

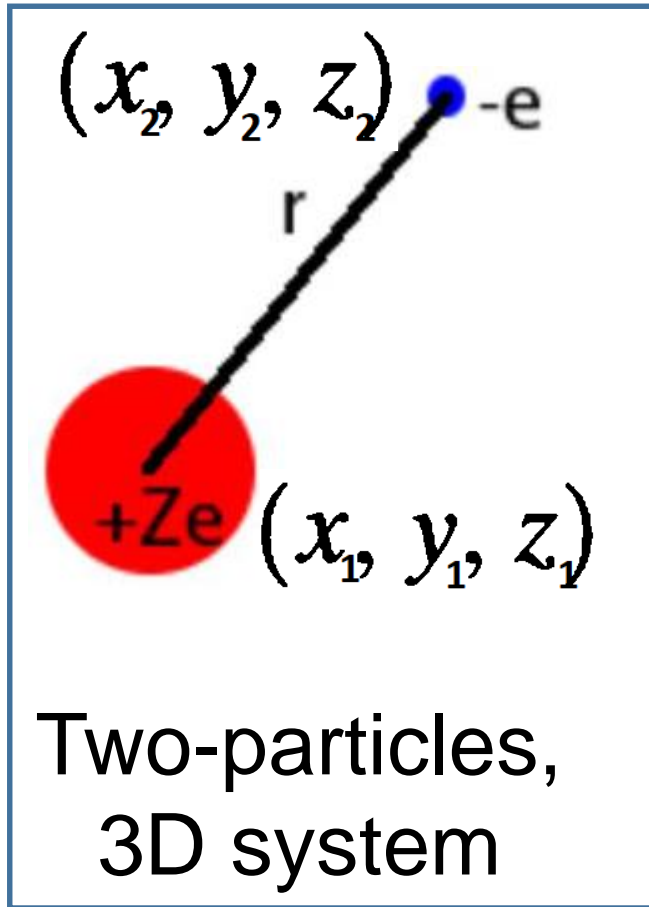
The Structure of atoms

FOCUS 8

The Structure of Atoms

- ❑ Description of the arrangement of electrons in atoms.
- ❑ Basis for understanding the structures and properties of elements and their compounds.
- ❑ For the **Hydrogenic atoms** (H, He^+ , Li^{2+} , C^{5+} , U^{91+} etc), the Schrödinger equation can be **solved exactly**.
- ❑ These concepts are used to describe structures of many electron atoms and molecules.

The Solution of Hydrogenic atoms



Potential energy, $V = -\frac{Ze^2}{4\pi\epsilon_0 r}$

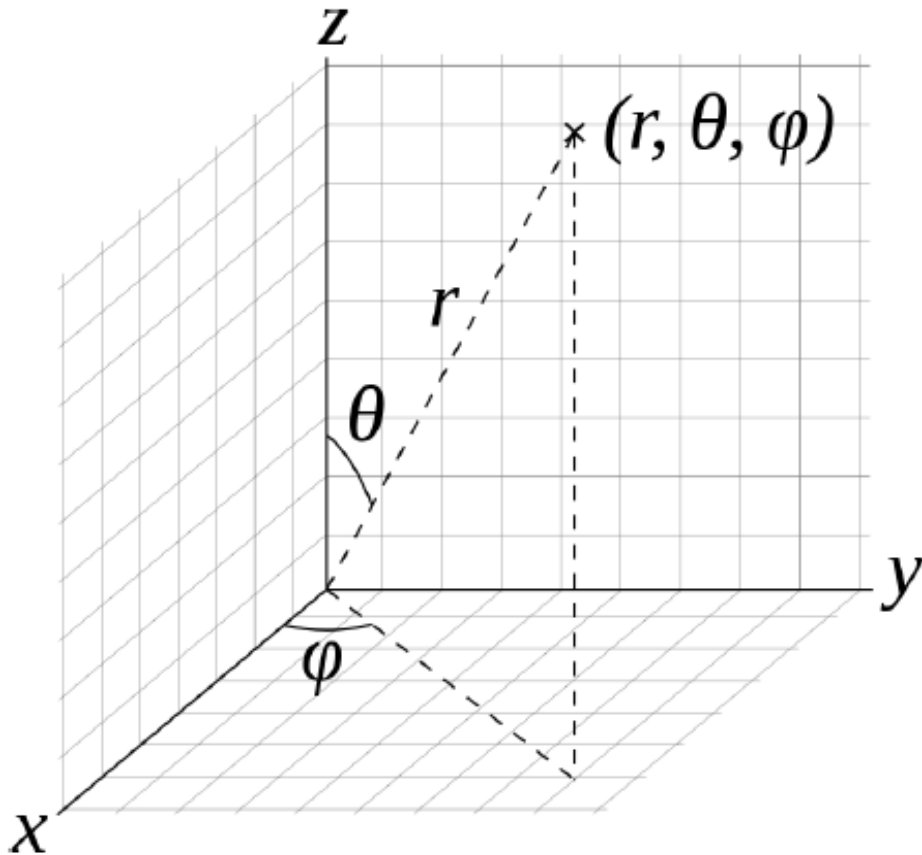
The Schrödinger equation:

$$\begin{aligned} & -\frac{\hbar^2}{2m_1} \left(\frac{\partial^2 \psi}{\partial x_1^2} + \frac{\partial^2 \psi}{\partial y_1^2} + \frac{\partial^2 \psi}{\partial z_1^2} \right) \\ & -\frac{\hbar^2}{2m_2} \left(\frac{\partial^2 \psi}{\partial x_2^2} + \frac{\partial^2 \psi}{\partial y_2^2} + \frac{\partial^2 \psi}{\partial z_2^2} \right) \\ & -\frac{Ze^2}{4\pi\epsilon_0 r} \psi = E\psi \end{aligned}$$

This is an example of a problem with a spherically symmetric potential-energy function.

Solution of Hydrogenic atom problem

Schrödinger equation for this problem is better solved in **spherical polar coordinate system** with proper boundary conditions.



$$x = r \cos \varphi \sin \theta,$$

$$y = r \sin \varphi \sin \theta,$$

$$z = r \cos \theta.$$

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

$$r \geq 0,$$

$$0^\circ \leq \theta \leq 180^\circ (\pi \text{ rad}),$$

$$0^\circ \leq \varphi < 360^\circ (2\pi \text{ rad})$$

Eigenvalues of Hydrogenic atom

$$E_n = -\frac{hcRZ^2}{n^2} \quad n = 1, 2, 3 \dots$$

Principal quantum no.

$$hcR = \frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \quad \mu = \frac{m_e m_N}{m_e + m_N}$$

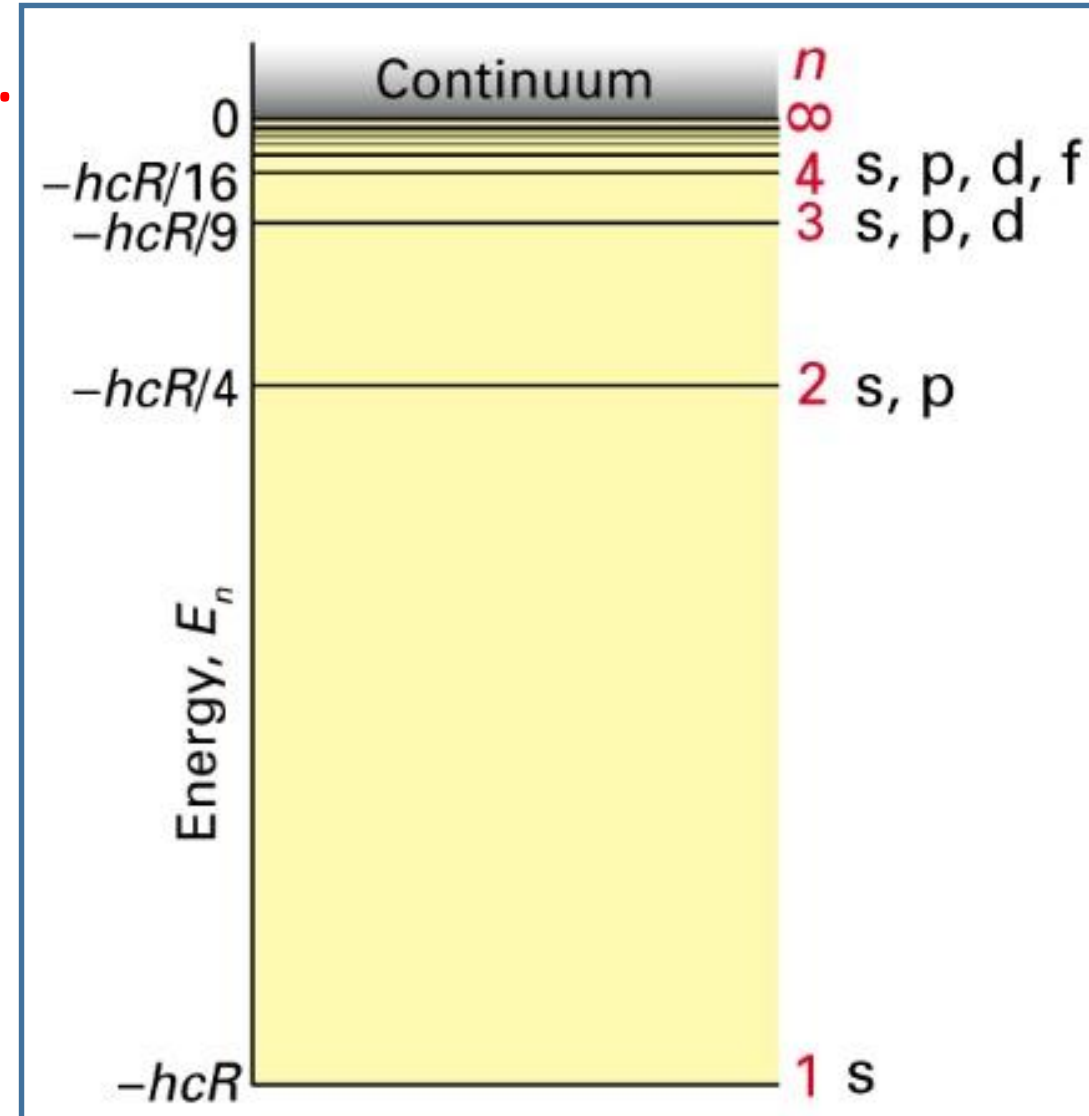
$E_n < 0$: Electron in an atom has lower energy than when it is free

For a transition:

$$\Delta E = E_2 - E_1 = hcRZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

This energy is carried out by a photon.

