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

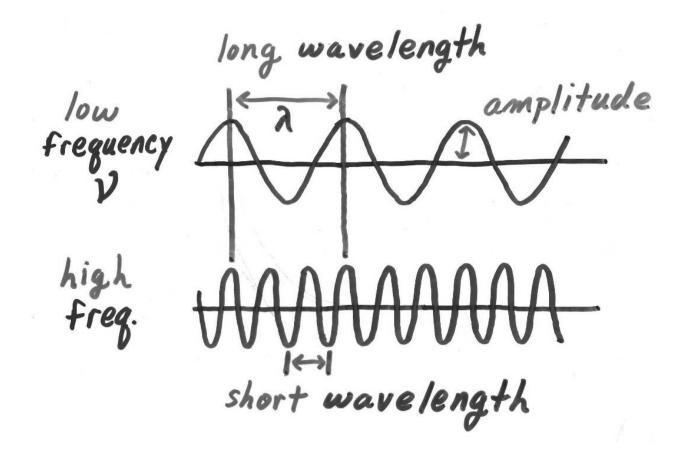
Radiant Energy

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

All move at the speed of light,

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

have wavelike characteristics

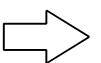


λ, wavelength distance between successive peaks

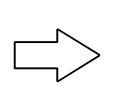
v, frequency number of complete
 wavelengths or cycles
 which pass a given point
 per second

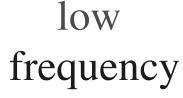
amplitude height of peak - related

to intensity of radiation

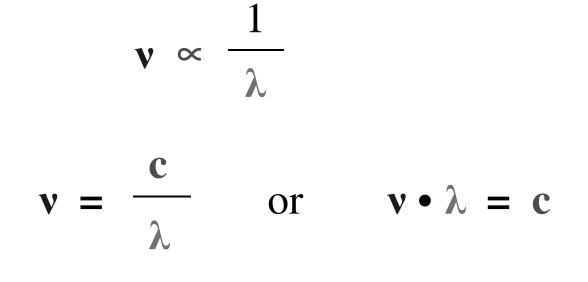






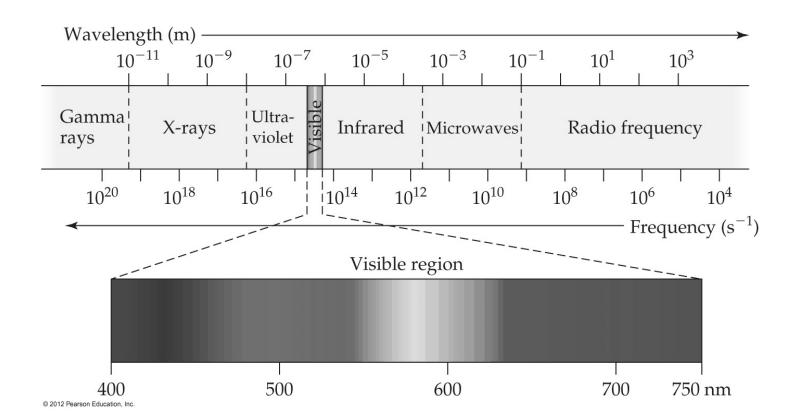


short wavelength high frequency



units for v

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



X-rays visible IR microwave radio

 λ (m) 10⁻⁹ 10⁻⁷ 10⁻⁵ 10⁻² 10²

 \mathbf{v} (s⁻¹) 10¹⁷ 10¹⁵ 10¹³ 10¹⁰ 10⁶

II) Quantized Energy and Photons

A) Plank's Theory

Energy changes are quantized

- discrete energy changes

 $\Delta E = n h v$ n = 1, 2, 3, 4, ...

