BRASS TRACKS OF CHEMISTRY

VISHESH BANSAL

M.Sc. Chemistry

TIET PATIALA (Punjab)

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Stories Matter

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PRELUDE

The ocean of knowledge is so deep and aggressive that the person who dives might have two phases. He might sink or reach his destination safely. Its correctly said, **“I’m having boats on my mind so I made one out of them... the boat; one that may either perish or hoist on the same ground. We are similar to that boat, in the maze of our life... we may either be like a captain getting through the hurdles or another captain that gets stuck between those hurdles and relinquishes, not knowing the destination is just beyond those high waves. Henceforth what we become is the mindset build by us”**

This attempt is to drive the reader to the destination of success in the world of chemistry. There are several aspects in chemistry like several streams and banks of ocean. This book is an attempt to serve this world of knowledge with a beautiful gift from my side with a prospective of making difficulties easily understood, rectified, and maintaining a streamlined flow of study in a well oriented direction.

Vishesh Bansal

REGARDS

I would like to extend my sincere gratitude to my family; my reputed institute TIET, and all my brothers and sisters for their invaluable contributions to this textbook. Their expertise, guidance, and support have greatly enriched the content and quality of this publication. Without their dedication and assistance, this textbook would not have been possible. This opportunity is the biggest achievement of my life. I have been very lucky to be a person to have such precious relations, be it my parents, teachers, friends, or siblings.

I am by heart thankful to my mother Dr. Artee Bansal, my father Dr. Vikram Bansal and my brother Aadik Bansal, who always supported me by his curiosity, patience and helping nature.

I express my heartfelt gratitude to my younger brother, Aadik Bansal, whose dedicated practical support, patience, and steady involvement played a vital role in shaping this book. His sincere efforts at every step provided a strong foundation and made many challenging parts easier.

Finally, I wish to express my deepest gratitude to my younger sister, Ashwika. Her curiosity, positivity, and gentle emotional strength remained a quiet yet powerful source of inspiration and balance throughout this journey.

Vishesh Bansal

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I take this opportunity to express my sincere gratitude to Mrs. Shikha Sharma, who was the first person to hold my hand in the astonishing world of chemistry. In her guidance I have completed my journey of graduation in chemistry. Her directions and support are like a light of knowledge, which let me grow up in a set direction in the field of chemistry.

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All the respected professors at Thapar Institute of Engendering and Technology, Patiala. Whose combined and competent guidance and expertise were invaluable throughout the writing process. Their insightful feedback and encouragement significantly shaped the content of this book.

Vishesh Bansal

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Director

FOREWORD

It is both a pleasure and a privilege to write a few introductory words for the book titled "Brass Tracks of Chemistry" authored by Mr. Vishesh Bansal. Chemistry, as a scientific discipline, has continually evolved through centuries of human curiosity, intellectual rigor, and experimental perseverance. Any sincere attempt to narrate this journey in a coherent and pedagogically meaningful manner deserves appreciation.

This first volume offers readers a thoughtful exploration of the conceptual foundations of science and the historical development of chemistry. Beginning with the philosophical question "What is Science," the author carefully guides the reader through the formative stages of chemical thought in "Precursors to Chemistry," and subsequently traces the intellectual evolution of the discipline in "Chemistry: The Root and Growth Process." The discussion on the "Element Classification Process" further highlights the remarkable human endeavor to organize the natural world into intelligible patterns, ultimately culminating in the periodic framework that lies at the heart of modern chemistry.

What makes this work particularly commendable is the author's independent scholarly effort in his own thinking and knowledge. Undertaking the preparation of a scientific text single-handedly, especially as a first edition and a first literary endeavor, reflects dedication, perseverance, and an admirable commitment to scientific education.

I hope that "Brass Tracks of Chemistry" will stimulate curiosity among students and provide a reflective perspective on how chemical knowledge has matured through systematic inquiry.

Such works play a valuable role in encouraging young minds to appreciate both the intellectual heritage and the evolving future of the chemical sciences.

I extend my best wishes to the author for this publication and for many more scholarly contributions in the years ahead.

Sudesh

(Sudesh Kumar Yadav)

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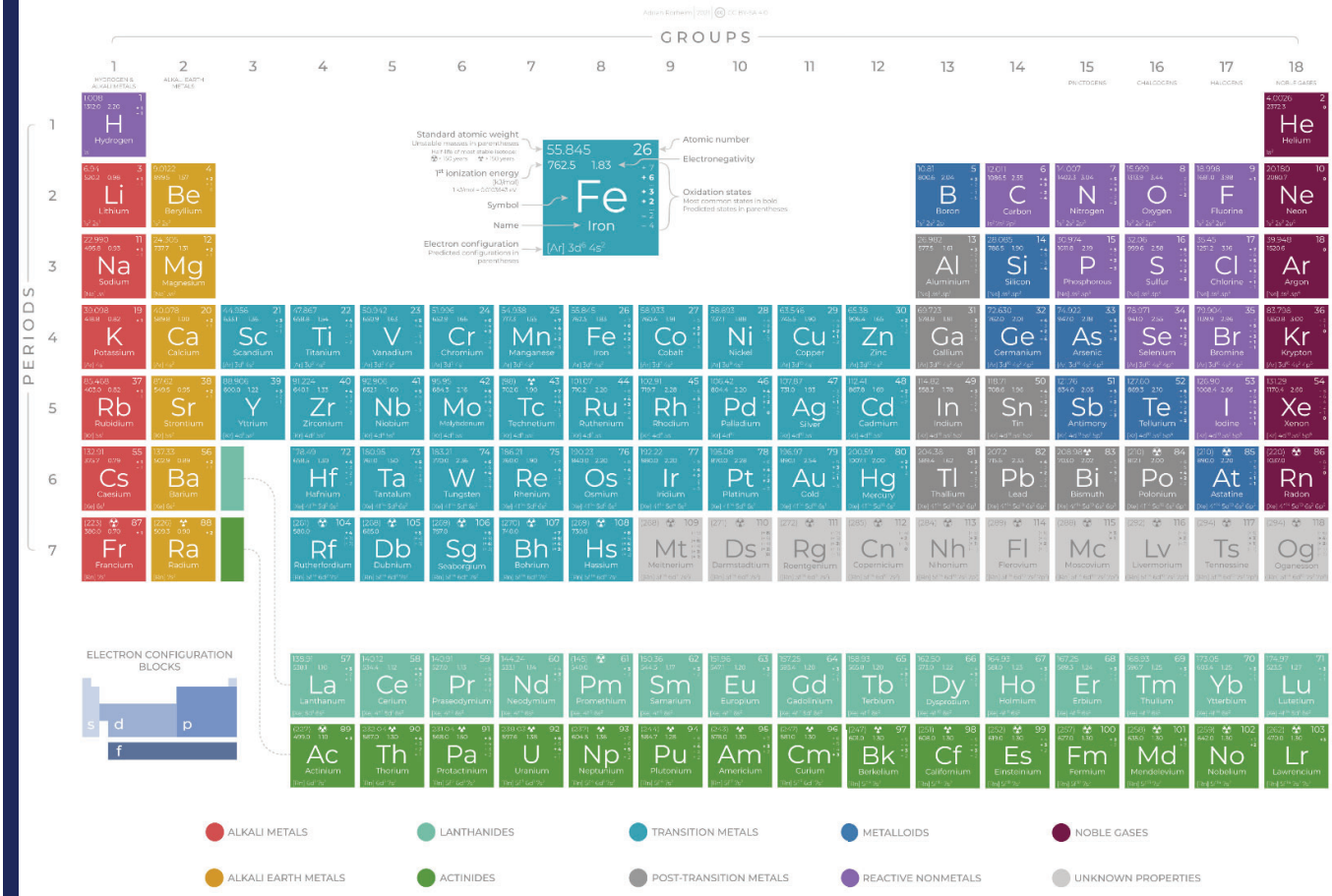

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I.

WHAT IS SCIENCE

Science is the study of processes and events that happen in nature, and summarising them in mathematical or theoretical statements. To do so, scientists follow the 'scientific method', which is a general method applied to observations in order to understand them easily.

Steps of this method include

1. Observation
2. Controlled Experiment
3. Analysis
    A. Qualitative Analysis
    B. Quantitative Analysis
4. Mathematical Modelling
5. Prediction
6. Verification/Falsification

THEORY: A scientific theory is an explanation of any naturally occurring event/phenomena, that has been tested repeatedly, and has been accepted despite criticism and scrutiny.

The fact it has withstood against such allegations proves it's reliability.

Sometimes a theory is experimentally proven under controlled conditions.

FACT: A basic statement of any observation.

A theory tries to explain a fact.

Fact	Theory
Things fall downwards when dropped.	Newton's theory of gravitation.

THEOREM: a theorem (in mathematics) is a logically proven statement which is used to prove other statements. The proof is logically made using other theorems and basic statements called "axioms". Example: the Pythagoras theorem. i.e. in a right-angled triangle, $base^2 + perpendicular^2 = hypotaneous^2$

LAW: It is the mathematical formulation of a theory that explains a fact example: 'newton's universal law of gravitation'. according to which,

$$F_G = \frac{Gm_1m_2}{r^2}$$

Associated Fact: there is a force of attraction between two bodies.

HYPOTHESIS: Hypothesis is in some way like a "theory", it's just not yet proven, neither experimentally nor logically using some other basic theories. It acts as the starting ground for further research. Note: an experiment for a hypothesis is not to prove the hypothesis true, just to make sure it can be true. Or in other words, an experiment for a hypothesis is to reject it, not completely accept it. Example: Prout's hypothesis.

PRINCIPLE: Principle is in some way a "law" which starts a chain of believes in the people of the field. Example: the uncertainty principle.

POSTULATE: A true statement which is believed to be true without any actual "proof". Sometimes interchangeable with "axiom" in science and mathematics. In science, a postulate is only acceptable if it leads to statements which further prove some natural phenomena with great agreement. Example: in science: postulates of the Bohr model of atom (these led to predictions which greatly agreed with observed things.), or in mathematics: $\boldsymbol{a = b \Rightarrow b = a}$

STATEMENT: A definition by a notable person regarding any subject. Example: the Clausius statement which states that: "heat does not flow spontaneously from a cool body to a hotter body. This statement is a direct result of the second law of thermodynamics, that is "energy tends to spread out".

COROLLARY: The direct consequence of a result. Example: the fact a lot of energy can be made from very less mass was *corollary* to the energy-mass relation made by Einstein, which was $E = mc^2$.

PROOF: A logical argument/algorithm (sequence of steps) which is used to come to the conclusion that any statement (mathematical or scientific) is true or not.

There is no final theory in science.

SCALES OF MEASUREMENT

A **scale of measurement** is a systematic way of assigning numbers or labels to a variable according to specific rules, so that its properties can be described and compared.

A **nominal scale** classifies data into categories without any order; in chemistry, examples include types of orbitals (s, p, d, f) or phases of matter.

An **ordinal scale** arranges data in a meaningful order but does not quantify the differences between them; for example, the Spectrochemical series ranks ligands by field strength without indicating how much stronger one is than another.

An **interval scale** has ordered values with meaningful differences but no true zero; for instance, temperature on the Celsius scale and values in the Electrochemical series allow comparison of differences but not ratios.

A **ratio scale** has all the properties of an interval scale along with a true zero, allowing meaningful ratios; examples in chemistry include mass, concentration, volume, and energy.

CONCLUSION: The type of scale depends on the meaning of zero and permitted operations, not on the scientific field.

The type of scale determines the mathematical operations and statistical methods that can be applied.

ON THE EXPERIMENTAL ORIGINS AND THEORETICAL FORMALIZATION OF SCIENTIFIC CONCEPTS

Theoretical frameworks in science do not arise in isolation; rather, they are the culmination of careful experimentation, critical observation, and sustained intellectual inquiry. The concepts encountered in theory are, in essence, distilled representations of prior experimental realities, formalized to provide coherence, predictive power, and deeper understanding. It is therefore natural that, while engaging with theoretical constructs, certain questions may emerge that appear unresolved or inaccessible within the immediate framework of the theory itself. Such questions often reflect the historical sequence of scientific development, wherein phenomena are first revealed through experiment and only subsequently interpreted through theory.

In this context, the interplay between experiment and theory assumes a deeper significance. As noted by **Albert Einstein**, ***"It is the theory which decides what we can observe,"*** while **Werner Heisenberg** reminds us that ***"What we observe is not nature itself, but nature exposed to our method of questioning."*** Together, these perspectives underscore that theory does not merely follow experiment, but also shapes the very manner in which experimental reality is perceived and understood, reflecting a dynamic and reciprocal relationship at the heart of scientific progress.

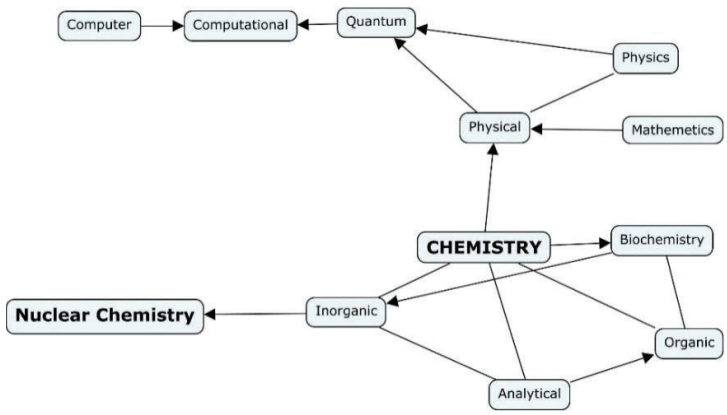
2.

PRECURSORS TO CHEMISTRY

ABSTRACT: The collection of all the basic definitions regarding all the concepts of all the other fields are included in the chapter. This chapter includes the meticulous study of the topics in branches of physics and mathematics. It also includes some concepts of literature used in the study of chemistry

CHEMISTRY- "The branch of science dealing with composition and properties of matter and the laws governing the effect of the physical and chemical changes on its composition and environment"

2A. DISCIPLINES OF CHEMISTRY



Chemistry is divided under different disciplines based on the prospect and directions of study. Mainly, it is classified under five major branches which are so much interconnected that without a detailed accounts of each, there's no clear distinction between them. As is depicted in the diagram it is clearly notable that the interconnections among the different fields of chemistry will be clear if we are able to understand the route of the journey. We will begin our journey of this beautiful world by learning some of the applications of the fields of mathematics and physics.

PHYSICAL CHEMISTRY: The branch of chemistry which deals with the application of the laws of physics on the atomic world. Physical chemistry hence deals with how changes in physical conditions, like temperature, pressure etc, effect substances and how they affect chemical reactions. Topics of study like thermodynamics fall under this field of chemistry.

INORGANIC CHEMISTRY: The chemistry of all the elements of the periodic table, explaining their physicochemical behaviour. Topics of study like chemical bonding fall under this field.

ORGANIC CHEMISTRY: The chemistry of bonding of carbon with elements like hydrogen, oxygen, nitrogen, halogens, silicon, sulphur is called organic chemistry provided hydrogen must be present in the compounds.

ORGANOMETALLIC CHEMISTRY: The chemistry of compounds showing a specific reaction sequence of oxidative addition, migratory insertion, ligand coordination, reductive elimination; with alteration of the oxidation state and coordination number of the metal and may or may not have bonds between carbon and metal in its initial phase.

NUCLEAR CHEMISTRY: The part of chemistry which deals with the study of nuclei and nuclear reactions using chemical methods.

BIOCHEMISTRY: Chemistry of biologically important compounds.

ENVIRONMENTAL CHEMISTRY: The chemistry of compounds affecting the environment.

MEDICINAL CHEMISTRY: The chemistry of medicinal compounds.

ANALYTICAL CHEMISTRY: chemistry dealing with the aspects of experimental environment, practical behaviour of compounds and the technicalities involved.

2B. THE BASIC PHYSICAL QUANTITIES

PHYSICAL QUANTITY: Any quantifiable characteristic of nature. Like the speed of a car. All physical quantities have some unit of measurement. Like km/h for speed. But there are basically seven physical quantities which have units that are called the base units. These quantities are those which are used to define all the other quantities in nature. In other words, these quantities are universally accepted to be used as the 'base' for all other units we come across.

Here we will be dealing with only six out of the seven fundamental quantities because luminous intensity has no examples in chemistry.

Sno.	Base quantity	Symbol	SI Units		Dimensions
			Name	Symbol	
1	Length	*L*	Metre	m	L
2	Mass	*M*	kilogram	kg	M
3	Time	t	second	s	T
4	Electric current	I	ampere	A	I
5	Thermodynamic temperature	*T*	kelvin	K	Θ
6	Amount of substance	n	mole	mol	N
7	Luminous intensity	I_v	candela	cd	J

Note: **kilogram** have lower case 'k'; **Not the UPPER CASE'K'.**

The unit of luminous intensity is candela with a symbol cd NOT Cd; Cd is the symbol of the element Cadmium with atomic number $Z = 48$.

The two more fundamental quantities are Plane angle and Solid angle which are included later on as Supplementary dimensionless quantities.

2C. LEXICON

Physical Property: The measurable quantities which describe the physical nature of a substance. Properties like the melting or boiling points of a substance are its physical properties.

Chemical Properties: The observable changes that describe the chemical nature (the chemical compositions or reactions towards other elements) of a substance. Like how burning paper leaves behind ash, but burning graphite leaves no residue.

2D. SOME PHYSICAL CONSTANTS

Some values which are important in measurement of many physical/chemical phenomena, are constant in magnitude independent of the way the experiment is conducted. Such values hold great importance in science. Some of these values important to chemistry are compiled here.

Name	**Symbol**	**Value**	**Units**
Avogadro's Constant	N_A	6.023×10^{23}	mol^{-1}
Bohr's Radius	a_0	5.29×10^{-11}	m
Boltzmann Constant	k_B	1.38×10^{-23}	JK^{-1}
		$8.617333262 \times 10^{-5}$	eVK^{-1}
Faraday's Constant	F	9.65×10^4 OR 96500	$Cmol^{-1} = F$

Gravitational Constant	G	6.67×10^{-11}	$m^3 s^{-2} kg^{-2}$ or $Nm^{-2} kg^{-2}$
Permeability Constant	m_0	1.26×10^{-6}	Hm^{-1}
Planck's Constant	h	6.626×10^{-34}	$J.s$
Rest Mass of Electron	m_e	$9.1 \times x10^{-31}$	Kg
		9.1×10^{-28}	g
Rest Mass of Neutron	m_n	1.675×10^{-27}	Kg
Rest Mass of Proton	m_p	$1.673 \times x10^{-27}$	Kg
Rydberg's Constant	R_H	$1.10 \times x10^7$ OR 109677	m^{-1}
Vacuum permeability	μ_0	$4\pi \times 10^{-7}$	Hm^{-1}
Vacuum permittivity	ε_0	$8.854 \times x10^{-12}$	Fm^{-1}
Charge on Electron/Proton	e	1.6×10^{-19}	C
		$4.803204712 \times 10^{-10}$	$statC(ESU, Fr)$
		$1.602176634 \times 10^{-20}$	$abC\ (EMU)$
Electron Magnetic Moment (Bohr's Magneton)	m_B	9.28×10^{-24}	JT^{-1}
Gravitational Acceleration	g	9.81	ms^{-2}
Speed of Light in Vacuum	c	$3 \times x10^8$	ms^{-1}
Electromagnetic moment	μ_e	-9.284×10^{-24}	JT^{-1}
Dirac's constant	$\hbar$	$1.054571596 \pm 0.000000078 \times 10^{-34}$	J. s
Gyromagnetic ratio of electron	γ_e	8.7954×10^{10}	Ckg^{-1}
Charge to mass ratio of electron	$\left(\frac{e}{m_e}\right)_{electron}$	1.82×10^{11}	
Charge to mass ratio of proton	$\left(\frac{e}{m_p}\right)_{proton}$	9.57×10^4	Cg^{-1}
Gas constant	R	0.0821	$LatmK^{-1}mol^{-1}$
			$dm^3 atmK^{-1}mol^{-1}$
		82.1	$cm^3 atmK^{-1}mol^{-1}$
		8.314	$JK^{-1}mol^{-1}$

		0.083	$barLmol^{-1}\ K^{-1}$
		8.314×10^7	$ergsK^{-1}mol^{-1}$
		62.397	$mmHg\ K^{-1}mol^{-1}$
g-factor of electron	g_e	2	
Euler's Constant	e	2.71828	
	e^0	1	
	e^{∞}	∞	
	$e^{-\infty}$	0	

NOTE: The value of the Gas constant R is the product of two universal constants; the Boltzmann Constant and the Avogadro's Constant given as $R = N_A \times k_B = 6.023 \times 10^{23} mol^{-1} \times 1.38 \times 10^{-23} JK^{-1} = 8.314 JK^{-1}mol^{-1}$.

For the expressions $e^x\ or\ \ln x\ or\ \log x$ the exponent or the value of $\boldsymbol{x}$ MUST BE A **Dimensionless** quantity.

2E. UNITS AND MEASUREMENTS ANALYSIS

The older conventional unit system have NO systematic relationships.

s.no.	Traditional Units
1	$1mile = 1760yards$
2	$1yard = 3feet$
3	$1foot = 12inch$
4	$1inch = 2.54cm$
5	$1cm = 10^{-2}m$

The universalization of the measurement systems is a very critical and crucial necessity for the study of any scientific discipline. This can be understood by the example of the unfortunate **Indian Airlines Flight 605** incident, which crashed due to the problem of units' understanding by pilots.

UNIT: The standard measurement of the physical quantities which is independent of natural phenomena. It should be of an appropriate size. It must easily reproducible. It should be defined with high accuracy without any confusion.

The modern system of units and measurement is metric system, i.e. the next higher or lower unit is brought by multiplication or division by ten. This is also a coherent system in which all the derived units are created by multiplication or division of single units. It is also a rational system with one unique unit for one type of quantity. The SI system is an example of the Ratio scale of measurement. It has easy practical applications. **SI system** stands for **"Système international d'unités".** It is **French**, meaning **"International System of Units."**. It is the **modern, globally accepted metric system** used in **science, engineering, and commerce**. Adopted officially in **1960** by the **General Conference on Weights and Measures (CGPM)**.

Another important measurement unit in chemistry is Å (Ångström) which is 10^{-10} m. it is used as a measurement of length at atomic levels i.e. $1Å = 10^{-10}m$. It was named after **Anders Jonas Ångström.** His priceless contribution to the measurement system helped us to get a closer look to the atomic world. Ironically **Anders Jonas Ångström** was a **Physicist** and **Astronomer.** The conversion of units:

$smaller\ unit \xrightarrow{10^{-x}} larger\ unit$

$larger\ unit \xrightarrow{10^{+x}} smaller\ unit$

Anders Jonas Ångström
(13 August 1814-21 June

SNO	EXPONENT	PREFIX	SYMBOL	EXAMPLE
1	10^{-30}	quecto	q	$1qHz = 10^{-30}Hz$
2	10^{-27}	ronto	r	$1rHz = 10^{-27}Hz$
3	10^{-24}	Yocto	y	$1\ ym = 10^{-24}\ m$
4	10^{-21}	Zepto	z	$1\ zm = 10^{-21}\ m$
5	10^{-18}	Atto	a	$1\ am = 10^{-18}\ m$
6	10^{-15}	Femto	f	$1\ fm = 10 - 15\ m$
7	10^{-12}	**pico**	**p**	$\mathbf{1\ pm = 10^{-12}\ m}$
8	10^{-9}	**nano**	**n**	$\mathbf{1\ nm = 10^{-9}\ m}$
9	10^{-6}	**micro**	**μ**	$\mathbf{1\ \mu m = 10^{-6}\ m}$
10	10^{-3}	**milli**	**m**	$\mathbf{1\ mm = 10^{-3}\ m}$
11	10^{-2}	**Centi**	**c**	$\mathbf{1\ cm = 10^{-2}\ m}$
12	10^{-1}	Deci	d	$1\ dm = 10^{-1}\ m$
13	10^{0}		m	1m
14	10^{1}	Deca	da	$1\ dam = 10m$
15	10^{2}	Hecto	h	$1\ hm = 10^{2}\ m$
16	10^{3}	kilo	k	$1\ km = 10^{3}\ m$
17	10^{6}	mega	M	$1\ Mm = 10^{6}\ m$
18	10^{9}	giga	G	$1\ Gm = 10^{9}\ m$
19	10^{12}	tera	T	$1\ Tm = 10^{12}\ m$
20	10^{15}	Peta	P	$1\ Pm = 10^{15}\ m$
21	10^{18}	Exa	E	$1\ Em = 10^{18}\ m$
22	10^{21}	Zeta	Z	$1\ Zm = 10^{21}\ m$
23	10^{24}	yotta	Y	$1YHz = 10^{24}Hz$
24	10^{27}	ronna	R	$1RHz = 10^{27}Hz$
25	10^{30}	quetta	Q	$1QHz = 10^{30}Hz$

METRE: The path length travelled by light in vacuum, during a time interval of $\frac{1}{299792458}$ of one second.

KILOGRAM: it is defined by the Planck's constant.

SECOND: The second is the duration of 9192631770 periods of the radiation corresponding to the transition between the two hyperfine lines of the Caesium 133 $^{133}_{55}Cs$ atom at rest at 0K temperature.

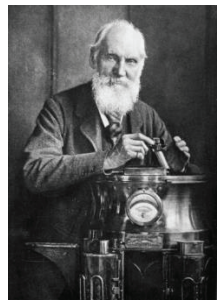
André Marie Ampère
(20 January 1775- 10 June 1836)

MOLE: The mole is the amount of a substance of a system which contain as many elementary entities as there are atoms in 0.012 kg of Carbon. 12.

AMPERE: The ampere is that constant current, which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross

section and placed 1 metre apart in vacuum, would produce a force of $2 \times 10^{-7} N$ in between them. It is named after André Marie Ampère.

KELVIN: The kelvin is the unit of thermodynamic temperature, corresponding to $\frac{1}{273.16}^{th}$ fraction of the thermodynamic temperature, of triple point of water with an isotopic composition of 0.0015576 moles of ${}^{2}_{1}H$ per mole of ${}^{1}_{1}H$, and 0.0003799 moles of moles of ${}^{17}_{6}O$ per mole of ${}^{16}_{6}O$, and 0.0020052 moles of moles of ${}^{18}_{6}O$ per mole of ${}^{16}_{6}O$. It is named after William Thomson, 1st Baron Kelvin.



William Thomson, 1st Baron Kelvin (26 June 1824- 17 December 1907)

CANDELA: The candela is the luminous intensity in a given direction, of a source that emits monochromatic radiation of frequency $540 \times 10^{12} Hz$ and has a radiant intensity in that direction of $\frac{1}{683}$watt per steradian.

In chemistry, some specific physical quantities and units are studied. There are two standardized conditions of temperature and pressure.

Lorenzo Romano Amedeo Carlo Avogadro di Quaregna e di Cerreto (9 Augst 1776-9 July 1856)

STP (Standard Temperature and Pressure): $T = 273K = 0℃$; $P = 1atm$.

NTP (Normal Temperature and Pressure): $T = 298K = 25℃$; $P = 1atm$.

CAPITALIZATION RULES AND NAMING CONVENTIONS FOR SI UNITS AND PREFIXES (INCLUDING UNITS NAMED AFTER SCIENTISTS)

SI symbols are case-sensitive: large prefixes use capitals, small prefixes use lowercase, unit symbols named after persons are capitalized, prefixes attach directly to units, and symbols are never pluralized or punctuated.

1. SI prefix symbols are case-sensitive. Prefix symbols must be written exactly as defined; a change in case changes the meaning.
2. Large multiples use CAPITAL letters. **kilo** is the **only SI prefix for a multiple** that uses a **lowercase symbol**.
3. Small multiples use lowercase letters.
4. Unit symbols named after people are capitalized. If an SI unit is named after a person, its symbol begins with a capital letter, but the **unit's name itself is lowercase.**
5. Unit symbols NOT named after people are lowercase.

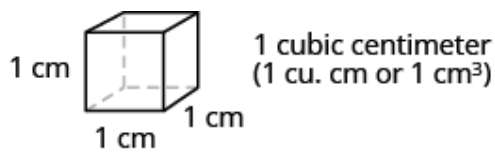
S.no	UNIT NAME	SYMBOL	SCIENTIST
1	newton	N	Isaac Newton
2	joule	J	James Prescott Joule
3	pascal	Pa	Blaise Pascal
4	watt	W	James Watt
5	volt	V	Alessandro Volta
6	coulomb	C	Charles-Augustin de Coulomb
7	ohm	Ω	Georg Simon Ohm
8	farad	F	Michael Faraday
9	henry	H	Joseph Henry
10	tesla	T	Nikola Tesla

11	weber	Wb	Wilhelm Eduard Weber
12	hertz	Hz	Heinrich Hertz
13	becquerel	Bq	Henri Becquerel
14	gray	Gy	Louis Harold Gray
15	sievert	Sv	Rolf Sievert
16	kelvin	K	William Thomson, 1st Baron Kelvin
17	ampere	A	André Marie Ampère
18	poise	P	Jean Léonard Marie Poiseuille
19	Dalton	Da	John Dalton
20	rutherford	Rd	Ernest Rutherford
21	curie	Ci	Marie Curie and Pierre Curie
22	franklin	Fr	Benjamin Franklin
23	Degree Celsius	°C	Anders Celsius
24	Degree Fahrenheit	°F	Daniel Gabriel Fahrenheit
25	Degree Rømer	°Rø	Ole Christensen Rømer
26	Degree Réaumur	°Re	René Antoine Ferchault de Réaumur
27	Degree Rankine	°R	William John Macquorn Rankine

6. Prefix + unit form a single symbol. **A prefix is attached directly to the unit symbol with no space and no change in case.**
7. Prefix symbols are never used alone
8. Symbols are NEVER pluralized and NEVER take a full stop.

VOLUME

It is the amount of three-dimensional space occupied by an object or enclosed by a surface. It is a measure of the size of a three-dimensional region and is expressed in cubic units, such as cubic meters (m^3) or (cm^3) or cc.



The different units of volume are related as:

$1ml = 1cm^3$

$1L = 1dm^3 = 10^3ml = 10^3cm^3$

$1m^3 = 10^3L = 10^6ml$

$1JPa^{-1} = 1m^3$

m^3 is the SI unit of volume. Litre is the laboratory unit of chemical measurement.

At STP 1 mole of all gases occupies 22.4L Volume

MASS

It is a measure of the amount of matter in a substance. It is mass which is affected by force.

Some of the important conversions of the units of mass is

$1g = 10^3mg$

$1kg = 10^3g$

$1lb = 453.592g$

$1g = 2.84 \times 10^{-3}lb.$

$1kg = 2.20lb$

$1amu = 1.66 \times 10^{-27}kg = 1.66 \times 10^{-24}g = 931MeV = 931 \times 10^6eV$

LENGTH

The SI unit of length is metre.

$1km = 10^3m = 10^5cm = 10^6mm$

$1\mu m = 10^{-6}m = 10^{-4}cm$

$1nm = 10^{-9}m = 10^{-7}cm$

$1Å = 10^{-10}m = 10^{-8}cm$

$1pm = 10^{-12}m = 10^{-10}cm$

$1fm = 10^{-15}m = 10^{-13}cm$

The symbol," refer to the unit inch.

$1" = 2.54cm$

$1cm = 0.39"$

SPEED AND ACCELERATION

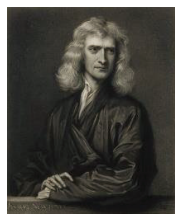
Speed is the time rate of change of length travelled by a body. And acceleration is the time rate of change in the speed of a body.

$v = \frac{ds}{dt}$ and $a = \frac{dv}{dt} = \frac{d^2s}{dt^2}$

FORCE

Force is a push or a pull. Applying force on a body means to produce an acceleration on it.
The unit of force is newton named after Sir Issac Newton. 1N force implies 1m/s^2 acceleration produced on it.

$1N = 1kgms^{-2}$
$1dyne = 1gcms^{-2}$
$1N = 10^5 dyne$



Sir Isaac Newton
(1643 – 1727)

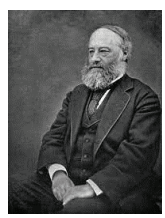
ENERGY

Energy is the ability to do work. Work is the measure of how much force was able to produce how much displacement in a body.

$W = E = \vec{F}.\vec{s} = |\vec{F}||\vec{s}| \cos\theta$

The SI unit of energy is joule named after James Prescott Joule. 1J energy, if does work of 1J on a body, means that the force doing the work was able to displace the object by 1m (given this force was also of 1N).

$1J = 1Pam^3 = 1Nm = 1kgm^2s^{-2}$
$1J = 10^7 ergs$
$1erg = 1gcm^2s^{-2}$
$1\ Cal\ =\ 4.184\ J$
$1Latm = 101.325J$
$1eV = 1.66 \times 10^{-19}J$
$1eV = 96.485kJmol^{-1}$



James Prescott Joule
(24 December 1818-11 October 1889)

PRESSURE

Pressure is the amount of force per unit area. It is measure of how much force is spread out on a body. SI unit of pressure is pascal. 1Pa pressure implies 1N of force on an area of 1m^2 $\left(P = \frac{F}{A}\right)$. Named after Blaise Pascal.

Pressure has great applications in hydraulic systems, which can seemingly increase force manifold. But the energy transferred is bound to remain same.

$1\text{atm} = 1.01325 \times 10^5\text{Pa} = 101.325\text{kPa} = 1.01\text{bar} = 76\text{cmHg}$
$= 760\text{mmHg} = 760\text{torr}$
$1bar = 10^5\text{Pa};\ 1Pa = 1Jm^{-3}$

Blaise Pascal
(19 June 1623-19 August 1662)

POWER

Power is the time rate of work done on a body by a force. Or in other words, the time rate of energy gained/lost by a machine/system.
The unit of Power is Watt named after James Watt who gave the term Power in 18th century. 1W power means a change in 1J per second.

James Watt
19 January 1736-
25 August 1819

COULUMB

It is a measure of the 'amount of charge'. Named after Charles Augustin de Coulomb

Form	Equals
1C	$2.9979 \times 10^9 statC = 2.9979 \times 10^9 esu = 2.9979 \times 10^9 Fr$
	$0.1 abC = 0.1 abcoulomb = 0.1 EMU$
1abC	$10C = 3 \times 10^{10} statC = 3 \times 10^{10} esu = 3 \times 10^{10} Fr$
1statC	$1Fr = 1esu = 3.33564 \times 10^{-10} C$
	$3.33564 \times 10^{-11} abC = 3.33564 \times 10^{-11} abcoulomb = 3.33564 \times 10^{-11} EMU$

1C charge is that amount of charge which travels through a cross section of a conductor, which is carrying 1amp current, measured over 1sec. $1C = 1As$.
There are a lot of units to consider. A concise table is given:
NOTE: The cgs unit of charge is known as esu (electrostatic unit) or statC (stat coulomb) OR Fr (franklin) named after Benjamin Franklin.

Charles Augustin de Coulomb
(14 June 1736-23 Augst 1806)

VOLTAGE

It is measured at a point. Voltage at a point is hence defined as 'that amount of energy spend per unit test charge (test charge is a theoretical, infinitesimally small positive charge and mass) in order to bring it from infinity (conventionally defined to be at potential of 0V) at very low speeds (so we don't increase overall energy as kinetic energy)'. $1V = 1J/C$.
Another important definition of voltage is that much energy spent in moving a unit charge (+1C) under the influence of a uniform 1N/C electric field by a displacement of 1m.

Alessandro Giuseppe Antonio
Anastasio Volta
(18 February 1745-5 March 1827)

Voltage difference between two points is the difference of the voltages at those points. And the voltage difference is the amount of energy spent in moving a unit positive charge from one of these points to the other.
Physically, it can be imagined to be a measure of how much charge is present at a point.
Named after Alessandro Giuseppe Antonio Anastasio Volta.
An important use of these definitions is in the use of defining the 'electron-Volt', which becomes much important when studying atomic structure.
The electron-Volt is a derived unit of energy, which is defined as the energy change in moving an electron by a voltage difference of $1eV = 1.6 \times 10^{-19} J = 1.6 \times 10^{-19} C \times 1V$.
Mathematical expressions in chemistry need not always be memorized; they can often be reconstructed by considering the units of the quantities involved, since dimensional consistency inherently constrains the permissible form of any valid relationship.

Blaise Pascal
(19 June 1623-
19 August 1662)

2F. PASCAL'S TRIANGLE

Blaise Pascal in the year 1654 devised a method to determine the values of $\binom{n}{r}$. This method uses a tool known as Pascal Triangle. Pascal Triangle is a triangular arrangement of numbers which are generated within the

matrix only with the help of existing numbers already present in the matrix using some rules. These numbers can be used as values of $\binom{n}{r}$.

In this section we will understand:

The method of constructing a Pascal Triangle.

Method of using the numbers in Pascal Triangle as values of $\binom{n}{r}$.

METHOD OF CONSTRUCTION OF PASCAL TRIANGLE

Note that a Lower Triangular Matrix is one in which n^{th} row contains n columns (or elements). for example, first row contains one element, second row contain two elements, third row contain three elements…. and so on……. for example,

*

* *

* * *

A Pascal Triangle is a Lower Triangular Matrix in which the numbers (or values) occupying different positions are determined by the following formula:

$$x_{i,1} = x_{i,i} = 1 \; \forall \; i$$

$$x_{i,j} = x_{(i-1),j} + x_{(i-1),(j-1)} : i > 2, 2 \leq j \leq (i-1)$$

where i is row number and j is column number.

This formula can be explained in simple language with the help of two rules as:

rule 1: the first and last number in each row is 1.

in the light of this rule, first two rows are fully defined as:

1

1 1

(Because these first two rows contain one and two elements respectively and these elements are all 1 being first and last elements of the rows)

From third row onward, the inner elements are calculated as follows:

rule 2: from third row onward, every inner element of a row is the sum of the element exactly above it (in the upper row) and the element to the left of that element (in the same upper row). (note that first and last element of every row are fixed to be 1 by using rule number one). Here is a ten row Pascal Triangle constructed using these two rules:

1

1 1

1 2 1

1 3 3 1

1 4 6 4 1

1 5 10 10 5 1

This is a very beautiful scheme using which we can construct the Pascal Triangle of any size.

METHOD OF USING THE NUMBERS IN PASCAL TRIANGLE AS VALUES OF $\binom{n}{r}$.

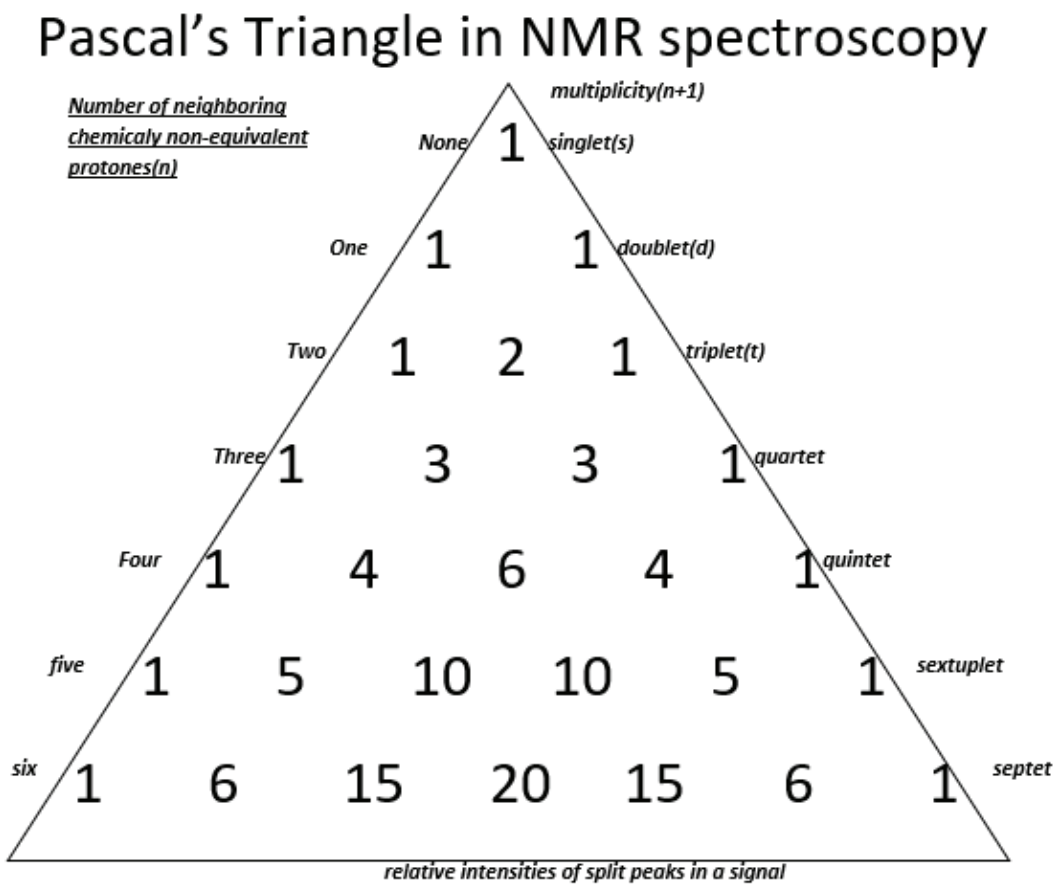
Now, we show how this triangle can be used to find out the values of $\binom{n}{r}$:

take n as row number and r as column number of the triangle and pick the value present at the designated location.

[Caution: Start counting row number (top to bottom) and column number (left to right) from zero.]

using this method, now we show what will be the value of $\binom{5}{2}$:

Here take row number as 5 and column number as 2. so, from the Pascal Triangle, the sixth row (start counting from zero number) and third column (start counting from zero number) is 10. So $\binom{5}{2} = 10$



COMBINATIONS

It is basically the number of ways to select 'r' things from a larger group of 'n' things, in the case when order of choosing does not matter. Like picking up 3 fruits from a bag of 5 unique ones. In this case, it does not matter how we pick up these fruits. Only thing that matters is that we pick up different fruits. Hence here, the number of ways to do so would be 10.

$$^{n}C_{r} = \frac{n!}{r!\,(n-r)!} = \frac{5!}{3! \times 2!} = 10$$

The combinatorial formula of all possible combinations of electronic microstates is used in the form

$$\Omega_{nl}\binom{4l+2}{N_{nl}} = \frac{(4l+2)!}{N_{nl}!\,[(4l+2)-N_{nl}]!}$$

Total angles in a geometry with n_{ATOMS} side atoms or ligands is given by

$$N_{\theta_{n_{ATOMS}}} = \frac{n_{ATOMS}!}{2!\,(n_{ATOMS}-2)!}$$

2F. GREEK ALPHABETS IN SCIENCE

There are several Greek symbols used to denote many physical quantities in both physics and chemistry. The meanings of each alphabet in all three fields are different and will be encountered with time. BLANK SPACES ARE LEFT TO SIGNIFY **"NO VALUE."**

English		Greek			
Upper Case	Lower Case	Upper Case	Lower Case	Name	Relations
A	a	A	α	Alpha	A
B	b	B	β	Beeta	B
C	c	Γ	γ	Gamma	G
D	d	Δ	δ	Delta	D

E	e	E	ε/ϵ	Epsilon	E
F	f	Z	ζ	Zeta	Z
G	g	H	η	Eta	E
H	h	Θ	θ/ϑ	Theta	T
I	i	I	ι	Iota	I
J	j	K	κ	Kappa	K
K	k	Λ	λ	Lambda	L
L	l	M	μ	Mu	M
M	m	N	ν	Nu	N
N	n	Ξ	ξ	Xi	
O	o	O	ο	Omicron	O
P	p	Π	π	Pi	P
Q	q	P	ρ	Rho	R
R	r	Σ	σ/ς	Sigma	S
S	s	T	τ	Tou	T
T	t	Y	υ	Upsilon	
U	u	Φ	ϕ/φ	Phi	
V	v	X	χ	Chi	
W	w	Ψ	ψ	Psi	
X	x	Ω	ω	Omega	
Y	y				
Z	z				

There are some Greek alphabets with two forms and the mathematical symbols that are very confusing and intermixed if not taken care of, these include the symbol:

Alpha (α) is a Greek alphabet but ∝ (proportion) is just a mathematical symbol as in

$x \propto y$ **NOT** $x \alpha y$.

Epsilon (ε/ϵ) is a Greek alphabet but ∈ (belongs to) is just a mathematical symbol as in

$1 \in \mathbb{N}$ **NOT** $1 \epsilon \mathbb{N}$.

Sigma (σ/ς) Theta (θ/ϑ) and Zeta (ζ) are different Greek alphabets in their alternative forms. Union (∪) is a mathematical symbol but Upsilon (υ) is a rarely used Greek alphabet. The RED coloured forms are not or rarely use in chemistry or physics.

LATIN MULTIPLICATIVE ADJECTIVES AND THEIR DERIVED SPECTROSCOPIC TERMS

The Latin origin, English translations and the usage in chemistry of some counting systems is explained through this table. Number before the 'signal peaks' denote that only a single signal contains that much number of peaks after splitting and the split signal is named as the terms listed in the 'Chemistry' column. These are used in the branch of spectroscopy called NMR (Nuclear Magnetic Resonance Spectroscopy).

Number	Latin	English	Chemistry	Meaning
1	Singulus	Single	Singlet	One signal peak
2	Duplus	Double	Doublet	Two signal peaks
3	Triplus	Triple	Triplet	Three signal peaks
4	Quadruplus	Quadruple	Quartet	Four signal peaks
5	Quintuplus	Quintuple	Quintet	Five signal peaks
6	Sextuplus	Sextuple	Sextet	Six signal peaks
7	Septuplus	Septuple	Septet	Seven signal peaks
8	Octuplus	Octuple	Octet	Eight signal peaks

2G. FUNCTIONS AND THEIR PLOTS

ODD FUNCTIONS: A function whose graph is symmetric about the origin is called an odd function. $F(X) = -F(-X) \Rightarrow \int_{-a}^{a} f(x)dx = 0$

EVEN FUNCTIONS: A function whose graph is symmetric about the y-axes is called an even function. $F(X) = F(-X) \Rightarrow \int_{-a}^{a} f(x)dx = 2\int_{0}^{a} f(x)dx$

2H. LOGARITHMS AND SQUARE ROOTS

Equations like $a^b = c$ can be dealt with in two different ways. One where, the output is the base, 'a' i.e. (root) and the other where, the output is the power b (logarithm). To get a, b; we can follow up as follows

1. Take the 'b^{th}' root of c, and get a.
2. Take the logarithm of c to the base a and get b.

In chemistry, we mostly encounter logarithm to the base 10. A very common point of error for students is taking log to the base e (natural log). Keep in mind to take the base as 10. Given is the base 10 log of some important values, and square roots of some numbers.

LOGARITHMS	SQUARE ROOTS
$\log 2 = 0.3010$	$\sqrt{2} = 1.414$
$\log 3 = 0.4771$	$\sqrt{3} = 1.732$
$\log 5 = 0.6989$	$\sqrt{5} = 2.236$
$\log 7 = 0.845$	$\sqrt{7} = 2.645$

2I. ERROR ANALYSIS

Measurements always have certain error or tolerance.

Errors may be of two types:

1. **Systematic error:** This is due to the system. The principle, instrument and observer make the system. Therefore, the Systematic errors are of three types.
   - **A.** Instrumental error: This is due to malfunctional instruments.
   - **B.** Technique error: Imperfect techniques.
   - **C.** Personal error: It is due to imperfect working of the person.

   We can rectify the systematic errors. These may be positive or negative in direction.
2. **Random error:** These are due to reasons beyond our control. It may be in any direction and cannot be rectified. Probability helps us to rectify Random errors.

PRECISION: The reproducibility of the data results of numerous measurements.

ACCURACY: It refers to the correctness of the data.

$Error = True\ value - Measured\ value$

The mean value is taken as true value

$$\bar{A} = \frac{\sum_{i=1}^{n} a_i}{n}$$

Now the accepted value is a

The absolute error $\Delta a_{ab} = \frac{\sum_{i=1}^{n} a_i}{n} - a$

The mean absolute error $\overline{\Delta a_{ab}} = \frac{\sum|\Delta a_{ab}|}{n}$

The percentage error/relative error

$$\Delta a_{\%} = \frac{\overline{\Delta a_{ab}}}{\bar{A}} \times 100 = \frac{\frac{\sum|\Delta a_{ab}|}{n}}{\frac{\sum_{i=1}^{n} a_i}{n}} \times 100 = \frac{\frac{\sum_{i=1}^{n} a_i}{n} - a}{a} \times 100$$

To write the measurements with error also called tolerance $a = \bar{A} \pm \overline{\Delta a_{ab}}$ or $a = \bar{A} \pm \Delta a_{\%}$

PROPAGATION OF ERRORS

Errors are always added up.

On addition or subtraction of two measurements, $a \pm b$ the value with tolerance is $a \pm b \pm (\Delta a + \Delta b)$

On multiplication or division of two measurements. Let the product $P = (a \pm \Delta a)(b \pm \Delta b)$, Let, $P = P \pm \Delta P$, Therefore, $\frac{\Delta P}{P} = \pm\left(\frac{\Delta a}{a} + \frac{\Delta b}{b}\right)$. All these are relative errors. Moreover, the percentage error of product is the sum of percentage errors of constituents.

$$\frac{\Delta P}{P} \times 100 = \pm\left(\frac{\Delta a}{a} \times 100 + \frac{\Delta b}{b} \times 100\right)$$

2J. SIGNIFICANT FIGURES & ERROR ANALYSIS: A CHEMISTRY PERSPECTIVE

Introduction In chemistry, precision and accuracy of measurements are as important as in physics. However, chemistry requires a distinct treatment of significant figures and error analysis because of its reliance on experimental techniques such as titrations, calorimetry, and spectroscopy. This module integrates both concepts in a chemistry-oriented way.

1. Significant Figures (SF)

Definition: Significant figures are the meaningful digits in a measured quantity that reflect its precision. These include all the Certain digits and the Uncertain digits.

Rules for Counting Significant Figures:

1. Non-zero digits are always significant (e.g., 345 g → 3 SF).
2. Zeros between non-zero digits are significant (e.g., 4005 mL → 4 SF).
3. Leading zeros are not significant (e.g., 0.0052 mol → 2 SF). In numbers with decimal point, the zeros to the **right** of the decimal point and to the **left** of the first nonzero digit are insignificant. Because they are just the placeholders for the specific position of the decimal point. E.g. 0.0024 have 2 S.F. The number in scientific notation explains the reason for 0.0024 have 2 S.F.; $0.0024 = 2.4 \times 10^{-2}$.
4. Trailing zeros after a decimal point are significant (e.g., 2.300 g → 4 SF).
5. Trailing zeros without a decimal point are ambiguous unless written in scientific notation.
6. In numbers with decimal point, the zeros after the decimal point are significant. E.g. 34.00 have 4 S.F.
7. if the number contains units; then the zeros after the last nonzero digit are significant. E.g. 20kg have 2 S.F.

Rules for Calculations:

• Multiplication/Division → Result has same SF as the least SF number.
• Addition/Subtraction → Result has same decimal places as least precise number.
• Logarithms → Number of SF in argument = number of decimal places in result.

2. Error Analysis

Errors are inevitable in chemical measurements. Understanding and minimizing them improves reliability of results.

Types of Errors:

• Systematic Errors: Consistent bias (e.g., burette with wrong calibration).
• Random Errors: Fluctuations due to uncontrolled factors (e.g., parallax).
• Gross Errors: Human mistakes (e.g., spilling a solution).

Absolute Error: $\Delta x_{absolute} = |x_{measured} - x_{true}|$

Relative Error: $\Delta x_{relative} = \frac{\Delta x_{absolute}}{x_{true}} \times 100\% = \frac{|x_{measured} - x_{true}|}{|x_{true}|} \times 100\%$

Propagation of Errors:

- Addition/Subtraction: Absolute errors add.
- Multiplication/Division: Relative errors add.
- Powers/Roots: Relative error multiplies by the power.

Chemistry Examples:

- Molarity calculation: 0.125 mol / 0.250 L = 0.500 M (3 SF).
- Titration: 24.35 mL – 23.15 mL = 1.20 mL (3 SF).
- Calorimetry: Error in ΔT propagates into calculation of $q = mC\Delta T$.

2K. VECTOR ALGEBRA

VECTOR: A quantity that has both size and direction.

SCALER: A physical quantity that is fully described by its magnitude (numerical value) and unit, without any, direction.

A. VECTOR ADDITION

The process is carried out when two vector quantities of similar nature are simultaneously acting on the body. Any vector can be redrawn anywhere in the space without alteration in both, its magnitude and direction

TRIANGLE LAW OF VECTOR ADDITION

If the two vectors are represented by two sides of a triangle, both in magnitude and direction, then, the resultant of the addition of these two vectors are represented, both in magnitude and direction, by third side of a triangle, taken in the opposite order.

Now by the application of the Pythagoras theorem the resultant $\vec{R}$ is given by

$$\overrightarrow{PS}^2 = \overrightarrow{PT}^2 + \overrightarrow{TS}^2$$

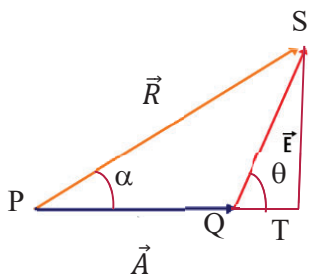
$$\overrightarrow{PS}^2 = \overrightarrow{(PQ + QT)}^2 + \overrightarrow{TS}^2 \qquad (1)$$

Now from ΔQST $\cos\theta = \frac{\overrightarrow{QT}}{\overrightarrow{QS}}$ (where θ is the angle between the directions of the two original vectors $\vec{A}$ and $\vec{E}$)

$$\overrightarrow{QT} = \overrightarrow{QS}\cos\theta = \vec{E}\cos\theta \qquad (2)$$

Now, $\sin\theta = \frac{\overrightarrow{ST}}{\overrightarrow{QS}}$

$$\overrightarrow{ST} = \overrightarrow{QS}\sin\theta = \vec{E}\sin\theta \qquad (3)$$



Combining the equations and solving

$$\vec{R}^2 = \left[|\vec{A}| + |\vec{E}|\cos\theta\right]^2 + |E|^2\sin^2\theta$$

$$|\vec{R}|^2 = |\vec{A}|^2 + |\vec{E}|^2\cos^2\theta + 2|\vec{A}||\vec{E}|\cos\theta + |\vec{E}|^2\sin^2\theta$$

$$|\vec{R}|^2 = |\vec{A}|^2 + |\vec{E}|^2[\cos^2\theta + \sin^2\theta] + 2|\vec{A}||\vec{E}|\cos\theta$$

$$|\vec{R}|^2 = |\vec{A}|^2 + |\vec{E}|^2 + 2|\vec{A}||\vec{E}|\cos\theta$$

$$|\vec{R}| = \sqrt{|\vec{A}|^2 + |\vec{E}|^2 + 2|\vec{A}||\vec{E}|\cos\theta}$$

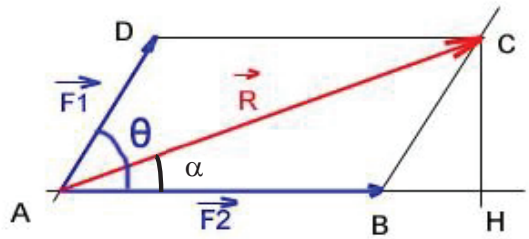
Where $|\vec{R}|$ is the magnitude of the vector called **Resultant;** its actually the result of addition of the two vectors.

$$\tan\alpha = \frac{|\vec{E}|\sin\theta}{|\vec{A}| + |\vec{E}|\cos\theta}$$

PARALLELOGRAM LAW OF VECTOR ADDITION

If the two vectors are represented by two adjacent sides of a parallelogram, both in magnitude and direction, then, the resultant of the addition of these two vectors are represented, both in magnitude and direction, by the diagonal of a parallelogram, passing through the same point

of contact of the tails of the two vectors. In a parallelogram ABCD, let two vectors $\overrightarrow{F_1}$ and $\overrightarrow{F_2}$ correspond to the two adjacent sides, AD and AB respectively of a parallelogram ABCD, both in magnitude and direction,
then,
The parallel sides of the parallelogram are equal i.e. $AB = CD = \overrightarrow{F_2}$ and similarly $AD = BC = \overrightarrow{F_1}$.



Now, the diagonal AC represent the vector R, which is the resultant of addition two vectors $\overrightarrow{F_1}$ and $\overrightarrow{F_2}$,
Now constructing a perpendiculars CH on AB at H,
Now by the application of the Pythagoras theorem in ΔAHC, we have,
$AH^2 + HC^2 = AC^2$
or $(AB + BH)^2 + HC^2 = AC^2$ (1)
or further in ΔBHC,
$\text{Cos}\,\theta = \frac{BH}{BC}$ (where θ is the angle between the directions of the two original vectors $\overrightarrow{F_1}$ and $\overrightarrow{F_2}$)
$BH = BC\,\text{Cos}\,\theta = \overrightarrow{F_1}\,\text{Cos}\,\theta$ (2)
$\text{Sin}\,\theta = \frac{CH}{BC}$
$CH = BC\,\text{Sin}\,\theta = |\overrightarrow{F_1}|\,\text{Sin}\,\theta$ (3)
Now combining (1), (2), (3), we have,
$\vec{R}^2 = \left[|\overrightarrow{F_2}| + |\overrightarrow{F_1}|\cos\theta\right]^2 + |\overrightarrow{F_1}|^2 \sin^2\theta$
$|\vec{R}|^2 = |\overrightarrow{F_2}|^2 + |\overrightarrow{F_1}|^2 \cos^2\theta + 2|\overrightarrow{F_1}||\overrightarrow{F_2}|\cos\theta + |\overrightarrow{F_2}|^2 \sin^2\theta$
$|\vec{R}|^2 = |\overrightarrow{F_2}|^2 + |\overrightarrow{F_1}|^2 [\cos^2\theta + \sin^2\theta] + 2|\overrightarrow{F_1}||\overrightarrow{F_2}|\cos\theta$
$|\vec{R}|^2 = |\overrightarrow{F_2}|^2 + |\overrightarrow{F_1}|^2 2|\overrightarrow{F_1}||\overrightarrow{F_2}|\cos\theta$
$|\vec{R}| = \sqrt{|\overrightarrow{F_2}|^2 + |\overrightarrow{F_1}|^2 2|\overrightarrow{F_1}||\overrightarrow{F_2}|\cos\theta}$
$\tan\alpha = \frac{|\overrightarrow{F_1}|\sin\theta}{|\overrightarrow{F_2}| + |\overrightarrow{F_1}|\cos\theta}$
Now for negative vector addition we have,
$|\vec{R}|^2 = |\vec{A}|^2 + |\vec{E}|^2 - 2|\vec{A}||\vec{E}|\cos\theta$

VECTOR COMPONENTS

Components of a vector signify the effect of that vector in the given directions.
Expressing any vectors in Unit vector form
$\vec{A} = \overrightarrow{a_x}\hat{\imath} + \overrightarrow{a_y}\hat{\jmath} + \overrightarrow{a_z}\hat{k}$
$\vec{B} = \overrightarrow{b_x}\hat{\imath} + \overrightarrow{b_y}\hat{\jmath} + \overrightarrow{b_z}\hat{k}$
$\vec{C} = \overrightarrow{c_x}\hat{\imath} + \overrightarrow{c_y}\hat{\jmath} + \overrightarrow{c_z}\hat{k}$
$\vec{R} = \vec{A} + \vec{B} + \vec{C} = (\boldsymbol{a_x + b_x + c_x})\hat{\imath} + (\boldsymbol{a_y + b_y + c_y})\hat{\jmath} + (\boldsymbol{a_z + b_z + c_z})\hat{k}$
$|\vec{R}| = |\vec{\boldsymbol{A}} + \vec{\boldsymbol{B}} + \vec{\boldsymbol{C}}| = \sqrt{(\boldsymbol{a_x + b_x + c_x})^2 + (\boldsymbol{a_y + b_y + c_y})^2 (\boldsymbol{a_z + b_z + c_z})^2}$
$\vec{A}_x$ and $\vec{A}_y$ are the rectangular components of $\vec{A}$ in x and y directions respectively. it implies $\vec{A}$ is **Resolved** into $\vec{A}_x$ and $\vec{A}_y$.
$\vec{A}_x = |\vec{A}_x|\cos\theta$

$\vec{A}_y = |\vec{A}_y| \sin\theta$

$\tan\alpha = \dfrac{|\vec{A}_y|}{|\vec{A}_x|}$

$$|\vec{R}| = |\vec{A} + \vec{B} + \vec{C}| = \sqrt{(a_x + b_x + c_x)^2 + (a_y + b_y + c_y)^2 (a_z + b_z + c_z)^2}$$

UNIT VECTOR

$$\hat{n} = \frac{\vec{n}}{|\vec{n}|}$$

PRODUCTS OF VECTOR QUANTITIES

There are two types of vector products:
1. DOT PRODUCT/ SCALER PRODUCT
2. CROSS PRODUCT/VECTOR PRODUCT

DOT PRODUCT

The dot product is the product of two vectors which provide a scaler quantity as the result of the product. The dot product of two vectors $\vec{A}$ and $\vec{B}$ is the product of the magnitude of the first vector $\vec{A}$ and the component of the second vector $\vec{B}$ in the direction of $\vec{A}$, i.e. $\vec{A}.\vec{B} = \text{AB}\cos\theta$. The dot product of two vectors gives scaler quantities. Example of a scalar product is Energy $W = E = \vec{F}.\vec{S} = |\vec{F}||\vec{S}|\cos\theta$

PROPERTIES OF DOT PRODUCT

1. The dot product of two equal (parallel) vectors is $\boldsymbol{A^2}$. The dot product of the unit vectors is dependent of the value of cosine of the angle between the two vectors. Therefore, we have,
   $\hat{\imath}.\hat{\imath} = \hat{\jmath}.\hat{\jmath} = \hat{k}.\hat{k} = 1$ $(\because\theta = 0^\circ \ \therefore \cos\theta = \cos 0^\circ = 1)$. The operation $\hat{\imath}.\hat{\imath} = \hat{\imath}^2$ is UNDEFINED!
2. $\vec{A}.\vec{B} = \vec{B}.\vec{A}$
3. The dot product of two perpendicular vectors is zero or if dot product of two vectors is zero then they are orthogonal. Therefore, we have, $\hat{\imath}.\hat{\jmath} = \hat{\jmath}.\hat{k} = \hat{k}.\hat{\imath} = 0$ $(\because\theta = 90^\circ \ \therefore \cos\theta = \cos 90^\circ = 1)$.

Therefore, For two vectors in terms of unit vectors $\hat{\imath}, \hat{\jmath}, \hat{k}$; then the multiplication is as:

$\vec{A}.\vec{B} = \text{AB}\cos\theta$

$\vec{A} = a_x\hat{\imath} + a_y\hat{\jmath} + a_z\hat{k}$

$\vec{B} = b_x\hat{\imath} + b_y\hat{\jmath} + b_z\hat{k}$

$\vec{A}.\vec{B} = |\vec{\text{A}}||\vec{\text{B}}|\cos\theta = (a_x\hat{\imath} + a_y\hat{\jmath} + a_z\hat{k}).(b_x\hat{\imath} + b_y\hat{\jmath} + b_z\hat{k}) = a_xb_x\hat{\imath} + a_yb_y\hat{\jmath} + a_zb_z\hat{k}$

$\cos\theta = \dfrac{\vec{A}.\vec{B}}{|\vec{\text{A}}||\vec{\text{B}}|}$

Volume is a Scaler quantity.

MATRICES

1. Matrix: A **matrix** is a rectangular arrangement of numbers, symbols, or functions, arranged in **Rows** and **Columns** and enclosed within **square brackets []**.

$$A = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix}$$

EXAMPLE

Identity Matrix: An **identity matrix** is a **square matrix** in which:

- All **diagonal elements = 1**
- All **non-diagonal elements = 0**

It is denoted by **I or E**.

$$I = E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

2. Order of a Matrix: The **order of a matrix** is defined by the **number of rows and number of columns** present in it.
If a matrix has **r rows** and **c columns**, its order is written as:

$$Order = r \times c$$

3. **Row:** A **row** is a **horizontal arrangement** of elements in a matrix.
4. **Column**: A **column** is a **vertical arrangement** of elements in a matrix.
5. **Character (Trace) of a Matrix χ_A:** The **character** (also called **trace**) of a **square matrix** is the **sum of its principal diagonal elements**. $\chi_A = \sum a_{ii}$.

6. **Rank of a Matrix**: The **rank of a matrix** is the **maximum number of linearly independent rows or columns** present in the matrix.

Before proceeding to the cross product, we need to know what we call a Determinant of a Matrix.

7. Determinant

The **determinant** is a **scalar quantity** associated with a **square matrix**. It provides important information about:

- Linear independence
- Invertibility of the matrix
- Solutions of simultaneous linear equations

EVALUATION OF DETERMINANT

1. General Form of a 3×3 Determinant

Let the matrix be:

$$|A| = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}$$

1. **Cofactor Expansion Rule**: The determinant of a **3×3 matrix** is evaluated by **expanding along any one row or any one column**.

(*Choose the row or column containing maximum zeros to simplify calculations.)

2. **Expansion Along First Row:** The expansion along the first row is done by multiplying the determinant of the square matrix formed by the remaining elements after hiding the first row and first column; with the element present at the junction point of the hidden row and column.

The signs while expanding are **fixed** as $(+)(-)(+)$

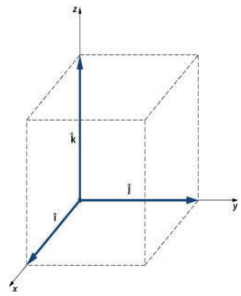
That is:

- First element → **positive**
- Second element → **negative**
- Third element → **positive**

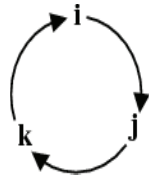
This comes from the factor $(-1)^{i+j}$

Therefore.

$$|A| = (-1)^{1+1} a_{11} \begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} + (-1)^{1+2} a_{12} \begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} + (-1)^{1+2} a_{13} \begin{vmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{vmatrix} = a_{11}(a_{22}a_{33} - a_{32}a_{23}) - a_{12}(a_{21}a_{33} - a_{23}a_{31}) + a_{13}(a_{21}a_{32} - a_{22}a_{31})$$



Cartesian unit



CROSS PRODUCT CYCLIC RULE

CROSS PRODUCT

The cross product is the product of two vectors which provide a vector quantity as the result of the product. The cross product of two vectors $\vec{A}$ and $\vec{B}$ is a single vector whose magnitude of the is the product of the magnitude of the two vectors and the sine of the angle between the two vectors $\vec{A}$ and $\vec{B}$.

$\vec{A} \times \vec{B} = |\vec{A}||\vec{B}| \sin\theta\, \hat{n}$ ($\hat{n}$ is a Unit vector)

$|\vec{A} \times \vec{B}| = |\vec{A}||\vec{B}| \sin\theta$

$\hat{\imath} \times \hat{\imath} = \hat{\jmath} \times \hat{\jmath} = \hat{k} \times \hat{k} = \vec{0}$ ($\because \theta = 0° \ \therefore \sin\theta = \sin 0° = 0$)

$\hat{\imath} \times \hat{\jmath} = \hat{k}$

$\hat{\jmath} \times \hat{k} = \hat{\imath}$

$\hat{k} \times \hat{\imath} = \hat{\jmath}$

CROSS PRODUCT CYCLIC RULE in Clockwise direction is Positive. Anticlockwise direction is negative.

The cross product can be calculated as:

$\vec{A} = \vec{A}_x\hat{\imath} + \vec{A}_y\hat{\jmath} + \vec{A}_z\hat{k}$

$\vec{B} = \vec{B}_x\hat{\imath} + \vec{B}_y\hat{\jmath} + \vec{B}_z\hat{k}$

$$\vec{A} \times \vec{B} = |\vec{A}||\vec{B}| \sin\theta\, \hat{n} = \begin{vmatrix} \hat{\imath} & \hat{\jmath} & \hat{k} \\ \vec{A}_x & \vec{A}_y & \vec{A}_z \\ \vec{B}_x & \vec{B}_y & \vec{B}_z \end{vmatrix} = \left[\hat{\imath}\begin{vmatrix} \vec{A}_y & \vec{A}_z \\ \vec{B}_y & \vec{B}_z \end{vmatrix} - \hat{\jmath}\begin{vmatrix} \vec{A}_x & \vec{A}_z \\ \vec{B}_x & \vec{B}_z \end{vmatrix} + \hat{k}\begin{vmatrix} \vec{A}_x & \vec{A}_y \\ \vec{B}_x & \vec{B}_y \end{vmatrix}\right]$$

$$= \left[\hat{\imath}\left(|\vec{A}_y||\vec{B}_z| - |\vec{A}_z||\vec{B}_y|\right) - \hat{\jmath}\left(|\vec{A}_x||\vec{B}_z| - |\vec{A}_z||\vec{B}_x|\right) + \hat{k}\left(|\vec{A}_x||\vec{B}_y| - |\vec{A}_y||\vec{B}_x|\right)\right]$$

The magnitude of the cross product can be given by

$$|\vec{A} \times \vec{B}| = \sqrt{\left(A_yB_z - A_zB_y\right)^2 + (A_zB_x - A_xB_z)^2 + \left(A_xB_y - A_yB_x\right)^2}$$

Two nonzero vectors are parallel if $\vec{A} \times \vec{B} = 0$.

$\otimes$ inward from the plane of rotation, clockwize and negative; • outward from the plane of rotation, anticlockwize and positive.

Further by combining the two laws we have,

$$|\vec{R}| = \sqrt{|\vec{A}|^2 + |\vec{E}|^2 + 2|\vec{A}||\vec{E}| \cos\theta}$$

$\vec{A}.\vec{E} = \mathrm{AE}\cos\theta$

$|\vec{A} \times \vec{B}| = -|\vec{B} \times \vec{A}|$

2L. MATRIX MULTIPLICATION

Matrix multiplication **AB is possible** when:

$(number\ of\ columns\ of\ A) = (number\ of\ rows\ of\ B)$ i.e. for a matric A of the order $r_A \times c_A$ and a matric B of the order $r_B \times c_B$;

$c_A = r_B$, the resultant matrix is of the order $r_A \times c_B$.

Row × Column Rule: Each element of the product matrix is obtained by:

Row of the first matrix × Column of the second matrix

That is:

- First row of A multiplies columns of B → first row of result
- Second row of A multiplies columns of B → second row of result
- Third row of A multiplies columns of B → third row of result.

The general form is:

$$A = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix}; B = \begin{bmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{bmatrix}$$

Therefore, each element of the resultant matrix is given by $C_{ij} = \sum_{k=1}^{n} a_{ik}b_{kj}$

$$AB = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix}\begin{bmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{bmatrix}$$

$$= \begin{bmatrix} (a_{11}b_{11} + a_{12}b_{21} + a_{13}b_{31}) & (a_{11}b_{12} + a_{12}b_{22} + a_{13}b_{32}) & (a_{11}b_{13} + a_{12}b_{23} + a_{13}b_{33}) \\ (a_{21}b_{11} + a_{22}b_{21} + a_{23}b_{31}) & (a_{21}b_{12} + a_{22}b_{22} + a_{23}b_{32}) & (a_{21}b_{13} + a_{22}b_{23} + a_{23}b_{33}) \\ (a_{31}b_{11} + a_{32}b_{21} + a_{33}b_{31}) & (a_{31}b_{12} + a_{32}b_{22} + a_{33}b_{32}) & (a_{31}b_{13} + a_{32}b_{23} + a_{33}b_{33}) \end{bmatrix}$$

2M. SCIENTIFIC NOTATION

ORIGIN AND EVOLUTION OF SCIENTIFIC NOTATION

Scientific notation, as used today, evolved gradually through centuries rather than being the product of a single inventor. It was developed to represent very large or very small numbers compactly, simplify calculations, compare magnitudes easily, and standardize scientific communication. Below is a concise historical timeline of the key contributors to scientific notation.

Archimedes (c. 287 BCE – c. 212 BCE): Used a form of powers of 10 to describe very large numbers in his work 'The Sand Reckoner'. He aimed to show that even enormous numbers could be logically represented using base 10.

Simon Stevin (1585): Introduced decimal fractions and promoted a decimal-based arithmetic system to simplify calculations. He laid the groundwork for base-10 scaling in mathematics and science.

John Napier (1614): Invented logarithms to simplify complex calculations, particularly in astronomy. His work brought the concept of exponents into common usage.

René Descartes (1637): Introduced modern exponential notation (e.g., x^3 for 'x cubed') in 'La Géométrie', providing a systematic way to express powers of 10.

Formalization in the 20th Century

The term 'scientific notation' became standardized in the early 20th century, especially with the rise of calculators and computers, which required a fixed format (e.g., 1.23E+06 for 1.23×10^6).

Purpose of Scientific Notation

To represent very large or very small numbers compactly
To simplify calculations using exponent rules
To compare magnitudes easily
To standardize scientific and engineering communication

Rules of Scientific Notation

Scientific notation is a way to write very large or very small numbers in the form $m \times 10^n$, where m is a number such that $1 \leq |m| < 10$ and n is an integer. This format helps in expressing numbers clearly and simplifies arithmetic operations.

Every number is written as $m \times 10^n$, where $1 \leq |m| < 10$ and n is an integer.

To convert a number to scientific notation, move the decimal point so that the resulting coefficient m is between 1 and 10.

Moving the decimal to the left makes n positive; moving it to the right makes n negative.

A negative number simply carries the negative sign in front of the coefficient.

Zero is usually written as 0.0×10^n (any n), but conventionally just 0.

In normalized form, the coefficient m always has exactly one non-zero digit before the decimal point.

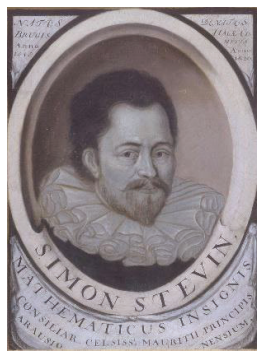
When multiplying numbers in scientific notation, multiply the coefficients and add the exponents.

When dividing, divide the coefficients and subtract the exponents.

To add or subtract, first express both numbers with the same exponent and then operate on the coefficients.

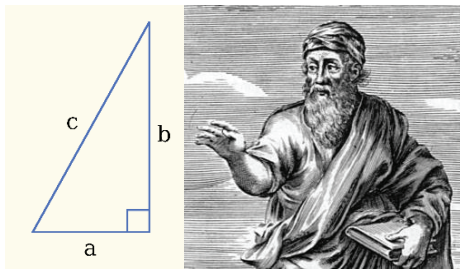
Examples

$4321.768 = 4.321768 \times 10^3$ (move decimal 3 places left)
$0.00000000751 = 7.51 \times 10^{-9}$ (move 9 places right)
$-53000 = -5.3 \times 10^4$ (negative number with proper format)
5.97×10^{24} (already in proper form).



Simon Stevin
(1548-1620)

2N. PYTHAGORUS THEORUM



PYTHAGORUS

Pythagorean theorem, states that the sum of the squares on the base (B) and perpendicular (P) sides of a right triangle is equal to the square on the hypotenuse (H) (the side opposite the right angle);

$H^2 = B^2 + P^2 \Rightarrow H = \sqrt{B^2 + P^2}$.

THE TRIGNOMETRIC RATIOS AND ANGLES

The six trigonometric ratios are defined as

$sin\theta = \left(\frac{P}{H}\right)$ $cos\theta = \left(\frac{B}{H}\right)$ $tan\theta = \left(\frac{P}{B}\right)$

$cosec\theta = \left(\frac{H}{P}\right)$ $sec\theta = \left(\frac{H}{B}\right)$ $cot\theta = \left(\frac{B}{P}\right)$

There are two different units for angles, namely degree and radian. There are related as $\pi rad = 180°$. The values of the sine and cosine functions at integral multiples of π, which frequently occur in phase-related chemical problems, are as:

$\sin n\pi = 0$ and $\cos n\pi = (-1)^n; n \in \mathbb{Z}.$

The corresponding values of the tangent, cotangent, secant, and cosecant functions at these angles are undefined, as their defining expressions involve division by zero.

2O. COMPLEX NUMBERS

Many chemical phenomena, particularly in quantum mechanics and spectroscopy, involve oscillations, waves, and phase relationships. Describing such behaviour using only real numbers is often inconvenient. Complex numbers provide a compact and efficient mathematical language for representing oscillatory and wave-like phenomena, and are therefore widely used in chemical theory.

