Hydrogen Atom

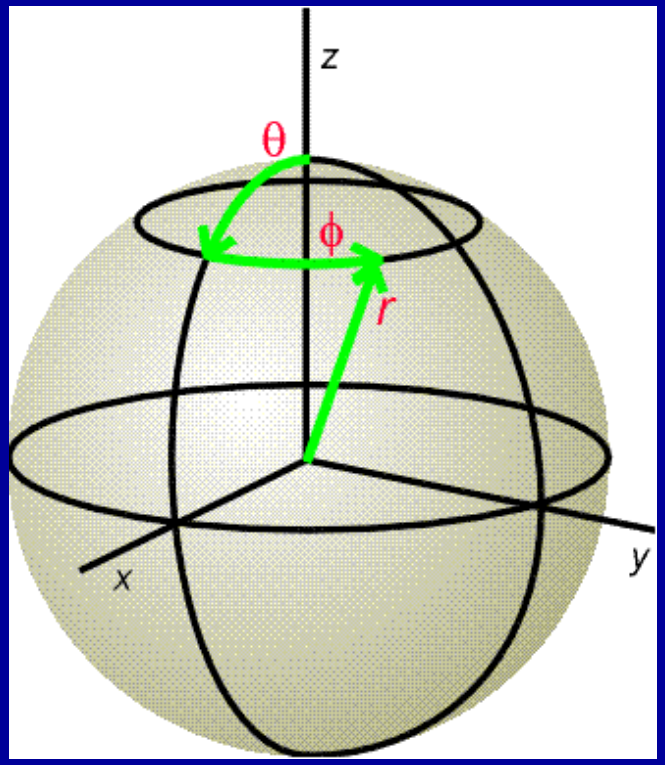
The simplest system: p + e

Schroedinger equation can be solved exactly

Spherical symmetry

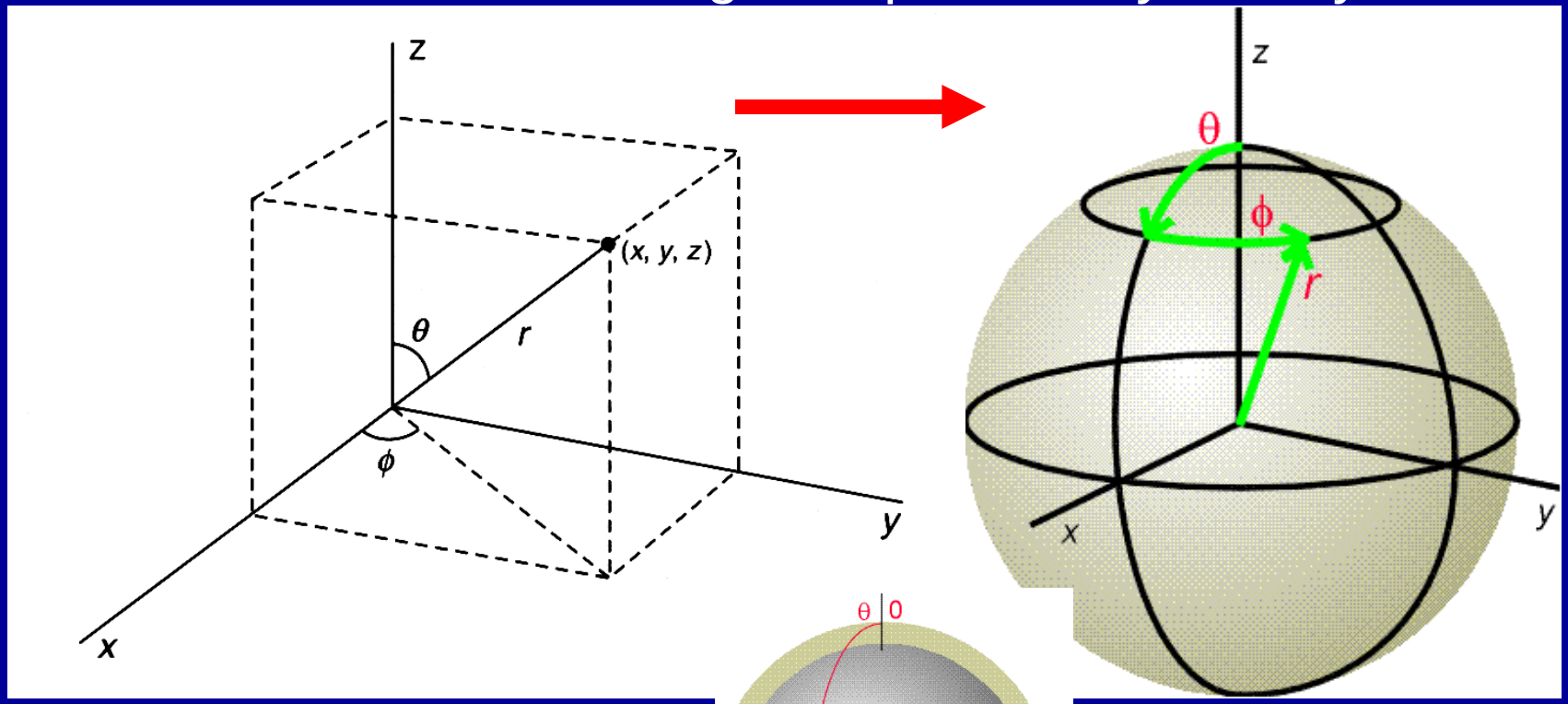
Potential energy between p + e

$$V = -\frac{e^2}{4\pi\varepsilon_0 r}$$

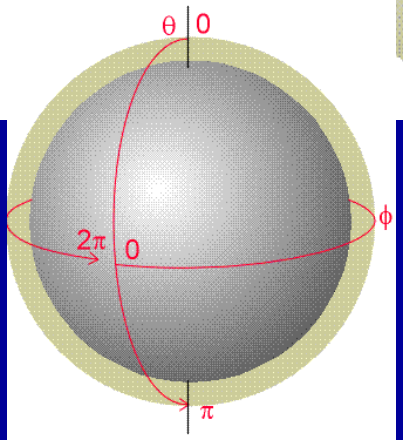


Polar Coordinates

Take advantage of spherical symmetry



$\Psi(x,y,z) \rightarrow \Psi(r,\theta,\phi)$



x = ?

y = ?

z = r cos q

Radial and Angular Part

$$\Psi_{n,\,l,\,m}(r,\theta,\phi) = N \times R_{n,\,l}(r) \times \chi_{l,\,m}(\theta,\phi)$$

Separation of variables

$R_{n,\,l}(r)$ = radial part of the wave function, depends only on distance from a nucleus - r

$\chi_{l,\,m}(\theta,\phi)$ = angular (angles) part of the wave function, depends only on direction - θ, ϕ

N = normalisation constant

In order to be $\int |\Psi|^2 \, dV = +1$

Normalisation condition - electron is definitely somewhere with probability = 1

Quantum Numbers

$R_{n,\,l}(r)$ depends on quantum numbers *n* and *l*

$\chi_{l,\,m}(\theta, \phi)$ depends on quantum numbers *l* and m_l

Principal quantum number *n*, (1 to ∞)

Angular momentum quantum number *l*, (0 to n –1)
l = 0 (s), 1 (p), 2 (d), 3 (f), 4 (g), 5 (h), ...

Magnetic quantum number m_l, (+ *l*, ...0, ... –*l*)
For each *l* there is (2*l* + 1) values of m_l

Magnetic spin quantum number m_s (±½)

Wave Functions of H atom

$$\varphi_{1,0,0} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

$$\varphi_{2,0,0} = \frac{1}{\sqrt{8\pi a_0^3}} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$$

$$\varphi_{2,1,0} = \frac{1}{4\sqrt{2\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \cos\theta$$

$$\varphi_{2,1,1} = -\frac{1}{8\sqrt{\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \sin\theta\, e^{i\phi}$$

$$\varphi_{3,0,0} = \frac{1}{3}\sqrt{\frac{1}{3\pi a_0^3}} \left[1 - \frac{2}{3}\frac{r}{a_0} + \frac{2}{27}\left(\frac{r}{a_0}\right)^2\right] e^{-r/3a_0}$$

$$\varphi_{3,1,m} = \frac{4}{27}\sqrt{\frac{2}{3a_0^3}} \frac{r}{a_0} \left(1 - \frac{1}{6}\frac{r}{a_0}\right) e^{-r/3a_0} Y_{1,m}(\theta,\phi)$$

$$\varphi_{3,2,m} = \frac{2}{81}\sqrt{\frac{2}{15a_0^3}} \left(\frac{r}{a_0}\right)^2 e^{-r/3a_0} Y_{2,m}(\theta,\phi)$$

- solution of Schrödinger equation
- complex function of coordinates x, y, z or better r, ϕ, θ
- no physical meaning
- positive and negative values
- $|\Psi|^2$ probability density of **finding electron** e

Radial Part of the Wave Function of H Atom

n	l	m_l	$R_{n,l}(r)$
1 (K)	0 (s)	0	$2\,(Z/a_0)^{3/2}\exp(-Zr/a_0)$
2 (L)	1 (p)	0	$2\,(Z/2a_0)^{3/2}\,(1-Zr/2a_0)\exp(-Zr/2a_0)$
2 (L)	1 (p)	±1	$2/\sqrt{3}\,(Z/2a_0)^{3/2}\,(Zr/2a_0)\exp(-Zr/2a_0)$

Electron Energy in H-type Atoms

$$E_n = -\frac{N_A \mu e^4}{8\varepsilon_0^2 h^2}\frac{Z^2}{n^2}$$

μ = reduced mass of nucleus-electron
e = elementary charge, ε_0 = permitivity of vacuum
Z – the higher a nucleus charge the stronger is an electron bound, the lower energy has, one-electron ions (He^+, Li^{2+},....)
n – the higher a principal number the less stable e is

Corresponds to Bohr's eq.!!

$$E_n = -E_0 \frac{Z^2}{n^2}$$

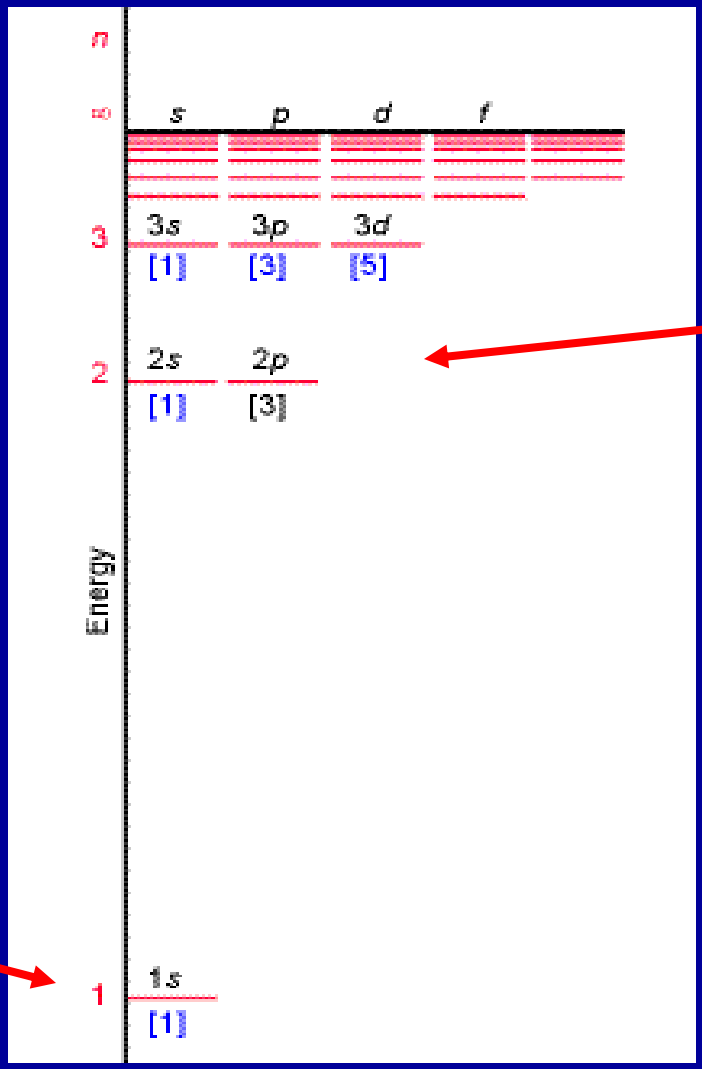
Electron Energy in H-type Atoms

$$E_n = -\frac{N_A \mu e^4}{8\varepsilon_0^2 h^2}\frac{Z^2}{n^2}$$

Energy depend ONLY on *n*

$E_1 = -13.6$ eV

(13.6 eV = 1 Ry)



$E_2 = ?$

Principal Quantum Number n

Gives the levels energy
Higher n has higher energy - less stable
n same as in the Bohr's model

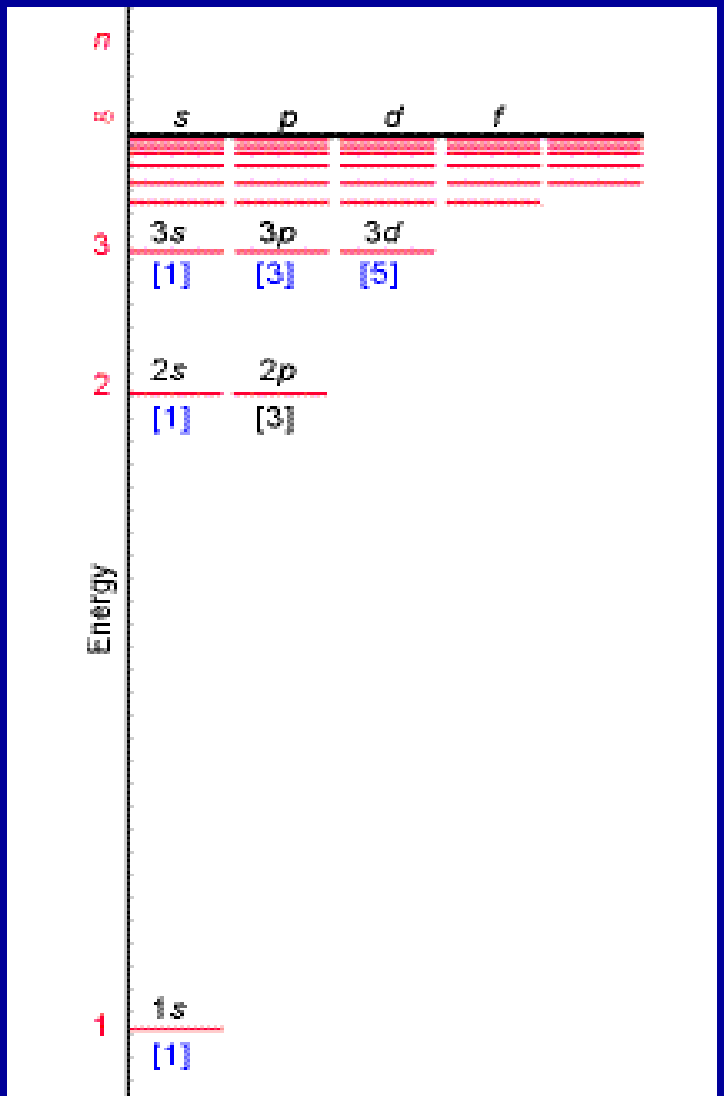
Attains values 1 to ∞

For each *n* there is n^2 of degenerate levels

$l = n - 1$

$$\sum (2l + 1) = n^2$$

$l = 0$



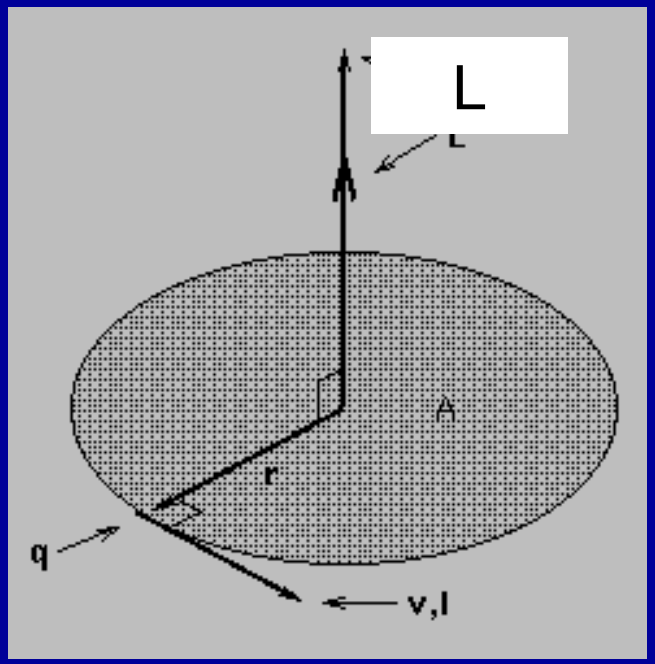
Orbital Angular Momentum

L = Orbital angular momentum (vector)

L = m × v × r = p × r

$$L = \hbar\sqrt{l(l+1)}$$

Describes movements of electrons in orbitals



Angular Momentum Quantum Number *l*

Type of orbital, (0 to n –1)

l	orbital
0	s
1	p
2	d
3	f
4	g
5	h
6	i
7	j
8	k

L = Orbital angular momentum

L = m × v × r

$$L = \hbar\sqrt{l(l+1)}$$

these orbitals are not filled by electrons in atoms in ground state

Magnetic Quantum Number m_l

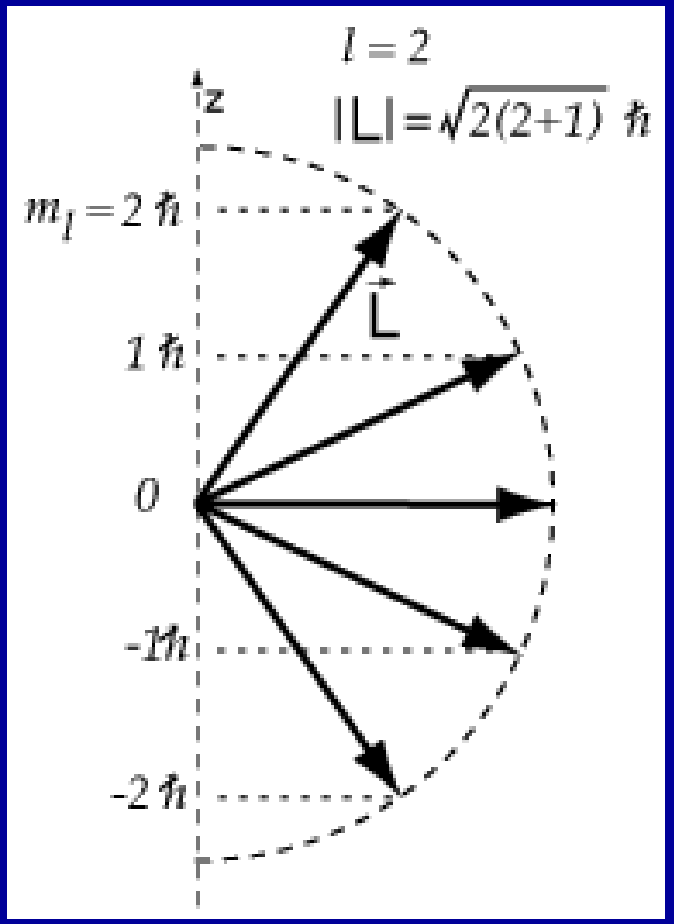
l	orbital	m_l
0	s	0
1	p	1, 0, –1
2	d	2, 1, 0, –1, –2
3	f	3, 2, 1, 0, –1, –2, –3
4	g	these orbitals are not filled by electrons in atoms in ground state
5	h	
6	i	

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

Quantization of Orbital Angular Momentum

$$L = \hbar\sqrt{l(l+1)}$$

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



For each n there is n^2 of degenerate levels

	s	p	d	f	g	h
l =	0	1	2	3	4	5
n = 1	1s					
n = 2	2s	2p				
n = 3	3s	3p	3d			
n = 4	4s	4p	4d	4f		
n = 5	5s	5p	5d	5f	5g	
n = 6	6s	6p	6d	6f	6g	6h