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

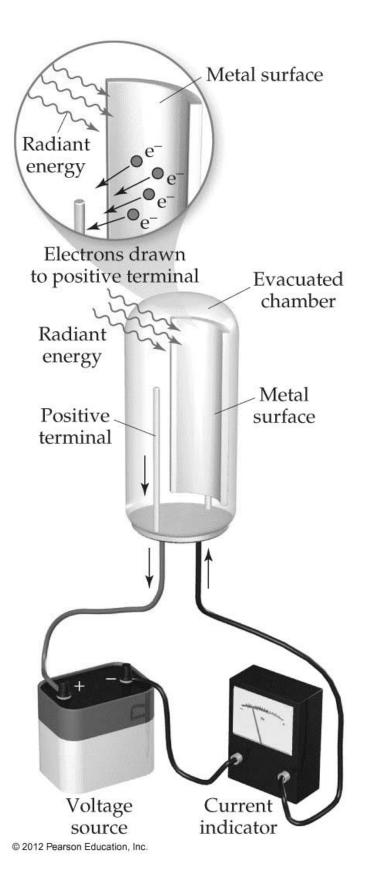
- radiant energy is quantized

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

high **v** (low λ) \Rightarrow high E

low **v** (high λ) \Rightarrow low E

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



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

$$E = h v = \frac{h c}{\lambda}$$

$$= \frac{(6.63 \times 10^{-34} \text{ Js})(3.00 \times 10^8 \text{ m/s})}{3.51 \times 10^{-7} \text{ m}}$$

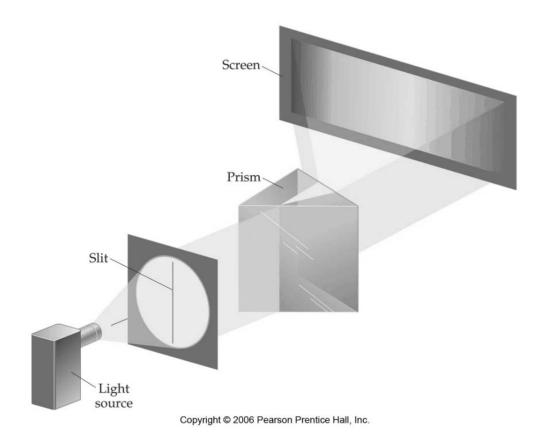
$$= 5.67 \times 10^{-19} \text{ J}$$

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)



2) monochromatic light

Light with a single wavelength - lasers

3) Line Spectra

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

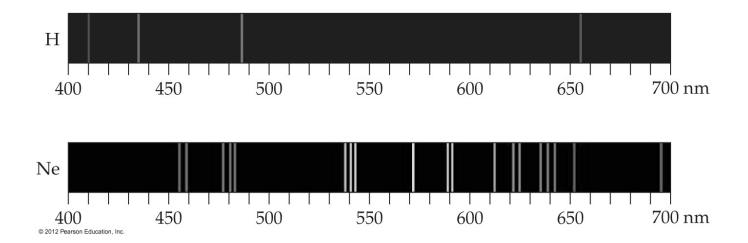
Passed through a prism see a series of narrow colored lines (specific λ 's)

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,

$$\frac{1}{\lambda} = \mathbf{R}_{\mathrm{H}} \left(\frac{1}{n_{1}^{2}} - \frac{1}{n_{2}^{2}} \right)$$

n₂ > n₁

Rydberg Constant $R_{\rm H} = 1.097 \text{ x } 10^7 \text{ m}^{-1}$

B) Bohr Model

1) Energy Levels & Orbits

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

$$\mathbf{r} = \mathbf{n}^2 \mathbf{a}_0$$
$$\mathbf{E}_n = -\mathbf{h} \, \mathbf{c} \cdot \mathbf{R}_{\mathrm{H}} \left(\frac{1}{n^2}\right)$$

n = principle quantum number

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

Bohr radius:

 $a_0 = 5.292 \text{ x } 10^{-11} \text{ m} = 0.5292 \text{ Å}$ h c • R_H = 2.180 x 10⁻¹⁸ J a) Ground State

