

Chapter 6

Electronic Structure of Atoms

The number & arrangement of e^- in an atom is responsible for its chemical behavior

I) The Wave Nature of Light

A) Electromagnetic Radiation

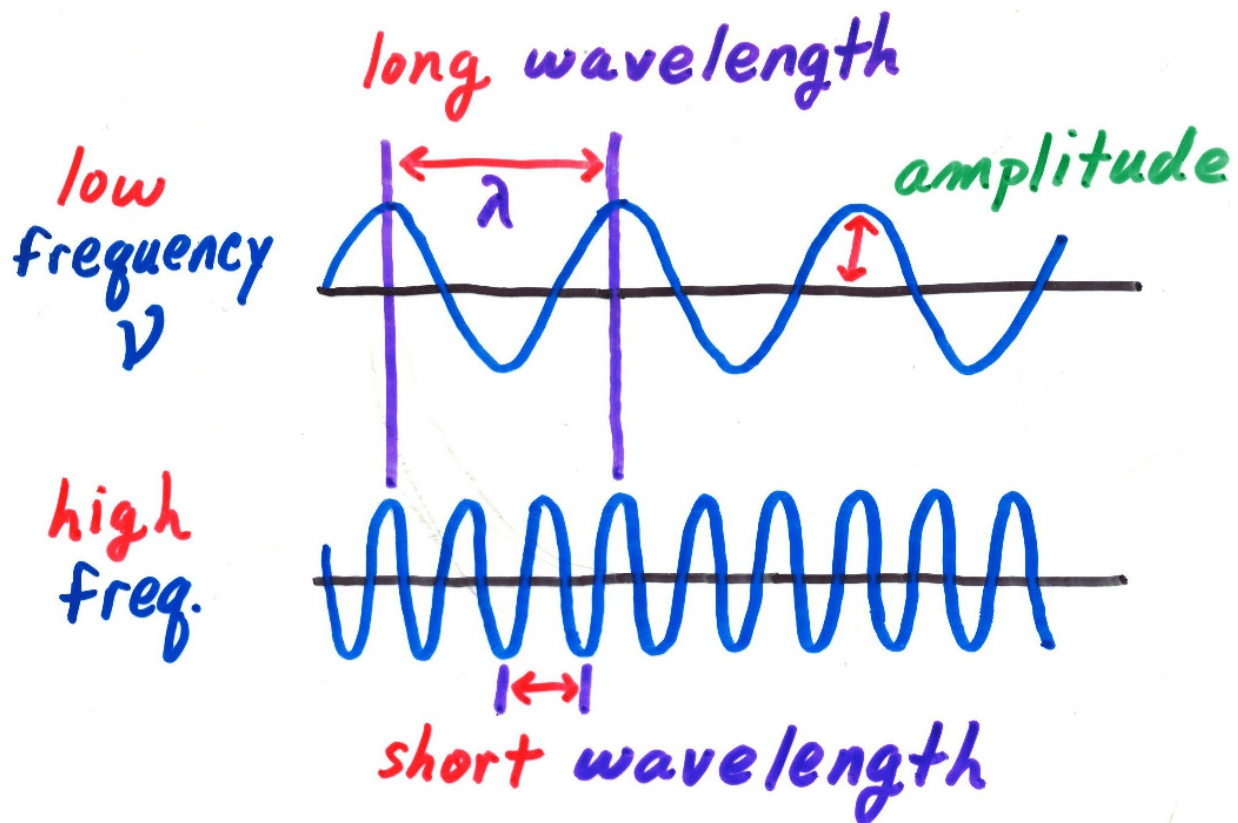
Radiant Energy

light, X-rays, UV, microwaves, etc.

All move at the speed of light,

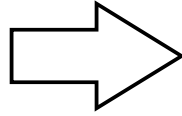
$$c = 2.99792 \times 10^8 \text{ m/s}$$

have wavelike characteristics



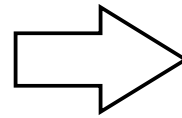
- λ , wavelength distance between successive peaks
- ν , frequency number of complete wavelengths or cycles which pass a given point per second
- amplitude height of peak - related to intensity of radiation

long
wavelength



low
frequency

short
wavelength



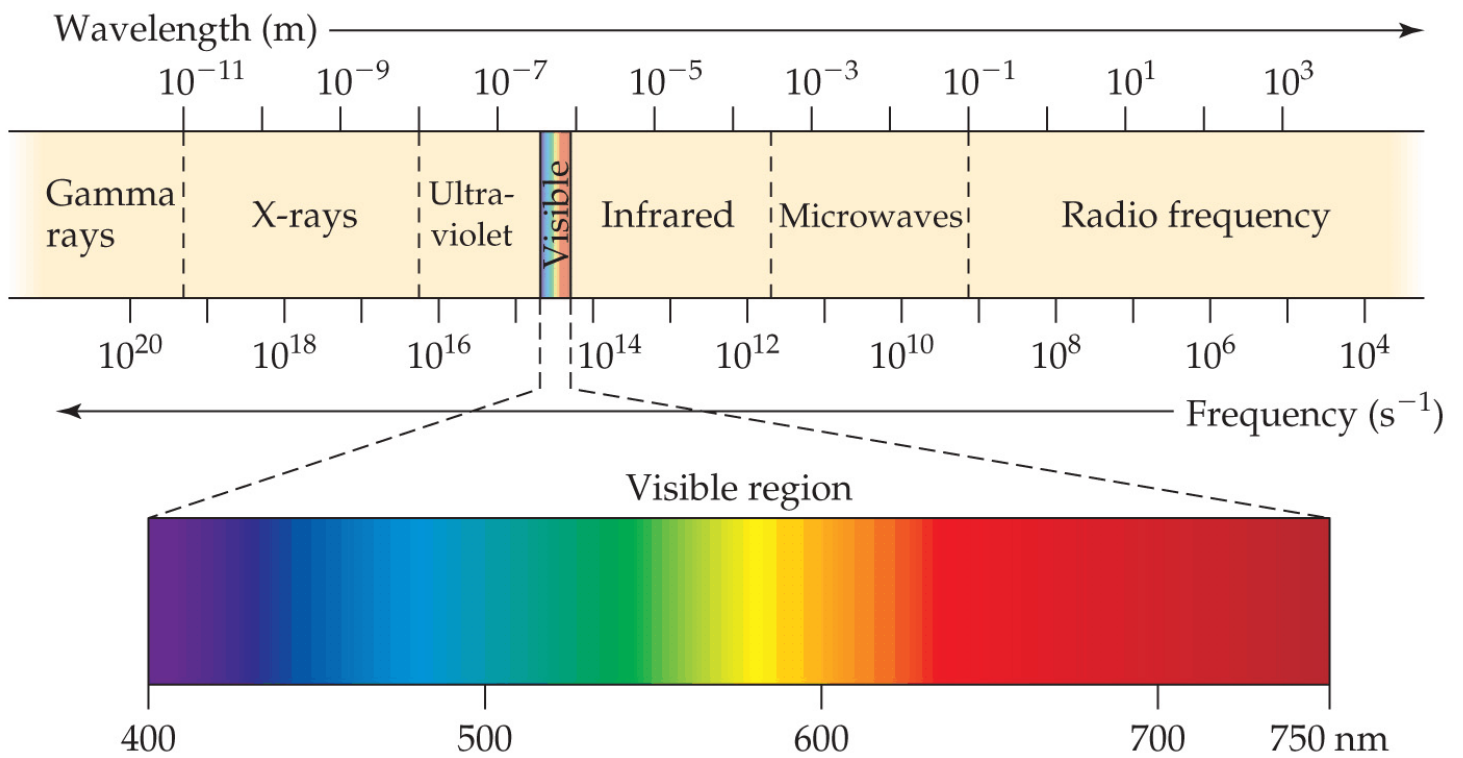
high
frequency

$$\nu \propto \frac{1}{\lambda}$$

$$\nu = \frac{c}{\lambda} \quad \text{or} \quad \nu \cdot \lambda = c$$

units for ν

s^{-1} ; cycles/s ; hertz, Hz



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X- rays **visible** IR microwave radio

λ (m) 10^{-9} 10^{-7} 10^{-5} 10^{-2} 10^2

ν (s^{-1}) 10^{17} 10^{15} 10^{13} 10^{10} 10^6

II) Quantized Energy and Photons

A) Plank's Theory

Energy changes are quantized

- discrete energy changes

$$\Delta E = n h \nu \quad n = 1, 2, 3, 4, \dots$$

Planck's constant

$$h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s},$$

Smallest increment of energy, at a given frequency, is termed a quantum of energy

B) Photoelectric Effect

A **minimum** **freq.** of **light** shining on a **metal** surface causes it to **emit** e^-

Einstein: energy is a stream of **particle like** energy **packets** called **photons**

