## Requisites of a satisfactory atom model:

The right atom model should be explain the characteristics of atom. Upto the first decade of twentieth century the following characteristics of of atoms were recorded:

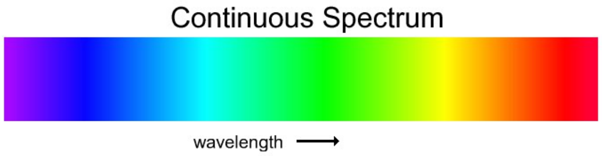
(i) Atoms are stable.

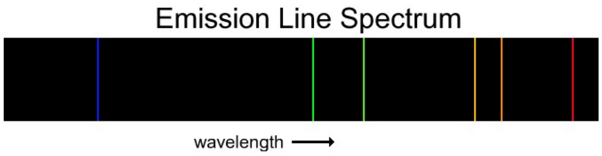
(ii) Atoms are electrically neutral.

(iii) The approximate radius of an atom was calculated to be in the range of $10^{-8}$ cm from the kinetic theory of gases.

(iv) Atoms give rise to discontinuous line spectrum.

## Continuous spectrum and discontinuous spectrum:





## Rutherford atom model (1911):

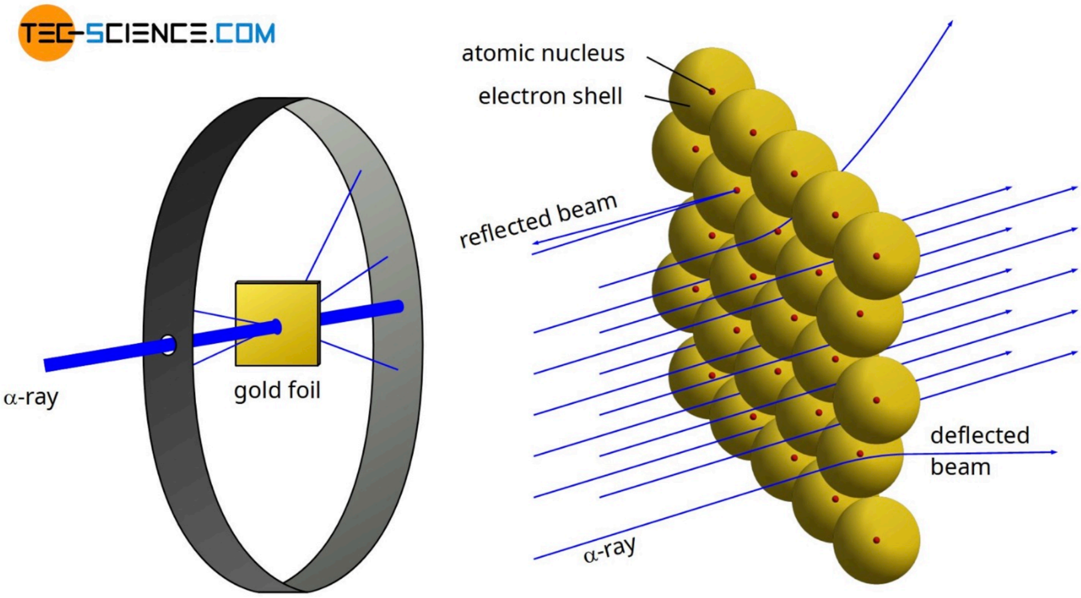
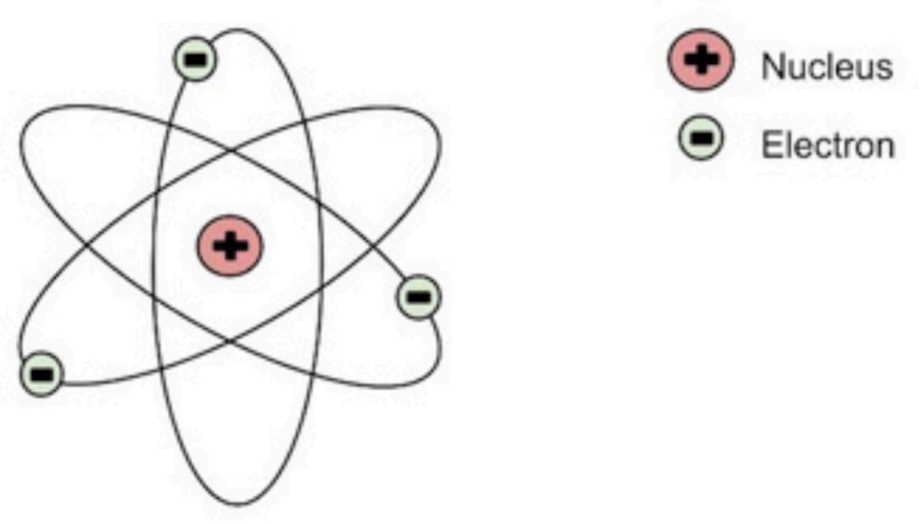


*Figure: Rutherford's gold foil experiment*



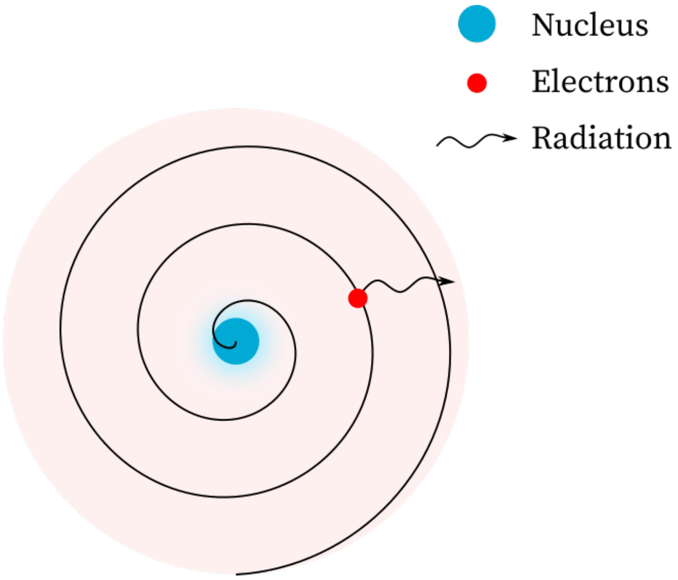
Rutherford Model of the Atom

## Electromagnetic theory

J.C. Maxwell (1870) showed that electricity, magnetism and light can be treated in terms of a single theory. His electromagnetic theory starts with the interaction between charged bodies in vacuum in terms of their associated electric and magnetic fields. According to this theory, oscillating electric and magnetic fields cause transmission of energy through space with the characteristics wave, the electromagnetic waves. The theory further states that electromagnetic radiation is produced by accelerated charged particles. The energy of the radiation is derived from the energy of the motion of the particle.

## Rutherford atom model vs electromagnetic theory:

Electromagnetic theory claimed that Rutherford atom model can not be stable and it does not give rise to discontinuous line spectrum.



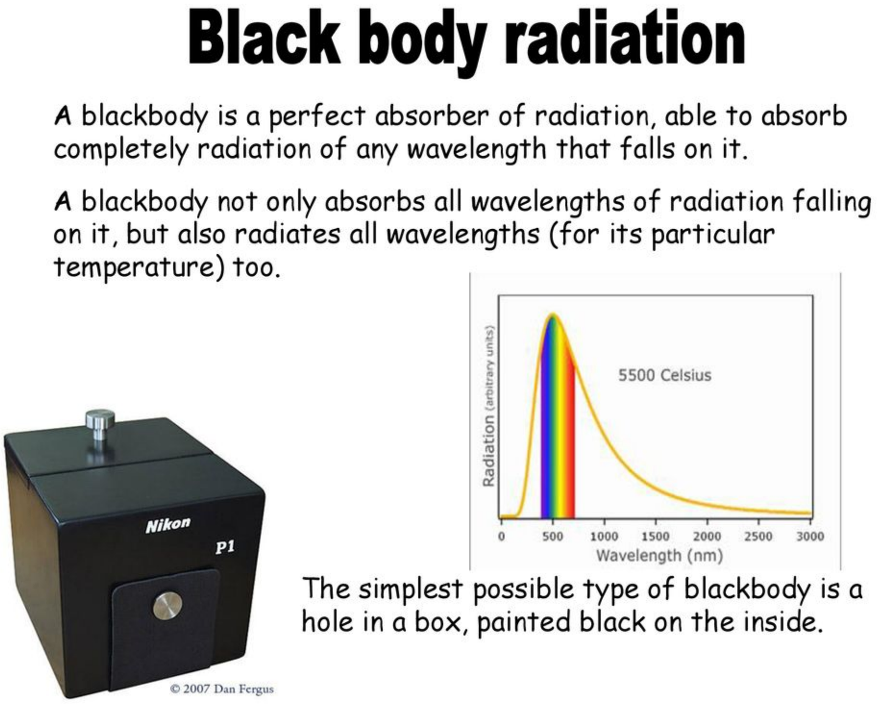
**This concludes:**

- Either Rutherford atom model was wrong or the electromagnetic theory was inadequate in this case.

- Rutherford atom model was based on definite experimental background. So, the position of electromagnetic theory was reconsidered by the scientists.

## CHALLENGES TO THE CLASSICAL ELECTROMAGNETIC THEORY

**1.**



**Black body radiation**

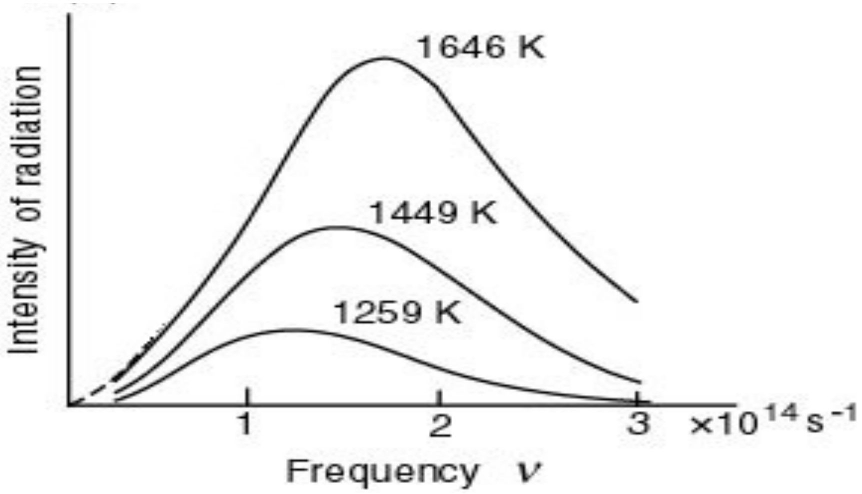
A blackbody is a perfect absorber of radiation, able to absorb completely radiation of any wavelength that falls on it.

A blackbody not only absorbs all wavelengths of radiation falling on it, but also radiates all wavelengths (for its particular temperature) too.

The simplest possible type of blackbody is a hole in a box, painted black on the inside.

The name "black body" is given because it absorbs radiation in all frequencies, not because it only absorbs.). It is an ideal emitter: at every frequency, it emits as much or more thermal radiative energy as any other body at the same temperature.The term *black body* was introduced by Gustav Kirchhoff in 1860 Black-body radiation is also called thermal radiation, *cavity radiation*, *complete radiation* or *temperature radiation*.

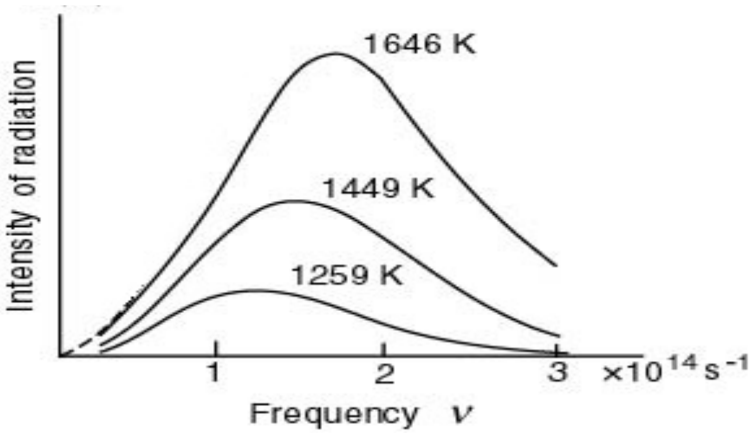
A black body in thermal equilibrium (that is, at a constant temperature) emits electromagnetic radiation called black-body radiation.



Experimentally, a uniformly heated hollow enclosure with a small opening may function as blackbody. Any radiation entering through the hole will be repeatedly reflected inside the cavity and will be nearly completely absorbed. When heated to constant temperature, the walls of the cavity will emit radiation. A portion of this will escape through the hole and can be studied for black body radiation.

**Characteristics of Blackbody Radiation**

1. Gaussian distribution curve: The radiant energy from a blackbody at constant temperature is distributed over different wavelengths. This is independent of the nature of the substance making the blackbody. The distribution of fraction of radiant energy emitted in different ranges of wavelength varies only with temperature. As the temperature is raised, the position of the maximum shifts towards shorter wavelength.



2. Wien's displacement law: The product of the wavelength corresponding to maximum intensity ($\lambda_{max}$) is inversely proportional to the absolute temperature of the body.

   $\lambda_{max} .T = 2.8976 \times 10^{-3}$ mK (where, $\lambda_{max}$ in meter ).

   (The max value for solar light is 500nm. What is the surface temperature of the sun?)

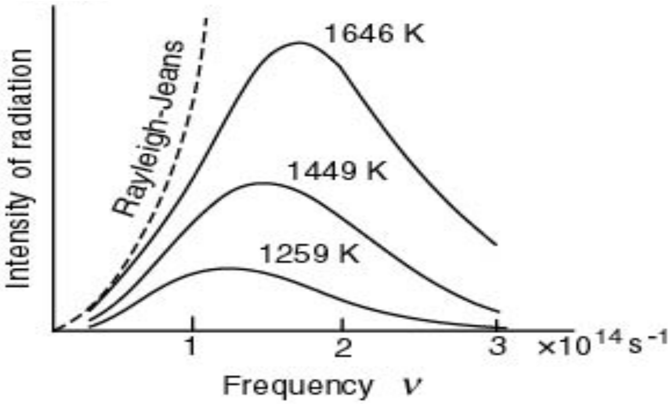
3. Stefan-Boltzmann law: The emissive power E of a black body at any temperature is proportional to fourth power of the absolute temperature of the blackbody.

   $E = \sigma T^4$ ($\sigma$ = Stefan-Boltzmann constant = $5.669 \times 10^{-18}$ W $m^{-2}$ $K^{-4}$).

**Blackbody radiation vs classical electromagnetic theory:**

According to classical electromagnetic theory (**Rayleigh-Jeans law**):

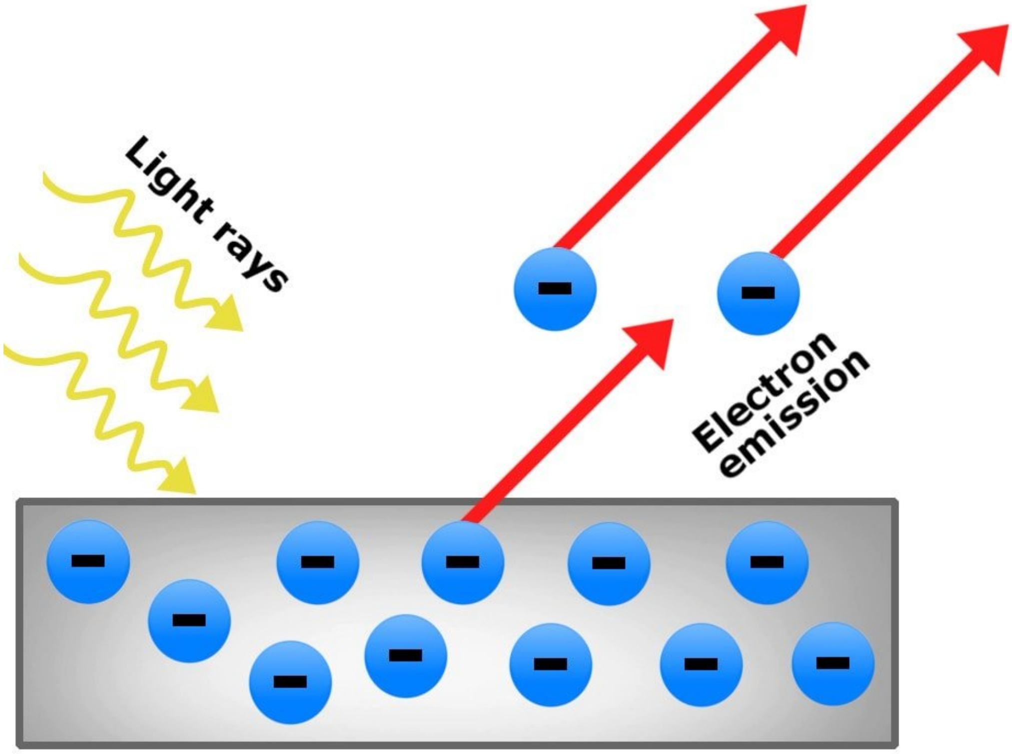
$\rho(\upsilon, T) = \frac{8\pi kT}{c^3}\upsilon^2 d\upsilon$ [where, $\rho(\upsilon, T)$ = density of radiative energy between frequency $\upsilon$ and $\upsilon + d\upsilon$]



The plot $\rho(\upsilon, T)$ vs $\upsilon$ does not match with the experimental blackbody

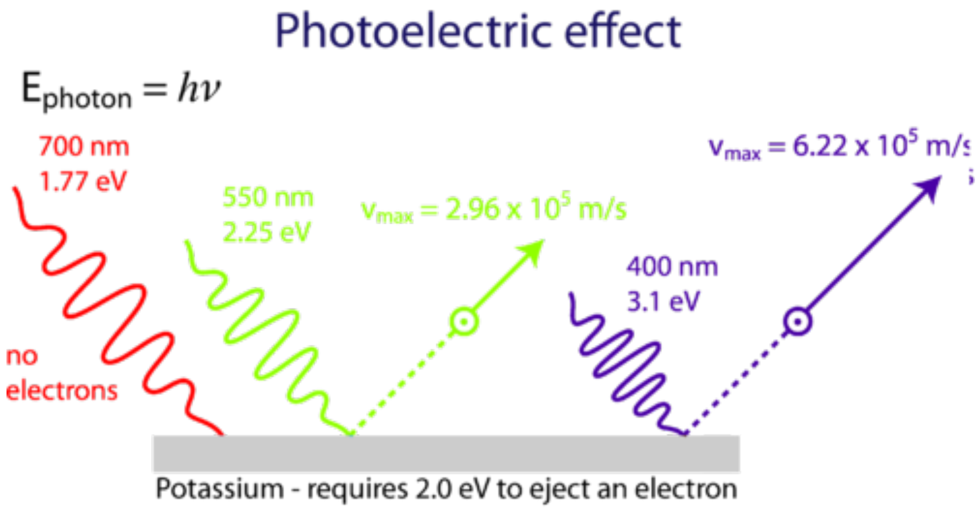
## CHALLENGES TO THE CLASSICAL ELECTROMAGNETIC THEORY

### 2. Photoelectric effect

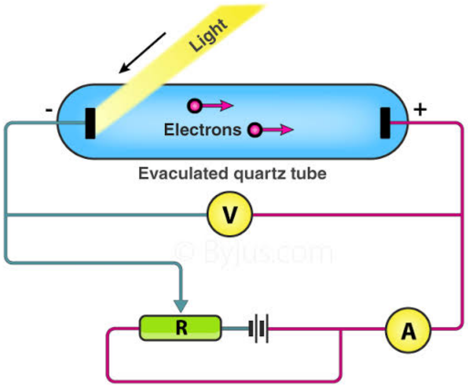


- When a light ray falls on the Metallic Surface, electrons in the metallic substance absorbs the energy of light and as a result, electrons get emitted from the metallic surface. This process is known as PHOTOELECTRIC EFFECT. Emitted electrons are known as Photoelectrons.
- The photoelectric effect was discovered in 1887 by the German physicist Heinrich Rudolf Hertz.
- In 1905, Albert Einstein formulate a new corpuscular theory to explain photoelectric effect and in 1921 awarded the Nobel prize in Physics for explaining the photoelectric effect.

