Chapter 6 – Electronic Structure

Chapter Outline

Review of wave properties (What is a wave?)

Electromagnetic spectrum (What is "light"?)

Atomic spectra/photoelectric effect (What causes light?)

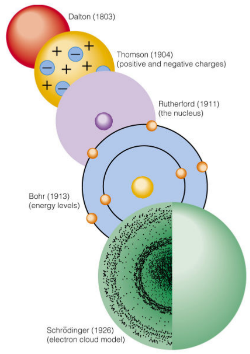
Bohr model of the atom (Simple model of the atom)

Rydberg equation (Describes light produced by hydrogen)

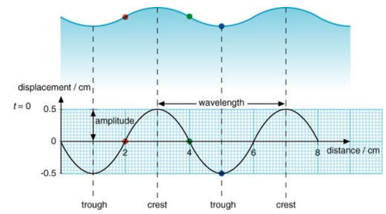
Wave mechanical model (Advanced model of the atom)

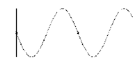
Quantum numbers

Periodic Trends



Wave Properties:





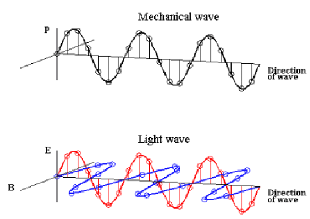
Velocity (distance/time): Translational speed of the wave.
Frequency (Cycles/Second; Hertz (Hz): The number of cycles per second that pass by some reference point
Period (time): Time required for one wave to pass (= 1/frequency)

Electromagnetic (Transverse) Waves: E and B Fields

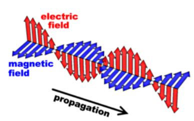
Light can be thought of as a wave of alternating electrical and magnetic fields.

The "E" is the electrical field and "B" is the magnetic field component.

EM wave are "self-propagating"



The phenomenon of diffraction is a wave-like property of light

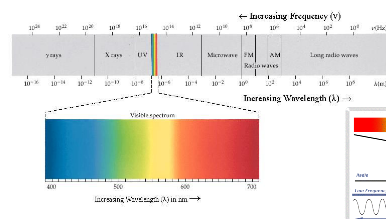


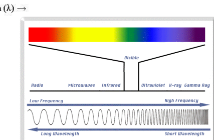
Regions of the Electromagnetic Spectrum

Increasing Energy

Increasing Wavelength

Increasing Frequency





Visible light runs between about 400-700nm

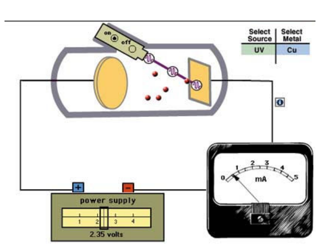
In mechanical waves, energy is carried on the amplitude of the wave

For light (EM radiation), energy is carried on the frequency of the wave.

This was determined through the photoelectric effect, explained by Einstein (1905)

Introduced the idea of the "photon" as a light "particle"

Light has both wave and particle properties

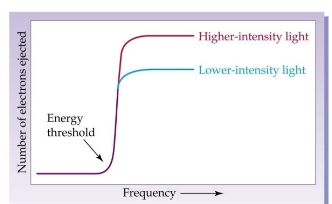


Video Clip

In Summary:

The frequency of the incident photon determines whether or not an electron of a particular metal will be ejected or not (Frequency $\propto$ Energy)

The amplitude of the photon (intensity) determines how many photons per unit time will be ejected (assuming they are ejected) (Intensity $\propto$ Current)



Summary of Equations:

$$c = \lambda\nu$$

Where:
c = speed of light = $3.0\text{x}10^8$m/s
λ = the wavelength (in meters)
ν = frequency (in s^{-1}, 1/s)
(Sometimes frequency is written with the symbol, f)

$$E = h\nu \text{ or } E = hc/\lambda$$

Where:
E = Energy (in joules)
h = Planck's constant ($6.626\text{x}10^{-34}$Js)

Example: Determine the frequency of a light wave with a wavelength of 650.nm.

