## Atom

Smallest particle of an element having the same chemical properties as bulk element.

## Atomic Structure:

What is it made of?
How does the interior of an atom look like?

A series of experiments and observations led to the current ‘model’ of the atom.

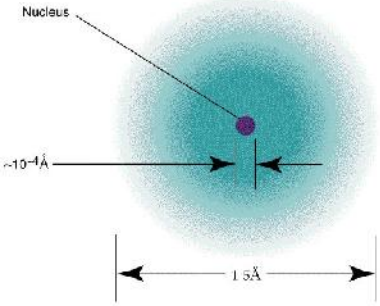
## Rutherford’s Nuclear Atom:

Atom: heavy positively charged small region
soft negatively charged large region.

#protons = # electrons; atom overall neutral.

Nucleus: protons + neutrons
virtually all mass in nucleus.

Soft sphere.



The nuclear constituents of an atom of a given element do not exchange during chemical and physical processes - exception - nuclear reactions.

Electrons however change partnerships during chemical reactions.

Our Focus - electronic environment of atoms.

Electron Organization in Atoms.
Electron Configurations.

*Key to understanding matter and their properties.*

Why alkali metals are very reactive and form +1 charged ions?

Why noble gases are very stable and un-reactive.

What is the theoretical basis of the Periodic Table.

Why nonmetallic elements join together by covalent bonds?

.

.

To understand the electronic structure (organization) of atoms - need a 'probe'.

The size of the atom is so small, the probe that would allow us an insight should be of comparable size as well.

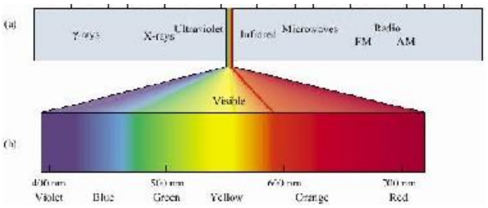
Looking at the size of the probes available, none that is familiar suits the job.

Visible light acts as an indirect probe.

Present day understanding of the structure of the electronic configuration is the result of studies of interaction of electromagnetic radiation (light) with atoms.

Visible light is only a small part of a broad 'spectrum' of electromagnetic radiation.

Electromagnetic Spectrum

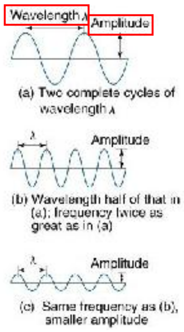


Most significant feature of e.m radiation - they are waves.

A wave is a 'repetition' of a property in a regular fashion.

Ocean wave - a photograph would illustrates this.

Wave length, λ & amplitude



(a) Two complete cycles of wavelength λ

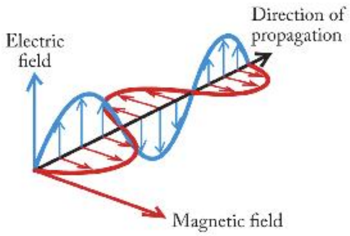
(b) Wavelength half of that in (a); frequency twice as great as in (a)

(c) Same frequency as (b), smaller amplitude

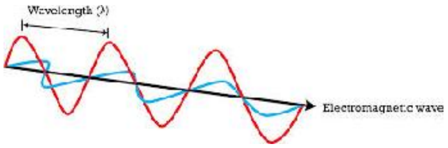
## Electromagnetic Radiation

Perpendicular oscillating fields:

- Electric
- Magnetic



http://www.youtube.com/watch?v=iLR_XuIk5iw



http://www.youtube.com/watch?v=iLR_XuIk5iw

Wave length (and frequency) with it's amplitude are the important characteristics of waves.

Electromagnetic radiation is a travelling wave.

Electromagnetic radiation travels through space (and some, thro' matter).

Velocity, in vacuum (~air); $c = 2.998\times10^{8}$ m/sec same for all types of e.m. radiation.

The visible region is commonly divided into 7 regions (violet, indigo,….red) – very, very approximate.

Each color has a unique wavelength (or unique frequency).

red limit ~700 nm
violet limit ~ 400 nm
in between - millions of wavelengths

$$\lambda\nu = c$$

Radiation is a form of energy.

The radiation energy is well defined.

The minimum amount of energy that a beam of radiation of frequency ν will carry is known as a ***Photon (energy packet)***.

The energy in a single photon = hν.
h = Planck's constant

hν is the smallest possible amount (packet) of energy from a beam of light of frequency ν
➡ QUANTUM of ENERGY = hν .
'Packets' of radiant energy = quanta
↑
Particle character of light.

Photon energy is quantized.

A single photon can have an energy of hν ***and no less and no more.***

A photon - energy packet - cannot be broken into fractions.

$h = 6.6260755 \times 10^{-34}$ J·s (Planck's constant)

A beam of radiation of frequency, ν, carries many 'packets' (photons) of energy.

Energy in a single photon: E = hν

*where h = Planck's constant = 6.63 × $10^{-34}$ J s*

Energy of a photon of radiation of $\lambda = 589nm$

$$\lambda = 589nm$$
$$\nu = \frac{2.998\times10^{8}ms^{-1}}{589\times10^{-9}m} = 5.09\times10^{14}s^{-1}$$
$$E = h\nu$$
$$= 6.63\times10^{-34}Js\times5.09\times10^{14}s^{-1}$$
$$\underline{= 3.37\times10^{-19}J}$$

Can you use 589 nm radiation to obtain energy of value;

$3.37 \times 10^{-19}$ J

$3.38 \times 10^{-19}$ J, $4.40 \times 10^{-19}$ J, $1.69 \times 10^{-19}$ J

$6.74 \times 10^{-19}$ J, $10.11 \times 10^{-19}$ J

Can you use 589 nm radiation to obtain energy of value;

$3.37 \times 10^{-19}$ J *1 photon*

$3.38 \times 10^{-19}$ J, $4.40 \times 10^{-19}$ J, $1.69 \times 10^{-19}$ J *no*

$6.74 \times 10^{-19}$ J *2 photons*
$10.11 \times 10^{-19}$ J *3 photons*

How much energy is contained in 1 mole of photons of radiation 589nm wavelength?

$$N_0 = 6.023\times10^{23}$$
$$E = h\nu$$
$$= 3.37\times10^{-19}J$$
$$\text{Energy in 1 mole of photons} = 3.37\times10^{-19}J\times6.023\times10^{23}$$
$$= 2.030\times10^{5}J$$

Photon energies are quantized.

A light ray is a stream of photons.

Each photon carries *h*¬ amount of energy.

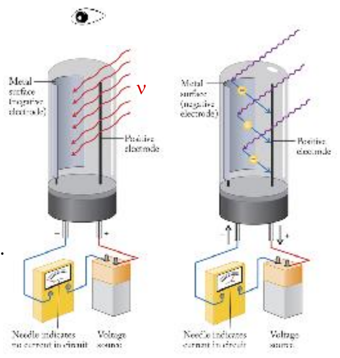
Amplitude is a measure of the brightness or intensity of the beam (number of photons/sec).

Frequency is characteristic of the ‘color’ of the radiation, and so is the wavelength.

## Photoelectric Effect:

Illuminating metal with electro-magnetic radiation releases electrons from metal surface.

If the electromagnetic radiation below a threshold energy, no electrons released.



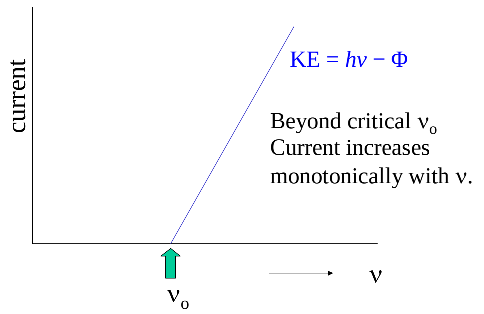
## Photoelectric effect

Application of the quantum (energy packet-photon) concept of photons - Photoelectric effect.

Metals exposed to radiation (light) emits electrons.

However, for each metal there is a *threshold radiation frequency*.

Below the threshold, electrons are not emitted, no matter how bright the radiation beam is.



$KE = h\nu - \Phi$

Beyond critical $\nu_o$
Current increases
monotonically with ν.

Work function: minimum energy required to release e− from metal surface: $\Phi = h\nu_0$

Photon energies are quantized (fact).