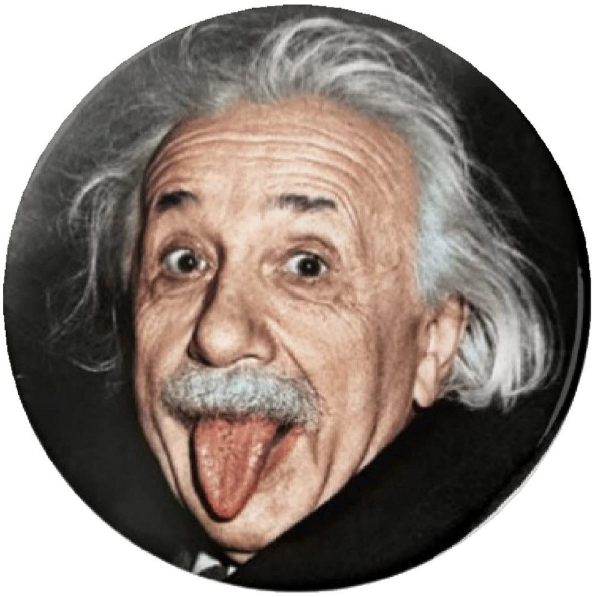
## Characteristics of Photoelectric effect



1. For a given metal surface, there exists a certain minimum frequency of incident radiation below which no photoelectrons are emitted. This frequency is called the *threshold frequency*.
2. Above the threshold frequency, the maximum kinetic energy of the emitted photoelectron depends on the frequency of the incident light, but is independent of the intensity of the incident light.
3. Increasing the frequency of the incident beam, keeping the number of incident photons fixed (this would result in a proportionate increase in energy) increases the maximum kinetic energy of the photoelectrons emitted. Thus, the stopping voltage increases.
4. If the intensity of the incident radiation of a given frequency is increased, there is no effect on the kinetic energy of each photoelectron.
5. The time lag between the incidence of radiation and the emission of a photoelectron is very small, less than $10^{-9}$ second.



## Photoelectric effect vs classical electromagnetic theory:



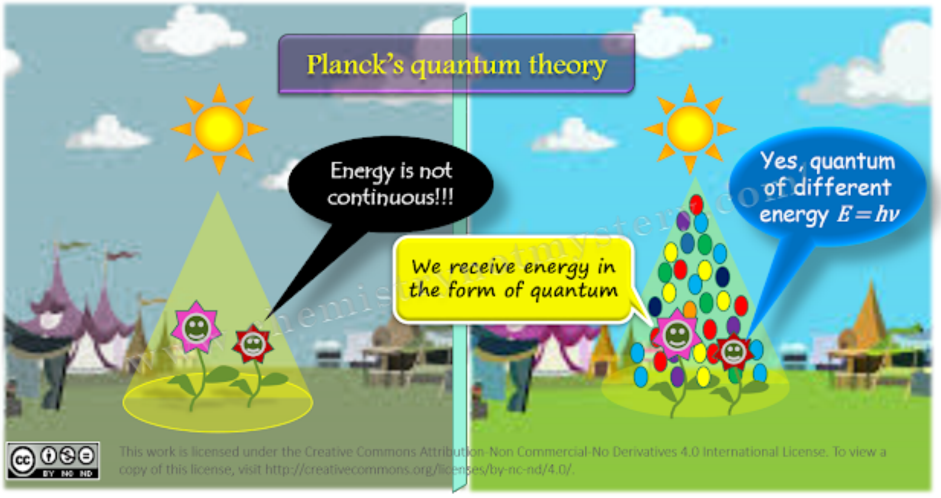
Albert Einstein puts forward the particle theory of the light (**hypothesised By Max Planck**) that later paved the way for the creation of the Quantum World.

- According to classical electromagnetic theory or classical wave theory, the photoelectric effect can be attributed to the transfer of energy from the light to an electron. From this perspective, an alteration in the intensity of light induces changes in the kinetic energy of the electrons emitted from the metal.
- According to classical electromagnetic theory, a sufficiently dim light is expected to show a time lag between the initial shining of its light and the subsequent emission of an electron.

### But……

- The experimental results did not correlate with either of the two predictions made by classical theory.
- Experiment showed that electrons are dislodged only by the impingement of light when it reached or exceeded a threshold frequency. Below that threshold, no electrons are emitted from the material, regardless of the light intensity or the length of time of exposure to the light.

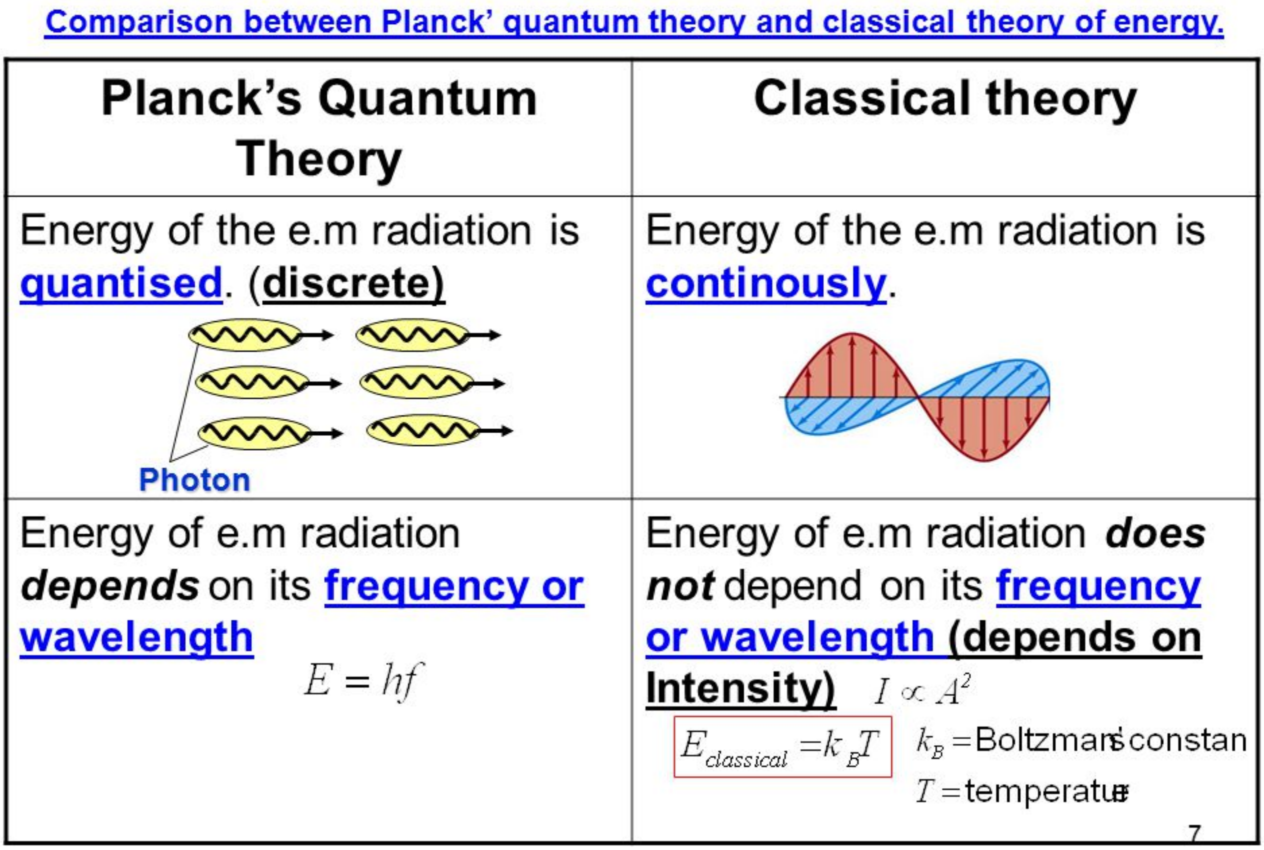
## Planck's quantum (hypothesis ) theory (1900)



Max Planck discarded the concept of continuous variation of energy among the oscillators of a black body and suggested quantum theory. According to this theory:

1. The energy of an oscillator cannot vary continuously but only by discrete amount. Hence an oscillator has definite energy level such as $\varepsilon_0$, $\varepsilon_1$, $\varepsilon_2$…etc.
2. The oscillator emitting a frequency $\upsilon$ can only radiate in units or quanta of the magnitude $h\upsilon$ where h is Planck's constant.
3. The energy levels of the oscillator can only be integral multiple of a quantum i.e.

$E_n = n h\upsilon$, where, n is an integer where its value is 1, 2, 3 … etc.



**Comparison between Planck' quantum theory and classical theory of energy.**

| **Planck's Quantum Theory** | **Classical theory** |
|---|---|
| Energy of the e.m radiation is **quantised**. (**discrete)**<br> | Energy of the e.m radiation is **continously**. |
| Energy of e.m radiation ***depends*** on its **frequency or wavelength**<br>$E = hf$ | Energy of e.m radiation ***does not*** depend on its **frequency or wavelength (depends on Intensity)** $I \propto A^2$<br>$\boxed{E_{classical} = k_B T}$ $k_B$ = Boltzmann's constant<br>$T$ = temperature |

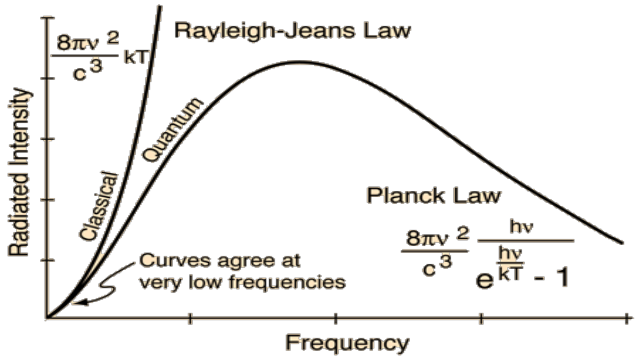
## Blackbody radiation in the light of Planck's quantum theory

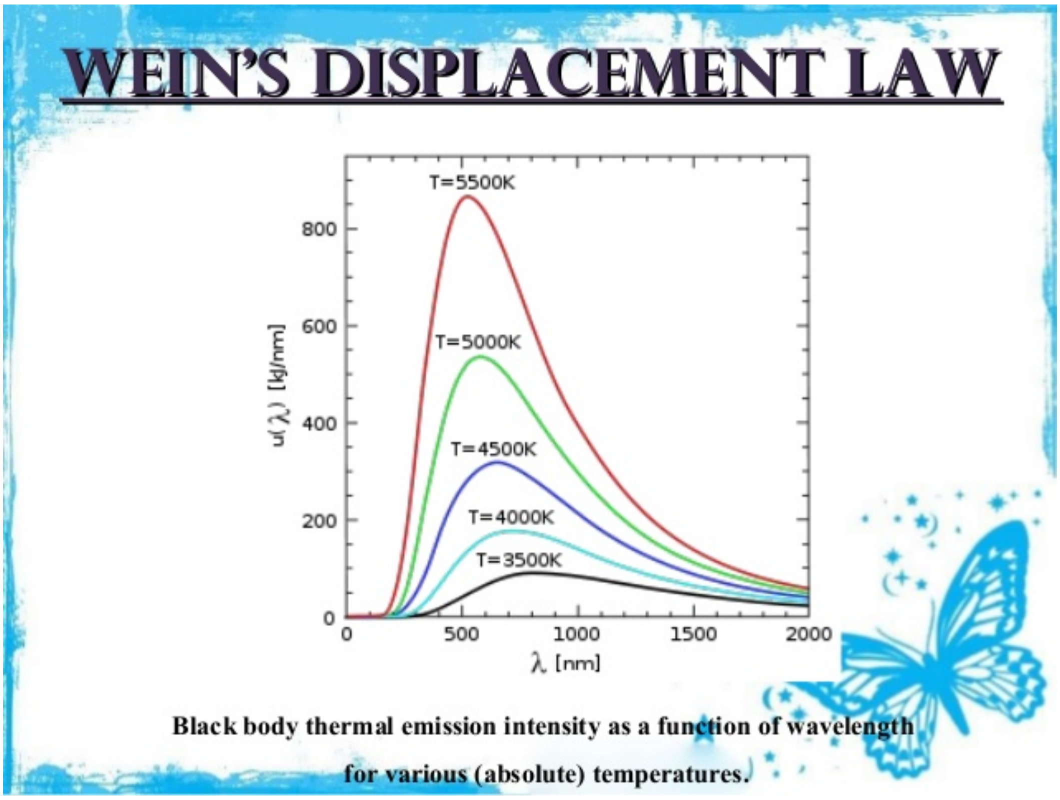
Using statistical thermodynamics Planck's quantum theory gives Planck's distribution law for blackbody radiation. According to Planck's distribution law:

$$\rho(\upsilon, T) = \frac{8\pi h\upsilon^3}{c^3}\frac{d\upsilon}{(e^{\frac{h\upsilon}{kT}} - 1)}$$

[where, ρ(υ, T) = density of radiative energy between frequency υ and υ+dυ].

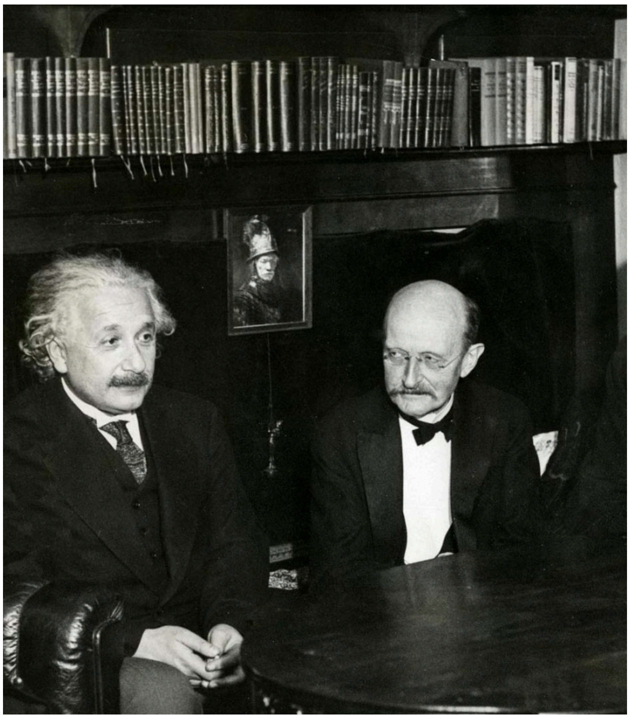
The plot ρ(υ, T) vs υ gives the Gaussian curve as like the experimental blackbody radiation curve. It suggests that Planck's quantum theory is more accurate than classical electromagnetic theory.




WEIN'S DISPLACEMENT LAW

Black body thermal emission intensity as a function of wavelength for various (absolute) temperatures.

## Photoelectric effect in the light of Planck's quantum theory



- In 1905, Einstein explained the facts about the photoelectric effect with quantum theory of radiation.

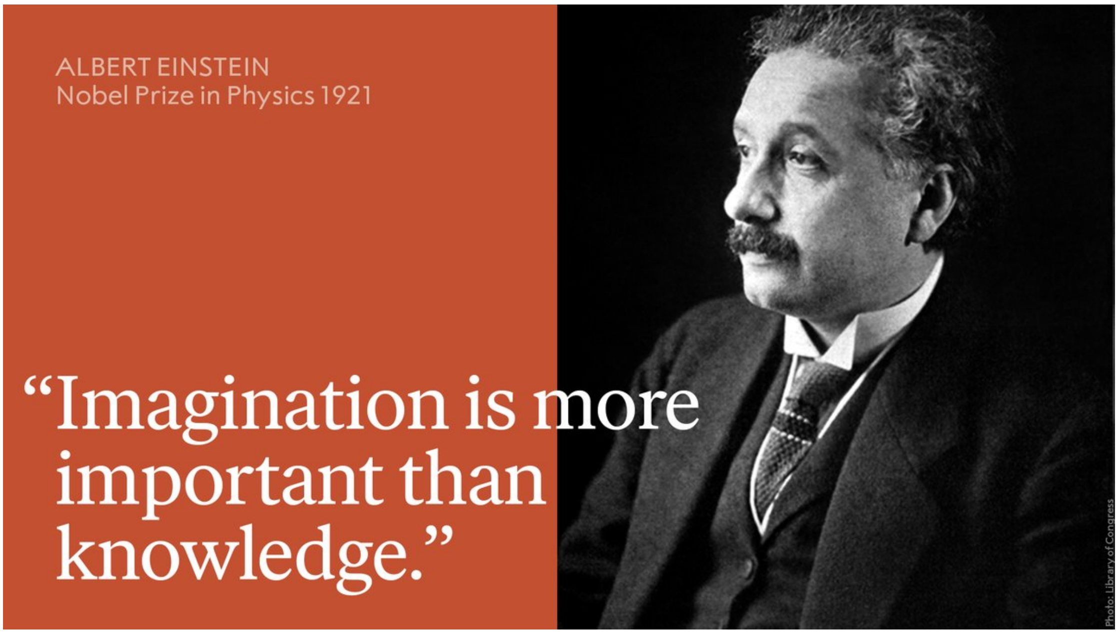
- Einstein proposed that radiant energy is not only absorbed or emitted in discrete units of quanta; it is also composed of such discrete units. The light itself consists of quanta or small corpuscles of energy equal to $h\upsilon$. When a light beam strikes a metal surface, the photons, each carrying energy $h\upsilon$, strikes the electrons.

- Now an electron will absorb the entire quantum of energy. If this energy of the quantum is greater than the binding energy (W) of the electron to the metal surface, the electron will be ejected instantly; the excess of the energy received from the photon will appear as the maximum kinetic energy of the electron. This is expressed in the photoelectric equation: $h\upsilon = \frac{1}{2} mv^2 + W$ where W is the photo-electric work-function of the metal.

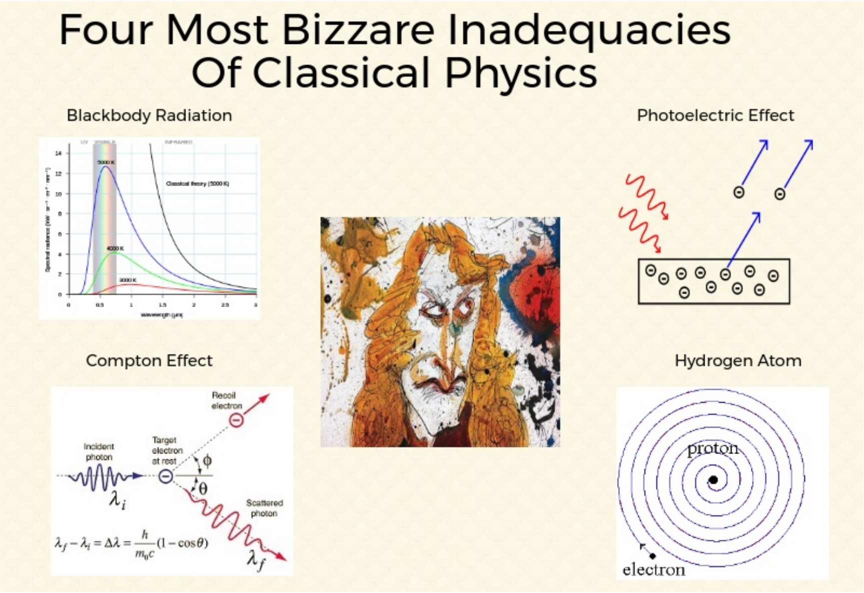
- No electron will be ejected when $h\upsilon < W$. The threshold frequency $\upsilon_o$ is then define as $h\upsilon_o = W$.

So, $\frac{1}{2} mv^2 = h(\upsilon - \upsilon_o)$.

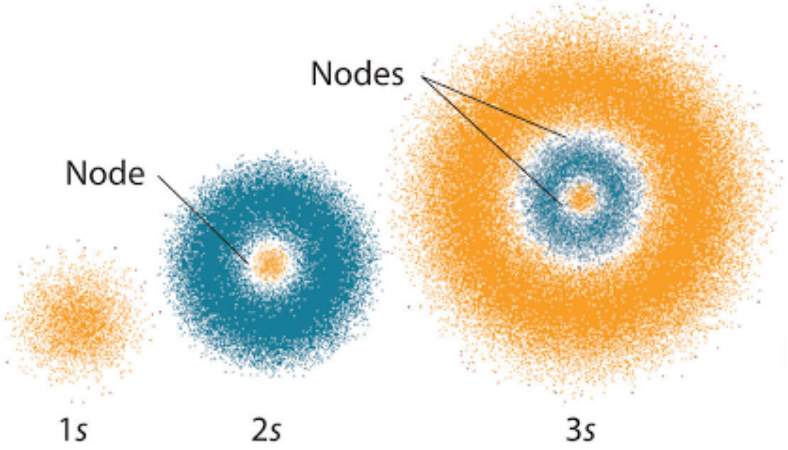
- Greater intensity means larger number of incident quanta per unit time. This will increase the number of electrons emitted and hence the current will be proportional to the intensity of light. But so long as the energy of a quanta $h\upsilon$ is fixed, the kinetic energy of the ejected electrons will remain the same.



**Einstein won his Nobel prize for showing that if a light is considered as a particle instead of a wave, whose energy is proportional to the associated frequency, then the photoelectric effect is fully explained.**


Four Most Bizzare Inadequacies Of Classical Physics

## About quantum mechanics......

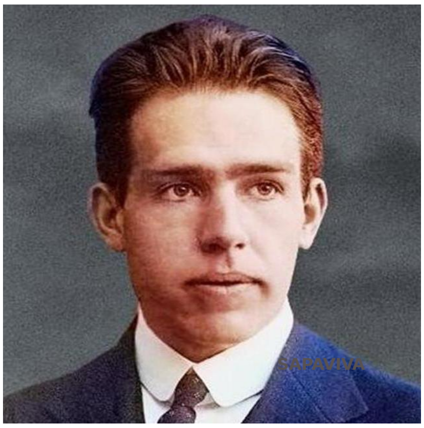


- The word *quantum* derives from the Latin, meaning "how great" or "how much".
- Max Planck considered his quantum hypothesis a mathematical trick to get the right answer rather than a sizable discovery.
- In 1905, Albert Einstein interpreted Planck's quantum hypothesis realistically and used it to explain the photoelectric effect.
- This phase is known as the old quantum theory. The theory is now understood as a semi-classical approximation to modern quantum mechanics.
- Modern quantum mechanics was born in 1925, when the German physicists Werner Heisenberg, Max Born, and Pascual Jordan developed matrix mechanics and the Austrian physicist Erwin Schrödinger invented wave mechanics.

