Lecture 18: Orbitals of the Hydrogen Atom

The material in this lecture covers the following in Atkins.

The structure and Spectra of Hydrogenic Atoms
13.2 Atomic orbitals and their energies
    (c) Shells and subshells
    (b) s-orbitals
    (c) Radial distribution function
    (d) p-orbitals
    (e) d-orbitals

Hydrogenic atomic orbitals

Lecture on-line
    Hydrogenic atomic orbitals (PDF Format)
    Hydrogenic atomic orbitals (PowerPoint)

Handout for this lecture

Audio-visuals on-line

key hydrogen orbitals (PowerPoint)(From the Wilson Group,***)

key hydrogen orbitals   (PDF)(From the Wilson Group,***)

Vizualization of atomic hydrogen orbitals (PowerPoint)
(From the Wilson Group,***)

Vizualization of atomic hydrogen orbitals (PDF)
(From the Wilson Group,***)

Slides from the text book (From the CD included in Atkins ,**)

Interactive Hydrogen Orbital Plots (For Mac users only)
(Visualizes all the
angular and radial wavefunctions of the hydrogen atom, *****)

The orbitals for the hydrogenic atom are given by

$$\psi_{nlm}(r,\phi,\theta) = R(r)_{nl} Y_{l,m}(\phi,\theta) \; ; \quad n = 1,2,3 \ldots$$

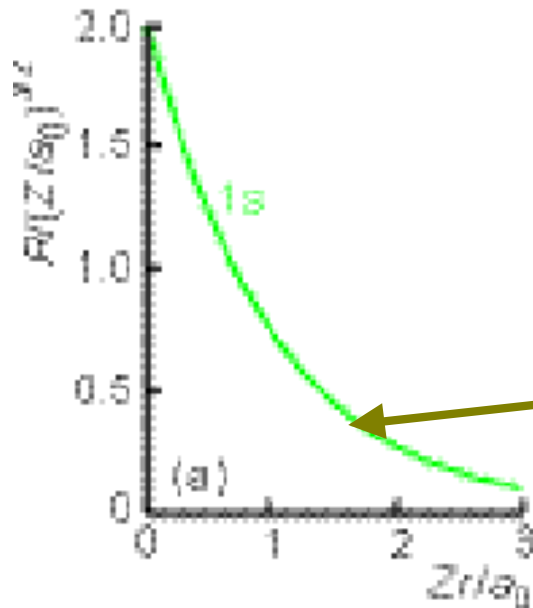$$l < \; n-1; \quad m = \; -l, \; -l+1, \; \ldots l-1, \; l$$

Where

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

are eigenfunctions to L^2 and L_z

With the radial part given as

$$R_{nl}(r) = N_{nl}\left(\frac{\rho}{n}\right)^l L_{n,l}(r) e^{-\rho/2n}$$

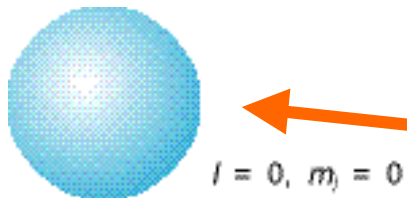# Hydrogen Levels

$$n = 1, \ l = 0$$

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

$$R_{1,0}(r) = 2\left(\frac{Z}{a_o}\right)^{3/2} e^{-\rho/2}$$

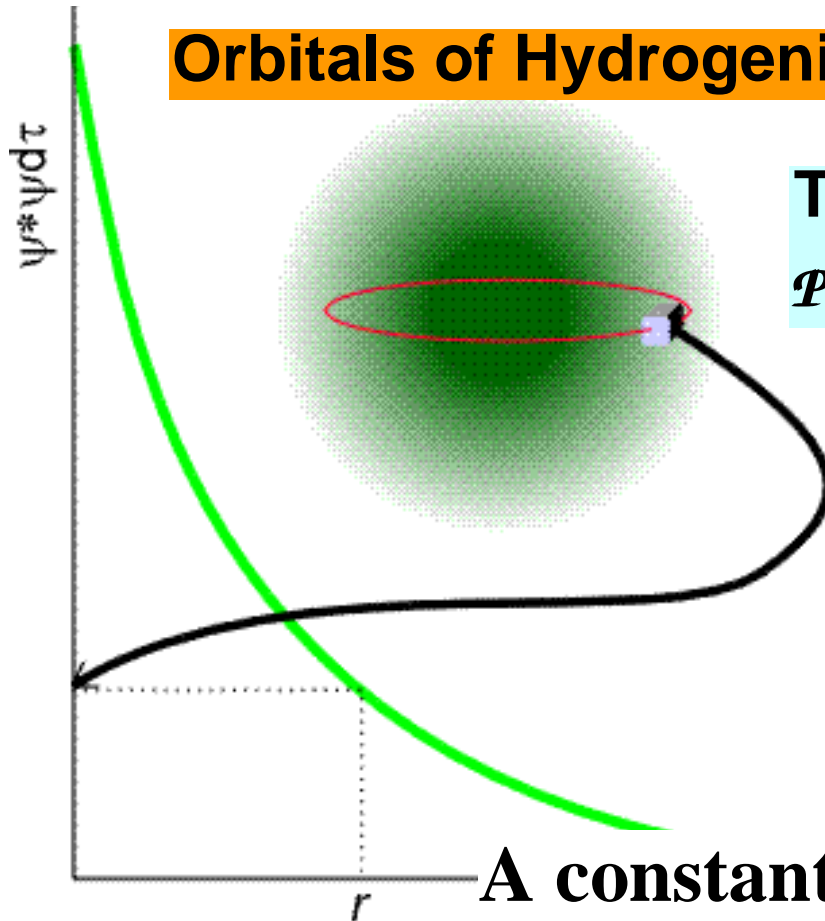No nodes. $R_{1,0}(r)$ everywhere positive

For $l = 0$ we have $m = 0$;

$$Y_{o,o} = \sqrt{\frac{1}{4\pi}}$$

Value of Y_{oo} is uniform over sphere

1s − orbital

ψ*ψdτ

r

The probability density
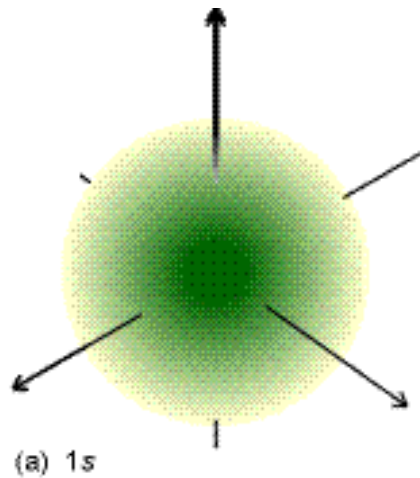
$$\mathcal{P}_{nlm}(r,\theta,\phi) = \psi_{nlm}(r,\theta,\phi)^* \, \psi_{nlm}(r,\theta,\phi)$$

$$\mathcal{P}_{1,00}(r,\phi.\theta) = 2\left(\frac{Z}{a_o}\right)^{3/2} e^{-\rho/2} Y_{00}{}^* \times$$

$$2\left(\frac{Z}{a_o}\right)^{3/2} e^{-\rho/2} Y_{00} = \frac{1}{\pi}\left(\frac{Z}{a_o}\right)^3 e^{-\rho}$$

A constant-volume electron-sensitive detector (the small cube) gives its greatest reading at the nucleus, and a smaller reading elsewhere. The same reading is obtained anywhere on a circle of given radius: the *s* orbital is spherically symmetrical.
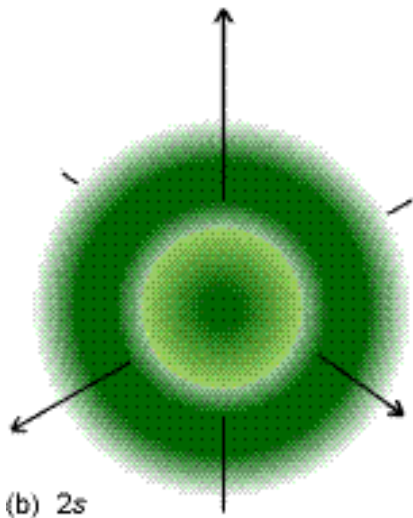
Orbitals of Hydrogenic Atom...prop.dens.

(a) 1s

(b) 2s

Representations of the 1s and 2s hydrogenic atomic orbitals in terms of their electron densities (as represented by the density of shading).

