

# CHAPTERS 7 & 8 Atomic Structure and Periodicity

## Electromagnetic Radiation

wave - a periodic disturbance through a medium

frequency  $\nu$  cycles per second

velocity of propagation

$$v = \lambda \nu$$

for electromagnetic radiation, velocity of propagation =  $c = 3.0 \times 10^8$  m/s or  $c = \lambda \nu$   
(see fig. 7.2, pg 281)

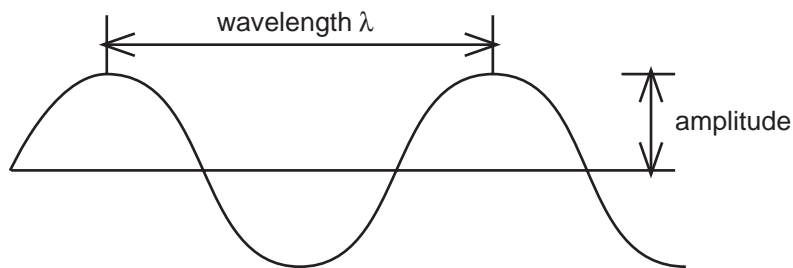


Figure on pg. 282 shows pickle emitting light at 589 nm due to excited Na atoms

$$\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^8 \text{ m/s}}{589 \times 10^{-9} \text{ m}} = 5.09 \times 10^{14} \text{ Hz}$$

## The Nature of Matter

By 1900, physicists believed they knew most about matter and energy, and that there was little yet to learn.

Max Planck - 1900 - attempted to explain the absorption and emission of light by hot bodies. Theories based on classical ideas of the continuous wave nature of light failed to give equations which fit the data.

Planck had to assume that energy could be lost or gained only in whole number multiples of  $h\nu$ , where  $h = 6.626 \times 10^{-34}$  Jsec

$$E = nh\nu$$

Energy is quantized; it can be absorbed or emitted in discrete bundles called quanta.

What is the energy of the quanta emitted by the pickle light?

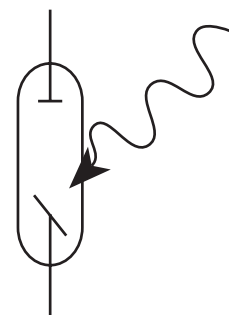
$$E = h\nu = (6.626 \times 10^{-34} \text{ Jsec})(5.09 \times 10^{14} \text{ Hz}) = 3.37 \times 10^{-19} \text{ J}$$

Photoelectric Effect - Albert Einstein - 1905

light shining on electrode causes electrons to be ejected, causing a photocurrent. It was found that the current increased with the intensity of the light, but that if the light were below a certain frequency, no current was produced regardless of the intensity of the light

Einstein proposed that light consisted of quanta of energy  $E = h\nu = \frac{hc}{\lambda}$

light behaves as if it is made up of discrete bundles called photons.



Einstein also derived  $E = mc^2$  or  $m = \frac{E}{c^2}$

If  $E = mc^2$  and  $E = h\nu$ , then  $mc^2 = h\nu$ . Since  $\nu = c/\lambda$ ,  $mc = h/\lambda$ . This equation relates the momentum of a photon (a particle property) with its wavelength (a wave property).

Since energy and matter are the same thing, Louis deBroglie proposed (1923) that, for a real particle with velocity  $v$ ,

$$mv = h/\lambda \quad \text{or} \quad \lambda = h/mv$$

For a 80 kg person running at 6.7 m/sec (a 4-min mile)

$$\lambda = h/mv = (6.626 \times 10^{-34} \text{ Jsec}) / (80 \text{ kg})(6.7 \text{ m/sec}) = 1.24 \times 10^{-36} \text{ m}$$

compared to nucleus,  $1 \times 10^{-15}$  m, this number is so small as to be meaningless.