Ionization Energy, $I = hcRZ^2$



Eigenfunctions of Hydrogenic atom

The wavefunctions (called **atomic orbitals**) can be written as

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

R: radial function
Y: angular function

n, l, m_l : **quantum nos.** arise due to restrictions (boundary conditions).

□ Principal quantum number: $n = 1, 2, 3, \dots$

Quantization of energy (E_n) $E_n = -hcRZ^2/n^2$

□ Orbital angular momentum quantum number: $l = 0, 1, 2, \dots, (n-1)$

Quantization of orbital angular momentum magnitude (J)

$$J = [l(l + 1)]^{1/2}\hbar$$

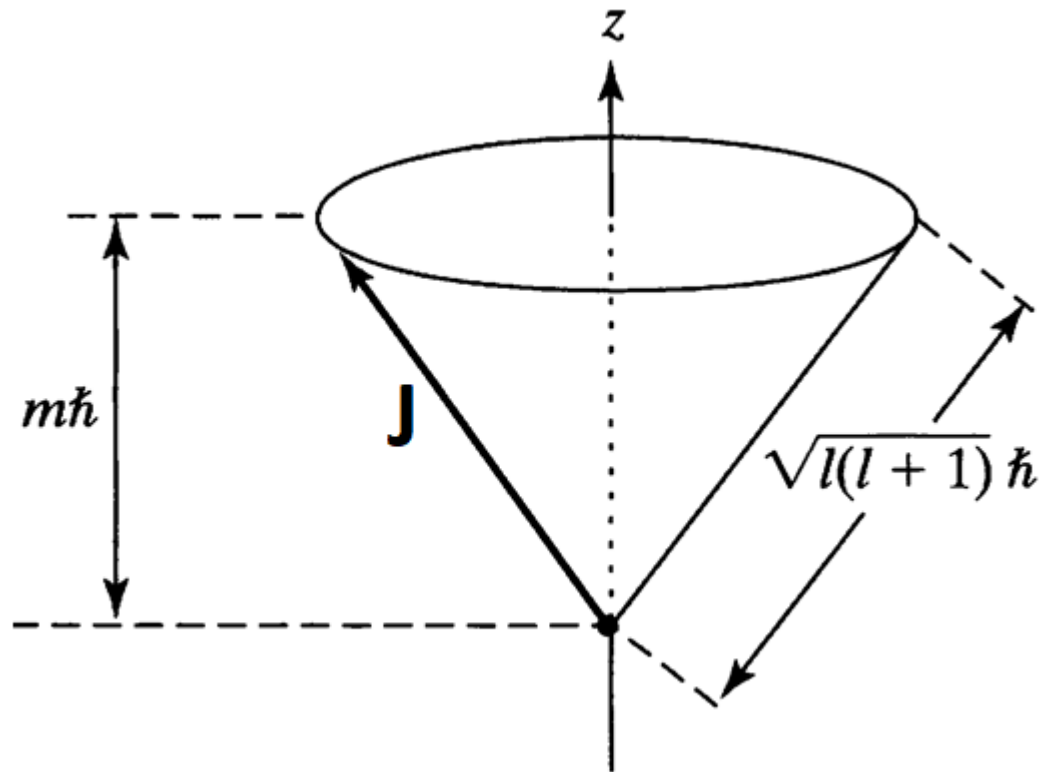
□ Magnetic quantum number: $m_l = -l, \dots, -2, -1, 0, 1, 2, \dots, l$

Quantization of orbital angular momentum direction $J_z = m_l \hbar$

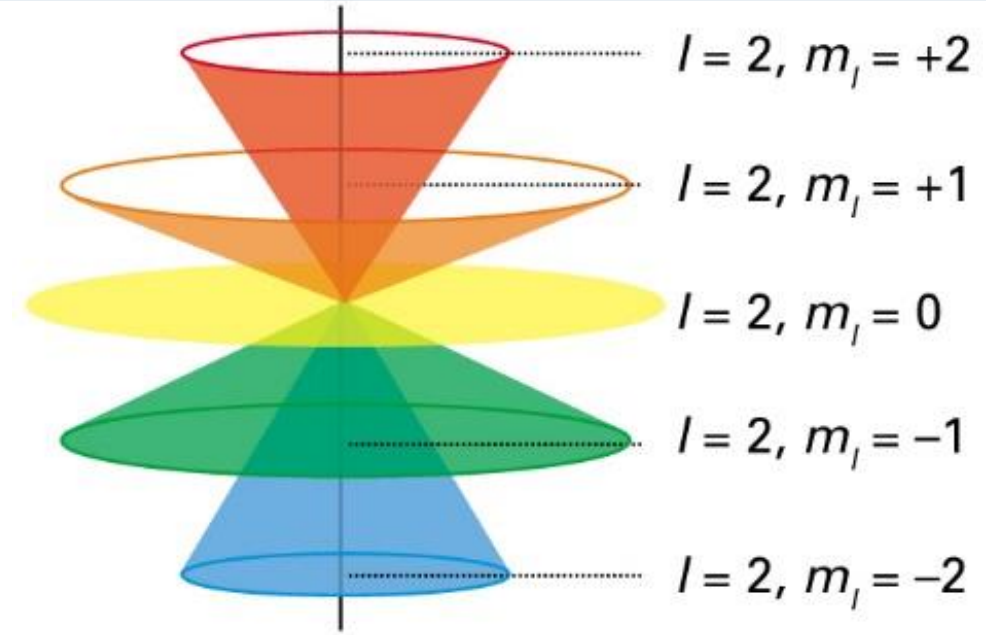
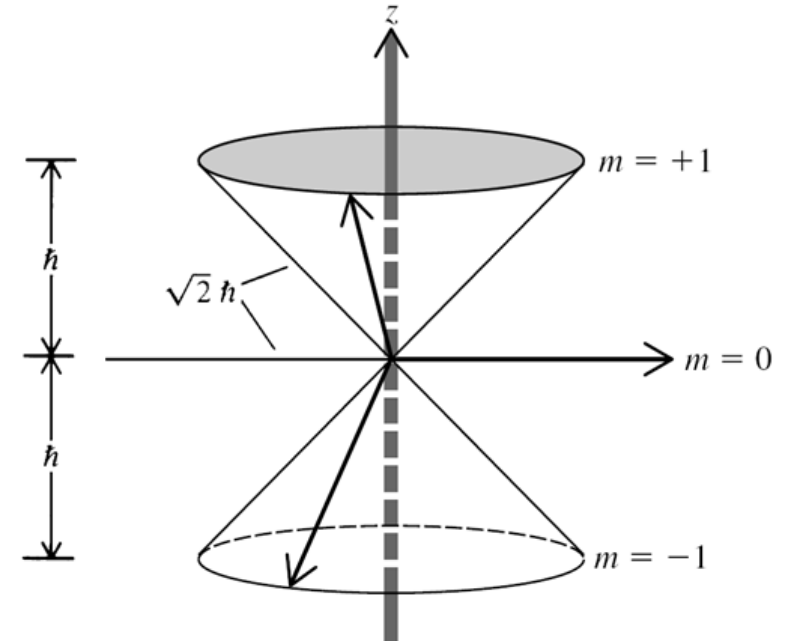
Orientation of orbital angular momentum

$$\mathbf{J} = [l(l + 1)]^{1/2} \hbar$$

$$J_z = m_l \hbar$$



For
 $l = 1$,
 $m_l = -1, 0, +1$



Degeneracy and mean radius of orbitals

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

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

$$m = -l, -l + 1, \dots, 0, \dots, l - 1, l$$

$$E_n = -\frac{hcRZ^2}{n^2}$$

States with different values of l or m , but the same value of n , have the same energy

(Degeneracy = n^2)

Mean radius: $\langle r \rangle_{n,l,m_l} = \frac{n^2 a_0}{Z} \left\{ 1 + \frac{1}{2} \left(1 - \frac{l(l+1)}{n^2} \right) \right\}$

Avg. distance

Increases with n^2
Decreases with Z

Mean distance of an electron from the nucleus in orbitals with $n = 3$:

$\langle r \rangle$ for $n = 3$		
$l = 0$ (s-orbital)	$l = 1$ (p-orbital)	$l = 2$ (d-orbital)
$\frac{27a_0}{2Z}$	$\frac{25a_0}{2Z}$	$\frac{21a_0}{2Z}$