The probability density

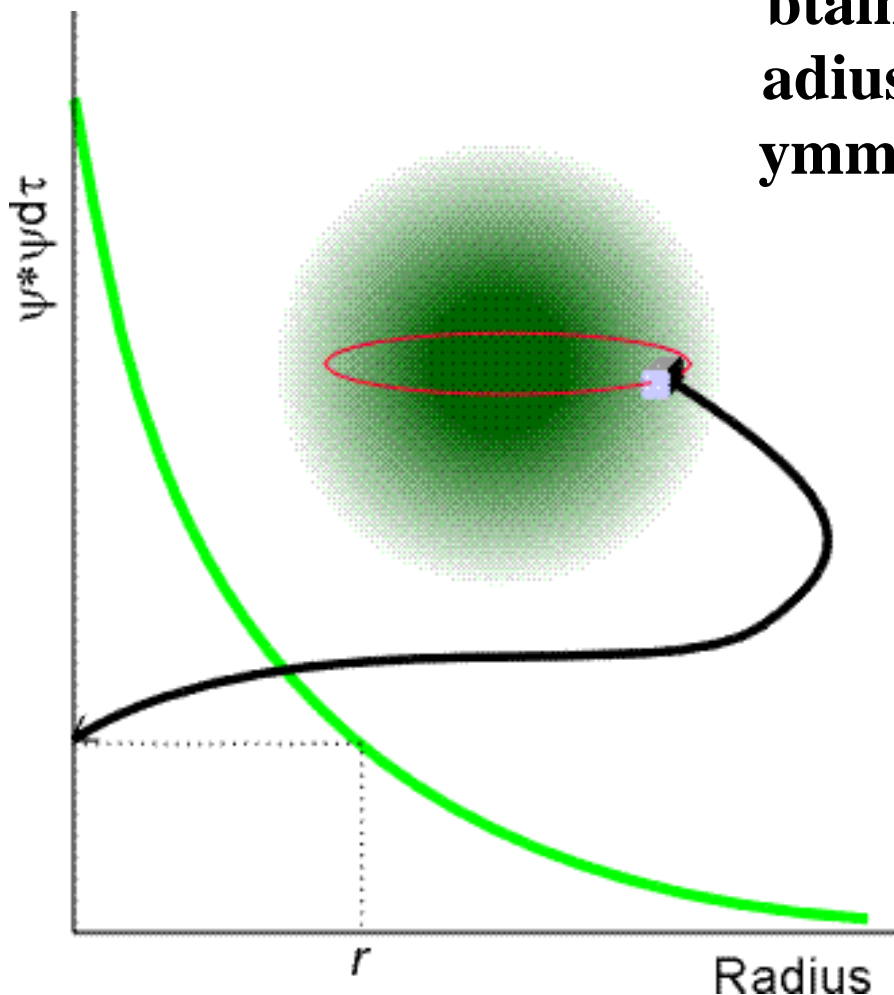$$\mathcal{P}_{nlm}(r,\theta,\phi) = \psi_{nlm}(r,\theta,\phi)\psi_{nlm}(r,\theta,\phi)$$

$$\mathcal{P}_{1,00}(r) = \frac{1}{\pi}\left(\frac{Z}{a_o}\right)^3 e^{-\rho}$$

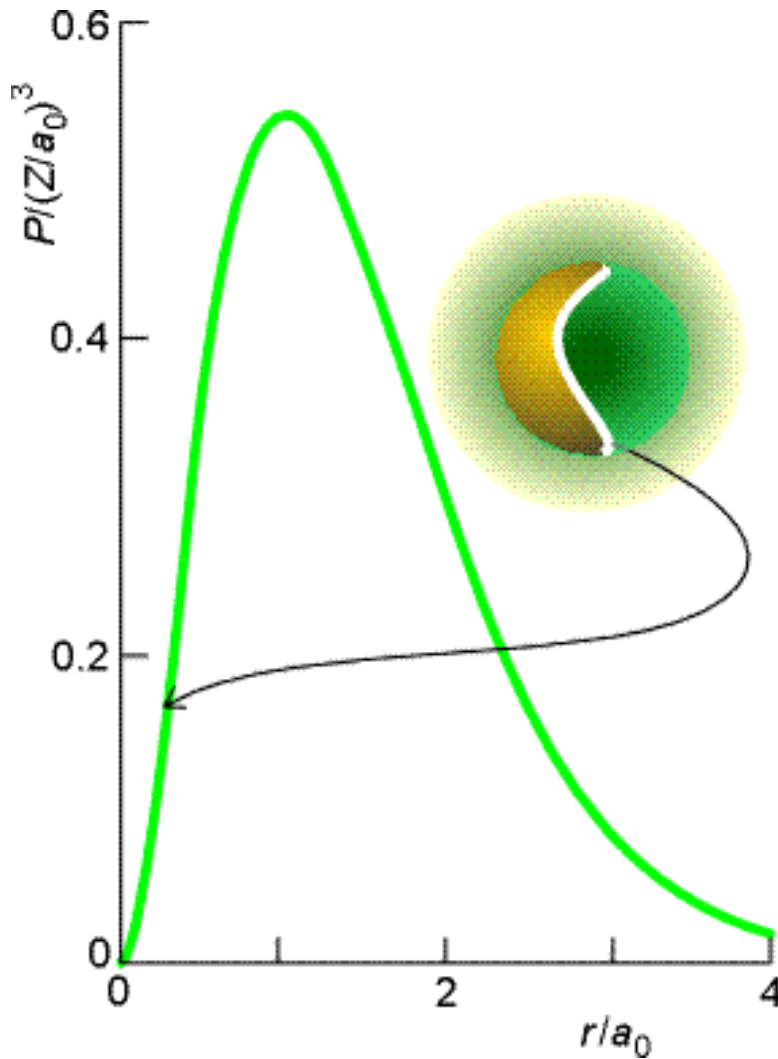$$\mathcal{P}_{200}(r) = \frac{1}{32\pi}\left(\frac{Z}{a_o}\right)^3 (2-\tfrac{1}{2}\rho)^2 e^{-\rho/2}$$

constant-volume electron-sensitive etector (the small cube) gives its greatest eading at the nucleus, and a smaller eading elsewhere. The same reading is btained anywhere on a circle of given adius: the *s* orbital is spherically ymmetrical.

$$\mathscr{P}_{1,00}(r, \phi.\theta) = 2\left(\frac{Z}{a_o}\right)^{3/2} e^{-\rho/2} Y_{oo} \times$$

$$2\left(\frac{Z}{a_o}\right)^{3/2} e^{-\rho/2} Y_{oo} = \frac{1}{\pi}\left(\frac{Z}{a_o}\right)^3 e^{-\rho}$$

he radial distribution function P gives the probability that the electron ill be found anywhere in a shell of radius r. For a 1s lectron in hydrogen, P is a aximum when r is equal to he Bohr radius a_0. The value f P is equivalent to the reading hat a detector shaped like a pherical shell would give as ts radius was varied.

