

Syllabus

Module	Syllabus
02 Quantum Chemistry	Historical development, Bohr's atomic model, de Broglie wavelength, Heisenberg uncertainty principle, Schrodinger equation, Wave function, particle in a box, Hydrogen atom, radial and angular solution to hydrogen atom, applications and limitations

The word ‘atom’ has been derived from the Greek word ‘*a-tomio*’ which means ‘uncut-able’ or ‘non-divisible’.

The atomic theory of matter was first proposed on a firm scientific basis by **John Dalton** in 1808.

According to Dalton’s atomic theory all the matters are made up of atoms, which are invisible.

All atoms of a given element are identical in mass, size, shape and chemical properties.

All atoms of a different elements have different masses, size and chemical properties.

Compounds are combinations of two or more different types of atoms in fixed ratio.

A chemical reaction is a rearrangement of atoms.

An atom can neither be created nor destroyed and can’t be interconverted.



Dalton’s atomic theory was able to explain the **law of conservation of mass, law of constant composition and law of multiple proportion** very successfully.

Failure of Dalton’s Atomic Theory

Dalton’s atomic theory failed to explain the results of many experiments.

For example: Substances like glass or ebonite when rubbed with silk or fur get electrically charged.

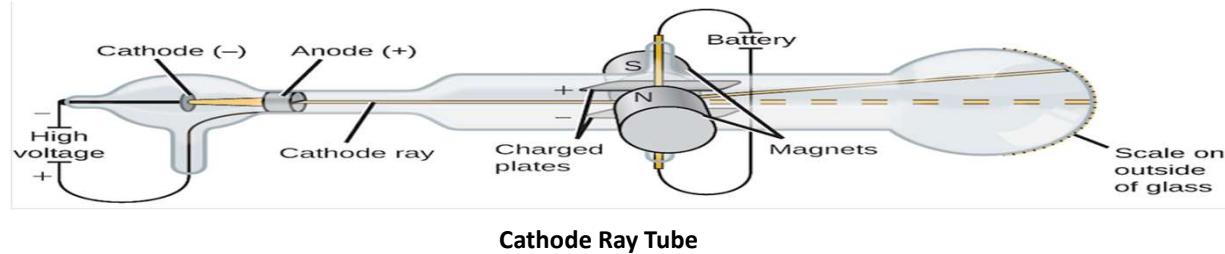
Dalton considered atom as the smallest unit of matter which is tiny, hard and could not be broken down further. This assumption got failed after some experiments in Physics (For e.g.- It was known that substances like glass or ebonite when rubbed with silk or fur get electrically charged).

Discovery of sub-atomic particles (Proton, Neutron and Electron)

Discovery of Electron by J. J. Thomson

Cathode ray tubes are sealed glass tubes from which most of the air has been evacuated. A high voltage is applied across two electrodes at one end of the tube, which causes a beam of particles to flow from the cathode (the negatively-charged electrode) to the anode (the positively-charged electrode).

The ray can be detected by painting a material known as **phosphors** onto the far end of the tube beyond the anode. The phosphors spark or emit light when impacted by the cathode ray.



Properties of the particles: Thomson placed two oppositely-charged electric plates around the cathode ray. The cathode ray was deflected away from the negatively-charged electric plate and deflected towards the positively-charged plate. This indicated that the cathode ray was composed of negatively-charged particles.

Effect of Magnetic Field: Thomson also placed two magnets on either side of the tube, and observed that this magnetic field also deflected the cathode ray. The results of these experiments helped Thomson determine the charge-to-mass ($e / m_e = 1.758820 \times 10^{11} \text{ CKg}^{-1}$) ratio of the cathode ray particles, which led to a fascinating discovery - the mass of each particle was much smaller than that of any known atom.

Cathode ray particles were given a more familiar name: **Electrons**.

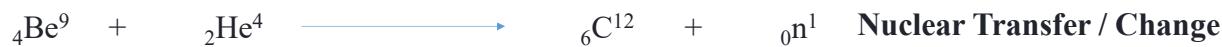
By Mullikan's oil drop method the charge on electron is 1.6×10^{-19} Coulomb.

Discovery of Proton by Goldstein

When high voltage charge passed between the electrodes in a discharge tube it was found that some rays were coming from the side of the anode which passed through the hole in the cathode and produce green fluorescence on the opposite glass wall coated with ZnS. These rays are called **anode rays or canal rays or positive rays**.

Discovery of Neutron by Chadwick

Chadwick bombarded thin sheet of Beryllium (Be) with α -particles then electrically neutral particles having mass slightly greater than proton are produced.

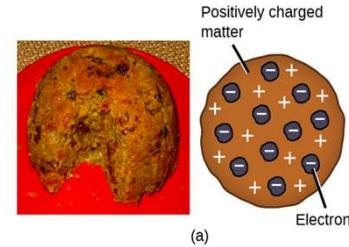


Name	Symbol	Absolute Charge (e)	Relative Charge	Mass/Kg
Electron	e	-1.6022×10^{-19}	-1	9.10×10^{-31}
Proton	p	1.6022×10^{-19}	+1	1.672×10^{-27}
Neutron	n	0	0	1.674×10^{-27}

Plum pudding Model of atom by J. J. Thomson

Thomson believed that overall charge on atom is neutral and there must be a source of positive charge within the atom.

Thomson proposed that atoms could be described as negative particles floating within a soup of diffuse positive charge. This model is called the **plum pudding / Watermelon model** of the atom.

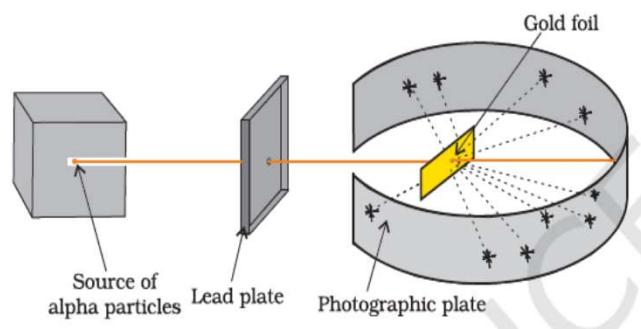


No. of electrons = No. of protons are equal in magnitude so that atom is electrically neutral.

Ernest Rutherford Atomic Model: The gold foil experiment

Rutherford fired a high energy stream of alpha α -particles (doubly charged helium nuclei ${}^4_2\text{He}^{2+}$) at a very thin sheet of pure gold (100 nm thickness); Gold is the most malleable & ductile metal among the metals. To study the deflection of α -particles, a fluorescent ZnS screen was kept around the gold sheet.

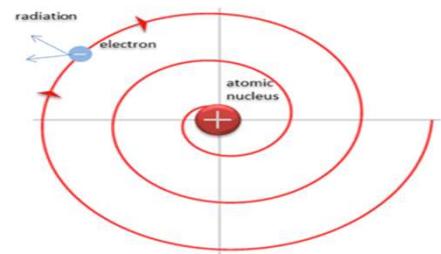
- A major fraction of the α -particles bombarded towards the gold sheet passed through the sheet without any deflection, and hence **most of the space in an atom is empty**.



- Some of the α -particles were deflected by the gold sheet by very small angles, The deflection must be due to enormous repulsive force showing that the **positive charge in an atom is not uniformly distributed**. **The positive charge in an atom is concentrated in a very small volume**.
- Very few (1 of 20000) of the α -particles were deflected back by 180° angle of deflection. So the **volume occupied by the positively charged particles in an atom is very small as compared to the total volume of an atom**. ($\text{radius}_{\text{atom}} = 10^{-10} \text{ m}$ and $\text{radius}_{\text{nucleus}} = 10^{-15} \text{ m}$).

Limitation of Rutherford Atomic Model

- Rutherford proposed that the electrons revolve around the nucleus in fixed paths called orbits. According to *Maxwell*, accelerated charged particles emit electromagnetic radiations and hence an electron revolving around the nucleus should emit electromagnetic radiation. This radiation would carry energy from the motion of the electron which will shrink the orbits. Ultimately the electrons would collapse in the nucleus. **An electron would collapse into the nucleus in less than 10^{-8} seconds**. So the Rutherford model was **could not explain the stability of an atom**.
- One of the drawbacks of the Rutherford model was also that he **did not say anything about the arrangement of electrons in an atom** which made his theory incomplete.
- Existence of certain definite lines in spectrum of hydrogen.



Nuclear Model of the Atom (α - particles Scattering Experiment)

Rutherford made following conclusions based on his experiment :-

- The positive charge must be localized over a very tiny volume of the atom (nucleus), which also contains most of the atom's mass. This explained how a very small fraction of the α - particles were deflected drastically, presumably due to the rare collision with a gold nucleus.
- Most of the α - particles passed straight through the gold foil, the atom must be made up of mostly empty space.
- The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called orbits. Thus, *Rutherford's model of atom resembles the solar system in which the nucleus plays the role of sun and the electrons that of revolving planets (Planetary Motion).*

Electrons and the nucleus are held together by electrostatic forces of attraction.

Conclusion: -

Rutherford proposed the nuclear model, in which an atom consists of a very small, positively charged nucleus surrounded by the negatively charged electrons. Based on the number of α - particles deflected in his experiment, Rutherford calculated that the nucleus took up a tiny fraction of the volume of the atom.

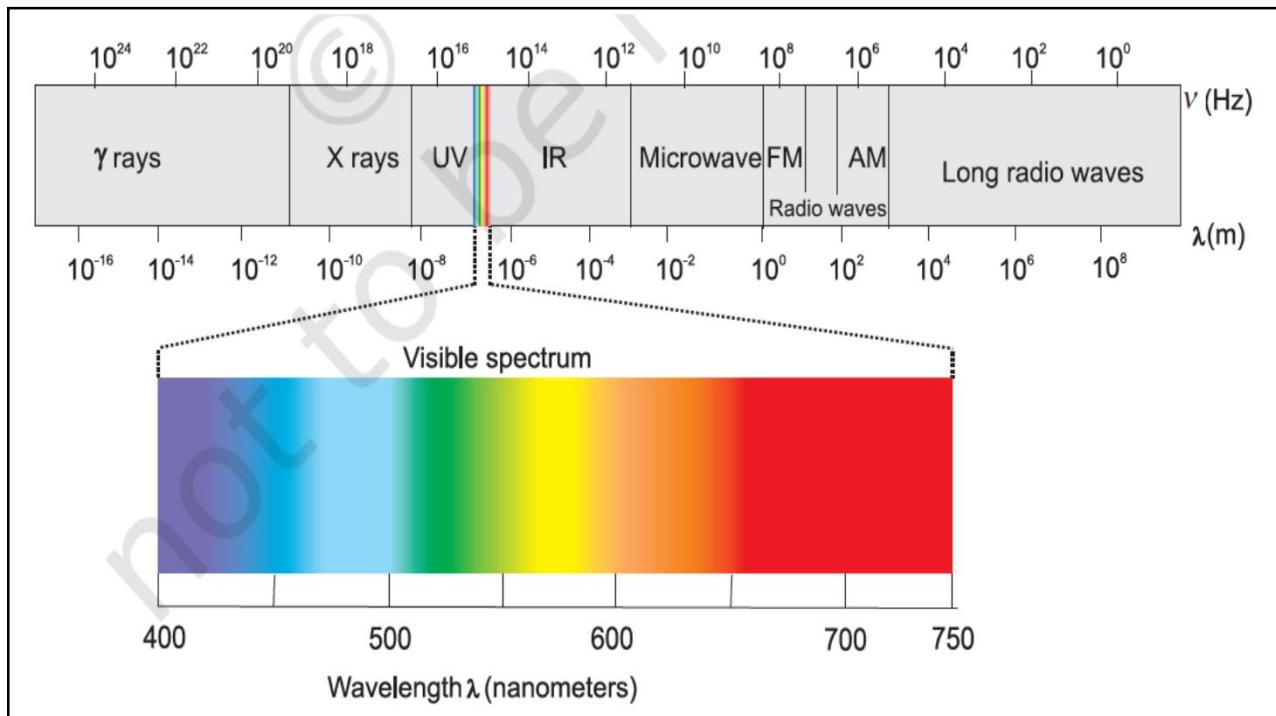
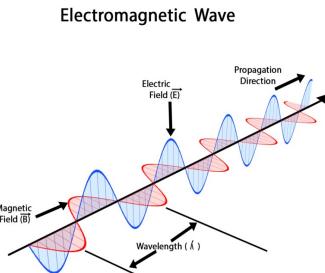
Dual Nature of Electromagnetic Radiation

James Maxwell (1870) suggested that when electrically charged particle moves under acceleration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the forms of waves called **electromagnetic waves or electromagnetic radiation**.

