Atomic Structure

Atomic models:

1. Thomson's Atomic mode (Plum-pudding model)
2. Rutherford's model
3. Bohr's model

Atomic terms: Atomic number
Atomic mass/Mass number

Nucleons : Protons and neutrons are collectively known as nucleons.

Isotopes : Atoms of the element with same atomic number but different mass number.

E.g. Hydrogen has three isotopes –

1. Protium / hydrogen : $_1H^1$ → atomic mass

atomic no. 1

2. Deuterium : $_1H^2$

^{2} → atomic mass

$_1$ → atomic no - 1

3. Tritium : $_1H^3$

^{3} → atomic mass - 3

$_1$ → atomic no - 1

	Atomic mass	Atomic no.	No. of protons	No. of electrons	No. of neutrons
Hydrogen $_1H^1$	1	1	1	1	0
Deuterium $_1H^2$	2	1	1	1	1
Tritium $_1H^3$	3	1	1	1	2

no. of neutrons differ.

Isotopic variation is due to the difference in number of neutrons.

But neutrons do not participate in chemical reaction.

Electrons participate in chemical reaction. However, in an isotope the number of electrons remain constant. So, isotope of an element will only differ in physical properties.

Chemical properties of isotopes remain the same.

Isobars: Atoms having the same atomic mass / mass number but different atomic no.

E.g. $_{15}P^{32}$ $_{16}S^{32}$

Chemical properties of isobars are different since they have different atomic no.

Isotones :

Atoms having the same no. of neutrons but different no. of protons or mass no.

e.g. $_{6}C^{14}$ $_{8}O^{16}$ $_{7}N^{15}$

$14 - 6 = 8$

$16 - 8 = 8$

$15 - 7 = 8$

atomic no.s are different.

Since the no. of protons ≠ no. of electrons ≠ constant, therefore isotones will show different chemical properties.

Isoelectronic: Atoms, molecules or ions having same no. of electrons

e.g. - N_2, CO, $CN^{\ominus}$

Nuclear isomers: Atoms with the same atomic number and same mass number but with different radioactive properties. Eg. - Uranium - X (half life 1.4 min)

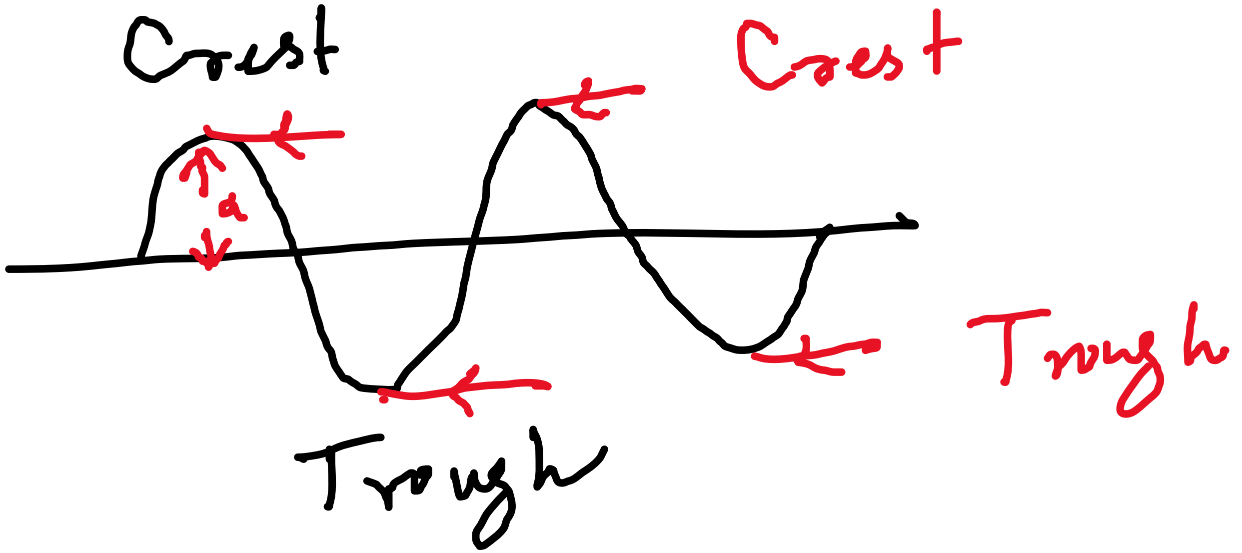
Uranium - Z (half life 6.7 h)

Isosters : Molecules having same number of atoms and also same number of electrons. Eg. N_2 CO

N_2 → nitrogen

CO → carbon-monoxide

Wave :



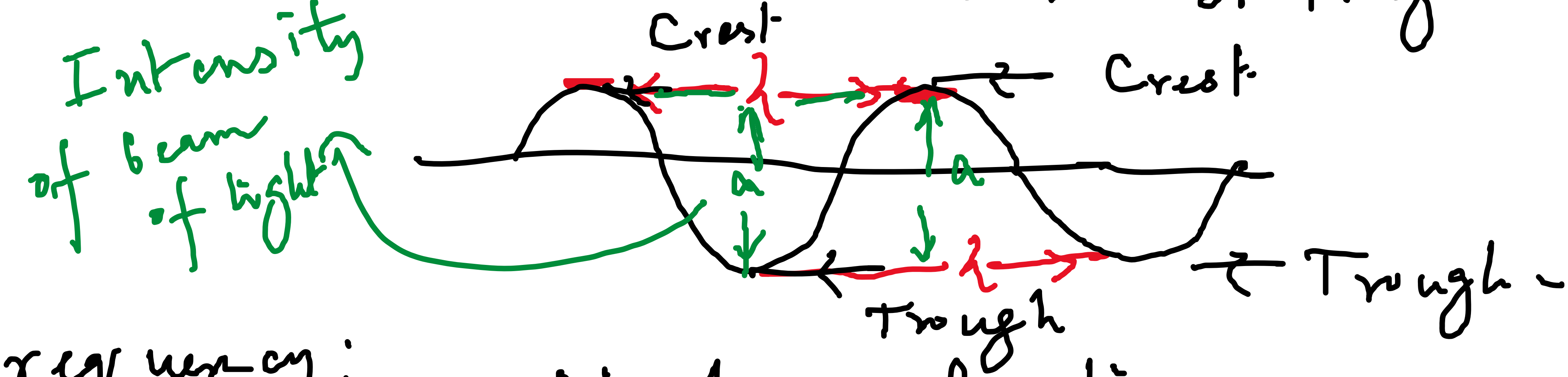
Wave: A wave is a kind of oscillation (disturbance) that travels through space and matter.

Wave motion transfers energy from one place to another.

Waves require some oscillating or vibrating source.

Wave length (λ) → lambda

Distance between two neighbouring crests or troughs



Frequency: ν

Number of times a wave passes through a given point in one second

$$\nu = \frac{c}{\lambda}$$

c → velocity of light

where ν = frequency

λ = wavelength

Wave number : Number of wavelength per cm.

cm → unit length

$$\frac{1}{\lambda}$$

Amplitude (a) : Height of the crest or depth of the trough

→ Amplitude is relate to intensity of wave

Electromagnetic waves

Radiations: radio waves, microwaves, infrared (IR), visible, ultraviolet (UV), x-rays, gamma rays

Bohr's model.

Bohr's model explain the spectral lines of the hydrogen atomic emission spectrum

In optics, spectrum is the arrangement according to wavelength of visible, ultraviolet and infrared light

Spectrum is the range of colors of wavelength energy sent out on a light source when viewed through a prism.

Band of 7 colors

White light → V I B G Y O R

↓

separates into its constituent colours

Spectroscopy gives us important information regarding the structure of an atom, molecule, ion and so on.

Bohr's model explains the spectral lines of the hydrogen atomic <u>emission</u> spectrum

↓ energy released.

In physics or chemistry, a quantum (plural: quanta) is the minimum amount of any physical entity (physical property) involved in an interaction.

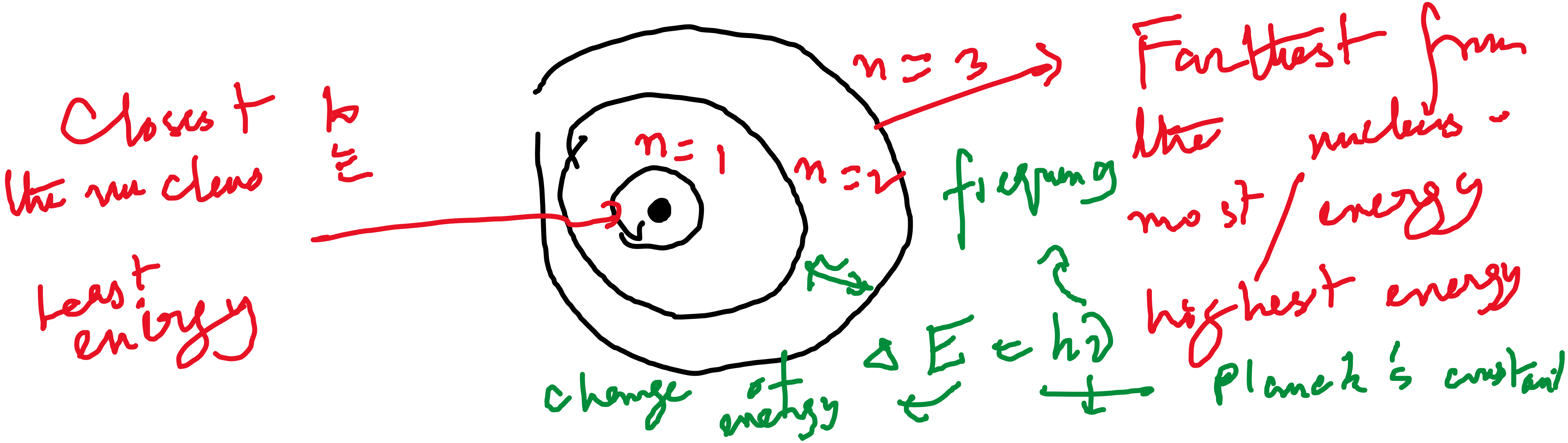
Quantization of energy and its influence on how energy and matter interact is part of the fundamental understanding and describing nature

While the electron of the atom remains in the ground state, its energy is unchanged. When the atom absorbs one or more quanta of energy, the electron moves from ground state orbit to excited state orbit that is further away. Energy levels are designated with the variable n

Bohr - Bury scheme : n = energy level.

Ground state is n = 1

First excited state n = 2 . . .

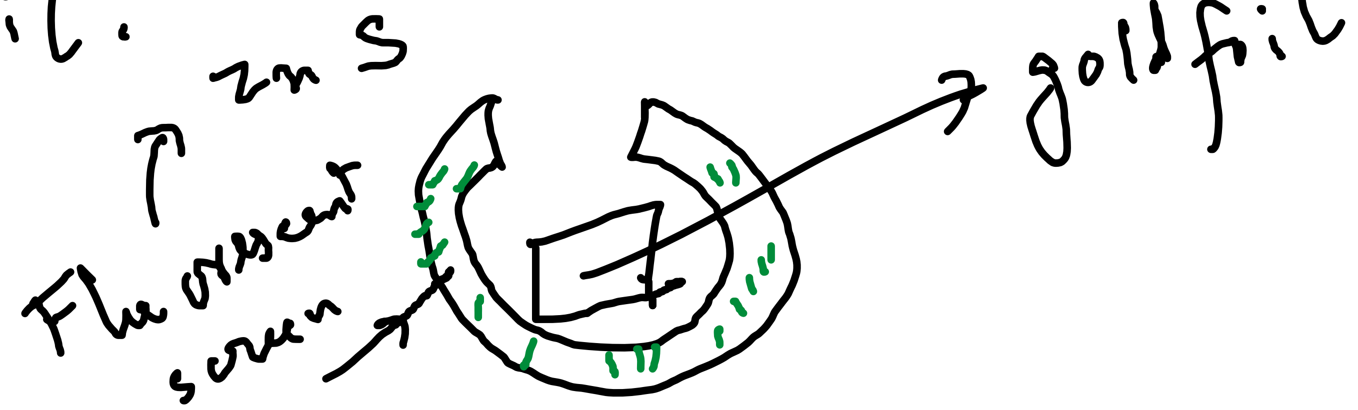


The energy that is gained by the atom is equal to the difference between two energy levels. When the atom relaxes back to a lower energy state, it releases energy that is again equal to the difference in energy of two orbits.

The Structure of Atom

Rutherford's Alpha 'α' Scattering Experiment

In this experiment, Rutherford directed a beam of α particles (+vely charged particles) towards a thin gold foil.



When an α particle struck the screen, tiny flashes of light were produced.

Important observation:

1. Most of the α particles, passed through the foil, without any deflection.
2. A small no. of α particles were deflected from their original path.

A few α particles were deflected by $90°$ or even wider angles.

3. A few α particles bounce back.

i.e. they were deflected through almost $180°$.

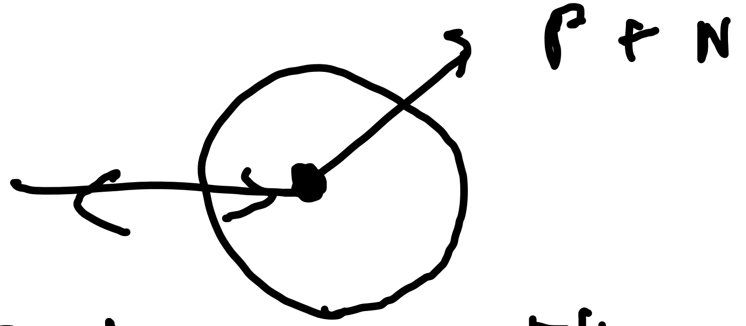
Inference / Conclusion:

1. As most of the α particles passed through the gold foil without any

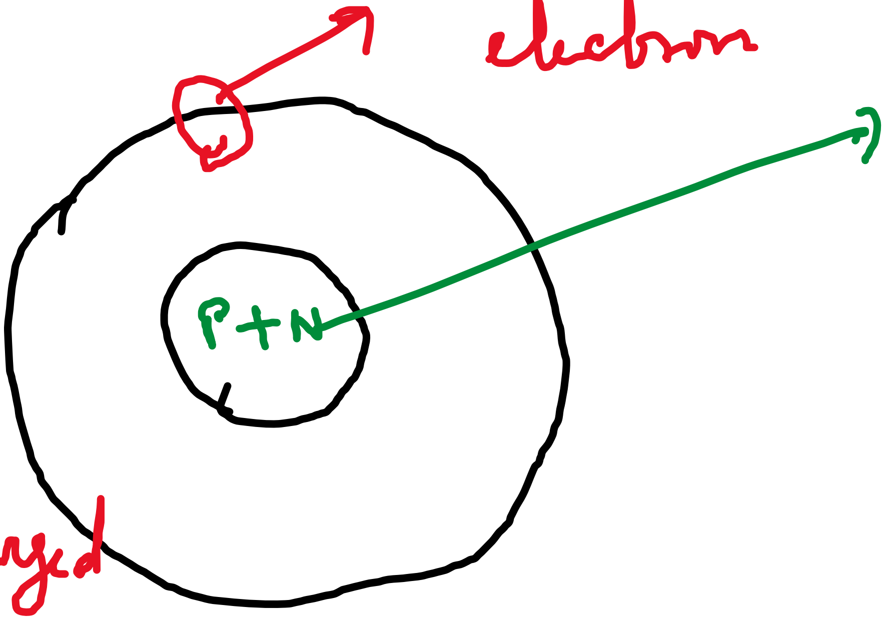
deviation, an atom consists of predominently empty space.