Shell structure of Hydrogenic atom

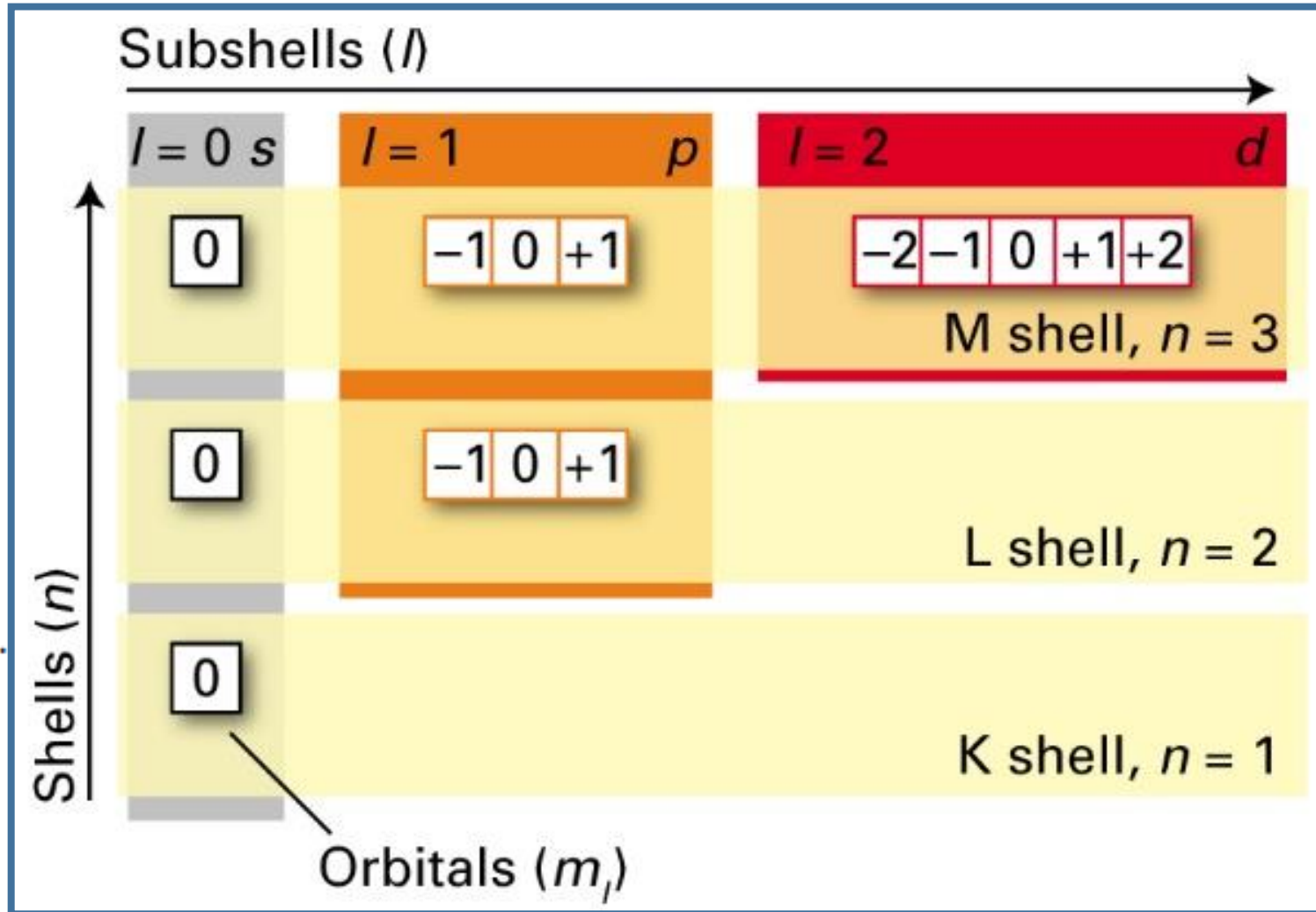
The degeneracy of all orbitals **with same n** and their **similar mean radii** form the basis for saying that they all belong to the same **shell** of atom.

Shell:

$n =$ 1 2 3 4 ...
 K *L* *M* *N* ...

Subshell:

$l =$ 0 1 2 3 4 5 6 ...
 s *p* *d* *f* *g* *h* *i* ...



The s-orbitals

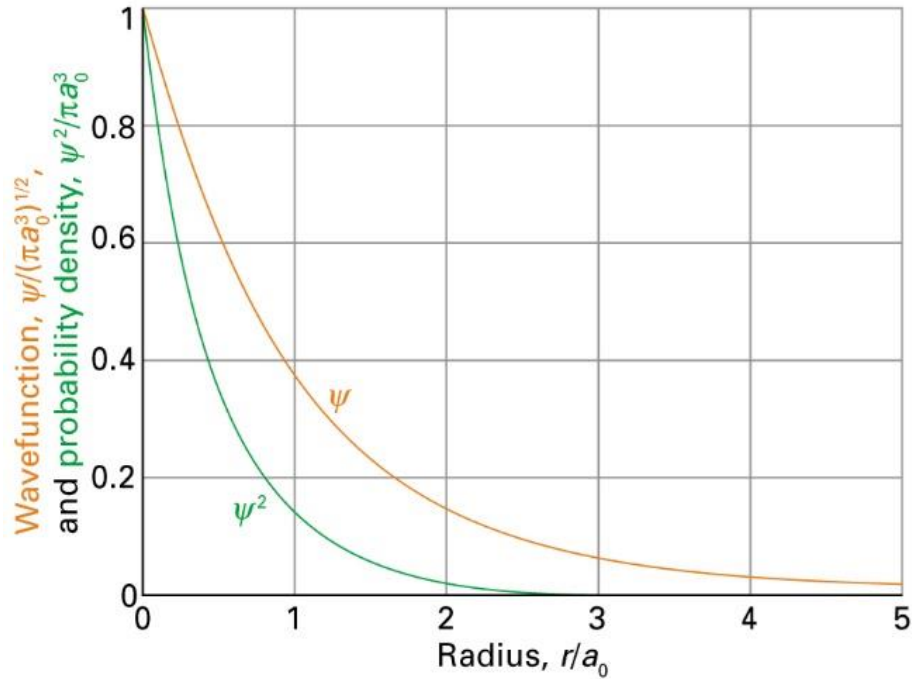
Recall, hydrogenic wavefunction:

(For 1s-orbital: $n = 1, l = 0, m_l = 0$)

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

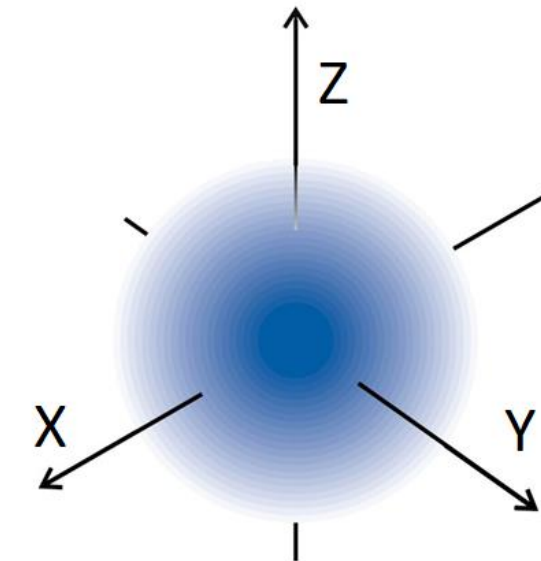
$$\begin{aligned}\psi_{100} \equiv \psi_{1s} &= \left[2(1/a_0^3)^{1/2} e^{-r/a_0} \right] \times \left[1/(2\pi^{1/2}) \right] \\ &= \left(1/(\pi a_0^3)^{1/2} \right) e^{-r/a_0}\end{aligned}$$

$$\begin{aligned}\text{Bohr radius } a_0 &= \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \\ &= 52.9 \text{ pm}\end{aligned}$$

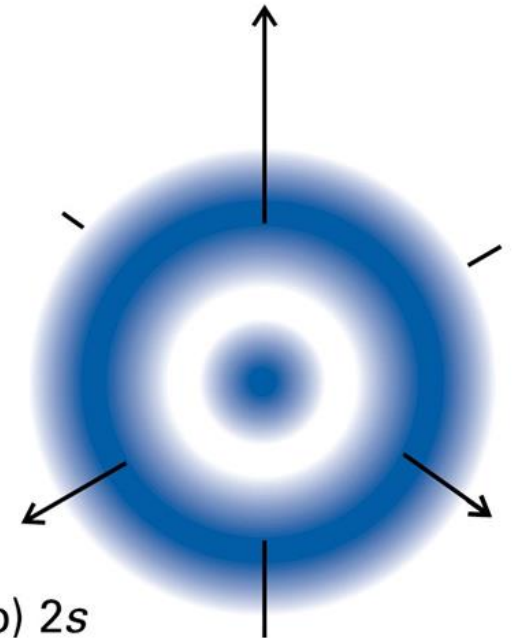


ψ_{1s} decays exponentially to zero from its maximum at the nucleus.

s-orbitals are spherically symmetrical



(a) 1s



(b) 2s

Probability of finding electron

What is the probability of finding an electron in a region of space with its coordinates lie in the ranges r to $r + dr$, θ to $\theta + d\theta$, and ϕ to $\phi + d\phi$?

