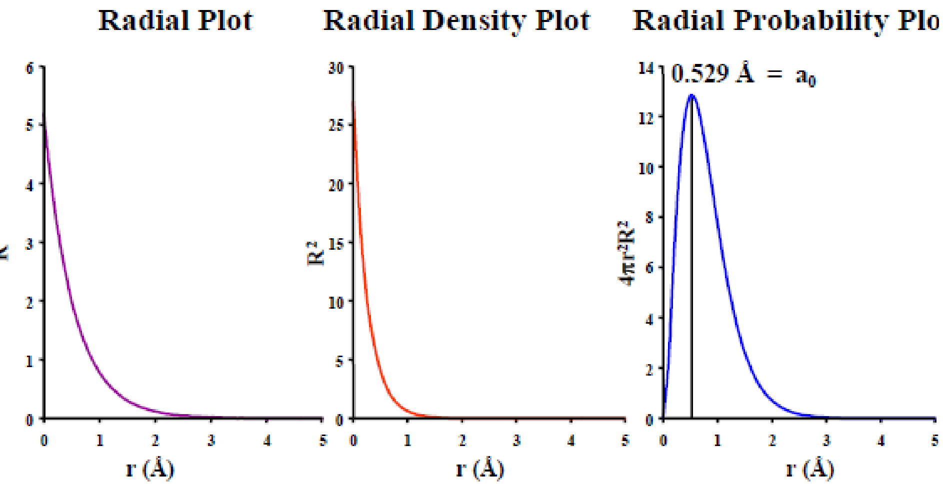
$R_{n,\ell}$ **Radial function**

R^2: Probability of **e⁻** at **r** from nucleus (in **all** directions)

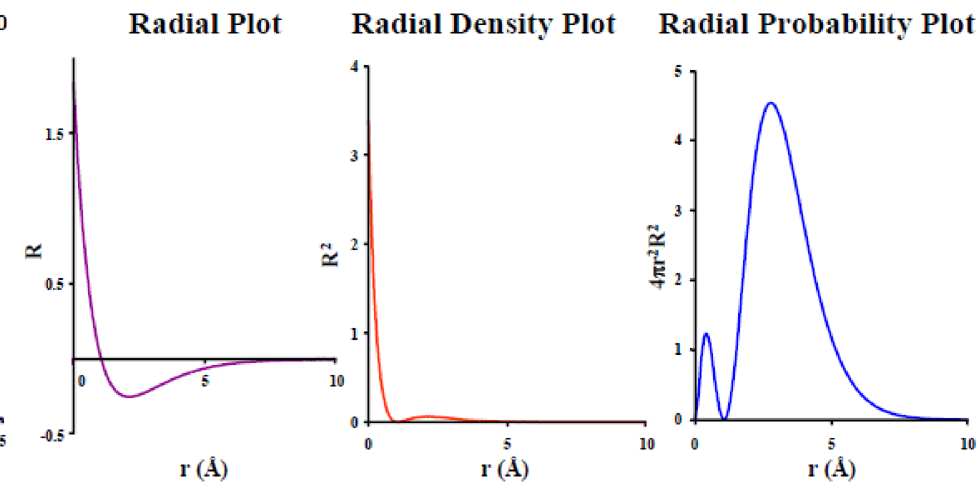
$\Theta(\theta)\Phi(\phi) = Y_{\ell, m_\ell}$ **Angular function (Spherical Harmonic)**

Y^2: Probability of **e⁻** at (θ, ϕ) from nucleus (out to infinity)