Orbitals of Hydrogenic Atom   Radial probability density
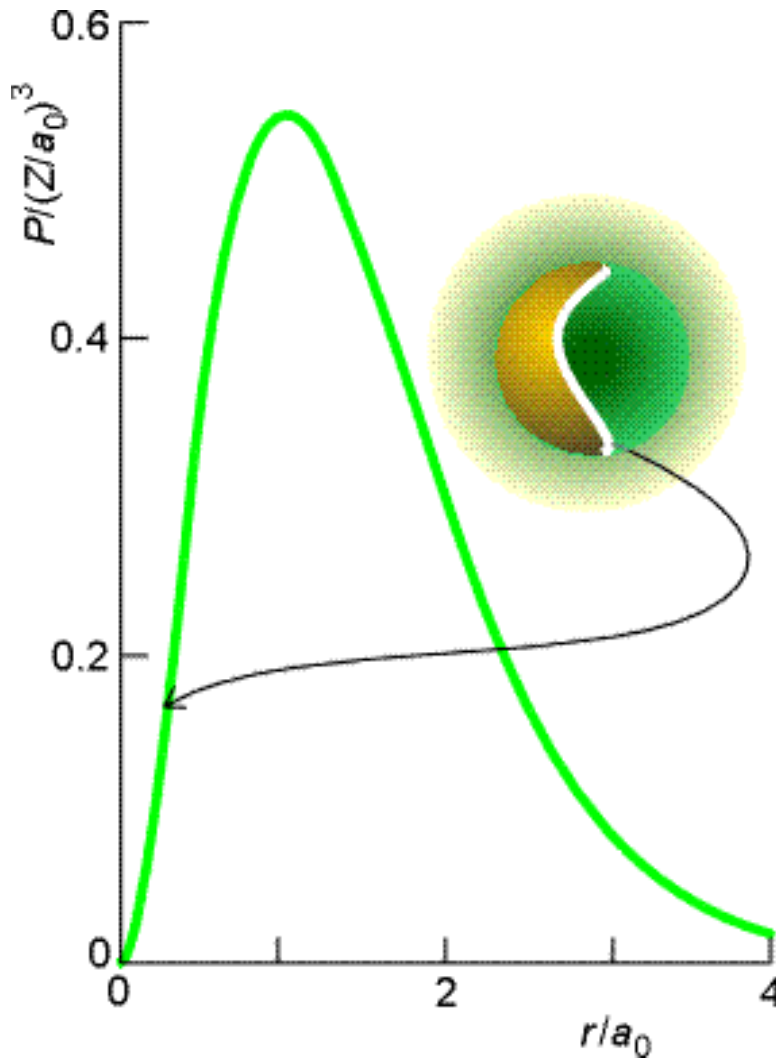
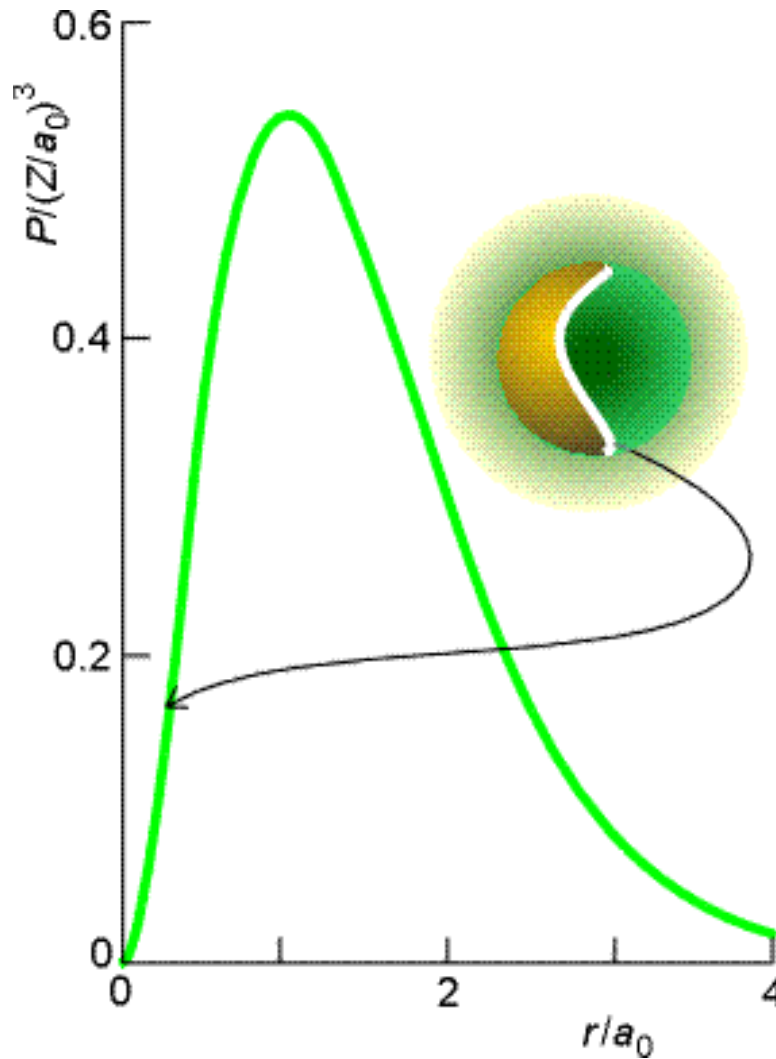The probability of finding the electron between r and $r + dr$ is :

$$P_{nl}(r)dr = \int_0^{2\pi} \int_0^{\pi} \mathscr{P}_{nlm}(r, \phi, \theta)dv$$

$$= \int_0^{2\pi} \int_0^{\pi} \mathscr{P}_{nlm}(r, \phi, \theta) r\sin\theta d\theta d\phi r^2 dr$$

$$= \int_0^{2\pi} \int_0^{\pi} |R_{nl}((r)|^2 Y_{lm}(\phi, \theta)|^2 \sin\theta d\theta d\phi r^2 dr$$

$$= 1 \times |R_{nl}((r)|^2 r^2 dr$$

Thus the radial probability density is

$$P_{nl}(r) = |R_{nl}((r)|^2 r^2$$

Orbitals of Hydrogenic Atom   Radial probability density

The radial probability density is

$$P_{nl}(r) = | R_{nl}((r) |^2 \, r^2$$

The most probable radius corrsponds to the maxima for $P_{nl}(r)$.

For 1s

$$r_{max} = \frac{a_o}{Z}$$

Orbitals of Hydrogenic Atom

Orbitals with increasing l are called

$$\psi_{n1m} = R_{n1}(r)Y_{1m}(\theta, \phi) \quad \text{p - orbitals} \quad m = -1, 0, 1$$

$$\psi_{n2m} = R_{n2}(r)Y_{2m}(\theta, \phi) \quad \text{d - orbitals} \quad m = -2, -1, 0, 1, 2$$
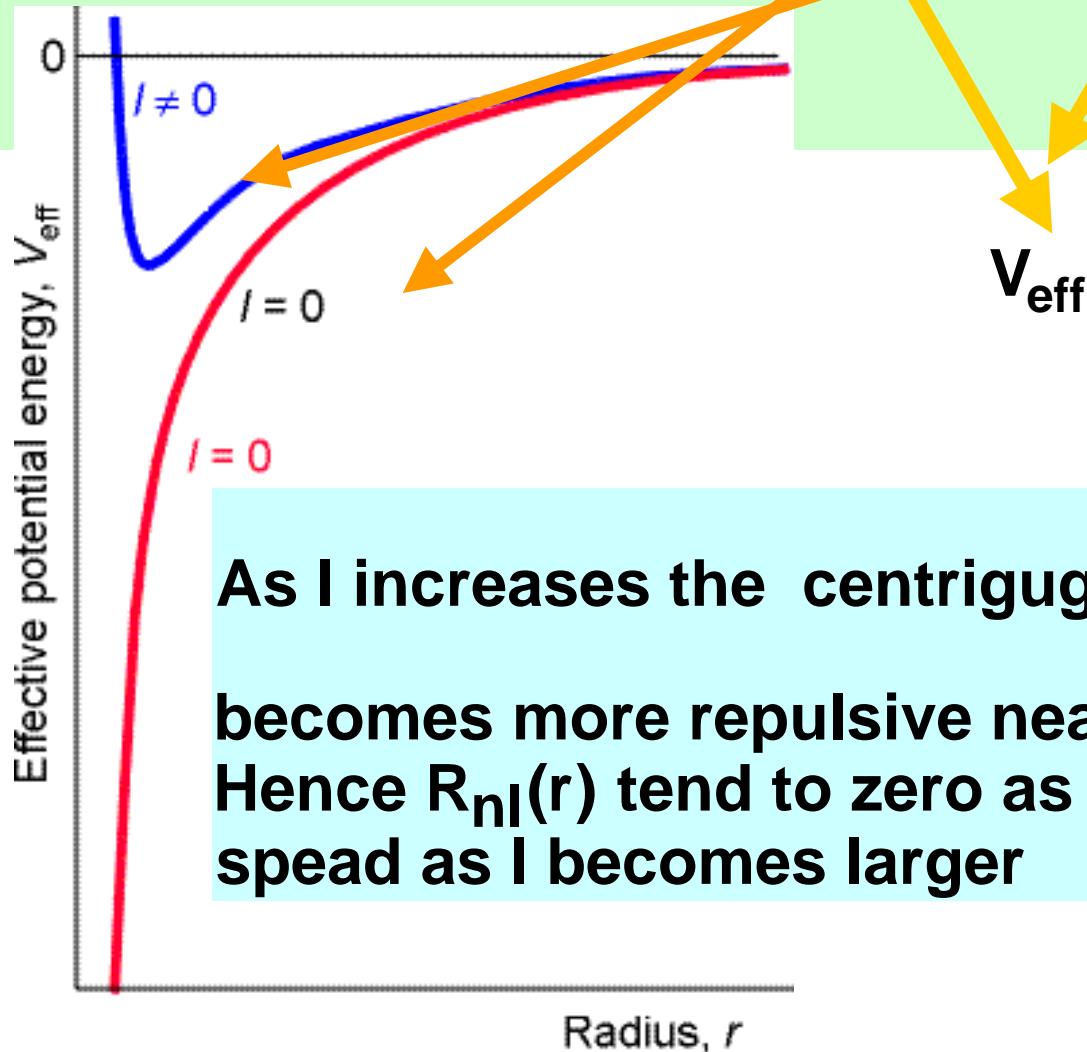
$$\psi_{n3m} = R_{n3}(r)Y_{3m}(\theta, \phi) \quad \text{f - orbitals} \quad m = -3, -2, -1, 0, 1, 2, 3$$