The number system that has the form of ι (iota) $\iota = \sqrt{-1}$ is known as the imaginary number system. The number system that has the form of ι (iota) $\iota = \sqrt{-1}$ along with the real part is known as the complex number system. A complex number is written as $\mathbb{C} = \pm a \pm \imath b$ where $a, b \in \mathbb{R}$. The complex conjugate is defined as $\mathbb{C}_1 = \pm a \pm \imath b \Rightarrow \mathbb{C}_1^* = \pm a \mp \imath b$. The product $\mathbb{C}_1\mathbb{C}_1^* = a^2 - b^2$ is always real and non-negative, a property that is essential in chemistry, since physically measurable quantities must be real.

Leonhard Euler (15 April 1707- 18 September 1783)

$\iota = \sqrt{-1} \Rightarrow \iota^2 = -1$

Every real number is complex number.

Purely real numbers have the imaginary part equal to zero, and vice versa.

ιb = bι (NOT the prefix bi-).

$\iota^n = \begin{cases} -1; n \in even\ numbers \\ -\iota; n \in odd\ numbers \end{cases}$

To represent oscillations and phase in a mathematically compact form, trigonometric functions are conveniently expressed using complex exponentials. The fundamental relation connecting trigonometric and exponential functions is given by Euler's formula $e^{\iota\theta} = \cos\theta + \iota \sin\theta$. Using this relation, the trigonometric functions may be written in exponential form as

A. $\sin\theta = \frac{e^{\iota\theta} - e^{\iota\theta}}{2\iota}$ **B.** $\cos\theta = \frac{e^{\iota\theta} + e^{\iota\theta}}{2}$ C. $\tan\theta = \frac{e^{\iota\theta} - e^{\iota\theta}}{\iota\left(e^{\iota\theta} + e^{\iota\theta}\right)}$ **D.** $\csc\theta = \frac{2\iota}{e^{\iota\theta} - e^{\iota\theta}}$ **E.** $\sec\theta = \frac{2}{e^{\iota\theta} + e^{\iota\theta}}$ **F.** $\mathbf{cot\,\theta} = \frac{\iota\left(e^{\iota\theta} + e^{\iota\theta}\right)}{e^{\iota\theta} - e^{\iota\theta}}$

CONDITIONS FOR THE EXACT DIFFERENTIALS

A differential is called exact if for $\boldsymbol{z = f(x, y)}$, the integral depends only on the initial and final states, not on the path.

Now for $\boldsymbol{z = f(x, y)}$

Its total differential is $\boldsymbol{dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy}$

Let $\boldsymbol{M = \left(\frac{\partial z}{\partial x}\right)_y}$; $\boldsymbol{N = \left(\frac{\partial z}{\partial y}\right)_x}$ $\boldsymbol{dy}$

$\boldsymbol{\Rightarrow dz = Mdx + Ndy}$

For the above expression to be an exact differential

$\boldsymbol{\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} \Rightarrow \left[\frac{\partial}{\partial y}\left(\left(\frac{\partial z}{\partial x}\right)_y\right)\right]_x \left[\frac{\partial}{\partial x}\left(\left(\frac{\partial z}{\partial y}\right)_x\right)\right]_y}$ (Clairaut's theorem)

The equality of the mixed partial derivatives follows from Clairaut's theorem of multivariable calculus, proposed by Alexis Claude Clairaut in 1740. It forms the mathematical basis for many thermodynamic relations used in chemistry. In thermodynamics, exact differentials correspond to **state functions** such as U, H, G, S, A. whereas quantities such as heat (q) and work (w) are **path-dependent** and represented by inexact differentials. These conditions are a bases of the thermodynamic relations such as $dU = TdS - PdV$

At this point we are present at the exact depth to which we need to sink in with regards to the knowledge and understanding of the prerequisites required from the peripheral disciplines.

Alexis Claude Clairaut (13 May 1713-17 May 1765)

3

CHEMISTRY: THE ROOT AND GROWTH PROCESS

ABSTRACT: This chapter covers all the historical account of the atomic structure from the Dalton's atomic theory to the quantum mechanical model of the atom. The time period of 1661-1932 is being encompassed in the chapter.

Democritus
(460–370 B.C.E.)

3A. ANCIENT PHILOSOPHY OF ATOMISM

Atomism is a natural philosophy centralised to the idea that the physical universe is composed of fundamental indivisible microscopic particles. Since 450 B.C. the idea of an atom was proposed by some Greek and Indian philosophers. These include some prominent Greek figures like, Leucippus, Democritus (460–370 B.C.E.) and Epicurus (341–270 B.C.E.). There was one ancient Indian natural scientist and philosopher **Kaṇāda**; who worked on the ideology of atomism. He gave his ideology in the Sanskrit text called 'Kaṇādasutra'.

Epicurus
(341–270 B.C.E.)

3B. DALTON'S ATOMIC THEORY

Our story begins with the emergence of the first modern scientific explanation about the composition of matter and the concept of 'Atom' (the word 'atom' comes from Greek word '*atomos*', meaning uncuttable). Which was the first scientific approach towards the structure of the atom; and was pioneered by John Dalton in year 1807-1808. John Dalton (6 September 1766-27 July 1844) was an English Chemist, Physicist and Meteorologist. His Contributions in Chemistry were the base for most of future discoveries. The most Important one of them was his atomic model. He is sometimes referred to as the **Father of The Modern Atomic Theory.** Dalton's atomic theory was one of the first theories that came out regarding how or what an atom was and looked like. He gave this theory in 1807-1808, when he published 'A New System of Chemical Philosophy' in 1808. In this work he used "the ultimate particles of all homogeneous bodies are perfectly alike in weight, figure, etc. In other words, every particle of water is like every other particle of water, every particle of hydrogen is like every other particle of hydrogen, etc." It was based on some postulates and experimental laws.

JOHN DALTON
(6 September 1766-27 July 1844)

3C. POSTULATES

Dalton's Atomic Theory is Based on 6 major postulates.

1. All Matter is composed of unique but specific types of indivisible tiny particles called *'ATOMS'*.

2. Atoms of two different elements are different in mass and size and atoms of same elements are similar in mass and size.
3. Atom cannot be created or destroyed (Law of Conservation of mass)
4. Atoms are the Fundamental Units of Matter that take part in Chemical Reactions.
5. Atoms of Different elements may combine to produce molecules or compounds.
6. Atom of same elements may combine in different whole number ratio to make different compounds

The atomic theory successfully explained the two laws of chemical combination. i.e.
1. Law of Conservation of Mass
2. Law of Constant Proportions

Dalton was the first person to point out the distinction between the 'fundamental particles' of 'Elements' called 'ATOMS' and those of 'Compounds' called 'MOLECULES'.

THE TERMINOLOGY

MATTER: Anything that occupies space and has mass.

ELEMENT: It's the smallest unit of matter which combines to form matter in the macro world. It's that smallest unit of matter that is composed of a unique type of atoms and cannot be further decomposed into smaller units.

COMPOUND: The different substances formed by the combination of different elements.

The terms 'Element' and 'Compound' were first coined by Robert Boyle in 1661.

Robert Alexander Boyle
(5 February 1627- 10 January 1692)

LIMITATIONS OF DALTON'S ATOMIC THEORY

The concept of indivisibility of atom was not true due to the discovery of three fundamental sub atomic particles i.e. Electron, proton and neutron. The concept that atoms of same element have same mass was also false due to the discovery of Isotopes. The concept that atoms of different elements are different in all aspects was discarded by the discovery of Isobars. The concept that atoms combine in simple whole number ratios was contradicted in complex organic molecules such as sugars (sucrose) e.g.

$C_{12}H_{22}O_{11}$

The theory fails to explain the existence of allotropes e.g. coal, graphite and diamond.

John Dalton also gave his laws but he was unsuccessful in corelating in his theory to these laws which were:

Law of Multiple Proportions

Law of Partial Pressure

DALTON'S OTHER CONTRIBUTIONS

Dalton also gave some symbols for elements known at his time. These symbols were implied in writing the chemical equations. There were some special names for these 20 elements.

THE OLD AND MODERN NAMES OF THE ELEMENTS OF DALTON'S ERA

S. NO.	ATOMIC NUMBER	OLD NAME	TODAY'S SYMBOLS	TODAY'S NAMES
1	1	HYDROGEN	H	HYDROGEN
2	6	CARBON	C	CARBON

3	7	AZOTE	N	NITROGEN
4	8	OXYGEN	O	OXYGEN
5	11	SODA	Na	SODIUM
6	12	MAGNESIA	Mg	MAGNISIUM
7	15	PHOSPHORUS	P	PHOSPHORUS
8	16	SULFUR	S	SULPHER
9	19	POTASH	K	POTASSIUM
10	20	LIME	Ca	CALCIUM
11	26	IRON	Fe	IRON
12	29	COPPER	Cu	COPPER
13	30	ZINC	Zn	ZINC
14	38	STROTIAN	Sr	STRONTIUM
15	47	SILVER	Ag	SILVER
16	56	BARYTES	Ba	BARIUM
17	78	PLATINA	Pt	PLATINUM
18	79	GOLD	Au	GOLD
19	80	MERCURY	Hg	MERCURY
20	82	LEAD	Pb	LEAD

These names were continued until a new system of representation was not introduced by Jons Jakob Berzelius in 1803. In this system the element's name was abbreviated in two latter symbols example Au for Gold etc. some elements were given some special names. Names also tell us the geographical distribution of elements.

3D. THE LATIN AND MODERN ENGLISH NAMES OF THE ELEMENTS

The use of Latin in scientific nomenclature reflects the need for a universal, stable, and non-evolving linguistic system for identifying elements and compounds across all languages and regions. In chemistry, this tradition is preserved through standardized element names and symbols, where each element is assigned a globally accepted name and abbreviation that ensures clarity and consistency in scientific communication. This system eliminates ambiguity that could arise from regional or common names and allows chemists worldwide to refer to the same substance without linguistic barriers. The nomenclature is also historically rooted in classical language conventions used during the formative development of modern chemistry, which established a structured framework that continues to support precise classification, documentation, and exchange of chemical knowledge across disciplines. As emphasized in his reform of chemical notation (1813–1814), Jöns Jacob Berzelius advocated that chemical symbols must be simple, systematic, and universally applicable for scientific use. This principle aligns with the broader scientific ethos of evidence-based validation, famously captured in the Latin motto of the Royal Society, ***"Nullius in verba"*** ("take nobody's word for it"), which underscores the commitment to verification, clarity, and universally reliable scientific standards.

Jöns Jacob Berzelius (20 Augst 1779-7 Augst 1848)

S. No.	ATOMIC NUMBER	SYMBOL	LATIN NAME	ENGLISH NAME
1	11	Na	Natrium	Sodium
2	19	K	Kalium	Potassium
3	26	Fe	Ferrum	Iron
4	29	Cu	Cuprum	Copper

5	47	Ag	Argentum	Silver
6	50	Sn	Stannum	Tin
7	51	Sb	Stibium	Antimony
8	74	W	Wolfrum	Tungsten
9	79	Au	Aurum	Gold
10	80	Hg	Hydrargyrum	Mercury
11	82	Pb	Plumbum	Lead

Due to irregularities in the ways of naming elements, a need was felt to make things universal and systematic. To ensure a single convention was agreed upon worldwide in naming of elements (and other chemistry concepts), the IUPAC was setup.

Hence, Dalton was the first to give a scientific explanation of the atom. But there were some properties that Dalton's theory failed to explain. Hence, a need was felt for a new model, so, the next attempt was made by Joseph John Thomson who introduced the atomic model sometimes called the "Plum-Pudding Model" or the "Watermelon-Seed Model", in 1904. The discovery of the first sub-atomic particles i.e. the electron, and the discovery of a spontaneous decay of atoms leads to this model. The story takes a twist at this point. Three major scientists come in the picture to solve the mystery of this spontaneous decay of atoms. We will first learn the contributions by the three pioneers before discussing any further development of the atomic structure.

Maria Salomea Sklodowska Curie (7 November 1867- 4 July 1934)

The Human Behind the Atomic Model

Marie Curie's discovery of radioactivity demonstrated that the atom is not a static or indivisible entity, but a structure containing immense internal energy. This insight played a crucial role in the development of modern atomic models. In July 1934, Marie Curie quietly departed from this world, leaving behind a scientific legacy that continues to guide chemistry, physics, and medicine. Her life stands as a reminder that the progress of science is often built upon patience, integrity, and silent sacrifice, devoted entirely to scientific work

In 1896 Antoine Henri Becquerel who was interested in phosphorescence (emission of light of a colour because of an exposure of an object to another coloured light); hence, he started attempting to find a connection between phosphorescence and the newly discovered X-rays by Wilhelm Conrad Röntgen who in late 1895, during the experiment, found that the Crookes tubes he had been using to study cathode rays emitted a new kind of invisible ray that was capable of penetrating through black paper. As Becquerel knew about X-rays, he thought that phosphorescent materials might emit penetrating X-ray-like radiation when illuminated by bright sunlight. For these experiments he had some phosphorescent materials including some uranium salts (which was actually potassium uranyl sulfate crystals, specifically potassium uranyl sulfate dihydrate $\boldsymbol{K_2UO_2(SO_4)_2.2H_2O}$). Throughout the first weeks of February, Becquerel layered photographic plates with coins etc, wrapped this setup in thick black paper, placed phosphorescent materials on top, and placed this whole thing in bright sun light for

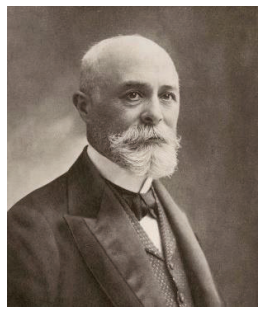
several hours. The developed plate showed shadows of the objects. On 24 February he reported his first results. However, the 26 and 27 February were dark and overcast during the day, so Becquerel left his layered plates in a dark cabinet for these days. He proceeded to develop the plates on 1 March and then made his astonishing discovery:

The object shadows were just as distinct when left in the dark as when exposed to sunlight. Both William Crookes and Becquerel's 18-year-old son, Jean Antoine Edmond Marie Becquerel, witnessed the discovery. It is an example of Serendipity (an unplanned fortunate discovery). By May 1896, after other experiments involving non-phosphorescent uranium salts, Becquerel arrived at the correct explanation, that the penetrating radiation were emitted by the uranium itself, without any need for excitation by an external energy source, i.e. spontaneously. There followed a period of intense research into radioactivity, including the determination that the element thorium is also radioactive and the discovery of additional radioactive elements polonium and radium by Maria Salomea Sklodowska Curie (Marie Curie) and her husband, Pierre Curie, whose collaborative work reflected equal dedication to scientific truth. Maria Salomea Sklodowska Curie coined the term 'radioactivity' in 1898 while studying uranium rays first observed by Henri Becquerel, reflecting, as described in *Madame Curie* by Eve Curie, a life lived for an idea. The 1903 Nobel Prize in Physics was awarded to Henri Becquerel, Pierre Curie, and Marie Curie for their pioneering research on radiation phenomenon discovered by Becquerel (radioactivity). A second Nobel Prize in Chemistry in 1911 was also awarded to Marie Curie due to her work on isolation of Radium as Radium-226 ($^{226}_{88}Ra$) and Polonium as Polonium-210 ($^{210}_{84}Po$) from pitchblende (Uraninite). These isotopes are formed by the natural decay of uranium-238 $^{238}_{92}U$.

Pierre Curie (15 May 1859-19 April 1906)

The Experimental Mind Behind Radioactivity

Pierre Curie's pioneering work on magnetism, crystallography, and radiation laid essential experimental foundations for the study of radioactivity. His precise measurements and insistence on scientific rigor strongly supported the early understanding of atomic structure and energy. Pierre Curie's life reflects the quiet strength of experimental science; were careful observation and integrity guide discovery.



Antoine Henri Becquerel
(15 December 1852-25 August 1908)

To summarize the discussion, we can say that the discovery of spontaneous radioactivity by Henri Becquerel and its systematic investigation by Marie and Pierre Curie revealed that atoms possess internal sources of enormous energy, contradicting the idea of atoms as stable, uniform entities proposed in early models. These findings led Rutherford to locate this activity in a small, dense nucleus, forming the nuclear model of the atom. Bohr later introduced quantum postulates to explain the stability of this nuclear atom. The work of Irène and Frédéric Joliot-Curie further confirmed the nuclear nature of atoms by demonstrating artificial radioactivity. Radioactivity forced the nuclear atom into existence, while quantum mechanics explained how electrons behave around it. Marie Curie's discovery of new elements arose from a serendipitous observation: certain uranium minerals were more radioactive than uranium itself, a fact she alone recognized as evidence of unknown matter. The discovery of radioactivity by Becquerel and Curie demonstrated that

Alessandro Giuseppe Antonio Anastasio Volta
(18 February 1745-5 March 1827)

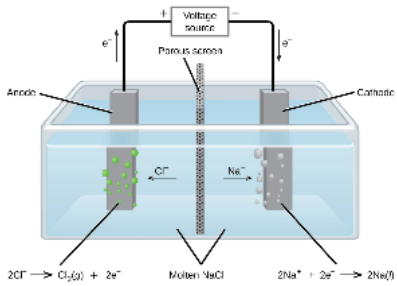
atoms possess internal structure and energy, thereby contradicting Dalton's indivisible atom and paving the way for development of modern atomic models, a progress often built upon patience and quiet perseverance. Concludingly, we can say that the discovery of spontaneous radioactivity by Henri Becquerel Marie Curie is widely known as **Founder of Radiochemistry.**

Julius Plücker
(16 June 1801-
22 May 1868)

Before discussing the further details of the discovery of the electron, there are some peculiar terms which we must know. These are as follows:

Electrode: A Conducting Rod which is used to conduct electricity across the electrolyte (compound that gets ionized in aqueous or molten state) The first electrodes were devised by **Alessandro Giuseppe Antonio Anastasio Volta** around the 1800s.

Cathode: A Negatively Charged Electrode. It attracts the Cation. This is the Electrode where Reduction occurs. Cathode is made from two Greek words, 'Kato' + 'Hodos'. 'Kato' means 'Down' and 'Hodos' means path. Hence, Cathode is the 'Down-Path' (Which attracts the ion that goes 'Down' i.e. the cation). The name can also be interpreted as the Electrode where the charge for the species goes 'down', i.e. decreases, becomes more negative (definition of reduction).

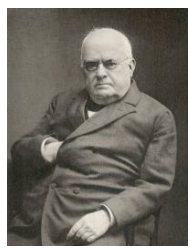


Anode: A Positively Charged Electrode. It attracts the Anion. This is the Electrode where Oxidation occurs. Anode is, again, made from two Greek words, '*Ano' + 'Hodos'*. *'Ano'* means 'up' and *'Hodos'* means path. Hence, Anode is the 'Up-Path' (Which attracts the ion that goes 'up' i.e. the anion) The name can also be interpreted as the Electrode where the charge for the species goes 'up', i.e. increases, becomes more positive.

EXAMPLE

NaCl in an aqueous medium with positive and negative electrodes and an applied voltage of around 4V causes the "electrolysis" (i.e. electrical disintegration into its constituents) of NaCl molecules to give Na metal and Cl_2 gas.

$$NaCl \xrightarrow{\approx 4V} Na + Cl_2$$



Johann Wilhelm Hittorf
(27 March 1824-
28 November 1914)

Discharge Tubes: A Discharge tube is just a packing of a low-pressure gas about $0.001\ atm$. It is equipped with two Electrodes maintained at a very high voltage of around 10,000V, at either end. In these circumstances, the gaseous atoms 'ionize', i.e. lose an electron, and the ionized gas is then manipulated into producing various results.

In our context, most of the "Discharge tubes" are "Crookes Tubes", named after English Physicist Sir William Crookes, who, with other scientists made these tubes in around 1869-1875.

The Terms "Anion", "Cation", "Anode", "Cathode" was Coined by William Whewell.

Sir William
Crookes
(17 June 1832-4
April 1919)

Phenomenon: Crookes Tubes, or the Discharge tubes, show the Phenomenon of cathode and anode rays and other processes.

Cathode Rays: Originate from Cathode (Negative Electrode) They are made up of Electrons (a discovery by J.J. Thomson). They accelerate towards the Anode (Positive Electrode) and hence produce Glow on the glass tube behind the Anode.

Cathode Ray: History

Julius Plucker, Jean Baptiste Perrin and Johann Wilhelm Hittorf were the first people to observe these rays in Crookes Tubes (Discharge tubes) in 1859, and later named by Eugen Goldstein as "Kathodenstrahlen" or "Cathode Rays".

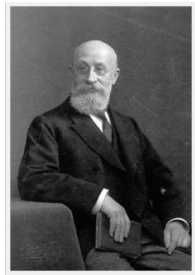
Jean Baptiste Perrin in 1895 conducted a crucial experiment in showing that cathode rays are composed of negatively charged particles what we now call electrons.

Benjamin Franklin (27 January 1706 – 17 April 1790)

CATHODE RAY: THEORY

The setup for a Cathode Ray is that there is a discharge tube with very low pressure, about $0.001\ atm \cong 10^{-4} atm$, and very high voltage, around 10,000V.

The residual gaseous atoms in the discharge tube get ionized (lose an electron) and the positive ions of the gas atoms (i.e. the gas atoms cations) get accelerated towards the Cathode and hit it at enough speed to knock off Electrons from it. These Electrons get accelerated towards the Anode (Positive Electrode) to cast a shadow on the glass walls. This beam of Electrons is the "Cathode Ray". These Rays get deflected in Electric and Magnetic fields, which was the base used by J.J. Thomson to calculate the charge to mass ratio of the Electron.

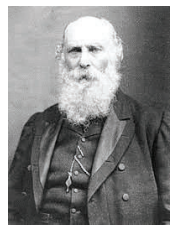


Eugen Goldstein (5 September 1850- 25 December 1930)

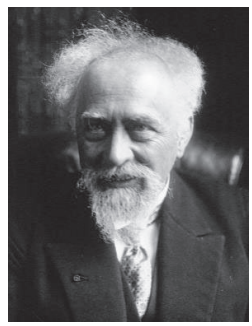
Note: Although Cathode Rays were discovered, it wasn't known what they were made up of. Some scientists thought they were composed of particles, some thought they were energy. This was cleared by J.J. Thomson, who carefully adjusting electric and magnetic fields in his Cathode Ray experiment, calculated the charge to mass ratio for the Cathode Rays proving they were made of a particle.

PERRIN'S EXPERIMENT

1. **Perrin Tube Experiment (1895):** Perrin constructed a modified Crookes tube (discharge tube) with a small metal cylinder (collector) placed inside the path of cathode rays. The cylinder was connected to an electroscope. In this experiment, he determined the nature of cathode rays.
2. **Experimental Setup:** Perrin used a modified Crookes tube. Two metal electrodes, the cathode (negative) and anode (positive), were fitted at opposite ends. When high voltage was applied, cathode rays were emitted from the cathode and travelled in straight lines toward the anode. Perrin placed a small metallic collector (a hollow cylinder) in the path of the rays and connected it to an electroscope.
3. **Working Principle:**
   1. When high voltage is applied, cathode rays (invisible beams) emerge from the cathode.
   2. The rays travel in straight lines toward the anode.
   3. Perrin placed a small metal collector in their path.
   4. On proceeding with the experiment, he noticed some sort of deflection in the connected electroscope.
   5. This proved that the ***charges are constituents of matter.***
4. **Observation:** When cathode rays struck the metal collector, the electroscope became negatively charged.



George Johnstone Stoney (15 February 1826-5 July 1911)



Jean Baptiste Perrin (30 September 1870- 17 April 1942)

5. **Conclusion**: This experiment confirmed that cathode rays carry negative electric charge. This discovery laid the foundation for J.J. Thomson's measurement of the charge-to-mass ratio of the electron in 1897 and ultimately the modern understanding of atomic structure.

IMPACT ON CHEMISTRY AND PHYSICS

1. Confirmed the particulate nature of cathode rays → atoms contain smaller, negatively charged components.

2. Laid groundwork for J.J. Thomson's discovery (1897): measurement of $\frac{e}{m}$ ratio identification of electron. The value he calculated turned out to be $\mathbf{1.758820 \times 10^{11} Ckg^{-1}}$. Millikan, in 1909 performed his oil drop experiment, which also supported this value.

3. Influence on Atomic Theory and Chemical Structure: Helped establish modern concepts of subatomic structure and bonding.

Eugene Goldstein discovered Canal rays **NOT protons** (a common confusion).

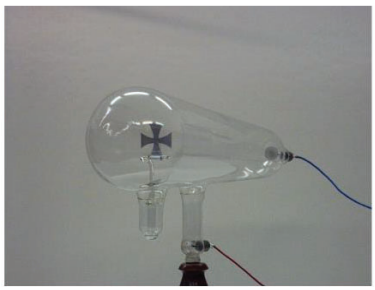
CHARACTERISTICS OF CATHODE RAYS

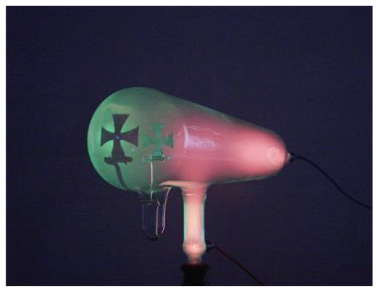
1. These travel in a straight line.
2. These are particles in nature.
3. They have mechanical properties.
4. The cathode rays show properties independent of the nature of the experimented gas and cathode material.
5. These are deflected by electric and magnetic fields in such a way as they contain the negatively charged particles. These particles were called electrons by George Johnstone Stoney. This deflection depends on the charge of the particles, mass of the particles and the electric field strength.
6. They have ionizing effects.
7. They produce fluorescence on glass, zinc sulphide, and photographic plates.
8. They can produce X-Rays when they strike a metallic surface called anticathode.

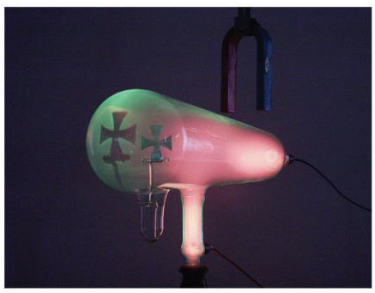
ANODE RAY: THEORY

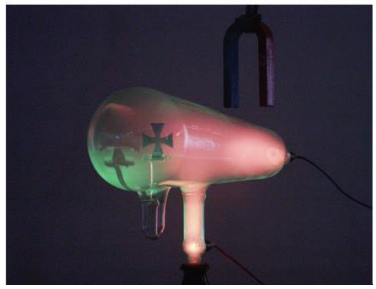
Appear to Originate from the Anode (Positive Electrode). They are made up of Nuclei of the residual gas atoms. They accelerate towards the Cathode (Negative Electrode) and hence produce Glow on the glass tube behind the Cathode. They were discovered by Eugen Goldstein in 1886. The setup is much like the Cathode Rays, consisting of a Discharge tube. A key difference is just that the Cathode in this Experiment is perforated. The mechanism for Anode Rays is that due to some natural processes, a few ions always exist in a gaseous sample. In an electric field, these ions are accelerated and hit other neutral atoms, knocking off their electrons. This makes Cations of the Gas atoms, which get accelerated towards the Cathode. In the Cathode Ray experiment, these cations upon hitting the Cathode caused Electrons to escape the Cathode, but here, because the Cathode was perforated, it caused the Cations to go behind the Cathode and hit the glass wall.

Note: Though Goldstein discovered the Anode Rays, it was not yet known what these rays were made up of. Because the charge to mass ratio for each different gas taken in the tube was different. So unlike Cathode Rays, where J.J. Thomson calculated the charge to mass ratio, here it was not possible, because scientists were not able to conclude that Anode rays were made up from a fundamental particle like Cathode Rays were. Calling these Rays "Anode Rays" may give the idea that they originate from the Anode. This is not the case. Because in "Cathode Rays", the Rays actually originated from the Cathode, but here, the Rays are NOT actually originating from the Anode, but are just an illusion for the same. They are actually just the residual gas atoms in the tube.

1. 

2. 

3. 

4. 

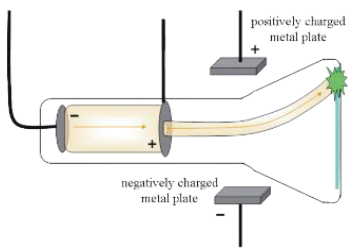
Images By Zátonyi Sándor, (ifj.) - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=10345950

CHARACTERISTICS OF ANODE RAYS

1. These travel in a straight line.
2. These are particles in nature.
3. They have mechanical properties.
4. They have heating properties.
5. These are attracted towards the negative terminal.
6. They have positive charge.

3E. THE DISCOVERY OF ELECTRON

Electron was theorized by George Johnstone Stoney in 1874 and discovered by Joseph John Thomson in 1897. In the late second half of the 19th century, the "cathode rays" were, though known, not still completely understood. Some physicists believed the rays were made of particles, while others, like Hertz and Goldstein believed they were a form of wave, or an electromagnetic radiation. This confusion was cleared in 1897 by J.J. Thomson, who calculated the charge by mass ($\frac{e}{m}$) ratio of the cathode rays. He also proved that the charges were particles, not waves. (Perrin's experiment was not enough to prove this); ending the debate and concluding the rays were made of negatively charged particles which he called "corpuscles", but were later named "electron" in accordance to Stoney's postulate of the existence of them. Joseph John Thomson got a noble prize in 1906 for the discovery of electron. Today we know about some properties of these small subatomic particles which have widespread universal applications, even in the modern era of quantum theory.



These properties are: -

Mass: $9.1 \times 10^{-31} kg \approx \frac{1}{1800} Da$

Charge: $-1\ e = -1.6 \times 10^{-19} C$

Symbol: The electron have two different symbols β^- or e^-, because in chemical and atomic processes the electron is usually denoted by the symbol e^-. However, in nuclear chemistry and nuclear physics the same particle is often represented by the symbol β^-. The difference in notation does not indicate a different particle but rather a difference in **origin and physical context**. The symbol e^-, refers to the ordinary electron present in atoms and involved in chemical bonding, ionization, and spectroscopic processes. In contrast, β^-, denotes an electron that is **emitted from the atomic nucleus during beta decay**, a radioactive process in which a neutron is transformed into a proton with the emission of an electron and an antineutrino. This classification of radiation into α, β, and γ types was first introduced by **Ernest Rutherford**, and later studies showed that β radiation consists of high-speed electrons. Thus, although β^- and e^-, represent the **same fundamental particle**, the two symbols are used to distinguish between electrons involved in **ordinary atomic processes** and those **produced in nuclear transformations**.

There are some of the universal applications that we can understand in depth due to our clear concepts about the existence of electron.

Reactions: They are the main reason behind Chemical reactions in General Chemistry.

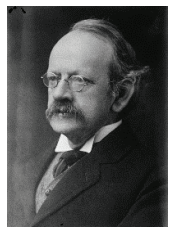
Nuclear Chemistry: Electron Capture and β-Decay could only by understood by discovery of Electron

ESR Spectra: This technique of Spectroscopy (which helps in determination of structures of compounds) is only due the presence of Electrons.

3F. THOMSON'S MODEL

PROPOSITION

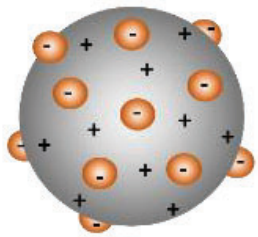
It was given in 1904 by Joseph John Thomson after he discovered electrons in 1897. This model was one of the first models which actually explained the structure of the atom. He made this model according to two key points of his time, i.e. the existence of the electron, and that the atom as a whole, was electrically neutral. It is also sometimes called the "Plum-Pudding Model" or the "Watermelon-Seed Model".



Joseph John Thomson (18 December 1856-30 August 1940)

THEORY

According to the Model, the atom is a Positively Charged *Sphere with Electrons Embedded in the Sphere, like Plums in a Christmas Pudding, or Seeds in a Watermelon.* At his time, Protons were not discovered, though Canal rays were. So, his Model did not account for the existence of the Proton, which was one of the Limitations of his model of the atom.



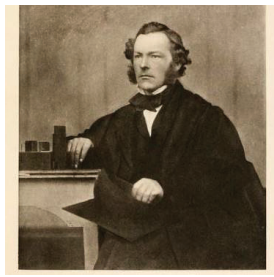
LIMITATIONS

Many future experiments, and the later discovery of the Proton disproved Thomson's Model of the atom and new models were later given, most notably by Ernest Rutherford. Thomson's model of the atom introduced the concept of internal structure by proposing the presence of electrons embedded in a positively charged sphere. Although it successfully explained some electrical properties of matter, subsequent experimental findings, particularly Rutherford's scattering experiment motivated the development of a more structured atomic model.

The Thomson's model could explain the electrical neutrality of atom.

At this point we are in a secure position to explore the story behind the 'Planetary model of atom.' Before going to the details of the same, which is also called the 'Rutherford's model of

atom', we first need to understand the details of the discovery of proton. Joseph John Thomson was awarded the 1906 Physics Nobel Prize for the discovery of electron.



Sir George Gabriel Stokes
(13 Augst 1819-1 February 1903)

3G. MILLIKAN'S OIL DROP EXPERIMENT

The discovery of the first subatomic particle, the electron was a turning point in the understanding of chemical properties of matter. The calculation of the $\frac{e}{m}$ ratio in 1897 by Joseph John Thomson, was the inspiration behind the Millikan's oil drop experiment. This experiment was first carried out by Robert Andrews Millikan and Harvey Fletcher in 1909 to calculate the elementary electric charge, for which Robert Andrews Millikan became the 1923 physics Nobel laureate. The Millikan's oil drop experiment was an attempt in support of the value $\frac{e}{m} = 1.758820 \times 10^{11} Ckg^{-1}$. The first attempt of this calculation was made by Sir Franz Arthur Friedrich Schuster in 1890 assuming the ionic nature of Cathode rays. The attempt of calculation of this ratio was also made by Joseph John Thomson, in an instrument which he called as parabola spectrograph.

NOTE: Today, an instrument that measures the mass-to-charge ratio of charged particles is called a mass spectrometer.

The experiment was to observe the tiny, vacuum pump oil droplets between the two parallel, horizontally placed, capacitor plates.

THE APPARATUS

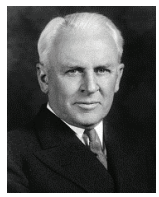
Sir William Watson

1. **Metal plates:** The experiment takes place in a chamber between two parallel metal plates with opposite charges. In the absence of the voltage the oil droplets fall undergo a freefall under the effect of gravity. In this state their terminal velocity is measured to calculate their mass. The top plate is typically positively charged and the bottom plate is negatively charged, creating an electric field that opposes gravity and can be adjusted to hold a negatively charged oil drop stationary. The lower plate is often grounded, while the upper plate receives the adjustable voltage. The electric field's effect on the oil droplet is balanced against the force of gravity to determine the droplet's charge. A variable DC voltage between 0 to 500V is applied across these plates to create an electric field. A digital voltmeter is connected to accurately measure the voltage applied between the plates. The upper plate has a small aperture to allow the oil mist to enter the space between the plates, as well as for light to enter and for a microscope to observe the droplets.
2. **Oil atomizer:** A sprayer releases fine droplets of oil into the chamber. These droplets can acquire a charge from the friction of the spraying process or by exposure to X-rays.
3. **Microscope or camera:** A microscope or a camera connected to a computer is used to view the tiny, individual oil droplets as they move between the plates.

Sir Franz Arthur Friedrich Schuster
(12 September 1851-14 October 1934)

OPERATING PRINCIPLE

1. **Sample injection:** The oil mist was sprayed between the two charged capacitor plates fitted in an air-filled chamber.
2. **Droplet suspension:** The voltage is adjusted until the upward electric force on a negatively charged drop balances the downward gravitational force.


Robert Andrews Millikan (22 March 1868-19 December 1953)

3. **Charge measurement:** By measuring the voltage required to suspend or control the drop's motion, and using its terminal velocity to determine its mass, the charge on the drop can be calculated.
4. **Elementary charge determination:** The experimenters found that the charges on all droplets were integer multiples of a fundamental unit of charge, which they identified as the charge of a single electron.
5. **Observation**: The motion of the oil droplets was observed under microscope.
6. **Procedure**: The droplets start to rise upwards due to the greater value of the upward electrical force $\vec{F}_E$ as per the Coulomb's law or Coulomb's inverse-square law which states that "The force of attraction or repulsion between two electric charges along a straight line is directly proportional to the product of the charges and inversely proportional to the square of the distance between them." Given by Charles-Augustin de Coulomb in 1785.


Harvey Fletcher (11 September 1884-23 July 1981)

$$\vec{F}_E = \frac{q_1 q_2}{4\pi\varepsilon_0 r^2} = k_e \frac{q_1 q_2}{r^2} = 9\times10^9 \frac{q_1 q_2}{r^2}$$

Where ($\varepsilon_0 = 8.85\times10^{-12} C^2 N^{-1} m^{-2}$)

This leads to the potential $V = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$ ($\because V = \vec{F}.\vec{s} \Rightarrow \int Fds$)

The gravitational force is given according to Newton's law of gravitation, which states that every particle in the universe attracts every other particle with a force that is directly proportional to the product of their masses and inversely proportional to the square of the distance between them. This can be expressed mathematically as:

$$\vec{F}_G = G\frac{m_1 m_2}{r^2} = 6.67\times10^{-11}\frac{m_1 m_2}{r^2}$$

The electrical force is very strong as compared to the gravitation as

$\vec{F}_E = \frac{q_1 q_2}{4\pi\varepsilon_0 r^2} = k_e \frac{q_1 q_2}{r^2} = 9\times10^9 \frac{q_1 q_2}{r^2} > \vec{F}_G = G\frac{m_1 m_2}{r^2} = 6.67\times10^{-11}\frac{m_1 m_2}{r^2}$.

The Coulomb's law in its vector form can be stated as follows:

$$\vec{F}_E = \frac{q_1 q_2(\overrightarrow{r_2} - \overrightarrow{r_1})}{4\pi\varepsilon_0|\overrightarrow{r_2} - \overrightarrow{r_1}|^3}$$

According to the principle of superposition the force on a single charge is vector sum of forces due to other charges around the charge under observation.

$$\overrightarrow{(F_E)_\iota} = \frac{1}{4\pi\varepsilon_0}\left[\sum_{j=1}^{n}\frac{q_i q_j(\overrightarrow{r_{ij}})}{|\overrightarrow{r_{ij}}|^3}\right]$$

The force between two charges is independent of the presence of any other charge.

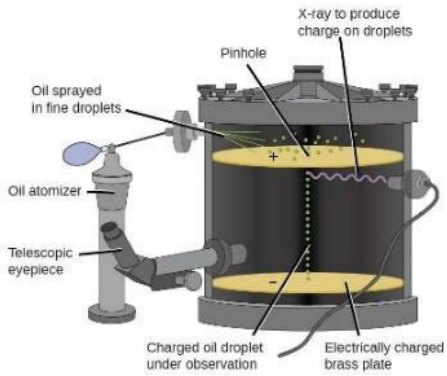
Now, this law can be derived similarly as the Newton's Universal law of Gravitation. But the proportionality constant must take the differences produced by the medium into consideration, therefore we have the above formula. The constant ε_0 is called Permittivity of free space (no medium). But Permittivity ε is a characteristic of the medium between two charges which decrease the force between them. This law is applicable on point charges. One drop is kept stuck in the middle by alternatively switching-on and off the voltage. This drop plays the role of the sample whose terminal velocity is calculated by using the Stokes' law given by Sir George Gabriel Stokes, (also known as Founder of Modern Fluid Dynamics; Pioneer of Optics and Light Polarization Studies) in 1851. It states that the viscous drag on a spherical object moving through a fluid depends on the speed, shape of the object and the viscosity coefficient of the fluid. The term viscous drag can be defined as follows:

When there is relative motion between the two adjacent layers of the fluid, a force of reaction develops to oppose the applied force responsible for the flow of the liquid. This opposing force is called the viscous drag. Viscous drag is a tangential force to the liquid layer. The property of fluid to develop this viscous drag is called viscosity. This force is governed by:

Newton's law of viscosity states that the shear stress in a fluid is directly proportional to the velocity gradient.

$$\vec{F}_u = -\eta A \frac{dv}{dl}$$

Where, η is the coefficient of viscosity and is defined as the force per unit area sufficient to create a unit of velocity gradient. It has a unit of Nsm^{-2}.



Oil drop	Charge in coulombs (C)
A	4.8×10^{-19} C
B	3.2×10^{-19} C
C	6.4×10^{-19} C
D	1.6×10^{-19} C
E	4.8×10^{-19} C

Stokes' law is mainly for a small spherical body which is moving in the given fluid media. However buoyant force appears by the virtue of the presence of a body in the given fluid media.

Now:

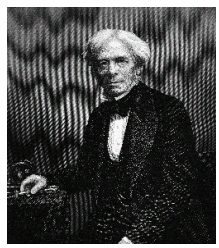
$\vec{F}_u = 6\pi\eta r v = 18.8\eta r v$ (the constant 6π is an experimental quantity)

Where: η: viscosity of the air

$\vec{F}_u$ is called the viscous drag

r: radius of the drop

v_a: terminal velocity of the drop in absence of the electric field.



Michael Faraday (22 September 1791- 25 August 1867)

Under applied force, the velocity of the drop in air keeps on increasing, increasing the viscous drag. After some time, a time comes when all these forces, the gravitational, buoyant and the viscous forces become equal. The increment of velocity stops and the velocity becomes uniform. This velocity is called the terminal velocity. The terminal velocity is the maximum velocity of the drop after the termination of acceleration at equilibrium of the gravitational and the viscous forces.

$$v_a = \frac{2r^2(\rho_{oil} - \rho_{air})g}{9\eta}$$

This value of the terminal velocity can be derived as follows:

$\vec{F}_u = 6\pi\eta r v$

The downward force of gravity experienced by an oil drop is its weight

$w = mg = V\rho_{oil}g$

The upward forces are the buoyancy and the viscous drag.

The buoyancy and viscous drag of the medium is: $V\rho_{air}g + 6\pi\eta r v_a$

Charles Augustin de Coulomb (14 June 1736-23 August 1806)

Now at equilibrium net fore becomes zero and acceleration is ceased.

$V\rho_{oil}g = V\rho_{air}g + 6\pi\eta r v_a$

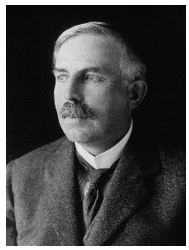
(v_a: terminal velocity of the drop in absence of the electric field)

Further

$v_a = \frac{mg}{6\pi\eta r} = \frac{w}{6\pi\eta r}$ (neglecting the buoyant force)

If we take the buoyant force in the calculation then the downward force will be decreased as:

The density of oil drop is ρ_{oil} and that of air is ρ_{air}



Ernest Rutherford
(30 August 1871- 19 October 1937)

The new value of the net force is $(\rho_{oil} - \rho_{air})\boldsymbol{V}g$ (V: volume)

$w = V(\rho_{oil} - \rho_{air})g$

$\Rightarrow v_a = \dfrac{(\rho_{oil} - \rho_{air})Vg}{6\pi\eta r}$

Now, the volume of the spherical drop is given by

$\boldsymbol{V} = \dfrac{4}{3}\pi r^3$

Substituting we get

$v_a = \dfrac{2r^2(\rho_{oil} - \rho_{air})g}{9\eta} = \dfrac{2.18r^2(\rho_{oil} - \rho_{air})g}{\eta}$

Where: w: weight of the oil droplet
r: radius of the oil droplet
g: acceleration due to gravity
ρ_{oil}: density of oil
ρ_{air}: density of air

Further at equilibrium

$\vec{F}_E = w$

After restarting the electric field, the electric force on the droplet

$\vec{F}_E = q\vec{E}$

Where: q: charge on the droplet
E: electric field strength of the capacitor

For parallel plates

$\vec{E} = \dfrac{V}{d}$

Where: V: Potential Difference
d: distance between the plates

by changing V, the drop attains a new terminal velocity v_p.

$w - qE = 6\pi\eta r v_p = \left|\dfrac{v_p}{v_a}\right| w$

The electric field was adjusted to suspend the drop in the centre. This leads to the **Charge: $\boldsymbol{1\,e = -1.6 \times 10^{-19} C}$.**

This experiment leads to the value of the fundamental electric charge e. This fundamental electric charge was used by the law of conservation of charge given by Sir William Watson in 1746 and Benjamin Franklin in 1747. This was proved by Michael Faraday in 1843. This law states that the total amount of electric charge in a closed system remains constant. The law can be mathematically written as $q = ne$

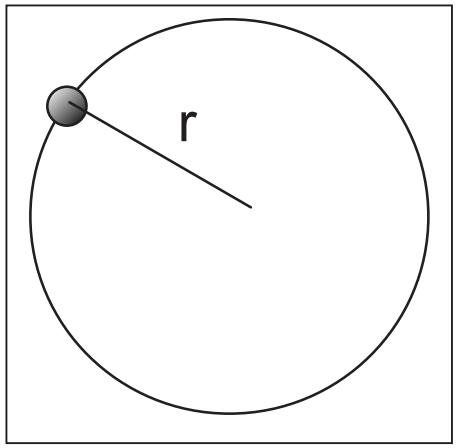
Where: q: total charge
n: number of charged particle

if $n = N_A$ then, $q = N_A e = 96500C = 1F = 1faraday.$

In this equation F is called Faraday's constant.

Robert Andrews Millikan is widely known as the Discoverer of the Elementary Electric Charge; Experimental Pioneer of the Electron. He was awarded the 1923 Physics Nobel Prize.

MAGNETISM OF THE ELECTRON



Two quantum properties, i.e., intrinsic spin and the orbital motion; correspond to the origin of magnetism, or magnetic dipole moment of an electron. The negative charge of an electron along with these two forms of angular momentum, causes it to act like a tiny, spinning bar magnet. This interacts with the external magnetic fields of the spectrometer.

The total magnetic moment (μ) is the vector sum of its spin and orbital moments: $\overrightarrow{\mu_{eff}} = \overrightarrow{\mu_s} + \overrightarrow{\mu_l}$.

This is an intrinsic property of the electron and is often the dominant source of magnetism in many materials.

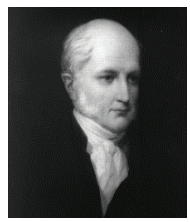
Current flowing due to electron is $I = -\frac{e}{T} = -e\nu = -\frac{e\omega}{2\pi}$

The electron is revolving in a circle of circumference $2\pi r$, with a velocity v.

The time period T of rotation is $T = \frac{2\pi r}{v}$

The magnetic dipole moment of current in a circular coil

$$\vec{\mu} = nIA = -\frac{e}{T}A = -\frac{e}{\frac{2\pi r}{v}}A = -\frac{ev\pi r^2}{2\pi r} = \frac{erv}{2}$$



Willian Prout
(15 January 1785-
9 April 1850)

Now we know that the angular momentum of a rotating body is $\vec{L} = mvr$, therefore for electron

$$\mu = -\frac{ervm_e}{2m_e} = -\frac{\vec{L}e}{2m_e}$$

The negative sign is for the opposite directions of $\vec{\mu}$ and $\vec{L}$.

The ratio $\gamma = \frac{\vec{\mu}}{\vec{L}}$ is called gyromagnetic ratio of electron.

$\gamma_e = \frac{e}{2m_e} = \frac{1.66\times10^{-19}C}{2\times9.11\times10^{-31}kg} = \frac{1.758820\times10^{11}Ckg^{-1}}{2} = 8.7954 \times 10^{10}Ckg^{-1}$.

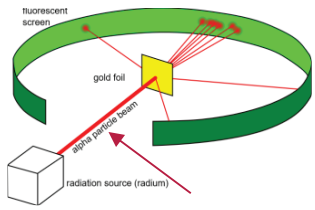
Sir Ernest Marsden
(19 February 1889-15
December 1970)

PROTON DISCOVERY

Protons were initially hypothesized by an English Chemist Willian Prout. His hypothesis was that the Hydrogen atom was the only fundamental particle in nature and that all the other elements that exist will only contain Hydrogen multiple times. He called this fundamental object 'protyle'. He made this hypothesis on his observation that all the atomic masses were integral multiples of hydrogen atom. This is known as Prout's Hypothesis, given in 1815-1816 through two papers he published. This also influenced Rutherford into believing that the Hydrogen ion (H^+) was a fundamental to all elements. In 1911, Rutherford proposed his 'Rutherford's Atomic Model' In fact, the first reported nuclear reaction (in 1919), accomplished by Rutherford. was $\mathbf{^{14}_{7}N + \alpha \rightarrow {}^{17}_{8}O + p^+}$ (p^+ stands for proton). This 'p' was written as H^+ by Rutherford.

Hantaro Nagaoka
(19 August 1865-
11 December 1950)

Though Canal Rays were much earlier (even before the discovery of the electron) observed, the charge to mass (q/m) ratio was different for each gas taken in the discharge tube and hence could not be given the status of being composed of one single particle like the Cathode Rays were.



COLLIMATOR

Though the Thomson Model was the prevailing model at the time, it was not universally accepted. A Japanese scientist Hantaro Nagaoka (長岡 半太郎; ながおか はんたろう) even rejected his model by saying that opposite charges cannot penetrate each other. He even gave his own model, the '*Saturnian model'*, in which the central nucleus was huge, and had around 10,000 electronic charges. But the later Rutherford model was much more accepted.

The Rutherford's Model of the atom is the 3rd step in the development of the model of the atom. It was next after J.J. Thomson's model and it led Neils Bohr to give his model which was very influential. It is based on experimental findings and some postulates. The experiment is the "Gold-Foil experiment"

3H. THE GOLD FOIL EXPERIMENT

The Gold foil experiments were a consequence of Rutherford's classification of radiations in α,β,γ radiations in 1899 based on their penetrating power:


Johannes Wilhelm "Hans" Geiger (30 September 1882- 24 September 1945)

The alpha rays (α-rays) were easily absorbed, carried a positive charge, and showed high ionizing power. They were deflected in a magnetic field toward the negative plate.

The beta rays (β-rays) were more penetrating than alpha rays, requiring thicker aluminium to stop. They carried a negative charge and deflected toward the positive plate in a magnetic field.

The gamma rays (γ-rays) were highly penetrating, passing through thick metal, and were not deflected by magnetic fields, indicating they were electrically neutral. These were included in his classification in 1903 after Paul Ulrich Villard studied them in 1900.

The Gold foil experiments were a a series of experiments conducted in 1910s by Hans Geiger and Ernest Marsden under Rutherford's guidance at the University of Manchester. These experiments lead to the "Rutherford's Model". They are also sometimes called the "Geiger-Marsden Experiments".

THE APPARATUS

The experiment was to project α-Particles on a thin Gold Foil (about 1000 atoms thick) and note the deflections in the rays. The source was some radioactive element like Radium that emitted α-Rays. The rays were a beam of α-particles accelerated to a speed of approximately $1.5 \times 10^7 ms^{-1}$.

In the apparatus between the source and screen, there was a device known as collimator, made of Lead and was used to narrow down the beam. It absorbs all the α-Particles, except those travelling in the appropriate desired direction. On the other side of the source a ZnS (Zinc Sulphide) screen was present.

From the source, at some distance a pin-hole was made to make the emitted rays a narrow beam. Then the gold foil was placed. Then the rays would hit the Zinc Sulphide screen. It is a property of ZnS that when it is hit by α-Particles, it produces fluorescence (i.e. it glows).

WHAT SHOULD HAVE HAPPENED

Now, if the Thomson model was correct, the α-Particles should've gone straight through the foil with no deflections. That was because of several reasons Rutherford deduced. They were: As solid matter does not exist at the quantum level, the α-Particles would not bounce back. The electric field of the Thomson atom could not deflect α-Particles to a noticeable degree, as these particles are very heavy and were moving fast. According to Coulomb, the more volume in

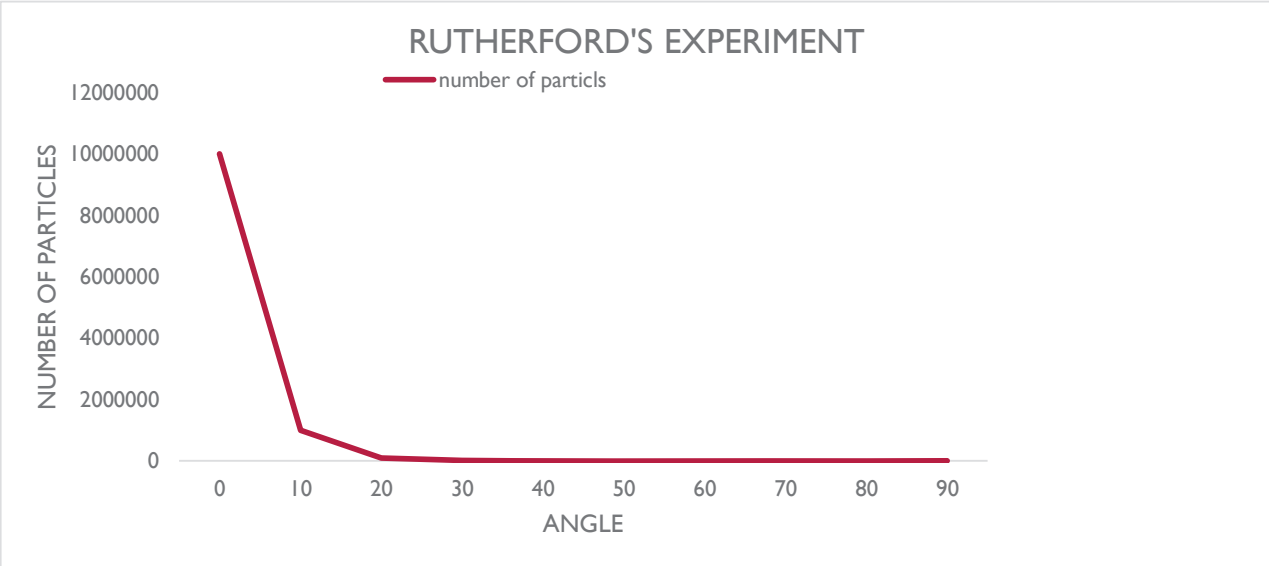
which a charge is dispersed, lesser will be the strength of the field at the surface. And the Gold atom, as Rutherford calculated, was big enough for no deflections to happen. So, at most the deflections would be in fractions of degrees.

WHAT HAPPENED

The actual outcomes were far different from the expected results. 3 main observations were made:

- Most of the particles went straight through
- Some got deflected at small angles
- Very few (about 1 in 20000) rebounded

The first observation did follow Thomson's model, but it could not explain the 2nd and 3rd observation, which inspired Rutherford to go on to devise his own model.
Rutherford even remarked at this as:



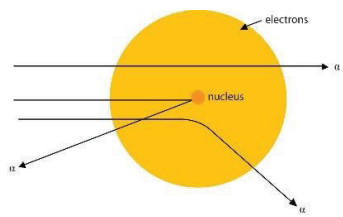
"It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you."

He also remarked that
"All science is either physics or stamp collecting."

POSTULATES

The three observations from the experiment lead to some postulates given by Rutherford for his Atomic Model. They were:

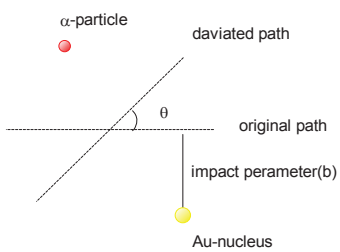
- Most of the atom is empty.
- Small deflections in a few numbers of particles, showing that the positive charge occupied very little space. The even smaller fraction of rebounded particles showed that the entire mass of the atom must've been concentrated in a very small region.



FEATURES

The model he devised, hence had the following features:

- The positive charge is in the centre of the atom called the 'nucleus'
- The electron revolves around the nucleus in circular paths.
- The size of the nucleus is very small compared to the atom (whose size was from the nucleus to the valence orbit).
- The electron and the nucleus are held together by electrostatic forces of attractions.



It is worth to address a serious question that Why Rutherford choose gold foil only as a suitable material for his experiments not any other foil like aluminium.
The main reason behind choosing gold is to make the foil as thin as possible. The thickness of the gold foil used in Rutherford experiment is approximately 1000 atoms thick which is approximately $4 \times 10^{-5} cm = 4 \times 10^{-7} m$.
To avoid the overlapping of the cross-section areas of two adjacent nuclei.
To make the α-particle suffer its entire deflection due to the encounter with only one atom, without any velocity loss.
The thickness of the thinnest gold foil is approximately 2 atomic layer thick i.e. $0.47nm = 4.7Å$
The gold foil is highly malleable due to its FCC structures and the existence of large number of slip systems. Gold have atomic mass 197u. Hence, it's so heavy that it remains stationary during the α-particles' collision.
α-particles are basically helium nuclei i.e. ${}_2^4He^{2+}$.
The property determining the experimental conditions of the experiment is called the *impact parameter* which is defined as the perpendicular distance of closest approach between the direction of α-particle and the gold nucleus and is given by:

$$b = \frac{Ze^2 \cot\left(\frac{\theta}{2}\right)}{4\pi\varepsilon_0\left(\frac{mv^2}{2}\right)} = \frac{Ze^2 \cot\left(\frac{\theta}{2}\right)}{2\pi\varepsilon_0(mv^2)} = \frac{4.6 \times 10^{-28} Z \cot\left(\frac{\theta}{2}\right)}{(mv^2)}$$

The distance of closest approach is the distance between the α-particle, travelling in the line of the nucleus and the gold nucleus. This gave the approximation of the size of nucleus.
This experiment was a specific example of what is known as Coulomb scattering caused by the electrostatic repulsions between the two like charges.

THE FORCE BETWEEN α-PARTICLE AND GOLD NUCLEUS

$\overrightarrow{F_E} = \frac{q_1 q_2}{4\pi\varepsilon_0 r^2} = \frac{2Ze^2}{4\pi\varepsilon_0 r^2}$, for gold $Z = 79$

For kinetic energy of α-particle $E_K^{\alpha} = V_{\alpha} = \frac{2Ze^2}{4\pi\varepsilon_0 r}$

DRAWBACKS

Rutherford's nuclear model, based on his gold foil experiment, provided a revolutionary understanding of atomic structure by introducing the concept of a dense central nucleus. While it resolved key shortcomings of Thomson's model, it did not adequately explain the stability of atoms or discrete spectral lines, thereby paving the way for Bohr's refinements.

ENERGY CONSIDERATIONS

The electron is a charged particle. The Rutherford model says that it is revolving (i.e. in circular motion, which is continuously accelerated because of continuous change in direction). Now, Maxwell's theory suggests that such a system should continuously radiate energy (as his theory says that charged particles under acceleration radiate electromagnetic radiation) this loss is governed by the equation called the Larmor Formula, developed by Sir Joseph Larmor. It works according to the equation $P = \frac{e^2 a^2}{6\pi\varepsilon_0 c^3}$, where P is the power lost by the accelerated charge accelerated by the acceleration a. therefore, the electron should fall into the nucleus (calculation showed that this should only take 10^{-18} seconds).
Another drawback was that it did not say anything about the distribution of the electron in the atom (i.e. how far is the electron, its energy etc.). His model also failed to account for the line spectra of atom.
These drawbacks inspired Neils Bohr to make his own model of the atom.

Sir Joseph Larmor
(11 July 1857-19 May 1942)

THE PROTON

Here, we must know, that it was the **Nucleus** that Rutherford discovered from the Gold-Foil experiment, not the proton or the neutron. He didn't know what is inside the nucleus.

As we know, firstly Prout said that the Hydrogen atom is present in other atoms' nuclei (Prout's hypothesis, 1815). Then, Rutherford discovered the nucleus (1911). Then in 1917, Rutherford performed experiments upon observing H-atoms produce scintillations on the ZnS screen when α-Particles would strike air at a distance α-Particles could not travel, but H-atoms could. When these experiments were done on Nitrogen, the effects were larger. The reaction was ${}^{14}_{7}\mathrm{N} + \alpha \rightarrow {}^{17}_{8}O + p$. Now this 'p' was the H^+ according to Rutherford. So, the reaction becomes ${}^{14}_{7}\mathrm{N} + \alpha \rightarrow {}^{17}_{8}O + H^+$.

If Rutherford's model was true, the atom would have collapsed in approximately 10^{-8}s.

PROPERTIES

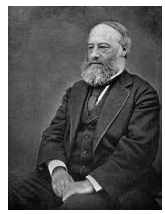
Mass: $\mathbf{1.6 \times 10^{-27}\ kg \approx 1\ Da = \frac{1}{1837} m_e}$

Charge: $\mathbf{1\ e = 1.6 \times 10^{-19} C}$

Symbol: $\mathbf{H^+}$ **or** $\mathbf{p^+}$

Rutherford is widely known as the 'Father of Nuclear Physics' OR 'Discoverer of the Atomic Nucleus' OR 'Discoverer of the Proton'.

Here its worthy to point out that the discoveries till now in our journey of the development of the atomic structure involved only some observations and analysis. Also, all these models have a unique importance of their own but to proceed in our study of this topic, it's important to first detour into some more concepts, where we can get some more important and prerequisite knowledge of physics. The Bohr's model, although was countered at some point before, but to continue with it, we must make ourselves comfortable with some more topics. The different aspects of physics and chemistry unite in this model. The story begins with the story of discovery of the electromagnetic waves and the in-depth knowledge of this field. So, we will begin from the basic terminology.



James Prescott Joule (24 December 1818-11 October 1889)

3I. ENERGY

Energy can be of many forms, mainly mechanical (including potential and kinetic energy), heat energy, light energy, chemical energy, electrical energy etc. In chemistry, energy is the ability of a molecule to change its, or its neighbouring molecule's structure, to attain stability. Any system tends to gain minimum energy and hence be more stable

Unit: The unit for energy (Joules) is named after James Prescott Joule, who showed that mechanical work is directly related to heat. He even gave the mechanical equivalent of heat $(1\ Cal = 4.184\ J)$

WAVES

Periodic motion: a motion which repeats its state after a fixed interval of time

Oscillatory motion: TO and FRO motion with an appreciable amplitude (if the amplitude is less, it will be called vibrational motion).

WAVE: It is a pattern created by a disturbance by which the energy of the disturbance propagates through a medium, with no displacement of the particles in that direction

OR

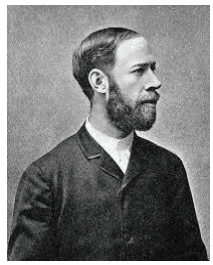
A wave is a propagating dynamic disturbance (change from equilibrium) of one or more quantities. Periodic waves oscillate repeatedly about an equilibrium (resting) value at some frequency.

Time period (T): Time taken to reattain the state of motion.

Frequency: Number of oscillations per unit time (ν=1/T). It is expressed in hertz (Hz) named after Heinrich Rudolf Hertz.

Amplitude: maximum deviation/displacement from its mean position

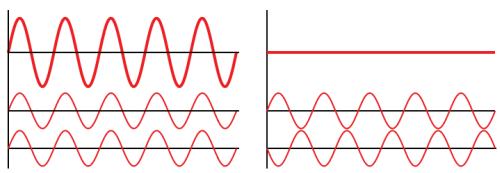
Phase: a physical quantity which helps to express the state of a body in a periodic motion. It is the argument which when calculated with the wave function gives out the state of the wave (i.e. amplitude of the particles, and their velocity).
Wavelength: the minimum distance between two particles in the same phase.
Transverse wave: when the particles executing wave motion are displaced perpendicularly to the direction of propagation of wave. E.g.: Light.
Longitudinal wave: when the particles are displaced parallel to the direction of propagation of wave. Eg: sound
Mechanical waves: these waves need a medium for propagation. E.g.: sound



Heinrich Rudolf Hertz (22 February 1857-1 January 1894)

Electromagnetic wave: waves which do not need a medium to propagate. E.g.: light. These waves have 2 perpendicular fields/components, namely the electrical and magnetic. Generally, the electrical component of these waves interacts with matter. These waves travel at the speed of light. These waves behave like particles and waves both (dual nature).
Interference: When two waves of same frequency, wavelength and approaching from same or opposite direction superimpose, they "interfere" and make new waves. Two waves can interact in 2 different ways:

- **Constructive interference:** when the crests and troughs (of both) of the two waves are on the same side, they add up and "constructively interfere". Or, when the two waves differ by a phase of $2n\pi$ or even multiple of π.
- **Destructive interference:** when the crest of first wave and trough of the other wave line up, the cancel and "destructively interfere". Or, when the phase difference is $(2n+1)\pi$ or odd multiple of π.
- The concept of interference is the basis behind bonding in molecules (Molecular Orbital Theory). This is a type of redistribution of energy. The interfering waves are called coherent waves.

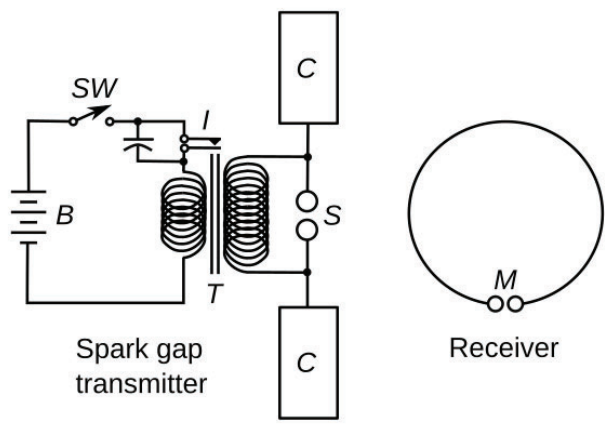


Constructive interference | Destructive interference

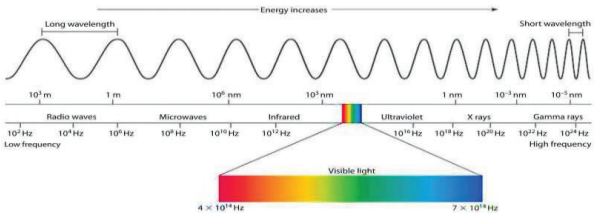
Below is given the order of electromagnetic waves in increasing energy. The order also follows increasing frequency, or decreasing wavelength. These concepts were given by Max Planck, which we shall study soon.

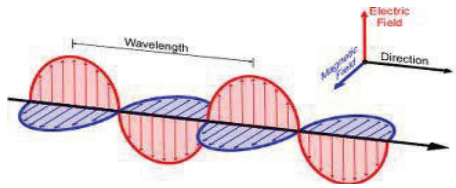
The order is as follows:

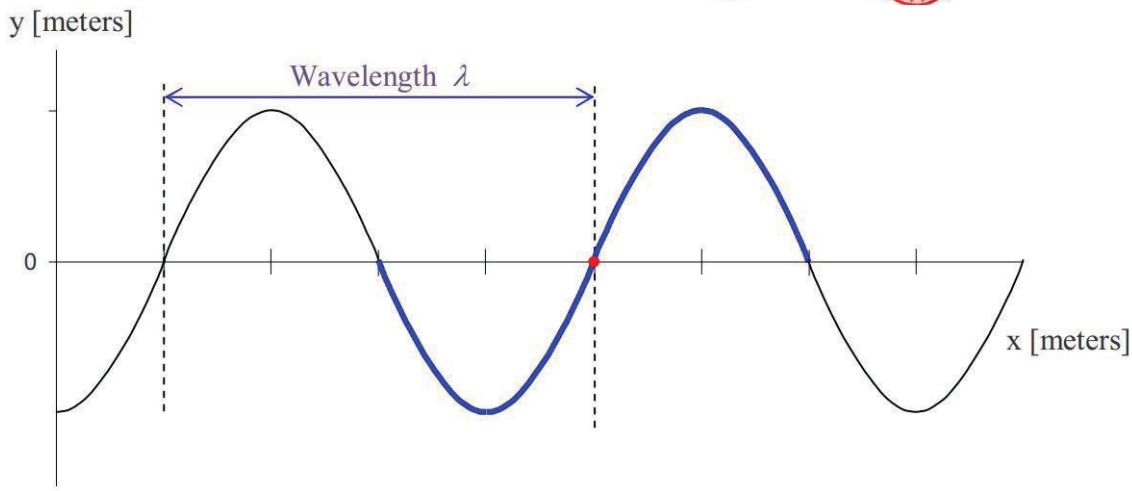
A. RADIO WAVES
B. MICROWAVES
C. INFRARED WAVE (IR)
D. VISIBLE
E. ULTRAVIOLET (UV)
F. X-RAY
G. GAMMA RAYS (γ-RAYS)
H. COSMIC WAVES



HERTZ'S EXPERIMENTAL APPARATUS







THE THEORY OF NATURE OF LIGHT

We shall deal with two main ideologies. One that treated light as a stream of particles, while the other treated light as wave. Both hold their own significance, and had their own shortcomings.

THE CORPUSCULAR THEORY OF LIGHT

The corpuscular theory of light is a historical scientific theory that postulates that light is made up of tiny particles, or corpuscles, which are emitted by luminous objects. This theory played a pivotal role in the early understanding of the nature of light and its behaviour.

ORIGINS AND EARLY IDEAS

1. **Ancient Roots:** The idea that light is composed of particles can be traced back to ancient Greek Philosophers such as *Empedocles* and *Democritus* proposed that vision involves particles emitted by objects that interact with the eyes. However, these ideas were speculative and lacked empirical support.

Empedocles
(490 B.C.E.-430

2. **Islamic Golden Age:** In the 10th century, Ibn al-Haytham (Alhazen) in his Book of Optics rejected the idea of emission from the eye and laid the foundation for later optical theories. While he did not explicitly propose a particle theory, his rigorous analysis of light's behaviour influenced later thinkers.

Abū ʿAlī al-Ḥasan ibn al-Haytham
(c. 965 – c. 1040 CE)

Development in the Scientific Revolution

1. Renaissance Contributions: During the Renaissance, natural philosophers began revisiting the nature of light in a systematic manner. The invention of the telescope and the microscope heightened interest in optics.

2. Isaac Newton (17th Century): The corpuscular theory of light, primarily developed by Isaac Newton, was based on a series of logical postulates that explained the behaviour of light in terms of tiny, discrete particles called corpuscles. These postulates were stranded in Newton's mechanical philosophy and aimed to explain the phenomena of reflection, refraction, and other optical behaviours. Below is a detailed

explanation of the key postulates Newton's formulation of the corpuscular theory being the most influential and detailed expression of this idea. He presented it in his book Opticks (1704).
Key tenets of Newton's theory:

- Light consists of small, discrete particles emitted by luminous sources.
- These particles travel in straight lines at high speeds and interact with matter to produce phenomena such as reflection and refraction.
- Newton explained refraction as resulting from the varying attraction of these particles by different media.

Newton's theory was partly inspired by his belief in mechanical philosophy, which emphasized the behaviour of particles and forces.
Here's a detailed account of his corpusclar theory:

1. Light Consists of Tiny Particles (Corpuscles)

- Light is composed of minute, discrete, and weightless particles called corpuscles.
- These corpuscles are emitted by luminous objects (e.g., the Sun, candles) and travel at high velocities in straight lines.
- The corpuscles are too small to be affected by gravity, which allows them to travel vast distances without being pulled back to their source.

2. Light Travels in Straight Lines

- Corpuscles move in straight paths unless they encounter a surface or medium that alters their trajectory.
- This explains phenomena such as sharp shadows and rectilinear propagation of light.
- The straight-line motion was supported by the observation that objects cast well-defined shadows.

3. Interaction with Surfaces: Reflection

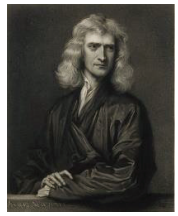
- When corpuscles strike a smooth, reflective surface (like a mirror), they bounce back following the laws of reflection.
- Newton postulated that the angle of incidence equals the angle of reflection because the corpuscles collide elastically with the surface.
- This behaviour was likened to a ball bouncing off a hard surface.

4. Interaction with Transparent Media: Refraction

- When corpuscles enter a different medium (e.g., from air to water or glass), they are subjected to a force exerted by the medium that changes their velocity and direction.
- Newton explained refraction by suggesting that the medium exerts an attractive force on the corpuscles:
- In denser media, this force increases the speed of the corpuscles, causing them to bend toward the normal.
- Conversely, in less dense media, the speed decreases, bending the light away from the normal.

5. Different Colours Correspond to Different Corpuscle Properties

- Newton proposed that the colour of light is determined by the size or other properties of the corpuscles.
- For example:
    - Red light corpuscles might be larger or less energetic than blue light corpuscles.
    - This idea was an attempt to explain the spectrum of colours observed in phenomena like rainbows.



Sir Isaac Newton
(1643 – 1727)

6. Transparency and Opacity

- The corpuscles can pass through transparent media (like glass) because the spaces between the particles of the medium are large enough to allow them to pass unimpeded.
- In opaque objects, the corpuscles are absorbed or blocked by the material, preventing light transmission.

Robert Hooke
(28 July 1635–14 March 1703)

7. **Light and Heat**

- Newton suggested that light corpuscles might also carry energy, explaining the warming effect of sunlight. However, he did not develop this idea fully, leaving it as a speculative aspect of his theory.

8. No Interaction Between Corpuscles

- Corpuscles do not interact or collide with each other during their motion.
- This postulate was necessary to explain why beams of light can cross each other without interference, maintaining their independent paths.

9. Weightlessness and High Speed

- The corpuscles were assumed to be extremely small and weightless, which allowed them to travel vast distances at immense speeds.
- Newton believed that the speed of light was finite and very high, which was later confirmed experimentally.

Strengths of the Postulates

These postulates successfully explained:

- The rectilinear propagation of light.
- Reflection and refraction phenomena.
- The dispersion of light into colours using a prism.

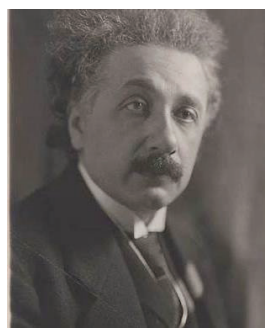
Limitations of the Postulates

Despite their success in explaining some optical phenomena, the corpuscular theory faced significant challenges:

- It could not explain diffraction and interference, which were better accounted for by the wave theory.
- The prediction that light travels faster in denser media was contradicted by later experiments showing the opposite.
- The theory could not explain phenomena such as polarization or the wave-like behaviour of light.

Modern Perspective

While the corpuscular theory was eventually supplanted by the wave theory and later quantum mechanics, its postulates were an essential step in understanding of light. Modern physics reconciles the particle and wave properties of light through the concept of photons in quantum theory, combining aspects of both theories, of Newton and Huygens. We shall encounter Huygens' theory for light later on, when we study on a detailed account for wave theory.



Albert Einstein
(14 March 1879-
18 April 1955)

Support for the Theory

Newton's explanation of reflection and refraction was mathematically consistent with his theory. The sharp shadows cast by objects and the rectilinear propagation of light seemed to support the idea of light as particles.

Empirical Contradictions

Newton's theory could not adequately explain certain optical phenomena, such as the interference patterns of light and its ability to bend around obstacles (diffraction). Additionally, the varying speed of light in different media, as measured later, was inconsistent with Newton's predictions.

19th Century Decline

1. (1801) Thomas Young

Thomas Young demonstrated that light exhibits interference patterns, a hallmark of wave behaviour.

This experiment provided strong evidence against the particle nature of light and for the wave theory.

2. Augustin-Jean Fresnel and James Clerk Maxwell

Fresnel further developed the wave theory, providing mathematical models for diffraction and polarization. In the mid-19th century, James Clerk Maxwell's electromagnetic theory described light as an electromagnetic wave, firmly establishing the wave theory over the corpuscular theory.

REVIVAL AND MODERN PERSPECTIVE

1. Quantum Theory and Photons: In the early 20th century, quantum mechanics revived aspects of the particle theory in a new form. Albert Einstein's explanation of the photoelectric effect (1905) introduced the concept of photons, quanta of light that exhibit both particle-like and wave-like properties.

This dual nature of light unified aspects of both the corpuscular and wave theories under the framework of quantum mechanics.

Thomas Young (13 June 1773-10 May 1829)

LEGACY OF THE CORPUSCULAR THEORY

The corpuscular theory was an essential step in the evolution of optical science. Although it was ultimately superseded by the wave and later quantum theories, it:

- Encouraged rigorous investigation into the behaviour of light.
- Highlighted the need for empirical validation in scientific theories.
- Laid the groundwork for the concept of photons in modern physics.
- Newton's corpuscular theory, though incomplete, remains a testament to the iterative nature of scientific progress and the interplay of competing ideas in the advancement of knowledge.

WAVE THEORY OF LIGHT

The wave theory of light is a cornerstone in the history of optics and physics, explaining light as a propagating wave rather than a stream of particles. This theory emerged as a significant alternative to the corpuscular theory of light and became foundational for modern physics. Below is a detailed historical account of the wave theory, from its origins to its eventual dominance.

Francesco Maria Grimaldi (2 April 1618-28 August 1663)

Early Ideas on Light as a Wave

1. **Ancient Philosophies:** Greek philosophers like Empedocles suggested that light moves and spreads out, hinting at a wave-like behaviour. However, no formal wave theory existed at the time. Aristotle believed in a continuous medium transmitting light, but his ideas were more philosophical than scientific.