**Sample questions**

1. What is 'black body radiation'? How Planck's quantum theory explains the fact 'black body radiation'?
2. The λmax value of a star light is 480 nm. What is the surface temperature of the star?
3. What is 'photo-electric effect'? How Planck's quantum theory explains the fact 'photo-electric effect'?
4. What is 'Planck's quantum theory'?

## Niels Henrik David Bohr

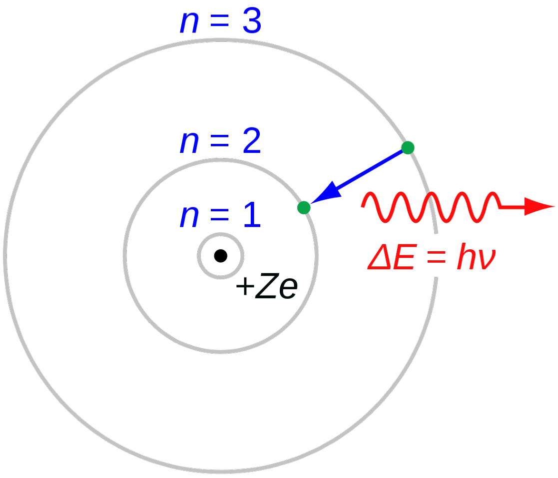


- **Niels Bohr** (7 October 1885 – 18 November 1962) was a Danish physicist who made foundational contributions to understanding atomic structure and quantum theory, for which he received the Nobel Prize in Physics in 1922.
- The element bohrium was named after him.
- He was part of the British mission to the Manhattan Project. He was involved with the establishment of CERN.

- Bohr met Margrethe Nørlund in 1910 and married in 1912.
- His son Aage Bohr (1922 – 2009) was became a successful physicist, and in 1975 was awarded the Nobel Prize in physics.

## Bohr's model of the atom (1913):

**This model also known as Rutherford–Bohr model. The model's key success lay in explaining the Rydberg formula for the spectral emission lines of atomic hydrogen.**



1. There exists only a number of permitted orbits in which electrons can exist outside of the nucleus. These permitted orbits are restricted by the quantum condition that the angular momentum of the electrons in the circular path about the nucleus must be an integral multiple of $\frac{h}{2\pi}$ where h is Planck's constant.

   Angular momentum = I. ω = (m.r$^2$).$\frac{v}{r}$ = m.v.r =$n$ . $\frac{h}{2\pi}$ (where, n= 1, 2, 3…..).
2. When an electron revolve along such orbits, the energy of the electron remain unchanged.
3. When an electron jumps from an orbit with energy $E_2$ to an orbit of energy $E_1$ ($E_2>E_1$), the difference of energy is emitted in the form quantised radiation *i.e.* $E_2-E_1 = h\upsilon$

## Basic formulas ofBohr's atom model:

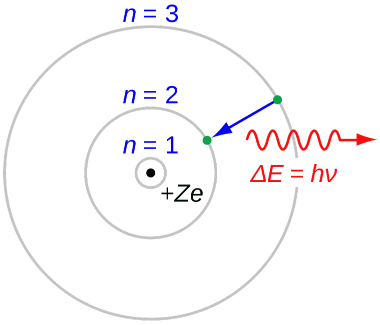
(i) In the Bohr orbits, the centrifugal force is balanced by the columbic attraction force.

Centrifugal force = $\dfrac{mv^2}{r}$

Columbic attraction force = $\dfrac{Ze^2}{4\pi\varepsilon_0 r^2}$

So, $\dfrac{mv^2}{r} = \dfrac{Ze^2}{4\pi\varepsilon_0 r^2}$ .........(1)

Again from quantum restriction: mvr = $n \cdot \dfrac{h}{2\pi}$ .......(2)



(ii) For hydrogen like atom, $r_n = \dfrac{\varepsilon_0 n^2 h^2}{\pi m Z e^2}$

For hydrogen atom, $r_1 = 0.529 \times 10^{-10}$ m

For hydrogen like atom, $r_n = \dfrac{n^2}{Z} \times 0.529 \times 10^{-10}$ m

(iii) For hydrogen like atom, $E_n = -\dfrac{1}{8}\dfrac{Z^2 e^4 m}{\varepsilon_0^2 n^2 h^2}$

For hydrogen atom, $E_1 = -13.6$ eV

For hydrogen like atom, $E_n = -13.6 \times \dfrac{Z^2}{n^2}$ eV

★The negative sign of energy indicates that the electron is bound to the atomic system by this amount of energy. If the electron is to be freed from the influence of the nucleus work equal to the magnitude of E has to be done. This is known as ionisation energy (IE).

★IE= $13.6 \times \dfrac{Z^2}{n^2}$ eV/atom= $13.6 \times \dfrac{Z^2}{n^2} \times 1.602 \times 10^{-19} \times 6.022 \times 10^{23}$ J/mole

(iv) Velocity of electron in nth orbit, $v_n = \frac{Ze^2}{2\varepsilon_0 n h}$

For hydrogen atom velocity of electron in 1st orbit, $v_1$ = 2.188 x $10^6$ m.s$^{-1}$

For hydrogen like atom general formula, $v_n = \frac{Z}{n}$ x 2.188 x $10^6$ m.s$^{-1}$

**Some constants and their values in SI and CGS unit**

| Constant | Symbol | SI unit | CGS unit |
|---|---|---|---|
| Planck's constant | h | 6.626 x $10^{-34}$ J.s | 6.626 x $10^{-27}$erg.s |
| Mass of electrom | $m_e$ | 9.109 x $10^{-31}$ kg | 9.109 x $10^{-28}$ g |
| Mass of proton | $m_p$ | 1.6726 x $10^{-27}$ kg | 1.6726 x $10^{-24}$ g |
| Mass of neutron | $m_n$ | 1.6749 x $10^{-27}$ kg | 1.6749 x $10^{-24}$ g |
| Charge of electron | e | 1.602 x $10^{-19}$ C | 4.8 x $10^{-10}$ esu |
| Electron volt | eV | 1.602 x $10^{-19}$ J | 1.602 x $10^{-12}$ erg |
| Permitivity vacuum | $\varepsilon_o$ | 8.854 x $10^{-12}$ C$^2$N$^{-1}$m$^{-2}$ | -------------- |

**Some atomic units (a.u.)**

| **Quantity** | **Value** |
|---|---|
| Mass | 1 a.u. = mass of an electron = 9.109 x $10^{-31}$ kg |
| Length | 1 a.u. = radius of 1st Bohr orbit of H atom = 0.529 x $10^{-10}$ m |
| Charge | 1 a.u. = charge of an electron = 1.602 x $10^{-19}$ C |
| Energy | 1 a.u. = twice the ionization energy of hydrogen atom = 27.12 eV |
| Speed | 1 a.u. = the speed of an electron in the 1st Bohr orbit of hydrogen atom<br>= 2.188 x $10^6$ m.s$^{-1}$ |
| Time | 1 a.u. = the period of rotation of an electron in 1st Bohr orbit of hydrogen atom= 2.42 x $10^{-17}$ s. |

**Q. Why Bohr's theory cannot be applied for multi electronic system?**

**Ans.** The main foundation of Bohr's theory is electron rotates around the nucleus in a particular orbit by balancing the centrifugal force and columbic attraction force only. It is true only for one electronic system. For multi-electronic system, besides centrifugal force and columbic attraction force there also exist electron-electron repulsive forces (shielding and de-shielding) in the extra nuclear part of an atom which was not considered for the formulation energy expression from Bohr's postulates. Hence Bohr's theory cannot be applied for multi electronic system.

Bhor's theory can be apply for multi-electronic system by substituting the nuclear charge by effective nuclear charge (with the help of Slater's rule).

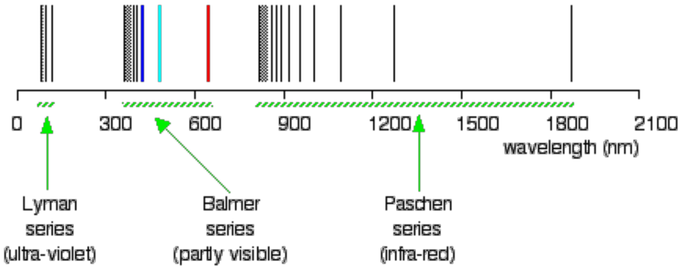
**Practice set-I**

1. Energy of an excited electron of $He^+$ ion is -6.04 eV. Calculate the angular momentum of that excited electron from Bohr's theory.
2. Obtain an expression for the total energy of an electron in the $He^+$ ion on the basis of Bohr's equation for energy levels of single electron system. Calculate second ionisation energy of He.
3. The radius of the third Bohr orbit of hydrogen like atom is 476 pm. Calculate the radius of the fourth orbit.
4. If energy of an electron in an excited hydrogen atom be -1.51 eV. What will be the angular momentum of the electron?
5. Calculate the principal quantum number where the electron is revolving in a hydrogen atom when its kinetic energy is $217.945 \times 10^{20}$ J.

## Balmer series (1885)( visible spectrum of hydrogen atom):

**Johann Jakob Balmer** (1 May 1825 – 12 March 1898) was a Swiss mathematician best known for his work in physics, the Balmer series of Hydrogen atom.

When an electric discharge is passed through hydrogen gas kept at a low pressure in a discharge tube, the radiation emitted being resolved shows the existence of a number of lines of definite wavelengths in the ultraviolet, visible and infra-red regions. This is emission spectrum of hydrogen.



Balmer's series was discovered first, other five spectral series discovered later.

**Balmer's equation:** $\lambda = K.\frac{n^2}{n^2-4}$ …………….(i)

where K is a constant for the whole series having the value 364.6 nm and n is an integer like 3, 4, 5, 6….

When, n=6, λ= 410 nm

n= 5, λ= 434 nm

n=4, λ= 486.1 nm

n=3, λ= 656.2 nm

## Rydberg formula (1888):

**Johannes (Janne) Robert Rydberg** (8 November 1854 – 28 December 1919) was a Swedish physicist mainly known for devising the Rydberg formula, in 1888, which is used to describe the wavelengths of photons (of visible light and other electromagnetic radiation) emitted by changes in the energy level of an electron in a hydrogen atom.

In atomic physics, the Rydberg formula was primarily presented as a generalisation of the Balmer series for electron transition of hydrogen. The formula directly generalises the equation used to calculate the wavelengths of the hydrogen spectral series. As stressed by Neils Bohr, expressing results in terms of wave number, not wavelength, was the key to Rydberg's discovery.

Rydberg, the Swedish physicist generalises the Balmer's observation as:

Wave number = $\frac{1}{\lambda}$ = A - $\frac{R}{(n+\alpha)^2}$..........(ii)

Where, R = Rydberg constant = 1.096775 x $10^7$ $m^{-1}$

A and α are constant for a particular series of an element. A and α depend on nature of elements and spectral series.

## Balmer's equation in the form of Rydberg equation:

Wave number = $\frac{1}{\lambda} = \frac{1}{K} - \frac{4}{Kn^2} = A - \frac{R}{(n+\alpha)^2}$…..(iii)

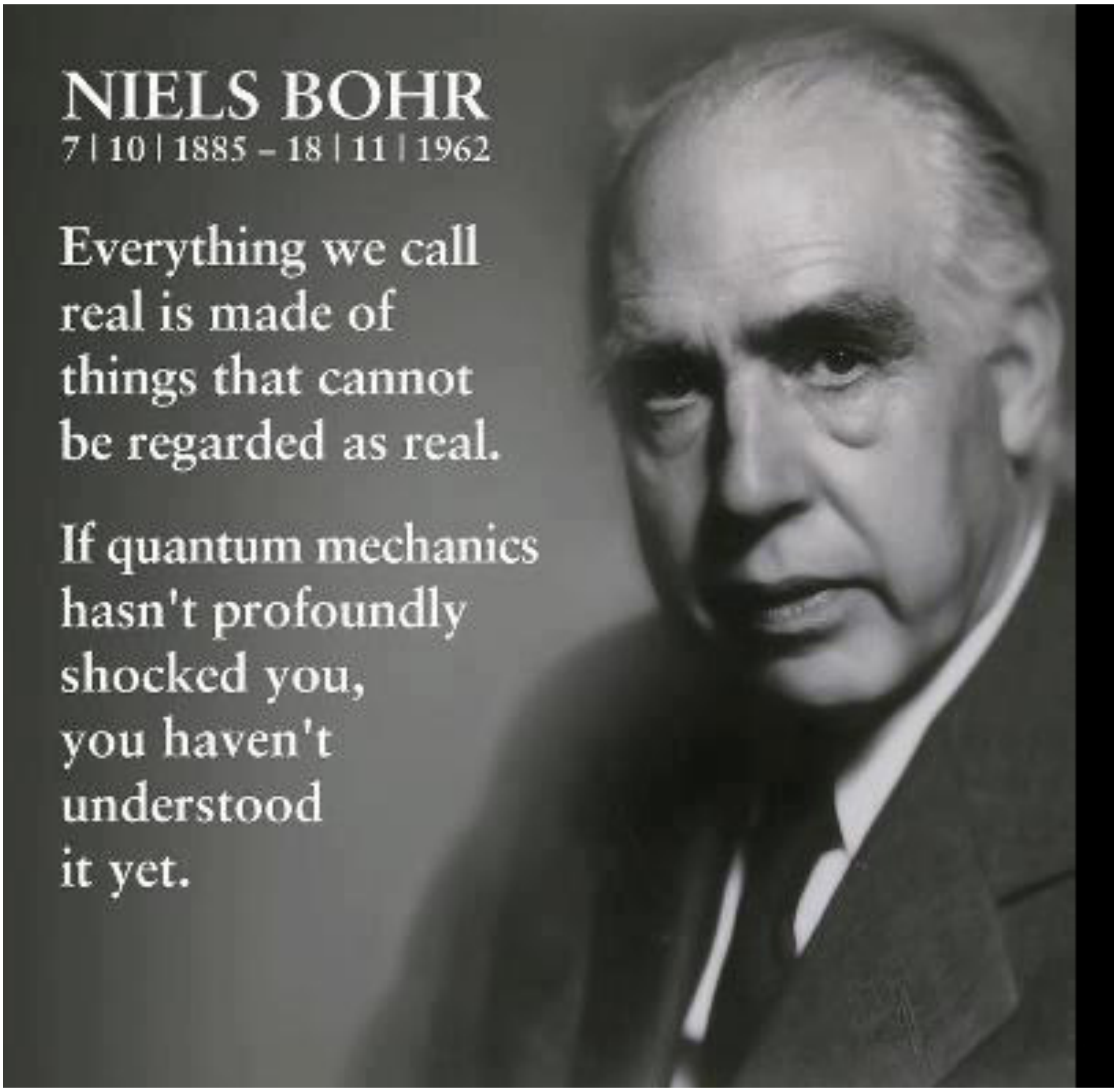
Comparing equation (ii) and equation (iii), we see

$A = \frac{1}{K}$ , $R = \frac{4}{K}$ and $\alpha = 0$.

Now, equation (iii) can be rewrite as,

$$\frac{1}{\lambda} = \frac{4}{K} \cdot \frac{1}{4} - \frac{4}{K} \cdot \frac{1}{n^2}$$

Or, $\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$



## Interpretation of the spectrum of atomic hydrogen from Bohr atomic model :

$E_{n_1} = -\frac{1}{8}\frac{mZ^2e^4}{{}^{2}_{o}n_1^2h^2}$ and $E_{n_2} = -\frac{1}{8}\frac{mZ^2e^4}{{}^{2}_{o}n_2^2h^2}$ where, $n_2 > n_1$.

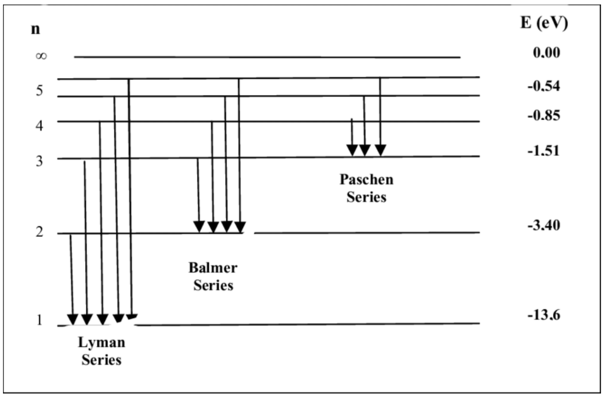
If an electron initially excited to higher orbit ($n_2$), then returns to the lower orbit ($n_1$). Then the difference of energy will be emitted in the form of radiation and give rise to a spectral line. The frequency of this line will be given by

$$h\nu = \Delta E = E_{n_2} - E_{n_1} = \frac{1}{8}\frac{mZ^2e^4}{{}^{2}_{o}h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\text{Or, wave number} = \frac{}{C} = \frac{1}{8}\frac{mZ^2e^4}{{}^{2}_{o}h^3C}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\text{Or, wave number} = R.\ Z^2.\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Where, $R = \frac{1}{8}\frac{me^4}{{}^{2}_{o}h^3C}$ = Rydberg constant = $1.096775 \times 10^7\ m^{-1}$.

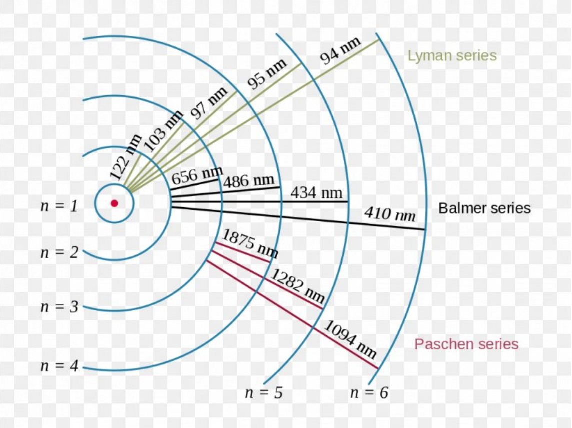


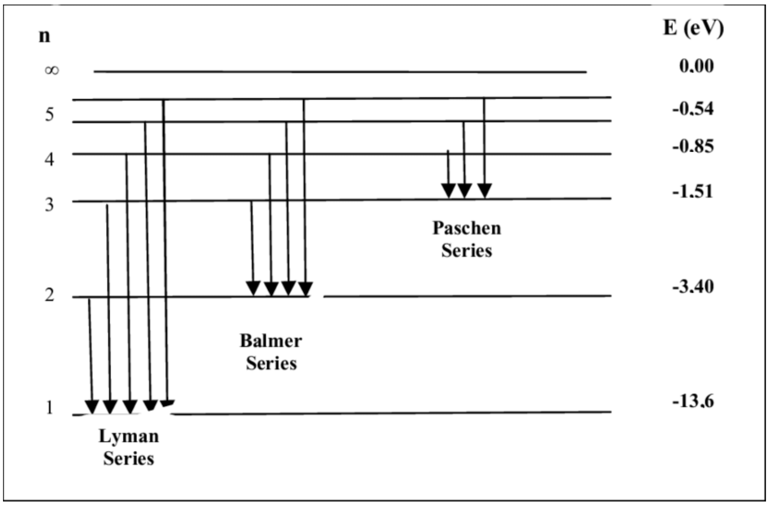
- ✤**The energy levels become gradually closer as n increases. Finally they converge to a limit. Correspondingly, the lines in the spectrum approach each other more closely until they merge into a continuum.**
- ✤**For large quantum numbers, the behaviour of the atom tends to that which would be expected from the classical theory. This is known as Bohr's correspondence principle.**

## Hydrogen spectrum series:

| Final orbit ($n_f$) | Initial orbit ($n_i$) | Spectrum series |
|---|---|---|
| 1 | 2, 3, 4, 5, ….. | Lyman series |
| 2 | 3, 4, 5, 6…… | Balmer series |
| 3 | 4, 5, 6,…… | Paschen series |
| 4 | 5, 6, 7… | Brackett series |
| 5 | 6, 7, 8…. | Pfund series |
| 6 | 7, 8, 9….. | Humphreys series |

Lyman series lays in the ultraviolet region, Balmer series in the visible region and other series in the infra-red region.





## Isotopic shift of atomic spectra:

**Angular momentum:** $mvr = n \cdot \frac{h}{2\pi}$

Moment of inertia: $I = mr^2$

We know from the exact angular momentum calculation method that for more precise calculation we should replace 'm' by $\frac{\mathrm{mM}}{(\mathrm{m}+\mathrm{M})}$.

★Reduced mass (μ)= $\frac{\mathrm{mM}}{(\mathrm{m}+\mathrm{M})}$.