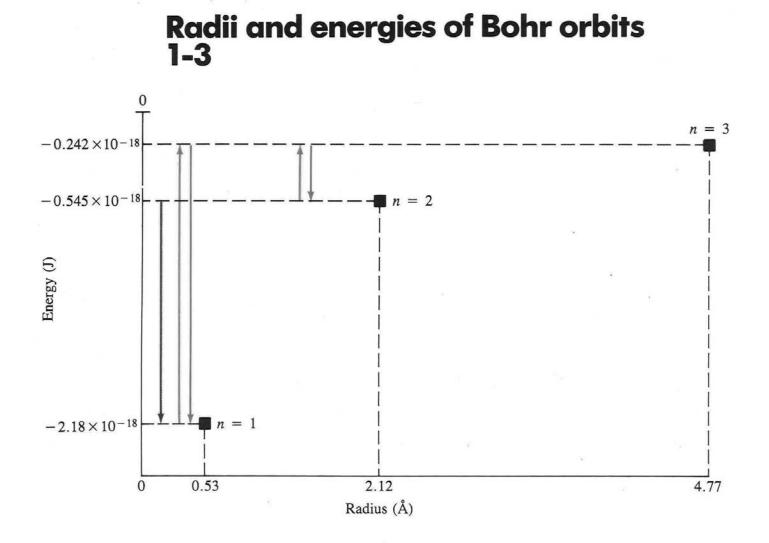
e in n = 1 orbit closest to nucleus

largest value of $1/n^2$

most negative E

* Lowest energy level

Note: most neg. E represents most stable state



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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 **=** ∞

e⁻ completely separated from nucleus

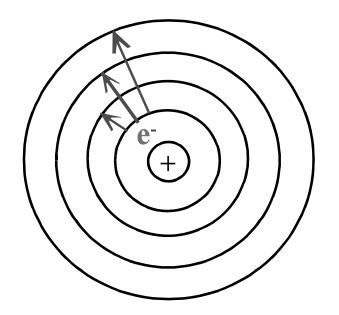
$$\mathbf{E}_{\infty} = -\mathbf{h} \, \mathbf{c} \cdot \mathbf{R}_{\mathrm{H}} \left(\frac{1}{\infty} \right) = 0$$

2) Energy Transitions

a) Absorption of Energy

e⁻ absorbs energy

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

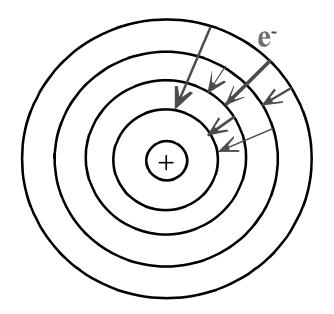


b) Emission of Energy - light

e⁻"falls" to lower level

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

a photon





c) Energy Changes

Energy diff. between orbits

$$\Delta E = E_{f} - E_{i} = \frac{-h \mathbf{c} \cdot R_{H}}{n_{f}^{2}} - \frac{-h \mathbf{c} \cdot R_{H}}{n_{i}^{2}}$$

$$\Delta E = -h c \cdot R_{H} \left(\frac{1}{n_{f}^{2}} - \frac{1}{n_{i}^{2}} \right)$$

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

1)
$$n_f > n_i$$

 $\Delta E > 0$, E inc.

Absorption

2) $n_{f} < n_{i}$

 $\Delta E < 0$, E dec.

Emission

3)
$$n_f = \infty$$

complete removal of e⁻ Ionization $H(g) \longrightarrow H^{+}(g) + e^{-}$ $n_{i} = 1 \qquad n_{f} = \infty$ $\Delta E = h c \cdot R_{H} \left(\frac{1}{1^{2}}\right) = 2.180 \text{ x } 10^{-18} \text{ J}$

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

1

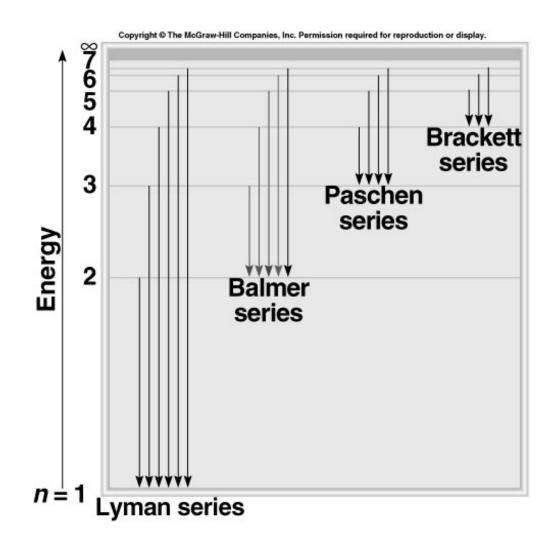
$$E_{\text{photon}} = -\Delta E_{\text{em}} = \mathbf{h} \, \mathbf{v} = \frac{\mathbf{h} \, \mathbf{c}}{\lambda}$$
$$\mathbf{v} = \mathbf{c} \cdot \mathbf{R}_{\text{H}} \left(\frac{1}{n_{\text{f}}^2} - \frac{1}{n_{\text{i}}^2}\right)$$
or
$$\frac{1}{\lambda} = \mathbf{R}_{\text{H}} \left(\frac{1}{n_{\text{f}}^2} - \frac{1}{n_{\text{i}}^2}\right)$$