2. **Renaissance Foundations:** During the Renaissance, scientists like Robert Hooke and Francesco Maria Grimaldi began investigating light's properties. Grimaldi discovered and named diffraction (1665), observing that light bends around obstacles; an effect difficult to explain using the particle theory.

Christian Huygens (14 April 1629- 8 July 1695)

Development of the Wave Theory

Christiaan Huygens (1690) The wave theory of light was formally introduced by Dutch physicist Christiaan Huygens in his book ***Traité de la Lumière (Treatise on Light).***

Huygens' Principle

Each point on a wavefront act as a source of secondary spherical wavelets. The wavefront at a later time is the envelope of these wavelets.

Huygens successfully explained reflection and refraction using his principle.

He proposed that light waves propagate through a medium called the **luminiferous ether** (an invisible substance filling all space).

Wave Theory's Early Challenges Huygens' theory initially failed to gain widespread acceptance because it could not explain the rectilinear propagation of light as convincingly as Newton's corpuscular theory.

The authority of Isaac Newton and the success of his corpuscular theory overshadowed Huygens' wave model for nearly a century.

André Marie Ampère (20 January 1775- 10 June 1836)

Revival of the Wave Theory

1. **Thomas Young (1801)** English scientist Thomas Young revived the wave theory by demonstrating the interference of light through his famous double-slit experiment.

Key Observations:

When light from a single source passed through two slits, it created an interference pattern of bright and dark fringes on a screen.

This pattern could only be explained if light consisted of waves that could constructively and destructively interfere.

Young's experiment was a direct challenge to the particle theory, as particles would not create such patterns.

2. **Augustin-Jean Fresnel (1815–1827)** French physicist Fresnel further developed the wave theory by providing a detailed mathematical framework for diffraction and polarization.

Fresnel's equations showed how light behaves in complex interactions with obstacles, validating the wave model.

He explained the phenomenon of polarization by proposing that light waves are transverse; meaning the oscillations occur perpendicular to the direction of propagation.

Hans Christian Ørsted (14 August 1777-9 March 1851)

Empirical Confirmation

1. **François Arago's Experiments:** Augustin-Jean Fresnel and Dominique François Jean Arago conducted experiments to test predictions of the wave theory, such as the Arago Spot: a bright point at the centre of a shadow cast by a circular object, due to diffraction. The successful observation of the Arago Spot provided strong support for the wave theory.

2. **Emergence of Electromagnetic Theory:** In the mid-19th century, James Clerk Maxwell unified the theories of electricity and magnetism, demonstrating that light is an electromagnetic wave.

Maxwell's equations described light as oscillating electric and magnetic fields propagating through space at the speed of light. This discovery eliminated the need for the hypothetical luminiferous ether and solidified the wave theory's dominance.

Challenges to the Wave Theory

1. **Photoelectric Effect (20th Century):** Experiments on the photoelectric effect showed that light interacts with matter as discrete packets of energy, or photons. This behaviour could not be explained solely by the wave theory, leading to the development of quantum mechanics.

2. **Wave-Particle Duality:** In the early 20th century, Albert Einstein reconciled the wave and particle theories by proposing that light exhibits wave-particle duality. Quantum theory showed that light behaves as both a wave and a particle depending on the context.

Dominique François Jean Arago
(26 February 1786-
2 October 1853)

Legacy of the Wave Theory

The wave theory of light played a crucial role in advancing the understanding of optical phenomena. Its principles are still foundational in many fields, including:

1. **Optics:** Phenomena like diffraction, interference, and polarization are explained by the wave theory.
2. **Electromagnetic Theory:** Maxwell's work on electromagnetic waves built on the wave theory's foundation.
3. **Modern Physics:** Quantum mechanics incorporates the wave-like behaviour of light, acknowledging its dual nature.

SUMMARY OF CONTRIBUTIONS

- Huygens introduced the wave theory and principles of wave propagation.
- Young demonstrated interference, providing empirical support.
- Fresnel developed mathematical models for diffraction and polarization.
- Maxwell established light as an electromagnetic wave, solidifying the theory's scientific foundation.

THE ELECTROMAGNETIC WAVE THEORY

The electromagnetic wave theory of light, formulated in the 19th century, revolutionized the understanding of light by uniting optics with electromagnetism. This theory, pioneered by James Clerk Maxwell, demonstrated that light is an electromagnetic wave—a phenomenon of oscillating electric and magnetic fields propagating through space. Below is a detailed historical account of this theory.

Foundations of Electromagnetic Theory

The electromagnetic wave theory of light emerged from advancements in the study of electricity, magnetism, and optics:

1. **Early Discoveries in Electricity and Magnetism:** In the 18th and early 19th centuries, scientists like Benjamin Franklin, Charles-Augustin de Coulomb, and Hans Christian Ørsted laid the groundwork for understanding electricity and magnetism.

In 1820, Ørsted discovered that a current-carrying wire produces a magnetic field, revealing a connection between electricity and magnetism.

2. **Faraday's Contribution:** In the 1830s, Michael Faraday discovered electromagnetic induction, showing that a changing magnetic field produces an electric field.

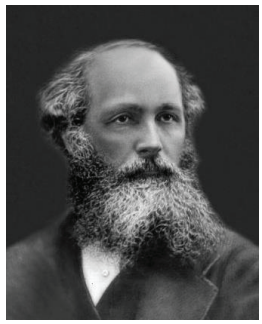
Faraday introduced the concept of field lines to describe electric and magnetic forces, providing a visual framework for electromagnetic phenomena.

1. **James Clerk Maxwell's Unified Theory:** The electromagnetic wave theory was formalized by James Clerk Maxwell in the 1860s:
2. The electromagnetic wave theory of light, developed by James Clerk Maxwell, describes light as an electromagnetic wave composed of oscillating electric and magnetic fields that propagate through space. Below are the detailed postulates of the theory, followed by the derivation of the electromagnetic wave equations from Maxwell's equations.

Augustin-Jean Fresnel
(10 May 1788-14 July 1827)

Postulates of the Electromagnetic Wave Theory

1. **Light is an Electromagnetic Wave**: Light consists of oscillating electric and magnetic fields that are mutually perpendicular and perpendicular to the direction of wave propagation.
2. **Transverse Nature**: Both electric and magnetic fields are transverse waves, meaning their oscillations are perpendicular to the direction of wave propagation.
3. **Self-Sustaining Nature:** A time-varying electric field generates a magnetic field, and a time-varying magnetic field generates an electric field. This mutual generation allows electromagnetic waves to propagate without a medium.
4. **Speed of Light:** The speed of light in a vacuum is determined by the electric permittivity and magnetic permeability of free space.
5. **Wave Properties:** Electromagnetic waves exhibit wave phenomena like reflection, refraction, diffraction, interference, and polarization.
6. **No Medium Required:** Unlike mechanical waves, electromagnetic waves do not require a medium for propagation and can travel through a vacuum.



James Clerk Maxwell (13 June 1831-5 November 1879)

Key Results

1.Light is an electromagnetic wave propagating at a finite speed.

2.Electric and magnetic fields are coupled and oscillate perpendicularly to each other and the direction of propagation.

3.Maxwell's theory unified optics and electromagnetism, showing that visible light is part of a broader electromagnetic spectrum.

This derivation is the cornerstone of classical electromagnetism and underpins modern physics and engineering.

MAXWELL'S EQUATIONS

Maxwell unified four equations of electricity and magnetism from contemporary scientists, that describe the behaviour of electric and magnetic fields in the years 1861 to1865

1. **Gauss's Law for Electricity:** Electric charges produce electric fields. Given by Johann Carl Friedrich Gauss in 1835, published in 1867 (posthumous publication). It states that the electric flux through a closed surface is equal to the total charge enclosed by the surface divided by the permittivity of free space. Here is a highly simplified derivation of the same:
   The mathematical definition of electric field is
   $E = \frac{q}{4\pi\varepsilon_0 r^2}$
   And electric flux is $\phi_E = E.A$
   Therefore,
   $\phi_E = \frac{q}{4\pi\varepsilon_0 r^2} A = \frac{\rho}{\varepsilon_0}\ (as\ A = 4\pi r^2)$
   $\nabla . E = \oint E.dA = \frac{\rho}{\varepsilon_0}$

Johann Carl Friedrich Gauss (30 April 1777-23 February 1855)

2. **Gauss's Law for Magnetism:** Magnetic monopoles do not exist; magnetic field lines form closed loops. The net magnetic flux through the closed surface is zero. This law was based on the studies of electromagnetic induction by Michael Faraday in 1831 and Johann Carl Friedrich Gauss in 1835. It was finalized by James Clerk Maxwell in the year 1864.

$$\nabla . B = \oint B . dA = 0$$

3. **Faraday's Law of Electromagnetic Induction:** A changing magnetic field induces an electric field.

$$\nabla . E = -\frac{\partial B}{\partial t} \Rightarrow \oint Edl = \frac{d\phi_B}{dt} = -\frac{d}{dt}\oint BdA$$

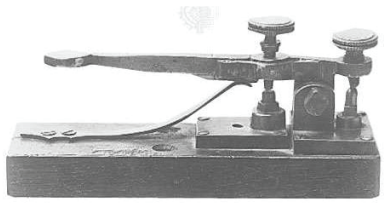
4. **Ampère-Maxwell Law** A changing electric field produces a magnetic field. André Marie Ampère in 1826.

$$\frac{d\phi_E}{dt} = \frac{dEA}{dt} = \frac{d\left(\frac{\rho}{\varepsilon_0}\right)}{dt} \Rightarrow i_d = \varepsilon_0 \frac{d\phi_E}{dt}$$

$$\nabla . B = \oint Bdl = \mu_0(I_C + I_D) = \mu_0 I_C + \mu_0 \varepsilon_0 \frac{d}{dt}\oint E . dA = \mu_0 J + \mu_0 \varepsilon_0 \frac{\partial E}{\partial t}.$$

The equation $\oint Bdl = \mu_0 I_C$ is called the Ampère's law.

Samuel Finley Breese Morse (27 April 1791-2 April 1872)



Electric Telegraph

These equations mathematically unified electricity and magnetism into a single framework. This unification have the most important application in communication known as the Morse Code. The transmission of signals across distance is not merely an achievement of invention, but a manifestation of the profound unity between electricity and magnetism—first illuminated through the work of André-Marie Ampère, deepened by the experimental insights of Michael Faraday, and ultimately unified into a complete theoretical framework by James Clerk Maxwell, later confirmed through the experiments of Heinrich Hertz; within this emerging understanding, the idea of transmitting thought itself through invisible forces took shape in the early 1830s in the mind of Samuel Finley Breese Morse. In close collaboration with Alfred Vail, was realized by 1837–1838 as a practical system of electric telegraphy, wherein a language of dots and dashes represented letters and numbers through controlled electrical pulses, accompanied by crucial improvements to the telegraph apparatus; first demonstrated publicly on January 6, 1838, in Morristown, New Jersey, and subsequently in New York, this system attained its historic culmination on May 24, 1844, when Morse transmitted the first official long-distance message—"What hath God wrought"—from Washington, D.C., to Baltimore, marking the birth of long-distance electrical communication; although Morse received the patent and enduring recognition, Vail's essential refinements endowed the code with its efficiency and clarity, and the system was later standardized as International Morse Code in 1865, ensuring its global adoption, while its essence remained unchanged—a quiet, rhythmic language in which meaning travels not through substance, but through the measured intervals of signal and silence.

INTERNATIONAL MORSE CODES' CHART

ALPHABETS	MORSE CODE	NUMBERS	MORSE CODE	SYMBOLS	NAMES	MORSE CODE	SPECIAL SIGNALS	MORSE CODE
A	.-	0	-----	.	Period	.-.-.-	SOS	... --- ...
B	-...	1	.----	,	Comma	--..--	AR (End)	.-.-.
C	-.-.	2	..---	?	Question	..--..	SK (End Contact)	...-.-

D	-..	3	...--	'	Apostrophe	.----.	BT (Pause)	-...-
E	.	4	....-	!	Exclamation	-.-.--		
F	..-.	5	.....	/	Slash	-..-.		
G	--.	6	-....	(	Left Bracket	-.--.		
H	....	7	--...	)	Right Bracket	-.--.-		
I	..	8	---..	&	Ampersand	.-...		
J	.---	9	----.	:	Colon	---...		
K	-.-			;	Semicolon	-.-.-.		
L	.-..			=	Equal	-...-		
M	--			+	Plus	.-.-.		
N	-.			-	Hyphen	-....-		
O	---			_	Underscore	..--.-		
P	.--.			"	Quotation	.-..-.		
Q	--.-			$	Dollar	...-..-		
R	.-.			@	At Sign	.--.-.		
S	...							
T	-							
U	..-							
V	...-							
W	...-							
X	-..-							
Y	-.--							
Z	--..							

PREDICTION OF ELECTROMAGNETIC WAVES

Maxwell realized that oscillating electric and magnetic fields could sustain each other and propagate through space as a wave.

He calculated the speed of these waves and found it matched the known speed of light (approximately $3 \times 10^{8} ms^{-1}$; $c = \frac{1}{\sqrt{\mu_0 \varepsilon_0}}$).

This led Maxwell to propose that light is an electromagnetic wave.

Characteristics of Electromagnetic Waves

1. **Nature of the Wave:** Electromagnetic waves consist of oscillating electric and magnetic fields that are:

Perpendicular to each other

Perpendicular to the direction of propagation (transverse waves).

2. **Wave Properties:** Electromagnetic waves exhibit properties such as:

Reflection: Bouncing off surfaces.

Refraction: Changing direction in different media.

Diffraction: Bending around obstacles.

Interference: Superposition of waves leading to constructive or destructive patterns.

Spectrum

The electromagnetic wave theory explains not only visible light but also other forms of electromagnetic radiation, such as radio waves, microwaves, infrared, ultraviolet, X-rays, and gamma rays.

Experimental Validation

1. **Heinrich Hertz's Experiments (1887):** Hertz confirmed the existence of electromagnetic waves by generating and detecting radio waves, which exhibited the same properties as light waves (e.g., reflection, refraction, and interference).

This experimental evidence provided direct support for Maxwell's theory. Heinrich Rudolf Hertz is widely known as Father of Electromagnetic Waves or Discoverer of Radio Waves.

2. **Wave Properties of Light:** The electromagnetic wave theory successfully explained phenomena like:

Diffraction and interference, previously described by the wave theory of Huygens, Fresnel, and Young.

Polarization, as the oscillations of electric and magnetic fields can occur in specific directions.

Implications and Advancements

1. **Elimination of the Luminiferous Ether:** Earlier wave theories suggested that light waves propagate through a medium called the ether. Maxwell's equations showed that electromagnetic waves do not require a material medium; they can propagate through the vacuum of space.

2. **Technological Applications:** Maxwell's work laid the foundation for modern technologies like radio, television, and radar, which rely on the propagation of electromagnetic waves.

Challenges and Extensions

1. **Photoelectric Effect:** In the early 20th century, experiments showed that light can eject electrons from metal surfaces (the photoelectric effect). This phenomenon could not be explained by the wave theory.

Albert Einstein proposed that light consists of discrete packets of energy called photons, introducing the concept of wave-particle duality.

2. **Wave-Particle Duality:** Quantum mechanics reconciled the wave and particle nature of light, showing that light behaves as both a wave and a particle depending on the context.

Legacy of the Electromagnetic Wave Theory

1. **Integration with Quantum Theory:** While Maxwell's theory describes the macroscopic behaviour of light and electromagnetic waves, quantum electrodynamics (QED) provides a more comprehensive understanding at the microscopic level.

2. **Scientific and Technological Impact:** The electromagnetic wave theory revolutionized physics and paved the way for numerous advancements, including:

Modern communication systems (e.g., radio, television, and mobile networks).

Medical imaging technologies (e.g., X-rays and MRI). Space exploration (e.g., radio telescopes and satellite communication).

Summary

The electromagnetic wave theory of light, established by James Clerk Maxwell and confirmed by Heinrich Hertz, unified optics with electromagnetism and provided a comprehensive framework for understanding light as an electromagnetic wave. While it faced challenges with the advent of quantum mechanics, it remains a cornerstone of classical physics and a critical milestone in the development of modern science.

THE ELECTROMAGNETIC WAVES

There are various stories of the discoveries of these electromagnetic waves. There have been drastic amount of research and efforts of various people behind such a sophisticated and systematised electromagnetic spectrum, which is today used as a key to the door of the branch of physics called electromagnetics, and finds application in much useful networking technologies today.

COSMIC RAYS

Victor Francis Hess (24 June 1883- 17 December 1964) Cosmic Rays

These were discovered on 7 Aug 1912 by Victor Francis Hess, during his 7th ballon flight of the year. When Becquerel discovered radioactivity, it was believed that ionization of atmospheric molecules happened only by radiation of radioactive elements on earth's surface. Theodore Wulff, upon inventing the electrometer (device to measure rate of ion production), he found higher radiation at the top of the Eiffel tower than at its base. This led him to believe some extra radiation must be coming from somewhere, which increased ions. Then, Dominico Pacini also did some experiments on similar ways, and measured ionization rate 3 meters under water, and found a less production rate. So, he concluded there must be some outer radiation above which could explain this. These 2 experiments happened in 1909 and 1911 respectively. Then finally, another scientist Victor Hess, in 1912 took the Wulff electrometer on a balloon at a height of 5000+ meters and measured the rate, to find that there is an increase in it (he did this independently of Wulff). It was eclipse on that day, which meant this increase could not have been because of the sun's radiation (much of it was blocked by the moon, enough to make the conclusion that some outer radiation must be playing some role). Hess received the noble price in 1936 for this discovery. The term cosmic ray was later coined by Robert Millikan. Jacob Clay proved that cosmic rays are charged particles, based on his observation of increment of measurement readings on sailing farther from the equator during his trip back to Netherlands and then he proposed that cosmic rays are deflected by the geomagnetic field and they are charged particles rather than photons. This proposal was generally accepted by 1932. This proved the fact that the Cosmic rays are not a part of the actual electromagnetic spectrum. But these are actually high energy particles which sometimes strike the Earth's atmosphere and are deflected to the outer space by the magnetic field of the Earth.

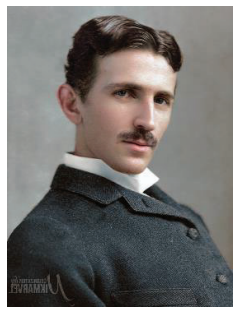
Paul Ulrich Villard (28 September 1860-13 January 1934) γ rays

GAMMA RAYS (γ-Rays)

In 1900, Villard noticed a radiation of more energy from radium, more energetic than beta or alpha rays, as previously discovered by becquerel and Rutherford. But Villard did not name this ray as a fundamentally different ray. That was done by Rutherford in 1903.

This ray was first thought to be a ray of particles. Rutherford named them gamma rays (γ-Rays), in accordance to the already known alpha rays (α-rays) and beta rays (β-rays).

Villard's experiment using these rays in magnetic fields showed no deflection, which (along with later discoveries) led these scientists to conclude these are also electromagnetic waves.



Nikola Tesla (9/10 July 1856-7 January 1943)

X-RAYS

X-rays were discovered on 8 November 1895 by Wilhelm Conrad Röntgen. Prior to his work, several scientists had unknowingly observed related phenomena but did not systematically investigate or identify them. Notably, Nikola Tesla explored electrical discharges, and earlier, experiments by Arthur Goodspeed and William Nicholson Jennings on 22 February 1890 accidentally produced images later recognized as early X-ray photographs, though their significance was not understood at the time.

After Röntgen's death, many of his laboratory notes were destroyed, making the exact reconstruction of his discovery incomplete.

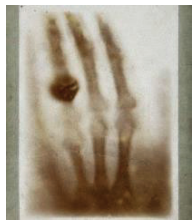
Wilhelm Conard Röntgen (27 March 1845-10 February 1923) X-rays

However, the essential sequence is well established. While working with a Crookes tube, Röntgen covered it with black cardboard to block visible light. He observed that a nearby screen coated with barium platinocyanide began to fluoresce, indicating the presence of an unknown penetrating radiation. Realizing that these rays could pass through opaque materials, he began systematic investigations into their properties.

Anna Bertha Ludwig (1839–1919)

He demonstrated that these rays could penetrate various substances, though to differing extents, and even produce images of internal structures. In his own words, **"I have called these rays X-rays, in order to indicate that their nature is unknown."** He further demonstrated their remarkable properties by producing an image of the bones of a hand on a photographic plate one of the earliest and most famous radiographs.

One such image, known as *Hand mit Ringen* ("Hand with Rings"), depicted the hand of his wife, Anna Bertha Ludwig. Upon seeing the image, she is widely reported to have exclaimed, *"I have seen my death!"* a statement that, while historically popular, is not firmly documented in primary sources.



Hand with Rings

Although the term "Röntgen rays" was proposed and adopted in several languages, Röntgen himself discouraged its use. In English, the radiation came to be known simply as X-rays.

CHERECTERESTICS OF X-RAYS

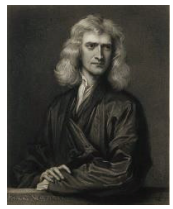
These are the observations from Rontgen's original report. Many substances show fluorescence with X-rays.

- Photographic plates are affected by these rays
- Almost all substances are more or less transparent to the X-rays.
- These travel in a straight line, and are undeflected by the magnetic fields.
- X- rays discharge both positively and negatively charged bodies.
- X-rays are generated when a solid body is struck by the cathode rays.

Johann Wilhelm Ritter
(16 December 1776-23 January 1810)
UV Rays

UV RAYS

In Feb 1801, Johann Wilhelm ritter observed a radiation just after the end of the visible spectrum (which is actually the reason for the name ultra violet, i.e. beyond violet) to darken AgCl-soaked paper more quickly than visible rays. He wrote a letter to a German science journal *Annalen der Physik* and named then de-oxidizing rays. They were later once called chemical rays (although some scientists were against this name, notably John William Draper, who named them tithonic rays) as well, but finally the name ultraviolet was accepted.



Sir Isaac Newton
(1643-1727)
Visible

VISIBLE LIGHT

Newton first in 17th century divided colour into its constituents, and used the word spectrum (Latin for appearance) in his book '*Optick*' in its sense we now know. It was the early 19th century that the visible spectrum got more definite in its meaning when UV and IR rays were discovered. Thomas young in 1802 was first to measure wavelength of different colours.

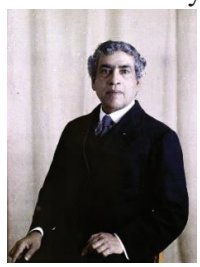
Besides the spectrum, light itself has a long history of different theories explaining its constitution.

Sir William Herschel (born Friedrich Wilhelm Herschel) (15 November 1738-25 August 1822)

IR RAYS

Previously it was known that fire can emit some form of invisible heat, other than the visible rays. In 1681, Edme Mariotte showed that glass let through visible sunlight, but obstructed this form of heat. In 1800, Sir William Herschel discovered these rays and these were named 'heat rays' by him. He was actually studying heat produced by different colours of light by blocking sunlight from some filters. He noticed varying temperatures, so took a prism to measure the heat of different colours of light. He then unknowingly placed his thermometer beyond red light, to notice a 1-degree increase (although IR rays are weaker in energy than visible rays, IR rays can more readily be absorbed by atoms which is the reason IR rays provide more heating sensation than visible rays). This led to the discovery of IR rays, and these were named heat rays previously. But alongside chemical rays (which were named to UV), these were also renamed to IR (infra-red, that is behind red).

Infrared



Jagadish Chandra Bose (30 November 1858-23 November 1937)

MICROWAVES

After Maxwell suggested the existence of electromagnetic waves via his theory of electromagnetism, he and Heinrich Hertz did experiments to notice the existence of these waves. Hertz discovered radio waves to be electromagnetic in nature in 1888. Then he and maxwell tried generating waves of higher frequencies, in the microwave region. In 1894, Jagadish Chandra Bose finally made microwaves of frequency of 60 GHz. Independently, some other scientists also did the same in Russia or England etc.

It was later in the 1940s, that the microwaves became usable for communications.

Guglielmo Giovanni Maria Marconi (25 April 1874-20 July 1937)

RADIO WAVES

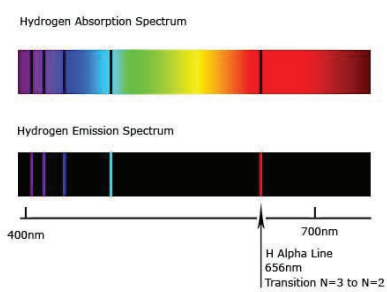
When Maxwell predicted the existence of electromagnetic waves, Hertz discovered them by producing radio waves in 1887. They were originally called hertzian waves, but were renamed to radio waves in 1912, as their use in radios was established by that time. First practical use of radio waves was in 1894-95 by Guglielmo Giovanni Maria Marconi.

SPECTRUM

Spectra: White light is not a single colour. It contains a continuous range of wavelengths (λ) or wavenumbers (1/λ), each of which represents a different colour such as:

1. Longer wavelength → Red
2. Medium wavelength → Green
3. Shorter wavelength → Blue/Violet.

When white light is broken down into these constituent colours, it forms the spectrum. When this light is obstructed such that only a few component colours are not passed, it forms a spectrum of the substance. These obstructions are done when white light is passed through a sample which has the substance whose 'spectra' we want to observe. What happens is that this substance will absorb energy from the light in the form of some constituent colours, and only allow certain colours to pass. E.g., out of the 7 constituent colours, say a substance absorbs only red light. So, it will allow all the rest 6 colours to pass



which will later form its spectra. This type of spectra where a light of a particular wavelength is absorbed, and rest constituents are allowed to pass to form a spectrum, is called absorption spectra; but when excited atoms release their absorbed energy in the form of light to form a spectrum, it is called an emission spectra. The spectra are like a fingerprint for an element or a molecule.

Here's a detailed account of what happens:

A compound appears of the particular colour in two situations

A. The compound absorbs one wavelength and appears to be of the colour of the reflected wavelengths. These reflected wavelengths combine to form a particular colour, called the complementary colour of the absorbed wavelength. This is 'selective absorption'.
B. It reflects only one colour and absorbs all the other colours from the visible light spectrum. This is a phenomenon of selective reflection. This is a result of other properties of light such as reflection of scattering.

Example A:

1. If a compound absorbs orange light (i.e. one narrow wavelength region) from the visible light spectrum then this absorption also corresponds to the reflection of all the remaining colours of the light spectrum. The mixture of all these reflected colours correspond to the perception of the human eye that the compound is of Blue colour which is nothing but the complimentary colour of the absorbed Orange colour. The compound $[Cu(H2O)_6]^{2+}$ absorbs orange and appears blue.
2. $KMnO_4$ absorbs green (due to Planck's postulate) and the remaining wavelengths form the purple colour that the human eye perceives, because purple colour of the $KMnO_4$ solution is produced because the absorbed wavelength (green) is removed, and the rest of the light is what your eye sees.

This case is explained by the PLANCK'S POSTULATE, which states that Light can be absorbed or emitted only in discrete packets (quanta) of energy: $E = h\nu$.

This means:

A molecule/ion can absorb only those photons whose energy matches the energy difference between two of its allowed energy levels.

In transition metal complexes or molecules:

The electrons have fixed energy gaps between levels.

If the gap corresponds to the energy of orange photons i.e. $E=h\nu_{orange}$

Only orange light is absorbed.

No other colour matches the energy gap, so they cannot be absorbed.

This case is perfectly explained by Planck's postulate.

The colour absorbed = energy level difference.

This is why spectroscopy exists—because absorption matches quantized energy levels. This is the basis of spectroscopy.

We shall study Planck's postulate soon.

Example B:

If a compound reflects Blue light from the spectrum. Blue paint absorbs red+green, reflects only blue.

Note: In chemistry and spectroscopy, the wavenumbers are preferred because these values are directly related to the energy.

H-Spectra

The substance is said to be excited when it has absorbed some constituent colours. On December 14, 1900 Max Karl Ernst Ludwig Planck introduced his quantum theory which helped us to understand the nature of the 6 spectral line series observed in the H-spectrum.

According to this theory, basically, light energy always flows in a quantized manner. This can be understood through a stair-ramp analogy.
Imagine a staircase with a ramp parallel to it. A ball of mass m is pushed downward from each in two experiments. Now, when the ball is pushed from the staircase the potential energy of the ball is proportional to the hights of the stairs. Hence the energy is quantized i.e. have discreate values of mgh_1, mgh_2 etc.
But when the ball is pushed from the ramp the energy can have any arbitrary value. Hence, its referred to be continuous. Before the emergence of Planck's quantum theory some scientist believed energy to be continuous, as was in the classical wave theory of light established by Christian Huygens in 1678 and later published in 1690. This wave theory had some validity due to which it survived for 200 years. But Planck proved energy to be quantized, which this theory failed to explain.
William Allen Miller in 1833 demonstrated that additional dark lines appear in the sun's spectrum when sunlight passes through gases in a laboratory.
Jean Bernard Léon Foucault in 1849 noticed a line similar to the D line of the solar spectrum when investigating the spectrum of an arc between two carbon electrodes.
Robert Wilhelm Eberhard Bunsen and **Gustav Robert Kirchhoff in** the 1860s established the link between chemical elements and their unique spectral patterns. They also established the technique of analytical spectroscopy.
Johannes Stark in 1913 discovered the splitting of spectral lines in an electric field, now called the Stark effect. Spectral lines are highly atom-specific and can be used to identify the chemical composition of any medium. They are also used to determine the physical conditions of stars and other celestial bodies. The German physicist **Gustav Robert Kirchoff** (1824–1887) and chemist **Robert Wilhelm Eberhard von Bunsen** (1811–1899) discover that spectral lines are unique to each element. 1860–1861: Kirchoff and Bunsen discover the elements caesium and rubidium using their new technique of spectral analysis. The Zeeman effect is first observed in 1896 by **Pieter Zeeman**, which stated that spectral lines deflect in presence of magnetic fields.

LIMITATIONS OF WAVE THEORY OF LIGHT

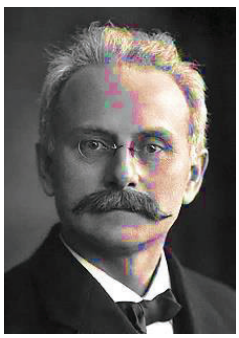
Blackbody radiation: Classical wave theory predicted an infinite amount of energy at high frequencies (ultraviolet catastrophe) which contradicted experimental observations of blackbody radiation spectra, prompting the development of Planck's quantum theory.
Photoelectric effect: This phenomenon, where electrons are ejected from a metal when illuminated by light, **could not** be explained by the wave model as it suggested that light energy should be distributed continuously across the wavefront, not concentrated in discrete packets.
Particle-like behaviour: Experiments like the Compton effect further demonstrated that light can exhibit particle-like momentum, which could not be fully explained by the wave model alone.
Line spectra of atoms: The theory cannot explain the line spectra of atoms, particularly hydrogen. The line spectr is basically a spectrum which contains some lines on analysis with a spectrophotometere.
The story of the discovery of the concept of line spectra of atoms dates back to **William Hyde Wollaston** who in 1802, was the first to note dark features in the solar spectrum.
Joseph von Fraunhofer In 1814, Fraunhofer independently rediscovered the lines and measured their wavelengths.

ELECTROMEGNETIC WAVES SPECTRUM KEY

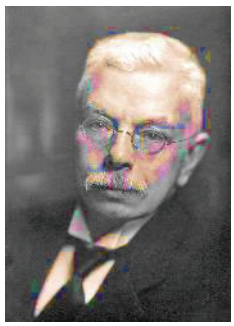
Name	Discoverers	Year of discovery	FREQUENCY (Hz)	Wavelength λ	Spectroscopy	Effects	Source	Detector	Danger	Use
Cosmic rays	Victor Franz Hess	1912	10^{23}			Burned				
Gamma rays (γ-Rays)	Paul Ulrich Villard	1900	10^{20}-10^{24}	6×10^{-15}	**Mössbauer spectroscopy**	Change of nuclear configuration Study of inorganic compounds o Iron (Fe), and Tin (Sn)	Radioactivity	γ-Ray Film	Cell mutation and cancer	Medical tracers and cancer killers (radiotherapy)
X-rays	Wilhelm Conard Rontgen	1895	10^{17}-10^{20}	1pm-1nm	XRD	Change of electronic configuration for the core electrons	Sudden retard of high energy electrons	X-ray film		Medical imaging of skeletal defects
UV Rays	Johann Wilhelm Ritter	22 February 1801	10^{15}-10^{17}	1nm-400nm	Raman spectroscopy and fluorescence and phosphorescence	Homo-diatomic molecules Change of molecular configuration	Atomic excitation spark and gas discharge lamp	Film	Sunburns, skin cancer (UVA cause **Melanoma** and UVB cause Squamous cell carcinoma and basal cell carcinoma	Bactericidal, Bluetooth
Visible	Isac Newton	1665	4-7.5x10^{14}	400-800nm			Atomic excitation spark and flame	Eyes, Electronic devices	Burning and Blindness	Photography human vision

Infrared	William Herschel	1800	$10^{13}10^{14}$	2.5-750μm OR 2.5-25μm	Vibrational spectroscopy.	Bond length, Isotopes	Atomic and molecular excitation	Electronic devices, Thermometers	Burning	Remote controls, magic eye
Microwaves	Arno Allan Penzias and Robert Woodrow Wilson	1964	$3x10^{11}$-10^{13}	1mm-0.1mm	High: Rotational Spectroscopy Low: Electron Spin Resonance (ESR)	Reaction intermediates (free radical, carbenes etc.)	Oscillating currents in vacuum tubes	Antina LCR Cricut		RADAR, Communication, food heating
Radio waves	Heinrich Rudolf Hertz	1887	3(kHz)-3,000 GHz	0.1-10000	NMR spectroscopy	All magnetic nuclei.	Oscillating LC Cricut			
Electron waves			50-60	$5-6\times10^{6}$			AC Cricut			

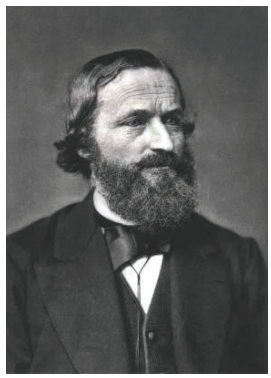
VISIBLE LIGHT			**SPECTRUM OF VISIBLE LIGHT**					
ABSORBED COLOUR	**TRANSMITTED COLOUR**	**ABSORBED WAVELENGTH**	**ABSORBED COLOUR**	λ (nm)	Frequency (Hz)	Energy per Photon (J)	Energy (eV)	Energy per Einstein ($kJ\cdot mol^{-1}$)
VIOLET	YELLOW-GREEN	300-400nm	VIOLET	405	7.40×10^{14}	4.90×10^{-19}	3.06	295.37
BLUE	YELLOW	450-495nm	INDIGO	445	6.74×10^{14}	4.46×10^{-19}	2.79	268.82
GREEN	VIOLET	495-570nm	BLUE	470	6.38×10^{14}	4.23×10^{-19}	2.64	254.52
YELLOW	BLUE	570-590nm	GREEN	510	5.88×10^{14}	3.89×10^{-19}	2.43	234.56
ORANGE	GREEN-BLUE	590-620nm	YELLOW	570	5.26×10^{14}	3.48×10^{-19}	2.18	209.87
RED	BLUE-GREEN	620-750nm	ORANGE	550-590	5.08×10^{14}	3.37×10^{-19}	2.10	202.76
			RED	650	4.61×10^{14}	3.06×10^{-19}	1.91	184.04



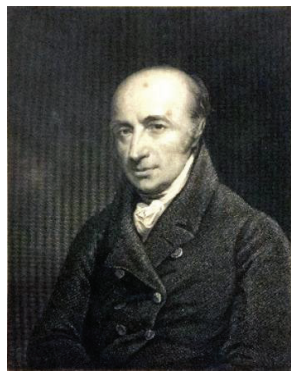
Pieter Zeeman
(25 May 1865-9 October 1943)



Johannes Stark
(15 April 1874-21 June 1957)



Gustav Robert Kirchhoff
(12 March 1824-17 October 1887)



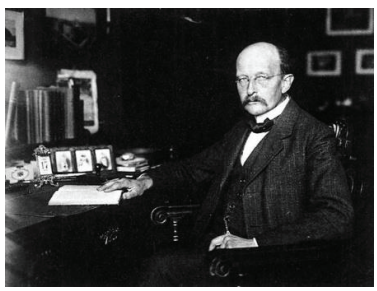
William Hyde Wollaston
(6 August 1766-22 December 1828)

Joseph von Fraunhofer
(6 March 1787-7 June 1826)

Jean Bernard Léon Foucault
(18 September 1819-11 February 1868)

Robert Wilhelm Eberhard Bunsen
(30 March 1811-16 August 1899)

Satyendra Nath Bose
(1 January 1894-4 February 1974)



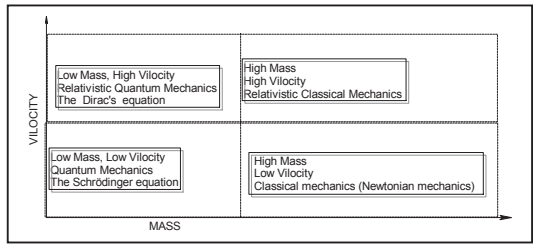
Max Karl Ernst Ludwig Planck
(23 April1858-4 October 1947)

Brook Taylor
(18 Augst 1685-29 December 1731)

3J. THE PLANCK'S QUANTUM THEORY

Classical mechanics provides an accurate description of macroscopic systems in the limit where velocities are much smaller than the speed of light. However, classical mechanics fails under the following conditions:

At microscopic (atomic and subatomic) scales where the concept of continuous energy breaks down.

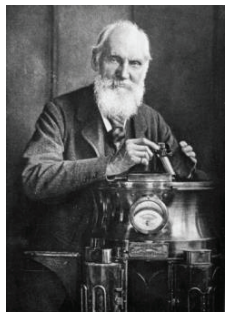


At velocities comparable to the speed of light where the assumptions of absolute space and time are invalid.

The failure at microscopic scales led to the development of quantum theory, while the failure at very high velocities necessitated the theory of relativity. In relativistic mechanics the relativistic mass/ energy momentum correction is introduced as $m = \frac{m_0}{\sqrt{1-\frac{v^2}{c^2}}}$.

Quantum theory was initiated by Planck in 1900, while the theory of relativity was proposed by Einstein in 1905.

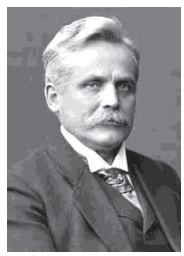
This gives the division of the scientific world into four major domains depending on the relative masses and velocities associated with the systems of interest.



William Thomson, 1st Baron Kelvin (26 June 1824- 17 December 1907)

At the close of the nineteenth century, classical physics appeared to present a nearly complete and unified description of natural phenomena. Yet, as Lord Kelvin observed in 1900, **"The beauty and clearness of the dynamical theory, which asserts heat and light to be modes of motion, is at present obscured by two clouds."** These "clouds" signified unresolved inconsistencies within classical theory most notably the failure to explain blackbody radiation and the implications of the Michelson–Morley experiment. Far from minor anomalies, these difficulties marked the limits of classical understanding and set the stage for the emergence of quantum theory and relativity, fundamentally transforming the conceptual foundations of modern physics.

But in the same year there was a ground breaking proposal of the quantum theory by Max Plank, which showed we still had much to discover. The Planck's quantum theory was introduced on 14 December 1900.



Wilhelm Carl Werner Otto Fritz Franz Wien (13 January 1864-30 August 1928)

There are several postulates of the Planck's quantum theory. Most notably, that energy travels in the form of packets called quantum (or quanta for plural).

The value of energy carried is $E = nh\nu$

Where:

- n- number of quanta released from the source
- h-Planck's constant
- ν-frequency of the quantum

This equation is known as:

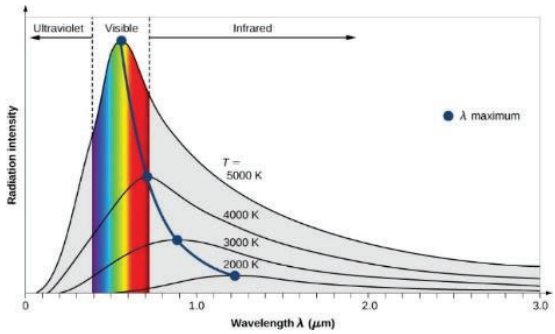
- Plank's relation
- Plank's energy-frequency relation
- Plank's equation
- Plank's formula
- Plank-Eisenstein relation

John William Strutt, 3rd Baron Rayleigh (12 November 1842- 30 June 1919)

This can be further extended as

$$E = \frac{nhc}{\lambda}$$

This equation helps us to prove what is known as the Planck's Radiation law introduced on October 19, 1900. This law connects the experimental results of the Wien's law given by Wilhelm Carl Werner Otto Fritz Franz Wien in 1893 and the Raleigh Jenes law, which was



given by John William Strutt, 3rd Baron Rayleigh (1904 Physics Nobel Prize) in the year 1900 and developed further in the year 1905 by both John William Strutt, 3rd Baron Rayleigh and Sir James Hopwood Jeans.
These laws are a part of Black body radiation studies.
These laws can be derived according to the sequence of steps:
Any black body can have discreate amount of energy, depending on oscillation frequency.

$$E = nh\nu = \frac{nhc}{\lambda}$$

If $n = N_A$ (Avogadro's number) then,

$$E = \frac{N_A hc}{\lambda(m)} = \frac{0.1197}{\lambda(m)} = 1Einstein$$

He derived an equation for energy of a black body at a wavelength λ known as Plank's radiation law, introduced on 19 October 1900.

$$E_\lambda = \frac{8\pi hc}{\lambda^5 (e^{\frac{hc}{\lambda k_B T}} - 1)}$$

From this equation both these laws can be proven (Wien's law and Rayleigh-Jean's law)
Both these laws are special cases of the Planck's Radiation law.
Assumption:

At smaller values of λT, $e^{\frac{8\pi hc}{\lambda k_B T}} \gg 1$
∴1 in the denominator can be ignored

$$E_\lambda = \frac{8\pi hc}{\lambda^5 e^{\frac{hc}{\lambda k_B T}}} \Rightarrow \frac{8\pi hc}{\lambda^5} e^{\frac{-hc}{\lambda k_B T}}$$ (Wien's spectral distribution law)

Now consider the case when λT is large, then expanding by binomial theorem i.e.
$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots,\ -\infty < x < \infty = 1 + \sum_{i=1}^{n} \frac{x^i}{i!}$ (Brook Taylor formally introduced the Taylor series in 1715. This was formulated by James Gregory (James Gregorie))

Sir James Hopwood Jeans
(11 September 1877-16 September 1946)

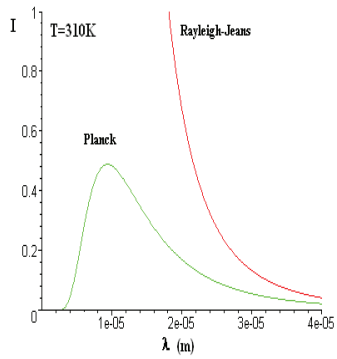
Let $x = \frac{hc}{\lambda k_B T}$

$$e^{\frac{hc}{\lambda kT}} = 1 + \frac{hc}{\lambda k_B T}\ \ (as\ \lambda T\ is\ large, x \ll 1)$$

Hence, $e^{\frac{hc}{\lambda kT}} - 1 = \frac{hc}{\lambda k_B T}$

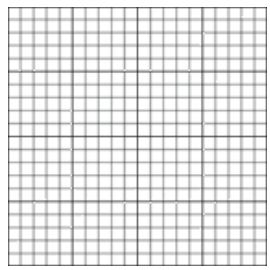
Hence, $E_\lambda = \frac{8\pi hc\lambda k_B T}{hc\lambda^5} = \frac{8\pi k_B T}{\lambda^4} = \frac{3.47\times10^{-22}T}{\lambda^4}$ (Raleigh Jenes law)

The phenomenon of failure of the Raleigh Jenes law at lower wavelength is called the Ultraviolet catastrophe. The term Ultraviolet catastrophe was first used in 1911 by Paul Ehrenfest.



Derivation of Planck's Radiation law: Satyendra Nath Bose used classical methods to derive the Plank's radiation Law. As the energy of a black body is quantized. Therefore, for a black body consisting of N number of small fragments called **oscillators** have collisions of energies $0, h\nu, 2h\nu, 3h\nu \ldots . nh\nu$ for $N_0, N_1, N_2, N_3 \ldots N_n$ number of particles respectively. **Oscillators** can be understood by the check analogy which can be depicted as the oscillators are considered similar to a checker board fragments. Actually, these are a group of particles vibrating with a definite constant value of energy i.e. 0, hν, 2hν…. nhν etc. in the photograph all the small white square has group of particles vibrating with a definite constant value of energy i.e. $0, h\nu, 2h\nu \ldots . nh\nu$ etc.

$\therefore E = nh\nu = \frac{nhc}{\lambda}$ (1)



According to the Maxwell Boltzmann distribution law

$N_i = N_0 e^{\frac{-E_i}{k_B T}}$ $(N_0 \, is \, number \, of \, particles \, with \, ground \, state \, energy)$(2)

Also,

$$N = \sum_{i=0}^{\infty} N_i$$

Combining (1) & (2) in the expression for N:

$N = N_0 + N_0 e^{\frac{-h\nu}{k_B T}} + N_0 e^{\frac{-2h\nu}{k_B T}} + N_0 e^{\frac{-3h\nu}{k_B T}} \ldots .$ (3)

$N = N_0 \left(1 + e^{\frac{-h\nu}{k_B T}} + e^{\frac{-2h\nu}{k_B T}} + e^{\frac{-3h\nu}{k_B T}}\right) \ldots .$

$(1 - e^{-x})^{-1} = 1 + \sum_{i=1}^{n} e^{-ix}$

$N = \frac{N_0}{1 - e^{\frac{-h\nu}{k_B T}}}$ (4)

Note that the total energy $E = nh\nu$,

Hence, $E = N_1 h\nu + 2N_2 h\nu + \cdots$

$E = h\nu(N_1 + 2N_2 + 3N_3 \ldots)$ .... (5)

Combining (3) & (4)

$E = N_0 h\nu \left(e^{\frac{-h\nu}{k_B T}} + 2e^{\frac{-2h\nu}{k_B T}} + 3e^{\frac{-3h\nu}{k_B T}} \ldots\right)$

$E = N_0 h\nu e^{\frac{-h\nu}{k_B T}} \left(1 + 2e^{\frac{-h\nu}{k_B T}} + 3e^{\frac{-2h\nu}{k_B T}} \ldots\right)$

Colin Maclaurin
(1698-1746)

Let $y = e^{\frac{-h\nu}{k_B T}}$

$E = N_0 h\nu e^{\frac{-h\nu}{k_B T}}(1 + 2y + 3y^2 + 4y^3 \ldots) = N_0 h\nu e^{\frac{-h\nu}{k_B T}}(1 - y)^{-2} = \frac{N_0 h\nu e^{\frac{-h\nu}{k_B T}}}{1 - y^2}$

(Maclaurin series)

$E = N_0 h\nu \frac{e^{\frac{-h\nu}{k_B T}}}{\left(1 - e^{\frac{-h\nu}{k_B T}}\right)^2}$ (6) [total energy of N oscillations]

For average energy per oscillation divide eqn (6) by (4)

James Gregory
(James Gregorie)
(1638-1675)

$$\bar{E} = \frac{E}{N} = \frac{\frac{N_0 h\nu e^{\frac{-h\nu}{k_B T}}}{\left(1 - e^{\frac{-h\nu}{k_B T}}\right)^2}}{\frac{N_0}{\left(1 - e^{\frac{-h\nu}{k_B T}}\right)}} = \frac{h\nu e^{\frac{-h\nu}{kT}}}{1 - e^{\frac{-h\nu}{k_B T}}}$$

Paul Ehrenfest
(18 January 1880-
25 September 1933)

Compiling further

$$\bar{E} = \frac{E}{N} = \frac{h\nu e^{\frac{-h\nu}{k_B T}}}{1 - e^{\frac{-h\nu}{k_B T}}} \qquad (7)$$

Multiply-divide (7) with $e^{\frac{-h\nu}{k_B T}}$

$$\bar{E} = \frac{E}{N} = \frac{h\nu}{e^{\frac{-h\nu}{k_B T}} - 1}$$

(According to classical mechanics $\bar{E} = 3k_B T$)

Ludwig Eduard
Boltzmann
(20 February 1844-5
September 1906)

if number of oscillations per unit volume having frequency ν→ν+dν is $\frac{8\pi\nu^2 d\nu}{c^3}$ (8) then average energy per unit volume or energy density is obtained by multiplying (8) and (7)

$$\bar{E}dn = \frac{h\nu e^{\frac{-h\nu}{k_B T}}}{1 - e^{\frac{-h\nu}{k_B T}}} \times \frac{8\pi\nu^2 d\nu}{c^3}$$

Putting $\nu = \frac{c}{\lambda}$ and $d\nu = -\frac{c}{\lambda^2} d\lambda$ we have

$\bar{E}dn = \frac{8\pi hc}{\lambda^5 e^{\frac{hc}{k_B T}} - 1} d\lambda$ Boltzmann Energy emitted by the black body

$$\boldsymbol{E_\lambda = \frac{8\pi hc}{\lambda^5 (e^{\frac{hc}{\lambda k_B T}} - 1)}}$$ (Planck's Radiation law)

Let $C_1 = 8\pi hc$ and $C_2 = \frac{hc}{k_B}$

$\therefore \bar{E}_\lambda = \frac{C_1 \lambda^{-5}}{e^{\frac{C_2}{\lambda T}} - 1}$

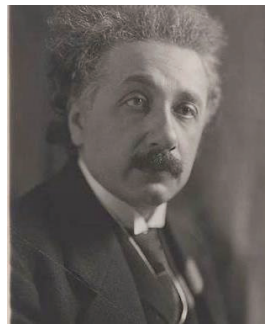
Ludwig Eduard Boltzmann is called the Father of Statistical Mechanics.

Max Karl Ernst Ludwig Planck is widely known as the Father of Quantum Theory and was awarded the 1918 Physics Nobel Prize.

"New scientific truth does not triumph by convincing its opponents and making them see the light, but rather because its opponents eventually die, and a new generation grows up that is familiar with it."

-Max Planck.

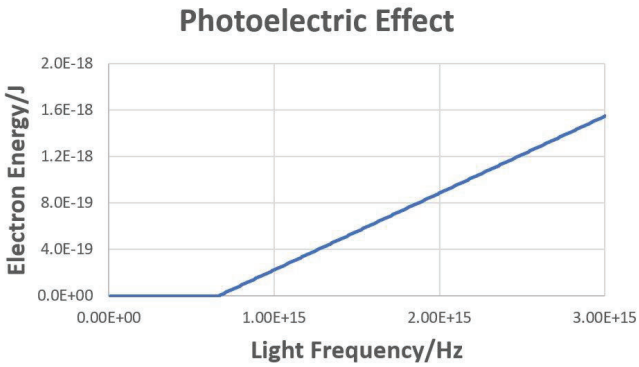
Wien's law given by Wilhelm Carl Werner Otto Fritz Franz Wien is known as "Founder of Blackbody Radiation Theory". He received the 1911 Physics Nobel Prize.



Albert Einstein
(14 March 1879-
18 April 1955)

3K. THE PHOTOELECTRIC EFFECT

The photoelectric effect (first reported by Hertz in 1887, and the photoelectric formula later given by Einstein) proved the quantization of energy successfully. It's the emission of the most loosely bound electron from the surface of a metal. It was discovered in 1887 by Heinrich Rudolf Hertz (name of the unit of frequency). During the experiment on electromagnetic waves, Hertz noticed that the sparks occur more frequently



in the air gap of the transmitter when the UV-rays were directed towards one of the metal balls used in the experiment. It was proved soon by Philipp Eduard Anton von Lenard that the emission of electron depends on the frequency of the radiation not on its intensity. According to the Planck's quantum theory the intensity of the radiation is the number of photons striking the surface per unit area per second. Photons are basically quanta of light. Now according to Planck's quantum theory, the energy of these photons $E = nh\nu$. This emission energy depends on the frequency of the photons hence, it was observed that, howsoever intense light of a frequency lower than a particular minimum threshold value might be fallen; no emission is observed but, when the frequency just crosses this threshold, the emission starts. This threshold value is known as work function of the metal. This was proposed by Albert Eisenstein in 1905. The kinetic energy of photoelectron is given by

$$E = \frac{m_e v_e^2}{2} = h\nu - W = h\nu - h\nu_0 = h(\nu - \nu_0) = hc\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right) = 1.9878 \times 10^{-25}\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)$$

$$E = h\nu_0 + eV_r \Rightarrow h\nu = h\nu_0 + eV_r \Rightarrow h\nu - h\nu_0 = eV_r = h(\nu - \nu_0) = eV_r$$

$$V_r = \frac{hc}{e}\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right) = 1.2 \times 10^{-6}\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right) joules$$

V_r is the retarding potential. The minimum negative potential applied to the positive plate to stop the current. It is proportional to frequency.

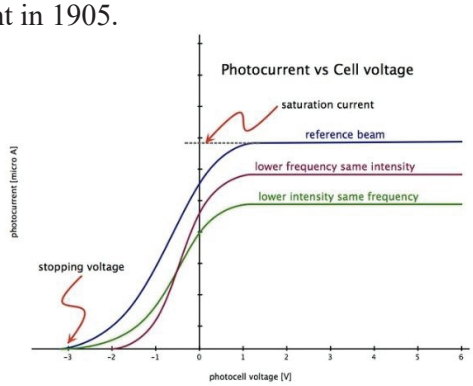
The work function of the metal is the minimum energy needed to eject an electron from a metal surface. Its relation with threshold frequency and wavelength is: $W = h\nu_0 = \frac{hc}{\lambda_0}$.

The velocity of the ejected electron in this effect is

$$v = \sqrt{\frac{2(h\nu - W)}{m_e}} = \sqrt{\frac{2(h\nu - h\nu_0)}{m_e}} = \sqrt{\frac{2h(\nu - \nu_0)}{m_e}} = \sqrt{\frac{2hc(\lambda_0 - \lambda)}{m_e \lambda \lambda_0}} = 660\sqrt{\frac{(\lambda_0 - \lambda)}{\lambda \lambda_0}}$$

EXPERIMENTAL OBSERVATION OF THE PHOTOELECTRIC EFFECT

Philipp Lenard was the first to carry out a systematic quantitative study of the photoelectric effect, extending Heinrich Hertz's 1887 discovery. His work (1899–1902) provided the experimental basis for Albert Einstein's photon theory of light in 1905.



In Lenard's experiment, two plane metal plates were mounted in an evacuated quartz-window discharge tube (since quartz transmits ultraviolet light, unlike glass). The plate at the negative terminal is coated with a photosensitive metal like potassium (K) or sometimes sodium (Na). The UV-rays were incident on the Anodic plate. The negative ions emitted by this plate are attracted toward the Cathodic plate called collector plate. The resulting electric current can be detected by a galvanometer fitted in the circuit. Now, if the positive potential is varied, the current varies with it, increasing as the potential increases and vice versa. Ultimately the potential is reached where the current becomes maximum, called saturation current. Opposing to this, if a negative potential is applied to the collector plate, at some potential V_r called retarding or stopping potential, the current drops to zero.

A. Experiments and Observations

Wilhelm Ludwig Franz Hallwachs
(9 July 1859-20 June 1922)

Between 1899 and 1902, Lenard published his results in *Annalen der Physik*. His key findings were:

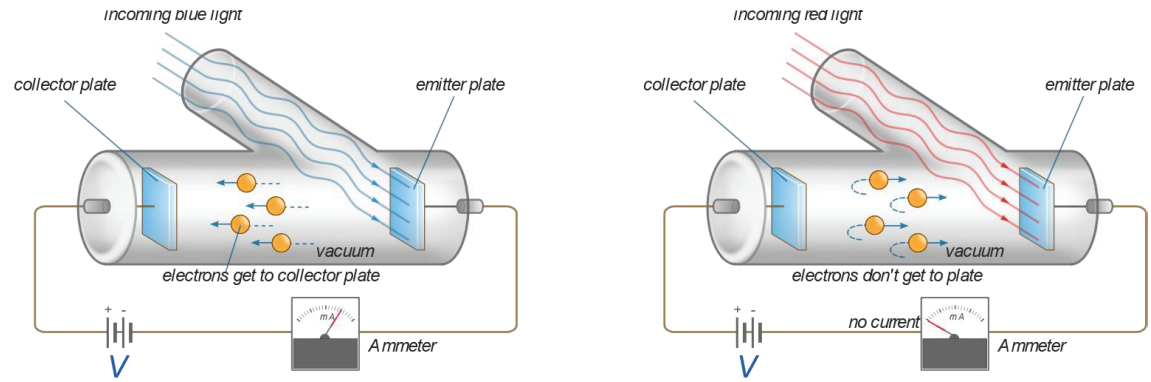
1. Emission of electrons (photoelectrons): When UV light strikes the potassium cathode, electrons are emitted instantly.
2. Effect of Intensity: Increasing light intensity increases the number of photoelectrons, but not their individual energies.
3. Effect of Frequency: Only light above a threshold frequency causes emission. Below threshold, no electrons are emitted regardless of intensity.
4. Kinetic Energy and Stopping Potential: By applying a reverse voltage, Lenard measured the stopping potential needed to halt photoelectrons, allowing him to estimate their maximum kinetic energy.
5. Instantaneous Emission: No measurable time lag between light exposure and electron emission.

Philipp Eduard Anton von Lenard
(7 June 1862-20 May 1947)

B. Significance

Lenard's experiments demonstrated clear limitations of classical wave theory of light. However, he did not provide a theoretical explanation. In 1905, Albert Einstein explained Lenard's results using the concept of light quanta (photons), earning him the 1921 Nobel Prize in Physics.

Conclusion: The stopping potential is proportional to frequency of the incident light, and the strength of current is proportional to the intensity of incident light.



The photoelectric effect provides direct experimental evidence for the particle nature of light. Albert Eisenstein was awarded the 1921 Physics Nobel Prize.

3L. BOHR'S ATOMIC MODEL

The combined strategies of the Rutherford's model and the Planck's quantum theory led to the incarnation of the Bohr's model in the 2nd half of the year 1913, when Niels Henrik David Bohr (Father of Atomic Physics/Founder of the Bohr's Atomic Model), published three consecutive papers now known as 'the trilogy' between July to November 1913. He quoted in 1928: **"Anyone who is not shocked by quantum theory has not understood it."**

In this model he used several quantum mechanical derivations for strengthening the arguments on the energy quantization in the atom. John William Nicholson's contribution into the model was of the postulate of angular momentum quantization: $mvr_n = \frac{nh}{2\pi}$.

Niels Henrik David Bohr
(7 October 1885-18 November 1962)

Other postulates were: the velocity of electron is negligible as compared to that of light and its mass is small than that of nucleus, the revolution path was considered elliptical. The most important of the postulates was that there is no energy radiation during the revolution of the electron.

This was a short introduction into the postulates. We shall now see a more detailed treatment of these:

Note: Despite the shared family name, the Bohr Effect in physiology and the Bohr atomic model in physics are distinct discoveries by father and son, respectively. This similarity makes them confusing but it is a common misconception.

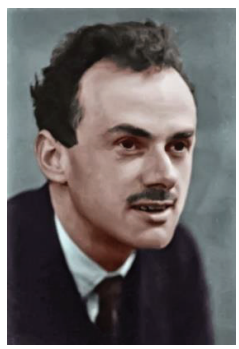
Christian Harald Lauritz Peter Emil Bohr (1855–1911) (Father): Discovered the Bohr Effect i.e. how haemoglobin's oxygen-binding depends on CO_2 and pH.

Niels Henrik David Bohr (1885–1962) (Son):
Developed the Bohr atomic model having quantized electron orbits explaining atomic stability and spectra.

Christian Harald Lauritz Peter Emil Bohr (14 February 1855-3 February 1911)

Karl Manne Georg Siegbahn (3 December 1886-26 September 1978)

Charles Glover Barkla (7 June 1877-23 October 1944)



Paul Adrien Maurice Dirac (PA.M. Dirac) (8 Augst 1902-20 October 1984

POSTULATES

- No retardation in the electron motion if it stays in a given orbit. This implies that an electron can revolve in an atom without emission of energy (radiation of energy) if it stays at a certain position called the non-radiating orbits or **stationary state**. Moreover, this is because the electron energy and probability are independent of time, as proven by the quantum mechanical model of atom. This eliminates the electromagnetic theory of physics in which every accelerated charge radiates energy.
- If the electron is moved from one orbit to another, it either radiated or absorbs energy in a sudden manner called quantum jumps. The direction of the flow of energy depends on the process of absorption or emission. If the electron is moved away from the nucleus opposing the coulombic attraction, then the energy is absorbed. It's emitted in the opposite process. The energy of the photon absorbed depends on the energy gap between the two energy levels of the two states i.e. the ground and the excited state of the atom. The photon of energy that exactly coincides with the energy gap cause an electronic transition. The energy gap is governed by the equation which is also called the **Bohr's frequency condition**.

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

  The electron can be found in the orbits where the angular momentum of the electron is some integral multiple of $\frac{h}{2\pi}$ i.e.

  $\vec{L} = m_e v_n r_n = \frac{nh}{2\pi} = n\hbar$ (Bohr's quantum restriction)

Where $\hbar = \frac{h}{2\pi}$. It is called Dirac's constant given by Paul Adrien Maurice Dirac (PA.M. Dirac, or simply, *Dirac*) in 1928.

- $\hbar = 1.054\ 571\ 628{\times}10^{-34}$ Js $= -6.582\ 118\ 99\ {\times}10^{-16}$ eVs
- it is pronounced as h-bar ($\hbar$)
- m mass of electron
- v tangential velocity
- r radius of the orbit
- n Principal quantum number ($n \in \mathbb{N}$)

Bohr's orbits are denoted by the uppercase KLMN etc. this was first used by Charles Glover Barkla in his paper published in 1911 titled 'The *Spectra of the Fluorescent Röntgen Radiations'*. Karl Manne Georg Siegbahn republished it in 1916 from when this is known as Siegbahn notations. Bohr's model obeys Newton's laws of motion.

Sir John Ambrose Fleming (29 November1849-18 April 1945)

It is applicable for hydrogen and **hydrogen like particles** like He^{+}, Li^{2+}, Be^{3+}. Generally, any atom is written as $^{ATOMIC\ MASS}_{ATOMIC\ NUMBER}SYMBOL^{CHARGE}_{ATOMICITY}$ where z is atomic number; A is atomic mass $\pm q$ is its charge and X is a general symbol for elements and Atomicity is ONE therefore we have $^{A}_{Z}X^{\pm q}$. For **hydrogen like or hydrogenic particles it generalizes as** $^{A}_{Z}X^{(Z-1)+}$.

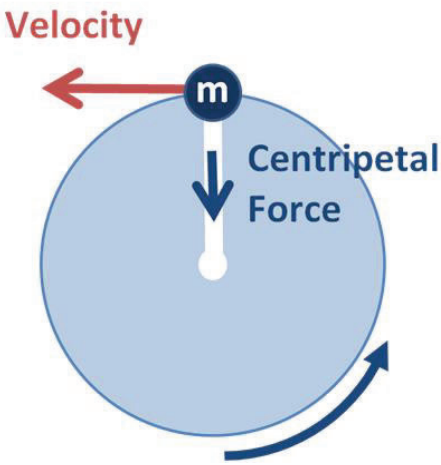
MATHEMATICAL TREATEMENT OF THE BOHR'S MODEL

A. **Radius of the orbit**

Bohr combined the classical forces in Newtonian mechanics and the electrostatic attraction. Let an electron of mass m_e and charge e are revolving in an orbit of radius r_n around the nucleus with a charge Ze,

Where Z is the atomic number,

At equilibrium the Columbic electrostatic attraction is balanced by the centrifugal force.



In classical mechanics the centrifugal force acting on a rotating body can be defined as the pseudoforce directed away the centre of the circle due to the circular motion and the centripetal force is equal and opposite to the centrifugal force, directed towards the centre of the circle due to the circular motion. This function is performed by the Columbic electrostatic attraction force acting between the electron and proton in the atom. This is the similarity of the Bohr's atomic model with the planetary motion (where, gravitational force act as centripetal force among the celestial bodies) and hence it is called the Planetary model of atom. ($\because$ negligible gravitational force between electron and proton)

The Columbic electrostatic attraction is:

$$\overrightarrow{F_E} = \frac{q_1 q_2}{4\pi\varepsilon_0 r_n^2}$$

The force acts in the direction from the proton to the electron and is denoted as $\overrightarrow{(F_E)_{ep}}$, which symbolizes the force acting on electron and is exerted by the proton. This complex symbol is denoted as $\overrightarrow{F_E}$ for simplification of the derivation.

The centrifugal force is:

$$\overrightarrow{F_C} = \frac{mv^2}{r_n}$$

This can be derived as follows:

By geometry a circle is a two-dimensional plane figure consisting of a set of all points that are equidistant from a fixed central point. This fixed distance is called the radius, and the fixed point is the center of the circle. The curved boundary itself is known as the circumference.

The small distance travelled by a body in a circular motion is given by x and it makes a small angle θ at the centre of the cirle, called as linear displacement x, and angular displacement θ respecively.

Now by geometry the angle at the centre θ is given by

$$Angle = \frac{Arc\ length}{Radius} \Rightarrow \theta = \frac{x}{r}$$

$\Rightarrow \vec{x} = \vec{\theta} \times \vec{r}$

The radius r, linear displacement x, and angular displacement θ, are all vector quantities.
Angular displacement θ is in Radian coined by James Thomson, brother of Lord Kelvin.
The axes of rotation is at the centre and normal to the plane of rotation. Therefore, all the quantities related to circular motion such as Angular displacement θ, Angular vilocity ω, Angular momentum L, torque τ are axeal vector quantities, as dipected by the right hand curl rule, given by Sir John Ambrose Fleming in 19th century.
⊗ inward from the plane of rotation, clockwise and negative; • outward from the plane of rotation, anticlockwise and positive.

Now angular velocity is anglular displacemnt in a unit time (one second). $\vec{\omega} = \frac{d\vec{\theta}}{dt}$. It is an axeal vector quantity expressed in rads^{-1}.
Now the angular velocity can be related with linear velocity as

$\vec{x} = \vec{\theta} \times \vec{r}$

Devide by t on both sides

$\frac{\vec{x}}{t} = \frac{\vec{\theta}}{t} \times \vec{r}$

Further,

$\vec{v} = \vec{\omega} \times \vec{r}$

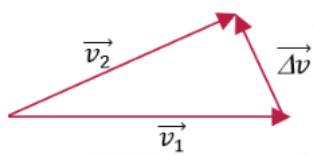
$\omega = \frac{v}{r}$

Next we have the frequency of rotation number of cycles per seconds **ν**, time period (T) is the time to complete one cycle. $\boldsymbol{\nu} = \frac{\mathbf{1}}{\mathrm{T}}$

$\omega = \frac{v}{r} = \frac{2\pi}{T} = 2\pi\nu$, Thus the angular velocity and the angular frequency are same.
Now, further the angular acceleration α is the rate of change of angular velocity. It is expressed rads^{-2}.

$\vec{\alpha} = \frac{d\vec{\omega}}{dt} = \frac{d\left(\frac{v}{r}\right)}{dt} = \frac{dv}{rdt} = \frac{a}{r} \Rightarrow \vec{a} = \vec{\alpha} \times \vec{r}$ (in vector notation)

At uniform **speed** a different acceleration called centripital acceleration as the velocity in a circular motion is changing and hence, circular motion is accelerated motion.



Now by the triangle law of vector addition we have,

$\overrightarrow{v_2} = \overrightarrow{v_1} + \overrightarrow{\Delta v}$

$\overrightarrow{v_2} - \overrightarrow{v_1} = \overrightarrow{\Delta v}$

$\overrightarrow{\Delta v}$ is change in velocity hence, it represents acceleration and is normal to the direction of velocity (as we start to take infinitesimally small changes in velocity), towards the centre.
Now by geometry The Tangent-Radius Theorem states that a radius drawn to the point of tangency is perpendicular to the tangent line at that point, forming a 90° angle. Therefore the angle between the two velocities is equal to the angle subtended by the arc at the centre which is the Angular displacement θ.
Now, from the two equations,

$\theta = \frac{\Delta v}{v_1} = \frac{x}{r} \Rightarrow \Delta v = \frac{x v_1}{r}$

Now dividing by t we have

$\frac{\Delta v}{\Delta t} = \frac{xv}{r\Delta t}$

$a = \frac{v.v}{r} = \frac{v^2}{r}$ is the centripital acceleration.
Bohr combined the classical forces in Newtonian mechanics, from Newton's Second Law of Motion,

"The time rate of change of the momentum of a body is equal in both magnitude and direction to the force imposed on it".
Further by definition the momentum of a body is given by $\vec{p} = m\vec{v}$
Therefore for Newton's Second Law of Motion we have,

$$\vec{F} \propto \frac{d\vec{p}}{dt} = m\frac{d\vec{v}}{dt} = ma$$

$$\vec{F} = k\frac{d\vec{p}}{dt}$$

$$\vec{F} = km\frac{d\vec{v}}{dt}$$

$\vec{F} = ma$ (k=1)
Now the centripital acceleration is $a = \frac{v^2}{r}$
Therefore

$$\overrightarrow{F_C} = \frac{mv^2}{r_n}$$

Now, at equilibrium the Columbic electrostatic attraction is balanced by the centrifugal force,

$$\overrightarrow{F_E} = \overrightarrow{F_C} \Rightarrow \frac{q_1 q_2}{4\pi\varepsilon_0 r_n^2} = \frac{mv^2}{r_n} \ (m = m_e)$$

$$\therefore r_n = \frac{Ze^2}{4\pi\varepsilon_0 mv^2} \qquad (8)$$

(Z is the atomic number and e is the electronic charge magnitude)

$$v_n = \frac{Ze^2}{\sqrt{4\pi\varepsilon_0 m_e r_n}}$$

Therefore,

$$\vec{L} = m_e v_n r_n = \frac{nh}{2\pi} = m_e \frac{Ze^2}{\sqrt{4\pi\varepsilon_0 m_e r_n}} r_n$$

Further,

$$v_n = \frac{2\pi e^2}{4\pi n\varepsilon_0 h} = \frac{e^2}{2n\varepsilon_0 h}$$

For first orbit,

$$v_0 = \frac{e^2}{2\varepsilon_0 h} = \frac{(1.6\times10^{-19}C)^2}{2\times6.626\times10^{-34}Js\times8.85\times10^{-12}C^2N^{-1}m^{-2}} = 2.18\times10^6 ms^{-1}$$

(Bohr's velocity)
This is 0.0027% of the speed of light. Therefore, the Schrödinger's wave equation is valid.
According to Bohr's quantum restriction i.e. $mvr_n = \frac{nh}{2\pi} = n\hbar$ (where $\hbar = \frac{h}{2\pi}$,) which he calculated by trial and error.

$$v_n = \frac{nh}{2\pi m_e r_n} = \frac{n\hbar}{m_e r_n} \qquad (9)$$

Further,

$$r_n = \frac{n^2}{m_e}\frac{h^2}{2\pi}\frac{4\pi\varepsilon_0}{e^2} = \frac{2n^2h^2\varepsilon_0}{m_e e^2}$$

For first orbit,

$$r_n = \frac{2h^2\varepsilon_0}{m_e e^2} = \frac{2\times8.85\times10^{-12}C^2N^{-1}m^{-2}(6.626\times10^{-34}Js)^2}{(9.1\times10^{-31}kg)(1.6\times10^{-19}C)^2} = 3.3\times10^{-10}m = 3.3\text{Å}$$

This calculation is the one Rutherford did, but this is not the true first orbit radius in Bohr's model. The calculation for that follows. The 3.3Å value is actually the de-Broglie wavelength λ_D for an electron in Bohr's first orbit.
From (8) & (9)

$$r_n = \frac{Ze^2}{4\pi\varepsilon_0 m_e\left[\frac{n^2h^2}{4\pi^2m^2r_n^2}\right]}$$

After simplification and rearrangement

$$r_n = \left[\frac{\varepsilon_0}{\pi m_e}\left(\frac{h}{e}\right)^2\right]\left(\frac{n^2}{Z}\right) = \left[\frac{4\pi\varepsilon_0}{m_e e^2}\hbar^2\right]\left(\frac{n^2}{Z}\right) \qquad (10)$$

This proves that the radii of the next higher orbit increase by a proportion of n^2

Further putting all the corresponding values

$\varepsilon_0 = 8.85\times10^{-12}C^2N^{-1}m^{-2}$

$m_e = 9.1\times10^{-31}kg$

$h = 6.626\times10^{-34}Js$

$e = 1.6\times10^{-19}C$

$$r_n = \left[\frac{\varepsilon_0}{\pi m_e}\left(\frac{h}{e}\right)^2\right] = \left[\frac{8.85\times10^{-12}C^2N^{-1}m^{-2}\times(6.626\times10^{-34}Js)^2}{9.1\times10^{-31}kg\times(1.6\times10^{-19}C)^2\pi}\right] = .53\times10^{-10}m = .53\text{Å}$$

$$= 5.3\times10^{-11}m = 53pm$$

This radius is known as the Bohr's radius and is denoted by a_0

Now putting the values for velocity by combining (9) and (10) we have,

$$v_n = \frac{nh}{2\pi m_e\left[\frac{\varepsilon_0}{\pi m_e}\left(\frac{h}{e}\right)^2\right]\left(\frac{n^2}{Z}\right)} = \frac{Z\pi m_e nhe^2}{2\pi m_e\varepsilon_0 h^2n^2} = \frac{Ze^2}{2\varepsilon_0 hn}$$

This predicts that the velocity of electrons in the next higher orbit fall down in the proportion to $\frac{1}{n}$

Now for the first Bohr's orbit of hydrogen atom we have,

$$v_n = \frac{e^2}{2h\varepsilon_0} = \frac{(1.6\times10^{-19}C)^2}{2\times8.85\times10^{-12}C^2N^{-1}m^{-2}\times6.626\times10^{-34}Js} = 2.18\times10^6ms^{-1}$$

We can directly put the value of the Bohr's radius in the expression of velocity as well, to reach the same value as

$$v_n = \frac{nh}{2\pi m_e r_n}$$

Now for the first Bohr's orbit of hydrogen atom we have,

$$v_n = \frac{h}{2\pi m_e a_0} = \frac{6.626\times10^{-34}Js}{2\pi\times9.1\times10^{-31}kg\times5.3\times10^{-11}m} = 2.18\times10^6ms^{-1}$$

The value of gravitational force between electron and proton according to Newton's law of gravitation

$$\vec{F}_G = G\frac{m_e m_n}{{a_0}^2} \quad G = 6.67\times10^{-11}Nm^{-2}kg^{-2}$$

$$\vec{F}_G = \frac{6.67\times10^{-11}\times1.67\times10^{-27}\times9.11\times10^{-31}}{(5.3\times10^{-11})^2} = 3.61\times10^{-47}N$$

Here we reach to the standard simplified equation for radius of the Bohr's orbit i.e.

$$\boldsymbol{r_n = a_0\left(\frac{n^2}{Z}\right) \Rightarrow a_0 = .53\times10^{-10}m = 53pm = 0.53\times10^{-8}cm\ (n = Z = 1)}$$

Further,

The kinetic energy of the electron is given by:

$$E_K = \frac{m_e v^2}{2} = \frac{Ze^2}{8\pi\varepsilon_0 r}$$

On putting r, we get,

$$E_K = \frac{Ze^2}{8\pi\varepsilon_0\left[\frac{\varepsilon_0}{\pi m_e}\left(\frac{h}{e}\right)^2\right]\left(\frac{n^2}{Z}\right)} = \frac{Z^2 m_e e^4}{8\varepsilon_0^2 h^2 n^2}$$

Johann Jakob Balmer (1 May 1825-12 March 1898)

Now for the first Bohr's orbit of hydrogen atom we have,

$$E_K = \frac{m_e e^4}{8\varepsilon_0^2 h^2} = \frac{9.1\times10^{-31}kg \times (1.6\times10^{-19}C)^4}{8(8.85\times10^{-12}C^2N^{-1}m^{-2})^2(6.626\times10^{-34}Js)^2} = 2.18 \times 10^{-18}J$$

The potential energy of electron attracted towards the proton will be negative for every finite value of r and become zero at $r \to \infty$, and it's given by

$$V_e = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

On putting r, we get,

$$V_e = -\frac{Ze^2}{4\pi\varepsilon_0\left[\frac{\varepsilon_0}{\pi m_e}\left(\frac{h}{e}\right)^2\right]\left(\frac{n^2}{Z}\right)} = -\frac{Z^2 m_e e^4}{4\varepsilon_0^2 h^2 n^2}$$

Now for the first Bohr's orbit of hydrogen atom we have,

$$V_e = -\frac{m_e e^4}{4\varepsilon_0^2 h^2} = \frac{9.1\times10^{-31}kg \times (1.6\times10^{-19}C)^4}{4(8.85\times10^{-12}C^2N^{-1}m^{-2})^2(6.626\times10^{-34}Js)^2} = -4.3 \times 10^{-18}J$$

Now the total energy $E = E_K + V_e = -\frac{Ze^2}{8\pi\varepsilon_0 r}$. This total energy is also known as the binding energy of electron

Johannes Robert Rydberg (8 November 1854-28 December 1919)

B. Energy of the revolving electron

The total energy of the electron is the sum of kinetic and potential energy (defined as the work done in bringing a positive charge from infinity to a point (at r_n in the present case)) which are:

$E_P = \int_\infty^n \overrightarrow{F_E}\, dr_n = \frac{Ze^2}{4\pi\varepsilon_0 r_n^2} dr = -\frac{Ze^2}{4\pi\varepsilon_0 r_n}$ the negative sign shows that work is done on the electron.

$$E_n = \frac{Ze^2}{8\pi\varepsilon_0 r_n} - \frac{Ze^2}{4\pi\varepsilon_0 r_n} = -\frac{Ze^2}{8\pi\varepsilon_0 r_n}$$

Putting r_n from (10)

$$E_n = -\left[\frac{m_e e^4}{8\varepsilon_0^2 h^2}\right]\left(\frac{Z^2}{n^2}\right) = -\left[\frac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2}\right]\left(\frac{Z^2}{n^2}\right)$$

Putting the corresponding values

$$\boldsymbol{E_n = \left[\frac{9.1\times10^{-31}kg(1.6\times10^{-19}C)^4}{8(8.85\times10^{-12}C^2N^{-1}m^{-2})^2(6.626\times10^{-34}Js)^2}\right]\left(\frac{Z^2}{n^2}\right) = -2.18\times10^{-18}\left(\frac{Z^2}{n^2}\right)J}$$

$$\boldsymbol{= -21.8\times10^{-19}\left(\frac{Z^2}{n^2}\right)Jatom^{-1} = -1313.3\left(\frac{Z^2}{n^2}\right)kJmol^{-1}}$$

$$\boldsymbol{= -13.6\left(\frac{Z^2}{n^2}\right)eVatom^{-1} = -R_H\left(\frac{Z^2}{n^2}\right)cm^{-1}}$$

$$\boldsymbol{= -1.09\times10^5\left(\frac{Z^2}{n^2}\right)cm^{-1} = -R_H hc\left(\frac{Z^2}{n^2}\right)J = -0.5\left(\frac{Z^2}{n^2}\right)a.u.}$$

The energy of the electron **Increases** on **Increasing** the value of the Principal quantum number. For hydrogen atom the energy of different orbits is

$$\boldsymbol{E_n = -2.18\times10^{-18}\left(\frac{Z^2}{n^2}\right)J = \frac{-21.8\times10^{-19}}{n^2}Jatom^{-1} = \frac{-1313.3}{n^2}kJmol^{-1} = \frac{-13.6}{n^2}eVatom^{-1}}$$

Now, for the first orbit of the hydrogen atom

Theodore Lyman IV (23 November 1874-11 October 1954)

$\boldsymbol{E_n = -13.6\ eVatom^{-1}}$ **(Ground state)**

Now, for the second orbit of the hydrogen atom

$\boldsymbol{E_n = -3.4\ eVatom^{-1}}$

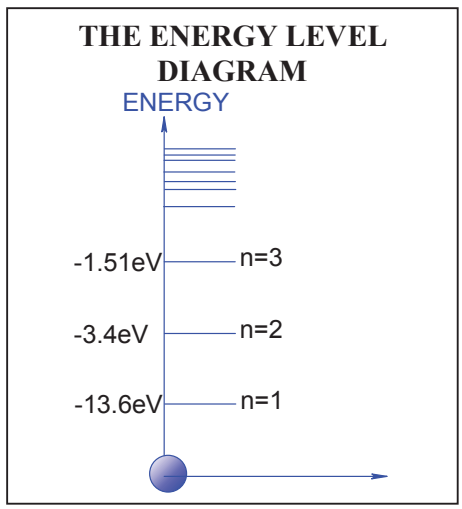
Now, for the third orbit of the hydrogen atom

$\boldsymbol{E_n = -1.51\ eVatom^{-1}}$

The negative sign in the energy expression reflects the choice of zero energy for a hydrogen-like atom as the state in which the electron is completely free at infinite separation from the nucleus, where the Coulomb interaction vanishes. All stationary states described by the Rydberg formula therefore correspond to bound states whose total energies lie below this reference level, implying that external energy must be supplied to remove the electron from the atom. The dependence of the energy on Z^2arises from the strength of the Coulomb attraction between the nucleus and the electron, while the inverse proportionality or variation with n^2ensures that higher quantum states, which are spatially more extended and hence less strongly bound, possess energies that increase toward zero as n increases. Consequently, the form $\boldsymbol{E_n = -13.6\left(\frac{Z^2}{n^2}\right)eVatom^{-1}}$ is a direct physical outcome of Coulomb binding and quantum confinement, and is fully consistent with energy conservation, which applies to energy differences rather than absolute energy values. This leads to the energy level diagram of the hydrogenic atom.