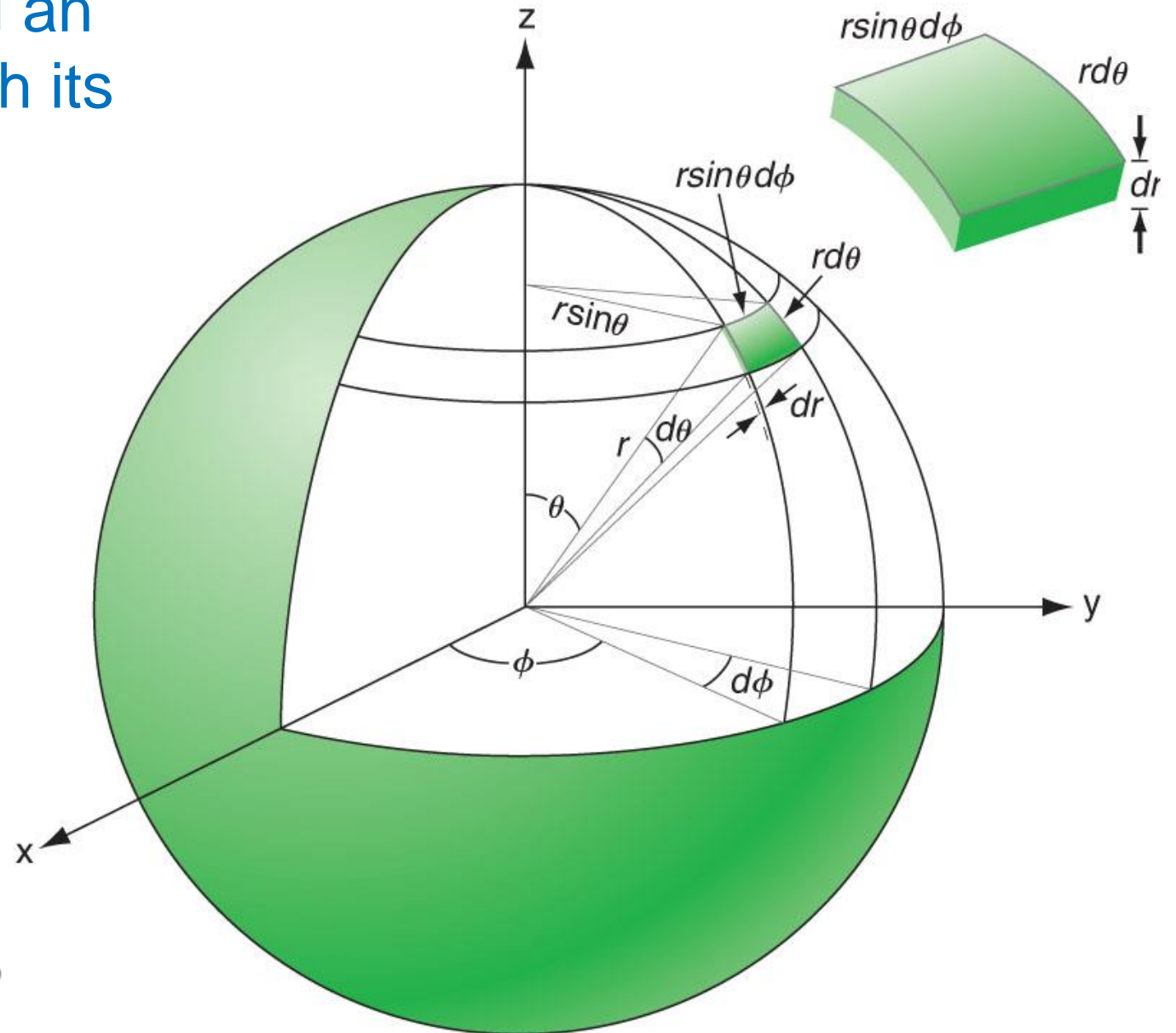
$$\text{Probability} = |\psi|^2 d\tau$$

Where,

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

$$\text{Probability} =$$

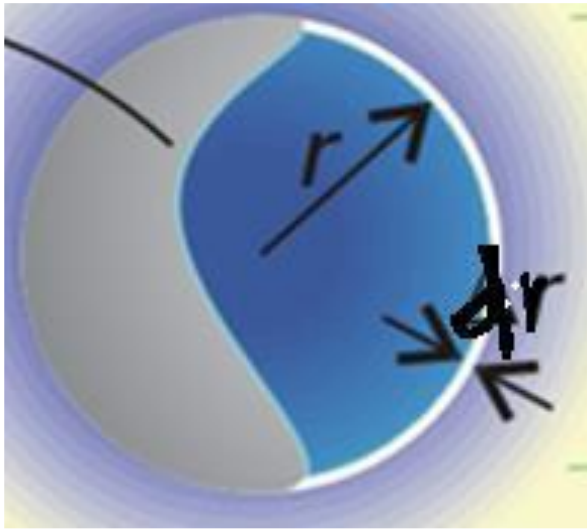
$$= [R_{nl}(r)]^2 |Y_l^m(\theta, \phi)|^2 r^2 \sin \theta dr d\theta d\phi$$



Probability of finding electron

The probability of finding the electron in a region of space with its coordinates lie in the ranges r to $r + dr$, θ to $\theta + d\theta$, and ϕ to $\phi + d\phi$ is

$$\begin{aligned}\text{Probability} &= |\psi|^2 d\tau, \text{ where } d\tau = r^2 \sin \theta dr d\theta d\phi \\ &= [R_{nl}(r)]^2 |Y_l^m(\theta, \phi)|^2 r^2 \sin \theta dr d\theta d\phi\end{aligned}$$



Now, What is the probability of finding the electron in a thin spherical shell centered at the origin, of inner radius r and outer radius $r + dr$?

$$\begin{aligned}\text{Probability} &= [R_{nl}(r)]^2 r^2 dr \int_0^{2\pi} \int_0^{\pi} |Y_l^m(\theta, \phi)|^2 \sin \theta d\theta d\phi \\ &= [R_{nl}(r)]^2 r^2 dr\end{aligned}$$

Area = $4\pi r^2$, thickness = dr

So Prob = $|\psi|^2 \times 4\pi r^2 dr$.

Radial Distribution Function P(r)

Probability of finding the electron between two spherical shells of thickness r and $r + dr$

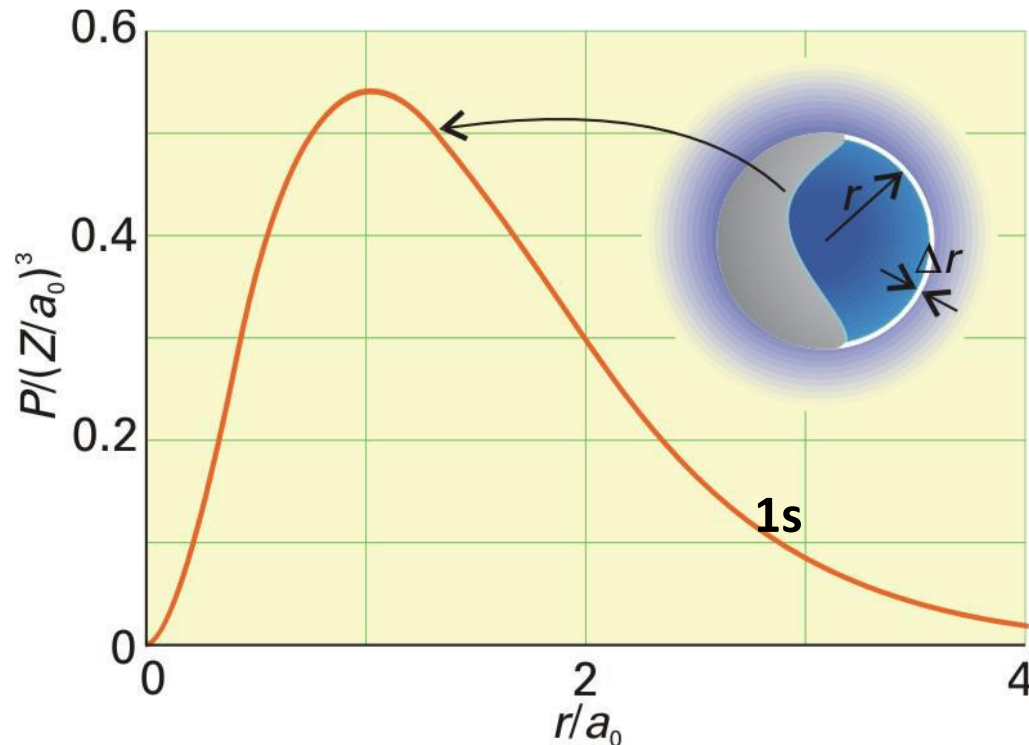
$$= [R_{nl}(r)]^2 r^2 dr = P(r) dr$$

Radial distribution function (RDF)