Magnetic Spin Quantum Number m_s

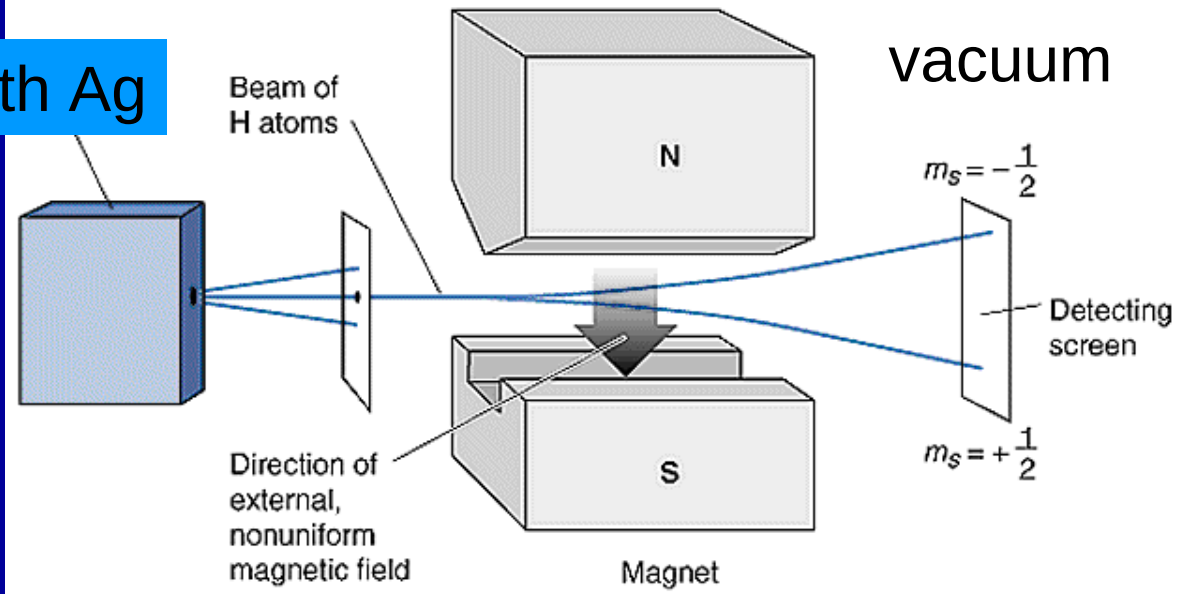
Stern-Gerlach experiment

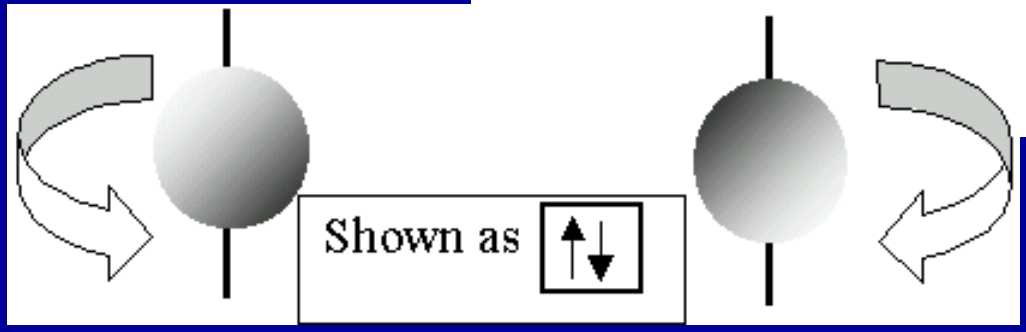
Inhomogeneous magnetic field

Furnace with Ag

vacuum

S = spin momentum



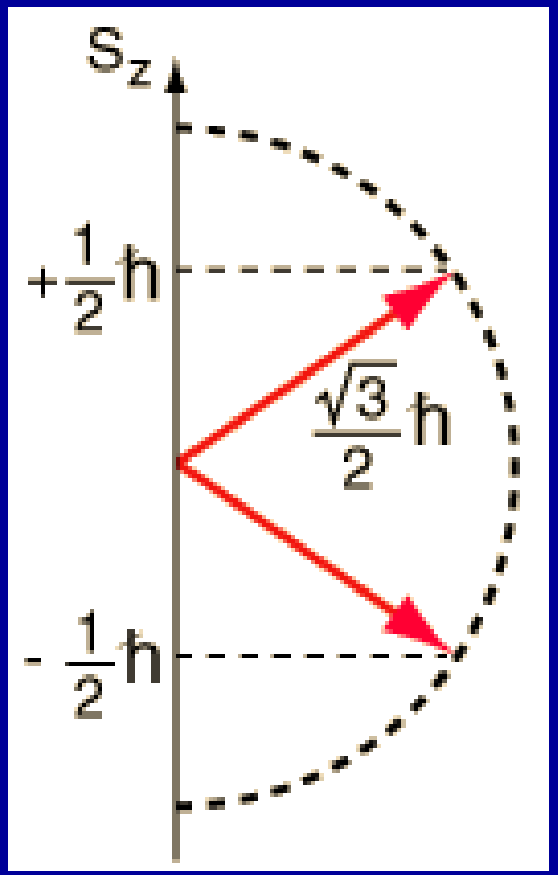


$S = h/2\pi\,[s\,(s+1)]^{1/2}$

$s = 1/2$

$S_Z = m_s\, h/2\pi$

Magnetic Spin Quantum Number m_s

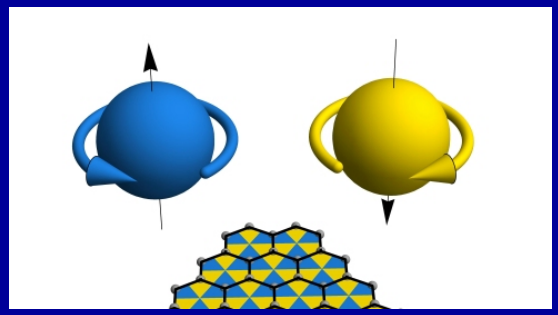


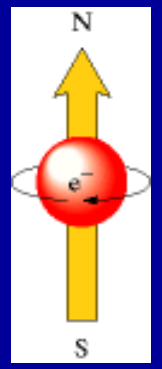
$S = h/2\pi\ [s\ (s+1)]^{½}$

$s = ½$

$S_Z = m_s\ h/2\pi$

$m_s = \pm ½$



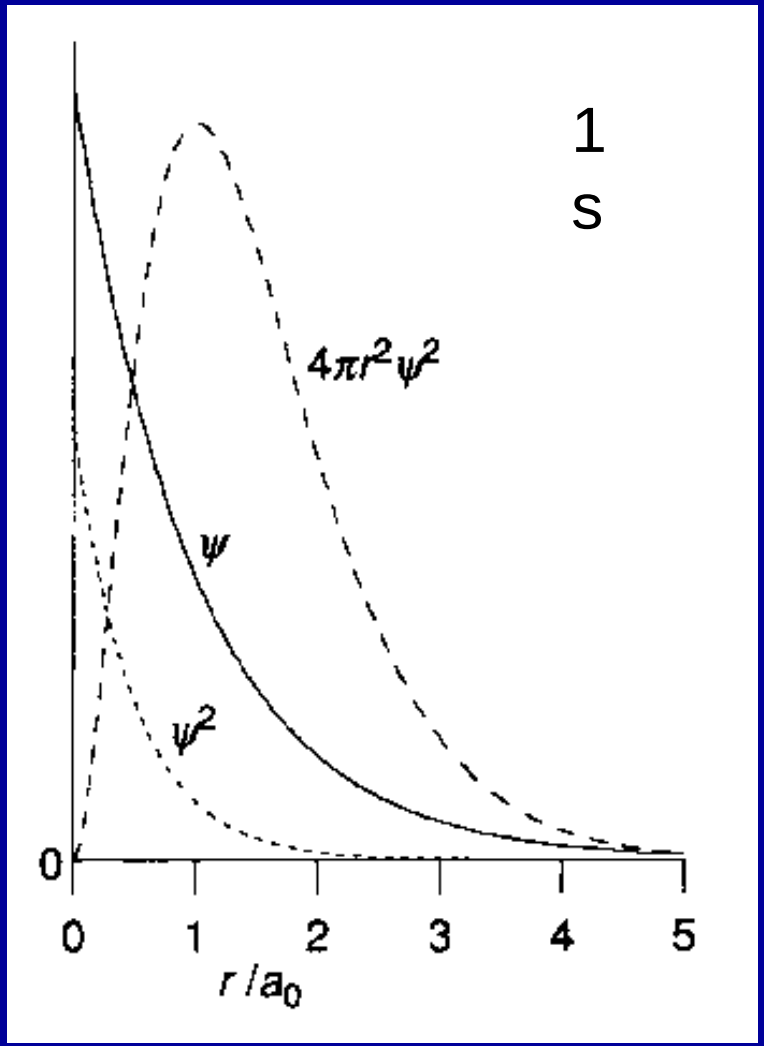


Ψ = Wave Functions

Ψ = solution of Schrödinger equation

$|\Psi|^2$ = probability density of **e**

$|\Psi|^2 dV$ = probability density of finding electron e in volume dV = distribution of electron density



Probability Density

Polar coordinates

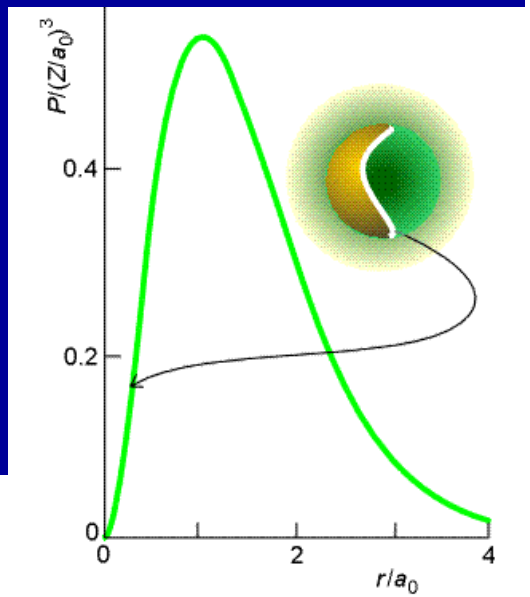
$R_{n,l}(r)$ radial function

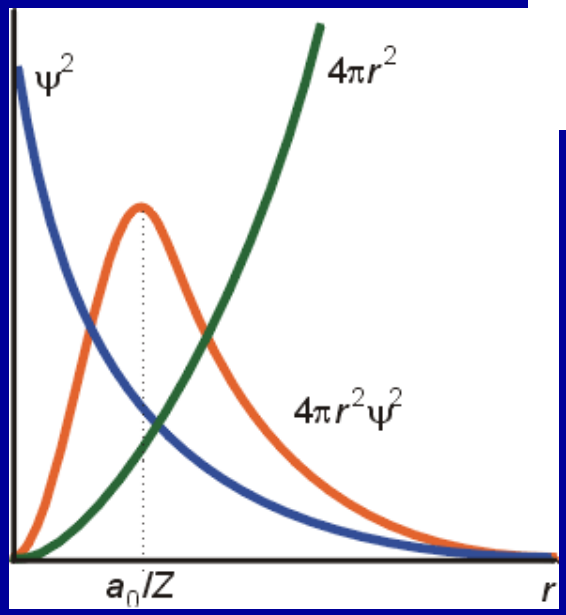
$dV = 4\pi r^2\, dr$ (spherical layer of thickness dr)

Radial distribution function

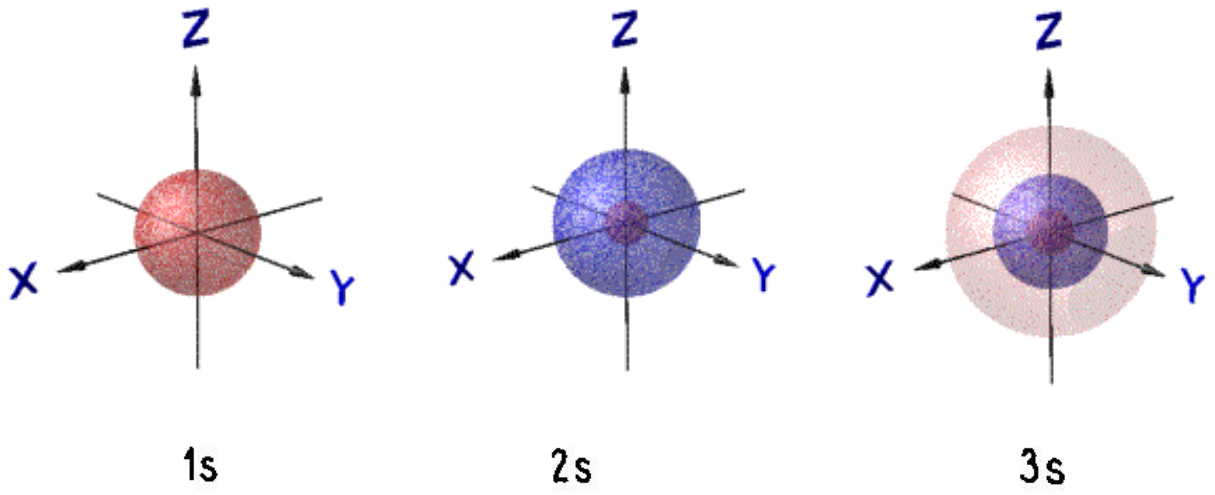
$P = 4\pi r^2 |\Psi|^2\, dr = 4\pi r^2 R^2_{n,l}(r)\, dr$

P = probability density
of finding electron e
in volume
of spherical layer
of thickness dr
In a distance r





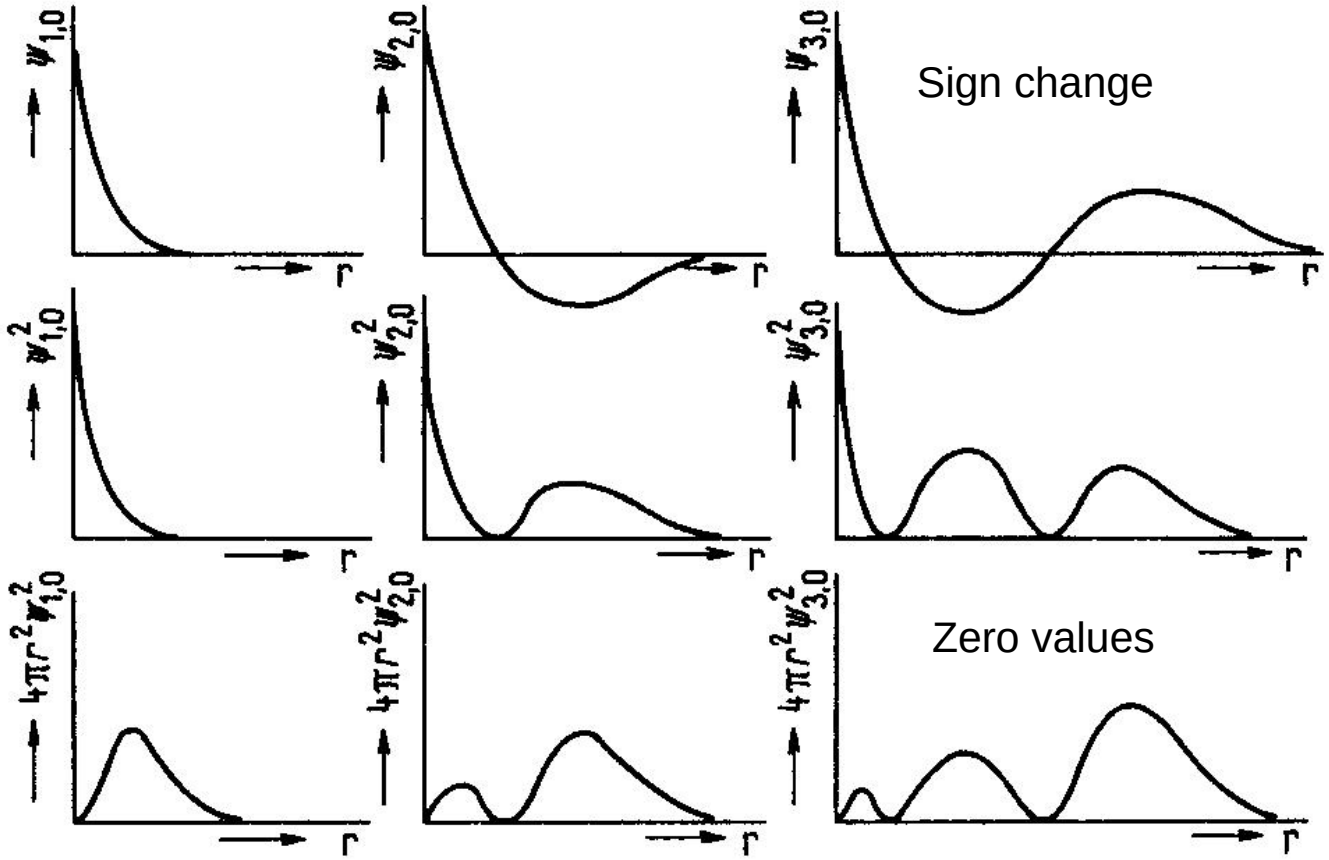
Orbital



Wave Functions

Probability density

Radial distribution function

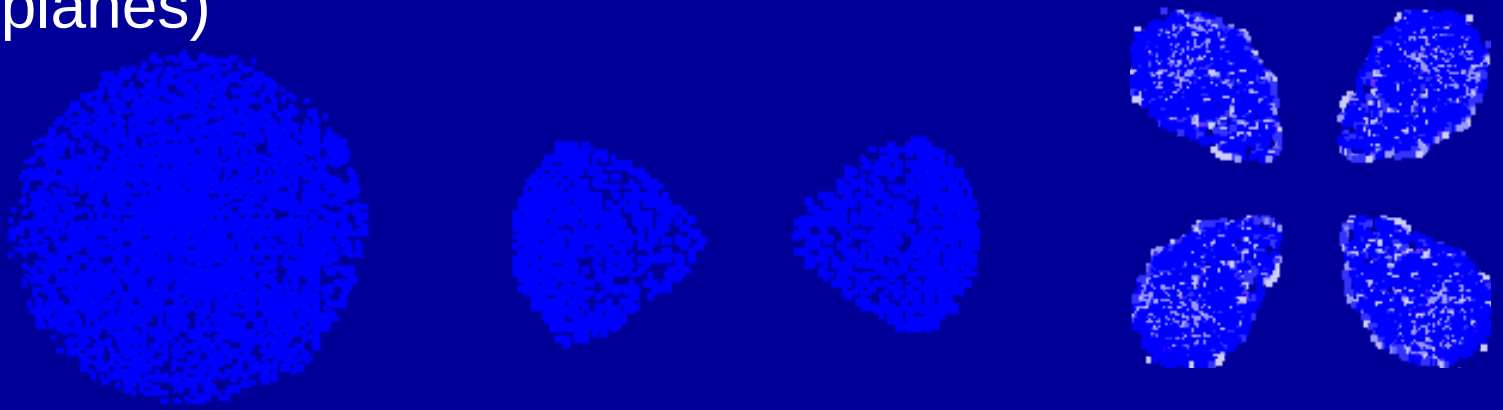


Orbitals

Position of electrons cannot be established – Heisenberg's principle – only probability

Radial function – probability of finding e in a direction away from nucleus (to r = ∞) and number of nodes = zero values of radial distribution function

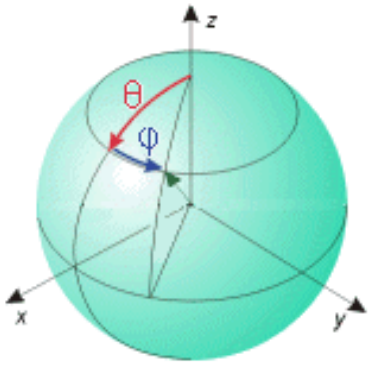
Angular function = shape of orbitals (number of nodal planes)



s - Orbitals

$R_{n,l}(r)$ = Radial function, depends on *r* only

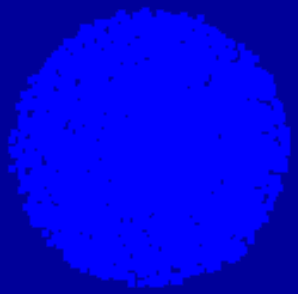
$\chi_{l,m}(\theta, \phi)$ = angular function, is **a constant** for s-orbitals ($l = 0$) = SPHERICAL SHAPE