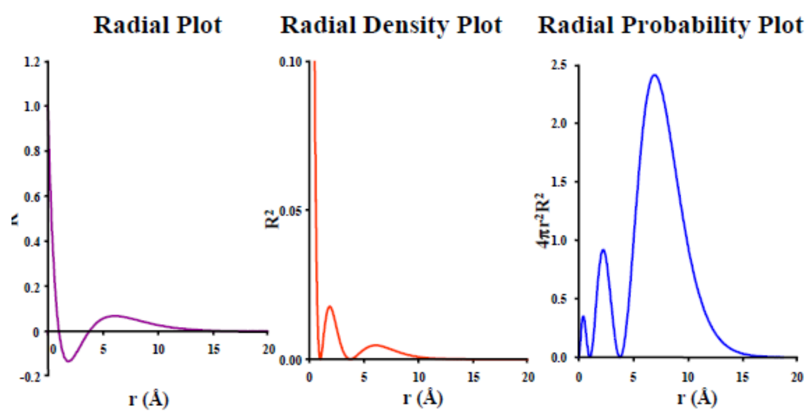
Radial Plots of the 1*s* Orbital



Radial Plots of the 2*s* Orbital



Radial Plots of the 3*s* Orbital



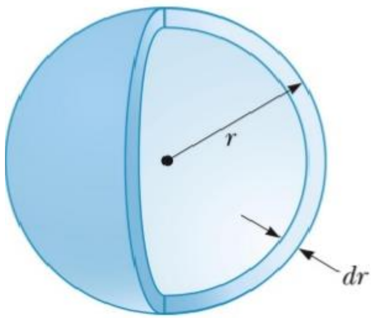
Graphical representation of radial wave function

Radial plots:- $R_{n,l}$ is maximum at the nucleus. It can have +ve and –ve values. It becomes 0 at $r = 0$ for $l > 0$. It increases with 'r' and tends to attain zero as 'r' tends to infinity.

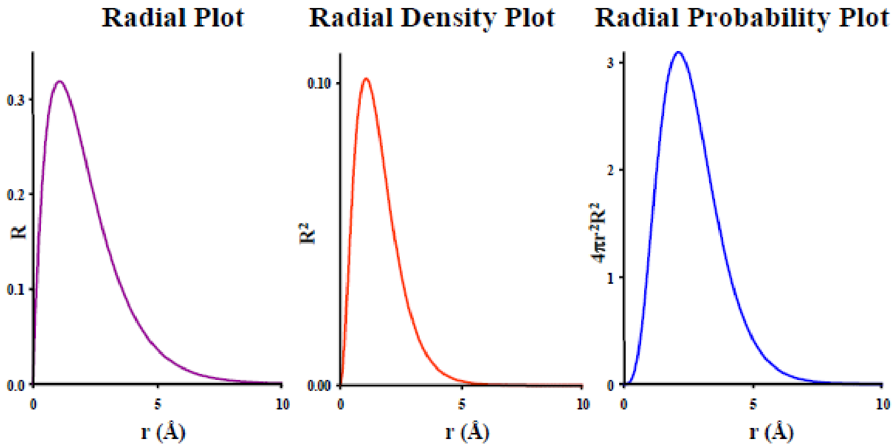
Probability density plots:- A plot of $R^2_{n,l}$ against 'r' represents the probability of finding electron(radial probability density). But $R^2_{n,l}$ at 'r' is equal to zero which is not true.

Radial probability distribution plots: This gives the probability of finding electron in a spherical shell of thickness 'dr' surrounding the nucleus.

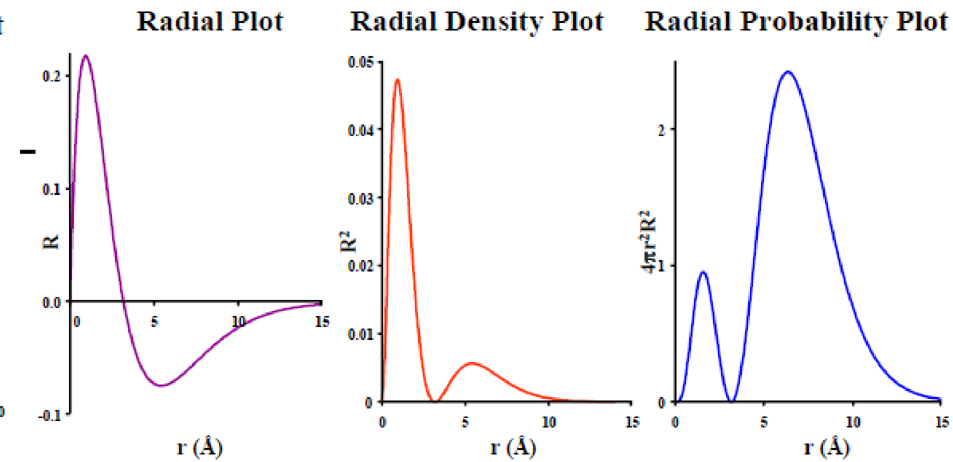
$$\text{Radial probability} = R^2_{n,l}\,dV = 4\pi r^2\,dr$$