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

$$\frac{1}{\lambda} = R_{\rm H} \left(\frac{1}{n_{\rm f}^2} - \frac{1}{n_{\rm i}^2} \right)$$

Balmer Series (visible):

 $n_{f} = 2$



IV) Wave Behavior of Matter

A) de Broglie

Matter should have wave prop.

For photons:

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

From Einstein:

$$E = m c^2$$

$$\lambda = \frac{h}{mc}$$

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

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

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

 Ex 2: Calculate the de Broglie wavelength for an electron moving at a speed of 3 x 10⁶ m/s.

$$(6.63 \text{ x } 10^{-34} \text{ J} \cdot \text{s})$$

 $\lambda = \frac{1}{(9.11 \text{ x } 10^{-31} \text{ kg}) (3 \text{ x } 10^{6} \text{ m/s})}$

 $= 2.43 \times 10^{-10} \text{ m}$ (0.243 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.

- $\Delta x =$ uncertainty in position
- Δp = uncertainty in momentum (mv)

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

Limit on simultaneously measuring position and momentum (speed).

V) Quantum Mechanics

Impose wave properties on e⁻

A) Schrödinger's Wave Equation

Total energy of H-atom is sum of K.E. and P.E.

Time-Independent Sch. Eqn.: (in one dimension)

 $-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{d x^2} + V(x) \psi(x) = E \psi(x)$ K.E. P.E. Total E

 $\hbar = h/2\pi$

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

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	shape	orientation
and		of an
distance		orbital
from nucleus		

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

There is a 4th quantum no.

m_s: spin

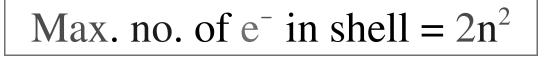
1) Principal quantum number, n

Determines:

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

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

Larger n ⇒ farther shell is from nucleus & higher energy



- n = 1 $2(1)^2 = 2 e^-$
- n = 2 $2(2)^2 = 8 e^{-1}$

2) <u>Azimuthal q. n. , ℓ</u> (Angular Momentum q.n.) identifies subshell (energy sublevels) defines shape of orbital # subshells in a shell = n $\ell = 0, 1, 2, \dots (n-1)$ Subshell designated by letters: $\ell = 0 \quad 1 \quad 2 \quad 3 \quad 4 \dots$ s p d f g **#**e⁻ in subshell 2 6 10 14 18 $2(2\ell + 1)$

If n = 4 $\ell = 0, 1, 2, 3$ 4s 4p 4d 4f

n^{th}	no. of		max	total # e⁻
shell	subshells		# e ⁻ by	in
(n)	(= n)	designation	subshell	shell $(2n^2)$
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_e

Describes orientation of orbital in space

 $m_{\ell} = +\ell, ..., 0, ..., -\ell$ 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 ℓ +1)