For an electron ( $9.11 \times 10^{-31}$  kg) with a velocity of  $6.7 \times 10^6$  m/sec

$$\lambda = h/mv = (6.626 \times 10^{-34} \text{ Jsec}) / (9.11 \times 10^{-31} \text{ kg})(6.7 \times 10^6 \text{ m/sec}) = 1.1 \times 10^{-10} \text{ m} = 0.11 \text{ nm}$$

This is in the range of x-rays. Atoms are  $1 \text{ \AA}$  to  $2 \text{ \AA}$  ( $0.1 - 0.2 \text{ nm}$ ) in diameter, and a regular crystal (such as NaCl) acts as a diffraction grating for X-rays, causing a diffraction pattern.

At Bell labs, in 1927, an electron beam was diffracted through a Ni crystal and found to exhibit a diffraction pattern nearly identical to an X-ray diffraction pattern. This shows that electrons display both particle and wave properties.

## The Atomic Spectrum of Hydrogen

A rainbow, or the light passing through a diffraction grating or prism is a continuous spectrum of light. Under some conditions, atoms and molecules are seen to absorb or emit discrete wavelengths rather than continuous spectra of light. This is called a line spectrum. (fig. 7.6, pg. 288). This means that there are only certain energy levels that the H atom can have, the energy of H is quantized.

$$E = h\nu = \frac{hc}{\lambda}$$

## The Bohr Model



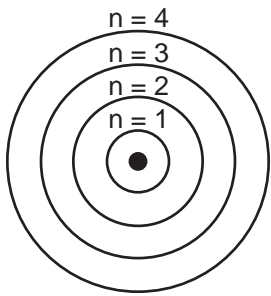
In the old planetary model, electrons were believed to orbit the nucleus like planets around the sun; however, a charged particle moving in a circle generates a magnetic field which opposes the current, thus radiating energy. This would cause the orbit to decay and the electron to spiral into the nucleus in about  $10^{-7}$  seconds

1913 Neils Bohr proposed a model of the H atom in which angular momentum is quantized.

$$mvr = \frac{nh}{2\pi} \quad \text{where } m = \text{mass of electron} \quad n = 1, 2, 3, 4 \dots$$

$v$  = velocity of electron  
 $r$  = radius of orbit

$$h = 6.626 \times 10^{-34} \text{ J sec}$$

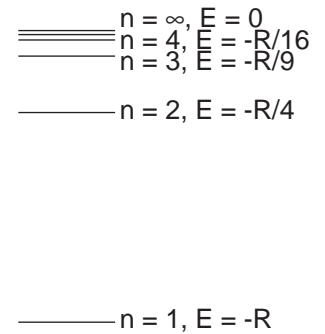


From the classical centripetal and electrostatic forces,

$$E = -\frac{2e^4 \pi^2 m}{n^2 h^2} = -R \frac{1}{n^2}$$

where  $R = 2.178 \times 10^{-18}$  J (Rydberg constant)

Zero energy corresponds to the energy of a free (unattached) electron. Negative energy corresponds to a bound electron.



Transitions between energy levels require  $E = E_{\text{fin}} - E_{\text{init}}$

For a transition from level 3 to level 2,  $E = E_2 - E_3$

$$E_2 = -R \frac{1}{2^2} = -(2.178 \times 10^{-18} \text{ J})(0.25) = -5.445 \times 10^{-19} \text{ J}$$

$$E_3 = -R \frac{1}{3^2} = -(2.178 \times 10^{-18} \text{ J})(0.111) = -2.420 \times 10^{-19} \text{ J}$$

$$E = (-5.445 \times 10^{-19} \text{ J}) - (-2.420 \times 10^{-19} \text{ J}) = -3.025 \times 10^{-19} \text{ J}$$

(negative because the electron is losing energy)

This energy change requires the emission of a photon with exactly the right energy

$$E_{\text{photon}} = |E_{\text{electron}}| = hc/\lambda$$

$$\lambda = hc/E = (6.626 \times 10^{-34} \text{ J sec})(3.0 \times 10^8 \text{ m/sec}) / (3.025 \times 10^{-19} \text{ J}) = 6.571 \times 10^{-7} \text{ m}$$

compare with figure 7.6, pg. 288 orange line at 656 nm

The Bohr model gives good results only for 1 - electron atoms.