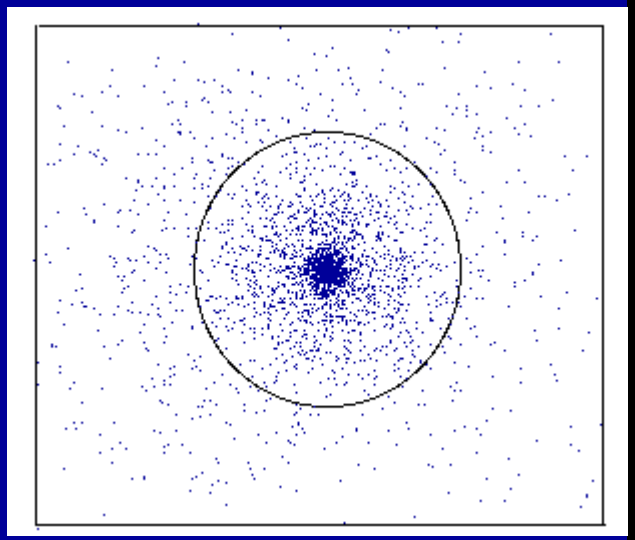


$\psi^2_{0,0}$

$Y_{0,0} = (1/4\pi)^{1/2}$

Atomic Orbital 1s

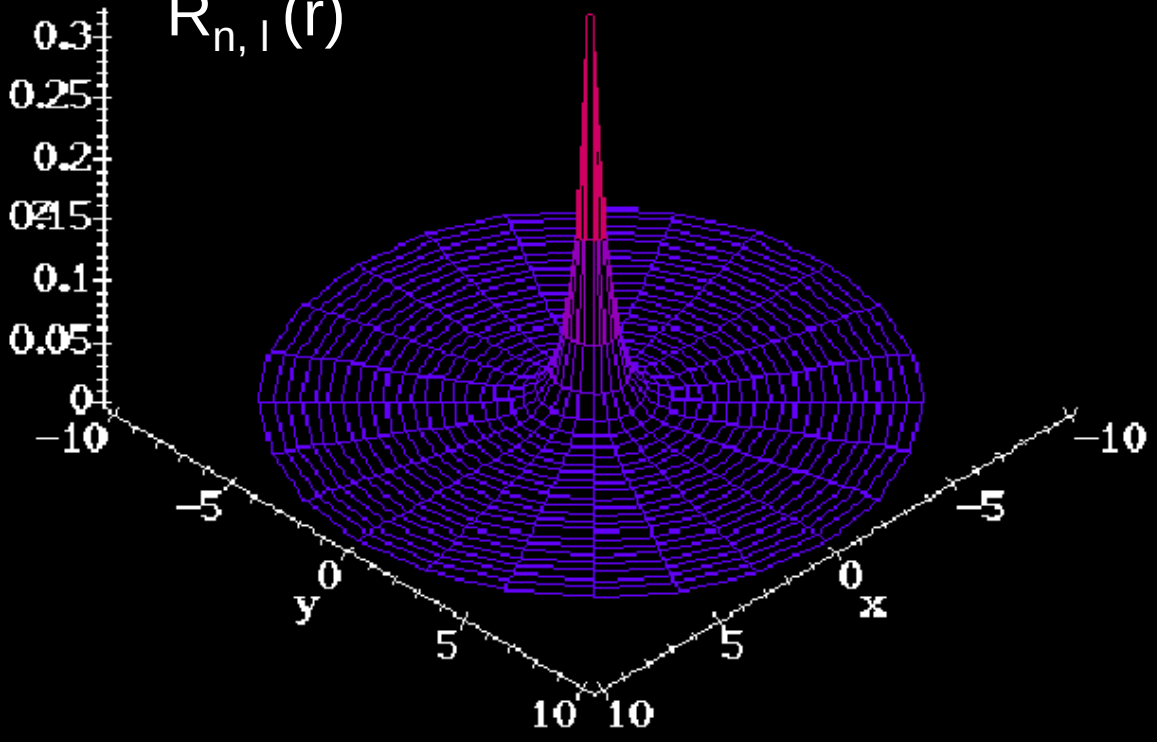




Wave Function 1s

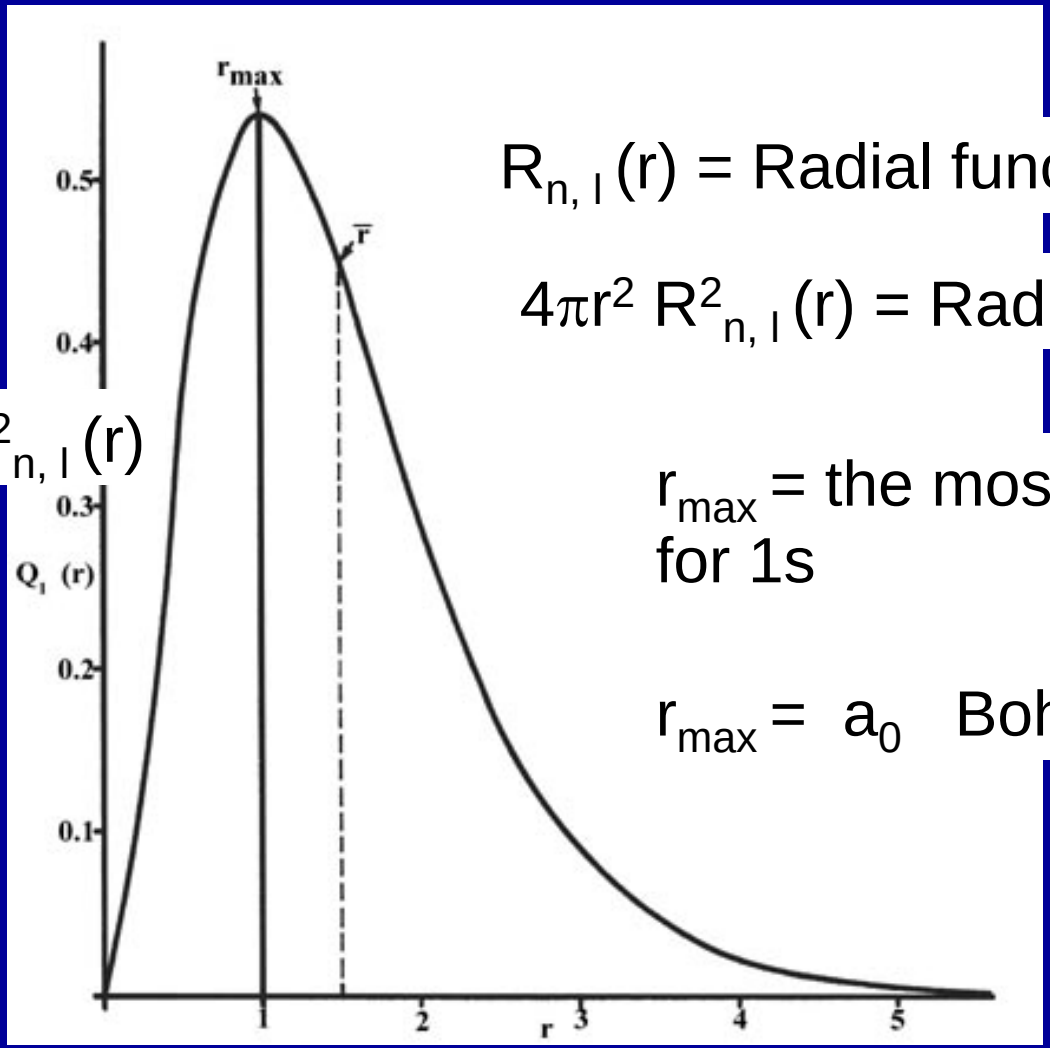
$R_{n,l}(r)$

$n = 1, l = 0$



Radial Distribution Function

$4\pi r^2 R^2_{n,l}(r)$

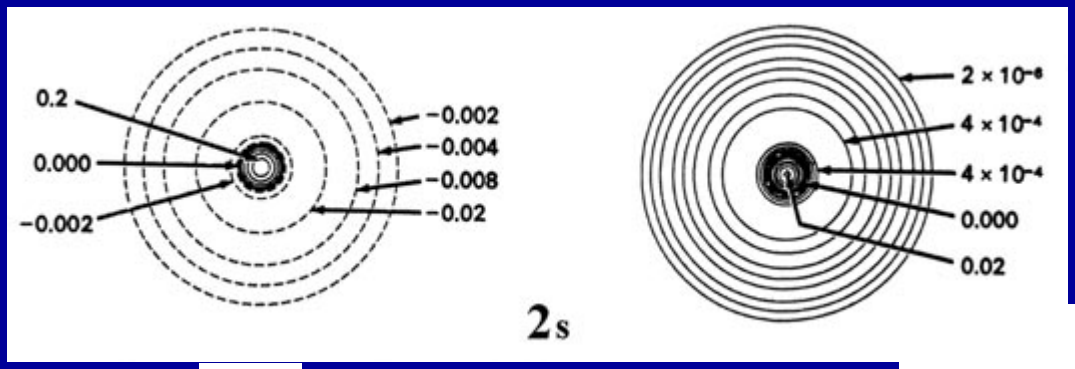


$R_{n,l}(r)$ = Radial function of H atom

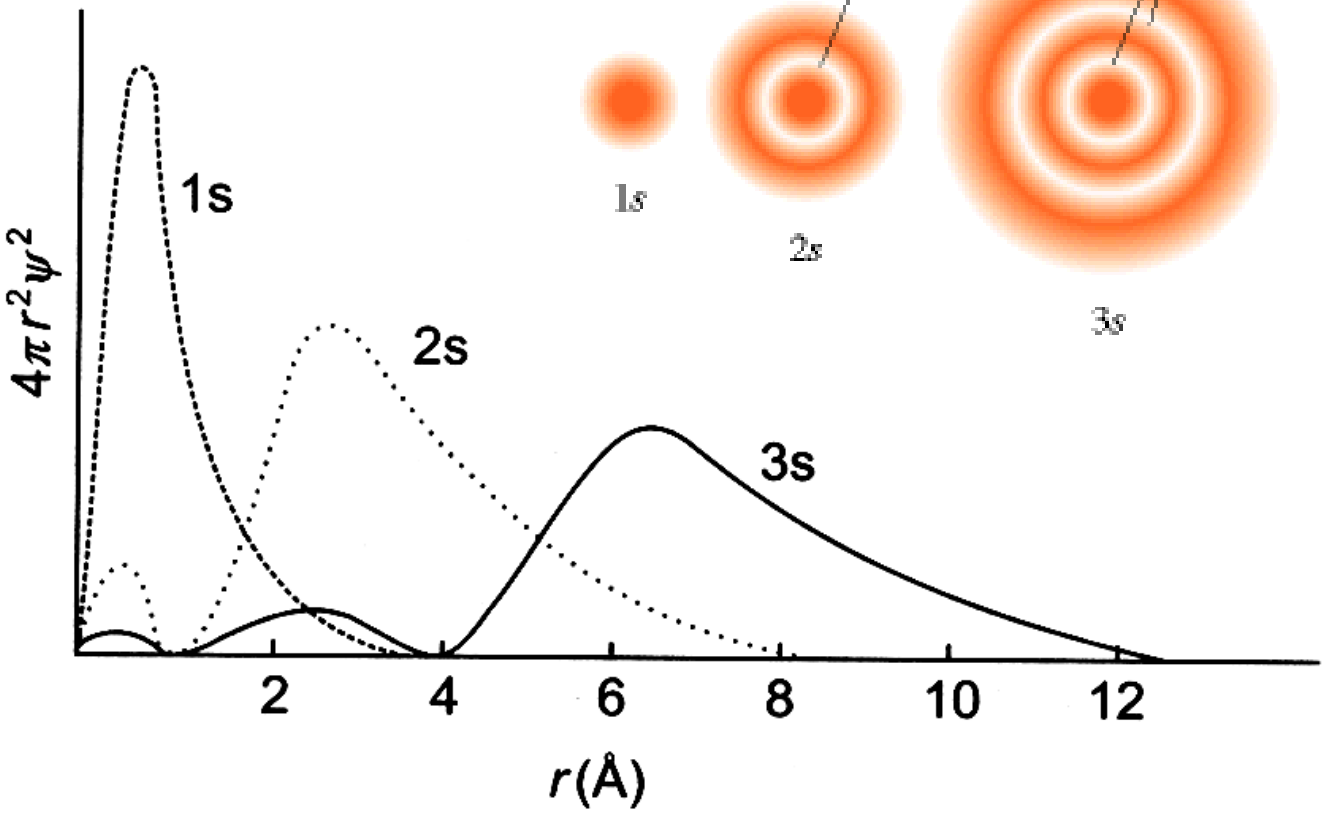
$4\pi r^2 R^2_{n,l}(r)$ = Radial distribution function

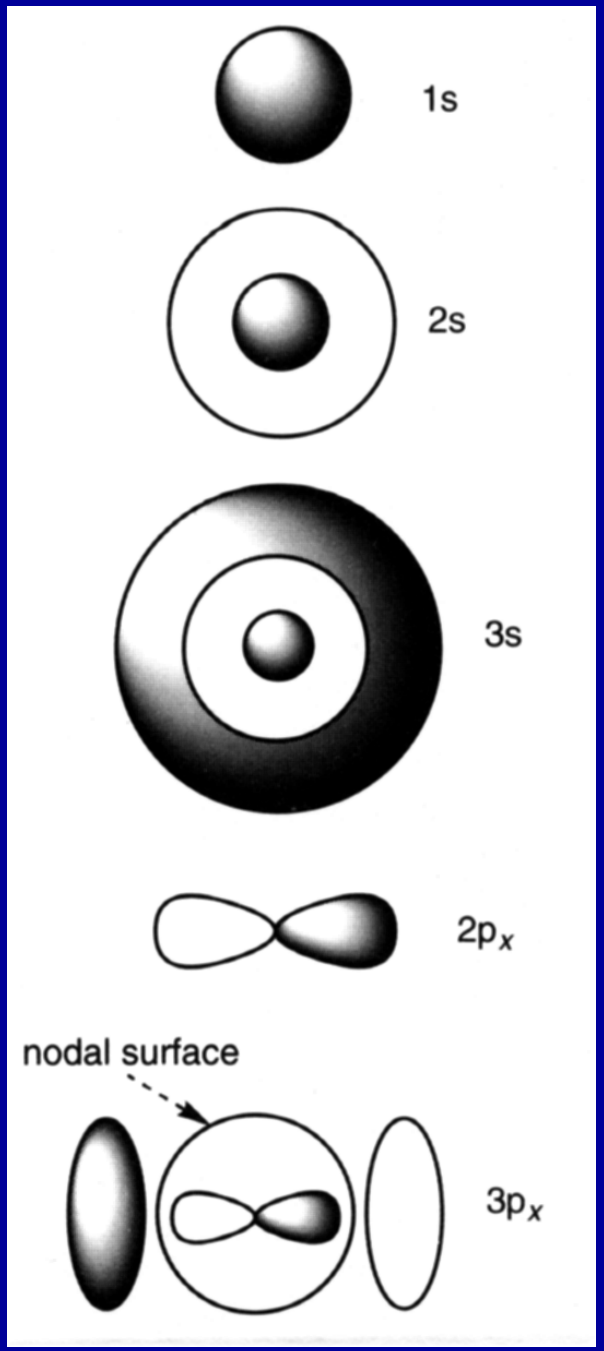
r_{max} = the most probable radius for 1s

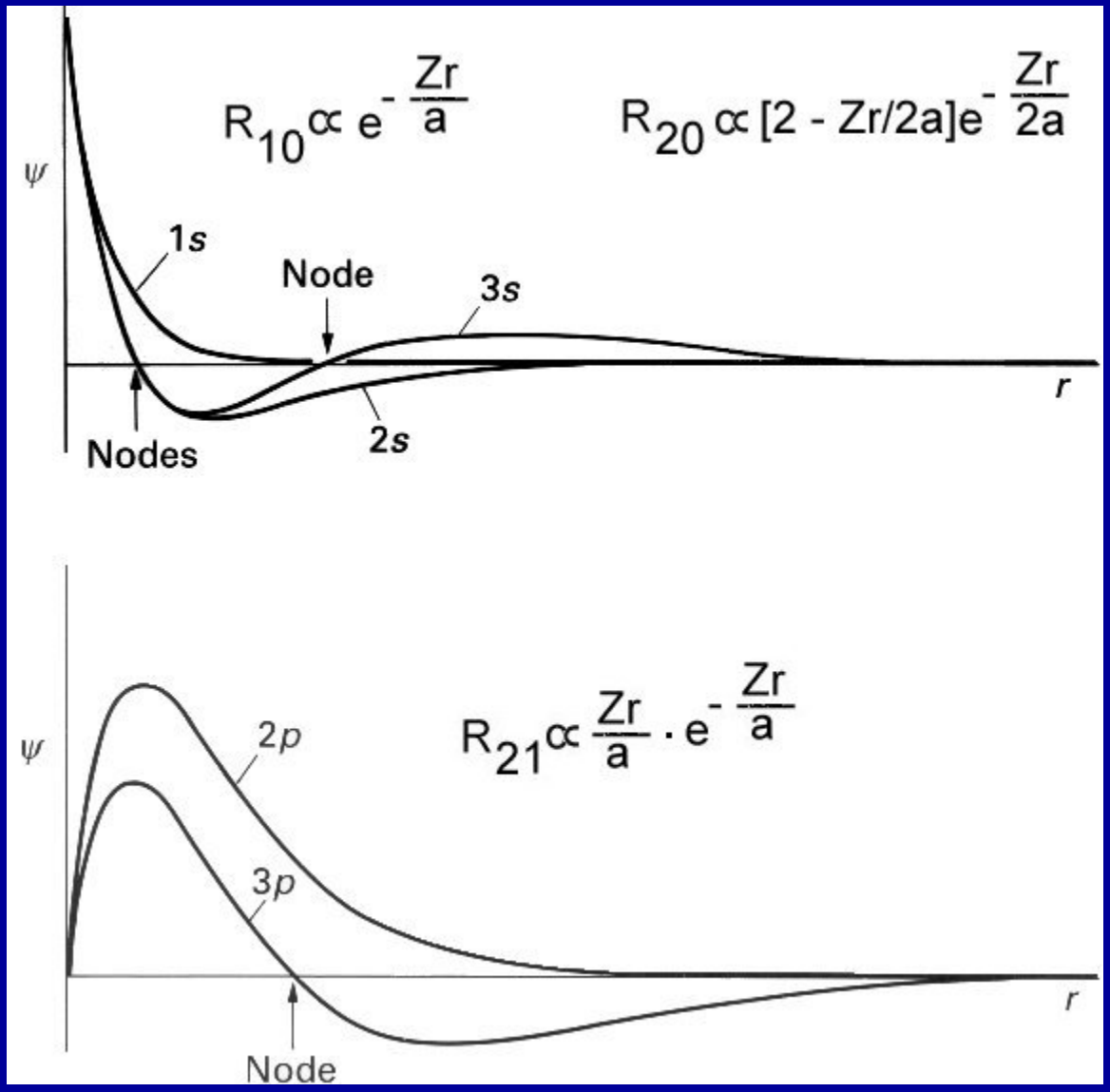
$r_{max} = a_0$ Bohr's radius



$4\pi r^2 R^2_{n,l}(r)$ = Radial distribution function

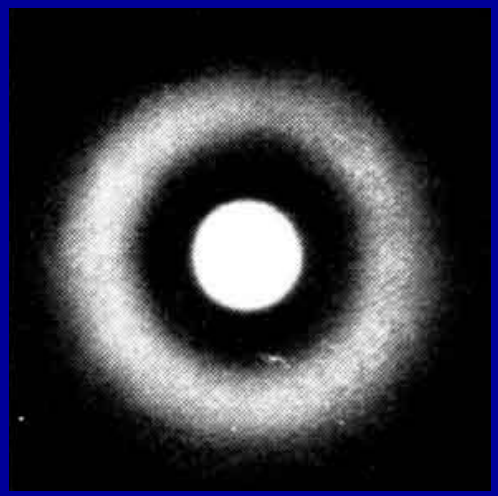



1s
2s
3s
2p$_x$
nodal surface
3p$_x$


$R_{10} \propto e^{-\frac{Zr}{a}}$
$R_{20} \propto [2 - Zr/2a]e^{-\frac{Zr}{2a}}$
ψ
1s
Node
3s
r
Nodes
2s
ψ
2p
3p
$R_{21} \propto \frac{Zr}{a} \cdot e^{-\frac{Zr}{a}}$
r
Node

Nodes

- **Wavefunction changes sign**
- **Radial distribution function has zero value**

