QUANTUM CHEMISTRY - THEORY

Introduction:

The classical mechanics includes Newtonian laws of motion of macroscopic bodies, Maxwell's theory of electricity, magnetism and electromagnetic radiation, thermodynamics and the kinetic theory of gases. In the late nineteenth century, it was felt that this classical mechanics was found not successful to explain the behaviour of the sub-atomic particles. Such phenomena are black body radiation, photoelectric effect, Compton effect, spectrum of H-atom, etc.

In the history, first classical theory fails to explain the observed frequency distribution of radiation energy emitted by a hot body. To explain the phenomenon, in Dec 14, 1900, Max Planck presented his revolutionary theory to the Berlin Physical Society. He proposed the quantum nature of electromagnetic radiation. According to this theory, radiation is assumed to be composed of bundles of discrete energy packets; each is called quantum or photon. The energy of the photon,

$$\varepsilon_{photon} = h\nu = \frac{hc}{\lambda},$$

where ν is the frequency of the radiation and h is called Planck's constant and its value is 6.626×10^{-27} erg sec, c is the velocity of light in vacuum and its value is 3×10^{10} cm/sec and λ is its wave length of the light.
If a photon undergoes interaction with matter, either it can be completely absorbed transferring all its energy (photo electric effect) or it may transfer part of its energy and its frequency is adjusted to a lower value, thereby maintaining particle character (Compton Effect).

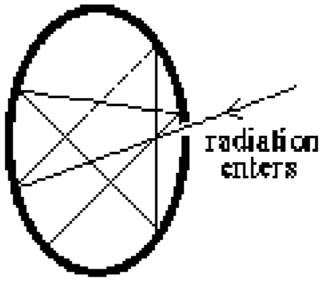
Intensity of the radiation is a measure of number of photons falling per unit time and it has no concerned with individual photon energy. The energy of the photon is independent of its intensity and is dependent only on its frequency. This concept is contrary to the classical ideas where radiation is considered purely as waves and energy is estimated by the intensity of the wave disturbance, dependent on the physical properties of the medium.

In 1905, Einstein used this theory to explain successfully the photoelectric effect in which emission of electrons from metal surface occurs by irradiation of light. In 1913, Niels Bohr developed his theory of H-atom assuming the quantization of angular momentum of the electron rotating in a circular path keeping nucleus at the centre.
In 1924, de Broglie used the idea of quantum theory to explain the wave-particle duality of the radiation.
The development of the subject up to 1925 is based on assumptions and is called 'quantum theory'.
In 1926, Erwin Schrödinger and Heisenberg independently developed quantum mechanics based on rigid mathematical model. Thus the subject developed after 1925, is called quantum mechanics.

Black Body Radiation

What is black body?

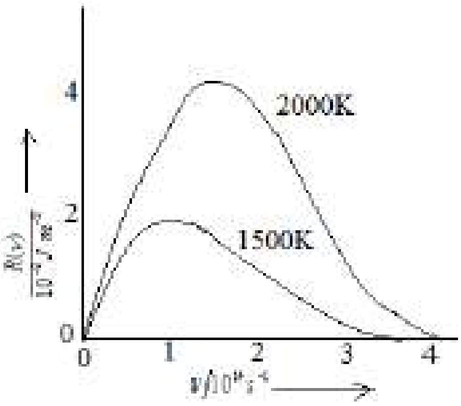
When radiation falls on an object, a part of it is reflected, a part is absorbed and the remaining part is transmitted. This is due to the fact that no object is a perfect absorber.
In contrast to this, we may visualize a black body which completely absorbs all the radiations that incident on it and retain all the radiant energy that strikes it.
For experimental purposes, a black body is generally a metallic surface with cavity blackened inside with a tiny hole. Radiation that enters the hole is repeatedly reflected within the cavity. At each reflection, a certain fraction of radiation is absorbed by the cavity walls and the large number of reflections causes virtually all the incident radiation to be absorbed. Such a material is called a black body and a nearest approach of a perfect absorber of radiation.



Criteria of the black body radiation:

A black body is not only a perfect absorber, but also is an idealized radiator. When the radiant energy absorbed by the body is equal to the heat emitted; the system will be in thermal equilibrium. Thus, when the cavity is heated, its walls emit radiation and a tiny portion of which escapes through the hole. Radiation emitted by such a body at constant temperature is known as black body radiation. It can be shown that the rate of radiation emitted per unit surface area of the black body is a function of only its temperature and is independent of the material of which black body is made up (Kirchhoff in 1859).

Experimental observations: Radiant energy may be analyzed by passing it through a prism and breaking it up into radiations of various frequencies. The energy associated with different frequencies can be measured. The usual practice is to measure the amount of black body radiant energy emitted in a given narrow frequency range. The frequency distribution of the emitted radiation is described by the function $R(\nu)$, where $R(\nu)d\nu$ is the energy with frequency in the range ν to $\nu + d\nu$ that is radiated per unit times per unit surface area of the black body. Some experimentally observed $R(\nu)$ vs. ν curves at two T are shown by the adjoining figure.



(1) Distribution function per unit frequency, $R(\nu)$ is more at high temperature than at low temperature. It is a function of temperature and frequency (ν). Experimentally, it is found that at any temperature T, $R(\nu)$ increases with ν, reaches a maximum and then falls off to zero.

(2) As T increases, the maximum in $R(\nu)$ shifts to higher frequencies.
As we find that when a metal rod is heated, it first glows red then orange-yellow, then white, then blue-white.(White light is a mixture of all colors).
Our bodies are not so hot to emit visible light, but it emits infrared radiation.

Raleigh formulation: In June, 1900, Lord Raleigh attempted to derive the theoretical expression for the function, $R(\nu)$. He used the equipartition of energy theorem (Classical theory) and formulated $R(\nu) = \left(2\pi kT/c^2\right)\nu^2$. The result is found absurd as it predicts the amount of energy emitted would increase without limit as ν increases which are contrary to the experimental observations.

Plank's Radiation Law: Radiation is emitted by any substance at any temperature due to oscillation of its particles, so each particle acts as an oscillator. These oscillators vibrate with certain frequency which is also equal to the frequency of the radiation they emit. Planck proposed the following two postulates relating to quantum nature of radiation emitted by the oscillators present in the black body.