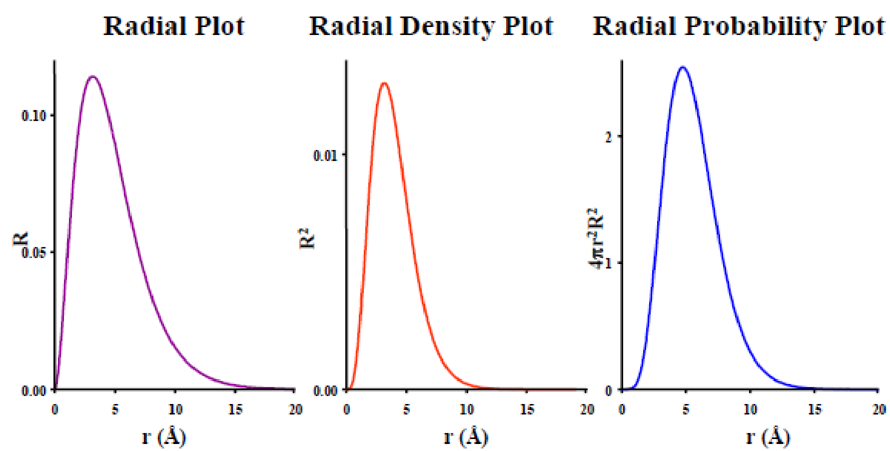
Radial Plots of the 2*p* Orbital



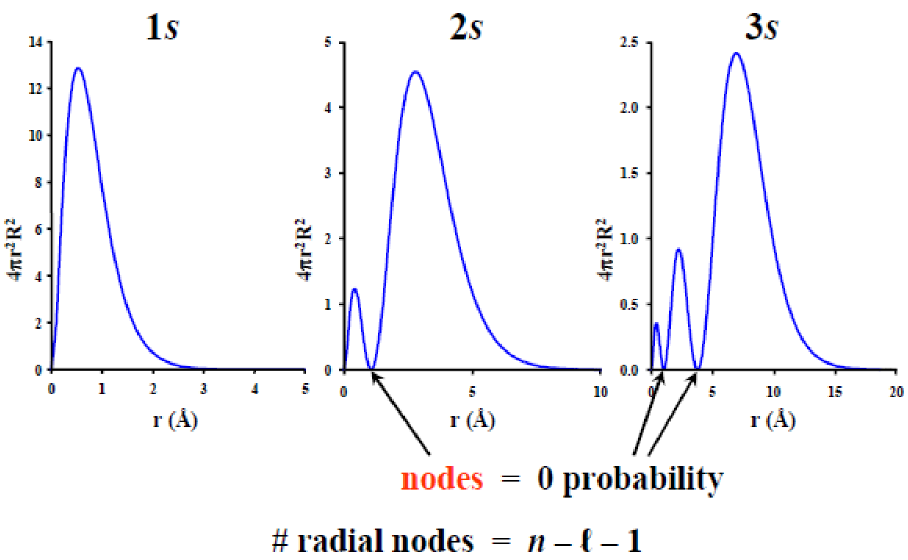
Radial Plots of the 3*p* Orbital



Radial Plots of the 3*d* Orbital