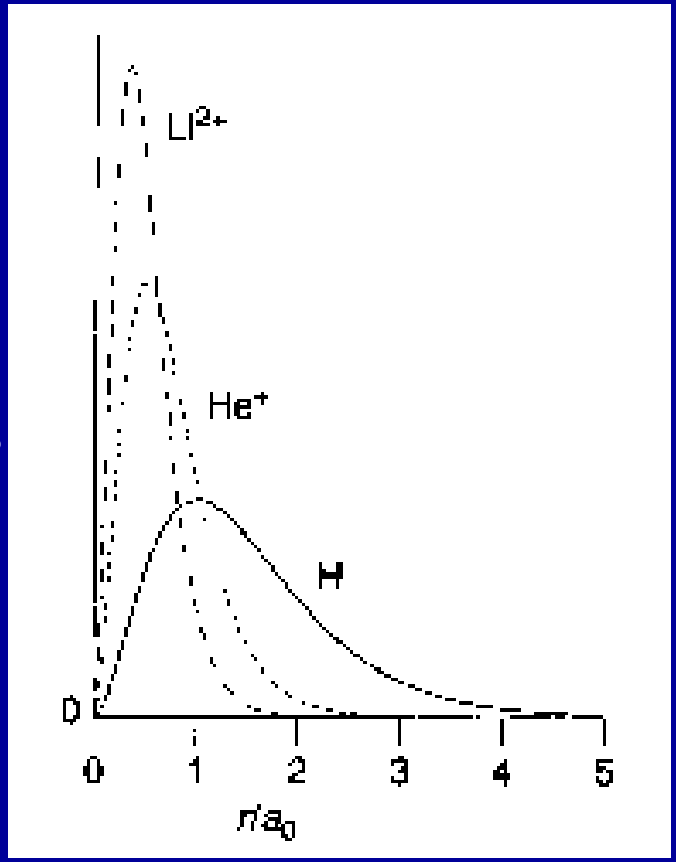


Number of nodes = $n - l - 1$

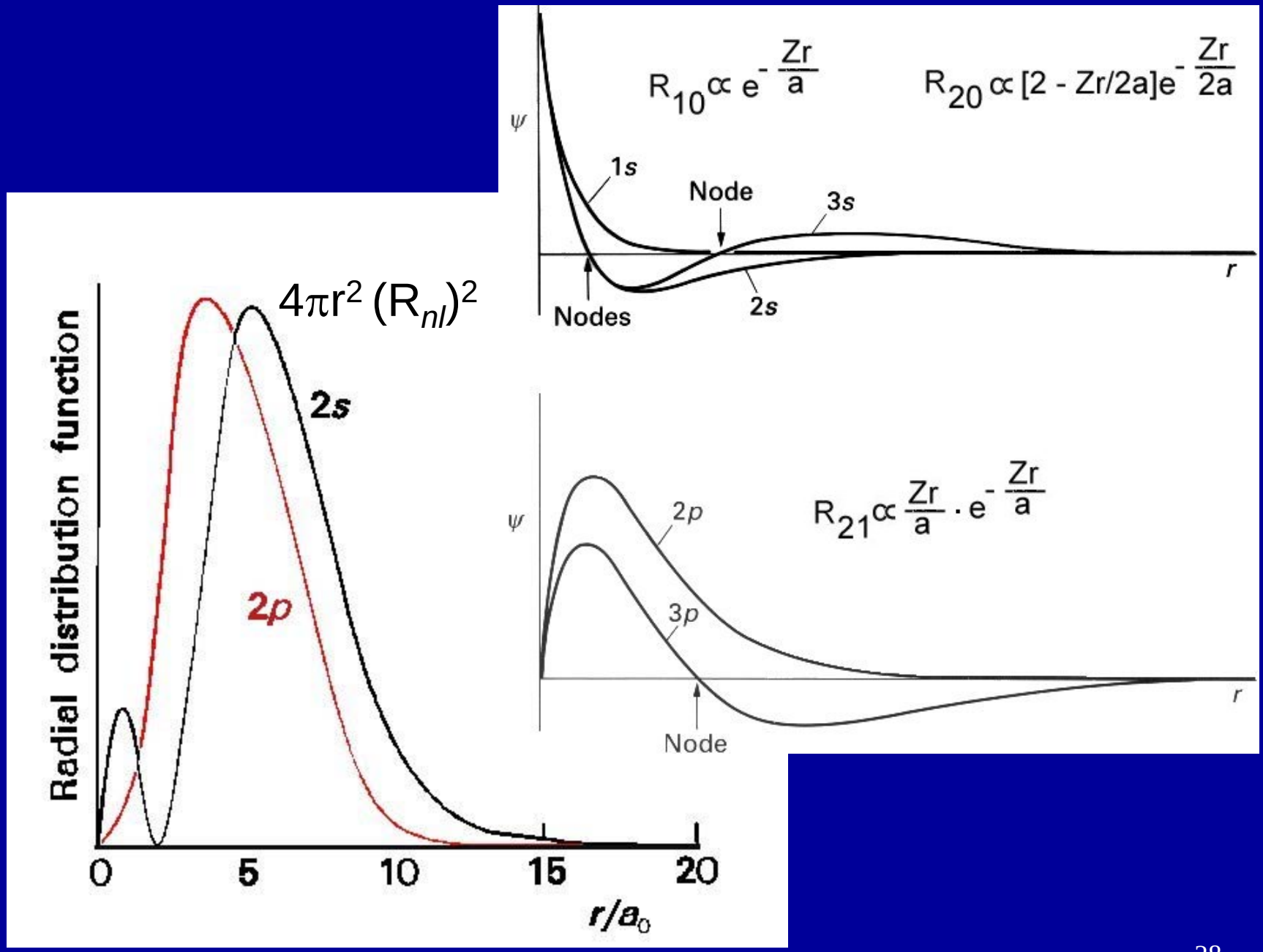
Effect of Z Radial Function s

$$R_{n,l}(r) = 2\sqrt{\left(\frac{Z}{a_0}\right)^3}\exp\left(-\frac{Zr}{a_0}\right)$$

Radial distribution function 1s



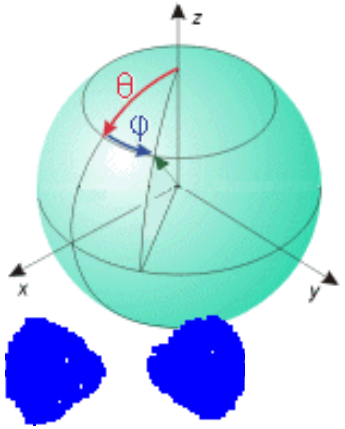
With increasing nucleus charge the maximum of radial distribution function approaches closer to the nucleus


$R_{10} \propto e^{-\frac{Zr}{a}}$
$R_{20} \propto [2 - Zr/2a]e^{-\frac{Zr}{2a}}$
ψ
1s
Node
3s
r
Nodes
2s
$4\pi r^2 (R_{nl})^2$
Radial distribution function
2s
2p
0
5
10
15
20
r/a_0
ψ
2p
3p
$R_{21} \propto \frac{Zr}{a} \cdot e^{-\frac{Zr}{a}}$
r
Node

Angular Wave Function

Angular wave function gives the shape of orbitals

The same for all values of n



$\psi^2_{1,0}$

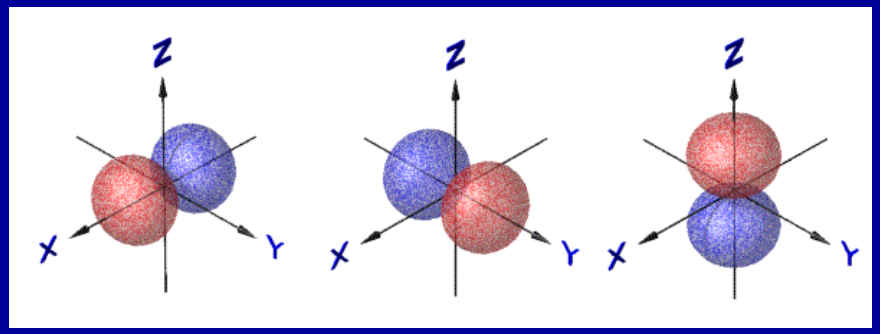
$\psi^2_{1,\pm1}$

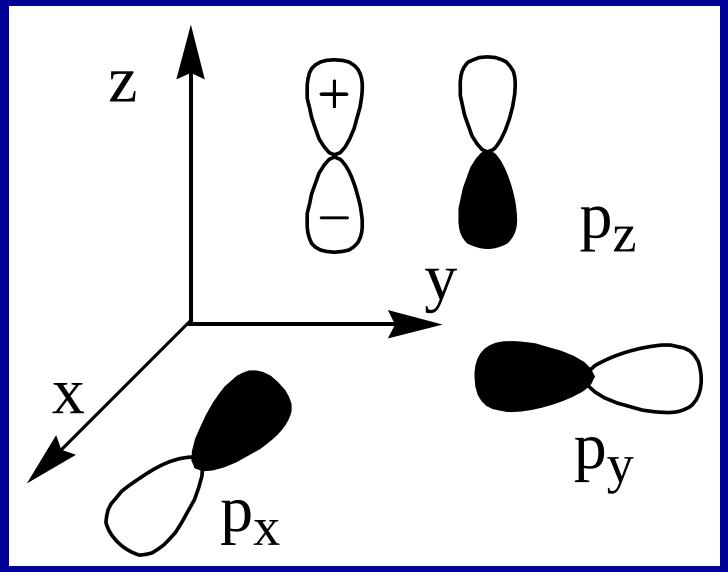
$$Y_{1,0} = (1/4\pi)^{1/2}\, 3^{1/2} \cos\theta$$

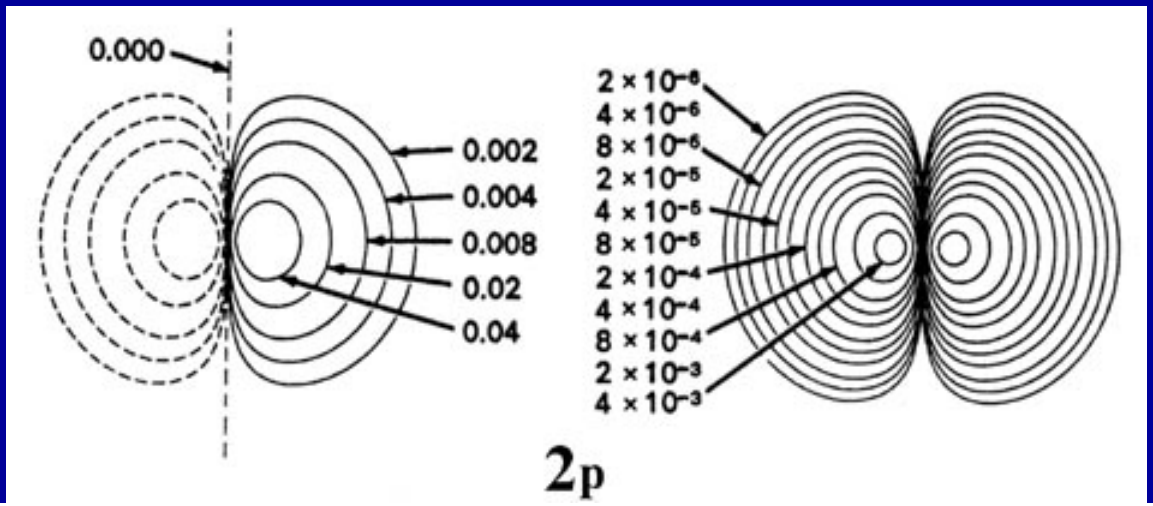
$$Y_{1,\pm1} = (1/4\pi)^{1/2}\, (\mp 3/2)^{1/2} \sin\theta\, e^{\pm i\varphi}$$

