

Quantum Atom: Atomic Structure, Electron Configuration, and Periodicity

Equations:

$$\lambda\nu = c$$

$$E = h\nu \quad \text{energy of photon}$$

$$\Delta E = h\nu \quad \text{difference of energy levels}$$

$$\lambda = h/p$$

$p = mu$ (momentum and particle wavelength) \rightarrow deBroglie Relation

$(\Delta p)(\Delta x) \approx h \rightarrow$ The Heisenberg Uncertainty Principle

$$1/\lambda = R_H(1/n_\ell^2 - 1/n_u^2)$$

$\ell = \text{lower} \quad u = \text{upper}$

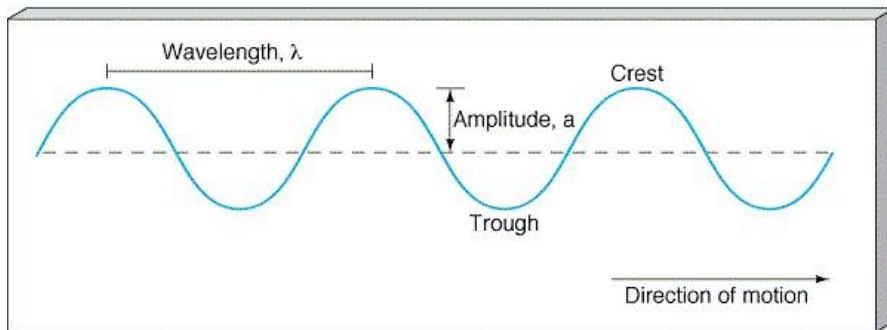
where h is Planck's constant $h = 6.63 \times 10^{-34} \text{ J s}$
and c is speed of "light" $c = 3.00 \times 10^8 \text{ m/s}$

Electromagnetic Radiation

Positive and negative particles are attracted (electrostatic attraction) so what keeps electrons (negative) separated from (positive) nucleus?

First idea is electron in orbit like the planet (common image but WRONG).
Small systems behave much differently than everyday world.

Before we can understand models for structure of atoms and "Quantum World" We need to look at electromagnetic radiation and atomic spectra.



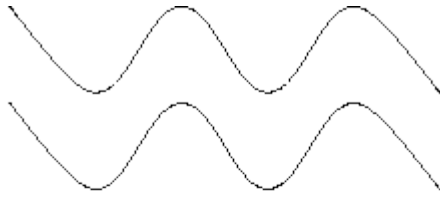
http://physics.uoregon.edu/~courses/BrauImages/Chap03/FG03_003.jpg

amplitude (a) = height of the crest brightness proportional to a^2

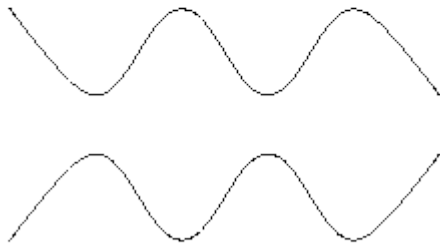
frequency (ν) = cycles of waves that pass a fixed point per unit of time (s^{-1})
Hertz (Hz) means the same as waves per second or (s^{-1})
 ν is the Greek letter nu

wavelength (λ) = length of one cycle
units can be (m) or (cm = 10^{-2} m) or (nm = 10^{-9} m)
 λ is the Greek letter lambda

Interference Property of Waves



Constructive interference



Destructive interference

http://theory.uwinnipeg.ca/mod_tech/node125.html

Velocity, Wavelength and Frequency

Speed that wave moves is how many waves per second (ν) times length of wave (λ)

$\nu = 2 \text{ Hz}$ 2 cycles/s

$\lambda = 10 \text{ m}$ 10 m apart

$\nu = 1 \text{ ms}^{-1}$ $\nu = \lambda\nu = 20 \text{ m/s}$

$\nu = \lambda\nu$

Electromagnetic radiation travels at the speed of light (c) = $3.00 \times 10^8 \text{ m/s}$

so $c = \lambda\nu$ for electromagnetic radiation

So if know: λ can get ν
 ν can get λ

Types of Electromagnetic Radiation include:

Length of	λ (m)	ν (s^{-1})	c (m/s)	
Gamma <	1×10^{-10}	3×10^{18}	3.8×10^8	High energy

x-rays	<	1×10^{-8}	3×10^{16}		
Ultraviolet	<	3.8×10^{-7}	7.9×10^{14}		
Visible	<	7.6×10^{-7}	3.9×10^{14}		
Infrared	<	1×10^{-3}	3×10^{11}		
Microwave	<	1×10^{-1}	3×10^9		
TV radio	<	5.5×10^2	5.5×10^5		Low Energy

In the above note that x-rays are roughly less than 1×10^{-8} but longer than 1×10^{-10} m and so on for other examples ultraviolet less than 3.8×10^{-7} but more than 1×10^{-8} m, etc., etc.