R_{nl} is a solution to

$$-\frac{\hbar^2}{2\mu}\{\frac{\delta^2 R_{nl}(r)}{\delta^2 r} + \frac{2}{r}\frac{\delta R_{nl}(r)}{\delta r}) + \{-\frac{Ze}{4\pi\varepsilon_o r} + \frac{\hbar^2 l(l+1)}{2\mu m r^2} \}R_{nl}(r) = ER_{nl}(r)$$


V_{eff}

As l increases the centrigugal term $\dfrac{\hbar^2 l(l+1)}{2\mu m r^2}$

**becomes more repulsive near nucleus at small r. Hence $R_{nl}(r)$ tend to zero as r → o with increasing spead as l becomes larger**

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.
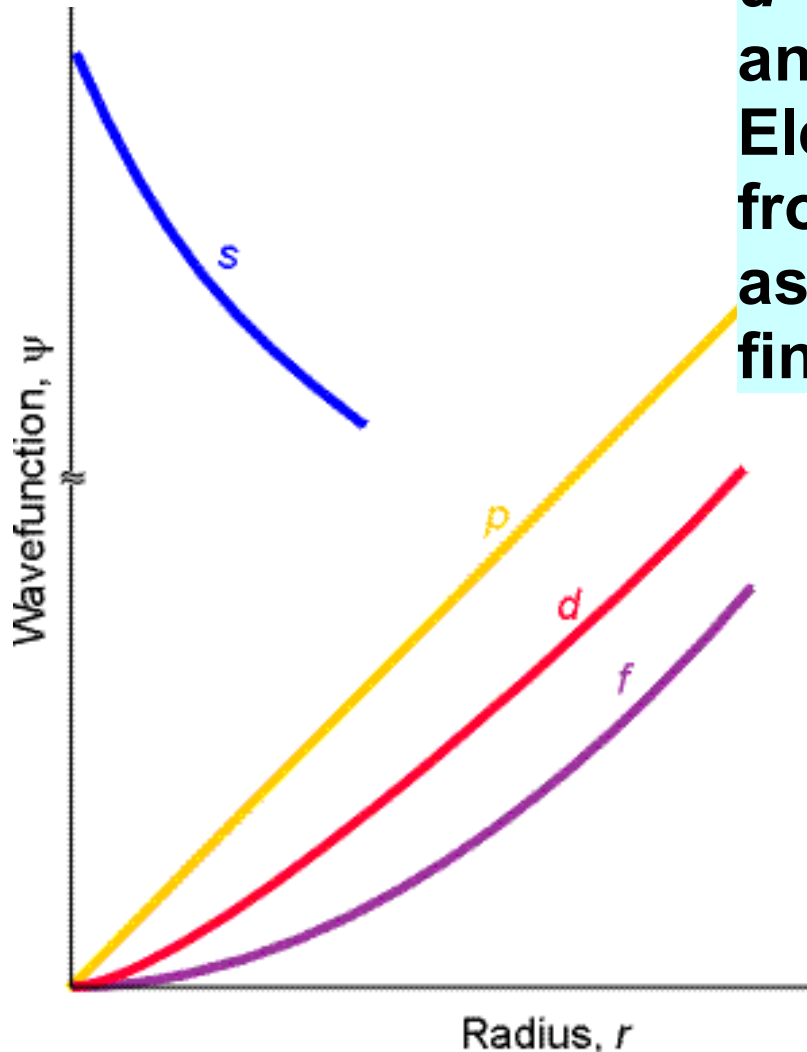
Orbitals of Hydrogenic Atom

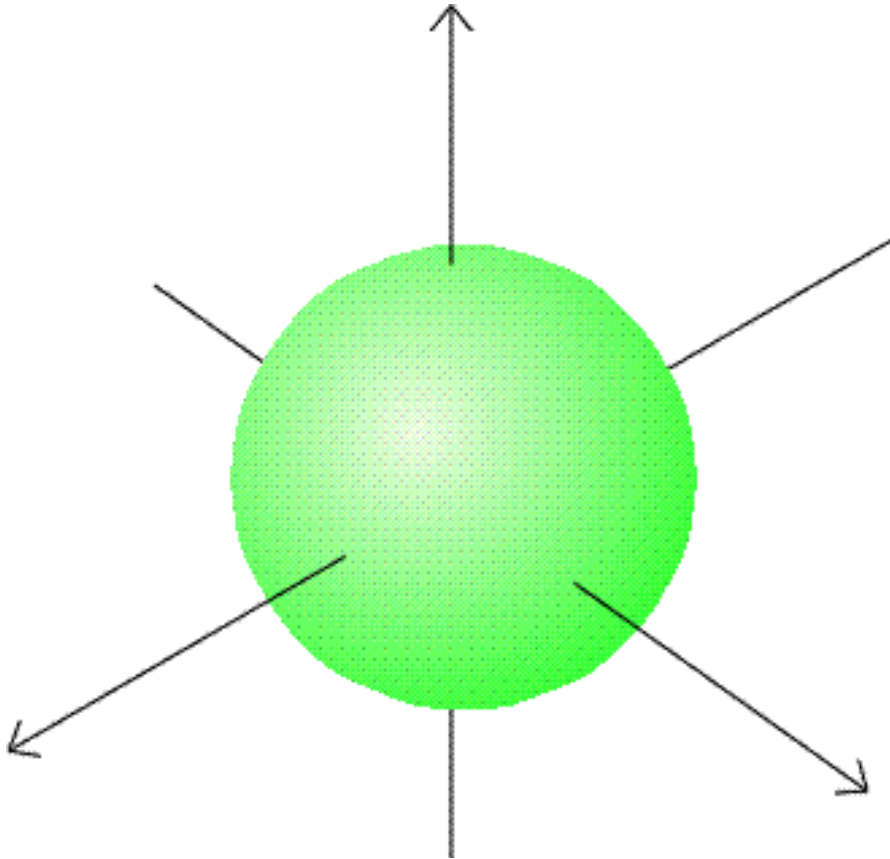## Mean radius
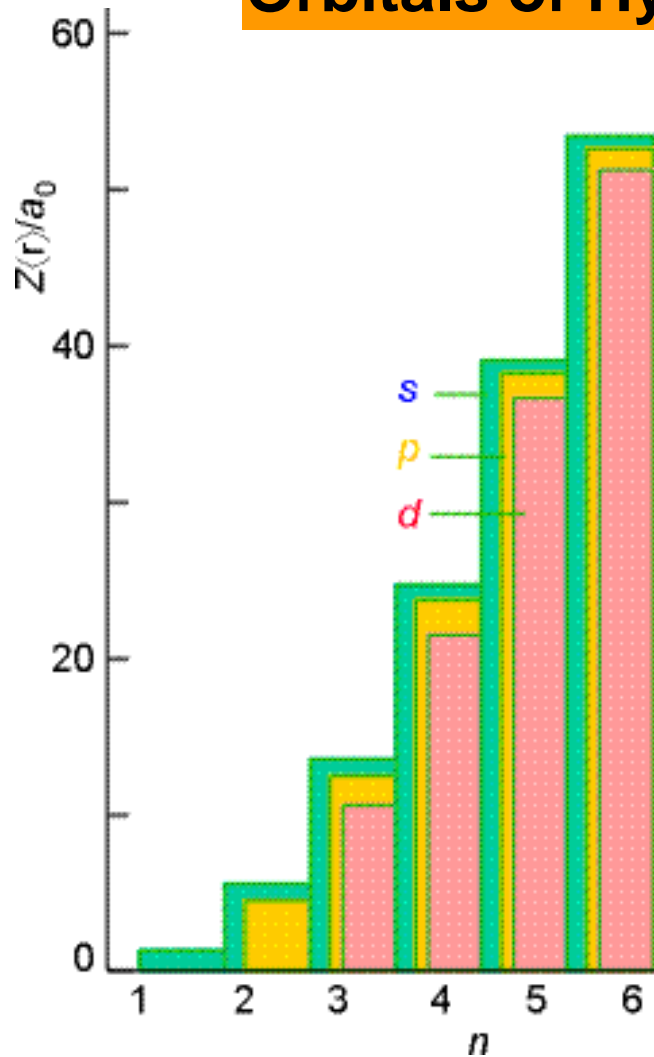
The mean radius is given as the espectation value

$$< r >= \int \psi_{nlm} r \psi_{nlm} dv$$

For the hydrogenic atom

$$< r >_{nl} = n^2 \left\{ 1 + \frac{1}{2}(1 - \frac{l(l+1)}{n^2} \right\} \frac{a_o}{Z}$$

he variation of the mean radius of a ydrogenic atom with the principal and rbital angular momentum quantum umbers. Note that the mean radius lies in he order $d < p < s$ for a given value of n.