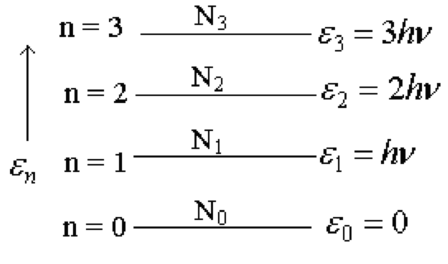
(1) An oscillator absorbs or emits radiation discontinuously, in the form of energy packets, called quanta or photons. Radiation behaves like a stream of particles, possessing mass, momentum and energy.
The energy of each quantum radiation is given as

$$\varepsilon = h\nu,$$

where ν is the frequency of radiation emitted by the oscillator and h is called Planck's constant.
The value of h in SI system is 6.626×10^{-34} Js and in cgs system its value is 6.626×10^{-34} Js.

(2) The oscillator has definite amount of energy in discrete energy levels. The energy of the nth energy level will be integral multiple of a quantum. i.e.

$$\varepsilon_n = nh\nu,$$



where n = 0, 1, 2, 3, etc, up to very high value tending to ∞.
The population of oscillators at different energy levels is given in the adjoining figure. The relative population with reference to ground level (n = 0) is given by Boltzmann distribution law, $N_n/N_0 = e^{-\Delta\varepsilon/kT}$ or, $N_n = N_0\, e^{-\Delta\varepsilon/kT}$, where $\Delta\varepsilon = \varepsilon_n - \varepsilon_0 = \varepsilon_n$ as $\varepsilon_0 = 0$. So, $N_n = N_0\, e^{-\varepsilon_n/kT}$ and $\varepsilon_n = nh\nu$.
Thus, $N_n = N_0\, e^{-nh\nu/kT}$.

The average energy of the oscillators is $\bar{\varepsilon} = E/N$, E is the total energy and N is the total number of oscillators in the black body. This can be written as,

$$\bar{\varepsilon} = \frac{N_0\,\varepsilon_0 + N_1\,\varepsilon_1 + N_2\,\varepsilon_2 + N_3\,\varepsilon_3}{N_0 + N_1 + N_2 + N_3} = \frac{\Sigma N_n\,\varepsilon_n}{\Sigma N_n} = \frac{\Sigma N_0\, e^{-nh\nu/kT} \times nh\,\nu}{N_0\, e^{-nh\nu/kT}} = h\nu\,\frac{\Sigma n e^{-nh\nu/kT}}{\Sigma e^{-nh\nu/kT}}$$

or, $\bar{\varepsilon} = h\nu \dfrac{e^{-h\nu/kT} + 2e^{-2h\nu/kT} + 3e^{-3h\nu/kT} ----}{1+e^{-h\nu/kT}+e^{-2h\nu/kT}+e^{-3h\nu/kT} ----} = h\nu\dfrac{x+2x^2+3x^3+....}{1+x+x^2+x^3+....}$, where $e^{-h\nu/kT} = x$.

Now taking the summation, we get $\bar{\varepsilon} = h\nu\dfrac{x(1-x)^{-2}}{(1-x)^{-1}} = h\nu\dfrac{x}{(1-x)} = h\nu\dfrac{1}{\left(\dfrac{1}{x}-1\right)}$ or, $\bar{\varepsilon} = \dfrac{h\nu}{e^{h\nu/kT}-1}$.

[Mathematics: Let $S = 1+x+x^2+x^3+....$ or, $xS = x+x^2+x^3+....$, subtracting the two we get $S\,(1-x) = 1$ or, $S = (1-x)^{-1}$. Similarly, $x+2x^2+3x^3+....$ = $x\left(1+2x+3x^2+....\right)$. Again, let $S = 1+2x+3x^2+....$ or, $x\,S = x+2x^2+3x^3....$, subtracting, we get $S = (1-x)^{-2}$. Thus, $x+2x^2+3x^3+.... = x(1-x)^{-2}$]

The number of oscillators per unit area of the cavity wall within frequency range ν to $\nu+d\nu$ is given by

$dN = \dfrac{2\pi\nu^2}{c^2}d\nu$, where c is the velocity of light in vacuum ,equal to 3 × 10^8 m/s.

Thus, the energy distribution, $R(\nu)d\nu$ within frequency range ν to $\nu+d\nu$ is equal to the product of the number of oscillators per unit area (dN) and the average energy of each oscillator ($\bar{\varepsilon}$).

$R(\nu)d\nu = dN\times\bar{\varepsilon} = \dfrac{2\pi\nu^2}{c^2}d\nu\times\dfrac{h\nu}{e^{h\nu/kT}-1} = \dfrac{2\pi h}{c^2}\times\dfrac{\nu^3}{e^{h\nu/kT}-1}d\nu$. Thus, $R(\nu)d\nu = \dfrac{2\pi h}{c^2}\times\dfrac{\nu^3}{e^{h\nu/kT}-1}d\nu$.

In terms of wavelength (λ), the distribution, $R(\lambda)\,d\lambda = \dfrac{2\pi hc^2}{\lambda^5}\times\dfrac{1}{e^{hc/\lambda kT}-1}d\lambda$ as $|d\nu| = \dfrac{c}{\lambda^2}d\lambda$.

Thus, the energy distribution function within unit frequency range of the black body radiation is given by

$$R(\nu) = \frac{2\pi h}{c^2}\times\frac{\nu^3}{e^{h\nu/kT}-1}.$$

Taking, $\dfrac{2\pi h}{c^2} = A_1$ and $\dfrac{h}{k} = A_2$, we get the distribution function, $R(\nu) = A_1\nu^3\times\dfrac{1}{e^{A_2\nu/T}-1}$.

Thus at lower frequency (ν), the non-exponential term (ν^3) dominates and $R(\nu)$ increases with the increase of ν. But at higher frequency, the exponential term $\left(\dfrac{1}{e^{A_2\nu/T}-1}\right)$ dominates and $R(\nu)$ decreases with increase of ν. So, $R(\nu)$ increases with the increase of ν passes through maximum and then drops almost to zero.