Note that: Shorter wavelength \rightarrow Higher Frequency \rightarrow High Energy

Ex. If frequency of light is 4.00×10^{14} Hertz or (s^{-1}), then what is the wavelength (m, nm)?

$$c = \lambda \nu$$

$$c / \nu = \lambda$$

$$= \frac{3.00 \times 10^8 \text{ ms}^{-1}}{4.0 \times 10^{14} \text{ s}^{-1}} = 7.5 \times 10^{-7} \text{ m} \quad \text{or} \quad 7.5 \times 10^{-7} \text{ m} (10^9 \text{ nm/m}) = 750 \text{ nm}$$

And what is the energy per photon?

$E = h \nu$ where h is Planck's constant $h =$

$$E = (6.63 \times 10^{-34} \text{ Js})(4.0 \times 10^{14} \text{ s}^{-1})$$

$$E = 2.65 \times 10^{-19} \text{ J for 1 photon}$$

$$2.65 \times 10^{-19} \text{ J} (6.02 \times 10^{23} / \text{mol}) = 1.60 \times 10^5 \text{ J/mol} = 160 \text{ kJ/mol (mol of photons!)}$$

Spectroscopy

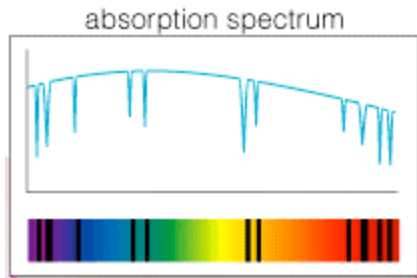
Atomic spectra is used to study energy levels occupied by electrons in an atom

Prism or grating is used to separate light into different wavelengths

Continous emissions spectrum- white light (Tungsten in light bulb)

Discontinous emission spectrum- bright lights on dark background

Discrete Energies



<http://www.astro.washington.edu/labs/hubblelaw/nowgalaxies.html>

Why is energy absorbed at discrete wavelengths?

1900-1905 Max Planck and Albert Einstein

Radiant Energy is discontinuous and comes in increments of energy or quanta or particles given off photons

Radiant Energy is quantized

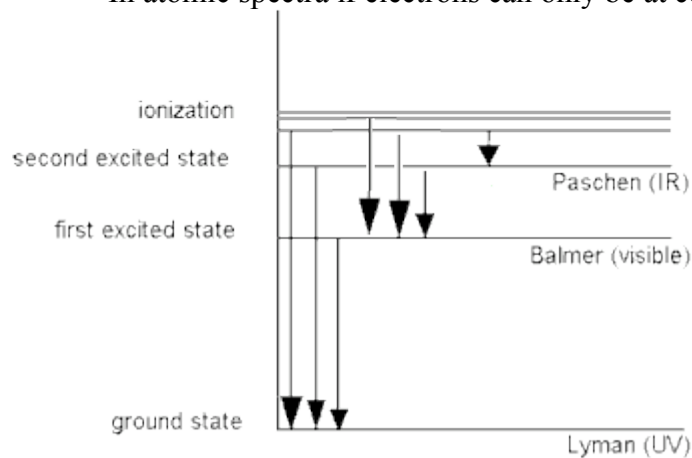
$$E = hv \quad h = 6.63 \times 10^{-34} \text{ Js} = \text{Planck's constant}$$

Light is not just like waves but also like particles

Bohr Model

More Energy \rightarrow Higher Frequency \rightarrow Shorter Wavelength

In atomic spectra if electrons can only be at certain discrete energies



<http://online.cctt.org/physicslab/content/Phy1/lessonnotes/atomic/atomicmodelsandspectra.asp>

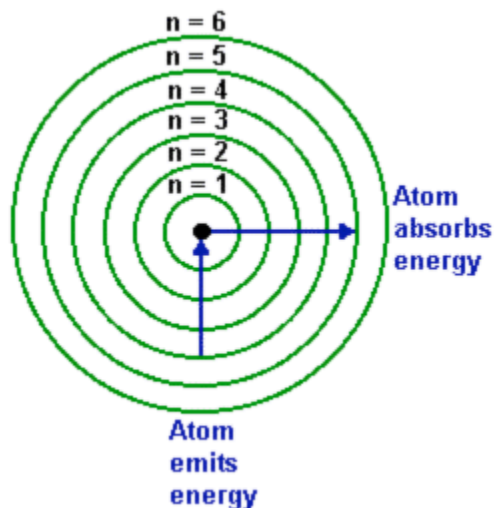
Explained Observation that

$$1/\lambda = R_H(1/n_l^2 - 1/n_u^2)$$

$$R_H = \text{Rydberg constant} = 109,678 \text{ cm}^{-1}$$

Lyman	$n_1=1$	$n_2 = 2, 3, 4, 5, 6$	ultraviolet
Balmer	$n_1=2$	$n_2 = 3, 4, 5, 6$	visible
Paschen	$n_1=3$	$n_2 = 4, 5, 6$	infrared