Answer:

$\nu = c/\lambda$

$\nu = (3.00\text{x}10^8\text{m/s})/(6.50\text{x}10^{-7}\text{m})$

$\nu = 4.62\text{x}10^{14}\text{s}^{-1}$

Example: Calculate the energy of a photon with a wavelength of 500.nm. Express your answer in joules. How much energy is there in units of kJ/mol of photons?

Answer:

$E = hc/\lambda$

$E = (6.626\text{x}10^{-34}\text{Js})(3.00\text{x}10^8\text{m/s})/(5.00\text{x}10^{-7}\text{m}) = 3.98\text{x}10^{-19}$J/photon

The energy per mole of photons is

$(3.98\text{x}10^{-19}\text{J/photon})(6.022\text{x}10^{23}\text{photons/mole}) = 2.40\text{x}10^5$J/mol or 240.kJ/mol

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Example: A 60.W, monochromatic laser beam gives off photons of wavelength 650.nm. How long does it take for 2.5moles of these photons to be given off? (Hint: Power (in watts) = work/time (in J/s))
b. How many moles of photons are given off per second?

Answer:

$E = hc/\lambda = (6.626\text{x}10^{-34}\text{Js})(3.0\text{x}10^8\text{m/s})/6.50\text{x}10^{-7}\text{m}$

$= 3.06\text{x}10^{-19}$J/photon

$(3.06\text{x}10^{-19}\text{J/photon})((6.022\text{x}10^{23}\text{photons/mol})(2.5\text{mol}) =$

$4.60\text{x}10^5$J

$4.60\text{x}10^5\text{J} / 60\text{J/s} = 7673.4\text{s}$ $\quad$ /3600s/h = 2.13h

b. $2.5\text{mol} / 7673.4\text{s} = 3.3\text{x}10^{-4}$mol/s

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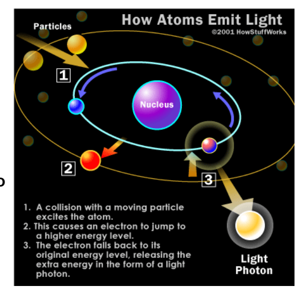
What is light and how is it produced?

Light is pure energy that can be transported through space.

EM energy is produced when an electron in a lower orbit (energy state) is "excited" to a higher energy state by absorbing some form of energy (heat, electrical, etc.)

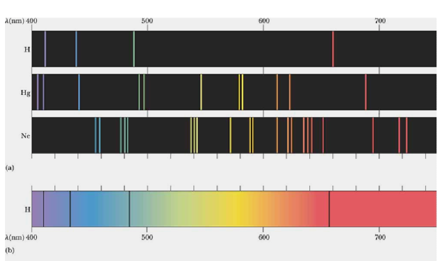
Upon the transition back down to its "ground state" (normal orbit), the energy that it loses in doing so is given off as some form of electromagnetic radiation, whose energy (frequency) depends on the energy "jump" the electron makes.



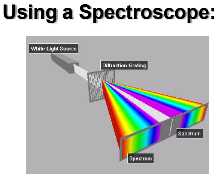
Spectral Lines and the Quantum Model of the Atom

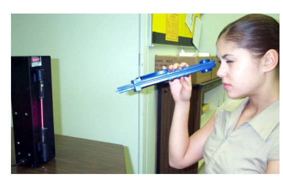
Classical physics predicted that when a rarefied (low pressure) gas is heated, it should give off light of all wavelengths (since all energy level transitions (jumps) should be possible)

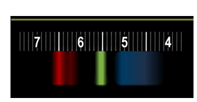
In practice, only specific wavelengths appeared (spectral lines)



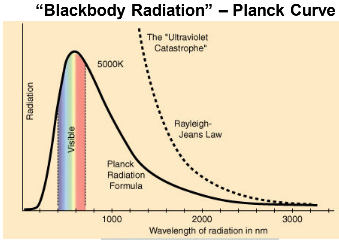
Using a Spectroscope:



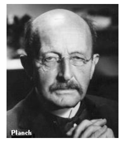




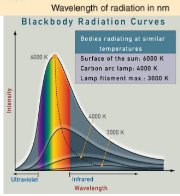
"Blackbody Radiation" – Planck Curve

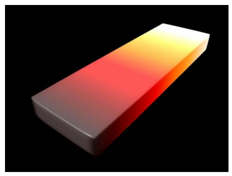


Max Planck



Energy must exist as tiny packets of energy which Planck called "quanta".