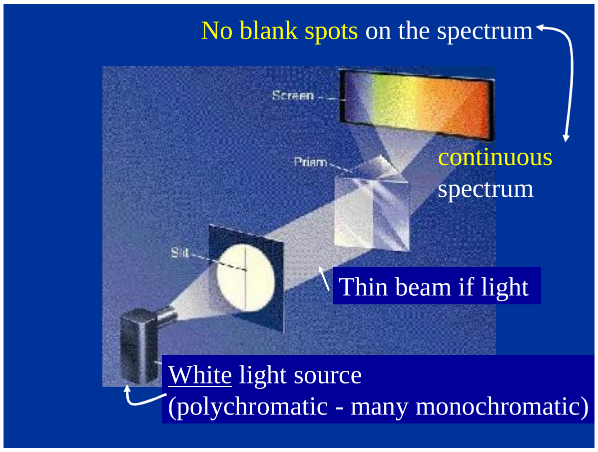
Quantization: discreteness of energy.

Atomic systems interact with photons only if they can use the entire photon.

Beyond the critical photon frequency, of the photon energy $h\nu$, $h\nu_0$ is expended to remove the electrons from the metal surface.

Energy from the one photon is consumed by one electron.

If the energy of a photon is less than the minimum energy needed to extract the electron (i.e. $\nu < \nu_0$), such photons will not be used and an electron would not come out; regardless how many photons of less energy ($< h\nu_o$) is provided.

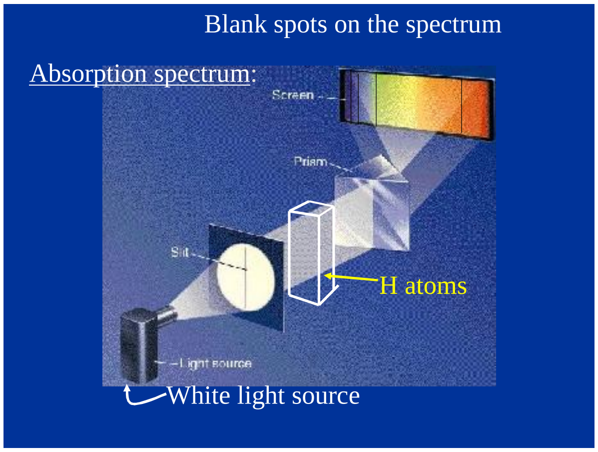


No blank spots on the spectrum

continuous spectrum

Thin beam if light

White light source
(polychromatic - many monochromatic)



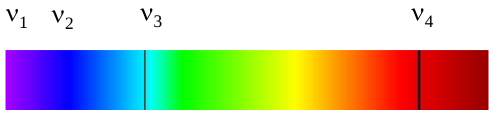
Blank spots on the spectrum

Absorption spectrum:

H atoms

White light source

Hydrogen line spectra:



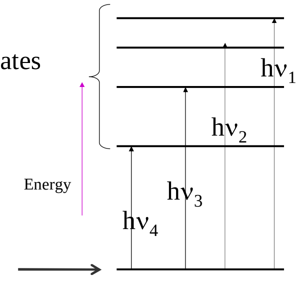
Absorption spectrum of H
Visible region.

The dark lines are the frequencies lost from the white light; continuous spectrum.

H atoms absorbed them.

H atoms absorb only well defined frequencies/ photons/quanta/energy packets.

In doing so H atom raises its energy by a well defined quantum of energy values.



Excited states

Ground state
Stable atoms

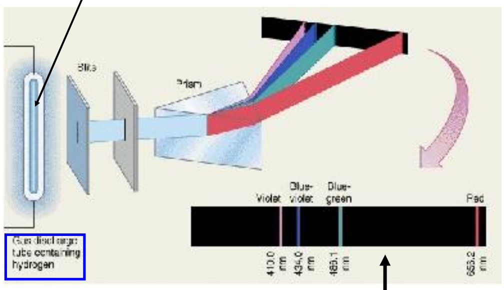
The most likely particle to absorb the photon is the electron (high probability- think of nuclear size and electron 'cloud' size).

Energy is absorbed in discrete amounts; quanta.

Once energy is absorbed by an atomic (molecular) system, the system reaches new states (energy levels) of well defined energy values
– ***quantization of energy states***)

---

Energized H atoms



H Line (emission) *spectrum*
(visible part)

---

Energy is absorbed and emitted in discrete amounts; quanta.

Emission spectrum of H atoms contain *only a few* well specified colors (monochromatic) and appear as lines from the experimental arrangement.

Line spectrum. Regions of blank spaces exist.

Spectrum is reproducible.

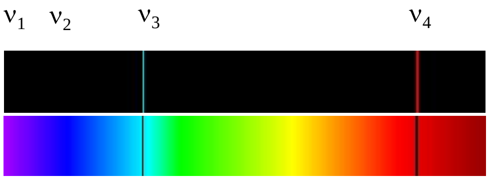
---

Energized atoms emits energy achieve a more stable lower energy states. The emitted energies are discrete too.

Emission spectrum of hydrogen

---

Emission spectrum of hydrogen



The frequencies of absorption and emission match perfectly.

---

The state with the lowest energy of atomic/ molecular system = Ground state.

Once photon energy is absorbed/emitted in atomic (molecular) systems, the 'new (final) state' energy of the system is shifted exactly up/down by the energy value of the photon, relative to the energy of the 'state at the start (initial)'.

Atom energy/electron energy raised due to Photon (light) *absorption*.

Atom energy/electron energy lowered due to Photon (light) *emission*.

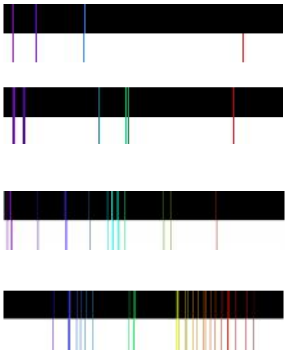
Balmer (1885)

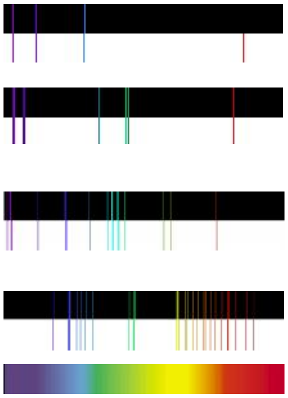
a empirical formula to relate frequencies observed in H spectrum.

$$\neg = C\left(\frac{1}{4}-\frac{1}{n^2}\right) \qquad n > 2$$

$$C = 3.29\times10^{15}\,s^{-1} \qquad \text{note}$$

BALMER GAVE NO EXPLANATION !!!



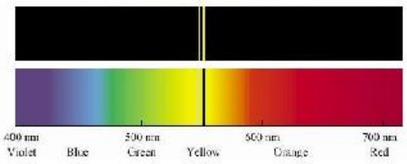


Emission spectra of some elements

***In absorption spectra a black space will be seen wherever a bright line appear in the emission spectra.***

Balmer.exe

Emission spectrum of sodium



Absorption spectrum of sodium

*NOTE THE COMPLIMENTARY NATURE of the two types of spectra.*

Bohr Theory of H atom:

Rutherford atom + Solar system
+ Planck's quantization idea.

Departure from Newtonian mechanics.

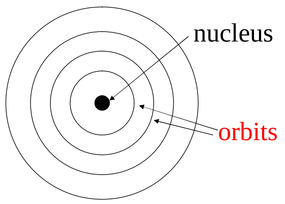
Bohr Theory of H atom:

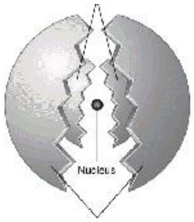
Electrons move in spherical ***orbits*** around the nucleus. In doing so, so long as the electron stays in the orbit the electron does not lose or gain energy.

The radii of the spherical ***orbits*** are well defined. (only certain radii can exist). Electron in an **orbit** has a well defined **specific energy**. i.e. energy quantized.

(Orbit - a place in which electron can exist/reside, is called an “allowed” energy state.)