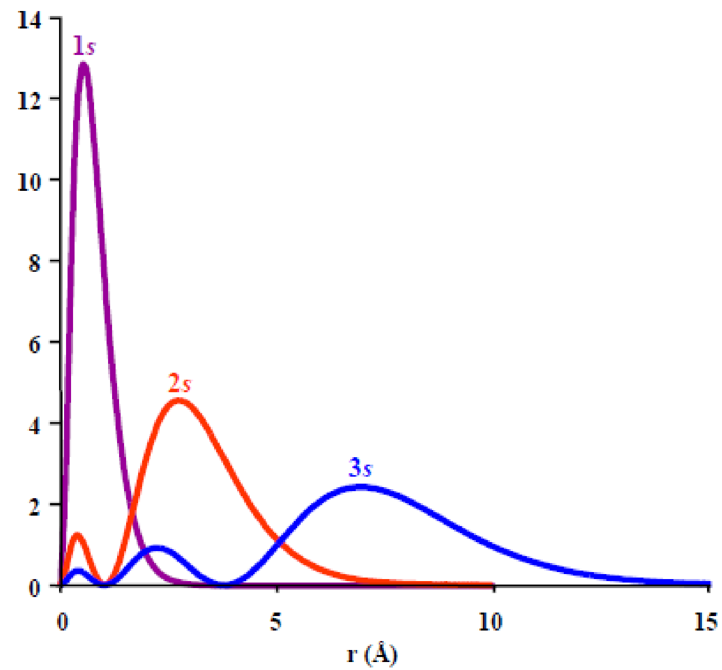


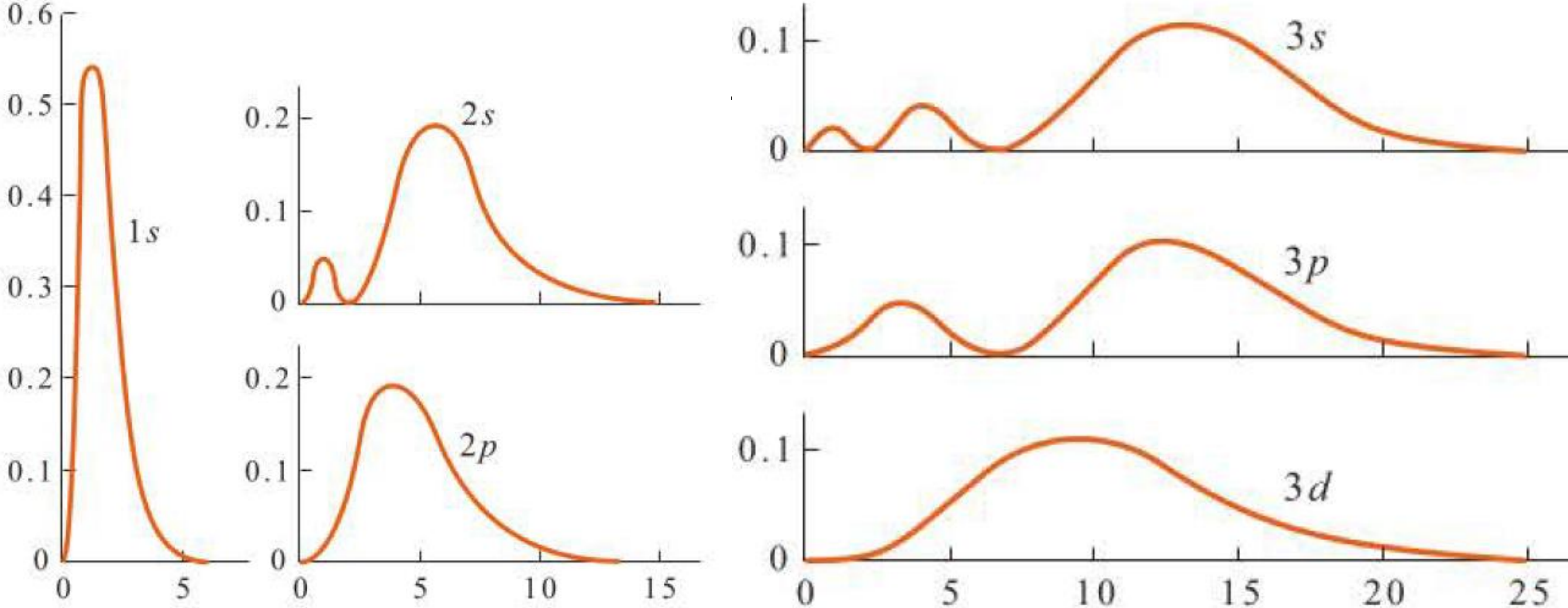
Nodes



The points at which the radial probability is zero are called nodes

Size of orbitals