2. The deflection of a small no. of α particles suggest that there must be some positive charge in an atom, which is not uniformly distributed. This positive charge is concentrated in a small core, called as nucleus.

(3) The fact that only a few α particles bounced back suggests that the heavy, positively charged nucleus occupies a small fraction of the total volume of the atom.



Based on this observations, Rutherford proposed a model, which has the following features



electron

proton + neutron } nucleus

Proton : +ve

Electron : -ve

Neutron : non charged

The total no. of protons within the nucleus = the no. of electrons outside the nucleus.

H → 1 electron

atomic no. is - 1

Atomic Mass/Mass number

Atomic no.

Mass no. = Total no. of protons + neutrons in an atom.

Atomic no. = No. of protons or no. of electrons.

Atomic no. = Atomic mass − No. of neutrons
↓ Z
↓ A

<u>Rutherford model</u>: (1) An atom consists of extremely small, heavy,

positively charged core called nucleus, which is located at the center of the atom. The entire mass of the atom is concentrated within the nucleus.

(2) The -vely charged electrons surround the nucleus of an atom and revolve around the nucleus in circular orbits, just as the planets revolve around the Sun.

(3) Rutherford's model of the atom resembled the Solar System. Therefore, it is also called as the Planetary Model of atom.

Limitation:

Rutherford's model was unable to justify the stability of an atom.

Bohr's atomic model

1913, Niels Bohr

Bohr's atomic model

Bohr accepted that whole mass of atom is concentrated in the nucleus and the presence of electrons outside the nucleus.

1. Electron's revolve around the nucleus in circular paths called orbits or energy shells.

2. The orbits or energy shells are associated with definite energy levels.

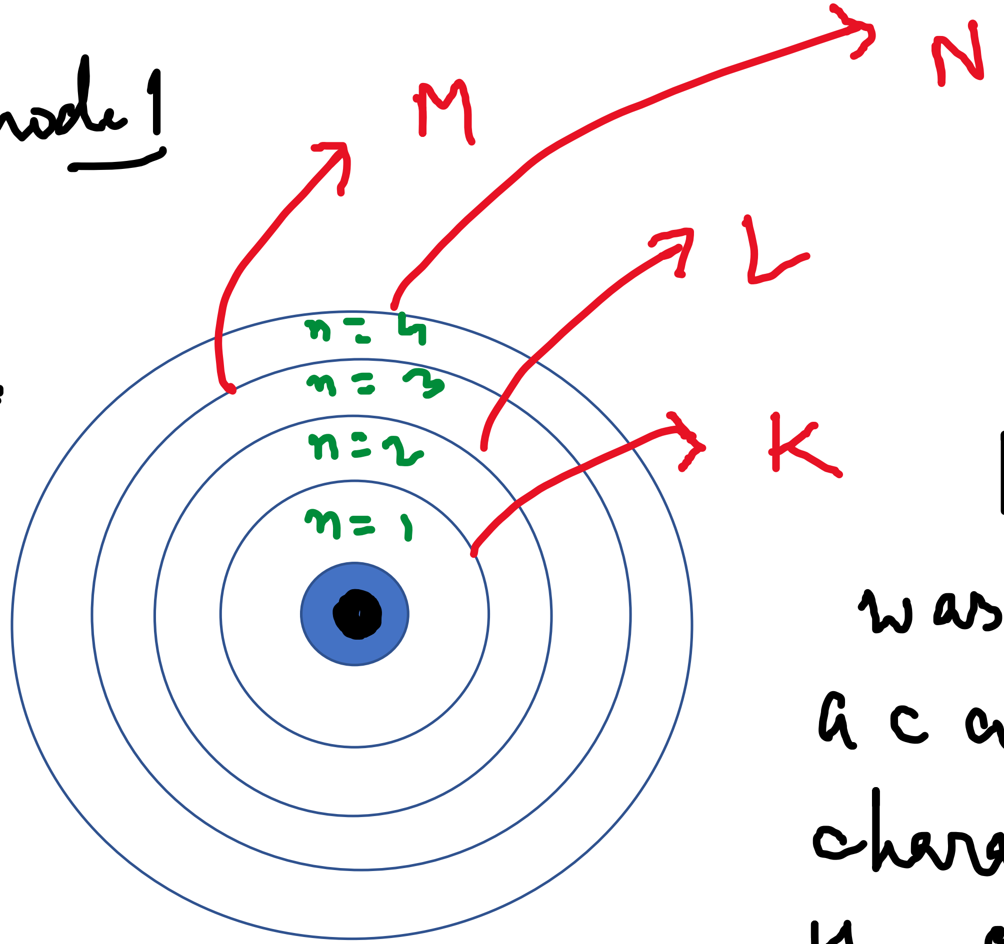
These energy shells are represented by numbers 1, 2, 3, 4 ⟶ starting from the innermost, or the symbols K, L, M, N

(3) Different orbits possess different energies.

(4) The energy of an orbit increases as it moves away from the nucleus.

(5) The energy difference between one orbit and another orbit is constant.

Bohr's model



Bohr's model was successful because it was able to account for the characteristics of H atom.

Limitation:

Bohr's model was unable to explain the characteristics of elements other than H.

Breakthrough: Quantum theory of atomic theory.

1. J. J. Thomson → electron

2. Rutherford → Nucleus

3. Bohr → Energy level

4. Chadwick → Neutron → non-charged

Combined Postulates

1. Atoms consist of subatomic particles - electron, proton & neutron.

② Atom → Nucleus

→ Empty space (extra-nuclear region)

③ . Nucleus = Protons + Neutrons

Protons + Neutrons → Nucleons (collective term)

Total mass of atom is concentrated within the nucleus considering electrons have negligible mass.

Nucleus is +vely charged due to the presence of protons.

(3) Circular path → Electrons revolve
↓
Extranuclear orbits

Orbits are fixed imaginary paths associated with a fixed amount of energy.

(4) Atom is electrically neutral.

$$^{A}_{Z}X$$

- A → mass no.
- Z → atomic no.
- X → element

mass no → A

atomic no. → Z

no. of protons → P

no. of electrons → E

no. of neutrons → N

Element	Symbol	Z	A	P	E	N (A − Z)
Hydrogen	H	1	1	1	1	0
Helium	He	2	4	2	2	2
Boron	B	5	11	5	5	6
Nitrogen	N	7	14	7	7	7
Fluorine	F	9	19	9	9	10
Sodium	Na	11	23	11	11	12

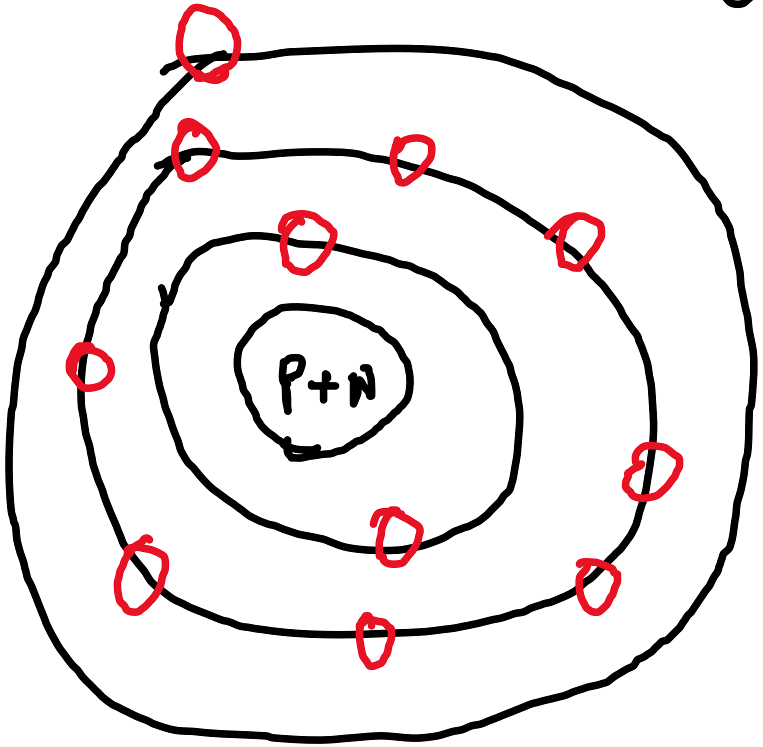
Bohr Bury Scheme

11 Na

32
+ 18
+ 8
+ 2
60

$2n^2$ n = integer

K $n=1$
L $n=2$
M $n=3$
N $n=4$



$2n^2$

$n = 1 \rightarrow K$

$2 \cdot 1^2 = 2$

$2n^2$ $n = 2$

$2 \cdot 2^2 = 8$

M: $n = 3$

$2 \cdot 3^2 = 2 \times 9 = 18$

N = $n = 4$

$2 \cdot 4^2 = 32$

K : 19 atomic no :

Argon → inert gas

~~2, 8, 9~~

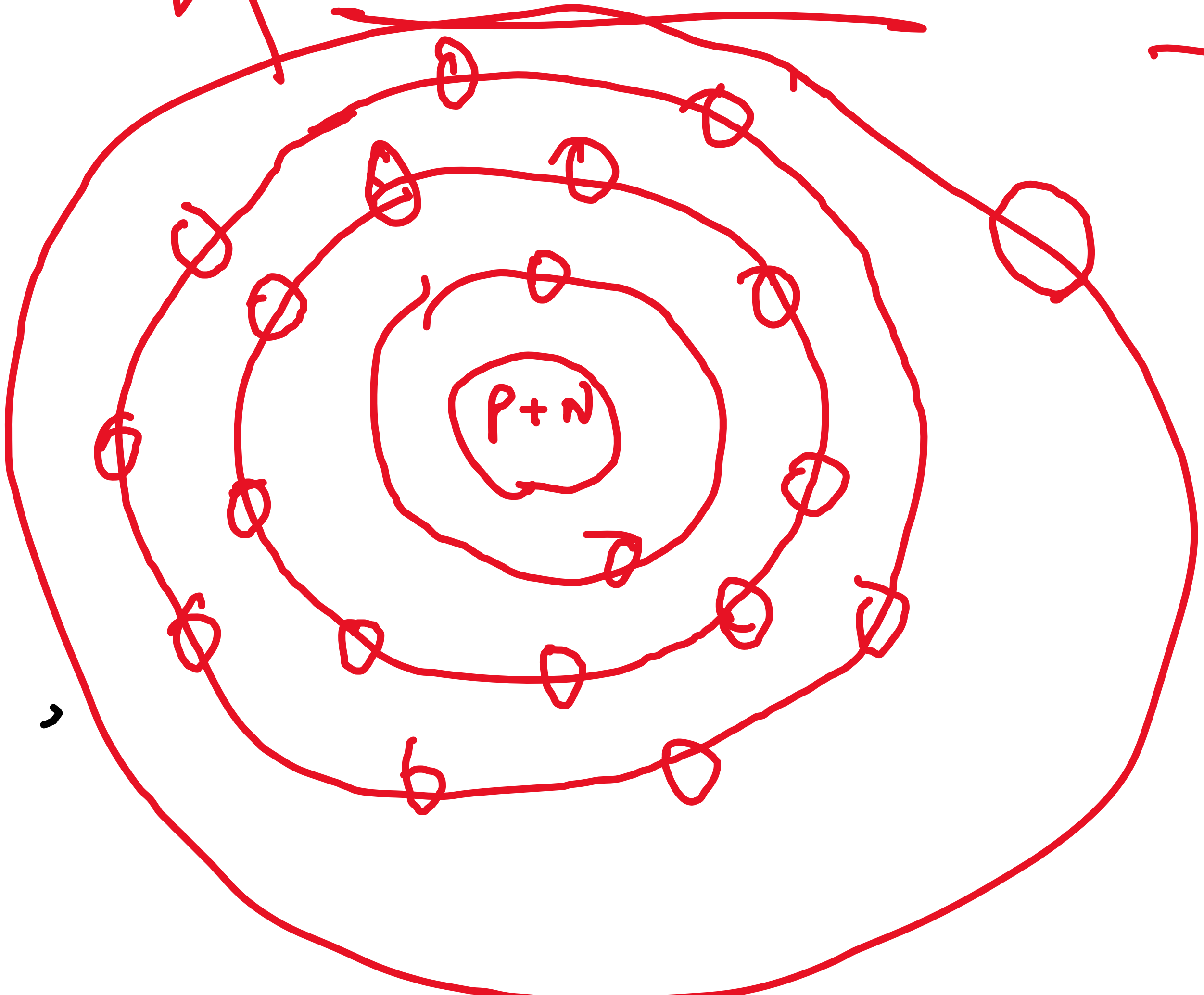
K, L, M, N

2, 8, 8, 1

Octet rule

↓

outermost orbit should not have more than 8 electrons



(18)

2, 8, 8

Atomic Structure

Wave : 1. Wavelength λ

2. Frequency ν $\qquad c = \nu\lambda$

3. Velocity c

Atomic spectra of hydrogen

$$\frac{1}{\lambda} = \bar{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where R_H = Rydberg constant

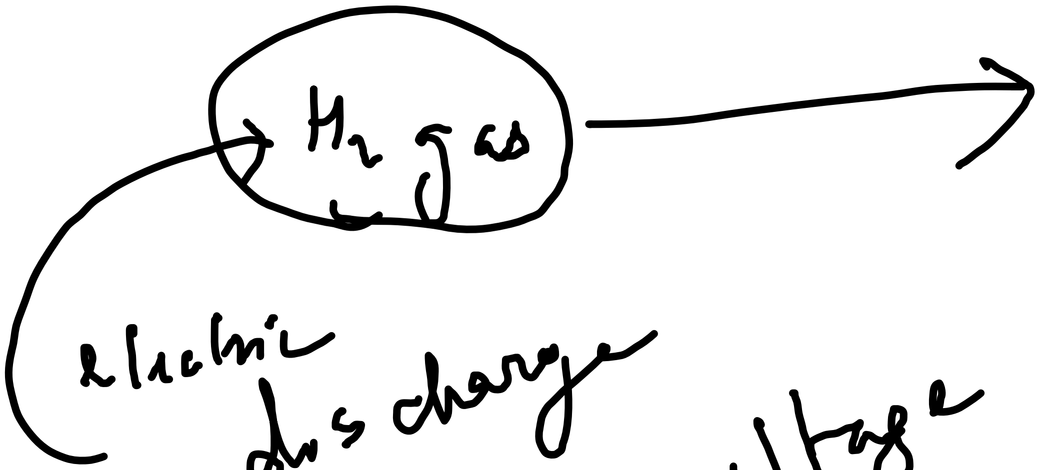
(109678 cm^{-1})

n_1 n_2 are integers

Line spectra

Objects at high temperature emit a continuous spectrum of electromagnetic radiation. When pure samples of individual elements are heated, a different type of spectrum is observed

For e.g. if a high voltage electric discharge is passed through a sample of hydrogen gas at low pressure the resulting individual isolated H atom caused by the dissociation of H_2 emit a red light.



Red light emitted.

i) high voltage

ii) low pressure

} Colour of the light emitted is not much dependant on the temperature of the gas in the tube

The light emitted by H is red because of its four characteristic line.

Most intense line in the spectrum is red ~ 656 nm ~ visible range

Emitted light → Passed through prism

↓

Only a few narrow lines

↓

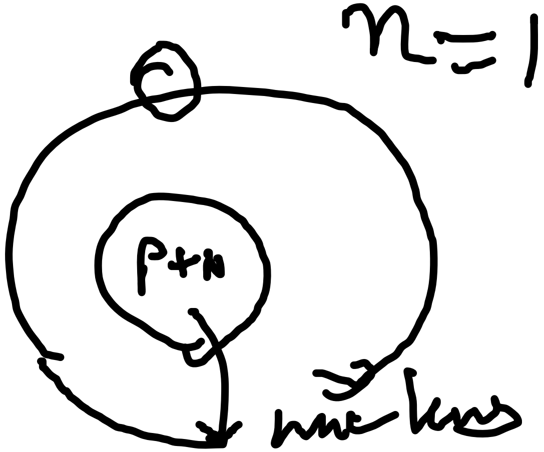
Line spectrum

Line spectrum is a spectrum in which light of only certain wavelength is emitted or absorbed rather than a continuous range of wavelength

The different colors of light produced by emission spectra of different elements enable their identification.