The experimental curve, $R(\nu)$ vs. ν is explained by the Planck's formulation of black body radiation.

It also explains that $R(\nu)$ increases with increase of T so, $R(\nu)$ is a function of ν and T .

Thus Planck's formulation, based on quantum theory, successfully explains the experimental observations of black body radiation.

Quantum result of Planck is reduced to classical result of Raleigh when $h\to 0$.

Max Planck planned to take $h\to 0$ in his result and found that his expression is reduced to Raleigh' expression that is based on the energy equipartition theorem.

Expanding the Planck's distribution function, we get

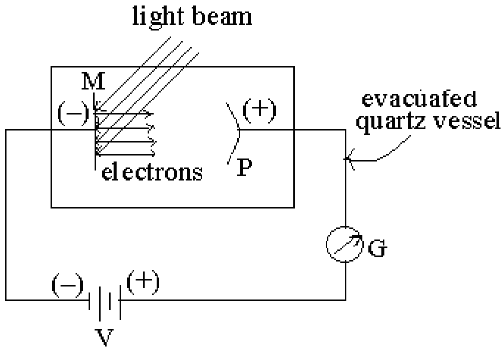
$$R(\nu) = \frac{2\pi h}{c^2}\times\frac{\nu^3}{\left[1+\dfrac{h\nu}{kT}+\left(\dfrac{h\nu}{kT}\right)^2+--\right]-1} = \frac{2\pi h}{c^2}\times\frac{\nu^3}{\dfrac{h\nu}{kT}} = \left(\frac{2\pi kT}{c^2}\right)\times\nu^2 .$$

But Raleigh expression fails to explain the experimental observations and so the correct expression can be obtained only when Planck's constant, $h\neq 0$.

Photo-electric Effect

The effect: It is the emission of electrons from a clean surface of some metals (like Na, K, Zn, etc) when light of suitable frequency falls on the metal plate. The ejected electrons are called photo-electrons. Visible light is used for the alkali metal surface, near ultra-violet light for other metals and extreme ultra-violet for other substances besides metals.

Experimental set-up: In 1888, Henry and Millikan performed the experiment with a beam of visible and ultra-violet light which falls on a clean surface of a metal in an almost evacuated vessel. They found that electrons are emitted from the metal surface if radiation of suitable frequency is used.



M = metal surface on which light is allowed to fall.

P = electron collector plate and is made anode (+ve) to accelerate the release of electrons.

G = galvanometer to record the current (photocurrent) i. This i is directly proportional to the rate of electrons emitting.

V = potential difference applied across M and P by using a battery.

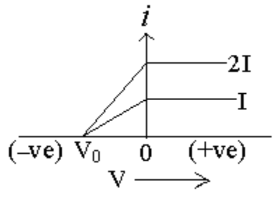
When M is made (–ve) and P is (+ve), electrons are accelerated towards P.

When P is made (–ve) and M is (+ve), electrons are retarded.

Observations of the experiment:

(1) There is no time-lag between the falling of light on the metal plate and ejecting of electrons from the plate. That is, the process is instantaneous.

(2) For monochromatic radiation of fixed frequency, the photocurrent (i) increases with the intensity (I) of radiation. When V is (+ve) [i.e. P = (+ve) and M = (–ve)], i reaches saturation value and if intensity (I) of light is doubled, photocurrent strength (i) also becomes doubled.



ν is fixed but I is varied

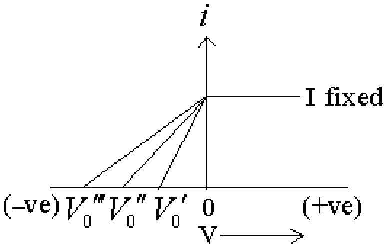
When V is made (–ve) [i.e. P = (–ve) and M = (+ve)], current strength decreases rapidly and becomes zero at a particular value of V, called stopping potential (V_0).

Since V_0 potential is required to stop the electrons of having maximum speed (v), then V_0 is a measure of KE of electrons, i.e, $eV_0 = ½ mv^2$

Stopping potential and KE :

This observation helps conclude that for fixed frequency of radiation, i depends on I of light. V_0 and hence KE of the ejecting electrons does not depend on intensity of radiation used.

(3) For fixed intensity of light, the photocurrent strength (i) remains unchanged but stopping potential (V_0) increases with increase of radiation frequency (ν).

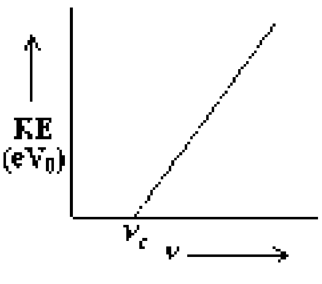


I is fixed but ν is varied

As $\nu''' > \nu'' > \nu'$, $V_0''' > V_0'' > V_0'$.

This concludes that the KE of the emitted electrons (½ mv^2) increases with the increase of radiation frequency and photocurrent strength (i) remains unaffected.

(4) Again if the frequency of radiation is decreased continuously, it is found that photocurrent (i) stops abruptly when the frequency becomes below a certain value (ν_c) for a given metal surface. This particular frequency is called threshold or cut-off frequency below which there is no emission of electrons regardless of intensity of light used. This cut-off frequency is the characteristic property of the metal.



In brief, we may summarize the observations as given below:

(1) The process is instantaneous i.e. there is no time-lag between irradiation and ejection of electrons from the metal plate.

(2) When frequency (ν) of radiation is kept fixed and intensity (I) is increased, photocurrent (i) is also proportionately increased.

(3) When I is kept fixed and ν is increased, stopping potential (V_0) is increased linearly and thus KE of the electrons (½ mv^2) is also increased since KE (½ mv^2) = eV_0.

(4) There is threshold or cut-off frequency (ν_c) below which there is no photoelectric effect of the metal what ever high the intensity light beam is used. This frequency is the characteristic property of the metal used.

Main features of the classical theory of light:

Main contents of the classical theory of light are as follows:

(1) Light beam propagates as wave and the system absorbs energy of the light continuously.

(2) Energy of the light beam depends on its intensity and intensity depends on the amplitude of the light wave.