Bohr Model Hydrogen Atom



(<http://library.thinkquest.org/C006669/media/Chem/img/bohr.gif>)

Electrons in fixed orbits around nucleus

Electrons in orbit do not gain or lose energy

When electron jumps from one orbit to another
Gain or lose set amount of energy
(drop to lower level then emits energy)
(jump to lower level then absorb energy)

Bohr used classical physics to balance electrostatic attraction with centrifugal force away from center and derived equation

$$E = -A(1/n^2) \quad n = \text{quantum number}$$

main energy level 1, 2, 3, 4 ...

$$\Delta E = E_2 - E_1$$

$$\Delta E = -A/n_2^2 - -A/n_1^2 \quad A = 2\pi m e^4 z^2 / h^2 = \text{mass charge of electron}$$

$$\Delta E = A(1/n_1^2 - 1/n_2^2)$$

Recall: $\Delta E = h\nu$ $\lambda\nu = c$

$$\Delta E = h(c/\lambda) = A(1/n_1^2 - 1/n_2^2)$$

$$1/\lambda = A/hc(1/n_1^2 - 1/n_2^2)$$

His theory agreed exactly with his known Rydberg constant
Explained Balmer, Paschen, Lyman Experiment

Important Ideas but does not work for other atoms (more than one electron) need NEW physics

Wave Mechanics

Modern Electronic Theory

After description of radiant

Electromagnetic radiation waves Matter Particles

1924 DeBroglie suggested that all matter in motion must have wavelike properties

light \rightarrow wavelike characteristic \rightarrow frequency (diffraction)
particle characteristic \rightarrow photons (photoelectric effect)

$$\lambda = h/p \quad p = \text{momentum} = mv = (\text{mass})(\text{velocity}) \quad (\text{kg m/s})$$

Units: λ = meters (m) and h/p = Js/ (kg m/s)

Larger the particle then λ is very small relative to particle atoms
 \therefore macroscopic ignore, microscopic important!

Electron particles can be diffracted, they act like waves

Heisenberg Uncertainty Principle

Basically do not know exactly where electrons are

Impossible to exactly determine the momentum and position of object
X-rays observe the position, disrupt momentum

Not exact but probable position

$$(\Delta x)(\Delta p) = h/4\pi = (\Delta p)(\Delta x)$$

Quantum Mechanics

Provides a unified description of the atomic and everyday world

Physics prior to 1930 could explain cannonballs but not electrons

Schrödinger equation relates $H\Psi = E\Psi$

Ψ = Position E = Total Energy H = Hamiltonian Operator

Total energy is the sum of kinetic and potential energy

Ψ wave function the region in space that the electron is most likely to be found in
this region related to the orbital

Ψ^2 gives probable electron density

Transition absorb energy electron change orbitals and has higher energy

Use results of hydrogen atom for other atoms

Calculation predicts location in space in which electron is most likely
found and energy of electron

Orbitals → location of electrons

Shape is indicated by letter s, p, d, f

s orbital is spherical

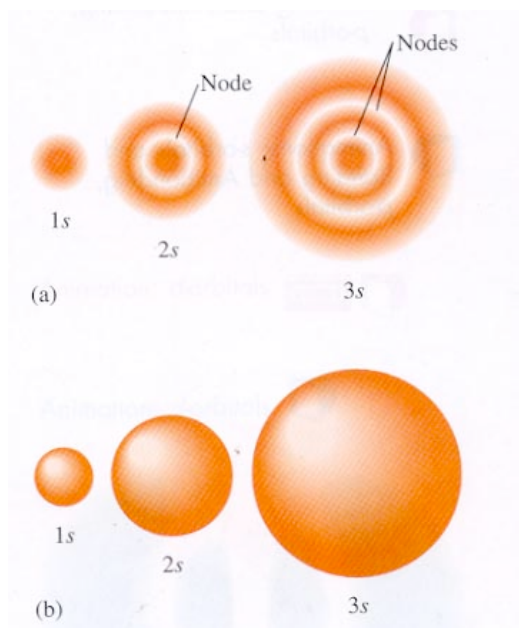
Cannot say where an electron is but only where it is likely to be