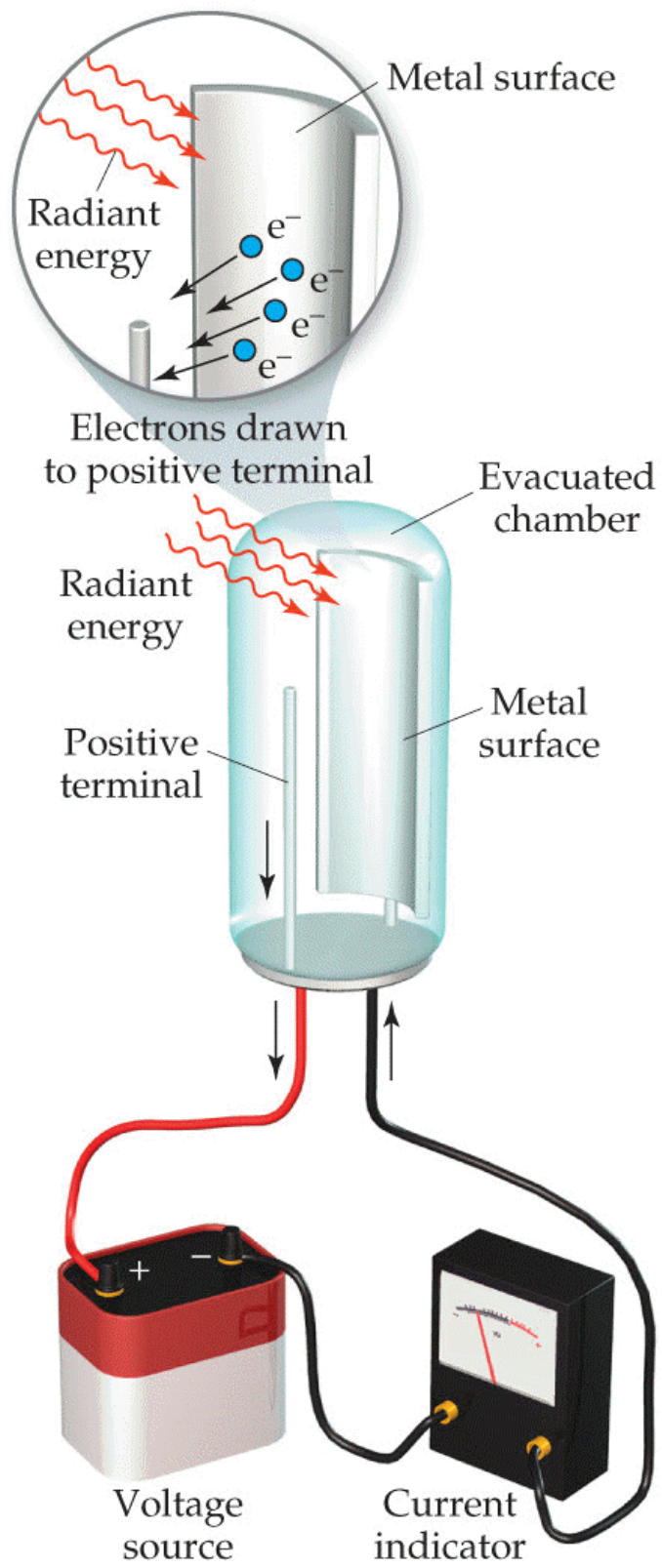
- radiant energy is **quantized**

$$E_{\text{photon}} = h \nu = \frac{h c}{\lambda}$$

high ν (**low** λ) \Rightarrow **high** E

low ν (**high** λ) \Rightarrow **low** E

Note : **duality** of **light** - behaves **both** as a **wave** and **particle**



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1) Ex: A laser emits a signal with a wavelength of 351 nm. Calculate the energy of a photon of this radiation.

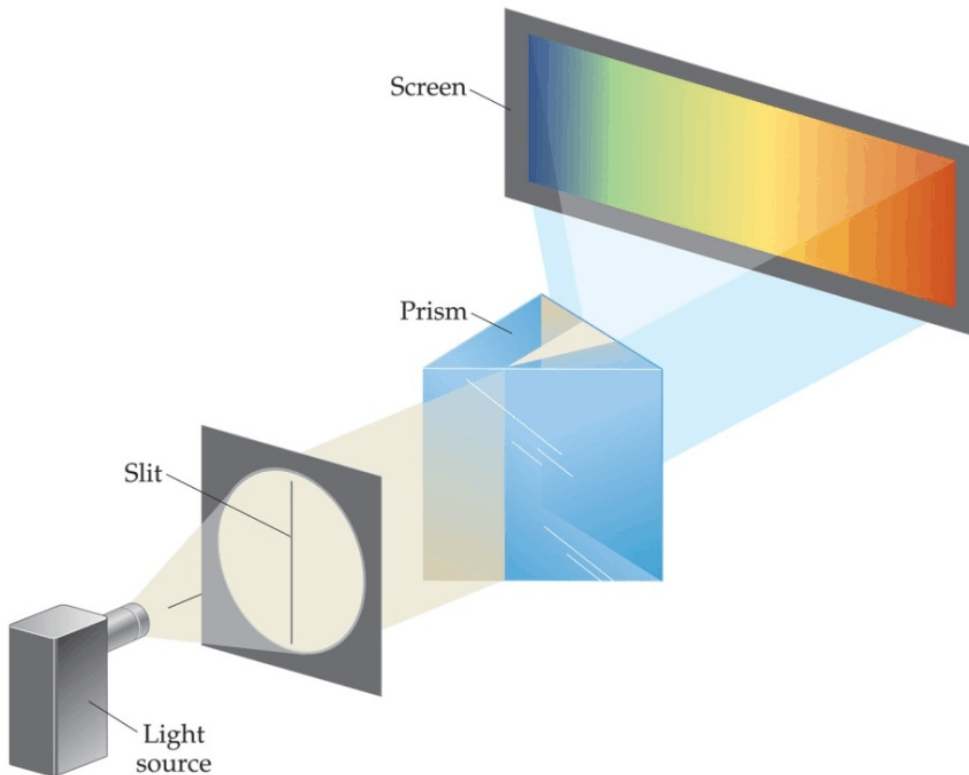
$$\begin{aligned} E &= h \nu = \frac{h c}{\lambda} \\ &= \frac{(6.63 \times 10^{-34} \text{ Js})(3.00 \times 10^8 \text{ m/s})}{3.51 \times 10^{-7} \text{ m}} \\ &= 5.67 \times 10^{-19} \text{ J} \end{aligned}$$

III) Line Spectra and the Bohr Model

A) Line Spectra

1) **White** light passing through a **prism** results in **band** called a

continuous spectrum (**rainbow**)



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2) monochromatic light

Light with a **single** wavelength

- lasers

3) Line Spectra

discharge tube - atom **absorbs** energy
& it can later **emit** it as light

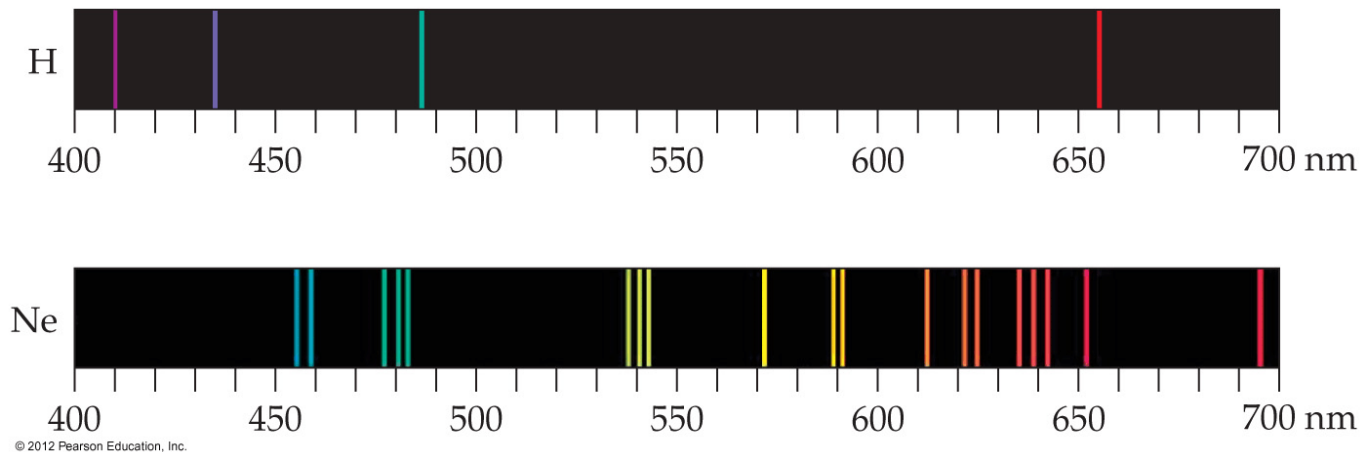
Passed through a prism see a
series of **narrow** colored lines
(**specific** λ 's)

Line Spectrum

Each **line** associated with a
particular energy and color

Different elements give different & distinctive line spectra

- characteristic of a particular element
- use to identify elements



B) Rydberg Equation

Wavelengths of lines in hydrogen spectrum given by,

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

$$n_2 > n_1$$

Rydberg Constant

$$R_H = 1.097 \times 10^7 \text{ m}^{-1}$$

B) Bohr Model

1) Energy Levels & Orbits

e^- is restricted to certain energy levels corresponding to spherical orbits, w. certain radii, about the nucleus

$$r = n^2 a_0$$

$$E_n = -hc \cdot R_H \left(\frac{1}{n^2} \right)$$

n = principle quantum number

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

Bohr radius:

$$a_0 = 5.292 \times 10^{-11} \text{ m} = 0.5292 \text{ \AA}$$

$$hc \cdot R_H = 2.180 \times 10^{-18} \text{ J}$$

a) Ground State

e^- in $n = 1$ orbit
closest to nucleus

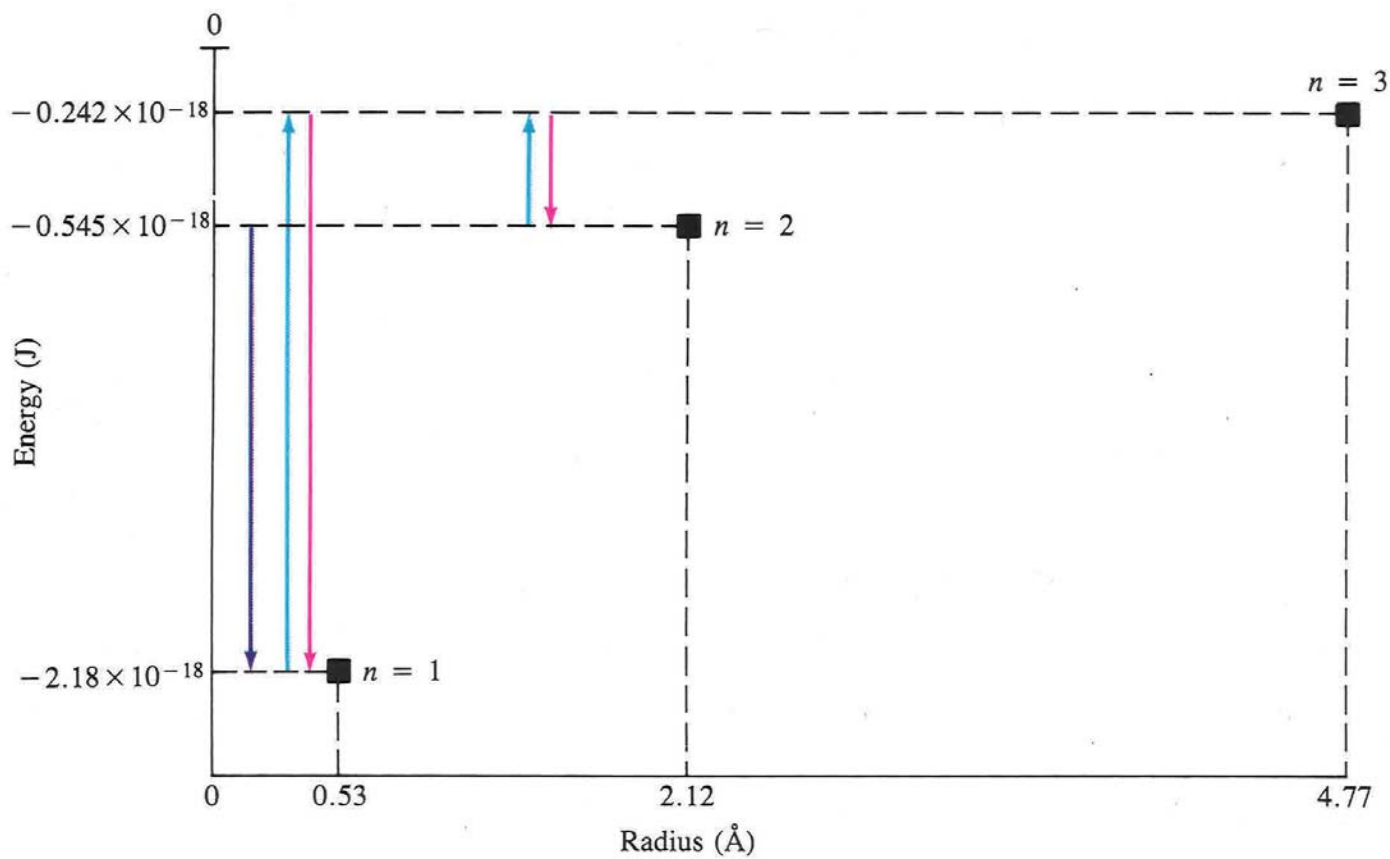
largest value of $1/n^2$

most negative E

* Lowest energy level

Note: most neg. E represents
most stable state

Radii and energies of Bohr orbits 1-3



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by Brown/Le May/Bursten

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b) Excited States

$$n > 1$$

higher energy

less neg. E, less stable

inc. distance from nucleus

$$r \propto n^2$$

c) Zero-Point of Energy

$$n = \infty$$

e^- completely separated
from nucleus

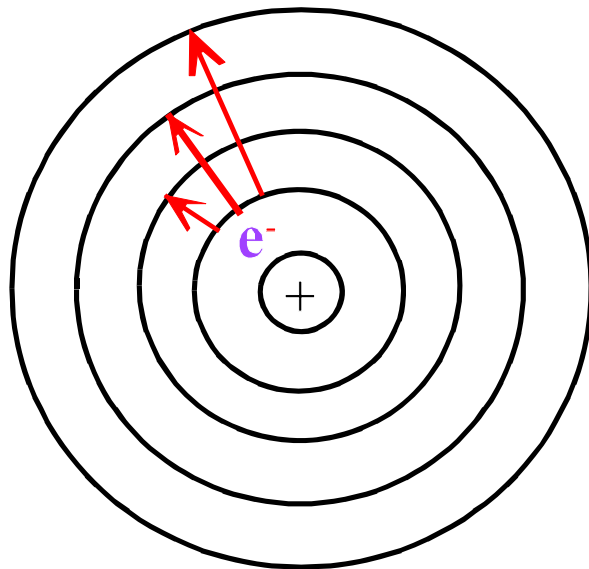
$$E_{\infty} = -hc \cdot R_H \left(\frac{1}{\infty} \right) = 0$$

2) Energy Transitions

a) Absorption of Energy

e^- absorbs energy

- jumps to higher energy levels, farther from nucleus
- Excited State

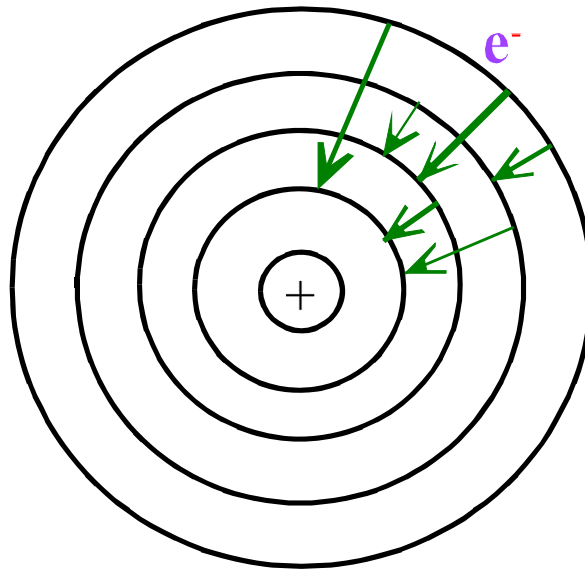


b) Emission of Energy - light

e^- “falls” to lower level

- emits the energy diff. as
a quantum of light,

a photon



$$E_{\text{photon}} = - \Delta E_{\text{emission}} = h \nu = \frac{h c}{\lambda}$$

c) Energy Changes

Energy diff. between orbits

$$\Delta E = E_f - E_i = \frac{-hc \cdot R_H}{n_f^2} - \frac{-hc \cdot R_H}{n_i^2}$$

$$\Delta E = -hc \cdot R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$\Delta E = -2.180 \times 10^{-18} \text{ J} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

1) $n_f > n_i$

$$\Delta E > 0, \quad E \text{ inc.}$$

Absorption

$$2) \quad \underline{n_f < n_i}$$

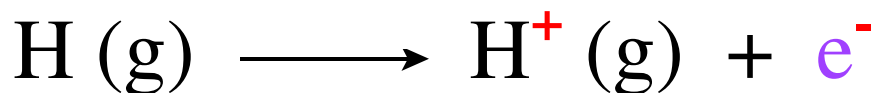
$$\Delta E < 0, \quad E \text{ dec.}$$

Emission

$$3) \quad \underline{n_f = \infty}$$

complete removal of e^-

Ionization



$$n_i = 1 \quad n_f = \infty$$

$$\Delta E = h c \cdot R_H \left(\frac{1}{1^2} \right) = 2.180 \times 10^{-18} \text{ J}$$

d) Energy of a Photon

Energy of a photon emitted when e^- “drops” to a lower energy level is related to freq. (wavelength) of radiation

$$E_{\text{photon}} = -\Delta E_{\text{em}} = h\nu = \frac{hc}{\lambda}$$

$$\nu = c \cdot R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

or

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

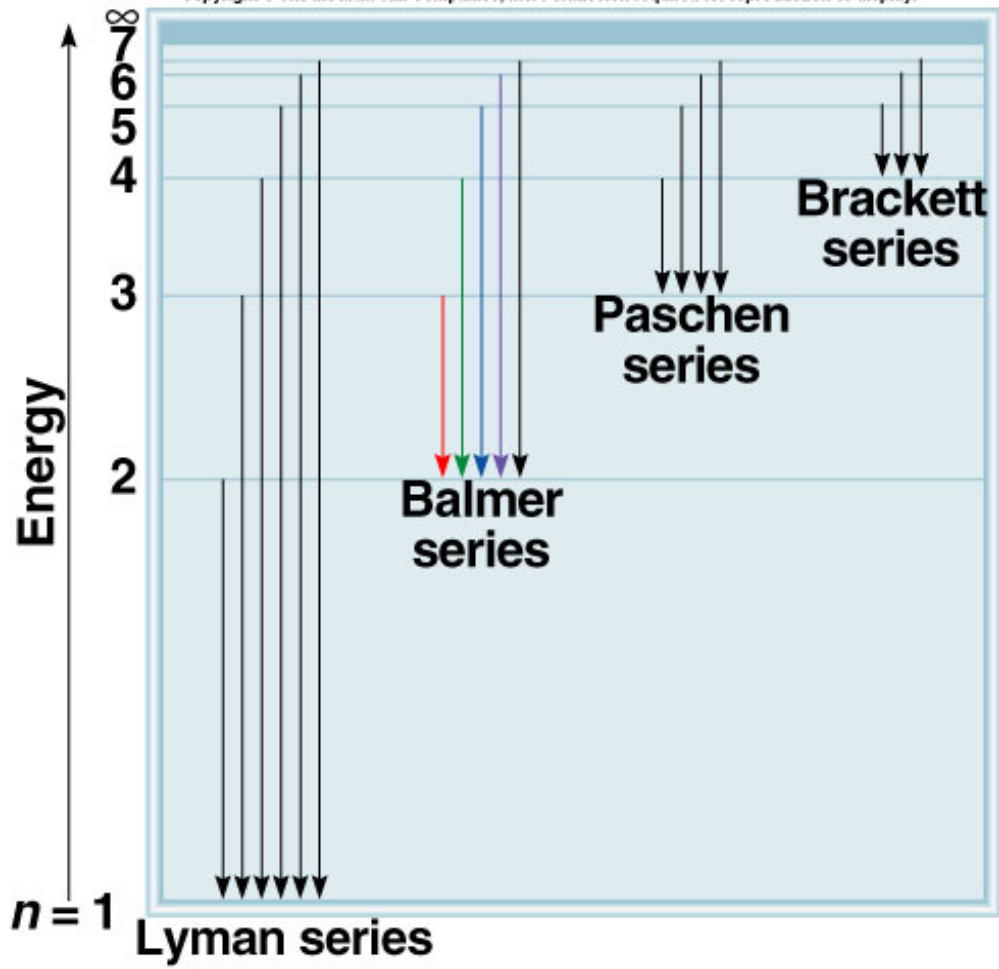
e) Ex : Calc. the wavelength of a line in the visible spectrum for which $n_i = 3$.