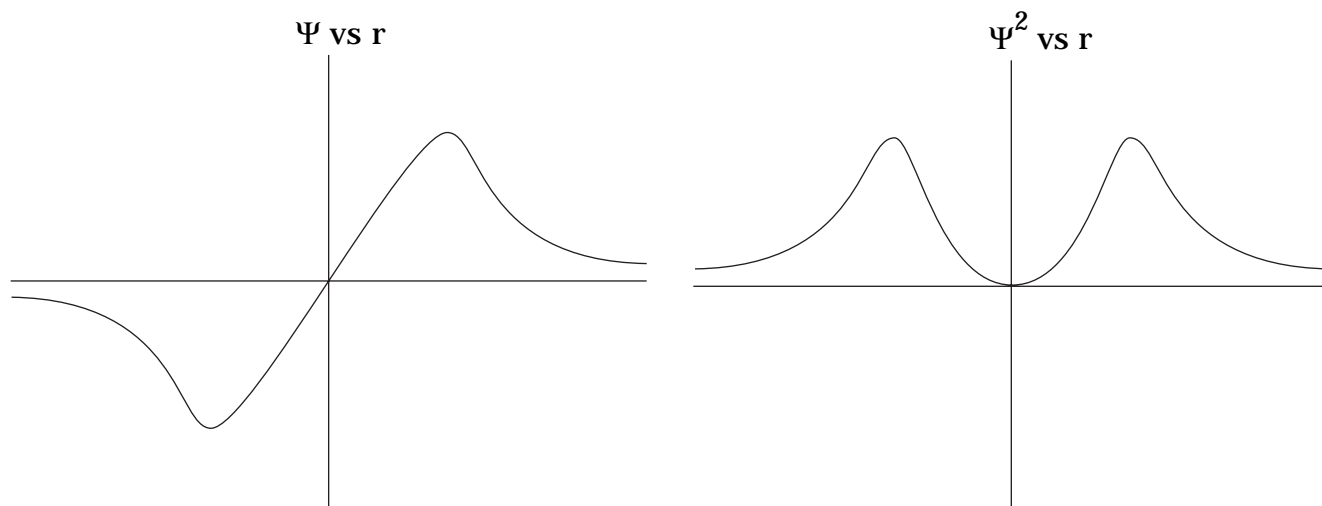
### The Quantum Mechanical Model of the Atom

Erwin Schroedinger attempted to describe an electron's behavior by emphasizing the wave aspect rather than the particle aspect.

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V)\Psi = 0 \quad \text{time independent Schroedinger equation}$$

$\Psi$  is the wave function, a function which gives the amplitude of the electron wave as a function of x, y, z, t. E is the energy operator and V is the potential energy operator. The solution of the Schroedinger equation gives an infinite number of solutions (just as the Bohr model of the H atom gave an infinite number of orbits). Each of these is called an orbital, and can be described by a set of 3 numbers called quantum numbers, which are analogous to the number n in the Bohr model.

The physical properties of the electron (charge and mass) are correlated to the value of  $\Psi^2$  (the wave intensity)



The electron acts like a cloud distributed through space everywhere the value of  $\Psi^2$  is nonzero.

Orbital - a volume of space which an electron cloud may occupy

### Quantum Numbers

Principle Quantum Number  $n = 1, 2, 3, 4, \dots$

$n$  determines the size of the electron cloud and the energy of the orbital  
electrons with the same value of  $n$  are said to be in the same shell

Angular Momentum Quantum Number  $l = 0, 1, 2, 3, \dots, n-1$

$l$  determines the shape of the orbital (angular distribution of the electron cloud)  
electrons with the same value of  $l$  are said to be in the same subshell

each shell has 1 more subshell as the previous shell (the  $n^{\text{th}}$  shell has  $n$  subshells)

$n = 1$	$l = 0$		
$n = 2$	$l = 0$		
	$l = 1$		
$n = 3$	$l = 0$		
	$l = 1$		
	$l = 2$ , etc.		
$l = 0$	1	2	3
subshell = s	p	d	f
	sharp,	principle,	diffuse, fine

shell and subshells are identified as 1s, 2s, 2p, 3d, 4f, etc.