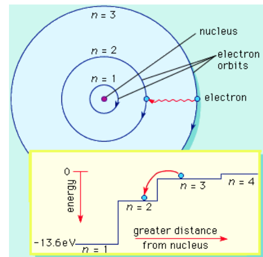


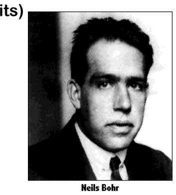


$E \propto \nu^2 kT$

Bohr Model of the Atom

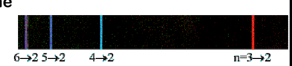
Explained spectral lines by predicting that orbits in an atom must be "quantized" (can only have specific orbits)

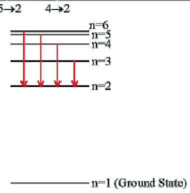




The Balmer Series of Hydrogen

The difference in energy between the two levels equals the energy of the photon given off. $\Delta E = h\nu$





For the hydrogen atom, the frequency of a photon emitted is given by the Rydberg equation:

$\Delta E = R_H\ (1/n_{lo}^2 - 1/n_{hi}^2)$ or

$\nu = R_H/h\ (1/n_{lo}^2 - 1/n_{hi}^2)$

$R_H = 2.180\times10^{-18}$J $h = 6.626\times10^{-34}$Js

The maximum number of electrons allowed in any ring is given by $2n^2$, where n is the ring number (1 = innermost ring).

Absolute energy for any level n is given by $E = -R_H(1/n^2)$

Example:

In a hydrogen atom, an electron is excited from $n_1 \rightarrow n_5$ level. The downward transition is composed of two jumps; $n_5 \rightarrow n_2$ and $n_2 \rightarrow n_1$

Calculate the energy absorbed by the electron on the upward transition.

Calculate the energies and frequencies of the photons emitted on the downward transitions.

Comment on the relationship between the energy absorbed by the atom and the energy released by the photons.

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Calculate the energy absorbed by the electron on the upward transition.

Calculate the energies and frequencies of the photons emitted on the downward transitions.

Comment on the relationship between the energy absorbed by the atom and the energy released by the photons.

Answer:

$\Delta E = R_H\ (1/n_{lo}^2 - 1/n_{hi}^2) = 2.180\times10^{-18}\text{J}\ (1/1^2 - 1/5^2) = 2.093\times10^{-18}\text{J}$

$n_5 \rightarrow n_2 = 2.180\times10^{-18}\text{J}\ (1/2^2 - 1/5^2) = 4.578\times10^{-19}\text{J}$
$\nu = E/h = 4.578\times10^{-19}\text{J}/6.626\times10^{-34}\text{Js} = 6.909\times10^{14}\text{Hz}$

$n_2 \rightarrow n_1 = 2.180\times10^{-18}\text{J}\ (1/1^2 - 1/2^2) = 1.635\times10^{-18}\text{J}$
$\nu = E/h = 1.635\times10^{-18}\text{J}/6.626\times10^{-34}\text{Js} = 2.468\times10^{15}\text{Hz}$

The energy out = energy in

Example:
In a hydrogen atom, a Balmer series line is produced corresponding to a photon with a frequency of 6.909×10^{14}Hz. From which Bohr orbit ring did the electron jump from?

$\Delta E = R_H\ (1/n_{lo}^2 - 1/n_{hi}^2)$ or

$\nu = (R_H/h)\ (1/n_{lo}^2 - 1/n_{hi}^2)$

$R_H = 2.180\times10^{-18}$J $h = 6.626\times10^{-34}$Js

Answer:

$6.909\times10^{14}\text{Hz} = [2.180\times10^{-18}\text{J}/6.626\times10^{-34}\text{Js}](1/2^2 - 1/n_{hi}^2)$

n_{hi} = **5**

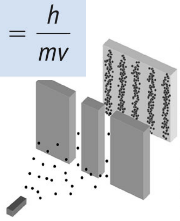
Wave Properties of the electron

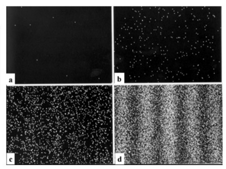
If light has particle properties (photons), can particles have wave properties?