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Balmer Series (visible):

$$n_f = 2$$

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IV) Wave Behavior of Matter

A) de Broglie

Matter should have wave prop.

For photons:

$$E_{\text{photon}} = h \nu = \frac{h c}{\lambda}$$

From Einstein:

$$E = m c^2$$

$$\lambda = \frac{h}{m c}$$

wavelength for photon traveling at c
with an effective mass, m

B) de Broglie Wavelength for Particles

$$\lambda = \frac{h}{m v}$$

v = velocity of the particle

h (6.63×10^{-34} J•s) is extremely small so λ is too small for macroscopic particles.

λ can only be detected for particles w. very small mass,

i.e. e^- ($m = 9.11 \times 10^{-28}$ g)

1) Ex 1: Calculate the de Broglie wavelength for a 907.2 kg car moving at a speed of 96.6 km/hr.

$$\lambda = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})}{(907.2 \text{ kg}) (26.83 \text{ m/s})}$$
$$= 2.72 \times 10^{-38} \text{ m}$$

2) Ex 2: Calculate the de Broglie wavelength for an electron moving at a speed of 3×10^6 m/s.

$$\lambda = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})}{(9.11 \times 10^{-31} \text{ kg}) (3 \times 10^6 \text{ m/s})}$$
$$= 2.43 \times 10^{-10} \text{ m} \quad (0.243 \text{ nm})$$

X-rays

C) Heisenberg Uncertainty Principle

The wave-particle duality of matter makes it impossible to precisely measure both the position and momentum of an object.

Δx = uncertainty in position

Δp = uncertainty in momentum (mv)

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

Limit on simultaneously measuring position and momentum (speed).

1) Wave Functions

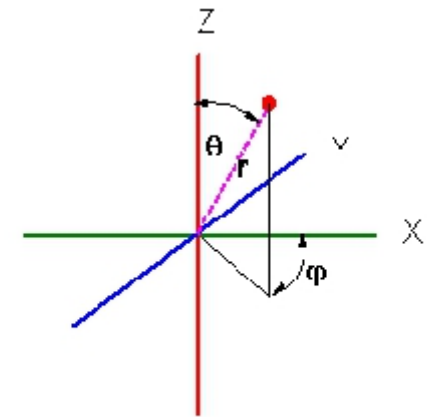
Get a series of solutions to the wave eqn.

wave functions, ψ

Each ψ corresponds to a specific energy & describes a region about the nucleus, an orbital, in which an e^- w. that energy may be found

ψ has no direct physical meaning

The general equation for ψ for H in polar coordinates is:



Polar coordinate system

$$\psi_{(n,l,m,r,\theta,\phi)} = \sqrt{\frac{(n-l-1)!}{n((n+l)!)^3}} \left(\frac{1}{na_0}\right)^{\frac{3}{2}+l} r^l e^{\left(\frac{-r}{na_0}\right)} (n+l)! \left(\sum_{i=0}^{n-l-1} \frac{(-1)^i (n-l)! \left(\frac{2r}{na_0}\right)^i}{(n-l-1-i)!(2l+1+i)!i!} \right) \bullet$$

$$\sqrt{(2l+1)(l-|m|)!(l+|m|)!} \sin(\theta)^{|m|} \left(\sum_{i=0}^{l-|m|} \frac{(l!)^2 (\cos\theta - 1)^{l-|m|-i} (\cos\theta + 1)^i}{(l-i)!i!(l-|m|-i)!(|m|+i)!} \right) e^{im\phi} \left(\frac{1}{\sqrt{\pi l!}} \right)$$

Can only determine the **probability** of **finding** e^- in a certain **region** of **space** at a given instant,

ψ^2 **probability density**

Electron density

Greater where e^- spends **more** of its **time**.

Probability of finding an e^- is **high** in regions of **high** e^- **density**

B) Orbitals & Quantum Numbers

ψ represents an orbital and has 3 characteristic quantum numbers associated with it,

n	l	m_l
energy and distance from nucleus	shape	orientation of an orbital

The first 3 arise naturally from the solution of the Sch. Eqn.

There is a 4th quantum no.

m_s : spin

1) Principal quantum number, n

Determines:

- energy level
- average distance from nucleus
- Identifies the shell

$$n = 1, 2, 3, 4, \dots$$

Larger n \Rightarrow farther shell is from nucleus & higher energy

$$\text{Max. no. of } e^- \text{ in shell} = 2n^2$$

$$n = 1 \quad 2(1)^2 = 2 e^-$$

$$n = 2 \quad 2(2)^2 = 8 e^-$$

$$n = 3 \quad 2(3)^2 = 18 e^-$$

n^{th} shell (n)	no. of subshells (= n)	designation	max # e ⁻ by subshell	total # e ⁻ in shell ($2n^2$)
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1	1	1s	2	2
2	2	2s, 2p	2+6	8
3	3	3s, 3p, 3d	2+6+10	18
4	4	4s, 4p, 4d, 4f	2+6+10+14	32

3) Magnetic q.n., m_ℓ

Describes orientation of orbital in space

$$m_\ell = +\ell, \dots, 0, \dots, -\ell$$

integer values from $+\ell$ to $-\ell$

possible values = # orbitals in
for m_ℓ a subshell

$(2\ell + 1)$ orbitals in a subshell

Total # orbitals in shell $n = n^2$

orbital contains a max. of $2 e^-$

max. # e^- in subshell = $2(2\ell + 1)$

a) Ex:

$$\ell = 0$$

$$m_\ell = 0;$$

s subshell has
1 orbital

max # e⁻

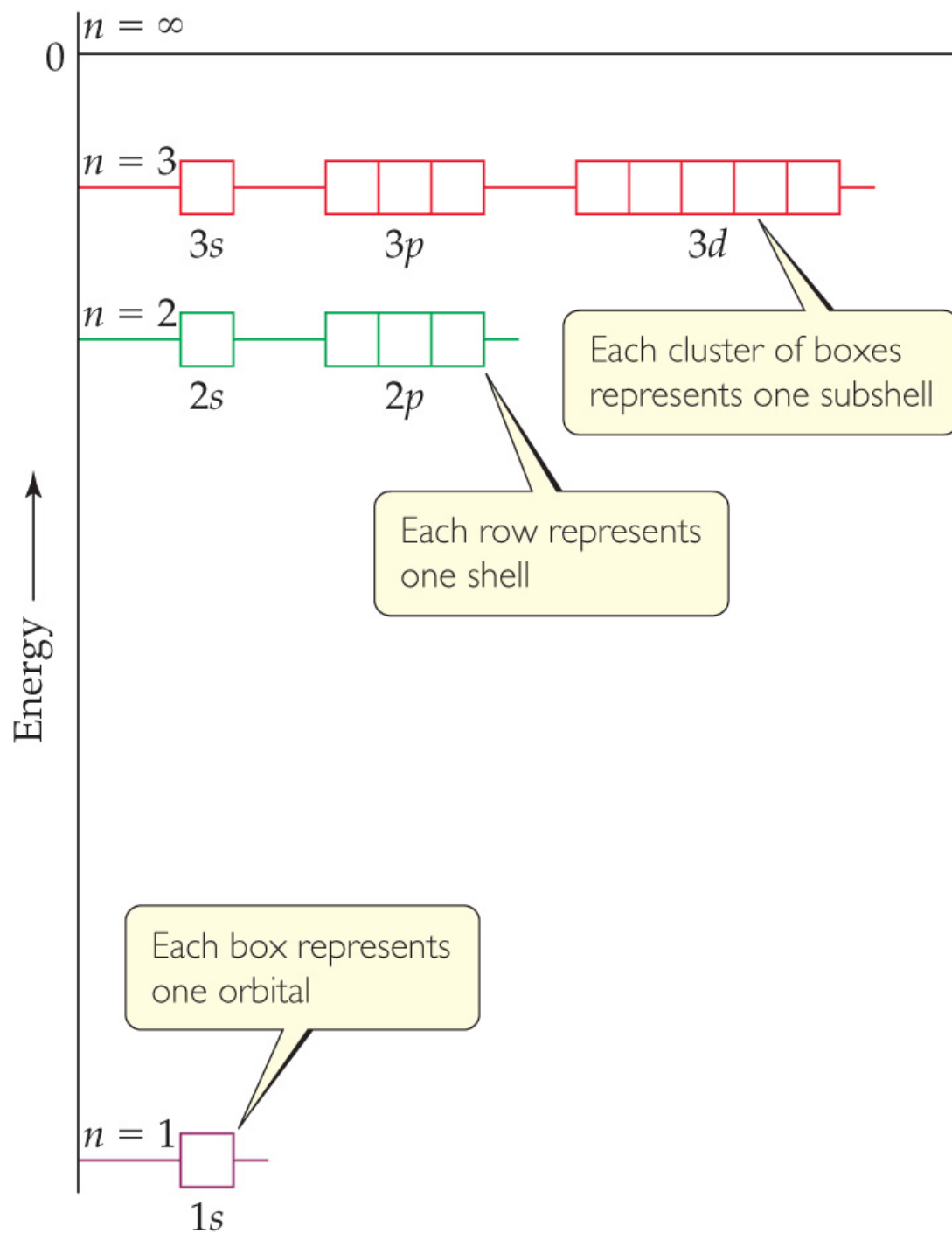
<u>ℓ</u>	<u>subshell</u>	<u># orbitals</u>	<u>in subshell</u>
0	s		
1	p		
2	d		
3	f		
4	g		
5	h		

TABLE 6.2 • Relationship among Values of n , l , and m_l through $n = 4$

n	Possible Values of l	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1s	0	1	1
2	0	2s	0	1	4
	1	2p	1, 0, -1	3	
3	0	3s	0	1	9
	1	3p	1, 0, -1	3	
	2	3d	2, 1, 0, -1, -2	5	
4	0	4s	0	1	16
	1	4p	1, 0, -1	3	
	2	4d	2, 1, 0, -1, -2	5	
	3	4f	3, 2, 1, 0, -1, -2, -3	7	