Magnetic Quantum Number  $m_l = -l, \dots, -1, 0, 1, 2, \dots, +l$

$m_l$  determines the orientation of an orbital

each subshell has 2 more orbitals than the previous subshell  
(the  $l$  subshell has  $2l + 1$  orbitals)

n = 1	l = 0	1s	$m_l = 0$
n = 2	l = 0	2s	$m_l = 0$
	l = 1	2p	$m_l = -1, 0, +1$
n = 3	l = 0	3s	$m_l = 0$
	l = 1	3p	$m_l = -1, 0, +1$
	l = 2	3d	$m_l = -2, -1, 0, +1, +2$
n = 4	l = 0	4s	$m_l = 0$
	l = 1	4p	$m_l = -1, 0, +1$
	l = 2	4d	$m_l = -2, -1, 0, +1, +2$
	l = 3	4f	$m_l = -3, -2, -1, 0, +1, +2, +3$

## Orbital Shapes and Energies

Orbital shapes are defined as the volume of space which contains 90% of the electron cloud density. Each orbital is a 3-dimensional wave, where the energy of the wave is related to the number of nodes (areas where  $\Psi = 0$ ). Nodes can be planar surfaces, spherical surfaces, or more complicated surfaces.

The Principle quantum number  $n$  determines how many nodes there are:  $n-1$  nodes.

The Angular Momentum quantum number  $l$  determines how many of the nodes are planar surfaces:  $l$  planar surfaces,  $n - l - 1$  spherical surfaces.

s orbitals ( $l = 0$ ) have no planar nodes, so they are spherically symmetric

p orbitals ( $l = 1$ ) have 1 planar node, so they have a peanut or dumbbell shape

d orbitals ( $l = 2$ ) have 2 planar nodes ( $90^\circ$  apart), so they have a cloverleaf shape

f orbitals ( $l = 3$ ) have 3 planar nodes ( $90^\circ$  apart), so they have a double cloverleaf shape

Higher order orbitals have spherical nodes in addition to planar nodes.

For hydrogen,  $E$  depends only on  $n$ . The types of nodes have no effect on  $E$  so all orbitals in the same shell have the same energy (as in the Bohr atom). For multielectron atoms, the shape does have an effect on the energy.

For H (only) (1s) (2s 2p) (3s 3p 3d) (4s 4p 4d 4f) ...

## Electron Spin and the Pauli Principle

Spin Quantum Number  $m_s = +1/2, -1/2$

$m_s$  determines the magnetic moment of the electron

Pauli Exclusion Principle: no two electrons can have the same set of 4 quantum numbers ( $n, l, m_l, m_s$ )

Each orbital can hold up to two electrons, if they have opposite spins.

n = 1	l = 0	1s	$m_l = 0$	1 orbital	2 electrons
n = 2	l = 0	2s	$m_l = 0$	1 orbital	2 electrons
	l = 1	2p	$m_l = -1, 0, +1$	3 orbitals	6 electrons
n = 3	l = 0	3s	$m_l = 0$	1 orbital	2 electrons
	l = 1	3p	$m_l = -1, 0, +1$	3 orbitals	6 electrons
	l = 2	3d	$m_l = -2, -1, 0, +1, +2$	5 orbitals	10 electrons
n = 4	l = 0	4s	$m_l = 0$	1 orbital	2 electrons
	l = 1	4p	$m_l = -1, 0, +1$	3 orbitals	6 electrons
	l = 2	4d	$m_l = -2, -1, 0, +1, +2$	5 orbitals	10 electrons
	l = 3	4f	$m_l = -3, -2, -1, 0, +1, +2, +3$	7 orbitals	14 electrons

## Polyelectronic Atoms

For atoms with more than one electron, the Schrodinger equation cannot be solved exactly because of problems with electron-electron repulsion. As an approximation, each electron can be treated as if it were alone, and attracted to the nucleus by an effective nuclear charge which includes the nuclear attraction and the other electrons' repulsions

$$Z_{\text{eff}} = Z - (\text{electronic repulsion})$$

This allows a calculation of orbitals which are similar to those of the 1 electron H atom, but vary in energy. In particular, subshells within a shell are found not to be degenerate.