(3) Energy of the light beam does not depend on its frequency (ν). With increase of frequency, light will be more penetrating due to shorter wave length and it adds to the color of the light beam.

Attractive potential of the electrons in the metal:

Electrons on the surface of the metal are free to move from atom to atom and that gives rise to electrical conductivity to the metal. These electrons, however, can not come out of the metal surface at normal temperature. This is due to the fact that when they try to be ejected outwards, they have (+ve) ions behind which exert enough Coulombic attraction at the surface. Only when the electrons pick up sufficient energy by absorption of light and overcome attractive potential, they come out of the metal surface.

[Similar phenomenon also occurs when the metal is sufficiently heated so that the electrons acquire enough kinetic energy to overcome attractive potential for emission from the metal surface].

Failure of the classical theory to explain the observations:

Classical theory of light fails to explain the observations of photoelectric effect.

Observation (1):

When light beam falls on the metal plate, the electrons on the surface under exposure absorbs energy continuously. It will take time for the electrons to acquire sufficient energy to overcome the Coulombic attractive potential. Thus there should have some time-lag and the process should not be instantaneous.

Observation (2):

With fixed frequency (ν) of light, when intensity (I) is increased, it means that higher energy light beam falls on the electrons. So the KE of the electrons should increase but not the photocurrent (i) strength that depends on the number of electrons ejecting.

Observation (3):

With fixed intensity (I) of light beam, when frequency (ν) is increased, the energy of the light beam is not increased and so KE of the electrons should not increase.

Observation (4):

According to classical theory, there should not exist any threshold or cut-off frequency (ν_c), since even low frequency but high intensity should favour the ejection of electrons from the metal plate under the exposure of light.

Success of quantum theory:

In 1905, Albert Einstein explained the photoelectric effect very nicely on the basis of Planck's quantum theory of light. According to this theory, light is composed of discrete particles, called photons each of having energy $h\nu$. When a photon of energy $h\nu$ is incident on the metal surface, it gives up its entire energy to the electron on the surface. The entire energy of photon is absorbed by the single electron on the metal surface. Einstein suggested that a portion of the absorbed energy is utilized to liberate the electron from the metal plate by overcoming the attractive potential, called work function (ω). This attractive potential depends on the nature of the metal from which the electrons are ejecting. The rest part of the absorbed energy of photon imparts the electron for its KE (½ mv^2). Thus, Einstein's famous photoelectric equation is

$$h\nu = \omega + (1/2)mv^2$$

From the experiment it is seen that when $\nu = \nu_c$, KE = 0, hence $h\nu_c = \omega$ and the equation becomes

$$h\nu = h\nu_c + (1/2)mv^2$$

This equation explains all the characteristics of the photoelectric effect.

Observation (1):

This explains irradiation and ejection of electrons occur instantaneously. The electrons immediately eject as soon as light falls on it.

Observation (2):

According to quantum theory, increase of intensity with no change in frequency increases the number of photons falling per unit time. As more number of photons falls, more number of electrons are ejected from the metal plate per unit time. Thus the photocurrent strength (i) is also increased proportionately.

Observation (3):

When frequency of light is increased with no change of intensity, electrons absorb photons of higher energy and so KE of the ejected electrons are increased, i.e. $\frac{1}{2} mv^2 = h\nu - h\nu_c$. Thus KE of the emitted electrons is linearly increased with frequency of light (ν), so stopping potential (V_0) is also increased.

Observation (4):

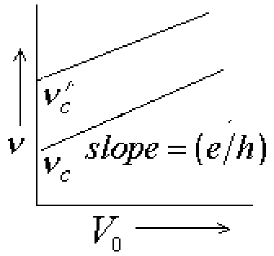
The equation also explains the existence of threshold frequency (ν_c). When $\nu < \nu_c$, there will be no ejection of electrons and no photoelectric effect as the energy of the photon ($h\nu_c$) absorbed by the electron is not sufficient to overcome the attractive potential. Since $\omega = h\nu_c$, so ν_c is a measure of the attractive potential of the metal and it is a characteristic property of the metal surface used.

Experimental verification:

Difficulty in testing the equation is the need to maintain a very clean surface of the metal. Though Einstein's theory of photoelectric effect agrees well with the observations qualitatively, it was R A Millikan in 1916 who made an accurate quantitative test of the equation. Replacing KE ($\frac{1}{2} mv^2$) by eV_0, we have the equation

$$h\nu = h\nu_c + eV_0 \quad \text{or,} \quad \nu = \nu_c + (e/h)V_0 .$$

Millikan used different frequency of light (ν) and determined the stopping potentials (V_0).



When the frequency of light (ν) is plotted against stopping potentials (V_0), a straight line is obtained with intercept equal to the cut-off frequency (ν_c) and slope equal to (e/h). Millikan verified the equation and had shown that different metals used for experiment show different intercepts but identical slope. This is due to the fact that different metals have different cut-off frequencies and hence have the different intercepts. The slopes contain universal constants and hence have same value for all the metals. Millikan also determined the value of Planck's constant (h) from the slope as he already determined the charge of the electron by his famous oil-drop experiment. The value of h, he found equal to 6.625×10^{-27} erg sec.

This proves the correctness of Einstein's photoelectric equation and incidentally gives a decisive evidence in support of the particle nature (atomic nature) of light.

Importance of the effect:

Photoelectric effect is widely used in the construction of photoelectric cell which converts light energy into electric energy. This type of effect is also utilized in photospectrometer to determine the intensity of light.

Work function and Ionization energy:

It is seen that work function (ω) i.e. work or energy required to remove the electron from the surface of a metal is less than the ionization potential (IP) i.e. work or energy required to remove electron from an isolated gaseous atom in its ground state of energy.

In the metal, other electrons on the surface repel the electron to be removed and hence ω is less than IP of the isolated gaseous atom in its lowest energy state.