Orbitals of Hydrogenic Atom

The boundary surface of an *s* orbital, within which there is a 90 per cent probability of finding the electron.

Orbitals of Hydrogenic Atom   Angular part

Let us now look at the angular part of the p - functions

$$\psi_{nlm}(r, \phi, \theta) = R(r)_{nl} Y_{l,m}(\phi, \theta)$$
$$n = 2, l = 1$$

$$m = -1, 0, 1$$

$$\psi_{211}(r, \phi, \theta) = R(r)_{21} Y_{1,1}(\phi, \theta) = -R(r)_{21}\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi}$$

$$\psi_{210}(r, \phi, \theta) = R(r)_{21} Y_{1,0}(\phi, \theta) = R(r)_{21}\left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

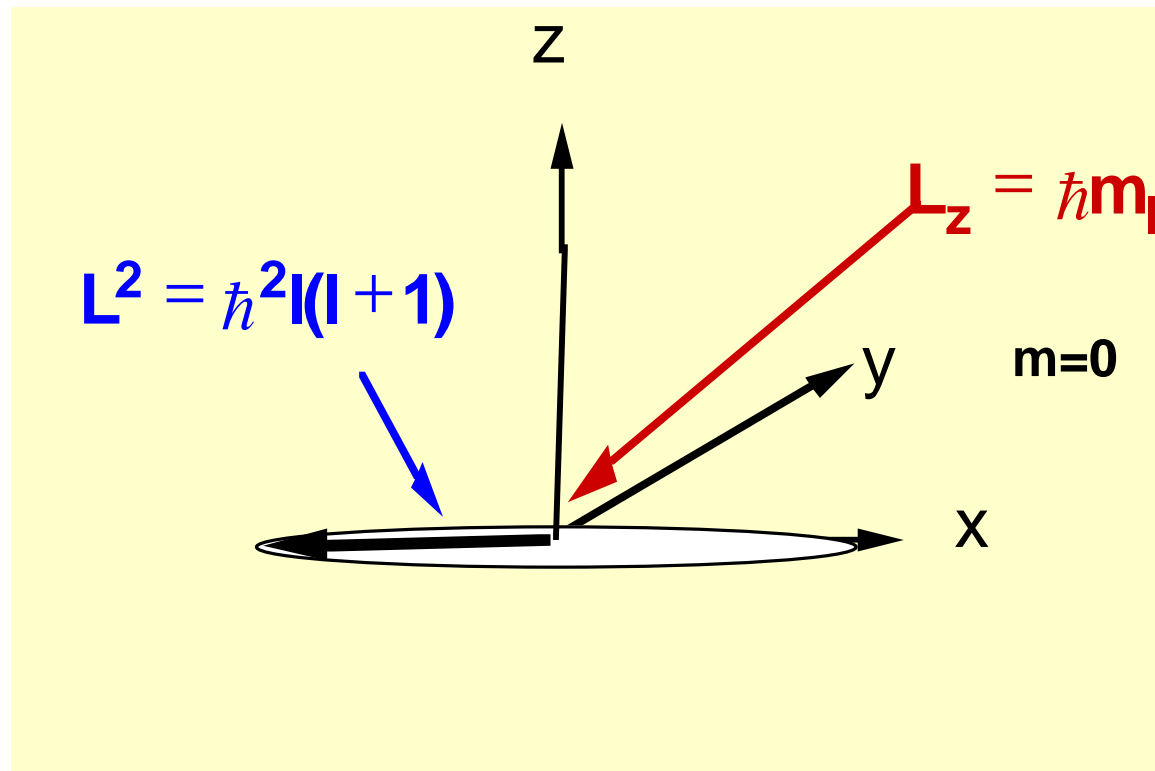$$\psi_{21-1}(r, \phi, \theta) = R(r)_{21} Y_{1,-1}(\phi, \theta) = R(r)_{21}\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{-i\phi}$$

$$\psi_{210}(r, \phi, \theta) = R(r)_{21}\left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \qquad I = 1, m = 0$$

The electron has an angular momentum $\vec{L}$ such that $L * L = \hbar^2 I(I+1)$

The z-component of $\overleftarrow{L}$ is $L_z = o$

$$L_z = \hbar m_I$$

$$L^2 = \hbar^2 I(I+1)$$
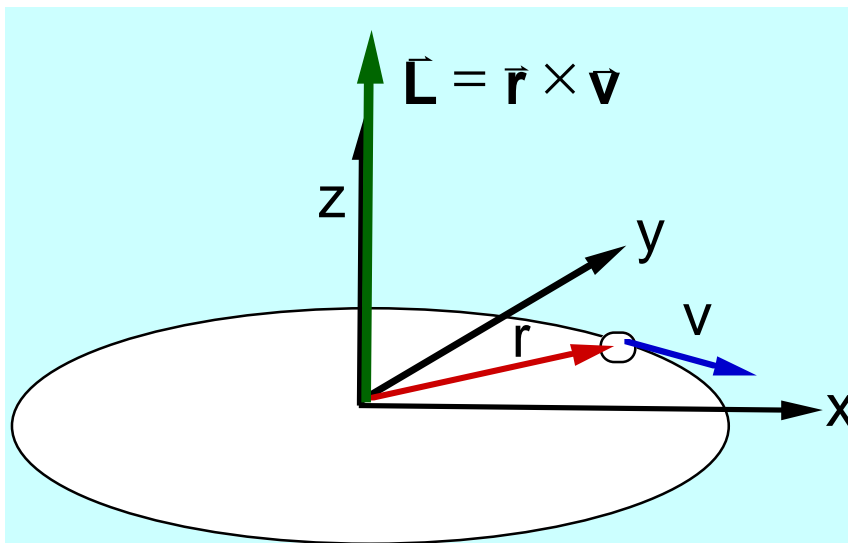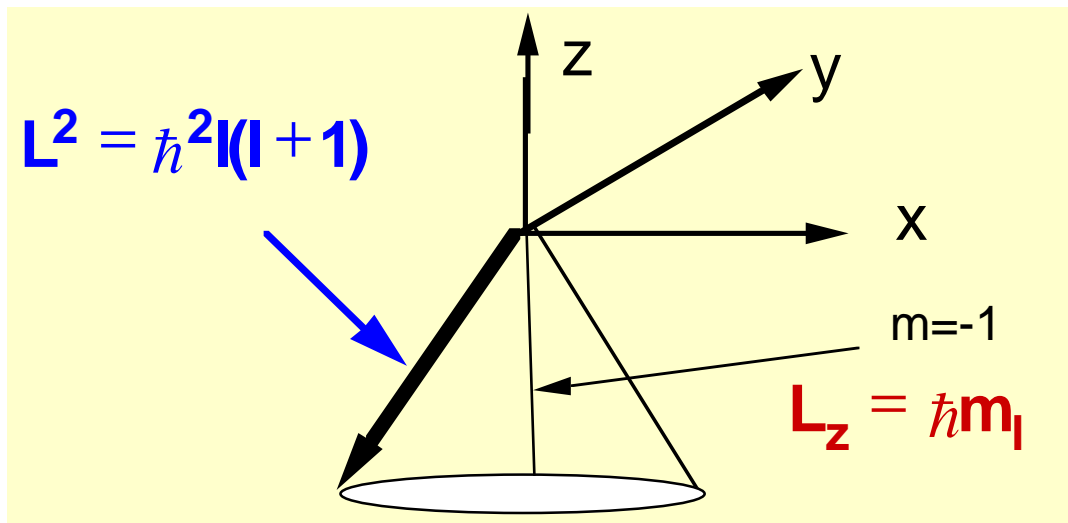
m=0

z

y

x

Orbitals of Hydrogenic Atom

Angular part

$$\psi_{211}(r, \phi, \theta) = -R(r)_{21}\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\, e^{i\phi}$$

$l = 1, m = 1$

The electron has an angular momentum $\vec{L}$ such that $L * L = \hbar^2 l(l+1)$

The z - component of $\overleftarrow{L}$ is $L_z = \hbar$

$\vec{L} = \vec{r} \times \mathbf{v}$

$L^2 = \hbar^2 l(l+1)$

$L_z = \hbar m_l$

$L^2 = \hbar^2 l(l+1)$

$$\psi_{21-1}(r, \phi, \theta) = R(r)_{21}\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{-i\phi}$$ $I = 1, m = -1$