## The History of the Periodic Table

Johann Dobereiner (1780 - 1849) - triads : sets of three elements with similar properties

John Newlands (1864) octaves: noticed that elements seemed to repeat properties in groups of eight.

Julius Lothar Meyer (german, 1830 - 1895) and Dmitri Mendeleev (russian, 1834 - 1907) "modern" periodic table. Mendeleev gets most credit because he used the chart to predict the properties of yet undiscovered elements Ga, Sc, Ge. Elements listed in order repeat chemical and physical properties periodically originally listed by increasing mass, now by atomic number.

## The Aufbau Principle and the Periodic Table

Aufbau (building up) principle: the electronic structure of an atom can be determined by adding one electron to the atom before it.

H	$1s^1$	electron configuration	$\uparrow$	orbital diagram		
He	$1s^2$	$\uparrow\downarrow$				
Li	$1s^2 2s^1$	$\uparrow\downarrow$	$\uparrow$			
Be	$1s^2 2s^2$	$\uparrow\downarrow$	$\uparrow\downarrow$			
B	$1s^2 2s^2 2p^1$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	—	—
C	$1s^2 2s^2 2p^2$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	—
N	$1s^2 2s^2 2p^3$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$
O	$1s^2 2s^2 2p^4$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$
F	$1s^2 2s^2 2p^5$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$
Ne	$1s^2 2s^2 2p^6$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$

Hund's Rule: Electrons enter orbitals in a subshell singly, with parallel spin, until each orbital is half full before pairing up.

Valence Shell: the outermost occupied shell

Valence Electrons: electrons in the outermost occupied shell

Core electrons (inner shell electrons): electrons in all shells smaller than the valence shell

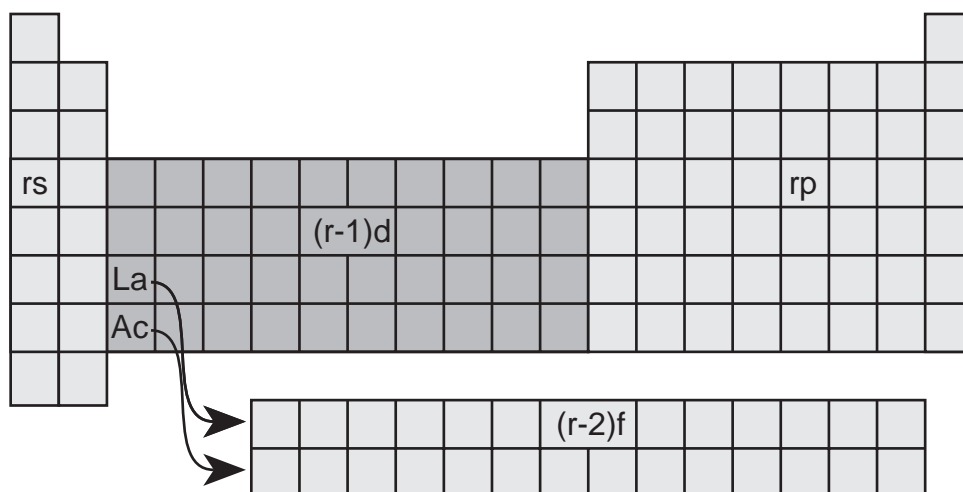
Na:[Ne] 3s<sup>1</sup>  
 Mg:[Ne] 3s<sup>2</sup>  
 Al:[Ne] 3s<sup>2</sup> 3p<sup>1</sup>  
 Si:[Ne] 3s<sup>2</sup> 3p<sup>2</sup>  
 P:[Ne] 3s<sup>2</sup> 3p<sup>3</sup>  
 S:[Ne] 3s<sup>2</sup> 3p<sup>4</sup>  
 Cl:[Ne] 3s<sup>2</sup> 3p<sup>5</sup>  
 Ar:[Ne] 3s<sup>2</sup> 3p<sup>6</sup>