"Matter Waves" Based on the (Louis) DeBroglie Equation

Where, λ is the DeBroglie Wavelength, h is the Planck constant, 6.626×10^{-34}Js and mv is the momentum of the particle (m = mass in kg; v = velocity in m/s)

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

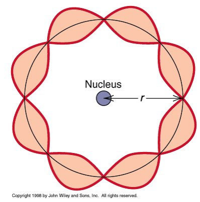


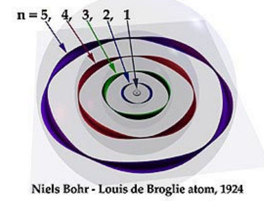


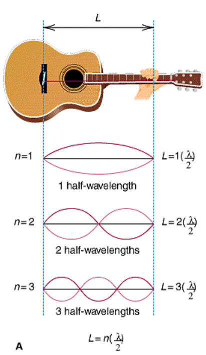
DeBroglie's Interpretation of the Bohr Model of the Atom

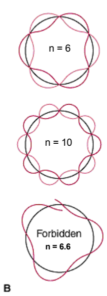
Allowed orbits have a circumference related to nλ/2

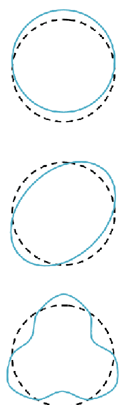
2πr =nλ/2, where n is an integer number



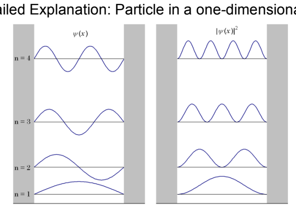








Optional Detailed Explanation: Particle in a one-dimensional Box of Length, L.



Permitted Standing wavelengths

$$\lambda = \frac{2L}{n} \quad n = 1,2,3 \quad \textit{total nodes} = n+1$$

Wave function:

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad n = 1,2,3...$$

Ψ^2 function: Probabilities of particle in a one-dimensional box.

$$\Psi_n^{\,2}(x) = \frac{2}{L}\sin^2\left(\frac{n\pi}{L}x\right)$$

Wave Mechanical Model of the Atom

Interpretation of the DeBroglie Wavelength

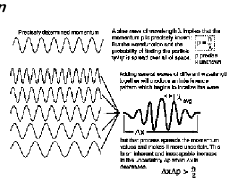
About the same time as DeBroglie (1927) Werner Heisenberg developed what became known as the Heisenberg Uncertainty Principle. It stated:

There is a fundamental limit that nature puts on our ability to measure both the position and momentum of an object simultaneously.

The equation is given by:

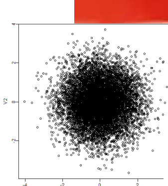
$\Delta x \Delta mv \geq h/4\pi$

where Δx is the uncertainty in the position and Δmv is the uncertainty in the momentum (often velocity).



The result of these two ideas is that there is a certain "fuzziness" or statistical uncertainty associated with determining the position and/or momentum of an object.

Analogy: When the race car is in motion, to what precision can you determine the instantaneous position of the vehicle?



Scatter Plot (probability density)

Example:

Calculate the wavelength associated with a neutron having a mass of 1.675×10^{-24}g and a kinetic energy of 6.21×10^{-21}J. (Recall that the kinetic energy of a moving particle is $E = ½ mv^2$.)

Answer:

$KE = ½ mv^2$ $\quad 6.21 \times 10^{-21} J = ½ (1.67 \times 10^{-27} kg)(v^2)$

$v = 2727.11 m/s$

$\lambda = h / mv \quad = (6.626 \times 10^{-34} Js) / (1.67 \times 10^{-27} kg)(2727.11 m/s)$

$= 1.45 \times 10^{-10} m$ = .145nm (1.45Å, angstroms)

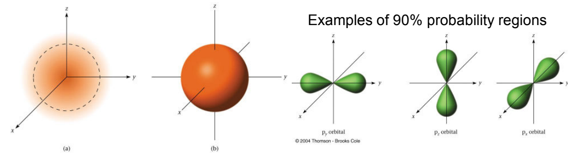
Note: 1 angstrom = 10^{-10}m

The Schrodinger Wave Equation

Erwin Schrodinger - Derived the wave function (a.k.a. wave equation), represented by Ψ (psi). This equation describes the **quantum energy state** of a particular electron in an atom.