Light is a form of radiation having wave characteristics and are associated with oscillating electrical and magnetic field perpendicular to each other.

Electromagnetic radiations don't require any medium for propagation and can move in vacuum.

Electromagnetic radiations are of various types which differ in frequency and constitutes electromagnetic spectrum.



Each electromagnetic radiation will have characteristic frequency, wave length and wave number (No. of waves per unit length).

Some of the phenomenon like diffraction and interference can't be explained by corpuscular/particle theory.

Classical Physics fail to explain the following phenomenon -

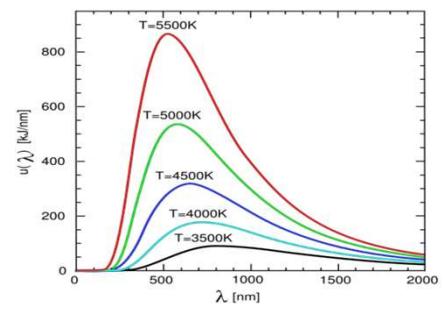
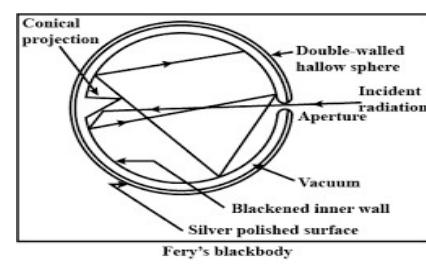
- ✓ Nature of emission of radiation from hot body (Black Body Radiation).
- ✓ Ejection of electron from metal surface when radiation strikes it (Photoelectric Effect).
- ✓ Variation of heat capacity of solids as a function of temperature.
- ✓ Line spectra of Hydrogen atom.

Black Body Radiation (Thermal Radiation / Cavity Radiation / Complete Radiation / Temperature Radiation)

A black body is an idealized physical body that absorbs all incident electromagnetic radiation, regardless of frequency or angle of incidence. **It absorbs all colors of light.** A black body also emits black-body radiation.

The energy that the blackbody absorbs heats it up, and then it will emit its own radiation. The only parameter that determines how much light the blackbody gives off and at what wavelengths & at what **temperature**.

Energy is emitted or absorbed by a molecule in the form of a discrete quantities called Quantum. $E = h\nu$



Hot objects emit electromagnetic radiations over a wide range of wavelengths. At high temperatures, an appreciable proportion of radiation is in the visible region of the spectrum. As the temperature is raised, a higher proportion of short wavelength (blue light) is generated.

Application: Heating of Iron

when an iron rod is heated in a furnace, it first turns to dull red and then progressively becomes more and more red as the temperature increases.

As this is heated further, the radiation emitted becomes white and then becomes blue as the temperature becomes very high. This means that red radiation is most intense at a particular temperature and the blue radiation is more intense at another temperature.

The intensities of radiations of different wavelengths emitted by hot body depend upon its temperature.

Planks Quantum Theory

Planck assumed that radiation could be sub-divided into discrete chunks of energy. He suggested that atoms and molecules could emit or absorb energy only in discrete quantities and not in a continuous manner.

He gave the name quantum to the smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation.

The energy (E) of a quantum of radiation is proportional to its frequency (ν) and is expressed by equation $E = h\nu$

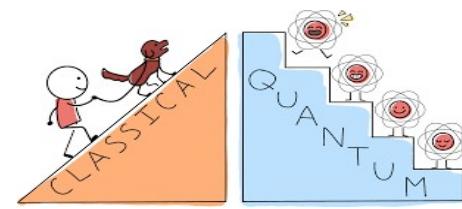
The proportionality constant, ' h ' is known as Planck's constant and has the value 6.626×10^{-34} J s.

Planck was able to explain the distribution of intensity in the radiation from black body as a **function of frequency or wavelength at different temperatures**.

Quantization of light

Classical Mechanics: Any real value of energy is allowed.
Energy can be continuously varied.

Quantum Mechanics: Not all the values of energy is allowed. Energy is discrete (quantized).



The quantization of light refers to **light behaving as quanta or photon, which is like a packet of energy**. A quanta carries an energy that is dependent on frequency and Planck's constant; $E = h\nu$.

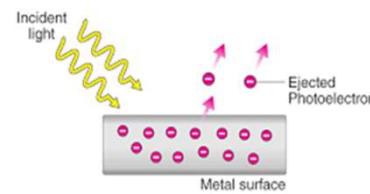
The energy can take any one of the values from the following set, but cannot take on any values between them. $E = 0, h, 2h, 3h, \dots nh, \dots$

Einstein applied the concept of quantized energy to light. Photons are absorbed or emitted by electron jumping from one quantum state to another.

Photoelectric Effect / Photoemission

The photoelectric effect is a phenomenon in which electrons are ejected from the surface of a metal when light is incident on it. These ejected electrons are called photoelectrons.

There is no time lag between the striking of light beam and the ejection of electrons from the metal surface.



Number of electrons ejected is proportional to the intensity or brightness of light.

No photoelectric effect is not observed below characteristic minimum frequency ν_0 (threshold frequency). At a frequency $\nu > \nu_0$, the ejected electrons come out with certain kinetic energy which increase with the increase of frequency of the incident light used.

Application of Photoelectric Effect / Photoemission

One of the manifestations of wave theory of matter is photoelectric effect. The doors in the mall stops closing or opens when you move towards it. Similarly, an alarm may sound or light may turn on when there is some movement (motion detection). Such devices work by responding to an interruption in the beam of light.

A beam of light is made to shine on a photocathode which emits photo-electrons and a current is constituted. When the beam of light is interrupted, the flow of electrons stops and the current is cut off. When the current stops, the movement of the door stops. In motion-detection devices, a light may turn on (at night) or an alarm might be set.

Einstein defined the photoelectric effect using Planks Quantum Theory

Electrons in the metal are held by some attractive forces and to overcome these forces certain minimum amount of energy is required which is the characteristic of the metal. This is called photoelectric work function (W_0)

The striking photon must have energy equal to or greater than this work function (W_0). The minimum energy required to eject the electron is $E = hv$

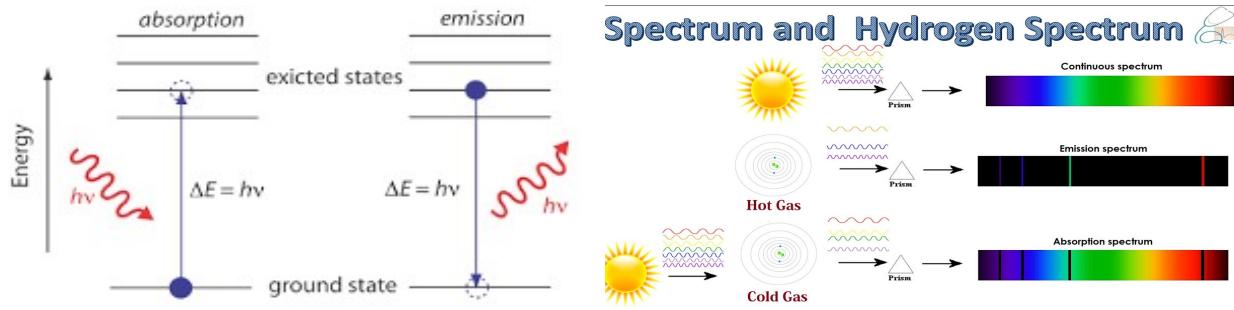
According to the quantum theory the energy of photon (E) is directly proportional to frequency (v). So incident photon should have minimum frequency is called Threshold Frequency or Critical frequency (v_0).

$$h v_0 = W_0$$

Difference in energy transferred as the kinetic energy of the photoelectron $= (hv - hv_0)$
Kinetic energy of ejected electron $= hv - hv_0 = h(v - v_0)$

Continuous Spectrum, Emission Spectra & Absorption Spectra

Continuous Spectrum: A spectrum having no apparent breaks or gaps throughout its wavelength range.



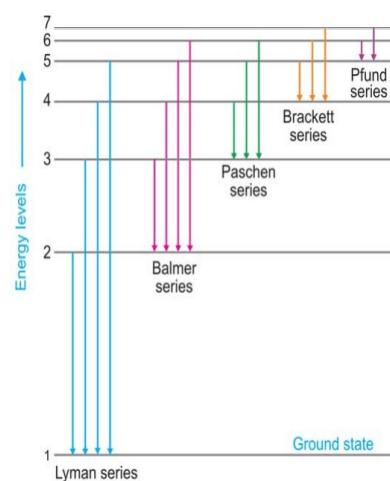
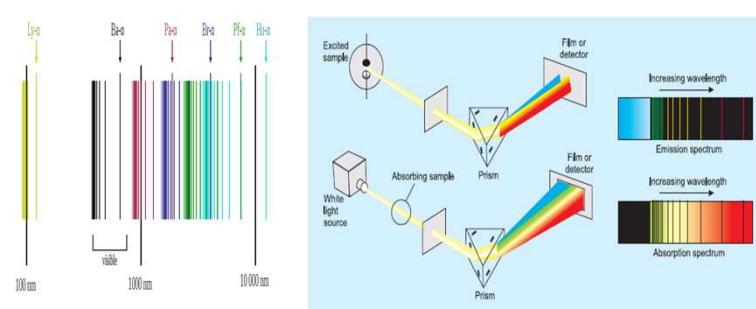
Emission Spectrum: A spectrum of the electromagnetic radiation emitted by a source.

Absorption Spectra: A spectrum of electromagnetic radiation transmitted through a substance, showing dark lines or bands due to absorption at specific wavelengths.

Line Spectrum of Hydrogen

When an electric discharge is passed through gaseous hydrogen, the H_2 molecules dissociate and the energetically excited hydrogen atoms produced emission spectrum of *discrete frequencies*.

The first five series of lines that correspond to $n = 1, 2, 3, 4, 5$ are known as Lyman, Balmer, Paschen, Brackett and Pfund series respectively.



The hydrogen spectrum consists of several series of *lines* named after their discoverers. Balmer showed in 1885 on the basis of experimental observations that if spectral lines are expressed in terms of wavenumber, then the visible lines of the hydrogen spectrum obey the following formula:

$$\bar{v} = 109,677 \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \text{ cm}^{-1} \quad \text{Where } n = 3, 4, 5, \dots$$

Johannes Rydberg, noted that all series of lines in the hydrogen spectrum could be described by the following expression :

$$\bar{v} = 109,677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ cm}^{-1} \quad \text{Where } n_1 = 1, 2, 3, \dots \\ n_2 = n_1 + 1, n_1 + 2, n_1 + 3, \dots$$

Series	n_1	n_2	Spectral Region
Lyman	1	2,3,...	Ultraviolet
Balmer	2	3,4,...	Visible
Paschen	3	4,5,...	Infrared
Brackett	4	5,6,...	Infrared
Pfund	5	6,7,...	Infrared

Where R = Rydberg Constant for Hydrogen atom = 109.677 cm⁻¹

The first five series of lines that correspond to $n_1 = 1, 2, 3, 4, 5$ are known as Lyman, Balmer, Paschen, Bracket and Pfund series, respectively,

Bohr's Model for Hydrogen Atom

The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called orbits. These orbits are arranged concentrically around the nucleus.