Ground state

When hydrogen is unexcited, its electron is in the first energy level i.e. the level which is closest to the nucleus.



When hydrogen is excited, hydrogen molecules are first broken up into hydrogen atoms and electrons are promoted to the next energy level.

$$\frac{1}{\lambda} = \bar{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

R_H → Rydberg constant

n_1	n_2	spectral series	spectral region
1	2, 3, 4...	Lyman	UV
2	3, 4, 5...	Balmer	Visible
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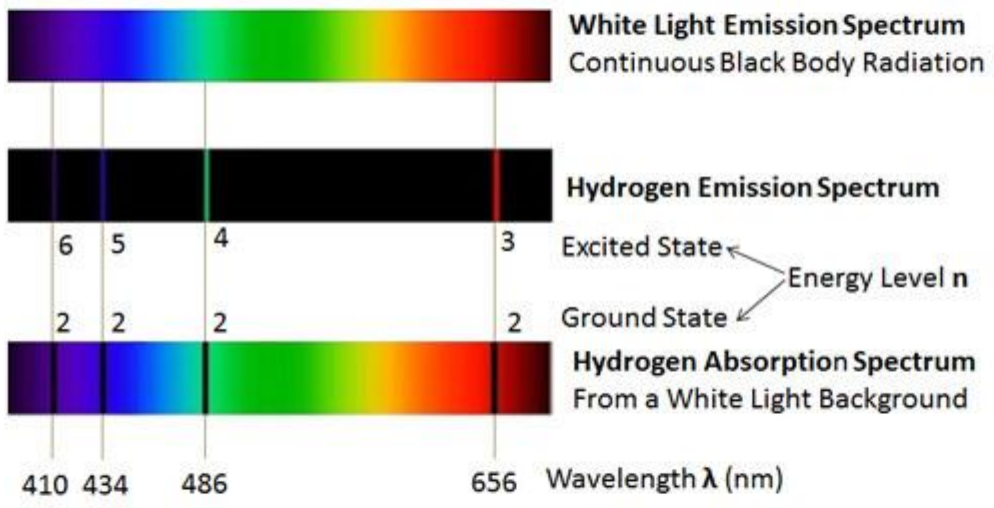
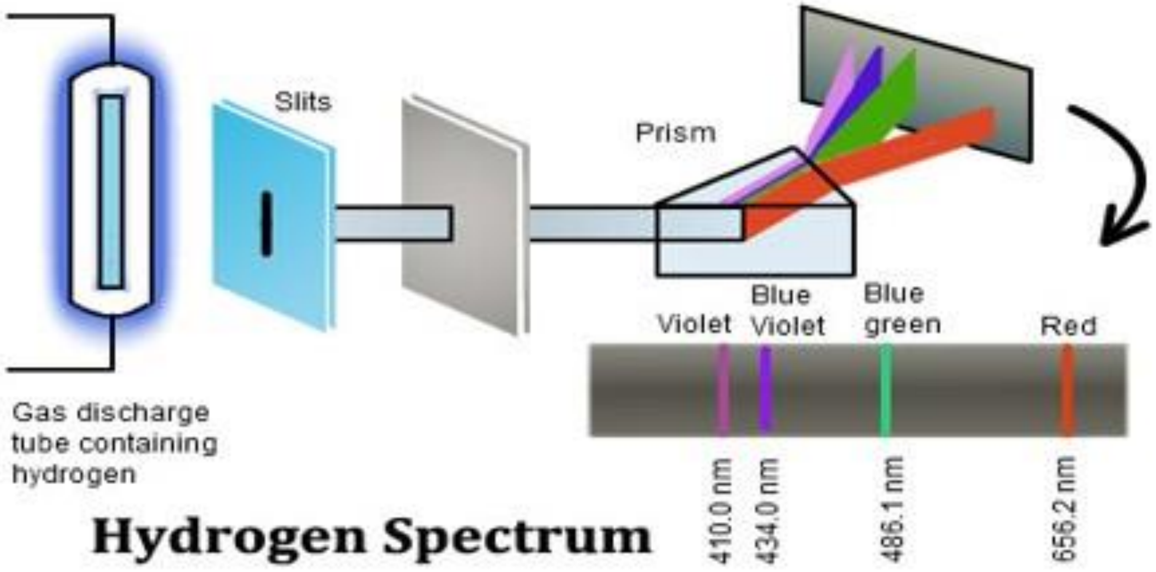
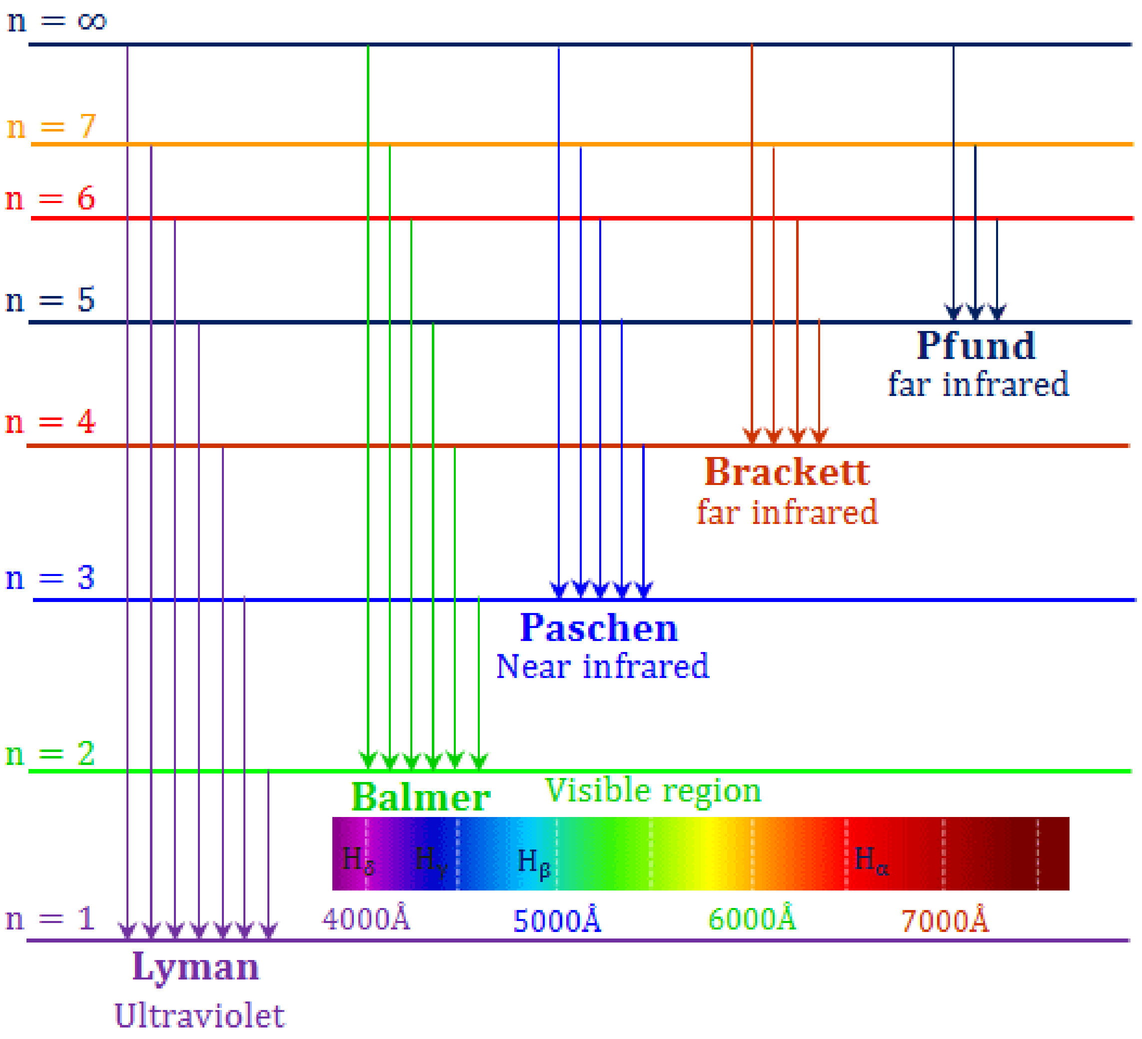
Atomic Spectral Lines







Photoelectric Effect

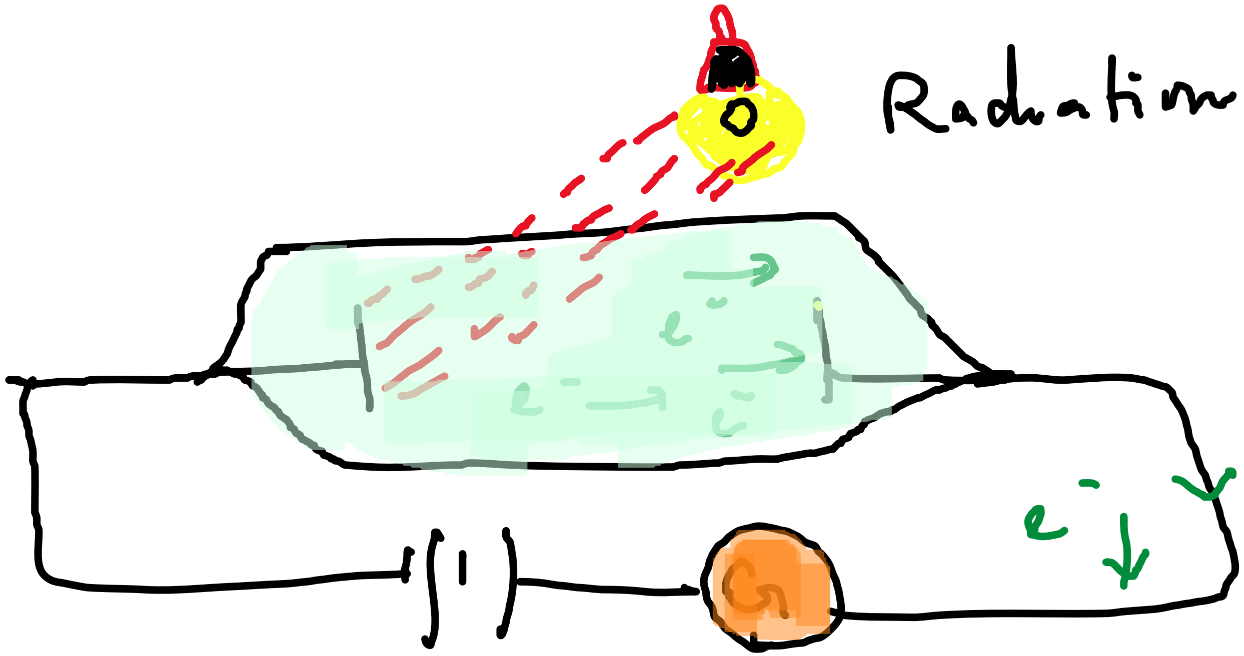
Photoelectric effect is a phenomenon in which electrically charged particles are released from or within a material when it absorbs electromagnetic radiation. The effect is often defined as the ejection of electrons from a metal plate when light falls on it.

Study of photoelectric effect is important because it led to important steps in the understanding of quantum nature of light and electrons.

Matter → Particle, Wave

Wave - particle duality.

Photoelectric effect is widely used to investigate electron energy levels in matter.



1. Ejection of electrons takes place from the surface of metal when light of a suitable frequency falls on it.

2. Minimum frequency required for ejection of electron is called threshold.

frequency (ν_0).

(3) Energy of the ejected electrons is directly proportional to the frequency of radiation.

(4) Number of electrons ejected per second depends on the intensity of radiation.

(5) $h\nu - h\nu_0 = \frac{1}{2}mv^2$

$h\nu_0$ → threshold frequency

$h\nu$ → energy

$\frac{1}{2}mv^2$ → energy of ejected electrons frequency

threshold frequency

velocity

$$h\nu - h\nu_0 = \frac{1}{2} m_e v^2$$

kinetic energy

energy of electromagnetic

Threshold

mass of electron

Wave

Particle

Wave Particle duality.

Quantum mechanics

Classical Mechanics

h = Planck's constant

Planck's quantum theory

Substances radiate or absorb energy discontinuously in the form of packet.

The smallest packet of energy is called quantum.

In case of light, the quantum is known as photon.

Plural – quanta

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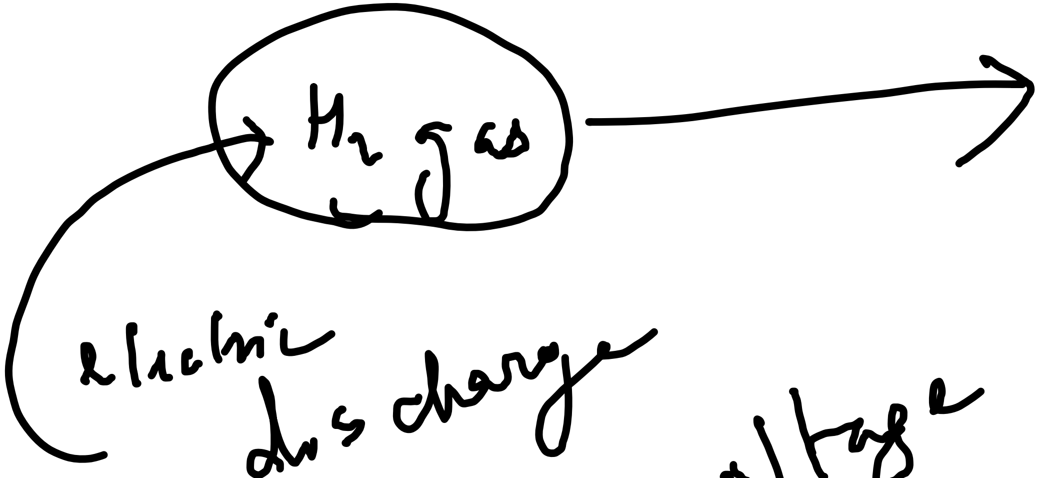

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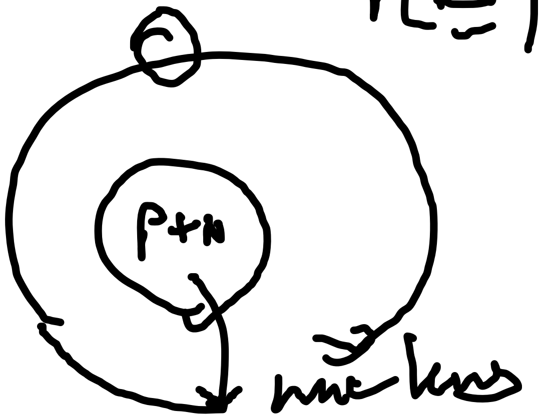