Psi squared (Ψ^2) gives the 90% probability region (3-dimensional space) for finding an electron with a particular quantum energy state (set of 4 quantum numbers). These regions are known as **orbitals**

Examples of 90% probability regions



Electrons are not particles orbiting in a ring, but they are "waves of probability" that exist within a region of space around the nucleus.

Each electron's quantum state is determined by four fundamental properties

Principal Quantum Number (n)

Description: Determines the ***overall energy*** of the level. Analogous to the ***average distance*** away from the nucleus.

Possible values: n = 1, 2, 3,… (integer numbers)

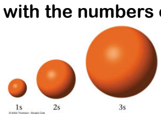
Angular Momentum (Azimuthal) Quantum Number (*ℓ*)

Description: Determines the ***shape*** of the ***sub-level*** orbital

Possible values: *ℓ* = 0 to (n-1)

There are also letters associated with the numbers of *ℓ*: 0 (s), 1 (p), 2 (d), 3 (f), 4 (g), …

s = sharp, p = principal,
d = diffuse, f = fine.

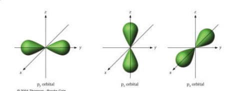


Note: There is a difference between an orbit and an orbital

Magnetic Quantum Number (m_ℓ)

Description: Determines the ***spatial orientation*** of the sub-level orbital

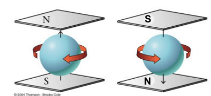
Possible Values: -*ℓ*…0…+*ℓ*



Spin Quantum Number (m_s)

Description: Determines the ***spin orientation*** of the electron in an orbital

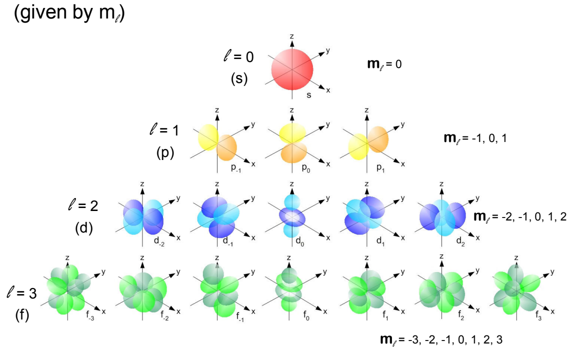
Possible Values: $m_s = \pm ½$

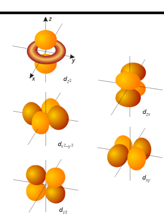


Each orbital can contain a maximum of 2 electrons

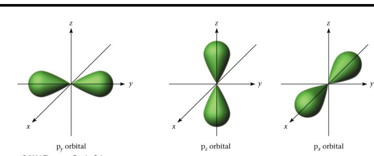
Orbitals (90% probability regions)

Energy sub-levels (given by *ℓ*) and orbitals within the sub-levels (given by m_ℓ)

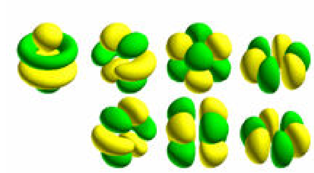




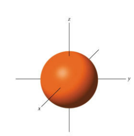
d-sublevel orbitals



p-sublevel orbitals



f-sublevel orbitals



s-sublevel orbital

In Summary

To describe the quantum state of an electron in an atom you must identify:

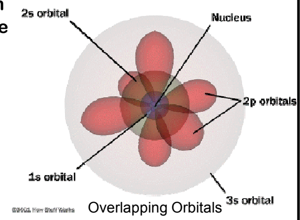
The energy level (n)(given by the period on the periodic table)

The energy sub-level (ℓ)(given by the "group" position on the periodic table.