p - Orbitals

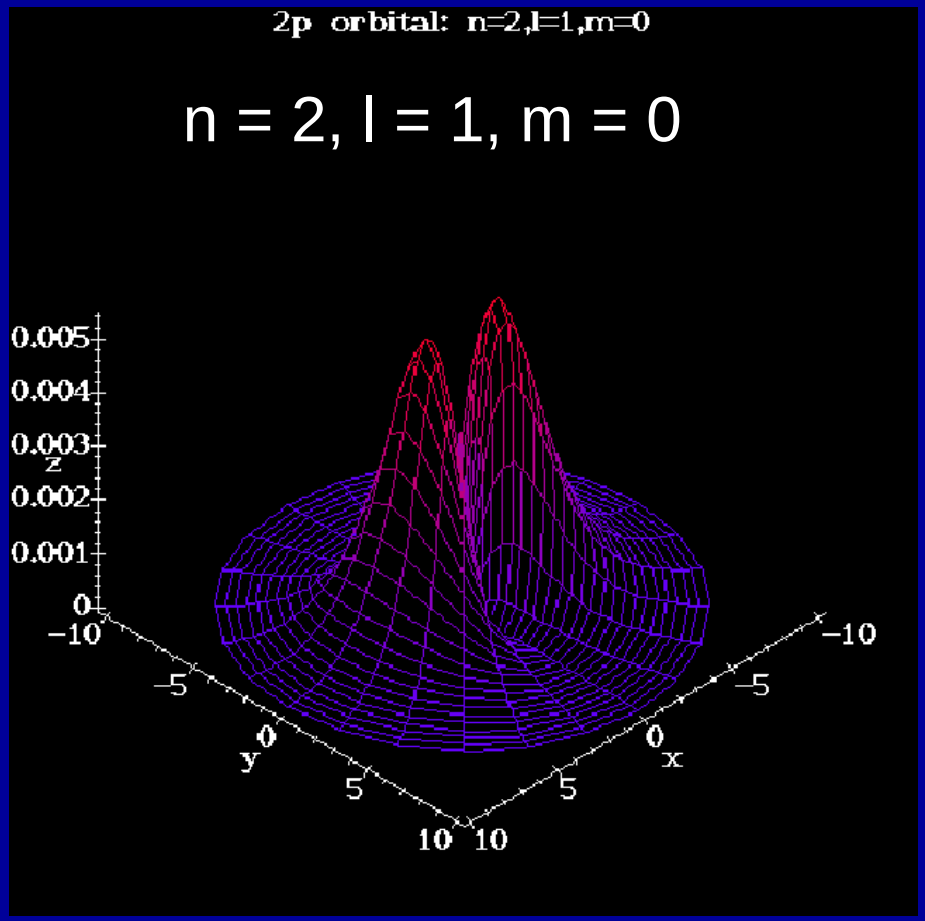
n = 2, l = 1, m = 1,0,–1



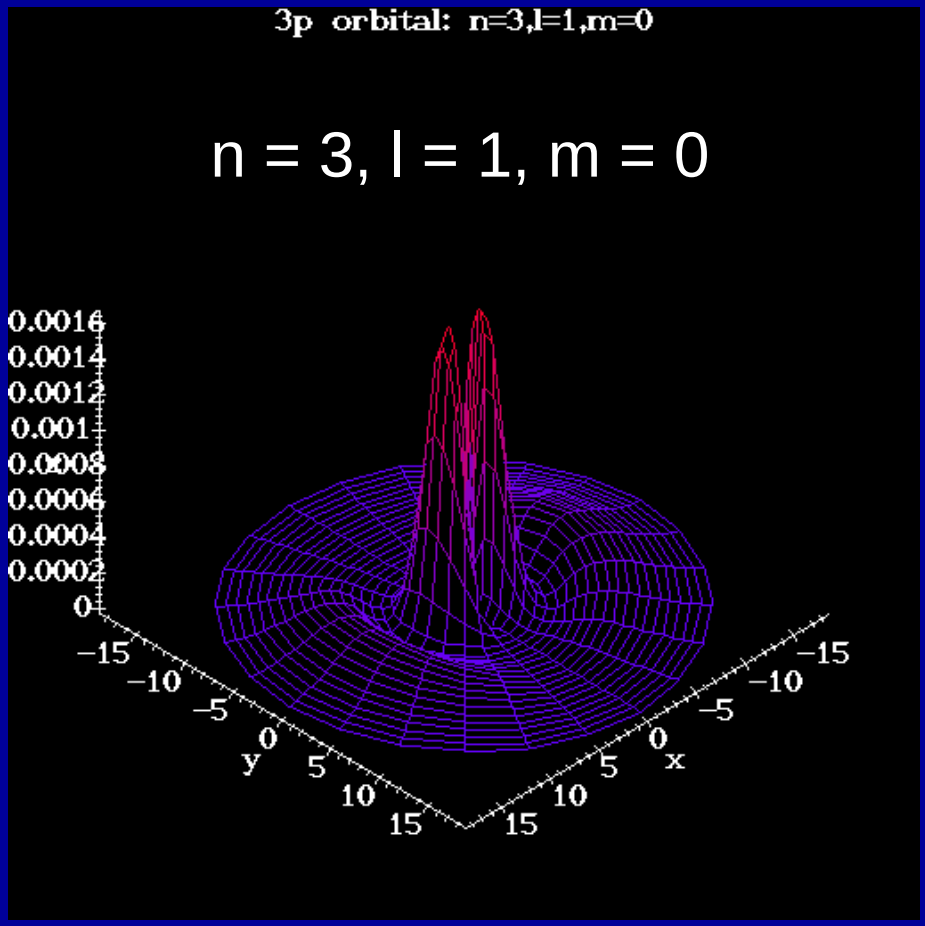


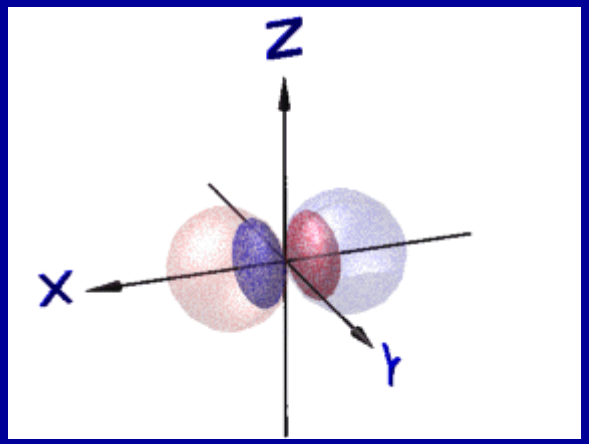


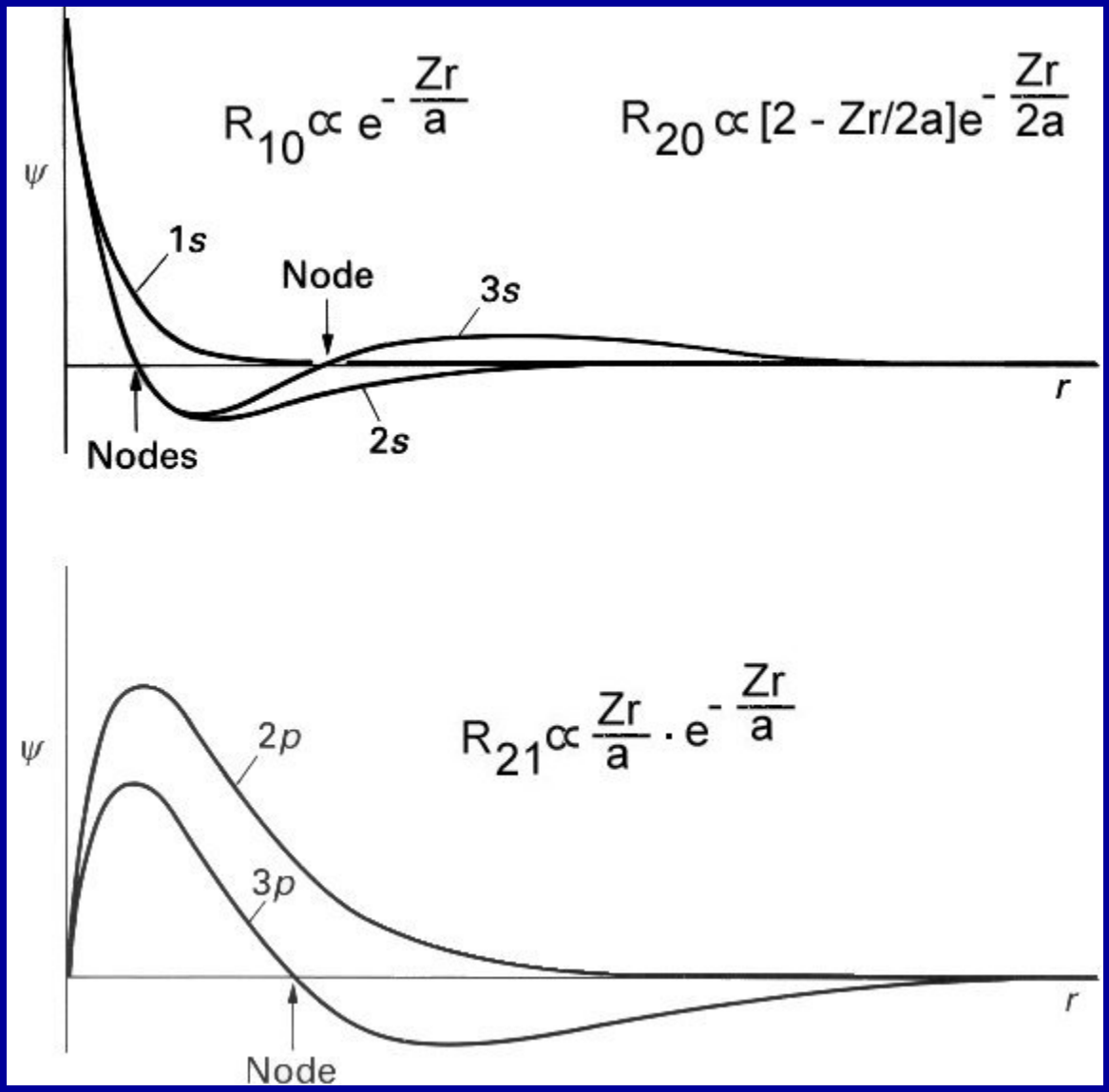
2p - orbitals



3p - orbitals

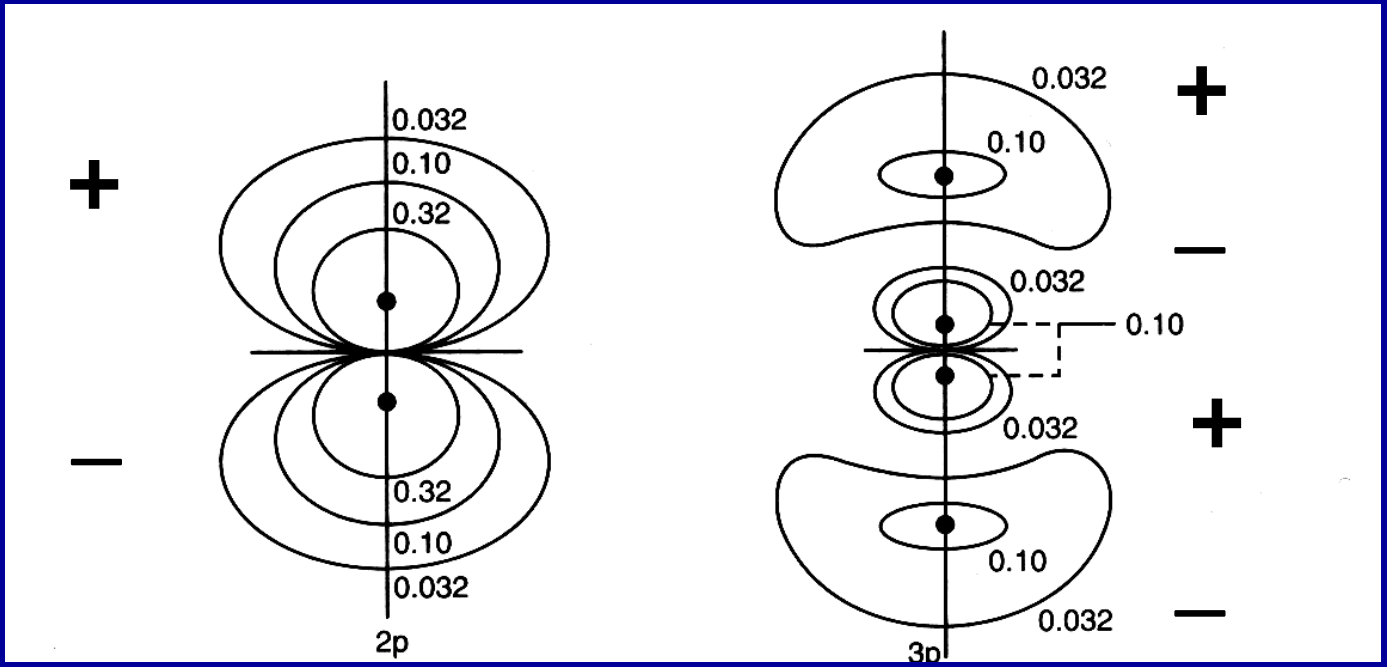



Z
X
Y

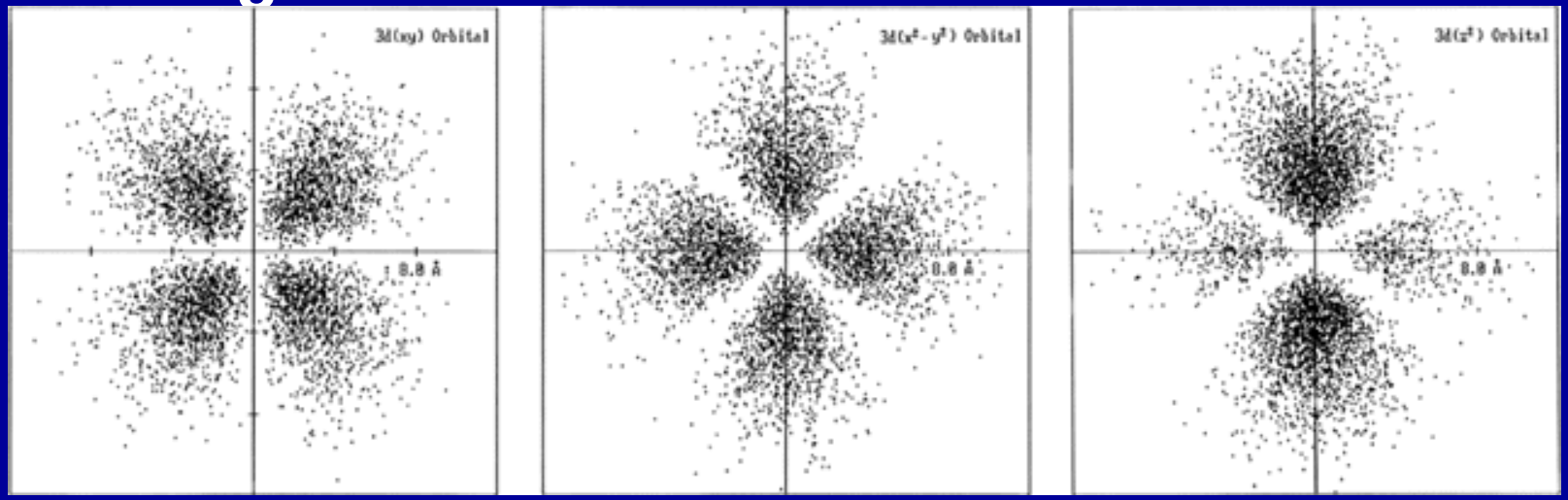

$R_{10} \propto e^{-\frac{Zr}{a}}$
$R_{20} \propto [2 - Zr/2a]e^{-\frac{Zr}{2a}}$
ψ
1s
Node
3s
r
Nodes
2s
ψ
2p
$R_{21} \propto \frac{Zr}{a} \cdot e^{-\frac{Zr}{a}}$
3p
r
Node

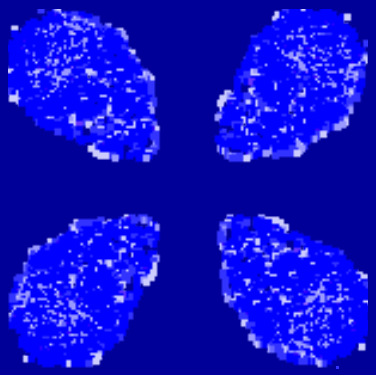
2p - orbitals **3p - orbitals**

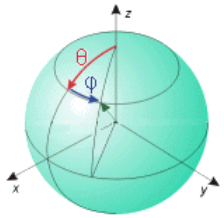
Wave Function = Radial × Angular

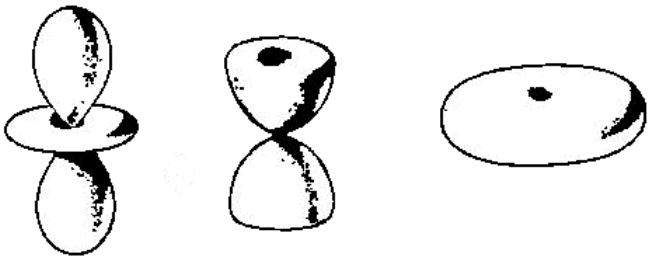


Angular Wave Function of d-Orbitals









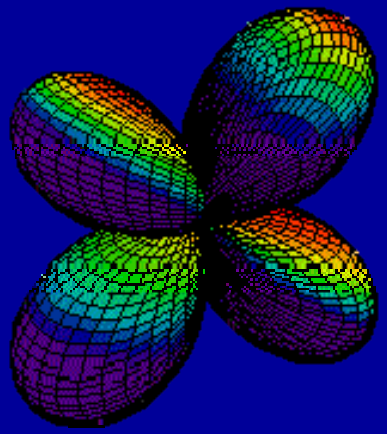
$\psi^2_{2,0}$ $\psi^2_{2,\pm1}$ $\psi^2_{2,\pm2}$

$$Y_{2,0} = (1/4\pi)^{1/2} (5/4)^{1/2} (3\cos^2\theta - 1)$$

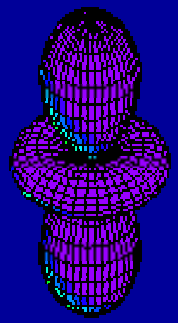
$$Y_{2,\pm1} = (1/4\pi)^{1/2} (\mp 15/4)^{1/2} \cos\theta \sin\theta \, e^{\pm i\varphi}$$

$$Y_{2,\pm2} = (1/4\pi)^{1/2} (15/8)^{1/2} \sin^2\theta \, e^{\pm 2i\varphi}$$

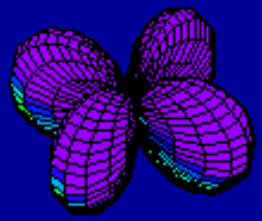
d - Orbitals

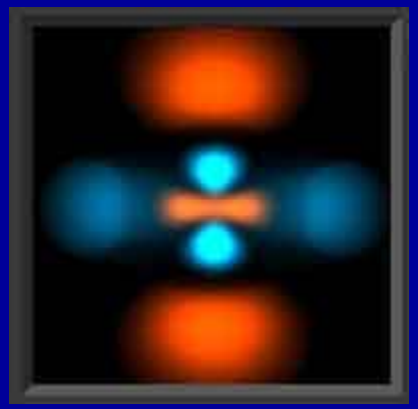


d_{z^2}

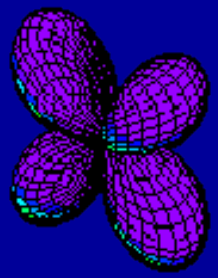


$d_{x^2-y^2}$

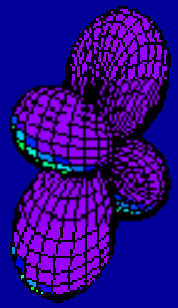




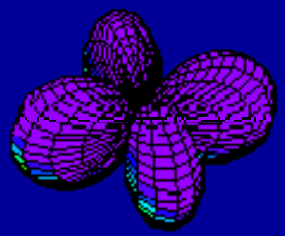
d_{yz}



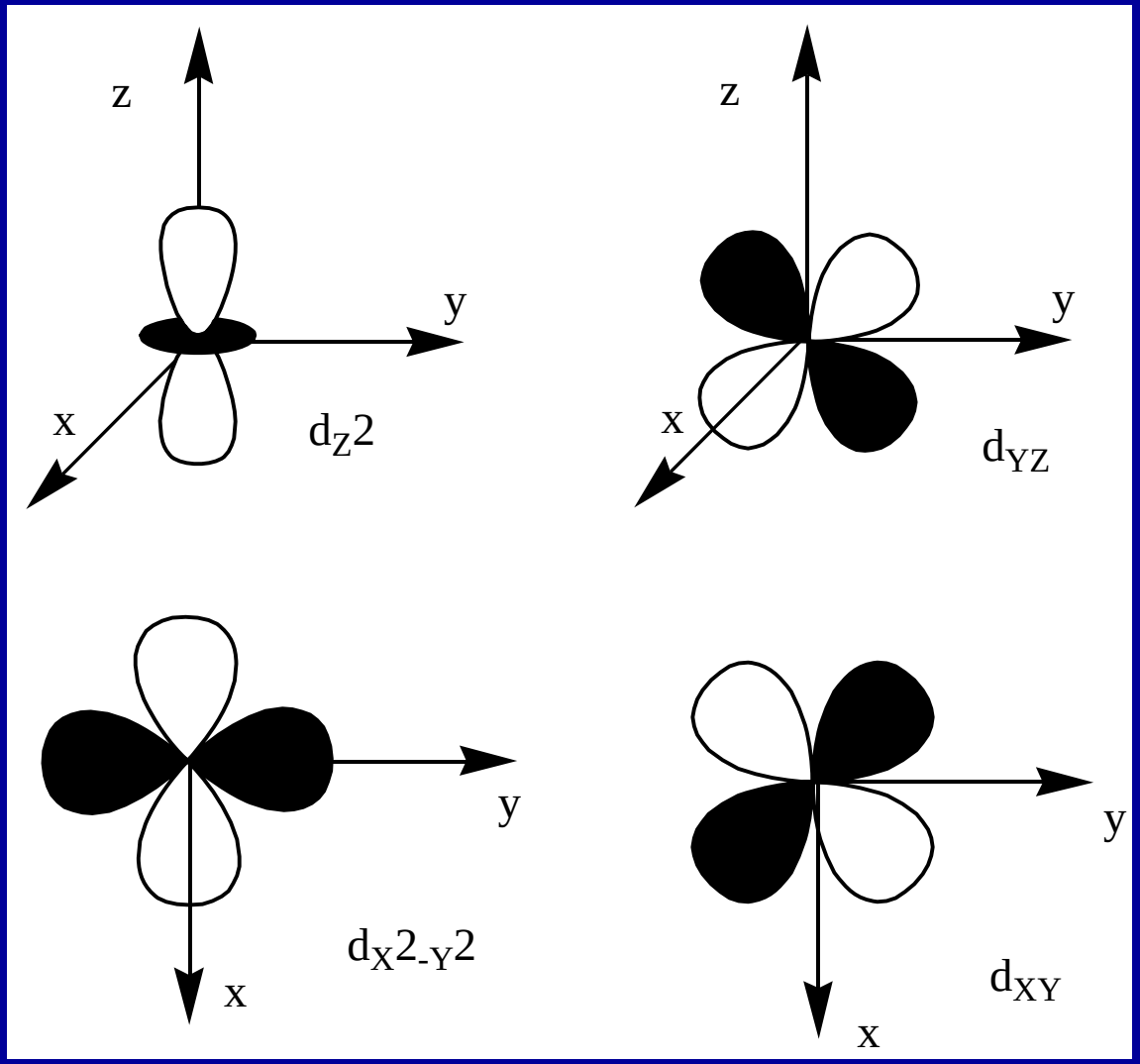
d_{xz}



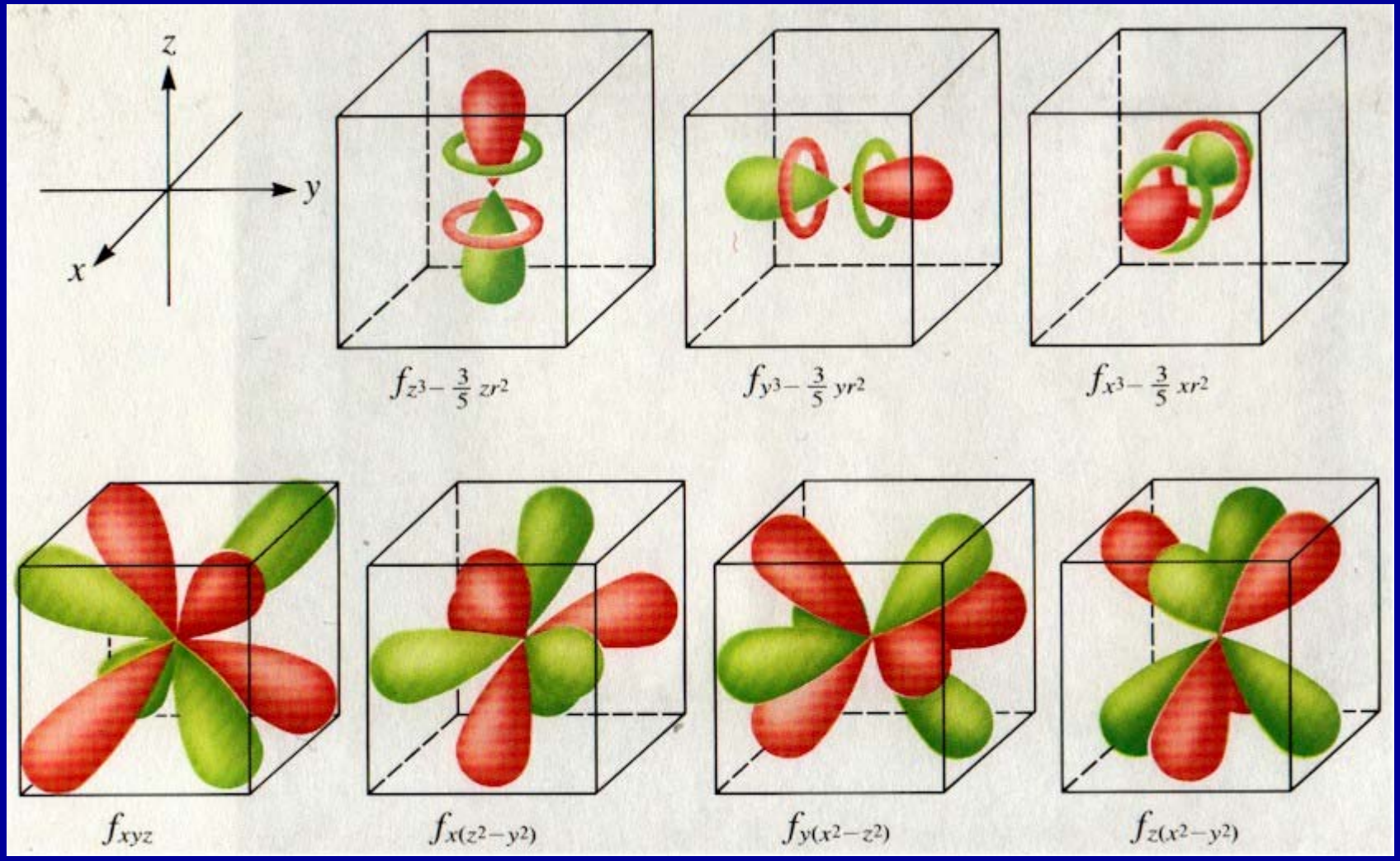
d_{xy}



d - Orbitals

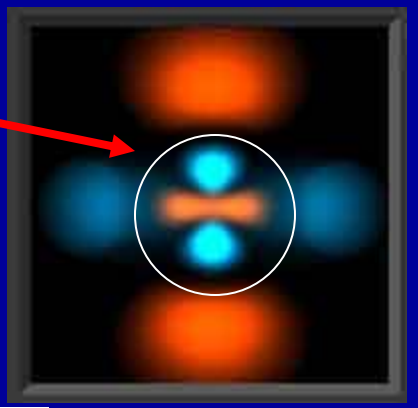


f - Orbitals


z
y
x
$f_{z^3-\frac{3}{5}zr^2}$
$f_{y^3-\frac{3}{5}yr^2}$
$f_{x^3-\frac{3}{5}xr^2}$
f_{xyz}
$f_{x(z^2-y^2)}$
$f_{y(x^2-z^2)}$
$f_{z(x^2-y^2)}$