---

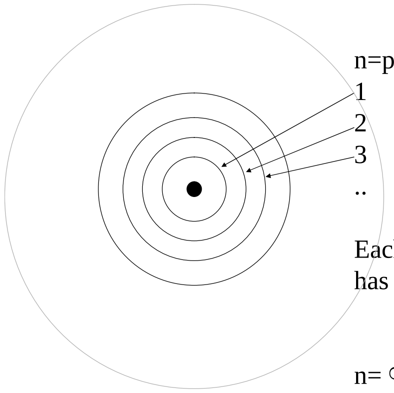




An electron in an orbit acquires the energy of the orbit of residence.

Energy of orbits increases with the radius.

---



n=principal quantum number

1
2
3
..

Each allowed state has a unique n.

n= ∞

---

As a general principle, ***attractions lower energy and repulsion increase energy.***

The most stable ‘state’ of any system is when the energy of the system is at it’s lowest.

---

The nucleus is positive and electrons are negative.

They, attract each other.

Thus the best possible (i.e. stable) orbit(s) for electron(s) are the ones closest to the nucleus.

Electrons arranging with the most stable arrangement (electrons in orbits closest to nucleus) - ground state.

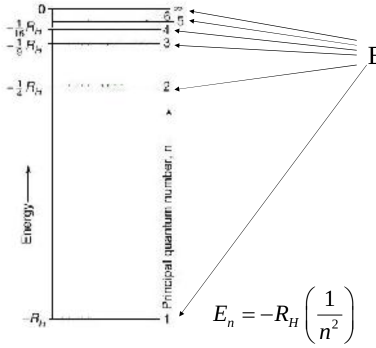
---

Energy of the electron in a Bohr orbit n;

$$E_n = -R_H\left(\frac{1}{n^2}\right) \qquad \text{n} = 1,2,3,4,...$$

$R_H = 2.18\times10^{-18}\,J$ :Rydberg constant

$r_n \sim n^2$ :$r_n$ = radius of the $n^{th}$ orbit



Energy levels

$$E_n = -R_H\left(\frac{1}{n^2}\right) \qquad n = 1,2,3,4,...$$

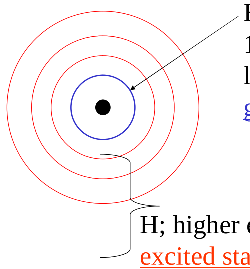
Energy of the orbit closest to the nucleus is the lowest.

Energy increases with n.

The electrons closest to the nucleus are the most attracted, attraction diminishes as orbital becomes larger.

As a general principle, ***attractions lower energy and repulsion increase energy.***

The most stable 'state' of any system is when the energy of the system is at it's lowest.

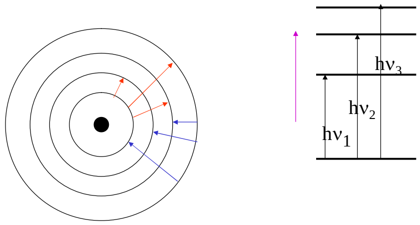


H atom ;
1- electron system,
lowest energy state
ground state

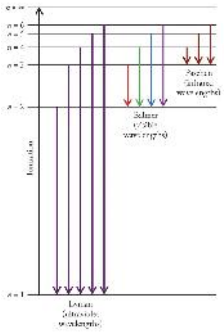
H; higher energy states
excited states

Transitions of electrons can occur between allowed energy states only.

Energy associated with electronic transitions ΔE for H atom.



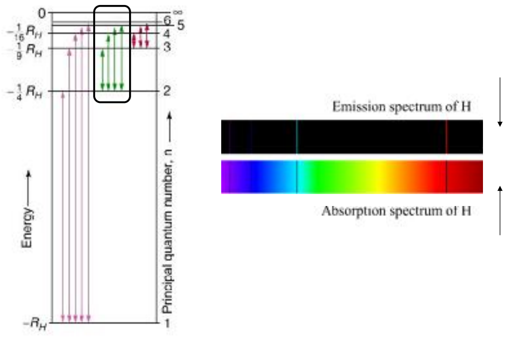
$$\Delta E = -2.178\times10^{-18}\ J\left(\frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2}\right)$$



Show electron **transitions** (*i.e.*, movement of electrons between energy levels).

↑ = absorption of energy.

↓ = emission of energy.



Electronic States

- Energy Level:
  - An allowed energy state that an electron can occupy in an atom.
- Ground State:
  - Lowest energy level available to an electron in an atom.
- Excited State:
  - Any energy state above the ground state.

Transition from lower energy orbit to higher energy orbit; demand (absorb) energy.

Transition from higher energy orbit to lower energy orbit; loses (emit) energy.

True for all systems (including atoms).

The energy absorbed/emitted is exactly equal to the energy difference between the orbit energies.

$$E_f - E_i = \Delta E = h\nu$$

During the electron transitions, photons of appropriate energy is absorbed/emitted.

Energy of transition (H like) between $n_i$ and $n_f$ and associated frequency;

$$E_f - E_i = \Delta E = h\nu$$

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

$$\frac{R_H}{h} = C \qquad \leftarrow \text{Balmer formula C!!!}$$

$n_i<n_f$ absorption of photons (energy)

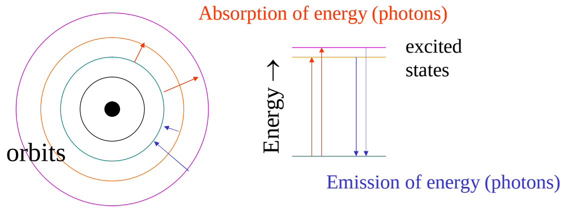
$\nu>0$

$n_i>n_f$ emission of photons (energy)

$\nu<0$

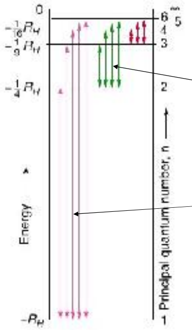
$$\nu = \left(3.2881\times10^{15}\,s^{-1}\right)\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$\frac{1}{\lambda} = \left(1.0097\times10^{-2}\ nm^{-1}\right)\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$



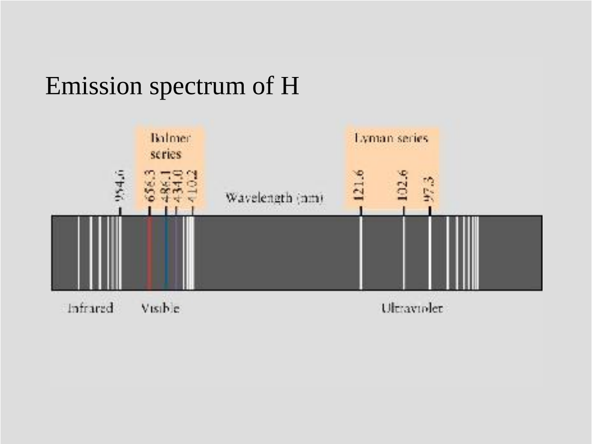
Energy of each orbit is discrete (quantized).
Therefore their energy differences are quantized.
Transitions are associated with photons of frequency ν with equal to the energy difference.

$$E_f - E_i = \Delta E = h\neg$$



Balmer series
visible region

Lyman Series



Emission spectrum of H

## The Bohr Model

Electrons in H atoms:

- Occupy discrete energy levels and exist only in the available energy levels.
- May move between energy levels by either absorbing or emitting energy.
- Energy levels designated by a specific value for *n* (principal quantum number).
- Difference between energy levels ($\Delta E$):

$$\Delta E = -2.178\times10^{-18}\ J\left(\frac{1}{n^2_{\text{final}}} - \frac{1}{n^2_{\text{initial}}}\right)$$

All energy levels of any atom are of definite energies; ***Quantization of energy levels/states***.

Bohr theory is followed perfectly by H like species only!! H, $He^+$, $Li^{+2}$, $Be^{+3}$ etc.

## Beyond the Bohr Model

Bohr theory considers electron to be a charged particle.

Electron has particle properties - true.

Moving electrons has *wave properties* as well.

The electrons must be treated as entities exhibiting both particle properties and wave properties to arrive at a realistic picture of the atomic ‘system’.

Wave-particle duality:

All matter are associated with a wave.

Therefore all matter/particles/masses will have wave length.

De Broglie matter waves - ª; (De Broglie wave length).

$$ª = \frac{\mathrm{h}}{\mathrm{mv}}$$

The wave length of a matter wave is inversely proportional to it's momentum, mv.