The spatial orientation of the electron (m_ℓ)(given by the orbital shapes)

The spin of the electron (m_s)(one of two possible values)

Orbitals are "nested" (overlapping) like these wooden dolls



Overlapping Orbitals

Examples of possible values

Energy Level (n)	Azimuthal Number (ℓ) (0 to n-1)	Magnetic Number (m_ℓ) ($-\ell$…0…$+\ell$)	Spin Number (m_s) + ½, - ½	Possibilities
1	0 (s)	0	+ ½ , - ½	2
2	0 (s) 1 (p)	0 -1, 0, +1	+ ½ , - ½ + ½ , - ½	2 6
3	0 (s) 1 (p) 2 (d)	0 -1, 0, +1 -2, -1, 0, +1, +2	+ ½ , - ½ + ½ , - ½ + ½ , - ½	2 6 10

Electron filling in an atom is governed by three principles:

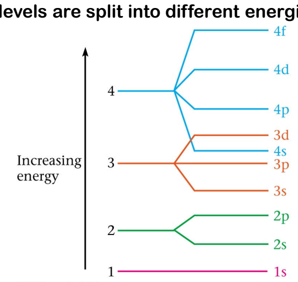
Aufbau Principle - Electrons fill energy positions from lowest to highest.

Hund's Rule - When filling orbitals within an energy sub-level, electrons fill orbitals singly before pairing.

Pauli Exclusion Principle - Each electron in an atom must have a unique set of quantum numbers for that atom. Put another way: **No two electrons in a given atom can possess the same set of four quantum numbers.**

Electrons within the same energy sub-level are said to be "**degenerate**" because their energies are all the same.

For atoms with more than one electron, the energy sub-levels are split into different energies.



Energy for multi-electron atoms.

Note: For hydrogen, all sublevels of a given energy level have the same energy (i.e. are degenerate).

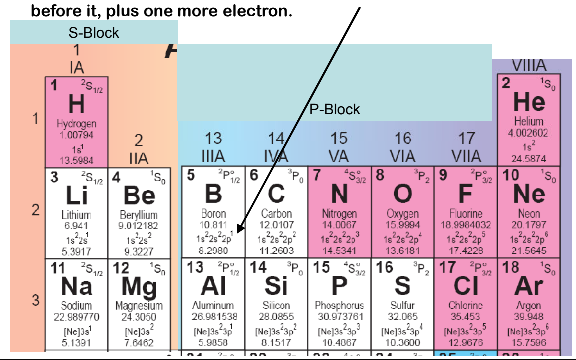
Spectroscopic Notation

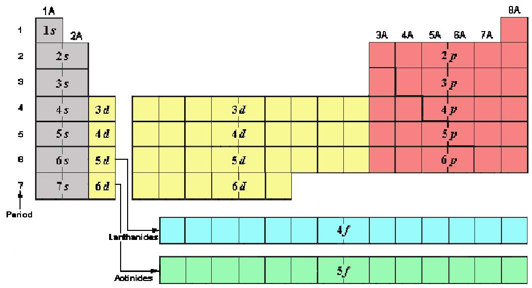
One way of designating the electron configuration in an atom denotes the principal energy level, sublevel and the number of electrons in the sublevel (written as a superscript). It does not differentiate between m_ℓ and m_s values.

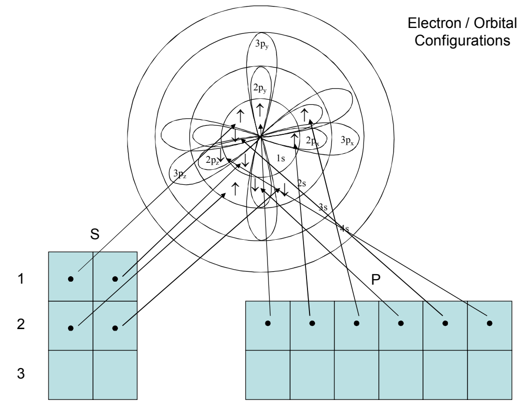
Example: Give the spectroscopic notation for the sodium atom (assume ground state electron configuration)

Answer: $1s^2 2s^2 2p^6 3s^1$

The periodic table is laid out to help you identify the "quantum state" for a particular electron in an atom. In most cases, each atom has the same electron configuration as the one that came before it, plus one more electron.