The energy of an electron in the orbit does not change with time. However, the electron will move from a lower stationary state to a higher stationary state when required amount of energy is absorbed by the electron.

The electron will moves from higher stationary state to lower stationary state when energy is emitted. The energy change does not take place in a continuous manner.

The amount of energy emitted or absorbed is equivalent to the energy difference between two stationary states i.e. $\Delta E = E_2 - E_1$. the frequency of radiation absorbed or emitted $v = \Delta E/h$.

The angular momentum of an electron is quantized i.e. $m_e v r = n \cdot h / 2\pi$; $n=1,2,3, \dots$

Where m_e = mass of electron, v = velocity of electron, r = radius of the orbit in which electron is moving, n = No. of orbit

An electron can move only in those orbits for which its angular momentum is integral multiple of $h/2\pi$, i.e. angular momentum is quantized and transition of electron takes place from one quantized value of angular to another.

Bohr's theory can also be applied to the ions containing only one electron, similar to that present in hydrogen atom. For example, He^+ , Li^{2+} , Be^{3+} and so on. The energies of the stationary states associated with these kinds of ions (also known as hydrogen like species)

Limitation of Bohr's Model for Hydrogen Atom

- ✓ It fails to explain the finer details of the hydrogen atom spectrum like (doublet, that is two closely spaced lines).
- ✓ This model is also unable to explain the spectrum of atoms other than hydrogen, for e.g. helium atom which possesses only two electrons.

- ✓ Fails to explain the splitting of spectral lines in the presence of magnetic field (Zeeman effect) or an electric field (Stark effect).

Zeeman effect: - In the presence of magnetic field spectral line gets split up into closely spaced lines.

Stark effect: - Splitting of lines under the effect of applied electrical field.

- ✓ It could not explain the ability of atoms to form molecules by chemical bonds and the shape of molecules.
- ✓ It could not explain the 3-D structure of atom
- ✓ Bohr's model of atom was not in accordance with de-Broglie and Heisenberg's Uncertainty Principle

Dual Nature of Matter or de Broglie's Equation or Particle Wave Duality

de Broglie, proposed that matter, like radiation, should also exhibit dual behavior i.e., both particle and wavelike properties.

As the photon has momentum & wavelength, electrons should also have momentum as well as wavelength.

de Broglie's relationship between wavelength (λ) and momentum (p) of a material particle.

$$\lambda = \frac{h}{mv} = \frac{h}{p}; \quad v = c/\lambda \quad \text{-----equ^n 1}$$

The de Broglie equation is applicable to all material objects but it has significance only in case of microscopic particles. This is because the wavelength produced by a bigger particle (say a ball) using Eq. (1) comes out to be too small to be observed. Only particles like electrons, atoms etc. give an observable value of λ according to Eq. (1).

Heisenberg's Uncertainty Principle

It states that it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron.

$$\Delta x * \Delta p \geq h/4\pi$$

$$\Delta x * \Delta(mv) \geq h/4\pi \quad \text{or} \quad \Delta x * \Delta v \geq h/4\pi m$$

Collective reasons for the failure of Bohr's Model: Bringing it altogether

Bohr model of the hydrogen atom not only ignores dual behavior of matter but also contradicts Heisenberg uncertainty principle.

Bohr model of the atom can't be extended to other atoms.

Calculate energy of one mole of photons of radiation whose frequency is 5×10^{14} Hz.

Solution

Energy (E) of one photon is given by the expression

$$E = hv$$

$$h = 6.626 \times 10^{-34} \text{ J s}$$

$$f = 5 \times 10^{14} \text{ S}^{-1} \text{ (given)}$$

$$E = (6.626 \times 10^{-34} \text{ J s}) \times (5 \times 10^{14} \text{ S}^{-1})$$

$$= 3.313 \times 10^{-19} \text{ J}$$

Energy of one mole of photons

$$= (3.313 \times 10^{-19} \text{ J}) \times (6.022 \times 10^{23} \text{ mol}^{-1})$$

$$= 199.51 \text{ kJ mol}^{-1}$$

A 100 watt bulb emits monochromatic light of wavelength 400 nm. Calculate the number of photons emitted per second by the bulb.

Solution

Power of the bulb = 100 watt

$$= 100 \text{ J s}^{-1}$$

$$\text{Energy of one photon } E = hv = hc/\lambda$$

$$= 6.626 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ m s}^{-1}$$

$$400 \text{ } 10^{-9} \text{ m}$$

$$= 4.969 \times 10^{-19} \text{ J}$$

Number of photons emitted

$$100 \text{ J s}^{-1}$$

$$4.969 \times 10^{-19}$$

$$= 2.012 \times 10^{20} \text{ s}^{-1}$$

Introduction to Quantum Chemistry & it's application

Outline

Classical Mechanics & Quantum Mechanics

Schrodinger Equation

Wave Function

Application: Particle in a box

: Hydrogen atom

Radial & Angular Solution to Hydrogen atom

Applications & Limitations

Classical Mechanics: The branch of science based on Newton's Law of motion & Maxwell's electromagnetic wave theory to explain phenomenon related the motion and energy is known as Classical Mechanics or Newtonian Mechanics.

According to Classical Mechanics it is possible to simultaneously determine the position and velocity of a moving particle but Heisenberg's uncertainty principle contradicts this theory.

Classical Mechanics assumes that the energy is emitted or absorbed in continuous manner but Plank's Quantum theory says that the emission or absorption of energy takes place in discontinuous manner in the form of packets of energy called **quanta**.

Limitation of Classical Mechanics : Fails to explain the satisfactory explanation for the following phenomenon –

Black Body Radiation

Photoelectric Effect

Atomic & Molecular Spectra

Heat Capacities of Solids [Dulong & Petit Formula ($c * M = 3R$)]

Classical Mechanics is applicable to objects of appreciable size (**macroscopic particles**) but fails to explain the motion of microscopic objects like electrons, atoms and molecules.

Classical Mechanics is applicable to macroscopic objects such as falling stone, orbiting planets which have particle nature and it ignores the concept of dual nature of matter and uncertainty principle for microscopic objects.

It's necessary to devise a new mechanics which takes into account de Broglie's dual nature of matter and Heisenberg's uncertainty principle and applicable on microscopic particles like electron and atomic nuclei.

The exact position of moving object such as orbit of electron around the nucleus of an atom is replaced by a function which determines the probability of the object being in particular position.

These probability functions satisfy differential equations which are similar to those representing the variation of the amplitude of a wave.

The new mechanics is referred as ***Wave Mechanics or Quantum Mechanics.***

The branch of science which takes into consideration dual nature of matter, Plank's Quantum Theory and Heisenberg's uncertainty principle and applicable to microscopic particles is known as Quantum Mechanics.

The Schrodinger Wave Equation is the core of Quantum Mechanics and can be derived directly or on the basis of certain postulates of quantum mechanics.



Erwin Schrödinger developed the fundamental equation of Quantum Mechanics & awarded by Nobel Prize in 1933.

Classical Mechanics	Quantum Mechanics
(i) It deals with macroscopic (big) particles.	It deals with microscopic (small) particles.
(ii) It is based upon Newton's laws of motion.	It takes into account Heisenberg's uncertainty principle and de Broglie concept of dual nature of matter.
(iii) It is based on Maxwell's electromagnetic wave theory according to which any amount of energy may be emitted or absorbed continuously.	It is based on Planck's quantum theory according to which only discrete values of energy are emitted or absorbed.
(iv) The state of the system is defined by specifying all the forces acting on the particles as well as their positions and velocities (momenta).	It gives probabilities of finding particles at various locations in space.

Sinusoidal Wave Equation

Consider the motion of a wave (say ocean wave) in a particular direction, say x-axis. At any time t , the upward displacement of the wave, represented by y , is the function of position x and time t , i.e. $y = f(x, t)$.

Waves of many shapes are formed in nature and the most common form is Sinusoidal Wave. The electric & magnetic fields associated with electromagnetic radiation is also Sinusoidal wave.

A sine waves travelling in 'x' direction with velocity 'v', wave length ' λ ', frequency ' v ' and amplitude 'A' is defined mathematically as

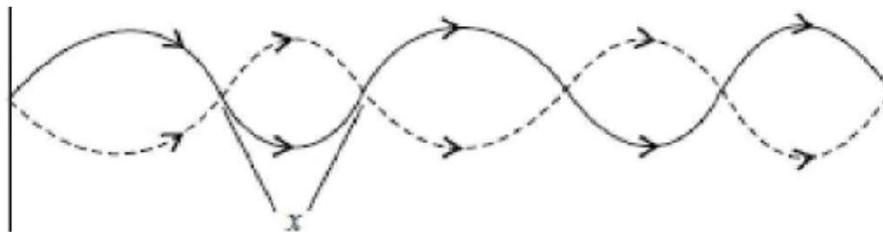
$$y = A \sin\left[\frac{2\pi}{\lambda}(x - vt)\right] = A \sin\left[2\pi\left(\frac{x}{\lambda} - vt\right)\right] \quad \{\because v = \nu\lambda\}$$

Here 'y' is a wave function and this equation gives information of displacement 'y' at any point 'x' and time 't'.

Stationary or Standing Wave

Suppose a string is stretched between two fixed points and a wave is allowed to travel along the string in one direction. When the wave reaches the other end, it is diverted in the opposite direction with the same wavelength, speed and amplitude. In this process, the string is divided into a number of vibrating segments. Such a vibrating motion is called ***stationary or standing wave***.

Point 'x' representing zero amplitude are called **nodes**.



Main Features of Quantum Mechanical Model of Atom

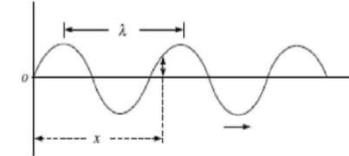
- ❖ The energy of electrons in an atom is quantized i.e. electrons can have only certain specific values of energy in an atom. The existence of quantized electronic energy state is the result of the wave properties of electrons.
- ❖ The exact position & velocity of electron in an atom can't be determined simultaneously. So it is impossible to determine the exact trajectory of the electron in an atom. Therefore we consider the **probability of finding the electron at different positions in an atom**.
- ❖ Wave function (ψ) for an electron in atom represent an atomic orbital. Atomic orbital is associated with definite amount of energy and many wave functions and atomic orbitals are possible for an electron. An orbital can't contain more than 2 electrons.
- ❖ All the information about electron in an atom can be determined from the orbital wave function (ψ).
- ❖ Probability of finding an electron at a point within the atom (Probability Density) = $|\psi_x|^2$

Schrodinger Wave Equation

Consider a simple wave motion similar to the vibration of a stretched string travelling along x-axis, with velocity 'v'. If 'ω' is the amplitude of wave function then at any point 'x' and time 't' the Schrodinger Wave Equation is defined as -

Time Independent Schrodinger Wave Equation
for motion in one direction (i.e. along x-axis)

$$\frac{\partial^2 f(x)}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} f(x)$$



Time Independent Schrodinger Wave Equation
for motion in three direction or 3-D, (x, y, z)

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m(E - V)}{\hbar^2} \psi = 0$$