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Energy Levels in the H atom



$n = 1$ shell has one orbital

$n = 2$ shell has two subshells composed of four orbitals

$n = 3$ shell has three subshells composed of nine orbitals

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VI) Representations of Orbitals

ψ has **no** direct physical meaning

ψ^2 probability density
(electron density)

probability of finding e^- at
a given point in space

$(4\pi r^2) \psi^2$ radial probability density

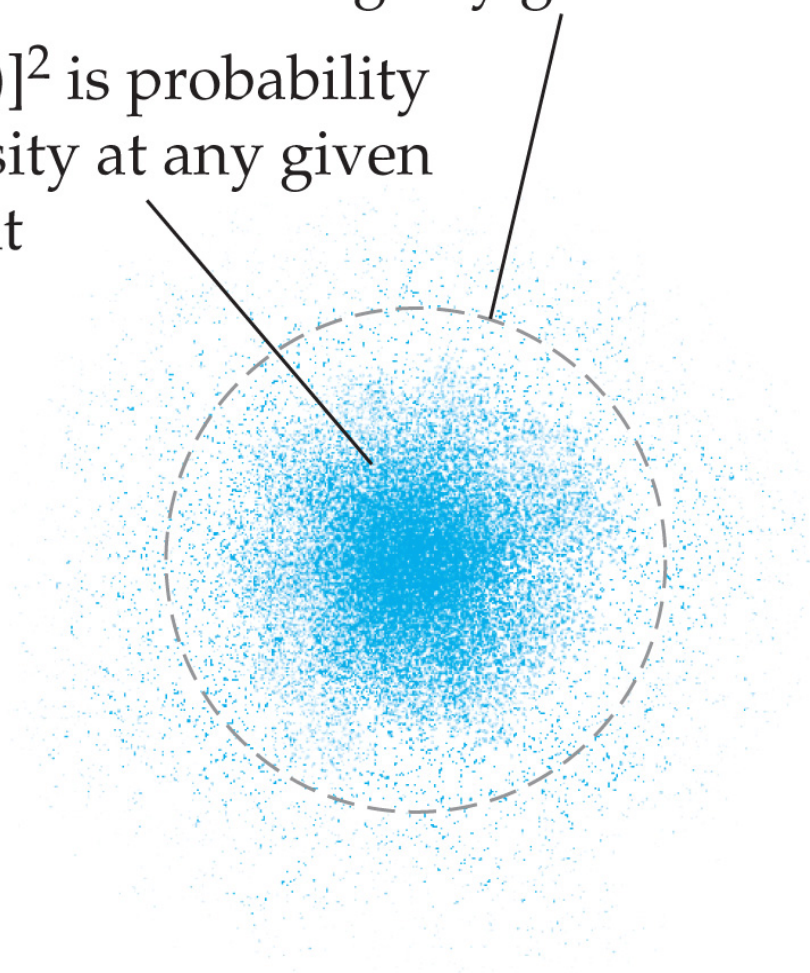
probability of finding e^- at a
specific distance, r , from the
nucleus

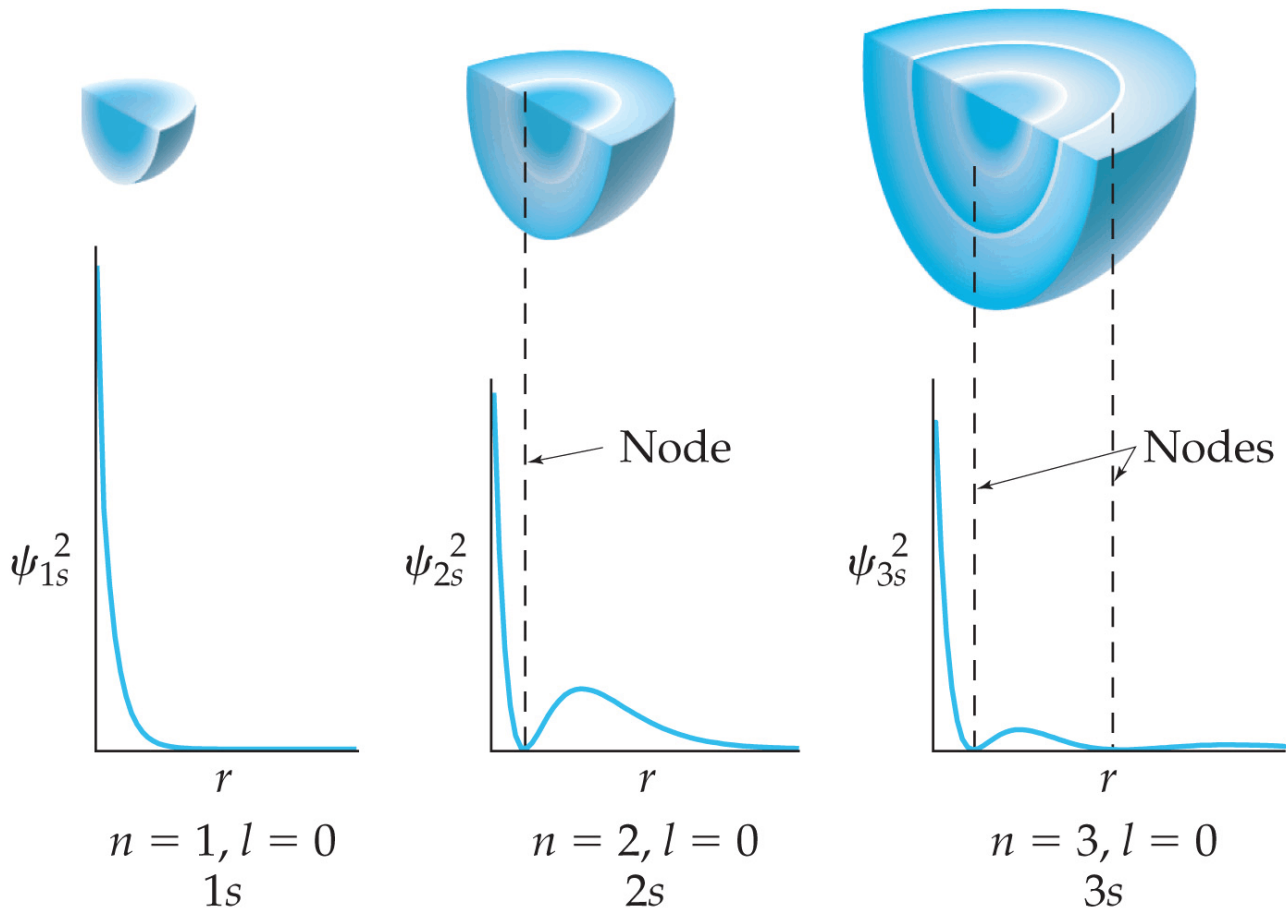
A) s orbitals

$l = 0$ All s orb. are spherical

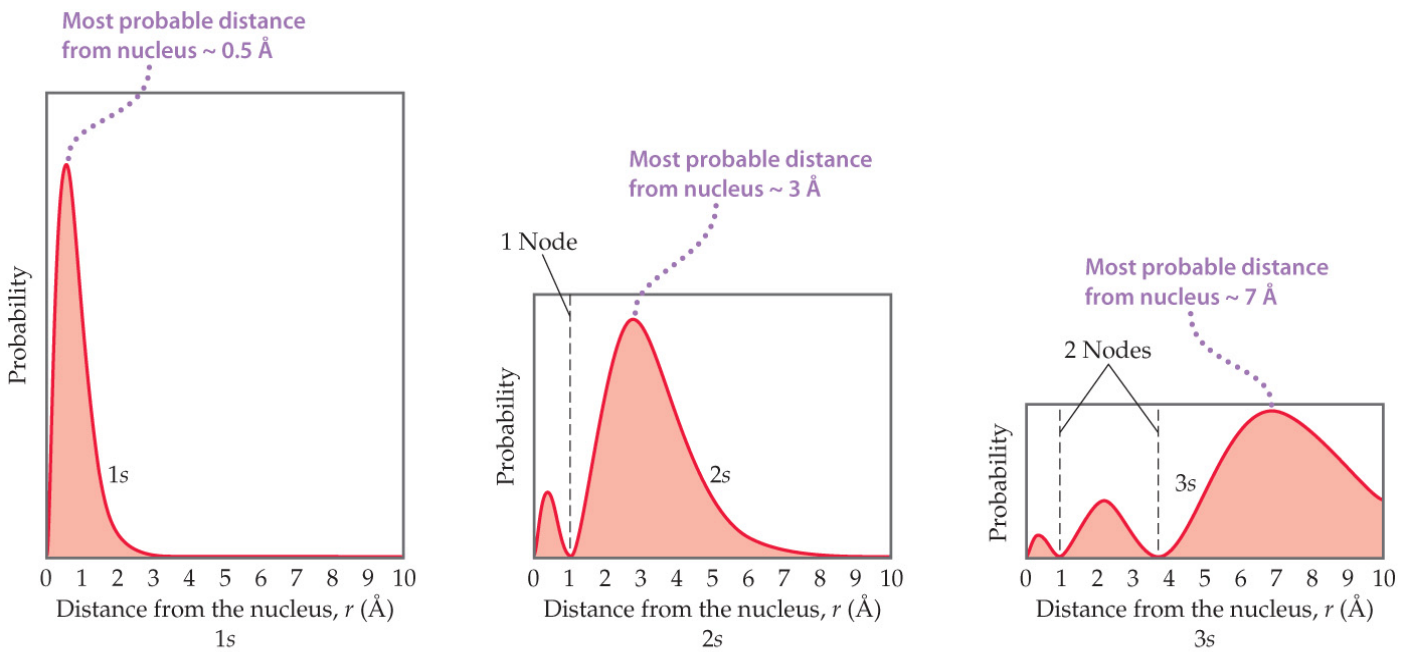
$4\pi r^2[\psi(r)]^2$ is radial probability function = sum of all $[\psi(r)]^2$ having any given value of r

$[\psi(r)]^2$ is probability density at any given point





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1) 3 trends from radial prop. dist.