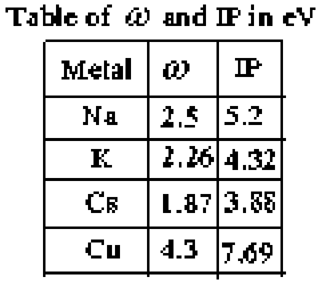


Table of ω and IP in eV

Metal	ω	IP
Na	2.5	5.2
K	2.26	4.32
Cs	1.87	3.88
Cu	4.3	7.69

Problem: The threshold frequency (ν_c) of photoelectric emission for a certain metal is 10^{15} Hz. Calculate the cut-off wavelength and work function. Calculate also KE, velocity and stopping potential when radiation of λ = 1800 Å is incident on the surface.

Answer: λ_c **= 3000 Å,** ω **= 4.13 eV, KE = 2.78 eV,** ν **= 9.6 × 10^7 cm/sec, V_0 = 2.78 V.**

Problem: Light of frequency ν is found to eject electrons of velocity v_e from a clean potassium surface in vacuum. Which of the following is true concerning the phenomenon?

(A) The frequency ν is most likely in the infrared region.
(B) This phenomenon is best explained theoretically by using the wave model of light.
(C) The minimum energy required to remove the electron from the metal is $h\nu -$ ½ mv^2
(D) Light of frequency 2ν will eject electrons of velocity $2v_e$.
(E) A more intense light source of frequency ν will eject electrons with a velocity greater than v_e.

Answer: (C) **[GRE sample question]**

Problem: When Li is irradiated with light, the KE of the ejected electrons is 2.935×10^{-19} J for λ = 300.0 nm and 1.280×10^{-19} J for λ = 400.0 nm. Calculate (a) Planck's constant (b) the threshold frequency and (c) work function of Li.

Answer : (a) $h = 6.625\times10^{34}$ J s **(b)** $\nu_c = 5.564\times10^{14}$ Hz **(c)** ω = 3.7×10^{-19} J.

Action small and action large

A dynamic particle may have several variables associated with its motion. Such variables are position, momentum, angular momentum, azimuthal angle (for rotating system), energy, time, etc. When the product of two such variables has the dimension of Planck constant (h), the pair of variables are called conjugate variables, or canonically conjugate variables. These pair of variables are intricately related to each other. Such pair of variables are linear momentum and position, angular momentum (p_φ) and azimuthal angle (φ), energy (ε) and time (t).

The product of the two canonically conjugate variables is called 'action' (or characteristic action of the dynamic particle, Jc). The Planck's constant (h) is called 'action constant'. When Jc is much larger than h ($i.e\ Jc >> h$), it is called 'action-large' and when $Jc \approx h$, it is called 'action small'. Jc or h has the dimension, ML^2T^{-1}. Motion of electron in the atomic or molecular system exerts 'action-small' while motion of a macroscopic body is 'action-large'. Quantum mechanics could be used to explain or interpret the motion of action-small while classical mechanics is sufficient to interpret the motion relating to 'action-large'.

When a particle is executing periodic motion i.e. when any one or both of the conjugate variables will be repeating after certain fixed time or distance interval, the characteristic action integrated over one period of motion is called action integral or phase integral. It is denoted by $\oint J_C$.

These are $\oint p_x\,dx$, $\oint p_\varphi d\varphi$ and $\oint E\,dt$.

Wilson - Sommerfeld Quantization rule:

In 1915, W. Wilson and A. Sommerfeld proposed a general rule independently to predict the energy values of stationary states of a periodic system.

The rule states that $\oint p_k dq_k = n_k h$, where q_k is the variable along the k th degree of freedom which is repeating after a fixed time or distance interval and p_k is its conjugate variable along that degree of motion.
n_k = quantum number along this degree of motion = 0, 1, 2, 3, etc i.e., any positive integer including zero.
It is stated in detail as

"For system executing periodic motion, the phase integral of the conjugated pair of variables in each degree of freedom will be integral multiple of Planck's constant i.e. $\oint p_k dq_k = n_k h$. p_k and q_k are some periodic functions of time, or any case p_k remains constant, q_k will have the periodicity but not necessarily with respect to time.

When an election is moving in an elliptical path keeping the nucleus at any of foci of H-atom then according to the Sommerfeld model, both distance (r) of the electron from the nucleus and azimuthal angle (φ) vary periodically with time and so,

$$\oint p_r dr = n_r h \quad \text{and} \quad \oint p_\varphi d\varphi = n_\varphi h,$$

where n_r = radial quantum number and n_φ = azimuthal quantum number.

Applications:

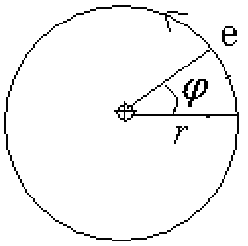
This quantization rule is used to predict the expression of the discrete values of certain properties of the dynamic particles executing periodic motion. Such cases may happen to Bohr model of electron-motion in H-atom, the rigid free-axis rotation, particle in one-dimensional box, simple harmonic oscillation, etc.

(1) Bohr H-atom:

According to Bohr's concept of H-atom, electron is rotating in a circular path with nucleus at the centre. Radial distance (r) remains constant while azimuthal angle (φ) varies periodically with range 0 to 2π.

The conjugate variable of azimuthal angle is angular momentum (p_φ) which remains constant for the motion. Thus, Wilson- Sommerfeld quantization rule for the motion of electron is

$$\oint p_\varphi d\varphi = nh \text{ or, } p_\varphi \int_0^{2\pi} d\varphi = nh \quad \text{or,} \quad p_\varphi = nh/2\pi.$$



This is one most important postulate of Bohr for H-atom. It means that angular momentum of the election in H-atom takes only certain discrete values and it does not change continuously. It will be $h/2\pi$, $2h/2\pi$, $3h/2\pi$, etc, but no value between $h/2\pi$ and $2h/2\pi$ or $2h/2\pi$ and $3h/2\pi$

This quantum condition of p_φ leads to the expression of discrete energy values of H-atom. The velocity (v) and radius (r) of the circular orbits also take certain discrete values.

But $p_\varphi = mvr$, so $mvr = nh/2\pi$ so, $v = nh/2\pi mr$ or, $v^2 = n^2h^2/4\pi^2m^2r^2$.