Schrodinger Wave Equations
Let us consider a simple wave similar to vibration of stretching wave travelling along x-axis and at time t, the equation for such wave is defined as -

$$\frac{\partial^2 \omega}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \omega}{\partial t^2} \quad \text{--- eqn ①}$$

where ω = Amplitude of the wave at any time t travelling with velocity 'v' and depends on ' ω ' & ' t '
i.e. $\omega = f(x) f'(t)$ eqn ②

for stationary wave/Standing Wave

$$f(t) = A \sin 2\pi V t \quad \text{--- eqn ③}$$

where A = constant, equal to the maximum amplitude of wave,
V = velocity

Putting the value from eqn (3) in eqn (2)

$$\omega = f(x) A \sin 2\pi V t \quad \text{--- eqn ④}$$

Differentiating above eqn twice w.r.t x

$$\frac{\partial^2 \omega}{\partial x^2} = -4\pi^2 V^2 A \sin 2\pi V t \cdot f(x) \quad \text{--- ⑤}$$

Putting the value from eqn (4) in eqn (5)

$$\frac{\partial^2 \omega}{\partial x^2} = -4\pi^2 V^2 f(x) f'(t) \quad \text{--- ⑥}$$

Now, differentiating eqn ② twice w.r.t t

$$\frac{\partial^2 \omega}{\partial x^2} = \frac{\partial^2 (f(x) f'(t))}{\partial x^2} \quad \text{--- ⑦}$$

Putting the value from eqn (6) & (7) in eqn (1)

$$\frac{\partial^2 f(x)}{\partial x^2} f'(t) = -4\pi^2 V^2 f'(t) \times \frac{1}{V^2} + f''(t)$$

∴ velocity $v = V\lambda$ $f''(t) = -4\pi^2 V^2 f'(t) \times \frac{1}{V^2} + f''(t)$

$\boxed{v = \text{frequency}, \lambda = \text{wavelength}}$

This Schrodinger wave eqn. in one direction.

$$\frac{\partial^2 \psi(x)}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} \psi(x) + f(x) \quad (8)$$

For extending above eqn to the wave medium in 3D
the amplitude function $f(x)$ needs to be replaced by $\psi(x, y, z)$
which represents amplitude function for three coordinates.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2} \psi \quad [m = \text{mass of particle}, v = \text{velocity}]$$

By de-Broglie's eqn: $\lambda = \frac{h}{mv}$

Putting the value from above eqn:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2}{h^2/m^2 v^2} \psi \quad \text{Schrodinger eqn. 3D}$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2 v^2 m^2}{h^2} \psi \quad \text{eqn. 9}$$

Total energy (E) = Kinetic Energy + Potential Energy

$$E = \frac{1}{2} mv^2 + V \quad \text{eqn. 10}$$

$$mv^2 = 2(E - V) \quad \text{eqn. 10}$$

Putting the value from eqn. 10 in eqn. 9

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2 m}{h^2} \cdot 2(E - V) \psi$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{8\pi^2 m}{h^2} (E - V) \psi$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

This is Schrodinger wave eqn. in 3D

Operators

Operators are the mathematical instruction or procedure to be carried out on a function to get another functions.

Laplacian Operators: This is a very common operator used in quantum mechanics. It is represented by

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Schrodinger Wave Equation

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m (E - V)}{h^2} \psi = 0 \quad \nabla^2 \psi + \frac{8\pi^2 m (E - V)}{h^2} \psi = 0$$

Hamiltonian Operators:

$$\left(\frac{-\hbar^2}{8\pi^2 m} \nabla^2 + V \right) \psi = E \psi$$

Hamiltonian Operator (\hat{H}) Total Energy

Brief form of Schrodinger Wave Equation

$$\hat{H}\psi = E\psi$$

Schrodinger Wave Equation based on the Postulates of Quantum Mechanics

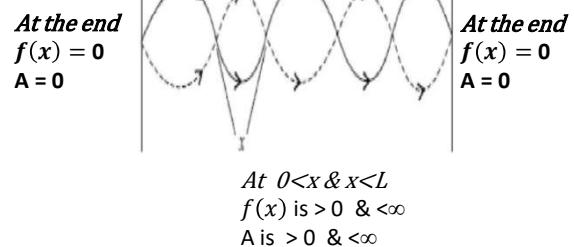
$$\nabla^2 \psi + \frac{8\pi^2 m}{\hbar^2} (E - V) \psi = 0$$

Where
 $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$
Laplacian Operator

Eigen Values & Eigen Functions (Wave Function)

(Fig – 01)

For a stationary (or standing) wave in a stretched string, the amplitude function $f(x)$ can have **significance only for certain definite values of λ** & it should satisfy the conditions (Fig – 01).



The Schrodinger wave equation is a second-order differential equation can have a number of solutions for the amplitude function ψ but **only those values of ψ** are acceptable and have significance which correspond to **some definite values of the total energy E** . Such values of the total energy E are called **Eigen values**. These values are also called **proper values** or **characteristic values**. The corresponding values of the function ψ are called **Eigen functions** or **wave functions**.

Eigen Functions of Schrodinger Wave Function

For stretched string Eigen functions of Schrodinger Wave Equation are those functions which satisfy following conditions –

- For each value of the variable x, y, z , there is only one **definite value** of the function ψ . i.e ψ should be single valued and finite.
- ψ should be continuous i.e. ψ should not change with change in variables (x, y, z).
- $\Psi = 0$ at infinity.

Functions which when operated on by an operator (\hat{a}) are merely multiplied by some constant then various values of (\hat{a}) are called **Eigen Values or Characteristic Values of the operator**.

When functions is $\Psi = \sin kx$ on which **operated** d/dx operates then

$$\frac{d\Psi}{dx} = \frac{d}{dx}(\sin kx) = k \cos kx$$

$\cos kx \neq \Psi$, Hence **d/dx is not the operator of d/dx** $\Psi = \sin kx$

Let us consider d^2/dx^2 is the operator for $\Psi = \sin kx$ then $d^2/dx^2 = -k^2 \Psi$

d^2/dx^2 is said to be the operator for $\Psi = \sin kx$ and $-k^2$ is known as Eigen Value.

Exercise:

Find out the operator for the wave function $\Psi = e^{imx}$. Prove different Eigen operators have different Eigen values for the same function.

Problems on Eigen Value & Eigen function of Wave function

Problem: Show that the function $\psi = \cos ax \cos by \cos cz$ is an eigen function of the Laplacian operator. What is the corresponding eigen value?

Interpretation of Wave function

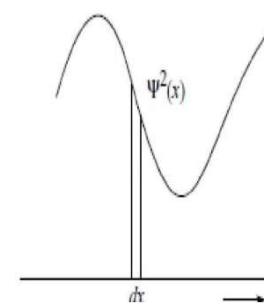
The function ψ by itself does not give any valuable information regarding the movement or position of the microscopic particle since some functions contain imaginary parts in their definitions.

The product $(\psi \times \psi^*)$ (the product of multiplying a complex number by its complex conjugate) is a real number. The quantity $|\psi \times \psi^*|$ or $|\psi|^2$ represents the probability of finding a particle in the small length “ dx ” at a position x and time t called **Probability amplitude $P(\psi)$** .

Born interpretation

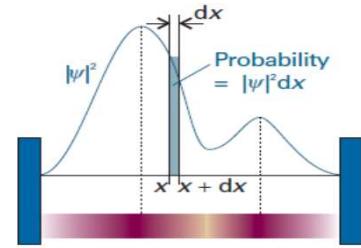
Born suggested that the square of the amplitude of the electron wave, i.e. ψ^2 at any point gives the intensity of the electron wave at that point. However, keeping in view the Heisenberg's uncertainty principle, the **intensity of the electron at any point** may be interpreted as the **probability of finding the particle electron at that point**.

Total probability of finding particle in small space dx at any time 't' is always equal to one. This is called Conservation of Probability.



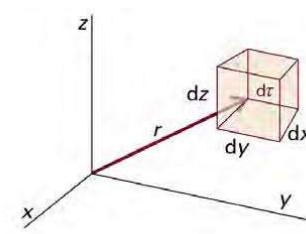
ψ^2 gives the electron density at any given point. Since the region around the nucleus which represents the electron density at different points is called an orbital, the wave function for an electron in an atom is called **orbital wave function** or simply **atomic orbital**.

For a one-dimensional system: – The probability of finding a particle between x and $x+dx$ is proportional to $|\psi_x \times \psi_x^*| dx$ or $|\psi_x|^2$. It represents the probability of finding a particle in the small length “ dx ” at a position x and time t .



For 3-Dimensional System: -

A particle free to move in three dimensions (for e.g., an electron near a nucleus in an atom) the wave function depends on the point $d\tau$ with coordinates x, y , and z .



If the wave function of a particle has the value ψ at some point r , then the probability of finding the particle in an infinitesimal volume $d\tau = dx dy dz$ at that point is proportional to $|\psi|^2 d\tau$.

Particle with un-normalized wave function at some instant of time ‘t’

$$\Psi(x, t) = a^2 - x^2, \quad -a \leq x \leq a$$

$$\Psi(x, t) = 0, \quad |x| > a$$

Normalized Wave Function

The product $\int \psi \times \psi^*$ (ψ = Probability Amplitude) (the product of multiplying a complex number by its complex conjugate) is a real number.

$$\text{i.e. } \int \psi \times \psi^* dx = 1; \quad dx = \text{Small area/volume}$$

The wave function satisfying the above equation is said to be normalized and $|\psi \times \psi^*|^2$ is known as **Probability Distribution Function and 1/N is known as Normalization Constant.**

In some cases the integration $\int \psi \times \psi^*$ (ψ = Probability Amplitude) is found to be equal to constant, say 'N'.

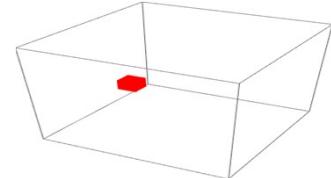
$$\text{i.e. } \int \psi \times \psi^* dx = N; \quad dx = \text{Small area/volume}$$

$$1/N \int \psi \times \psi^* dx = 1$$

$$\text{Or } \int \left(\frac{1}{N^{1/2}} \psi \right) \left(\frac{1}{N^{1/2}} \psi^* \right) dx = 1$$

$\frac{1}{N^{1/2}}$ is called the normalization constant and function $(\frac{1}{N^{1/2}} \psi)$ is called normalization function.

- ✓ In QM the particle is distributed in the space like a wave.
- ✓ In any space we can't find out the position of any particle but we can find out probability of finding the particle at any point in space.



Orthogonal Wave Function

If ψ_i and ψ_j are two wave Eigen functions then

if $\int \psi_i \psi_j^* dx = 1$, functions are said to be Normalized

if $\int \psi_i \psi_j^* dx = 0$, functions are said to be mutually orthogonal

Wave functions which are both normalized and orthogonal are said to be orthonormal.

Table 8.1 The Schrödinger equation

For one-dimensional systems:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

Where $V(x)$ is the potential energy of the particle and E is its total energy. For three-dimensional systems

$$-\frac{\hbar^2}{2m} \nabla^2\psi + V\psi = E\psi$$

where V may depend on position and ∇^2 ('del squared') is

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

In systems with spherical symmetry three equivalent forms are

$$\begin{aligned}\nabla^2 &= \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{r^2} \Lambda^2 \\ &= \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2} \Lambda^2 \\ &= \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \Lambda^2\end{aligned}$$

where

$$\Lambda^2 = \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta}$$

In the general case the Schrodinger equation is written

$$H\psi = E\psi$$

where H is the hamiltonian operator for the system:

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V$$

For the evolution of a system with time, it is necessary to solve the time-dependent Schrödinger equation:

$$H\Psi = i\hbar \frac{\partial\Psi}{\partial t}$$

Quantization

The Born interpretation puts severe restrictions on the acceptability of wave functions.

The principal constraint is that ψ must not be infinite anywhere but it should be finite everywhere.