Radial Probability

Sum of Ψ^2 at distance r

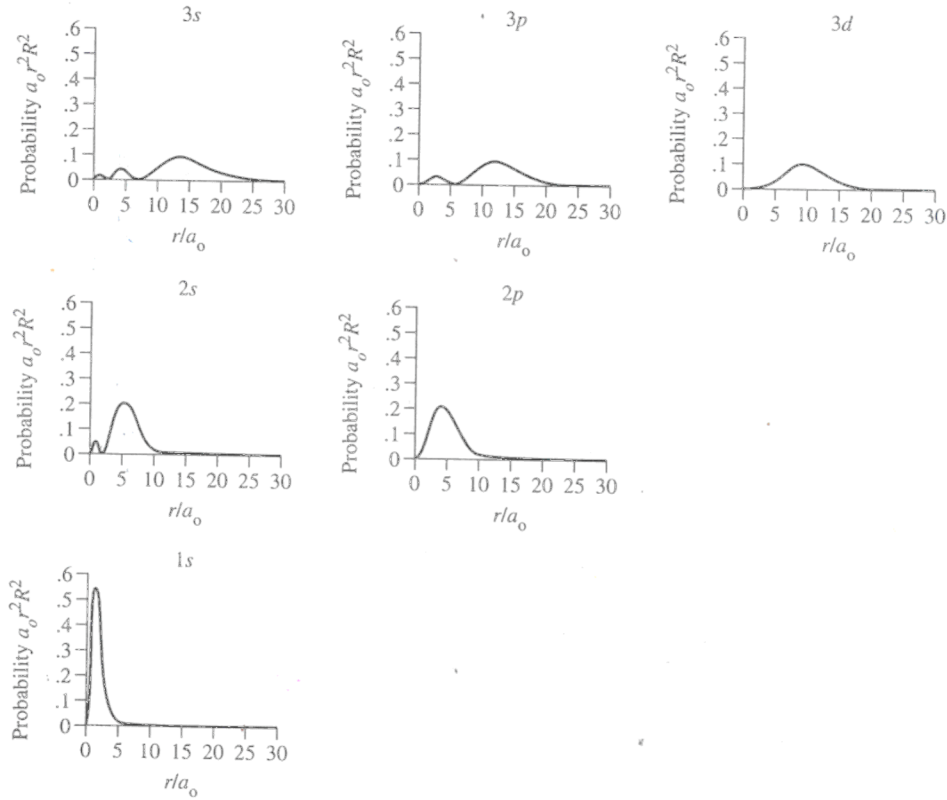
Surface of sphere $4\pi r^2 \Psi^2 =$ radial distribution function
 \therefore Size of an atomic orbital increases as the principle quantum number increases

$n =$ primary (principle) quantum number (1, 2, 3 ...) = main energy level



<http://www.chemistry.uvic.ca/chem222/Notes/lect3v1.htm>

Radial Wave function of Electron



<http://www.physicsarchives.com/atomicphysics.htm>

Types of orbitals → s, p, d, f
 $\ell = 0, 1, 2, 3$

2 electrons per orbital

		Quantum Numbers				
		<u>n</u>	<u>ℓ</u>			
	4p	—	—	—	4	1
	3d	—	—	—	—	—
↑ Energy	4s	—			4	0
	3p	—	—	—	3	1
	3s	—			3	0
	2p	—	—	—	2	1
	2s	—			2	0
	1s	—			1	0

Ordering can change slightly

Same energy for hydrogen

Separate with more electrons

Because of order of penetration

$$ns \geq np \geq nd \geq nf$$

Example Electron Configuration

	1s	2s	2p	3s	Electron Configuration
H	↑ —				$1s^1$
He	↑↓ —				$1s^2$
Li	↑↓ —	↑ —			$1s^2 2s^1$ [He] $2s^1$
Be	↑↓ —	↑↓ —			$1s^2 2s^2$
B	↑↓ —	↑↓ —	↑ —	—	$1s^2 2s^2 2p^1$
C	↑↓ —	↑↓ —	↑ ↑ — —	—	$1s^2 2s^2 2p^2$
N	↑↓ —	↑↓ —	↑ ↑ ↑ — — —		$1s^2 2s^2 2p^3$
O	↑↓ —	↑↓ —	↑↓ ↑ ↑ — — —		$1s^2 2s^2 2p^4$
F	↑↓ —	↑↓ —	↑↓ ↑↓ ↑ — — —		$1s^2 2s^2 2p^5$
Ne	↑↓ —	↑↓ —	↑↓ ↑↓ ↑↓ — — —		$1s^2 2s^2 2p^6$
Na	↑↓ —	↑↓ —	↑↓ ↑↓ ↑↓ — — —	↑ —	$1s^2 2s^2 2p^6 3s^1$ [Ne] $3s^1$

Chemical properties of elements are determined by electron configuration

Xenon Xe [Kr] $5s^2 4d^{10} 5p^6$

Cesium Cs [Xe] $6s^1$

Barium Ba [Xe] $6s^2$

Lanthium La [Xe] $6s^2 5d^1$

Cerium Ce [Xe] $6s^2 5d^1 4f^1$

Proseodymium Pr [Xe] $6s^2 4f^3$

Exception occur in filling f order, Expect $6s^2 5d^1 4f^2$

More Exceptions

Half filled and filled subshells have unusual stability

Examples:

Chromium (Cr) $4s^2 3d^4 \rightarrow 4s^1 3d^5$

Copper (Cu) $4s^2 3d^9 \rightarrow 4s^1 3d^{10}$

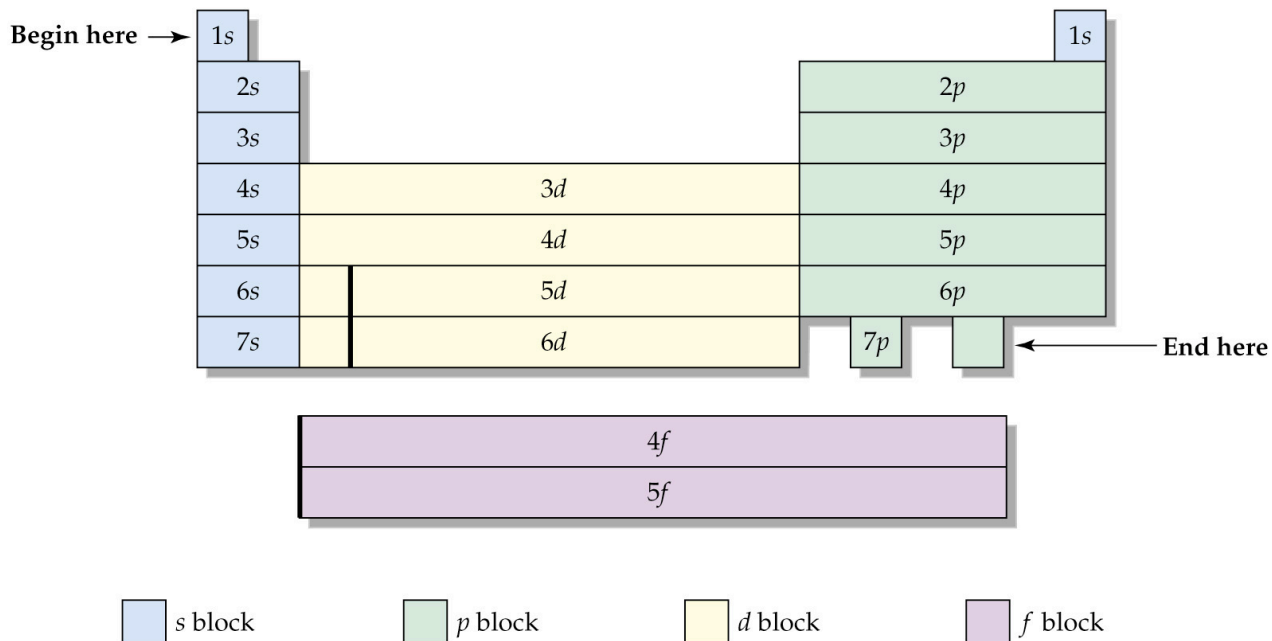
Others: Pd, Ag, Mo

If can move 1 electron to get filled or half-filled d subshell will do so.

Know Normal Order and Exceptions!

Exceptions increase s go to higher weight elements

Periodic Table



(http://wps.prenhall.com/wps/media/objects/602/616516/Media_Assets/Chapter05/Text_Images/FG05_18.JPG)

Quantum Numbers

Alternate way to specify type of orbital other than 1s, 2p etc
Orbital Designation

Specify the probable location and energy of electron found in orbitals

More complicated than just $n= 1, 2, 3...$

As go across periodic table add protons for new element also add electron

Specify the type of orbital for each electron

Principle Quantum Number	shell	n
Angular momentum Quantum Number	subshell	ℓ
Magnetic Orbital Quantum Number	orbital	m_ℓ
Magnetic Spin Quantum Number	spin	m_s

shell	n	1, 2, 3, 4 ...	main energy level
subshell	ℓ	0, 1, 2...(n-1)	type of orbital, sublevel
orbital	m_ℓ	+ ℓ , +1 ℓ , 0	specific orbital
spin	m_s	+1/2, -1/2	a specific electron spin

Pauli Exclusion Principle says no two electrons within the same atom can have the same four quantum numbers

	n	ℓ	m_ℓ	m_s	<u># of electrons</u>
1s	1	0	0	+1/2	2
2s	2	0	0	+1/2	2
2p	2	1	+1, 0, -1	+1/2	6