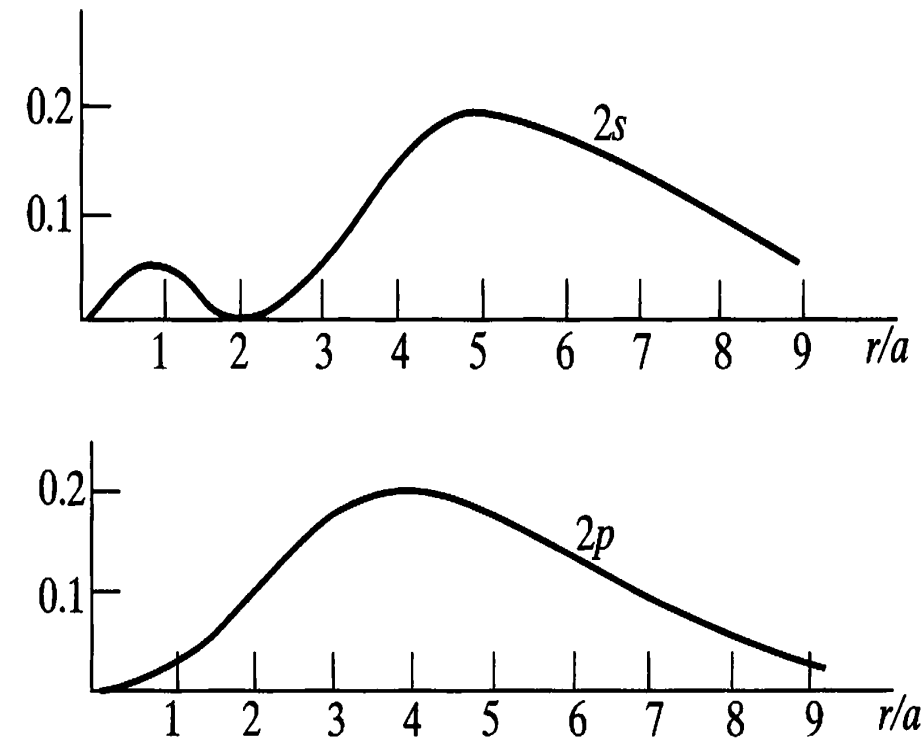
$$P(r) = [R_{nl}(r)]^2 r^2$$

For spherically symmetric orbitals,

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

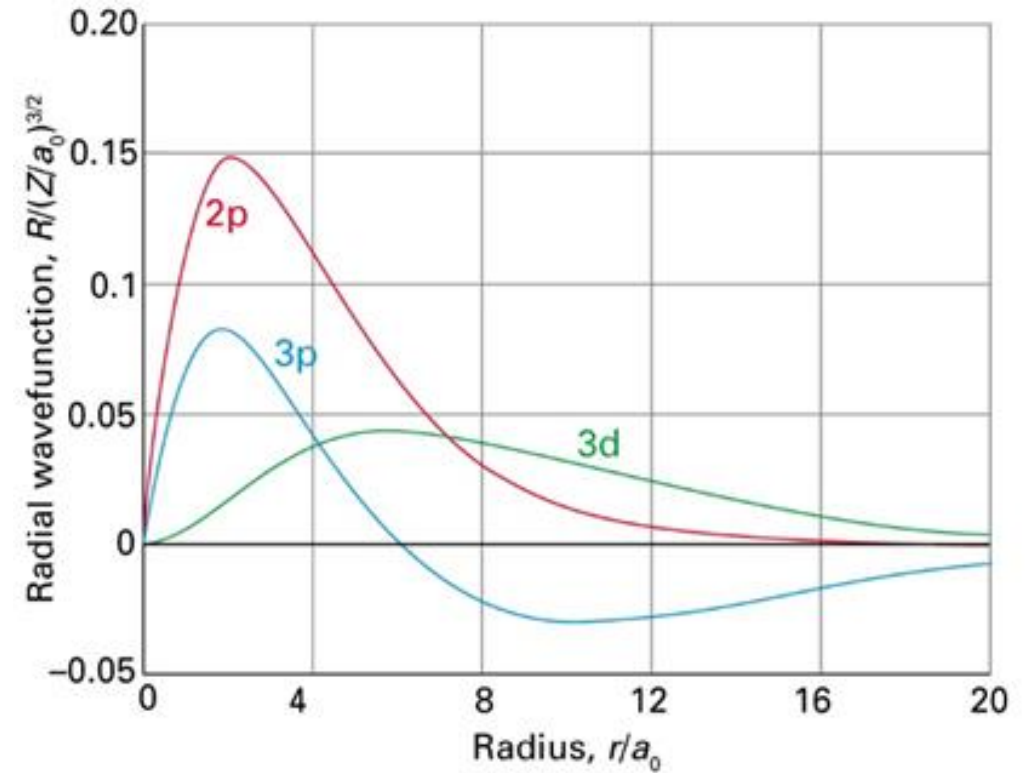
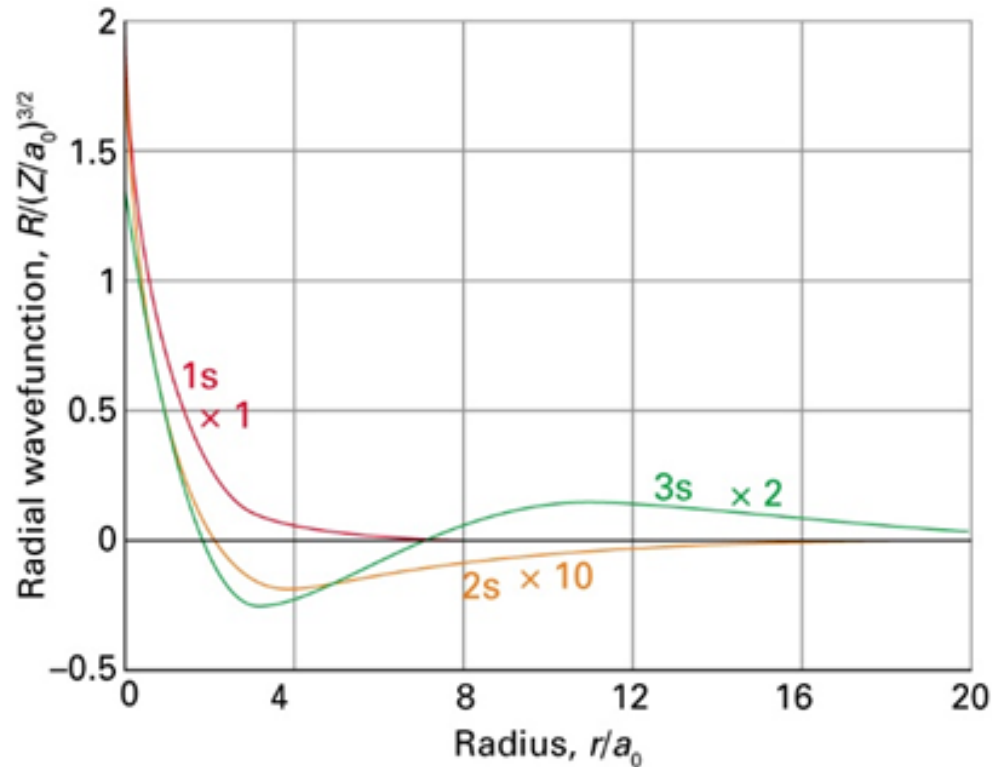


Thus, the RDF gives the probability that an electron will be found anywhere in a shell of radius r and thickness Δr regardless of angle.



Radial Wavefunctions

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



$$R_{1s} = 2 \left(\frac{Z}{a} \right)^{3/2} e^{-Zr/a}$$

$$R_{2s} = \frac{1}{\sqrt{2}} \left(\frac{Z}{a} \right)^{3/2} \left(1 - \frac{Zr}{2a} \right) e^{-Zr/2a}$$

$$R_{3s} = \frac{2}{3\sqrt{3}} \left(\frac{Z}{a} \right)^{3/2} \left(1 - \frac{2Zr}{3a} + \frac{2Z^2 r^2}{27a^2} \right) e^{-Zr/3a}$$

**Number
of
radial node
=
(n - l - 1)**

$$R_{2p} = \frac{1}{2\sqrt{6}} \left(\frac{Z}{a} \right)^{5/2} r e^{-Zr/2a}$$

$$R_{3p} = \frac{8}{27\sqrt{6}} \left(\frac{Z}{a} \right)^{3/2} \left(\frac{Zr}{a} - \frac{Z^2 r^2}{6a^2} \right) e^{-Zr/3a}$$

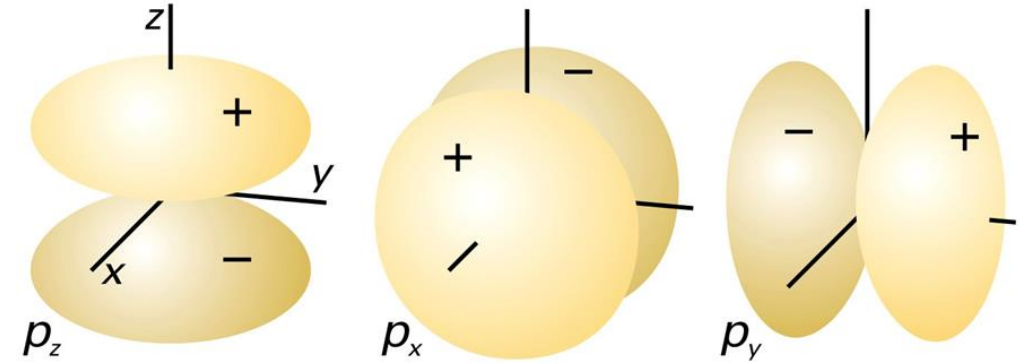
$$R_{3d} = \frac{4}{81\sqrt{30}} \left(\frac{Z}{a} \right)^{7/2} r^2 e^{-Zr/3a}$$

Other Hydrogenic Wavefunctions

The p-orbitals ($l = 1$):

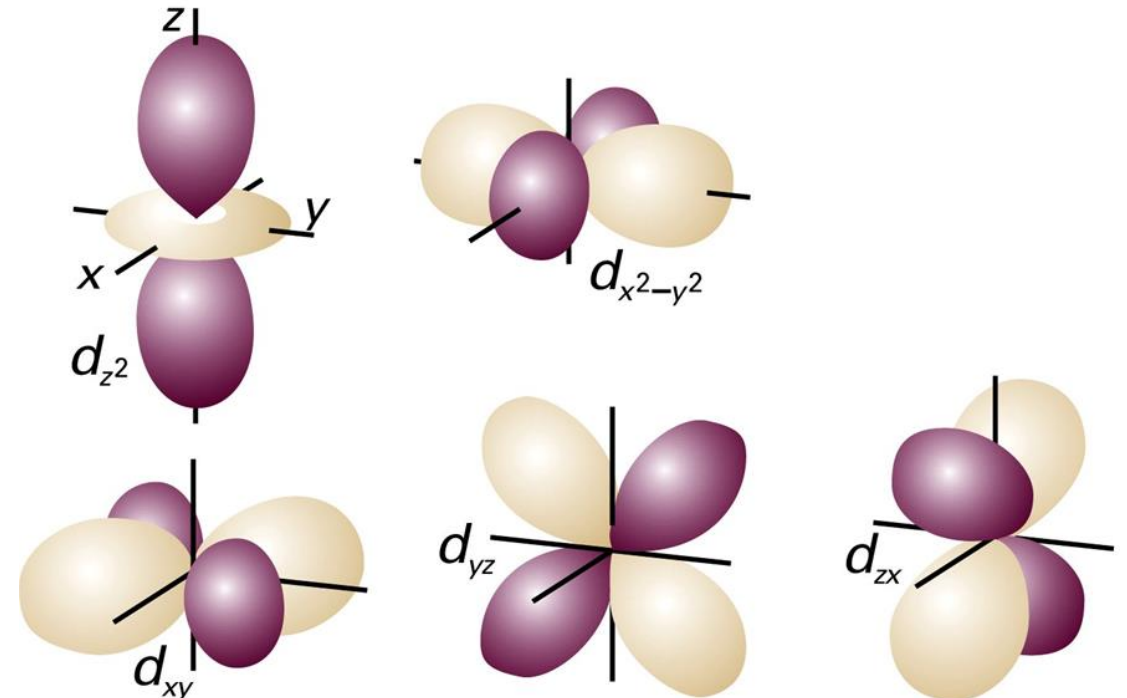
$$\begin{aligned}\psi_{2p_z} &= \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta \times \frac{1}{2} \left(\frac{1}{6a_0^3}\right)^{1/2} \frac{r}{a_0} e^{-r/2a_0} \\ &= \left(1/32\pi a_0^5\right)^{1/2} r \cos \theta e^{-r/2a_0}\end{aligned}$$

\swarrow \searrow
 $\psi_{2p_x} \rightarrow \sin \theta \cos \varphi$ $\psi_{2p_y} \rightarrow \sin \theta \sin \varphi$



The d-orbitals ($l = 2$):

$$\begin{aligned}3d_{z^2} &= \frac{1}{81(6\pi)^{1/2}} \left(\frac{Z}{a}\right)^{7/2} r^2 e^{-Zr/3a} (3 \cos^2 \theta - 1) \\ 3d_{x^2-y^2} &= \frac{1}{81(2\pi)^{1/2}} \left(\frac{Z}{a}\right)^{7/2} r^2 e^{-Zr/3a} \sin^2 \theta \cos 2\phi \\ 3d_{xz} &= \frac{2^{1/2}}{81\pi^{1/2}} \left(\frac{Z}{a}\right)^{7/2} r^2 e^{-Zr/3a} \sin \theta \cos \theta \cos \phi\end{aligned}$$



See Table 8A.1 for more orbitals

Original solutions:

$$\psi_{2p_{-1}} = \frac{1}{8\pi^{1/2}} \left(\frac{Z}{a} \right)^{5/2} r e^{-Zr/2a} \sin \theta e^{-i\phi}$$

$$\psi_{2p_0} = \frac{1}{\pi^{1/2}} \left(\frac{Z}{2a} \right)^{5/2} r e^{-Zr/2a} \cos \theta$$

$$\psi_{2p_1} = \frac{1}{8\pi^{1/2}} \left(\frac{Z}{a} \right)^{5/2} r e^{-Zr/2a} \sin \theta e^{i\phi}$$