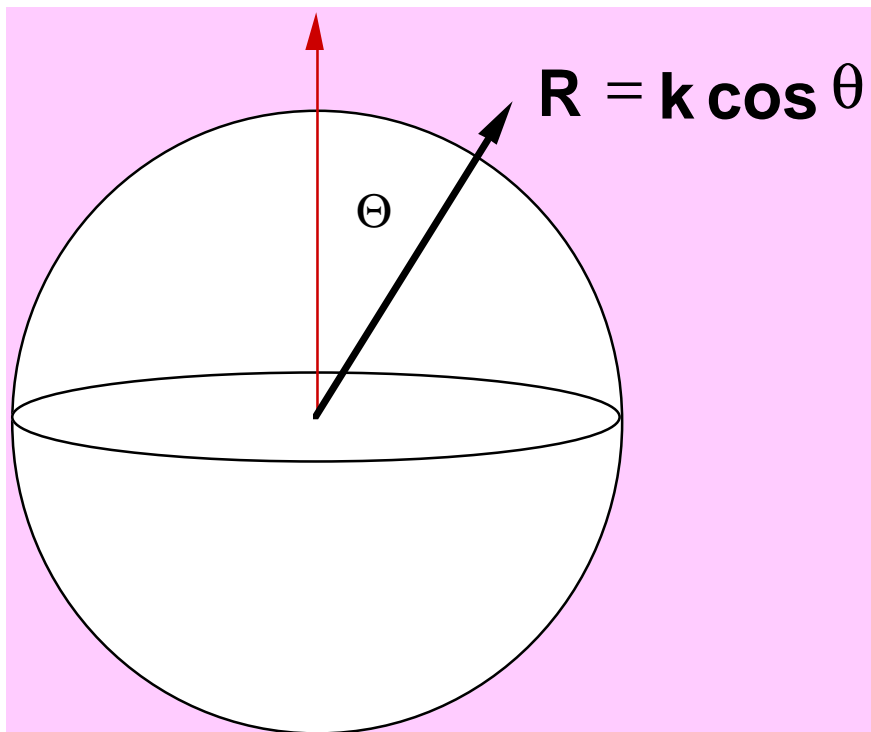The electron has an angular momentum $\vec{L}$
such that $L * L = \hbar^2 I(I+1)$
The z - component of $\overleftarrow{L}$ is $L_z = -\hbar$

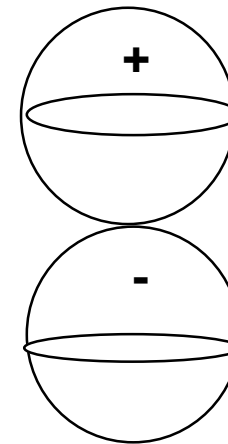$$L^2 = \hbar^2 I(I+1)$$

$$L_z = \hbar m_I$$

m=-1

z   y

x

Real orbitals

Plotting angular part of

$$\psi_{210}(r, \phi, \theta) = R(r)_{21}\left(\frac{3}{4\pi}\right)^{1/2} \cos\theta = 2p_z$$

$$R = k\cos\theta$$

Θ

+

-

Draw vector $\vec{R}$ of length $k\cos\theta$ through each point (θ, ϕ) on sphere

Draw surface through all vectors R

The remaining two orbitals are complex

$$\psi_{211}(r, \phi, \theta) = -R(r)_{21}\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta[\cos\phi + i\sin\phi]$$

$$\psi_{21-1}(r, \phi, \theta) = R(r)_{21}\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta[\cos\phi - i\sin\phi]$$

However by linear combinations we can get the real orbitals

$$2p_x = \frac{1}{\sqrt{2}}\{\psi_{211} - \psi_{21-1}\} = R(r)_{21}\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\cos\phi$$

$$2p_y = \frac{i}{\sqrt{2}}\{\psi_{211} + \psi_{21-1}\} = R(r)_{21}\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\sin\phi$$
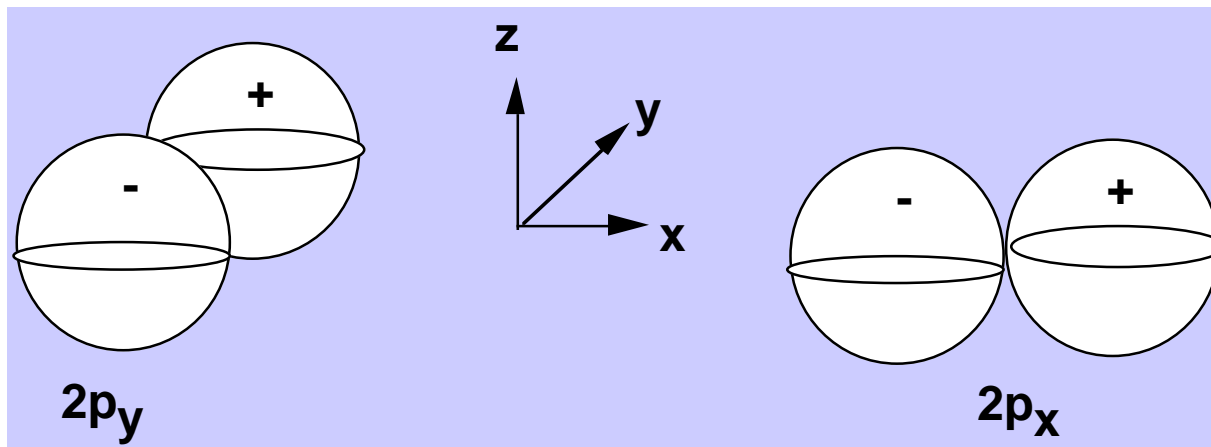
Orbitals of Hydrogenic Atom   Angular part

$$2p_x = \frac{1}{\sqrt{2}} \{\psi_{211} - \psi_{21-1}\} = R(r)_{21}\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\cos\phi$$
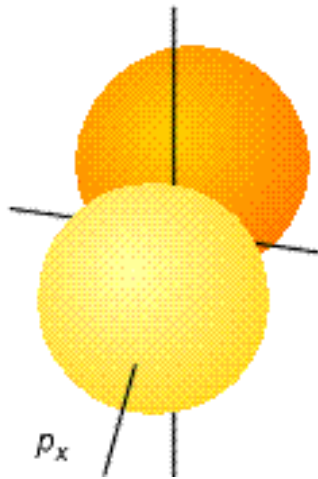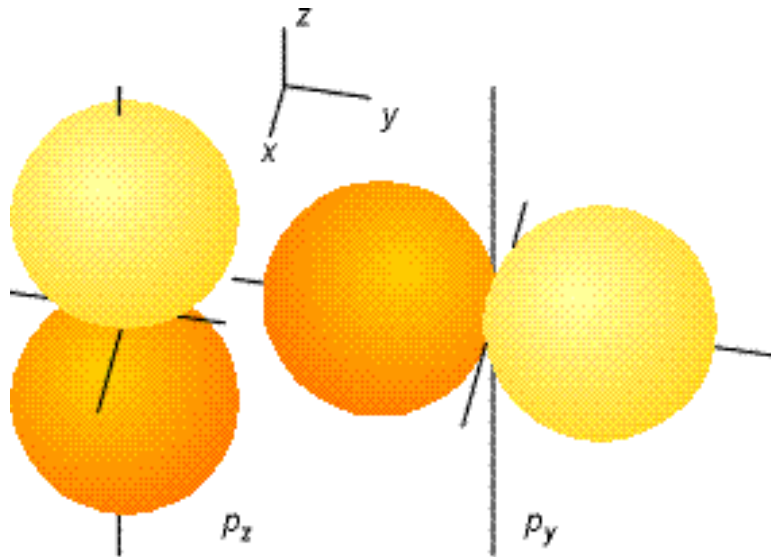
$$2p_y = \frac{i}{\sqrt{2}} \{\psi_{211} + \psi_{21-1}\} = R(r)_{21}\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\sin\phi$$