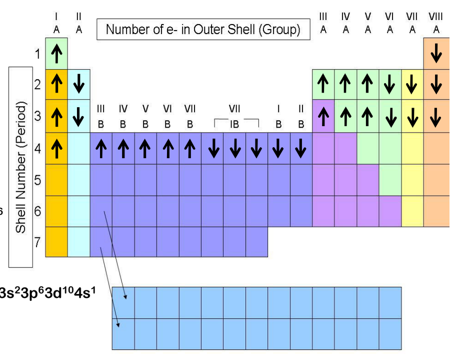






Orbital Filling

H – $1s^1$
He – $1s^2$
Li – $1s^22s^1$
Be – $1s^22s^2$
B – $1s^22s^22p^1$
C – $1s^22s^22p^2$
N – $1s^22s^22p^3$
O – $1s^22s^22p^4$
F – $1s^22s^22p^5$
Ne – $1s^22s^22p^6$



Cu – $1s^22s^22p^63s^23p^63d^{10}4s^1$

Condensed Spectroscopic Notation

Uses the previously occurring noble gas as the starting point for writing the notation

For instance:

Sulfur can be written as

$1s^22s^22p^63s^23p^4$

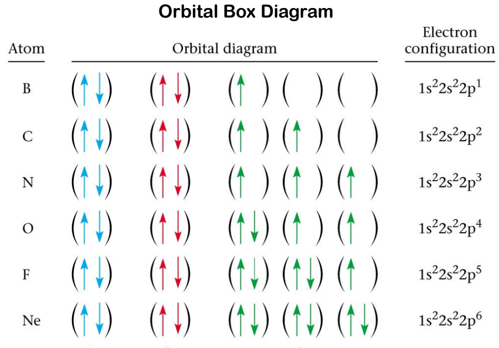
Or, since neon's notation is $1s^22s^22p^6$ you can write

$[Ne]3s^23p^4$

Important: Only noble gases can be used in brackets!

Alternate Method of Representing Electron Arrangements

Orbital Box Diagram



Electron Arrangements in Monoatomic Ions

Noble gases have completely filled s and p (outermost) sublevels for a total of 8 electrons (known as an **octet**)[two for He since it has no p-sublevel]

Outermost electrons (highest n number) are known as **valence** electrons. Other electrons are known as **core** electrons

Bonding normally occurs at the valence electron level

Ions generally form to achieve a noble gas "octet"

For the main group elements (A groups) the group number gives the number of valence electrons in the atom.

Transition metals lose electrons from the outermost n level first (e.g. 4s electrons removed before 3d electrons)(Add e^- by increasing energy take away e^- by highest n)

Common Exceptions to Orbital Filling

Happens commonly with transition metals

Because of energy considerations, electrons are sometimes "promoted" from an s-sublevel valence electron to a d-sublevel to half-fill or fill that sublevel

Example:

The expected spectroscopic notation for chromium (Cr) is: $1s^22s^22p^63s^23p^64s^23d^4$ but the actual notation is:

$1s^22s^22p^63s^23p^64s^13d^5$ *
this half-fills the d-sublevel making it more stable

*Note: The more common way of writing the notation now is by principal energy level: $1s^22s^22p^63s^23p^63d^54s^1$

Examples:

1. Give the spectroscopic, condensed spectroscopic and orbital box diagram for Arsenic (As)
2. Copper (Cu) behaves similar to chromium as explained on the previous slide. Predict and write the spectroscopic and condensed spectroscopic notation for copper.
3. Give the full spectroscopic notation for gallium, Ga, in its 3+ charge state.

Answers:

1. $1s^22s^22p^63s^23p^63d^{10}4s^24p^3$
[Ar]$3d^{10}4s^24p^3$
(↓↑) (↓↑) (↓↑)(↓↑)(↓↑) (↓↑) (↓↑)(↓↑)(↓↑) (↓↑)(↓↑)(↓↑)(↓↑)(↓↑) (↓↑) (↑)(↑)(↑)
1s 2s 2p 3s 3p 3d 4s 4p

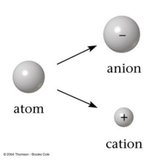
2. $1s^22s^22p^63s^23p^63d^{10}4s^1$ [Ar]$3d^{10}4s^1$
3. $1s^22s^22p^63s^23p^63d^{10}$(same as Argon noble gas config.)