3s	3	0	0	+1/2	2
3p	3	1	+1, 0, -1	+1/2	6
3d	3	2	+2, +1, 0, -1, -2	+1/2	10

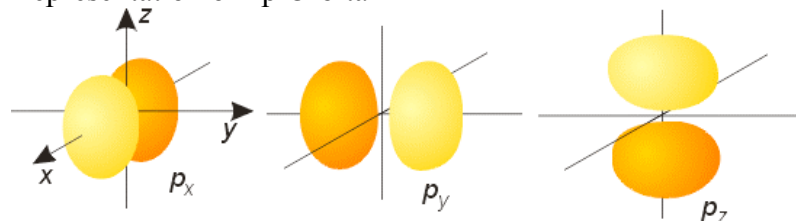
Filling of orbitals by Aufbau Principle → lowest energy upward

Hunds Rule → electrons unpaired as much as possible
 For the same type of orbital, electrons go in separate ones first

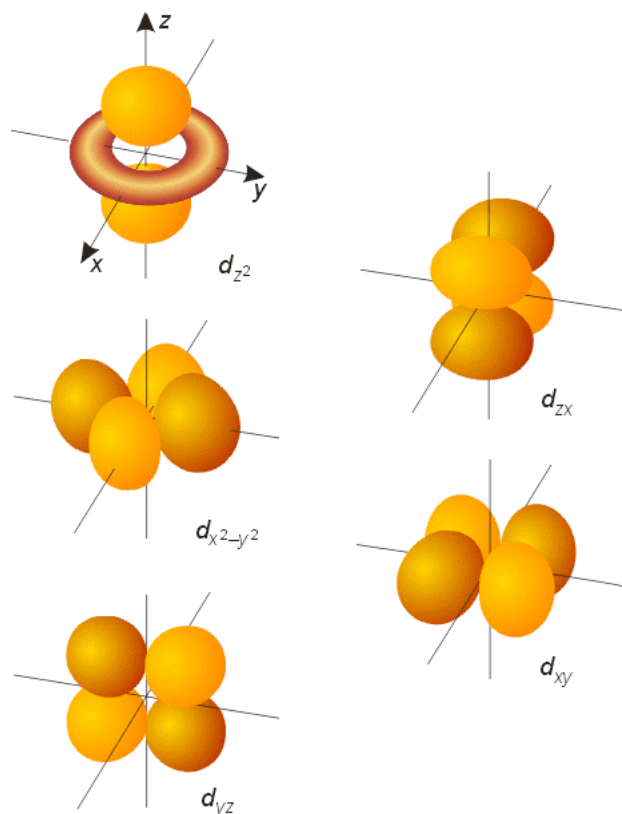
Indicate electronic configuration with electronic notation

- n = 1, 2, 3, 4...
- ℓ = 0 s
- = 1 p p_x, p_y, p_z
- = 2 d d_{x²-y²}, d_{z²}, d_{xy}, d_{xz}, d_{yz} subscripts to indicate orbital
- = 3 f

Representation of 2p Orbital



Representation of the 3d Orbital

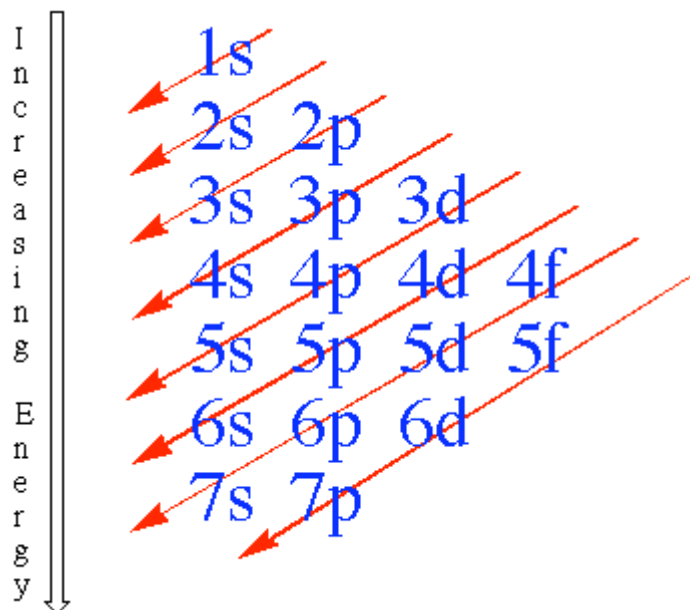


(<http://www.chemistry.uvic.ca/chem222/Notes/lect3v1.htm>)

s	$m_\ell = 0$
p	$m_\ell = -1, 0, +1$
d	$m_\ell = -2, -1, 0, +1, +2$
f	$m_\ell = -3, -2, -1, 0, +1, +2, +3$

n, ℓ, m_ℓ specify one particular orbital

Filling in electrons lowest to highest energy



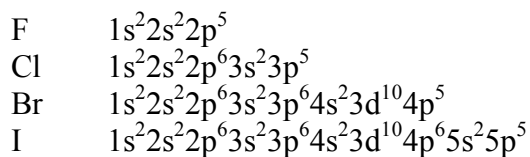
<http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson36.htm>

Electron Configuration Continued...