So particles with large masses will have very small ª values.

So particles with very small masses will have very large ª values.

Moving electrons are associated with ª values comparable to the atom size.

Electrons:

$$ª = \frac{\mathrm{h}}{\mathrm{mv}} \qquad \mathrm{h} = 6.63 \times 10^{-34}\, Js$$

$$\mathrm{m}_e = 9.11 \times 10^{-31} kg$$

$$\mathrm{v}_e = 5.97 \times 10^{6} \frac{m}{s}$$

$$ª = 1.22 \times 10^{-10} m = 0.122 nm$$

ª compares to the size of atoms!

Matter waves come into prominence only for subatomic particles *not* macroscopic particles.

Wave properties are significant at atomic level.

Heisenberg's Uncertainty Principle:

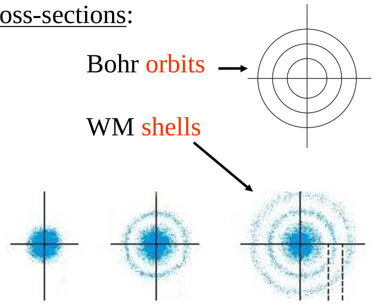
The simultaneous exact determination of position and momentum (velocity) of sub atomic particles is impossible.

There is an uncertainty in the position of the electrons in an atom.

Bohr atom - position very precise, on the surface of a sphere – orbits (major drawback!!).

Wave mechanics: incorporates the wave - particle duality of subatomic particles into the theory of atoms.

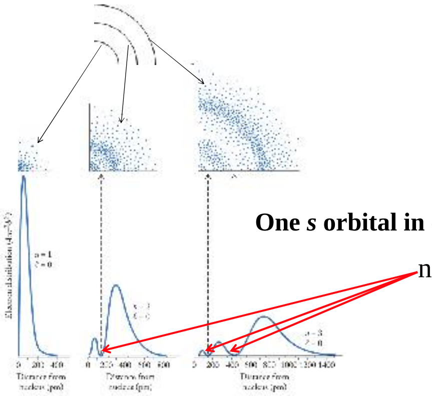
The picture of the atom changes from spaces like spherical orbits of well defined radii to a more diffuse, cloud like spaces.



Cross-sections:

Bohr orbits

WM shells



**One *s* orbital in each shell.**

nodes

Norton & Company

Wave mechanics: each shell identified by the principal quantum number n. (n =1,2,3,…) ~ Bohr orbits.

Each shell is made up of sub-shells, identified by a quantum number *l*, azimuthal quantum number. *l* = 0, 1, ..(n-1)

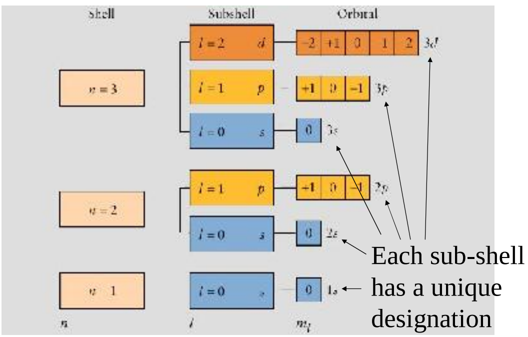
Each sub-shell is made up of orbitals, identified by a quantum number $m_l$, magnetic quantum number. $m_l = l, (l-1), 0, -l$

Quantum Numbers

**TABLE 7.1** Quantum Numbers of the Orbitals in the First Four Shells

| Value of *n* | Allowed Value of ℓ | Subshell Label | Allowed Values of $m_\ell$ | Number of Orbitals in: Subshell | Shell |
|---|---|---|---|---|---|
| 1 | 0 | s | 0 | 1 | 1 |
| 2 | 0 | s | 0 | 1 | |
| | 1 | p | −1, 0, +1 | 3 | 4 |
| 3 | 0 | s | 0 | 1 | |
| | 1 | p | −1, 0, +1 | 3 | |
| | 2 | d | −2, −1, 0, +1, +2 | 5 | 9 |
| 4 | 0 | s | 0 | 1 | |
| | 1 | p | −1, 0, +1 | 3 | |
| | 2 | d | −2, −1, 0, +1, +2 | 5 | |
| | 3 | f | −3, −2, −1, 0, +1, +2, +3 | 7 | 16 |

*n* *l* $m_l$



Each sub-shell has a unique designation

Sub-shell designation: *number letter*

*n* *s* *l = 0*
*p* *l = 1*
*d* *l = 2*
*f* *l = 3*

For a given shell, n:

The total number of orbitals = $n^2$

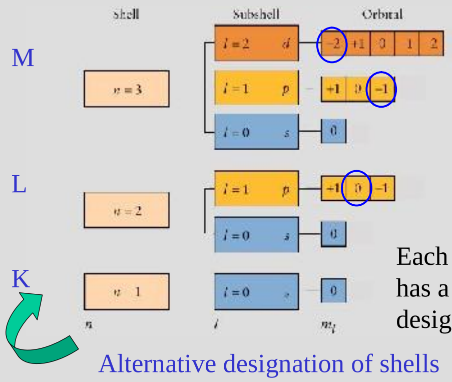
For a given sub-shell, *l*:

Total number of orbitals = $2l + 1$

Orbital designation: *number letter*$_{number}$

*shell=pqn* *subshell* $m_{l\ value}$

*e.g.* $2p_{+1}$



Each orbital has a unique designation

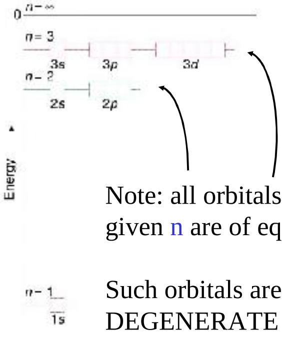
Alternative designation of shells

An electron in an orbital is assigned the relevant n, *l*, and $m_l$ value.

Orbitals are the spaces where electrons can reside in an atom.***

Energies of orbitals are quantized.

Hydrogen atom orbital energy diagram



Note: all orbitals in a given n are of equal energy.

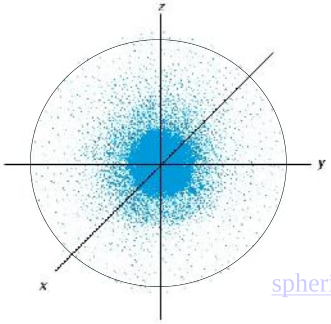
Such orbitals are said to be DEGENERATE

Energetically; 1s<2s=2p<3s=3p=3d< 4s=4p=4d=4f<..

Hydrogen ground state: 1s orbital occupied.
Excited state: any other orbital occupied

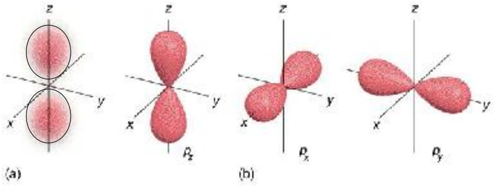
Orbitals have well defined shapes.

s orbital (electrons diffused in space)



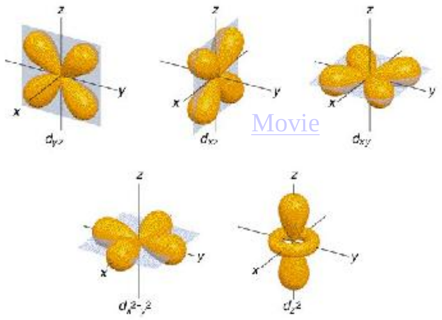
spherical

The orbitals in a sub-shell, collectively forms a *spherical* space.



dumb-bell shaped

The orbitals in a sub-shell, collectively forms a *spherical* space.



Movie

Movie

The quantum numbers gives us information:

n  average energy, radius of the shell; both increases with n

*l* shape of the sub-shell

$m_l$ orientation of the orbital in 3-dimension

Multi-electron atoms:

Repulsion between electrons and the unequal attraction of the nucleus and different sets of electrons changes the energy order from that of H.

The electrons in orbitals away from the nucleus are *less* attracted to the nucleus due to;

a. increased average distance of the electron from the nucleus

b. screening (S) of outer electrons by inner ones such electrons feel a lesser positive charge of the nucleus;  $Z_{eff} = Z - S$.