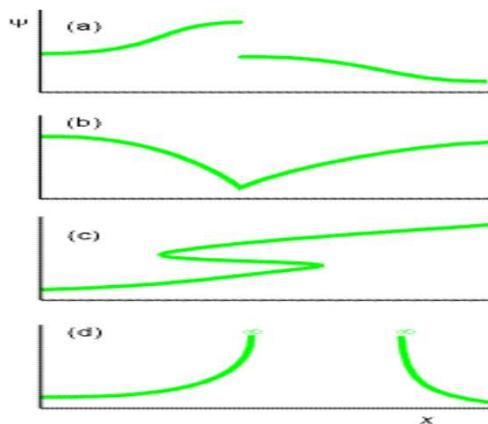
If ψ is infinite then $N \int \psi \times \psi^* \neq 1$ and solution will be infinite and $N = 0$

If the solution of SE gives more than one value of $N \int \psi \times \psi^*$ at a single point then such solution is unacceptable as ψ can't have more than one value at the same point.

The wave function ψ must have single valued i.e. it should have one value at each point of space.

A particle must possess only certain energies, otherwise its wave function would be physically unacceptable i.e. *the energy of a particle is quantized*.

Quantization of ψ means only certain wave function and energies are allowed and rest are forbidden.



The wave function must satisfy stringent conditions for it to be acceptable.

- (a) Unacceptable because it is not continuous;
- (b) unacceptable because its slope is discontinuous;
- (c) Unacceptable because it is not single-valued;
- (d) unacceptable because it is infinite over a finite region.

Particle in a box

A particle in a box provides us the application of Schrodinger wave equation to the translational motion of a particle like an electron, atom, etc. It also explains as to why the energies associated are quantized.

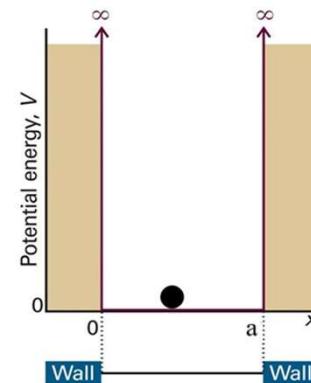
The motion of the particle in a one-dimensional box is like the flow of an electron in a wire but still it is called “particle in a box”

System

Consider a particle of mass ‘m’ in 1-D box of length ‘a’ and moves in the range of $x = 0$ to $x = a$.

Particle can't escape from the box as Potential Energy (PE) outside the box $V_x = \infty$ for $x = 0$ and $x = a$ (Walls)

Potential Energy (PE) inside the box is $V_x = 0$ for $0 < x < L$.



1-D Schrodinger Equation

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}(E - V)\psi = 0$$

- ✓ Ψ is the function of 'x' coordinate
- ✓ Outside the box $V = \infty$, therefore $\psi = 0$ which means particle can't go outside.

For a particle within the box, $V = 0$ $\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}E\psi = 0$ -----equⁿ 1

For the given state of the system the value of 'E' is constant $\frac{8\pi^2m}{h^2}E = k^2$

Putting the value of 'E' in equation 1, then

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0$$

This is second order differential equation with general solution of following form

$$\psi = A \sin kx + B \cos kx$$
 -----equⁿ 2

The values of ' Ψ ' depends on the value of A, B and k and all the values are not acceptable. Only those values are acceptable which follows the boundary conditions i.e. $0 \leq x, x \leq aL$.

$$\psi = A \sin \left(\frac{n\pi}{a} \cdot x \right)$$
 -----equⁿ 3

$$E = \frac{n^2 h^2}{8ma^2}$$
 -----equⁿ 4

Equation (3) and (4) are the solutions of Schrodinger Wave Equation of a particle in 1-D box.

Max Born Restrictions on system: Particle in a box

Schrodinger wave equation can have infinite solutions. For general solution

$$\psi = A \sin kx + B \cos kx \quad \text{For any value of } A, B, K \longrightarrow \text{Values of } \psi \text{ and } E \text{ will be infinite}$$

According to Born Restrictions only certain wave function and energies are allowed and rest are forbidden.

Outside the box - $x < 0, x > L$, Potential Energy $V = \infty$; Particle will not exist and $|\psi|^2 = 0$ or $\psi = 0$.

Ψ must be a continuous function

Boundary conditions: At $x = 0$ then $\psi = 0$ and $x = a$ then $\psi = 0$

Effect of Boundary conditions

When $x = 0$

$$\Psi = A \sin kx + B \cos kx \quad \leftarrow \begin{array}{l} \sin 0 = 0 \text{ and } \cos 0 = 1 \\ \text{equ}^n 1 \end{array}$$

then

$$\Psi = B$$

But according to boundary condition At $x = 0$ then $\psi = 0$

If $\psi = 0$

$$B = 0$$

Putting the value in equⁿ 1

$$\Psi = A \sin kx$$

When $x = a$

$$\Psi = A \sin ka = 0$$

If $a = 0$ then $\psi = 0$
For all values of x

Contradicts Born interpretation that
particle must be somewhere

ka must be choose so that $\sin ka = 0$
 $ka = n\pi$ (Ka = integral multiple of π)
 $n = 1, 2, 3, \dots$
 $n \neq 0$

Justify Born interpretation

K is restricted to discrete set of values

$$k = \frac{n\pi}{a}$$

$$\varphi = A \sin \frac{n\pi}{a}$$

Allowed wave function

$$\Psi = A \sin \frac{n\pi}{a}$$

Normalization of wave function: $A = (\frac{2}{a})^{1/2}$

$$\Psi_n = (\frac{2}{a})^{1/2} \sin \frac{n\pi}{a}$$

For $0 < x < a$

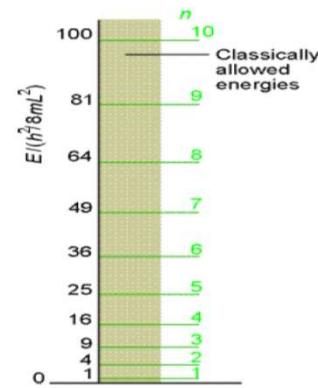
Allowed Energies

$$E_n = \frac{k^2 h^2}{2m}$$

$$E_n = \frac{n^2 \pi^2 h^2}{2ma^2}$$

The energies and wave functions are labelled with the ‘quantum number’ n . A **quantum number** is an integer (in some cases a half-integer) that labels the state of the system.

With the help of ‘quantum number’ n we can calculate energy (E) and wave function (ψ).



$$\int A^2 \sin^2 \frac{n\pi}{a} = \left(\frac{a}{2} - \frac{\sin 2a}{4} + c \right)$$

$$A^2 \left(\frac{a}{2} - \frac{\sin 2a}{4} + c \right) = 1$$

$$\left(\frac{\sin 2a}{4} \right) = 0$$

Properties of Wave function in 1-D Box

Wave functions are standing waves

$$\Psi_n = \left(\frac{2}{a}\right)^{1/2} \sin \frac{n\pi}{a}$$

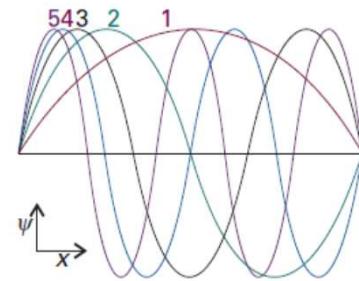
Wave functions of a particle in 1-D box is sin function with same amplitude and different wavelength.

Shortening of wavelength (λ) results in sharp average curvature of the wave function and increase in kinetic Energy of the particle.

Successive wave function possesses one more half wavelength & hence they have shorter wavelength

No. of Nodes (Points where wave function passes through zero i.e. ψ_0) increases with the increase in 'n' so that ψ_n has $(n-1)$ nodes.

No. of Nodes = $(n-1)$ then $\psi_1 \rightarrow 0, \psi_2 \rightarrow 1, \psi_3 \rightarrow 2 \dots$



Energies of Wave function in 1-D Box

When a particle in 1-D box moves between the walls of the box then in any given period it spends half of the its time in travelling left and half travelling to right.

Reason: $n \neq 0$ then lowest energy of the particle can't be zero

The lowest energy is called Zero Point Energy (ZEP) $E_1 = \frac{h^2}{8ma^2}$

We Know that

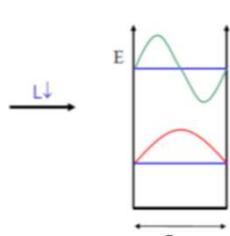
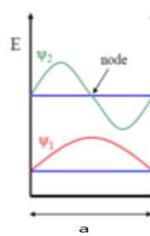
$$E_n = \frac{n^2 \pi^2 h^2}{2ma^2}$$

So we can say

$$E_n \propto \frac{n^2}{a^2}$$

When

$\uparrow E_n$ then $\uparrow n$ (More nodes in ψ_n)



- $\uparrow E_n$ then $\downarrow a$ (Shorter Wavelength)
- $\uparrow n$ or $\downarrow a$ (Curvature of ψ_n \uparrow)
- $\uparrow KE$
- $\uparrow E_n$

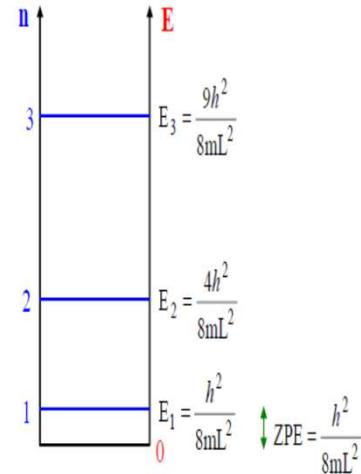
❖ $E_n \propto n^2$

Energy levels will further get apart as the value of 'n' increases

Zero Point Energy: Lowest Energy of the particle in 1-D box

❖ $ZEP = E_{\min} = E_n = \frac{h^2}{8mL^2}$

In *Classical Mechanics* $E_{\min} = 0$ is possible but in *Quantum Mechanics* $E_{\min} = 0$ corresponds to $\psi = 0$ everywhere (Which is not possible & forbidden because particle must exist somewhere in 1-D box)



The physical origin of the zero-point energy can be explained in two ways -

First, the uncertainty principle requires a particle to possess kinetic energy if it is confined to a finite region ($0 < x, x < L$): the location of the particle is not completely indefinite, so its momentum cannot be precisely zero. Hence it has non-zero kinetic energy.

Second, if the wave function is to be zero at the walls ($x=0, x=L$) but smooth, continuous and non-zero everywhere, then it must be curved and curvature in a wave function implies the possession of kinetic energy.

Probability Density for a particle in 1-D Box

The probability density of a particle in 1-D box is given by -

$$\psi^2(x) = \frac{2}{L} \sin^2 \frac{n\pi x}{L}$$

The probability density of a particle (P_x) between x and $x+dx$ given by -

$$\int \psi^2 dx = \int \frac{2}{L} \sin^2 \left(\frac{n\pi x}{L} \right) dx$$

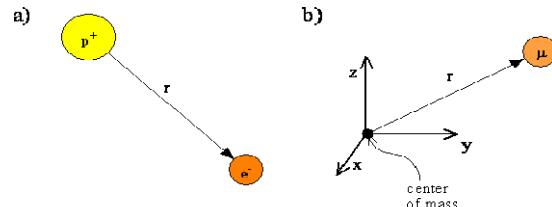
The probability density of a particle in 1-D box is not uniform i.e. $\psi_n^2 = 0$ at walls $x=0$ & $x=L$ $\psi_n^2 = 0$ at the nodes.