C. Frequency of radiation for excitation

In the process of excitation of electron, the energy is actually absorbed in a quantized manner with a frequency corresponding to the energy gape between the two states. This energy and the frequency of the radiation is governed by the Rydberg's formula. The Bohr's theory explains the emission spectra of Hydrogen on the same grounds. The Rydberg's formula was introduced by Johannes (Janne) Robert Rydberg (also known as Founder of the Spectroscopic Theory) in 1888. First regularities in a spectrum were proposed by him in 1889 as a result of his studies on doublet spectra of alkalis.



$$\boldsymbol{\overline{v} = \frac{1}{\lambda} = \frac{\nu}{c} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]Z^2}$$

The Rydberg's constant is derived by combining the Panck's quantum theory and the energy of electronic transition.

$$\Delta E = \frac{me^4}{8\varepsilon_0^2 h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]Z^2$$

$$\bar{\nu} = \frac{me^4}{8\varepsilon_0^2 ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]Z^2$$

$$\boldsymbol{\overline{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]Z^2}$$

$$\boldsymbol{R_H} = \frac{me^4}{8\varepsilon_0^2 ch^3} = \frac{(9.1\times10^{-31}kg)(1.6\times10^{-19}C)^4}{8(8.85\times10^{-12}C^2N^{-1}m^{-2})^2(3\times10^8 ms^{-1})(6.626\times10^{-34}Js)^3}$$

$$= 1.097\times10^7 m^{-1} = 109677 cm^{-1}$$

The numerically active form of the Rydberg formula is

$$\boldsymbol{\overline{v} = \frac{1}{\lambda} = \frac{\nu}{c} = 1.097\times10^7 m^{-1}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]Z^2}$$

Different atoms have different characteristics and a prominent characteristic is the light absorbed or emitted by the atom. These spectra are produced by the transitions of electrons.

Dr. Walther Heinrich Wilhelm Ritz (22 February 1878- 7 July 1909)

The spectra act as the fingerprint of that atom. The formation of the hydrogen emission spectra series is now explained based on the Rydberg's formula, also known as Rydberg Ritz combination principle because it was further advanced by Walther Heinrich Wilhelm Ritz in 1908 according to which if the electron falls to the first orbit n=1 then the formation of the **Lyman series** is observed which was first introduced by Theodore Lyman IV between 1906-1914.

Further if the electron falls to the second orbit from a higher one then the **Balmer series** is observed introduced by Johann Jakob Balmer in 1885. Similarly, when the electron falls to the third orbit $n = 3$, the formation of **Paschen series** is observed introduced by Louis Carl Heinrich Friedrich Paschen in 1908. **Bracket series** is observed when electron falls to fourth orbit, introduced by Friedrich Sumner Brackett in 1922. August Herman Pfund introduced the **Pfund series** in 1924. It's observed when an electron falls to the fifth orbit. **Humphreys series** is observed when electron transition takes place from higher energy state to the sixth orbit. It was introduced by Curtis Judson Humphreys in 1953.

Lyman-alpha, denoted by **Ly-α**, is a spectral line of hydrogen (or, more generally, of any one-electron atom) in the Lyman series. It is emitted when the atomic electron transitions from an $n = 2$ state to the ground state ($n = 1$), where n is the principal quantum number. In hydrogen, it has a wavelength of $1215.67\ \text{Å} = 121.567\ nm = 1.21567 \times 10^{-7}\ m$ corresponding to a frequency of about 2.47×10^{15} Hz, which places Lyman-alpha in the ultraviolet (UV) region of the electromagnetic spectrum. More specifically, Ly-α lies in vacuum UV (VUV), characterized by a strong absorption in the air.

On similar bases:

- n = 3 to n = 2 is called Balmer-alpha or Br α
- n = 4 to n = 2 is called Balmer-beta or Br β
- n = 5 to n = 2 is called Balmer-gamma or Br γ.

For the Lyman series the naming convention is:

- n = 2 to n = 1 is called Lyman-alpha or Ly α
- n = 3 to n = 1 is called Lyman-beta or Ly β.

One of the methods of production of the spectrum is to pass a high voltage electric discharge through the desired gas filled at a pressure of 1-2 mmHg in an electrode equipped glass tube called discharge tube as is used in the Neon signs. The wavelengths can be measured by an instrument called interferometer.

In the series the lines get closer and dimmer (less intense).

Lyman series is given by $\overline{\boldsymbol{\nu}} = \frac{\mathbf{1}}{\boldsymbol{\lambda}} = \boldsymbol{R_H}\left[\frac{1}{1} - \frac{1}{n_2^2}\right]$ where n_2 starts from 2.

Balmer series is given by $\overline{\boldsymbol{\nu}} = \frac{\mathbf{1}}{\boldsymbol{\lambda}} = \boldsymbol{R_H}\left[\frac{1}{4} - \frac{1}{n_2^2}\right]$ where n_2 starts from 3.

Paasschen series is given by $\overline{\boldsymbol{\nu}} = \frac{\mathbf{1}}{\boldsymbol{\lambda}} = \boldsymbol{R_H}\left[\frac{1}{9} - \frac{1}{n_2^2}\right]$ where n_2 starts from 4.

Bracket series is given by $\overline{\boldsymbol{\nu}} = \frac{\mathbf{1}}{\boldsymbol{\lambda}} = \boldsymbol{R_H}\left[\frac{1}{16} - \frac{1}{n_2^2}\right]$ where n_2 starts from 5.

Pfund series is given by $\overline{\boldsymbol{\nu}} = \frac{\mathbf{1}}{\boldsymbol{\lambda}} = \boldsymbol{R_H}\left[\frac{1}{16} - \frac{1}{n_2^2}\right]$ where n_2 starts from 6.

Louis Carl Heinrich Friedrich Paschen (22 January 1865-25 February 1947)

THE BOHR MEGNETON

Now from Bohr's quantum restriction i.e. $\vec{L} = mvr_n = \frac{nh}{2\pi} = n\hbar$, for first Bohr's orbit $n = 1$, the magnetic dipole moment of electron μ is given by

$$\gamma = \frac{\vec{\mu}}{\vec{L}} = 8.8 \times 10^{10} Ckg^{-1}$$

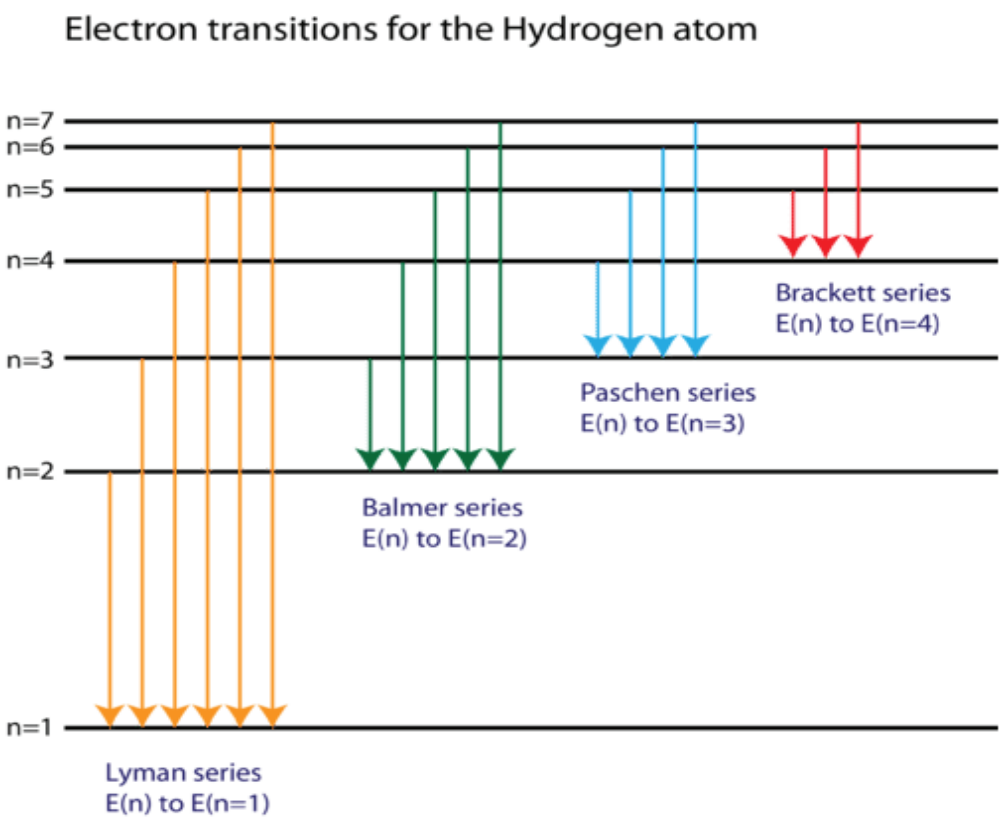
$$\overrightarrow{\mu_B} = \frac{eh}{4\pi m_e} = \frac{1.66\times10^{-19}C\times6.626\times10^{-34}Js}{4\pi\times9.11\times10^{-31}kg} = \frac{e\hbar}{2m_e} = \frac{1.66\times10^{-19}C\times1.054\,571\,628\times10^{-34}\,\text{Js}}{2\times9.11\times10^{-31}kg} = \gamma_e\vec{L} = \frac{\gamma_e h}{2\pi}$$
$$= \frac{8.7954\times10^{10}Ckg^{-1}\times6.626\times10^{-34}Js}{2\pi} = 9.27\times10^{-24}Am^2 = 9.27\times10^{-24}JT^{-1} = 1BM$$
$$= 1Bohr's\ megneton$$

THE BALMER SERIES OF HYDROGEN ($(n_1 = 2); Z = 1$

Line	λ (Å)	n_2	$\overline{v} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$	COLORS
H_α	6563.1	3	15233	Red
H_β	4860.9	4	20565	Blue-green (Teal)
H_γ	4340.5	5	23033	Blue
H_δ	4101.7	6	24373	Violet
H_ε	3970.1	7	25181	Near-violet
H_ζ	3889.05	8		Near-violet / UV
H_η	3835.38	9		Near-UV
H_θ	≅3797.9	10		UV
H_∞	3646	∞	27420	UV (Balmer limit)

The spectral series are encountered in a specific spectral region as shown in the table.

SPECTRAL SERIES	SPECTRAL REGION
Lyman series	**ULTRA VIOLET**
Balmer series	**ULTRA VIOLET-VISIBLE**
Paasschen series	**INFRARED**
Bracket series	
Pfund series	
Humphreys series	



BOHR'S CORRESPONDENCE PRINCIPLE

"It seems possible to throw some light on the outstanding difficulties by trying to trace the analogy between the quantum theory and the ordinary theory of radiation as closely as possible."

-Bohr 1918

"Although the process of radiation cannot be described on the basis of the ordinary theory of electrodynamics … there is found, nevertheless, to exist a far-reaching correspondence between the various types of possible transitions between the stationary states on the one hand and the various harmonic components of the motion on the other hand."

-Bohr 1923- 1924

"The demonstration of the asymptotic agreement between spectrum and motion gave rise to the formulation of the 'correspondence principle,' according to which the possibility of every transition process connected with emission of radiation is conditioned by the presence of a corresponding harmonic component in the motion of the atom. Not only do the frequencies of the corresponding harmonic components agree asymptotically with the values obtained from the frequency condition …, but also the amplitudes of the mechanical oscillatory components give in this limit an asymptotic measure for the probabilities of the transition processes on which the intensities of the observable spectral lines depend."

-Bohr 1925

This can be concluded to:

At higher values of n the results of quantum mechanics approach the same values as those of the classical mechanics. This is called the Bohr's correspondence principle and was postulated by Bohr in 1923.

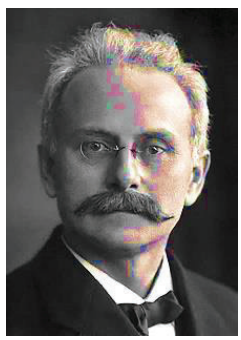
BOHR'S COMPLEMENTARITY PRINCIPLE

Bohr first introduced the Principle of Complementarity in September 1927-1928 during his Como Lecture, delivered at the Volta Conference on Electrons and Photons in Como, Italy, organized to celebrate Alessandro Volta's centenary. It states that:

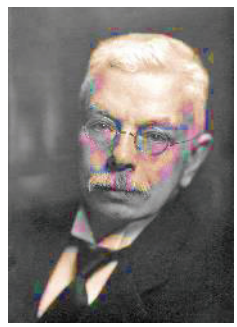
"The evidence obtained under different experimental conditions cannot be comprehended within a single picture, but must be regarded as complementary in the sense that only the totality of the phenomena exhausts the possible information about the object."

This general principle is applied concretely to atomic phenomena, where Bohr explains:

"The description of atomic phenomena has a complementary character, since the various experimental arrangements which disclose the wave or the particle aspects of the atomic entities are mutually exclusive, yet both are necessary for a complete account of the phenomena."



Pieter Zeeman (25 May 1865-9 October 1943)



Johannes Stark (15 April 1874-21 June 1957)

-Neils Bohr 1928

DOCTRINE OF CLASSICAL CONCEPTS

"However far the phenomena transcend the scope of classical physical explanation, the account of all evidence must be expressed in classical terms."

— Niels Bohr, 1949

MERITS OF THE BOHR'S THEORY

The Bohr's theory has numerous important advantages. It helped to reach more accurate results of many properties.

- **Ionization Potential:** it is the potential needed to ionize, or take out an electron from an atom. It can be calculated using the Rydberg's formula.

$$E_{ionization} = -21.8 \times 10^{-19} \left(\frac{Z^2}{n^2}\right) Jatom^{-1}$$
$$= -21.8 \times 10^{-19} Z^2 Jatom^{-1}$$
$$(n, Z = 1)$$

- It explains the Mosley's law also called the Modern Periodic Law.
- It explains the atomic stability by the concept of stationary states, bypassing the electromagnetic theory which was the main demerit of the Rutherford's model. It also explains the isotopic shift and the mass spectroscopy.

Hendrik Antoon Lorentz
(18 July 1853-4 February 1928)

LIMITATIONS OF THE BOHR'S THEORY

While the model proposed by Niels Bohr marked a profound and remarkably successful breakthrough, it remains subject to certain limitations that were subsequently addressed within the framework of quantum mechanics. Bohr's atomic model offered critical advancements by introducing quantized electron orbits and successfully explaining the hydrogen emission spectrum. However, as experimental evidence accumulated, it became evident that certain atomic phenomena lay beyond its scope. These were later addressed by more generalized quantum mechanical principles.

- The Bohr's theory was unable to explain the hyperfine spectra of the hydrogen atom.

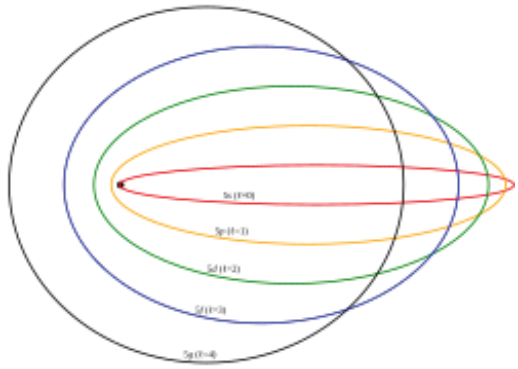
It was also not able to explain the Zeman effect which is the splitting of a spectral line into several components in the presence of a static external magnetic field. It is produced as a consequence magnetic field and the magnetic field associated with the electron (by the virtue of its spinning and orbital motion) proposed by Pieter Zeeman, in 1896 and Stark Effect which is the splitting of a spectral line into several components in the presence of a static electric field proposed by Johannes Stark in 1913. Johannes Stark is known as the Founder of experimental electro spectroscopy. He was awarded the 1919 Physics Nobel Prize. Pieter Zeeman is known as the Founder of experimental magneto spectroscopy. He was awarded the 1902 Physics Nobel Prize, shared with Hendrik Antoon Lorentz.

Niels Henrik David Bohr was awarded the 1922 Physics Nobel Prize for his atomic model.

BOHR AND THE ATOMIC BOMB: HISTORICAL FACTS VS MISCONCEPTIONS

Although Niels Bohr's atomic model laid the foundation stone for profounder understanding nuclear structure, his active participation, with other scientists, in the development of the atomic bomb has often been misunderstood. They were NOT bomb-makers. Bohr himself was a moral voice during one of science's darkest turning points. After escaping Nazi-occupied Denmark in 1943, he visited Britain and the United States of America to advise on the Allied Nuclear Project; yet his purpose was never, arm making, but to ensure international openness and post-war control of atomic energy. He repeatedly warned that secrecy and rivalry would endanger humanity more than any scientific discovery itself.

In later reflections, Bohr described science as *"A human adventure into the unknown"* that carries ethical duties equal to its intellectual achievements. The tragedy he witnessed was not of his making, but of a world unprepared for the power that his and others' insights had unlocked. Far from losing dignity, Bohr's legacy lies in his insistence that knowledge must always be joined with conscience a lesson that continues to guide scientific responsibility today.



In 1916 Arnold Johannes Wilhelm Sommerfeld proposed another atomic model called the Bohr-Sommerfeld model. It is an extension of the Bohr's atomic model by incorporating the orbit shape concept and the second quantum number called as the azimuthal quantum number. It was an attempt to explain the fine structure of the line spectra of hydrogen.

3M. THE COMPTON EFFECT

This scattering effect was discovered by Arthur Holly Compton in the year 1923. It is the quantum mechanical explanation of the scattering of high frequency X-ray photons through their interaction with charged particles. Interaction of such a high frequency X-ray photons release the most loosely bound valence electrons from atoms or molecules. The Compton effect occurs at electron level. After interaction the wavelength of the photon is increased, reducing its energy. The scattered photon has a greater wavelength than the incident photon. This increase of wavelength is called Compton's shift. The energy of the photon gets transferred to the electron creating a "Compton recoil electron". If the recoiling particle initially carried more energy than the photon has, the reverse would occur. This is known as **inverse Compton scattering**, in which the scattered photon increases in energy. In the original Compton's experiment, the energy of the X-Ray photon was ≈ 17 keV. This energy was significantly larger than the binding energy of the electrons. Therefore, the electrons are approximately free after scattering. Wu Youxun verified the Compton effect. Compton effect demonstrates the fact that, light cannot be explained purely as a wave phenomenon.

Arthur Holly Compton (10 September 1892-15 March 1962)

$\Delta\lambda = \lambda' - \lambda \propto \theta$

There is smaller Compton's shift at smaller scattering angles and larger at larger angles. This shifting of wavelength can be explained by assuming that the electromagnetic radiations are composed of photons not electromagnetic waves. The Compton scattering is due to the inelastic collisions of the photons and electrons.

Now from Plank's postulate

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

Now further from relativity we have

$$E = pc$$

$$p = \frac{E}{c} = \frac{h\nu}{c} = \frac{h}{\lambda}$$

now further the energy of electron is

$$\boldsymbol{E_e = m_e c^2}$$

Now the energy of the scattered photon is

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

$$p' = \frac{h\nu'}{c}$$

Now the energy of the scattered electron is,

$$\boldsymbol{E'_e = \sqrt{m_e^2 c^4 + p_e^2 c^4}}$$

Now by the law of linear momentum we have,

$$\vec{p} = \overrightarrow{p'} + \overrightarrow{p_e}$$

$$\overrightarrow{p_e} = \vec{p} - \overrightarrow{p'}$$

Applying $|\vec{R}|^2 = |\vec{A}|^2 + |\vec{E}|^2 - 2|\vec{A}||\vec{E}|\cos\theta$ we have,

$p_e^2 = p^2 + p'^2 - 2pp'\cos\ \theta$

$p_e^2 = \left(\frac{h\nu}{c}\right)^2 + \left(\frac{h\nu'}{c}\right)^2 - 2\left(\frac{h\nu}{c}\right)\left(\frac{h\nu'}{c}\right)\cos\theta = \left(\frac{h}{c}\right)^2\left[\nu^2 + \nu'^2 - 2\nu\nu'\cos\ \theta\right]$

Applying the conservation of energy we have,

$\boldsymbol{E_e} + E = E' + \boldsymbol{E'_e}$

$h\nu + \boldsymbol{m_e c^2} = h\nu' + \sqrt{\boldsymbol{m_e^2 c^4} + \boldsymbol{p_e^2 c^4}}$

On squaring and rearranging we have,

$[h(\nu - \nu') + \boldsymbol{m_e c^2}]^2 = \boldsymbol{m_e^2 c^4} + \boldsymbol{p_e^2 c^4}$

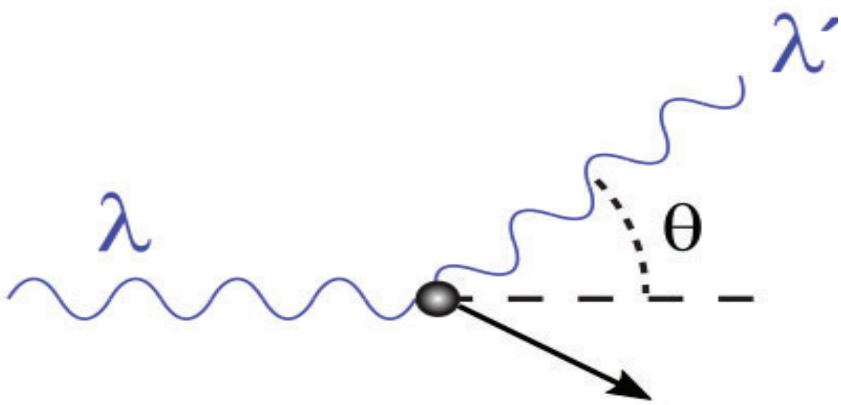
After further mathematical treatment we have,

$$\lambda' - \lambda = \Delta\lambda = \frac{h}{m_e c}(1 - \cos\theta) = \lambda_C(1 - \cos\theta) = 2.42 \times 10^{-12} m(1 - \cos\theta)$$
$$= 2.43pm(1 - \cos\theta) = 0.0243\text{Å}(1 - \cos\theta)$$

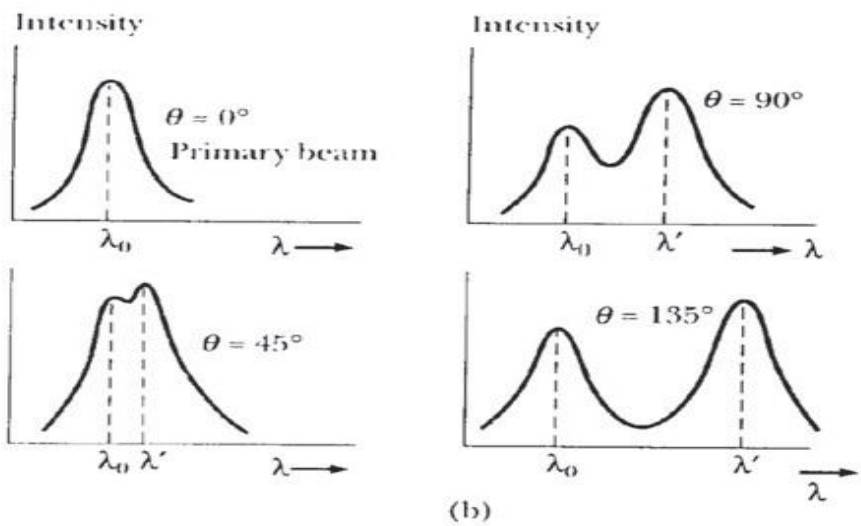
$\lambda_C = 2.42 \times 10^{-12} m = 2.43pm = 0.0243$Å is called Compton wavelength.

$$\frac{E_K}{E} = \frac{\Delta\lambda}{\lambda + \Delta\lambda}$$

The Compton effect dominates for the high energy photons. The black body radiation, photoelectric effect and the Compton effect deduce the particle nature of electromagnetic



Compton scattering experimental scheme



Compton scattering experimental observation

radiation. The experiments like diffraction, interference, deduce the wave nature of electromagnetic radiation. Arthur Holly Compton is called the Father of X-Ray Quantum Physics. Arthur Holly Compton was awarded the 1927 Physics Nobel Prize.

3N. THE de-BROGLIE HYPOTHESIS

The de-Broglie hypothesis proposed by Louis Victor Pierre Raymond, 7th Duc de Broglie (Father of the matter waves) in 1923-24 in his doctorate thesis **"Recherches sur la théorie des quanta ("Research on Quantum Theory") (1924)".** In this thesis he proposed the idea of matter waves. This is a unique idea of that time. It can be stated as; "similar to the behaviour of light (radiation) which have both a nature of particle and a wave, matter also have a wave nature with an associated wavelength λ which can be calculated by $\lambda = \frac{h}{mv}$ where h Plank's constant; m is mass of the particle and v is its velocity." It was derived by combining the Einstein energy mass equation and the Plank's quantum theory as:

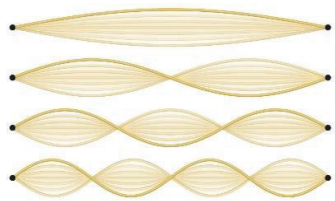
Louis Victor Pierre Raymond, 7th Duc de Broglie
(15 August 1892-19 March 1987)

$E = mc^2$

$E = nh\nu = \frac{nhc}{\lambda}$

$\therefore mc^2 = \frac{nhc}{\lambda}$

$\therefore \lambda = \frac{nh}{mv}$



Further this confirms the Bohr's quantization condition which can be proved by the analyses of the standing waves.

Standing wave possess energy but they do not ***propagate*** energy. The condition for the production of the standing wave is two waves with same wavelength, frequency, speed and medium, travelling in opposite direction.

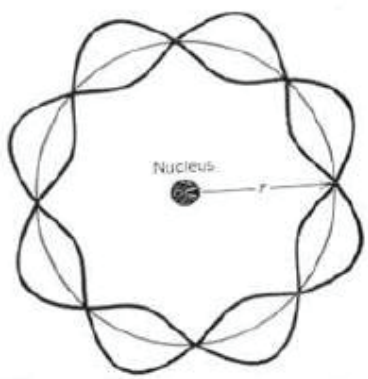
The electron revolving around the nucleus is associated with a de-Broglie wave of wavelength $l = n\lambda; n \in \boldsymbol{W}$

This produces the stationary waves in the total circumference therefore, $2\pi r = n\lambda$

Where n is the no. of cycles in each circle.

$\therefore 2\pi r = \frac{nh}{mv} = n\lambda_D$

The circumference of the permitted stationary state orbit is an integral multiple of the de-Broglie wave of wavelength associated with the electron present in that particular orbit. This condition leads to the constructive interference.



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

According to Bohr's quantum restriction i.e. $mvr_n = \frac{nh}{2\pi}$

The de-Broglie hypothesis was demonstrated by the results of Davison-Germer experiments, Thomsons experiments and the interference patterns obtained in the Young's double slit experiment with electron. It further explains why electrons cannot reside in the nucleus.

We know that

$mvr = \frac{h}{2\pi} \Rightarrow v = \frac{h}{2\pi mr} = \frac{6.626 \times 10^{-34} Js}{2 \times 3.14 \times 9.1 \times 10^{-31} kg \times 10^{-15} m} =$
$1.15 \times 10^{11} ms^{-1}$ which is not possible as $c = 3 \times 10^8 ms^{-1}$

According to Bohr's quantum restriction i.e. $mvr_n = \frac{nh}{2\pi} \Rightarrow 2\pi r_n = \frac{nh}{m_e v_n} = \lambda_D$

The de-Broglie wavelength λ_D for an electron in Bohr's first orbit is

$$\lambda_D = 2\pi r_n = \frac{nh}{m_e v_n} \Rightarrow 2\pi\left[\frac{\varepsilon_0}{\pi m_e}\left(\frac{h}{e}\right)^2\right]\left(\frac{n^2}{Z}\right) = \frac{nh}{m_e \frac{e^2}{2h\varepsilon_0}}$$

On further simplification we have,

$$\lambda_D = 2\pi\left[\frac{\varepsilon_0}{\pi m_e}\left(\frac{h}{e}\right)^2\right]\left(\frac{n^2}{Z}\right) = \frac{nh}{m_e \frac{Ze^2}{2\varepsilon_0 hn}}$$

On further simplification, from both the above expressions, we have,

$$\lambda_D = \frac{2\varepsilon_0 n^2 h^2}{Z m_e e^2}$$

Alternatively,

For the non-relativistic case,

$$\lambda_D = \frac{h}{mv} = \frac{h}{m_e v_n} = \frac{h}{m_e \frac{Ze^2}{2\varepsilon_0 hn}} = \frac{2\varepsilon_0 nh^2}{Z m_e e^2}$$

$$\lambda_D = \frac{h}{\sqrt{2mE_K}} = \frac{h}{\sqrt{2m_e \frac{m_e e^4}{8\varepsilon_0^2 h^2}}} = \frac{2\varepsilon_0 h^2}{m_e e^2}$$

Now for the first Bohr's orbit of hydrogen atom we have,

$$\lambda_D = \frac{2\varepsilon_0 h^2}{m_e e^2} = \frac{2 \times 8.85 \times 10^{-12} C^2 N^{-1} m^{-2} (6.626 \times 10^{-34} Js)^2}{(9.1 \times 10^{-31} kg)(1.6 \times 10^{-19} C)^2} = 3.3 \times 10^{-10} m = 3.3\text{Å}$$

Moreover, we cannot even experience this phenomenon in macroscopic world because even if we take a 100-gram golf ball shot by $100 ms^{-1}$ have

$$\lambda_D = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{100 \times 10^{-3} \times 100} = 6.626 \times 10^{-35} m$$

The velocity of a body of mass of an electron will be greater than the speed of light at a de Broglie wavelength equal to the Planck's length $l_p = \sqrt{\frac{\hbar G}{c^3}} = 1.61 \times 10^{-35} m$

Putting, $\lambda_D = l_p = 1.61 \times 10^{-35} m$

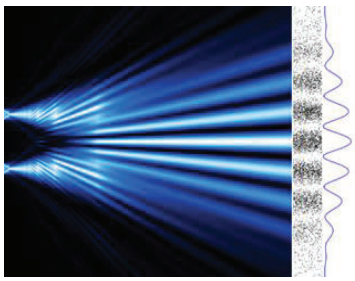
$$\lambda_D = \frac{h}{m_e v} = 1.61 \times 10^{-35} m = \frac{6.626 \times\times 10^{-34} J.s}{9.11 \times 10^{-31} kg.v} \Rightarrow v = 4.54 \times 10^{31} ms^{-1}$$

The de Broglie wavelength can be related to energy in the following way by incorporating different relations od energy.

$$\lambda_D = \frac{h}{mv} = \frac{h}{p} = \frac{h}{\sqrt{2mE_K}} = \frac{h}{\sqrt{2mE}} = \sqrt{\frac{h}{2m\nu}} = \frac{h}{\sqrt{2mqV}}$$

Using the molar mass and putting the relation of given mass m and molar mass M $M = \frac{M}{N_A}$, de Broglie wavelength can be written as $\lambda_D = \frac{h}{mv} = \frac{hN_A}{Mv} = \frac{3.99 \times 10^{-10}}{M(kg)v(ms^{-1})} = \frac{3.99 \times 10^{-7}}{M(g)v(ms^{-1})}$

Louis de Broglie was awarded the 1929, Physics Nobel Prize.



The double slit experiment with electrons

Thomas Young (13 June 1773-10 May 1829)

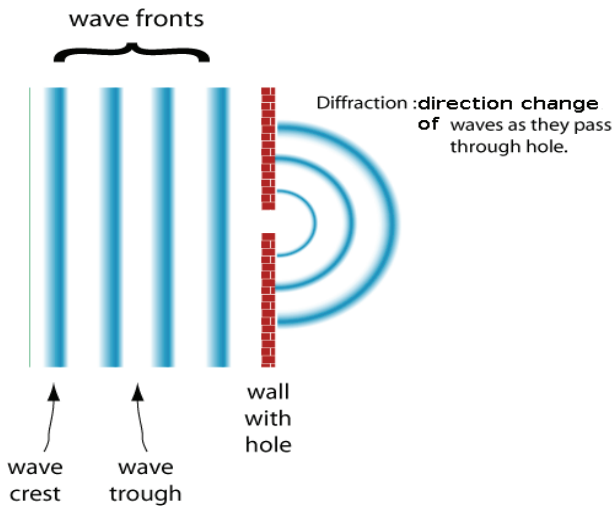
George Paget Thomson (G.P. Thomson) (3 May 1892-10 September 1975)

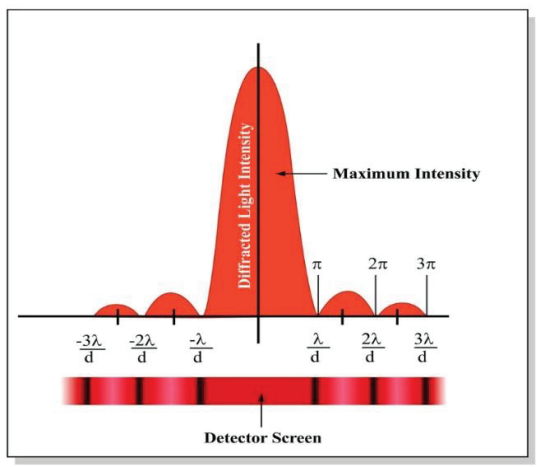
DIFFRACTION OF ELECTROMEGNETIC WAVES

Diffraction refers to a wave characteristic in which when light passes over an obstacle, it bends towards the shadow area. This gives some bright and dark fringes at the end of the shadow area. The term diffraction was given by Francesco Maria Grimaldi. The diffraction of light of wavelength λ is $d \sin\theta$. θ is the angle of elevation of the fringes. It is observed that the dark point if $d \sin\theta = n\lambda$. This is the superposition principle according to which, for linear systems, the response to multiple stimuli or influences acting simultaneously is the algebraic or vector sum of the individual responses to each stimulus.

For displacement. sources in the opening are divided in two parts in both of which there are two corresponding sources with a destructively superposing path difference of $\frac{\lambda}{2}$. This gives a dark point. If θ is small then $\theta = \sin\theta$, therefore, $d.\theta = \lambda$, therefore, $\theta = \frac{\lambda}{d}$. For the screen at a distance D and the distance of the normal to the screen from the slit and the first dark as h, the width of the central bright is given by $2h = \frac{2\lambda D}{d}$. If a particle is under effect of more than one waves simultaneously, the net displacement is equal to the sum of all the individual displacements given by all the waves.

In this case The first bright after central is observed because the path difference is $\frac{3\lambda}{2}$. First $\frac{1}{3}$ waves have destructive superposition with second set of $\frac{1}{3}$ waves, but the last set of $\frac{1}{3}$ waves have no superposition and they make first bright after central bright with an elevation of $\theta = \frac{3\lambda}{2d}$. Now in general the dark fringe is at an elevation of $\theta = \frac{n\lambda}{d}$, and at a distance $h = \frac{n\lambda}{d}D$. Now for brights $\theta =$

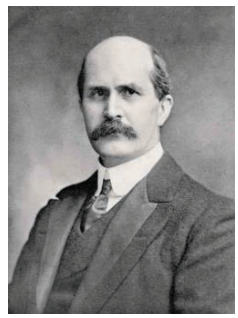




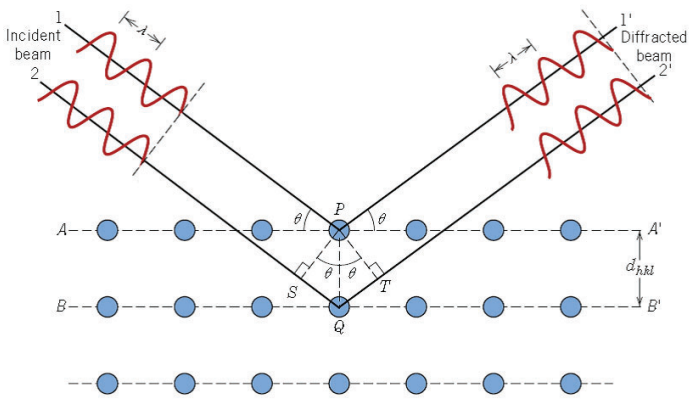
$\frac{(2n+1)\lambda}{2d}$, the hight of nth bright fringe $h = \frac{(2n+1)\lambda}{2d} D$. The width of the bright and dark fringes is $\frac{\lambda}{d} D$. The intensity of the fringes is given by the diagrams as shown.

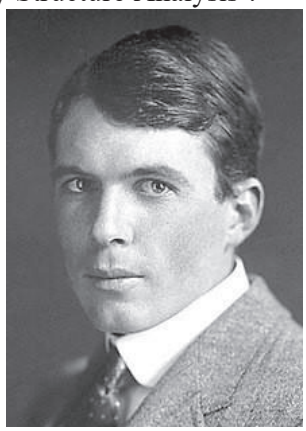
3O. THE X-RAY DIFFRACTION EXPERIMENT

The X-ray diffraction experiment is based on the diffraction of waves. This diffraction by the crystalline solids is governed by the Bragg's law; also known as Wulff–Bragg's condition or Laue–Bragg interference given in 1913 by Sir William Lawrence Bragg and his father Sir William Henry Bragg. This was after the discovery of a specific pattern of the reflected X-rays with specific wavelengths; incident at some specific angles on the crystalline specific solids. To explain this result Sir William Lawrence Bragg considered the crystal as a set of discrete parallel planes separated by a constant parameter d called the grating constant, which is the interplanar distance. He proposed that the incident X-ray radiation would produce a Bragg peak if reflections of the various planes, constructively interfered. Lawrence Bragg on 11 November 1912 proposed that the constructive interference would be observed when the phase difference will be an integral multiple of 2π. This further leads us to the Bragg's law $2d \sin\theta = n\lambda$. This is the condition of a maxima in the diffraction pattern. Sir William Lawrence Bragg shared the 1915 Physics Nobel Prize with his Father Sir William Henry Bragg, and became the youngest Nobel Laureate in Physics winning the 1915 Physics Nobel Prize at the age of 25 years. Both, Sir William Lawrence Bragg and Sir William Henry Bragg are jointly referred as 'Pioneers of X-ray Crystallography/ Founders of X-ray Structure Analysis'.



Sir William Henry Bragg (2 July 1862-12 March 1942)





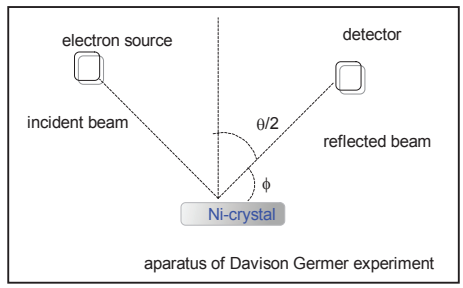
Sir William Lawrence Bragg (31 March 1890-1 July 1971)

3P. THE DAVISSON–GERMER EXPERIMENT

It was carried out in between 1923-27 by Clinton Joseph Davisson and Lester Halbert Germer. In this experiment a **54eV** monoenergetic electron beam was scattered through a **Ni** crystal using a similar apparatus with that of the Bragg's apparatus. They found that on sticking electrons on the crystal surface at an angle ϕ; they are reflected at a certain angle θ (angle between the incident and reflected rays) with a maximum intensity at $\theta = 50°$. this confirmed that a bulk of electrons were scattered with a well-defined trajectory

Clinton Joseph Davisson (1881–1958) and Lester Halbert Germer (1896–1971)

and these are recorded by the detector as an interference pattern which was due to a constructive interference of electrons. The interplanar distance of a Ni crystal is 2.03Å. θ is the angle of the incidence and the maxima is obtained when the reflected beam is at 50° to the incident beam, therefore, the angle θ is given by $\theta = \frac{50^\circ}{2} = 25^\circ$. Now, from the Bragg's law i.e. $2d \sin\theta = n\lambda$, putting $n = 1$ we have $2 \times 2.03 \times 10^{-10} m \sin 25^\circ = \lambda$



aparatus of Davison Germer experiment

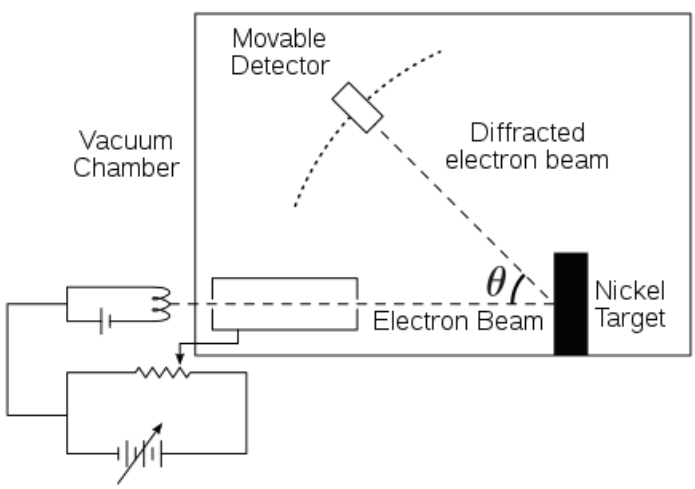
$\boldsymbol{\lambda = 1.72 \times 10^{-10} m = 1.72}$Å

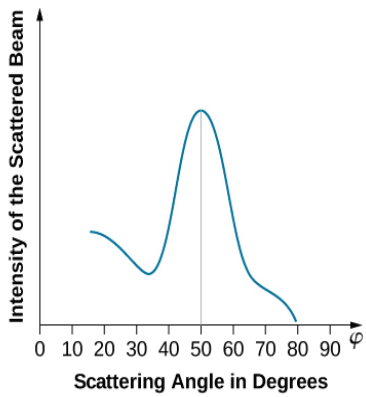
The kinetic energy of the electrons is $E_K = 54eV = \frac{p^2}{2m_e}$

Now, according to the de-Broglie hypothesis $\lambda_D = \frac{h}{\sqrt{2m_e E_K}} = \frac{6.626\times10^{-34} Js}{\sqrt{2\times\times9.11\times10^{-31}\times54\times1.6\times10^{-19}}} = 1.67 \times 10^{-10} m = 1.67$Å.

The Davisson–Germer experiment is the experimental analogue that demonstrates the wave nature of particles, as predicted by the de Broglie hypothesis; just as the photoelectric effect demonstrates the particle nature of light.

Clinton Joseph Davisson shared the 1937 Physics Nobel Prize with George Paget Thomson (G.P. Thomson).

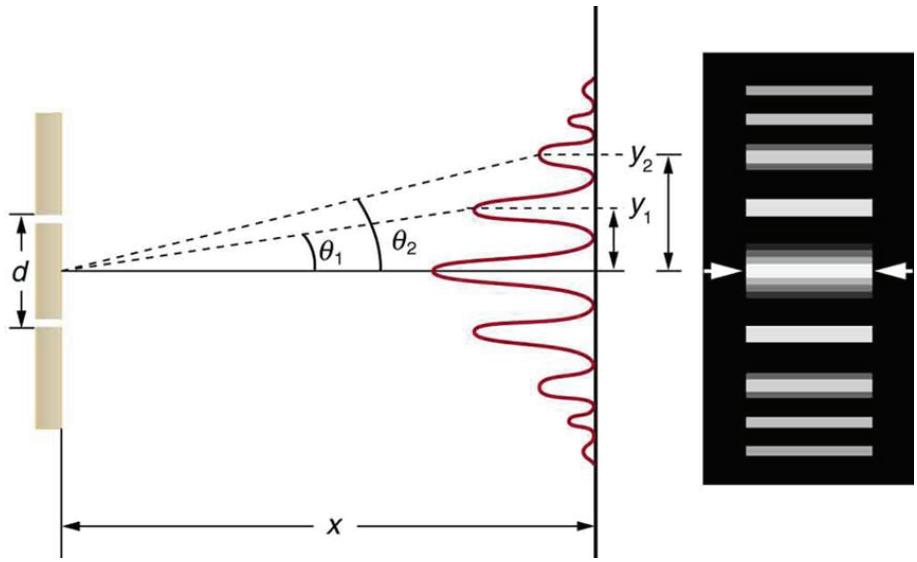




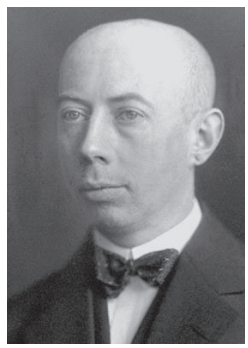
YOUNG'S DOUBLE SLIT EXPERIMENT

It was performed by Thomas Young in 1801. It leads to an interference pattern of light passing through two slits of small sizes. The light waves are coherent and monochromatic in nature. The two slits act as coherent sources plated at a gap d. A screen is placed at a distance D. At a point which is equidistant from the two sources there is a bright spot called as the Central bright fringe. Another point at a hight h from the centre point receive waves with a path difference given by the expression $\frac{2hd}{2D} = \frac{hd}{D}$. The hight of dark fringe $h_{dark} = \frac{(2n-1)\lambda D}{2d}$ $(n \in \mathbb{N})$. The hight of dark fringe $h_{bright} = \frac{n\lambda D}{d}$ $(n \in \mathbb{N})$. The fringe width is given by $W_B = W_D = \frac{\lambda D}{d}$. The width of bright fringe is the distance between the two consecutive dark points. The width of

dark fringe is the distance between the two consecutive bright points. All fringes have the same width. In interference fringes the energy is conserved and redistributed.



3Q. THOMSON'S EXPERIMENT

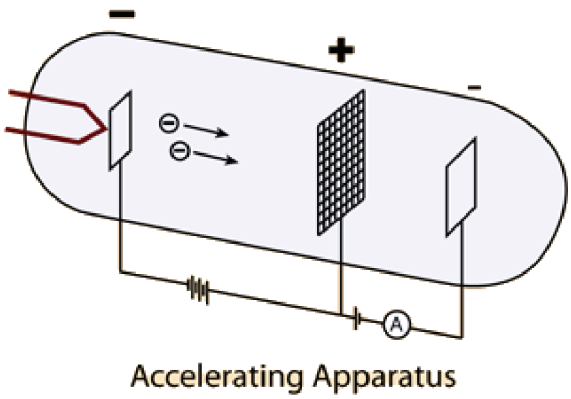


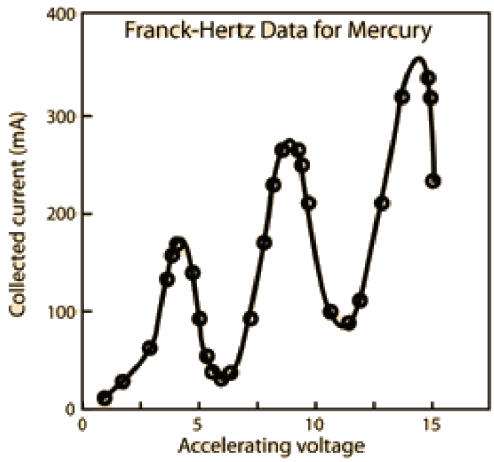
Gustav Ludwig Hertz (22 July 1887-30 October 1975)

In 1926 Thomson's experiment carried out by George Paget Thomson (G.P. Thomson). This experiment on a polycrystalline thin film reached he similar observations a of the Davisson–Germer experiment. The double-slit experiment in 1801 by Thomas Young. When the Young's double slit experiment was carried out with electron beam, it showed an interference pattern which is possible for electromagnetic waves when both the slits were opened simultaneously. But when the phenomenon was observed, it transformed back to the expected classical behaviour. It confirms a dual nature of electron. Scientist already knew of the particle nature (due to it having mass and being quantized. 2.5 electrons do not make sense) of electron and these experiments confirm its wave nature with a de-Broglie wavelength associated with it. It also leads to the most basic indeterministic nature of quantum mechanics and the formulation of the **Heisenberg's Uncertainty Principle.** Based on these experiments the modern quantum mechanical model of atom was developed. James Franck and Gustav Ludwig Hertz, nephew of the physicist Heinrich Rudolf Hertz (on whose name the unit of wave frequency hertz is named) proved the quantum nature of atom on 24 April 1914 through the Franck-Hertz experiment. In this experiment electrons were bombarded at a speed of 1.3 million ms^{-1}, through a mercury vapour cloud kept in a specially designed vacuum tube apparatus. Electrons at this constant speed lost 4.9eV energy which ultimately retarded their speeds to rest; faster electrons do not come to rest but they also loose the same amount of energy and the slower electrons bounce back. This amount of kinetic energy corresponds to the wavelength of UV light (calculated by the formula *hv*). This constant nature of the energy loss proved the quantized nature of energy in the atoms. This also disproved the assumption of the classical electromagnetic theory, that electrons can be bound to the atomic nucleus by any amount of energy and; a revolving electron should release the energy and atom should collapse, which in fact disproved the Rutherford's atomic model. James Franck and Gustav Ludwig

James Franck (26 Augst 1882-21 May 1964)

Hertz are together known as Pioneers of experimental quantum physics. They were awarded the shared 1925 Physics Nobel Prize.





3R. HEISENBERG'S UNCERTAINTY PRINCIPLE OR INDETERMINACY PRINCIPLE

A major limitation of the Bohr's theory was the **Heisenberg's Uncertainty Principle** which was proposed by Werner Karl Heisenberg (Founder of Matrix Mechanics OR Originator Of Uncertainty Principle) in February 1927. It states that

"The more precisely the position is determined, the less precisely the momentum is known in this instant, and vice versa."

— Werner Heisenberg, 1927

OR

No one can predict the position and momentum of the microscopic particles more accurately and precisely. It would always have an uncertainty of $\frac{h}{4\pi} = \frac{\hbar}{2}$.

Werner Karl Heisenberg
(5 December 1901-
1 February 1976)

This can be derived by the equation for minima or dark spot which is $d \sin\theta = n\lambda$

The width of the slit corresponds to the uncertainty of the position of the electron

Further on vector calculation of the momentum $\Delta p = p \sin\theta = \frac{p\lambda}{\Delta x}$

Now from the de-Broglie relation

$\Delta x . \Delta p = h$ (imperial relation NOT EXACT)

$\Delta x . \Delta p \geq \frac{h}{4\pi} = \frac{\hbar}{2}$.

$\Delta x . \Delta v \geq \frac{h}{4\pi m} = \frac{\hbar}{2m}$

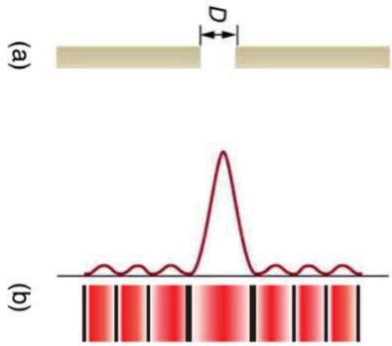
If we put $m = mass\ of\ electron = 9.1 \times 10^{-31} kg$

Then $\Delta x . \Delta v \geq 5.8 \times 10^{-5}$

Further we can also relate the energy or frequency of the particle and the time in the same manner as:

$\Delta \nu . \Delta t \geq \frac{h}{4\pi} = \frac{\hbar}{2}$. Where $\Delta \nu$ is the uncertainty in frequency and Δt uncirtainity in relaxation time from retuning from excited to the ground state.

The quantities which form a pair of uncertainty principle are called canonical variables.



The shortcomings of the Bohr's theory are explained by the combined results of Davison-Germer experiments, Thomsons experiments, de-Broglie hypothesis and the quantum mechanical model of atom. Mainly this explains the Zeeman and Stark effects encountered in the emission spectra of hydrogen.

From **Werner Heisenberg's autobiography** *Physics and Beyond: Encounters and Conversations* (original German title: *Der Teil und das Ganze, 1969*). Heisenberg's own words (translated into English, since the original was in German):

On his meeting with Tagore ***"When I was in India, I had long conversations with Rabindranath Tagore about the new quantum theory and its philosophical implications. Tagore explained to me that it was the tradition of Indian thought to regard the apparent contradictions of the world as different aspects of one and the same reality."*** On the Ganges and the philosophical acceptance of quantum mechanics:

"As I walked along the banks of the Ganges in the evening, I often thought about these conversations. It seemed to me as if the river carried away my doubts, and I began to feel that the philosophical ideas of quantum theory were much easier to accept."

The Heisenberg's Uncertainty Principle, which is a fundamental phenomenon in the microscopic world, becomes insignificant in the macroscopic world. This is due to the negligible values of uncertainties for massive systems.

For a 1kg object, $\Delta x.\Delta v \geq \frac{h}{4\pi m} \Rightarrow \Delta x.\Delta v = \frac{h}{4\pi} = 5.27 \times 10^{-35}$. This value is extremely smaller than the size of the atomic nucleus. If only the uncertainty is of the order of 10^{-35}, then this is so small that macroscopic systems are not influenced by the principle's effect.

The directional nature of the uncertainty principle is a consequence of the canonical commutation relations, which are non-zero only for position and momentum components along the same direction. Equivalently, since a particle is represented by a wave packet, localization within a finite region of space requires the superposition of waves with different wavelengths. This necessarily introduces a spread in the corresponding momentum component, which is related to the wave number through the de Broglie relation. A detailed wave-packet analysis shows that the product of position and momentum uncertainties satisfies the relation of a nonzero commutator in a given direction i.e. $[\hat{x}, \widehat{p_x}] = \imath\hbar \neq 0$. This means that the two observables namely the linear momentum and the position in the direction if linear momentum cannot be calculated simultaneously and accurately.

Heisenberg was awarded the 1932, Physics Nobel Prize.

3S. QUANTUM MECHANICAL MODEL OF ATOM

The quantum mechanical model of the atom emerged from intense discussions and debates among some of the greatest physicists of the 20th century—many of whom are captured together in this historic photograph from the Fifth Solvay Conference, Brussels, October 1927

The need for a new model arose when classical physics failed to explain the behaviour of electrons within the atom, particularly their stability and discrete energy levels. Building upon earlier ideas such as quantization, the framework of quantum mechanics was developed to describe matter at microscopic scales. In this formulation, electrons are no longer viewed as particles moving in fixed orbits, but as entities described by wavefunctions, whose behavior is governed by mathematical laws. The work of Erwin Schrödinger introduced a wave equation that provides a complete description of the allowed states of an electron, while Werner Heisenberg established fundamental limits on the precision with which certain pairs of physical properties can be known. Together, these ideas form the foundation of the quantum mechanical model of the atom, replacing certainty with probability and redefining our understanding of atomic structure. Quantum chemistry provides the theoretical framework that bridges the fundamental laws of physics with chemical phenomena, enabling a rigorous explanation of experimental observations at the atomic and molecular level and forming the conceptual foundation of the quantum mechanical model of the atom.

INTRODUCTION

On 27 January 1926 Erwin Rudolf Josef Alexander Schrödinger (Founder of Wave Mechanics) proposed the quantum mechanical model of atom also called the wave mechanical model of atom. This model was based on the results of previous experiments and a complex equation called the Schrödinger's wave equation, which plays the same pivotal role in quantum mechanics as the Newton's laws in classical mechanics. This equation is a second order partial differential equation, that describes the matter waves. The Schrödinger's wave equation gives the same results at macroscopic limit as Newton's laws in classical mechanics. This approach treats electrons as a dual characteristic identity having both particle and wave nature.

WAVEFUNCTION

In 1926, **Erwin Schrödinger**, in his formulation of Wave Mechanics within Quantum Mechanics, introduced the function **ψ**, referred to as the **wave function** (*Wellenfunktion*), which describes the quantum state of a system.

Waves are a type of pattern of disturbance created in a medium which carries the energy from one point to another.

Wavefunction is a complex mathematical function which satisfies the equation and describes the state of a quantum particle. It is not a physical like the electric or magnetic fields or propagating pressure differences in sound wave. This complex function contains some information about the quantum particle's position, energy etc.

Wavefunctions are multiplicative in nature and energy is additive in nature. Wavefunction is a vector quantity.

SCHRÖDINGER'S WAVE EQUATION

Schrödinger's wave equation can have various forms as:

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$$

$$\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\psi+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$$

$$\nabla^2\psi_{(n,l,m)}(x,y,z)+\frac{8\pi^2 m}{h^2}(E-V)\psi_{(n,l,m)}(x,y,z)=0$$

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\psi+V\psi=E\psi$$

$$-\frac{\hbar^2\nabla^2\psi}{2m}+V\psi=E\psi$$

$$\left[-\frac{\hbar^2\nabla^2}{2m}+V\right]\psi=E\psi$$

The first term $-\frac{\hbar^2\nabla^2}{2m}$ corresponds to the kinetic energy.

The second term $V(x,y,z)$ corresponds to the potential energy.

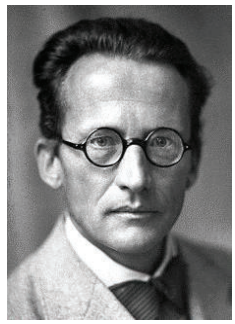
$\hat{H}\psi_{(n,l,m)}(x,y,z)=E\psi_{(n,l,m)}(x,y,z)$

(The Time Independent Schrödinger's Wave Equation in Cartesian plane).

$$\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi_{(n,l,m)}(r,\theta,\phi)+\frac{8\pi^2 m}{h^2}(E-V)\,\Psi_{(n,l,m)}(r,\theta,\phi)=0$$

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi_{(n,l,m)}(r,\theta,\phi)+V\,\Psi_{(n,l,m)}(r,\theta,\phi)=E\,\Psi_{(n,l,m)}(r,\theta,\phi)$$

(Schrödinger's wave equation in polar coordinates).



Erwin Rudolf Josef Alexander Schrödinger (12 August 1887- 4 January 1961)

Schrödinger, in his various writings quoted his words inspired by the philosophies of **Upanishads** and the parallel ideas also present in **Shrimad Bhagwat Geeta.** His words explaining the philosophies behind the wave mechanical model of the atom are cited here:

"The multiplicity is only apparent; in truth there is only one mind."

"Consciousness is never experienced in the plural, only in the singular."

"Hence this life of yours which you are living is not merely a piece of the entire existence, but in a certain sense the whole."

"Vedanta teaches that consciousness is singular; all happenings are played out in one universal consciousness and there is no multiplicity of selves."

"The total number of minds in the universe is one. In fact, consciousness is a singular of which the plural is unknown."

Time independent Schrödinger's wave equation can be represented in an alternate generalized form with the *Dirac* notation as $\hat{H}|\Psi\rangle = E|\Psi\rangle$.

The time-independent Schrödinger equation constitutes an eigenvalue problem for the *Linear Hermitian Hamiltonian operator*, whose eigenvalues represent the allowed energies of the stationary states of the system. The general eigenvalue equation is represented as $\hat{A}\psi = k\psi$ where k is a Nonzero constant value. The function ψ is called eigen function and the operator $\hat{A}$ is called the eigen operator. Hamiltonian operator is eigen operator. In the eigenvalue equation $\hat{A}\psi = k\psi$, the quantity k is called the **eigenvalue** of the operator $\hat{A}$ and ψ is the corresponding **eigenfunction**. The eigenfunction ψ\psiψ is generally a function of spatial coordinates (and possibly time), whereas the eigenvalue aaa is a **constant scalar quantity** associated with that eigenfunction. Thus, the eigenvalue does not depend on spatial variables or on the functional form of ψ\psiψ; rather, it represents the fixed numerical factor by which the eigenfunction is multiplied when acted upon by the operator. Consequently, each admissible eigenfunction of a given operator corresponds to a definite constant eigenvalue.

Although quantum mechanics admits several simplified model systems, the description of atomic structure is developed here directly from the physically real Coulomb potential of the atom.

Robert Sanderson Mulliken (7 June 1896-31 October 1986)

A Hermitian operator is one that is equal to its adjoint, represented as $\int_{-\infty}^{\infty} \psi^* \hat{A}\,\psi d\tau = \int_{-\infty}^{\infty} \psi \hat{A}^*\,\psi^* d\tau$. A Hermitian operator possesses real eigenvalues i.e. for A Hermitian operator the eigenvalue equation is represented as $\hat{A}\psi = k\psi; k \in \mathbb{R}$. The Hamiltonian operator is Hermitian to ensure that the energy spectrum and expectation values are real and physically meaningful. Also, the Hamiltonian represents the total energy of the system which must be a real observable.

Note: The terminology was introduced by Paul Dirac to represents a generalized inner product, symbolically written as $\langle\psi|\phi\rangle$; in this notation, $\langle\psi|$ denotes the dual vector corresponding to the quantum state $|\psi\rangle$ (called ket). The terminology used in the literature is conventional; in this book, a greater emphasis is placed on the mathematical structure and meaning rather than spoken labels. A helpful way to remember the syntax is that the inner product $\langle\psi|\phi\rangle$ may be viewed as a bracket composed of a left component and a right component. In most applications of quantum mechanics, the ket $|\psi\rangle$ serves as the fundamental representation of a quantum states.

DERIVATION OF TIME INDEPENDENT SCHRÖDINGER'S WAVE EQUATION

This equation can be derived by using the equation of a standing wave because the wave associated with electron can have a state of standing wave with infinite number of standing wave patterns. This state is also referred to as the stationary state in quantum mechanics. All type of waves arises due to some oscillatory motion, simplest of which is the Simple Harmonic Motion (SHM). In SHM, a given physical quantity (also known as the amplitude function or wave function (ϕ)) attains a constant value after a periodic time interval as the wave progresses, and is a function of space coordinates $(x, y, z)$and time (t). the wave has the corresponding properties.

λ wavelength

T time period

ν frequency $\nu = \frac{c}{\lambda} = \frac{1}{T}$

$\bar{\nu} = \frac{1}{\lambda}$ ($\bar{\nu}$ Is the wave number i.e. number of waves per unit length.)

The periodic nature of the properties of waves suggests the presence of oscillating sine or cosine functions of x, t. such expression of amplitude function ϕ is governed by the general differential wave equation, which can be derived by the following algorithm:

$$\frac{\partial^2\phi}{\partial x^2}=\frac{\partial^2\phi}{v^2\partial t^2}$$

This wave equation can be represented in three dimensions as

$$\frac{\partial^2\phi}{\partial x^2}+\frac{\partial^2\phi}{\partial y^2}+\frac{\partial^2\phi}{\partial z^2}=\frac{\partial^2\phi}{v^2\partial t^2}=\nabla^2\phi=\frac{\partial^2\phi}{v^2\partial t^2}$$

The amplitude function ϕ can be written as a product of two component functions $\phi(x,t)=\psi(x)T(t)$ and this time function can be written as $T(t)=e^{2\pi\iota\nu t}$

Putting the values we have,

$$\frac{\partial^2\phi(x,t)}{\partial x^2}=\frac{\partial^2\phi(x,t)}{v^2\partial t^2}$$

$$\frac{\partial^2\psi(x)T(t)}{\partial x^2}=\frac{\partial^2\psi(x)T(t)}{v^2\partial t^2}$$

$$\frac{\partial^2\psi(x)e^{2\pi\iota\nu t}}{\partial x^2}=\frac{\partial^2\psi(x)e^{2\pi\iota\nu t}}{v^2\partial t^2}$$

$$e^{2\pi\iota\nu t}\frac{\partial^2\psi(x)}{\partial x^2}=\psi(x)\frac{\partial^2 e^{2\pi\iota\nu t}}{v^2\partial t^2}$$

$$e^{2\pi\iota\nu t}\frac{\partial^2\psi(x)}{\partial x^2}=\frac{(2\iota\pi\nu)^2e^{2\pi\iota\nu t}}{v^2}\psi(x)$$

$$\frac{d^2\psi(x)}{dx^2}=-\frac{4\pi^2\nu^2\psi}{v^2}$$

$$v=\nu\lambda$$

$$\frac{d^2\psi}{dx^2}=-\frac{4\pi^2\psi}{\lambda^2}$$

Jean Baptiste le Rond d'Alembert (17 November 1717-29 October 1783)

Using the de-Broglie hypothesis of wave particle duality, Schrödinger in 1926 proposed that the microscopic particles like electrons behave as standing waves and derived the equation by putting the values of de-Broglie wavelength in the equation $\frac{d^2\psi}{dx^2}=-\frac{4\pi^2\psi}{\lambda^2}$ which results as

$$\frac{d^2\psi}{dx^2}=-\frac{4\pi^2p_x^2\psi}{h^2}$$

From the law of energy conservation $E=V+KE$ (V potential energy KE kinetic energy)

$$KE=\frac{p^2}{2m}\Rightarrow p^2=2m(E-V)$$

Putting the values of p^2 we get

$$\frac{d^2\psi}{dx^2}=-\frac{8\pi^2m(E-V)\psi}{h^2}$$

On summing up all the components we get the standard form of the Schrödinger's wave equation

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2m}{h^2}(E-V)\psi=0$$

$$\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\psi+\frac{8\pi^2m}{h^2}(E-V)\psi=0$$

$$\nabla^2\Psi_{(n,l,m)}(x,y,z)+\frac{8\pi^2m}{h^2}(E-V)\Psi_{(n,l,m)}(x,y,z)=0$$

Where ∇ (nabla) is called the Laplacian operator named after Pierre-Simon, Marquis de Laplace (known for the Laplace correction in Newton's formula for speed of sound)

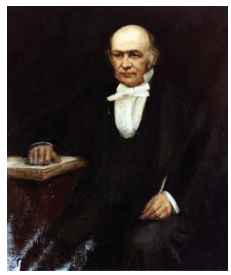
$$\boldsymbol{\nabla}\cdot\boldsymbol{\nabla}\psi = \nabla^2\psi = \frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2} = \frac{1}{r^2\sin\theta}\left[\sin\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin\theta}\frac{\partial^2\psi}{\partial\varphi^2}\right]$$

Laplacian in Cartesian and spherical coordinates.

$$\left[\nabla^2+\frac{8\pi^2m}{h^2}(E-V)\right]\Psi_{(n,l,m)}(x,y,z)=0$$

$\hat{H}\,\Psi_{(n,l,m)}(x,y,z) = E\,\Psi_{(n,l,m)}(x,y,z)$ (where $\hat{H}$ is called the Hamiltonian named after Sir William Rowan Hamilton).

ALTERNATIVE FORM OF THIS TIME INDEPENDENT SCHRÖDINGER'S WAVE EQUATION



Sir William Rowan Hamilton (3/4 August 1805-2 September 1865)

This Time independent Schrödinger's wave equation can be represented in an alternate form with some modifications as:

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2m}{h^2}(E-V)\psi=0$$

$$\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\psi+\frac{8\pi^2m}{h^2}(E-V)\psi=0$$

$$\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\psi=-\frac{8\pi^2m}{h^2}(E-V)\psi$$

$\because$ We know that $\hbar=\frac{h}{2\pi}\Rightarrow\hbar^2=\frac{h^2}{4\pi^2}$, $\frac{8\pi^2m}{h^2}=\frac{2m}{\hbar^2}$

The equation $\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\psi=-\frac{8\pi^2m}{h^2}(E-V)\psi$ can be rewritten as

$$\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\psi=-\frac{2m}{\hbar^2}(E-V)\psi$$

Further,

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\psi=E\psi-V\psi$$

$$\Rightarrow-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\psi+V\psi=E\psi$$

Now another modification is done After incorporation of the Coulomb's potential energy and thus, we have,

$$\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\psi+\frac{8\pi^2m}{h^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi=0$$

As $r=\sqrt{x^2+y^2+z^2}$

$$\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\psi+\frac{8\pi^2m}{h^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0\sqrt{x^2+y^2+z^2}}\right)\psi=0$$

Note: The Schrödinger equation has two equivalent forms because the reduced Planck constant is defined as $\hbar=\frac{h}{2\pi}$, using either h or $\hbar$ is purely an algebraic rewriting and does not change any physical predictions. Quantum mechanics is fundamentally a theory of waves, phases, and rotations, in which quantities such as angular frequency ω wave number k and angular momentum arise naturally and are most cleanly expressed using $\hbar$. Writing the equation in the $\hbar$-form removes unnecessary factors of 2π, leads to simpler and more natural expressions for quantum operators and commutation relations, and aligns the theory with its underlying rotational and phase-based structure, which is why the $\hbar$-form is universally preferred despite both forms giving identical results.

Now the Time independent Schrödinger's wave equation in polar coordinates take a similar form after a similar modification as:

$$\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi_{(n,l,m)}(r,\theta,\phi)+\frac{8\pi^2 m}{h^2}(E-V)\,\Psi_{(n,l,m)}(r,\theta,\phi)=0$$

Similarly, after incorporation of the Coulomb's potential energy we have,

$$\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi_{(n,l,m)}(r,\theta,\phi)+\frac{8\pi^2 m}{h^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi_{(n,l,m)}(r,\theta,\phi)=0$$

Now the equation with V as potential energy can be transformed as

$$\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi_{(n,l,m)}(r,\theta,\phi)=-\frac{8\pi^2 m}{h^2}(E-V)\,\Psi_{(n,l,m)}(r,\theta,\phi)$$

$\because$ We know that $\hbar = \frac{h}{2\pi} \Rightarrow \hbar^2 = \frac{h^2}{4\pi^2}, \frac{8\pi^2 m}{h^2} = \frac{2m}{\hbar^2}$

$$\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi_{(n,l,m)}(r,\theta,\phi)=-\frac{2m}{\hbar^2}(E-V)\,\Psi_{(n,l,m)}(r,\theta,\phi)$$

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi_{(n,l,m)}(r,\theta,\phi)=(E-V)\,\Psi_{(n,l,m)}(r,\theta,\phi)$$

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi_{(n,l,m)}(r,\theta,\phi)=E\,\Psi_{(n,l,m)}(r,\theta,\phi)-V\,\Psi_{(n,l,m)}(r,\theta,\phi)$$

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi_{(n,l,m)}(r,\theta,\phi)+V\,\Psi_{(n,l,m)}(r,\theta,\phi)=E\,\Psi_{(n,l,m)}(r,\theta,\phi)$$

Now another modification is done After incorporation of the Coulomb's potential energy and thus, we have,

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi_{(n,l,m)}(r,\theta,\phi)-\frac{Ze^2}{4\pi\varepsilon_0 r}\Psi_{(n,l,m)}(r,\theta,\phi)=E\,\Psi_{(n,l,m)}(r,\theta,\phi)$$

NOTE: After substitution of the relation $r=\sqrt{x^2+y^2+z^2}$ in the polar form of the Time independent Schrödinger's wave equation it transforms to an inseparable and unsolvable complex form

$$-\frac{\hbar^2}{2m}\left[\frac{1}{(x^2+y^2+z^2)}\frac{\partial}{\partial r}\left((x^2+y^2+z^2)\frac{\partial}{\partial r}\right)+\frac{1}{(x^2+y^2+z^2)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{(x^2+y^2+z^2)sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi_{(n,l,m)}(r,\theta,\phi)$$
$$-\frac{Ze^2}{4\pi\varepsilon_0\sqrt{x^2+y^2+z^2}}\Psi_{(n,l,m)}(r,\theta,\phi)=E\,\Psi_{(n,l,m)}(r,\theta,\phi)$$

On substituting the Laplacian in the two forms of the Time independent Schrödinger's wave equation we have,

$$-\frac{\hbar^2}{2m}\nabla^2\psi+V\psi=E\psi$$

$$\Rightarrow \hat{H}\,\Psi_{(n,l,m)}(x,y,z)=E\,\Psi_{(n,l,m)}(x,y,z)$$

Now for generalized quantum states the Time independent Schrödinger's wave equation can be represented in an alternate form with the *Dirac* notation as $\hat{H}|\Psi\rangle = E|\Psi\rangle$

ψ defined as a wave function having a substantial information about electron.