Where 2= main level number, p= sublevel letter, 3= electrons in sublevel

Electronic Configuration of Halogens



Outer electrons similar orbitals, so properties the same, combine with alkali metal
NaF, NaCl, NaBr

Abbreviated Electronic Configuration

F [He] 2s²2p⁵
 Cl [Ne] 3s²3p⁵
 Br [Ar] 3d¹⁰4s²4p⁵
 I [Kr] 4d¹⁰5s²5p⁵

Paramagnetic → attracted external magnetic field (unpaired electrons)

Diamagnetic → not attracted (slightly repelled) external magnet (all paired electrons)

Nonmetals → gain electrons (Electron Affinity more negative)

Metal → lose electrons (low ionization energy)

Metals transfer electrons to oxygen to form ionic oxides which act as bases

Nonmetals share electrons with oxygen, covalent-oxides act as acids

Called Isoelectronic noble gas or Pseudo-noble gas

Electron with highest n value is lost first (except for Lathanides)

Atomic and Ionic Sizes

Determine spectroscopy, math models include size, radius

Atomic radii based on bond distance

Cl-Cl is 198 pm apart so the radius for Cl is $198\text{pm}/2 = 99\text{ pm}$

C-Cl is 176 pm apart so radii $176-99 = 77\text{ pm}$ radius for C

The general trend for Atomic Radius is that it increases right to left across the periodic table and increases from top to bottom.

Reason: down- filling shell so farther from nucleus

across- within shell remove e- and proton so remaining electrons are not held as tightly

Ionic Radius in crystals like table salt have alternating negative-positive ions

Shielding



(<http://www.webelements.com/webelements/elements/text/Li/econ.html>)

The effective nuclear charge $\sim +1$

Representative elements change more than transition change in d and f

Size is fairly flat in filling d and f orbitals since these are not outermost electrons

Lanthanide contraction

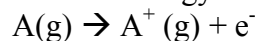
<u>Left</u>	Periodic Table	<u>Right</u>
Lose e-		Gain e-
Cation		Anion
Become smaller		Become larger
Fe = 117 pm		Cl = 99 pm
Fe ²⁺ = 75 pm		Cl ⁻ = 181 pm
Fe ³⁺ = 60 pm		

Electron cloud responsible for size

X-ray diffraction to determine separation between nuclei in atomic crystals

Ionization Energy and Electron Affinity

First Ionization Energy \rightarrow energy to remove 1 outer electron



Use beam of electrons to knock off electron to form ion

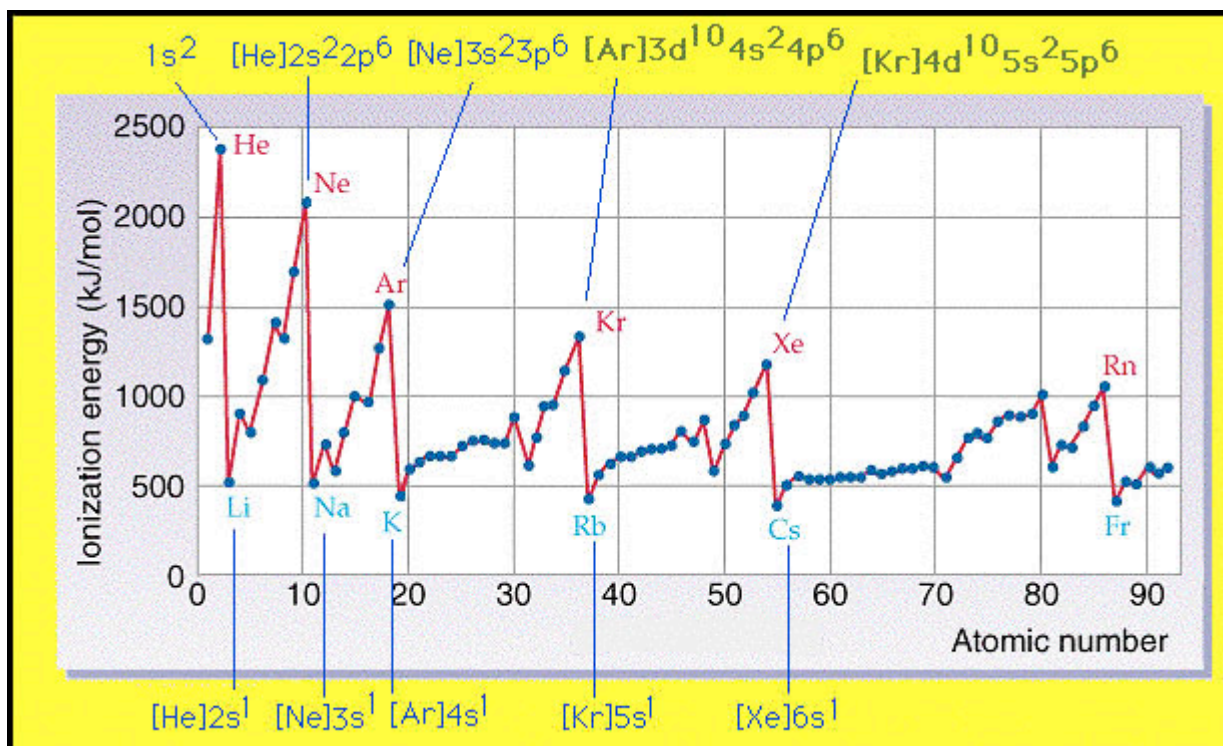
Exothermic- energy given off (-), electron moves down a level