For *shells* $Z_{eff}$ decreases with increasing n.

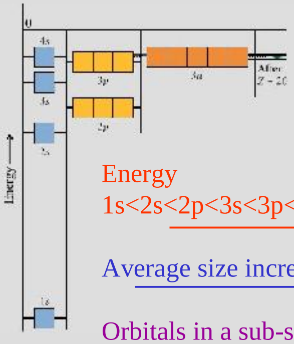
For *sub-shells in a shell* $Z_{eff}$ decreases with increasing *l; s more attracted than p, …d…f…*

Energetically; 1s<2s<2p<3s<3p<4s<3d<4p<..

Energy of the sub-shells in a shell are equal,

i.e. energywise; $np_x = np_y = np_z$ and
$nd_{xy} = nd_{yz} = nd_{xz} = nd_{z2} = nd_{x2-y2}$, …

## Multi-electron atoms electron energy diagram:

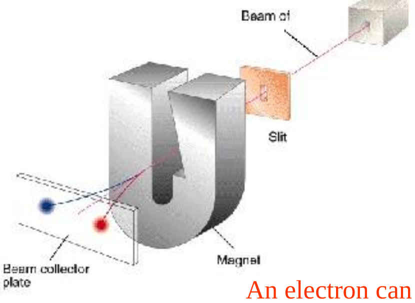


Energy
1s<2s<2p<3s<3p<4s<3d<…

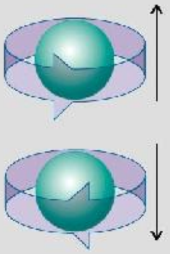
Average size increases

Orbitals in a sub-shell are degenerate (equal in energy)

## Spin: A unique property of electrons:



An electron can spin in only two directions.



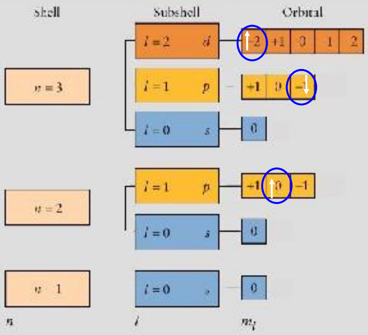
Anti-clockwise
$m_s = +1/2$

Clockwise
$m_s = -1/2$

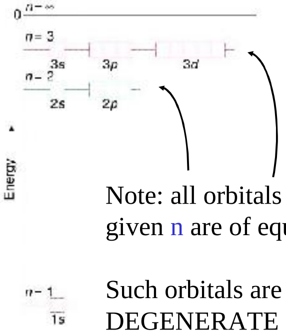
Spin quantum number, $m_s$

Note: $m_s$ can take only two values, ±1/2.

An electron in an orbital is assigned the relevant n, *l*, $m_l$ and $m_s$ value. *4 quantum numbers*



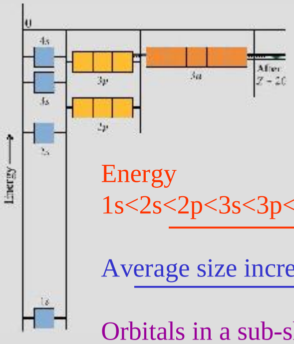
## Hydrogen atom orbital energy diagram



Note: all orbitals in a given n are of equal energy.

Such orbitals are said to be DEGENERATE

Multi-electron atoms electron energy diagram:

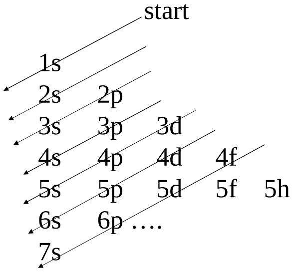


Energy
1s<2s<2p<3s<3p<4s<3d<…

Average size increases

Orbitals in a sub-shell are degenerate

Orbital occupation; Electron configuration of multi-electron systems. Ground state.



Sub shell filling order.
*Aufbau filling order; ground state.*

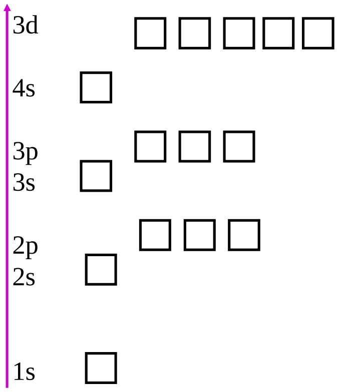
Follow the rules given below:

1. Pauli Principle: No two electrons in an atom can have the same set of four quantum numbers.
*Result: maximum # electrons in a orbital = 2, with electrons having opposite spins.*

2. Aufbau Build-up Principle: In it's most stable state the electrons occupy the lowest energy levels.
*Result: Electrons fill orbitals from bottom up the energy ladder.*

3. Hunds Rule: For degenerate orbitals the lowest energy (most stable/ground state) is when the spin is maximized.

*Result: Degenerate orbitals fill singly first and then pair up.*



Electron configuration:

Electron occupation representation.

e.g Li - $1s^2 2s^1$

short form [He] $2s^1$ (inert gas notation)

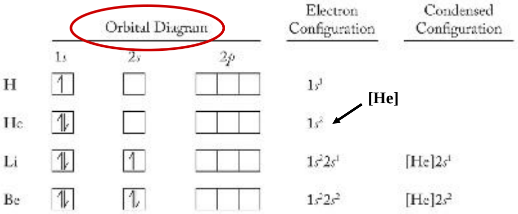
[closest preceding inert gas] rest

*core electrons* *valence electrons*

## Electron Shells and Orbitals

- Orbitals with the exact same energy are **degenerate**.
- **Core electrons** are the electrons in the filled, inner shells and less in an atom and they are not involved in chemical reactions.
- **Valence electrons** are the electrons in the outermost shell of an atom and they have the most influence on the atom's chemical behavior.

## Electron Configurations:

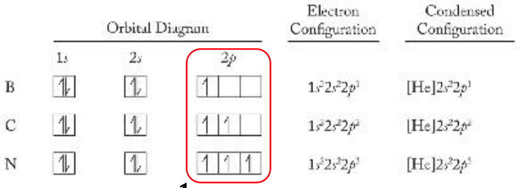


|  | Orbital Diagram 1s | Orbital Diagram 2s | Orbital Diagram 2p | Electron Configuration | Condensed Configuration |
|---|---|---|---|---|---|
| H | [↑] | [ ] | [ ] [ ] [ ] | $1s^1$ |  |
| He | [↑↓] | [ ] | [ ] [ ] [ ] | $1s^2$ |  |
| Li | [↑↓] | [↑] | [ ] [ ] [ ] | $1s^22s^1$ | $[\mathrm{He}]2s^1$ |
| Be | [↑↓] | [↑↓] | [ ] [ ] [ ] | $1s^22s^2$ | $[\mathrm{He}]2s^2$ |

[He]

-noble gas notation-

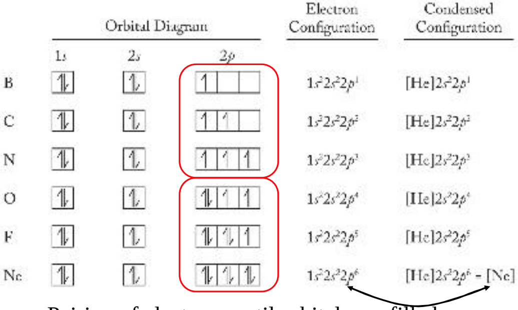
## Electron Configurations:



|  | Orbital Diagram 1s | Orbital Diagram 2s | Orbital Diagram 2p | Electron Configuration | Condensed Configuration |
|---|---|---|---|---|---|
| B | [↑↓] | [↑↓] | [↑] [ ] [ ] | $1s^22s^22p^1$ | $[\mathrm{He}]2s^22p^1$ |
| C | [↑↓] | [↑↓] | [↑] [↑] [ ] | $1s^22s^22p^2$ | $[\mathrm{He}]2s^22p^2$ |
| N | [↑↓] | [↑↓] | [↑] [↑] [↑] | $1s^22s^22p^3$ | $[\mathrm{He}]2s^22p^3$ |

Hund's Rule for filling of degenerate orbitals.