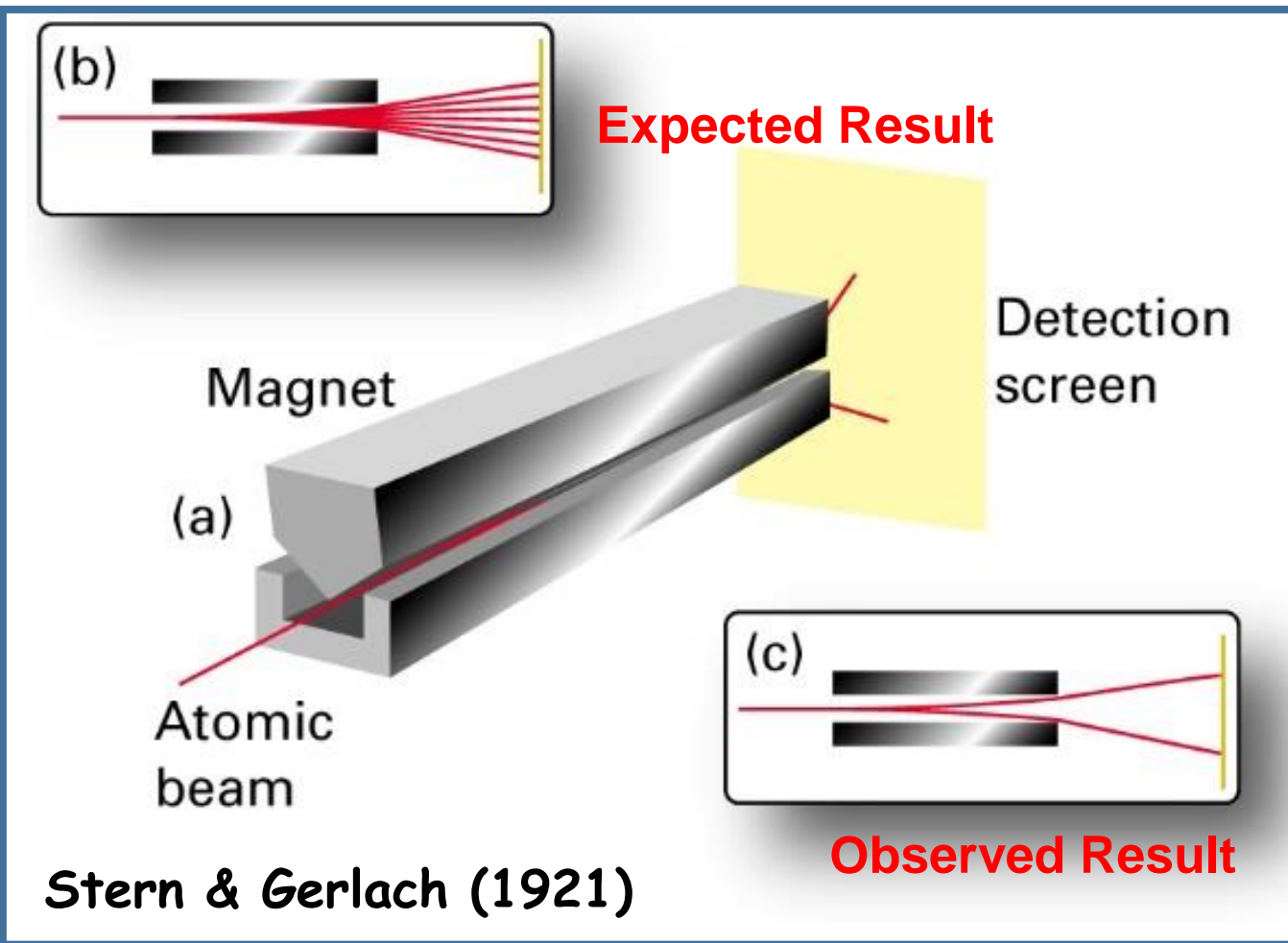
Combine these two functions to obtain real functions:

$$\psi_{2p_x} \equiv \frac{1}{\sqrt{2}} (\psi_{2p_{-1}} + \psi_{2p_1}) = \frac{1}{4\sqrt{2}\pi} \left(\frac{Z}{a} \right)^{5/2} r e^{-Zr/2a} \sin \theta \cos \phi$$

$$\psi_{2p_y} \equiv \frac{1}{i\sqrt{2}} (\psi_{2p_1} - \psi_{2p_{-1}}) = \frac{1}{4\sqrt{2}\pi} \left(\frac{Z}{a} \right)^{5/2} r \sin \theta \sin \phi e^{-Zr/2a}$$

Electron Spin

Shot silver ($Z=47$) beam through an inhomogeneous magnetic field

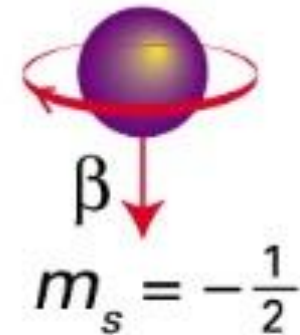
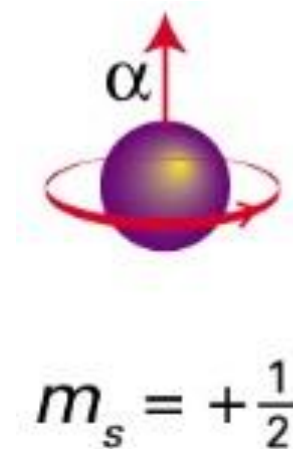
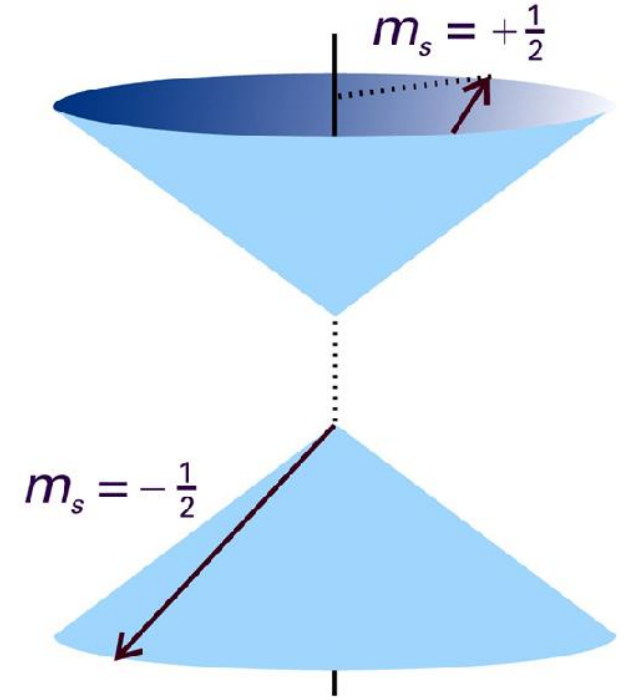


- ❑ This **intrinsic angular momentum** of the electron is called its **spin**.
- ❑ Electron spin is described by spin quantum number ($s = 1/2$).
- ❑ It is a quantum mechanical phenomenon - NO classical counterpart.

Observed angular momentum was due to the motion of the electron about its own axis.

Electron Spin

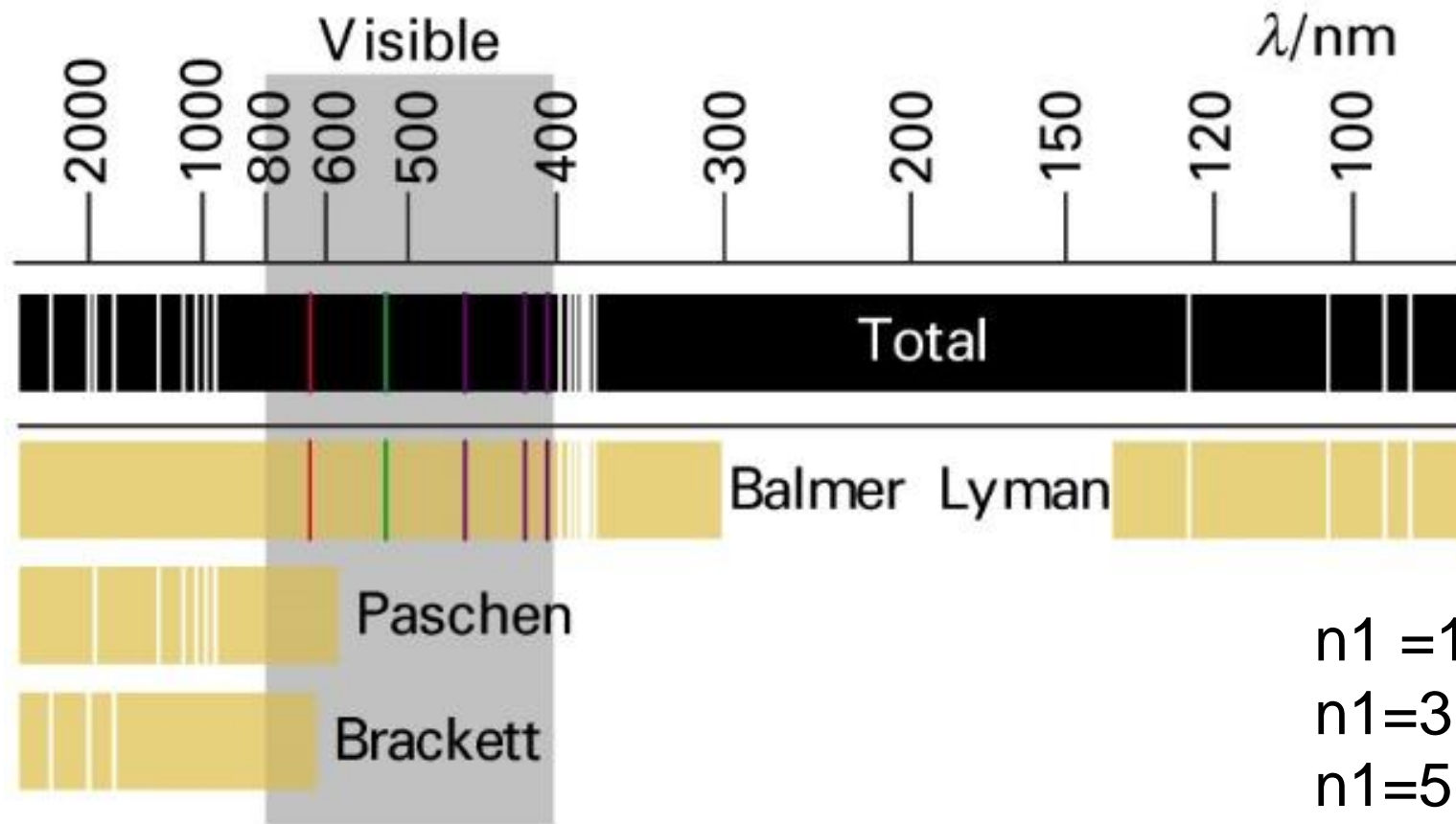
- ❑ Described by spin Quantum number $s = 1/2$
- ❑ The magnitude of the spin angular momentum is $(3^{1/2}/2)\hbar$
- ❑ Two allowed spin states of electron $m_s(+1/2$ or $-1/2)$
- ❑ Directions of spin are opposite



Can be clockwise or counterclockwise

The permitted energies of hydrogenic atoms

The spectrum of atomic hydrogen - excited H atoms emit light of discrete frequencies, producing a series of 'lines'.



$$\Delta E = h\nu = hc\tilde{\nu}$$

Rydberg (1890)

$$\tilde{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

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

$n_1 = 1$ Lyman,

$n_1 = 3$ Paschen,

$n_1 = 5$ Pfund

$n_1 = 2$ Balmer,

$n_1 = 4$ Brackett,

$n_2 > n_1$

During a transition, a photon (with its one unit of angular momentum) is generated.