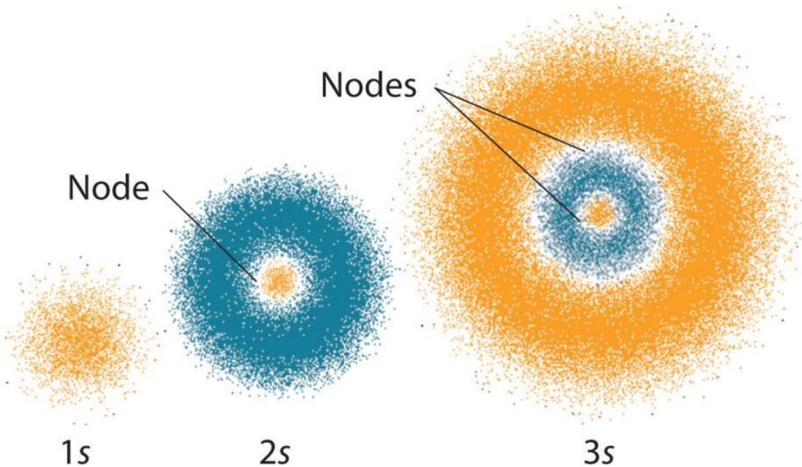


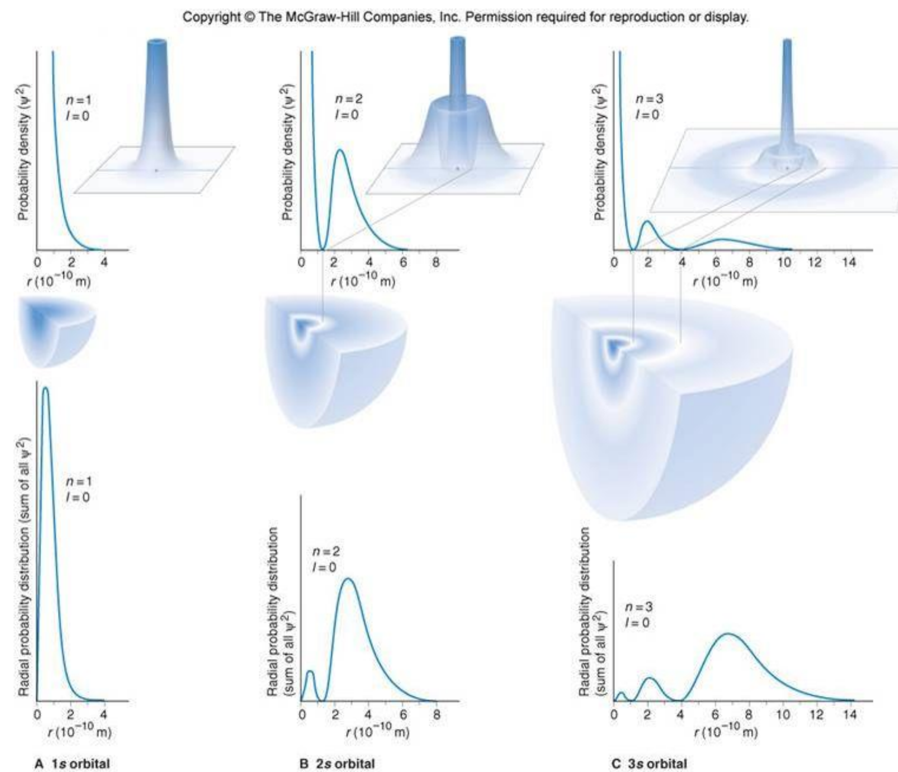
The probability densities $r^2[R_{nl}(r)]^2$ associated with the radial parts of the hydrogen atomic wave functions.