For any wave function to be acceptable it should be:

- Finite and Square integrable.
- Single valued
- Real valued
- Continuous
- Normalized i.e. the total probability should be unity $\int_{-\infty}^{\infty}\psi\psi^* d\tau = \langle\psi|\psi\rangle = 1$ (where dτ is a small 3D volume element including all 3 coordinates x, y, z). ψ^* is the complex conjugate of ψ. $\psi\psi^* = |\psi|^2$, only when the wavefunction is real; for complex wavefunctions of the form $a+\imath b$, it must be evaluated using the rules of complex conjugation. The normalization condition of the wave function of the hydrogen atom in polar coordinates is $\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\left|\Psi_{(n,l,m)}(r,\theta,\phi)\right|^2 r^2\sin\theta\,dr\,d\theta\,d\phi =$

1The general condition of normalization leads to the expression for the normalization constant as $N = \frac{1}{\sqrt{\int_{-\infty}^{\infty} \psi\psi^* d\tau}}$. This expression leads to

$N = \frac{1}{\sqrt{\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} \left|\psi_{(n,l,m)}(r,\theta,\phi)\right|^2 r^2 \sin\theta dr d\theta d\phi}}$.

The Volume elements of Hydrogen atom is $d\tau = dxdydz = r^2 \sin\theta dr d\theta d\phi$

- It should be orthogonal to another wave function i.e. $\oint \psi_i \psi_j d\tau = \left\langle \psi_i \middle| \psi_j \right\rangle = 0$

The overall condition is called Orthonormalization condition denoted as $\oint \psi_i \psi_j d\tau = \left\langle \psi_i \middle| \psi_j \right\rangle = \delta_{ij} = \begin{cases} 0, if\ i \neq j\ (\text{orthogonality}) \\ 1, if\ i = j\ (\text{normalization}) \end{cases}$

The δ_{mn} is known as Kronecker delta given by Leopold Kronecker in the year 1868.
It should have a continuous first derivative function.
ψ^2 defines the probability of finding the electron in a given space.
The space where the probability of finding the electron i.e. ψ^2 is maximum is called an **orbital** and where ψ^2 is zero that space is called **node.**
Note: As the '*one-electron orbital wave function*' was a mouthful to say, in 1932 R. S. Mullikan gave the term 'orbital'. The time independent Schrödinger's wave equation leads to atomic structure and electronic configurations through the definition of the wavefunction and the value of energy, and the time dependent Schrödinger's wave equation

$i\hbar \frac{d\psi(x,t)}{dt} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2} + V(x,t)\psi(x,t) \Rightarrow \hat{H}\psi(t) =$
$i\hbar \frac{d\psi(t)}{dt} \Rightarrow \hat{H}|\Psi(t)\rangle = i\hbar \frac{d|\Psi(t)\rangle}{dt}$ leads to the concepts of Spectroscopy (a branch of physical chemistry derived from Quantum chemistry).

Pierre Simon Marquis de Laplace (23 March 1749-5 March 1827)

SCHRÖDINGER'S WAVE EQUATION IN POLAR COORDINATES

For hydrogen atom the Time independent Schrödinger's wave equation

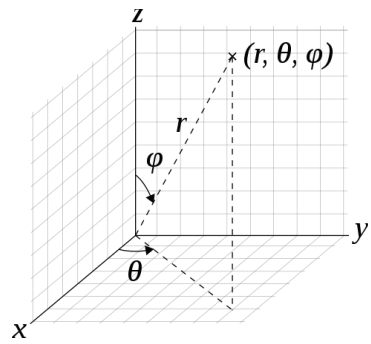
$$\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]\psi + \frac{8\pi^2 m}{h^2}\left(E + \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi = 0$$

And $r = \sqrt{x^2 + y^2 + z^2}$

$$\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]\psi + \frac{8\pi^2 m}{h^2}\left(E + \frac{Ze^2}{4\pi\varepsilon_0\left(\sqrt{x^2 + y^2 + z^2}\right)}\right)\psi = 0$$

And this expression cannot be further treated using separation of variables method.
Since the atom is spherical in nature, it's better to use the spherical polar coordinates, (r, θ, ϕ) instead of the standard Cartissian coordinates, (x, y, z) to solve the Schrödinger's wave equation. Moreover, we face a mathematical constraint of $\sqrt{(x + y + z)} \neq \sqrt{x} + \sqrt{y} + \sqrt{z}$ i.e., root is not a linear operator.
The Time independent Schrödinger's wave equation can be represented in an alternate form in the Polar coordinates using the relations:

$x = r\sin\theta\cos\phi$ (1)
$y = r\sin\theta\sin\phi$ (2)
$z = r\cos\theta$ (3)
$r^2 = x^2 + y^2 + z^2$ (4)
$r = \sqrt{x^2 + y^2 + z^2}$ (5)



$\tan\theta = \frac{\sqrt{x^2+y^2}}{z}$ (6)

$\tan\phi = \frac{y}{x}$ (7)

Partially Differentiating (4) w.r.t. x, we have,

$$\frac{\partial r^2}{\partial x} = \frac{\partial(x^2+y^2+z^2)}{\partial x} = 2r\frac{\partial r}{\partial x} = 2x$$

$$\Rightarrow \frac{\partial r}{\partial x} = \frac{x}{r}$$

Now from (1)

$\frac{\partial r}{\partial x} = \sin\theta\cos\phi$ (8)

Similarly, Partially Differentiating (4) w.r.t. y, we have,

$$\frac{\partial r^2}{\partial y} = \frac{\partial(x^2+y^2+z^2)}{\partial y} = 2r\frac{\partial r}{\partial y} = 2y$$

$$\Rightarrow \frac{\partial r}{\partial y} = \frac{y}{r}$$

Now from (2)

$\frac{\partial r}{\partial y} = \sin\theta\sin\phi$ (9)

Partially Differentiating (4) w.r.t. z, we have,

$$\frac{\partial r^2}{\partial z} = \frac{\partial(x^2+y^2+z^2)}{\partial z} = 2r\frac{\partial r}{\partial z} = 2z$$

$$\Rightarrow \frac{\partial r}{\partial z} = \frac{z}{r}$$

Now from (3)

$\frac{\partial r}{\partial z} = \cos\theta$ (10)

Now applying the chain rule we have,

$\frac{\partial \psi}{\partial x} = \frac{\partial \psi}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial \psi}{\partial \theta}\frac{\partial \theta}{\partial x} + \frac{\partial \psi}{\partial \phi}\frac{\partial \phi}{\partial x}$ (11)

$\frac{\partial \psi}{\partial y} = \frac{\partial \psi}{\partial r}\frac{\partial r}{\partial y} + \frac{\partial \psi}{\partial \theta}\frac{\partial \theta}{\partial y} + \frac{\partial \psi}{\partial \phi}\frac{\partial \phi}{\partial y}$ (12)

$\frac{\partial \psi}{\partial z} = \frac{\partial \psi}{\partial r}\frac{\partial r}{\partial z} + \frac{\partial \psi}{\partial \theta}\frac{\partial \theta}{\partial z} + \frac{\partial \psi}{\partial \phi}\frac{\partial \phi}{\partial z}$ (13)

Further, from (3) we have,

$\cos\theta = \frac{z}{r}$ (14)

Therefore, on Differentiating (3) w.r.t. x, we have,

$$\frac{\partial\cos\theta}{\partial x} = \frac{\partial\left(\frac{z}{r}\right)}{\partial x} = -\sin\theta\frac{\partial\theta}{\partial x} = -\frac{z}{r^2}\frac{\partial r}{\partial x} = -\frac{r\cos\theta}{r^2}\sin\theta\cos\phi$$

$$\Rightarrow \frac{\partial\theta}{\partial x} = \frac{\cos\theta\cos\phi}{r}$$ (15)

Now, Partially Differentiating (7) w.r.t. x, and using (1) & (2) we have,

$$\frac{\partial\tan\phi}{\partial x} = \frac{\partial\left(\frac{y}{x}\right)}{\partial x} = \sec^2\phi\frac{\partial\phi}{\partial x} = -\frac{y}{x^2} = -\frac{r\sin\theta\sin\phi}{(r\sin\theta\cos\phi)^2}$$

On further simplification we have,

$\frac{\partial\phi}{\partial x} = -\frac{\sin\phi}{r\sin\theta}$ (16)

Partially Differentiating (11) w.r.t. y, and reinstalling (3) we have,

$$\frac{\partial\cos\theta}{\partial y} = \frac{\partial\left(\frac{z}{r}\right)}{\partial y} = \sin\theta\frac{\partial\theta}{\partial y} = -\frac{z}{r^2}\frac{\partial r}{\partial y} = -\frac{r\cos\theta\sin\theta\sin\phi}{r^2}$$

On further simplification we have,

Leopold Kronecker
(7 December 1823-
29 December 1891)

$\frac{\partial\theta}{\partial y} = -\frac{\cos\theta\sin\phi}{r}$ (17)

Now, Partially Differentiating (7) w.r.t. y, and using (1) we have,

$$\frac{\partial \tan\phi}{\partial y} = \frac{\partial\left(\frac{y}{x}\right)}{\partial y} = \sec^2\phi\frac{\partial\phi}{\partial y} = \frac{1}{x}$$

On further simplification we have,

$\frac{\partial\phi}{\partial y} = \frac{1}{r\sin\theta\cos\phi\sec^2\phi} = \frac{\cos\phi}{r\sin\theta}$ (18)

Now, further to find $\frac{\partial\theta}{\partial z}$, we differentiate (3) w.r.t. z, and apply the product rule, and therefore we have,

$$\frac{\partial z}{\partial z} = \frac{\partial(r\cos\theta)}{\partial z}$$

$$\Rightarrow \cos\theta\frac{\partial r}{\partial z} - r\sin\theta\frac{\partial\theta}{\partial z} = 1$$

$$\Rightarrow \cos^2\theta - r\sin\theta\frac{\partial\theta}{\partial z} = 1$$

$$\Rightarrow \sin^2\theta = -r\sin\theta\frac{\partial\theta}{\partial z}$$

$\Rightarrow \frac{\partial\theta}{\partial z} = -\frac{\sin\theta}{r}$ (19)

Further from (7) we have,

$\frac{\partial\phi}{\partial z} = 0$ (20)

Putting the values from equations (15-20) in (11), we have,

$\frac{\partial\psi}{\partial x} = \sin\theta\cos\phi\frac{\partial\psi}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial\psi}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial\psi}{\partial\phi}$ (21)

Similarly, Putting the values from equations (15-20) in (12), we have,

$\frac{\partial\psi}{\partial y} = \sin\theta\sin\phi\frac{\partial\psi}{\partial r} - \frac{\cos\theta\sin\phi}{r}\frac{\partial\psi}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial\psi}{\partial\phi}$ (22)

Similarly, Putting the values from equations (15-20) in (13), we have,

$\frac{\partial\psi}{\partial z} = \cos\theta\frac{\partial\psi}{\partial r} - \frac{\sin\theta}{r}\frac{\partial\psi}{\partial\theta}$ (23)

Now calculating the second derivatives we have,

$$\frac{\partial^2\psi}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{\partial\psi}{\partial x}\right) = \frac{\partial}{\partial x}\left(\frac{\partial\psi}{\partial r}\frac{\partial r}{\partial x}\right) + \frac{\partial}{\partial x}\left(\frac{\partial\psi}{\partial\theta}\frac{\partial\theta}{\partial x}\right) + \frac{\partial}{\partial x}\left(\frac{\partial\psi}{\partial\phi}\frac{\partial\phi}{\partial x}\right) = \frac{\partial}{\partial r}\left(\frac{\partial\psi}{\partial x}\frac{\partial r}{\partial x}\right) + \frac{\partial}{\partial\theta}\left(\frac{\partial\psi}{\partial x}\frac{\partial\theta}{\partial x}\right) + \frac{\partial}{\partial\phi}\left(\frac{\partial\psi}{\partial x}\frac{\partial\phi}{\partial x}\right) \quad (24)$$

Now by combining the 22-term values of equations (11-24) and the values from the similar calculations for $\frac{\partial^2\psi}{\partial y^2}, \frac{\partial^2\psi}{\partial z^2}$, we get our final equation with $\psi = \psi_{(n,l,m)}(r,\theta,\phi)$ as:

$$\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi_{(n,l,m)}(r,\theta,\phi) + \frac{8\pi^2 m}{h^2}(E-V)\Psi_{(n,l,m)}(r,\theta,\phi) = 0 \quad (25)$$

This equation can be modified further by multiplication with r^2 and putting V as the Columb's potential

$$\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi_{(n,l,m)}(r,\theta,\phi) + \frac{8\pi^2 mEr^2}{h^2}\psi_{(n,l,m)}(r,\theta,\phi) + \frac{2\pi Ze^2 r}{\varepsilon_0 h^2}\psi_{(n,l,m)}(r,\theta,\phi) = 0$$

(Schrödinger's wave equation in polar coordinates). It helps to derive the orbital wave function values.

THE HYDROGEN ATOM

The hydrogen atom is the crown jewel of the Schrödinger's quantum mechenical atomic model. The hydrogen atom is the simplest atom in the periodic table. It consists of a heavy positively charged nucleus and a density of one negatively charged orbiting electron. The nature of the interaction between the nucleus and the electron is given by the Coulombic interaction which corresponds to the Potential energy $\hat{V} = -\frac{e^2}{4\pi\varepsilon_0 r}$. The time-independent Schrödinger equation obtained above for the hydrogen atom is a partial differential equation whose solutions determine the allowed states of the electron. To obtain these solutions, the equation is first

converted to the spherical polar coordinates, because hydrogen atom is the three dimentional probability distribution problem.

$$\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi_{(n,l,m)}(r,\theta,\phi)+\frac{8\pi^2 m}{h^2}(E-V)\,\Psi_{(n,l,m)}(r,\theta,\phi)=0$$

This equation modifies to

$$\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi_{(n,l,m)}(r,\theta,\phi)-\frac{2m}{\hbar^2}(V-E)\,\psi_{(n,l,m)}(r,\theta,\phi)=0$$

This equation can be modified further by multiplication with r^2 and putting V as the Columb's potential

$$\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi_{(n,l,m)}(r,\theta,\phi)+\frac{8\pi^2 mEr^2}{h^2}\psi_{(\mathrm{n,l,m})}(r,\theta,\phi)+\frac{2\pi Ze^2 r}{\varepsilon_0 h^2}\psi_{(\mathrm{n,l,m})}(r,\theta,\phi)=0$$

Now this modified version is separated into spatial components and solved to arrive at the final wavefunction of the hydrogen atom. Having established the mathematical framework of quantum mechanics, we now turn to the first real physical system that can be treated exactly within quantum theory; the hydrogen atom and hydrogen-like (hydrogenic) species such as He^+ and Li^{2+}.

The Volume elements of Hydrogen atom is $d\tau = dxdydz = r^2\sin\theta drd\theta d\phi$ Provided, $0 < r < \infty; 0 < \theta < \pi$, and $0 < \phi < 2\pi$

Using the separation of variables the wavefunction can be written as a product of three components:

$$\psi_{(n,l,m)}(x,y,z) = \psi_{(n,l,m)}(r,\theta,\phi) = R_{nl}(r)Y_l^m(\theta,\phi) = R_{n,l}(r)\Theta_l^m(\theta)\Phi_m(\phi)$$

This can be further solved by writing the value of ψ as

$\psi_{(n,l,m)}(r,\theta,\phi) = R_{nl}(r)Y_l^m(\theta,\phi) = R_{n,l}(r)\Theta_l^m(\theta)\Phi_m(\phi)$ and applying the method of separation of variables.

The equation becomes

$$\left\{\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]+\left(\frac{8\pi^2 mEr^2}{h^2}+\frac{8\pi^2 mZre^2}{4h^2\pi\varepsilon_0}\right)\right\}R_{nl}(r)Y_l^m(\theta,\phi)=0$$

Before writing the complete final wavefunction of the Hydrogen atom we take a separate mathematical analysis of the Radial and Agular parts of the wavefunction. From the Schrödinger's wave equation in polar coordinates. This modified equation further separates into two multiplicative wavefunctions

$$\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi_{(n,l,m)}(r,\theta,\phi)+\frac{8\pi^2 mEr^2}{h^2}\psi_{(\mathrm{n,l,m})}(r,\theta,\phi)+\frac{2\pi Ze^2 r}{\varepsilon_0 h^2}\psi_{(\mathrm{n,l,m})}(r,\theta,\phi)=0$$

We can resolve the wave function $\psi_{(\mathrm{n,l,m})}(r,\theta,\phi)$ into the Radial and Agular parts of the wavefunction as $\psi_{(n,l,m)}(r,\theta,\phi) = R_{n,l}(r)\Theta_l^m(\theta)\Phi_m(\phi) = R_{nl}(r)Y_l^m(\theta,\phi)$

Now using this in the equation we get

$$\left[\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]+\frac{8\pi^2 mEr^2}{h^2}\psi_{(\mathrm{n,l,m})}(r,\theta,\phi)+\frac{2\pi Ze^2 r}{\varepsilon_0 h^2}\right]R_{nl}(r)Y_l^m(\theta,\phi)=0$$

Now after separation of variables we can rewrite the equation as

$$\left[\frac{1}{R_{nl}(r)}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{8\pi^2 mEr^2}{h^2}+\frac{2\pi Ze^2 r}{\varepsilon_0 h^2}\right]R_{nl}(r)\right]+\left[\frac{1}{Y_l^m(\theta,\phi)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\right]Y_l^m(\theta,\phi)=0$$

The radial part can be written as $\left\{\frac{1}{R_{nl}(r)}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right]+\left(\frac{8\pi^2 mEr^2}{h^2}+\frac{8\pi^2 mZre^2}{4h^2\pi\varepsilon_0}\right)\right\}R_{nl}(r)$

The angular part can be written as $\left\{\frac{1}{Y_l^m(\theta,\phi)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\right\}Y_l^m(\theta,\phi)$

These two separated equations can be combined as

$$\left\{\frac{1}{R_{nl}(r)}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right]+\left(\frac{8\pi^2 mEr^2}{h^2}+\frac{8\pi^2 mZre^2}{4h^2\pi\varepsilon_0}\right)\right\}R_{nl}(r)=\left\{\frac{1}{Y_l^m(\theta,\phi)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\right\}Y_l^m(\theta,\phi)$$

Equivalently, $\left\{\frac{1}{R_{nl}(r)}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right]-\frac{2m}{\hbar^2}(V-E)\,\psi_{(n,l,m)}(r,\theta,\phi)\right\}=-\left\{\frac{1}{Y_l^m(\theta,\phi)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\right\}$

The two can be equal only when both hr LHS and RHS are equal to some constants.

RADIAL WAVEFUNCTION

This component of the wavefunction talks about the variation of probability along the radial distance of the electron from the nucleus.

after separation of variables we can rewrite the equation for The radial part can be written as $\left\{\frac{1}{R_{nl}(r)}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right]+\left(\frac{8\pi^2 mEr^2}{h^2}+\frac{8\pi^2 mZre^2}{4h^2\pi\varepsilon_0}\right)\right\}R_{nl}(r)$ which after rearrangements becomes $\left\{\frac{1}{R_{nl}(r)}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right]-\frac{2mr^2}{\hbar^2}(V(r)-E)\right\}R_{nl}(r)=l(l+1)$ (1)

Now applying the substitution method

Let $R_{nl}(r)=\frac{u}{r}\Rightarrow\frac{dR_{nl}(r)}{dr}=\frac{r\frac{du}{dr}-u}{r^2}\Rightarrow r^2\frac{dR_{nl}(r)}{dr}=r\frac{du}{dr}-u$ (2)

Further, on differentiating we get $\frac{d}{dr}\left(r^2\frac{dR_{nl}(r)}{dr}\right)=\frac{d}{dr}\left(r\frac{du}{dr}-u\right)=r\frac{d^2u}{dr^2}$ (3)

Now on substituting the above transforms the equation (1) becomes

$$\left\{\frac{r^2}{u}\frac{d^2u}{dr^2}-\frac{2mr^2}{\hbar^2}(V(u)-E)\right\}R_{nl}(r)=l(l+1)$$

Multiplying by $\frac{u}{r^2}$ we get $\left\{\frac{d^2u}{dr^2}-\frac{2mu}{\hbar^2}(V(u)-E)\right\}R_{nl}(r)=\frac{u(l(l+1))}{r^2}$

After some rearrangements we get $-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}+\left[V(r)+\frac{\hbar^2\left(l(l+1)\right)}{2mr^2}\right]u=E.u$

Now putting the Coulombic potential $\hat{V}=-\frac{e^2}{4\pi\varepsilon_0 r}$ we have $-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}+\left[-\frac{e^2}{4\pi\varepsilon_0 r}+\frac{\hbar^2\left(l(l+1)\right)}{2mr^2}\right]u=E.u$ (4)

Now after further rearrangements and putting $\sqrt{-\frac{2mE}{\hbar^2}}=k$ (the energy of a bound quantum system is negative), we get $-\frac{1}{k^2}\frac{d^2u}{dr^2}+\frac{mue^2}{2\pi\varepsilon_0 r\hbar^2k^2}-\frac{\left(l(l+1)\right)}{k^2r^2}u=u$

Edmond Nicolas Laguerre
(9 April 1834- 14 August 1886)

Now let $\frac{me^2}{2\pi\varepsilon_0\hbar^2k}=\rho_0$ and $\rho=kr$

Therefore, after some rearrangements we get $\frac{d^2u}{d\rho^2}=\left[1-\frac{\rho_0}{\rho}+\frac{\left(l(l+1)\right)}{\rho^2}\right]u$ (5)

Now analysing the asymptotic behaviour of the above differential equation, we put two conditions

1. $\rho\to\infty$ we get, $\frac{d^2u}{d\rho^2}=u(\rho)$

This equation have a solution of the form $u(\rho)=Ae^{-\rho}+Be^{\rho}$ but this Be^{ρ} is not acceptable by quantum mechanical constraints therefore we have a solution of the form $u(\rho)=Ae^{-\rho}$.

2. $\rho\to 0$ we get, $\frac{d^2u}{d\rho^2}=\frac{\left(l(l+1)\right)u(\rho)}{\rho^2}$

This equation have a solution of the form $u(\rho)=C\rho^{l+1}+D\rho^{-l}$ but this $D\rho^{-l}$ is not acceptable by quantum mechanical constraints therefore we have a solution of the form $u(\rho)=C\rho^{l+1}$.

Combining 1 and 2 we have $u(\rho)\sim e^{-\rho}\rho^{l+1}$

Now multiplying the above equation with a function $v(\rho)$ to combine the two behaviours with its behaviour in the midway values, we get, $u(\rho)\sim e^{-\rho}v(\rho)\rho^{l+1}$

Now resubstituting $u(\rho)\sim e^{-\rho}v(\rho)\rho^{l+1}$ in the radial wavefunction of the Schrodinger equation (5) and after a rigorous mathematical deviations we get, $e^{-\rho}\rho^l\left\{\left(\rho\frac{d^2v}{d\rho^2}+2(l+1-\rho)\frac{dv}{d\rho}\right)+\left(\frac{\left(l(l+1)\right)}{\rho}-2(l+1)+\rho\right)v\right\}$ (6)

Now again resubstituting (6) in the radial wavefunction of the Schrodinger equation (5) and after a rigorous mathematical deviation we get, $\left\{\left(\rho\frac{d^2v}{d\rho^2}+2(l+1-\rho)\frac{dv}{d\rho}\right)+\left(\rho_0-2(l+1)\right)v\right\}=0$ (7)

Now this can be written as a power series sum as $v(\rho)=\sum_{j=0}^{\infty}a_j\rho^j$ (8)

This leads to $\frac{d}{dx}v(\rho)=\sum_{j=0}^{\infty}(j+1)a_{j+1}\rho^j$ and further $\frac{d^2v(\rho)}{d\rho^2}=\sum_{j=0}^{\infty}j(j+1)a_{j+1}\rho^{j-1}$ (9)

Now resubstituting in (7) FROM (8) and (9) we get,

$\sum_{j=0}^{\infty}j(j+1)a_{j+1}\rho^j+2(l+1)\sum_{j=0}^{\infty}(j+1)a_{j+1}\rho^j-2\sum_{j=0}^{\infty}(j+1)a_{j+1}\rho^{j+1}+\left(\rho_0-2(l+1)\right)\sum_{j=0}^{\infty}a_j\rho^j=0$ (10)

On further comparisons we finally get something known as the recursion relation which can be written as $a_{j+1} = \frac{2(l+1+j)-\rho_0}{(j+1)\{j+2(l+1)\}} a_j$ (11)

Now if $j \to \infty$ then this recursion relation simplifies to $a_{j+1} = \frac{2}{(j+1)} a_j \Rightarrow a_j = \frac{2^j}{j!}\mathbf{A_0}$

Now $v(\rho) = \sum_{j=0}^{\infty} a_j \rho^j = \sum_{j=0}^{\infty} \frac{2^j}{j!} a_0 \rho^j = a_0 e^{\rho}$

Now $u(\rho) \sim e^{-\rho} v(\rho) \rho^{l+1} = a_0 e^{\rho} \rho^{l+1}$ but this is not acceptable in its raw form because of the quantum mechanical constraints therefore we have a solution for a Finite terminating power series which can be done by putting $a_{j+1} = 0 \Rightarrow 2(l+1+j) - \rho_0 = 0 \Rightarrow 2(l+1+j_{max}) = \rho_0$ (12)

Now let $l + 1 + j_{max} = n$ (13)

Therefore, $2n = \rho_0 \; n \in \mathbb{N}$

Now the energy becomes

$E_n = -\left[\frac{m_e e^4}{8\varepsilon_0^2 h^2}\right]\left(\frac{Z^2}{n^2}\right) = -\left[\frac{m_e e^4}{32\pi^2 \varepsilon_0^2 \hbar^2}\right]\left(\frac{Z^2}{n^2}\right) = \frac{-13.6}{n^2}$. this n is known as the Principal Quantum Number.

Also, the Bohr's radius $a_0 = \left[\frac{4\pi\varepsilon_0}{m_e e^2}\hbar^2\right] = 0.529\text{Å}$

Remark: This exact energy spectrum—emerging here from the full machinery of quantum mechanics was once intuited by Niels Bohr stands as a quiet testament to the depth of his physical insight.

Now further from $\rho = kr$; $u(\rho) \sim e^{-\rho} v(\rho) \rho^{l+1}$ and $R_{nl}(r) = \frac{u}{r}$ we get

$$R_{nl}(r) = \frac{e^{-\frac{r}{na_0}}}{r}\left(\frac{r}{na_0}\right)^{l+1} v\left(\frac{r}{na_0}\right)$$

Now for ground state $R_{nl}(r) = \frac{\mathbf{a_0} e^{-\frac{r}{na_0}}}{a_0}$

Now on normalization $\int_0^{\infty} |R_{nl}(r)|^2 r^2 dr = 1 \Rightarrow \int_0^{\infty} \left|\frac{\mathbf{A_0} e^{-\frac{r}{na_0}}}{a_0}\right|^2 r^2 dr = 1 = \frac{\mathbf{A_0^2}}{a_0^2}\int_0^{\infty} e^{-\frac{2r}{na_0}} r^2 dr$

the expression simplifies by using the identity $\int_0^{\infty} x^2 e^{-cx} dx = \frac{2}{c^3}$ to $R_{10}(r) = R_{1s}(r) = \frac{2e^{\frac{-r}{a_0}}}{(a_0)^{\frac{3}{2}}}$

The normalized radial part of the wavefunction is solved by the Laguerre polynomial, and the solution is expressed in the form $R_{nl}(r) = N_{nl}\left(\frac{2r}{na_0}\right)^l e^{-\frac{Zr}{na_0}} L_{n-l-1}^{2l+1}$ and after using the identity $\int_0^{\infty} e^{-x} x^{k+1} [L_m^k(x)]^2 dx = \frac{[(m+k)!]}{m!}(2m+k+1)$ this becomes

$$R_{nl}(r) = \sqrt{\left(\frac{2Z}{na_0}\right)^3 \left[\frac{(n-l-1)!}{2n[(n+l)!]}\right]}\left(\frac{2Zr}{na_0}\right)^l e^{-\frac{Zr}{na_0}} L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_0}\right)$$

On normalizing the wavefunction for 1s orbital we get $\psi_{1s} = \frac{e^{\frac{-r}{a_0}}}{\sqrt{\pi}(a_0)^{\frac{3}{2}}}$ and the radial part of this wavefunction is given by

$R_{nl}(r) = R_{10}(r) = \frac{2e^{\frac{-r}{a_0}}}{(a_0)^{\frac{3}{2}}}$. Similarly, for 2s orbital

$\psi_{2s} = \frac{e^{\frac{-r}{2a_0}}}{4\sqrt{2\pi}(a_0)^{\frac{3}{2}}}\left(2 - \frac{r}{a_0}\right)$, therefore, $R_{20}(r) = \frac{e^{\frac{-r}{2a_0}}}{(2a_0)^{\frac{3}{2}}}\left(2 - \frac{r}{a_0}\right)$.

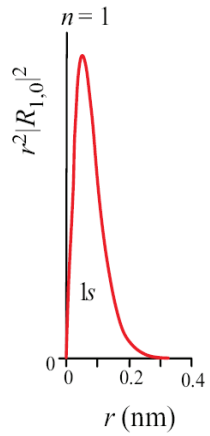
Some radial wavefunctions are listed

ORBITAL	Principal Quantum Number (n)	Azimuthal Quantum Number (l)	RADIAL WAVEFUNCTION $R_{nl}(r)$
1s	1	0	$R_{10}(r) = \frac{2e^{\frac{-r}{a_0}}}{(a_0)^{\frac{3}{2}}}$

2s	2	0	$R_{20}(r) = \frac{e^{\frac{-r}{2a_0}}}{2\sqrt{2}(a_0)^{\frac{3}{2}}}\left(2 - \frac{r}{a_0}\right)$
2p	2	1	$R_{21}(r) = \frac{re^{\frac{-r}{2a_0}}}{2\sqrt{6}(a_0)^{\frac{5}{2}}}$
3s	3	0	$R_{30}(r) = \frac{2e^{\frac{-r}{3a_0}}}{81\sqrt{3}(a_0)^{\frac{3}{2}}}\left(27 - 18\frac{r}{a_0} + 2\left(\frac{r}{a_0}\right)^2\right)$
3p	3	1	$R_{31}(r) = \frac{8e^{\frac{-r}{3a_0}}}{27\sqrt{6}(a_0)^{\frac{5}{2}}}\left(r - \frac{r^2}{6a_0}\right)$
3d	3	2	$R_{32}(r) = \frac{4r^2e^{\frac{-r}{3a_0}}}{81\sqrt{30}(a_0)^{\frac{7}{2}}}$

Maxima And Physical Significance

In many problems of chemistry and physics, the physically meaningful value of a quantity corresponds not merely to where a function exists, but where it becomes most significant. Mathematically, such points are identified as maxima or minima of a function, obtained by setting its first derivative equal to zero i.e. $\frac{df(x)}{dx} = 0$, and applying appropriate conditions. In quantum mechanics, observable probabilities are represented by functions, and the most likely or most probable physical outcomes are therefore determined by locating the maxima of probability distributions. Consequently, the concept of maxima is not a purely mathematical tool but a fundamental method for extracting measurable physical information from wavefunctions, such as the most probable distance of an electron from the nucleus.



Since the principal and azimuthal quantum numbers determine the radial part of the wavefunction, it is natural to ask at what distance from the nucleus the electron is most likely to be found. In quantum mechanics, the position of an electron is described probabilistically rather than by definite orbits. For a hydrogen-like atom, after separation of the Schrödinger wavefunction into radial and angular parts, as $\psi(r, \theta, \phi) = \psi_{(n,l,m)}(r, \theta, \phi) = R_{n,l}(r)\Theta_l^m(\theta)\Phi_m(\phi) = R_{nl}(r)Y_l^m(\theta, \phi)$ the probability of finding the electron between r and $r + dr$, irrespective of direction, is given by the radial probability distribution $P_{nl}(r)dr = r^2|R_{nl}(r)|^2dr$. The most probable radius is defined as the value of r where, $P_{nl}(r)$ is maximum. For the ground state of hydrogen atom, i.e. 1s orbital where, $n = 1; l = 0$, the radial wavefunction is given as $R_{10}(r) = R_{1s}(r) = \frac{2e^{\frac{-r}{a_0}}}{(a_0)^{\frac{3}{2}}}$. This corresponds to the relation of radial probability distribution

$P_{nl}(r)dr \propto r^2e^{\frac{-r}{a_0}}$. Differentiation with respect to r and putting the first derivative equal to zero i.e. $\frac{d}{dr}\left[\frac{4r^2e^{\frac{-2r}{a_0}}}{(a_0)^3}\right] = 0$ yields the most probable radius where the probability of finding the electron is maximum $(r_{mp})_{1s} = a_0$, called the Bohr's radius. The most probable radius calculated using the curve known as the radial probability distribution plots.

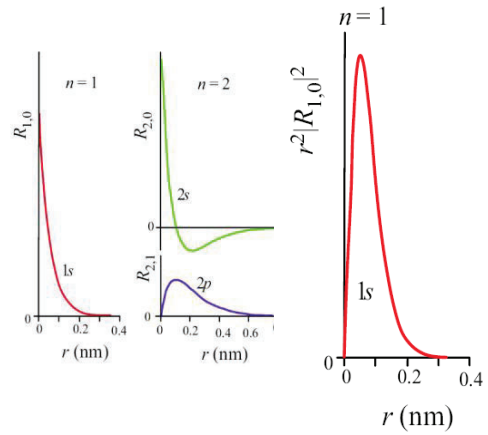
Similarly, for 2s orbital we have

$R_{20}(r) = R_{2s}(r) = \frac{e^{\frac{-r}{2a_0}}}{2\sqrt{2}(a_0)^{\frac{3}{2}}}\left(2 - \frac{r}{a_0}\right)$, therefore, the procedure of differentiation yields $\frac{d}{dr}\left[\frac{r^2e^{\frac{-r}{2a_0}}}{8(a_0)^3}\left(2 - \frac{r}{a_0}\right)^2\right] = 0$, after a rigorous mathematical solution leads to two different values of the most probable radius $(r_{mp})_{2s} = (3 \pm \sqrt{5})a_0$. These values are $\left((r_{mp})_{2s}\right)_1 = 0.77a_0$ and

$\left(\left(r_{mp}\right)_{2s}\right)_2 = 5.23a_0$ There is a radial node at $r = 2a_0$. Similarly, the most probable radius of 2p orbital is given by the process of putting $R_{21}(r) = R_{2p}(r) = \frac{re^{\frac{-r}{2a_0}}}{2\sqrt{6}(a_0)^{\frac{5}{2}}}$ in the differential $\frac{d}{dr}\left[\frac{r^4 e^{\frac{-r}{a_0}}}{24(a_0)^5}\right] = 0$ leads to the value $\left(r_{mp}\right)_{2p} = 4a_0$.

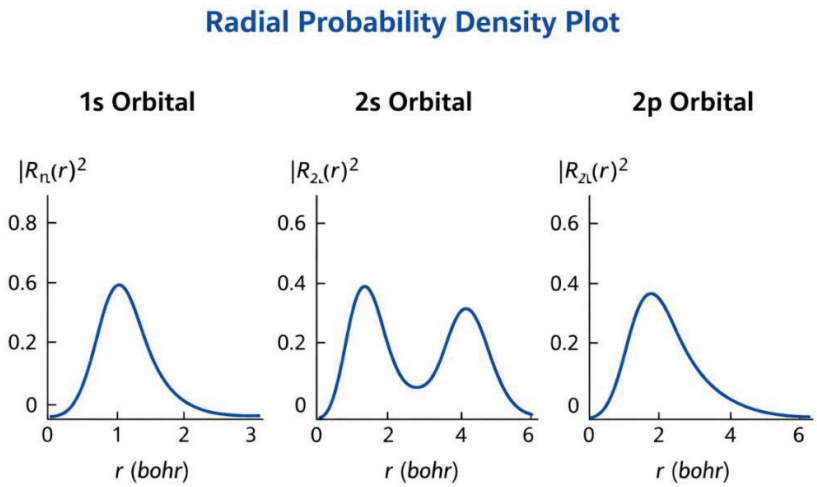
When the radial wavefunction is plotted we get three different types of plots namely

A. RADIAL WAVEFUNCTION PLOT: This is the plot of the raw radial wavefunction $R_{nl}(r)$ against the radial distance r. It shows the oscillatory behaviour and **nodes** of the wavefunction and accounts for the phase change of the wavefunction.



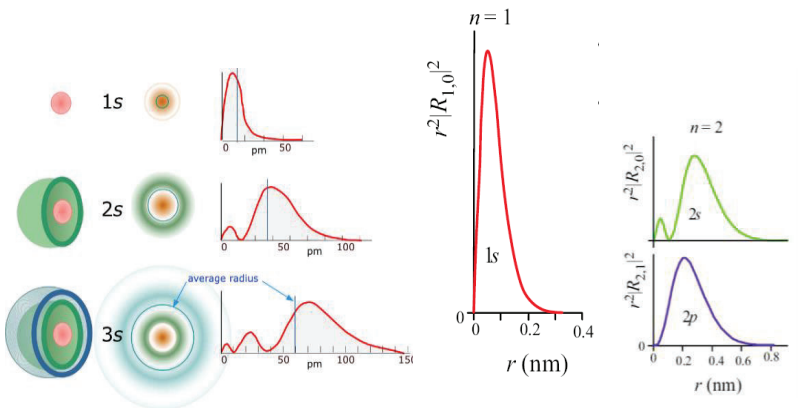
A. RADIAL WAVEFUNCTION PLOT

B. RADIAL PROBABILITY DENSITY PLOT: This plots the square of the radial wavefunction $|R_{nl}(r)|^2$. Shows where the electron is most likely to be found at a certain distance r, ignoring the spherical volume factor.



B. RADIAL PROBABILITY DENSITY PLOT

C. TOTAL RADIAL PROBABILITY PLOT OR RADIAL DISTRIBUTION PLOT: This includes the spherical volume factor $4\pi r^2$ sometimes just $r^2|R_{nl}(r)|^2$ without 4π. It gives the probability of finding the electron at a distance r in a spherical shell of radius r. The peak of this plot gives the most probable radius r_{mp}. This trend of the radial probability plots leads to the fact that the effective nuclear charge Z_{eff}, and the radial distance r are approximately inversely related for regions beyond the most probable radius r_{mp}. At distances $r > r_{mp}$, the electron is influenced primarily by the net positive charge of the nucleus after shielding by inner electrons. In this region, the radial probability decreases exponentially, and the electron's average



C. TOTAL RADIAL PROBABILITY PLOT OR RADIAL DISTRIBUTION PLOT

distance from the nucleus scales roughly as $Z_{eff} \propto \frac{1}{r^2}$. Within r_{mp}, this simple inverse relationship does not hold, because the electron is in the rising part of the radial distribution where the wavefunction behaviour is dominated by penetration effects rather than shielding.

Caution: The most probable radius is a quantum-mechanical probability maximum and must not be interpreted as a fixed circular orbit or identified with the Bohr model's electron path. Nevertheless, it is remarkable that the radius obtained from the quantum-mechanical probability maximum for the ground state coincides numerically with the Bohr radius, highlighting the deep physical insight of Niels Bohr, whose early model, though semi-classical, anticipated an essential feature later justified rigorously by quantum mechanics.

ANGULAR WAVEFUNCTION OR SPHERICAL HARMONICS OF HYDROGEN ATOM

So far, the radial wavefunction determines how the probability of finding an electron varies depending on its distance from the nucleus, the complete spatial description of an atomic orbital requires understanding how this probability is distributed in different directions, which is provided by the spherical harmonics, which are just the standing waves on spherical surface.

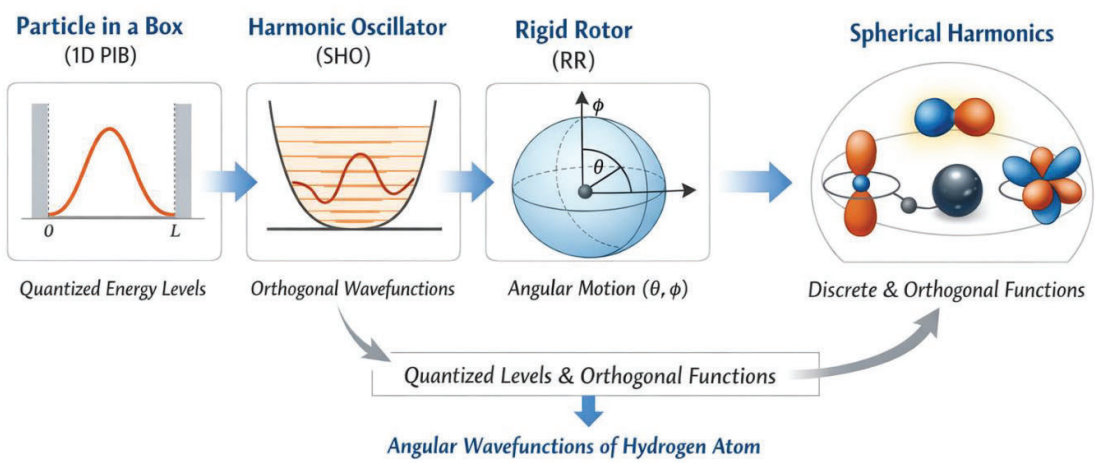
CONNECTING SIMPLE QUANTUM SYSTEMS TO ANGULAR WAVEFUNCTIONS

Before we study the angular wavefunctions of the hydrogen atom, it is useful to recall a few simple quantum systems:

1. Particle in a Box (1D PIB): A particle confined in a one-dimensional box can occupy only specific energy levels given by $E_n = \frac{n^2h^2}{8ma^2}$, for a box of length a. This happens because the wavefunction must satisfy boundary conditions at the walls of the box. In the hydrogen atom, the electron's motion is similarly restricted by the geometry of space, giving rise to **quantized energy levels** for both radial and angular motion.

2. Simple Harmonic Oscillator (SHO): The harmonic oscillator has discrete energy levels given by $\boldsymbol{E = \left(v_x + \frac{1}{2}\right) h\nu;\ v \in W}$ and corresponding wavefunctions that are **orthogonal**, meaning they are independent and do not overlap. The angular wavefunctions of the hydrogen atom, called **spherical harmonics**, share this property of orthogonality.

3. Rigid Rotor (RR): In a rigid rotor, a particle moves only on the surface of a sphere, with a fixed distance from a central point. Its energy depends on the angles θ (polar) and φ (azimuthal). The solutions of this system are the **spherical harmonics** $Y_l^m(\theta, \phi)$, which also describe the angular motion of the electron in a hydrogen atom. These functions are defined on the surface of a sphere and are both discrete and orthogonal. The energy of a rigid rotor is given in terms of the azimuthal quantum number (also called orbital angular momentum quantum number) by $E_l = \frac{h^2}{8\pi^2 I}\big(l(l+1)\big) = \frac{\hbar^2}{2I}\big(l(l+1)\big)$.



The angular part of the hydrogen atom Schrödinger equation, which is governed entirely by the square of the angular momentum operator, $\hat{L}^2$. Since the Hamiltonian depends on the angular coordinates only through this operator, it introduces no angular eigenfunctions beyond those already defined by angular momentum itself. Consequently, the spherical harmonics arise fundamentally as eigenfunctions of $\hat{L}^2$. and they appear in the hydrogen atom because the angular dependence of the Hamiltonian is proportional to this operator. This relationship may be expressed compactly as: $\hat{H}Y_l^{|m|}(\theta,\phi) = \frac{1}{2I}\hat{L}^2 Y_l^{|m|}(\theta,\phi) = \frac{\hbar^2}{2I}\big(l(l+1)\big) \Rightarrow \hat{L}^2 Y_l^{|m|}(\theta,\phi) = \hbar^2\big(l(l+1)\big)$. As the total wavefunction of hydrogen atom can be separated in radial and angular components as $\psi_{(n,l,m)}(r,\theta,\phi) = R_{nl}(r)Y_l^m(\theta,\phi)$ similarly the angular part of the wavefunction is itself composed of two components and can be written as $Y_l^m(\theta,\phi) = \Theta_l^m(\theta)\Phi_m(\phi)$. Where, $\Phi_m(\phi)$ is called the azimuthal function and $\Theta_l^m(\theta)$ is called the co-latitudinal function Therefore, the total wavefunction can also be written as a product of three independent wavefunctions as $\psi_{(n,l,m)}(r,\theta,\phi) = R_{n,l}(r)\Theta_l^m(\theta)\Phi_m(\phi)$. Now again applying the separation of variables to the angular part and putting $Y_l^m(\theta,\phi) = \Theta_l^m(\theta)\Phi_m(\phi)$ in $\left\{\frac{1}{Y_l^m(\theta,\phi)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\right\}Y_l^m(\theta,\phi)$ we finally get $\left\{\frac{1}{\Theta(\theta)}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + l(l+1)\sin^2\theta\right]\right\} = m^2$, and $\frac{\partial^2\Phi(\phi)}{\partial\phi^2} = -m^2$. This equation has a solution of the form $\Phi_m = Ae^{\iota m\phi}$, which after normalization gives $\Phi_m(\phi) = \frac{e^{\iota m\phi}}{\sqrt{2\pi}}$ which is also obtained by the solution of the Time independent Schrödinger's wave equation for the Rigid rotor model. We have four identities to write the spherical harmonics:

$\sin\theta = \frac{e^{\iota\theta} - e^{\iota\theta}}{2\iota}$ **B.** $\cos\theta = \frac{e^{\iota\theta} + e^{\iota\theta}}{2}$ **C.** $e^{\iota m\phi} = \cos m\phi$ **D.** $e^{-\iota m\phi} = \sin m\phi$

The spherical harmonics for different atomic orbitals can be listed using the general form $Y_l^{|m|}(\theta,\phi) = N_l^{|m|}\sin^{|m|}\theta\cos^{l-|m|}\theta\, e^{\iota m\phi}$, and the identities A-D as

Orbital	Spherical harmonics (angular wavefunction of H-atom) $Y_l^{\|m\|}(\theta,\phi)$
s-orbital	$Y_0^0(\theta,\phi) = \frac{1}{2\sqrt{\pi}}$
p_z-orbital	$Y_1^0(\theta,\phi) = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
p_x-orbital	$Y_1^1(\theta,\phi) = -\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{\iota\phi} = -\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\cos\phi$
p_y-orbital	$Y_1^{-1}(\theta,\phi) = \frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{-\iota\phi} = \frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\sin\phi$
$d_{(x^2-y^2)}$-orbital	$Y_2^2(\theta,\phi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\, e^{2\iota\phi} = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\cos 2\phi$
d_{xz}-orbital	$Y_2^1(\theta,\phi) = -\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta\, e^{\iota\phi} = \sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\cos\phi$
d_{z^2}-orbital	$Y_2^0(\theta,\phi) = \frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$
d_{yz}-orbital	$Y_2^{-1}(\theta,\phi) = \frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta\, e^{-\iota\phi} = \frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta\sin\phi$
d_{xy}-orbital	$Y_2^{-2}(\theta,\phi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\, e^{-2\iota\phi} = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\sin 2\phi$

$f_{x(x^2-3y^2)}$ and $f_{y(3x^2-y^2)}$ orbitals	$Y_3^{-3}(\theta,\phi)=\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta\, e^{-3\iota\phi}$
$f_{x(x^2-3y^2)}$ and f_{xyz} orbitals	$Y_3^{-2}(\theta,\phi)=\frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta\cos\theta\, e^{-2\iota\phi}$
f_{xz^2} and f_{yz^2} orbitals	$Y_3^{-1}(\theta,\phi)=\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta\,(5\cos^2\theta-1)e^{-\iota\phi}$
f_{z^3} orbital	$Y_3^{0}(\theta,\phi)=\frac{1}{4}\sqrt{\frac{7}{\pi}}(5\cos^3\theta-3\cos\theta)$
f_{xz^2} and f_{yz^2} orbitals	$Y_3^{1}(\theta,\phi)=-\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta\,(5\cos^2\theta-1)e^{\iota\phi}$
$f_{z(x^2-y^2)}$ and f_{xyz} orbitals	$Y_3^{2}(\theta,\phi)=\frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta\cos\theta\, e^{2\iota\phi}$
$f_{x(x^2-3y^2)}$ and $f_{y(3x^2-y^2)}$ orbitals	$Y_3^{3}(\theta,\phi)=-\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta\, e^{3\iota\phi}$

The factor $e^{\iota m\phi}$ represents the phase rotations about the z-axe. The factor $e^{\iota m\phi}$ determines the value of the Magnetic Quantum Number ($\boldsymbol{m_\ell}$), because although the terms $\sin^{|m|}\theta\cos^{l-|m|}\theta\, e^{\iota m\phi}$ include m in their expressions but this term, $e^{\iota m\phi}$ results in the quantization of the *orientation* of the angular momentum, as it gives rise to discrete allowed orientations of the angular momentum without affecting its magnitude.. These values of Spherical harmonics (angular wavefunction of H-atom) $Y_l^{|m|}(\theta,\phi)$ leads to the conclusions about the shapes of the atomic orbitals. The values of Spherical harmonics for s-orbital is independent of ϕ,θ; therefore, s-orbital is non directional in nature and spherical in shape, which can also be explained by combining the radial and angular wavefunctions of 1s orbital as $Y_0^0(\theta,\phi)=\frac{1}{2\sqrt{\pi}}$ and $R_{10}(r)=\frac{2e^{\frac{-r}{a_0}}}{(a_0)^{\frac{3}{2}}}$ giving $\psi_{1s}=\frac{e^{\frac{-r}{a_0}}}{\sqrt{\pi}(a_0)^{\frac{3}{2}}}$. Similarly, by plotting the value of $\cos\theta$ we get the dumbbell shape of the p_z-orbital. In the vector model of orbital angular momentum, the magnitude of the angular momentum is $\left|\hat{L}\right|=\sqrt{l(l+1)}\hbar$ while its projection along the z-axis is quantized as $\left|\hat{L}_z\right|=m\hbar$. This permits a semi-classical interpretation in which the polar angle θ the same angle that appears in spherical polar coordinates and hence in the spherical harmonics $Y_l^{|m|}(\theta,\phi)$ and represents the angle between the angular momentum vector $\hat{L}$ and the z-axis. The relation between θ,l and m is then given by $\cos\theta=\frac{m}{\sqrt{l(l+1)}}$. This expression illustrates the space quantization of the **angular momentum vector**, indicating that $\hat{L}$ can assume only discrete orientations with respect to the reference axis. It must be emphasized that this angle θ refers solely to the orientation of $\hat{L}$ and should not be interpreted as describing the spatial orientation or shape of atomic orbitals. The shapes, nodal planes, and directional characteristics of orbitals such as p_x, p_y, p_z arise from the angular wavefunctions (spherical harmonics) themselves, not from the vector model of angular momentum.

For the solution of the θ part of the spherical harmonics or the co-latitudinal function, we have $\left\{\frac{1}{\Theta(\theta)}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+l(l+1)\sin^2\theta\right]\right\}=m^2$

After rearrangements It becomes

$$\left[\left(\frac{\sin^2\theta}{\Theta(\theta)}\frac{\partial^2\Theta(\theta)}{\partial\theta^2}\right)+\frac{\sin\theta\cos\theta}{\Theta(\theta)}\frac{\partial\Theta(\theta)}{\partial\theta}+l(l+1)\sin^2\theta-m^2\right]=0$$

$$\left[\left(\sin^2\theta\frac{\partial^2\Theta(\theta)}{\partial\theta^2}\right)+\sin\theta\cos\theta\frac{\partial\Theta(\theta)}{\partial\theta}+l(l+1)\sin^2\theta-m^2\right]\Theta(\theta)=0$$

The Associated Legendre polynomials are the solutions for the equation

$$\frac{d}{dx}\left[(1-x^2)\frac{d}{dx}P_l^m(x)\right]+\left[l(l+1)-\frac{m^2}{(1-x^2)}\right]P_l^m(x)=0$$

The Associated Legendre polynomials are given by

$$P_l^m(x)=(-1)^m(1-x^2)^{\frac{m}{2}}\frac{d^m}{dx^m}P_l(x)$$

Equivalently, $\boldsymbol{P_l^{|m|}(\xi)=\left(1-\xi^2\right)^{\frac{|m|}{2}}\frac{d^{|m|}P_l(\xi)}{d\xi^{|m|}}}$

This $P_l(x)$ is called the Legendre polynomials and are given by the Rodrigues' formula as $P_l(x)=\frac{1}{2^l l!}\frac{d^l}{dx^l}[(x^2-1)^l]\quad(l\in W)$

Adrien Marie Legendre (18 September 1752-10 January 1833)

Equivalently,$P_l(\xi)=\frac{1}{2^l l!}\frac{d^l}{d\xi^l}\left(\xi^2-1\right)^l$

$\xi^2=\boldsymbol{\cos\theta}$

After some substitutions and rearrangements, we get

$$P_l^m(x)=\frac{(-1)^m}{2^l l!}(1-x^2)^{\frac{m}{2}}\frac{d^{l+m}}{dx^{l+m}}[(x^2-1)^l]$$

By applying the Orthonormalization condition $\oint\psi_i\psi_j d\tau=\left\langle\psi_i\middle|\psi_j\right\rangle=\delta_{ij}=\begin{cases}0\,,if\ i\neq j\ (\text{orthogonality})\\1,if\ i=j\ (\text{normalization})\end{cases}$ on The Associated Legendre polynomials $P_l^m(x)$, we have

$N^2\oint\left(P_l^m(x)\right)^2=1$

The normalization constant $N=\sqrt{\left[\left(\frac{2l+1}{2}\right)\left(\frac{(l-|m|)!}{(l+|m|)!}\right)\right]}$

The normalized angular wave function is termed as the spherical harmonics and is given by

$$\boldsymbol{\Theta(\theta)_{l,|m|}=P_l^{|m|}(\cos\theta)\sqrt{\left[\left(\frac{2l+1}{2}\right)\left(\frac{(l-|m|)!}{(l+|m|)!}\right)\right]}}$$

$$\boldsymbol{Y_l^{|m|}(\theta,\phi)=\Theta(\theta)_{l,|m|}\Phi_m(\phi)=P_l^{|m|}(\cos\theta)\sqrt{\left[\left(\frac{2l+1}{4\pi}\right)\left(\frac{(l-|m|)!}{(l+|m|)!}\right)\right]}e^{\iota m\phi}}$$

$$\boldsymbol{P_l^{|m|}(\cos\theta)=\left(1-\cos^2\theta\right)^{\frac{|m|}{2}}\frac{d^{|m|}}{d(\cos\theta)^{|m|}}\left[\frac{1}{2^l l!}\frac{d^l}{d(\cos\theta)^l}\left(\cos^2\theta-1\right)^l\right]}$$

The complete general form of spherical harmonics is given as:

$$\boldsymbol{Y_l^{|m|}(\theta,\phi)=(-1)^m\sqrt{\left[\left(\frac{2l+1}{4\pi}\right)\left(\frac{(l-|m|)!}{(l+|m|)!}\right)\right]}\left(1-\cos^2\theta\right)^{\frac{|m|}{2}}\frac{d^{|m|}}{d(\cos\theta)^{|m|}}\left[\frac{1}{2^l l!}\frac{d^l}{d(\cos\theta)^l}\left(\cos^2\theta-1\right)^l\right]e^{\iota m\phi}}$$

Now combining the radial and the angular parts we have

$$\psi_{(n,l,m)}(r,\theta,\phi)=R_{nl}(r)Y_l^{|m|}(\theta,\phi)$$

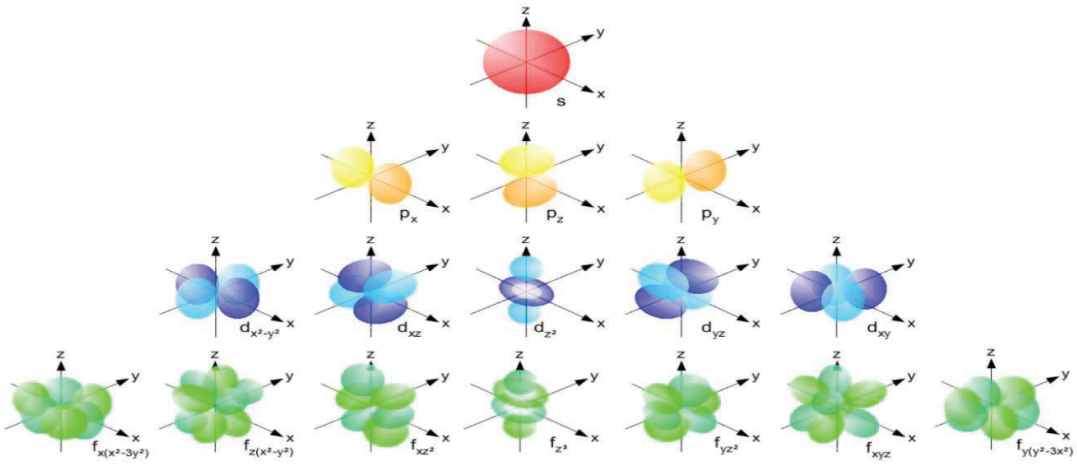
$$=\sqrt{\left(\frac{2Z}{na_0}\right)^3\left[\frac{(n-l-1)!}{2n[(n+l)!]}\right]}\left(\frac{2Zr}{na_0}\right)^l e^{-\frac{Zr}{na_0}}L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_0}\right)(-1)^m\sqrt{\left[\left(\frac{2l+1}{4\pi}\right)\left(\frac{(l-|m|)!}{(l+|m|)!}\right)\right]}(1$$

$$-\cos^2\theta)^{\frac{|m|}{2}}\frac{d^{|m|}}{d(\cos\theta)^{|m|}}\left[\frac{1}{2^l l!}\frac{d^l}{d(\cos\theta)^l}\left(\cos^2\theta-1\right)^l\right]e^{\iota m\phi}$$

Angular Part and Orbital Shapes in Hydrogen Atom

The angular part of the hydrogen atom wavefunction determines the shapes and orientations of atomic orbitals. the radial component governs the variation of the probability along the radial

direction. Among the two angular components, the θ component governs the variation of the probability along the longitudinal direction and the ϕ component governs the variation of the probability along the latitudinal direction. The characteristic forms of the s, p, d, and f orbitals arise directly from the specific sine and cosine functions present in the angular part of the normalized wavefunction, which describe the spatial distribution of electron probability. While the radial part governs the size and distance of the electron cloud from the nucleus, the angular part defines its directional pattern, giving each orbital its unique geometry, such as the spherical s orbitals, the dumbbell-shaped p orbitals, and the more complex d and f orbital shapes.



ATOMIC ORBITALS

QUANTUM NUMBERS: FIXED BY THEORY, UNDEFINED IN SPACE

For a given principal quantum number n, quantum mechanics strictly determines the allowed values of the angular momentum quantum number l and the magnetic quantum number m through the eigenvalue equations of the angular momentum operators. However, these quantum numbers do not define a unique classical orientation or spatial shape of the orbitals. The quantum number l fixes only the magnitude of the orbital angular momentum, while m specifies its projection along a chosen axis; the remaining components remain intrinsically uncertain. Consequently, although the values of l and m are mathematically well defined, their physical manifestation in space is not uniquely defined prior to measurement. The familiar real orbitals therefore arise from particular linear combinations of the degenerate spherical harmonic states, chosen for convenience and symmetry rather than imposed by quantum mechanical treatment. The final equation can be written as:

$$\psi_{n,l,m}(\vec{r},\Theta,\Phi) = \psi_{space}\psi_{spin} \Rightarrow \psi_{n,l,m}(\vec{r},\Theta,\Phi) = R_{n,l}(r)Y_l^{|m|}(\theta,\phi,\sigma) = R_{n,l}(r)\Theta(\theta)\Phi(\phi)\Sigma(\sigma)$$

$$= \left[\underbrace{(-1)^{|m|}\sqrt{\left(\frac{2}{na_0}\right)^3\left[\frac{(n-l-1)!\,(2l+1)(l-|m|)!}{2n[(n+l)!]^3}\right]}\left(\frac{2r}{na_0}\right)^l e^{-\frac{r}{na_0}}\left[\sum_{k=0}^{n-l-1}\frac{(-1)^k}{k!}\left(\frac{2r}{na_0}\right)^k\binom{n+l}{n-l-1-k}\right]}_{Normalization\ constant} \right.$$

$$\left. \left[(1-\cos^2\theta)^{\frac{|m|}{2}}\frac{d^{|m|}}{d(\cos\theta)^{|m|}}\left[\frac{1}{2^l l!}\frac{d^l}{d(\cos\theta)^l}(\cos^2\theta-1)^l\right]e^{\iota m\phi}\right]\begin{cases}\binom{1}{0}, m_s = +\frac{1}{2}\\ \binom{0}{1}, m_s = -\frac{1}{2}\end{cases} \right]$$

The unit of wave function ψ is $m^{-\frac{3}{2}}$.

The wavefunction have no significance of its own, it is just a mathematical function which contains the information of the quantum particle, (electron in this case). Using the ground-state wavefunction of the hydrogen atom obtained from the Schrödinger equation, the uncertainties in position and momentum can be evaluated. The result $\Delta x \Delta p_x = \frac{\sqrt{3}}{2}\hbar = 0.86\hbar > \frac{\hbar}{2}$ and

therefore satisfies the Heisenberg uncertainty principle. Schrödinger was awarded the 1933, Physics Nobel Prize, shared with P.A.M. Dirac.

3T. BORN'S STATISTICAL INTERPRETATION

Max Born (Father of Quantum Mechanics' Probabilistic Interpretation) in 1926 introduced the Born's statistical interpretation of the wavefunction. It states that, "The wave-function does not represent a physically observable classical wave but a 'wave of probability'. The square of the absolute value of the wave-function gives the probability density – that is, the probability per unit of length (or volume) to find the particle in an area of the space."

Max Born
(11 December 1882-5 January 1970)

"The motion of particles follows the laws of probability, but the probability itself propagates in accordance with the law of causality."

— Max Born, 1926

OR

The *probability density of finding a particle at a specific position is equal to the absolute square* $|\psi|^2$ *of its wavefunction at that position.* Quantum mechanics is probabilistic. Max Born was awarded the 1954 Physics Nobel Prize, shared with Walther Wilhelm Georg Bothe. The official Nobel Prize wording "For his fundamental research in quantum mechanics, especially for his statistical interpretation of the wave function."

THE COPENHAGEN INTERPRETATION

"The Copenhagen Interpretation was developed primarily at Niels Bohr's Institute in Copenhagen, Denmark; brought together Bohr's principle of complementarity, Born's statistical interpretation of the wavefunction, and Heisenberg's uncertainty principle to form a coherent framework for quantum mechanics. It emphasizes that quantum phenomena cannot be fully described by classical concepts alone, and that the outcomes of measurements are fundamentally probabilistic. However, Einstein famously objected to this intrinsic randomness, remarking that "God does not play dice."

Enrico Fermi
(29 September 1901-28 November 1954)

In quantum mechanics, an electron in an atom is described by a wave, and therefore physical quantities such as position and momentum do not possess definite pre-existing values. An atomic orbital provides a probability distribution rather than a specific trajectory. When a measurement is repeated over many identically prepared atoms, the results vary, but their probability-weighted mean approaches a definite value, known as the average (expectation) value given by the equation $\int \psi^* \hat{A}\, \psi d\tau$. This equation yields a general form for the average value of the distance r i.e. $\langle \hat{r} \rangle$ for any given orbital which is given as $\langle \hat{r} \rangle_{nl} = \frac{n^2 a_0}{Z}\left[1 + \frac{1}{2}\left(1 - \frac{l(l+1)}{n^2}\right)\right] \Rightarrow \frac{a_0}{2Z}(3n^2 - \{l(l+1)\})$. This indicates the combined effect of n and l on radius as the average radius depends on both n and ℓ reflecting the combined radial and angular character of the hydrogenic wavefunction. Observable atomic properties are predicted through such averages. Average radial values (hydrogen ground state) $\langle \hat{r} \rangle = \frac{3}{2} a_0 \qquad \langle \hat{r}^2 \rangle = 3a_0^2$

Otto Stern
(17 February 1888-17 Augst 1969)

These represent the average size and spatial spread of the electron cloud, not the result of a single measurement.

3U. QUANTUM NUMBERS

In general, we know that the atom is structured as $ATOM \rightarrow SHELLS/ORBITS \rightarrow SUBSHELL \rightarrow ORBITALS \rightarrow SPIN - STATES \rightarrow ELECTRON$. But in quantum chemistry we solve the Schrödinger's wave equation. After a complex solution of the different Schrödinger's wave equations, through complex computational calculations the four values obtained are called quantum numbers. The set of four quantum numbers play the same role as the American address system. From the Schrödinger's wave equation, while calculating the wave functions of the different atomic orbitals of hydrogen atom, the wave function ψ is written as $\psi(r,\theta,\phi) = \psi_{(n,l,m)}(r,\theta,\phi) = R_{n,l}(r)\Theta_l^m(\theta)\Phi_m(\phi) = R_{nl}(r)Y_l^m(\theta,\phi)$.

Where $Y_l^m(\theta,\phi) = \Theta_l^m(\theta)\Phi_m(\phi)$. The spherical harmonics are the solutions of the angular part of the wave functions of the different atomic orbitals of hydrogen atom.

The wave function $\psi(r,\theta,\phi)$ is divided into Radial part and Angular part (also called The Spherical Harmonics). Each of these provide us with specific values of different quantum numbers. ψ(r,θ,ϕ) gives the values in terms of the three quantum numbers n, l, m out of which the first two i.e. n, l are given by the radial part R(r). and the spherical harmonics give the values of l, m. The values of l, m are given by the Θ(θ) part of the angular part of ψ and, the value of m is also given by the Φ(ϕ) part of ψ. These are introduced by Niels Henrik David Bohr, Arnold Johannes Wilhelm Sommerfeld, Wolfgang Ernst Pauli, George Eugene Uhlenbeck and Samuel Abraham Goudsmit in the period 1913-25. These are of 4 types:

1. **Principal Quantum Number (n):** It was introduced by Bohr in 1913. It is the number of the shell in which the electron is present. It gives information about the distance of the electron from the nucleus i.e. the atomic size. The corresponding spaces are called shells or orbits. Their energy is quantized therefore these are referred to as the Stationary states. $n \in \mathbb{N}$. The shell positions are the radial probability maxima. It also explains the degeneracy of orbitals. For hydrogenic atoms the energy of the orbitals depends just on the values of the Principal Quantum Number (n) and for multielectron atom it depends on the sum of the values of Principal Quantum Number (n) and Azimuthal Quantum Number (l).
2. **Azimuthal Quantum Number (l):** It was introduced by Sommerfeld in 1914-15. It tells about the movement of the electron in the space around the nucleus. It varies from $0 \; to \; n-1; l \in \mathbb{Z}$. The corresponding 3D spaces are called subshells.

AZIMUTHAL QUANTUM NUMBERS AND SUBSHELLS

Principal Quantum Number (n)	Azimuthal Quantum Number (l)	Name
1	0	s
2	0	s
	1	p
3	0	s
	1	p
	2	d
4	0	s
	1	p
	2	d
	3	f

Azimuthal Quantum Number (l) talks about the total angular momentum for a given subshell as $L = \sqrt{l(l+1)}\hbar \Rightarrow L^2 = l(l+1)\hbar^2$

ORBITAL	Azimuthal Quantum Number (l)	$L^2 = l(l+1)\hbar^2$	$L = \sqrt{l(l+1)}\hbar$
s	0	0	0

p	1	$2\hbar^2$	$\sqrt{2}\hbar$
d	2	$6\hbar^2$	$\sqrt{6}\hbar$
f	3	$12\hbar^2$	$\sqrt{12}\hbar = 2\sqrt{3}\hbar$

For hydrogenic atomic orbitals, the azimuthal quantum number l determines the highest power of $\cos\theta$ in the angular wavefunction and the lowest power of r^l in the radial wavefunction.

The number of subshells in a given shell is equal to its Principal Quantum Number (n) of the shell, (shell number). This shell number corresponds to the period number.

Joseph von Fraunhofer
(6 March 1787-7 June 1826)

3. **Magnetic Quantum Number (m_ℓ):** It was introduced by Sommerfeld in 1914-15. It tells about the orientation movement of the electron in the space around the nucleus. It varies from $-l\ to\ l; m \in \mathbb{Z}$.The corresponding 3D spaces are called orbitals.

The number of Orbitals in a given **Shell** n^2. Therefore, the number of electrons in a given shell is given by $2n^2$.

The number of Orbitals in a given l^{th} **Subshell** is given by the equation $\sum \boldsymbol{m_\ell} = \mathbf{2}\boldsymbol{l} + \mathbf{1}$**.** It gives the z-component of angular momentum as $\widehat{L_z} = m\hbar$

4. **Spin Quantum Numbers (s and m_s):** The concept of electron spin was introduced to explain certain features of atomic spectra, such as the spectral lines of alkali metals especially for sodium havingclosely spaced doublets, known as the sodium D-lines first observed in the solar spectrum by Joseph von Fraunhofer. that could not be accounted for by the three quantum numbers obtained from the Schrödinger wave equation. The existence of such doublets indicated that an additional degree of freedom must be associated with the electron. It was introduced in 1925 by Wolfgang Ernst Pauli, George Eugene Uhlenbeck and Samuel Abraham Goudsmit, proposed that the electron possesses an intrinsic angular momentum called **spin, characterized by the spin quantum number** $\boldsymbol{s} = \pm\frac{\mathbf{1}}{\mathbf{2}}$. Spin is an inherent property of microscopic particles and has no true classical analogue; it is purely a quantum mechanical phenomenon. The orientation of this spin angular momentum relative to a chosen axis is described by the **spin magnetic quantum numb** $\boldsymbol{m_s} = \pm\frac{1}{2}$. The particles with half-integral spin values are called Fermions. The electrons are also Fermions. These two values correspond to the two possible orientations of the electron's spin angular momentum. Because the spin quantum number has two possible values, an atomic orbital can accommodate a maximum of two electrons with opposite spins, in accordance with the **Pauli exclusion principle proposed by Wolfgang Ernst Pauli**.

George Eugene Uhlenbeck
(6 December 1900-31 October 1988)

Charles Janet
(15 June 1849-
7 February 1932)

In quantum mechanics, the components of the electron spin angular momentum are represented by operators whose matrix representations are known as the **Pauli spin**

matrices $\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$; $\sigma_y = \begin{bmatrix} 0 & -\imath \\ \imath & 0 \end{bmatrix}$; $\sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$.

Ralph Kronig (10 March 1904-16November 1995)

These matrices describe the behaviour of a particle with a spin of $\frac{1}{2}$, and satisfy important relations, $\sigma_x \sigma_y = \imath\sigma_z;\ \sigma_y \sigma_z = \imath\sigma_x;\ \sigma_z \sigma_x = \imath\sigma_y$; which reflect the fundamental commutation relations of angular momentum operators in quantum mechanics. Both these states are degenerate in an atom in ground state i.e., of same energy. Spin is an intrinsic property of atoms, nuclei and electrons etc. Ralph Kronig in 1925, suggested the electron spin as the physical interpretation of the two valued Paoli's degree of freedom, which ultimately lead to the formulation of the Pauli's exclusion principle. The number of electrons in any orbital is equal to the total number of spin orientations possible for an electron. Total number of particles in an orbital is equal to $2s + 1$. For electron the Total number of particles in an orbital is equal to

$2s + 1 \Rightarrow \left[2\left(\frac{1}{2}\right) + 1\right] = 2$. Therefore, **Any Orbital contains Only two electrons!**

Any solution of the Schrödinger's wave equation gives ONLY THREE quantum numbers n, l, m_ℓ respectively.

FERMIONS

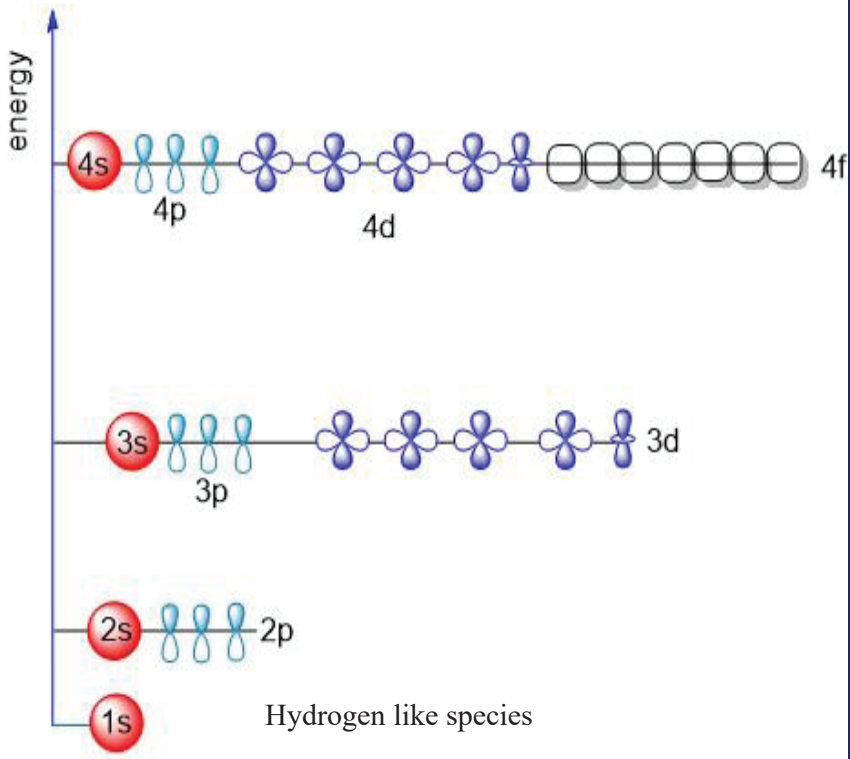
The quantum numbers n, l, m_ℓ *and* $\boldsymbol{m_s}$, completely specify the state of an individual electron in an atom. However, electrons are indistinguishable particles possessing, a half-integral intrinsic spin $\boldsymbol{m_s} = \pm\frac{1}{2}$, and therefore belong to the class of particles known as fermions. As a consequence of their fermionic nature, *The total wavefunction of a multi-electron system must be antisymmetric* with respect to the exchange of any two electrons i.e. $\psi(1,2) = -\psi(2,1)$. This requirement is not imposed by the Schrödinger equation itself but is a fundamental quantum condition arising from electron spin. The antisymmetric character of the electron wavefunction underlies the Pauli exclusion principle, governs the manner in which electrons are distributed among atomic orbitals, and forms the conceptual basis for the Aufbau principle, Hund's rule, exchange energy, and the electronic structure of multi-electron atoms. The term Fermion was coined by P.A.M. Dirac after Enrico Fermi.

AUFBAU PRINCIPLE or $n + l$-Rule

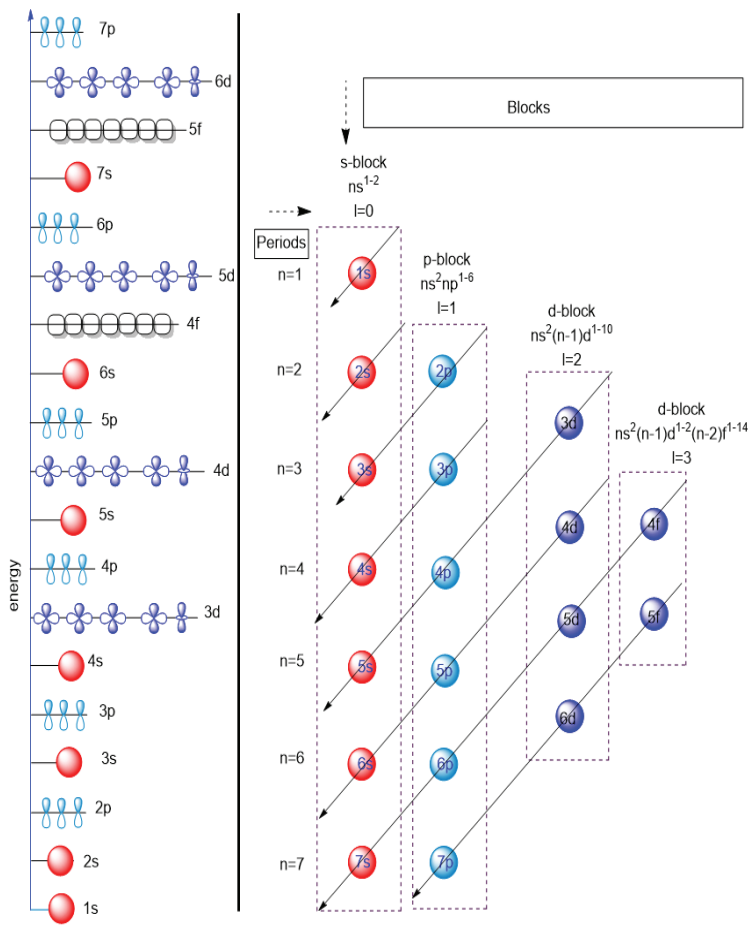
The radial wavefunction $R_{nl}(r)$ is obtained from the radial part of the Schrödinger equation and represents the wave nature of an electron as a function of its distance r from the nucleus. Since the wavefunction itself is not directly observable, the quantity $|R_{nl}(r)|^2$ gives the probability density at a distance r. However, because electrons occupy three-dimensional space and the volume of a spherical shell increase with r^2, the actual probability of finding an electron at a distance r is proportional to $r^2|R_{nl}(r)|^2$. This quantity, known as the radial distribution function, provides the most physically meaningful description of electron distribution in an atom and is particularly useful for comparing orbital penetration and relative orbital energies. These ideas help explain the order of filling of atomic orbitals described by the Aufbau principle. Having understood how the radial distribution function reflects the actual probability of finding an electron and how orbital penetration influences relative energies, we can now examine the systematic filling of orbitals. The Aufbau principle provides a convenient guideline for the order in which electrons occupy these orbitals, based on their energies.