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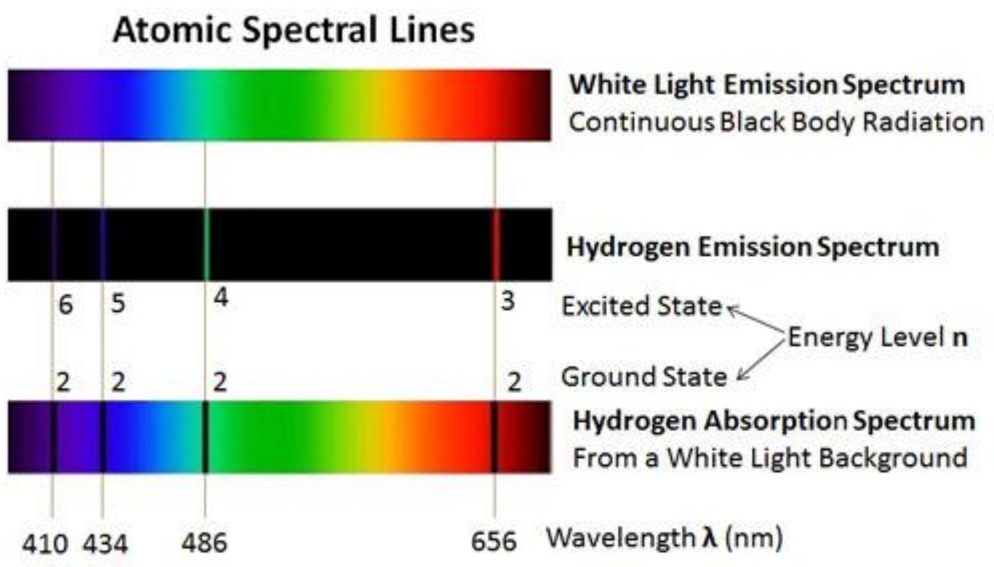
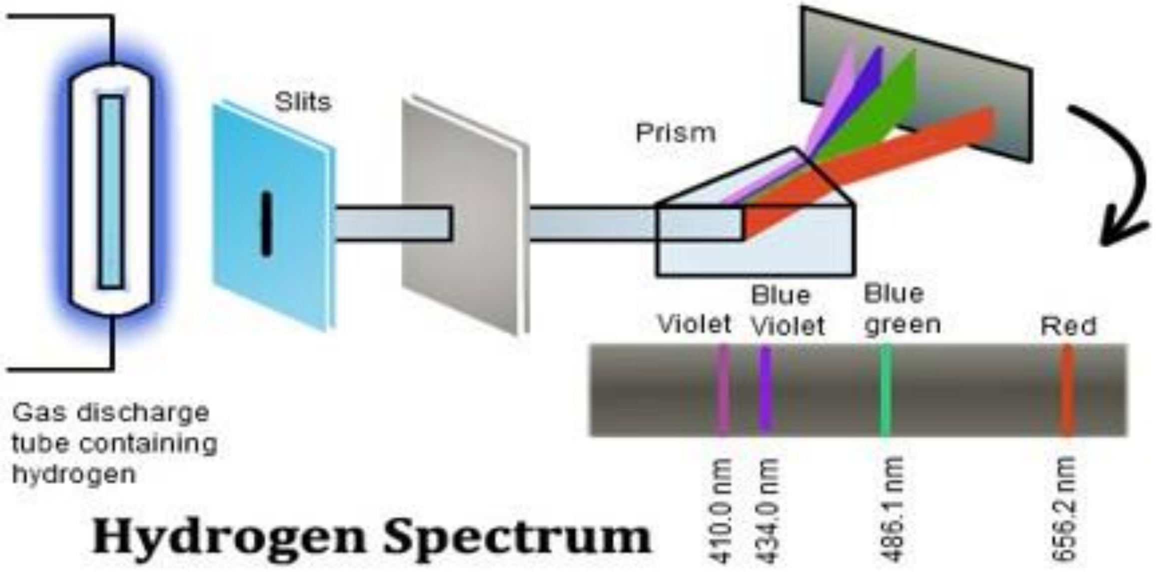
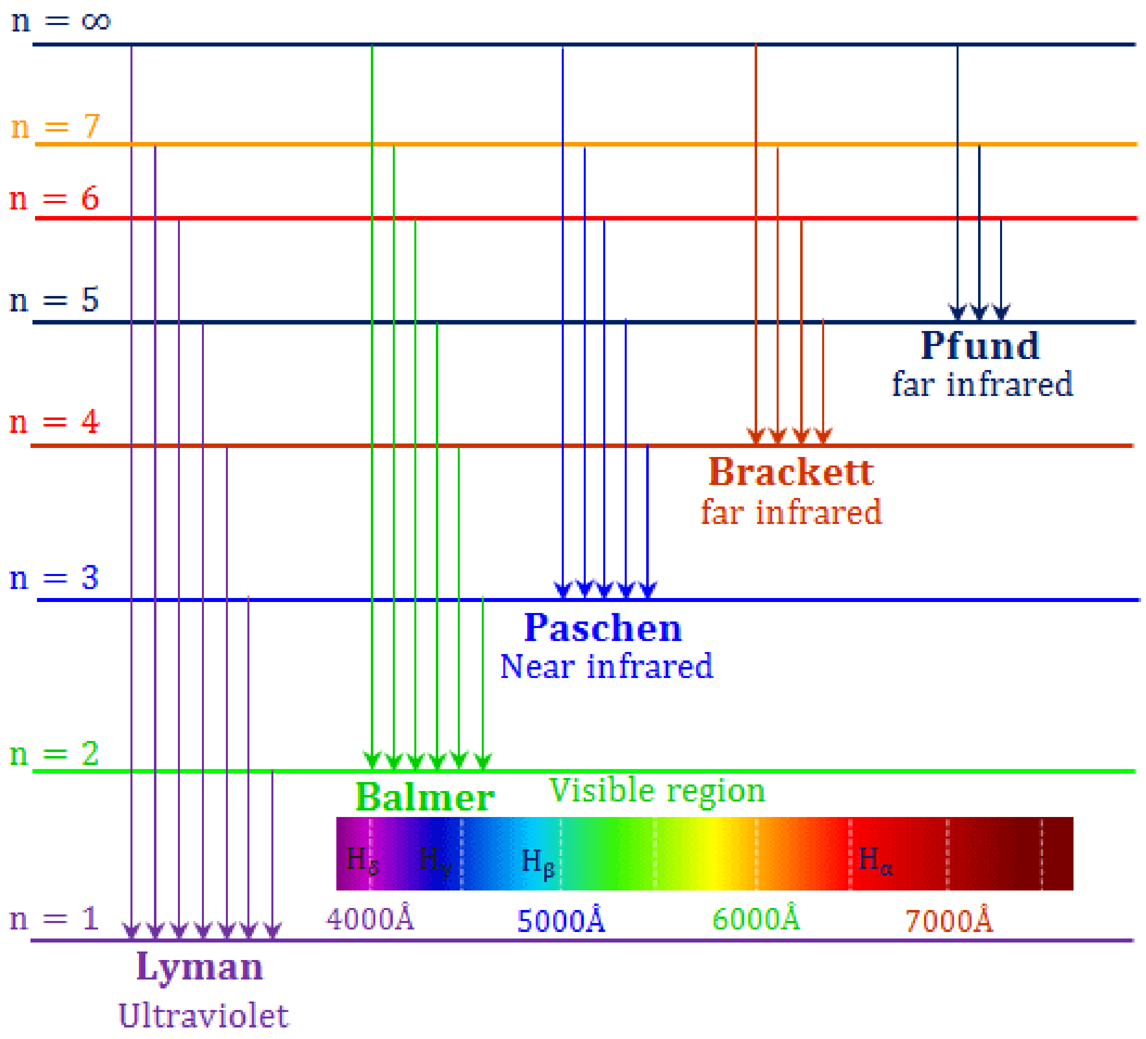

Atomic Spectral Lines
White Light Emission Spectrum
Continuous Black Body Radiation
Hydrogen Emission Spectrum
6
5
4
3
Excited State
Energy Level n
Ground State
2
2
2
2
Hydrogen Absorption Spectrum
From a White Light Background
410
434
486
656
Wavelength λ (nm)


Slits
Prism
Gas discharge tube containing hydrogen
Violet
Blue Violet
Blue green
Red
410.0 nm
434.0 nm
486.1 nm
656.2 nm
Hydrogen Spectrum


n = ∞
n = 7
n = 6
n = 5
n = 4
n = 3
n = 2
n = 1
Pfund
far infrared
Brackett
far infrared
Paschen
Near infrared
Balmer
Visible region
Hδ
Hγ
Hβ
Hα
4000Å
5000Å
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7000Å
Lyman
Ultraviolet

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Matter

Particle ← Matter → Wave

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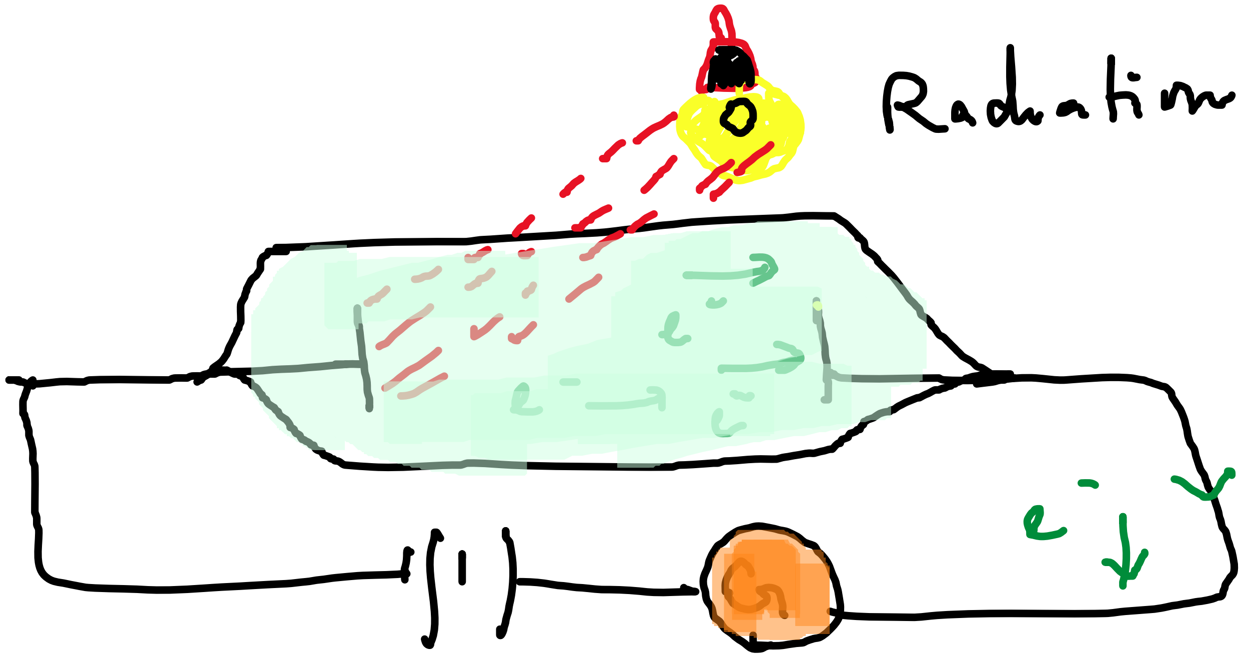

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$\frac{1}{2}mv^2$ → energy of ejected electrons

$$h\nu - h\nu_0 = \frac{1}{2} m_e v^2$$

- $h\nu$ — energy of electromagnetic (frequency)
- $h\nu_0$ — threshold frequency
- v — velocity
- $\frac{1}{2} m_e v^2$ — kinetic energy
- m_e — mass of electron

energy of electromagnetic → Wave → Quantum mechanics

Threshold → Particle → Classical Mechanics

Wave Particle duality.

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where n = + ve integer —

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Photoelectric effect

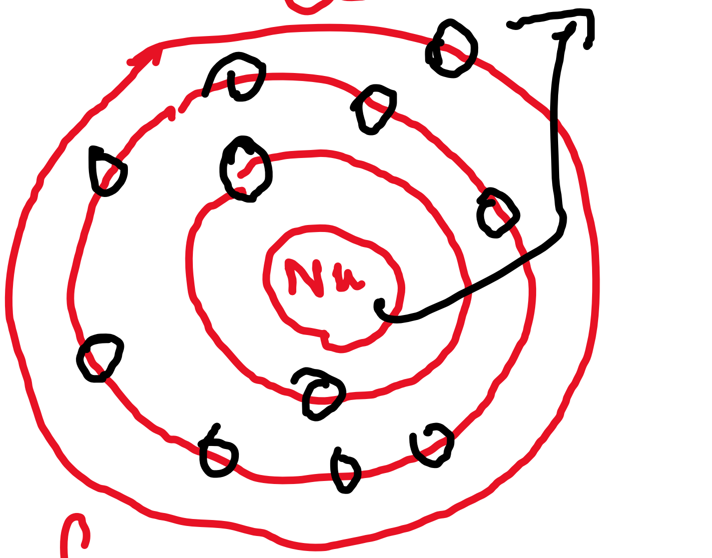
Bohr's model

de Broglie equation

Bohr's atomic model

1. Electrons revolve around the nucleus in circular orbits of fixed energy.

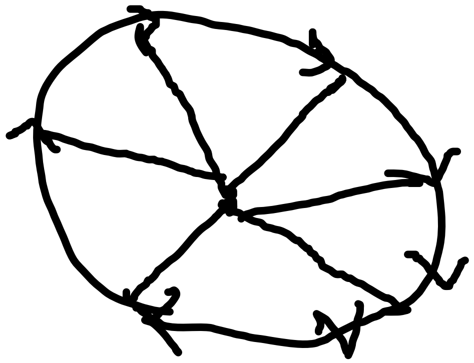
2. Electrons revolve only in those orbits whose angular momentum (mvr) is an integral multiple of $\frac{h}{2\pi}$ where h = Planck's constant

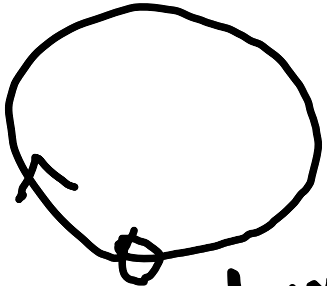


Na

Momentum = mass x velocity

Linear motion





Circular motion :

Electrons have angular momentum

Angular momentum = Circular motion

$m v \cdot r$ where

r = radius of the path

$$mvr = \frac{nh}{2\pi}$$

where

$n = 1, 2, 3 \ldots\ldots$ any integers .

3. Electrons absorb energy in the from of electromagnetic radiation. (EMR) when it jumps from lower energy level (ground state) to higher energy level (excited state) and vice versa.

Energy absorbed or released in an electron jump $(\Delta E) = E_2 - E_1 = h\nu$

$$\Delta E = E_2 - E_1 = h\nu$$

Energy absorbed or released in an electron jump, $\Delta E = h\nu$.

Limitations of Bohr's theory.

1. Failed to explain the spectra of atoms having more than one electron.
2. Failed to account for the splitting of spectral line source of a spectrum.

that is placed in a strong magnetic or electrical field.

3. Dual nature of particle and uncertainty principle was ignored in Bohr's atomic model.

de-Broglie equation

where m = mass
v = velocity

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

mv → momentum

Heisenberg's uncertainty principle : $p = m \times v$

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

where

Δx = Change in position

Δp = " " momentum

$$\Delta x \times \Delta v \geq \frac{h}{4\pi m}$$

It is impossible to determine simultaneously, the exact position and exact momentum of an electron.

Atomic Structure -

1. Thomson's plum pudding model.
2. Chadwick's discovery of neutron
3. Rutherford's model
4. Wave :- Atomic spectrum of hydrogen.
5. Photoelectric effect
6. Plank's quantum theory
7. Bohr's atomic model .
8. de - Broglie equation

9. Heisenberg's uncertainty principle -

10. Quantum Number - A quantum no. is a value that is used when describing the energy levels available to atoms & molecules.