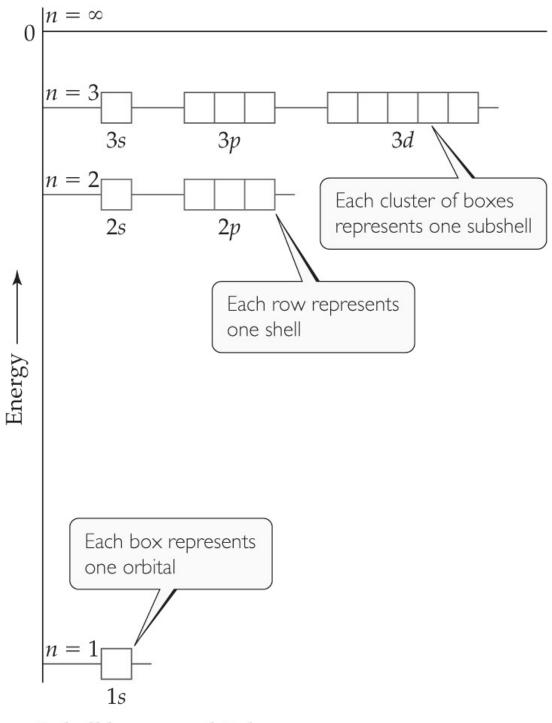
	a) <u>Ex:</u>		
	$\ell = 0$	$m_{\ell} = 0;$	s subshell has 1 orbital
<u>l</u> s	<u>ubshell</u>	<u># orbitals</u>	max # e ⁻ in subshell
0	S		
1	р		
2	d		
3	f		
4	g		
5	h		

n	Possible Values of <i>l</i>	Subshell Designation	Possible Values of <i>m</i> _l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	15	0	1,	1
2	0	2 <i>s</i>	0	1	
	1	2 <i>p</i>	1, 0, -1	3	4
3	0	35	0	1	
	1	3р	1, 0, -1	3	
	2	3 <i>d</i>	2, 1, 0, -1, -2	5	9
4	0	4s	0	1	
	1	4 <i>p</i>	1, 0, -1	3	
	2	4d	2, 1, 0, -1, -2	5	
	3	4f	3, 2, 1, 0, -1, -2, -3	7	16

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

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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 © 2012 Pearson Education, Inc.

VI) Representations of Orbitals

ψ has no direct physical meaning

ψ² 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

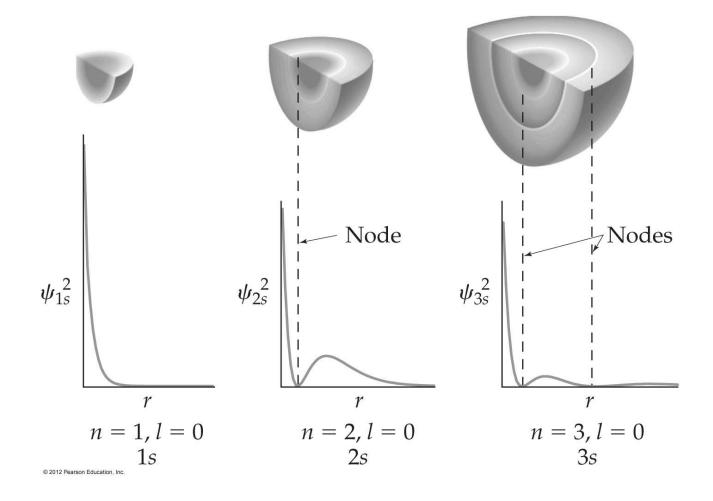
A) <u>s orbitals</u>

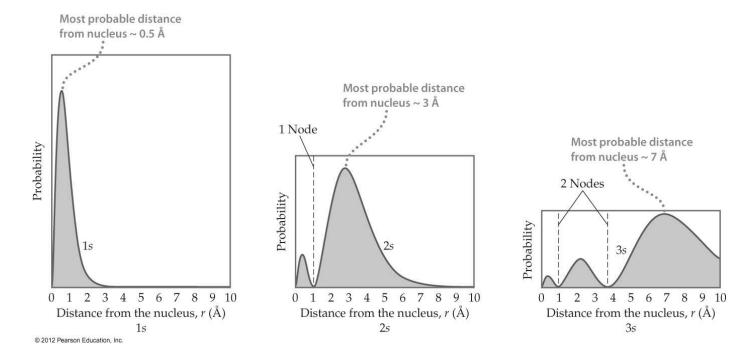
$\ell = 0$ All s orb. are spherical

 $4\pi r^2 [\psi(r)]^2$ 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) <u>3 trends from radial prop. dist.</u>