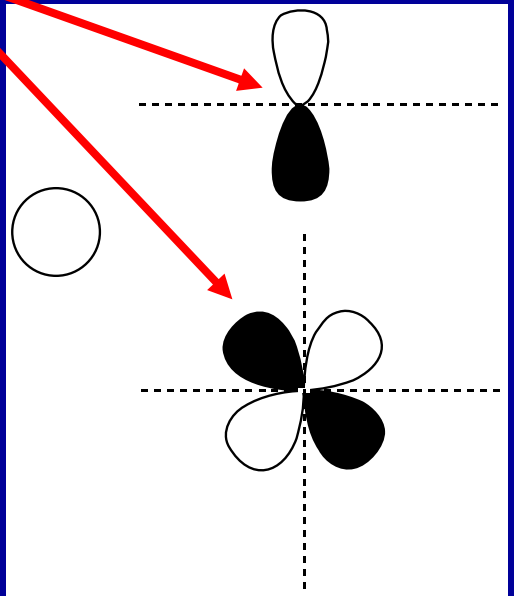
Nodes

Spherical nodes = $n - l - 1$
for s, p, d, f,....
***Radial* wave function**



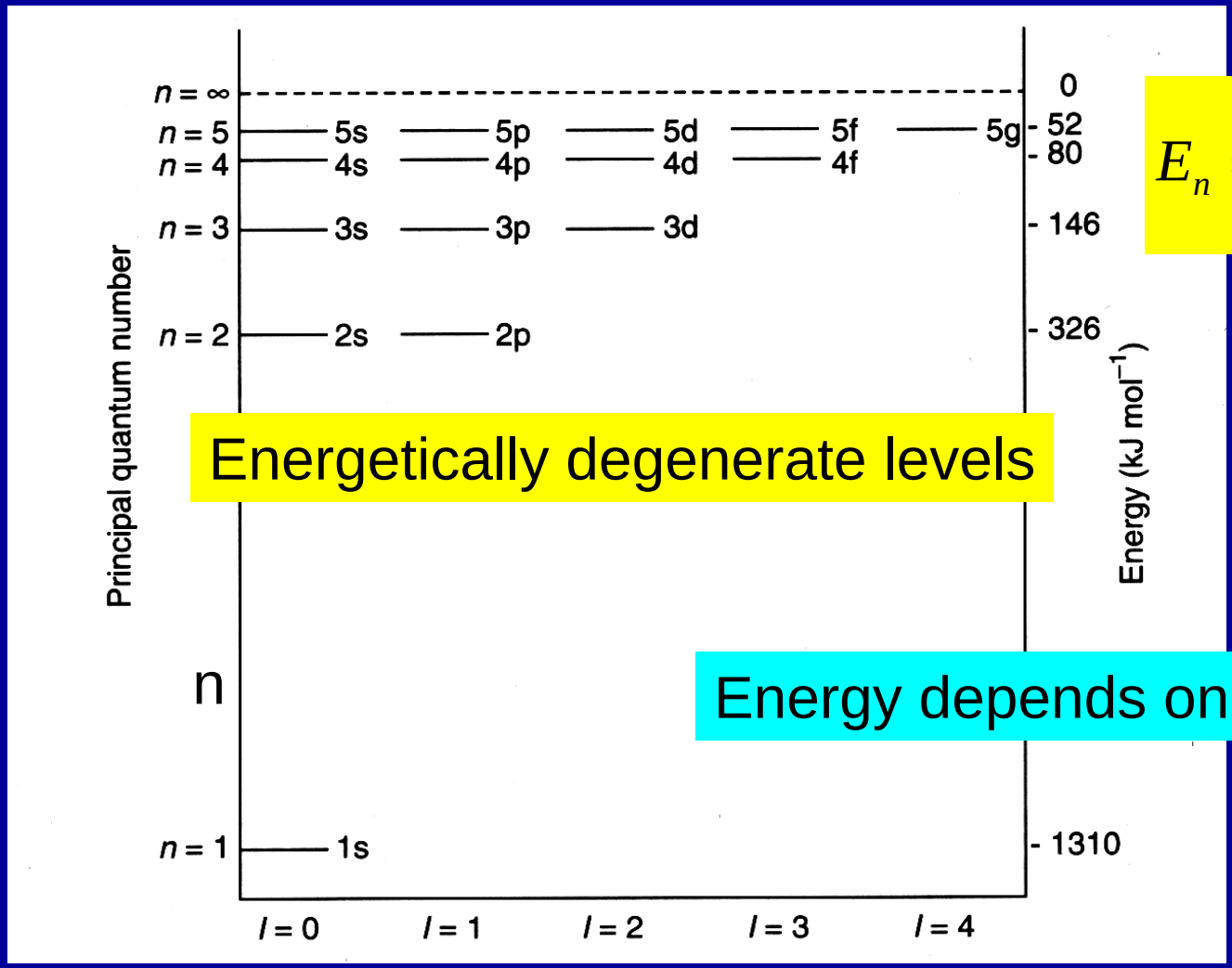
Nodal planes
***Angular* wave function:**

Orbital	no.
s	0
p	1
d	2
f	3
.	.
.	.



Only s-orbitals have non-zero value of wave function at the nucleus

Energy of H-Atom Orbitals

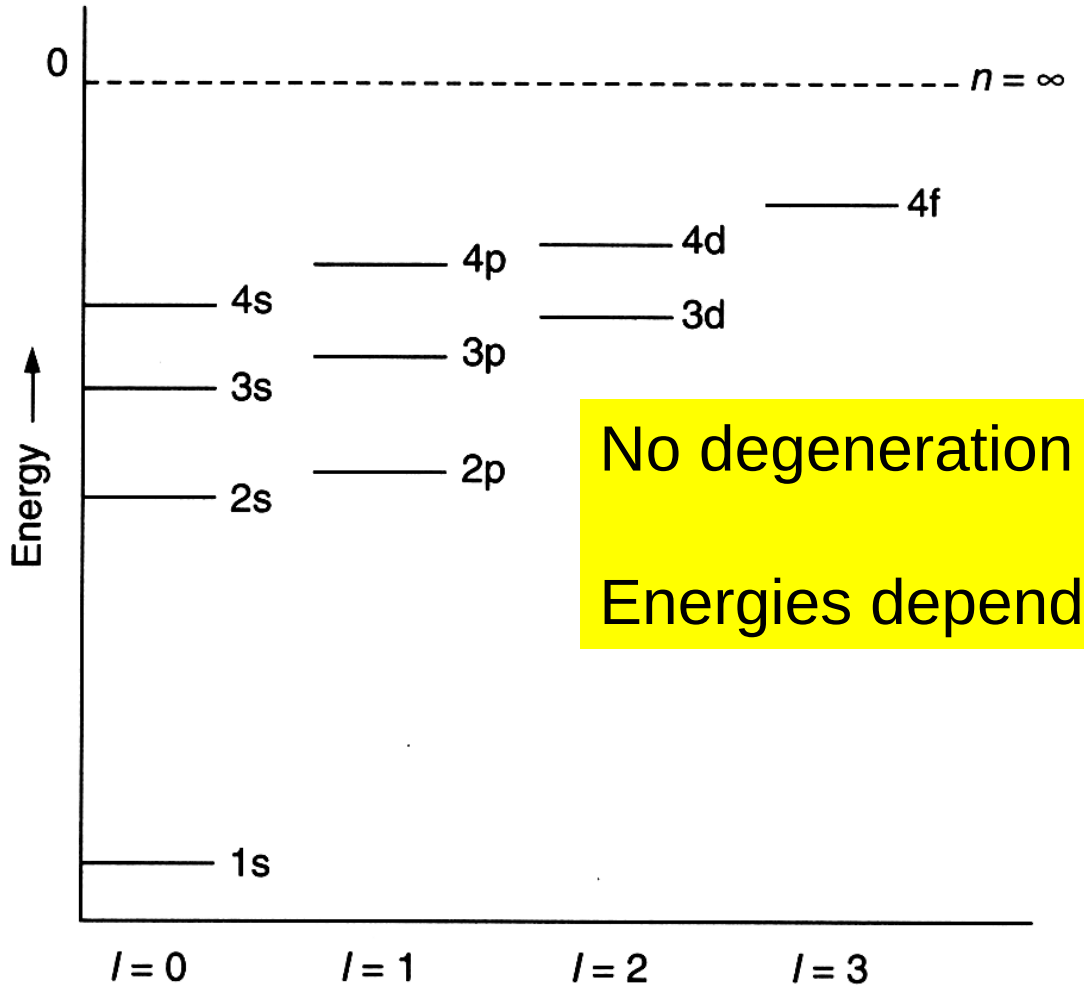


$$E_n = -\frac{N_A \mu e^4}{8\varepsilon_0^2 h^2}\frac{Z^2}{n^2}$$

Energetically degenerate levels

Energy depends only on ***n***

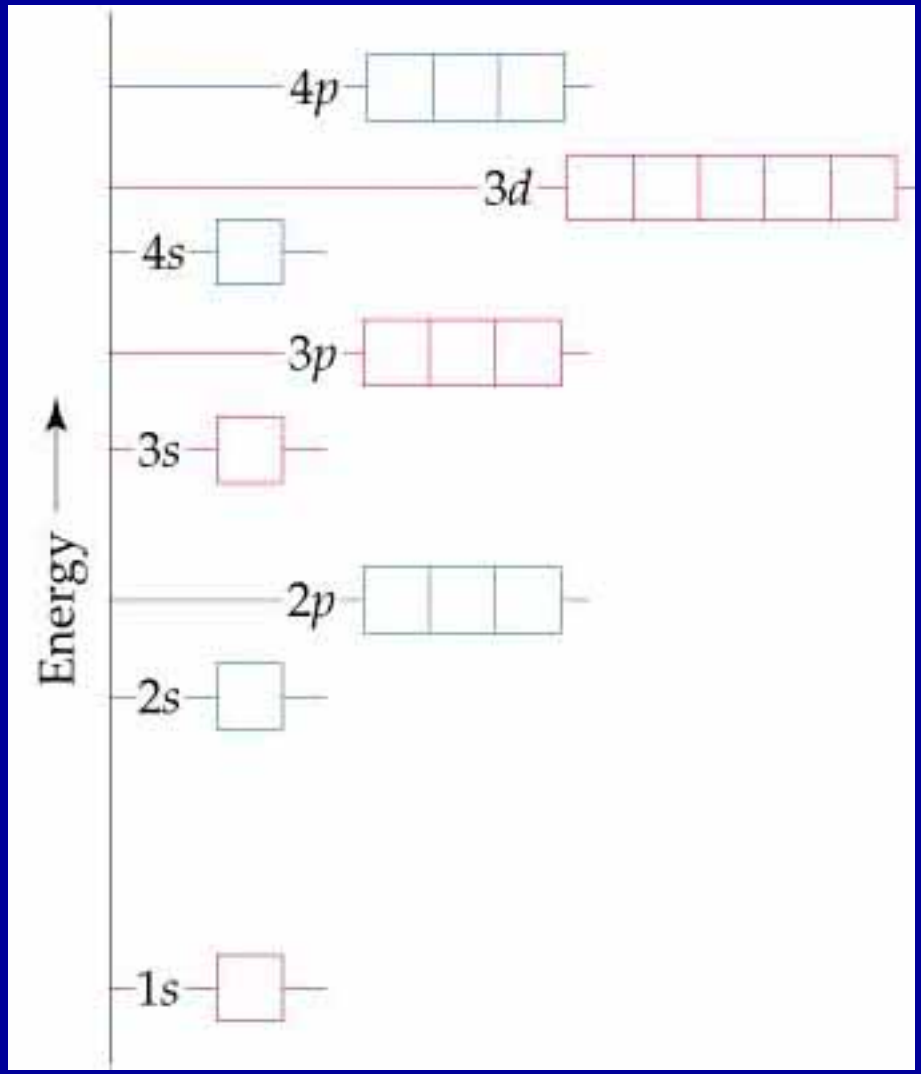
Energy Levels in Many-Electron Atoms



No degeneration

Energies depend on ***n*** and ***l***

Energy Levels in Many-Electron Atoms



More stable orbital has a lower energy

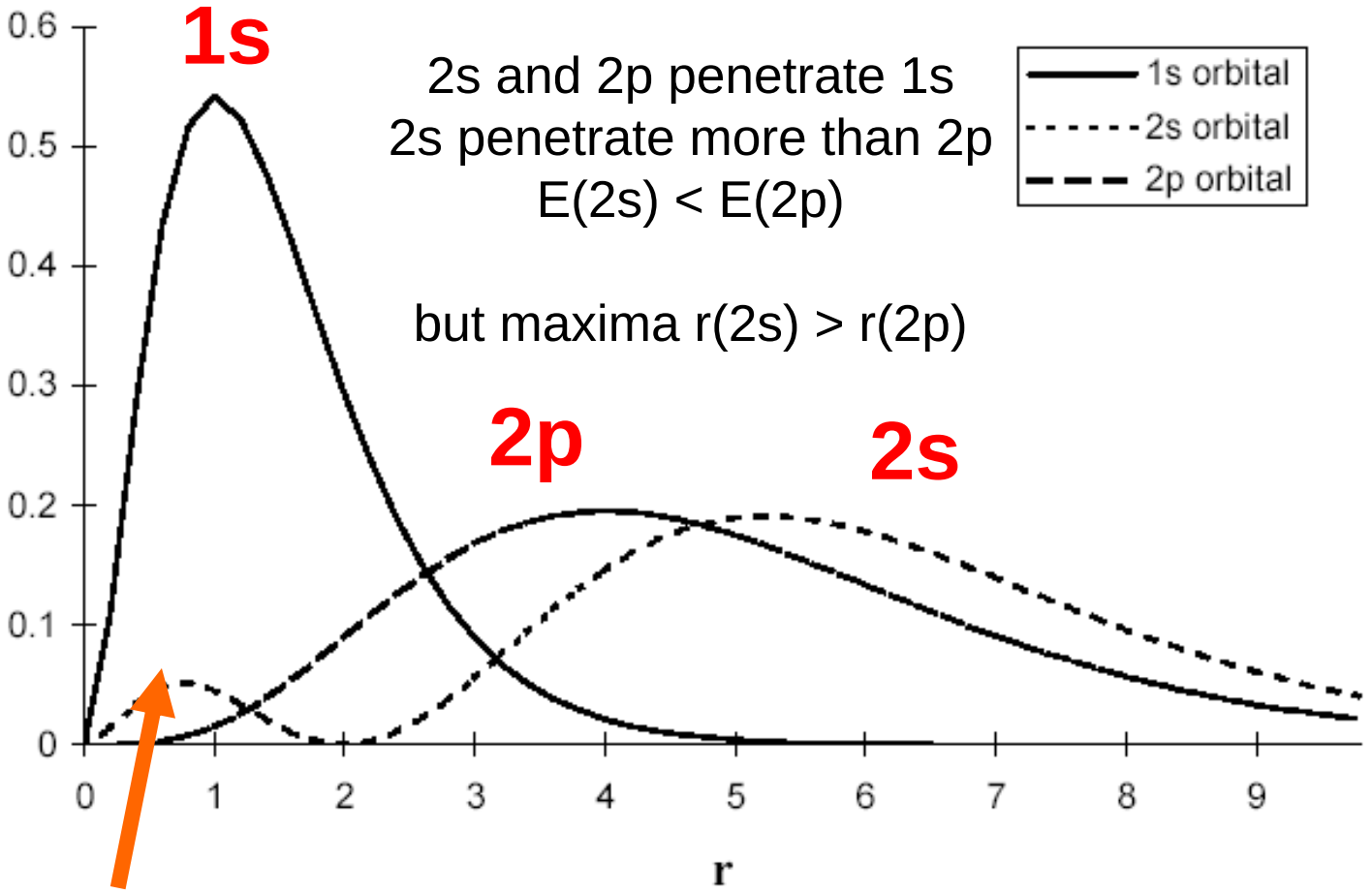
Madelung's Rule (up to Ca)

1. Lower for $(n + l)$
2. When $n + l$ same lower n

3p 4s

4p 3d

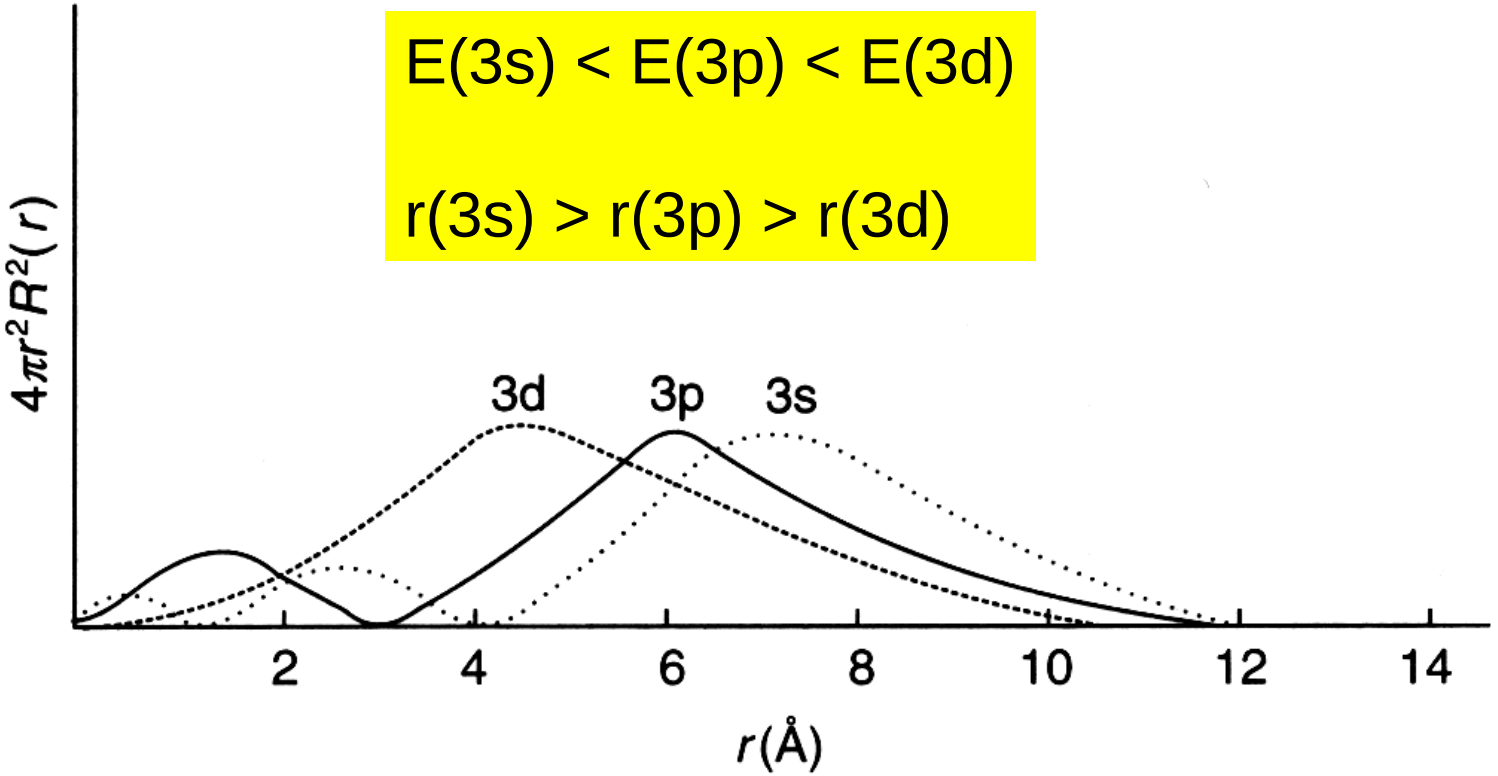
Many-Electron Atoms
Penetration and Screeneing



Relative Energies of s, p, d Orbitals

E(3s) < E(3p) < E(3d)

r(3s) > r(3p) > r(3d)



Slater's Orbitals

Orbitals for many-electron atoms - approximate

- orbitals (wave functions) of hydrogen type
- angular part: same as for H
- radial part:

$R(r) = N\, r^{n^*-1} \exp(-Z^* r/n^*)$

Z^* = A charge acting on an electron
= Nucleus charge (Z+) – charge of other electrons
n^* = effective quant. number (for K, L, M = n)

$E_i = -N\,(Z^*_i / n_i)$ N = 1313 kJ mol $^{-1}$

Efective Nucleus Charge

$Z^* = Z - \sigma$

σ = screening constant, sum for all electrons

(1s)(2s,2p)(3s,3p)(3d)(4s,4p)(4d)(4f)(5s,5p)(5d)(5f)...