The German word *Aufbauprinzip*, literally means "building-up principle". It should be carefully noted that it's not named for a scientist. The Aufbau principle is the principle of filling of electrons in the atom in a definite energy sequence. It was introduced by Bohr in early 1920s. It states that the atomic orbitals are filled in the **increasing order of the energy of the orbitals.** The order is decided on the bases of the $n + l$-rule. This rule states that the orbitals with lower value of the sum of the **Principal** and the **Azimuthal Quantum Numbers** are occupied prior to those with the higher values. For two orbitals with the same $n + l$ value the one with the lower n-value are occupied preferentially. Some other scientists also made a significand contribution to the formulation of this Aufbau principle. In their honour this is known by their names as listed along with the corresponding contributions.

- This rule is known as Madelung rule after Erwin Madelung who in 1936 proposed the rule of the order of filling of atomic orbitals.
- This rule is known as Janet rule after Charles Janet in the honour of his contributions in the field of periodic classification by introduction of a periodic table based on the $n + l$ values in



Hydrogen like species



AUFBAU PRINCIPLE or $n + l$-Rule

1930. It's referred to as the left-step table.

- This rule is known as Wiswesser's rule after William Joseph Wiswesser who in 1945 proposed the mathematical equation satisfying the This rule is known as Klechkovsky rule after Vsevolod Mavrikievich Klechkovsky who in 1961 explained the importance of the sum $n + l$ based on the Thomas–Fermi model of the atom. It was named after Llewellyn Hilleth Thomas and Enrico Fermi who proposed it in 1927 This model is considered as the precursor of the modern world Density Functional theory (DFT). Increasing order as proposed by this principle $W(n,l) = n + l - \frac{l}{l+1}$. This exactly fitted with the Madelung rule.
- Enrico Fermi (Father of Nuclear Physics/ Pioneer of Neutron-Induced Radioactivity/ Architect of the First Nuclear Reactor) was awarded the 1938 Physics Nobel Prize.
- The orbitals 1p, 2d are not possible because the Azimuthal Quantum Number (l) varies from $0\ to\ n-1$.
- For single electron species (hydrogen like species), the energy depends only on n-values.
- The $\boldsymbol{n+l}$-Rule is applicable for multielectron systems only. Because of stronger interelectronic repulsions caused by the electromagnetic field interactions, leading to splitting of the degeneracy of the different orbitals.

In 1971 the complete Madelung rule was derived from a similar potential by Yury N. Demkov and Valentin N. Ostrovsky. Further there is an experiment known as the Stern–Gerlach experiment after Otto Stern (Father of Molecular Beam Experiments/ Co-discoverer of Space Quantization (Stern–Gerlach Experiment)/ Pioneer of Experimental Quantum Physics) and Walther Gerlach who conducted it in 1921-22. It was based on the Bohr–Sommerfeld model, which was proposed in 1915-16. This experiment used a silver atom to test the quantization in the direction of angular momentum of the electrons. This experiment was performed years **before** George Eugene Uhlenbeck and Samuel Abraham Goudsmit hypothesized the spin quantum number. In 1927, T.E. Phipps and J.B. Taylor reproduced the effect using hydrogen atoms in their ground state, thereby eliminating any doubts that may have been caused by the use of silver atoms.
Otto Stern was awarded the 1943 Physics Nobel Prize.

Wolfgang Ernst Friedrich Pauli
(25 April 1900-15 December 1958)

PAULI'S EXCLUSION PRINCIPLE

It was introduced by Wolfgang Ernst Pauli in January 1925. It states that **"No two electrons in an atom can have the same set of all four quantum numbers."** Therefore, any two electrons in an atom must differ in at least one quantum number. As a consequence, electrons may occupy different orbitals (characterized by different n, l, m_l) or, if they are in the same orbital, they must have opposite spins, with spin quantum numbers $m_s = \pm\frac{1}{2}$

Note: This relationship is just a convention. The spins magnetic moment of an electron is $\mu = 2\sqrt{|s(s+1)|}$. Consequently, any orbital accommodate maximum of two electrons with paired and opposite spins. Pauli was awarded the 1945, Physics Nobel Prize.

HUND'S RULE OF MAXIMUM MULTIPLICITY

This rule was proposed by Friedrich Hermann Hund (Father of the Hund's Rules/Pioneer of Quantum Chemistry; also contributed in Molecular Orbital Theory (M.O.T.)) in 1925 by the observation of the atomic spectra. It states that for a given electronic configuration the term with highest multiplicity has the lowest energy. For a given electronic configuration. The lowest energy configuration is the one with highest spin multiplicity. If two or more orbitals of equal energy are available, then electron will occupy them singly first; and then, pairing may occur.

It concludes that while filling of the orbitals, all the degenerate orbitals should be singly occupied before the pairing of electrons is started i.e. Oxygen cannot have a configuration given in left side of the attached figure.
It must have its configuration as B.
Similar constraint is applied all-over the study of chemistry. Electrons are indistinguishable from each other. These are only arranged in a well-defined symmetry. This arrangement is called the electronic configuration. The electronic configuration in general is represented by $[Nobel\ Gas]nl^{N_{nl}} = [Ng]nl^{N_{nl}}$.
Here,

- n Principal Quantum Number
- l Azimuthal Quantum Number
- N_{nl} total electrons in the given configuration

$[Ng]$ the symbol of the noble gas containing the number of electrons nearest to the given element. If two or more different states (wave function solutions) share a common energy value, then they are called degenerate states. Higher the stability, lower is the energy of the configuration.

Friedrich Hermann Hund (4 February 1896-31 March 1997)

The Right Configuration is Correct

EXCHANGE ENERGY

The extra additional stability of exactly half filled and completely filled electronic configurations is due to the exchange energy. The s orbitals are Not considered in this explanation of stability
The orbitals are not like a 3D object but it's just an electromagnetic field of electron's influence in which the electron have a definite high probability of being present along with the de Broglie wave associated with it.
Electron revolve at such a high speed that these become undetectable similar to the blades of a fan rotating at its maximum speed. Electrons are indistinguishable from each other. These are only arranged in a well-defined symmetry. This arrangement is called the electronic configuration. The orbital wave functions are of different phases across the nodal plane, represented by the +, - signs in the orbital lobes. The orbitals have a definite symmetry depending on the positions of the change of the phase of the wave function ψ. This is referred as the orbital is gerade or ungerade. These two German words mean even and uneven respectively. If the flip of the coordinates of the given point leads to the wave function of the same phase, then the orbital is said to be gerade and if the operation leads to a wave function with opposite phase, then the orbital is said to be ungerade therefore the s and d orbitals are gerade and the p, f orbitals are ungerade. The orbitals with even l value are gerade and those with odd are ungerade. This implies that
Gerade (g): An orbital (or wavefunction) is gerade if it does not change sign under inversion i.e. $\psi(-r) = +\psi(r)$
Ungerade (u): An orbital (or wavefunction) is ungerade if it changes sign under inversion i.e.$\psi(-r) = -\psi(r)$
As the value of n increases the size of the orbital increase leading to an increase in its diffused nature. This results in some electronic configurations that occur in some elements and it seems that they go against the standard Aufbau principle. But actually, they get extra stabilized due to the release of energy as exchange energy. The various exceptional electronic configurations are summarized.

EXCEPTIONAL ELECTRONIC CONFIGURATIONS

The exceptional electronic configurations are summarized in this table. The exact electronic configurations of atoms are established through quantum-mechanical calculations and verified by experimental spectroscopic techniques.

Atomic number	Symbol	Name	Expected configuration (Madelung's Rule)	Experimental configuration
24	Cr	Chromium	$[Ar]3d^4 4s^2$	$[Ar]3d^5 4s^1$
29	Cu	Copper	$[Ar]3d^9 4s^2$	$[Ar]3d^{10} 4s^1$
41	Nb	Niobium	$[Kr]4d^3 5s^2$	$[Kr]4d^4 5s^1$
42	Mo	Molybdenum	$[Kr]4d^4 5s^2$	$[Kr]4d^5 5s^1$
44	Ru	Ruthenium	$[Kr]4d^6 5s^2$	$[Kr]4d^7 5s^1$
45	Rh	Rhodium	$[Kr]4d^7 5s^2$	$[Kr]4d^8 5s^1$
46	Pd	Palladium	$[Kr]4d^8 5s^2$	$[Kr]4d^{10}$
47	Ag	Silver	$[Kr]4d^9 5s^2$	$[Kr]4d^{10} 5s^1$
57	La	Lanthanum	$[Xe]4f^1 6s^2$	$[Xe]5d^1 6s^2$
58	Ce	Cerium	$[Xe]4f^2 6s^2$	$[Xe]4f^1 5d^1 6s^2$
64	Gd	Gadolinium	$[Xe]4f^8 6s^2$	$[Xe]4f^7 5d^1 6s^1$
78	Pt	Platinum	$[Xe]4f^{14} 5d^8 6s^2$	$[Xe]4f^{14} 5d^9 6s^1$
79	Au	Gold	$[Xe]4f^{14} 5d^9 6s^2$	$[Xe]4f^{14} 5d^{10} 6s^1$
89	Ac	Actinium	$[Rn]5f^1 7s^2$	$[Rn]6d^1 7s^2$
90	Th	Thorium	$[Rn]5f^2 7s^2$	$[Rn]6d^2 7s^2$
91	Pa	Protactinium	$[Rn]5f^3 7s^2$	$[Rn]5f^2 6d^1 7s^2$
92	U	Uranium	$[Rn]5f^4 7s^2$	$[Rn]5f^3 6d^1 7s^2$
93	Np	Neptunium	$[Rn]5f^5 7s^2$	$[Rn]5f^4 6d^1 7s^2$
96	Cm	Curium	$[Rn]5f^8 7s^2$	$[Rn]5f^7 6d^1 7s^2$

The exceptional configuration of chromium can be explained on the bases of exchange energy and magnetism of the electron. The experimentally verified electronic configuration of chromium is $[Ar]3d^5 4s^1$ because this configuration is stable due to the exchange energy and symmetric distribution of electrons. The small energy gap between the 3d and 4s orbitals allows the shifting of electrons. On the other hand, the experimental value of magnetic moment helps us to justify the correctness of the experimentally verified electronic configuration of chromium. The experimental value of magnetic moment of chromium is given by the results of the Dirac's equation of relativistic quantum mechanics, developed by P.A.M Dirac in 1928, and, the Quantum Electrodynamics (QED) which leads to the, value of g-factor of electron as $g_e = 2$. This further leads to the equation $\mu = 2\sqrt{|s(s+1)|}$ which after putting $s = \frac{n}{2}$, gives $\mu = \sqrt{|n(n+2)|}$. This equation leads to the experimental value of magnetic moment of chromium by putting $n = 6$ as $\mu = \sqrt{|n(n+2)|} = \sqrt{|6(6+2)|} = 6.93 B.M.$

Schrodinger in 1926 showed that it is the difference in energy levels of orbitals which decide the position of electron and not the energy level of an individual orbital which decide the position of the electron. This is verified by spectroscopic experiments. Hence, the low energy gap between the 3d and 4s orbitals of chromium, corresponds to the concepts of stability of half-filled orbitals. All the other exceptional configurations are mostly explained based on the energy difference between the different orbitals. The diagram shows the shapes of different s orbitals and the two types of plots i.e. the wavefunction plots and the probability distribution plots of various atomic orbitals. These are obtained as graphical representations of the wavefunction solutions of the Time Independent Schrödinger's Wave Equation.

ORBITAL DESCRIPTION

The solution of the Schrodinger wave equation provides us with four quantum numbers. Three of which, namely Principal Quantum Number (n), Azimuthal Quantum Number (l) and the Magnetic Quantum Number (m) are combined to reach what we know as orbitals through the step of subshell. The combination of the first two quantum numbers gives us the subshell. The further consideration of the spatial orientation factors represented by Magnetic Quantum Number (m) give us the orbitals. Various subshells have fixed number of orbitals. These

orbitals have fixed value of m corresponding to a fixed orientation in space. The names of these subshells are s, p, d, f due to this nature of the transition lines in the complete atomic spectra. The different orbitals with their corresponding wave functions can be summarized. The f-orbitals have wave function values more complex than these mentioned in the above chart. Therefore, some computational techniques are used to create the shapes of these orbitals and to solve for the ψ-value of the seven f-orbitals. orbitals are actually, just energy levels. There are infinite number of orbits/shells, subshells, orbitals with every atom, but those of suitable energy participates in the electronic configuration and chemical properties.

SUMMARY TABLE OF ELECTRONIC CONFIGURATION

All the wavefunctions in this table are Normalized.

NORMALIZATION

The normalization condition of the wave function of the hydrogen atom in polar coordinates is $\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\left|\Psi_{(n,l,m)}(r,\theta,\phi)\right|^2 r^2\sin\theta dr d\theta d\phi = 1$

The general condition of normalization leads to the expression for the normalization constant as $N = \frac{1}{\sqrt{\int_{-\infty}^{\infty}\psi\psi^* d\tau}}$. This expression leads to $N = \frac{1}{\sqrt{\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\left|\Psi_{(n,l,m)}(r,\theta,\phi)\right|^2 r^2\sin\theta dr d\theta d\phi}}$. This solves to give the normalized wavefunctions of different atomic orbitals. The best illustration is for the ground state of 1s orbital of hydrogen atom as:

$\psi = e^{\frac{-r}{a_0}}$

$$N = \frac{1}{\sqrt{\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\left|\Psi_{(n,l,m)}(r,\theta,\phi)\right|^2 r^2\sin\theta dr d\theta d\phi}}$$

Putting the values we have $\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\left|e^{\frac{-r}{a_0}}\right|^2 r^2\sin\theta dr d\theta d\phi$

This transforms to $\int_{r=0}^{\infty} r^2\left|e^{\frac{-r}{a_0}}\right|^2 dr\int_{\theta=0}^{\pi}\sin\theta d\theta\int_{\phi=0}^{2\pi} d\phi$

$\Rightarrow\int_{r=0}^{\infty} r^2 e^{\frac{-2r}{a_0}} dr\int_{\theta=0}^{\pi}\sin\theta d\theta\int_{\phi=0}^{2\pi} d\phi$

Now for the angular component ϕ the integral yields 2π

The component $\int_{r=0}^{\infty} r^2 e^{\frac{-2r}{a_0}} dr\int_{\theta=0}^{\pi}\sin\theta d\theta\int_{\phi=0}^{2\pi} d\phi$ becomes $2\pi\int_{r=0}^{\infty} r^2 e^{\frac{-2r}{a_0}} dr\int_{\theta=0}^{\pi}\sin\theta d\theta$

The component $\int_{r=0}^{\infty} r^2 e^{\frac{-2r}{a_0}} dr$ can be solved by using the identity of gamma functions i.e. $\int_0^{\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}} = \frac{\Gamma(n+1)}{a^{n+1}}$ and $\Gamma(n+1) = n!$ We have,

$$\frac{\Gamma(2+1)}{\left(\frac{2}{a_0}\right)^{2+1}} = \frac{2!}{\left(\frac{2}{a_0}\right)^{2+1}} = \frac{2}{8}a_0^3$$

Now the component $\int_{\theta=0}^{\pi}\sin\theta d\theta$ can be integrated by basic integration identity, and the solution is $-\cos\theta$

On applying limits and the identity $\cos n\pi = (-1)^n; n\in\mathbb{Z}$

$-(\cos\pi - \cos 0) = -(-1-1) = 2$

The overall product becomes $\frac{2}{8}a_0^3\times 2\times 2\pi$

$\Rightarrow\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\left|e^{\frac{-r}{a_0}}\right|^2 r^2\sin\theta dr d\theta d\phi = \pi a_0^3$

Therefore,

$$N = \frac{1}{\sqrt{\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\left|\Psi_{(n,l,m)}(r,\theta,\phi)\right|^2 r^2\sin\theta dr d\theta d\phi}} = \frac{1}{\sqrt{\pi a_0^3}} = \frac{1}{\sqrt{\pi}(a_0)^{\frac{3}{2}}}$$

The normalized wavefunction for the 1s orbital of hydrogen atom is $\psi_{1s} = \frac{e^{\frac{-r}{a_0}}}{\sqrt{\pi}(a_0)^{\frac{3}{2}}}$

Azimuthal Quantum Number (l)	Subshell			Magnetic Quantum Number (m)	Orbitals
	Atomic orbitals	Ionic terms $^{2S+1}L_J$	Molecular terms		
0	s	S	Σ	0	s
1	p	P	Π	-1	p_y
2	d	D	Δ	0	p_z
3	f	F	Φ	1	p_x
The different symbols corresponding to the same values of the Azimuthal Quantum Number (l) are context sensitive in nature. The complete table of L-values for the Ionic terms $^{2S+1}L_J$ is attached in the end of this orbital description table.				0	d_{z^2}
				2	$d_{(x^2-y^2)}$
				1	d_{xz}
				-1	d_{yz}
				-2	d_{xy}
				-3	$f_{y(3x^2-y^2)}$
				-2	$f_{z(x^2-y^2)}$
				-1	f_{yz^2}
				0	f_{z^3}
				1	f_{xz^2}
				2	f_{xyz}
				3	$f_{x(x^2-3y^2)}$

Subshell	Nature of spectral lines	Number of orbitals	Number of electrons	Shape of the subshell	Symmetry
s	Sharp	1	2	Spherical	Gerade (g)
p	Principal	3	6	Dumbbell	Ungerade (u)
d	Diffused	5	10	Double dumbbell	Gerade(g)
f	fundamental	7	14	Tetrahedral	Ungerade(u)

Orbitals	Wavefunctions ($\psi_{n,l,m}^{r,\theta,\phi}$)
1s	$\psi_{1s} = \frac{e^{\frac{-r}{a_0}}}{\sqrt{\pi}(a_0)^{\frac{3}{2}}}$
2s	$\psi_{2s} = \frac{e^{\frac{-r}{2a_0}}}{4\sqrt{2\pi}(a_0)^{\frac{3}{2}}}\left(2 - \frac{r}{a_0}\right)$
$2p_y$	$\psi_{2p_y} = \frac{re^{\frac{-r}{2a_0}}}{8a_0\sqrt{\pi}(a_0)^{\frac{3}{2}}}\sin\theta e^{\iota\phi}$
$2p_z$	$\psi_{2p_z} = \frac{re^{\frac{-r}{2a_0}}}{4a_0\sqrt{2\pi}(a_0)^{\frac{3}{2}}}\cos\theta$
$2p_x$	$\psi_{2p_x} = \frac{re^{\frac{-r}{2a_0}}}{8a_0\sqrt{\pi}(a_0)^{\frac{3}{2}}}\sin\theta e^{\iota\phi}$
$3s$	$\psi_{3s} = \frac{e^{\frac{-r}{2a_0}}}{81\sqrt{3\pi}(a_0)^{\frac{3}{2}}}\left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{(a_0)^2}\right)$

$3p_y$	$\psi_{3p_y} = \frac{re^{-\left(\frac{r}{3a_0}+\iota\phi\right)}}{81a_0\sqrt{\pi}(a_0)^{\frac{3}{2}}}\left(6-\frac{r}{a_0}\right)\sin\theta$
$3p_z$	$\psi_{3p_z} = \frac{r\sqrt{2}e^{\frac{-r}{3a_0}}}{81a_0\sqrt{\pi}(a_0)^{\frac{3}{2}}}\left(6-\frac{r}{a_0}\right)\cos\theta$
$3p_x$	$\psi_{3p_x} = \frac{re^{\left(\iota\phi-\frac{r}{3a_0}\right)}}{81a_0\sqrt{\pi}(a_0)^{\frac{3}{2}}}\left(6-\frac{r}{a_0}\right)\sin\theta$
$3d_{z^2}$	$\psi_{3d_{z^2}} = \frac{r^2e^{-\left(2\iota\phi+\frac{r}{3a_0}\right)}}{162a_0^2\sqrt{\pi}(a_0)^{\frac{3}{2}}}\sin^2\theta$
$3d_{(x^2-y^2)}$	$\psi_{3d_{(x^2-y^2)}} = \frac{r^2e^{-\left(\iota\phi+\frac{r}{3a_0}\right)}}{81a_0^2\sqrt{\pi}(a_0)^{\frac{3}{2}}}\sin\theta\cos\theta$
$3d_{xz}$	$\psi_{3d_{xz}} = \frac{r^2e^{-\left(\frac{r}{3a_0}\right)}}{81a_0^2\sqrt{6\pi}(a_0)^{\frac{3}{2}}}(3\cos^2\theta-1)$
$3d_{yz}$	$\psi_{3d_{yz}} = \frac{r^2e^{\left(\iota\phi-\frac{r}{3a_0}\right)}}{81a_0^2\sqrt{\pi}(a_0)^{\frac{3}{2}}}\sin\theta\cos\theta$
$3d_{xy}$	$\psi_{3d_{xy}} = \frac{r^2e^{\left(2\iota\phi-\frac{r}{3a_0}\right)}}{162a_0^2\sqrt{\pi}(a_0)^{\frac{3}{2}}}\sin^2\theta$
f_{z^3}	$\psi_{f_{z^3}} = \sqrt{\frac{Z^3}{4^8a_0^35040}}\left(\frac{2Zr}{4a_0}\right)^3e^{-\frac{Zr}{4a_0}}\sqrt{\frac{7}{16\pi}}(5\cos^3\theta-3\cos\theta)$
f_{xz^2} f_{yz^2}	$\psi_{f_{xz^2}} = \psi_{f_{yz^2}} = \sqrt{\frac{Z^3}{4^8a_0^35040}}\left(\frac{2Zr}{4a_0}\right)^3e^{-\frac{Zr}{4a_0}}\mp\sqrt{\frac{21}{64\pi}}\sin\theta(5\cos^2\theta-1)e^{\pm\iota\phi}$
f_{xyz} $f_{z(x^2-y^2)}$	$\psi_{f_{xyz}} = \psi_{f_{z(x^2-y^2)}} = \sqrt{\frac{Z^3}{4^8a_0^35040}}\left(\frac{2Zr}{4a_0}\right)^3e^{-\frac{Zr}{4a_0}}\sqrt{\frac{105}{32\pi}}(\sin^2\theta\cos\theta)e^{\pm\iota\phi}$
$f_{x(x^2-3y^2)}$ $f_{y(3x^2-y^2)}$	$\psi_{f_{x(x^2-3y^2)}f_{z^3}} = \psi_{f_{y(3x^2-y^2)}} = \sqrt{\frac{Z^3}{4^8a_0^35040}}\left(\frac{2Zr}{4a_0}\right)^3e^{-\frac{Zr}{4a_0}}\mp\sqrt{\frac{35}{64\pi}}(\sin^3\theta)e^{\pm3\iota\phi}$

L-values	0	1	2	3	4	5	6
Terms	S	P	D	F	G	H	I

The labels s, p, d, f for atomic orbitals originate from early spectroscopy experiments in the late 19th and early 20th centuries. Spectroscopists observed patterns in atomic emission lines and described them as sharp (s), principal (p), diffuse (d), and fundamental (f). These terms initially described the appearance of spectral lines rather than electron orbitals. Later, with the development of quantum mechanics, these labels were adopted to denote the different shapes of orbitals corresponding to azimuthal quantum numbers.

s$\Rightarrow l=0\Rightarrow$spherical shape, sharp lines

p$\Rightarrow l=1\Rightarrow$dumbbell shape, principal lines

d$\Rightarrow l=2\Rightarrow$ cloverleaf-shaped, “diffuse” lines

s$\Rightarrow l=0\Rightarrow$complex shape and fundamental lines

Thus, the letter system connects **spectroscopic observations** with **orbital shapes**, providing both a historical and quantum-mechanical context.

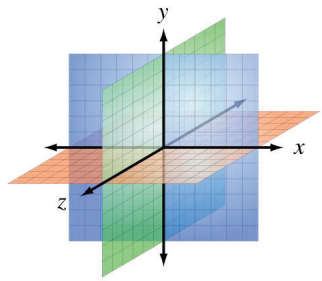
For the chemical studies the linear combinations of the last two wave functions of the orbitals $f_{x(x^2-3y^2)}$ and $f_{y(3x^2-y^2)}$, designated by

$$\psi_{f_{x^3-3xy^2}} = \sqrt{\frac{Z^3}{4^8 a_0^3 5040}}\left(\frac{2Zr}{4a_0}\right)^3 e^{-\frac{Zr}{4a_0}}\sqrt{\frac{35}{64\pi}}(\sin^3\theta\cos 3\phi)$$

for the combination $f_{x^3-3xy^2}$, and by

$$\psi_{f_{y(3x^2-y^2)}} = \sqrt{\frac{Z^3}{4^8 a_0^3 5040}}\left(\frac{2Zr}{4a_0}\right)^3 e^{-\frac{Zr}{4a_0}}\sqrt{\frac{35}{64\pi}}(\sin^3\theta\sin 3\phi)$$

For $f_{y(3x^2-y^2)}$. both these equations leads to the same orbitals but the format is altered to eleminate the immaginary ι component. This leads to the highly diffused nature of the f orbitals which in turn leads to many unexpected trends and behavioural differences in the f orbitals as compaired to those in the rest of the s, p, d orbitals.



OCTANTS

Every subshell has a fixed number of nodes which are classified into distinct categories based on the arrangement.

1. **Radial nodes:** The nodes which are present along the internuclear axes of the orbital. These define the boundary of the different orbitals of different n values. The radial wavefunction is zero at these points. The number of radial nodes in a given orbital $n_r = \boldsymbol{n} - l - 1$.
2. **Angular nodes:** The nodes present around the nucleus in an orbital at fixed angle. Number of angular nodes is given by the values of the azimuthal quantum number l. These are also called the nodal planes. These are the planes passing through the nucleus at which the probability of finding the electron of the corresponding orbital is zero.

Orbital (nl)	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s	7p
Angular nodes	0	0	1	0	1	2	0	1	2	3	0	1	2	3	0	1	2	0	1
Radial nodes	0	1	0	2	1	0	3	2	1	0	4	3	2	1	5	4	3	6	5
Total nodes	0	1	1	2	2	2	3	3	3	3	4	4	4	4	5	5	5	6	6

Total number of nodes in a given orbital is given by $n - l - 1 + l = n - 1 \Rightarrow n_t = n - 1$.

All the d orbitals have angular nodes in the form of nodal planes.

Plane	xy	yz	xz
Null component	$Z = 0$	$X = 0$	$Y = 0$

I. The number of nodal planes in s orbital is zero.

II. The number of nodal planes in p orbital is one.
   a. The xy plane is a nodal plane for p_z orbital.
   b. The xz plane is a nodal plane for p_y orbital.
   c. The yz plane is a nodal plane for p_z orbital.

III. The number of nodal planes in d orbital is two.
   a. xz, yz planes are nodal planes for d_{xy} orbital.
   b. xz, xy planes are nodal planes for d_{yz} orbital.
   c. xy, yz planes are nodal planes for d_{xz} orbital.
   d. For the $d_{(x^2-y^2)}$ there exist a special nodal plane described by two properties. Firstly, it is perpendicular to the xy plane and moreover it is inclined at an angle of 45° with the x and y axes.
   e. The d_{z^2} orbitals have two nodal cones instead of nodal planes.

There are some more characteristics of the d orbitals.

- These are grouped into two classes based of their orientation in the Cartesian coordinate system.
- The d_{xy}, d_{xz} and d_{yz} orbitals are known as the non-axial orbitals as the lobes are aligned between the axes.
- The $d_{(x^2-y^2)}$ and d_{z^2} orbitals are known as the axial orbitals as the lobes are aligned along the x, y and z-axes.

IV. The seven f orbitals also contain nodes which can be described as different coordinates' descriptions.

a. The f_{z^3} orbital have two lobes along the z axes and two doughnut shaped lobes surrounding them in the xy plane. This orbital possesses conical nodal surfaces. These are symmetrical about the z axes.

b. The f_{xyz} orbital have eight lobes with alternating signs. These lobes are oriented at the octants of the coordinate axes. These have the xy, yz and xz planes as the nodal planes because they have one of the components equal to zero**.**

As the 2D space is divided into four quadrants by the 2 axes. Similarly, the three planes divide the space into eight octants.

- **The octants of a three-dimensional coordinate system:** The octants of a three-dimensional coordinate system are the eight divisions of space created by the three axial planes:
- **First octant**: It is the front right top region where all coordinates are positive $(+x, +y, +z)$.
- **Second octant**: It is the front left top region where $(-x, +y, +z)$
- **Third octant**: It is the back left top region where the x and y coordinates are negative, and z is positive $(-\mathrm{x}, -\mathrm{y}, +\mathrm{z})$.
- **Fourth octant**: It is the back right top region where the x and z are positive, and y is negative. $(+\mathrm{x}, -\mathrm{y}, +\mathrm{z})$
- The 5th -8th octants are mirror images of the 1st-4th octants in the negative z axes half of the coordinate system.
- **Fifth octant**: The x and are positive, and z is negative $(+x, +y, -z)$.
- **Sixth octant:** $(-x, +y, -z)$.
- **Seventh octant:** $(-\mathrm{x}, -\mathrm{y}, -\mathrm{z})$.
- **Eighth octant:** $(+\mathrm{x}, -\mathrm{y}, -\mathrm{z})$.

c. The $f_{x(x^2-3y^2)}$ orbital have six lobes with four of them present in the xy plane and the rest two along the x axes. The yz plane with $X = 0$ and a diagonal plane with $x^2 - 3y^2 = 0$, act as nodal planes.

d. The $f_{y(3x^2-y^2)}$ orbital have six lobes with four of them present in the xy plane and the rest two along the y axes. The xz plane with $y = 0$ and a diagonal plane with $3x^2 - y^2 = 0$, act as nodal planes.

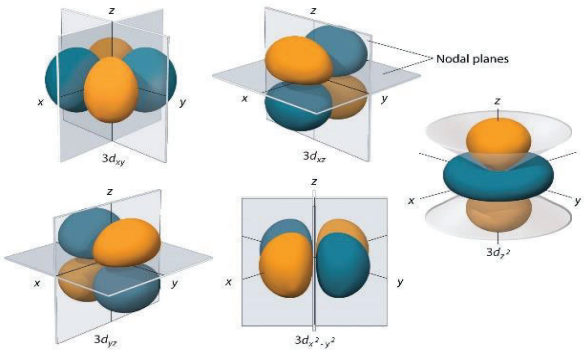
e. The $f_{z(x^2-y^2)}$ orbital have four lobes extending in between x and y axes in the xy plane with additional component along the z axes. The xy plane with $z = 0$ and a diagonal plane with $x^2 - y^2 = 0$, act as nodal planes.

f. The f_{xz^2} orbital have six lobes with four of them present in the xz plane and the rest two along the z axes. The yz plane with $x = 0$ and a conical angular node in the xz plane act as nodal planes.

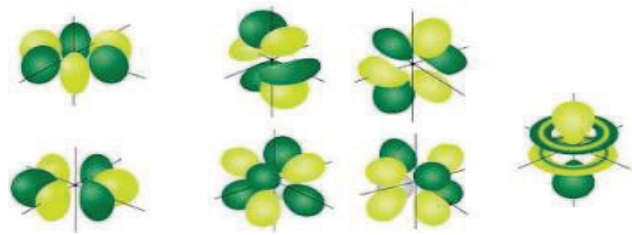
g. The f_{yz^2} orbital have six lobes with four of them present in the yz plane and the rest two along the z axes. The xz plane with $Y = 0$ and a conical angular node in the yz plane act as nodal planes.

h. These nodal surfaces account for the symmetry properties of the f orbitals and aid us in determining the orbital interactions in the variety of the f block elements' compounds and complexes.

This discussion leads to the following shapes of the d and f prbitals.

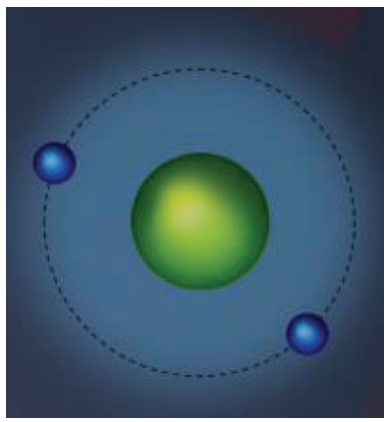


D ORBITALS WITH SYMITRY PLANES



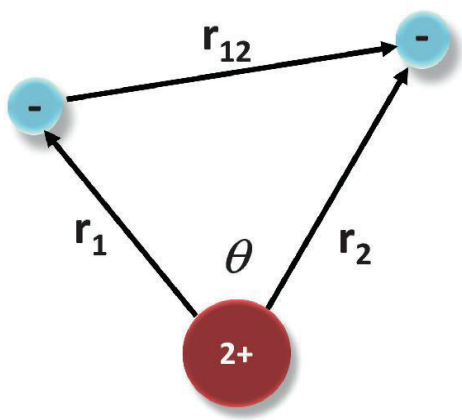
THE F ORBITALS

The quantum mechanical model represents a comprehensive and fundamental description of atomic structure. Incorporating wave-particle duality, probabilistic interpretation, and mathematical formalism, it builds upon the foundational insights of earlier models offering a unified framework capable of explaining a broad spectrum of atomic and subatomic phenomena.



Helium Atom

The Schrödinger's wave equation for Hydrogen atom could explain the spectrum of Hydrogen atom, without violating the Heisenberg's Uncertainty Principle. The Zeman effect (splitting of a spectral line into several components in the presence of a static external magnetic field. It is produced as a consequence magnetic field and the magnetic field associated with the electron by the virtue of its spinning and orbital motion.) proposed by Pieter Zeeman, in 1896 and Stark effect (splitting of a spectral line into several components in the presence of a static electric field) proposed by Johannes Stark in 1913, because of the Magnetic Quantum Number (m) obtained as a solution of the Schrödinger's wave equation for Hydrogen atom. However, the position and a finer splitting of the spectral line could not be explained by the three quantum numbers $n, l, \boldsymbol{m_\ell}$. This could however be explained by the new quantum number $J = |L \pm S|$ where, $L = \sum l$ is the total Azimuthal Quantum Number, and $S = \sum s$ is the total spin Quantum Number. George Eugene Uhlenbeck and Samuel Abraham Goudsmit hypothesized the spin quantum number and fitted the explanation of the splitting in the two components of electron spin with $s = \pm\frac{1}{2}$. This was proved by the Stern–Gerlach experiment. But Albert Einstein proved the electron spin as an intrinsic property rather than a spin in a true sense of motion. From here it is concluded after some more calculation that the degeneracy



Helium Atom

of the spatial orbitals is n^2 which is relevant for hydrogenic atoms only and for multielectron systems, we know that each electron have two spins hence, each orbital can accommodate two electrons. This leads to the famous Bohr Bury scheme just tells us about the total number of electrons that can be filled in the shell or energy level of the energy corresponding to the Principal Quantum Number (n), and is given by the equation $2n^2$.

For multi-electron atoms the time independent Schrödinger's wave equation can be expressed as:

Helium is a two electron species

Hence, has electron-electron repulsions

So, it needs special treatment (2 ways):

1.Approximation

2. Actual treatment

True Hamiltonian is:

$$\widehat{H} = \widehat{T_N} + \widehat{T_{e_1}} + \widehat{T_{e_2}} + \hat{V}$$

$$\widehat{H} = -\frac{\hbar^2\nabla_N^2}{2m_N} - \frac{\hbar^2\nabla_{e_1}^2}{2m_e} - \frac{\hbar^2\nabla_{e_2}^2}{2m_e} + \left(-\frac{Z_A e^2}{4\pi\varepsilon_0 r_1} - \frac{Z_A e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}\right)$$

$$\widehat{H} = \frac{e^2}{4\pi\varepsilon_0 r_{12}} - \frac{\hbar^2\nabla_N^2}{2m_N} - \frac{\hbar^2\sum_{i=1}^{2}\nabla_i^2}{2m_e} - \frac{Z_A e^2}{4\pi\varepsilon_0}\sum_{i=1}^{2}\frac{1}{r_i}$$

In atomic units In atomic units, we consider the constant values as follows:

S. No.	Symbol	Quantity	Value in SI	Value in Atomic Units (a.u.)
1	m_e	Mass Of Electron	$9.110 \times 10^{-31} kg$	1
2	e	Charge Of Electron	$1.602 \times 10^{-19} C$	
3	t	Time	$2.419 \times 10^{-17} s$	
4	$\hbar = \frac{h}{2\pi}$	Dirac's Constant (Atomic Momentum Unit)	$1.055 \times 10^{-34} Js$	
5	a_0	Bohr's Radius (Atomic Distance Unit)	$5.292 \times 10^{-11} m$	
6	E_H	Hartree (Atomic Energy Unit)	$4.360 \times 10^{-18} J$	
7	$4\pi\varepsilon_0$	Vacuum Permittivity	$1.113 \times 10^{-10} C^2 J^{-1} m^{-1}$	
8	h	Planck's Constant	$6.626 \times 10^{-34} Js$	2π
9	c	Speed of Light	$2.998 \times 10^{8} ms^{-1}$	137.036
10	$\alpha = \frac{1}{c} = \frac{e^2}{4\pi\varepsilon_0 c\hbar}$	Fine Structure Constant	0.00729735	0.00729735
11	$\mu_B = \frac{e\hbar}{2m_e}$	Bohr magneton	$9.274 \times 10^{-24} JT^{-1}$	0.5
12	μ_N	Nuclear magneton	$5.051 \times 10^{-27} JT^{-1}$	$2.723 \times 10^{-4} JT^{-1}$
13	$\mu_0 = \frac{4\pi}{c^2}$	Vacuum Permeability	$1.257 \times 10^{-6} Ns^2 C^{-2}$	$6.692 \times 10^{4} Ns^2 C^{-2}$

Therefore, we get the Time Independent Schrödinger's wave equation in the form:

$$\widehat{H} = \frac{1}{r_{12}} - Z\left(\frac{1}{r_1} + \frac{1}{r_2}\right) - \frac{1}{2}\left[\frac{\nabla_N^2}{m_N} + \nabla_1^2 + \nabla_2^2\right]$$

After applying the **"Infinite nuclear mass approximation"** or **"Fixed nucleus approximation"**

$\widehat{H} = -\frac{1}{2}\left[\frac{\nabla_N^2}{m_N} + \nabla_1^2 + \nabla_2^2\right]$ Where the $\frac{1}{r_{12}}$ term has been ignored.

NOTE: The Atomic Units $(a.u.)$ are actually completely different units as well as completely different concepts.

- The $\hat{V}$ term has 3 terms, 2 for nucleus-electron attraction (in –ve), and 1 for electron-electron repulsion (in +ve).
- Applying atomic units means to write them as 1 and then later calculating other units accordingly.
- As seen, applying atomic units has made the rather complex Hamiltonian to a much more neat and simpler Hamiltonian, easier to work with. The more exact solution of the equation can be found through the use of computational techniques such as Hartree–Fock (HF) method named after Douglas Rayner Hartree and Vladimir Aleksandrovich Fock or the Density Functional Theory (DFT), Variation theory, Perturbation theory etc.

VARIATION OF ORBITAL ENERGIES AND ELECTRON FILLING IN MULTI-ELECTRON ATOMS

In multi-electron atoms, electrons are described by standing-wave wavefunctions in the wave-mechanical model, developed by Erwin Schrödinger, within the framework of nonrelativistic quantum mechanics; the resulting atomic orbitals therefore represent probability distributions (the square of the wavefunction who's integral over a region gives the probability of finding the electron) rather than rigid shells. Strictly speaking, in multi-electron atoms orbitals are not exact eigenfunctions of the many-electron Hamiltonian but approximate one-electron functions arising from mean-field treatments of interelectron interactions. The approximate sequence in which these orbitals are occupied is given to a good approximation, by the Aufbau principle, commonly expressed through the $\boldsymbol{n+l}$-rule, according to which orbitals with smaller $\boldsymbol{n+l}$ values are filled first and, when these values are equal, the orbital with the smaller principal quantum number n is filled earlier. Although the angular momentum quantum number increases in the order $\mathrm{s} < \mathrm{p} < \mathrm{d} < \mathrm{f}$, the extent of penetration of penetration toward the nucleus follows the reverse trend $s > p > d > f$. Orbitals with greater penetration experience a larger effective nuclear charge Z_{eff} and may therefore possess lower energy even when they belong to a higher principal shell. **Because these orbitals arise from overlapping standing-wave probability distributions whose wavefunctions extend throughout the atom, allowing higher-n orbitals to penetrate into regions closer to the nucleus, electrons already present in outer orbitals do not form a barrier preventing occupation of inner orbitals, consistent with the principle that electrons occupy orbitals in the arrangement that minimizes the total energy of the atom. Consequently, orbitals of the type $\boldsymbol{ns}$ may be filled before inner orbitals such as** $(n-1)d$ and $(n-2)f$. Therefore, we get the general electronic configurations as tabulated:

Block	Electronic configurations
s-block	ns^{1-2}
p-block	ns^2np^{1-6}
d-block	$(n-1)d^{1-10}ns^{1-2}$
f-block	$(n-2)f^{1-14}(n-1)d^{0-1}ns^2$

Orbital energies are determined by the combined effects of electron–electron repulsion, shielding, and nuclear attraction, and since these interactions vary with electronic configuration, the energies of orbitals in multi-electron atoms are not fixed. Therefore, the energy difference between orbitals ΔE ultimately governs the exact electronic configuration of the atom. Consequently, the Aufbau sequence represents only the **approximate order of electron addition**, whereas the actual energy ordering in a completed atom may differ. In general, electrons occupy the available orbitals in the arrangement that **minimizes the total energy of the atom**, so the relative energies of orbitals depend not only on their quantum numbers but also on the electronic configuration of the atom itself.

3V. NEUTRON

Existence: The Neutron is a subatomic particle, which constitutes the 'Nucleon' or 'Nucleus' along with the Proton.

Symbol: Neutron is represented by the symbol 'n' *or* '^1n'

Mass: The mass of a Neutron is approximately equal to that of the Proton; i.e. $1.6 \times 10^{-27}\ kg = 1\ Da$.

APPLICATIONS

- Neutrons are the main reason for the existence of 'Isotopes'.
- Neutrons helped greatly to achieve nuclear energy.
- Of use in the field of Medical Science.

DISCOVERY

At that time, the proton was known, but neutrons were not. But scientists knew from Rutherford's Gold-Foil experiment that the entire mass of the atom was concentrated in a small but dense sphere in the centre of the atom. It was also known that the mass of the electron is negligible. Hence, to account for the mass of atoms, a '**Nuclear-Electron Hypothesis**' was given (in 1920s). According to this hypothesis, an atom has that many protons as is its mass number, and an according number of electrons embedded inside the nucleus to give that atom its associated nuclear charge, and the rest of the electrons were orbiting like normal. So, for example, a Carbon-12 atom would have 12 protons inside its nucleus along with 6 'internal electrons' embedded inside the nucleus and the rest 6 electrons would orbit the nucleus. Base for this hypothesis was that in β-decay, electron is removed from the nucleus. This '**Nuclear-Electron Hypothesis**' undoubtably had many problems associated with it.

Heisenberg's Principle: if the electron was inside the nucleus, the uncertainty in speed of the electron would become more than the speed of light. It would be also energetically unfavorable for opposite charges to exist so closely/penetrate each other.

If the electron was in the nucleus, the β-decay electron would have an energy much higher (~200 MeV) but actual energy is only ~2MeV. These problems were not encountered at the time, and the 'Nuclear-Electron' hypotheses was accepted and was even used by Rutherford to explain the existence of some particles. In this process, he proved the existence of a particle with 1 mass and 0 charge (while explaining existences of other particles). This was the neutron, as was named by **'William Draper Harkins'** in 1921. This was much like 'Prout's Hypotheses' i.e. they believed this was the case, but was later proven true (that it exists, just not how Rutherford explained it). Rutherford and Chadwick immediately started experiments to prove the existence of the 'Neutron' but had no success. Elsewhere, in Germany, scientists found that hitting Lithium, Beryllium, Boron and with α-Particles emitted something, which was electrically neutral and very penetrating. Scientists thought this radiation must be γ-rays (of purely energy and no particles) but that was not the case, because this new type of radiation was more penetrating than gamma rays. Then in Paris, when similar experiments were made, and the rays were made to fall on paraffin wax (a hydrocarbon with readily available high amounts of Hydrogen), Protons were ejected with very high energies. This proved that these rays were not gamma rays either because for gamma rays to eject Protons from paraffin wax, an impossibly high amount of energy for the gamma rays was required. Finally, hearing about these experiments in Paris, Chadwick performed them himself. He then calculated the mass of the rays responsible for ejecting protons and these rays were of Neutrons.

Sir James Chadwick
(20 October 1891-24 July 1974)

The experiment conducted by Chadwick was (i.e. the one done in Paris):

$${}^{9}_{4}Be + {}^{4}_{2}He \rightarrow {}^{12}_{6}C + {}^{1}_{0}n$$

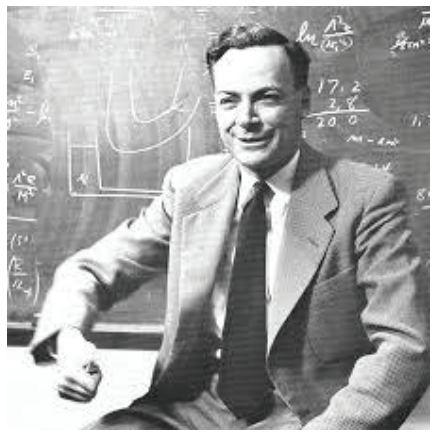
Chadwick was given the Nobel Prize in Physics for this discovery in 1935.

THE LONG QUEST FOR THE NATURE OF THE ATOM

The development of atomic structure exhibits a striking two-phase evolution: a prolonged technological and conceptual bottleneck of nearly a century following John Dalton's atomic theory (1803–1808), during which atoms were regarded as indivisible due to limited experimental capability, and a subsequent extraordinary period of rapid advancement between 1900 and 1932. This 32-year surge was driven by the convergence of powerful experimental techniques—such as cathode ray experiments, spectroscopy, and radioactivity studies—and deep theoretical crises in classical physics, which failed to explain fundamental issues such as atomic stability and discrete spectral lines. Classical theory predicted that orbiting electrons should continuously radiate energy and collapse into the nucleus, making atomic stability impossible, thereby exposing a profound inconsistency in the existing framework. The resolution began with the discovery of the electron by J. J. Thomson and the nuclear model proposed by Ernest Rutherford, which established the existence of a dense, positively charged nucleus. However, Rutherford's model still could not explain stability or spectral regularities. A decisive breakthrough came with Niels Bohr, who introduced quantized energy states, demonstrating that atomic stability arises only when electrons occupy discrete, non-radiating orbits. Although successful for hydrogen, this model remained limited and phenomenological. A deeper and more general understanding emerged with the advent of quantum mechanics, initiated by Max Planck and Albert Einstein, and fully developed through the wave mechanics of Erwin Schrödinger and the uncertainty principle of Werner Heisenberg. In this transition from deterministic trajectories to probabilistic description, the tension with classical intuition was famously articulated by Albert Einstein in his 1926 correspondence with Max Born: **"God does not play dice."** This statement captured the philosophical resistance to inherent probabilism at the heart of quantum theory. Yet the new framework prevailed, replacing certainty of trajectories with statistical amplitudes and wavefunctions as the fundamental description of matter.

At a deeper interpretational level, Niels Bohr clarified the epistemological shift demanded by quantum theory, emphasizing the limits of classical language itself. As he stated: **"There is no quantum world. There is only an abstract quantum physical description. It is wrong to think that the task of physics is to find out how Nature is. Physics concerns what we can say about Nature."** In this framework, electrons are no longer treated as particles in fixed orbits but as wave-like entities described by atomic orbitals, where energy levels and spatial distributions arise naturally from fundamental equations rather than assumptions. This quantum-mechanical model resolved the long-standing problem of electronic structure and atomic stability that had persisted since Dalton's era. Nevertheless, it also revealed new unresolved questions regarding the composition and stability of the atomic nucleus. These questions were ultimately addressed with the discovery of the neutron by James Chadwick in 1932, completing the modern understanding of atomic structure. Thus, the apparent "94-year gap" represents not scientific stagnation but a foundational phase of conceptual and technological preparation, while the subsequent "32-year explosion" reflects a rapid and interconnected convergence of experimental discovery and theoretical innovation that ultimately established the quantum-mechanical description of the atom and completed the modern atomic model.

CONCLUSION



Richard Phillips Feynman
(11 May 1918-15 February 1988)

The study of atomic structure, as presented in this text, establishes the fundamental principles necessary for understanding chemical behavior, electronic configurations, and the spectral properties of atoms, forming a coherent and sufficient framework for standard instruction. Milestones such as Schrödinger's wave mechanics and Chadwick's discovery of the neutron mark critical advances in this development; however, they do not signify the cessation of inquiry in atomic physics. Rather, within the defined scope of this text, these foundations mark the boundary beyond which contemporary research extends into nuclear structure, subatomic particles, quantum electrodynamics, exotic atoms, and quantum information science—domains essential to the advancing frontier yet typically reserved for graduate study and specialized investigation. Thus, the material presented here represents a foundational framework, while recognizing that the exploration of atomic phenomena continues to evolve through successive refinements driven by experimental discovery. As **Albert Einstein** observed, ***"The important thing is not to stop questioning. Curiosity has its own reason for existing,"*** a spirit that propels inquiry beyond established boundaries. In this context, **Paul Adrien Maurice Dirac** (1929) stated, ***"The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved."*** Yet, as **Richard Phillips Feynman** remarked, ***"I think I can safely say that nobody understands quantum mechanics,"*** and indeed, ***"What I cannot create, I do not understand,"*** underscoring that the boundary of knowledge is not defined by the absence of laws, but by the limits of their application and comprehension. Together, these insights capture both the power and the limitation of our knowledge: not its completion, but the enduring challenge that continues to drive the progress of theoretical and computational chemistry.

EACTION ZONE

Numerical Answer Type Questions (NATs)

1. A. Calculate the radii of the first three Bohr's orbits of the hydrogen atom? The values of constants are

$h = 6.6262 \times 10^{-34} Js$
$m_e = 9.1091 \times 10^{-31} kg$
$e = 1.60210 \times 10^{-19} C$
$\varepsilon_0 = 8.854185 \times 10^{-12} A^2 kg^{-1} m^{-3}$

B. Use the calculated radii to find the velocity of electron in these orbits?

Solution: A. The radius of the three orbits can be calculated by the equation:

$$r_n = \left[\frac{\varepsilon_0}{\pi m_e}\left(\frac{h}{e}\right)^2\right]\left(\frac{n^2}{Z}\right)$$

For the first orbit of hydrogen $n = 1, Z = 1$

Therefore,

$$r_n = \left[\frac{\varepsilon_0}{\pi m_e}\left(\frac{h}{e}\right)^2\right] = \frac{8.854185 \times 10^{-12} A^2 kg^{-1} m^{-3}}{9.1091 \times 10^{-31} kg \pi}\left(\frac{6.6262 \times 10^{-34} Js}{1.60210 \times 10^{-19} C}\right)^2 = 0.529 Å$$

For the second orbit of hydrogen $n = 2, Z = 1$

Therefore,

$$r_n = \left[\frac{\varepsilon_0}{\pi m_e}\left(\frac{h}{e}\right)^2\right] n^2 = 4\frac{8.854185 \times 10^{-12} A^2 kg^{-1} m^{-3}}{9.1091 \times 10^{-31} kg \pi}\left(\frac{6.6262 \times 10^{-34} Js}{1.60210 \times 10^{-19} C}\right)^2 = 2.12 Å$$

For the third orbit of hydrogen $n = 3, Z = 1$
Therefore,

$$r_n = \left[\frac{\varepsilon_0}{\pi m_e}\left(\frac{h}{e}\right)^2\right] n^2 = 9\,\frac{8.854185\times10^{-12}A^2kg^{-1}m^{-3}}{9.1091\times10^{-31}kg\pi}\left(\frac{6.6262\times10^{-34}Js}{1.60210\times10^{-19}C}\right)^2 = 4.76\text{Å}$$

B. The corresponding velocities can be calculated by the equations

$$v_n = \frac{Ze^2}{2\varepsilon_0 hn}$$

For the first orbit of hydrogen $n = 1, Z = 1$
Therefore,

$$v_n = \frac{e^2}{2\varepsilon_0 h} = \frac{(1.60210\times10^{-19}C)^2}{2\times8.854185\times10^{-12}A^2kg^{-1}m^{-3}\times6.6262\times10^{-34}Js} = 2.19\times10^6 ms^{-1}$$

For the second orbit of hydrogen $n = 2, Z = 1$
Therefore,

$$v_n = \frac{(1.60210\times10^{-19}C)^2}{2\times2\times8.854185\times10^{-12}A^2kg^{-1}m^{-3}\times6.6262\times10^{-34}Js} = 1.09\times10^6 ms^{-1}$$

For the third orbit of hydrogen $n = 3, Z = 1$
Therefore,

$$v_n = \frac{(1.60210\times10^{-19}C)^2}{3\times2\times8.854185\times10^{-12}A^2kg^{-1}m^{-3}\times6.6262\times10^{-34}Js} = 7.2\times10^5 ms^{-1}$$

2. The Balmer series of spectral lines of hydrogen appears in the visible region. What is the lowest energy level from which these electronic transition start? What electronic transition correspond to the spectral lines of 379nm and 430nm respectively?

Solution: The Balmer series of spectral lines of hydrogen appears in the visible region according to the Balmer's formula:

Balmer series is given by $\bar{\nu} = \frac{1}{\lambda} = R_H\left[\frac{1}{4} - \frac{1}{n_2^2}\right]$ where n_2 starts from 3.

Further, electronic transition correspond to the spectral line of 379nm is given by the equation

$$\frac{1}{\lambda} = R_H\left[\frac{1}{4} - \frac{1}{n_2^2}\right] \Rightarrow \frac{1}{379\times10^{-9}m}$$

$$= 1.097\times10^7 m^{-1}\left[\frac{1}{4} - \frac{1}{n_2^2}\right] \Rightarrow \frac{1}{379\times10^{-9}m\times1.097\times10^7 m^{-1}}$$

$$= \left[\frac{1}{4} - \frac{1}{n_2^2}\right] \Rightarrow \frac{1}{n_2^2} = \frac{1}{4} - \frac{1}{379\times10^{-9}m\times1.097\times10^7 m^{-1}} =$$

Further, electronic transition correspond to the spectral line of 430nm is given by the equation

$$\frac{1}{\lambda} = R_H\left[\frac{1}{4} - \frac{1}{n_2^2}\right] \Rightarrow \frac{1}{430\times10^{-9}m} = 1.097\times10^7 m^{-1}\left[\frac{1}{4} - \frac{1}{n_2^2}\right] \Rightarrow \frac{1}{379\times10^{-9}m\times1.097\times10^7 m^{-1}}$$

$$= \left[\frac{1}{4} - \frac{1}{n_2^2}\right] \Rightarrow \frac{1}{n_2^2} = \frac{1}{4} - \frac{1}{430\times10^{-9}m\times1.097\times10^7 m^{-1}} \Rightarrow n$$

$$= \frac{1}{\sqrt{\left(\frac{1}{4} - \frac{1}{430\times10^{-9}m\times1.097\times10^7 m^{-1}}\right)}} = 10$$

The transition corresponding to 379nm occurs from 10→2.
Now for 430nm after calculation we get that the transition for 434nm is 5→2; not for 430nm.

3. What is the wavenumber and wavelength in the spectral series of hydrogen for first transitions in Lyman, Balmer, Paasschen series?

Solution: The spectral series of hydrogen spectrum obey the following equations.

Lyman series is given by $\overline{\boldsymbol{v}} = \frac{\mathbf{1}}{\boldsymbol{\lambda}} = \boldsymbol{R_H}\left[\frac{1}{1} - \frac{1}{n_2^2}\right]$ where n_2 starts from 2.

Balmer series is given by $\overline{\boldsymbol{v}} = \frac{\mathbf{1}}{\boldsymbol{\lambda}} = \boldsymbol{R_H}\left[\frac{1}{4} - \frac{1}{n_2^2}\right]$ where n_2 starts from 3.

Paasschen series is given by $\overline{\boldsymbol{v}} = \frac{\mathbf{1}}{\boldsymbol{\lambda}} = \boldsymbol{R_H}\left[\frac{1}{9} - \frac{1}{n_2^2}\right]$ where n_2 starts from 4.

The wavenumbers are:

Lyman series; $\overline{\boldsymbol{v}} = \frac{\mathbf{1}}{\boldsymbol{\lambda}} = \boldsymbol{R_H}\left[\frac{1}{1} - \frac{1}{n_2^2}\right]$

For first transition

$$\overline{\boldsymbol{v}} = \frac{\mathbf{1}}{\boldsymbol{\lambda}} = \boldsymbol{R_H}\left[1 - \frac{1}{4}\right] = 1.097\times10^7 m^{-1}\left[1 - \frac{1}{4}\right] = \frac{3 \times 1.097\times10^7 m^{-1}}{4}$$
$$= 8.175 \times 10^6 m^{-1}$$

Balmer series is given by $\overline{\boldsymbol{v}} = \frac{\mathbf{1}}{\boldsymbol{\lambda}} = \boldsymbol{R_H}\left[\frac{1}{4} - \frac{1}{n_2^2}\right]$

For first transition

$$\overline{\boldsymbol{v}} = \frac{\mathbf{1}}{\boldsymbol{\lambda}} = \boldsymbol{R_H}\left[\frac{1}{4} - \frac{1}{9}\right] = 1.097\times10^7 m^{-1}\left[\frac{1}{4} - \frac{1}{9}\right] = \frac{5 \times 1.097\times10^7 m^{-1}}{36}$$
$$= 1.5 \times 10^6 m^{-1}$$

Paasschen series is given by $\overline{\boldsymbol{v}} = \frac{\mathbf{1}}{\boldsymbol{\lambda}} = \boldsymbol{R_H}\left[\frac{1}{9} - \frac{1}{n_2^2}\right]$

For first transition

$$\overline{\boldsymbol{v}} = \frac{\mathbf{1}}{\boldsymbol{\lambda}} = \boldsymbol{R_H}\left[\frac{1}{9} - \frac{1}{16}\right] = 1.097\times10^7 m^{-1}\left[\frac{1}{9} - \frac{1}{16}\right] = \frac{7 \times 1.097\times10^7 m^{-1}}{144}$$
$$= 5.3 \times 10^5 m^{-1}$$

For the wavelengths

Lyman series $\lambda_{Lym} = \frac{1}{8.175\times10^6 m^{-1}} = 1.22 \times 10^{-7} m$

Balmer series $\lambda_{Balm} = \frac{1}{1.5\times10^6 m^{-1}} = 6.7 \times 10^{-7} m$

Paasschen series $\lambda_{Pasten} = \frac{1}{5.3\times10^5 m^{-1}} = 1.8 \times 10^{-6} m$

4. Given $r_{n+1} - r_{n-1} = 2r_n$ find the value of n if these are the radii of the respective orbits?

Solution: The radius of the Bohr's orbits in hydrogen atom is

$$r_n = \frac{2n^2h^2\varepsilon_0}{m_e e^2}$$

Therefore, $r_{n+1} - r_{n-1} = 2r_n$

$$\Rightarrow \frac{2(n+1)^2h^2\varepsilon_0}{m_e e^2} - \frac{2(n-1)^2h^2\varepsilon_0}{m_e e^2} = 2\frac{2n^2h^2\varepsilon_0}{m_e e^2}$$

$$\Rightarrow (n+1)^2 - (n-1)^2 = 2n^2$$

Applying the identities of $(a+b)^2 = a^2 + b^2 + 2ab$ and $(a-b)^2 = a^2 + b^2 - 2ab$ we have,

$$(n^2 + 1 + 2n) - (n^2 + 1 - 2n) = 2n^2$$

On simplifying we have,

$n = 2$.

5. The energy of separation of electron in Li^{2+} is 30.6eV, find the number of waves produced by the electron?

Solution: The radius of the Bohr's orbits in hydrogen atom is

$$r_n = \left[\frac{\varepsilon_0}{\pi m_e}\left(\frac{h}{e}\right)^2\right]\left(\frac{n^2}{Z}\right)$$

The energy of the hydrogen atom is

$$\boldsymbol{E_n = -13.6\left(\frac{Z^2}{n^2}\right) eVatom^{-1}}$$

For $Li^{2+}; Z = 3$

$$\boldsymbol{30.6 = -13.6\left(\frac{3^2}{n^2}\right) eVatom^{-1}}$$

$$\text{n} = \sqrt{\frac{13.6 \times 9}{30.6}} = 2$$

The radius of the second orbit of Li^{2+} is given by

$$r_n = \left[\frac{\varepsilon_0}{\pi m_e}\left(\frac{h}{e}\right)^2\right]\left(\frac{n^2}{Z}\right)$$

Therefore,

$$r_n = \frac{8.85 \times 10^{-12}}{9.11 \times 10^{-31}\pi}\left(\frac{6.626 \times 10^{-34}}{1.66 \times 10^{-19}}\right)^2 \frac{2^2}{3} = 6.5 \times 10^{-11} m$$

The velocity of this electron is

$$v_n = \frac{Ze^2}{2\varepsilon_0 hn} = \frac{3 \times (1.66 \times 10^{-19})^2}{2 \times 8.85 \times 10^{-12} \times 6.626 \times 10^{-34} \times 2} = 3.5 \times 10^6 ms^{-1}$$

The number of waves of electron are given by

$$2\pi r = n\frac{h}{mv} \Rightarrow \frac{2mvr\pi}{h} = n$$

$$n = \frac{2\pi \times 6.5 \times 10^{-11} m \times 9.11 \times 10^{-31} kg \times 3.5 \times 10^6 ms^{-1}}{6.626 \times 10^{-34}} = 2$$

This electron is associated with two de-Broglie waves with wavelength

$$\lambda_D = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{9.11 \times 10^{-31} kg \times 3.5 \times 10^6 ms^{-1}} = 2 \times 10^{-10} m = 2\text{Å}$$

6. Calculate the number of waves created by an electron in one complete revolution in nth orbit of hydrogen. If, the ratio of the de-Broglie wavelength associated with the electron moving in nth orbit and 2nd orbit is 1.5?

Solution: The velocity of this electron is

$$v_n = \frac{Ze^2}{2\varepsilon_0 hn}$$

The de-Broglie wavelength associated with the electron

$$\lambda_D = \frac{h}{mv} = \frac{h}{m_e v_n} = \frac{h}{m_e \frac{Ze^2}{2\varepsilon_0 hn}} = \frac{2\varepsilon_0 nh^2}{Zm_e e^2}$$

For second orbit of hydrogen

$$\lambda_D = \frac{2 \times 8.85 \times 10^{-12} \times 2 \times (6.626 \times 10^{-34})^2}{9.11 \times 10^{-31} kg \times (1.66 \times 10^{-19})^2} = 6.2 \times 10^{-10} m = 6.2\text{Å}$$

The ratio of the two wavelengths is 1.5 i.e.

$(\lambda_D)_{n^{th}} = 1.5 \times 6.2\text{Å} = 9.3\text{Å}$

The number of waves is

$$\lambda_D = \frac{2\varepsilon_0 nh^2}{Zm_e e^2} \Rightarrow 9.3\text{Å} = \frac{2\varepsilon_0 nh^2}{Zm_e e^2}$$

For hydrogen $Z = 1$

$$9.3\text{Å} = \frac{2\varepsilon_0 nh^2}{Zm_e e^2} = \frac{2 \times 8.85 \times 10^{-12} \times n \times (6.626 \times 10^{-34})^2}{9.11 \times 10^{-31} kg \times (1.66 \times 10^{-19})^2}$$

$$n = \frac{9.3 \times 10^{-10} m \times 9.11 \times 10^{-31} kg \times (1.66 \times 10^{-19} C)^2}{2 \times 8.85 \times 10^{-12} \times (6.626 \times 10^{-34})^2} = 3$$

7. Calculate the value of $A = \frac{E_{1,2}}{2E_{2,1}}$ where $E_{n,Z}$ is the energy of the n^{th} orbit of the hydrogenic species with atomic number Z?

Solution: The energy of electron is given by

$$\boldsymbol{E_{n,Z} = -2.18 \times 10^{-18} \left(\frac{Z^2}{n^2}\right) Jatom^{-1}}$$

Now, $A = \frac{E_{1,2}}{2E_{2,1}}$

$$E_{1,2} = -2.18 \times 10^{-18} \left(\frac{2^2}{1^2}\right) Jatom^{-1} = -2.18 \times 10^{-18} \times 4 = -8.72 \times 10^{-18} Jatom^{-1}$$

$$E_{2,1} = -2.18 \times 10^{-18} \left(\frac{1^2}{2^2}\right) Jatom^{-1} = \frac{-2.18 \times 10^{-18}}{4} = -5.4 \times 10^{-19} Jatom^{-1}$$

$$2E_{2,1} = -1.09 \times 10^{-18} Jatom^{-1}$$

$$A = \frac{E_{1,2}}{2E_{2,1}} = \frac{-8.72 \times 10^{-18} Jatom^{-1}}{-1.09 \times 10^{-18} Jatom^{-1}} = 8$$

8. A photon of energy 4.5eV strikes on a metal of work function 3eV. If the uncertainty in position is $\frac{25}{4\pi}$Å, find the uncertainty in measurement of the de-Broglie wavelength in Å?

Solution: The kinetic energy of photoelectron is given by

$$\frac{m_e v_e^2}{2} = h\nu - W$$

$$v_e^2 = \frac{2(h\nu - W)}{m_e} \Rightarrow v_e = \sqrt{\frac{2(h\nu - W)}{m_e}} = \sqrt{\frac{2(4.5-3) \times 1.66 \times 10^{-19}}{9.11 \times 10^{-31}}} =$$

$$p = m_e v_e = 9.11 \times 10^{-31} \times 7.4 \times 10^5 = 6.74 \times 10^{-25}$$

Now according to the Heisenberg's Uncertainty Principle

$$\Delta x . \Delta v = \frac{h}{4\pi m}$$

We have $\Delta x = \frac{25}{4\pi}$Å

Therefore,

$$\Delta p = \frac{h}{4\pi \Delta x} = \frac{h}{4\pi \frac{25}{4\pi} \times 10^{-10}} = \frac{h}{25 \times 10^{-10}} = \frac{6.626 \times 10^{-34}}{25 \times 10^{-10}} = 2.65 \times 10^{-25}$$

Now according to the de-Broglie hypothesis

The de-Broglie wavelength associated with the electron

$$\lambda_D = \frac{h}{p}$$

The maximum and minimum values of p can be calculated as

$$p_{max} = p + \Delta p = 6.74 \times 10^{-25} + 2.65 \times 10^{-25} = 9.39 \times 10^{-25}$$

$$p_{min} = p - \Delta p = 6.74 \times 10^{-25} - 2.65 \times 10^{-25} = 4.09 \times 10^{-25}$$

$$\Delta\lambda_D = (\lambda_D)_{max} - (\lambda_D)_{min} = \frac{h}{p_{min}} - \frac{h}{p_{max}} = \frac{6.626 \times 10^{-34}}{4.09 \times 10^{-25}} - \frac{6.626 \times 10^{-34}}{9.39 \times 10^{-25}} = 9.14\text{Å}.$$

9. The de Broglie wavelength foe He atom travelling at $1000 ms^{-1}$is?

Solution: The de Broglie wavelength foe He atom travelling at $1000 ms^{-1}$ is given by the relation $\lambda_D = \frac{3.99 \times 10^{-7}}{M(g) v(ms^{-1})}$

$$\Rightarrow \lambda_D = \frac{3.99 \times 10^{-7}}{4 \times 1000} = 99.7 \times 10^{-12} m.$$

10. The uncertainty in the speed of a moving electron is? (Given $h = 6.63 \times 10^{-34} Js$ and $m_e = 9.1 \times 10^{-31} kg$)

Solution: The uncertainty in the speed of a moving electron is by

$$\Delta x . \Delta v = \frac{h}{4\pi m}$$

We have $\Delta x = 100pm$

Therefore, $\Delta v = \frac{h}{4\pi m \Delta x} \Rightarrow \Delta v = \frac{6.63\times10^{-34}Js}{4\pi\times9.1\times10^{-31}kg\sim\times100pm} = \frac{6.63\times10^{-34}Js}{4\pi\times9.1\times10^{-31}kg\times100\times10^{-12}m} = 5.79\times10^{5}ms^{-1}$

11. The number of photons emitted per nanosecond by a deuterium lamp of 400nm and 1 microwatt (Given $h = 6.626\times10^{-34}Js$ and $c = 3\times10^{8}ms^{-1}$)?

Solution: The number of photons emitted per nanosecond by a deuterium lamp of 400nm and 1 microwatt is given by the formula

$E = \frac{nhc}{\lambda}$ and we know $E = P.t$ therefore, we have, $P.t = \frac{nhc}{\lambda} \Rightarrow n = \frac{P.t.\lambda}{hc} = \frac{10^{-6}W\times10^{-9}s\times400\times10^{-9}m}{6.626\times10^{-34}Js\times3\times10^{8}ms^{-1}} = 2012$photons.

12. The de Broglie wavelength foe Argon atom (mass $40gmol^{-1}$) travelling at $250ms^{-1}$is --- pm?

Solution: The de Broglie wavelength foe Argon atom travelling at $250ms^{-1}$ is given by the relation $\lambda_D = \frac{3.99\times10^{-7}}{M(g)v(ms^{-1})} \Rightarrow \lambda_D = \frac{3.99\times10^{-7}}{40\times250} = 39.9\times10^{-12}m = 39.9pm.$

4.

ELEMENT CLASSIFICATION PROCESS

ABSTRACT: This chapter covers the development of classification schemes in chemical history from 1808 to 1932, highlighting their essential role in organizing elements systematically, revealing patterns in properties, and enabling predictive understanding that shaped the foundation of modern chemistry.

MATTER: Anything that occupies space and has mass.

The terms 'Element' and 'Compound' were first coined by Robert Alexander Boyle in 1661.

Robert Alexander Boyle
(5 February 1627- 10 January 1692)

ELEMENT: a group of atoms with same properties, determined by the number of protons in it. All atoms in an element sample show same behaviour physically and chemically, and have same composition on the subatomic level.

Now, as we studied, developments in atomic structure were increasing rapidly, all the same time as new elements were being discovered. As the number of elements increased, it became increasingly difficult to keep track and study of each of them separately. Moreover, most properties of many elements were same or similar, which made chemists increasingly feel that there is a need for some type of classification. This is what we shall study from here on.

The story of the discovery of different elements and the compounds is rooted in the story of the development of their different classification schemes developed in the chemical history. This is to cover the era from 1817-1913.

4A. CLASSICAL PERIODIC TABLE

DÖBEREINER TRIADS

Johann Wolfgang Döbereiner
(13 December 1780-24 March 1849)

In 1817 Johann Wolfgang Döbereiner **noticed that for some elements of his time, for three Consecutive elements, the arithmetic mean of atomic masses of two elements was equal to the mass of the middle element arranged in 'Triads' and** introduced the very primitive classification system in the chemical history. It was based on the law which states that 'Chemically analogous elements arranged in increasing order of their atomic weights formed well marked groups of three called Triads in which the atomic weight of the middle element was found to be generally the arithmetic mean of the atomic weight of the other two elements in the triad.'

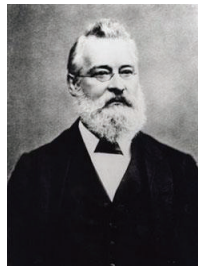
- ^{7}Li ^{23}Na ^{39}K
- ^{35}Cl ^{80}Br ^{127}I
- ^{40}Ca ^{87}Sr ^{137}Ba
- ^{32}S ^{79}Se ^{127}Te

The similar trend is followed in today's periodic table by

- ^{45}Sc ^{48}Ti ^{51}V *d-block*
- ^{139}La ^{140}Ce ^{141}Pr *f-block*

Limitations: The rule did not follow for all the elements.

Jean Baptiste André Dumas in 1857 published a table of 32 elements along with their relationships.



John Alexander Reina Newlands (26 November 1837-29 July 1898)

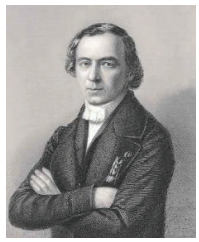
NEWLAND'S LAW OF OCTAVE

John Alexander Reina Newlands gave the law of octave in 1865. He stated that if the chemical elements are arranged according to increasing atomic weight, those with similar physical and chemical properties occur after each interval of seven elements.

1	2	3	4	5	6	7
Li	Be	B	C	N	O	F
8	9	10	11	12	13	14
Na	Mg	Al	Si	P	S	Cl
15	16					
K	Ca					

Limitations: After the Discovery of Noble Gases, periodicity happened after every 9th element instead of 8th. So, though still being true, some other advancements were again made.

William Odling in 1864 drew a table with 17 columns and 57 elements



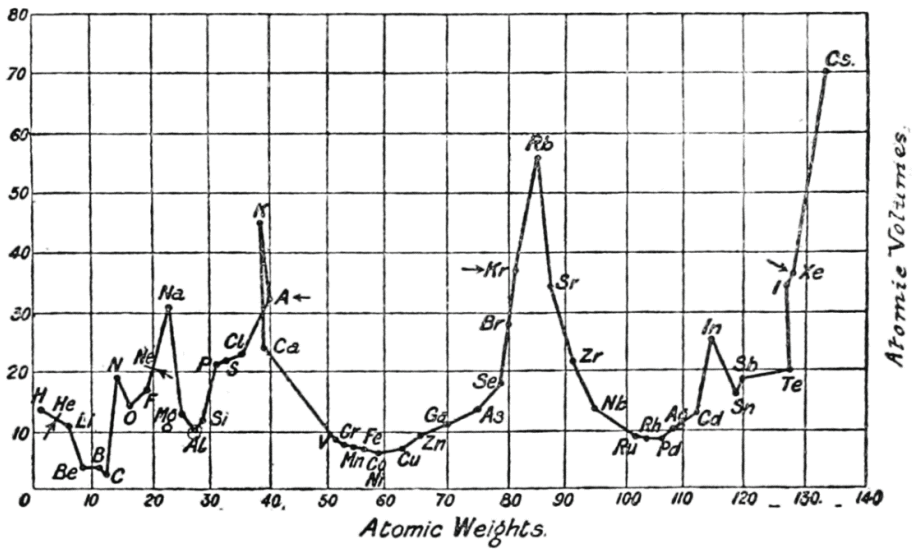
Jean Baptiste André Dumas (14 July 1800- 10 April 1884)

THE LOTHAR MEYER CURVE

Julius Lothar Meyer created the Lothar Meyer Curve in 1869. It was a plot between Atomic Weight and Atomic Volume. He then noticed some periodicity in that curve.

CHARACTERISTICS

- The peaks were occupied by Alkali Metals
- Ascending Part of the Curve was occupied by Noble gases and Halogens
- Descending Part of the Curve was occupied by Alkali Earth Metals
- Minima of the Curve was Occupied by d-block Transition Metals.



Julius Lothar Meyer (19 Augst 1830-11 April 1895)

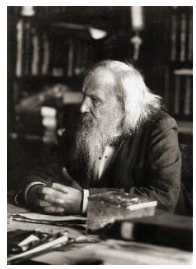
Limitations: It was not so practical to be of any physical importance. It also turns out to be difficult to remember.

MENDELEEV'S PERIODIC LAW

In 1869 Dmitri Ivanovich Mendeleev (often called the father of periodic table) gave the first Periodic Law. His Law stated that the periodicity in the properties of elements was in order of increasing atomic masses. In 1871 he modified his table after the discovery of 10 elements namely.