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

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

nodes = n - 1

spherical nodes = $n - \ell - 1$

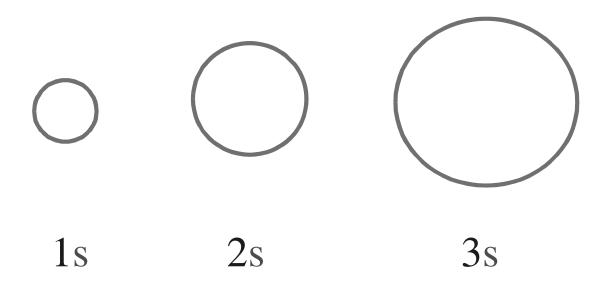
angular nodes $= \ell$

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

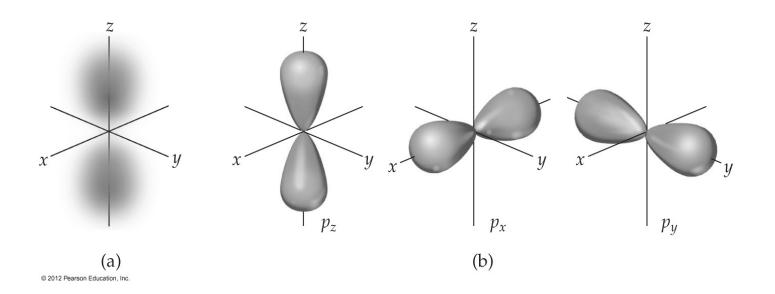
B) p orbitals

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



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

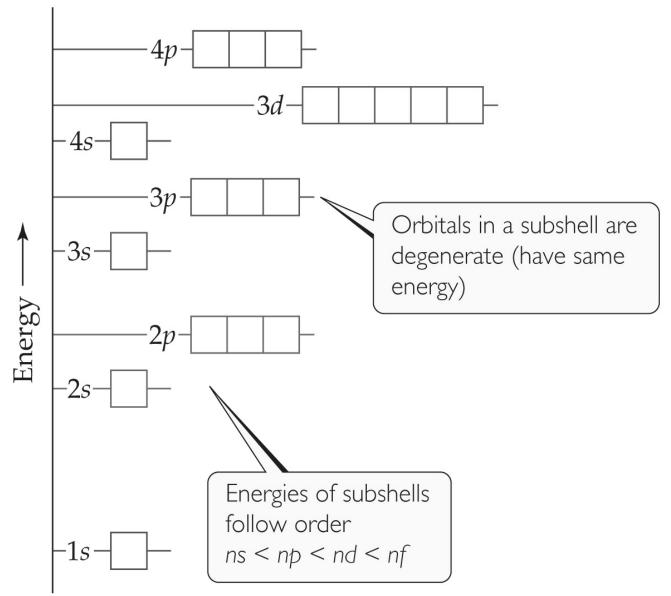
Many-e⁻ atoms:

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	-1/2
up	down
1	

B) Pauli Exclusion Principle

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

n, ℓ , m_{ℓ} , m_{s}

Look at 1s orbital

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

can have only $2e^{-1}$ 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

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

2) Subshell, ℓ (shape of orbital)

subshells in shell = n

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

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

3) Orbitals, m_{ℓ} (orientation)

 $m_{\ell} = +\ell, ..., 0, ..., -\ell$

orb. in shell =
$$n^2$$

 $(2\ell + 1)$ orbitals in a subshell max. # e⁻ in subshell = 2 ($2\ell + 1$)

4) <u>Spin, m_s</u>

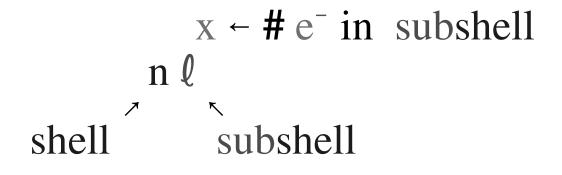
+1/2(1) -1/2(1)

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

	$\ell =$	0	1	2	3	4	5
subshell letters		S	р	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



- $_1$ H $1s^1$
- $_2$ He $1s^2$
- ₆C 1s 2s 2p

A) <u>Ex</u>: Consider sulfur, $_{16}$ S : 16 e⁻

$$_{16}S$$
 $1s^2 2s^2 2p^6$ _____ $3s 3p$

valence shell (outer shell)