Slater's rules

e on the right does not screen, no contribution to σ
Within a group screens 0.35 (1s only 0.30)
n – 1 (s,p) screens 0.85
n – 2 and lower screens 1.00
If an electron is in d or f, all on the left screens 1.00

Efective Nucleus Charge

Z^* = Efective Nucleus Charge

$Z^* = Z - \sigma$

A charge acting on an electron

= Nucleus charge (Z^+) – charge of other electrons

K $(1s)^2(2s,2p)^8(3s,3p)^8(3d)^1$

$\sigma(3d) = 0 \times (0.35) + 8 \times 1.00 + 10 \times 1.00 = 18$

$Z^* = 19 - 18 = 1$

K $(1s)^2(2s,2p)^8(3s,3p)^8 (4s)^1$

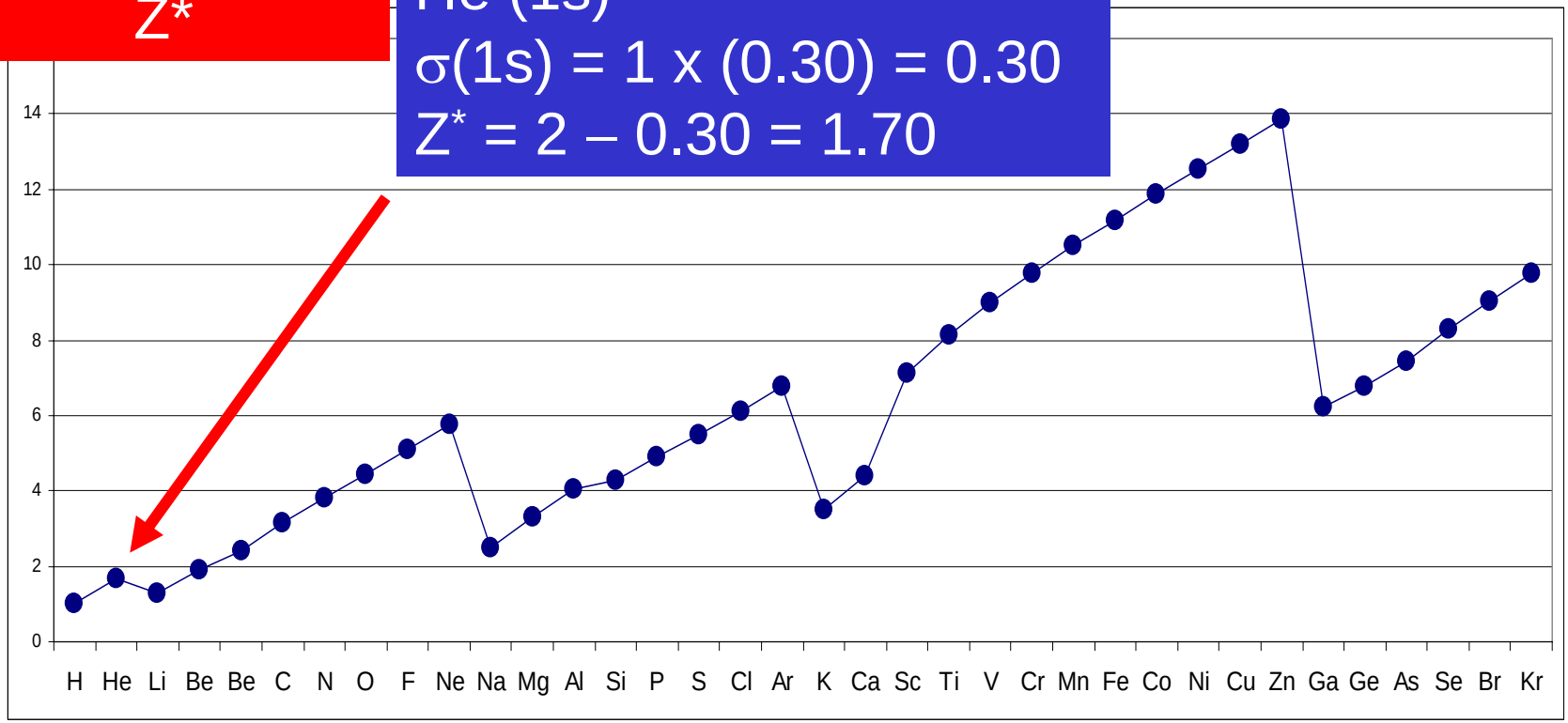
$\sigma(4s) = 0 \times (0.35) + 8 \times 0.85 + 10 \times 1.00 = 16.8$

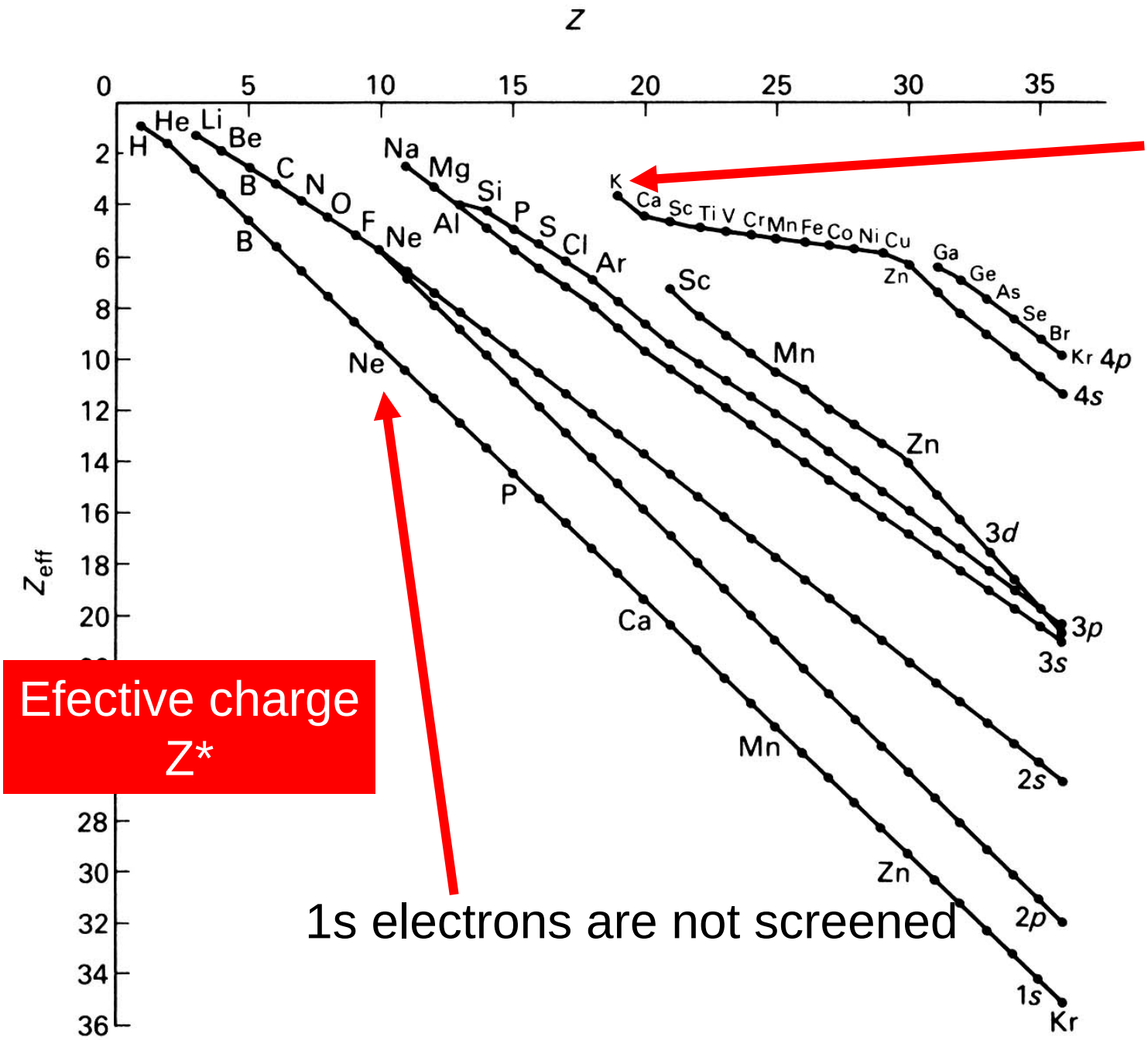
$Z^* = 19 - 16.8 = 2.2$

Efective Nucleus Charge

Efective charge
Z*

He $(1s)^2$
$\sigma(1s) = 1 \times (0.30) = 0.30$
$Z^* = 2 - 0.30 = 1.70$



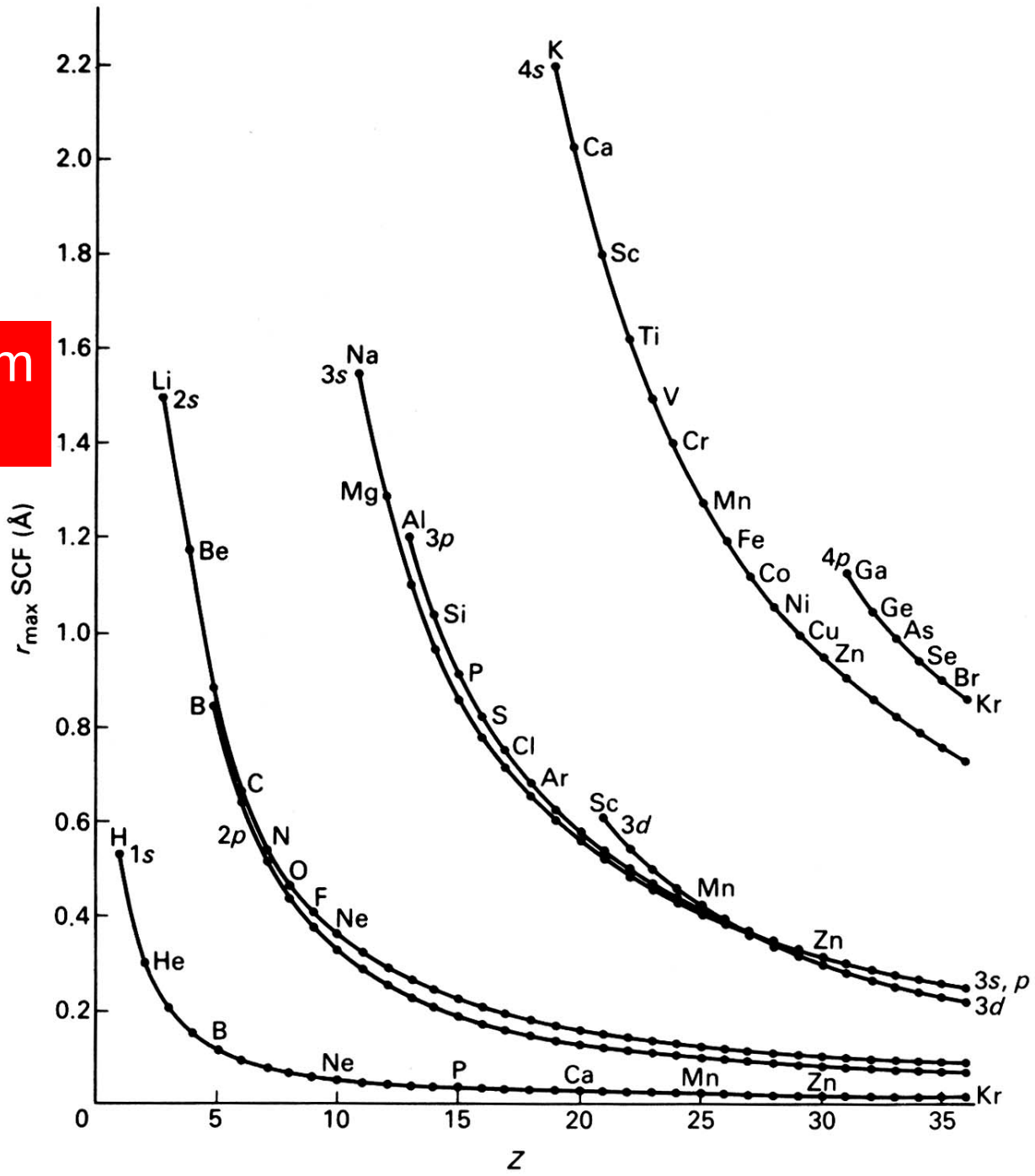


Other electrons are screened

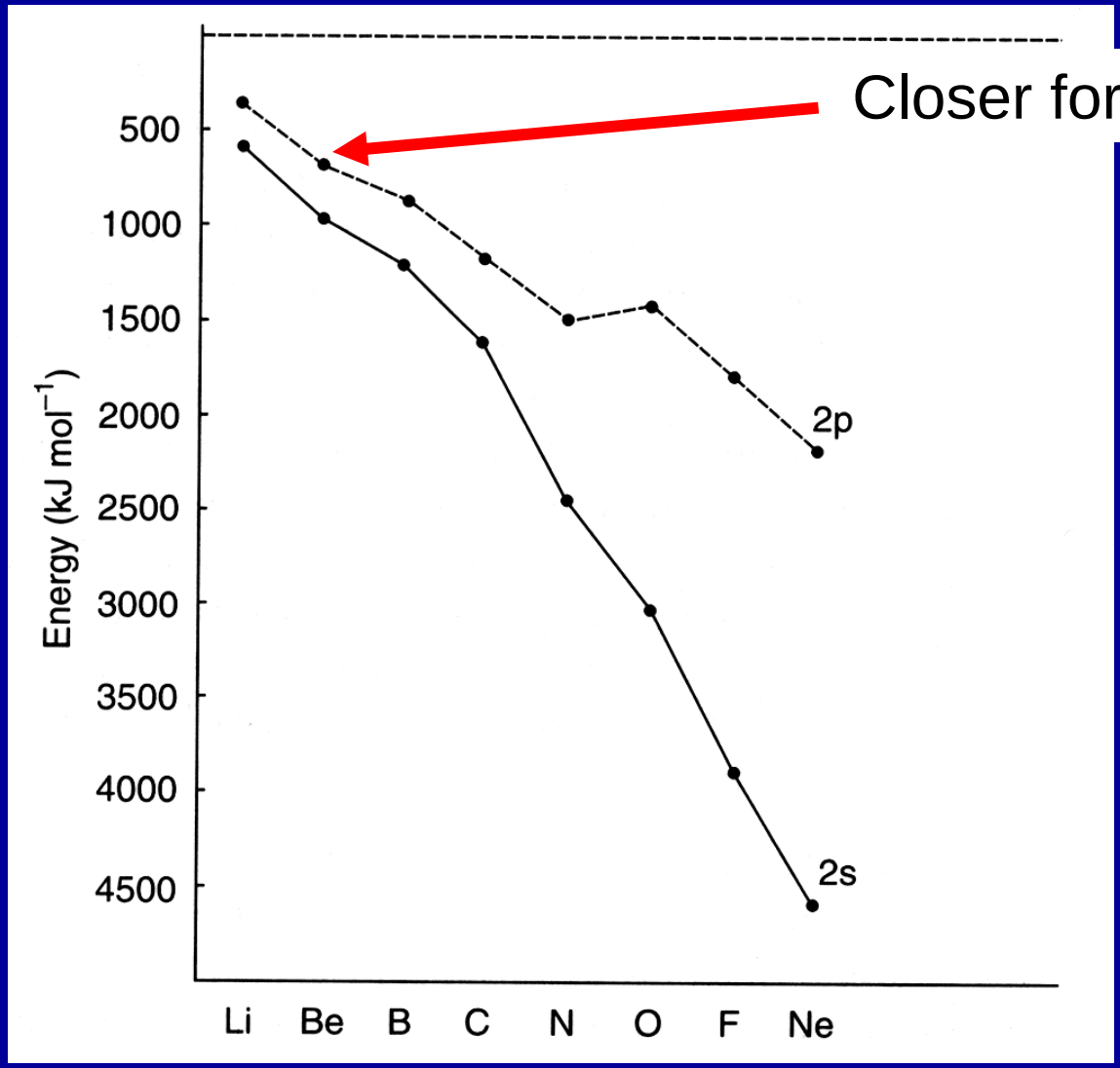
Radius of maximum electron density

r(2s) > r(2p)

r(3s) ~ r(3p)



Energies of 2s and 2p Orbitals

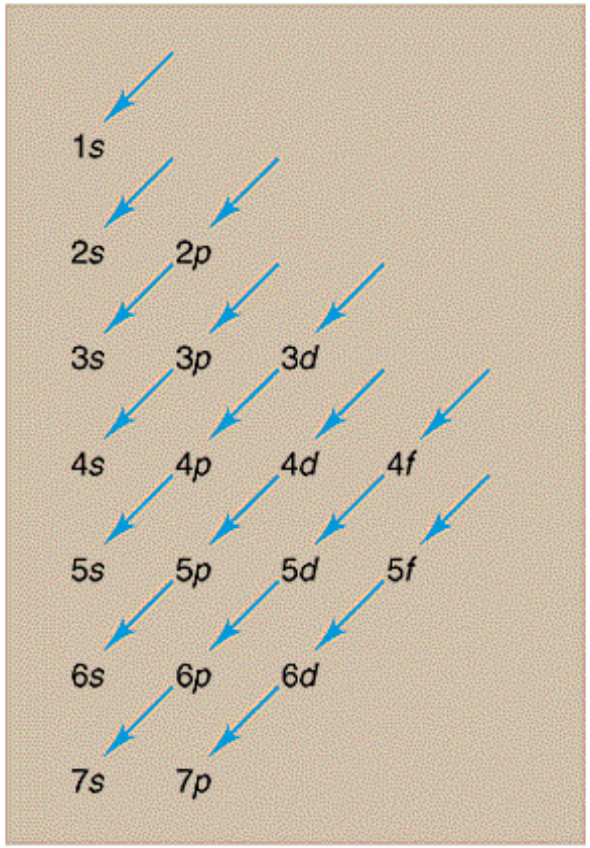


Electron Configurations of Ground State Atoms

Aufbau Principle:
Electron levels are filled by electrons in the order of increasing energy, to maintain the lowest atom energy

Pauli Principle:
Two electrons cannot have all 4 quantum numbers the same

Hund's Rule:
In degenerate orbitals, the state with maximum unpaired electrons is the most stable

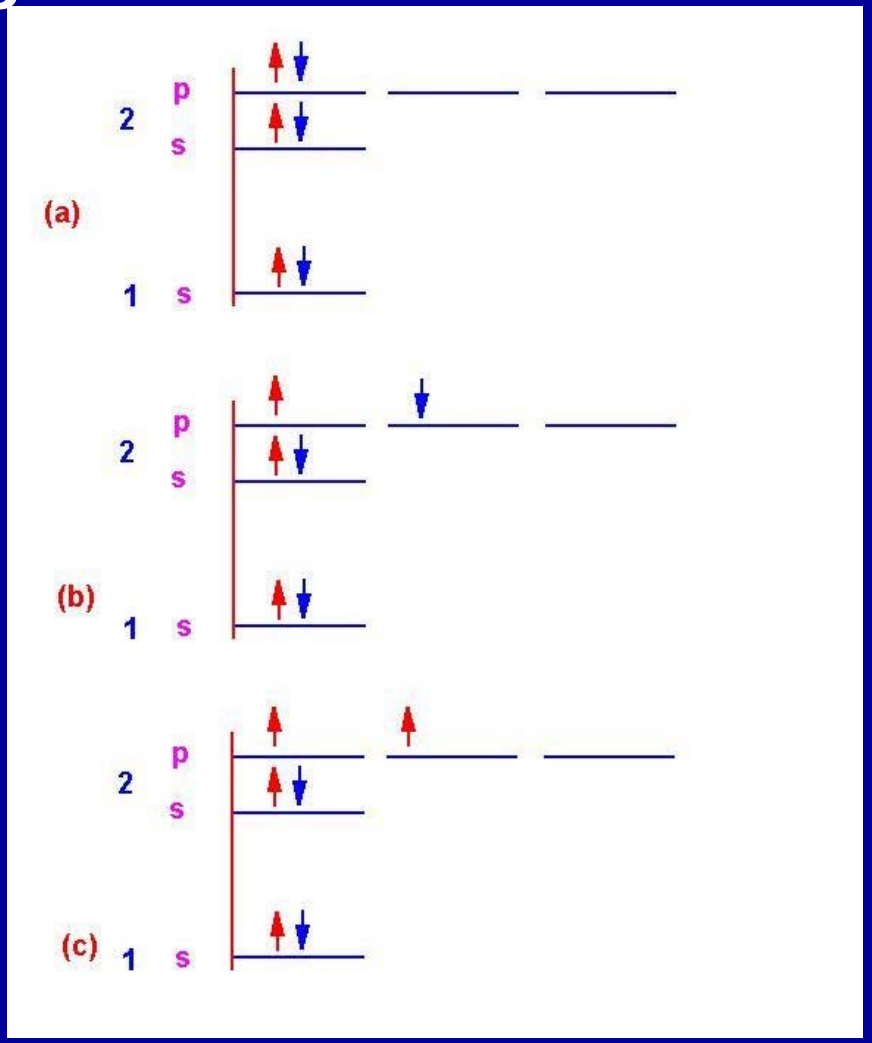


1																	18
1 **H** 1.0079	2											13	14	15	16	17	2 **He** 4.0026
3 **Li** 6.941	4 **Be** 9.0122											5 **B** 10.811	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.180
11 **Na** 22.990	12 **Mg** 24.305	3	4	5	6	7	8	9	10	11	12	13 **Al** 26.982	14 **Si** 28.086	15 **P** 30.974	16 **S** 32.065	17 **Cl** 35.453	18 **Ar** 39.948
19 **K** 39.098	20 **Ca** 40.078	21 **Sc** 44.956	22 **Ti** 47.867	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.845	27 **Co** 58.933	28 **Ni** 58.693	29 **Cu** 63.546	30 **Zn** 65.38	31 **Ga** 69.723	32 **Ge** 72.64	33 **As** 74.922	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.798
37 **Rb** 85.468	38 **Sr** 87.62	39 **Y** 88.906	40 **Zr** 91.224	41 **Nb** 92.906	42 **Mo** 95.96	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.76	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57-71 *	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89-103 #	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (266)	107 **Bh** (264)	108 **Hs** (270)	109 **Mt** (268)	110 **Ds** (281)	111 **Rg** (272)	112 **Uub** (285)	113 **Uut** (284)	114 **Uuq** (289)	115 **Uup** (288)	116 **Uuh** (291)		118 **Uuo** (294)