## Electron Configurations:



|  | Orbital Diagram 1s | Orbital Diagram 2s | Orbital Diagram 2p | Electron Configuration | Condensed Configuration |
|---|---|---|---|---|---|
| B | [↑↓] | [↑↓] | [↑] [ ] [ ] | $1s^22s^22p^1$ | $[\mathrm{He}]2s^22p^1$ |
| C | [↑↓] | [↑↓] | [↑] [↑] [ ] | $1s^22s^22p^2$ | $[\mathrm{He}]2s^22p^2$ |
| N | [↑↓] | [↑↓] | [↑] [↑] [↑] | $1s^22s^22p^3$ | $[\mathrm{He}]2s^22p^3$ |
| O | [↑↓] | [↑↓] | [↑↓] [↑] [↑] | $1s^22s^22p^4$ | $[\mathrm{He}]2s^22p^4$ |
| F | [↑↓] | [↑↓] | [↑↓] [↑↓] [↑] | $1s^22s^22p^5$ | $[\mathrm{He}]2s^22p^5$ |
| Ne | [↑↓] | [↑↓] | [↑↓] [↑↓] [↑↓] | $1s^22s^22p^6$ | $[\mathrm{He}]2s^22p^6$ - [Ne] |

Pairing of electrons until orbitals are filled.

## Electron Configurations of the Fourth Period

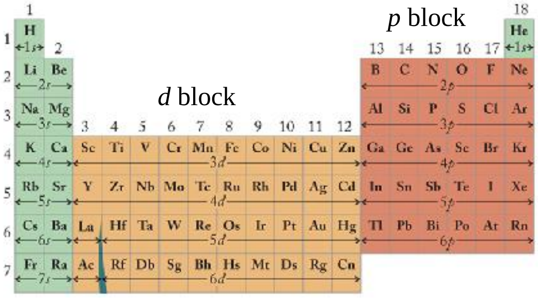
[Ar]

| | | |
|---|---|---|
| K | $1s^22s^22p^63s^23p^64s^1$ | or $[\mathrm{Ar}]4s^1$ |
| Ca | $1s^22s^22p^63s^23p^64s^2$ | or $[\mathrm{Ar}]4s^2$ |
| Sc | $1s^22s^22p^63s^23p^64s^23d^1$ | or $[\mathrm{Ar}]4s^23d^1$ |
| Ti | $1s^22s^22p^63s^23p^64s^23d^2$ | or $[\mathrm{Ar}]4s^23d^2$ |
| V | $1s^22s^22p^63s^23p^64s^23d^3$ | or $[\mathrm{Ar}]4s^23d^3$ |
| Cr | $1s^22s^22p^63s^23p^64s^13d^5$ | or $[\mathrm{Ar}]4s^13d^5$ |
| Mn | $1s^22s^22p^63s^23p^64s^23d^5$ | or $[\mathrm{Ar}]4s^23d^5$ |
| | • • • | |
| Cu | $1s^22s^22p^63s^23p^64s^13d^{10}$ | or $[\mathrm{Ar}]4s^13d^{10}$ |

**Note:** the deviations

Reason - later

## Periodic Table: *s*, *p*, and *d* Blocks



|  | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | H |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | He |
| 2 | Li | Be |  |  |  |  |  |  |  |  |  |  | B | C | N | O | F | Ne |
| 3 | Na | Mg |  |  |  |  |  |  |  |  |  |  | Al | Si | P | S | Cl | Ar |
| 4 | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| 5 | Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| 6 | Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| 7 | Fr | Ra | Ac | Rf | Db | Sg | Bh | Hs | Mt | Ds | Rg | Cn |  |  |  |  |  |  |

Periodic table arranged based on electron configurations.

The valence electron configuration is similar for elements in a given group.

The main reason why the properties of elements in a group are similar.

Across a given period (group to group) the outer shell fills from left to right.

| Li | Be | B | C |
|---|---|---|---|
| [He] $2s^1$ | [He] $2s^2$ | [He] $2s^2\ 2p^1$ | [He] $2s^2 2p^2$ |

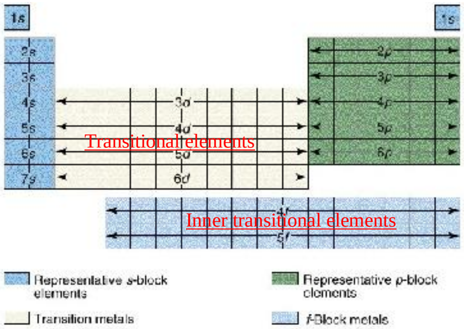
-noble gas notation/condensed configuration-

Down a group (period to period) a higher shell (n) fills. But same type of shell and filling in all cases.

H $1s^1$
Li [He] $2s^1$
Na [Ne] $3s^1$
K [Ar] $4s^1$
.
.

Transitional elements:
Inner d sub-shells fills.
*(n-1)d filled after ns and before np.*

Inner transitional elements:
Inner f sub-shells fills
*partial filling of upper d and s complicates the order of filling.*



Note: valence shell n = period #
Valence shell configuration same for elements in a period.

Ion electron configurations:

s and p block - electrons are added or taken off to attain noble gas configuration.

Metals lose electrons.
Nonmetals gain electrons.

Species with identical electron configurations are termed iso-electronic.

Ion electron configurations:

transition metals - ns electrons removed before any (n-1)d electrons are removed, usually.

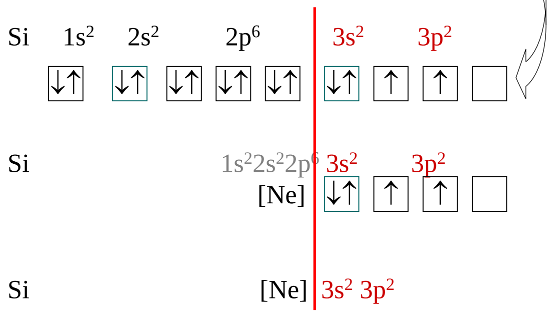
Fe $\rightarrow$ $Fe^{+2}$ + 2e
$[Ar]3d^6 4s^2 \rightarrow [Ar]3d^6$

Fe $\rightarrow$ $Fe^{+3}$ + 3e
$[Ar]3d^6 4s^2 \rightarrow [Ar]3d^5$

---

Orbital Diagram:

A representation of electron occupation in orbitals, (shows spin orientation)



Si $1s^2$ $2s^2$ $2p^6$ | $3s^2$ $3p^2$
↓↑ ↓↑ ↓↑ ↓↑ ↓↑ | ↓↑ ↑ ↑ ☐

Si $1s^2 2s^2 2p^6$ | $3s^2$ $3p^2$
[Ne] | ↓↑ ↑ ↑ ☐

Si [Ne] | $3s^2$ $3p^2$

---

Magnetism:

Species with unpaired electrons exhibit magnetism (*paramagnetic* species), such species interact with magnetic fields when encountered. Unpaired spins acts as tiny magnets.

Fe $[Ar]3d^6 4s^2$
4 unpaired e
$Fe^{+2}$ $[Ar]3d^6$

$Fe^{+3}$ $[Ar]3d^5$ 5 unpaired e

---

Magnetism:

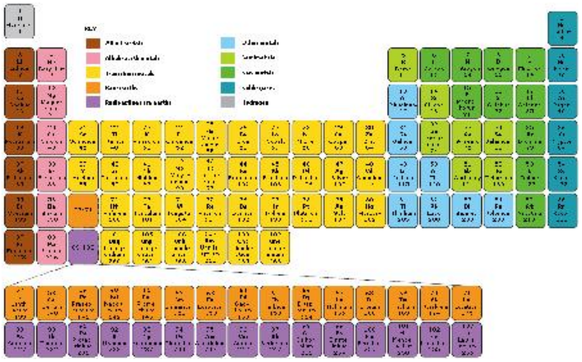
A spinning electron is like a magnet.
If two electrons spin in opposite directions, no net spin (magnetism).

Species with all paired electrons exhibit no magnetism (*diamagnetic* species).

Ferromagnetics: substances with permanent magnetism. Clustering of atoms (domains) with unpaired electrons with parallel alignment.