The orbitals $2p_x$ and $2p_y$ have the same energies and eigenvalues to L^2 as ψ_{211} and ψ_{21-1} . However only the latter are eigenfunctions of L_z
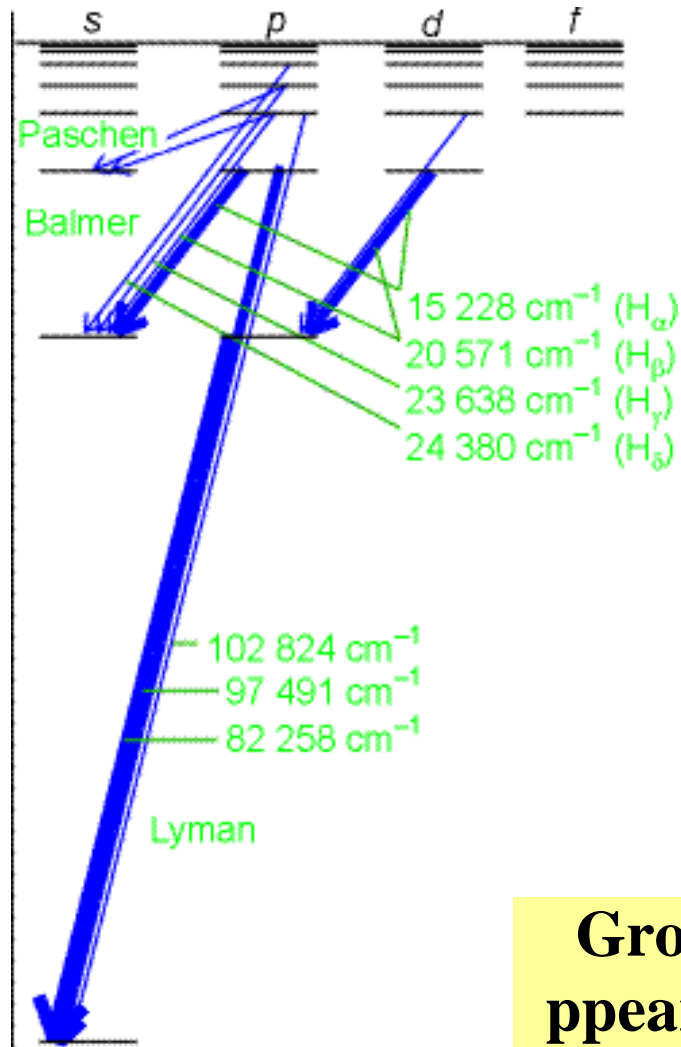
The boundary surfaces
of *p* orbitals. A nodal
plane passes through
the nucleus and
separates the two lobes
of each orbital.
The dark and light areas denote
regions of opposite sign
of the wavefunction.

Orbitals of Hydrogenic Atom

Transitions

In transitions between
 different energy levels of
the hydrogenic atom
 the following selection
rules apply

$\Delta l = \pm 1$
 $\Delta m = 0, \pm 1$

   Grotrian diagram that summarizes the
ppearance and analysis of the spectrum of
tomic hydrogen. The thicker the line, the
   ore intense the transition.

**What you need to learn from
this lecture about the hydrogen atom
for the quizz and the final exam**

Understand how the
balance between kinetic
energy and potential
energy shapes R_{nl}
Fig.13.10

The behaviour of $R_{nl}(r)$ near
the nucleus (Fig 13.16)

The definition of the radial
distribution function
$P(r) = r^2 R(r)^2$ and how it
is used to calculate the
expaction values $<r^n>$

Memorize the relation between
real p-orbitals (p_x, p_y, p_z) and
imaginary p-orbitals (p_o, p_{-1}, p_1).
Understand the physical
difference. Understand
plots of (p_x, p_y, p_z).

Same for d and f great,
but not required

Selection rules for electronic
transitions in thehydrogen atom
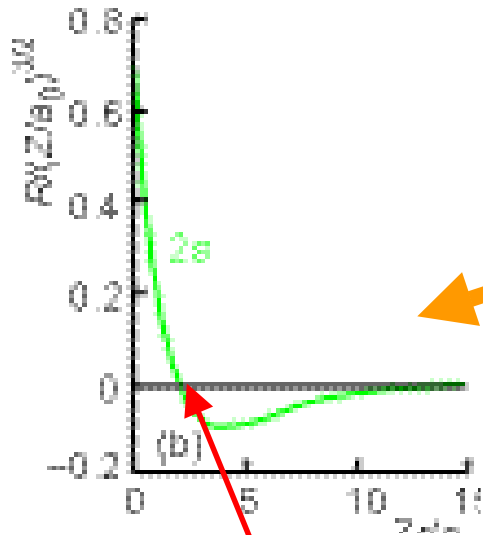
$\Delta l = \pm 1$
$\Delta m = o, \pm 1$

$n = n_o$, $l = 0$

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

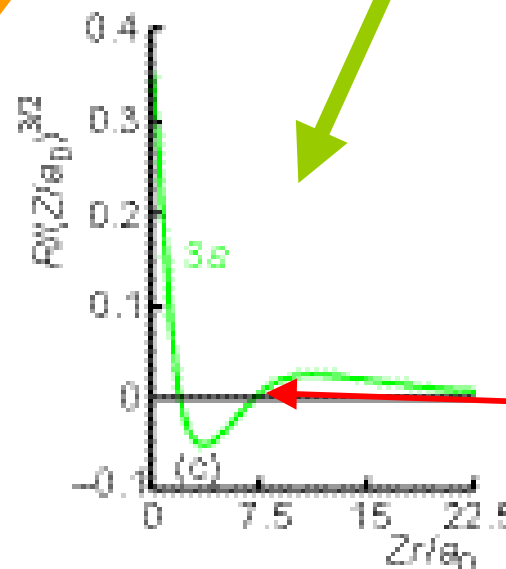For $l = 0$ we have $m = 0$;

$$Y_{o,o} = \sqrt{\frac{1}{4\pi}}$$

$$R_{20}(r) = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_o}\right)^{3/2}(2 - \frac{1}{2}\rho)e^{-\rho/4}$$

$$R_{30}(r) = \frac{1}{9\sqrt{3}}\left(\frac{Z}{a_o}\right)^{3/2}(6 - 2\rho + \frac{1}{9}\rho^2)e^{-\rho/6}$$

One node at

$$(2 - \frac{1}{2}\rho) = 0$$

with $\rho = 2Zr/a_o$

node : $2a_o / Z$

two nodes at

$$(6 - 2\rho + \frac{1}{9}\rho^2) = 0$$

with $\rho = 2Zr/a_o$

nodes : $1.9a_o / Z$

and $7.1Zr/a_o$

Appendix : Orbitals of Hydrogenic Atom..why nodes

$n = n_o, \; l = 0$

$\psi_{n_o,o,o}(\phi, \theta) = R_{n_o,o}(r) Y_{o,o}((\phi, \theta)$

Why has $R_{nl}(r)$ n - 1 nodes ?

We have seen previously that any two independent solutions to the Schrödinger equation must be orthogonal :

$\int \psi_i \psi_j dv = \partial_{ij}$

Thus any two s - orbitals $R_{n'o}Y_{oo}$ and $R_{no}Y_{oo}$ must be orthorgonal

$$\int\limits_{0}^{2\pi} \int\limits_{0}^{\pi} \int\limits_{0}^{\infty} R_{n'o}Y_{oo}R_{n'o}Y_{oo}dv = 0$$

$$\int_{0}^{2\pi} \int_{0}^{\pi} \int_{0}^{\infty} R_{n'o}Y_{oo}R_{n'o}Y_{oo}\,dv = 0$$

$$\int_{o}^{2\pi} \int_{o}^{\pi} Y_{oo}Y_{oo}\,\sin\theta\,d\theta\,d\phi \int_{o}^{r} R_{n'o}(r)R_{no}(r)r^2\,dr = 0$$

$$1 \qquad\qquad \int_{o}^{r} R_{n'o}(r)R_{no}(r)r^2\,dr = 0$$

Y_{oo} normalized
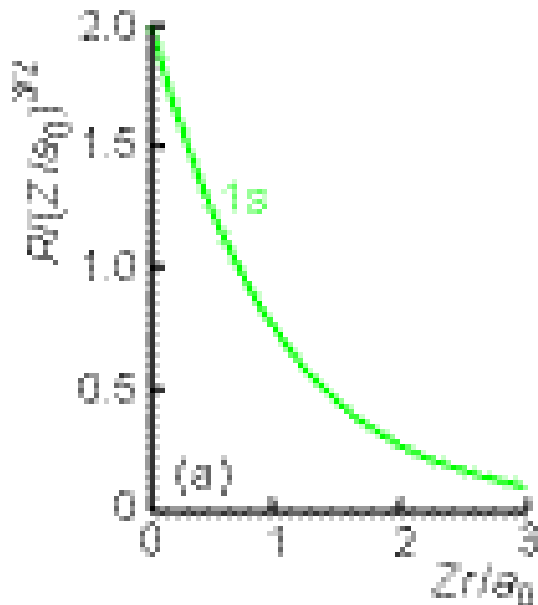
The R_{1o} function is positive every where