Schrodinger Equation for Hydrogen Atom

The hydrogen atom, consisting of an electron and a proton, is a two-particle system. Similar type of system are H, He⁺, Li²⁺, Be³⁺

The internal motion of two particles (Proton & Electron) around their center of mass (**position defined relative to an object or system of objects i.e. $m_1r_1+m_2r_2$**) is equivalent to the motion of a single particle with a reduced mass (**The equations of motion of two mutually interacting bodies can be reduced to a single equation describing the motion of one body in a reference frame centered in the other body, $\mu=m_1*m_2/m_1+m_2$**).

This reduced particle is located at r , where r is the vector specifying the position of the electron relative to the position of the proton. The length of r is the distance between the proton and the electron, and the direction of r is given by the orientation of the vector pointing from the proton to the electron.



a) The proton (p⁺) and electron (e⁻) of the hydrogen atom.
b) Equivalent reduced particle with reduced mass μ at distance r from center of mass.

Consider 3-D motion of electron with respect to the nucleus (p⁺) then total energy of the system can be defined as

$$\hat{H} = \hat{T} + \hat{V}$$

Coulomb's Potential Energy or
Central Potential Energy

Kinetic Energy $\hat{T} = -\frac{\hbar^2}{2\mu} \nabla^2$

Potential Energy $\hat{V} = V(r) = \frac{-Ze^2}{4\pi\epsilon_0 r}$

Where

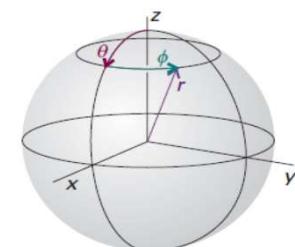
μ is the reduced mass $\mu = \frac{m_e \cdot m_N}{m_e + m_N} \approx m_e$

$\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$

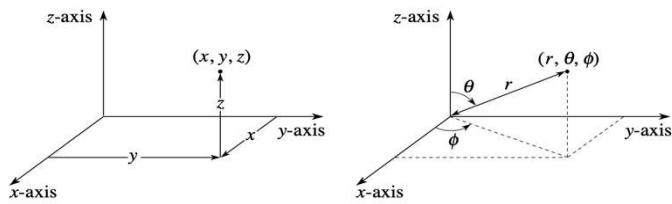
$r = \sqrt{x^2 + y^2 + z^2}$

Due to the spherical symmetry of atom the position of electron can be defined in spherical coordinates (r, θ, ϕ) rather than Cartesian coordinates (x, y, z).

Due to the spherical symmetry wave function can be represented as the product of radial and angular component.



$$\begin{aligned}
 x &= r \sin \theta \cos \phi \\
 y &= r \sin \theta \sin \phi \\
 z &= r \cos \theta \\
 r &= \sqrt{x^2 + y^2 + z^2}
 \end{aligned}$$



Time independent Schrodinger wave equation in spherical coordinates for electrons around the positively charged nucleus.

$$\Psi(r, \theta, \phi) = R(r) * Y(r, \theta, \phi)$$

Radial Wave function Angular Wave function

The **Spherical Harmonic $\Psi(\theta, \phi)$** functions provide information about where the electron is around the proton, and the **radial function $R(r)$** describes how far the electron is away from the proton.

A solution for both radial and angular wave functions [$R(r)$ and $Y(\theta, \phi)$] with energy ' E_n ' depends on only one quantum number n (Principle Quantum Number), although others (l, m & s) are required for the proper description of the wave function.

$$E_n = -\left(\frac{\mu e^4}{8\hbar^2 \epsilon_0^2} \right) \cdot \left(\frac{Z^2}{n^2} \right)$$

The hydrogen atom wave functions, $\psi(r, \theta, \phi)$ are called atomic orbitals. An atomic orbital is a function that describes one electron in an atom. The wave function with $n = 1, l = 0$ is called the 1s orbital, and an electron that is described by this function is said to be in the 1s orbital, i.e. have a 1s orbital state.

The constraints on ' n ', ' l ' and ' m ' are imposed during the solution of the hydrogen atom. Schrödinger equation explain why there is a single 1s orbital, why there are three 2p orbitals, five 3d orbitals, etc.

Quantum Numbers

Total 04 Quantum numbers (n, l, m and s) are used to describe completely the movement and trajectories of each electron within the atom.

The combination of all the quantum numbers of all electrons in an atom is described by a wave function that obeys Schrodinger Wave Equation.

Each electron in an atom has unique set of all the quantum numbers i.e. No two electrons will have same set of quantum numbers.

Quantum numbers determine the electronic configuration of an atom, probable location of electron in an orbital, ionization energy and atomic radii.

Quantum numbers are:

- 1) Principle Quantum Number
- 2) Azimuthal Quantum Number or Orbital Angular Momentum Quantum Number
- 3) Magnetic Quantum Number
- 4) Spin Quantum Number

Principle Quantum Number (n)

Principle quantum number is the main energy level occupied by the electron. Energy levels are the fixed distances from the nucleus of an atom.

As the value of 'n' increases the average distance of electron from nucleus also increases. Negatively charged electron is present in first orbit ($n=1$) is strongly attracted towards the positively charged nucleus as compared to an electron present in outermost orbit. Hence electron with high value of 'n' can be removed easily.

All orbitals with the **same value of 'n'** together constitute an **electronic shell** or All the wave function (ψ) having same value of 'n' constitutes the principle shell.

n	1	2	3	4
Shell	K	L	M	N

For given value of n , l can have ' n ' values ranging from 0 to $(n-1)$.

For each value of n , orbitals with the same value of $\ell = (n-1)$ together constitute an electronic sub-shell.

Each sub-shell consists of $(2\ell+1)$ orbitals, each with a different m_ℓ value.

ℓ	0	1	2	3
Sub-shell	s	p	d	f
No. orbitals	1	3	5	7

Possible combination of shells & subshells

n	1	2	3	4
1	0	1	2	3
Shell	K	L	M	N
Subshell	s	p	d	f
No. of orbitals	1	3	5	7

n	$\ell \rightarrow$	0	1	2	3	...
1	1s					
2	2s	2p				
3	3s	3p	3d			
4	4s	4p	4d	4f		
...						

Total No. of orbitals in a shell ' n ' is n^2

Total No. of electrons in a shell ' n ' is $2n^2$

Azimuthal Quantum Number (l)

It gives information about the shape / region an electron occupies (Orbital Shape). The value of ' l ' varies from 0 to $(n-1)$ i.e. it depends on the value of ' n '.

All the wave function (ψ) having same value of ' n ' and ' l ' forms a sub-shell which will have same shape but different orientation in space.

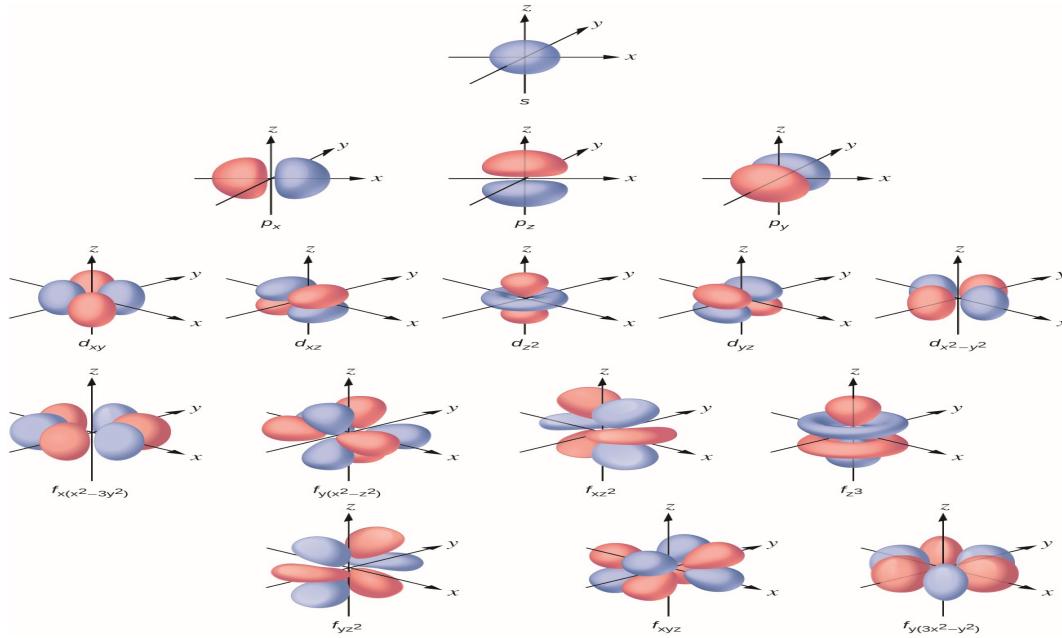
Magnetic Quantum Number (m)

Magnetic quantum number is describes the orbital orientation in space. For a given value of ' l ' magnetic quantum number will have $(2l+1)$ values.

Each wave function with an allowed combination of n , l , and m values describes an atomic orbital i.e. An electron will have particular spatial distribution.

For a given set of quantum numbers, each principal shell has a fixed number of subshells and each subshell has a fixed number of orbitals.

Shapes of Atomic Orbitals



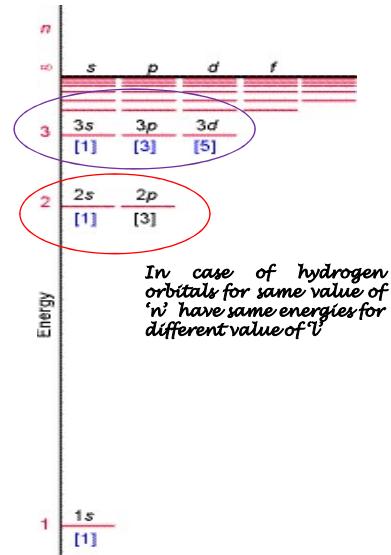
Solutions of the Schrödinger Wave Equation for a One-Electron Atom

n	ℓ	m_ℓ	Orbital	Solution	n	ℓ	m_ℓ	Orbital	Solution
1	0	0	1s	$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma}$	3	0	0	3s	$\psi_{3s} = \frac{1}{81\sqrt{3\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (27 - 18\sigma + 2\sigma^2) e^{-\sigma/3}$
2	0	0	2s	$\psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (2 - \sigma) e^{-\sigma/2}$	3	1	0	3p _z	$\psi_{3p_z} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (6\sigma - \sigma^2) e^{-\sigma/3} \cos \theta$
2	1	0	2p _z	$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \cos \theta$	3	1	± 1	$\begin{cases} 3p_x \\ 3p_y \end{cases}$	$\psi_{3p_x} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (6\sigma - \sigma^2) e^{-\sigma/3} \sin \theta \cos \phi$
2	1	± 1	$\begin{cases} 2p_x \\ 2p_y \end{cases}$	$\psi_{2p_x} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \sin \theta \cos \phi$	3	2	0	3d _{z^2}	$\psi_{3d_{z^2}} = \frac{1}{81\sqrt{6\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3} (3 \cos^2 \theta - 1)$
				$\psi_{2p_y} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \sin \theta \sin \phi$	3	2	± 1	$\begin{cases} 3d_{xz} \\ 3d_{yz} \end{cases}$	$\psi_{3d_{xz}} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3} \sin \theta \cos \theta \cos \phi$
					3	2	± 2	$\begin{cases} 3d_{xy} \\ 3d_{x^2-y^2} \end{cases}$	$\psi_{3d_{xy}} = \frac{1}{81\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3} \sin^2 \theta \sin 2\phi$
									$\psi_{3d_{x^2-y^2}} = \frac{1}{81\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3} \sin^2 \theta \cos 2\phi$

Note: $\sigma = Zr/a_0$, where $Z = 1$ for hydrogen; $a_0 = \epsilon_0 h^2/\pi me^2 = 5.29 \times 10^{-11}$ m.