Again when the election moves, the centrifugal force $\left(mv^2/r\right)$ balances the centripetal force $\left(Ze^2/r^2\right)$ of the election, and so $mv^2/r = Ze^2/r^2$ or, $v^2 = Ze^2/mr$. Equating v^2, we have $r = n^2h^2/4\pi^2mZe^2$. Putting the value of r in the expression of v, we get $v = nh/\left[2\pi m\left(n^2h^2/4\pi^2mZe^2\right)\right]$ or, $v = \frac{2\pi Ze^2}{nh}$.

Thus, both r and v are quantized, certain discreet circular paths are allowed. The total energy of the electron in H-atom, $E = KE + PE$. $KE = \frac{1}{2}mv^2$ but $\frac{mv^2}{r} = \frac{Ze^2}{r^2}$ so, $mv^2 = \frac{Ze^2}{r}$ and $KE = \frac{Ze^2}{2r}$.

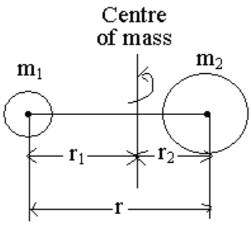
The PE $= -\int_\infty^r \left(-\frac{Ze^2}{r^2}\right)dr = Ze^2\int_\infty^r \frac{dr}{r^2} = Ze^2\left[-\frac{1}{r}\right]_\infty^r = -Ze^2/r$. Putting the expression of KE and PE, we get

$$E = \frac{Ze^2}{2r} - \frac{Ze^2}{r} = -\frac{Ze^2}{2r} \quad \text{but } r = \frac{n^2h^2}{4\pi^2mZe^2} \quad \text{hence, } E_n = -\frac{2\pi^2mZ^2e^4}{n^2h^2}$$

For H-atom, Z =1 and m is replaced by reduced mass of H-atom μ, where $\mu = \frac{m_n m_e}{m_n + m_e}$ which is very close to m_e. Thus it is seen that the energy of H-atom is quantized and it takes certain discreet values. ($-$ve) sign of the energy signifies that the electron is bound within the atom and energy is required to remove electron from the atom.

(2) Rigid rotator

A rigid rotator is a dumb-bell shaped body in which two spheres are connected by rod of very thin breadth. The system rotates about an axis passing through the centre of mass and perpendicular to the line joining the two masses m_1 and m_2. Axis of rotation is assumed to be free, i.e. it may attain any rotation in space.



The moment of inertia of the rigid rotator, $I = m_1r_1^2 + m_2r_2^2$ but according to the figure, $m_1r_1 = m_2r_2$ (condition of centre of mass) or, $m_1r_1 + m_2r_1 = m_2r_1 + m_2r_2$ or, $r_1(m_1+m_2) = m_2(r_1+r_2) = m_2r$ so, $r_1 = \frac{m_2}{m_1+m_2}.r$. Similarly, $r_2 = \frac{m_1}{m_1+m_2}r$.

Putting this values of r_1 and r_2 in I, we get,

$I = m_1\left(\frac{m_2}{m_1+m_2}r\right)^2 + m_2\left(\frac{m_1}{m_1+m_2}r\right)^2 = \frac{m_1m_2}{m_1+m_2}r^2 = \mu r^2$, where $\mu = \frac{m_1m_2}{m_1+m_2}$, called reduced mass of the rotator. The reduced mass of the system is not the total mass of the system; it measures the contribution of rotating ability of the spheres.

Let $m_2 \gg m_1$ then $\mu \approx \frac{m_1m_2}{m_2} \approx m_1$, it is more close to the smaller mass of the sphere. It means that lighter body contributes mainly to the rotational process i.e. lighter body moving and heavier body remains almost stationary. If $m_1 = m_2 = m$, then $\mu = m/2$ i.e. both spheres contribute equally to the process of rotation.

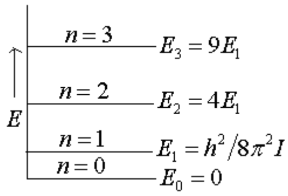
For this system, the angle of rotation (φ) changes periodically within the range $0\ to\ 2\pi$. The conjugate variable corresponding to φ is p_φ which remains constant during the rotation.

The Wilson-Sommerfeld quantization rule for the system is, $\oint p_\varphi\, d\varphi = nh$ or, $\int_0^{2\pi} p_\varphi d\varphi = nh$

or, $p_\varphi \int_0^{2\pi} d\varphi = nh$ or, $p_\varphi = n\left(\frac{h}{2\pi}\right)$. The angular momentum is thus quantized.

The energy of the rotator, E = KE + PE but for this rigid rotator, PE = 0 as no force is acting on the system. Thus, E = KE = ½ μv^2 but, $v = \omega r$, where ω is angular velocity. Thus, $E = \tfrac{1}{2}\mu\omega^2r^2 = \tfrac{1}{2}\left(\mu r^2\right)\omega^2$

or, E = $\frac{1}{2}I\omega^2 = {(I\omega)^2}/{2I}$, but $I\omega = p_\varphi$ thus, $E = {p_\varphi^2}/{2I}$.



Putting the expression, $p_\varphi = n\left(\frac{h}{2\pi}\right)$, we have energy of the rotator, $E = \frac{n^2h^2}{8\pi^2 I}$.

This system is analogous to the rotation of diatomic molecule and the connecting thin rod is compared to the chemical bond binding the two atoms in the molecule.

However, energy of the rotator can be formulated in another way by using the quantum condition of p_φ.

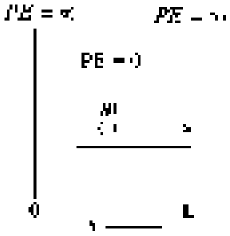
$$E = KE = \frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2 = \frac{1}{2}m_1\left(\omega r_1\right)^2 + \frac{1}{2}m_2\left(\omega r_2\right)^2 = \frac{1}{2}\omega^2\left(m_1r_1^2 + m_2r_2^2\right) = \frac{1}{2}I\omega^2 = \frac{(I\omega)^2}{2I} = \frac{p_\varphi^2}{2I},$$

but $p_\varphi = n\left(\frac{h}{2\pi}\right)$. Thus putting the value of p_φ, we have energy of the rotator, $E = \frac{n^2h^2}{8\pi^2 I}$.