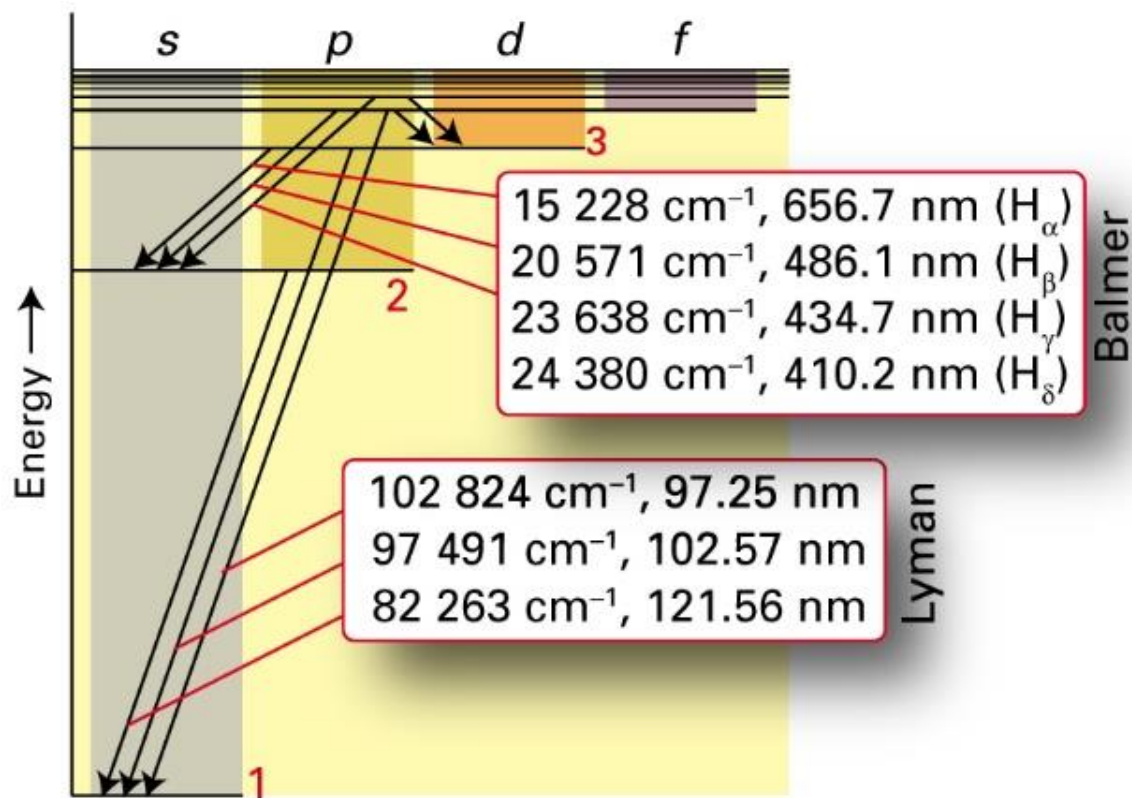
Selection Rules for transitions

To compensate for the angular momentum carried away by photon, the angular momentum of electron must change by one unit.

Selection rule: $\Delta l = \pm 1, \Delta m_l = 0, \pm 1$

Transitions

$d(l=2) \rightarrow s(l=0)$: **Not allowed**
 $s(l=0) \rightarrow p(l=1)$: **Allowed**



The Grotrian Diagram

Transition dipole moment

$$\mu_s = \int \psi_f \hat{\mu} \psi_i d\tau$$

$\mu_s \neq 0$, transition is allowed

$\mu_s = 0$, transition is not allowed

Self-Study Portions

Topic 8B: Many electron atoms

Topic 8C: Periodic Trends of atomic properties

Many-electron Atoms

- ❑ All electrons interact with one another
- ❑ Schrödinger equation is very complicated

Orbital approximation:

(Exact wavefunction) $\psi \approx \psi(1)\psi(2)\psi(3) \dots \psi(n)$

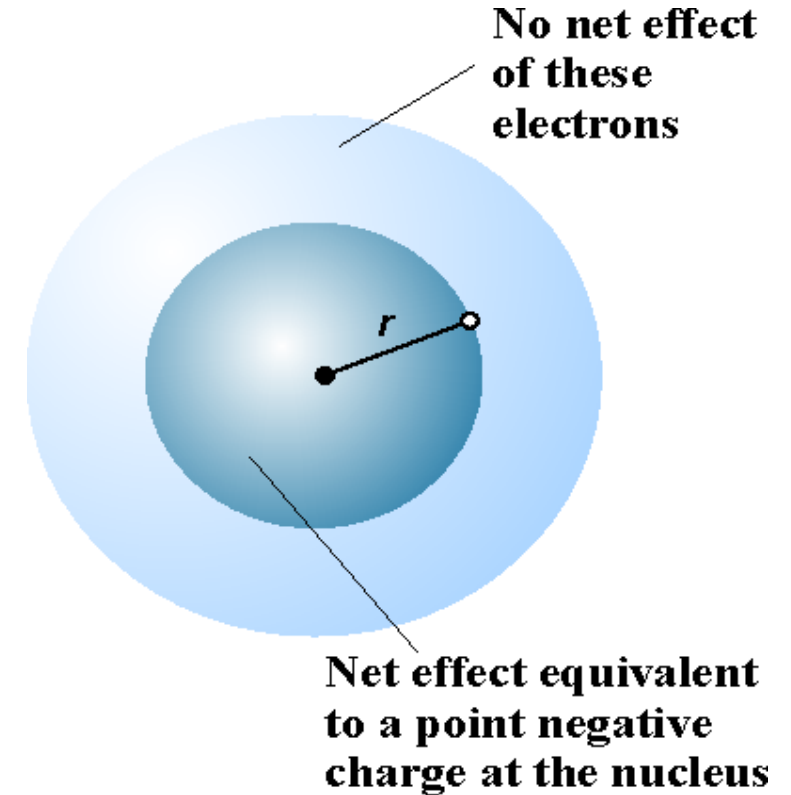
Pauli Principle:

- Not more than two electrons can occupy one orbital
- Spins must be paired when two electrons occupy one orbital
- **Paired spins**-zero net spin angular momentum

Penetration and shielding

Lowest energy configuration of Li \rightarrow [He]2s¹ or [He]2p¹ ?

- 2s, 2p orbitals are nondegenerate unlike hydrogenic atoms
- Electron at distance r from nucleus experiences repulsion
- This is modelled as point negative charge on the nucleus with magnitude equal to charge of electrons within a sphere of radius r
- Ze is changed to $Z_{\text{eff}}e$
- Shielded nuclear charge

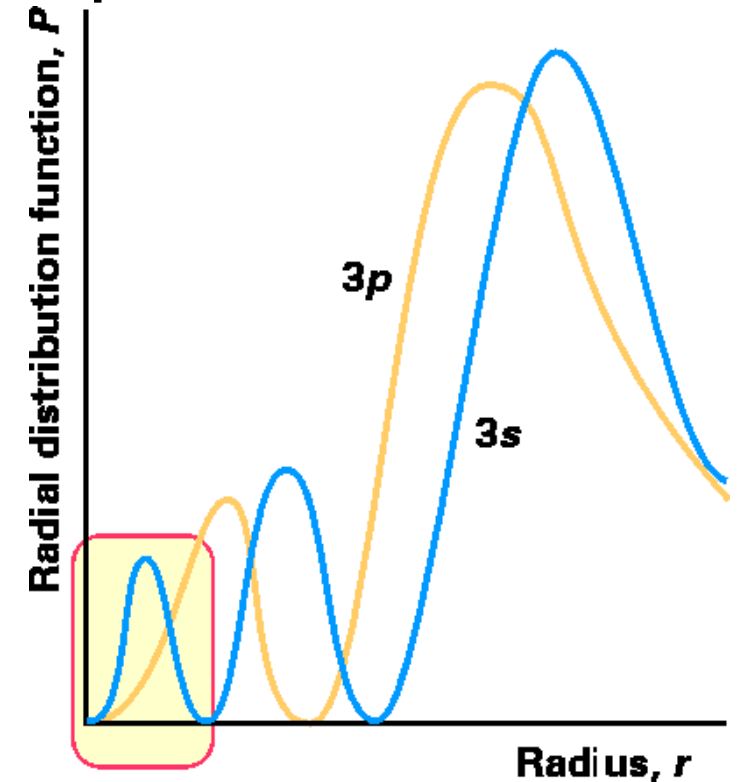


Penetration and shielding

Effective nuclear charge experienced by s and p electrons are different

S electron:

- Greater penetration through inner shells than p electron
- More likely to be found close to nucleus than p electron
- Experiences less shielding, larger Z_{eff}



The order of energies of orbitals in same shell (n) is **$s < p < d < f$**

- Individual orbitals of a given subshell are degenerate
- They all have same radial character
- They all experience same effective nuclear charge