Angular wave functions and shapes of orbitals

s Orbitals: Angular Part

ℓ	m_ℓ	$Y(\theta,\phi)$
0	0	$\frac{1}{2\sqrt{\pi}}$





$$p_z = \left(\frac{3}{4\pi}\right)^{1/2} R_{n1}(r)\cos\theta$$

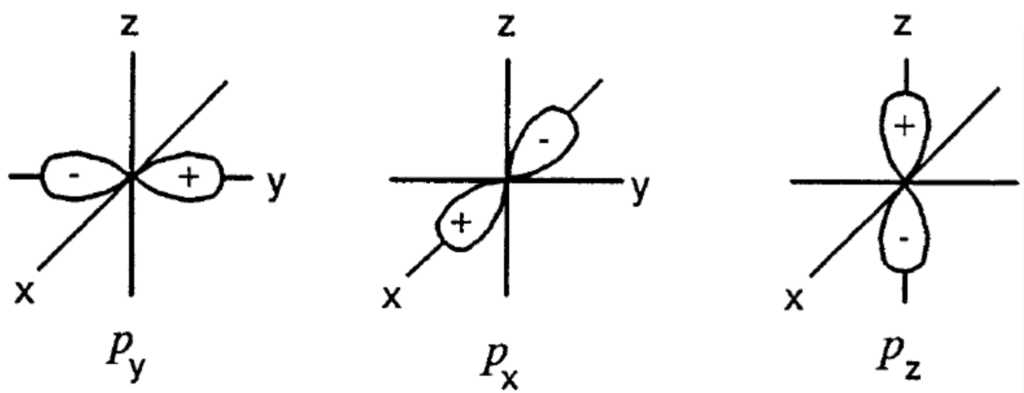
$$p_+ = -\left(\frac{3}{8\pi}\right)^{1/2} R_{n1}(r)\sin\theta\, e^{i\phi}$$

$$p_- = \left(\frac{3}{8\pi}\right)^{1/2} R_{n1}(r)\sin\theta\, e^{-i\phi}$$

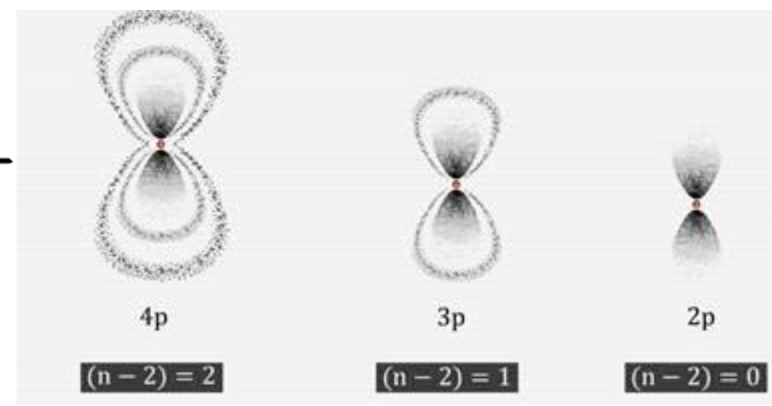
$$p_x = \frac{1}{\sqrt{2}}(p_- - p_+) = \left(\frac{3}{4\pi}\right)^{1/2} R_{n1}(r)\sin\theta\cos\phi$$

$$p_y = \frac{i}{\sqrt{2}}(p_- + p_+) = \left(\frac{3}{4\pi}\right)^{1/2} R_{n1}(r)\sin\theta\sin\phi$$

It is usual to depict the real and imaginary components, and to call these orbitals p_x and p_y:



(a) (b) (c)



$$d_{z^2} = d_0 \sim (3\cos^2\theta - 1) \sim 3z^2 - 1$$

$$d_{xz} = \frac{d_{+1} + d_{-1}}{\sqrt{2}} \sim \sin\theta\cos\theta\cos\varphi \sim xz$$

$$d_{yz} = -i\,\frac{d_{+1} - d_{-1}}{\sqrt{2}} \sim \sin\theta\cos\theta\sin\varphi \sim yz$$

$$d_{x^2-y^2} = \frac{d_{+2} + d_{-2}}{\sqrt{2}} \sim \sin^2\theta\cos 2\varphi \sim \sin^2\theta(\cos^2\varphi - \sin^2\varphi) \sim x^2 - y^2$$

$$d_{xy} = -i\,\frac{d_{+2} - d_{-2}}{\sqrt{2}} \sim \sin^2\theta\sin 2\varphi \sim \sin^2\theta\cos\varphi\sin\varphi \sim xy$$

Real wavefunction (not normalized)[a]
$\psi(3d_{z^2}) = \sigma^2 e^{-\sigma/3}(3\cos^2\theta - 1)$
$\psi(3d_{xz}) = \sigma^2 e^{-\sigma/3}\sin\theta\cos\theta\cos\phi$
$\psi(3d_{yz}) = \sigma^2 e^{-\sigma/3}\sin\theta\cos\theta\sin\phi$
$\psi(3d_{x^2-y^2}) = \sigma^2 e^{-\sigma/3}\sin^2\theta\cos 2\phi$
$\psi(3d_{xy}) = \sigma^2 e^{-\sigma/3}\sin^2\theta\sin 2\phi$