★**Now, corrected energy expression in Bohr's orbit**

$$= -\frac{1}{8}\frac{\mu e^4 Z^2}{\varepsilon_0^2 n^2 h^2}$$

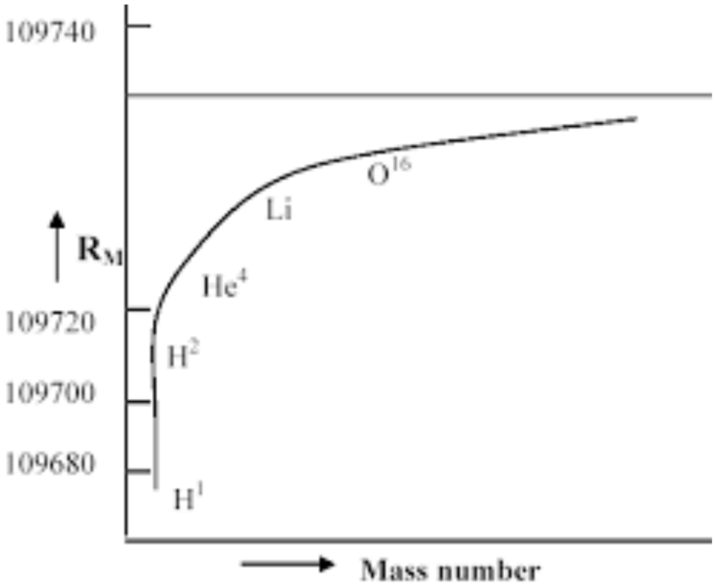
★So, corrected Rydberg constant ($R_{corr.}$) = $\frac{1}{8}\frac{e^4}{\varepsilon_o^2 h^3 C} \cdot \frac{\mathrm{mM}}{(\mathrm{m}+\mathrm{M})}$

[where, m= mass of electron and M= mass of nucleus].

Or, $R_{corr.} = \frac{1}{8}\frac{e^4}{\varepsilon_o^2 h^3 C} \cdot \frac{m}{(1+\frac{m}{M})}$.......(i)

★Now, if we consider the mass of nucleus infinite compare to the mass of electron (for heavier elements, $\frac{m}{M} = 0$), then corresponding Rydberg constant is $R_{\propto}$ (= $1.097373 \times 10^7\ m^{-1}$).

$$R_{\propto.} = \frac{1}{8}\frac{m\,.\,e^4}{\varepsilon_o^2 h^3 C} \quad ..........(ii)$$



★Comparing eqn. (i) and eqn.(ii), we see that

$$R_{corr.} = \frac{R}{(1+\frac{m}{M})} \quad .............(iii)$$

★For the lighter elements, the $\frac{m}{M}$ value cannot be ignore and its value is different for different isotopes of an element; and hence the $R_{corr}$ values are different for different isotopes of an element. So the wavelengths of the same transition are not same for the different isotopes of an element. This is called isotopic shift of atomic spectrum.

## Problem:

The Hα line of Balmer series in the spectrum of hydrogen occurs at 656.28 nm. Calculate the separation of this line in the spectrum of deuterium.

## Hints.

$$\frac{wavenumberforhydrogenatom}{wavenumberfordeuteriumatom} = \frac{R_H}{R_D}$$

**Practice set-II**

1. The wavelength of the first line of the Lyman series for hydrogen is identical to that of the second line of the Balmer series for some hydrogen like 'X'. Identify the ion and also find the ionisation energy of the ion.

2. Calculate the isotopic shift in terms of wavelength for the $H_\alpha$ line of $^1H$ and $^3H$ in the Balmer series. (Given, $R_\propto = 1.097373 \times 10^7\ m^{-1}$)

3. How does the concept of nuclear motion correct the Rydberg's constant? What are the experimental evidences to support this correction?

4. Compute the difference in wavelength for transition n=1 to n=2 in H and D.

5. Calculate the value of the longest wavelength of line in the Lyman series of hydrogen spectrum.

6. The second line ($H_\beta$) in Balmer series has wavelength 486.2 nm. Calculate the Rydberg constant in $cm^{-1}$.

## Merits of Bohr's atom model:

### (i) Stability of atom:

It explains the stability of atoms while it is lacking in the Rutherford's model. The instability in the Rutherford's model is overcome by incorporating the concept of stationary state.

### (ii) Prediction of frequency of the spectral lines:

The model not only explain the origin of the spectral lines in different series but also gives mathematical formulations which nicely fit the experimental observations at least made on the instruments of low resolving power.

### (iii) Rydberg constant:

Calculated value of R nicely agrees with the experimental one.

### (iv) Spectra of isotopes:

By considering the nuclear motion, the spectral shifts for the isotopes of lighter elements such as hydrogen for which masses of isotopes differ significantly are experimentally verified.

### (v) Determination of $\frac{m_e}{m_p}$ ratio:

By measuring Rydberg constant and using $R_{\text{corr.}} = \frac{1}{8\varepsilon_o^2 h^3 C} \frac{e^4}{} . \frac{m}{(1+\frac{m}{M})}$, $\frac{m_e}{m_p}$ ratio can be evaluated.

## Demerits of Bohr's atom model:

### (i) 2D concept.

### (ii) Involvement of both classical and quantum mechanics:

Here the principles of both quantum mechanics and classical mechanics have been taken into consideration as and when required. Hence, theoretically the model cannot be supported.

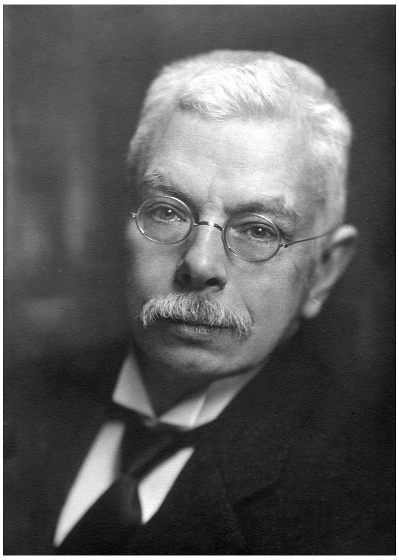
### (iii) Applicable for only hydrogen like system.

### (iv) Fine spectra of the spectral lines:

The model can explain the origin of the spectral lines along with their frequencies when they observed with the instrument of low resolving power. But actually each single line is consisting of a number of fine lines which are closely packed. This has been observed by using instrument of very high resolving power. These cannot be explaining by Bohr's theory.

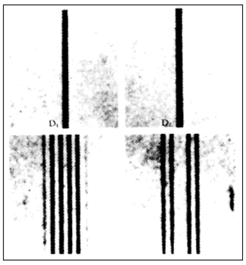
### (v) Zeeman effect and Stark effect:

The single line in the spectrum is found to split into a number of closely spaced lines in the presence of an external magnetic field (Zeeman Effect) and electric field (Stark Effect). Such splitting cannot find any support from the Bohr's theory.



**Pieter Zeeman (25.05.1865 to 09.10.1943)**

## Zeeman Effect



- Effect produced by a strong magnetic field on the light emitted by a radiant body is called Zeeman effect; it is observed as a **splitting** of its spectral lines. It was first observed (1896) by Pieter **Zeeman**. The breakthrough resulted in Zeeman receiving the 1902 Nobel Prize in Physics with former instructor Hendrik Antoon Lorentz.

- Historically, one distinguishes between the **normal** and an **anomalous Zeeman effect** (discovered by Thomas Preston). The anomalous effect appears on transitions where the net spin of the electrons is non-zero. It was called "anomalous" because the electron spin had not yet been discovered, and so there was no good explanation for it at the time that Zeeman observed the effect.

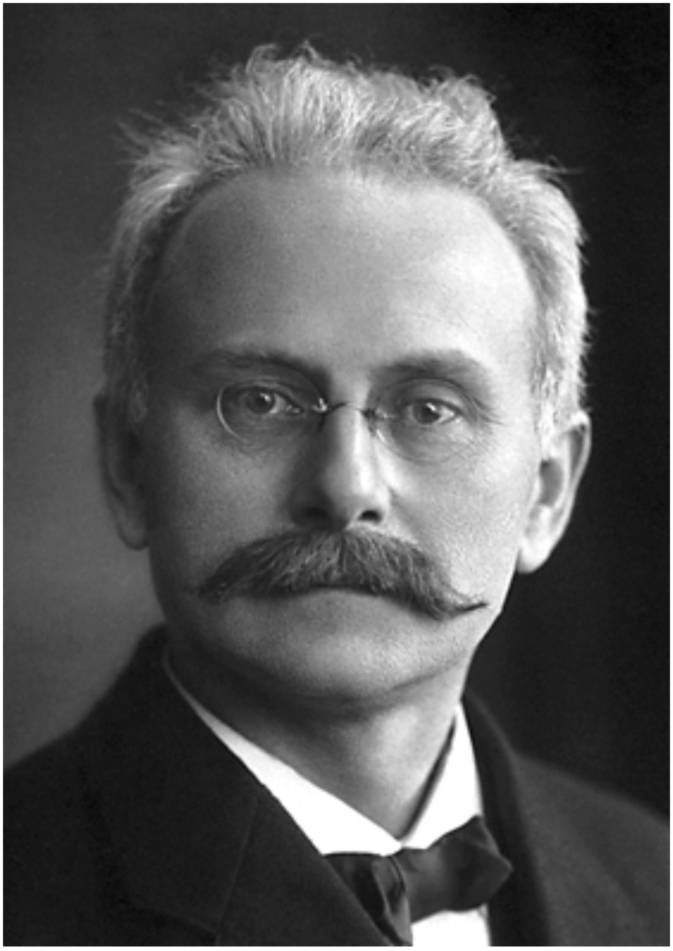
- According to **Zeeman effect**, the l = 1 energy level will be splitted into into 2l+1 = 3 levels, when the atom is placed in the presence of magnetic fields.

## Stark effect:

- The **Stark effect** is the shifting and splitting of spectral lines of atoms and molecules due to the presence of an external electric field. It is the electric-field analogue of the Zeeman effect, The effect is named after the German physicist Johannes Stark, who discovered it in 1913.

- It was independently discovered in the same year by the Italian physicist Antonino Lo Surdo, and in Italy it is thus sometimes called the **Stark–Lo Surdo effect**.

- The discovery of this effect contributed importantly to the development of quantum theory and was rewarded with the Nobel Prize in Physics for Johannes Stark in the year 1919.



**Johannes Stark** (15.04.1874 to 21.06.1957)

## (vi) Intensity of spectral line:

Bohr's atomic theory does not say anything about the intensity of spectral lines.

## Arnold Sommerfeld

Arnold Sommerfeld was a famous atomic physicist and mathematician who is known mostly for his work on atomic theory in the field of quantum mechanics and for mentoring more recipients of the Nobel Prize in Physics than any other physicist. **He was nominated for the Nobel Prize 84 times, more than any other physicist (including Otto Stern, who got nominated 82 times), but he never received the award.** He introduced the second quantum number (azimuthal quantum number) and the third quantum number (magnetic quantum number). He also introduced the fine-structure constant and pioneered X-ray wave theory.

| | |
|---|---|
| **Born** | Arnold Johannes Wilhelm Sommerfeld<br>5 December 1868<br>Königsberg, Kingdom of Prussia |
| **Died** | 26 April 1951 (aged 82)<br>Munich, West Germany |

Four of Sommerfeld's doctoral students, Werner Heisenberg, Wolfgang Pauli, Peter Debye, and Hans Bethe went on to win Nobel Prizes, while others, most notably, Walter Heitler, Rudolf Peierls, Karl Bechert, Hermann Brück, Paul Peter Ewald, Eugene Feenberg, Herbert Fröhlich, Erwin Fues, Ernst Guillemin, Helmut Hönl, Ludwig Hopf, Adolf Kratzer, Otto Laporte, Wilhelm Lenz, Karl Meissner, Rudolf Seeliger, Ernst C. Stückelberg, Heinrich Welker, Gregor Wentzel, Alfred Landé, and Léon Brillouin became famous in their own right. Three of Sommerfeld's postdoctoral students, Linus Pauling, Isidor I. Rabi and Max von Laue, won

Nobel Prizes, and ten others, William Allis, Edward Condon, Carl Eckart, Edwin C. Kemble, William V. Houston, Karl Herzfeld, Walther Kossel, Philip M. Morse, Howard Robertson, and Wojciech Rubinowicz went on to become famous in their own right. Walter Rogowski, an undergraduate student of Sommerfeld at RWTH Aachen, also went on to become famous in his own right. Max Born believed Sommerfeld's abilities included the "discovery and development of talents. Albert Einstein told Sommerfeld: "What I especially admire about you is that you have, as it were, pounded out of the soil such a large number of young talents.Sommerfeld's style as a professor and institute director did not put distance between him and his colleagues and students. He invited collaboration from them, and their ideas often influenced his own views in physics. He entertained them in his home and met with them in cafes before and after seminars and colloquia. Sommerfeld owned an alpine ski hut to which students were often invited for discussions of physics as demanding as the sport.

In 1928/1929, Sommerfeld traveled around the world with major stops in India, China, Japan, and the United States.

As for Sommerfeld’s once patriotic views, he wrote to Einstein shortly after Hitler took power: "I can assure you that the misuse of the word ‘national’ by our rulers has thoroughly broken me of the habit of national feelings that was so pronounced in my case. I would now be willing to see Germany disappear as a power and merge into a pacified Europe.

# Arnold Sommerfeld revised Niels Bohr's model of the atom in 1915

- Sommerfeld showed that another number is needed to describe electron orbits besides the shell number ($n$). This is known as the azimuthal quantum number ($\ell$).

- The azimuthal quantum number describes the orbital angular momentum of an electron, which defines the 'shape' of the orbit. Bohr had assumed that orbits would be circular, but Sommerfeld showed that they could take as many shapes.

- The maximum number of electrons that are allowed to have the same shape in each shell = $2(2\ell+1)$.

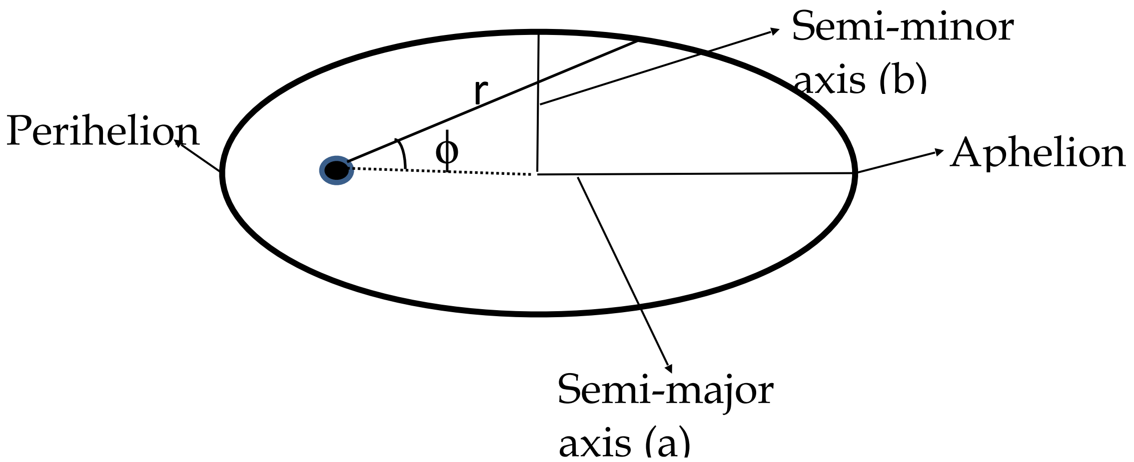
- In 1920, Sommerfeld realised that another number was needed to describe the Zeeman effect. Sommerfeld realised that the same $\ell$ shape can have different orientations in space defined by the magnetic quantum number ($m$). The maximum number of different orientations = $2\ell+1$.

- A magnetic field causes electrons of the same energy, which would otherwise produce a single spectral line, to have different energies depending on their orientation with respect to the magnetic field. In the case of a cloud of hydrogen atoms, the transition from the second to the first shell produces three lines as about 1/3 gain energy, 1/3 loose energy, and 1/3 are unaffected by the presence of the magnetic field. This explained the normal Zeeman effect.

- Sommerfeld was still unable to explain the anomalous Zeeman effect. This is a term used to describe spectra that split into more than three lines in the presence of a magnetic field, and it is more likely to occur in lines made from atoms with an odd number of electrons in their outer shell. This meant that many scientists still did not accept that electrons have orbits that are defined by quantised positions and directions in space. Paul Dirac would later explain the anomalous Zeeman effect using another quantum number, $s$.

## Sommerfeld's first modification:

**(i) Elliptic orbits**: In general, the electrons are revolving around the nucleus in some specific elliptic paths with different eccentricities (ε).



Eccentricity (ε) = $\sqrt{1 - (\frac{b}{a})^2}$

**(ii) Quantum restriction:** If the position of a revolving electron around the nucleus at any instant is (r, ϕ) where r is the radius vector measured from the nucleus and ϕ is the angle between the radius vector and fixed axis (say, X - axis), then only certain elliptic orbits will be allowed which satisfy the conditions:

$$\oint P_\phi d\phi = k.h \text{ and } \oint P_r dr = n_r.h$$

Here integrals are taken over one cycle, $P_\phi$ and $P_r$ are angular and radial momentum of electrons respectively and, **k and $n_r$ are two positive integer, called azimuthal and radial quantum numbers.**

k and $n_r$ are related as $n = k + n_r$

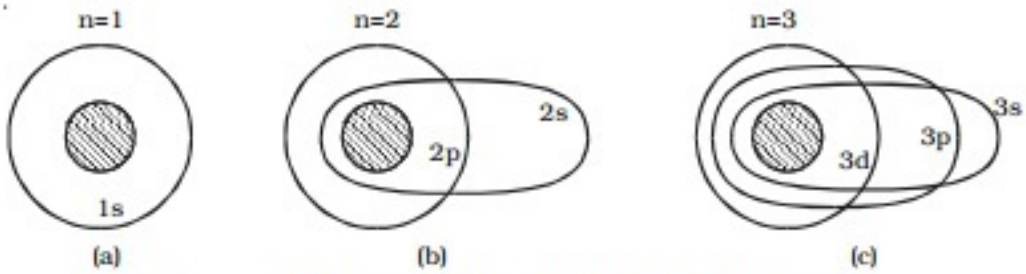
For a given orbit (n), values of k = 1, 2.....n and values of $n_r$= (n-1), (n-2).....0 respectively.

| k | 1 | 2 | 3 | 4 | n |
|---|---|---|---|---|---|
| $n_r$ | (n-1) | (n-2) | (n-3) | (n-4) | 0 |
| l (from wave mechanics) | 0 | 1 | 2 | 3 | (n-1) |
| Name of orbit | s | p | d | f | |

## Shapes of sub-orbits in different principal energy levels:

$$\frac{a}{b} = \frac{Semi-majoraxis}{Semi-minoraxis} = \frac{n}{k} = \left(\frac{n_r+k}{k}\right)$$

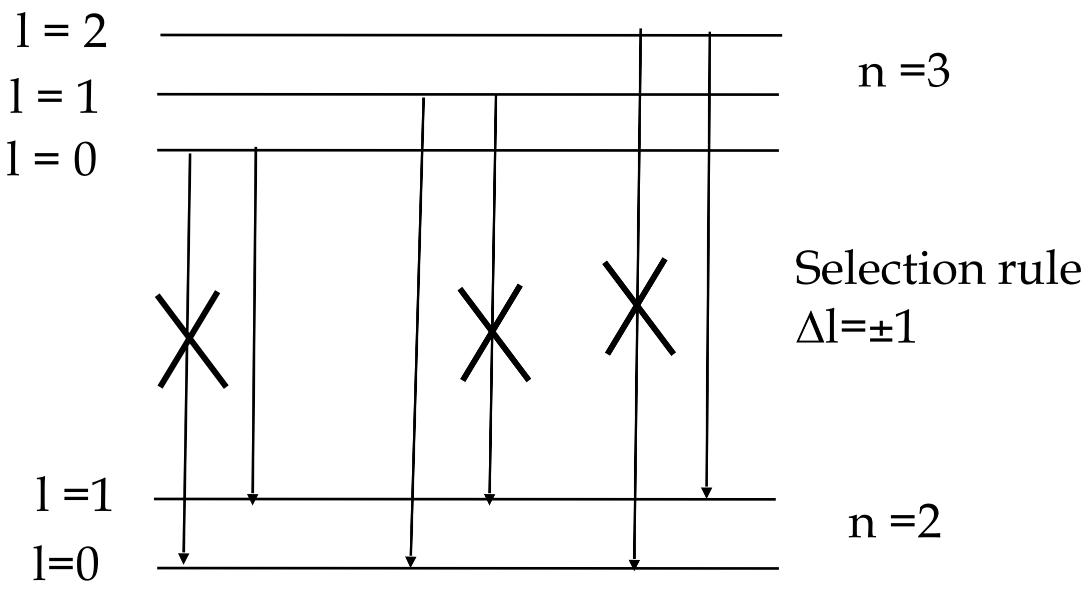
For a particular value of n, as the value of k increases ellipticity of the orbit decreases and for the highest value of k, it becomes a circular orbit. So, the minimum value of k, is the most elliptic in nature.