Endothermic- energy taken in (+), electron moves up a level

Put energy into atom to ionize so + sign

$$1\text{eV} = 1.602 \times 10^{-19} \text{ J} = 96.5 \text{ kJ/mol}$$

Observe Ionization Energies versus Atomic Number Graph



<http://www.iun.edu/~cpanhd/C101webnotes/modern-atomic-theory/images/ionization-energy.jpg>

The general trend is one of increasing ionization energy from right to left across the periodic table and increase from bottom to top

Reason: Up- electron from lower level (closer to nucleus) is more difficult to remove
 Across- have higher positive nuclear charge and so more attraction to nucleus

For alkali metal most of positive charge is shielded
 Ex showing this is Francium Atomic Model:



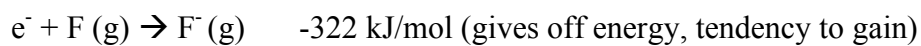
http://pittsford.monroe.edu/pittsfordmiddle/rountree/rounweb_1_02/connimage_2.jpg

Second and Third Ionization Energy require more energy
But largest jump is after valence

Na	1 valence, outer shell electron
Mg	2
Al	3

Electron Affinity

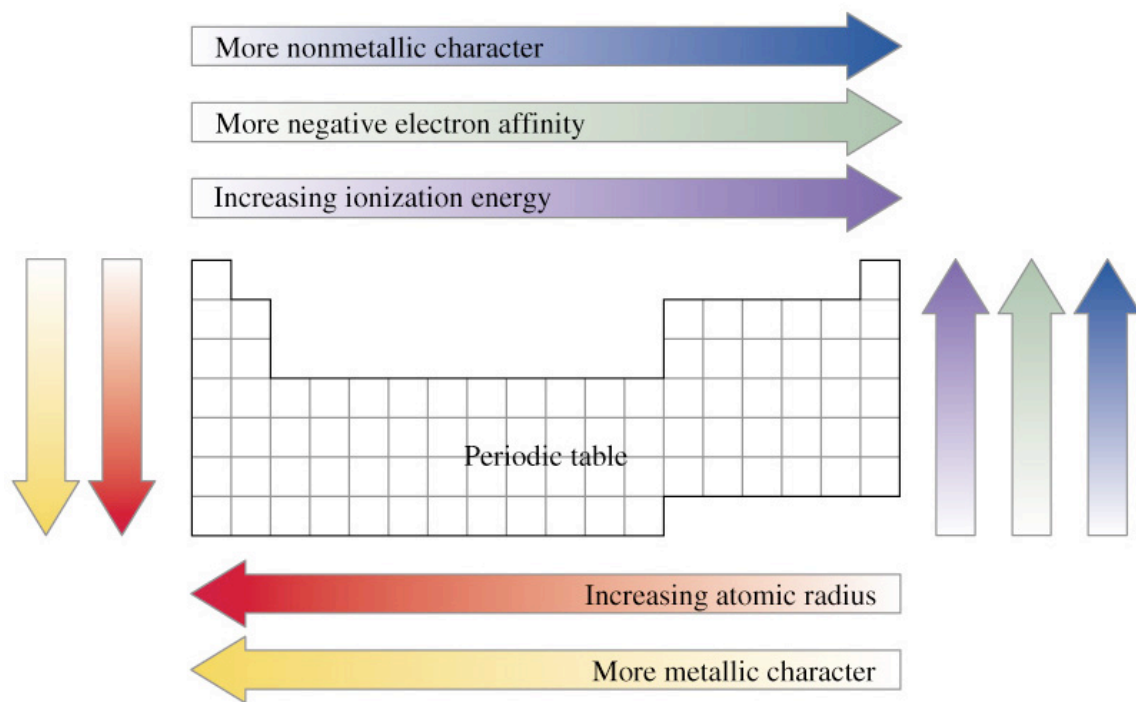
Energy to add electron



Halogens have strong tendency to GAIN electrons

Otherwise there is not a clear pattern

Summary of Periodic Trends



(http://cwx.prenhall.com/bookbind/pubbooks/hillchem3/medialib/media_portfolio/08.html)