Problem: The bond length for H ^{19}F is 91.68 ×10^{-12} m. Where does the axis of rotation intersect the molecular axis? **[Ans. 87.096 ×10^{-12} m away from H-atom]** **[Burdwan Univ. 2015]**

(3) Particle in one-dimensional box

Let us consider a particle of mass m which is constrained to move in one dimensional rectangular box of length L. It is assumed that no force is acting on the particle except during collision at the wall it rebounds elastically.



The position (x) of the particle is periodically within the length 0 to 2L.

The conjugate variable of x is x- component linear momentum$\left(p_x\right)$.

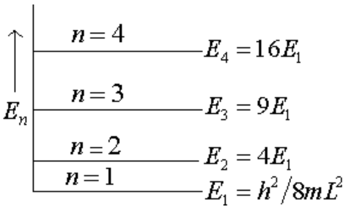
The Wilson-Summerfield quantization rule when applied to the system becomes

$\int_0^{2L} p_x dx = nh$ but p_x remains constant since velocity of the particle remains constant as no force is acting on it, thus, $p_x \int_0^{2L} dx = nh$ or, $p_x \times 2L = nh$ or, $p_x = {nh}/{2L}$,

where n = 1, 2, 3, etc excluding zero.

This states that certain x- component momentum values are allowed for the particle executing periodic motion in a box. The energy of the particle, E = KE + PE but PE = 0. (As no force is acting on the system).

so, $E = \frac{1}{2} m v_x^2 = \frac{(m v_x)^2}{2m} = \frac{p_x^2}{2m} = \frac{(nh/2L)^2}{2m}$ or, $E_n = \frac{n^2 h^2}{8mL^2}$.



This shows that the total energy of the particle is quantized and it takes certain discrete values only, though in classical theory it is assumed that energy of the system changes continuously.

This energy difference between two successive energy levels (i.e. $n \to n+1$) is

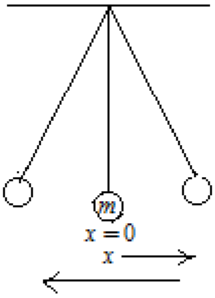
$$\Delta E = E_{n+1} - E_n = (n+1)^2 \frac{h^2}{8mL^2} - \frac{n^2 h^2}{8mL^2} \quad \text{or,} \quad \Delta E = \frac{(2n+1)h^2}{8mL^2}.$$

This shows that for macroscopic body of large mass (m), $\Delta E \to 0$ and energy then changes continuously. Conjugated polyenes could be viewed as one dimensional box in which π- electrons are moving to and fro motions periodically within the chain length L. For example, in $CH_2 = CH - CH = CH_2$, L = end to end chain length of the molecule. m = mass of the electron.

(4) Simple harmonic Oscillator:

One dimensional oscillation is viewed as a particle of mass m oscillating along x- axis through an equilibrium position $(x = 0)$ with restoring force F_x.

For simple harmonic oscillator, this restoring force F_x is proportional to the displacement (x) from the mean position i.e. $F_x \propto x$ or, $F_x = -k\,x$, where k is restoring force constant, ($-$) sign is added to indicate that restoring force is acting in opposition to the displacement of the particle.

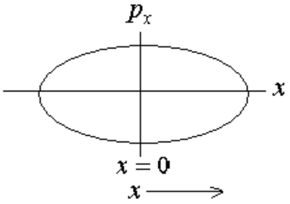


The potential energy $(PE) = -\int_0^x F_x dx = -\int_0^x (-kx) dx$ or, $(PE) = \frac{1}{2} kx^2$.

This indicates that the PE follows parabolic curve with x. Wilson-Sommerfeld quantization rule can be applied to the motion of simple harmonic oscillator (SHO) as $\oint p_x dx = nh$, where n = 0, 1, 2, 3, etc.

In this system both x and p_x are varying with time. p_x is maximum, when x = 0 and p_x = 0 when x is maximum. The value of the phase integral $\oint p_x \, dx$ can be obtained by graphical method or by direct integration.

(a) Graphical method: The energy of the system, E = KE + PE = $= \frac{p_x^2}{2m} + \frac{1}{2} kx^2$ or, $\frac{x^2}{(2E/k)} + \frac{p_x^2}{2mE} = 1$.

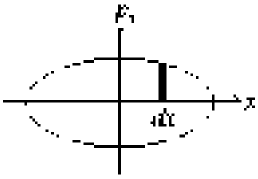


This is an equation of ellipse with coordinate axes, x and p_x.

The semi major axis (a), = $\sqrt{(2E/k)}$ and semi minor axis $(b) = \sqrt{2mE}$.

The displacement (x) and the momentum (p_x) of the oscillator at any instant are represented by the coordinates of a particular point on this ellipse. During one complete oscillation, the above point describes a complete cycle on the ellipse in the phase plane. It should be noted that the ellipse, we are talking about, does not represent the orbit of any real particle. The positions of the different points on the ellipse are the pictorial representation of the mathematical relationship between the position (x) and momentum (p_x) of the oscillator at different instant of time. That is, the points are the phase path for the linear oscillator.

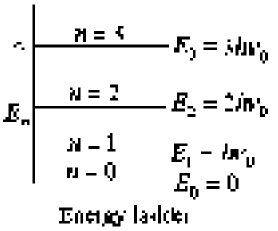
The area of the ellipse $= \pi ab = \pi \times \sqrt{\frac{2E}{k}} \times \sqrt{2mE} = 2\pi E \sqrt{\frac{m}{k}}$ or, $E \Big/ \left(\frac{1}{2\pi} \sqrt{\frac{k}{m}} \right) = \frac{E}{\nu_0}$, since $\frac{1}{2\pi}\sqrt{\frac{k}{m}}$ is ν_0, the frequency of the oscillator.

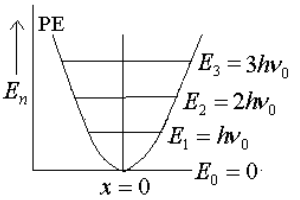


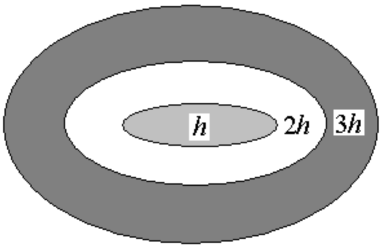
Again, the area of the stripe in the phase diagram = $p_x\, dx$ and is called unit action. When the oscillator completes one motion, the stripe covers the whole ellipse. Thus the total area of the ellipse can also be represented as $\oint p_x\, dx$, thus $\oint p_x\, dx = E/\nu_0$ by comparing the area of the ellipse in both the cases.