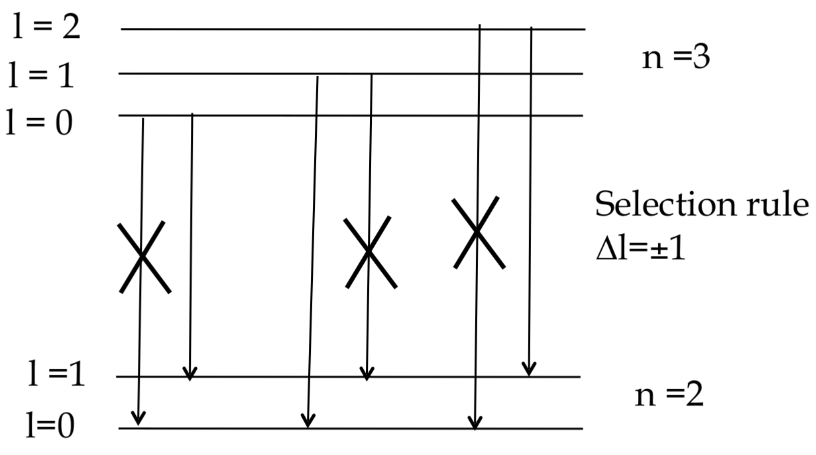
Various sub-shells for the electrons

## Fine spectrum of first line of Balmer series:

There are 3 sub-orbit for n=3 and 2 sub-orbit for n=2. So there are 3 X 2 = 6 possible transitions between these two orbits.

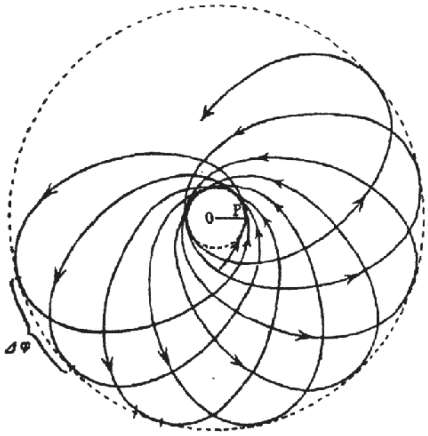


But due to the restriction of selection rule, the $H_\alpha$ line of Balmer series consists of three fine closely space lines.

| Bohr's atom model | Sommerfeld's first modification |
|---|---|
| It fails to explain the fine spectrum. |  <br>It explains the three fine lines in $H_\alpha$ of Balmer series. But this modification does not give any idea about the energy of the sub-orbits. So, all the three transitions will have same energy, i.e. effectively one line will appear. Thus, it also fails to explain the fine spectrum. |

## Sommerfeld's second modification (Relativistic correction):

**Precession:** The slow movement of the axis of a rotating body around another axis due to torque acting to change the direction of first axis.



According to theory of relativity:

$$m = \frac{m_0}{\sqrt{1-\frac{v^2}{c^2}}}$$

Where, $m_0$ = rest mass, m= mass at velocity v and c= velocity of light. When v=c, then m= ∝.

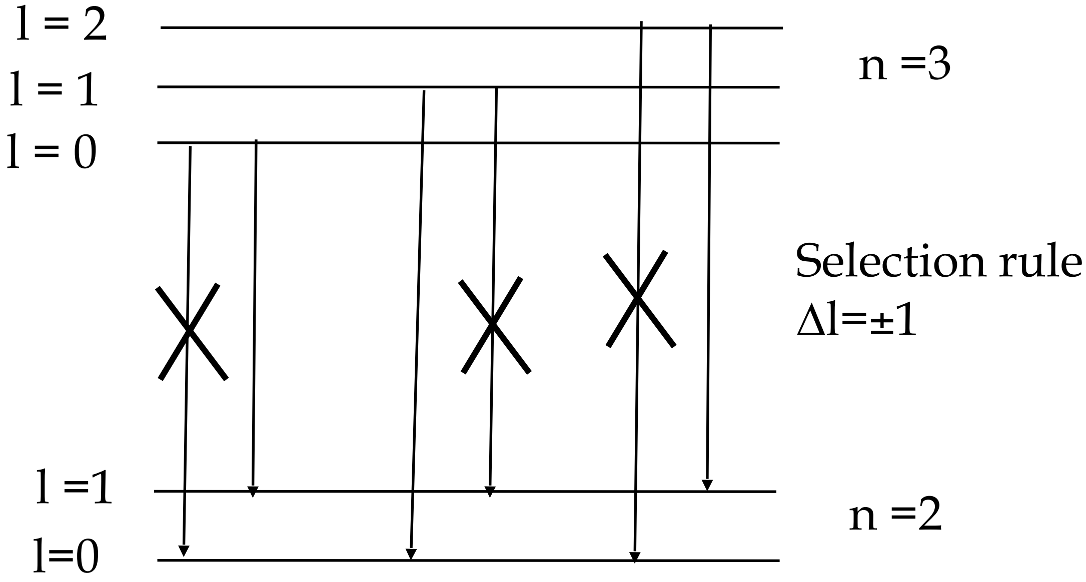
Now, the velocity of electron (v) = $\left(\frac{Ze^2}{4\pi\varepsilon_0 mr}\right)^{1/2}$

In the elliptic sub-orbits, the distance between the electron and nucleus changes constantly and hence the velocity of the electron changes continuously. Velocity of electron is maximum at perihelion position and velocity of electron is minimum at aphelion position. As a result, there is a continual mass variation and leads to generate a perturbation in the equilibrium force between electron and nucleus. Because of this fact, the path of the electron is rosette which is an ellipse whose major axis precesses slowly in the plane of the ellipse about an axis passing through one of its foci at which the nucleus is residing.

Now, $E_{(n,\,k)} = -\frac{me^4Z^2}{8\varepsilon_0^2 n^2 h^2}\left[1+\frac{a^2Z^2}{n}\left(\frac{1}{k}-\frac{3}{4n}\right)\right]$

Where, α = fine structure constant = $\frac{e^2}{2\varepsilon_0 ch} = \frac{1}{137}$.

In the above equation, the energy of a sub-orbit can be calculated. For a particular n, the energy of sub-orbit increases with increasing k. Hence, the fine structure of spectrum can be explained.



**Demerits of Sommerfeld's atom model:**

# Louis de Broglie

- **Louis Victor Pierre Raymond de Broglie, 7th duc de Broglie** 15 August 1892 – 19 March 1987)was a French physicist who made groundbreaking contributions to quantum theory.
- In his 1924 PhD thesis, he postulated the wave nature of electrons and suggested that all matter has wave properties. This concept is known as the de Broglie hypothesis, an example of wave–particle duality, and forms a central part of the theory of quantum mechanics.
- De Broglie won the Nobel Prize for Physics in 1929, after the wave-like behaviour of matter was first experimentally demonstrated in 1927 (**Davisson–Germer experiment** ).
- The 1925 pilot-wave model, and the wave-like behaviour of particles discovered by de Broglie was used by Erwin Schrödinger in his formulation of wave mechanics.
- De Broglie had intended a career in humanities, and received his first degree in history. Afterwards he turned his attention toward mathematics and physics and received a degree in physics. With the outbreak of the First World War in 1914, he offered his services to the army in the development of radio communications.

## De-Broglie hypothesis:

**Each particle has its associated matter waves or pilot waves which guide the particles, the wave length of such waves is given by λ= $\frac{h}{p}$ , where p is momentum and h is Planck's constant.**

This theory set the basis of wave mechanics. It was supported by Einstein, confirmed by the electron diffraction experiments of G P Thomson and Davisson and Germer, and generalized by the work of Schrödinger.

**Matter wave:** The wave associated with matter because of de Broglie hypothesis is called matter wave or pilot wave or de Broglie wave. The velocity of matter wave may less than the velocity of light. But the velocity of electromagnetic radiation is always equal to the velocity of light.

**Problem 1:** A bullet of 2 g mass is moving in the velocity of 300 m/s. Calculate the wavelength associated with the bullet?

**Problem 2:** Suppose an electron moving in 1/10th velocity of light. What will be the de-Broglie wavelength?

From the above two examples, it can be shown that de-Broglie wavelength is insignificant in the macroscopic world but it is very significant in the microscopic world.

## Relativistic de Broglie equation:

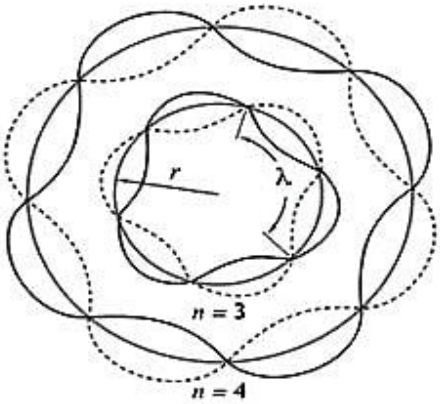
Matter wave length (λ) = $\dfrac{h}{\dfrac{m_o}{\sqrt{(1-\frac{v^2}{C^2})}}\,.\,v}$

## Bohr's hypothesis from de Broglie hypothesis

**The De Broglie Wavelength**

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

$\lambda$ = wavelength
$h$ = Planck's constant ($6.63 \times 10^{-34}$ J • s)
$p$ = momentum
$m$ = mass
$v$ = speed



2πr = n λ = n$\dfrac{h}{P}$ = n.$\dfrac{h}{mv}$

Or, mvr = n$\dfrac{h}{2\pi}$

## Problem:

1. Calculate the number of de Broglie wave length in the second Bohr's orbit.
2. Calculate the wavelength of an electron revolving in the 3rd Bohr orbit of hydrogen atom.
3. Prove that de Broglie wave length of any Bohr orbit is equal to 2πna$_{o.}$

   Hints.$r_n$= $\dfrac{\varepsilon_0 n^2 h^2}{\pi m Z e^2}$; $v_n$= $\dfrac{Ze^2}{2\varepsilon_0 n h}$

## Production of different wavelength using electron beam:

If an electron is kept at potential gradient V, the energy of the electron is equal to eV. Here, potential energy is zero. Now if the electron moves in the velocity v in this condition, then kinetic energy of the electron will $\frac{1}{2}mv^2$.

Now, $\frac{1}{2}mv^2 = eV$; or $mv = \sqrt{2meV}$

So, $\lambda = \frac{h}{\sqrt{2meV}}$

## Problems:

1. Calculate the wave length of an electron under potential gradient 150 volt.

# Werner Karl Heisenberg

**Werner Karl Heisenberg** (5 December 1901 – 1 February 1976) was a German theoretical physicist and one of the key pioneers of quantum mechanics. He published his work in 1925 in a breakthrough paper. In the subsequent series of papers with Max Born and Pascual Jordan, during the same year, this matrix formulation of quantum mechanics was substantially elaborated. He is known for the Heisenberg uncertainty principle, which he published in 1927. Heisenberg was awarded the 1932 Nobel Prize in Physics "for the creation of quantum mechanics".

He also made important contributions to the theories of the hydrodynamics of turbulent flows, the atomic nucleus, ferromagnetism, cosmic rays, and subatomic particles, and he was instrumental in planning the first West German nuclear reactor at Karlsruhe, together with a research reactor in Munich, in 1957. He was a principal scientist in the German nuclear weapons program during World War II. He travelled to occupied Copenhagen where he met and discussed the German project with Niels Bohr.

Following World War II, he was appointed director of the Kaiser Wilhelm Institute for Physics, which soon thereafter was renamed the Max Planck Institute for Physics. He was director of the institute until it was moved to Munich in 1958, when it was expanded and renamed the Max Planck Institute for Physics and Astrophysics.

Heisenberg was also president of the German Research Council, chairman of the Commission for Atomic Physics, chairman of the Nuclear Physics Working Group, and president of the Alexander von Humboldt Foundation.

He studied physics and mathematics from 1920 to 1923 at the Ludwig Maximilian University of Munich and the Georg-August University of Göttingen. At Munich, he studied under Arnold Sommerfeld and Wilhelm Wien. At Göttingen, he studied physics with Max Born and James Franck and mathematics with David Hilbert. He received his doctorate in 1923, at Munich under Sommerfeld. At Göttingen, under Born, he completed his habilitation in 1924 with a *Habilitationsschrift* (habilitation thesis) on the anomalous Zeeman effect.

Because Sommerfeld had a sincere interest in his students and knew of Heisenberg's interest in Niels Bohr's theories on atomic physics, Sommerfeld took Heisenberg to Göttingen to attend the Bohr Festival of June 1922. At the event, Bohr was a guest lecturer and gave a series of comprehensive lectures on quantum atomic physics. There, Heisenberg met Bohr for the first time, and it had a significant and continuing effect on him.

Heisenberg's doctoral thesis, the topic of which was suggested by Sommerfeld, was on turbulence; the thesis discussed both the stability of laminar flow and the nature of turbulent flow. The problem of stability was investigated by the use of the Orr–Sommerfeld equation, a fourth order linear differential equation for small disturbances from laminar flow. He briefly returned to this topic after World War II.

It was in Copenhagen, in 1927, that Heisenberg developed his uncertainty principle, while working on the mathematical foundations of quantum mechanics. On 23 February, Heisenberg wrote a letter to fellow physicist Wolfgang Pauli, in which he first described his new principle. In his paper on the principle, Heisenberg used the word "*Ungenauigkeit*" (imprecision), not uncertainty, to describe it.

## Interpretation of Quantum Theory

The development of quantum mechanics, and the apparent contradictory implications in regard to what is "real" had profound philosophical implications, including what scientific observations truly mean. In contrast to Albert Einstein and Louis de Broglie, who were realists who believed that particles had an objectively true momentum and position at all times (even if both could not be measured), Heisenberg was an anti-realist, arguing that direct knowledge of what is "real" was beyond the scope of science. Writing in his book *The Physicist's Conception of Nature,* Heisenberg argued that ultimately we only can speak of the *knowledge* (numbers in tables) which describes something about particles but we can never have any "true" access to the particles themselves.

We can no longer speak of the behaviour of the particle independently of the process of observation. As a final consequence, the natural laws formulated mathematically in quantum theory no longer deal with the elementary particles themselves but with our knowledge of them. **Nor is it any longer possible to ask whether or not these particles exist in space and time objectively ... When we speak of the picture of nature in the exact science of our age, we do not mean a picture of nature so much as a *picture of our relationships with nature*. ...Science no longer confronts nature as an objective observer, but sees itself as an actor in this interplay between man [*sic*] and nature.** The scientific method of analysing, explaining and classifying has become conscious of its limitations, which arise out of the fact that by its intervention science alters and refashions the object of investigation. In other words, method and object can no longer be separated

**Shortly after the discovery of the neutron by James Chadwick in 1932, Heisenberg submitted the first of three papers on his neutron-proton model of the nucleus. After Adolf Hitler came to power in 1933, Heisenberg was attacked in the press as a "White Jew". Supporters of *Deutsche Physik*, or Aryan Physics, launched vicious (inhuman) attacks against leading theoretical physicists, including Arnold Sommerfeld and Heisenberg. From the early 1930s onward, the anti-Semitic and anti-theoretical physics movement *Deutsche Physik* had concerned itself with quantum mechanics and the theory of relativity. As applied in the university environment, political factors took priority over scholarly ability, even though its two most prominent supporters were the Nobel Laureates in Physics Philipp Lenard and Johannes Stark**.

## Uncertainty principle

In quantum mechanics, the uncertainty principle (also known as Heisenberg's uncertainty principle) is any of a variety of mathematical inequalities asserting a fundamental limit to the precision with which the values for certain pairs of physical quantities of a particle, known as **complementary variables or canonically conjugate variables** such as position *x* and momentum *p*, can be predicted from initial conditions, or, depending on interpretation, to what extent such conjugate properties maintain their approximate meaning, as the mathematical framework of quantum physics does not support the notion of simultaneously well-defined conjugate properties expressed by a single value. The uncertainty principle implies that it is in general not possible to predict the value of a quantity with arbitrary certainty, even if all initial conditions are specified.

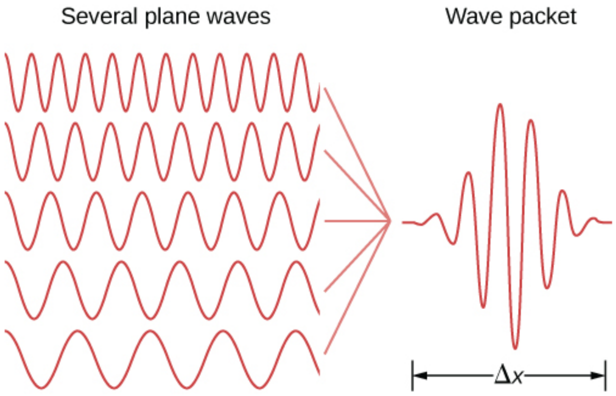
$$\Delta x.\ \Delta P \geq \frac{h}{4\pi}$$

($\hbar$ is the reduced Planck constant, $h/2\pi$).

**Historically, the uncertainty principle has been confused with a related effect in physics, called the observer effect,** which notes that measurements of certain systems cannot be made without affecting the system, that is, without changing something in a system. Heisenberg utilized such an observer effect at the quantum level as a physical "explanation" of quantum uncertainty. It has since become clearer, however, **that the uncertainty principle is inherent in the properties of all wave-like systems, and that it arises in quantum mechanics simply due to the matter wave nature of all quantum objects.** Thus, *the uncertainty principle actually states a fundamental property of quantum systems and is not a statement about the observational success of current technology*. It must be emphasized that *measurement* does not mean only a process in which a physicist-observer takes part, but rather any interaction between classical and quantum objects regardless of any observer.

Since the uncertainty principle is such a basic result in quantum mechanics, typical experiments in quantum mechanics routinely observe aspects of it. Certain experiments, however, may deliberately test a particular form of the uncertainty principle as part of their main research program. These include, for example, tests of number–phase uncertainty relations in superconducting or quantum optics systems. Applications dependent on the uncertainty principle for their operation include extremely low-noise technology such as that required in gravitational wave interferometers.

To illustrate the momentum-position uncertainty principle, consider a free particle that moves along the $x$-direction. The probability density is *uniform* and independent of time. The particle is equally likely to be found anywhere along the $x$-axis but has definite values of wavelength and wave number, and therefore momentum. The uncertainty of position is infinite (we are completely uncertain about position) and the uncertainty of the momentum is zero (we are completely certain about momentum). This account of a free particle is consistent with Heisenberg's uncertainty principle.



: Adding together several plane waves of different wavelengths can produce a wave that is relatively localized.

Similar statements can be made of localized particles. In quantum theory, a localized particle is modeled by a linear superposition of free-particle (or plane-wave) states called a **wave packet**. An example of a wave packet is shown in the above figure. A wave packet contains many wavelengths and therefore by de Broglie's relations many momenta—possible in quantum mechanics! This particle also has many values of position, although the particle is confined mostly to the interval Δx. The particle can be better localized (Δx can be decreased) if more plane-wave states of different wavelengths or momenta are added together in the right way (Δp is increased). Note that the uncertainty principle has nothing to do with the precision of an experimental apparatus. Even for perfect measuring devices, these uncertainties would remain because they originate in the wave-like nature of matter. The precise value of the product Δx.Δp depends on the specific form of the wave function. Interestingly, the Gaussian function (or bell-curve distribution) gives the minimum value of the uncertainty product.

Unlike the position uncertainty for the electron, the position uncertainty for the bowling ball is immeasurably small. Planck's constant is very small, so the limitations imposed by the uncertainty principle are not noticeable in macroscopic systems such as a bowling ball.

## Heisenberg's Uncertainty principle:

Uncertainty principle introduced in 1927, by the German physicist Werner Heisenberg. The uncertainty principle states that it is impossible to measure simultaneously the position and momentum of a microscopic element with desired accuracy (alternatively, the more precisely the position of some particle is determined, the less precisely its momentum can be predicted from initial conditions, and vice versa.). Mathematically the product of uncertainty in position ($\Delta x$) and uncertainty in momentum of a microscopic particle is always greater than a constant value. The value of constant was later on found to be $\frac{h}{4\pi}$.

So, $\Delta x . \Delta P \geq \frac{h}{4\pi}$

Now, $\Delta P = m . \Delta v$ [$\Delta v$ = uncertainty in velocity]

So, $\Delta v = \frac{h}{4\pi m . \Delta x}$

PROBLEM:

1. Calculate the uncertainty in position of an electron having $\Delta P = 10^{-3}P$, where P is momentum and velocity of electron is 1/10th of velocity of light.
2. Uncertainty in position of an electron is $10^{-8}$ m. What will be the uncertainty in velocity?
3. Prove that an electron cannot exist in the nucleus. (dimension of nucleus in the range of $10^{-14}$ m).
4. Prove that proton/neutron can exist in the nucleus.
5. Calculate the uncertainty in position of an electron having wavelength 600 nm. Uncertainty in wavelength is one parts per million.