---

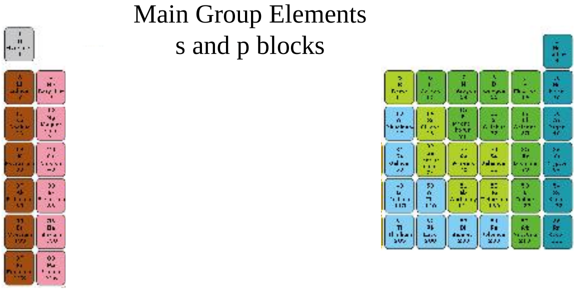
Periodic Table of Elements



http://www.infoplease.com/dk/science/encyclopedia/periodic-table.html

---

Main Group Elements
s and p blocks



http://www.infoplease.com/dk/science/encyclopedia/periodic-table.html

## Exceptions to Rule (anomalies):

29 Cu [Ar] $4s^23d^9$ ←expected [Ar] $4s^13d^{10}$
47 Ag [Kr] $5s^24d^9$ [Kr] $5s^14d^{10}$
Cr

*In stability*: completely filled subshells > half filled subshells> partially filled subshells

Reason: *symmetrical systems are more stable than unsymmetrical systems. And the c*loseness of energy in higher levels makes it energetically favorable.

---

## Electron Configurations: Ions

Formation of Ions:

Gain/loss of valence electrons to *achieve stable electron configuration* (filled shells, Noble gas/inert gas configuration [ ] – in general, $ns^2\ np^6$).

Cations:

$Na(g) \rightarrow Na^+(g) + e^-$

$[He]3s^1 \rightarrow [He] + e^-$

Anions:

$Cl(g) + e^- \rightarrow Cl^-(g)$

$[Ne]3s^23p^5 + e^- \rightarrow [Ne]3s^23p^6 = [Ar]$

---

## Iso-electronic Atoms/Ions

Main group elements form ions by gain/loss of $e^-$ needed to obtain noble gas configuration:

- $Mg \rightarrow Mg^{2+} + 2e^-$ = [Ne]
- $O + 2e^- \rightarrow O^{2-}$ = [Ne]

Atoms/Ions that have identical electron configurations are called **isoelectronic**:

- $Na^+$, $Mg^{2+}$, $O^{2-}$, $F^-$, Ne = $1s^22s^22p^6$
  $K^+$, $Cl^-$, $Ca^{2+}$, Ar = $1s^22s^22p^63s^23p^6$

---

## Cations of Transition Metals

Transition Metal Cations:

Loss of valence electrons (*s*) and, in some cases, *d* electrons to achieve stable configurations:

- Fe: $[Ar]4s^23d^6$
- $Fe^{2+}$: $[Ar]\cancel{4s^2}3d^6 \Rightarrow [Ar]3d^6$ (loss of valence $e^-$)
- $Fe^{3+}$: $[Ar]3d^6 \Rightarrow [Ar]3d^5$ (loss of one 3*d* = half-filled *d* subshell!)

---

## Periodic Properties of Elements

### 1. Electronic configuration:

[core electrons] *valence electrons*

e.g. K [Ar] $4s^1$

---

Elements in the same group (column) contain the *same number of electrons in same type of orbitals* in the outer most shell (valence shell); so the behave chemically similar.

H $1s^1$
Li [He] $2s^1$
Na [Ne] $3s^1$
K [Ar] $4s^1$

*The differences between them are the difference in outer most shells.*

Group 8A (IUPAC 18) - inert gases highly un-reactive.

Property attributed the extra stability of fully filled shells. $ns^2np^6$ configuration.

Electronically, there are *differences and similarities* between atoms from the same group.

Electronic structure forms the basis for the similarities and differences (inequalities) of the properties of the elements in the same group.

Electronic structure provides an explanation for the gradual variation of similar properties down a group.

## 2. Atom Radius:

The distance from the *nucleus to* the edge of the of the *atom* electron density, i.e. to the edge of the *outer most filled shell* (orbital).

## Facts (atoms/ions):

With Z increase, positive charge in the nucleus increases.

The shell size increases with n.

Inner shell electrons “shield” (screens) outer electrons.

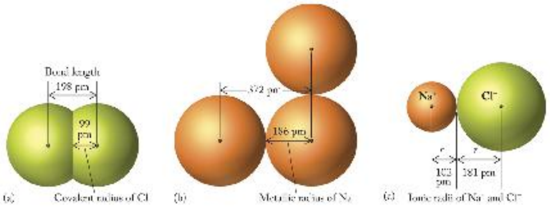
Screening (S) increases with the increase of the number of core electrons. $Z_{eff} = Z - S$.

## Sizes of Atoms/Ions

Covalent Radius of Atoms:

- Calculated based on distances between nuclei bonded together in molecules.
- For diatomic molecules, equal to **covalent radius** (one-half the distance between nuclei $X_2$).
- For metals, equal to **metallic radius** (one-half the distance between nuclei in metal lattice).
- For ions, **ionic radius.**.

## Atomic, Metallic, Ionic Radii

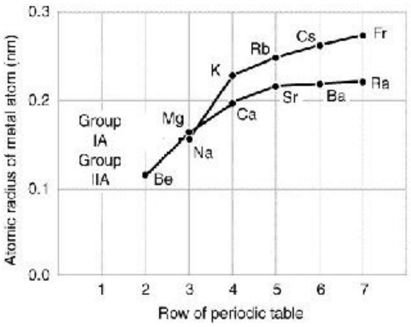


## Atom Radius in a group;

e.g.
H $1s^1$
Li [He] $2s^1$
Na [Ne] $3s^1$
K [Ar] $4s^1$
.
.

***increases down the group** (with increasing Z), because a new higher n (larger radius) level gets occupied and screening increases*.

## Atom Radius in a group;



## Atom Radius in a period;

e.g. period 2
Li [He] $2s^1$
Be [He] $2s^2$
B [He] $2s^2 2p^1$
C [He] $2s^2 2p^2$
.
.
***decreases across the period** (with increasing Z), because a same n level gets occupied but the nuclear charge Z increases, screening the same.*

## Ionic Radius:

The distance from the *nucleus to* the edge of the of the *ion* electron density.

Cations:

- Loss of electrons from valence shell orbitals, decrease in radius compared to atom.

Anions:

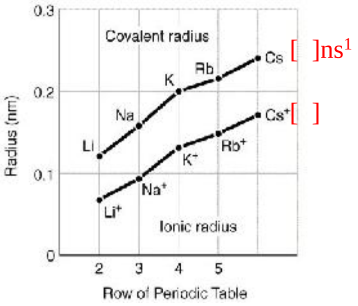
- Gain of electrons in valence shell orbitals, increase in radius compared to atom.

## Cation (positive) ion radius:

In positive ions the number of electrons are less than the protons.

Thus electron cloud shrinks, reducing the ion radius with respect to atom radius.

If the valence shell is emptied, the resulting ions radius shrinkage is very pronounced.



Li [He] 2s$^1$ $r_{Li} >> r_{Li}{}^{+}$

Be [He] 2s$^2$ $r_{Be} > r_{Be}{}^{+} >> r_{Be}{}^{+2}$

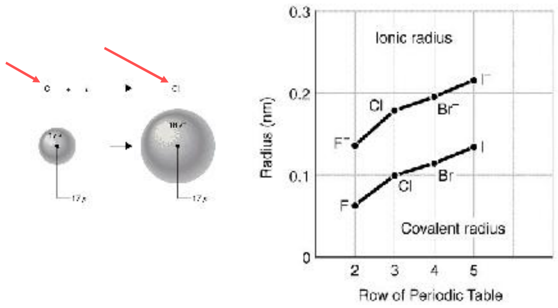
B [He] 2s$^2$2p$^1$ $r_B > r_B{}^{+} > r_B{}^{+2} >> r_{Be}{}^{+3}$

## Anion (negative) ion radius:

In negative ions the number of electrons are higher than that of protons, inter-electronic repulsion rises.

Electron cloud expands, increasing the ion radius with respect to atom radius.

Electrons fills up to completion of outer shell (to get ns$^2$np$^6$ configuration).

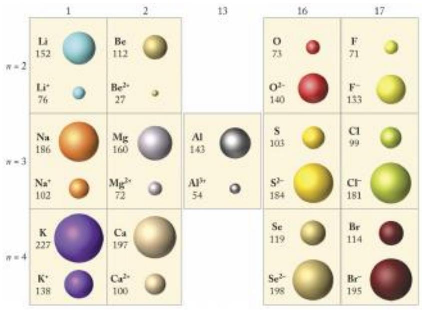


## Anion (negative) ion radius:

Down a group ion size inc. as $r_{ion}$ (and n) increases and $Z_{eff}$ remains ~constant.