K:[Ar] 4s<sup>1</sup>  
 Ca:[Ar] 4s<sup>2</sup>  
 Sc:[Ar] 4s<sup>2</sup> 3d<sup>1</sup>  
 Ti:[Ar] 4s<sup>2</sup> 3d<sup>2</sup>  
 V:[Ar] 4s<sup>2</sup> 3d<sup>3</sup>  
 Cr:[Ar] 4s<sup>1</sup> 3d<sup>5</sup>  
 Mn:[Ar] 4s<sup>2</sup> 3d<sup>5</sup>

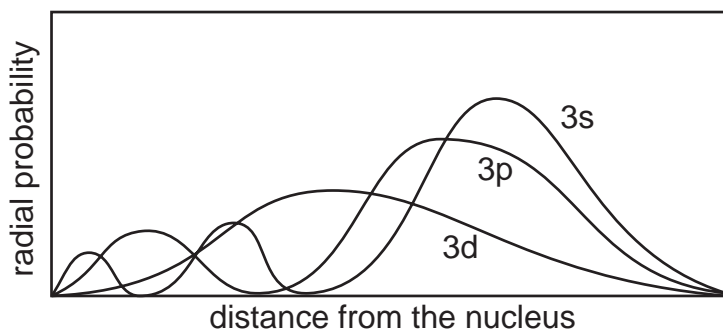
Fe:[Ar] 4s<sup>2</sup> 3d<sup>6</sup>  
 Co:[Ar] 4s<sup>2</sup> 3d<sup>7</sup>  
 Ni:[Ar] 4s<sup>2</sup> 3d<sup>8</sup>  
 Cu:[Ar] 4s<sup>1</sup> 3d<sup>10</sup>  
 Zn:[Ar] 4s<sup>2</sup> 3d<sup>10</sup>

Ga:[Ar] 4s<sup>2</sup> 3d<sup>10</sup> 4p<sup>1</sup>  
 Ge:[Ar] 4s<sup>1</sup> 3d<sup>10</sup> 4p<sup>2</sup>  
 As:[Ar] 4s<sup>2</sup> 3d<sup>10</sup> 4p<sup>3</sup>  
 Se:[Ar] 4s<sup>2</sup> 3d<sup>10</sup> 4p<sup>4</sup>  
 Br:[Ar] 4s<sup>2</sup> 3d<sup>10</sup> 4p<sup>5</sup>  
 Kr:[Ar] 4s<sup>1</sup> 3d<sup>10</sup> 4p<sup>6</sup>

Order of filling of subshells: **1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d 7p 8s**



### Further Development of the Polyelectronic Model



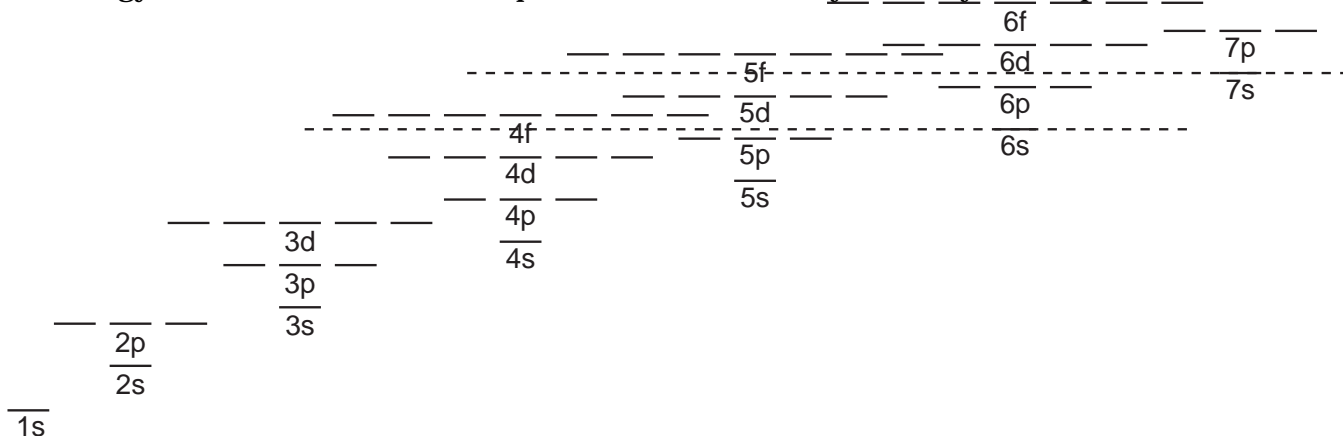
$$Z_{\text{eff}} = Z - \text{electron screening}$$

inner shell electrons are able to screen part or all of the nuclear charge, but this screening is offset by orbital penetration.

ns > np > nd > nf  
 most penetration    least penetration

Because of penetration, subshells within a shell are not degenerate, and always fill in the order s - p - d - f

The energy levels of the subshells split so much that they actually overlap between shells.