- Principal quantum no.
- Azimuthal quantum no.
- Magnetic quantum number
- Spin quantum no.

To completely describe an electron in an atom, four quantum numbers are needed.

Principal Quantum no. (n)

1. It tells us about the main shell in which the electron resides and the approximate distance of the electron from the nucleus. ✓

2. Maximum number of electrons that a shell can accomodate is $2n^2$.

1st shell : Principal quantum no. $n = 1$

Shell		Principal Quantum no (n)	No. of electrons that can be accommodated
K	1^{st}	$n = 1$	$2n^2$ i.e. $2 \cdot 1^2 = 2$
L	2^{nd}	$n = 2$	$2 \cdot 2^2 = 2 \cdot 4 = 8$
M	3^{rd}	$n = 3$	$2 \cdot 3^2 = 2 \cdot 9 = 18$
N	4^{th}	$n = 4$	$2 \cdot 4^2 = 2 \cdot 16 = 32$

Bohr bury scheme — The distribution of electrons in different orbits or shells is governed by a scheme known as Bohr bury scheme.

K shell → will accomodate a maximum of 2 electrons
($n = 1$)

L shell, $n = 2$ " " → 8 "

M " $n = 3$ " " → 18 "

2nd shell -

1st shell (2) (8)

From third shell (M or $n = 3$) onwards the shells become bigger. The third shell can accomodate as many as 18 electrons. In general, the maximum number of electrons that can be present in any shell is $2n^2$ where n is the no. of energy shell. However, the outermost shell of an atom cannot have more than 8 electrons and the shell next to the outermost shell can not have more than 18 electrons

This rule i.e. 8 electrons maximum in the outermost shell / valence shell is called Octet rule

Why octet? Because octet configuration is stable. All inert gas possess 8 electrons in their valence shell.

Azimuthal or angular momentum quantum number (l)

1. It represents the number of subshells present in the main shell
2. These subsidiary orbits within a shell are designated as s, p, d, f.
3. This tells us about the shape of subshell.
4. For a given value of n, there are n possible values of

starting from 0 to n - 1

Value of l	0	1	2	3	4
Subshell notation	s	p	d	f	g,

Magnetic Quantum no. (m)

It determines the number of preferred orientation of electrons present in a subshell.

For a given value of n there are n possible values of l starting from $0 - n-1$

$n = 2, \quad l = 0, 1$

$n = 3, \quad l = 0, 1, 2$

For a given value of l, there are $2l + 1$ possible values of m from $-l$ to $+l$

$l = 0$; s $\quad$ $l = 2$ d

$l = 1$; p $\quad$ $l = 3$ f

Value of l	0	1	2	3
Subshell	s	p	d	f
Values of m	0	−1, 0, +1	−2, −1, 0, +1, +2	−3, −2, −1, 0, 1, 2, 3

$2 \cdot 1 + 1$
$2 \cdot 0 + 1$
$0 + 1$
1

$2 \cdot 1 + 1 = 3$
$-1 \quad \rightarrow \quad +1$

$2 \cdot 2 + 1$
$= 5$
$-2 \quad\quad +2$
$-2, -1, 0, +1, +2$

$2 \cdot 3 + 1$
$= 7$
$-3, -2, -1, 0, +1, +2, +3$

The Spin Quantum no. —

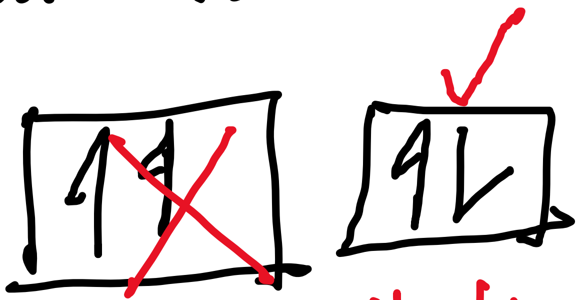
1. It determines the direction of spin of an electron in an orbit.

2. There are only two possible values for spin quantum no.

$$-\frac{1}{2} \quad + \frac{1}{2}$$

parallel ↑↑

↑ ↓



antiparallel

Electronic Configuration of an atom.

Orbital: It is defined as the space occupied by electrons around the nucleus of an atom where the probability of finding an electron is the maximum.

Quantum no.

- Principal 'n'
- Azimuthal 'l'
- Magnetic m or m_l
- Spin - s or m_s

Each value of l indicates the sub-energy level or subshell within the particular shell or energy level.

Subshell or subenergy level :

s , p , d , f , g

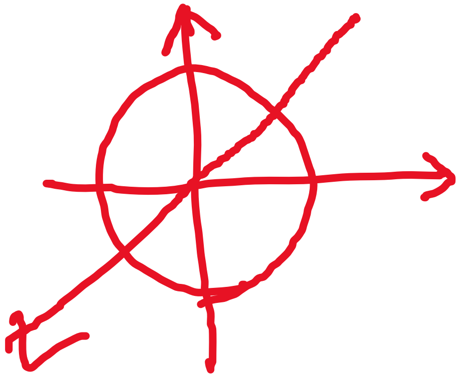
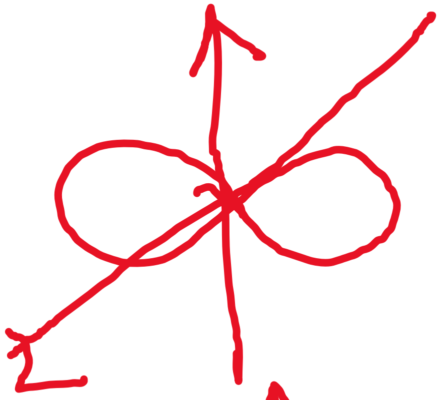
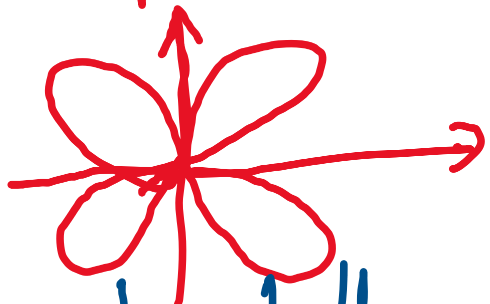
s → sharp

p → principal

d → diffused

f → fundamental

g → generalized

Subshell	Shape	Description
s - orbital		Spherically symmetrical -
p - orbital		Dumbbell shaped -
d - orbital		Double dumbbell -

f and g subshells are of complicated shape.

These shapes of subshells are not experimentally observed as these are 3D-plots of solution solution of Schrodinger wave eqn.

Magnetic quantum no:

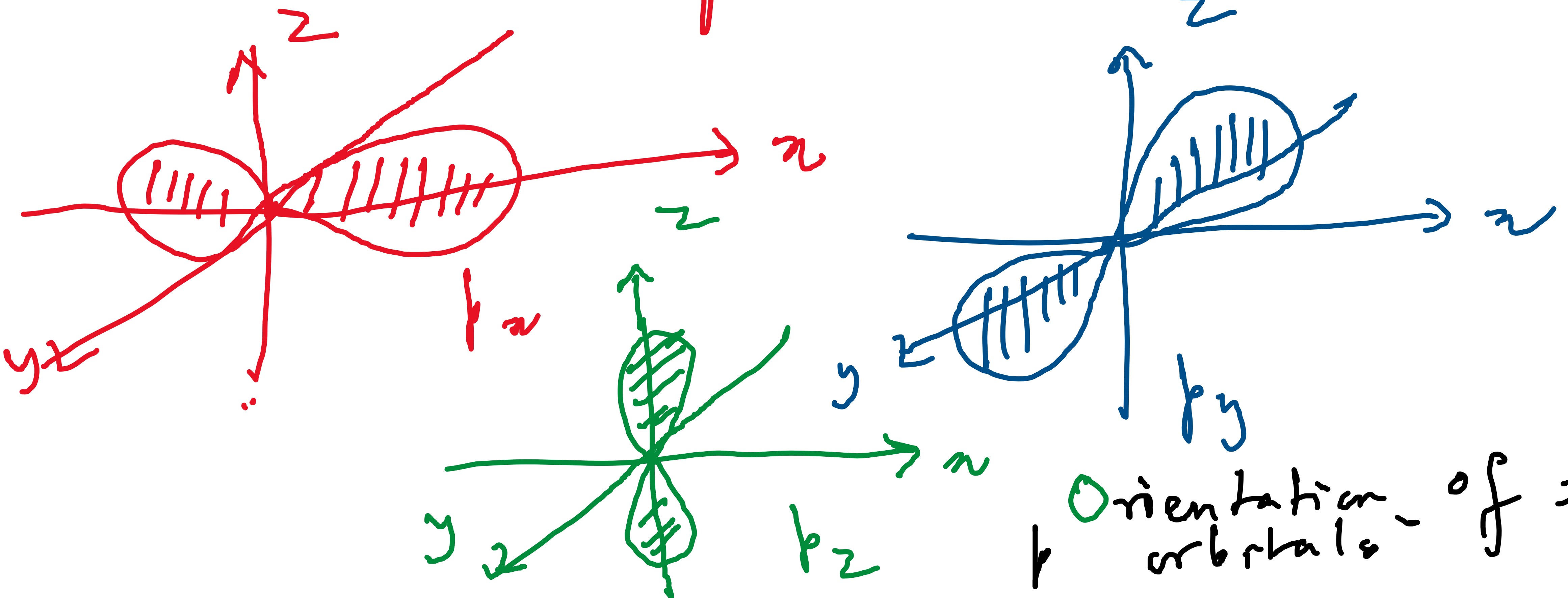
The values of m for a particular value of l varies from +l to -l including zero.

Value of l (n = 4)	Possible values of m	Total possible values
0	0	1 → s
1	+1, 0 −1	3 → p
2	−2, −1, 0, +1, +2	5 → d
3	−3, −2, −1, 0, +1, +2, +3	7 → f

Each possible orientation is considered as a particular orbital.

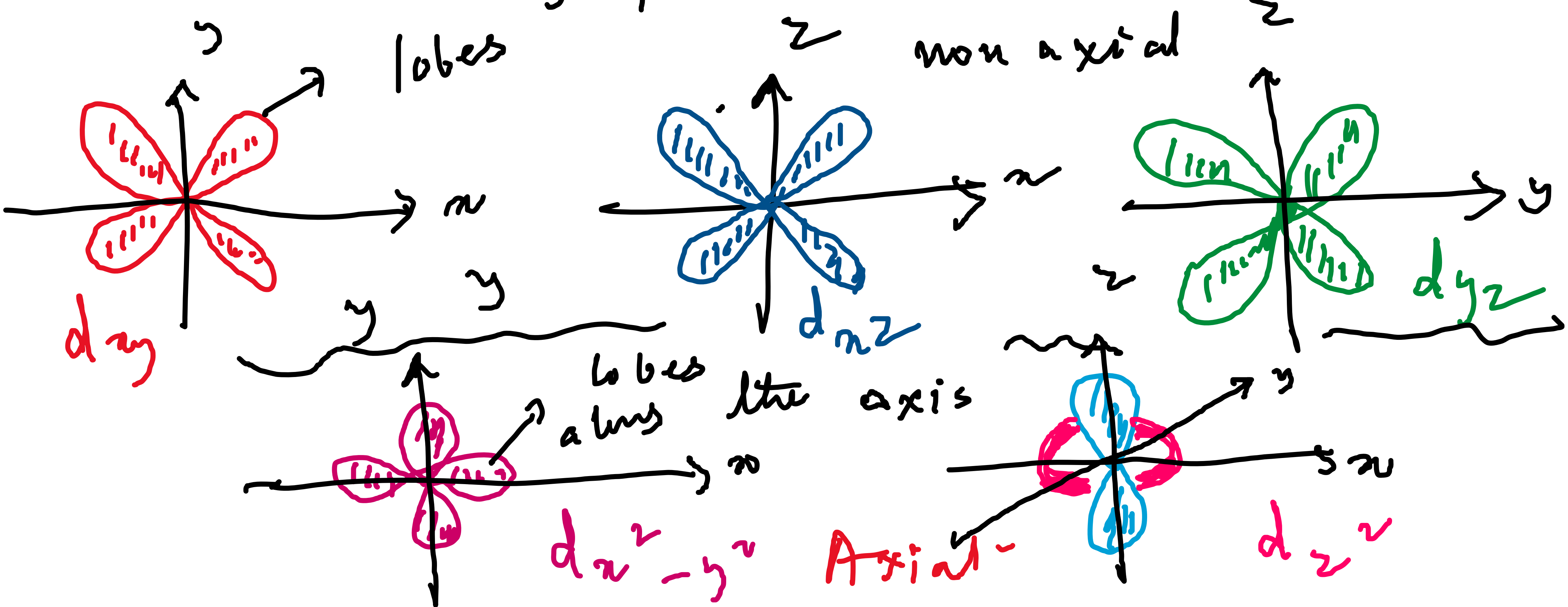
a. s − subshell consists of one orbital that is known as s − orbital.

b- p subshell consists of 3 orbitals that are known as p_x, p_y, and p_z orbitals along the respective axis.



Orientation of 3 p orbitals

c. d subshell consists of five orbitals that are known as – d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$, d_{z^2}



i) d_{xy}, d_{yz}, d_{zx} orbitals are known as non-axial d orbitals because the lobes of the orbitals are not available along the axis

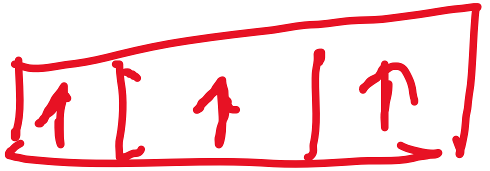
ii) $d_{x^2-y^2}$ and d_{z^2} are known as axial d orbitals because the lobes of the orbitals are along the axis.

Spin quantum no.

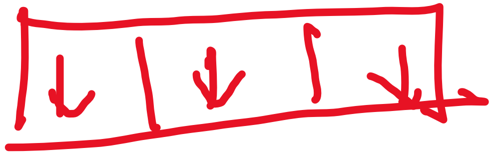
An electron is not only moving around the nucleus but also spinning about its own axis. It may spin either clockwise or anticlockwise.

anticlockwise

$$s = -\frac{1}{2} \quad -\frac{1}{2} \quad -\frac{1}{2}$$



or.



$$s = +\frac{1}{2} \quad +\frac{1}{2} \quad +\frac{1}{2}$$

clockwise spinning

Aufbau Principle

The electrons are filled up in the empty orbitals of an atom from the lowest energy orbital to the higher energy orbitals. The energy sequence of empty orbitals is –

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < ...... and

Sequence of filling energy levels

Shells

n = 1

n = 2

n = 3

n = 4

n = 5

n = 6

n = 7

n = 8

Possible subshells -

1s

2s 2p

3s 3p 3d

4s 4p 4d 4f

5s 5p 5d 5f 5g ...

6s 6p 6d 6f 6g ...

7s 7p

8s 8p

Energy order: 4f > 6s > 5p > 4d > 3d > 4s

Since energy of 3d level is greater than 4s level, while filling up electrons in an orbital, 4s level is filled up before the 3d level.

<u>Pauli's exclusion principle</u>

No two electrons in an atom can have the same values of all four quantum numbers.

An orbital in a subshell can accomodate a maximum of two electrons with opposit spin.

Shell number

$n = 1$, 1st shell

$l = n - 1$, $1 - 1 = 0$ (1s)

$m = 0$

No. of orbital 1 Max no. of electron

$1 \times 2 = 2$

$2n^2 = 2 \cdot 1^2 = 2$ → electron

$n = 2$

Possible values of l:

$2l + 1$: $2 \cdot 1 + 1 = 3$

2s

2p.