MENDELEEV'S PRIDICTIONS

Atomic number	Symbol	Name
21	Sc	Scandium
31	Ga	Gallium
32	Ge	Germanium
43	Tc	Technetium
75	Re	Rhenium
84	Po	Polonium
87	Fr	Francium
88	Ra	Radium
89	Ac	Actinium
91	Pa	Protactinium



Dmitri Ivanovich Mendeleev (27 February 1834-2 February 1907)

CHARACTERISTICS

- He divided his periodic table in groups and sub-groups along with periods.
- Some Elements with lower masses were placed after other elements with greater masses. Mendeleev did this thinking the measurement techniques might've been incorrect. Example: Iodine was placed after Tellurium, though being lighter.

Series	Zero Group	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
0	*x*								
1	*y*	Hydrogen H=1·008							
2	Helium He=4·0	Lithium Li=7·03	Beryllium Be=9·1	Boron B=11·0	Carbon C=12·0	Nitrogen N=14·04	Oxygen O=16·00	Fluorine F=19·0	
3	Neon Ne=19·9	Sodium Na=23·05	Magnesium Mg=24·1	Aluminium Al=27·0	Silicon Si=28·4	Phosphorus P=31·0	Sulphur S=32·06	Chlorine Cl=35·45	
4	Argon Ar=38	Potassium K=39·1	Calcium Ca=40·1	Scandium Sc=44·1	Titanium Ti=48·1	Vanadium V=51·4	Chromium Cr=52·1	Manganese Ma=55·0	Iron Fe=56·9 / Cobalt Co=59 / Nickel Ni=59 / (Cu)
5		Copper Cu=63·6	Zinc Zn=65·4	Gallium Ga=70·0	Germanium Ge=72·3	Arsenic As=75·0	Selenium Se=79	Bromine Br=79·95	
6	Krypton Kr=81·8	Rubidium Rb=85·4	Strontium Sr=87·6	Yttrium Y=89·0	Zirconium Zr=90·6	Niobium Nb=94·0	Molybdenum Mo=96·0	—	Ruthenium Ru=101·7 / Rhodium Rh=103·0 / Palladium Pd=106·5 / (Ag)
7		Silver Ag=107·9	Cadmium Cd=112·4	Indium In=114·0	Tin Sn=119·0	Antimony Sb=120·0	Tellurium Te=127	Iodine I=127	
8	Xenon Xe=128	Cæsium Cs=132·9	Barium Ba=137·4	Lanthanum La=139	Cerium Ce=140	—	—		— / — / — / (—)
9		—	—		—	—	—	—	
10	—	—	—	Ytterbium Yb=173	—	Tantalum Ta=183	Tungsten W=184	—	Osmium Os=191 / Iridium Ir=193 / Platinum Pt=194·9 / (Au)
11		Gold Au=197·2	Mercury Hg=200·0	Thallium Tl=204·1	Lead Pb=206·9	Bismuth Bi=208	—	—	
12	—	—	Radium Rd=224	—	Thorium Th=232	—	Uranium U=239		

MENDELEEV'S PREDICTIONS

Mendeleev was so confident in his law that he made several predictions for future elements, hence leaving empty spaces in his periodic table. And many of his predictions were even true.

Prediction	Atomic number	Symbol	Name	Predicted Atomic weight	Atomic weight	Density (gcm^{-3})	Oxide	CHLORIDE	Melting point (K)
Eka-Aluminium	31	Ga	Gallium	68	69.7	5.9	Ga_2O_3	$GaCl_3$	302.93
Eka-Silicon	32	Ge	Germanium	72	72.6	5.36	GeO_2	$GeCl_4$	1231
Eka-Manganese	43	Tc	Technetium	100	99				

Eka-Boron	21	Sc	Scandium	44	44.6	
Tri-Manganese	75	Re	Rhenium	190	186	
Dvi-Cesium	87	Fr	Francium	220	223	
Dvi-Tellerium	84	Po	Polonium	212	210	
Eka-Tantalum	91	Pa	Protactinium	235	231	

Limitations: Mendeleev contradicted himself by placing Iodine after Tellurium. Although Iodine was lighter than Tellurium. So, it was concluded that periodicity in properties of elements is not a function of their masses, but rather their atomic number. (Which was later given by Henry Moseley). To this point all the developmental studies are considered as **classical periodic table**.

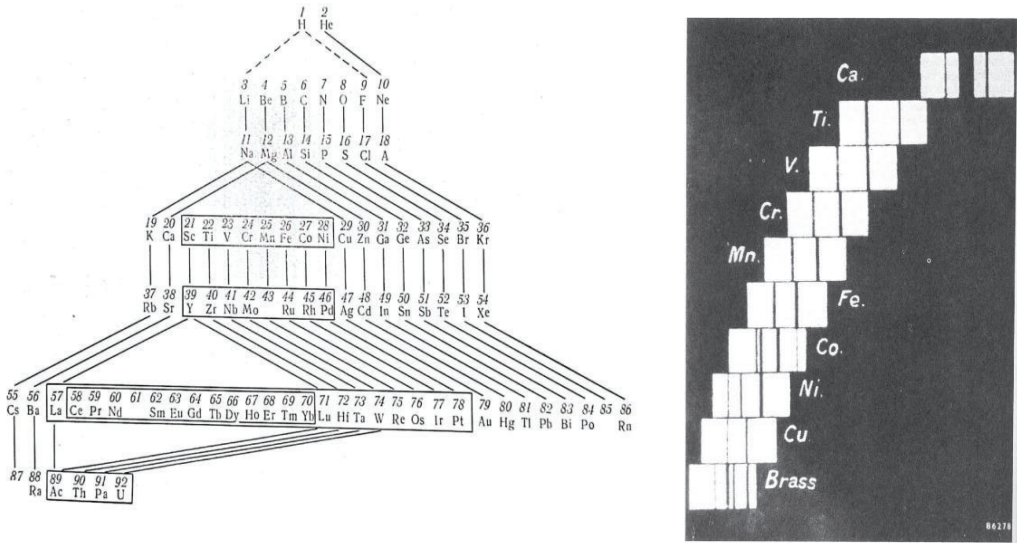
Antonius Johannes van den Broek (4 May 1870- 26 October 1926)

MODERN PERIODIC LAW

Henry Gwyn Jeffreys Moseley gave the modern periodic law in 1913 based on the X-Ray Studies. He conducted experiments by bombardment of electrode in a discharge tube with high energy electron beam. It generated two types of X-rays. The first type of X-rays produced a continuous, high-energy spectrum, whose frequency was proportional to the energy of the incident electron beam. The second type of X-rays produced a line spectrum superimposed on the continuous spectrum of the first type. But the line spectrum was a characteristic property of the material of the electrode. The modern periodic law states that periodicity in properties of elements is a function of their atomic numbers. This was an experimental law concerning the characteristic X-rays emitted by different elements. At the time of this experiment, the 'atomic number' was just merely the position of the element in the periodic table (given by Mendeleev). But the atomic number we know today is the number of Protons in the nucleus of the element. This was suggested by Antonius Johannes van den Broek, who concluded this from the Rutherford's model of atom. After van den Broek gave his prediction that the atomic number was equal to the positive charge on the nucleus, Moseley conducted his X-Ray experiment, and this did prove to be true. Moseley's law hence proved the physical importance of the atomic number given by van den Broek. The experiment led to Moseley's law which was that the square root of the frequency of the X-Ray emitted from an element was directly proportional to its atomic number, i.e. $\sqrt{\nu} \propto Z$ and is governed by $\sqrt{\nu} = A(Z - b)$. Further in terms of wavelength the equation can be expressed as $\sqrt{\frac{c}{\lambda}} = A(Z - b)$. This proved the physical importance of the 'atomic number' and hence, the modern periodic law. He studied many elements from Aluminum to Gold. After the modern Periodic Law, Neils Bohr, Henry Moseley and Charles Rugeley Bury sketched the design for the first Periodic table. Neils Bohr and Charles Bury also gave the Bohr-Bury scheme ($2n^2$). This scheme gives us an empirical formula of the total number of electrons in a given Bohr's orbit or shell. It does not give any description of the distribution of the elements in the periodic table. These are counted according some other equation that relates the principal quantum number the period number and the even-odd nature of its value.

Henry Gwyn Jeffreys Moseley (23 November 1887–10 August 1915)

The modern periodic law replaces the atomic weights by atomic number and hence it removes the unusual positioning of the elements K, Ar, Co, Ni, Te, I. This law also paved way for identification of new elements by spectral studies and their easier positioning in the periodic table. Lanthanoids and the elements Tc, Pm were the new elements identified afterwards.



The original modern periodic table and Mosley's stepladder graph

CALCULATION OF THE TOTAL NUMBER OF ELEMENTS IN A PERIOD AND THE ELEMENT'S POSITION IN THE PERIODIC TABLE

The Bohr Bury scheme just tells us about the total number of electrons that can be filled in the shell or energy level of the energy corresponding to the Principal Quantum Number (n). This may also be understood as that number of elements which have the valance electrons entering in the n^{th} orbit. The distribution of the electrons in the subshells is governed by the Aufbau Principle. This corresponds to the structure of the Periodic table as encountered and studied in the course of chemistry in the modern era. This can be understood according to the following algorithm.

- We know that n: Principal Quantum Number
- This also give the number of subshells present in the given energy level corresponding to the energy of the Bohr's orbit or shell.

Then,

- The total number of orbitals present are n^2.
- The number of orbitals in l^{th} subshell $2l + 1$ (l varies from $0\ to\ n - 1$).
- Maximum number of electrons that a single orbital can accommodate is given by the number of permitted spin states of an electron. For an electron only two spin states are permitted according to the Pauli's Exclusion Principle.
- The number of electrons that these orbitals can accommodate are $2n^2$.
- Further the distribution of the electrons in the subshells is governed by the Aufbau Principle.

∴ The number of elements in the given period of the periodic table depends on the value of the Principal Quantum Number according to two different equations depending whether n is even or odd. The highest value of Principal Quantum Number corresponds to the period number.

The number of subshells in the given shell is equal to its shell number; this shell number corresponds to the period number.

The number of Orbitals in a given **Shell** n^2. Therefore, the number of electrons in a given shell is given by $2n^2$.

The number of Orbitals in a given l^{th} **Subshell** is given by the equation $\sum \boldsymbol{m_\ell} = \boldsymbol{2l + 1.}$

A. For odd values of n

- The number of orbitals that can be filled $\left(\frac{n+1}{2}\right)^2$.

- The number of elements in the give period of the periodic table $2\left(\frac{n+1}{2}\right)^2$.

EXAMPLE: For 13TH Period of the periodic table, we have $2\left(\frac{n+1}{2}\right)^2 = 2\left(\frac{13+1}{2}\right)^2 = 98$

B. For even value of n

- The number of orbitals that can be filled $\left(\frac{n+2}{2}\right)^2$.
- The number of elements in the give period of the periodic table $2\left(\frac{n+2}{2}\right)^2$.

EXAMPLE: For 12TH Period of the periodic table, we have $2\left(\frac{n+2}{2}\right)^2 = 2\left(\frac{12+2}{2}\right)^2 = 98$

EXAMPLE: For 10TH Period of the periodic table, we have $2\left(\frac{n+2}{2}\right)^2 = 2\left(\frac{10+2}{2}\right)^2 = 72$

These formulas works for NEXT NEAREST EVEN numbers ONLY.

Now further the position of the element in the periodic table can be calculated according to the following algorithm.

- Write the atomic number of the element
- Write its ENERGETICALLY CORRECT electronic configuration

The highest value of Principal Quantum Number corresponds to the period number

Block: It is constituted by elements who have the same subshell for the entrance of the last electron, also called differentiating electron.

If this electron enters the s subshell of Outermost (Valence) shell, and leads to the $ns^{1-2} = ns^y$ configuration then the group number of the element is equal to the number of electrons in the s subshell of Outermost (Valence) shell; i.e. y.

EXAMPLE: For $[Xe]5s^1$, the element is an s-block element of 5th period and 1st group.

If this electron enters the p subshell and leads to the $ns^2np^{1-6} = np^y$ configuration then the group number of the element equal to twelve more than the number of electrons in the p subshell of Outermost (Valence) shell; i.e. $12 + y$.

EXAMPLE: For $[Xe]6s^24f^{14}5d^{10}6p^4$, the element is a p-block element of 6th period and 16th group.

EXAMPLE: For $[Xe]6s^24f^{14}5d^{10}6p^3$, the element is a p-block element of 6th period and 15th group.

If this electron enters the d subshell, of Penultimate shell and leads to the $ns^y(n-1)d^x$ configuration then the group number of the element is $x + y$.

EXAMPLE: For $[Kr]5s^14d^5$, the element is a d-block element of 5th period and 6th group.

For f-block elements the last electron must enter in the f-subshell of Antepenultimate shell. For f block elements the group number is always three.

EXAMPLE: For atomic number 45 ($Z = 45$), the electronic configuration is $[Kr]5s^24d^7$ is a d-block element of 5th period and 9th group.

PERIOD NUMBER	NUMBER OF ELEMENTS	PRINCIPAL QUANTUM NUMBER	BOHR BURREY SCHEME $2n^2$
1	2	1	2
2	8	2	8
3	8	3	18
4	18	4	32
5	18	5	50
6	32	6	72
7	32	7	98
TOTAL NUMBER OF ELEMENTS	118	TOTAL NUMBER OF ELEMENTS POSSIBLE	276

The electronic configurations of maximum elements can be predicted by the following table.

Shell / Period	Filled SUBSHELLS	Filled Orbitals	NUMBER OF ELECTRONS	Elements	Noble Gases		
					Atomic number	Symbol	name
1 / 1	1s	1	2	2	2	He	HELIUM
2 / 2	2s 2p	4	8	8	10	Ne	NEON
3 / 3	3s 3p	4	8	8	18	Ar	ARGON
4 / 4	4s 3d 4p	9	18	18	36	Kr	KRYPTON
5 / 5	5s 4d 5p	9	18	18	54	Xe	XENON
6 / 6	6s 5d 4f 6p	16	32	32	86	Rn	RADON
7 / 7	7s 6d 5f 7p	16	32	32	118	Og	OGANESSON

ALGORITHM TO WRITE THE CORRECT ELECTRONIC CONFIGURATIONS

Write the nearest noble gas in brackets.

Write the remaining orbitals energetically.

Then write the final configuration according to the Principal Quantum Numbers.

EXAMPLE 1: For Atomic number 27 ($Z = 27$), $[Ar]3d^7 4s^2$

EXAMPLE 2: For Atomic number 82 ($Z = 82$), $[Xe]4f^{14}5d^{10}6s^2 6p^2$

EXAMPLE 3: For Atomic number 42 ($Z = 42$), $[Kr]4d^5 5s^1$ (EXCEPTIONAL).

EXAMPLE 4: For Atomic number 84 ($Z = 84$), $[Xe]4f^{14}5d^{10}6s^2 6p^4$.

Inference: If the number of elements possible in a period gets equal to those predicted by the Bohr Burrey Scheme $2n^2$, for the 6th and 7th periods of the periodic table then the periodic will be completed in a true sense but due to some constraints and restrictions this is actually a hypothetical limit that can't be exactly touched. The constraints are as follows:

1. **Undiscovered Elements:** While the periodic table currently includes 118 confirmed elements, it is possible that elements with atomic numbers greater than 118 (in the so-called **"Island of Stability"**) may exist. These elements are predicted to be superheavy and potentially more stable than the elements near the end of the current table. However, they haven't been synthesized or observed yet.
2. **Limitations in Synthesizing Superheavy Elements:** The production of superheavy elements becomes increasingly challenging as atomic numbers increase due to their extremely short half-lives and the difficulty in experimental conditions required to create them. Thus, the periodic table is incomplete because these elements cannot yet be fully studied or characterized.
3. **Uncertainty About Element Properties:** For many heavy elements, especially those beyond uranium (the actinides), data about their chemical and physical properties is sparse or incomplete due to their instability and scarcity.
4. **Potential for Unknown Variations:** The structure of the periodic table is based on quantum mechanics, and it's possible that new discoveries in physics or chemistry could lead to modifications of its structure or the addition of new elements that don't fit neatly into the current model.

While the periodic table as we know it is one of the most complete and reliable scientific frameworks, its evolution continues as scientists push the boundaries of discovery.

The periodic table can be considered complete with reference to current scientific knowledge and understanding.

1. **Known Elements:** All naturally occurring elements and many synthetic ones have been discovered, characterized, and assigned places in the periodic table up to element 118 (Oganesson).
2. **Periodic Trends:** The table accurately reflects periodic trends, including atomic size, ionization energy, electronegativity, and chemical properties, based on the arrangement of elements by atomic number and electron configuration.

3. **Current Limits of Discovery:** While superheavy elements beyond 118 are theorized, they are not yet observed or confirmed. For now, the periodic table reflects the full extent of experimentally verified elements.
4. **Practical Utility:** The table is highly effective for predicting chemical behaviour, forming the foundation for modern chemistry, physics, and materials science.
Thus, for practical purposes and within the framework of contemporary science, the periodic table is considered "complete." However, it remains open to future updates as discoveries and technologies advance. The maximum possible number of elements in the periodic table is not definitively known, but it is theoretically limited by the physics of atomic nuclei and quantum mechanics.
Scientists estimate that the periodic table could potentially accommodate up to 170 elements or slightly more, though this remains speculative.
1. **Nuclear Stability Limits (Island of Stability):** As atomic numbers increase, nuclei become larger and less stable due to the repulsive force between protons (positive charges).
Beyond a certain size, the strong nuclear force (which binds protons and neutrons) is no longer sufficient to keep the nucleus stable.
However, some superheavy nuclei might exist in a hypothesized "island of stability," where certain combinations of protons and neutrons could create longer-lived elements.
2. **Quantum Mechanical Constraints**: The periodic table is built on the arrangement of electrons in atomic orbitals. In theory, elements could extend into the 8th period (beyond element 118) with new electron orbitals like **g-orbitals**. This could allow for up to 172 elements before running out of viable orbitals to house electrons.
3**.Proton-Drip Line**: Beyond a certain number of protons, nuclei may become too unstable to exist at all, even for fleeting moments. Current models suggest this limit could be around $Z = 126$ to 130, though some theorists propose it could extend slightly further.
4. **Experimental Challenges:** The creation of elements beyond 118 is increasingly difficult, as they exist for extremely short periods (fractions of a second) and require immense energy to synthesize.
5. **Hypothetical Limits:** Estimates vary, but many scientists suggest the practical limit of the periodic table might be around 170 to 200 elements, assuming stable or semi-stable configurations can be found.
While the exact number is uncertain, the periodic table's upper limit will ultimately depend on the interplay of nuclear stability, quantum mechanics, and advances in experimental techniques.
6. Limitations: Hydrogen’s Position is still disputed. Even today, it is not given any particular group as it shows similar properties with Alkali metals and Halogens. The primitive modern periodic table, made by Bohr, Moseley and Bury, was designed in a way in which the elements connected by lines are similar in properties, and Hydrogen had a line going to both alkali metals and halogens (refer figue on next page). In the long form of the periodic table theres more clarity of the periods and groups.
As a conclusion we may accept that the periodic table is complete as per the scope of the studies and for a specified discipline of research but its not a static and rigid frame with a seized research probability.

AN INTRODUCTION TO THE MODERN PERIODIC TABLE

The current way to classify and order elements known is the “Modern Periodic Table”. The modern periodic table is based on the modern periodic law given by Henry Moseley, i.e. “The Chemical and Physical Properties of Elements is a periodic function of their atomic numbers”. This law was the basis for the making of the modern periodic table by Neils Bohr, Henry Moseley and Charles Rugeley Bury.

CHARACTERISTICS

- This table is divided into 4 blocks, 7 periods and 18 groups.
- **Block**: It is constituted by elements who have the same subshell for the entrance of the last electron.
- **Period**: It is the Horizontal Division in the Periodic Table. It is constituted by elements with the same Valence Shell.
- **Group**: It is the Vertical Division in the Periodic Table. It is constituted by elements with same valence electron. All elements in the same group also have similar properties.
- Hydrogen shows properties of both Alkali Metals and Halogens, so placing it with both is justified, hence it is "floating" in the 1st Period between Group-1 and Group-17. It is also called the rogue element.
- Helium is placed in Group-18 along with all other noble gases (which are of *p-block*), but Helium is not a *p-block* element as its electronic configuration is $1s^2$.
- Group-1 elements are called the "Alkali Metals". i.e. The metals that form an "Alkali", or Base with water. They are found as Salts in Marine water.
- Group-2 elements are called the "Alkaline Earth Metals". i.e. The metals that form an "Alkali", or Base with water. They are found in the Earth's Crust as ores.
- *p-block* consists of all the non-metals, metalloids, halogens and noble gases (except He).
- Group 13 elements are called trials because of their tendency to form stable compounds with three bonds (their valency is three).
- Group 14 elements are called Crystallogens because of their crystalline solid allotropes.
- The Group-15 (Nitrogen Family) is known as "Pnictogen" which is derived from a Greek Word, which means "to choke", as Nitrogen and other Group-15 Hydrides have suffocating nature.
- Group-16 (Oxygen Family) is known as "Chalcogens" which is derived from a Latin word. Though the word literally means "Copper-former", but this is obviously misleading. The term can be interpreted as "ore-forming", as most metallic ores are with Oxygen and other Group-16 elements.
- Group-17 elements are known as "Halogens". The term "Halogen" was originally proposed for the element with the atomic number 17 (i.e. Chlorine) but the original name (Chlorine) prevailed. Later, another scientist "Jons Jacob Berzelius" (who is also known for giving the Chemical Notations used today, like writing H_2O and AgCl etc.) proposed to call the Group-17 "Halogens" all together. The word means "salt producer" as these elements react with metals to form salts. All Group-17 elements end with the suffix '–ine'.
- Group-18 elements are known as "Noble Gases" or Arogens. They were formerly called "inert gases". This term was dismissed because some elements in this Group do form compounds (most commonly knows are of Xenon).
- *d-block* elements are known as "transition elements" except Group-12 (i.e. Zn, Cd, Hg) because they have completely filled *d-subshell* in either neutral or ionic states. Hence, all transition elements are *d-block* elements, but all *d-block* elements are not transition elements.
- The three groups of the d block, namely group 8,9 and 10 form the **'hydride gap'** due to their relatively lesser tendency of hydride formation.
- Group-11 is known as "Coinage Metals" (i.e. Cu, Ag, Au).
- *f-block:* The *f-block* is placed at the bottom of the Periodic Table to avoid the overlengthening of the table which may cause inconvenience in reading the table, but all the *f-block* elements belong to **3rd Group** of the Periodic Table. This is so because, though they do not have the typical "similar electronic configuration", but just that they show similar properties and hence are concentrated into a single spot,

i.e. the Group-3, Period-6 and Period-7 Positions. Their properties are in fact so similar, it is very difficult to isolate each of them separately from an ore or a sample.

- f-block elements are also known as *"inner transition elements"*.
- All trans-bismuth elements are radioactive, and although trans-uranium elements were initially synthesized artificially, some of them are also found in nature in trace amounts.
- Technetium and Promethium are the only 2 pre-bismuth radioactive elements. In other words, Technetium and Promethium are the only elements with atomic number less than 83 that lack stable isotopes and are therefore inherently radioactive.
- Element with highest number of compounds in the whole periodic table is Carbon.
- Element with lowest number of compounds in the whole periodic table is Helium. Only one compound of Helium is discovered in outer space in 2019. It does not react at room temperature.
- For our surprise both these elements lie in the same 1st period of the periodic table.
- Gold is known as 'king of metals' as it's the oldest known most precious metal for mankind.
- Carbon is known as 'king of non-metals' as well as 'king of elements', as it's the element with maximum number of compounds in the whole periodic table (provided carbon as the central atom involved in the σ-skeleton of those approximately 10 million compounds).
- Mercury forms fewer types of compounds compared to many transition metals due to its limited oxidation states, but it is not the metal with the lowest number of compounds.
- Lanthanum $^{139}_{57}La$ is a d block element.

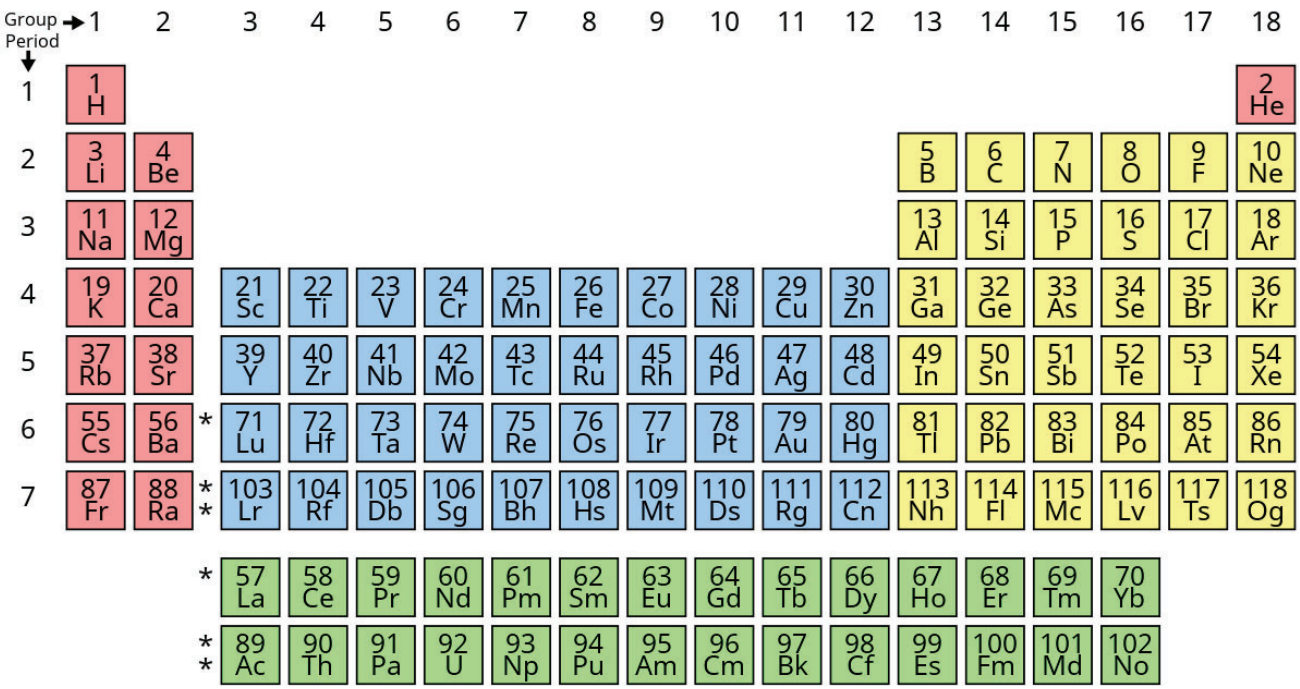
The *f-block* elements have two series which have 14 elements each and are named by two different spellings. Out of these two, one is lanthanides, which is the old spelling. The second spelling **Lanthanoids is the official IUPAC recommended spelling, (**IUPAC prefers the term "lanthanoids" instead of "lanthanides" to avoid confusion since "ides" usually refers to negatively charged ions). However, "lanthanides" remains widely accepted in the scientific community. As of February 2025, the International Union of Pure and Applied Chemistry (IUPAC) continues to recommend the terms "lanthanoids" and "actinoids" for the series of elements 57–71 and 89–103, respectively. The suffix "-oid" means "resembling". However, the terms "lanthanides" and "actinides" remain widely used in the scientific community.

- Elements from Hafnium to lead are called trans lanthanoids.
- **Note:** Lanthanum and Actinium are *d-block* elements, as they have $(n-1)d^1ns^1$ configurations.
- There are only 11 gaseous elements in the periodic table. (on standard temperature and pressure (STP).

s.no.	Atomic number	Symbol	Name
1	1	H	Hydrogen
2	2	He	Helium
3	7	N	Nitrogen
4	8	O	Oxygen
5	9	F	Fluorine
6	10	Ne	Neon
7	17	Cl	Chlorine
8	18	Ar	Argon
9	36	Kr	Krypton
10	54	Xe	Xenon
11	86	Rn	Radon

- There are only TWO liquid elements in the periodic table, Namely, MERCURY (Hg) and BROMINE (Br).

- Atomic radius is **not uniquely defined**, and reliable values are unavailable for many elements.
- Electrical conductivity is **well-defined mainly for stable solid elements**, not for all 118 elements.
- Earlier classifications treated elements beyond uranium as synthetic and recognized only the naturally occurring elements up to uranium (Z = 92), excluding elements such as Technetium Tc (Z=43) due to the absence of stable isotopes; however, modern understanding recognizes that even such elements occur naturally in trace amounts, and thus elements up to atomic number 94 are considered naturally occurring. Today, 118 elements have been identified, of which the first 94 occur naturally on Earth and the remaining are synthetic.[52-54]
- About 80 elements have at least one stable isotope.
- Out of 118 elements of the periodic table only **80** are stable natural elements.



Periodicity: The phenomenon of re-occurrence of certain properties after a fixed interval is called periodicity. The behavior of these properties on propagation in the periodic table is called trend. These trends are studied in two fissions. These trends require a specific systematic order of atomic number is chosen as the fixed order according to the Mossley's law. The periodicity can be divided into two different sections based on the division of the periodic table:

- ❖ **Periodicity of representative elements**
- ❖ **Periodicity of the transition elements**
- ❖ **Periodicity of the inner transition elements**

This periodicity is systematized in two different fissions:

- ✧ **Groupwise periodicity:** the variations of the properties on moving down the group (vertically downwards).
- ✧ **Period wise periodicity:** the variations of the properties on moving across a period (rightwards). This applies to the inner transition meals in a more defined manner.

At this point we have to survey a depth of the various atomic properties and their trends in the periodic table. There are many interdependent atomic properties that ae to be studied in this section. The periodic table systematize the study of the diverse physicochemical properties that vary with atomic number. The properties of elements are divided into the following categories:

- □ **ATOMIC PROPERTIES**
- □ **PHYSICAL PROPERTIES**

- **CHEMICAL PROPERTIES**

ATOMIC PROPERTIES

- The properties that are encountered in the study of the atomic structure of the element are called the atomic properties, these include:
- **Valance Electronic Configuration:** The configuration of the last shell of the elements. It has different generalized forms for different blocks of elements.

Block	Electronic configurations
s-block	ns^{1-2}
p-block	ns^2np^{1-6}
d-block	$(n-1)d^{1-10}ns^{1-2}$
f-block	$(n-2)f^{1-14}(n-1)d^{0-1}ns^2$

Atomic Radius: The atomic radius is defined as the distance from the nucleus to the outermost most loosely bound electron. Though this definition seems rigorous, it is not quite valid, as the electron exists as a cloud, we cannot define a distance to it from the nucleus. Moreover, the radius of a single isolated atom cannot be determined due to the constraints of the quantum mechanics. Moreover, the size of an atom is of the order of $10^{-10}m$, which is not possible to be isolated by ant technological equipment. So, different averages are used to define the size of an atom, or the atomic radius. Like Van der Waals radius, metallic radius, covalent radius and ionic radius. The concept of atomic radius is one of the foundation stone for the Bohr's atomic model. These four types of radii are a type of approximations expected to deal with the variation of the other properties reaching to accurately known results. Atomic radius is a waggly defined quantity since a tom have no well-defined boundary similar to a billiard ball, because according to the quantum mechanical model of atom the electron exists as a negatively charged charge density in the atom. Moreover, no atomic radii can be calculated in The Gaseous Phase, therefore, the experiment requires solidification. Due to the dual nature of electron, the atomic radius is to be considered in the four different forms:

1. **Van der Waals Radius:** It was proposed by Johannes Diderik van der Waals. It is defined for noble gases. It refers to the distance of closest approach between the neighbouring *non bonded molecules*. It's the distance between the valence shells of the neighbouring non bonded atoms of the neighbouring non bonded molecules. It gives a valuable insight in the close packing of crystals of the molecular compounds. It is directly proportional to the molecular weight of the compounds. E.g.
   1. Noble gases He, Ne, Ar etc. 2. Real gases Cl_2 etc. for the calculation of the radius, the two nearest centres of the two nonbonded molecules are considered. We can simplify it as $(r_{A-A})_V = \frac{(d_{A-A})_V}{2}$.
2. **Metallic Radius:** The metallic radius is defined as half the internuclear distance of the two nearest neighbouring atoms in the solid metallic element. It is also called the crystallographic radius. It is determined in solid crystals. We can simplify it as $(r_{A-A})_M = \frac{(d_{A-A})_M}{2}$.
   ***(More details are considered in the Solid-State Chemistry.)
3. **Covalent Radius:** The covalent radius is defined as half the internuclear distance between the nuclei of the two covalently bonded atoms in a non-metallic element. It was proposed by Irving Langmuir in 1919 and was first calculated for fluorene by Lawrence Olin Brockway. This was for homo-di-atomic molecules with a single covalent bond. This can be calculated Crystallography and the radius is given as $\boldsymbol{r_A = \frac{d_{A-A}}{2}}$.

For hetero-di-atomic molecules with a single covalent bond, the covalent radius is calculated in two ways

1. For Nonpolar Molecules without any electronegativity difference the covalent radius is calculated by $\boldsymbol{d_{A-B} = r_A + r_B}$.
2. For Polar Molecules with electronegativity difference the covalent radius is calculated by Schomaker-Stevenson equation, proposed by Vernon Schomaker and D.P. Stevenson which is as:

   $\boldsymbol{d_{A-B} = r_A + r_B - C|\chi_A - \chi_B|}$

   Where $C = 0.07$ for second period or 0.09 for higher periods.

   $\boldsymbol{d_{A-B}}$ is the bond length of the molecule A-B

This is due to the strong attractive force because of the electronegativity difference of the two covalently bound atoms e.g. HF. The values $\boldsymbol{d_{A-B}, r_A, r_B}$ are in angstrom (Å).

$\boldsymbol{r_A + r_B}$ is the sum of covalent radii of the atoms A and B.

$\boldsymbol{|\chi_A - \chi_B|}$ is the magnitude of the difference of electronegativities of the atoms A and B according to the Pauling scale.

The radii of the constituent atoms are calculated by taking the half of the bond lengths of the homo-di-atomic molecules A-A and B-B.

EXAMPLE: **If the internuclear distance of $\boldsymbol{F_2}$ is 144pm and HF is 92pm. Calculate the atomic radius of hydrogen. (Given $\boldsymbol{(\chi_H = 2.1)}$ and $\boldsymbol{(\chi_F = 4)}$)?**

ELUCIDATION: For $\boldsymbol{F_2}$ the internuclear distance is 144pm

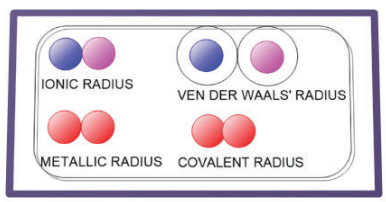
$\therefore$ The atomic radius of F is $\boldsymbol{r_F = \frac{144pm}{2}} = 72pm$

Similarly for HF the internuclear distance is 144pm

$\therefore$ The atomic radius of H is g9vn by using the Schomaker-Stevenson equation

$$\boldsymbol{d_{A-B} = r_A + r_B - C|\chi_A - \chi_B|}$$
$$\boldsymbol{d_{H-F} = r_H + r_F - 0.09|\chi_F - \chi_H|}$$
$$\boldsymbol{92 \times 10^{-2} = r_H Å + 72 \times 10^{-2} Å - 0.09|4 - 2.1|}$$
$$\boldsymbol{r_H = 0.371 Å}$$

4. **Ionic Radius:** It is related to the distance between the nearest neighbouring cations and anions in an ionic compound. Metals generally form cation by a process called oxidation due to the loss of the most loosely bound outermost valence electrons. The term oxidation was coined in 1697 by Georg Ernst Stahl in his theory of oxidation and reduction called the phlogiston theory. The metal cations are smaller than the atomic metals due to two reasons: The removal of the entire outermost shell of the atom during the ionization.



   A. The effective nuclear charge increases on the outermost electron after ionization because the Z number of protons now have to attract Z-n number of electrons, where n is the number of electrons left with the atom after ionization. Which further reduces the Ionic Radii of the cations.

Antoine-Laurent de Lavoisier
(26 August 1743-8 May 1794)

The anions are larger in size then the parent atoms as the effective nuclear is decreased due to the addition of one or more electrons to the parent atom. Because the Z number of protons now have to attract $Z + n$ number of electrons, where n is the number of electrons with the atom after reduction. This term reduction was also used by Antoine-Laurent de Lavoisier (Father of Chemistry) to describe the loss of weight of the metallic ore on strong heating for metal extraction.

✧ **Trends Groupwise periodicity:** The atomic radii increase down the group due to the increase the principal quantum number of the valance electron in the atom with a higher atomic number down the group.

- ✧ **Period wise periodicity:** The atomic radii decrease rightward across a period due to the increase in the effective nuclear charge on the valance electron in the next element lying rightwards in a period. On moving rightwards in a period, the atomic number of the element is increased by unity at each step, consequently the size of the atom gets contracted due to extra attraction on the outermost electron cloud of the valence electrons.**:** There is a periodicity in the variation of the atomic radius of the elements. This is consolidated in two different orders.

But the atomic radii seem to increase from 17^{th} to 18^{th} group but it should be kept in mind thar the noble gases have Van der Waals radius which is larger by definition itself.

The ionic size is a periodic property but it also has some exceptions which must be encountered to render an easier understanding of the effects dependent on these exceptions.

Although it's possible to accurately calculate the internuclear distance in a crystal through X-ray diffraction but the values of ionic radii are not accurately assigned to different ions. There are three main sets of ionic radii given by Goldschmidt, Linus Carl Pauling and Ahrens. All these ae calculated from the observed internuclear distance and have different allocation methods. The most recent and most accurate is the one proposed by Robert Day Shannon and Charles Thompson Prewitt in 1976. Necessary corrections are needed according to the charge, coordination number and geometry of the ion. The s-block and p-block ions are assumed to be spheres with a noble gas configuration. But in some cases, there is an extensive delocalization of the d-electrons. Therefore, the ionic radii are not are not absolute constants but are based on some approximations. In general, $\boldsymbol{Van\ der\ Waals\ Radius > Metallic\ Radius > Covalent\ Radius.}$ Some of the elements have their atomic radii in a specific order due to associated reasons:

$\boldsymbol{Be < Li < Mg < Na < Ca < Sr < Ba < K < Rb < Cs}$.

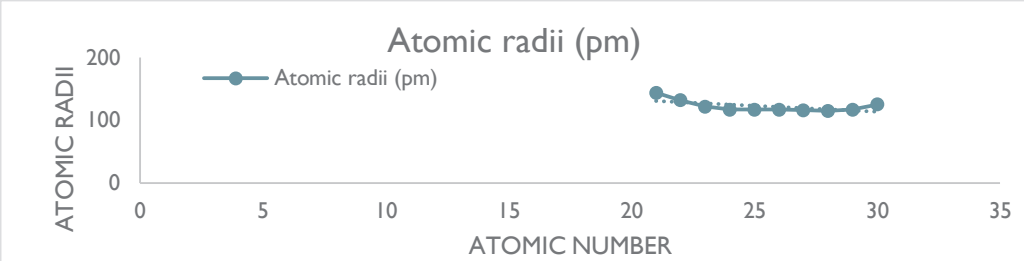
Expected order of atomic radii: $\boldsymbol{Ne > Li > Be > B > C > N > O > F}$

Modern research: $\boldsymbol{Ne > Li > Be > B > C > O > F > N}$

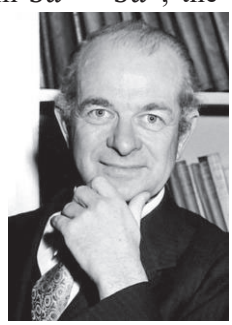
For same atom $Cation > Nutral > Anion$

In group 13 elements, B<Ga<Al<In≤ Tl, this is due to the fact that, Gallium is proceeded by 3d series metals, leading to a rapid overall decrease in size, therefore, Al>Ga. Thallium is proceeded by lanthanoid series metals, leading to In ≤ Tl. Further moving in the transition metals, the 3d series metals must show a regular decrease of size due to increase in size due to the increase in the effective nuclear charge on the valance electron in the next element lying rightwards in a period. But the actual experimental results show some deviations.

Atomic number	Symbol	Name	Electronic configurations	Atomic radii (pm)
21	Sc	Scandium	$[Ar]3d^1 4s^2$	144
22	Ti	Titanium	$[Ar]3d^2 4s^2$	132
23	V	Vanadium	$[Ar]3d^3 4s^2$	122
24	Cr	Chromium	$[Ar]3d^5 4s^1$	117
25	Mn	Manganese	$[Ar]3d^5 4s^2$	117
26	Fe	Iron	$[Ar]3d^6 4s^2$	117
27	Co	Cobalt	$[Ar]3d^7 4s^2$	116
28	Ni	Nickel	$[Ar]3d^8 4s^2$	115
29	Cu	Copper	$[Ar]3d^{10} 4s^1$	117
30	Zn	Zinc	$[Ar]3d^{10} 4s^2$	125



This is due to the imbalance in the nuclear attraction and the interelectronic repulsions in all these configurations. For the configurations $3d^1 - 3d^5$, the shielding effect is negligible, therefore the effective nuclear charge that is experienced by the electron Z_{eff} for these configurations is very high, decreasing the atomic size, as expected. From $3d^6 - 3d^8$, the shielding effect is approximately similar, which is intern approximately equal to the Z_{eff} giving these elements approximately equal sizes. Further in $3d^{10}$ the shielding effect is very high compared to the preceding configurations. Therefore, the atomic size shows an abnormal abrupt increase. This leads to the order: $Sc > Ti > V > Cr > Mn \cong Fe \cong Co > Ni < Cu < Zn.$ This trend cannot be explained theoretically by the Slater's Rules. This behaviour is known as the d-contraction, similar to the Lanthanoid contraction. Elements from Hafnium to lead are called trans lanthanoids. Here, the elements of the 5d series must be larger in size as compared to the 4d series, and, similarly, the 4d series must be larger in size as compared to the 3d series. But actually, this trend is a truth for the first three elements Sc, Y, La; having their atomic sizes in the same order $La > Y > Sc$. But, for the next elements the sizes are almost similar for the 4d and 5d series elements. Therefore, these elements are called Twins Elements.



Dr. Linus Carl Pauling
(28 February 1901-
19 August 1994)

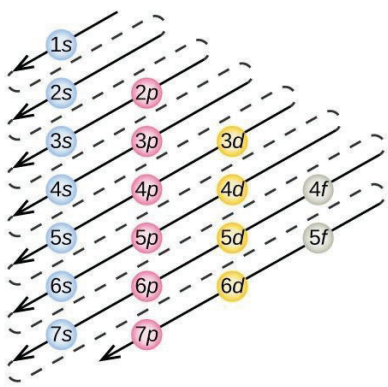
Linus Carl Pauling was the Father of Modern Chemical Bonding Theory; Founder of Quantum Chemistry. He is the only one to receive two unshared Nobel Prizes.

1. Nobel Prize in Chemistry (1954)
2. Nobel Peace Prize (1962)
3. Only Chemist to receive the Nobel Peace Prize.

- The ionic radii of the s block metal cations follow the order $Be^{2+} < Mg^{2+} < Li^{+} < Ca^{2+} < Na^{+} < Sr^{2+} < Ba^{2+} < K^{+} < Rb^{+} < Cs^{+}$.
- $P > S > N > O$
- $K > Ar > Na > Cl > Ne > F$
- $I^{+} < I < I^{-}$
- $H < F$
- $\boldsymbol{I^{-} > H^{-} > Br^{-} > Cl^{-} > F^{-}}$

ION	$\boldsymbol{F^{-}}$	$\boldsymbol{Cl^{-}}$	$\boldsymbol{Br^{-}}$	$\boldsymbol{H^{-}}$	$\boldsymbol{I^{-}}$
SIZE (nm)	0.13	0.18	0.19	0.208	0.216

This is because of the fact that the hydride ion has only one proton and two electrons are to be attracted which is a very difficult task leading to a drastic expansion.



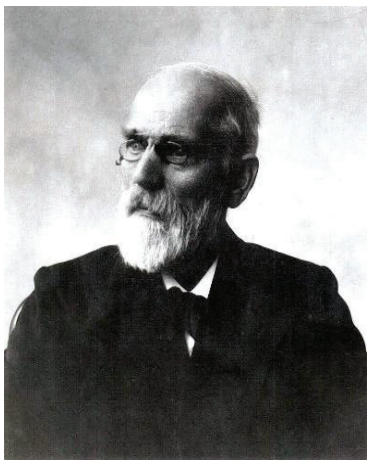
Expected order: $Li < Na < K < Rb < Cs < Fr$
Experimental order: $Li < Na < K < Rb < Fr < Cs$
his is due to relativistic contraction of s orbitals as explained by the quantum mechanics a phenomenon called quantum defect.

$$K^+ \approx Tl^+ \approx NH_4^+$$

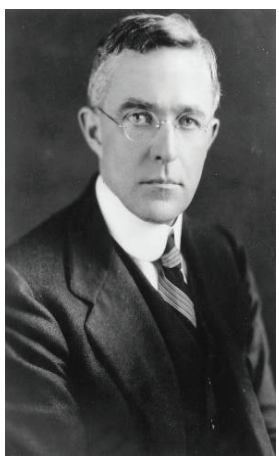
4B. CRITERIA OF ATOMIC SIZE ORDERING

1. Consider isoelectronic ions. Anions (size increase with increasing negative charge)>Neutral>Cations (size decrease with increasing positive charge).
   e.g. $N^- > O > F^+$
   $SIZE \propto \frac{NEGATIVE\ CHARGE}{POSITIVE\ CHARGE}$
   $N^{3-} > N^{2-} > N^- > N$
   $Cu^{3+} < Cu^{2+} < Cu^+ < Cu$
   $N^{3-} > O^{2-} > F^- > Ne > Na^+ > Mg^{2+} > Al^{3+}$
   $Br^- > Kr > Rb^+ > Sr^{2+}$
2. If same element with different oxidation state Anions (size increase with increasing negative charge)>Neutral>Cations (size decrease with increasing positive charge). e.g. $P^{5+}<P^{3+}<P<P^{3-}$.
   $S^{2-}>Ar>K^+>Ca^{2+}$.
3. If different elements are given then consider their shell number if the above two criteria failed. E.g. Cs>Sn>Al>Li
4. If shell numbers are same then consider the effective nuclear charge that is experienced by the electronZ_{eff}. Pseudo-noble gas>low atomic number>high atomic number atoms. E.g. $S^{2-} > Ar > Na > Si > Cl$.
   $Se^{2-}Br^- > Se > Br$
   $Al > P > Li > B$

A. Ionization Energy: It was discovered by Dmitri Ivanovich Mendeleev. Ionization enthalpy is the energy required to remove the most loosely bound electron (valance electron) from an isolated gaseous atom at 0K temperature, present in its ground state. But the absolute value of ionization energy cannot be calculated experimentally. Therefore, for the experimental purposes the **ionization enthalpy** is defined the other way. It is the molar internal energy change observed on removal of the most loosely bound electron (valance electron) from an isolated gaseous atom in its ground state at



Johannes Diderik van der Waals
(23 November 1837-9 March 1923)



Irving Langmuir
(31 January 1881-16 Augst1957)

Georg Ernst Stahl
(21 October 1660-14 May 1734)

0K temperature, present in its ground state. The ionization enthalpy is also called ionization potential, which is expressed in the unit **eVatom^{-1},** whereas the ionization enthalpy is expressed in the unit **kJmol^{-1}** or **kcalmol^{-1}**. It is an endothermic process and is therefore assigned a positive value according to the thermodynamic sign conventions. Thermodynamically the ionization enthalpy can be derived as:

ionization enthalpy $= (\Delta U)_{0K} = \Delta H - P\Delta V$

For this reaction the work done is zero $\therefore$

$P\Delta V = 0$ (no volume change)

$\therefore (\Delta U)_{0K} \cong \Delta H$

$\therefore (\Delta U)_{0K} \cong (\Delta H)_{0K}$

$\Delta H = C_p dT$ (Kirchhoff equation)

Further integrating we have, $\int_{0K}^{298K} d(\Delta H) = \Delta C_p \int_{0K}^{298K} dT$

$(\Delta H)_{298K} - (\Delta H)_{0K} = \Delta C_p \times 298K$

Further, for monoatomic gaseous species we have, $C_p = \frac{5R}{2} = \Delta C_p$ (both the gas and the cation are monoatomic)

Putting the values

$$(\Delta H)_{298K} - (\Delta H)_{0K} = \Delta C_p \times 298K = \frac{298K \times 5R}{2} = \frac{298K \times 5 \times 8.314 \times 10^{-3} kJK^{-1}mol^{-1}}{2} = 6.19 kJK^{-1}mol^{-1}$$

Further on rearranging we have, $(\Delta H)_{298K} = (\Delta U)_{0K} + 6.19 kJK^{-1}mol^{-1}$

The usual range of ionization enthalpy values is greater than $400 - 500\ kJK^{-1}mol^{-1}$

Therefore, we can neglect $6.19 kJK^{-1}mol^{-1}$ and directly write $(\Delta U)_{0K} \cong (\Delta H)_{298K}$

Greater the value of ionization enthalpy, the difficult it is to remove the electron from the atom. Ionization is Endothermic process. The atom is taken in gaseous state and is isolated to avoid the interference of other nuclei in the ionization process. The ejected electron is present in shell number infinity i.e. no influence of the nucleus. The general expression for the ionization process like $A \xrightarrow{IONIZATION} A^{n+}$ can be written as $\Delta H = \sum_{i=1}^{n} I_i$. The number of valence electrons of an atom are determined by the smaller values of ionization energy. If the energy values have an abrupt increase of approximately 10-times for the $(n+1)^{th}$ electron removal, then there are n number of valence electrons of that particular atom.

EXAMPLE The ionization of three s and p-block elements XYZ are given; Predict the number of valence electrons in each one?

ELEMENT	IE1	IE2	IE3	IE4
X	520	7298	1185	
Y	900	1757	14849	21007
Z	801	2427	3660	25026

ELUCIDATION: On a careful observation of the values of values of ionization enthalpies we can predict that

ELEMENT	X	Y	Z
VALENCE ELECTRONS	1	2	3

CONCLUSION If the $I_{n+1} \ggg I_n$ then the $(n+1)^{th}$ electron is being removed from the Noble gas configuration.

NOTE: The removal of electrons from an **'Atom'** is the process of ionization and the heterolytic cleavage of hydrogen bound to any electronegative element is Acidity of a **Molecule**. Therefore, the ionization can be expressed as $H \xrightarrow{IONIZATION} H^+$; But the acidity is like $H{-}Cl \xrightarrow[H_2O]{ACIDITY} H^+ + Cl^-$.

In ionization the electron extraction is from 1s-orbital of H-atom, whereas in acidity the protons escape due to the transfer of electrons to the antibonding σ^*-orbital of (say the H-Cl bond).

$$IONIZATION\ ENERGY \propto \frac{Z_{eff}.PENETATION\ POWER}{SIZE}$$

ALGORITHUM TO PRIDICT THE SEQUENCE OF IONIZATION ENTHALPY

1. Atoms having noble gas configuration have high ionization energy.

2.$PENETRATION\ POWER\ (s > p > d > f) > ELECTRONIC\ CONFIGURATION >$ **Effective Nuclear Charge** Z_{eff} for adjacent atoms.

Therefore, $Li < Be > B < C < N > O < F < Ne$

$Be^+ < C^+ < B^+ < N^+ < F^+ < O^+ < Ne^+ < Li^+$

$Se < S < Cl$

$C < O < N < F$

$Cu^+ > Zn^+ > Zn > Cu$

For the 3d-series the ionization enthalpy decreases as

$Zn > Fe > Co > Cu > Ni > Mn > Ti > V > Cr > Sc$

In general, in the periodic table, the ionization energy increases across the period due to increase of the Effective Nuclear Charge Z_{eff} and decreases down the group due to increase of atomic size.

NUCLEAR CHARGE

1. **Nuclear charge:** It is the net charge on the nucleus which can be calculated by adding up all the charge on the protons i.e. $q = Ze$. But in chemistry we follow the electronic charge e as a unit and take Z as a reference of the nuclear charge. This ideal charge is the exact charge on the nucleus that should be experienced by the electron under its influential field. But due to the presence of other electrons inner to the electron under observation, this charge is diluted to a certain extent. This diluted charge is known as **Effective Nuclear Charge** and the process of dilution is known as shielding effect. This shielding effect is governed by the Slater's Rules.
2. **Shielding effect of the core electron:** The shielding effect of the core electrons is calculated as the effective nuclear charge that is experienced by the electron under observation or at the atomic surface. This is designated as $Z_{eff} = Z^* = Z - \sigma = Z - s$. Further the shielding constant for an electron can be calculated as per the rules given by John Clarke Slater in 1930. These rules provide us with the values of the shielding constant σ.

The highest energy electrons are lost first as they require the least minimum amount of energy for ionization. Therefore, the electrons must be ionized in the reverse order of orbital filling according to the Aufbau principle. But this interpretation is restricted by the exceptional behaviour of the transition elements, because the relative energies of the 3d and 4s orbitals lie very close to each other. Therefore, the ns^2 electron are lost before the $(n-1)d$ or $(n-2)f$ electrons. This gives the common **+2** oxidation state to the transition metals. This also explains the exceptional electronic configurations of the coin age metals i.e. copper, silver and gold with an electronic configuration of the form $[Noble\ gas](n-1)d^9ns^1$ However, the metals have more than one oxidation states which are higher and lower than the common +2 oxidation state. But if the electron loss was as expected in the reverse order of orbital filling, then the electronic configurations of some ions would be other than the well-known configurations, e.g. Ga^{3+} should have a configuration of $[Ar]3d^84s^2$ but its actual configuration is $[Ar]3d^{10}$. Similarly, Zn^{2+} should have a configuration of $[Ar]3d^84s^2$

John Clarke Slater
(22 December 1900-
25 July 1976)

but its actual configuration is $[Ar]3d^{10}$. This can be explained on the bases of difference of the effective nuclear charge on these orbitals due to their distances from the atomic nucleus. The ionization enthalpy depends on various factors:

SLATER'S RULES

I. Write the given element in the format ${}_{ATOMIC\ NUMBER}SYMBOL^{CHARGE}$ which can be simplified as ${}_{Z}X^{N\pm}$.

II. Write the corresponding electronic configurations.
   A. In the normal order.
   B. Rearrange this configuration according to $(1s)(2s,2p)(3s,3p)(3d)(4s,4p)(4d)(4f)(5s,5p)$ ... etc.

III. Electrons in any group outer (at higher energy) to the group under consideration contributes nothing to the value of effective nuclear charge (Z_{eff}). This is due to the following:

I. Nature of Shielding by Inner Electrons:

Inner electrons present closer to the nucleus, are more effectively shielding for the positive charge of the nucleus because they lie between the nucleus and the outer electrons. These inner electrons repel outer electrons, reducing the net attractive force experienced by the outer electrons.

1. **Outer Electrons' Contribution to Shielding:** Outer electrons are located farther from the nucleus and do not 'block' the nucleus's positive charge for other outer electrons effectively. Since shielding depends on the ability of electrons to reduce the nuclear attraction felt by others, outer electrons provide negligible shielding for one another.

2. **Distance and Overlap:** Outer electrons are spatially further from the nucleus and from each other, leading to minimal overlap in their probability distributions. This reduced overlap means that their repulsion effect on other outer electrons is weak and does not significantly reduce the attractive force of the nucleus.

3. **Dominance of Inner Shell Shielding**: Inner-shell electrons are much closer to the nucleus and have a much greater effect in shielding because their negative charge is concentrated in regions where they can effectively reduce the nuclear charge felt by electrons in outer shells.

4. **Empirical Basis of Slater's Rules:** Slater's Rules assign zero shielding contribution to electrons in the same or higher energy levels (\(n\) values) relative to the electron being analysed. This empirical rule simplifies the calculation and reflects the fact that outer electrons are less effective at reducing the nuclear attraction for one another.

Conclusion

Outer electrons do not significantly shield each other because their spatial distribution, distance from the nucleus, and weak overlap prevent them from interfering with the nuclear attraction. Consequently, the effective nuclear charge experienced by an outer electron is largely determined by the actual nuclear charge reduced by the shielding effects of inner electrons.

IV. All the other electrons in the (ns,np) group (other than the one under observation) shield the one under observation to an extent of 0.35. This is not applied to the $1s$ group where the extent of shielding is 0.30.

V. All the electrons in the $(n-1)$ shell contribute 0.85 to the extent of shielding.

VI. All electrons in the $(n-2)$ or lower-shells shield to the extent of 1 each i.e. they shield completely.

VII. For electrons present in the $(nd)\ or\ (nf)$ groups the electrons in any group outer (at higher energy) to the group under consideration contributes nothing to the value of effective nuclear charge (Z_{eff}).

All the other electrons in the same group as the one under observation (other than the one under observation) shield the one under observation to an extent of 0.35.

VIII. The electrons in the left to the $(nd)\ or\ (nf)$ groups shield to an extent of 1 each.

These rules can be applied as per the following algorithm:

THE ALGORITHM

Write the given element in the format

$_{ATOMIC\ NUMBER}SYMBOL^{CHARGE}$ which can be simplified as $_{Z}X^{N\pm}$.

Write the corresponding electronic configurations: $[Ng]nl^{N_{nl}}$.

- In the normal order.
- Rearrange this configuration according to $(1s)(2s,2p)(3s,3p)(3d)(4s,4p)(4d)(4f)(5s,5p)$ ... etc.

To apply these rules the configuration should be rearranged further

Case 1: The electron under consideration lies in the $ns\ or\ np$ orbital.

1. The electronic configuration should be written by separating the electron under consideration as $(ns^2np^x)(np^1)$ etc.
2. Let number of electrons is given by the symbol N_{group}; $N_{group} = \sum \eta$ where η is the number of electrons in the orbitals present in the same group and the corresponding contributions be given by Φ_{group}

Now we have

$$Z_{eff} = Z^* = Z - \sigma = Z - s = Z - \left[\sum \boldsymbol{\Phi_{group} N_{group}} = \sum \left(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta}\right)\right]$$

EXAMPLE 1: **Calculate the Effective Nuclear Charge Z_{eff} for one 4s electron in Zn?**

ELUCIDATION: considering the example of Zn we proceed as

i. $_{Z}X^{N\pm} = {}_{30}Zn$

ii. $[Ar]3d^{10}4s^2$

iii. $(1s^2)(2s^22p^6)(3s^23p^6)(3d^{10})(4s^1)(\mathbf{4s^1})$ **(**electron under observation is shown in a **bold face**).

iv. Apply $Z_{eff} = Z^* = Z - \sigma = Z - s = Z - \left[\sum \boldsymbol{\Phi_{group} N_{group}} = \sum\left(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta}\right)\right]$ as $Z_{eff} = Z - \left[\sum\left(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta}\right)\right]$

$Z_{eff} = 30 - [(0.35 \times 1) + \{0.85(10 + 6 + 2)\} + \{1(6 + 2 + 2)\}] = 30 - 25.65 = 4.35$

Case 2: The electron under consideration lies in the nd or nf orbital.

The electronic configuration should be written by separating the electron under consideration as $(ns^2np^x)(nd^{y-1})(nd^1)$ etc.

EXAMPLE 2: **Calculate the Effective Nuclear Charge Z_{eff} for one 3d electron in Zn?**

ELUCIDATION: Considering the example of Zn, we proceed as

i. $_{Z}X^{N\pm} = {}_{30}Zn$

ii. $[Ar]3d^{10}4s^2$

iii. $(1s^2)(2s^22p^6)(3s^23p^6)(3d^9)(\mathbf{3d^1})(4s^2)$ **(**electron under observation is shown in a **bold face;** higher group electrons are shown in RED).

iv. Apply $Z_{eff} = Z^* = Z - \sigma = Z - s = Z - \left[\sum \boldsymbol{\Phi_{group} N_{group}} = \sum\left(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta}\right)\right]$ as $Z_{eff} = Z - \left[\sum\left(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta}\right)\right]$

v. $Z_{eff} = 30 - [(0.35 \times 9) + \{1(6 + 2 + 2 + 6 + 2)\}] = 30 - 21.15 = 8.85$

The Z_{eff} for 3d electron in Zn is 8.85 and that of 4s is 4.35 $\therefore Z_{eff}(3d) > Z_{eff}(4s)$ for Zn. This proves that the ionization of Zn leads to the loss of the 4s electron nd not of the strongly bound 3d electron. This is sometimes also interpreted the 3d orbital is completely filled and is therefore more stable. This also proves as an evidence to the interpretation that the dipositive Zn cation poses stronger attrition on its electron and hence its stable.

EXAMPLE 3: **Calculate the Effective Nuclear Charge Z_{eff} for one 2s electron in Li?**

ELUCIDATION: Considering the example of Li, we proceed as

i. $_{Z}X^{N\pm} = {}_{3}Li$

ii. $[He]2s^1$

$(1s^2)(2s^1)$

$$Z_{eff} = Z - \left[\sum\left(\Phi_{group}\sum\eta\right)\right]$$

$$Z_{eff} = 3 - [\{0.85(2)\}] = 3 - 1.7 = 1.3$$

EXAMPLE 4: **Calculate the Effective Nuclear Charge Z_{eff} for one 2s electron in He?**

ELUCIDATION: Considering the example of **He**, we proceed as

i. $_{Z}X^{N\pm} = {}_{2}He$

ii. $1s^2$

$(1s^2)$

$$Z_{eff} = Z - \left[\sum\left(\Phi_{group}\sum\eta\right)\right]$$

$$Z_{eff} = 2 - 0.3 = 1.7$$

EXAMPLE 5: **Calculate the Effective Nuclear Charge Z_{eff} for one 1s electron in H?**

ELUCIDATION: Considering the example of **?**, we proceed as

i. $_{Z}X^{N\pm} = {}_{1}H$

ii. $1s^1$

$(1s^1)$

$$Z_{eff} = Z - \left[\sum\left(\Phi_{group}\sum\eta\right)\right]$$

$Z_{eff} = Z$. For hydrogen there's no repulsion in the atom due to the presence of a single electron, therefore the whole charge is felt by the electron as a corresponding attraction force in hydrogen

EXAMPLE 6: **Calculate the Effective Nuclear Charge Z_{eff} for one 2s electron in Be or last electron of Beryllium?**

ELUCIDATION: Considering the example of **Be**, we proceed as

i. $_{Z}X^{N\pm} = {}_{4}Be$

ii. $[He]2s^2$

$(1s^2)(2s^2)$

$$Z_{eff} = Z - \left[\sum\left(\Phi_{group}\sum\eta\right)\right]$$

$$Z_{eff} = 4 - [\{0.35\} + \{0.85(2)\}] = 4 - 2.05 = 1.95$$

EXAMPLE 7: **Calculate the Effective Nuclear Charge Z_{eff} for one 2p electron in B?**

ELUCIDATION: Considering the example of **B**, we proceed as

i. $_{Z}X^{N\pm} = {}_{5}B$

ii. $[He]2s^2 2p^1$

$(1s^2)(2s^2)(2p^1)$

$$Z_{eff} = Z - \left[\sum\left(\Phi_{group}\sum\eta\right)\right]$$

$$Z_{eff} = 5 - [\{2 \times 0.35\} + \{2 \times 0.85\}] = 5 - 2.4 = 2.6$$

EXAMPLE 8: **Calculate the Effective Nuclear Charge Z_{eff} for one 2p electron in C?**

ELUCIDATION: Considering the example of **C**, we proceed as

i. $_{Z}X^{N\pm} = {}_{6}C$

ii. $[He]2s^2 2p^2$

$(1s^2)(2s^2)(2p^1)(2p^1)$

$$Z_{eff} = Z - \left[\sum\left(\Phi_{group}\sum\eta\right)\right]$$

$Z_{eff} = 6 - [\{3 \times 0.35\} + \{2 \times 0.85\}] = 6 - 2.75 = 3.25$

EXAMPLE 9: **Calculate the Effective Nuclear Charge Z_{eff} for one 2p electron in N?**

ELUCIDATION: Considering the example of **N**, we proceed as

i. $_{Z}X^{N\pm} = {}_{7}N$

ii. $[He]2s^2 2p^3$

$(1s^2)(2s^2)(2p^2)(2p^1)$

$$Z_{eff} = Z - \left[\sum \left(\Phi_{group} \sum \eta\right)\right]$$

$Z_{eff} = 7 - [\{4 \times 0.35\} + \{2 \times 0.85\}] = 7 - 3.1 = 3.9$

EXAMPLE 10: **Calculate the Effective Nuclear Charge Z_{eff} for one 2p electron in O?**

ELUCIDATION: Considering the example of **O**, we proceed as

i. $_{Z}X^{N\pm} = {}_{8}O$

ii. $[He]2s^2 2p^4$

$(1s^2)(2s^2)(2p^3)(2p^1)$

$$Z_{eff} = Z - \left[\sum \left(\Phi_{group} \sum \eta\right)\right]$$

$Z_{eff} = 8 - [\{5 \times 0.35\} + \{2 \times 0.85\}] = 8 - 3.45 = 4.55$

EXAMPLE 11: **Calculate the Effective Nuclear Charge Z_{eff} for one 2p electron in F?**

ELUCIDATION: Considering the example of **F**, we proceed as

i. $_{Z}X^{N\pm} = {}_{9}F$

ii. $[He]2s^2 2p^5$

$(1s^2)(2s^2)(2p^4)(2p^1)$

$$Z_{eff} = Z - \left[\sum \left(\Phi_{group} \sum \eta\right)\right]$$

$Z_{eff} = 9 - [\{6 \times 0.35\} + \{2 \times 0.85\}] = 9 - 3.8 = 5.2$

This proves that the effective nuclear charge Z_{eff} increases on moving from left to right in the periodic table.

EXAMPLE 12: **Calculate the Effective Nuclear Charge Z_{eff} for one 3s electron in Na?**

ELUCIDATION: Considering the example of **Na**, we proceed as

i. $_{Z}X^{N\pm} = {}_{9}F$

ii. $[Ne]3s^1$

$(1s^2)(2s^2)(2p^6)(3s^1)$

$$Z_{eff} = Z - \left[\sum \left(\Phi_{group} \sum \eta\right)\right]$$

$Z_{eff} = 11 - [\{8 \times 0.85\} + 2] = 11 - 8.8 = 2.2$

EXAMPLE 12: **Calculate the Effective Nuclear Charge Z_{eff} for one 4s electron in K?**

ELUCIDATION: Considering the example of **K** Li, we proceed as

i. $_{Z}X^{N\pm} = {}_{19}K$

ii. $[Ar]4s^1$

$(1s^2)(2s^2)(2p^6)(3s^2)(3p^6)(4s^1)$

$$Z_{eff} = Z - \left[\sum \left(\Phi_{group} \sum \eta\right)\right]$$

$Z_{eff} = 19 - [\{8 \times 0.85\} + 10] = 19 - 16.8 = 2.2$

Q. Why the last electron goes in 4s rather than 3d for K?

KEY: According to the Aufbau principle the 4s orbital is of lower energy than 3d orbital. This can be explained based on the concept of Effective Nuclear Charge Z_{eff} for 3d electron of K. The Effective Nuclear Charge Z_{eff} for 3d electron of K is less than that for its 4s electron as predicted by the Slater's Rules.

EXAMPLE 13: **Calculate the Effective Nuclear Charge Z_{eff} for the condition if it's one valence electron were in 3d instead of 4s for K?**

ELUCIDATION: Considering the example of **K**, we proceed as

i. $_{Z}X^{N\pm} = {}_{19}K$

$(1s^2)(2s^2)(2p^6)(3s^2)(3p^6)(3d^1)$

$Z_{eff} = Z - \left[\sum\left(\Phi_{group}\sum\eta\right)\right]$

$Z_{eff} = 19 - 18 = 1$. The Z_{eff} of 4s > Z_{eff} of 3d for K. Hence the 4s orbitals are of lower energy and are filed first before the filling of 3d orbitals. Partially we can say that the last electron of K will reside in 4s and not in 3d orbital.

EXAMPLE 14: **Calculate the Effective Nuclear Charge Z_{eff} for the last electron for Cl?**

ELUCIDATION: Considering the example of **Cl**, we proceed as

i. $_{Z}X^{N\pm} = {}_{17}Cl$

ii. $[Ne]3s^2$

iii. $(1s^2)(2s^2)(2p^6)(3s^2)(3p^5)$

iv. $Z_{eff} = Z - \left[\sum(\Phi_{group}\sum\eta)\right]$

v. $Z_{eff} = 17 - [\{6 \times 0.35\} + \{8 \times 0.85\} + 2] = 17 - 10.9 = 6.1.$

EXAMPLE 15: **Calculate the Effective Nuclear Charge Z_{eff} for the last electron for Cl^+?**

ELUCIDATION: Considering the example of **Cl^+**, we proceed as

$(1s^2)(2s^2)(2p^6)(3s^2)(3p^4)$

$Z_{eff} = Z - \left[\sum\left(\Phi_{group}\sum\eta\right)\right]$

$Z_{eff} = 17 - [\{5 \times 0.35\} + \{8 \times 0.85\} + 2] = 17 - 10.55 = 6.45.$

EXAMPLE 16: **Calculate the Effective Nuclear Charge Z_{eff} for the last electron for Cl^-?**

ELUCIDATION: Considering the example of Cl, we proceed as

$(1s^2)(2s^2)(2p^6)(3s^2)(3p^6)$

$Z_{eff} = Z - \left[\sum\left(\Phi_{group}\sum\eta\right)\right]$

$Z_{eff} = 17 - [\{7 \times 0.35\} + \{8 \times 0.85\} + 2] = 17 - 11.25 = 5.75.$

CONCLUSION

Shielding orbitals involved: the orbitals follow the decreasing order of the shielding effect as azimuthal quantum number ***l*** increases i.e. $s > p > d > f$, due to the diffused nature of the orbitals. Further for the d orbitals with electronic configurations having unpaired electrons (i.e.d^{1-5}) have a negligible shielding effect, and it is increased as the electrons start to pair up (i.e.d^{6-10}). Moreover, the d^{10} configuration have the maximum shielding elect. The configurationsd^6, d^7 and d^8 have almost similar shielding effects due to the difference of only one electron pair.

Species	Cl^-	Cl	Cl^+
Shielding constant σ	11.25	10.9	10.55
Z_{eff}	5.75	6.1	6.45

In this data from the anionic to cationic species the number of electrons decreased and the Z_{eff} is increased. Therefor higher the Z_{eff}, higher the attraction; higher the attraction smaller will be the size of ion. Therefore, the cations are smaller than the anion of the same element. this can be proved by using the example of gallium.

EXAMPLE 17: **Calculate the Effective Nuclear Charge Z_{eff} for the last electron for Ga?**

ELUCIDATION: Considering the example of **Ga**, we proceed as

i. ${}_{Z}X^{N\pm} = {}_{31}Ga$
ii. $[Ar]3d^{10}4s^{2}4p^{1}$
iii. $(1s^{2})(2s^{2})(2p^{6})(3s^{2})(3p^{6})(3d^{10})(4s^{2}4p^{1})$
iv. $Z_{eff} = Z - [\sum(\Phi_{group}\sum\eta)]$
v. $Z_{eff} = 31 - [\{2 \times 0.35\} + \{18 \times 0.85\} + 10] = 31 - 26 = 5.$

EXAMPLE 18: **Calculate the Effective Nuclear Charge Z_{eff} for the last electron for Ga^{+}?**

ELUCIDATION: Considering the example of **Ga^{+}**, we proceed as

i. ${}_{Z}X^{N\pm} = {}_{31}Ga$
ii. $[Ar]3d^{10}4s^{2}$
iii. $(1s^{2})(2s^{2})(2p^{6})(3s^{2})(3p^{6})(3d^{10})(4s^{2})$
iv. $Z_{eff} = Z - [\sum(\Phi_{group}\sum\eta)]$
v. $Z_{eff} = 31 - [\{0.35\} + \{18 \times 0.85\} + 10] = 31 - 25.65 = 5.35.$

EXAMPLE 19: **Calculate the Effective Nuclear Charge Z_{eff} for the last electron for Ga^{+3}?**

ELUCIDATION: Considering the example of **Ga^{+3}**, we proceed as

i. ${}_{Z}X^{N\pm} = {}_{31}Ga$
ii. $[Ar]3d^{10}$
iii. $(1s^{2})(2s^{2})(2p^{6})(3s^{2})(3p^{6})(3d^{10})$
iv. $Z_{eff} = Z - [\sum(\Phi_{group}\sum\eta)]$
v. $Z_{eff} = 31 - [\{9 \times 0.35\} + 18] = 31 - 21.15 = 9.85.$

Species	Li	Be	B	C	N	O	F
Z_{eff}	1.3	1.95	2.6	3.25	3.9	4.55	5.20

In a 2nd and 3rd period the Z_{eff} of next element is 0.65 more than that of previous one. For a group Z_{eff} first increases for 2nd to 3rd period and then become constant.

EXAMPLE 20: **Calculate the Effective Nuclear Charge Z_{eff} for the last electron for Na^{+}?**

ELUCIDATION: Considering the example of **Na^{+}**, we proceed as

i. ${}_{Z}X^{N\pm} = {}_{11}Na$
ii. $[Ne]3s^{1}$
iii. $(1s^{2})(2s^{2})(2p^{6})(3s^{1})$
iv. $Z_{eff} = Z - [\sum(\Phi_{group}\sum\eta)]$
v. $Z_{eff} = 11 - [\{7 \times 0.35\} + \{2 \times 0.85\}] = 11 - 4.15 = 6.85.$

EXAMPLE 21: **Calculate the Effective Nuclear Charge Z_{eff} for the last electron (4s electron) for Cu?**

ELUCIDATION: Considering the example of **Cu**, we proceed as

i. ${}_{Z}X^{N\pm} = {}_{29}Cu$
ii. $[Ar]3d^{10}4s^{1}$
iii. $(1s^{2})(2s^{2})(2p^{6})(3s^{2})(3p^{6})(3d^{10})(4s^{1})$
iv. $Z_{eff} = Z - [\sum(\Phi_{group}\sum\eta)]$
v. $Z_{eff} = 29 - [\{18 \times 0.85\} + 10] = 29 - 25.3 = 3.7.$

EXAMPLE 22: **Calculate the Effective Nuclear Charge Z_{eff} for the last electron for Cu^{+}?**

ELUCIDATION: Considering the example of **Cu^{+}**, we proceed as

i. ${}_{Z}X^{N\pm} = {}_{29}Cu$
ii. $[Ar]3d^{10}$
iii. $(1s^{2})(2s^{2})(2p^{6})(3s^{2})(3p^{6})(3d^{10})$
iv. $Z_{eff} = Z - [\sum(\Phi_{group}\sum\eta)]$

v. $Z_{eff} = 29 - [\{17 \times 0.35\} + 10] = 29 - 15.95 = 13.05.$

vi. Z_{eff} of pseudo noble gas configurations is more than the noble gas configurations

Species	Na^+	K^+	Cu^+
Z_{eff}	6.85	7.75	7.85

EXAMPLE 23: **Calculate the Effective Nuclear Charge Z_{eff} for one 3p electron in K^+?**

ELUCIDATION: Considering the example of $\mathbf{K^+}$, we proceed as

$(1s^2)(2s^2)(2p^6)(3s^2)(3p^6)$

$Z_{eff} = Z - \left[\sum \left(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta}\right)\right]$

L$Z_{eff} = 19 - [\{7 \times 0.35\} + \{8 \times 0.85\} + 2] = 19 - 11.25 = 7.75.$

EXAMPLE 24: **Calculate the Effective Nuclear Charge Z_{eff} for one 2s electron in B?**

ELUCIDATION: Considering the example of B, we proceed as

i. ${}_ZX^{N\pm} = {}_5B$

$(1s^2)(2s^2)(2p^1)$

$Z_{eff} = Z - \left[\sum \left(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta}\right)\right]$

L$Z_{eff} = 5 - [\{1 \times 0.35\} + \{2 \times 0.85\}] = 5 - 2.05 = 2.95.$

The Slater's constant is same for the 1s-orbital but the Effective Nuclear Charge Z_{eff} for different atoms depends on the atomic number Z.