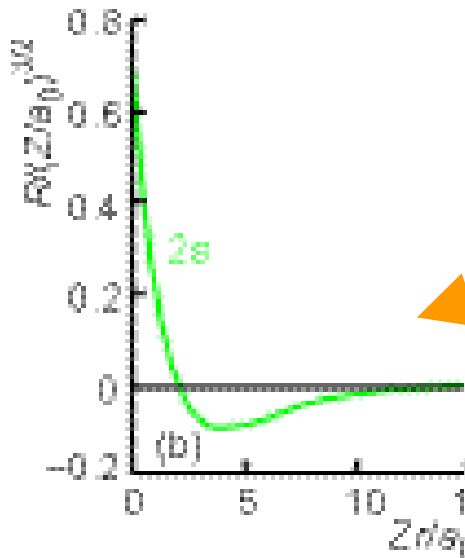$$R_{1,0}(r) = 2\left(\frac{Z}{a_o}\right)^{3/2} e^{-\rho/2}$$

Thus for R_{2o} to be orthogonal to R_{1o}

$$\int_{o}^{r} R_{1o}(r)R_{2o}(r)r^2 dr = 0$$

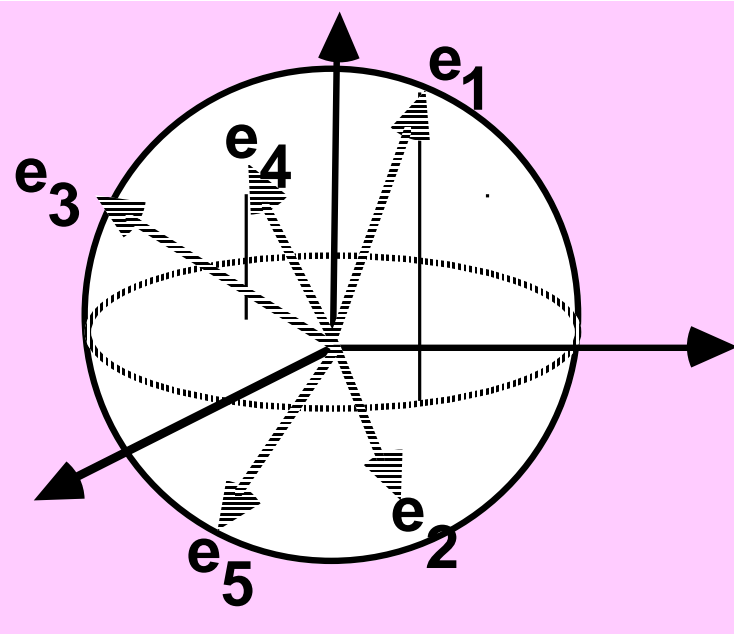**R_{20} must have positive and negative regions**

For R_{3o} to be orthogonal to R_{1o} and R_{20} two nodes are required etc...

$$R_{20}(r) = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_o}\right)^{3/2}(2 - \frac{1}{2}\rho)e^{-\rho/4}$$
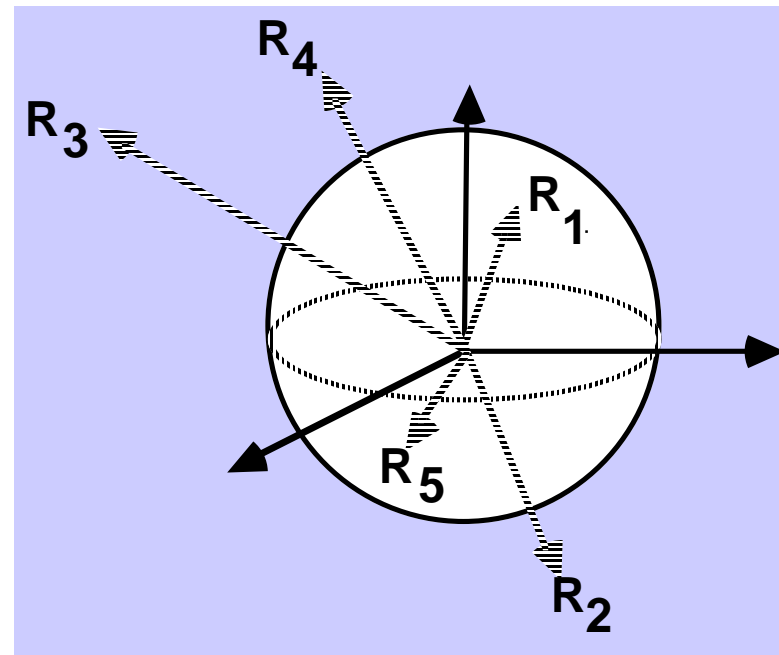
Appendix : Drawing Orbitals of Hydrogenic Atom   An aside
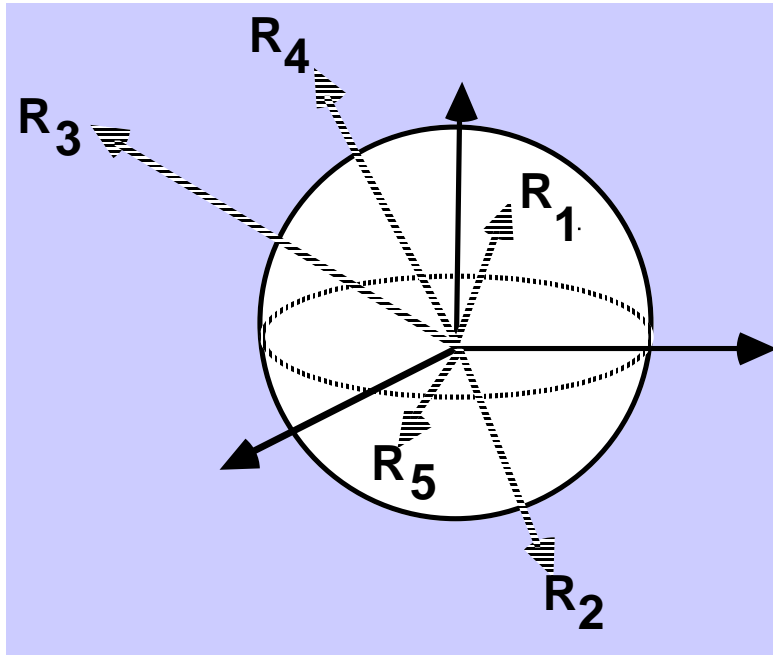
How do we plot Y_{lm} ?

Calculate the value of $Y_{lm}(\phi, \theta)$ at the position of each $\vec{e}_n$ (e.i for each ϕ_n, θ_n). Construct the vectors : $\overline{R}_1, \overline{R}_2, \overline{R}_3, ..\overline{R}_n$

where : $\vec{R}_n = \vec{e}_n Y_{lm}(\phi, \theta)$

Draw $\overline{R}_n$

Consider a unit sphere withradius 1. Draw a large number ofunit vectors from the origin ofthe sphere in different directions (e.i. different θ, ϕ) $\vec{e}_1, \vec{e}_2, \vec{e}_3, \vec{e}_4...\vec{e}_n$

R_4

R_3

R_1

R_5

R_2

Draw a surface through the endpoints of all $\vec{R}_n$.
This surface represents $Y_{lm}(\theta, \phi)$

For $Y_{oo}(\phi, \theta)$ we have

$$\vec{R}_n = \frac{1}{2\sqrt{\pi}} \vec{e}_n \text{ for all } n$$
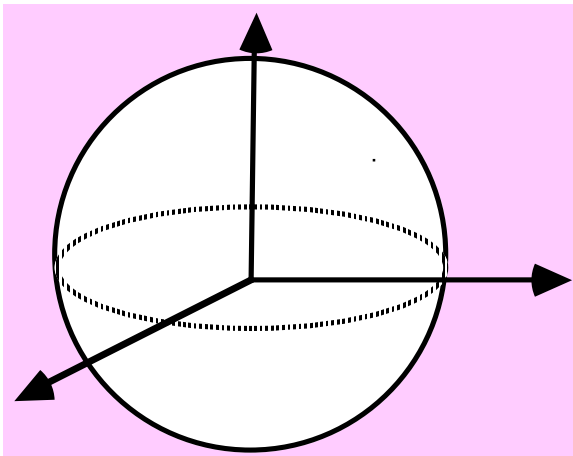
THus Y_{oo} representing the angular part of a ns function is represented by a sphere
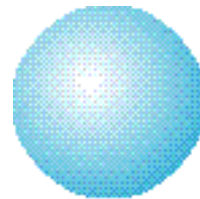
$l = 0, \; m_l =$

ns - orbital

We have that $Y_{oo}(\phi, \theta)$ is spherical e.u. the same for all ϕ_n, θ_n