Atomic Orbital Energy Diagram for H

- Orbital energies depend only on the principal quantum number n .
- For a given n value (shell), all sub-shells (l) and orbitals (m_l) have the same energy
– i.e. they are **degenerate**.

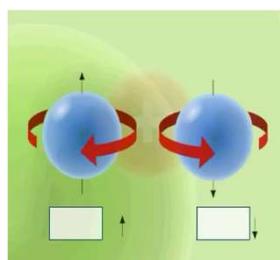


Spin Quantum Number (s)

The Spin Quantum Number (m_s) describes the angular momentum of an electron. An electron spins around an axis and has both angular momentum and orbital angular momentum. Since angular momentum is a vector, the Spin Quantum Number (s) has both a magnitude ($1/2$) and direction (+ or -).

Each orbital can only hold two electrons. One electron will have a $+1/2$ spin (Clockwise motion) and other will have a $-1/2$ spin (Counter Clockwise motion). For pairing of electrons in the orbitals the occupying electrons should have opposite spin.

Spin is the fundamental property of an electron like charge & mass



- The three quantum numbers (n , l , and m) that describe an orbital are integers: 0, 1, 2, 3.
- The principal quantum number (n) cannot be zero. The allowed values of n are therefore 1, 2, 3, 4...
- The angular quantum number (l) can be any integer between 0 and $n-1$.
- If $n = 3$, l can be either 0, 1, or 2.
- The magnetic quantum number (m) can be any integer between $-l$ and $+l$.
- If $l = 2$, m can be $-2, -1, 0, +1$, or $+2$.
- Orbitals that have same value of principal quantum number form a Shell(n).
- Orbitals within the shells are divided into subshell (l)

Application

- Computational chemistry is a rapidly growing field in chemistry.
 - ✓ Computers are getting faster.
 - ✓ Algorithms and programs are maturing.

- Some of the almost limitless properties that can be calculated with computational chemistry are:
 - ✓ Equilibrium and transition-state structures
 - ✓ dipole and quadrupole moments and polarizabilities
 - ✓ Vibrational frequencies, IR and Raman Spectra
 - ✓ NMR spectra
 - ✓ Electronic excitations and UV spectra
 - ✓ Reaction rates and cross sections
 - ✓ thermochemical data

Limitations

- Schrödinger Equation can only be solved exactly for simple systems.
 - ✓ Rigid Rotor, Harmonic Oscillator, Particle in a Box, Hydrogen Atom.

- For more complex systems (*i.e.* many electron atoms/molecules) we need to make some simplifying assumptions/approximations and solve it numerically.

- However, it is still possible to get very accurate results (and also get very crummy results).
 - ✓ In general, the “cost” of the calculation increases with the accuracy of the calculation and the size of the system.

Tools

- Software packages for performing electronic structure calculations.
 - ✓ MOLPRO, GAMESS, COLUMBUS, NWChem, MOLFDIR, ACESII, GAUSSIAN, ...
 - ✓ The different programs have various advantages and capabilities.

- We also have available to us **Gaussview** which is a GUI that interfaces with Gaussian for aiding in building molecules and viewing output.

Numerical on Planks Quantum Theory $E = h\nu \quad \nu = \frac{c}{\lambda}$

Calculate energy of one mole of photons of radiation whose frequency is 5×10^{14} Hz.

Solution

Energy (E) of one photon is given by the expression

$$E = h\nu$$

$$h = 6.626 \times 10^{-34} \text{ J s}$$

$$\nu = 5 \times 10^{14} \text{ s}^{-1} \text{ (given)}$$

$$E = (6.626 \times 10^{-34} \text{ J s}) \times (5 \times 10^{14} \text{ s}^{-1})$$

$$= 3.313 \times 10^{-19} \text{ J}$$

Energy of one mole of photons

$$= (3.313 \times 10^{-19} \text{ J}) \times (6.022 \times 10^{23} \text{ mol}^{-1})$$

$$= 199.51 \text{ kJ mol}^{-1}$$

A 100 watt bulb emits monochromatic light of wavelength 400 nm. Calculate the number of photons emitted per second by the bulb.

Solution

$$\begin{aligned} \text{Power of the bulb} &= 100 \text{ watt} \\ &= 100 \text{ J s}^{-1} \end{aligned}$$

$$\text{Energy of one photon } E = h\nu = hc/\lambda$$

$$= \frac{6.626 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ m s}^{-1}}{400 \times 10^{-9} \text{ m}}$$

$$= 4.969 \times 10^{-19} \text{ J}$$

Number of photons emitted

$$\frac{100 \text{ J s}^{-1}}{4.969 \times 10^{-19} \text{ J}} = 2.012 \times 10^{20} \text{ s}^{-1}$$

Source for Numerical: NCERT Chemistry Class XI

Numerical on relationship of c , v and λ

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

Problem 2.3

The Vividh Bharati station of All India Radio, Delhi, broadcasts on a frequency of 1,368 kHz (kilo hertz). Calculate the wavelength of the electromagnetic radiation emitted by transmitter. Which part of the electromagnetic spectrum does it belong to?

Solution

The wavelength, λ , is equal to c/v , where c is the speed of electromagnetic radiation in vacuum and v is the frequency. Substituting the given values, we have

$$\begin{aligned}\lambda &= \frac{c}{v} \\ &= \frac{3.00 \times 10^8 \text{ m s}^{-1}}{1368 \text{ kHz}} \\ &= \frac{3.00 \times 10^8 \text{ m s}^{-1}}{1368 \times 10^3 \text{ s}^{-1}} \\ &= 219.3 \text{ m}\end{aligned}$$

This is a characteristic radiowave wavelength.

The wavelength range of the visible spectrum extends from violet (400 nm) to red (750 nm). Express these wavelengths in frequencies (Hz). ($1\text{nm} = 10^{-9}\text{m}$)

Solution

Using equation 2.5, frequency of violet light

$$\begin{aligned}\nu &= \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{400 \times 10^{-9} \text{ m}} \\ &= 7.50 \times 10^{14} \text{ Hz}\end{aligned}$$

Frequency of red light

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{750 \times 10^{-9} \text{ m}} = 4.00 \times 10^{14} \text{ Hz}$$

The range of visible spectrum is from 4.0×10^{14} to 7.5×10^{14} Hz in terms of frequency units.

Calculate (a) wavenumber and (b) frequency of yellow radiation having wavelength 5800 Å.

Solution

(a) Calculation of wavenumber ($\bar{\nu}$)

$$\begin{aligned}\lambda &= 5800 \text{ Å} = 5800 \times 10^{-8} \text{ cm} \\ &= 5800 \times 10^{-10} \text{ m}\end{aligned}$$

$$\begin{aligned}\bar{\nu} &= \frac{1}{\lambda} = \frac{1}{5800 \times 10^{-10} \text{ m}} \\ &= 1.724 \times 10^6 \text{ m}^{-1} \\ &= 1.724 \times 10^4 \text{ cm}^{-1}\end{aligned}$$

(b) Calculation of the frequency (ν)

$$\bar{\nu} = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ m s}^{-1}}{5800 \times 10^{-10} \text{ m}} = 5.172 \times 10^{14} \text{ s}^{-1}$$

Numerical on de Broglie's Equation

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

The mass of an electron is 9.1×10^{-31} kg. If its K.E. is 3.0×10^{-25} J, calculate its wavelength.

Solution

Since K. E. = $\frac{1}{2} mv^2$

$$v = \left(\frac{2\text{K.E.}}{m} \right)^{1/2} = \left(\frac{2 \times 3.0 \times 10^{-25} \text{ kg m}^2 \text{s}^{-2}}{9.1 \times 10^{-31} \text{ kg}} \right)^{1/2}$$

$$= 812 \text{ m s}^{-1}$$

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ Js}}{(9.1 \times 10^{-31} \text{ kg})(812 \text{ m s}^{-1})}$$

$$= 8967 \times 10^{-10} \text{ m} = 896.7 \text{ nm}$$

Calculate the mass of a photon with wavelength 3.6 \AA .

Solution

$$\lambda = 3.6 \text{ \AA} = 3.6 \times 10^{-10} \text{ m}$$

Velocity of photon = velocity of light

$$m = \frac{h}{\lambda v} = \frac{6.626 \times 10^{-34} \text{ Js}}{(3.6 \times 10^{-10} \text{ m})(3 \times 10^8 \text{ ms}^{-1})}$$

$$= 6.135 \times 10^{-29} \text{ kg}$$

What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 m s^{-1} ?

According to de Broglie equation (2.22)

$$\lambda = \frac{h}{mv} = \frac{(6.626 \times 10^{-34} \text{ Js})}{(0.1 \text{ kg})(10 \text{ m s}^{-1})}$$

$$= 6.626 \times 10^{-34} \text{ m} (\text{J} = \text{kg m}^2 \text{ s}^{-2})$$

Calculations of Wavelength

Compare the wavelength for an electron (mass = 9.11×10^{-31} kg) traveling at a speed of $1.0 \times 10^7 \text{ m/s}$ with that for a ball (mass = 0.10 kg) traveling at 35 m/s.

Solution We use the equation $\lambda = h/mv$, where

$$h = 6.626 \times 10^{-34} \text{ J s} \quad \text{or} \quad 6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-2}$$

since

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

For the electron,

$$\lambda_e = \frac{6.626 \times 10^{-34} \frac{\text{kg m}^2}{\text{s}}}{(9.11 \times 10^{-31} \text{ kg})(1.0 \times 10^7 \text{ m/s})} = 7.3 \times 10^{-11} \text{ m}$$

For the ball,

$$\lambda_b = \frac{6.626 \times 10^{-34} \frac{\text{kg m}^2}{\text{s}}}{(0.10 \text{ kg})(35 \text{ m/s})} = 1.9 \times 10^{-34} \text{ m}$$

Numerical on Photoelectric Effect

When electromagnetic radiation of wavelength 300 nm falls on the surface of sodium, electrons are emitted with a kinetic energy of $1.68 \times 10^{-5} \text{ J mol}^{-1}$. What is the minimum energy needed to remove an electron from sodium? What is the maximum wavelength that will cause a photoelectron to be emitted?

The energy (E) of a 300 nm photon is given by

$$\begin{aligned} h\nu &= hc/\lambda \\ &= \frac{6.626 \times 10^{-34} \text{ J s} \times 3.0 \times 10^8 \text{ m s}^{-1}}{300 \times 10^{-9} \text{ m}} \\ &= 6.626 \times 10^{-19} \text{ J} \end{aligned}$$

$$\begin{aligned} \text{The energy of one mole of photons} \\ = 6.626 \times 10^{-19} \text{ J} \times 6.022 \times 10^{23} \text{ mol}^{-1} \\ = 3.99 \times 10^5 \text{ J mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{The minimum energy needed to remove} \\ \text{one mole of electrons from sodium} \\ = (3.99 - 1.68) \times 10^5 \text{ J mol}^{-1} \\ = 2.31 \times 10^5 \text{ J mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{The minimum energy for one electron} \\ = \frac{2.31 \times 10^5 \text{ J mol}^{-1}}{6.022 \times 10^{23} \text{ electrons mol}^{-1}} \\ = 3.84 \times 10^{-19} \text{ J} \end{aligned}$$

This corresponds to the wavelength

$$\begin{aligned} \therefore \lambda &= \frac{hc}{E} \\ &= \frac{6.626 \times 10^{-34} \text{ J s} \times 3.0 \times 10^8 \text{ m s}^{-1}}{3.84 \times 10^{-19} \text{ J}} \\ &= 517 \text{ nm} \end{aligned}$$

(This corresponds to green light)

The threshold frequency v_0 for a metal is $7.0 \times 10^{14} \text{ s}^{-1}$. Calculate the kinetic energy of an electron emitted when radiation of frequency $v = 1.0 \times 10^{15} \text{ s}^{-1}$ hits the metal.