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

¹⁶S 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⁻

$$_{16}S = 1s^2 2s^2 2p^6 3s^2 3p^4$$

completed subshells → [Ne] noble gas from previous period

[Ne]
$$3s^2 3p^4$$

 $1s^2 2s^2 2p^2 \Rightarrow []$

C) Orbital Diagrams

A dash _____ indicates an orbital

Use arrows, 1 or ↓ to indicate e⁻ with up or down spin

 $_{1}\text{H} \ 1\text{s}^{1} \ \frac{1}{1\text{s}}$; $_{2}\text{He} \ 1\text{s}^{2} \ \frac{1}{1\text{s}}$

 single e⁻ in an orbital, <u>1</u>, unpaired

paramagnetic substance

- unpaired e's
- attracted by magnetic field

$2 e^{-}$ in same orbital, <u>11</u>, paired

Diamagnetic substance

- all e⁻ paired
- not attracted by magnetic field

D) Hund's Rule

$$_{6}$$
C : 6 e⁻

 $1s^2 2s^2 2p^2 \implies [He] 2s^2 2p^2$

3 possible orbital diagrams:

[He]		 	 paired
	2s	2p	
[He]	$\frac{1}{2s}$	 2p	 unpaired diff. spin
[He]	<u>1</u> 2s	 2p	 unpaired same spin

<u>Hunds</u> <u>Rule</u>: 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.

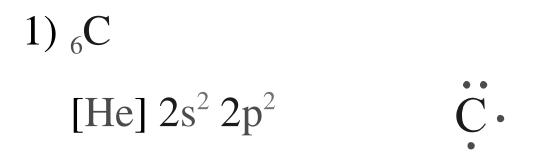
There are 4 s & p orb. & 4 positions about the symbol

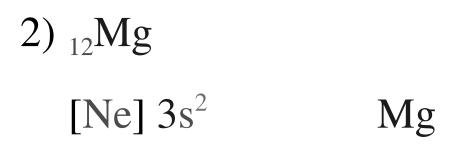
- treat like orb. diagrams

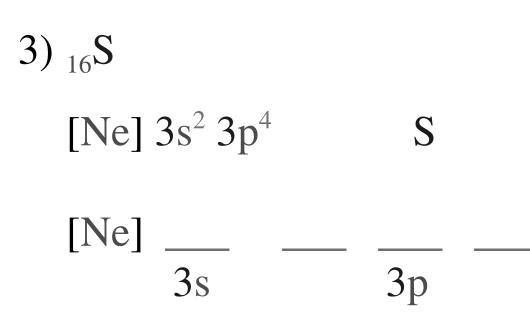
p p p

Note: only real useful for representative elements

A) <u>Ex's</u>: Draw e⁻ dot symbols







IX) Electron Conf & Periodic Table

Look a	at ₃₂ Ge
$1s^2$	$2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$
n = 4	5s
	4p
	3d
	4s
n = 3	3p
	3s
n = 2	2p
	2s
n = 1	1s

What was happening?

left, filling s orbright, filling p orb.2e⁻, 2 columns6e⁻, 6 columns

center, filling d orb 10e⁻, 10 columns

Period no. ⇒ n value of s & p subshells of valence shell

Group no. \Rightarrow # of valence e⁻

1s			1s
2s		-	+2p $+$
35			+3p $+$
4s <	- 3d	→ ≺	$-4p$ \rightarrow
5s <	-4d $-$	→ <	+5p $+$
6s <	- 5d	→ 	$-6p$ \rightarrow
7s -	- 6d	→ <	+7p $+$
-		+4f	>
			► ►
Representative <i>s</i> -elements	block	Represe element	entative <i>p</i> -block
Transition metals	3	f-Block	k metals
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A) <u>Ex's:</u>

1) $_{16}S$ Period no. Group no. 3 VI A



	IA	IIA	IIIB	IVB	VB	VIB	VIIB		VIIIB		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 $^{12}\mathrm{C})$

3) ₄₃Tc

4) ₈₂Pb

B) Exceptions

 ${}_{24}Cr = expect [Ar] 4s^{2} 3d^{4}$ find [Ar] $4s^{1} 3d^{5}$ ${}_{29}Cu = expect [Ar] 4s^{2} 3d^{9}$ find [Ar] $4s^{1} 3d^{10}$

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

¹/₂ filled & filled subshells are more stable.