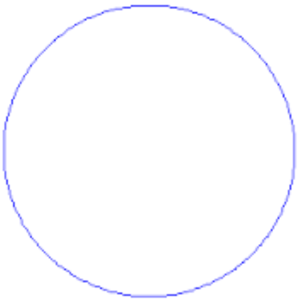
## Orbit from the point of Heisenberg's uncertainty principle:

So, $\Delta v = \dfrac{h}{4\pi m \,.\, \Delta x}$

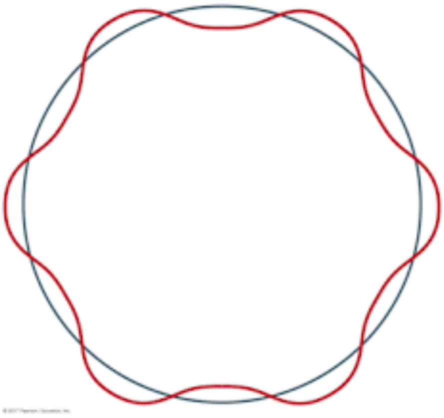
Or, $\Delta x = \dfrac{h}{4\pi m \,.\, \Delta v}$

There is always an uncertainty in the position of electron; it concludes electron cloud in the orbit instead of Bohr's trajectory path.

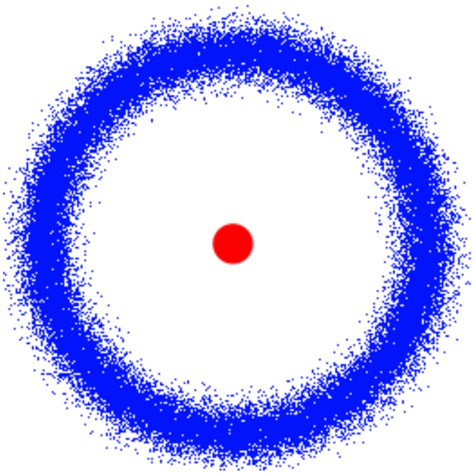
**Bohr atom**



**Bohr -de Broglie**



**Bohr -Heisenberg**



## Uncertainty in energy-time relation:

Another kind of uncertainty principle concerns uncertainties in simultaneous measurements of the energy of a quantum state and its lifetime,

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

Where, ΔE is the uncertainty in the energy measurement and Δt is the uncertainty in the lifetime measurement. The general meaning of the energy-time principle is that a quantum state that exists for only a short time cannot have a definite energy. The reason is that the frequency of a state is inversely proportional to time and the frequency connects with the energy of the state, so to measure the energy with good precision, the state must be observed for many cycles.

To illustrate, consider the excited states of an atom. The finite lifetimes of these states can be deduced from the shapes of spectral lines observed in atomic emission spectra. Each time an excited state decays, the emitted energy is slightly different and, therefore, the emission line is characterized by a *distribution* of spectral frequencies (or wavelengths) of the emitted photons. As a result, all spectral lines are characterized by spectral widths. The average energy of the emitted photon corresponds to the theoretical energy of the excited state and gives the spectral location of the peak of the emission line. Short-lived states have broad spectral widths and long-lived states have narrow spectral widths.

## *Dual nature of light*

| **Particle nature** | **Wave nature** |
|---|---|
| Photoelectric effect, Compton effect | Diffraction, reflection |

# Schrödinger Equation:

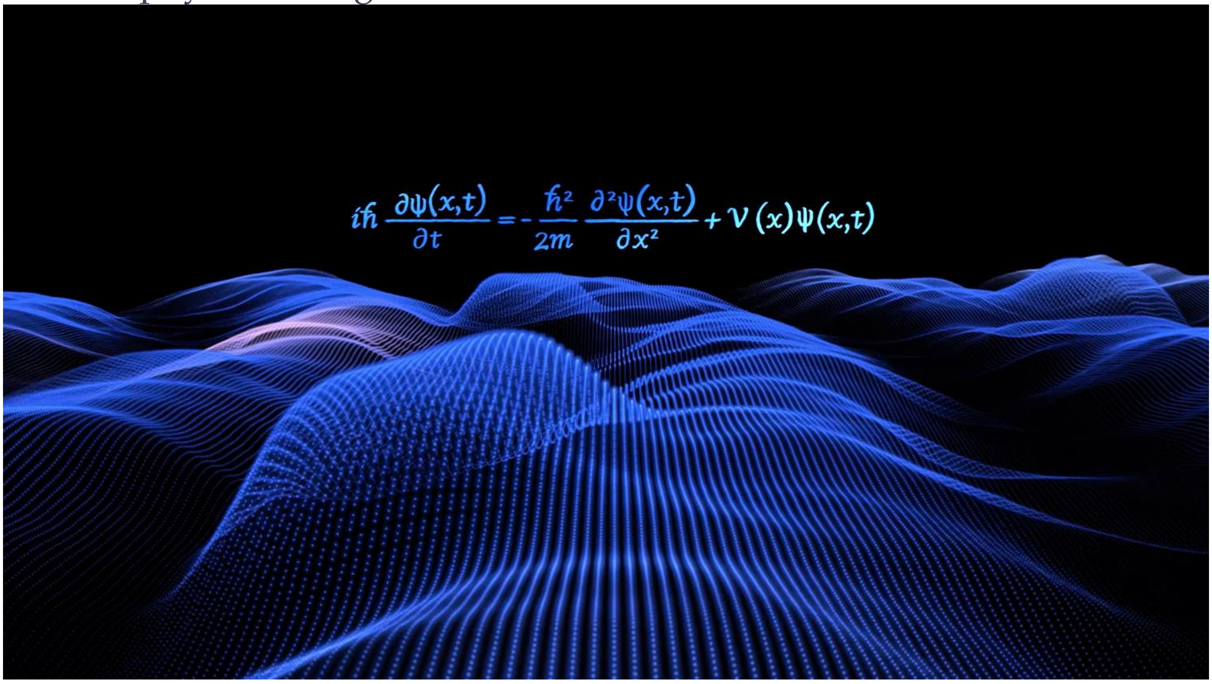
On 12th August 1887, a man who would go on to revolutionize not only the field of physics, but also biology, was born.

From a very young age, Erwin Schrödinger had shown immense talent for mathematics and physics. He also had interests in poetry and philosophy.

At the University of Vienna, Schrödinger met many talented physicists, including Ludwig Boltzmann's successor Fritz Hasenöhrl, and Franz Exner. Schrödinger mastered the concept of eigenvalues in continuous media, and did a lot of experimenting. During his time at the University of Zurich, Schrödinger published a lot of papers on thermodynamics. His greatest achievement, however, was yet to come.

Erwin Schrödinger was not happy with Niels Bohr's old quantum theory. As his background with eigenvalue problems would suggest, he believed that atomic spectra should be determined by some kind of eigenvalue problem.

He came up with an equation which could be used to find the energy states of an atom. The equation describes the Hamiltonian operator, which when operated on an abstract mathematical function called the wave function, produced energy as a result. The energy is an eigenvalue here. The time-dependent version of Schrödinger's equation also relates the Hamiltonian with time. This equation brought him the 1933 Nobel Prize in physics, along with Paul Dirac.



*Schrödinger's equation.*

The equation was revolutionary as it solved one of the greatest problems in the quantum-mechanical model of the atom. Schrödinger did not like Heisenberg's formulation of quantum mechanics – matrix mechanics – since it lacked visualization and was mostly mathematical. Schrödinger was inspired by de Broglie's idea of wave-particle duality. The solution to Schrödinger's equation is a wave that describes the quantum aspects of a system. The physical interpretation of this wave remains one of the greatest philosophical problems in modern physics.

The solution of Schrödinger's equation – the wave function for the system can, using Fourier analysis, be replaced by an infinite series of the wave functions of the individual states, which are natural harmonics of each other. The replacement waves describe the individual states of the quantum system, and their amplitudes give the relative importance of that particular state to the whole system.

Schrödinger's equation has been universally recognized as one of the greatest achievements of twentieth century science, containing much of physics and in principle, all of chemistry.

**Max Born would later discover that in an atom, the square of the wave function gives the probability of finding the electron in that region.**

**This replaced well-defined orbits in the atom with the concept of orbitals.** New concepts like hybridization were also discovered.

Schrödinger's theory, known as wave mechanics, also gave a complete description of the spectral lines of the hydrogen atom. (Solving Schrödinger's equation for atoms of elements with higher atomic numbers, however, is extremely complicated.)

It was widely accepted that matter exhibits both particle and wave properties. However, Schrödinger soon began to suspect this view. He wanted to go back to the classical idea of waves. He started to believe that waves alone can describe everything; particles were useless. Schrödinger proposed that a particle is just a wave group with small dimensions in all directions. However, Hendrik Lorentz pointed out that this wave would spread out with time, and cannot describe particles.

By that time, the widely accepted view held that quantum states exist in a superposition. Everything is thus reduced to probability by quantum mechanics. Schrödinger, however, was dissatisfied with this view. To demonstrate how absurd the idea is, he put forward a thought experiment. A cat is put in a box with a radioactive material and a poison bottle. The latter is connected to a hammer, which in turn is connected with a Geiger counter (a device which can detect radioactive decay). It is set such that if the radioactive substance decays, the hammer breaks the bottle and releases the poison, thus killing the cat. Otherwise, the cat lives. Since radioactive decay is purely probabilistic, quantum mechanics predicts that the cat should live in a superposition of two possible states – dead and alive. How can a cat be dead and alive at the same time? This is Schrödinger's famous cat paradox.

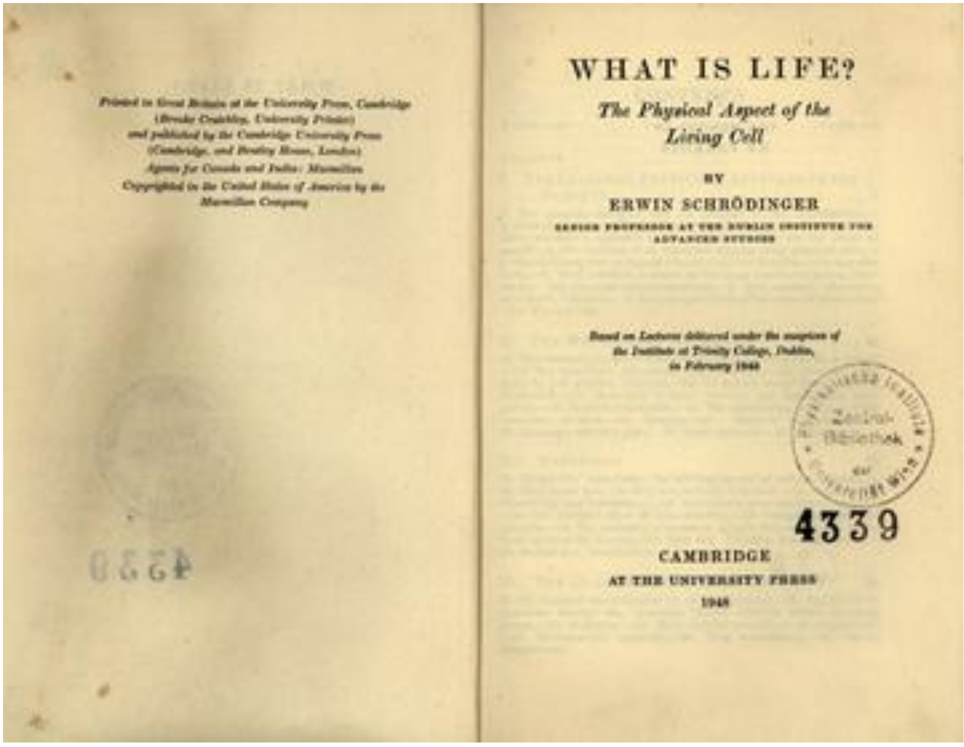
While Schrödinger believed that this thought experiment would disprove the idea of superposition and probability once and for all, it actually gave rise to many new interpretations of quantum mechanics. The philosophical implications of these interpretations remain a matter of intense debate.

*Schrödinger's cat.*

This is known as the measurement problem in quantum mechanics. Hugh Evertt's many-worlds interpretation holds that, as we open the box to look at the cat, we ourselves become entangled with the system. A version of us in this universe may see the cat alive, while some other version of us in some parallel universe might see a dead cat. Bohr, on the other hand, believed that the wave function of the cat collapses from a superposition of all possible states to a single state on observation. But what counts as observation? If we need an observer to exist in a distinct state, then is there a supreme observer or God? It is difficult to define observation and consciousness from the perspective of physics.

**Most of us are of the opinion that consciousness arises from biological interactions in the brain, and is best left to biology. Schrödinger was perhaps the first physicist who seriously took up the challenge of exploring consciousness from the perspective of the physical sciences.** Consciousness, for all we know, must be an emergent phenomena – a possible outcome that can be obtained when so many particles interact in some pattern. Schrödinger investigated this thoroughly and published his findings in a short but highly influential book.

**The name of the book is a question – and that question is as great a question as has ever confronted humankind. "What is life?" This book inspired Watson and Crick's work on DNA, which transformed biology and the medical sciences.**



WHAT IS LIFE?
*The Physical Aspect of the Living Cell*
BY
ERWIN SCHRÖDINGER

CAMBRIDGE
AT THE UNIVERSITY PRESS

"What is life?" by Schrödinger.

**In his book, Schrödinger investigated life from the perspective of physics, entropy and statistics. He used quantum theory and quantum jumps to explain mutations and other biological phenomena.** Finally, he finished the book with an epilogue on determinism and free will. In the epilogue, Schrödinger put forward his philosophy of oneness. Schrödinger was greatly influenced by the ideas of philosophers such as Baruch Spinoza and Arthur Schopenhauer.

**"Quantum physics thus reveals a basic oneness of the universe," he said. He believed that only one consciousness exists, and we are different manifestations of that same consciousness. He didn't imply religion or superstition. This view is actually possible under the laws of physics.**

"Consciousness is never experienced in the plural, only in the singular," Schrödinger wrote. "Even in the pathological cases of split consciousness or double personality, the two persons alternate, they are never manifest simultaneously. In a dream we do perform several characters at the same time, but not indiscriminately: we are one of them; in him we act and speak directly, while we often eagerly await answer or response of another person, unaware of the fact that it is we who control his movements and his speech just as much as our own. How does the idea of plurality arise at all? Consciousness finds itself intimately connected with, and dependent on, the physical state of a limited region of matter, the body. Now there is a great plurality of similar bodies. Hence the pluralization of consciousness or minds seems a very suggestive hypothesis… The only possible alternative is simply to keep to the immediate experience that consciousness is a singular of less is never which the plural is unknown; that there is only one thing and even in that what seems to be a plurality is merely a series of different personality aspects of this one thing… each of us has the indisputable impression that the sum total of his own experience and memory forms a unit, quite distinct from that of any other person. He refers to it as 'I' …'I' is that ground stuff upon which they [the facts little more than a collection of single data (experiences and memories), namely the canvas..] are collected… Yet there has been no intermediate break, no death. And even if a skilled hypnotist succeeded in blotting out entirely all your earlier reminiscences, you would not find that he had killed you. In no case is there a loss of personal existence to deplore. Nor will there ever be."

According to Schrödinger, consciousness is fundamental and cannot be accounted for in terms of anything else. Schrödinger's philosophy of oneness is also apparent in his quote: "The world is given to me only once, not one existing and one perceived. Subject and object are only one. The barrier between them cannot be said to have broken down as a result of recent experience in the physical sciences, for this barrier does not exist."

**Another physicist whose beliefs were very similar to Schrodinger's was Albert Einstein. Einstein and Schrödinger both wanted to find a unified theory of physics, without assuming quantum uncertainty to be true.** Einstein spent the last three decades of his life attempting to unify gravity with electromagnetism. Schrödinger worked on the same problem in isolation in the Institute for Advanced Studies in Dublin. He corresponded with Einstein, they supported and at times opposed each other, and both had great insights about unification. **However, neither succeeded in reaching their ultimate goal.**

**Today, the study of chaos theory and fractal geometry has provided us with new insights about the nature of consciousness, which can be an emergent phenomena.** Schrödinger, so many years back, had already formed the then-unusual idea that life was both orderly and complex. He saw aperiodicity as the source of life's special qualities. To quote James Gleick, "In Schrödinger's day, neither mathematics nor physics provided any genuine support for the idea. There were no tools for analyzing irregularity as a building block of life. Now those tools exist."

Schrödinger was exceptional in so many ways. He was a great physicist *and* a great philosopher, responsible for much of the research that goes on in physics today. He still lives among us, with his ideas, his discoveries – and, of course, in the fate of his unfortunate cat.

The Schrödinger equation is not the only way to study quantum mechanical systems and make predictions. The other formulations of quantum mechanics include matrix mechanics, introduced by Werner Heisenberg, and the path integral formulation, developed chiefly by Richard Feynman. Paul Dirac incorporated matrix mechanics and the Schrödinger equation into a single formulation.

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## Schrödinger Equation:

$$H\Psi = E\Psi$$

H = Hamiltonian operator
OR Energy operator
$= \left(-\frac{h^2}{8\pi^2 m}\nabla^2 + U\right)$

$\nabla^2$ = Laplacian operator
$= \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dZ^2}\right)$

U = Potential Energy
E = Total Energy (Eigen value)
$\Psi$ = Wave function (Eigen function)

## Alternative form Schrödinger wave equation:

$$\nabla^2\Psi + \frac{8\pi^2 m}{h^2}(E-U)\Psi = 0$$

# Eigen function and eigen value:

# Eigen function: Orbitals

Solution of the Schrödinger wave equation for an electron in an atom may yield a number of values for Ψ. But only those values of Ψ will be acceptable to us which are physically meaningful and obey certain conditions pertinent to the system. Such acceptable values are called orbitals. The discrete energy values ( eigen values) obtained for the electron corresponding to these orbitals ( eigen function) are the energy of the orbitals.

Selection of the acceptable values of Ψ is made according to the following conditions (Boundary conditions):

(i) Ψ must be single valued, because probability of finding the electron at any point must have only one value.

(ii) Ψ must be finite, an infinite value at appoint would mean that the electron is fixed there.

(iii) Ψ must be continuous with respect to its variables.

(iv) The first derivative Ψ with respect to its variables must be continuous with respect to its variables.

(v) The total probability of finding the electron over the whole space must be equal to 1 i.e. Ψ must be normalised.

$$\int_{-\infty}^{\infty} \Psi^2 \, dx \, dy \, dz = 1$$

$$\int_{-\infty}^{\infty} \Psi_1 \Psi_2 \, dx \, dy \, dz = 0$$

(vi) If $\Psi_1$ and $\Psi_2$ are two acceptable wave functions, then they must be orthogonal. Conditions of orthogonality is:

Orbital: Each acceptable value of the wave function Ψ obtained from the solution of Schrödinger wave equation represents an orbital.

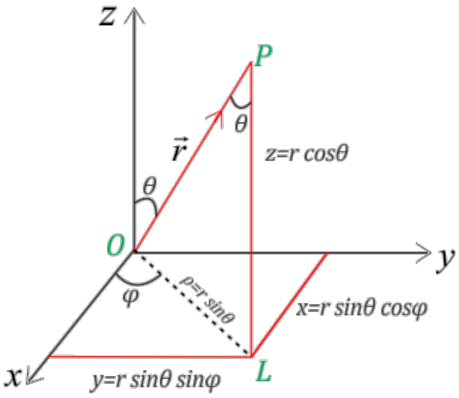
## Schrödinger wave equation:

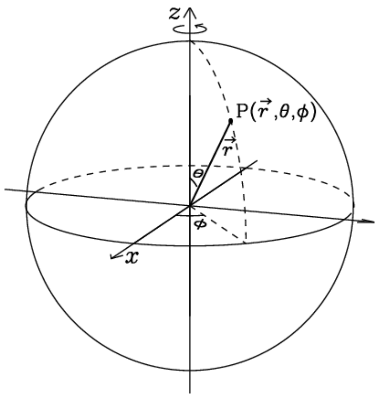
$$\nabla^2\Psi + \frac{8\pi^2 m}{h^2}(E-U)\Psi = 0$$

## 3D coordinate systems:

Any point within a sphere P can be define as P(x, y, z) or P(r, θ, φ).
Here,

- r is the radial distance of the point P from the origin O.
- θ is the angle between Z axis and OP. The value of θ is in between $0^0$ to $180^0$.
- φ is the angle between X axis and OL. The value of φ is in between $0^0$ to $360^0$.





$$\Psi_{\text{orbital}} = \Psi(r, \theta, \varphi)$$

The dependence of Ψ on r, θ and φ can be express as a product of three functions:

- $\Psi_r$ or $R(r)$
- $\Psi_\theta$ or $\Theta(\theta)$
- $\Psi_\phi$ or $\Phi(\phi)$

So,

$$\Psi_{r,\theta,\phi} = \Psi_r.\Psi_\theta.\Psi_\phi = R(r).\Theta(\theta).\Phi(\phi)$$

- R(r) or $\psi_r$ is a function of r (the radial distance from the nucleus). $\psi_r$ is known as radial part of wave function. Sometimes it is abbreviated by R. It depends on quantum numbers n and l.
- $\psi_\theta$ and $\psi_\varphi$ are the function of $\theta$ and $\varphi$ respectively; these are the angular part of wave function. They may also combined into a single wave function $\psi_{\theta\varphi}$. These functions are depend on the quantum number l and $m_l$.
- **Orbital wave function = (Radial part X Angular part).**

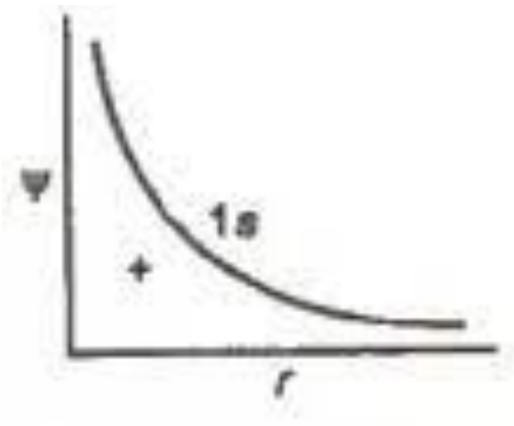
## Radial part of wave function R(r) or $\psi_r$ or R:

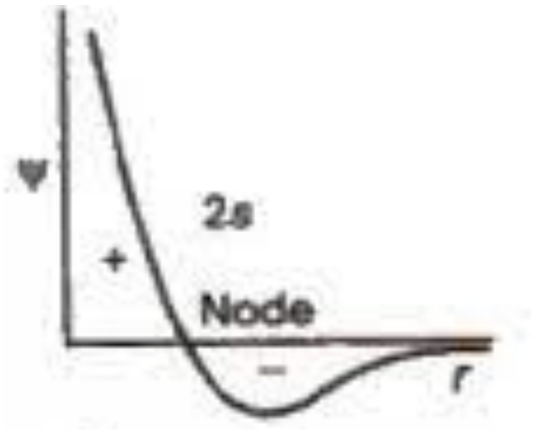
$$\begin{aligned}
R_{10} &= 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Zr/a_0} \\
R_{21} &= \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0} \\
R_{20} &= 2\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\left(1-\frac{Zr}{2a_0}\right) e^{-Zr/2a_0} \\
R_{32} &= \frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0} \\
R_{31} &= \frac{4\sqrt{2}}{3}\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right)\left(1-\frac{Zr}{6a_0}\right) e^{-Zr/3a_0} \\
R_{30} &= 2\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(1-\frac{2Zr}{3a_0}+\frac{2(Zr)^2}{27a_0^2}\right) e^{-Zr/3a_0}
\end{aligned}$$

Here, $a_0$ is the radius of first Bohr orbit of hydrogen atom which is equal to 0.0529 nm.