2s — 0

2p — 3 (+1, 0 −1)

Total no. of orbitals in second shell $= 1 + 3 = 4$

Total electrons =

$2 \times 4 = 8$

$2n^2 = 2 \cdot 2^2 = 2 \cdot 4 = 8$ ✓

Atomic Structure

Pauli's exclusion principle -

No two electrons in one atom can have the same values of all four quantum numbers or an orbital in a subshell can accomodate a maximum of two electrons of opposite spin.

N.B.: 1. The no. of orbitals present in a subshell is $2l+1$ where l = azimuthal quantum no.

ii) The total no. of electrons present in a subshell is - $2(2l+1)$

iii) Total no. of orbitals present in a shell is n^2

iv) Total no. of orbitals present in a shell is - $2n^2$.

Shell	K	L	M	N	O	P	Q	R
n =	1	2	3	4	5	6	7	8
n^2 =	1 (s)	4 (1s + 3p)	9 (1s + 3p + 5d)	16 (1s + 3p + 5d + 7f)				
$2n^2$ =	2	8	18	32	...	...	...	etc.

Hund's rule:

The degenerate orbitals will be filled by one electron each having same spin and then only pairing of electrons will take place.

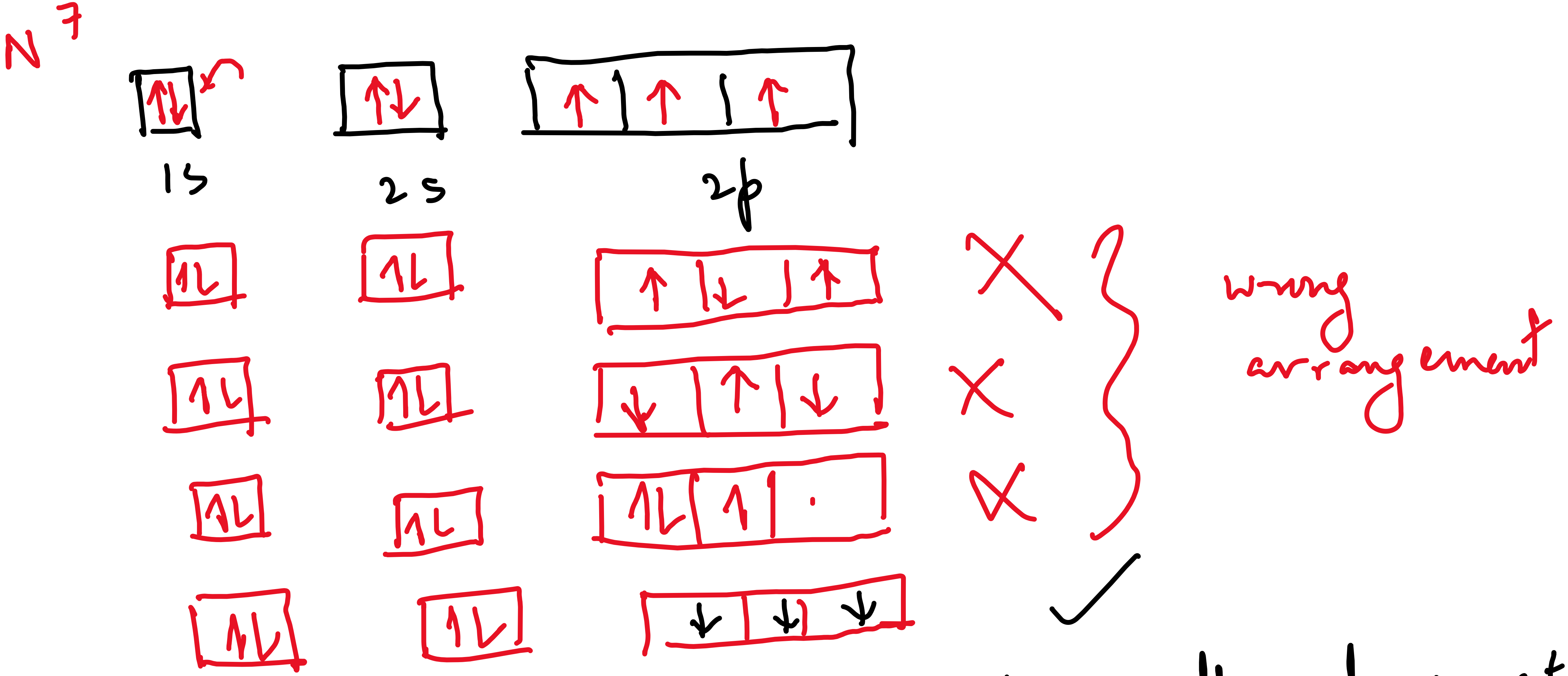
↓ orbitals having same energy

^{7}N :

$n = 2 \quad n^2 = 4 \quad 2n^2 = 8$ → max.

1s

3p.



The filling up of electrons in the degenerate orbitals will take place in such a way that the multiplicity (M) value will be maximum when M is defined as follows: $M = 2|S| + 1$

$s = +\frac{1}{2}$

$s = -\frac{1}{2}$

N: $1s$ [↑↓] $2s$ [↑↓] $2p$ [↑ | ↑ | ↑]

$s = +\frac{1}{2} - \frac{1}{2} = 0$ $\quad +\frac{1}{2} - \frac{1}{2} = 0$ $\quad S = +\frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{3}{2}$

$M = 2|S| + 1 = 2 \cdot \frac{3}{2} + 1 = 4$

Electronic configuration:

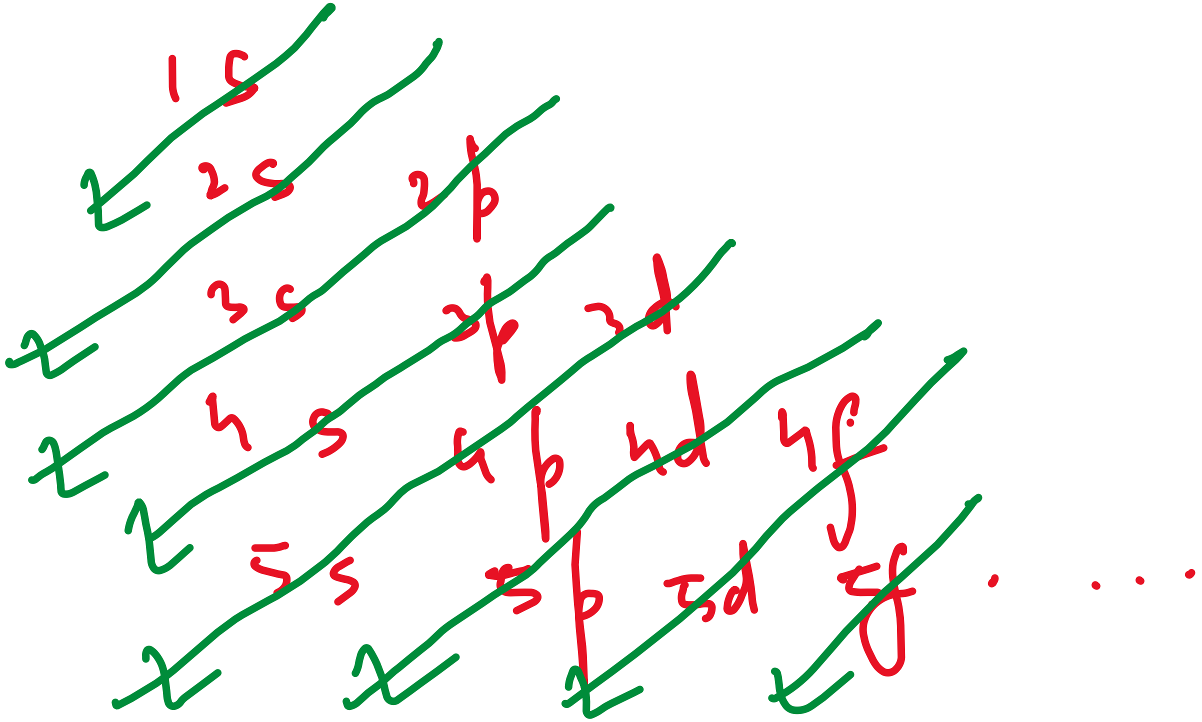
1. Aufbau's principle
2. Pauli's exclusion
3. Hund's rule of maximum spin multiplicity

[↓ | ↓ | ↓]

$S = -\frac{1}{2} - \frac{1}{2} - \frac{1}{2} = -\frac{3}{2}$

$M = 2 \cdot \frac{3}{2} + 1 = 4$

1s < 2s < 2p < 3s <
3p < 4s < 3d < 4p <
5s < 4d < 5p < ....



Atomic no. : 1

Subshells

Hydrogen $Z = 1$

$1s^1$

[↑] 1s

Helium $Z = 2$

$1s^2$

[↑↓]

Element	Atomic no. Z	Subshells 1s	2s	2p	3s	3p	3d	4s
Hydrogen $1s^1$	1	1						
Helium $1s^2$	2	2						
Lithium $1s^2, 2s^1$	3	2	1					
Beryllium $1s^2\ 2s^2$	4	2	2					
Boron $1s^2, 2s^2 2p^1$	5	2	2	1				
Carbon $1s^2, 2s^2 2p^2$	6	2	2	2				

Lithium: 1s [↑↓] 2s [↑] 2p [| |]

Beryllium: 1s [↑↓] 2s [↑↓] →

Max e

1 ← s = 2

3 ← p = 6

5 ← d = 10

7 ← f = 14

(n = 1) , → (n = 2)

separated by ','

C^6 :

$1s^2, 2s^2 2p^2$

1s: [↑↓]   2s: [↑↓]   2p: [↑ | ↑ |] (p_x p_y p_z)

$s = \frac{1}{2} + \frac{1}{2} = 1$

degenerate → same energy level.

p_x p_y p_z: [↑↓ | |]

$M = 2|s| + 1$

$= 2\left(\frac{1}{2} + \frac{1}{2}\right) + 1$

$= 2 \cdot 1 + 1 = 3$

$s = \frac{1}{2} - \frac{1}{2} = 0$ $M = 2 \cdot 0 + 1 = 1$

N^7 :

1s: [↑↓]   2s: [↑↓]   2p: [↑ | ↑ | ↑]

$1s^2, 2s^2 2p^3$

$3 = \frac{6}{2}$

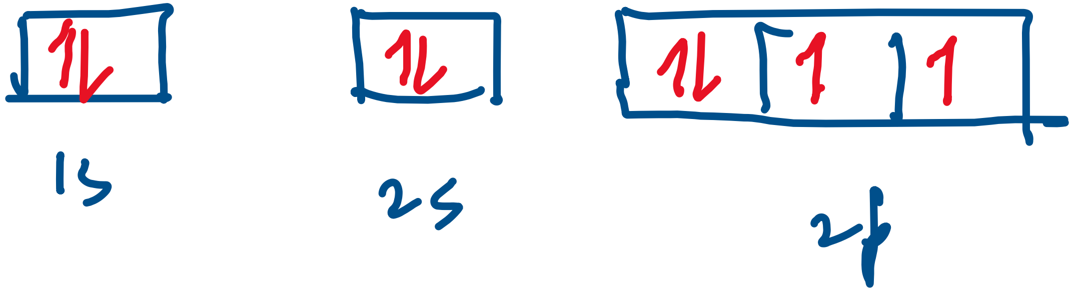
Half-filled orbital

stable

Oxygen: O^{8} :

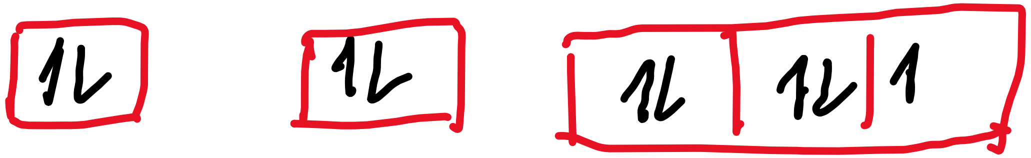
O^{16} → atomic mass

O_{8} → atomic no.



O : $1s^2, 2s^2 2p^4$

Fluorine : F^9

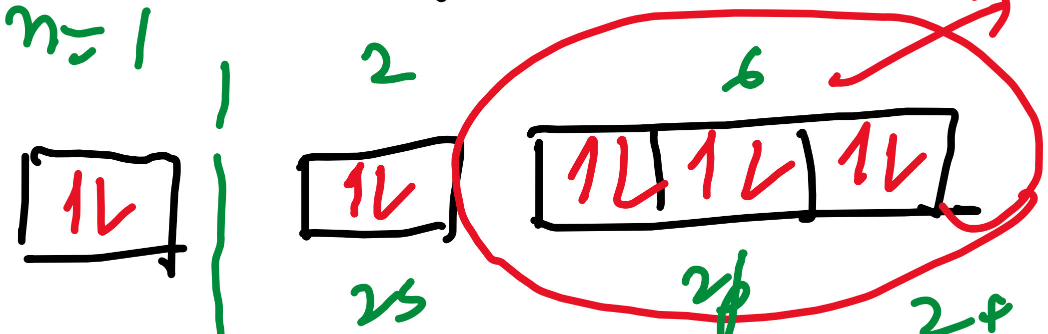


highly stable

F : $1s^2, 2s^2 2p^5$

Neon Ne^{10}

Ne:



fully filled orbital

stable octet 2+6

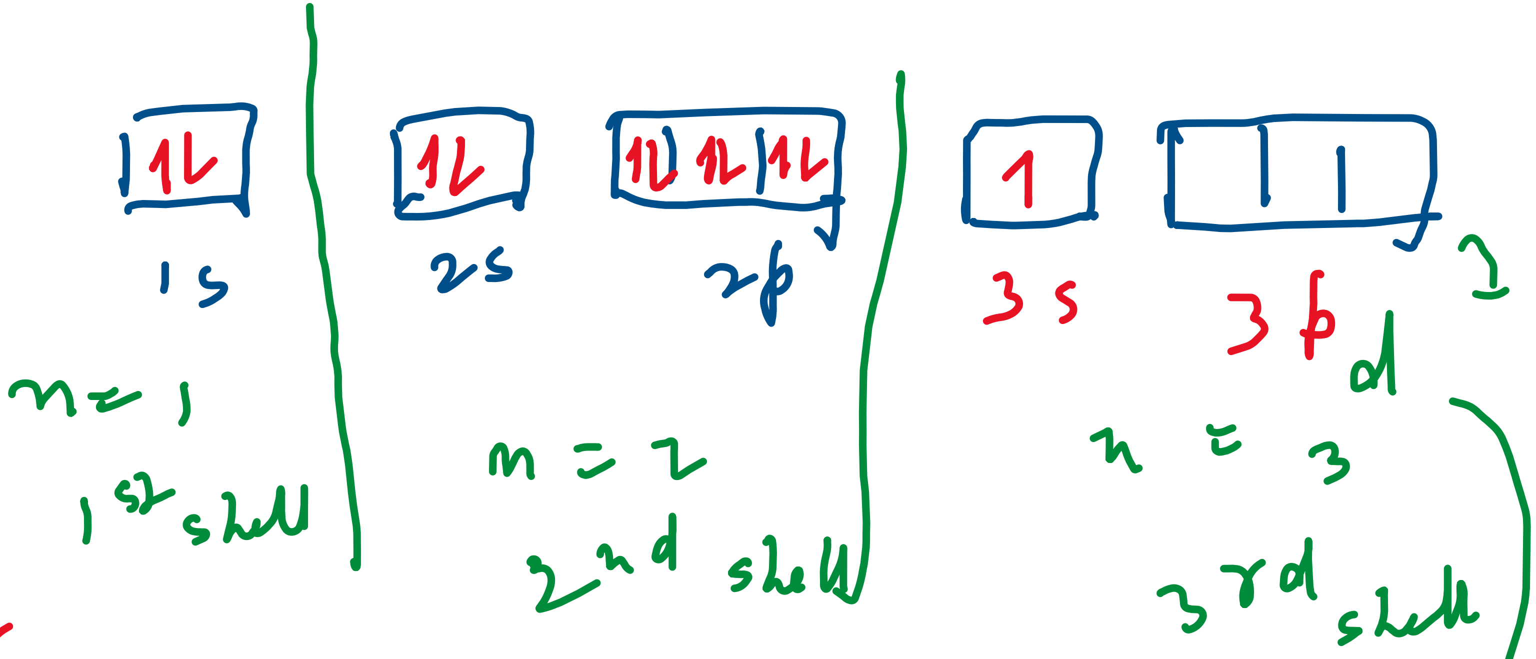
e = 8

neon is an inert gas

$1s^2, 2s^2 2p^6$

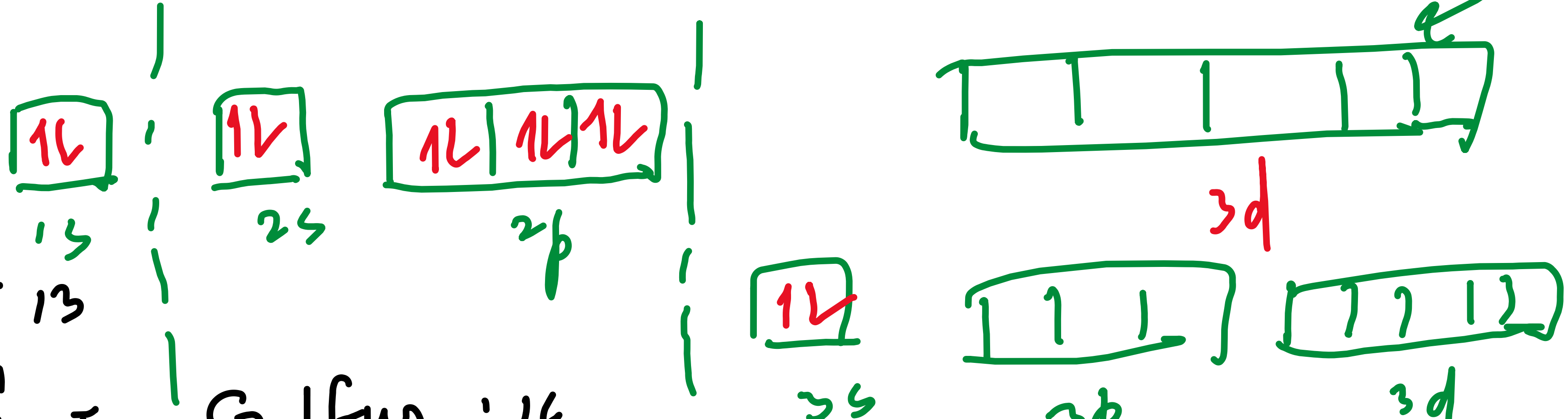
Sodium: $Z = 11$

$1s^2, 2s^2 2p^6, 3s^1$



Magnesium: $Z = 12$

Mg: $1s^2, 2s^2 2p^6, 3s^2$



H. W: Aluminium : 13
Silicon : 14
Phosphorus : 15.
Sulfur : 16
Chlorine : 17,
Argon : 18

Electronic Configuration

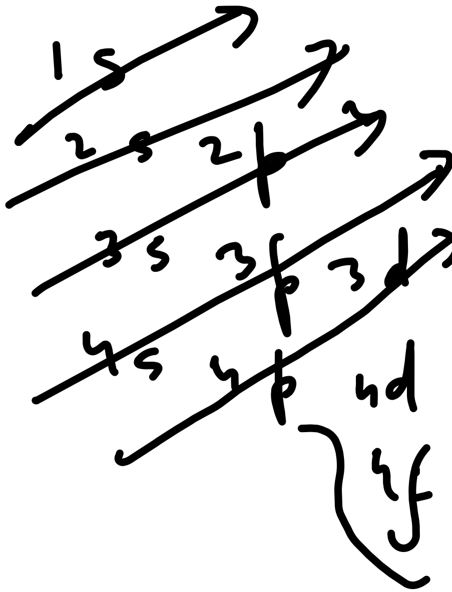
Element no: 19 Potassium : 'K'

$1s < 2s < 2p < 3s < 3p < 4s < 3d \ldots$

$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^1$

Ar

$[Ar] 4s^1$



Element no: 20 Calcium 'Ca'

$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2$

Element no: 21 Sc

$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2 3d^1$ → d orbital.

Element no: 22 Ti = Titanium.

$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2 3d^2$

Element no: 23 : V = Vanadium

$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2 3d^3$

Element no: 24 : Cr = Chromium

$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2 3d^4$ → X

Exception:

$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^1 3d^5$ ✱

Element no: 25 Manganese

$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2 3d^5$ → no exception

Element no: 26 Iron

$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2 3d^6$ → "

Element no. 27 Cobalt.

$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2 3d^7$ → "

Element no: 28 Nickel.

$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2 3d^8$ → "

Element no: 29 Copper.

$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2 3d^9$ → ✗

$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^1 3d^{10}$ exception.

Element with atomic no. 24 and 29 i.e. Chromium and Copper showed exception and did not follow Aufbau's principle.

Why such anomaly / exception:

d orbitals - 5 : $d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{z^2}$

Recap: i) The number of orbitals present in any subshell is $2l+1$.

For $M=3$, possible of l (designated subshell) is

$0\,(3s)$, $1\,(3p)$, $2\,(3d)$

K → $n=1$

L → $n=2$

M → $n=3$.

$2l+1$ for 3d level → $2\cdot2+1=5$

$-2, -1, 0, +1, +2$

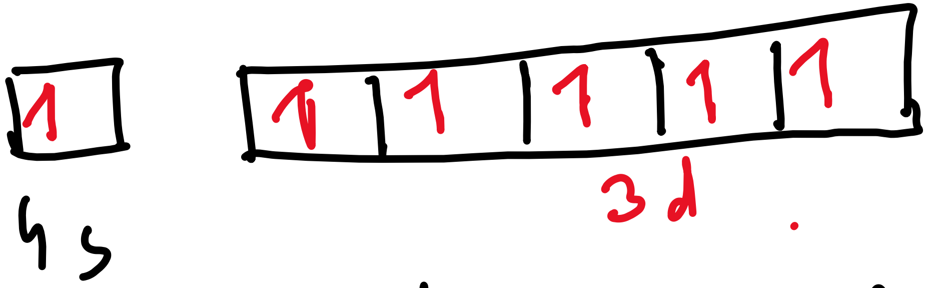
$-1 \rightarrow +1$

ii) The total no. of electrons in any subshell is — $2(2l+1) = 2\cdot5 = 10$

Chromium: Electronic configuration.

$1s^2, 2s^2 2p^6, 3s^2 3p^6$ $4s^1 3d^5$

$[Ar] 4s^1 3d^5$



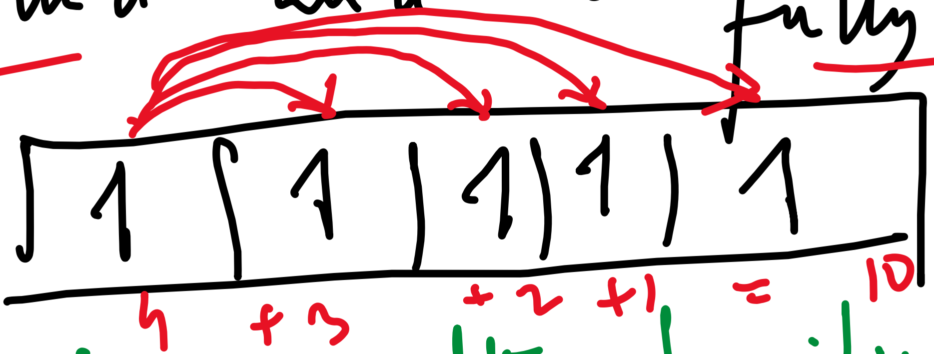
→ Half filled d level.

When a subshell is half-filled or full-filled it becomes highly stable.

The extra stability of the half-filled and full filled orbitals can be attributed to

i) The symmetrical leads to stability

ii) The exchange energy is more for half-filled and fully filled electrons.



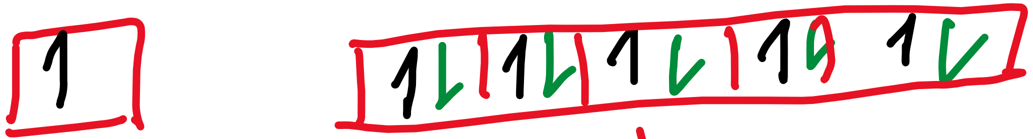
} Possible exchange

After exchanging the position between any two electrons, it gives the same configuration. During the exchange of position of electrons, some amount of energy is released which is known as exchange energy. More no. of exchange causes the release of more energy.

Half filled or full filled orbitals are highly stable

Cu : $1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^1 3d^{10}$

$= [Ar] 4s^1 3d^{10}$



4s 3d

} Full filled (orbital) stable.

Element no: 30 Zinc.

$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2 3d^{10}$ → stable

$d^1 - d^9$ → Transition elements

Elements whose atom has a partially filled d subshell or which can give rise to cations with an incomplete d subshell are called as transition elements

Cu : $[Ar] 4s^1 3d^{10}$

Cu_2O :

↓ x ↓ oxidation state − 2 : Total oxidation state in a molecule is 0

Cu_2O : Cu → x, O → -2

$$2x + (-2) = 0$$
$$\Rightarrow 2x - 2 = 0$$
$$\Rightarrow 2x = 2 \Rightarrow x = 1$$

Cu(I)

$CuSO_4$: Cu → x, S → $+6$, O → -2

$$x + 6 + 4 \times (-2) = 0$$
$$\Rightarrow x + 6 - 8 = 0$$
$$\Rightarrow x - 2 = 0 \Rightarrow x = 2$$

Summary: Cu shows two oxidation state – +I & +II.

Ionic state : Cu^{+}, Cu^{2+}

$Cu^+ \rightarrow Cu - e$ $Cu^{2+} \rightarrow Cu - 2e$

$Cu \rightarrow 29$ $Cu^+ : 28$ $Cu^{2+} : 27$

Cu : [Ar] $4s^1$ $3d^{10}$ → full filled

-e { Cu^+ : [Ar] $3d^{10}$ → " "

Cu^{2+} : [Ar] $3d^9$ incomplete d subshell

For d block elements first electrons are removed from s and then d subshell

[Ar] $4s^2$ → outermost

Ca

↙ calcium = [Ar]

Ca^{2+} : noble gas configuration → inert gas

highly stable

Ca^+ : [Ar] $4s^1$ } not stable

Ca^{2+} : [Ar] (all electrons from 4s here are removed)

Elements with atomic no. 21 – 29 are transition elements.

Features of transition elements:

1. Incomplete d subshell.
2. These elements give rise to colored ions.

Color arises due to d-d transfer or charge transfer:

$CuSO_4$: Blue vitriol. $FeSO_4$: Green vitriol

$Fe_2(SO_4)_3$: Brown :

3. Exhibit paramagnetism due to the presence of unpaired electrons.

Spin only magnetic moment (μ_s) $= \sqrt{n(n+2)}$

n = no. of unpaired electrons present in the species

Magnetic property:

1. Paramagnetic

Substances consisting of unpaired electrons is known as paramagnetic and is attracted by magnetic field

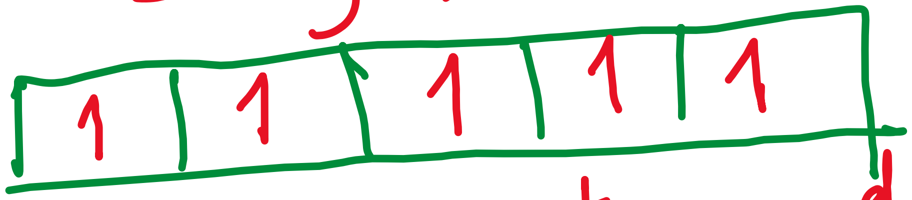
2. Diamagnetic

Paramagnetic substances are usually coloured

Diamagnetic: Substances consisting of no unpaired electrons is known as diamagnetic and it is not attracted by magnetic field.

$Mn : [Ar]\ 3d^5, 4s^2$ → s electrons will be removed to form Mn^{2+} cation.

$Mn^{2+} : [Ar]\ 3d^5$



unpaired → paramagnetic

magnetic property

$$\mu_s = \sqrt{n(n+2)}\ \text{B M.}$$

$$= \sqrt{5(5+2)}\ \text{B M}$$

$$= \sqrt{35}\ \text{B.M.} = 5.92\ \text{BM.}$$

Cu^{2+} has unpaired electron

B.M. ≡ Bohr magneton ≡ unit for magnetic dipole moment of electrons.

Cu^{29} : $[Ar]\ 4s^1\ 3d^{10}$

Cu is not paramagnetic

1L	1L	1L	1L	1L

$n = 0$

$$\mu_s = \sqrt{0(0+2)} = 0$$

④ Transition elements form coordination complex.

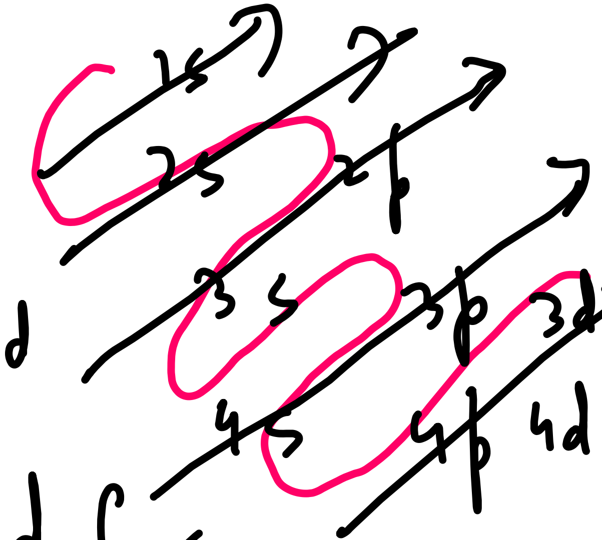
ATOMIC STRUCTURE

Fe : 26

$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2 3d^6$

Fe : $[Ar]\ 4s^2 3d^6$

Fe^{2+} : $[Ar]\ 3d^6$



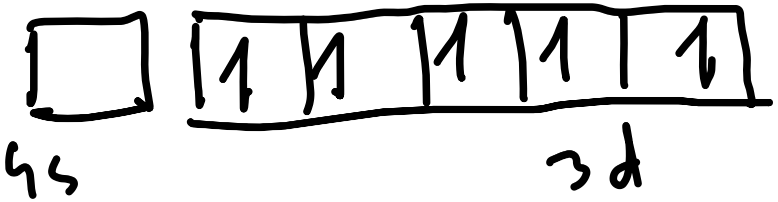
4s ↓ no electron

↓

electrons removed for ionisation

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

highly stable configuration



→ Half filled orbital

Fe^{3+} is more stable then Fe^{2+}.

$FeSO_4 \cdot 7H_2O$ $Fe_2(SO_4)_3$

↓ green vitriol.

↓ ferric sulfate

$Fe^{2+} \xrightarrow{[O]} Fe^{3+}$

ferrous → oxidised to ferric.