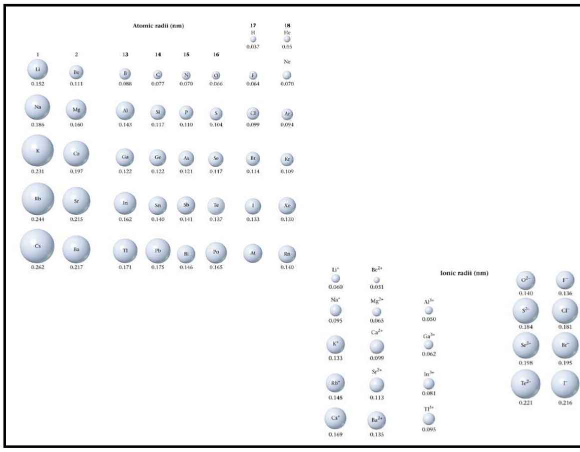
Periodic Trends (with reference to the periodic table)

Applies most accurately to the main group (A) elements

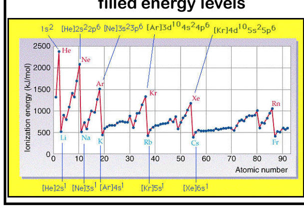
Atomic Radius: Distance from nucleus to outer electron cloud region
-Decreases to the right (due to increase in atomic (+) charge)
-Increases down (due to increasing energy layers (n-numbers) [like adding another layer to an onion]

Ionic radius: Size of an ionized atom
-An anion is always bigger than its parent atom (increase in electron repulsion)
-A cation is always smaller that its parent atom (surplus of positive charge relative to negative charge)





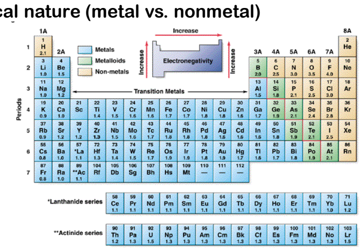
Ionization Energy (IE): Energy required to remove an electron from the gas phase of an atom (kJ/mol)
-Increases across the periodic table (increasing positive nuclear charge)
-Decreases down the periodic table (valence electrons further from nucleus; Core electron "shielding"
-Usually see big IE spikes from one energy level to another
-See smaller IE spikes removing electrons from half-filled energy levels



1	2	13	14	15	16	17	18
						H 1312	He 2372
Li 520	Be 900	B 801	C 1086	N 1402	O 1314	F 1681	Ne 2081
Na 496	Mg 738	Al 578	Si 786	P 1012	S 1000	Cl 1251	Ar 1520
K 419	Ca 590	Ga 579	Ge 762	As 944	Se 941	Br 1140	Kr 1351
Rb 403	Sr 550	In 558	Sn 709	Sb 832	Te 869	I 1009	Xe 1170
Cs 376	Ba 503	Tl 589	Pb 716	Bi 703	Po 812	At	Rn 1037

Electronegativity: Dimensionless scale. Gives the relative tendency for an atom in a bond with another atom to attract the bonding electrons towards it.

Increases on the periodic table to the right and up due to:
-Proximity of valence electrons to the nucleus
-Number of valence electrons
-Core electron shielding
-Chemical nature (metal vs. nonmetal)



Supplemental Question:

The ionization energy for fluorine is 1681kJ/mol. Calculate the energy in joules per atom.

Calculate the maximum photon wavelength that a fluorine atom could absorb to achieve this result.

$1{,}681{,}000\text{J/mol} \ (1\text{mol} / 6.022\times10^{23}\text{atoms})$
$= 2.791\times10^{-18}\text{J/atom}$

$E = hc/\lambda \qquad \lambda = hc/E$

$\lambda = (6.626\times10^{-34}\text{Js})(3.00\times10^{8}\text{m/s})/(2.791\times10^{-18}\text{J})$

$= 7.12\times10^{-8}\text{m} = 71.2\text{nm}$