a) Number of peaks inc. w. inc. n

$$\# \text{ peaks} = n$$

most probable distance further out & peaks get larger as move further from nucleus

b) Number of nodes inc. w. inc. n

points where the prob. is zero

$$\# \text{ nodes} = n - 1$$

$$\# \text{ spherical nodes} = n - \ell - 1$$

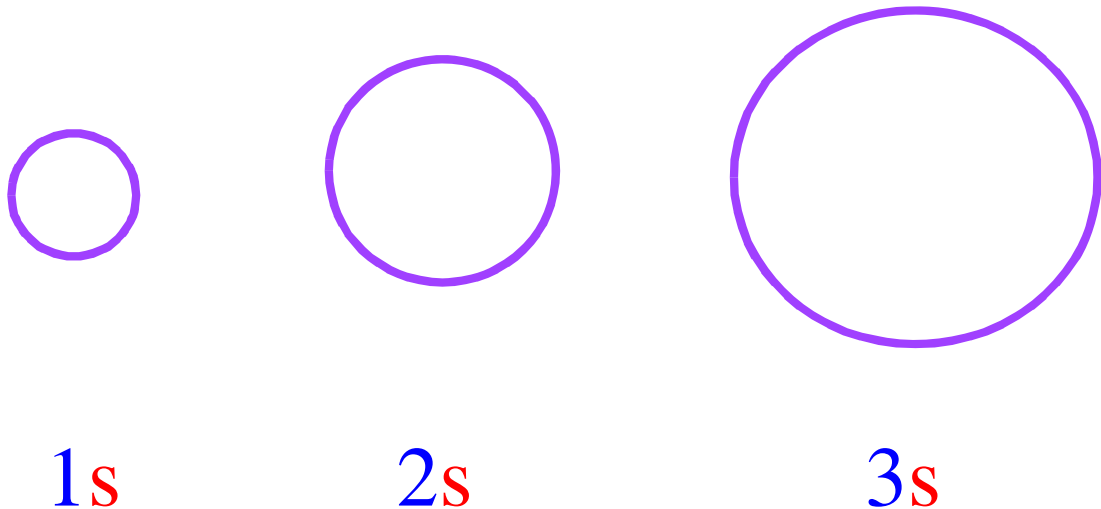
$$\# \text{ angular nodes} = \ell$$

c) e^- density spreads out w. inc. n

2) Contour Representation

represent a **volume** of space in which there is a **high probability** of finding the e^-

usually **90%**



e^- in orb. of **higher n** will be **greater** avg. **distance** from nucleus

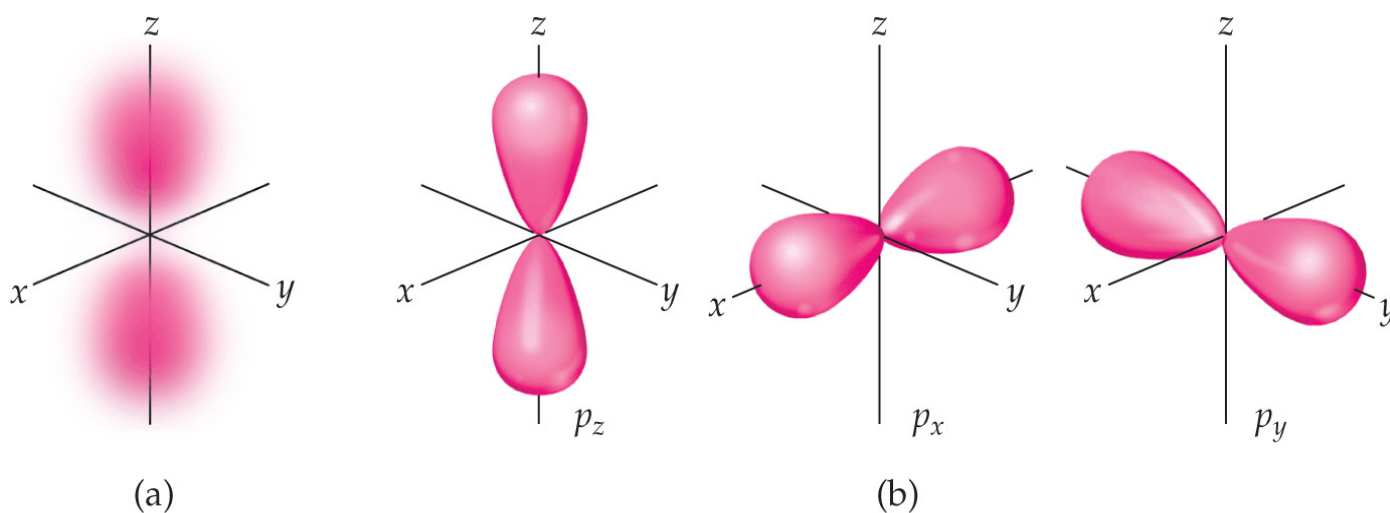
B) p orbitals

All p orbitals have 2 lobes pointing in opposite directions

dumbbell or teardrop

The 3 p orbs in a subshell differ in their orientation in space

- at right angles to each other



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VII) Many-Electron Atoms

H atom has only 1 e^-

E_{orb} depends on n and is determined by attraction between **positive proton** and **negative e^-** and average **distance** between them

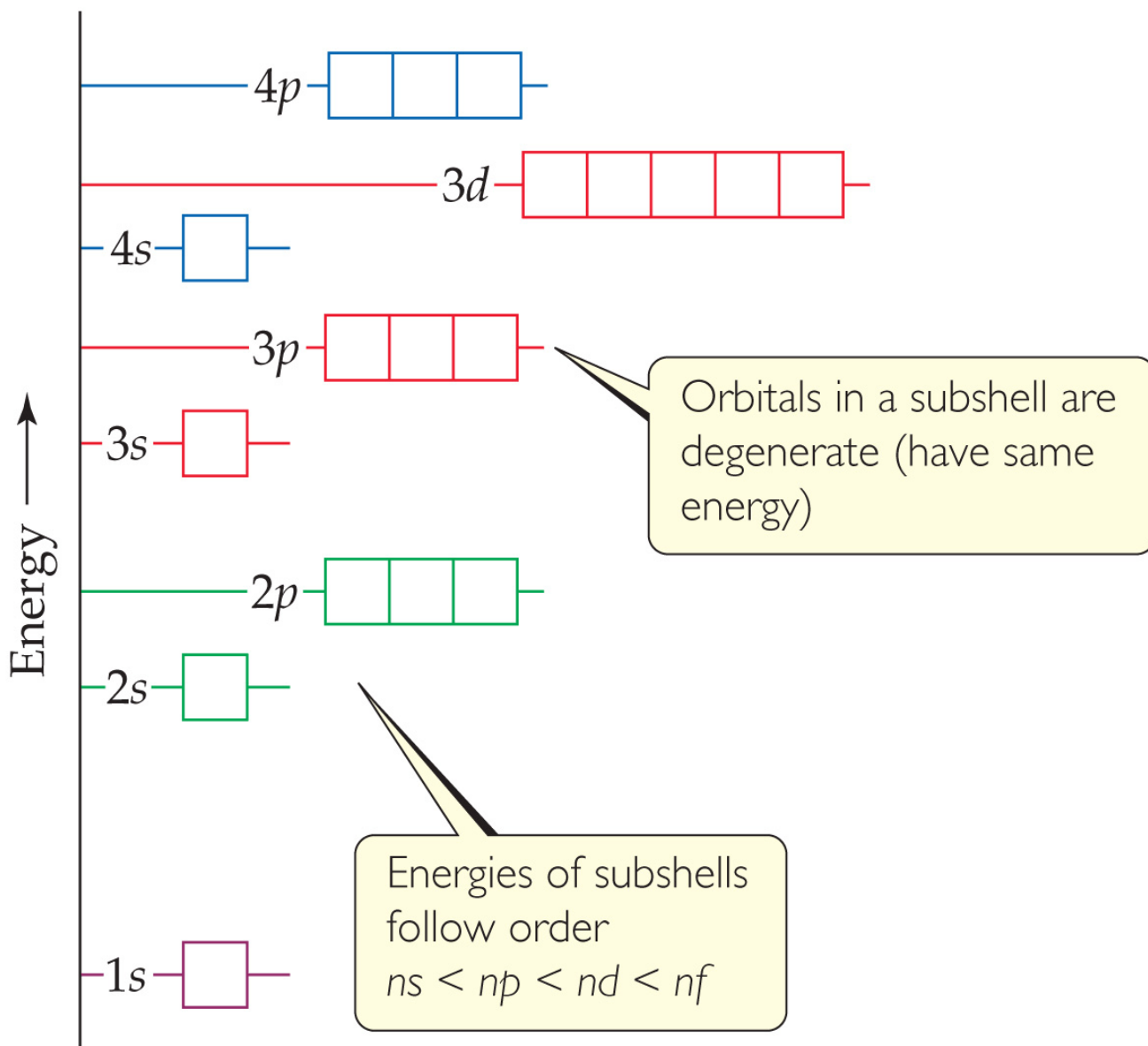
Many- e^- atoms:

Add $e^- - e^-$ **repulsions** to **E** & **diff. e^- -nucleus** attractions

Causes **subshells** to have **diff. E**

E_{orb} now depends on n and l

E of orbitals **w/in subshell** still **degenerate**



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A) Electron Spin

e^- “spins” about its own axis

- spinning charge generates a magnetic field

e^- only spin in either of 2 directions

quantized

electron spin q.n., m_s

+1/2

up

↑

-1/2

down

↓

B) Pauli Exclusion Principle

No 2 e^- in an atom can have same set of 4 quantum no.'s

$$n, \quad \ell, \quad m_\ell, \quad m_s$$

Look at 1s orbital

$$n = 1, \quad \ell = 0, \quad m_\ell = 0$$

can have only 2 e^- w. diff. values of m_s , $+1/2$ or $-1/2$

Limits max. # e^- in orbital to 2

- MUST have opposite spins

C) Summary of Quantum Numbers

1) Shell number, n

$$n = 1, 2, 3, 4, \dots$$

energy level & avg. distance
Period no. \Rightarrow highest n

$$\text{Max \# } e^- \text{ in shell} = 2n^2$$

2) Subshell, ℓ (shape of orbital)

$$\text{\# subshells in shell} = n$$

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

s, p, d, f, g, h....