* Lanthanide series	57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.05	71 **Lu** 174.97
# Actinide series	89 **Ac** (227)	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

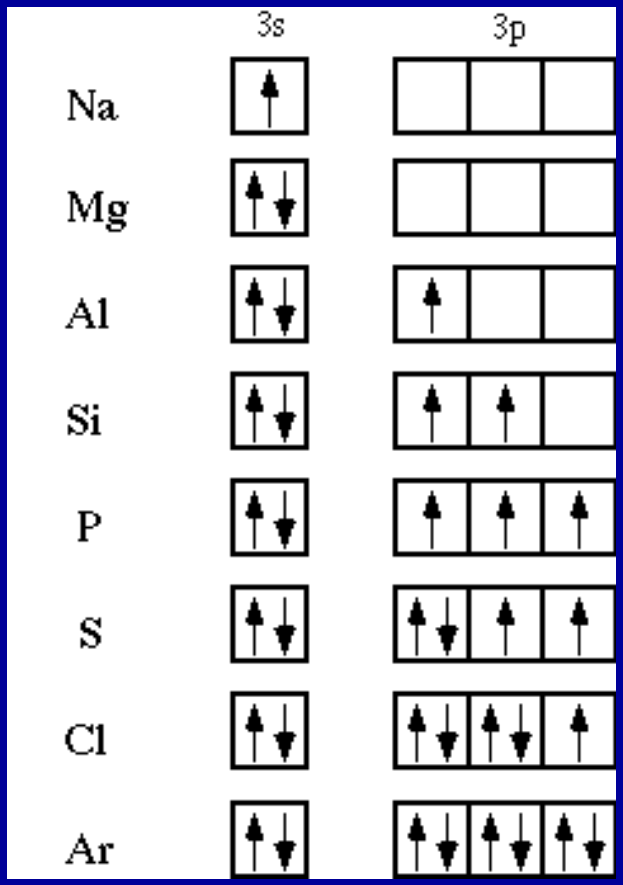
Electron Configurations of C

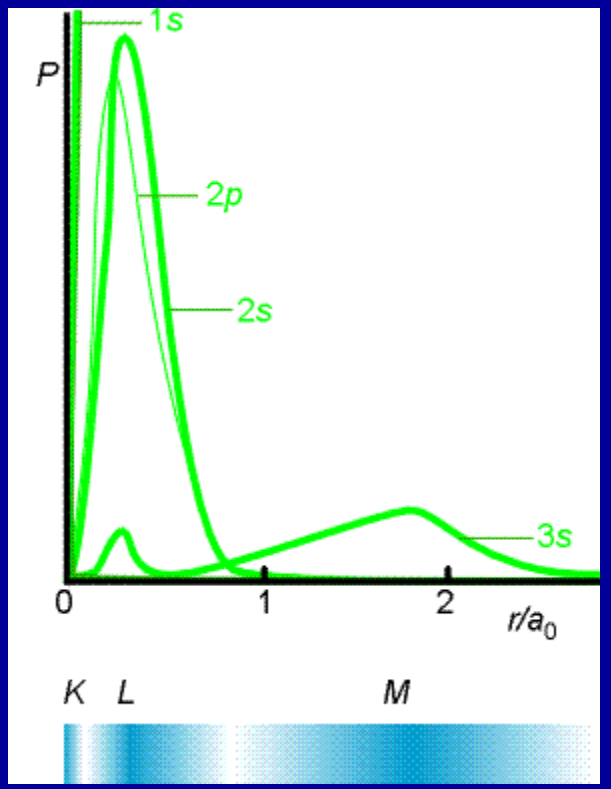
	1s	2s	2p		
a)	↑↓	↑↓	↑	↓	
b)	↑↓	↑↓	↑↑		
c)	↑↓	↑↓	↑	↑	
d)	↑↓	↑↓	↑↓		



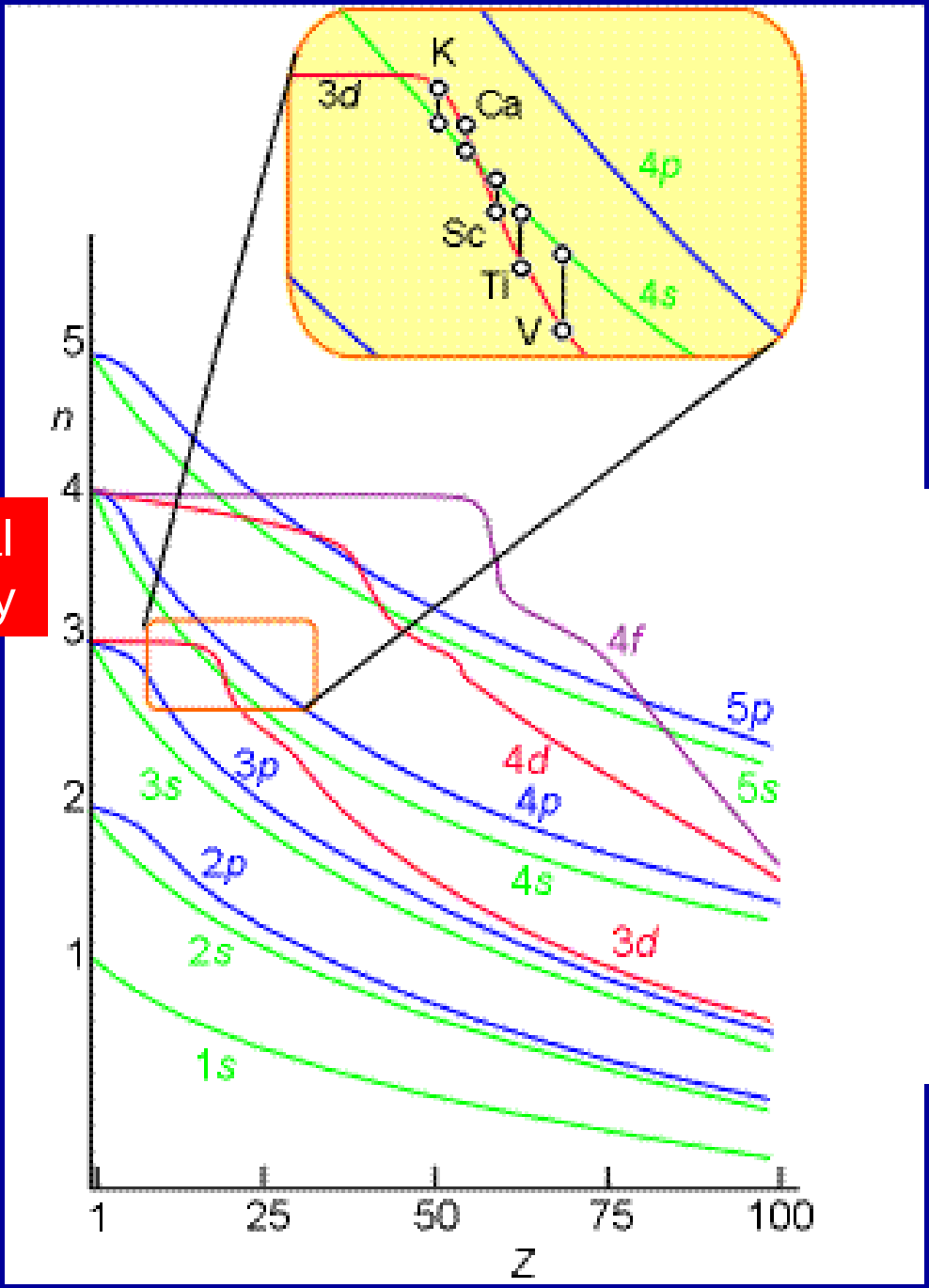
Electron Configurations of Valence Shell

(Ne)



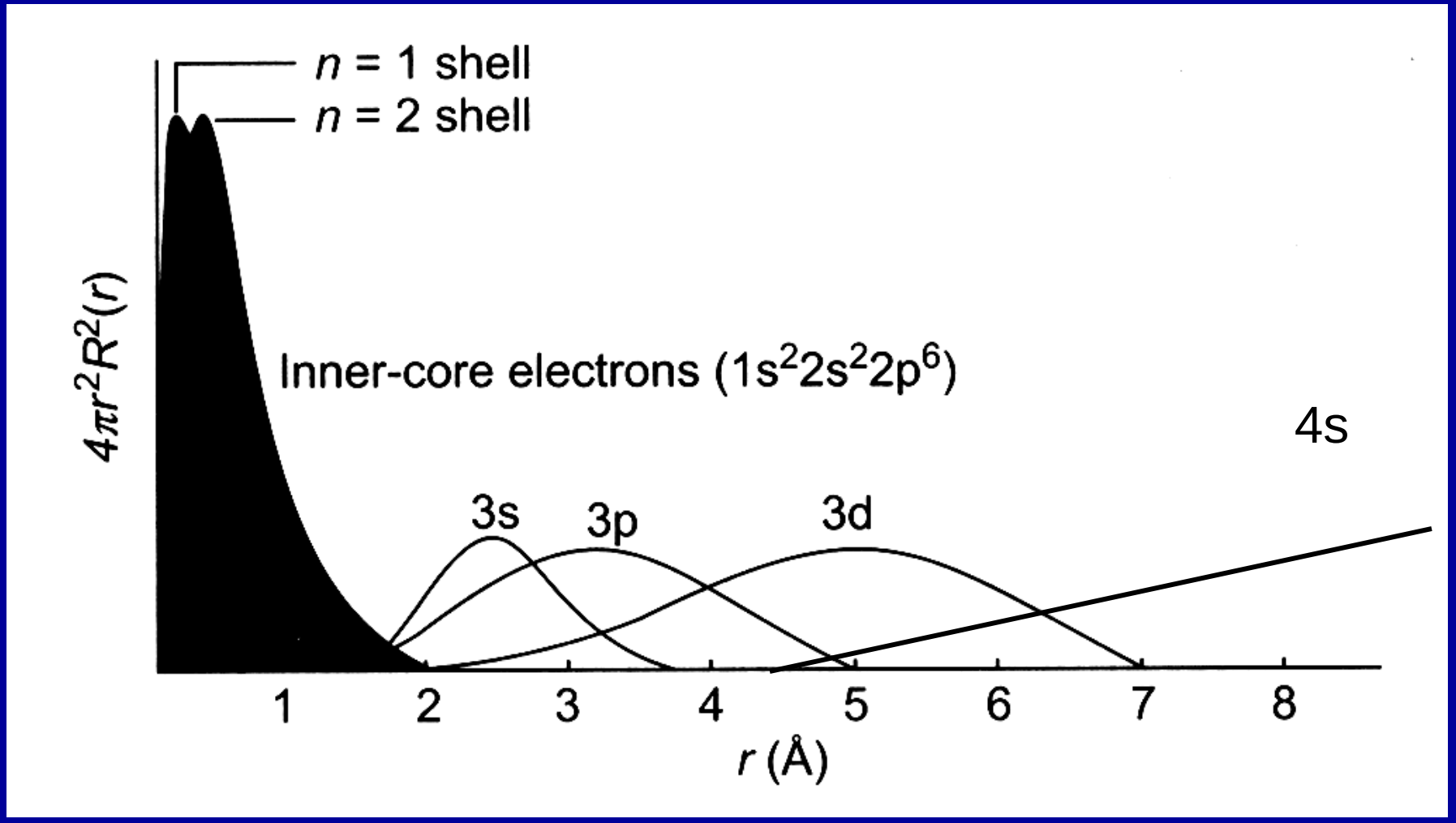


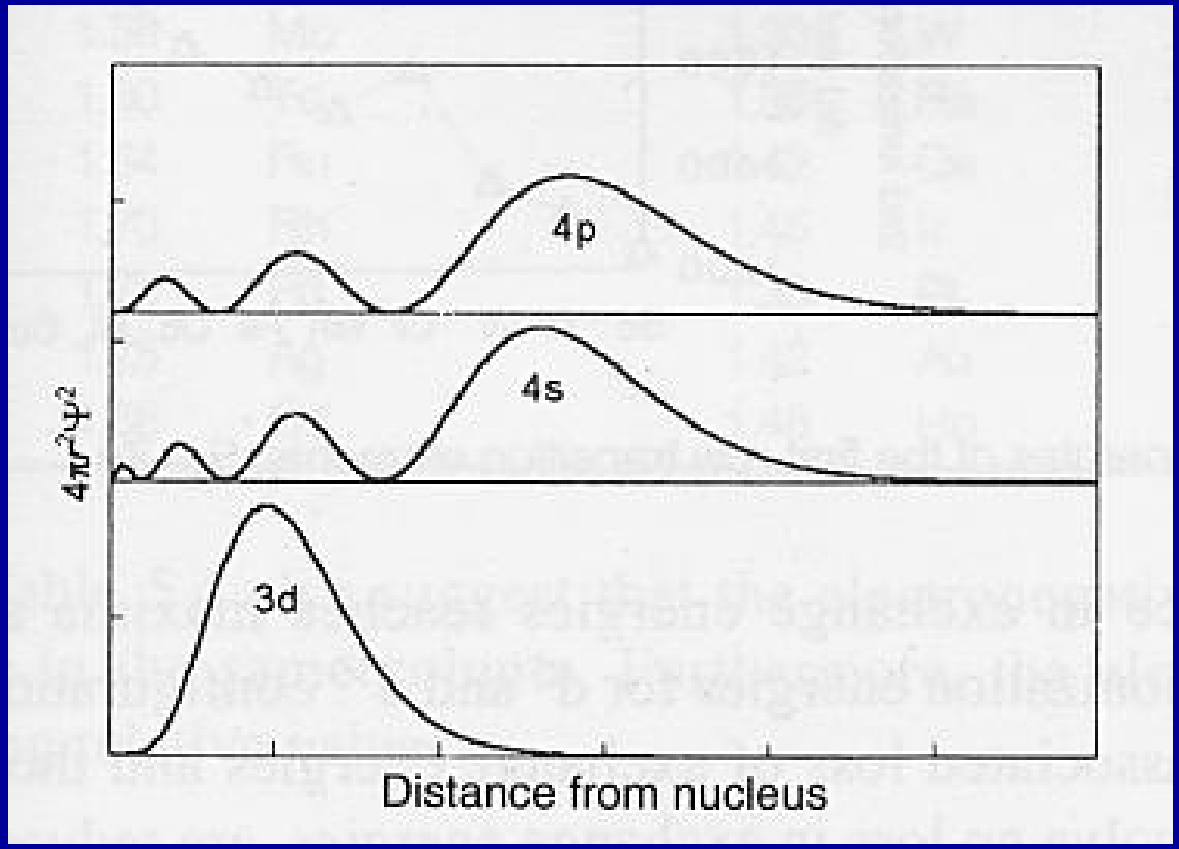
Orbital energy



Placing electrons in orbitals can change order of energy levels

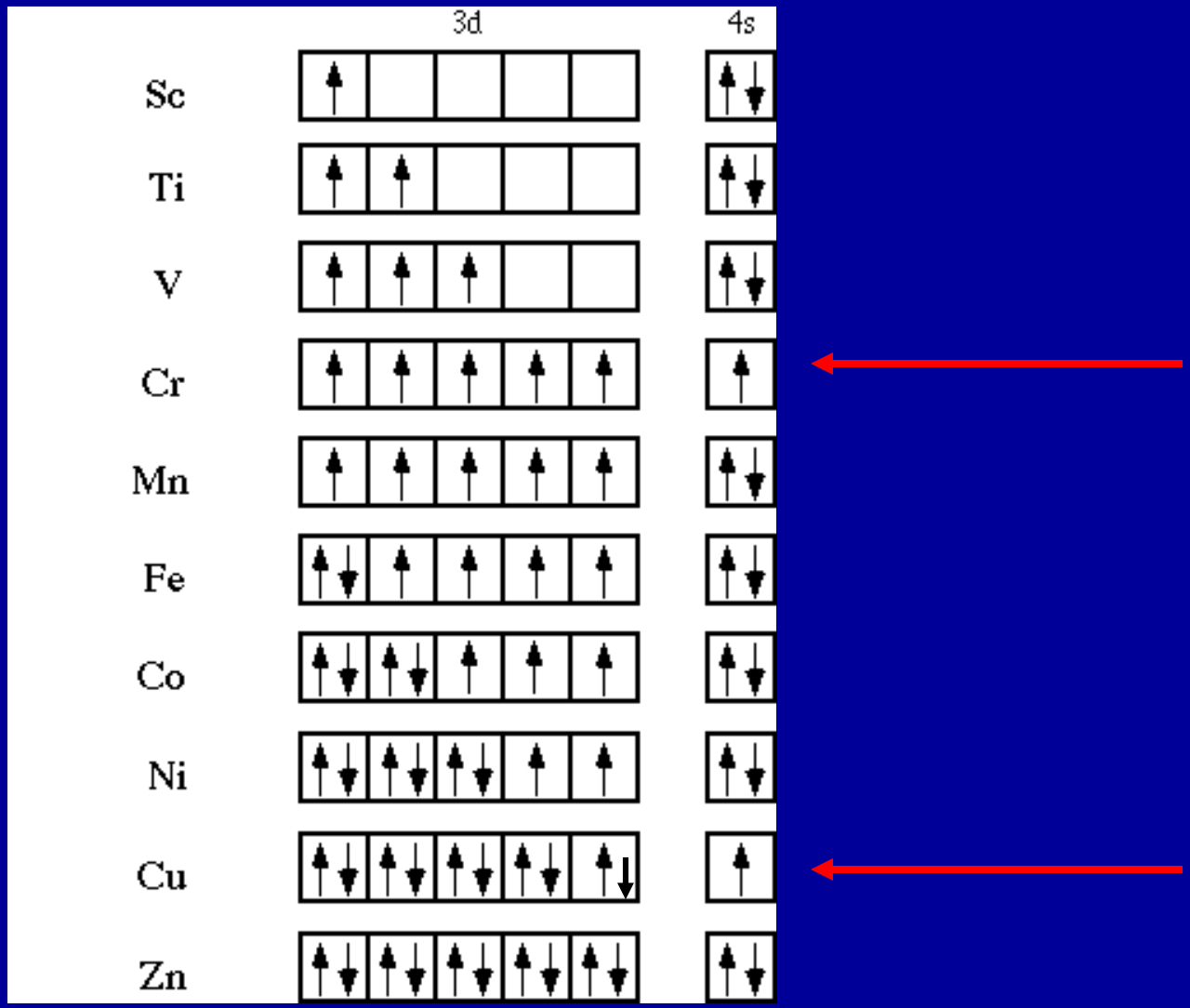
Starting at Sc, 3d orbitals have lower energy than 4s


n = 1 shell
n = 2 shell
Inner-core electrons (1s²2s²2p⁶)
4s
3s
3p
3d
4πr²R²(r)
1
2
3
4
5
6
7
8
r (Å)


4p
4s
3d
$4\pi r^2\psi^2$
Distance from nucleus

Electron Configurations of Valence Shell

(Ar)



Ionisation Energies