Problems

1. The third line in Balmer series corresponds to an electronic transition between which Bohr's orbit in hydrogen?

a) 5 → 3 b) 5 → 2 c) 4 → 3

d) 4 → 2

Correct option.

$$\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

In Balmer series electron jumps

from higher energy level to 2nd energy level. Hence, the third line from when electron jumps from fifth energy level to 2nd energy is $5 \rightarrow 2$.

(Q) The wave length of a spectral line for an electronic transition is — inversely related to –

i) the no. of electrons undergoing transition

ii) the nuclear charge of an atom.

iii) the difference in the energy of the energy levels involved in of the transition

iv) the velocity of electron undergoing the transition

Correct option: (iii)

$\Delta E = h\nu$ → Planck's constant

$E_2 - E_1 = \Delta E = h\nu$ → Frequency

$\Rightarrow \Delta E = h \cdot \frac{c}{\lambda}$ → velocity of light = constant

$E_2 - E_1 \propto \frac{1}{\lambda}$ $\lambda \propto \frac{1}{E_2 - E_1}$

wavelength

→ energy diff.

(3) If uncertainty in the position of an atom is 0, the uncertainty in its momentum will be

a) zero b) $\frac{h}{2\pi}$ c) $\frac{h}{4\pi}$ d) Infinity (Correct)

Soln

Heisenberg's uncertainty principle –

$$\Delta x \, \Delta p_x \geq \frac{h}{4\pi}$$

Δx → uncertainty in position

Δp_x → uncertainty in momentum.

h → Planck's constant

Heisenberg's uncertainty principle -

$$\Delta x \, \Delta p_x \geq \frac{h}{4\pi} \Rightarrow \Delta p_x \geq \frac{1}{\Delta x} \cdot \frac{h}{4\pi}$$

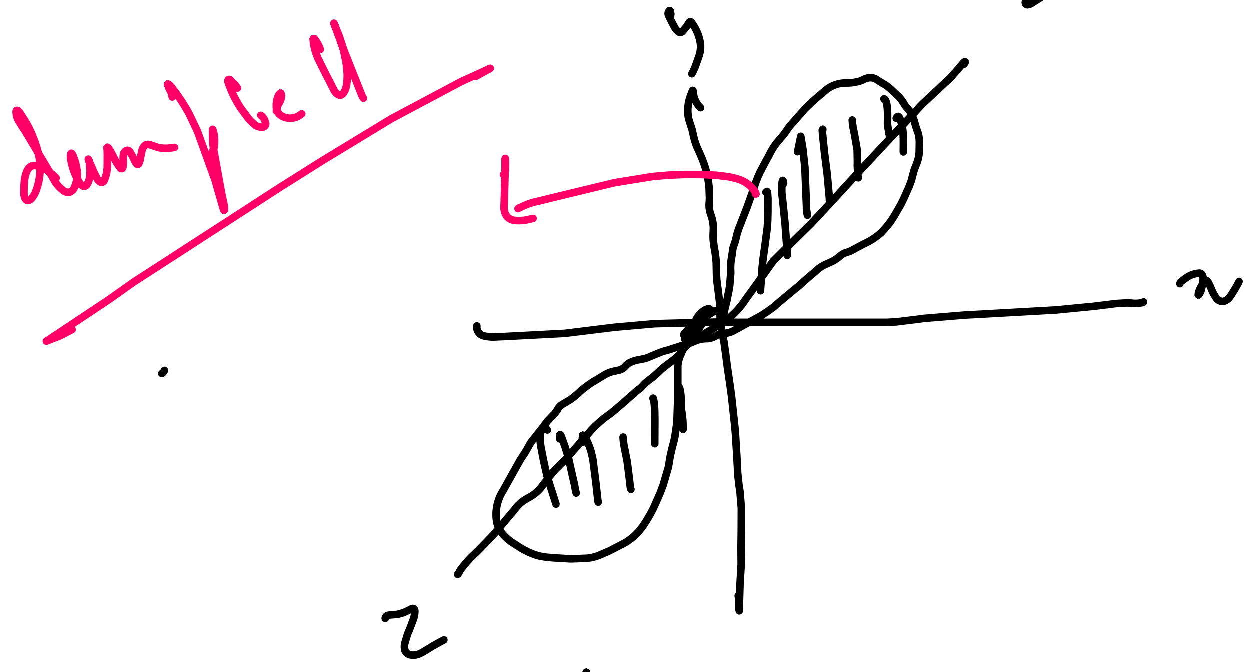
$$\therefore \Delta x = 0$$

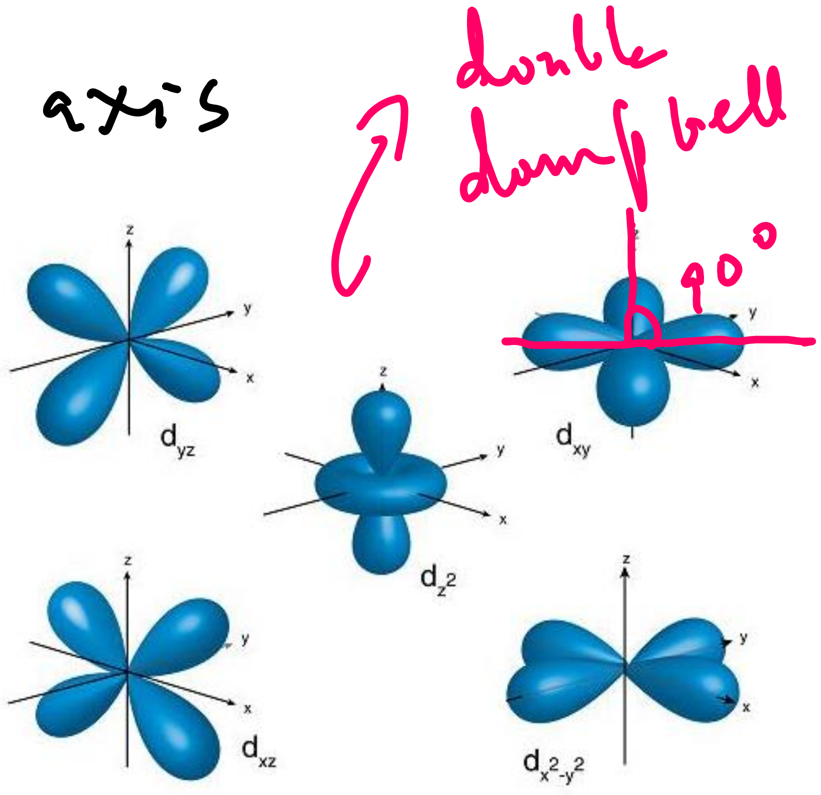
$$\therefore \frac{h}{4\pi} \times \frac{1}{\Delta x} = \infty$$ (infinity)

$$\therefore \Delta p_x \geq \infty$$

$\therefore$ Uncertainty in momentum is infinite

(4) (ii) p_z orbital lies along z axis





Lobes of d_{xy} orbital are at 90° with the z axis.

(5) What will be the wavelength of an electron moving with 1/10 th of the velocity of light?

6.626×10^{-34} J s

de-Broglie : $\lambda = \frac{h}{mv}$

Velocity of light = 3×10^{8} m/s.

Mass of electron = 9.1×10^{-31} kg.

$v = 3 \times 10^{8}$

$\frac{1}{10} v = \frac{3 \times 10^{8}}{10}$

Atomic Structure

1. Which one is the wrong statement? NEET-2017

a) de-Broglie's wavelength is given by $\lambda = \frac{h}{mv}$ where m = mass of the particle, v = group velocity of the particle.

b) The uncertainty principle is $\Delta E \times \Delta t \geq h/4\pi$

$\Delta x \, \Delta p_x \geq \frac{h}{4\pi}$

c) Half-filled and fully filled orbitals have greater stability due to greater exchange energy, greater symmetry and more balanced arrangement

d) (The energy of 2s orbital is less than the energy of 2p orbitals) in case of hydrogen like atoms.

Soln/

a) According to de-Broglie's equation,

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

where h = Planck's constant

m = mass, v = velocity

Thus, statement (a) is correct.

b) According to Heisenberg's uncertainty principle, the uncertainties of position Δx and momentum Δp are related as

$\Delta x \, \Delta p \geq \frac{h}{4\pi}$ → Heisenberg's uncertainty

momentum = mass × velocity

$\Delta p = m \, \Delta v$ (m → constant)

$\Rightarrow \Delta x \cdot m \Delta v \geq \frac{h}{4\pi}$

$\Rightarrow \Delta x \, \underline{m \, \Delta a} \cdot \Delta t \geq \frac{h}{4\pi}$

$\Rightarrow \Delta x \cdot F \cdot \Delta t \geq \frac{h}{4\pi}$

$\because F = m \, \Delta a$

acceleration (a) = $\frac{\text{change of velocity}}{\text{time}}$

$\frac{\Delta v}{\Delta t} = \Delta a$

$\Rightarrow \Delta v = \Delta a \cdot \Delta t$

Force = mass × acceleration.

$\underline{\Delta x \cdot F} \cdot \Delta t \geq \frac{h}{4\pi}$

Work = equivalent energy

Force × displacement

$\Rightarrow \Delta E \Delta t \geq \frac{h}{4\pi}$

another form of the eqn:

$\Delta x \cdot \Delta p_x \geq \frac{h}{4\pi}$

$\therefore \Delta E = F \cdot \Delta x$, where E = energy.

$\Delta x \Delta p_x = \Delta E \Delta t \geq \frac{h}{4\pi}$

∴ Statement (b) is correct.

Heisenberg's uncertainty; $\Delta x \Delta p_x \geq \frac{h}{4\pi}$

c) The half and fully filled orbitals have greater stability due to greater exchange energy, greater symmetry and more balanced arrangement. Thus statement (c) is correct.

d) For a single electronic species like H, energy depends on value of n and does not depend on l. Hence energy of 2s orbital and 2p orbital is equal in case of hydrogen like species. Therefore, statement

(d) is incorrect.

② Two electrons occupying the same orbital are distinguished by —

i) Magnetic Quantum no

ii) Azimuthal Quantum no.

iii) Spin quantum no.

iv) Principal quantum no.

(NEET-2016, Phase I)

Soln Two electrons occupying the same orbital has equal spin but the directions of their spin are opposite. Hence spin quantum no. s (represented as $+\frac{1}{2}$ and $-\frac{1}{2}$) distinguishes them.

③ How many electrons can fit in the orbital for which $n = 3$ and $l = 1$?

a) 2 b) 6 c) 10 d) 14

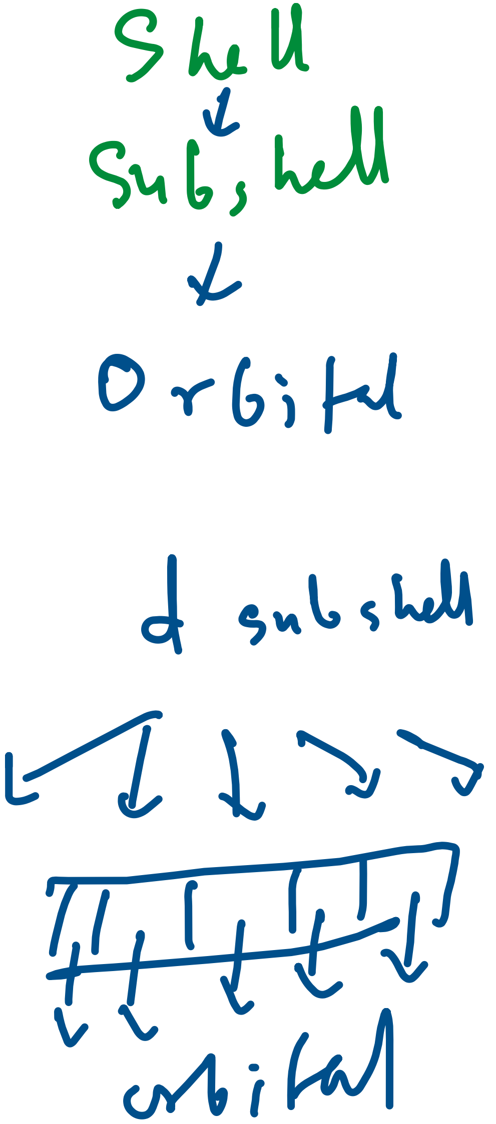
(NEET 2016 Phase II)

Soln

According to Hund's rule of maximum multiplicity an orbital can accomodate a maximum number of 2 electrons of exactly opposite spin $+\frac{1}{2}$ or $-\frac{1}{2}$.

Caution: To be noted →

The maximum number of electrons in an orbital do not depend upon the quantum numbers as given in question



4) Which is the correct order of increasing energy of the listed orbitals in the atom of titanium?

a) 3s < 4s < 3d < 3d

b) 4s < 3s < 3p < 3d

c) 3s < 3p < 3d < 4s

d) 3s < 3p < 4s < 3d

Soln:

According to Aufbau's principle,

3s < 3p < 3d < 4s

In neutral atoms, the approximate order in which subshells are filled is given by n + l rule, also known as the

1) Madelung rule (after Erwin Madelung)
2) Janet rule (" Charles Janet)
3) Klechkowsky " (" Vsevolod Klechkovsky)
4) Wiswesser's " (after William Wiswesser's rule)
5) Aufbau approximation.

Here n = principal quantum no. Ti : $1s^2, 2s^2 2p^6$ $3s^2 3p^6$ $4s^2$ $3d^2$

l = azimuthal " "

$l = 0, 1, 2, 3$

corresponding to s, p, d, f subshells.

The subshell ordering by this rule is —

$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < \ldots\ldots$ etc.

Other authors write the orbitals always in order of increasing n, such as Ti ($Z = 22$)

has the electronic configuration :-

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$ → 4s electrons are removed before d electrons

This can be called "leaving order" since if the atom is ionized, electrons leave approximately in the order 4s, 3d, 3p, 3s etc.

For a given neutral atom, the two notations are equivalent since the orbital occupancies have physical significance

(5) The number of d-electrons in Fe^{2+} (Z = 26) is not equal to the number of electrons in which of the following: → (6)

a) s-electrons in Mg (Z = 12) → (6)

b) p-electrons in Cl (Z = 17) → (11) ✓

~~c) d-electrons in Fe (Z = 26)~~ → (6)

d) p-electrons in Na (Z = 10) → (6)

Soln

Electronic configuration of Fe^{2+}

$Fe : Z = 26$

$Fe : 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

$= 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6, 4s^2$

$Fe^{2+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6, 4s^0$

$= [Ar] 3d^6 4s^0$

Number of d electrons in Fe^{2+} = (6)

∴ Mg — $1s^2, 2s^2 2p^6, 3s^2$

$Z = 12$

Total no. of s electrons = 6

Cl — $1s^2, 2s^2 2p^6, 3s^2 3p^5$

$Z = 17$

Total no. of p electrons = 11

Fe — $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6, 4s^2$

$Z = 26$

Total no. of d electrons = 6.

Na

$Z = 11$

$1s^2, 2s^2 2p^6, 3s^2$

Total p electrons = 6

Cl has 11 p electrons, which ≠ the number of 6 d electrons in Fe -

(18) An ion has 18 electrons in the outermost shell, it is -

a) Cu^+ b) Th^{4+}, Cs^+ d) K^+

Cu (29)   Th (90)   Cs (55)   K (19)

↓ Cu : 2, 8, 18, 1

Cu^+ = 2, 8, 18 → Cu^+ has 18 electrons in outermost shell → d, s

Th (90) = 2, 8, 18, 32, 18, 10, 2

Th_4^+ = 2, 8, 18, 32, 18, 8

Cs (55) = 2, 8, 18, 18, 8, 1 → 4s

Cs^+ = 2, 8, 18, 18, 8

K (19) = 2, 8, 8, 1 $K^{(+)}$: 2, 8, 8