EXAMPLE 25: **Calculate the Effective Nuclear Charge Z_{eff} for one 3p electron in Zn?**

ELUCIDATION: Considering the example of Zn, we proceed as

i. ${}_ZX^{N\pm} = {}_{30}Zn$

ii. $[Ar]3d^{10}4s^2$

iii. $(1s^2)(2s^2 2p^6)(3s^2 3p^6)(3d^9)(\mathbf{3d^1})(4s^2)$ **(**electron under observation is shown in a **bold face;** higher group electrons are shown in RED).

iv. Apply $Z_{eff} = Z^* = Z - \sigma = Z - s = Z - \left[\sum \boldsymbol{\Phi_{group}} \boldsymbol{N_{group}} = \sum\left(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta}\right)\right]$ as $Z_{eff} = Z - \left[\sum\left(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta}\right)\right]$

v. $Z_{eff} = 30 - [(0.35 \times 7) + 8 \times 0.85 + 2] = 30 - 11.25 = 18.75$

EXAMPLE 26: **Calculate the Effective Nuclear Charge Z_{eff} for one 3s electron in Zn?**

ELUCIDATION: Considering the example of Zn, we proceed as

i. ${}_ZX^{N\pm} = {}_{30}Zn$

ii. $[Ar]3d^{10}4s^2$

iii. $(1s^2)(2s^2 2p^6)(\mathbf{3s^2} 3p^6)(3d^9)(\mathbf{3d^1})(4s^2)$ **(**electron under observation is shown in a **bold face;** higher group electrons are shown in RED).

iv. Apply $Z_{eff} = Z^* = Z - \sigma = Z - s = Z - \left[\sum \boldsymbol{\Phi_{group}} \boldsymbol{N_{group}} = \sum\left(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta}\right)\right]$ as $Z_{eff} = Z - \left[\sum\left(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta}\right)\right]$

v. $Z_{eff} = 30 - [(0.35 \times 1) + 8 \times 0.85 + 2] = 30 - 9.15 = 20.85$

EXAMPLE 27: **Calculate the Effective Nuclear Charge Z_{eff} for one 2p electron in Zn?**

ELUCIDATION: Considering the example of Zn, we proceed as

i. ${}_ZX^{N\pm} = {}_{30}Zn$

ii. $[Ar]3d^{10}4s^2$

iii. $(1s^2)(2s^2\mathbf{2p^6})(3s^2 3p^6)(3d^9)(\mathbf{3d^1})(4s^2)$ **(**electron under observation is shown in a **bold face;** higher group electrons are shown in RED).

iv. Apply $Z_{eff} = Z^* = Z - \sigma = Z - s = Z - \left[\sum \boldsymbol{\Phi_{group} N_{group}} = \sum\left(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta}\right)\right]$ as $Z_{eff} = Z - \left[\sum\left(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta}\right)\right]$

v. $Z_{eff} = 30 - [(0.35 \times 7) + 2 \times 0.85] = 30 - 4.15 = 25.85$

EXAMPLE 28: **Calculate the Effective Nuclear Charge Z_{eff} for one 2s electron in Zn?**

ELUCIDATION: Considering the example of Zn, we proceed as

i. ${}_{Z}X^{N\pm} = {}_{30}Zn$

ii. $[Ar]3d^{10}4s^2$

iii. $(1s^2)(\mathbf{2s^2}2p^6)(3s^23p^6)(3d^9)(\mathbf{3d^1})(4s^2)$ (electron under observation is shown in a **bold face;** higher group electrons are shown in RED).

iv. Apply $Z_{eff} = Z^* = Z - \sigma = Z - s = Z - \left[\sum \boldsymbol{\Phi_{group} N_{group}} = \sum\left(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta}\right)\right]$ as $Z_{eff} = Z - \left[\sum\left(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta}\right)\right]$

v. $Z_{eff} = 30 - [(0.35 \times 1) + 2 \times 0.85] = 30 - 2.05 = 27.95$

EXAMPLE 29: **Calculate the Effective Nuclear Charge Z_{eff} for one 1s electron in Zn?**

ELUCIDATION: Considering the example of Zn, we proceed as

i. ${}_{Z}X^{N\pm} = {}_{30}Zn$

ii. $[Ar]3d^{10}4s^2$

iii. $(1s^2)(2s^2\mathbf{2p^6})(3s^23p^6)(3d^9)(\mathbf{3d^1})(4s^2)$ (electron under observation is shown in a **bold face;** higher group electrons are shown in RED).

iv. Apply $Z_{eff} = Z^* = Z - \sigma = Z - s = Z - \left[\sum \boldsymbol{\Phi_{group} N_{group}} = \sum\left(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta}\right)\right]$ as $Z_{eff} = Z - \left[\sum\left(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta}\right)\right]$

v. $Z_{eff} = 30 - 0.3 = 30 - 0.3 = 29.7$

The values of the Effective Nuclear Charge $Z_{eff}(4s) < Z_{eff}(3d) \ll Z_{eff}(3p)$, proves that the ionization of Zn is from 4s-orbital first and the closer we move to the nucleus the higher is the Effective Nuclear Charge $\boldsymbol{Z_{eff}}$ for the inner electrons.

EXAMPLE 30: **Calculate the Effective Nuclear Charge Z_{eff} for one 3p electron in K?**

ELUCIDATION: Considering the example of **K**, we proceed as

$(1s^2)(2s^2)(2p^6)(3s^2)(3p^6)(4s^1)$

$Z_{eff} = Z - \left[\sum\left(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta}\right)\right]$

$Z_{eff} = 19 - [\{7 \times 0.35\} + \{8 \times 0.85\} + 2] = 19 - 11.25 = 7.75.$

EXAMPLE 31: **Calculate the Effective Nuclear Charge Z_{eff} for one 3d electron in Cr?**

ELUCIDATION: Considering the example of Zn, we proceed as

i. ${}_{Z}X^{N\pm} = {}_{24}Cr$

ii. $[Ar]3d^54s^1$

iii. $(1s^2)(2s^22p^6)(3s^23p^6)(3d^4)(\mathbf{3d^1})(4s^1)$ (electron under observation is shown in a **bold face;** higher group electrons are shown in RED).

iv. Apply $Z_{eff} = Z^* = Z - \sigma = Z - s = Z - \left[\sum \boldsymbol{\Phi_{group} N_{group}} = \sum\left(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta}\right)\right]$ as $Z_{eff} = Z - \left[\sum\left(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta}\right)\right]$

v. $Z_{eff} = 24 - [(0.35 \times 4) + 18] = 24 - 19.4 = 4.6$

EXAMPLE 32: **Calculate the Effective Nuclear Charge Z_{eff} for one 4s electron in Cr?**

ELUCIDATION: Considering the example of Zn, we proceed as

i. ${}_{Z}X^{N\pm} = {}_{24}Cr$

ii. $[Ar]3d^54s^1$

iii. $(1s^2)(2s^2 2p^6)(3s^2 3p^6)(3d^4)(3d^1)(\mathbf{4s^1})$ **(**electron under observation is shown in a **bold face;** higher group electrons are shown in RED).

iv. Apply $Z_{eff} = Z^* = Z - \sigma = Z - s = Z - \left[\sum \boldsymbol{\Phi_{group} N_{group}} = \sum(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta})\right]$ as $Z_{eff} = Z - [\sum(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta})]$

v. $Z_{eff} = 24 - [(13 \times 0.85) + 10] = 24 - 21.05 = 2.95$

EXAMPLE 33: **Calculate the Effective Nuclear Charge Z_{eff} for one 3d electron in Cr^{3+}?**

ELUCIDATION: Considering the example of Zn, we proceed as

i. ${}_Z X^{N\pm} = {}_{24}Cr$

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

iii. $(1s^2)(2s^2 2p^6)(3s^2 3p^6)(3d^2)(\mathbf{3d^1})$ **(**electron under observation is shown in a **bold face;** higher group electrons are shown in RED).

iv. Apply $Z_{eff} = Z^* = Z - \sigma = Z - s = Z - \left[\sum \boldsymbol{\Phi_{group} N_{group}} = \sum(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta})\right]$ as $Z_{eff} = Z - [\sum(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta})]$

v. $Z_{eff} = 24 - [(2 \times 0.35) + 18] = 24 - 18.7 = 5.3$

EXAMPLE 34: **Calculate the Effective Nuclear Charge Z_{eff} for one 3d electron in Cr^{3+}?**

ELUCIDATION: Considering the example of Zn, we proceed as

i. ${}_Z X^{N\pm} = {}_{24}Cr$

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

iii. $(1s^2)(2s^2 2p^6)(\mathbf{3s^2} 3p^6)(3d^4)(3d^1)(4s^1)$ **(**electron under observation is shown in a **bold face;** higher group electrons are shown in RED).

iv. Apply $Z_{eff} = Z^* = Z - \sigma = Z - s = Z - \left[\sum \boldsymbol{\Phi_{group} N_{group}} = \sum(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta})\right]$ as $Z_{eff} = Z - [\sum(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta})]$

v. $Z_{eff} = 24 - [(1 \times 0.35) + 8 \times 0.85 + 2] = 24 - 9.15 = 14.85$

EFFECTIVE NUCLEAR CHARGE Z_{eff} ON THE ATOMIC SURFACE OR PERIPHERY

In Schrödinger's atom there is no real atomic surface; the "atomic surface" used in effective nuclear charge and electronegativity is a conventionally chosen boundary within a diffuse electron density, defined so that chemical behaviour can be compared and predicted. It is the point where the electron density reaches a minimum.

EXAMPLE 35: **Calculate the Effective Nuclear Charge Z_{eff} for one 2p subshell in N?**

ELUCIDATION: Considering the example of Zn, we proceed as

i. ${}_Z X^{N\pm} = {}_7 N$

ii. $[Ar]3d^{10} 4s^2$

iii. $(1s^2)(2s^2 2p^3)$

iv. Apply $Z_{eff} = Z^* = Z - \sigma = Z - s = Z - \left[\sum \boldsymbol{\Phi_{group} N_{group}} = \sum(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta})\right]$ as $Z_{eff} = Z - [\sum(\boldsymbol{\Phi_{group}} \sum \boldsymbol{\eta})]$

v. $Z_{eff} = 7 - [(0.35 \times 5) + 2 \times 0.85] = 7 - 3.45 = 3.55$

APPLICATIONS

The higher the value of the Effective Nuclear Charge, the closer will be the orbital to the nucleus and the energy of the orbital will be lower according to the Bohr's energy equation

$$\boldsymbol{E_n = -21.8x10^{-19}\left(\frac{Z^2}{n^2}\right)J = -21.8x10^{-19}\left(\frac{Z^2}{n^2}\right)Jatom^{-1} = -1313.3\left(\frac{Z^2}{n^2}\right)kJmol^{-1} = -13.6\left(\frac{Z^2}{n^2}\right)eVatom^{-1}}$$

The electrons are removed from the valance shells even though the 4s orbitals are filled before the 3d orbitals because the Z_{eff} value of completely filled 3d subshell is higher than the 4s subshell.

The higher the Z_{eff} value of a given orbital, the higher the ionization enthalpy.

The smaller the atomic size, the higher the ionization enthalpy.
The ionization enthalpy is more for stable electronic configurations i.e. half-filled and full filled electronic configurations, because it is the energy required to remove the electron from the atom and is given by the magnitude of the energy of the electron bound in the atom i.e. $I.E. = [E_n]$
The ionization enthalpy is more for electrons in orbitals with more penetration effect i.e. ionization enthalpy of $s > p > d > f$ orbitals for adjacent atoms only.
For successive ionization enthalpies, any atom have a set of ionization enthalpies having ionization enthalpies for each electron in a neutral atom i.e. $number\ of\ ionization\ enthalpies\ of\ a\ given\ atom\ =\ atomic\ number.$
Moreover $(\text{ionization enthalpy})_{next} > (\text{ionization enthalpy})_{previous}$ e.g. for Na $I_1<I_2<I_3$. This is always true, irrespective of the stability of electronic configurations, because of increased Z_{eff} value.
If $|I_{n+1} - I_n| > 17eV$, Then the Lower oxidation state is more stable. E.g. Sodium.
If $|I_{n+1} - I_n| < 11eV$, Then the Higher oxidation state is more stable. E.g. Magnesium.
If $11eV < |I_{n+1} - I_n| < 17eV$, Then the atom exists in variable oxidation states. E.g. d-block transition metals.

Limitation

1. Why such groupings are adopted.
2. In many electron atoms the Z_{eff} values do not concede with the experimental values.

✧ **Groupwise periodicity:** The atomic radii increase down the group due to the increase the principal quantum number of the valance electron in the atom with a higher atomic number down the group. Therefore, the ionization enthalpy decreases.

✧ **Period wise periodicity:** The atomic radii decrease rightward across a period due to the increase in the effective nuclear charge on the valance electron in the next element lying rightwards in a period. On moving rightwards in a period, the atomic number of the element is increased by unity at each step, consequently the size of the atom gets contracted due to extra attraction on the outermost electron cloud of the valence electrons. Therefore, the ionization enthalpy increases.

ATOMIC NUMBER	SYMBOL	NAME	ELECTRONIC CONFIGURATION
3	Li	LITHIUM	$[He]2s^1$
4	Be	BERYLLIUM	$[He]2s^2$
5	B	BORON	$[He]2s^2 2p^1$
6	C	CARBON	$[He]2s^2 2p^2$
7	N	NITROGEN	$[He]2s^2 2p^3$
8	O	OXYGEN	$[He]2s^2 2p^4$
9	F	FLUORINE	$[He]2s^2 2p^5$
10	Ne	NEON	$[He]2s^2 2p^6$

Examples

By a careful observation of the electronic configurations of the second and third period elements we can predict an order of the first ionization enthalpies as:
Li<B<Be<C<O<N<F<Ne. Na<Al<Mg<Si<S<P<Cl<Ar
The abnormalities can be explained on the bases of stability of:

* The penetration effect of s orbital is more than the p orbital. Therefore, a relatively higher effective nuclear charge Z_{eff} is experienced by the 2s electrons of beryllium because the 2s orbital is closer to the nucleus as compared to the 2p orbital. Therefore, the first ionization enthalpies of **B<Be** and **Al<Mg.**
* The half-filled electronic configurations are more stable than the partially filled electronic configurations. Therefore, the first ionization enthalpies of O<N and S<P

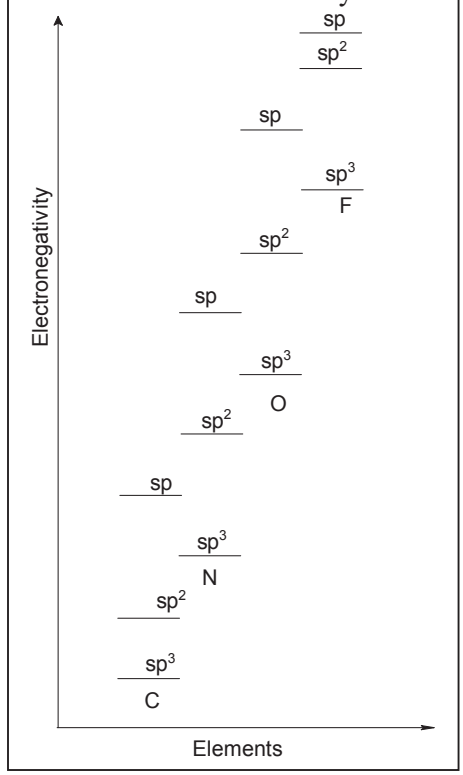
5. Isotopes have same size and same ionization enthalpies. The half-filled electronic configurations include p^3 d^5 and f^7 and NOT s^1, because the s orbitals are deeply buried in the tom and are already very close to the nucleus, which do not make any significant difference in the atomic properties to be studied based on the concept of stable electronic configurations. Moreover, this concept also for second and third periods only and not for the higher periods. This is due to the relatively larger atomic size of the heavier elements. The second ionization energy is in the order O>N as it becomes half-filled electronic configuration in O^+, due to the decrease of atomic size and increased effective nuclear charge $\boldsymbol{Z_{eff}}$. For charged species the ionization enthalpies increased with increased effective nuclear charge $\boldsymbol{Z_{eff}}$. Anions (size increase with increasing negative charge)<Neutral<Cations (size decrease with increasing positive charge). Consider isoelectronic ions. Anions (size increase with increasing negative charge)>Neutral>Cations (size decrease with increasing positive charge). Therefore, ionization enthalpies are in the order Cations> Neutral> Anions e.g. Be^{2+}>Li^+ >He>H. Elements with higher atomic number (corresponding to a higher principal quantum number) have a lower ionization enthalpy e.g. H>Li>Al>Sn. The d block has no fixed order of ionization enthalpies. Ga>Zn due to the penetration effect. Sc>Y>La due to increased atomic size. But in rest of elements in maximum (not all) cases 3d>4d<5d or 5d>3d>4d. It is an imperial concept.

B. Electronegativity: The electronegativity of an element is the relative tendency of the element to attract the *shared electron pair (bond pair)* when a chemical covalent bond is formed. It is denoted by χ, and is affected by the atomic number and the atomic radii of the elements. It is a simplified technique to estimate the magnitude of bond energy and the bond polarity. This was introduced by Jons Jakob Berzelius in 1811. Later, in 1932, Linus Carl Pauling, proposed a scale depending on the energies developed by the **Valance Bond Theory**. The electronegativity of an element is the property of that element when its atoms are present in a **molecule**. Caesium is the least electronegative element with $\chi_{\Gamma} = 0.79$, and fluorene is the most electronegative element with $\chi_{\Gamma} = 3.98$. This is the only relative term among all the other periodic properties. There are three main scales of measuring the Electronegativity of any element. these are Pauling electronegativity, Mulliken electronegativity, Allred–Rochow electronegativity scales.

Carbon is more electronegative then Most of the Metals in the periodic table.

ONE JUMP RULE

The rule was given by Linus Pauling. Applicable in groups with same side atoms Only!



$$\text{Electronegativity } (\chi) \propto \frac{Z_{eff} positive\ oxidation\ state.\ \%s - character}{size.negative\ oxidation\ state}$$

$\boldsymbol{\chi_{C_{sp^3}} < \chi_{C_{sp^2}} < \chi_{C_{sp}}}$ the subscripts show the Hybridizations of Carbon atoms.

ELECTRONEGATIVITY SCALES

Pauling electronegativity: It is a relative scale of electronegativity developed by Linus Carl Pauling in 1932. In this scale the electronegativity of Fluorine F ($\chi_F = 3.98$) is used as a reference. It is the most widely accepted scale of electronegativity. The reference point of the scale was hydrogen initially, with an electronegativity of 2.1, which was later revised to 2.20. another revision in the scale changed the reference to Fluorine F ($\chi_F = 3.98$). The calculation of electronegativity on the Pauling scale, it requires the values of two types of bond dissociation energies. Albert Louis Allred updated the scale and the revised values are used today for chemical analysis.

$\boldsymbol{D_{AB}}$ bond dissociation energy of the heteronuclear bond AB.

$\boldsymbol{D_{AA}}$ bond dissociation energy of the homonuclear bond AA.

$\boldsymbol{D_{BB}}$ bond dissociation energy of the homonuclear bond BB.

According to the Pauling electronegativity scale, the three quantities are related as:

$$D_{AB}^{Expected} = \frac{\boldsymbol{D_{AA} + D_{BB}}}{2}$$

But experimentally the relation is

$$D_{AB}^{Expected} > \frac{\boldsymbol{D_{AA} + D_{BB}}}{2}$$

This excess bond energy Δ is attributed to the ionic character of covalent bonds, as explained by dipole moment.

This excess bond energy Δ is defined by the concepts of geometric mean as

$$\Delta = \boldsymbol{D_{AB} - \sqrt{D_{AA}.D_{BB}}}$$

Pauling hypothesized that the electronegativity difference of the two bonded elements is proportional to the square root of the excess bond energy OR ionic resonance energy Δ.

Therefore,

$$\left|\Delta\chi_{A-B}\right| = \left|\chi_A - \chi_B\right|_P = k\sqrt{\Delta} = \sqrt{\boldsymbol{D_{AB} - \sqrt{D_{AA}.D_{BB}}}}$$

Now, the electronegativity difference can be calculated using different units of the bond dissociation energies as:

$$\left|\chi_A - \chi_B\right|_P = \sqrt{\boldsymbol{D_{AB} - \sqrt{D_{AA}.D_{BB}}}} \qquad \text{(energies in eV)}$$

$$\left|\chi_A - \chi_B\right|_P = 0.208\sqrt{\boldsymbol{D_{AB} - \sqrt{D_{AA}.D_{BB}}}} \qquad \text{(energies in } kcalmol^{-1}\text{)}$$

Pauling scale is the standard scale for electronegativity.

Mulliken electronegativity: Robert Sanderson Mulliken proposed the scale in 1934. The Mulliken electronegativity can only be calculated for an element whose electron affinity is known. This scale is called the absolute electronegativity scale.

In this scale:

$$\boldsymbol{\chi_M = \frac{E_i + E_{ea}}{2}} \qquad \text{(values in eV)}$$

$$\boldsymbol{\chi_M = 2.8\chi_P}$$

EXAMPLE: If the ionization energy and electron affinity of A is $2.7kJmol^{-1}$ and $4.3kJmol^{-1}$ respectively, the electronegativity of A in eV is ($1eV = 96.45kJmol^{-1}$)?

ELUCIDATION: From the Mulliken electronegativity relation

$$\chi_M = \frac{E_i + E_{ea}}{2} = \frac{\frac{2.7}{96.45} + \frac{4.3}{96.45}}{2} = 0.036eV$$

$$\chi_M = 2.8\chi_P$$

$$\Rightarrow \chi_P = \frac{\chi_M}{2.8} = \frac{0.036eV}{2.8} = 0.0129eV$$

Allred–Rochow electronegativity: Albert Louis Allred and Eugene George Rochow proposed the scale in 1958.
In this scale:

$\chi_{AR} = \frac{0.359Z_{eff}}{r_{cov}^2} + 0.744$ (Z_{eff} at periphery according to the Slater's rules) (r_{cov} in Å)

Robert Thomas Sanderson noticed a relation of the Mulliken electronegativity with some other atomic properties. His method was based on the reciprocals of atomic volume. He developed electronegativity equalization in 1951. Mulliken is known as Founder of Molecular Orbital Theory; Pioneer of Quantum Chemistry. He was awarded the 1966 Chemistry Nobel Prize.
EXAMPLE: Find the electronegativity of nitrogen if its covalent radius is 0.8 Å?
ELUCIDATION: We know, $\chi_{AR} = \frac{0.359Z_{eff}}{r_{cov}^2} + 0.744$
From the Slater's rules we have,
$Z_{eff} = 7 - [(5 \times 0.35) + (2 \times 0.85)] = 7 - 3.45 = 3.55$
Therefore, $\chi_{AR} = \frac{0.359Z_{eff}}{r_{cov}^2} + 0.744 = \frac{0.359 \times 3.55}{(0.8\text{Å})^2} + 0.744 = 2.735$

Allen electronegativity: The electronegativity is related to the average of the spectroscopic energies of the s and p electrons of the valence shells of free atoms. Therefore, the Allen electronegativity is sometimes referred to as the spectroscopic electronegativities.
In this scale:

$$\chi_{AR} = \frac{s\varepsilon_s + p\varepsilon_p}{s + p}$$

Where s,p are the number of electrons in the s and p orbitals of the valence shells, and ε_s and ε_p are the average of the spectroscopic energies of the s and p electrons of the valence shells of free atoms.

Periodic trend of electronegativity: The electronegativity increases from left to right across a period, not including the Noble gases of group 18. Therefore, Fluorine is the most electronegative element and Caesium is the least. There are however some disorderliness with this, as Gallium and Germanium have higher electronegativities than Aluminium and Silicon, respectively, because of the d-block contraction. Elements of the fourth period immediately after the first row of the transition metals have unusually small atomic radii because the 3d-electrons are not effective at shielding the increased nuclear charge, and smaller atomic size correlates with higher electronegativity. The anomalously high electronegativity of lead, in particular, when compared to thallium and bismuth, is an artifact of electronegativity varying with oxidation state. Its electronegativity conforms better to trends if it is quoted for the +2 state with a Pauling value of 1.87 instead of the +4 state.

APPLICATIONS

1. **Predation of acidity of hydracids**: Across the periods of the periodic table electronegativity determines therefore, the acidity as in $HF > H_2O > NH_3 > CH_4$ But down the group, atomic size dominates therefore, the acidity is in the order$HI > HBr > HCl > HF$, as the bond of HI is the weakest due to weak overlap of the 1s-5p-orbital, moreover the electron density of HI is least.
2. **Predation of Lewis basicity of hydracids:** Across the periods of the periodic table electronegativity determines therefore, the Lewis basicity of hydracids is in the order $HF < H_2O < NH_3$. But down the group, atomic size dominates therefore, the Lewis basicity of hydracids is in the order $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.
3. **Predation of Polarity:** $|\Delta\chi_{A-B}| = 0$, the molecule is nonpolar; $|\Delta\chi_{A-B}| \neq 0$, the molecule is polar. Higher the electronegativity difference, higher is the polarity E.g.$NH_3 > AsH_3 > PH_3$
4. The Hannay-Smith equation, used to estimate the percentage of ionic character in a covalent bond, was proposed by David B. Hannay and Clinton N. Smith in 1953 is based on the electronegativity difference, and is given as $\%ionic\ cherecter = 16|\chi_A - \chi_B|_P + 3.5|\chi_A - \chi_B|_P^2$

5. The electronegativity difference can be a factor to predict the acidity of oxoacids.
6. **Predation of the nature of oxides:** The electronegativity difference can be a factor to predict the nature of oxides. Oxides are of four types:

A. Acidic Oxides: These react with water to give an acidic aquas solution. E.g. non-metallic oxides e.g. Cl_2O_7,P_4O_{10}. There have a high oxidation state$\geq +3$. Higher the oxidation state higher is its basicity. $Acidity \propto electronegativity.oxidation\ state.Z_{eff}$. E.g. $Mn_2O_7 > CrO_3$

B. Basic Oxides: These react with water to give an alkaline aquas solution. E.g. metallic oxides e.g. Na_2O, CaO. These have a low oxidation state $\leq +2$. These give hydroxide ion OH^- in water. Lower the oxidation state higher is its basicity. $Basicity \propto \frac{1}{electronegativity.oxidation\ state.Z_{eff}}$

C. Neutral Oxides: These neither react with acids nor with bases. Examples include CO, NO, N_2O.

D. Amphoteric Oxides: These react with acids as well as bases.

SNO.	ATOMIC NUMBER	SYMBOL	NAME	AMPHOTERIC OXIDE
1	4	Be	BERYLLIUM	BeO
2	13	Al	ALUMINIUM	Al_2O_3
3	30	Zn	ZINC	ZnO
4	31	Ga	GALIUM	Ga_2O_3
5	32	Ge	GERMANIUM	GeO and GeO_2
6	33	As	ARSENIC	As_2O_3
7	49	In	INDIUM	In_2O_3
8	50	Sn	TIN	SnO and SnO_2
9	51	Sb	ANTIMONY	Sb_2O_3
10	82	Pb	LEAD	PbO and PbO_2
11	83	Bi	BISMUTH	Bi_2O_3

D. Metallic Character (electropositive character): Tendency to form cations by ionization. decreases across a period.

Groupwise periodicity: The atomic radii increase down the group due to the increase the principal quantum number of the valance electron in the atom with a higher atomic number down the group. Therefore, the ionization enthalpy decreases. Metallic character increases down the group.

Period wise periodicity: The atomic radii decrease rightward across a period due to the increase in the effective nuclear charge on the valance electron in the next element lying rightwards in a period. On moving rightwards in a period, the atomic number of the element is increased by unity at each step, consequently the size of the atom gets contracted due to extra attraction on the outermost electron cloud of the valence electrons. Therefore, the ionization enthalpy increases. Metallic character decreases across a period.

E. Reducing Power: in gaseous state the species with lower ionization enthalpy will oxidise first and will have a higher reducing power. Therefore, it's a good reducing gent (reductant).

Groupwise periodicity: The atomic radii increase down the group due to the increase the principal quantum number of the valance electron in the atom with a higher atomic number down the group. Therefore, the ionization enthalpy decreases. Metallic character increases down the group. Therefore, reducing power increases

Period wise periodicity: The atomic radii decrease rightward across a period due to the increase in the effective nuclear charge on the valance electron in the next element lying rightwards in a period. On moving rightwards in a period, the atomic number of the element is increased by unity at each step, consequently the size of the atom gets

contracted due to extra attraction on the outermost electron cloud of the valence electrons. Therefore, the ionization enthalpy increases. Metallic character decreases across a period. Therefore, reducing power decreases.

This is not work in electrochemical series due to the highly exothermic hydration (solvation) process. When all the valence electrons are removed then the ionization enthalpy value show an abrupt spike. This indicates that the number of valence electrons of an atom are equal to the number of ionizations before the spike appears.

F. ELECTRON GAIN ENTHALPY $(\Delta_{eg}H)$: The amount of energy, involved (absorbed or released), when an electron is added to an isolated gaseous atom. It may be positive (absorbed) as well as negative (released). The value of $(\Delta_{eg}H)$ is mostly negative except for Noble gases, exactly half-filled and completely filled configurations e.g. Alkaline Earth Metals (group 2). The process can be represented as $A \xrightarrow{e^-} A^-$. The second electron gain enthalpy is always Positive because the accommodation of an extra electron on an anion leads to strong interelectronic repulsions, e.g. Oxygen have highly positive $(\Delta_{eg}H) = 600kJmol^{-1}$ value. But, the species O^{2-} (oxide anion) exist, despite the formation of oxide anion is energetically forbidden but oxides exist because of the release of the energy known as Lattice energy which compensates the energy demand of the ionization of Calcium and electron gain of Oxygen.

G. ELECTRON AFFINITY (E_{ea}): The tendency of an isolated gaseous atom to accept one electron.

The two terms are related as $E_{ea} = -\Delta_{eg}H - \frac{5}{2}RT$

Further, ignoring the term $-\frac{5}{2}RT$ at room temperature, we have, $E_{ea} = -\Delta_{eg}H$.

The higher the energy absorption (positive) electron gain enthalpy, the lower is the electron affinity (lower tendency to accept the electron, (negative electron affinity)); e.g. Neon and the higher release of energy (negative) electron gain enthalpy, the higher is the electron affinity (higher tendency to accept the electron, (positive electron affinity)) e.g. Carbon.

FACTORS AFFECTING ELECTRON AFFINITY OR ELECTRON GAIN ENTHALPY

$E_{ea} \propto \Delta_{eg}H \propto \frac{Z_{eff}}{size}$

Element	Li	Na	K	Rb	Cs
$\Delta_{eg}HkJmol^{-1}$	-60	-53	-48	-47	-46

The electron gain enthalpy OR electron affinity decreases down the group. The electron gain enthalpy OR electron affinity increases across a period.

For second period the electron affinity is in the order $Ne < Be < N < B < Li < C < O < F$.

The 2s orbital is closer to nucleus therefore, the electron affinity of $B < Li$

The main exception for fluorine regarding its electron affinity is that its electron affinity is lower than chlorine, defying the general trend of decrease of the electron affinity down the group. This is because of the fact that Fluorine is smaller in size and in the electron, accepting process it has a stronger interelectronic repulsion factor; therefore, the electron affinity of $F < Cl$. Chlorine is the element with highest electron affinity in the whole periodic table.

Group 15 $As > Sb > Bi > P > N$

Group 16 $S > Se > Te > Po > O$

Group 17 $F < Cl > Br > I$

The elements with highest electronegativity and electron affinity lie in the same group (Group 17 (Halogen family)).

4C. IUPAC NOMENCLATURE OF THE ELEMENTS WITH AOMIC NUMBER GREATER THAN 100

There are some controversial names among the heavier elements with atomic numbers greater than hundred. To avoid these controversies IUPAC adapted some temporary rules for a systematic name for elements in the year 1978.

These rules are:

1. The name is related to the atomic number of the element through the numerical roots.

Number	0	1	2	3	4	5	6	7	8	9
Root	Nil	Un	Bi	Tri	Quard	Pent	Hex	Sept	Oct	Enn
Initial symbols	n	u	b	t	q	p	h	s	o	e

2. The roots are combined in the order of the digits of atomic number, and terminated by ium to complete the spelling of the name.

3. The final n in enn is deleted when it occurs before nil

4. The final I in bi and tri are deleted when they occur before ium.

5. The chemical symbol of the element is composed of the initial symbols for the numerical roots in the order of the digits of atomic number.

Atomic number	IUPAC NAMING			
	Temporary symbol	Temporary name	Official symbol	Official name
101	Unu	Unnilunium	Md	Mendelevium
102	Unb	Unnilbium	No	Nobelium
103	Unt	Unniltrium	Lr	Lawrencium
104	Unq	Unnilquardium	Rf	Rutherfordium
105	Unp	Unnilpentium	Db	Dubnium
106	Unh	Unnilhexium	Sg	Seaborgium
107	Uns	Unnilseptium	Bh	Bohrium
108	Uno	Unniloctium	Hs	Hassium
109	Une	Unnilennium	Mt	Meitnerium
110	Uun	Ununnilium	Ds	Darmstadtium
111	Uuu	Unununium	Rg	Roentgenium
112	Uub	Ununbium	Cn	Copernicium
113	Uut	Ununtrium	Nh	Nihonium
114	Uuq	Ununquardium	Fl	Flerovium
115	Uup	Ununpentium	Mc	Moscovium
116	Uuh	Ununhexium	Lv	Livermorium
117	Uus	Ununseptium	Ts	Tennessine
118	Uuo	Ununoctium	Og	Oganesson

4D. NAMING CONTROVERSIES OF CHEMICAL ELEMENTS

The names of elements and compounds are officially declared by IUPAC (International Union of Pure and Applied Chemistry). It's the supreme governing body of rules followed for correct and effective chemical analysis. Conventionally the rights of naming an element is safe with its discoverers but, sometimes the names are trapped in a controversy due to main reasons:

Who first developed the concrete conclusive evidence for the existence of an element or what evidence was in fact conclusive. Such controversies are resolved by the IUPAC rules of nomenclature of chemical elements with atomic number greater than 100. There are some more controversies and a story of their solutions.

1. **Vanadium:** It's the chemical element with atomic number 23. It was originally discovered by Andrés Manuel del Río Fernández in 1801. He found experimentally that it forms salts with a wide variety of colours, therefore, he named the element **Panchromium** (Greek for all colours). He later renamed this substance **Erythronium**, since most of the salts turned red when heated. In 1831 Nils

Gabriel Sefström, a Swedish chemist, rediscovered the element and was close to calling it **Vanadin** in Swedish which changed to **Vanadium** in other languages including German and English.

Ernest Orlando Lawrence (8 August 1901-27 August 1958)

2. **Niobium:** It's the element with atomic number 41. It was discovered by Charles Hatchett named it as Columbium in 1801. William Hyde Wollaston published '*On the Identity of Columbium and Tantalum' in 1809. Heinrich Rose* in 1846 discovered that tantalite contained another element whose properties were close to tantalum and named it Niobium. This name was officially adopted by IUPAC in 1950 after 100 years of controversy.
3. **Ytterbium:** it's a chemical element with atomic number 70. It was discovered by Jean Charles Galissard de Marignac in 1878. He called it as Ytterbium, but he actually assumed yetterbia as a new element which was actually an oxide mineral a mineral. Georges Urbain in 1907 isolated element 70 and element 71 from **Ytterbia**. He named element 70 **neoytterbium** ("new ytterbium") and called element 71 **lutecium**. Carl Auer von Welsbach suggested the names **Aldebaranium** (**Ad**), after the star Aldebaran (in the constellation of Taurus), for element 70 (**ytterbium**), and **cassiopeium** (**Cp**), after the constellation Cassiopeia, for element 71 (**lutetium**), but both proposals were rejected. **Neoytterbium** (element 70) was eventually reverted to ytterbium (following Marignac), and in 1949, the spelling of **lutecium** (element 71) was changed to **lutetium**.

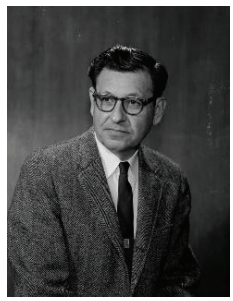
Carl Auer von Welsbach (1 September1858-4 Augst 1929)

At the time of discoveries of the elements with atomic numbers 102-109, there was a naming conflict between the Russian and American scientists. This was due to the situation of cold war at that time. To provide a solution to the conflict the IUPAC adapted a temporary system of nomenclature of elements which was working until the element's official name was declared by IUPAC. The names of elements with atomic numbers 104-106 were the major subject of controversial views of the two scientific communities. The controversy came to an end in 1997 when IUPAC officially named the elements with atomic numbers 107-109. This is sometimes also referred to as the **trans fermium wars**

Charles Hatchett (2 January 1765-10 March 1847)

Heinrich Rose (6 August 1795-27 January 1864)

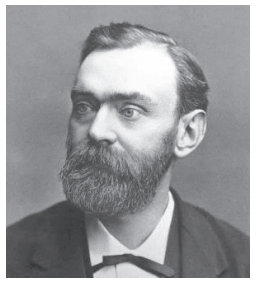
Otto Hahn (8 March 1879-28 July 1968)



Albert Ghiorso (15 July 1915-26 December 2010)

because it follows the nomenclature of the elements with atomic numbers greater than 100. The atomic number 100 is of the element Fermium.

4. **Nobelium:** It is the element with atomic number 102 and is named in the honour of Alfred Bernhard Nobel. He is the one on whose name is the world's largest prestigious Nobel prize exist. And moreover, he invented dynamite.
5. **Lawrencium:** It is the element with atomic number 103. It is named after Ernest Orlando Lawrence.
6. **Rutherfordium** is a synthetic chemical element; it has symbol **Rf** and atomic number 104. It is named after physicist Ernest Rutherford. This was first suggested by the US scientists. Before the official declaration of the now well-known name in 1997 by IUPAC, the name, '**Kurchatovium**' was suggested by the soviet scientists in the honour of Igor Vasilyevich Kurchatov who is also known as "father of the Russian atomic bomb".
7. **Dubnium:** It is an element with atomic number 105. It was named as **Nielsbohrium** (**Ns**) after Niels Bohr, by the soviets, and Hahnium after Otto Hahn but IUPAC declared the name **Dubnium.**
8. **Seaborgium:** It is an element with atomic number of 106. It was discovered simultaneously in June 1974 by soviets' team lead by **Georgii Nikolayevich Flyorov (Flerov),** reporting the production of $^{259}_{106}Sg$; and by Albert Ghiorso's American research group in September 1974 reporting the production of $^{263}_{106}Sg$. After the discovery the American research group suggested the now well-known name, **Seaborgium after** Glenn Theodore Seaborg. But the problem with the name was that Seaborg was still alive who passed away on February 25, 1999. Further in 1992 an international committee declared that there must be a share of credit between Berkeley and Dubna laboratories for the discovery. IUPAC adopted **unnilhexium** (**Unh**) as a temporary systematic element name. Afterwards this only name was recognized internationally. In India and some other countries before 1997, the names for the element 104 had a Soviet proposal kurchatovium and element 105 had an American proposal hahnium.
9. **Bohrium:** It is an element with atomic number 107. It was named as **Nielsbohrium** (**Ns**) after Niels Bohr. But this was a different proposal from the same proposal for Dubnium. IUPAC adapted **Unnilseptium (Uns)** as a temporary systematic name. in 1994 IUPAC suggested the use of Bohrium as a name for the element, in honour to Neils Bohr; but only using his surname. This was opposed due to some confusion with Boron which was



Alfred Bernhard Nobel (21 October 1833-10 December 1896)

Igor Vasilyevich Kurchatov (12 January 1903-7 February 1960)

Glenn Theodore Seaborg (19 April 1912- 25 February 1999)

Niels Henrik David Bohr (7 October 1885-18 November 1962)

called as Borium in languages like Latin. The name Bohrium was officially adapted as the name of the element 107 in the year 1997.

10. **Hassium:** IUPAC adapted a temporary name Unniloctium (Uno) as a systematic name of the element 108, which was named as Hassium After a German state of Hesse in 1997.
11. **Meitnerium:** The element 109 was named temporarily as Unnilennium (Une), which was changed to **Meitnerium in 1997** after **Lise Meitner**.

Lise Meitner
(7 November 1878-27 October 1968)

4E. INORGANIC ION

Ion: Any Charged Species other than the fundamental subatomic particles.

Cation: Positively Charged Ion. This species has less electrons than protons (by convention). Cation is also made from two words, '*Kato*' + 'Ion'. 'Ion' means 'To Go' and '*Kato*' means down (here, negative can be thought of as 'down' direction and a Cation goes towards the negative terminal). Cation is a result of an oxidation reaction (loss of electrons).

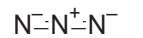
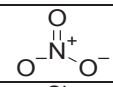
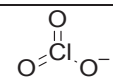
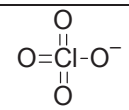
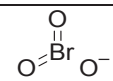
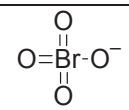
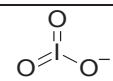
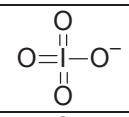
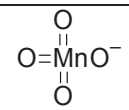
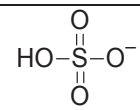
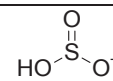
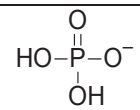
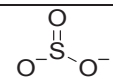
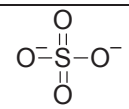
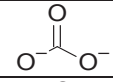
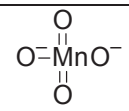
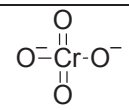
William Whewell
(24 May 1794-6 March 1866)

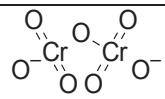
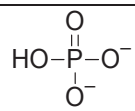
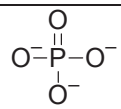
Anion: Negatively Charged Ion. This species has more electrons than protons (by convention). Anion is made from two words, '*Ano*' + 'Ion'. 'Ion' means 'To Go' and '*Ano*' means up (as positive can be thought of as 'up' direction and an Anion goes towards the positive terminal). Anion is a product of Reduction reaction (gain of electron). The Terms "Anion", "Cation", were Coined by William Whewell in 1834. There are a number of ions in inorganic chemistry which are classified in different classes in a specific order under different criteria depending on various properties.

THE INORGANIC IONS CLASSIFICATION KEY

ATOMIC			
VALANCY	ATOMIC NUMBER	SYMBOL	NAME
MONOVALENT	1	H^-	HYDERIDE
	9	F^-	FLUORIDE
	17	Cl^-	CHLORIDE
	35	Br^-	BROMIDE
	53	I^-	IODIDE
BIVALENT	8	O^{2-}	OXIDE
	16	S^{2-}	SULPHIDE
TRIVALENT	7	N^{3-}	NITRIDE
	15	P^{3-}	PHOSPHIDE

POLYATOMIC	
SYMBOL	NAME
CN^-	CYNIDE
ClO^-	HYPOCHLORIDE
NC^-	ISOCYNIDE
SCN^-	THIOCYNATE
NCS^-	ISOTHIOCYNATE
BrO^-	HYPOBROMIDE
IO^-	HYPOIODIDE
O^{2-}	SUPEROXIDE
$[Fe(CN)_6]^{3-}$	FERRICYNIDE
$[Fe(CN)_6]^{4-}$	FERROCYNIDE
C_2^{2-}	CARBIDE

VALANCY	SYMBOL	NAME	STRUCTURE
MONOVALENT	N_3^-	AZIDE	
	NO_2^-	NITRITE	
	NO_3^-	NITRATE	
	ClO_2^-	CHLORITE	
	ClO_3^-	CHLORATE	
	ClO_4^-	PERCHLORATE	
	BrO_2^-	BROMITE	
	BrO_3^-	BROMATE	
	BrO_4^-	PERBROMATE	
	IO_2^-	IODITE	
	IO_3^-	IODATE	
	IO_4^-	PERIODATE	
	MnO_4^-	PERMANGANATE	
	HSO_4^-	BISULPHATE	
	HSO_3^-	BISULPHITE	
	$H_2PO_4^-$	DIHYDROGEN PHOSPHATE	
BIVALENT	O_2^{2-}	PEROXIDE	
	SO_3^{2-}	SULPHITE	
	SO_4^{2-}	SULPHATE	
	CO_3^{2-}	CARBONATE	
	MnO_4^{2-}	MANGANATE	
	CrO_4^{2-}	CHROMATE	

	$Cr_2O_7^{2-}$	DICHROMATE	
	HPO_4^{2-}	HYDROGEN PHOSPHAT	
Trivalent	PO_4^{3-}	PHOSPHATE	

4F. DISCRIPTIVE FACTS ABOUT CHEMICAL ELEMENTS

1. Hydrogen forms covalent bonds through its single electron and exhibits both protic and hydridic behaviour.
2. Helium is chemically inert due to a filled 1s orbital.
3. Lithium is a small, highly polarizing alkali metal with pronounced covalent character in its compounds.
4. Beryllium forms predominantly covalent compounds due to high charge density.
5. Boron is electron-deficient and forms multicentre bonds.
6. Carbon forms stable chains and frameworks through strong C–C covalent bonding.
7. Nitrogen Favors multiple bonding and displays a wide range of oxidation states.
8. Oxygen is a strong oxidizing element with high electronegativity.
9. Fluorine forms highly polar bonds and stabilizes extreme oxidation states.
10. Neon is chemically unreactive under ordinary conditions.
11. Sodium readily forms Na^+ ions and ionic lattices.
12. Magnesium forms largely ionic compounds with significant covalent character.
13. Aluminium exhibits amphoteric behavior in its oxide and hydroxide.
14. Silicon forms extended covalent networks analogous to carbon.
15. Phosphorus displays structural diversity and variable coordination numbers.
16. Sulphur catenates readily and exhibits extensive allotropy.
17. Chlorine is a strong oxidant forming both covalent and ionic compounds. It is the element with highest electron affinity in the whole periodic table.
18. Argon is chemically inert owing to a closed valence shell.
19. Potassium is a highly electropositive metal with low ionisation energy.
20. Calcium forms stable ionic compounds and coordination complexes.
21. Scandium exhibits a dominant +3 oxidation state with ionic character.
22. Titanium forms stable oxides and shows variable coordination chemistry.
23. Vanadium displays multiple oxidation states with rich redox chemistry.
24. Chromium forms colored compounds due to d–d electronic transitions.
25. Manganese exhibits the widest range of oxidation states among transition metals.
26. Iron participates in reversible redox processes central to bioinorganic chemistry.
27. Cobalt stabilizes coordination complexes with diverse geometries.
28. Nickel forms stable complexes and catalyses hydrogenation reactions.
29. Copper readily interconverts between Cu^+ and Cu^{2+} oxidation states.
30. Zinc forms d^{10} complexes lacking ligand field stabilization energy.
31. Gallium melts near room temperature due to weak metallic bonding.
32. Germanium bridges metallic and non-metallic behaviour.
33. Arsenic displays metalloid character and variable bonding modes.
34. Selenium forms chain and ring allotropes with moderate electronegativity.
35. Bromine is a volatile molecular liquid with strong oxidising ability.
36. Krypton forms compounds only under extreme conditions.
37. Rubidium is a highly reactive alkali metal with weak metal–metal bonding.
38. Strontium forms ionic compounds resembling those of calcium.
39. Yttrium behaves as a typical trivalent transition metal.
40. Zirconium forms highly stable oxides and coordination compounds.
41. Niobium exhibits high resistance to corrosion through oxide passivation.
42. Molybdenum forms multiple metal–metal bonds in cluster compounds.
43. Technetium has no stable isotopes and displays rich coordination chemistry.

44. Ruthenium forms organometallic complexes used in catalysis.
45. Rhodium is a noble metal with exceptional catalytic efficiency.
46. Palladium absorbs hydrogen and catalyses C–C coupling reactions.
47. Silver forms linear coordination complexes and conducts electricity efficiently.
48. Cadmium forms soft-acid complexes with sulphur donors.
49. Indium exhibits metallic bonding with low lattice energy.
50. Tin shows allotropy and variable oxidation states (+2 and +4).
51. Antimony displays intermediate behaviour between metals and non-metals.
52. Tellurium forms covalent chains and exhibits semiconducting properties.
53. Iodine is a molecular solid with metallic lustre and soft oxidizing character.
54. Xenon forms stable compounds with fluorine and oxygen.
55. Cesium has the lowest ionisation energy among stable elements.
56. Barium forms insoluble sulfate and reactive oxides.
57. Lanthanum initiates the lanthanide contraction.
58. Cerium readily forms Ce^{4+} through oxidation.
59. Praseodymium forms coloured salts due to f–f transitions.
60. Neodymium exhibits strong magnetic behaviour.
61. Promethium is radioactive and absent from natural terrestrial matter.
62. Samarium forms mixed-valence compounds.
63. Europium stabilizes the +2-oxidation state unusually well.
64. Gadolinium has a high neutron capture cross-section.
65. Terbium forms luminescent compounds.
66. Dysprosium exhibits high magnetic anisotropy.
67. Holmium has one of the highest magnetic moments.
68. Erbium shows sharp f-electron emission bands.
69. Thulium is the least abundant stable lanthanide.
70. Ytterbium displays both +2 and +3 oxidation states.
71. Lutetium marks the end of the lanthanide series.
72. Hafnium closely resembles zirconium in chemical behaviour.
73. Tantalum resists corrosion due to a stable oxide layer.
74. Tungsten forms extremely strong metal–metal bonds and high-melting compounds.
75. Rhenium forms stable high-oxidation-state oxides.
76. Osmium is extremely dense and forms volatile tetroxide.
77. Iridium is highly inert and corrosion-resistant.
78. Platinum forms square-planar complexes and catalyse redox reactions.
79. Gold stabilizes soft-ligand coordination complexes.
80. Mercury exhibits weak metallic bonding resulting in liquid state.
81. Thallium Favors the +1 oxidation state due to inert pair effect.
82. Lead exhibits variable coordination and strong inert pair effects.
83. Bismuth forms weakly basic oxides and covalent compounds.
84. Polonium is radioactive and metallic in character.
85. Astatine displays halogen-like chemistry with metallic tendencies.
86. Radon is a radioactive noble gas.
87. Francium is extremely unstable and highly electropositive.
88. Radium forms radioactive alkaline earth compounds.
89. Actinium initiates the actinide series.
90. Thorium forms stable tetravalent compounds.
91. Protactinium shows complex actinide bonding behaviour.
92. Uranium forms linear uranyl species with strong U=O bonds.
93. Neptunium exhibits multiple oxidation states in solution.
94. Plutonium displays complex phase and redox chemistry.
95. Americium stabilizes the +3-oxidation state.
96. Curium behaves as a typical trivalent actinide.
97. Berkelium forms primarily +3 ionic compounds.
98. Californium is a strong neutron emitter.
99. Einsteinium is accessible only through nuclear synthesis.

100. Fermium exhibits actinide-like coordination chemistry.
101. Mendelevium exists only in trace synthetic quantities.
102. Nobelium stabilizes the +2-oxidation state unusually well.
103. Lawrencium exhibits relativistic effects in its valence shell.
104. Rutherfordium displays group-4-like chemistry.
105. Dubnium shows tantalum-like chemical behaviour.
106. Seaborgium forms volatile oxychlorides.
107. Bohrium exhibits rhenium-like properties.
108. Hassium forms a volatile tetroxide.
109. Meitnerium is known only from single-atom experiments.
110. Darmstadtium exhibits platinum-group character.
111. Roentgenium is expected to resemble gold chemically.
112. Copernicium shows weak metallic bonding.
113. Nihonium displays post-transition-metal behaviour.
114. Flerovium exhibits unusually low reactivity.
115. Moscovium shows strong relativistic effects.
116. Livermorium behaves as a heavy chalcogen.
117. Tennessine exhibits mixed halogen–metal character.
118. Oganesson shows significant deviation from noble-gas inertness due to relativistic effects.

CHEMISTRY: KNOWLEDGE, THOUGHT, AND LEGACY

From the earliest attempts at quantifying natural phenomena to the structured elegance of the modern periodic table, the development of chemistry has been a gradual refinement of how matter is described, measured, and understood. What began as observation and comparison evolved into a precise scientific language in which atoms, molecules, and their interactions are expressed through mathematical relationships. Over time, chemical equations and physical principles revealed an underlying order, bringing chemistry into deeper unity with the broader framework of physical science.

This transformation was neither sudden nor attributable to any single individual. Its foundations were established through centuries of inquiry and later strengthened by the atomic theories of John Dalton, J. J. Thomson, Ernest Rutherford, and Niels Bohr. The conceptual structure of the atom emerged progressively through their successive contributions. Dmitri Mendeleev's periodic classification unified the known elements into a coherent system, later refined by Henry Moseley's identification of atomic number as the fundamental ordering principle and further developed through the formulation of quantum mechanics.

Beyond experimental discovery and mathematical formulation lies a broader understanding of scientific knowledge itself. Scientific understanding is not only discovered but also constructed, communicated, and preserved through human effort. In this context, articulation plays a central role in intellectual progress, as reflected in the classical principles:

Docendo disco, scribendo cogito.
(I learn by teaching; I think by writing.)
Docendo discimus, scribendo cogitamus.
(We learn by teaching; we think by writing.)
Discere docendo; cogitare scribendo.
(To learn by teaching; to think by writing.)

These expressions emphasize that knowledge is clarified through explanation and stabilized through written form. Teaching refines understanding, while writing transforms thought into a durable intellectual structure.

A philosophical idea in intellectual history holds that human continuity may be understood through the persistence of ideas beyond individual existence. This idea is often expressed as: *"The only way one can hope to live after death is if one leaves something that posterity can remember him for."* In this spirit, **Isaac Newton** reflected with enduring clarity, **"If I have seen further, it is by standing on the shoulders of Giants."** Complementing this vision, **Marie Curie** affirmed with quiet resolve, **"Nothing in life is to be feared, it is only to be understood."** Scientific knowledge is cumulative, shaped not only by discovery but by perseverance and intellectual courage. The atomic models developed by John Dalton, J. J. Thomson, Ernest Rutherford, and Niels Bohr continue to form the conceptual foundation of modern chemistry, their contributions remaining integral to contemporary scientific understanding. Through teaching, writing, and discovery, scientific ideas are transformed into enduring structures of knowledge that extend beyond individual lifetimes. Thus, chemistry stands at the intersection of mathematics and matter—between numerical precision and material reality; where learning is refined through teaching, thought is clarified through writing, and knowledge, once formed, becomes part of the enduring intellectual legacy of those who shaped it:

Discere docendo; cogitare scribendo."

ADDENDUM: MATHEMATICAL IDENTITIES

Though mathematics is used in all fields of chemistry, and for that matter, science, in the context of physical chemistry the knowledge of some mathematical concepts become extremely important. All these concepts are summarised below.

Trigonometry										
ANGLES AND RATIO VALUES										
Angle → / Ratio ↓	0°	30°	45°	60°	90°	120°	135°	150°	180°	270°
$sin\theta = \left(\frac{P}{H}\right)$	0	$\frac{1}{2}$	$\frac{1}{\sqrt{2}}$	$\frac{\sqrt{3}}{2}$	1	$\frac{\sqrt{3}}{2}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2}$	0	-1
$cos\theta = \left(\frac{B}{H}\right)$	1	$\frac{\sqrt{3}}{2}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2}$	0	$-\frac{1}{2}$	$-\frac{1}{\sqrt{2}}$	$-\frac{\sqrt{3}}{2}$	1	0
$tan\theta = \left(\frac{P}{B}\right)$	0	$\frac{1}{\sqrt{3}}$	1	$\sqrt{3}$		$-\sqrt{3}$	-1	$-\frac{1}{\sqrt{3}}$	0	
$cosec\theta = \left(\frac{H}{P}\right)$		2	$\sqrt{2}$	$\frac{2}{\sqrt{3}}$	1	$\frac{2}{\sqrt{3}}$	$\sqrt{2}$	2		-1
$sec\theta = \left(\frac{H}{B}\right)$	1	$\frac{2}{\sqrt{3}}$	$\sqrt{2}$	2		2	$\sqrt{2}$	$\frac{2}{\sqrt{3}}$	-1	
$cot\theta = \left(\frac{B}{P}\right)$		$\sqrt{3}$	1	$\frac{1}{\sqrt{3}}$	0	$\frac{1}{\sqrt{3}}$	1	$\sqrt{3}$		0
Radian $\pi rad = 180°$	0	$\frac{\pi}{6}$	$\frac{\pi}{4}$	$\frac{\pi}{3}$	$\frac{\pi}{2}$	$\frac{2\pi}{3}$	$\frac{3\pi}{4}$	$\frac{5\pi}{6}$	π	$\frac{3\pi}{2}$

Trigonometric Identities		
CLASS	SNO	EQUATION
Angle sum	1	$Sin(A+B) = SinA.CosB + CosA.SinB$
	2	$Cos(A+B) = CosA.CosB - SinA.SinB$
	3	$Tan(A+B) = \frac{TanA + TanB}{1 - TanA.TanB}$
	4	$Cot(A+B) = \frac{CotA.CotB - 1}{CotA + CotB}$
Angle difference	5	$Sin(A-B) = SinA.CosB - CosA.SinB$
	6	$Cos(A-B) = CosA.CosB + SinA.SinB$
	7	$Tan(A-B) = \frac{TanA - TanB}{1 + TanA.TanB}$
	8	$Cot(A-B) = \frac{CotA.CotB + 1}{CotB - CotA}$
Sum of ratio	9	$SinA + SinB = 2Sin\left(\frac{A+B}{2}\right)Cos\left(\frac{A-B}{2}\right)$
	10	$CosA + CosB = 2Cos\left(\frac{A+B}{2}\right)Cos\left(\frac{A-B}{2}\right)$
Difference of ratios	11	$SinA - SinB = 2Cos\left(\frac{A+B}{2}\right)Sin\left(\frac{A-B}{2}\right)$
	12	$CosA - CosB = 2Sin\left(\frac{A+B}{2}\right)Sin\left(\frac{A-B}{2}\right)$
	13	$Sin2A = 2SinACosA = \frac{2TanA}{1 + Tan^2A}$

Double angle formula	14	$Cos2A = Cos^2A - Sin^2A = 1 - 2Sin^2A = 2Cos^2A - 1 = \frac{1 - Tan^2A}{1 + Tan^2A}$
	15	$Tan2A = \frac{2TanA}{1 - Tan^2A}$
Triple angle formula	16	$Sin3A = 3SinA - 4Sin^3A$
	17	$Cos3A = 4Cos^2A - 3CosA$
	18	$Tan3A = \frac{3TanA - Tan^3A}{1 - 3Tan^2A}$
Some other identities	19	$Sin(-\theta) = -Sin\theta$
	20	$Cos(-\theta) = Cos\theta$
	21	$Tan(-\theta) = -Tan\theta$
	22	$2SinASinB = Cos(A - B) - Cos(A + B)$
	23	$2SinACosB = Sin(A + B) + Sin(A - B)$
	24	$2CosACosB = Sin(A + B) - Sin(A - B) = Cos(A + B) + Cos(A - B)$
	25	$\cos^2 A + \sin^2 A = 1$
Reflections	26	$\sin(-\theta) = -\sin\theta$
	27	$\cos(-\theta) = \cos\theta$
	28	$\tan(-\theta) = -\tan\theta$
	29	$\csc(-\theta) = -\csc\theta$
	30	$\sec(-\theta) = \sec\theta$
	31	$\cot(-\theta) = -\cot\theta$
	32	$\sin\left(\frac{\pi}{2} - \theta\right) = \cos\theta$
	33	$\cos\left(\frac{\pi}{2} - \theta\right) = \sin\theta$
	34	$\tan\left(\frac{\pi}{2} - \theta\right) = \cot\theta$
	35	$\csc\left(\frac{\pi}{2} - \theta\right) = \sec\theta$
	36	$\sec\left(\frac{\pi}{2} - \theta\right) = \csc\theta$
	37	$\cot\left(\frac{\pi}{2} - \theta\right) = \tan\theta$
	38	$\sin(\pi - \theta) = \sin\theta$
	39	$\cos(\pi - \theta) = -\cos\theta$
	40	$\tan(\pi - \theta) = -\tan\theta$
	41	$\csc(\pi - \theta) = \csc\theta$
	42	$\sec(\pi - \theta) = -\sec\theta$
	43	$\cot(\pi - \theta) = -\cot\theta$
	44	$\sin\left(\frac{3\pi}{2} - \theta\right) = -\cos\theta$
	45	$\cos\left(\frac{3\pi}{2} - \theta\right) = -\sin\theta$
	46	$\tan\left(\frac{3\pi}{2} - \theta\right) = \cot\theta$
	47	$\csc\left(\frac{3\pi}{2} - \theta\right) = -\sec\theta$
	48	$\sec\left(\frac{3\pi}{2} - \theta\right) = -\csc\theta$
	49	$\cot\left(\frac{3\pi}{2} - \theta\right) = \tan\theta$
	50	$\sin(2\pi - \theta) = -\sin\theta$
	51	$\cos(2\pi - \theta) = \cos\theta$
	52	$\tan(2\pi - \theta) = -\tan\theta$
	53	$\csc(2\pi - \theta) = -\csc\theta$
	54	$\sec(2\pi - \theta) = \sec\theta$

	55	$\cot(2\pi-\theta) = -\cot\theta$
GENERAL		
Volume of sphere	56	$V = \frac{4}{3}\pi r^3$
Sidharth Acharya method	57	$x = \frac{-\mathrm{b} \pm \sqrt{\mathrm{b}^2 - 4\mathrm{ac}}}{2\mathrm{a}}$
Newton's law of gravitation	58	$F = G\frac{m_1 m_2}{r^2}, \quad G = 6.67 \times 10^{-11} Nm^{-2}kg^{-2}$
Expansion of e^x	59	$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots; -\infty < x < \infty$
Normal distribution	60	$F(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\left[\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2\right]}$
Exponential theorem	61	$e^x = 1 + \sum_{i=1}^{n} x^i$
Circle	62	$\boldsymbol{x^2 + y^2 = r^2}$
Sphere	63	$\boldsymbol{x^2 + y^2 + z^2 = r^2}$
Ellipse	64	$\left(\frac{x}{a}\right)^2 + \left(\frac{y}{b}\right)^2 = 1$
Ellipsoid	65	$\left(\frac{x}{a}\right)^2 + \left(\frac{y}{b}\right)^2 + \left(\frac{z}{c}\right)^2 = 1$
Pythagorean theorem	66	$h = \sqrt{b^2 + p^2}$
ALGEBRAIC IDENTITIES	67	$a^2 + b^2 = (a+b)^2 - 2ab$
	68	$a^2 - b^2 = (a+b)(a-b)$
	69	$(a+b)^2 = a^2 + b^2 + 2ab$
	70	$(a-b)^2 = a^2 + b^2 - 2ab$
	71	$(a+b+c)^2 = a^2 + b^2 + c^2 2ab + 2bc + 2ca$
	72	$\sqrt{ab} = \sqrt{a}\sqrt{b}$
	73	$\left(\sqrt{a} + \sqrt{b}\right)\left(\sqrt{a} - \sqrt{b}\right) = a - b$
Angles in a regular polygon	74	$\theta = \frac{(n_{sides} - 2) \times 360°}{n_{sides}}$
ARITHMETIC PROGRESSION		
N[th] term	75	$a_n = a + (n-1)d$
Sum	76	$S_n = \frac{n[2a + (n-1)d]}{2}$
GEOMETRIC PROGRESSION		
N[th] term	77	$a_n = ar^{n-1}$
Sum	78	$S_n = \frac{a(1-r^n)}{1-r} = \frac{a(r^n - 1)}{r-1}$
AVERAGE		
Arithmetic mean	79	$\bar{A} = \frac{\sum_{i=1}^{n} a_i}{n}$
Weighted average	80	$\overline{W} = \frac{\sum_{i=1}^{n} w_i a_i}{n}$

DIFFERENTIATION		
Constant	81	$\frac{d(C)}{dx} = 0$
Multiplication by a constant	82	$\frac{d(Cy)}{dx} = C\frac{dy}{dx}$
Addition	83	$\frac{d(Y+Z)}{dx} = \frac{dY}{dx} + \frac{dZ}{dx}$
Subtraction	84	$\frac{d(Y-Z)}{dx} = \frac{dY}{dx} - \frac{dZ}{dx}$
Product rule	85	$\frac{d(a.b)}{dx} = a\frac{db}{dx} + b\frac{da}{dx}$
Quotient rule	86	$\frac{d\left[\frac{a}{b}\right]}{dx} = \frac{b\frac{da}{dx} - a\frac{db}{dx}}{b^2}$
Chain rule	87	$\frac{df(g(x))}{dx} = \frac{df(g(x))}{dg(x)}\frac{dg(x)}{dx}$
Power rule	88	$\frac{dx^n}{dx} = nx^{n-1}$
Exponential rule	89	$\frac{de^x}{dx} = e^x$
	90	$\frac{de^{cx}}{dx} = ce^x$
	91	$\frac{de^{-cx}}{dx} = -ce^{-cx}$
Logarithmic	92	$\frac{dLn(x)}{dx} = \frac{1}{x}$
Trigonometric	93	$\frac{dSinA}{dx} = CosA$
	94	$\frac{dCosA}{dx} = -SinA$
	95	$\frac{dSincA}{dx} = cCoscA$
	96	$\frac{d\tan x}{dx} = \sec^2 x$
Cyclic rule	98	$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$
EULER'S RECIPROCITY RULE	99	$z = f(x,y)$ $\left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right]_y$
CHAIN RULE	100	$\frac{da^x}{dx} = a^x lna$
LOGARITHMS		
POWER RULE	101	$logx^n = nlogx$
QUOTIENT RULE	102	$Log\frac{x}{y} = Logx - Logy$
PRODUCT RULE	103	$Logxy = Logx + Logy$
EQUIVALANCE	104	$Log10 = Lne = 1$
CONVERSION FACTOR	105	$Lnx = 2.303Logx$
Meaning	106	$Logx = y; x = 10^y$
INTEGRALS		

Power rule	107	$\int x^n dx = \frac{x^{n+1}}{n+1}$
Logarithm rule	108	$\int \frac{1}{x} dx = Ln(x) + c$
Integration by parts	109	$\int f(x)g(x)dx = f(x)\int g(x)dx - \int \left[\frac{df(x)}{dx}\left[\int g(x)\,dx\right]\right]dx$
Trigonometric	110	$\int sinxdx = -cosx$
	111	$\int cosxdx = sinx$
	112	$\int sinaxdx = \frac{-cosax}{a}$
	113	$\int cosaxdx = \frac{sinax}{a}$
	114	$\int sin^2xdx == \frac{x}{2} - \frac{sin2x}{4}$
	115	$\int cos^2xdx == \frac{x}{2} + \frac{sin2x}{4}$
	116	$\int sin^2bxdx = \frac{x}{2} - \frac{sin2bx}{4b}$
	117	$\int xsin^2bxdx = \frac{x^2}{4} - \frac{xsin2bx}{4b} - \frac{cos2bx}{8b^2}$
	118	$\int cos^2bxdx = \frac{x}{2} + \frac{sin2bx}{4b}$
	119	$\int \sin ax \sin bx\, dx = \frac{\sin(a-b)x}{2(a-b)} - \frac{\sin(a+b)x}{2(a+b)}\ (a^2 \neq b^2)$
	120	$\int \sin ax \cos bx\, dx = -\frac{\cos 2bx}{4b}$
	121	$\int x^2 \sin^2 bx\, dx = \frac{x^3}{6} - \left(\frac{x^2}{4b} - \frac{1}{8b^3}\right)\sin 2bx - \frac{x\cos 2bx}{4b^2}$
	122	$\int xcos^2xdx = \frac{x^2}{4} + \frac{xsin2x}{4} + \frac{cos2bx}{8}$
	123	$\int xsinbxdx = \frac{sinbx}{b^2} - \frac{x}{b}cosx$
Rules	124	$\int f(ax+b)dx = \frac{F(ax+b)}{a}$
	125	$\int a^x dx = \frac{a^x}{lna}$
	126	$\int e^{cx} dx = \frac{e^{cx}}{c}$
	127	$\int e^{-cx} dx = -\frac{e^{-cx}}{c}$
	128	$\int e^x dx = e^x$
	129	$\int x^n e^{ax} dx = \frac{x^n e^{ax}}{a} - \frac{n}{a}\int x^{n-1} e^{ax} dx$
	130	$\int_0^\infty e^{-ax^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$

	131	$\int_0^\infty xe^{-ax^2}dx = \frac{1}{2a}$
	132	$\int_0^\infty x^n\, e^{-ax}dx = \frac{n!}{a^{n+1}} = \frac{\Gamma(n+1)}{a^{n+1}}$
	133	$\int_0^\infty x^2 e^{-ax^2}dx = \frac{1}{4}\sqrt{\frac{\pi}{a^3}}$
	134	$\int_0^\infty x^3 e^{-ax^2}dx = \frac{1}{2a^3}$
	135	$\int_0^\infty x^{2n} e^{-ax^2}dx = \frac{1.\bar{3}(2n-1)}{2^{n+1}}\sqrt{\frac{\pi}{a^{2n+1}}}$
	136	$\int_0^\infty x^{2n+1} e^{-ax^2}dx = \frac{n!}{2a^{n+1}}$
	137	$\int_1^\infty e^{-ax}dx = \frac{e^{-a}}{a}$
	138	$\int_0^1 e^{-ax}dx = \frac{1-e^{-a}}{a}$
	139	$\int_{-\infty}^{\infty} x^n\, e^{-aX^2}dx = \begin{cases} \frac{\Gamma\left(\frac{n+1}{2}\right)}{a^{\left(\frac{n+1}{2}\right)}}; n\ is\ Even \\ 0; n\ is\ Odd \end{cases}$
	140	$\int xe^{bx}dx = \left(\frac{x}{b} - \frac{1}{b^2}\right)e^{bx}$
	141	$\int x^2 e^{bx}dx = \left(\frac{x^2}{b} - \frac{2x}{b^2} + \frac{2}{b^3}\right)e^{bx}$
	142	$\int_0^\infty x^{2n} e^{-bx^2}dx = \frac{(2n)!}{2^{2n+1}n!}\sqrt{\frac{\pi}{b^{2n+1}}}$
	143	$\int_0^\infty x^2 e^{-cx}dx = \frac{2}{c^3}$
DIRAC DELTA FUNCTION	144	$\int_a^b f(x)\delta(x-m)dx = \begin{cases} f(m); a < m < b \\ 0; m < a\ or\ m > b \end{cases}$

THE CARTESIAN COORDINATE SYSTEM

The Cartesian coordinate system was developed by René Descartes in the 17th century (published in 1637). In this system there are four quadrants, which have their unique signs for value of x and y axes. These are numbered in anticlockwise direction as:

I. The values of x, y and all dix trigonometric rations are positive (ALL POSITIVE).
II. The values of y and sin θ are positive (SIN POSITIVE)
III. The values of tan θ are positive (TAN POSITIVE)
IV. The values of cos θ are positive (COS POSITIVE).

The trigonometric identity $Cos2A = Cos^2A - Sin^2A = 1 - 2Sin^2A = 2Cos^2A - 1$ is modified as $Cos^2A = \frac{(\cos 2A+1)}{2}$ and $sin^2A = \frac{(1-\cos 2A)}{2}$.

For the integration by parts $\int f(x)g(x)dx = f(x)\int g(x)dx - \int\left[\frac{df(x)}{dx}[\int g(x)\,dx]\right]dx$

In the integrals $\int_{-\infty}^{\infty} x^n\, e^{-aX^2}dx = \begin{cases} \frac{\Gamma\left(\frac{n+1}{2}\right)}{a^{\left(\frac{n+1}{2}\right)}}; n\ is\ Even \\ 0; n\ is\ Odd \end{cases}$ and $\int_0^{\infty} x^n\, e^{-ax}dx = \frac{n!}{a^{n+1}} = \frac{\Gamma(n+1)}{a^{n+1}}$,

the gamma function operates only on **POSITIVE NUMBERS.**

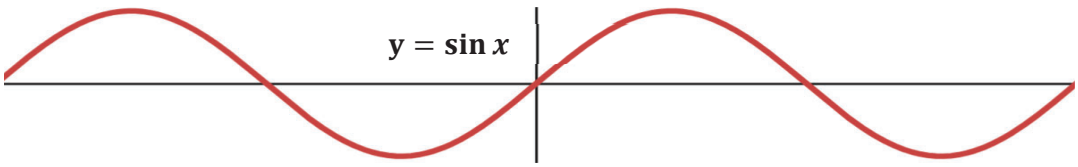
The preference of the functions is determined:

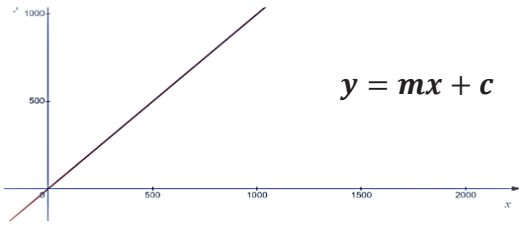
FUNCTION	**I**	**L**	**A**	**T**	**E**
NAME	INVERSE	LOGARITHM	ARITHMETIC	TRIGNOMETRIC	EXPONENTIAL

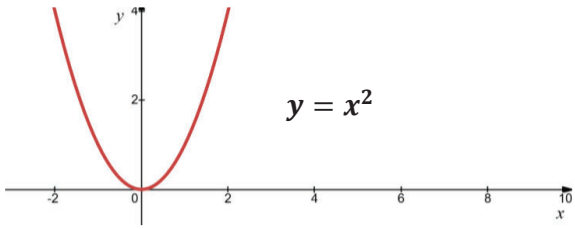
GRAPHS OF DIFFERENT FUNCTIONS

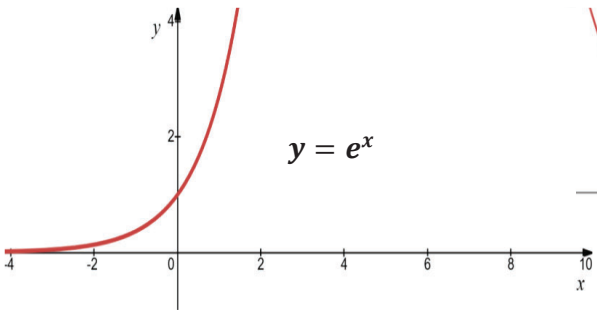
INTERCEPT: The point where the curve intersects the x or y-axes.

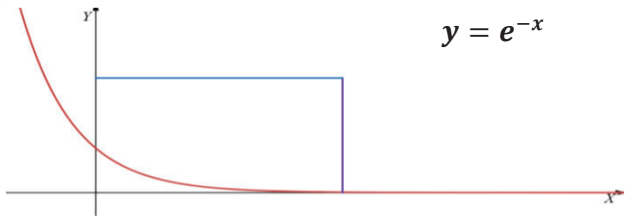
SLOPE: Slope (or gradient, often 'm') measures a line's steepness and direction, defined as the ratio of vertical change (rise) to horizontal change (run) between any two points on the line,

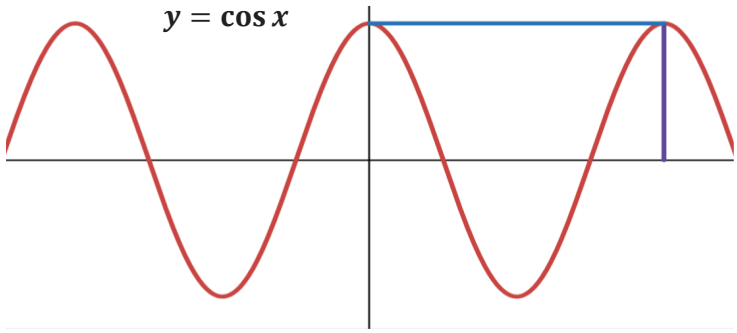


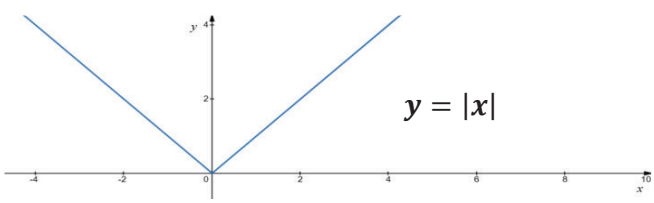


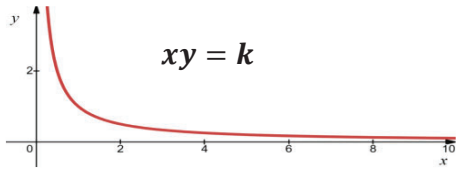












calculated as $\boldsymbol{m = \tan\theta = \frac{dy}{dx}}$. A positive slope means the line goes up from left to right, negative means down, zero is a flat horizontal line, and undefined is a vertical line.

$y = mx + c$	$\boldsymbol{y = x^2}$	$\boldsymbol{y = e^{-x}}$	$\boldsymbol{x^2 + y^2 = r^2}$	$\boldsymbol{y = \cos x}$	$\left(\frac{x}{a}\right)^2 + \left(\frac{y}{b}\right)^2 = 1$
$\boldsymbol{y = \lvert x \rvert}$	$\boldsymbol{y = e^x}$	$\boldsymbol{y = \sin x}$	$\boldsymbol{x^2 + y^2 + z^2 = r^2}$	$\boldsymbol{xy = k}$	$\left(\frac{x}{a}\right)^2 + \left(\frac{y}{b}\right)^2 + \left(\frac{z}{c}\right)^2 = 1$

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