As an approximation,  $Z_{\text{eff}} = Z - (\text{inner shell electrons})$

### Periodic Trends in Atomic Properties

**Atomic Radius** (324) [Covalent radius: determined from covalently bonded atoms]

Size decreases across a row, increases down a column (see fig. 7.36, pg 325)

Lanthanide Contraction

2.09	2.00	1.92	1.85	1.79	1.72	1.67	1.62	1.57	1.53
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
3.0	4.50	5.8	7.19	7.43	7.86	8.90	8.90	8.96	7.14
2.27	2.16	2.08	2.01	1.95	1.89	1.83	1.79	1.75	1.71
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
4.5	6.49	8.55	10.2	11.5	12.2	12.4	12.0	10.5	8.65
2.74	2.16	2.09	2.02	1.97	1.92	1.87	1.83	1.79	1.76
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
6.7	13.1	16.6	19.3	21.0	22.4	22.5	21.4	19.3	13.53

### Ions: Electron Configurations and Sizes

Metal atoms tend to lose all valence electrons to form cations

Nonmetal atoms tend to gain enough electrons to fill the outer s and p subshells

Ionic radius: cations are smaller than parent atom (see fig. 8.7, pg. 354)  
 anions are larger than parent atom  
 in an isoelectronic series, size decreases with Z  
 $\text{Mg}^{2+} < \text{Na}^+ < \text{Ne} < \text{F}^- < \text{O}^{2-}$

**Ionization Energy** (320): energy required to remove an electron from a gaseous atom in its ground state.



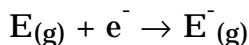
Ionization energy increases because of reduced electron-electron repulsion (increases  $Z_{\text{eff}}$ ) and more tightly bound shells/subshells



Ionization energy increases across a row and decreases down a column. Lowest for metals and highest for nonmetals.

metals lose (group number) electrons because these are the least tightly held

**Electron Affinity (323):** energy change when an electron is added to a gaseous atom in its ground state.



Electron affinities generally become more negative across a row and up a column.

### The Properties of a Group: The Alkali Metals

Information Contained in the Periodic Table (326) - Elements in the same group have the same outer electron (valence) configuration. Chemistry is determined by valence electron configuration. Electron configuration can be determined from position on the periodic table

Know: Alkali metals, Alkaline earth metals, halogens, noble gases, lanthanides, actinides, metals, non-metals, metalloids

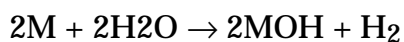
The Alkali Metals (328) - see table 7.8, pg.328

Properties of Five Alkali Metals								
Element	valence config	density at 25° (g/cm <sup>3</sup> )	mp ° C	bp ° C	1st ionization energy (kJ/mol)	atomic radius (pm)	ionic radius (pm)	hydration energy for cation (kJ/mol)
Li	2s <sup>1</sup>	0.53	180	1330	520	155	60	-510
Na	3s <sup>1</sup>	0.97	98	892	495	190	95	-402
K	4s <sup>1</sup>	0.86	64	760	419	235	133	-314
Rb	5s <sup>1</sup>	1.53	39	688	409	248	148	
Cs	6s <sup>1</sup>	1.87	29	690	382	267	169	

Density: mass usually increases faster than size, so density increases

mp and bp: usually not a clear correlation between mp/bp and position on the chart

Ionization energy: lowest on the chart. very reactive metals, never found in uncombined state.



reducing ability Cs > Rb > K > Na > Li, but in water, Li > K > Na because Li<sup>+</sup> is smaller and has a larger hydration energy.