Solution

According to Einstein's equation

$$\begin{aligned} \text{Kinetic energy} &= \frac{1}{2} m_e v^2 = h(v - v_0) \\ &= (6.626 \times 10^{-34} \text{ J s}) (1.0 \times 10^{15} \text{ s}^{-1} - 7.0 \times 10^{14} \text{ s}^{-1}) \\ &= (6.626 \times 10^{-34} \text{ J s}) (10.0 \times 10^{14} \text{ s}^{-1} - 7.0 \times 10^{14} \text{ s}^{-1}) \\ &= (6.626 \times 10^{-34} \text{ J s}) \times (3.0 \times 10^{14} \text{ s}^{-1}) \\ &= 1.988 \times 10^{-19} \text{ J} \end{aligned}$$

Problem: 1 - What is the energy in joules and electron volts of a photon of 420-nm violet light?

Problem: 2 - What is the maximum kinetic energy of electrons ejected from calcium by 420-nm violet light, given that the work function for calcium metal is 2.71 eV?

Solution - 1

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

Now substituting known values yields

$$\begin{aligned} E &= \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{420 \times 10^{-9} \text{ m}} \\ &= 4.74 \times 10^{-19} \text{ J} \end{aligned}$$

Converting to eV, the energy of the photon is

$$\begin{aligned} E &= (4.74 \times 10^{-19} \text{ J}) \left(\frac{1 \text{ eV}}{1.6 \times 10^{-19} \text{ J}} \right) \\ &= 2.96 \text{ eV.} \end{aligned}$$

Solution - 2

$$\begin{aligned} KE_e &= h\nu - \Phi \\ &= 2.96 \text{ eV} - 2.71 \text{ eV} \\ &= 0.246 \text{ eV.} \end{aligned}$$

Numerical on Bohr's Model for Hydrogen Atom

- The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by E , is given by:

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$$

- The angular momentum of an electron is quantized. In a given stationary state it can be expressed as in equation

$$m_e v r = n \cdot \frac{\hbar}{2\pi} \quad n = 1, 2, 3, \dots$$

- The radii of the stationary states are expressed as:

$$r_n = n^2 a_0$$

Where $a_0 = 52.9 \text{ pm}$ (The radius of the first stationary state called Bohr's orbit is 52.9 pm)

- Energy of electron:

$$E_n = -R_H \left(\frac{1}{n^2} \right) \quad n = 1, 2, 3, \dots$$

Where R_H (Rydberg Constant) = $2.18 \times 10^{-18} \text{ J}$

- Bohr's theory can also be applied to the ions containing only one electron, similar to that present in hydrogen atom. For example, He^+ , Li^{2+} , Be^{3+} and so on. The energies of the stationary states associated with these kinds of ions (also known as **hydrogen like species**) are given by the expression.

$$E_n = -2.18 \times 10^{-18} \left(\frac{Z^2}{n^2} \right) \text{ J}$$

Radius of Hydrogen like species (Ions containing one electron) $r_n = \frac{52.9(n^2)}{Z} \text{ pm}$

Where Z = Atomic Number

- Line spectrum of Hydrogen

Energy gap between two orbitals

$$\Delta E = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = 2.18 \times 10^{-18} \text{ J} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

Where n_i = Initial orbit and n_f = Final orbit

The **frequency (ν) in (Hz)** associated with the absorption and emission of the photon can be evaluated by using equation

$$\nu = 3.29 \times 10^{15} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

The **wave number ($\tilde{\nu}$) in (m^{-1})** associated with the absorption and emission of the photon can be evaluated by using equation

$$\tilde{\nu} = 1.09677 \times 10^7 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

Allowed Energies

$$E_n = \frac{n^2 \pi^2 h^2}{2ma^2}$$

What are the frequency and wavelength of a photon emitted during a transition from $n = 5$ state to the $n = 2$ state in the hydrogen atom?

Solution

Since $n_i = 5$ and $n_f = 2$, this transition gives rise to a spectral line in the visible region of the Balmer series. From equation (2.17)

$$\Delta E = 2.18 \times 10^{-18} J \left[\frac{1}{5^2} - \frac{1}{2^2} \right] \\ = -4.58 \times 10^{-19} J$$

It is an emission energy

The frequency of the photon (taking energy in terms of magnitude) is given by

$$\nu = \frac{\Delta E}{h} \\ = \frac{4.58 \times 10^{-19} J}{6.626 \times 10^{-34} Js} \\ = 6.91 \times 10^{14} Hz \\ \lambda = \frac{c}{\nu} = \frac{3.0 \times 10^8 m s^{-1}}{6.91 \times 10^{14} Hz} = 434 nm$$

Calculate the energy associated with the first orbit of He^+ . What is the radius of this orbit?

Solution

$$E_n = -\frac{(2.18 \times 10^{-18} J)Z^2}{n^2} \text{ atom}^{-1}$$

For He^+ , $n = 1$, $Z = 2$

$$E_1 = -\frac{(2.18 \times 10^{-18} J)(2^2)}{1^2} = -8.72 \times 10^{-18} J$$

The radius of the orbit is given by equation (2.15)

$$r_n = \frac{(0.0529 nm)n^2}{Z}$$

Since $n = 1$, and $Z = 2$

$$r_1 = \frac{(0.0529 nm)l^2}{2} = 0.02645 nm$$

Numerical on Heisenberg's Uncertainty Principle

Problem: An electron is confined to the size of a magnesium atom with a 150 pm radius. What is the **minimum** uncertainty in its velocity?

$$\Delta p \Delta x \geq \frac{\hbar}{2}$$

can be written

$$\Delta p \geq \frac{\hbar}{2 \Delta x}$$

and substituting $\Delta p = m \Delta v$ since the mass is not uncertain.

$$\Delta v \geq \frac{\hbar}{2 m \Delta x}$$

the relevant parameters are

- mass of electron $m = m_e = 9.109383 \times 10^{-31} \text{ kg}$
- uncertainty in position: $\Delta x = 150 \times 10^{-12} \text{ m}$

$$\Delta v \geq \frac{1.0545718 \times 10^{-34} \text{ kg m}^2/\text{s}}{(2)(9.109383 \times 10^{-31} \text{ kg})(150 \times 10^{-12} \text{ m})} \\ = 3.9 \times 10^5 \text{ m/s}$$

Problem: Determine the uncertainty in the position of the ball (163 gm) bowled at with velocity of 111 kph.

Problem: The hydrogen atom has a radius on the order of 0.05 nm. Assuming that we know the position of an electron to an accuracy of 1% of the hydrogen radius, calculate the uncertainty in the velocity of the electron using the Heisenberg uncertainty principle. Then compare this value with the uncertainty in the velocity of a ball of mass 0.2 kg and radius 0.05 m whose position is known to an accuracy of 1% of its radius.

For the electron the uncertainty in position (Δx) is 1% of 0.05 nm, or

$$\Delta x = (0.01)(0.05 \text{ nm}) = 5 \times 10^{-4} \text{ nm}$$

Converting to meters gives

$$5 \times 10^{-4} \text{ nm} \times \frac{10^{-9} \text{ m}}{1 \text{ nm}} = 5 \times 10^{-13} \text{ m}$$

The values of the constants are

$$m = \text{mass of the electron} = 9.11 \times 10^{-31} \text{ kg}$$

$$b = 6.626 \times 10^{-34} \text{ J s} = 6.626 \times 10^{-34} \frac{\text{kg m}^2}{\text{s}}$$

$$\pi = 3.14$$

For the ball, the uncertainty in position (Δx) is 1% of 0.05 m, or $5 \times 10^{-4} \text{ m}$. Thus the minimum uncertainty in velocity is

$$\Delta v = \frac{\Delta p}{m} = \frac{b}{\Delta x \cdot m \cdot 4\pi} = \frac{6.626 \times 10^{-34} \frac{\text{kg m}^2}{\text{s}}}{(5 \times 10^{-4} \text{ m})(0.2 \text{ kg})(4)(3.14)} \\ = 5 \times 10^{-31} \text{ m/s}$$

We can now solve for the uncertainty in momentum:

$$\Delta p = \frac{\hbar}{2 \cdot \Delta x} = \frac{h}{4\pi \cdot \Delta x} = \frac{6.626 \times 10^{-34} \text{ kg m}^2}{4(3.14)(5 \times 10^{-13} \text{ m})} \\ = 1.05 \times 10^{-22} \text{ kg m/s} \quad (\text{keeping extra significant figures})$$

Recalling that $p = mv$ and assuming that the electron mass is constant (ignoring any relativistic corrections), we have

$$\Delta p = \Delta(mv) = m\Delta v$$

and the uncertainty in velocity is

$$\Delta v = \frac{\Delta p}{m} = \frac{1.05 \times 10^{-22} \text{ kg m/s}}{9.11 \times 10^{-31} \text{ kg}} = 1.15 \times 10^8 \text{ m/s} = 1 \times 10^8 \text{ m/s}$$

Thus the uncertainty principle is negligible in the world of macroscopic objects but is very important for objects with small masses, such as the electron.

Problem: Assume that an electron is confined to a one-dimensional box 1.50 nm in length. Calculate the lowest three energy levels for this electron, and calculate the wavelength of light necessary to promote the electron from the ground state to the first excited state.

For $n = 1$ we get

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \quad E_1 = \frac{(1)^2(6.626 \times 10^{-34} \text{ J s})^2}{(8)(9.11 \times 10^{-31} \text{ kg})(1.50 \times 10^{-9} \text{ m})^2} = 2.68 \times 10^{-20} \text{ J}$$

Similarly, for $n = 2$ we get

$$E_2 = 1.07 \times 10^{-19} \text{ J}$$

And for $n = 3$ we get

$$E_3 = 2.41 \times 10^{-19} \text{ J}$$

Note that since

$$E_n = n^2 \frac{\hbar^2}{8mL^2} = n^2 E_1$$

then $E_2 = (2)^2 \frac{\hbar^2}{8mL^2} = 4E_1 \quad \text{and} \quad E_3 = 9E_1$

To calculate the wavelength of light necessary to excite the electron from level 1 to level 2 (the first *excited* state), we first need to obtain the energy difference between the two levels:

$$\Delta E = E_2 - E_1 = (n_2^2 - n_1^2) \frac{\hbar^2}{8mL^2} \\ = (3)(2.68 \times 10^{-20} \text{ J}) = 8.04 \times 10^{-20} \text{ J}$$

Then we find the wavelength required from the equation

$$\Delta E = \frac{hc}{\lambda}$$

Inserting the appropriate values gives

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.9979 \times 10^8 \text{ m/s})}{8.04 \times 10^{-20} \text{ J}} \\ = 2.47 \times 10^{-6} \text{ m} = 2470 \text{ nm}$$

Numerical on Quantum Numbers

Electron Subshells

For principal quantum level $n = 5$, determine the number of subshells (different values of ℓ) and give the designation of each.

Solution For $n = 5$ the allowed values of ℓ run from 0 to 4 ($n - 1 = 5 - 1$). Thus the subshells and their designations are

$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$
5s	5p	5d	5f	5g 

Food for thought

Q1: What is the wavelength of electromagnetic radiation that ejects 2.00-eV electrons from calcium metal, given that the work function is 2.71 eV? What type of electromagnetic radiation is this?

Q2: An unknown elemental metal has work function of 8.01×10^{-19} J. Upon illumination with UV light of wavelength 162 nm, electrons are ejected with velocity of at 3.5×10^4 m/s. What is the threshold wavelength? What is the work function in units of eV?

Q3: If the position of an electron is within the 10 pm interval, what is the uncertainty of the momentum?

Q4: If we know the velocity of an electron to within 3.5×10^7 m/s, then what is the uncertainty in its position?