### General features of Radial part of wave function:

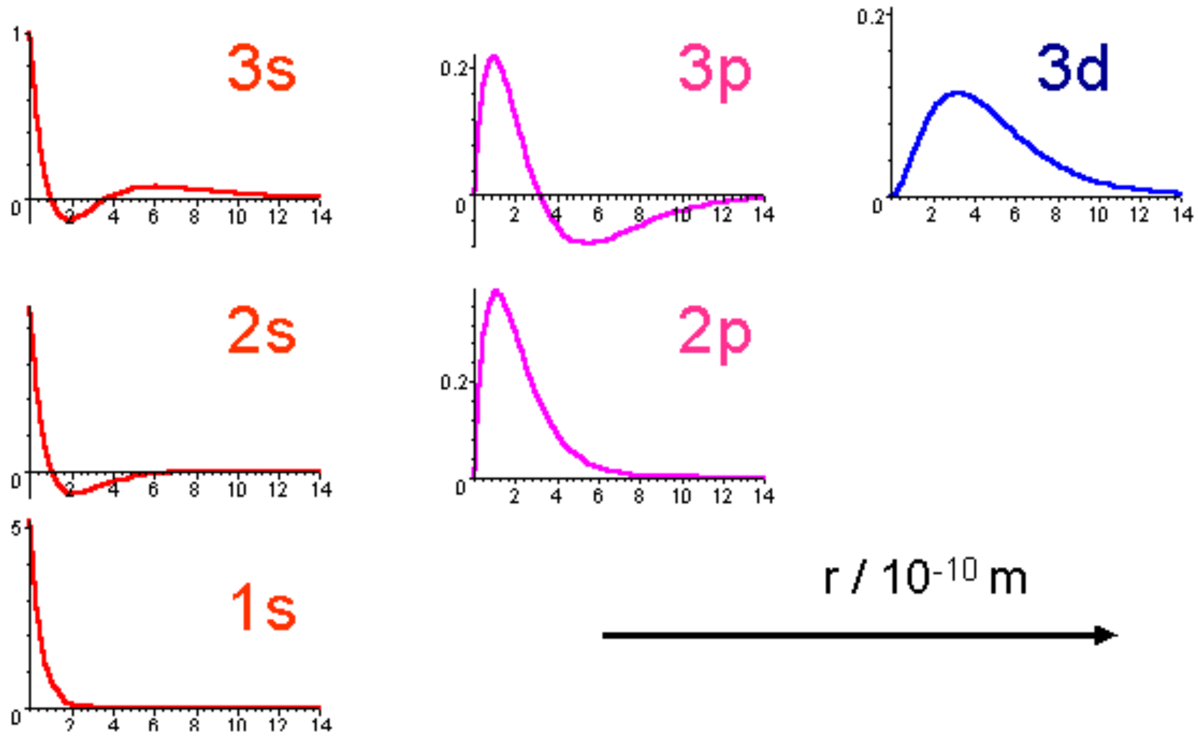
- All the functions decreases with r as $e^{-Zr/na_o}$. So, R(2s) has a slower rate of decay with r than R(1s). Thus the wave function of an orbital with higher n extends to a larger distance from the nucleus.
- The R function of 2s orbital will vanish when $(1-Zr/2a_o) = 0$ ie. at $r= 2a_o/Z$, the R(2s) =0. The function also changes its sign beyond these point which called 'node'.

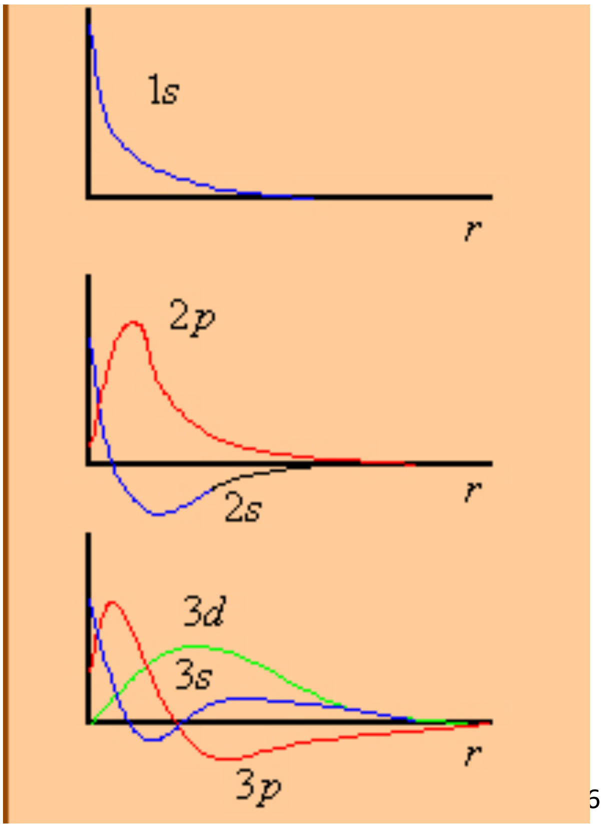




- An orbital designated by n and l has (n-l-1) number of nodes.

Electron wave functions of atomic hydrogen $R_{n\ell}(r)$





## Physical significance of ‘node’:

At the nodal points, there is no existence of the electron, but at both sides of the nodal point there is at finite probability of the existence of the electron. Now, the question arises how the electron passes from one side of the node to the other, when the electron is absent at the node. If the electron is considered to be particle then the question is fully valid, but if the electron is considered to be a standing wave then the problem does not arise as standing wave can exist at both side of a nodal point. Thus at the nodal point, the sign (+ or -) of the wave function changes.

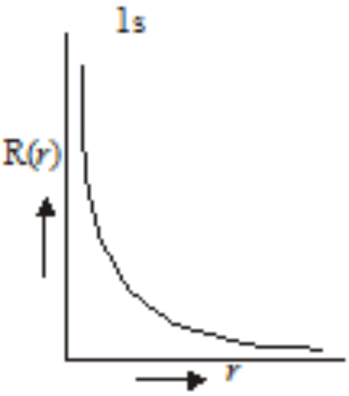
**Radial probability density, P(r):**

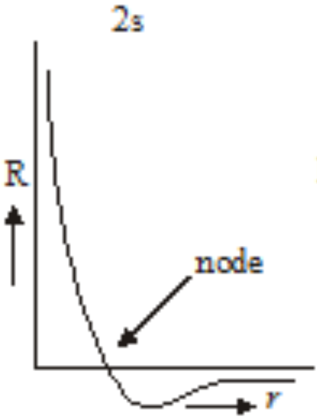
The probability of finding a particle at some point is proportional to the square of ψ . So the dependence of probability on the radial distance from the nucleus will be obtained from the square of the radial part of the wave function ie, $R^2$. $R^2$ is the probability density per unit volume.

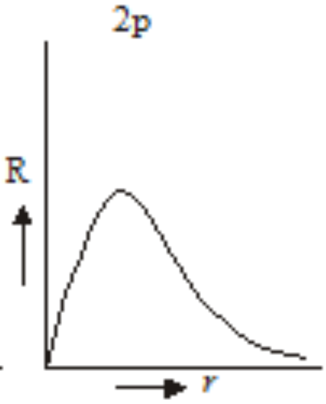
- **Total probability of the existence of the electron could in spherical shell bounded by concentric spheres of radius r and r+dr = P(r). dv = $R^2.4\pi r^2 \cdot dr$**
- **$R^2.4\pi r^2$ is called radial distribution function or radial probability distribution function (RDF).**

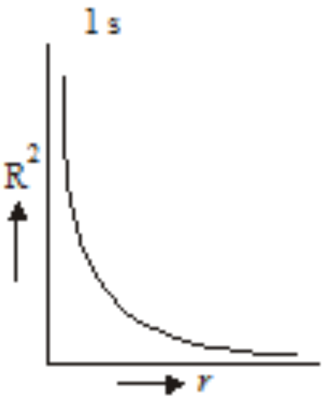
$$(RDF)_{1s} = 4\pi r^2 \cdot 4\left(\frac{Z}{a_0}\right)^3 e^{-\frac{2Zr}{a_0}}$$

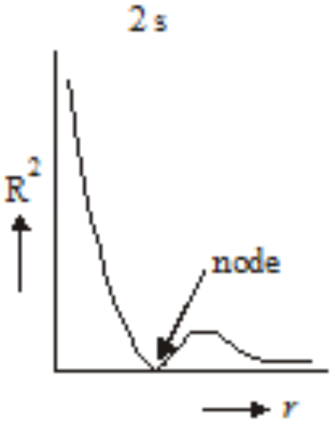
$$= 16\pi r^2 \left(\frac{Z}{a_0}\right)^3 e^{-\frac{2Zr}{a_0}}$$

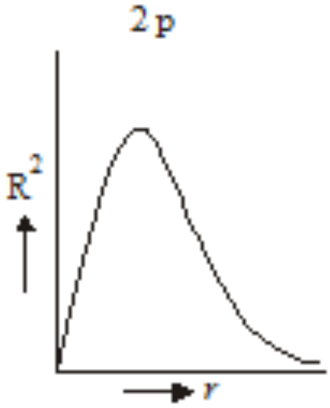

1s
R(r)
r

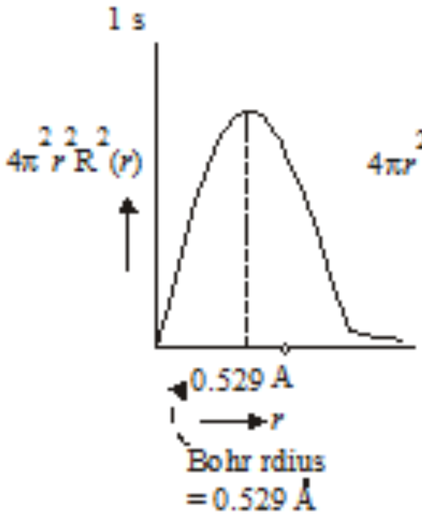

2s
R
node
r

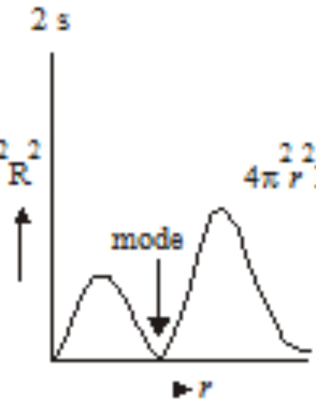

2p
R
r

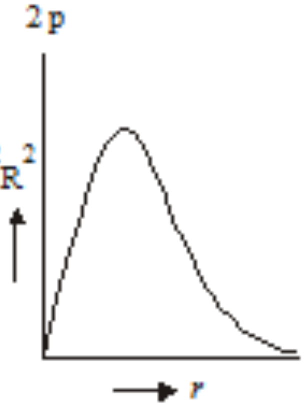

1 s
R2
r

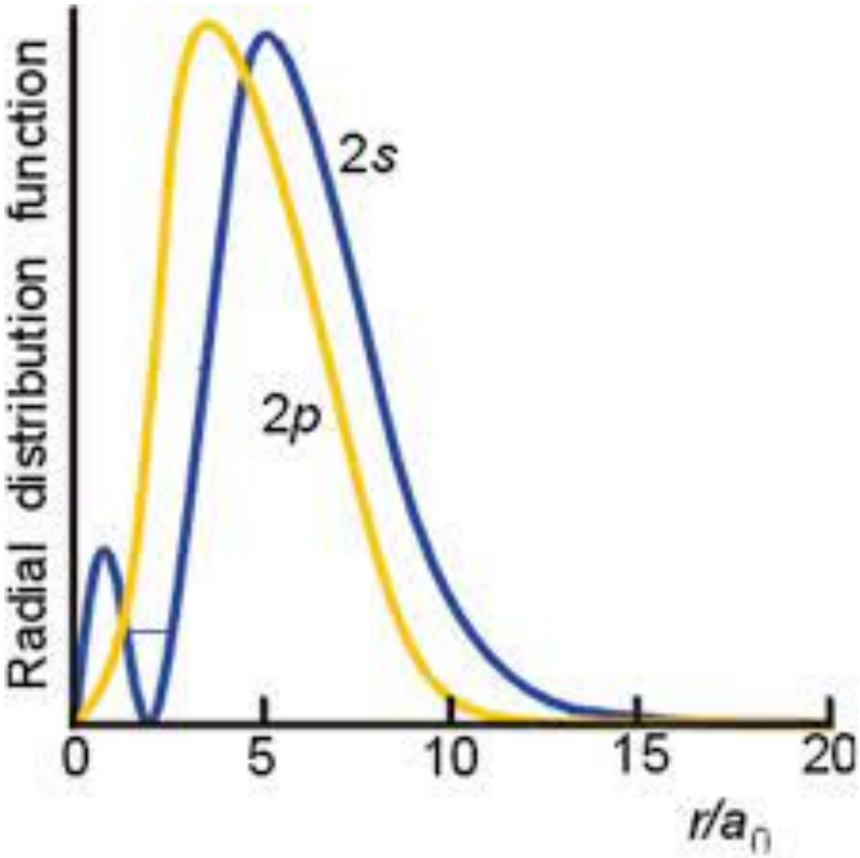

2 s
R2
node
r

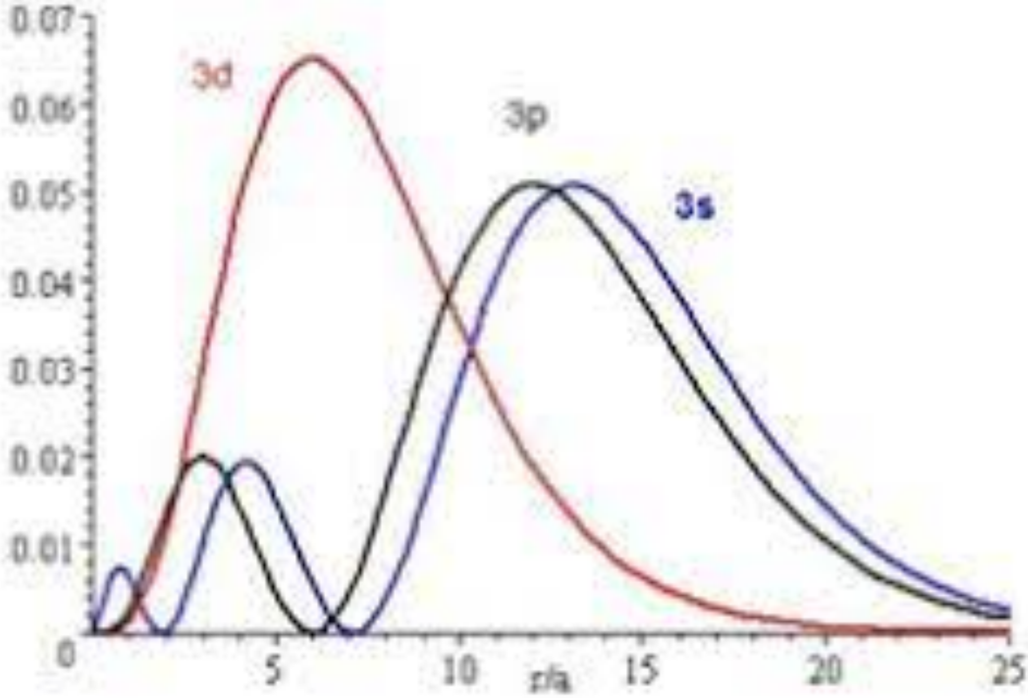

2 p
R2
r


1 s
4π2 r2 R2 (r)
0.529 Å
r
Bohr rdius
=0.529 Å


2 s
4πr2 R2
mode
r

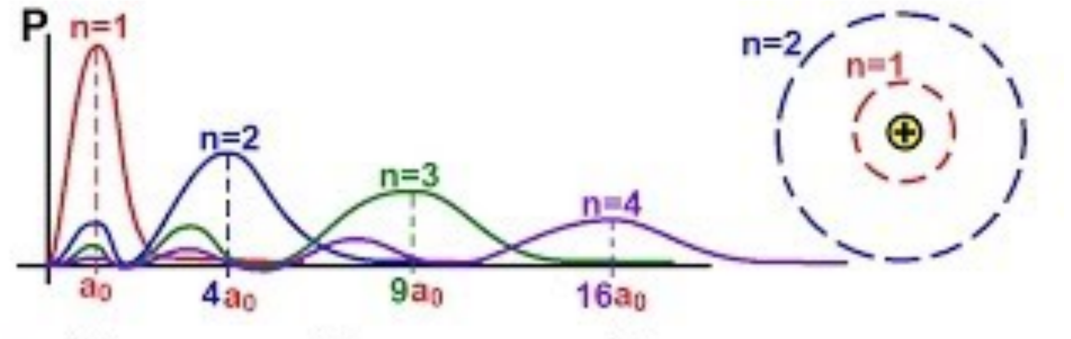

2 p
4π2 r2 R2
r


Radial distribution function
2s
2p
0
5
10
15
20
r/a0


0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
3d
3p
3s
5
10
r/a
15
20
25

## Qualitative features of these curves:

1. At r=0, R was not zero rather it had high value. But $R^2.4\pi r^2 = 0$ at this point, so the probability of finding the electron in the nucleus is zero.
2. The probability functions shows one maxima for 1s and more for higher orbitals. The maxima of the 1s orbital occurs at 0.0529 nm, the radius of the first Bohr orbit.
3. As r increases, R approaches zero exponentially and also does $R^2.4\pi r^2$ . This related to our idea of the size of an orbital. We also observe that the maximum electron density occurs at the larger distance as we pass 1s to 2s to 3s and so on. The total area under the curve equals to probability of 1. So the orbitals become more diffuse in nature.



*Plots of RDF vs r for different* ***s*** *orbitals.*

## Penetration:

The density functions of 2s, 3p , 3s etc. orbital have small but finite values within the curves of lower orbitals. The radial density of the 2s orbital spreads into the curves of 1s orbital, the 3s orbital spreads into 1s and 2s orbitals, and so on. This is termed as penetration of orbitals. This is the distribution of outer orbital's electron into inner orbitals. Presence of intranodal maxima at the lower distance from the nucleus is the measure of penetrating power of the orbital.
Penetrating order of orbitals: s>p>d>f.

As a consequence an electron in an outer orbital does not fully screened by the inner electrons from the nuclear charge. If the radial density of 2s orbital has been distributed completely outside the 1s orbital, the 2s electron would be completely screened by the 1s orbital. This variation in penetration influences mutual screening of the electrons and hence controls the effective nuclear charge as well as relative energy of the orbitals. The consequences are far reaching as we shall encounter the connection with ionisation energy, electronegativity, size, oxidation states etc.

## Slater's rules

In quantum chemistry, **Slater's rules** provide numerical values for the effective nuclear charge in a many-electron atom. Each electron is said to experience less than the actual nuclear charge, because of shielding or screening by the other electrons. For each electron in an atom, Slater's rules provide a value for the screening constant, denoted by *s*, *S*, or *σ*, which relates the effective and actual nuclear charges as Zeff=Z−s.