Along a period (among nonmetals), same charge -ve ion radius decreases because $Z_{eff}$ increases.

## Radii of Atoms and Ions



## 3. Ionization Energy

Some elements in their reactions give up and some accept electrons to form ions.

Thus the energy involved in such processes is of significance in chemistry.

Ease of the above processes favors the reactions occurring with such electron switching.

The easiest electrons to remove are in the valence shell (furthest from nucleus).

Ionization energy (IE) is the energy 'demand' to remove electrons from an atom/ion.

First ionization energy ($I_1$) is the IE involving the first electron as in;

$$M(g) \rightarrow M^+(g) + e^-(g) \qquad I_1 \qquad \Delta E > 0$$

Second ionization energy ($I_2$) is the IE involving the second electron as in;

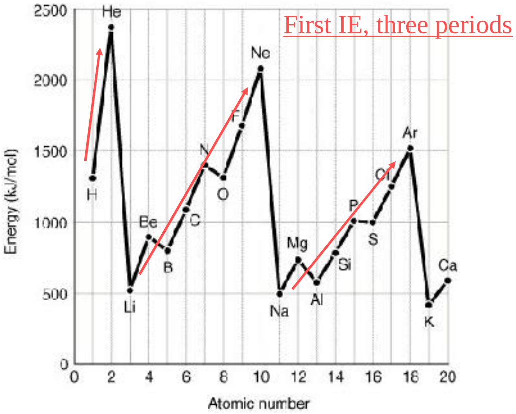
$$M^+(g) \rightarrow M^{+2}(g) + e^-(g) \qquad I_2 \qquad \Delta E > 0$$

This is a process demanding energy because e's are attracted to the nucleus.

Thus strongly attracted electrons are harder to remove to give positive ions.

Factors:
IE depends on are $Z_{eff}$, r (~n), elect. conf.

Larger $Z_{eff}$, smaller r (~smaller n) and stable elect. conf.; increases IE.


First IE, three periods

*The ionization energy increases along a period, from left to right,* because

$Z_{eff}$ = Z - S increases; Z increases, S remains constant.

Valence shell n is the same.

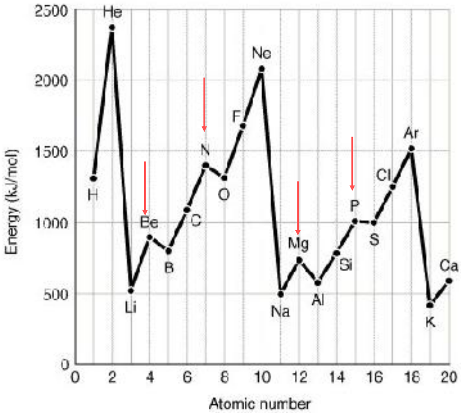
Valence shell electrons more attracted to the nucleus from L to R.

*The ionization energy decreases down a group, from top to bottom,* because

$Z_{eff}$ = (Z – S) no significant change down a group; as Z increases, S increases as well.

Valence shell n (distance to the nucleus) increases.

Valence shell electrons less attracted to the nucleus from top to bottom of a group.



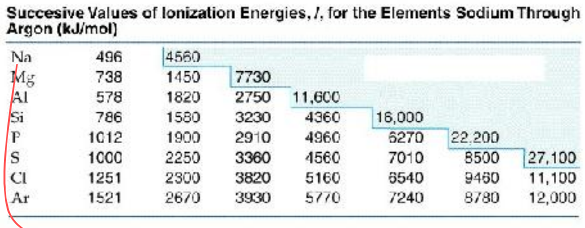
Other ionization energies of an atom.

$I_1 < I_2 < I_3 < I_4 < \ldots$ in general

$I_2$ onwards involve removing an electron from already positive species, renders difficult, hence ...

A step removing electron from a lower (n) shell is *extraordinarily difficult.* Reasons - extra stability of configuration of core electrons and lower $r_{ion}$.

And decreased S factor makes (Z – S) large making core electrons strongly attracted to nucleus..



**Succesive Values of Ionization Energies, *I*, for the Elements Sodium Through Argon (kJ/mol)**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Na | 496 | 4560 | | | | | |
| Mg | 738 | 1450 | 7730 | | | | |
| Al | 578 | 1820 | 2750 | 11,600 | | | |
| Si | 786 | 1580 | 3230 | 4360 | 16,000 | | |
| P | 1012 | 1900 | 2910 | 4960 | 6270 | 22,200 | |
| S | 1000 | 2250 | 3360 | 4560 | 7010 | 8500 | 27,100 |
| Cl | 1251 | 2300 | 3820 | 5160 | 6540 | 9460 | 11,100 |
| Ar | 1521 | 2670 | 3930 | 5770 | 7240 | 8780 | 12,000 |

$I_1$ $I_2$ $Na^{+2}$ not formed.

$I_1$ $I_2$ $I_3$ $I_4$

<u>4. Electron Affinity (EA):</u> is the energy released when an a species capture an electron.

First EA is the EA involving the first electron as in;

$$A(g) + e^-(g) \rightarrow A^-(g) \qquad EA_1 \qquad \Delta E < 0$$

Second EA is the EA involving the second electron is less negative than $EA_1$;

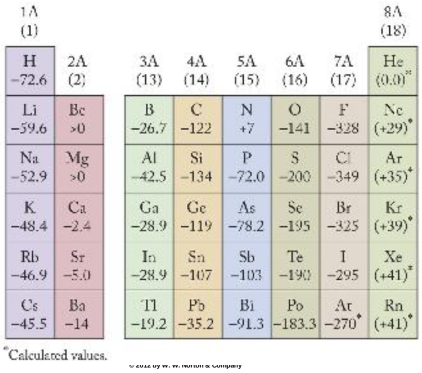
$$A^-(g) + e^-(g) \rightarrow A^{-2}(g) \qquad EA_2$$

Electron being *added is attracted* to the nucleus.

*Attractions leads to stability.*
*Attractions release energy.*
*The resulting 'product' is of lower energy.*
*Processes involving high energy releases are favored to happen (spontaneously).*

Larger $Z_{eff}$, smaller r, smaller n and stable elect. conf. attainment increases the magnitude of EA.

<u>Periodic Trends of (1st) EA</u>



| 1A (1) | 2A (2) | 3A (13) | 4A (14) | 5A (15) | 6A (16) | 7A (17) | 8A (18) |
|---|---|---|---|---|---|---|---|
| H −72.6 | | | | | | | He (0.0)* |
| Li −59.6 | Be >0 | B −26.7 | C −122 | N +7 | O −141 | F −328 | Ne (+29)* |
| Na −52.9 | Mg >0 | Al −42.5 | Si −134 | P −72.0 | S −200 | Cl −349 | Ar (+35)* |
| K −48.4 | Ca −2.4 | Ga −28.9 | Ge −119 | As −78.2 | Se −195 | Br −325 | Kr (+39)* |
| Rb −46.9 | Sr −5.0 | In −28.9 | Sn −107 | Sb −103 | Te −190 | I −295 | Xe (+41)* |
| Cs −45.5 | Ba −14 | Tl −19.2 | Pb −35.2 | Bi −91.3 | Po −183.3 | At −270* | Rn (+41)* |

*Calculated values.

<u>First EA</u>.

In a *group* magnitude of EA drops from top to bottom; larger r, larger n (elect. conf. & $Z_{eff}$, are same) decreases the magnitude of EA.

In a *period* magnitude of EA rises from left to right. Larger $Z_{eff}$, smaller r (~n) increases the magnitude of EA.

Attainment of noble gas elect conf. favors EA.

Higher the electron affinity more stable the ion formed.

Halogens have large EA values.

$Cl(g) + e(g) \rightarrow Cl^-(g)$ -349 kJ/mol
$Ar(g) + e(g) \rightarrow \boxed{Ar^-(g)}$ + value, do not occur easily;
why?

Metals are reluctant to accept electrons. Why?

5A elements (N, P etc) are not that eager to accept electrons forming isolated ions. Why?

Electron filling into atoms of nonmetals proceed toward attainment of inert gas conf. within limits.