Building up principle

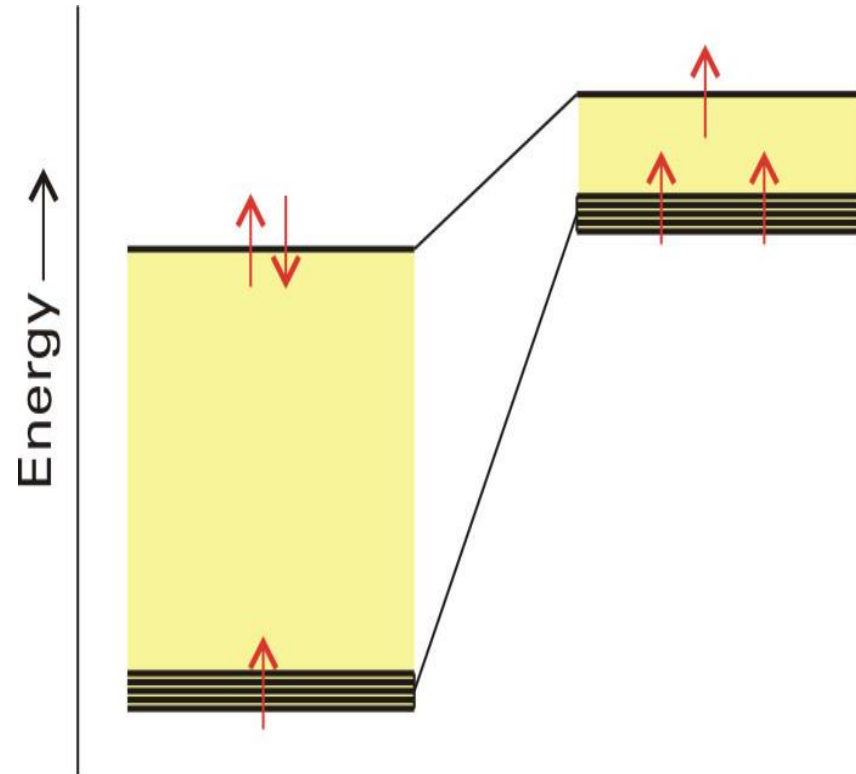
- The order of the occupation of orbitals
1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 5d 4f 6p.....
- Each orbital can accommodate up to 2 electrons
- Electrons occupy different orbitals of a subshell
Before doubly occupying any one
- An atom adopts a configuration with the greatest number of unpaired electrons, in ground state

Hund's rule

The occupation of d orbitals

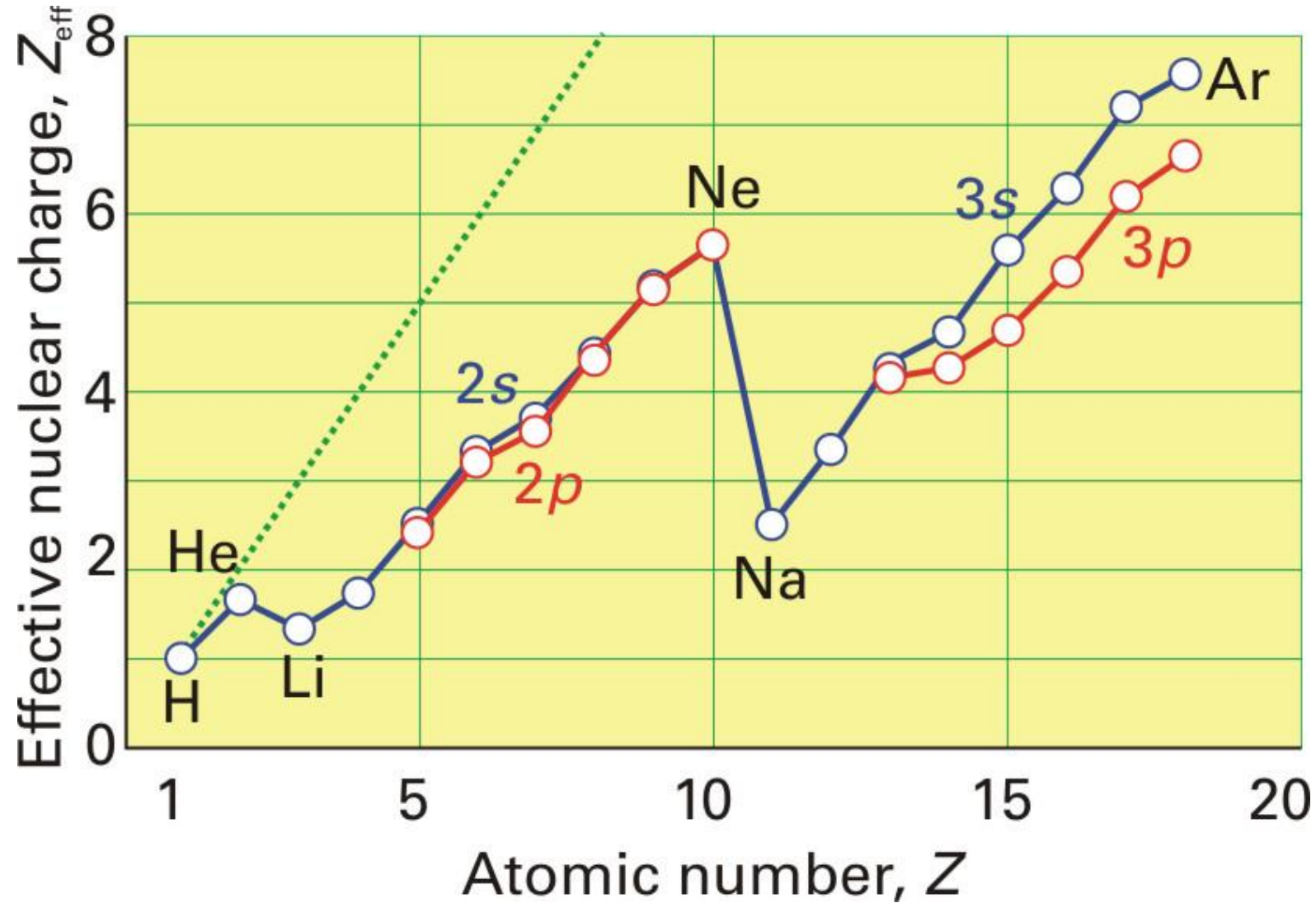
Sc(21): [Ar] 3d³ ??
or [Ar] 3d² 4s¹

Sc: [Ar] 3d¹ 4s²



The most probable distance of a 3d electron from the nucleus is less than that for a 4s electron.

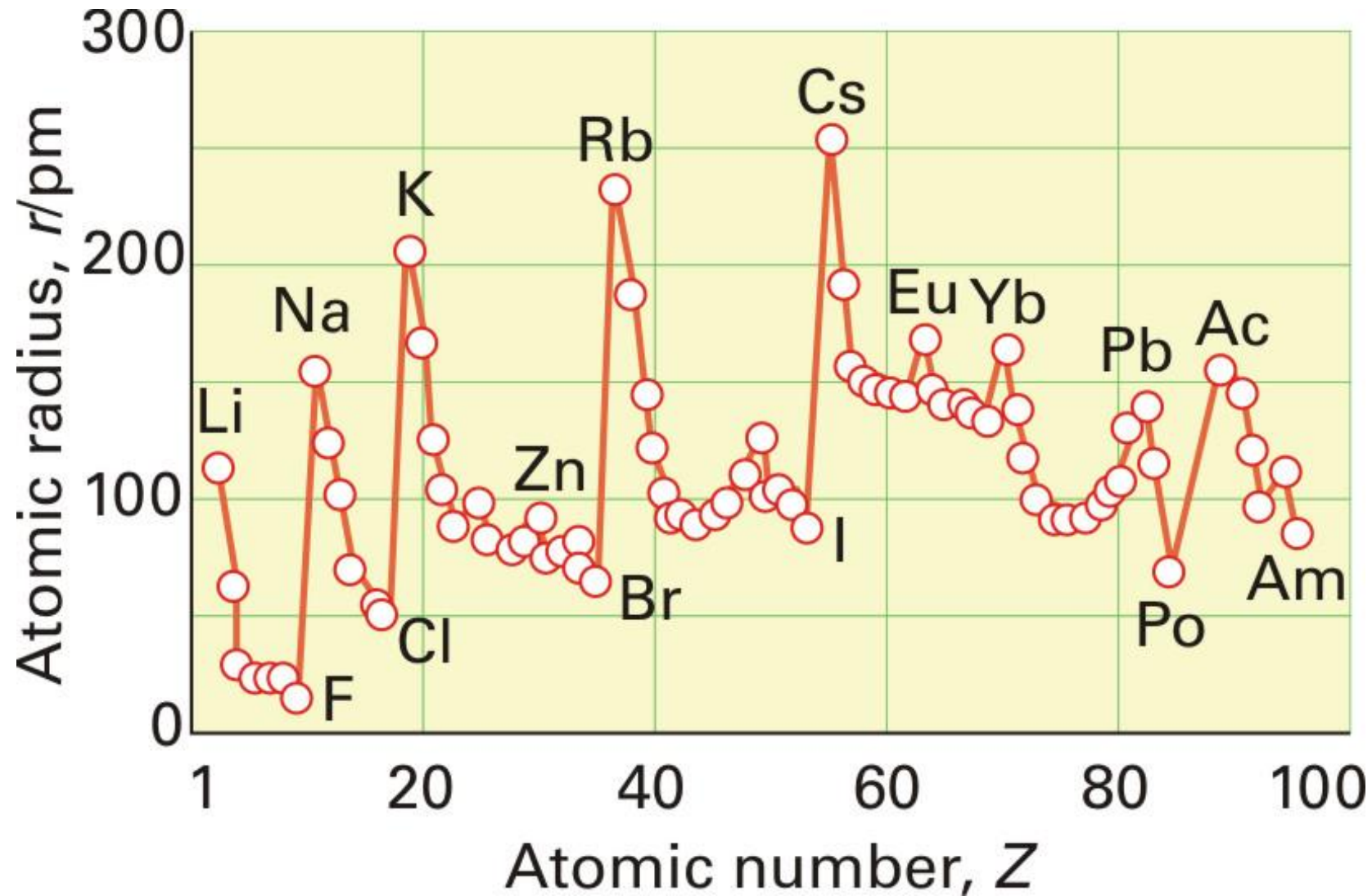
Periodic trends in atomic properties



Atomic radii of main-group elements, r/pm

Li	Be	B	C	N	O	F
157	112	88	77	74	66	64
Na	Mg	Al	Si	P	S	Cl
191	160	143	118	110	104	99
K	Ca	Ga	Ge	As	Se	Br
235	197	153	122	121	117	114
Rb	Sr	In	Sn	Sb	Te	I
250	215	167	158	141	137	133
Cs	Ba	Tl	Pb	Bi	Po	
272	224	171	175	182	167	

Periodic trends in atomic radii



Periodic trends in first ionization energies