$$\text{\# } e^- \text{ in subshell} = 2(2\ell + 1)$$

3) Orbitals, m_ℓ (orientation)

$$m_\ell = +\ell, \dots, 0, \dots, -\ell$$

$$\# \text{ orb. in shell} = n^2$$

$(2\ell + 1)$ orbitals in a subshell

$$\text{max. } \# e^- \text{ in subshell} = 2(2\ell + 1)$$

4) Spin, m_s

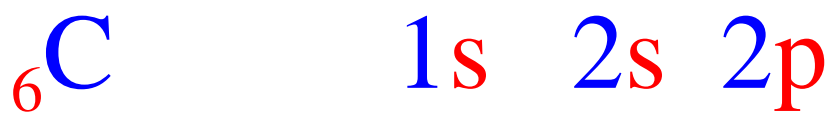
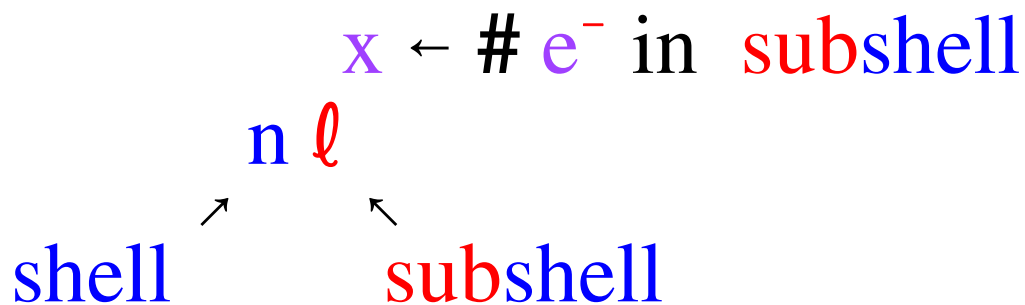
$$+1/2 (\uparrow) \quad -1/2 (\downarrow)$$

Subshell letters, # orbitals & max # e⁻ in subshell

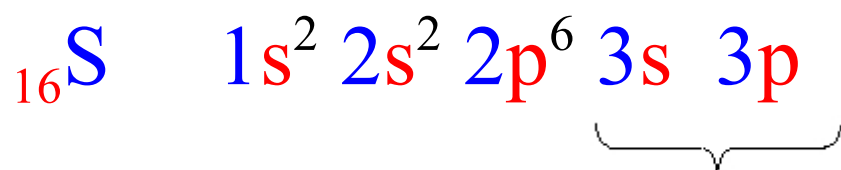
	$l =$	0	1	2	3	4	5
subshell letters		s	p	d	f	g	h ...
# orbitals in subshell		1	3	5	7	9	11 ...
max # e ⁻ in subshell		2	6	10	14	18	22 ...

VIII) Electron Configurations

Orbitals filled in order of **inc.** energy until **all e⁻** have been used



A) Ex: Consider sulfur, ${}_{16}\text{S} : 16 e^{-}$



valence shell
(outer shell)

${}_{16}\text{S}$ is in 3rd period ; $n_{\text{max}} = 3$

${}_{16}\text{S}$ is in group VI A, $6 e^{-}$ in outer
or valence shell

valence $e^{-} \Rightarrow e^{-}$ in outer or
valence shell

core $e^{-} \Rightarrow e^{-}$ in inner shells

Note: For representative elements

Period no. \Rightarrow n value of valence shell

Group no. \Rightarrow # of valence e^-

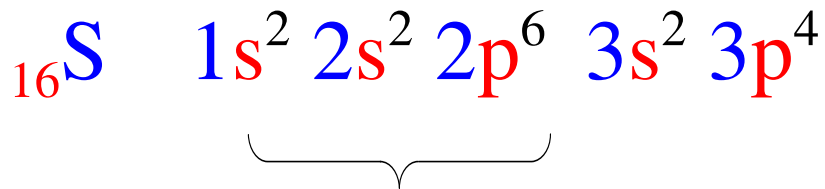
Elements in a group have similar chemical and physical properties

- same valence shell e^- configuration

e^- in outer shell are ones involved in chemical reactions

B) Shorthand Electron Configuration

Focus **attention** on **valence shell** e^-



completed subshells \Rightarrow **[Ne]**

noble gas from

previous period



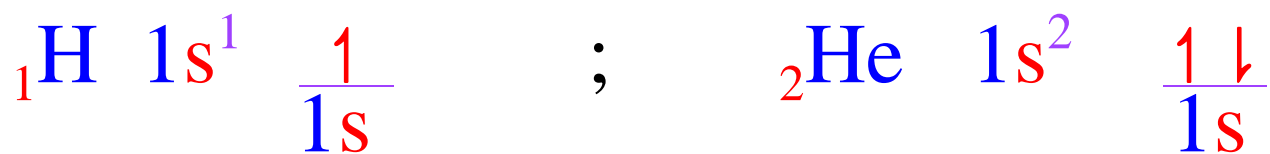
1) Ex: ${}_6\text{C}$



C) Orbital Diagrams

A **dash** indicates an **orbital**

Use **arrows**, \uparrow or \downarrow to indicate e^-
with **up** or **down spin**



1s 2s 2p



single e^- in an orbital, 1, unpaired

paramagnetic substance

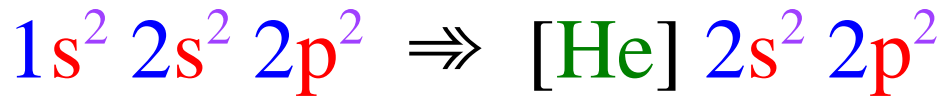
- unpaired e^- 's
- attracted by magnetic field

2 e^- in same orbital, 1↓, paired

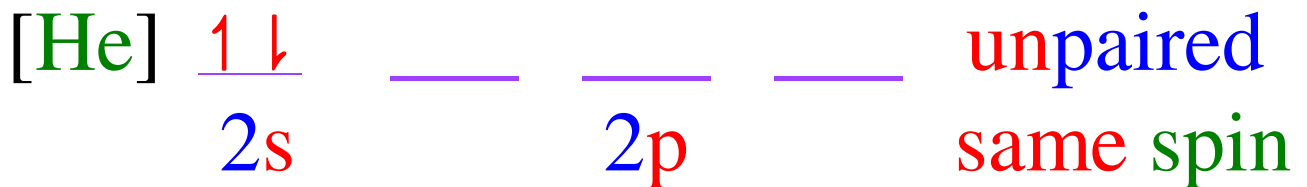
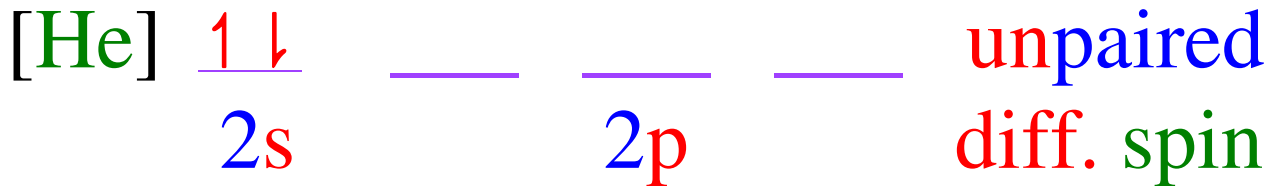
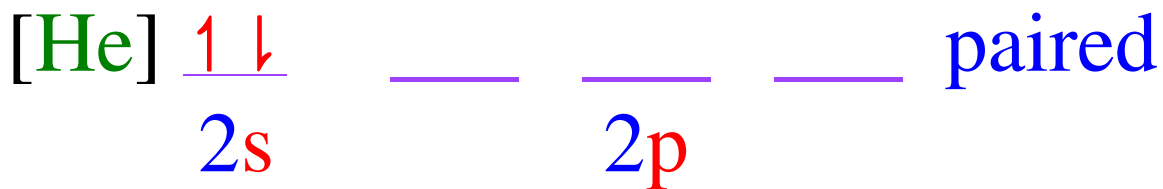
Diamagnetic substance

- all e^- paired
- not attracted by magnetic field

D) Hund's Rule



3 possible orbital diagrams:



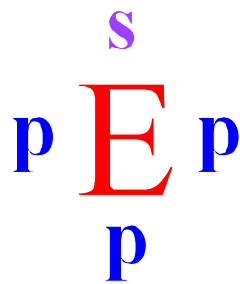
Hunds Rule: e^- occupy diff. orbitals of a subshell until all are singly occupied before e^- pairing occurs.

E) Electron-Dot Symbols

Represent e^- in the **s** & **p** orb. of the **valence shell** as **dots** arranged **around** the **symbol** of the **element**.