The rules were devised semi-empirically by John C. Slater and published in 1930.
Revised values of screening constants based on computations of atomic structure by the Hartree–Fock method were obtained by Enrico Clementi *et al* in the 1960s.

Firstly, the electrons are arranged into a sequence of groups in order of increasing principal quantum number n, and for equal n in order of in-

creasing azimuthal quantum number l, except that s- and p- orbitals are kept together...
[1s] [2s,2p] [3s,3p] [3d] [4s,4p] [4d] [4f] [5s, 5p] [5d] etc.
Each group is given a different shielding constant which depends upon the number and types of electrons in those groups preceding it.
The shielding constant for each group is formed as the *sum* of the following contributions:

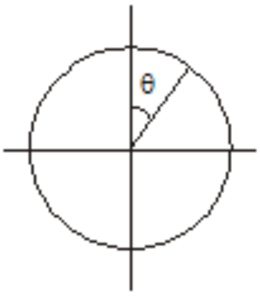
1. An amount of 0.35 from each *other* electron within the *same* group except for the [1s] group, where the other electron contributes only 0.30.
2. If the group is of the [ns, np] type, an amount of 0.85 from each electron with principal quantum number (n–1), and an amount of 1.00 for each electron with principal quantum number (n–2) or less.
3. If the group is of the [d] or [f], type, an amount of 1.00 for each electron "closer" to the nucleus than the group. This includes both i) electrons with a smaller principal quantum number than *n* and ii) electrons with principal quantum number *n* and a smaller azimuthal quantum number *l*.

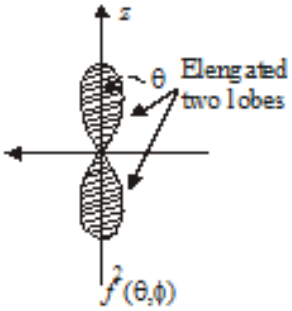
# Angular part of wave function( $\psi_{\theta\varphi}$):

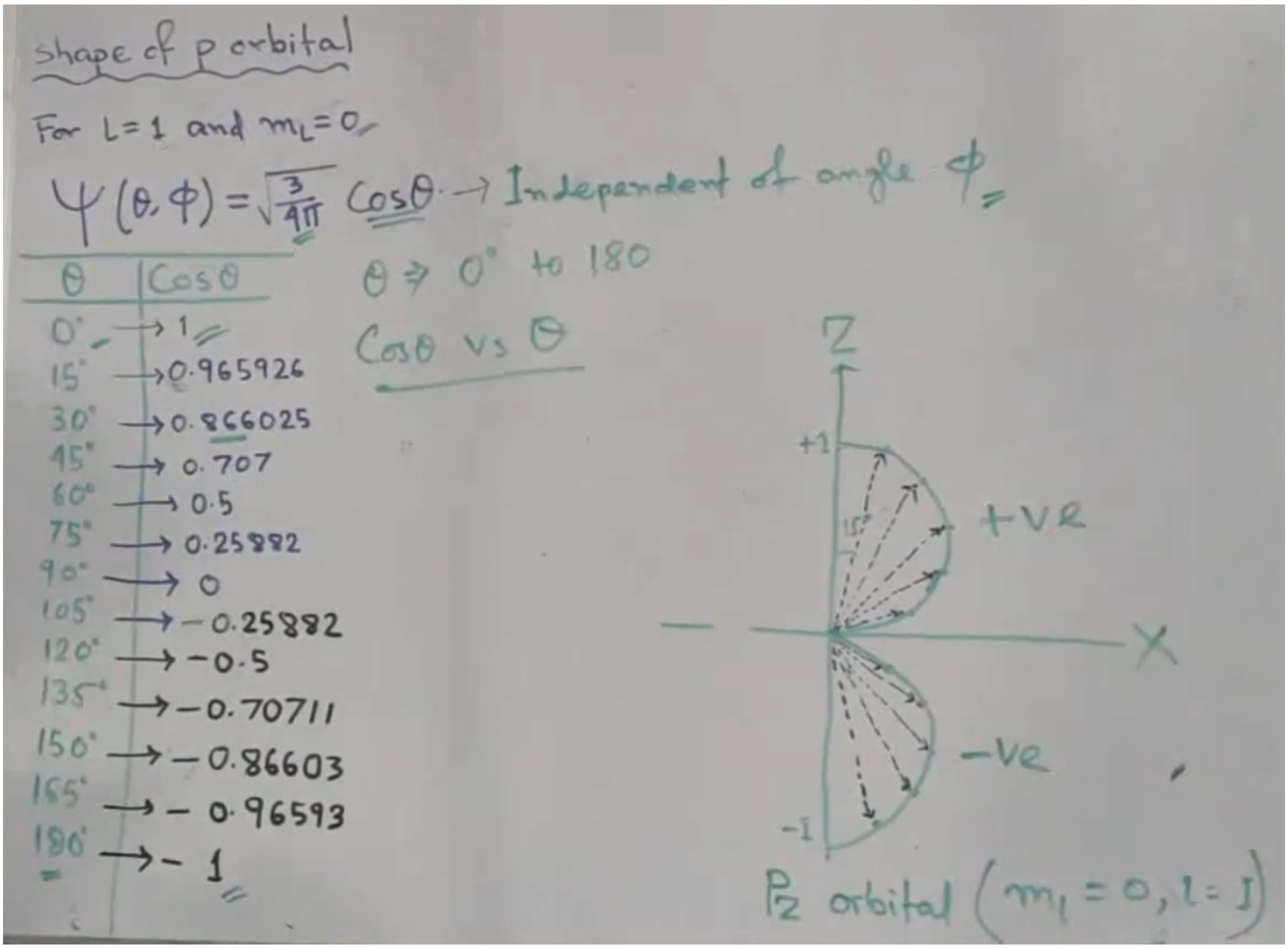
The angular part of wave function $\psi_{\theta\varphi}$ are independent of the value n. They primarily depend on the values of l and $m_l$. Orbitals mathematical functions and any attempt to picturise them carried little sense.

- **$\psi_{\theta\varphi}$ of s orbital = $(1/4\pi)^{1/2}$**
- **$\psi_{\theta\varphi}$ of $p_z$ orbital = $(3/4\pi)^{1/2}\cos\theta$**
- **$\psi_{\theta\varphi}$ of $p_x$ orbital = $(3/4\pi)^{1/2}\sin\theta\cos\varphi$**
- **$\psi_{\theta\varphi}$ of $p_y$ orbital = $(3/4\pi)^{1/2}\sin\theta\sin\varphi$**

The probability of finding an electron in a given direction is proportional to square of angular function. $\psi_{\theta\varphi}^2$ is called the angular probability function.







shape of p orbital

For L = 1 and $m_L = 0$

$\Psi(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\cos\theta \rightarrow$ Independent of angle $\phi$

$\theta \Rightarrow 0°$ to 180

Cosθ vs θ

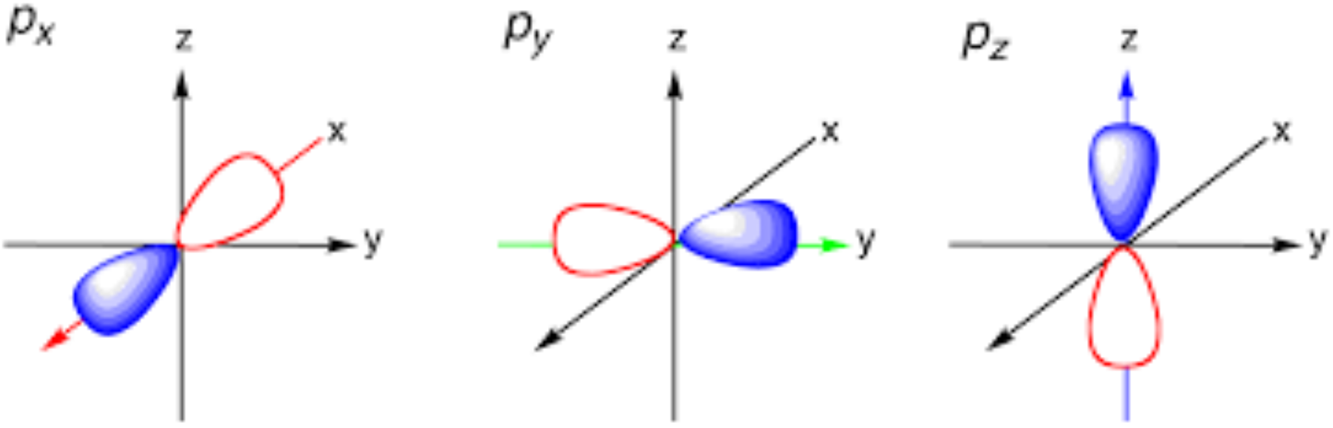
| θ | Cosθ |
|---|---|
| 0° | → 1 |
| 15° | → 0.965926 |
| 30° | → 0.866025 |
| 45° | → 0.707 |
| 60° | → 0.5 |
| 75° | → 0.25882 |
| 90° | → 0 |
| 105° | → −0.25882 |
| 120° | → −0.5 |
| 135° | → −0.70711 |
| 150° | → −0.86603 |
| 155° | → −0.96593 |
| 180° | → −1 |

$P_Z$ orbital $(m_l = 0, l = 1)$

**Considering the corresponding wave function sign (+ and -) describing the phase of the standing wave is extremely important from the standpoint of overlapping of the atomic orbitals. Overlapping in the same phase strengthens the bond while overlapping in the opposite phase weakens the bond.**

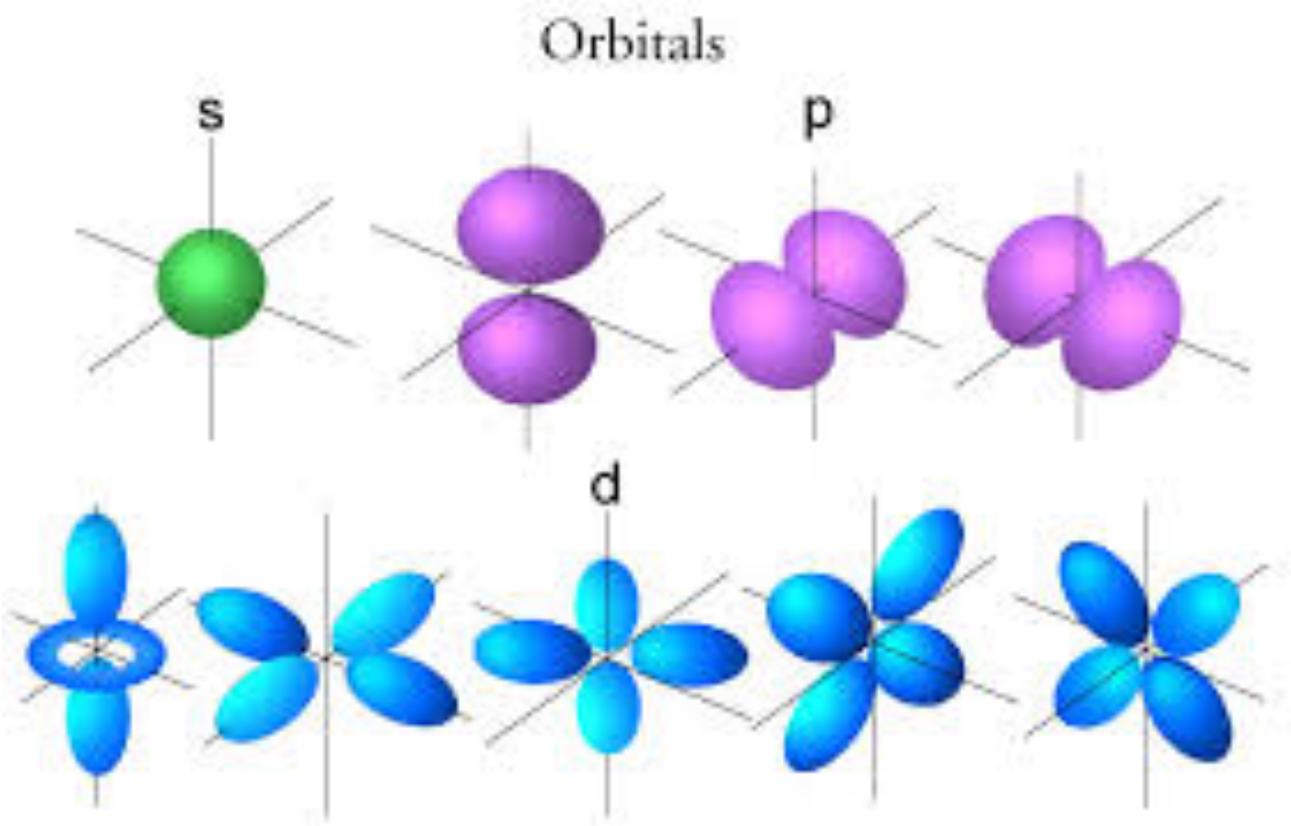
## Gerarde (g) and ungerade (u) orbitals:

- **Gerade means 'even' and ungerade means 'uneven'.**
- **The orbitals s and d are gerade orbitals. These are denoted as 'g' orbital.**
- **The orbitals p and f are ungerade orbitals. These are denoted as 'u' orbitals.**



The three p orbitals are aligned along perpendicular axes

## Angular probability function ($\psi_{\theta\varphi}^2$):



## Nodal surface:

Except s orbitals, for any other orbitals, in certain direction (ie., coordinates) the angular wave function may have zero values. Such coordinates define the angular nodal surface or nodal plane. In general there are (n-l-1) radial nodes in the radial distribution functions and there are l nodal surface (at r=0) in the angular distribution functions of all the orbitals.

## Exchange energy and extra stability of and fully filled orbitals

### Micro state

For a particular electronic configuration (say, $d^2$), the electrons can be arranged different way in the orbital. Each of the arrangement is called micro state of electronic arrangement. All the micro states may not have same energy. The micro state with lowest energy is called ground state of the electronic configuration.

#### Number of micro state

Number of micro-state of a given electronic configuration $= {}^{n}C_{r}$

$$= \frac{n!}{r!(n-r)!}$$

Where, n= electron capacity of the outer most sub shell

r = number of electron present in the outer most sub shell.

#### $d^2$ configuration:

Electron capacity (n) = 10

Number of electrons present (r) =2

Number of micro-state $= \dfrac{10!}{2!(10-2)!} = 45$

An electronic arrangement having least energy will be the most stable electronic arrangement of a given electronic configuration.

# Stability of different microstates

Stability of different microstates are govern by three factors:
- ✤ Exchange energy.
- ✤Pairing energy.
- ✤Spherical distribution of electronic charge.

## Exchange energy (E):

Mathematical calculation shows that if two electrons with parallel spin exchange their positions in space without undergoing change in their electronic arrangement, then there is a resultant decrease in energy. Such pairs of electrons with parallel spins within an orbit are called exchange pairs. The energy decrease per exchange pair is known as exchange energy. It is a negative energy.

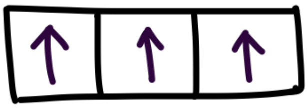
Number of exchangeable pairs = $^{x}C_{2}$

Where, x is the number of electrons with same spin.

Stability of an electronic arrangement increases with increasing the number of exchange pairs.

## Example 1:

Calculate the number exchange pairs and total exchange energy for the following $p^3$ configuration.



## Ans.

| | | |
|---|---|---|
| ↑ | ↑ | ↑ |

The no. of exchangeable electrons = 3

Number of exchangeable pairs = $^3C_2$ = 3

Exchange energy per exchange pair = -E

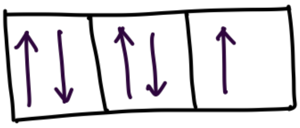
Total exchange energy= -3E

Total loss of energy = -3E

Stability of an electronic arrangement increases with increasing the number of exchange pairs.

## Example 2:

Calculate the number exchange pairs and total exchange energy for the following $p^5$ configuration.



**Ans.**

The no. of exchangeable electrons with upward spin is 3 and no. of exchangeable electrons with downward spin is 2.

Number of exchangeable pairs = ${}^3C_2 + {}^2C_2 = (3 + 1) = 4$

Exchange energy per exchange pair = -E

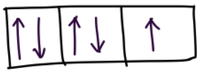
Total exchange energy= -4E

## Pairing energy (P):

The energy needed to paired up two electrons in an orbital is called pairing energy. It is a positive energy. Stability of an electronic arrangement **decreases** with increasing the pairing energy.

**Problem 1.**

Calculate the pairing of energy of the following $p^5$ configuration.



**Ans.**

Number of electron pair: 2

Pairing energy per electrons pair = P

Total pairing energy = 2P

### Problem 2

On the basis of exchange energy and pairing energy show that ground state $p^3$ configuration is more stable than ground state $p^4$ configuration.

**Ans.**

Ground state $p^3$ configuration:

The ground state $p^3$ configuration is presented as:

| | | |
|---|---|---|
| ↑ | ↑ | ↑ |

The no. of exchangeable electrons = 3

Number of exchangeable pairs = ${}^3C_2 = 3$

Exchange energy= -3E

Number of electron pair = 0

Total loss of energy = -3E

**For $p^4$ configuration:**

The ground state $p^4$ configuration is presented as:

| | | |
|---|---|---|
| ↑↓ | ↑ | ↑ |

The no. of exchangeable electrons = 3

Number of exchangeable pairs = ${}^3C_2 = 3$

Exchange energy= -3E

Number of electrons pair: 1

Pairing energy= P

Total loss of energy due to electron exchange and electron pairing = -3E + P

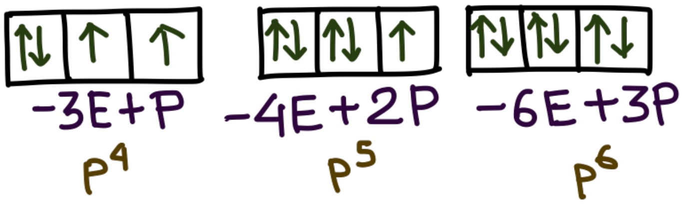
Lowest energy configuration is more stable. Comparing the energies of ground states of $p^3$ and $p^4$ systems, we see that the $p^4$ system is unstable by P amount of energy compare to $p^3$. So $p^3$ is more stable than $p^4$ configuration.

# Spherical distribution of electronic charge.

- A symmetrical or uniform distribution of electronic charge leads to decrease in energy and hence increase the stability of the system.
- Electronic arrangements with exactly half-filled or fully filled degenerate orbitals would be most stable in comparison with other arrangements.
- Relative stability of electronic arrangements in degenerate as well as non-degenerate orbitals is based on the combined effects of exchange energy, pairing energy and distribution of electronic charge in orbitals.

## Example 1.

Compare stability of the following configurations:

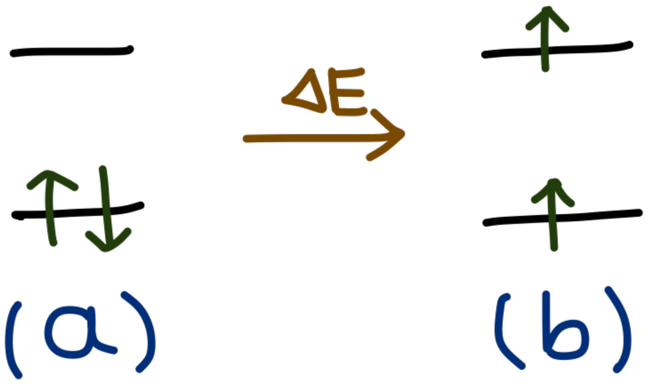


## Hints.

Until you know the exact values of E and P, the stability of the configurations can not be compare. Experimental data reveals that $p^6$ is more stable. This fact can be explain by considering the symmetrical distribution of electronic charge. In the $p^6$ configuration, all the electrons are symmetrically distributed. But in the other two configurations electrons are not symmetrically distributed.

## Promotional energy(ΔE):

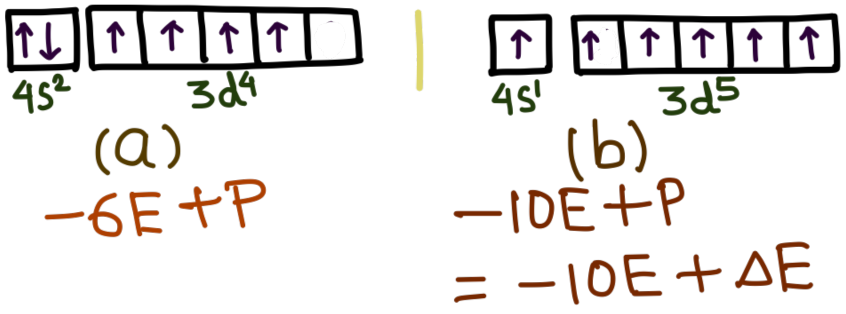
In order to promote an electron from an orbital of lower energy to an orbital of higher energy orbital, energy is required to supply from outside agency. This supplied energy (ΔE) is called promotional energy and is given a positive sign.



- ❖ Among these two configurations, (a) will be more stable if pairing energy is less than promotional energy.
- ❖ Configuration (b) will be more stable if pairing energy is higher than promotional energy.

### Electronic arrangement of Cr.

In the case of Cr, promotional energy is almost equal to pairing energy.



Configurations (b) is more stable.