There are **4 s** & **p** orb. & **4 positions** about the **symbol**

- treat like **orb. diagrams**



Note: only real **useful** for **representative elements**

A) Ex's: Draw e^- dot symbols

1) ${}_6\text{C}$



2) ${}_{12}\text{Mg}$

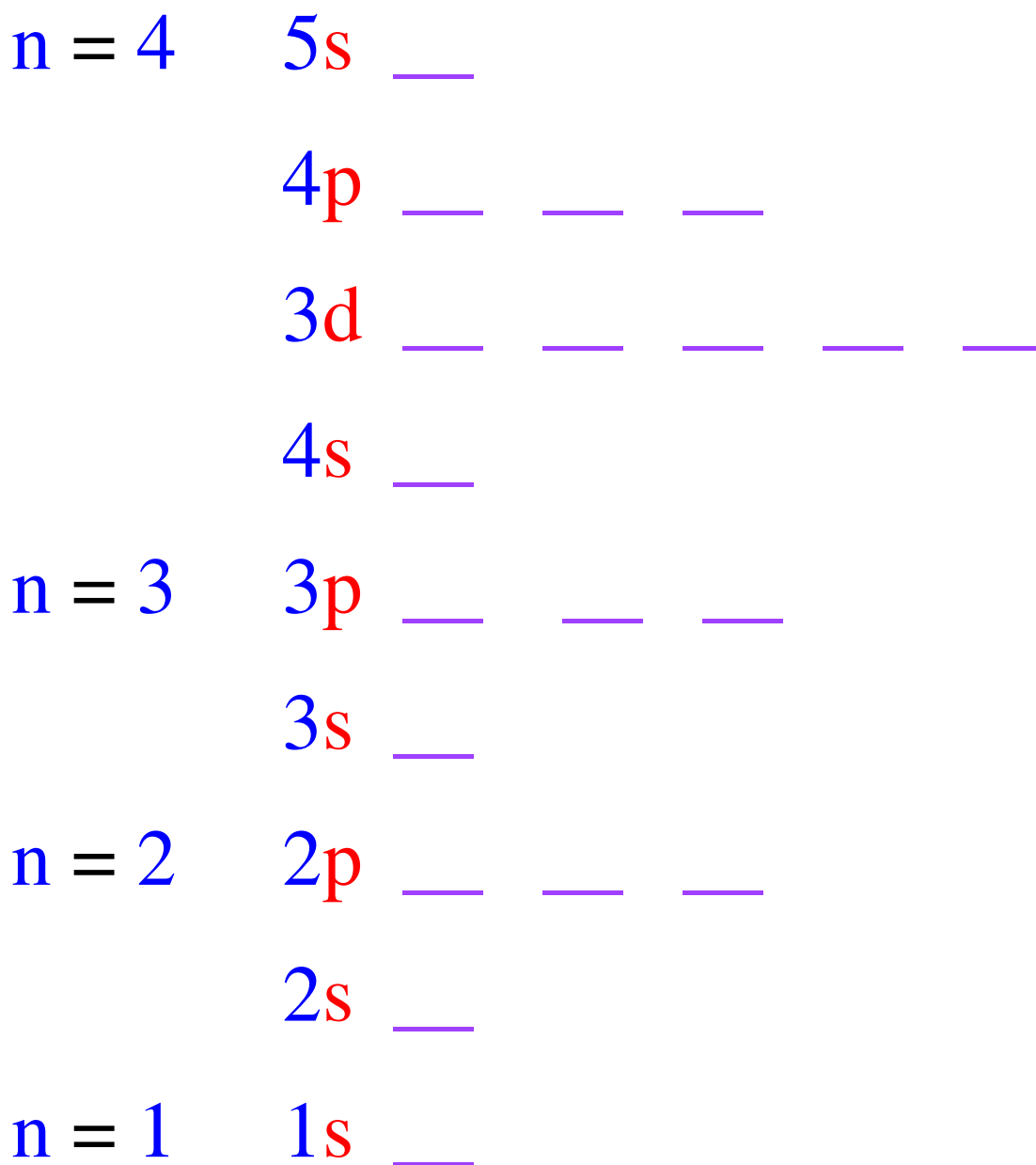


3) ${}_{16}\text{S}$



IX) Electron Conf & Periodic Table

Look at ${}_{32}\text{Ge}$



What was happening?

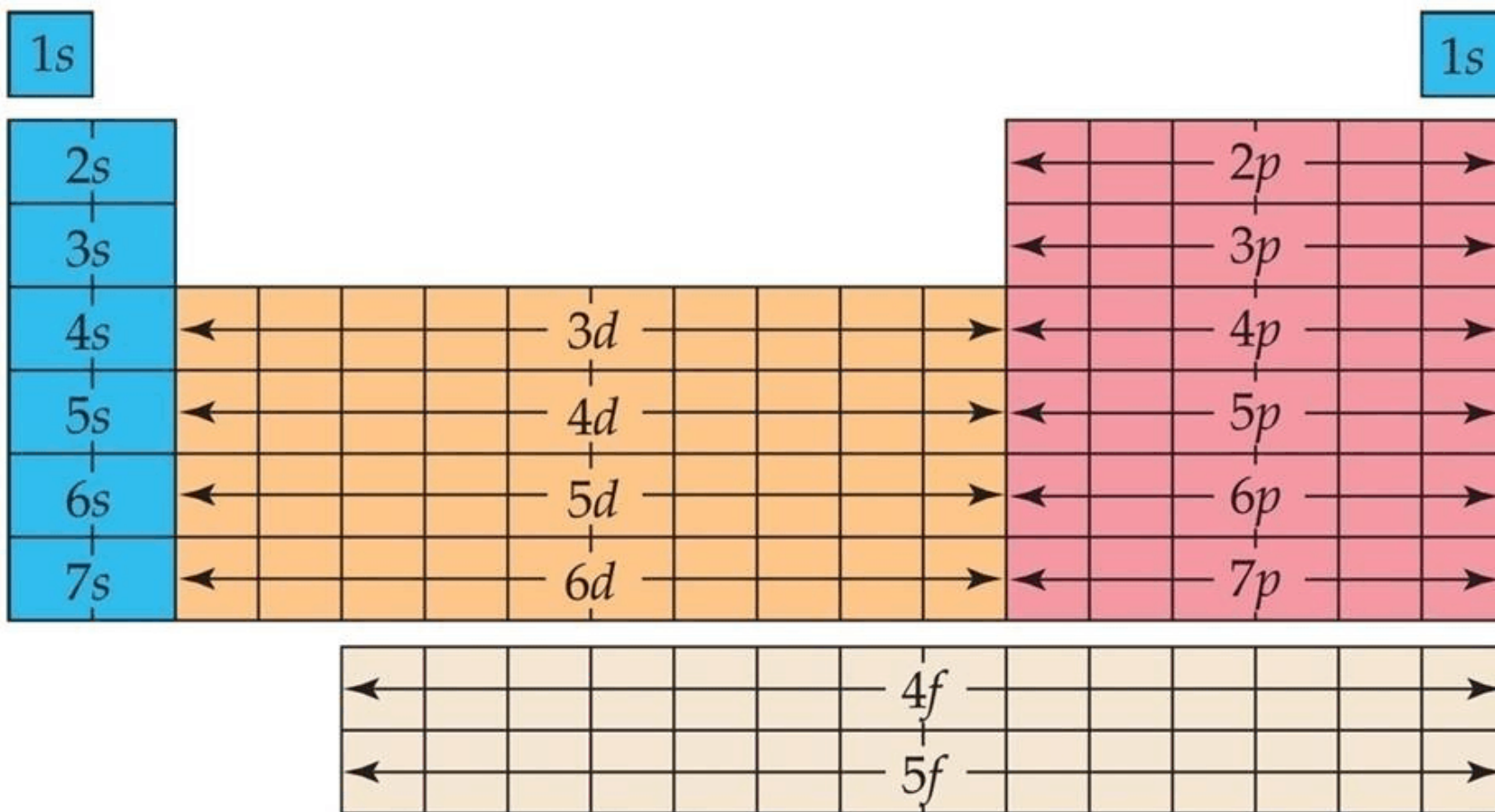
left, filling **s** orb
 $2e^-$, 2 columns

right, filling **p** orb.
 $6e^-$, 6 columns

center, filling **d** orb
 $10e^-$, 10 columns

Period no. \Rightarrow n value of **s** & **p**
subshells of **valence shell**

Group no. \Rightarrow # of **valence e^-**



Representative s-block elements

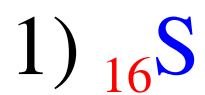
Transition metals

Representative p-block elements

f-Block metals

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A) Ex's:



Period no.
3

Group no.
VI A



	IA	IIA	IIIB	IVB	VB	VIB	VII B	VIII B					IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1.008 H 1																		4.003 He 2	
2	6.941 Li 3	9.012 Be 4												10.81 B 5	12.011 C 6	14.007 N 7	15.999 O 8	18.998 F 9	20.179 Ne 10	
3	22.990 Na 11	24.305 Mg 12												26.98 Al 13	28.09 Si 14	30.974 P 15	32.06 S 16	35.453 Cl 17	39.948 Ar 18	
4	39.098 K 19	40.08 Ca 20	44.96 Sc 21	47.88 Ti 22	50.94 V 23	52.00 Cr 24	54.94 Mn 25	55.85 Fe 26	58.93 Co 27	58.69 Ni 28	63.546 Cu 29	65.38 Zn 30	69.72 Ga 31	72.59 Ge 32	74.92 As 33	78.96 Se 34	79.904 Br 35	83.80 Kr 36		
5	85.47 Rb 37	87.62 Sr 38	88.91 Y 39	81.22 Zr 40	92.91 Nb 41	95.94 Mo 42	98 Tc 43	101.07 Ru 44	102.91 Rh 45	106.42 Pd 46	107.87 Ag 47	112.41 Cd 48	114.82 In 49	118.69 Sn 50	121.75 Sb 51	127.60 Te 52	126.90 I 53	131.39 Xe 54		
6	132.91 Cs 55	137.33 Ba 56	138.91 La 57	178.39 Hf 72	180.95 Ta 73	183.85 W 74	186.21 Re 75	190.23 Os 76	192.22 Ir 77	195.08 Pt 78	196.97 Au 79	200.59 Hg 80	204.38 Tl 81	207.2 Pb 82	208.98 Bi 83	209 Po 84	210 At 85	222 Rn 86		
7	223 Fr 87	226.03 Ra 88	227.03 Ac 89	261 Rf 104	262 Ha 105	263 Sg 106	262 Ns 107	265 Hs 108	266 Mt 109	269 110	272 111	277 112								

6	Lanthanide Series	140.12 Ce 58	140.91 Pr 59	144.24 Nd 60	145 Pm 61	150.36 Sm 62	151.96 Eu 63	157.25 Gd 64	158.93 Tb 65	162.50 Dy 66	164.93 Ho 67	167.26 Er 68	168.93 Tm 69	173.04 Yb 70	173.04 Lu 71
7	Actinide Series	232.04 Th 90	231.04 Pa 91	238.03 U 92	237.05 Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

A PERIODIC CHART OF THE ELEMENTS
(Based on ¹²C)

3) ${}_{43}\text{Tc}$

4) ${}_{82}\text{Pb}$

B) Exceptions



Reason: 4s and 3d are very close in energy. (Can act like degenerate orb)

$\frac{1}{2}$ filled & filled subshells
are more stable.