But Wilson-Sommerfeld quantization rule states that $\oint p_x dx = nh$.

So, $E/\nu_0 = nh$ or, $E_n = nh\nu_0$







The energy of SHO is quantized and the energy levels are equispaced. This is also called energy ladder. Quantum condition also asserts that the phase path of the harmonic oscillator can only be discrete set of ellipses which encloses the areas h, 2h, 3h, etc. The ellipse in between the two is not allowed.

(b) Mathematical method (Direct integration): The quantum condition for the system is $\oint p_x dx = nh$.

We have total energy, $E = KE + PE = p_x^2/2m + \frac{1}{2}kx^2$. At the two extreme points of the displacement (x_e), $E = PE = \frac{1}{2}kx_e^2$ since at these points, $KE = 0$ or, $x_e = \sqrt{2E/k}$. Thus the displacement of SHO ranges from $-x_e$ to $+x_e$ and so from $-\sqrt{2E/k}$ to $+\sqrt{2E/k}$ in one direction of the motion. The action integral for one complete motion of the oscillator is $2\int_{-\sqrt{2E/k}}^{+\sqrt{2E/k}} p_x\, dx = nh$.

But $E = p_x^2/2m + \frac{1}{2}kx^2$ so, $p_x = \sqrt{\left(E - \frac{1}{2}kx^2\right)2m}$. Putting the value in action integral, we get

$2\int_{-\sqrt{2E/k}}^{+\sqrt{2E/k}} \sqrt{2m\left(E - \frac{1}{2}kx^2\right)}\, dx = nh$. The integration, $I = 2 \times 2 \int_{0}^{+\sqrt{2E/k}} \sqrt{2m\left(E - \frac{1}{2}kx^2\right)}\, dx$,

[Since $F(x) = F(-x)$ so $F(x)$ = even function and hence $\int_{-a}^{+a} F(x)\, dx = 2 \times \int_{0}^{+a} F(x)\, dx$.]

Now the integration, $I = 4\sqrt{2m} \int_{0}^{+\sqrt{2E/k}} \sqrt{\left(E - \frac{1}{2}kx^2\right)}\, dx = 4\sqrt{2m} \times \sqrt{\frac{k}{2}} \int_{0}^{+\sqrt{2E/k}} \sqrt{\left(\frac{2E}{k} - x^2\right)}\, dx$

$$= 4\sqrt{mk} \int_{0}^{+\sqrt{2E/k}} \sqrt{\left(\frac{2E}{k} - x^2\right)}\, dx .$$

[Using standard integral rule of by parts, we get $\int\sqrt{a^2-x^2}\;dx=\frac{x}{2}\sqrt{a^2-x^2}+\frac{a^2}{2}\sin^{-1}\left(\frac{x}{a}\right)+C$].

Applying it in the integration, we get

$$I=4\sqrt{mk}\left[\frac{x}{2}\sqrt{\left(\frac{2E}{k}-x^2\right)}+\frac{2E}{2k}\sin^{-1}\left(\frac{x}{\sqrt{2E/k}}\right)\right]_0^{\sqrt{2E/k}}=4\sqrt{mk}\left[0+\frac{E}{k}\sin^{-1}1\right]=4\sqrt{mk}\times\frac{E}{k}\times\frac{\pi}{2}$$

$= 2\pi E\sqrt{m/k}$. Quantization rule states, $2\pi E\sqrt{m/k}=nh$ or, $E=nh\times\frac{1}{2\pi}\sqrt{k/m}$.

But, $\frac{1}{2\pi}\sqrt{k/m} = \nu_0$, the frequency of the oscillator. Thus the energy of the oscillator, $E=nh\nu_0$.

(3) Another method using energy-time conjugate variables:

The oscillator comes to a definite position after certain time interval (τ_0 , time period), where the frequency, $\nu_0=1/\tau_0$. So, the phase integral involving energy and time variables is $\oint Edt=nh$.

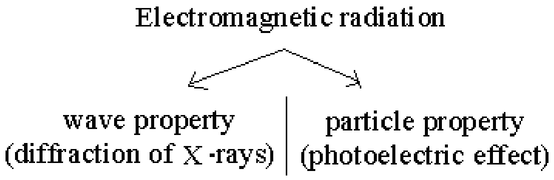
Time of the SHO ranges from 0 to τ_0 (time period). Thus, action integral, $\int_0^{\tau} Edt=nh$.

But E remains constant during the oscillation, so $E\int_0^{T} dt=nh$ or, $E=nh/\tau_0$ or, $E=nh\nu_0$.

Wave-Particle Duality

Wave aspect and particle aspect of radiation:

With the development of various experiments, it is conclusively proved that electromagnetic radiation has both wave aspects and particle aspects. Interference and diffraction of X-rays in Bragg experiment proves the wave nature while photoelectric effect, black body radiation can only be explained by the particle nature of radiation.



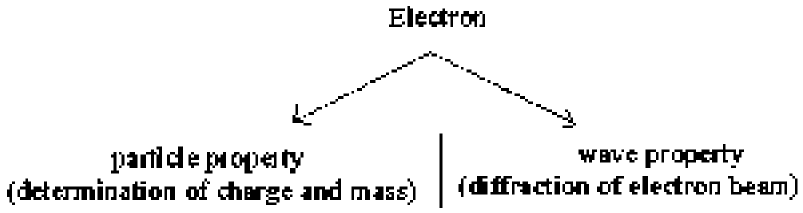
Thus light seems to exhibit dual nature behaving like waves in some situations and particle in other situations. Particles are localized in space while waves spread over space. These two aspects are contradictory. However, This condition is hidden in Planck's theory itself.

In Planck's equation $\varepsilon_{photon} = h\nu = hc/\lambda$, the quantity ε_{photon} is a particle concept but the wave length (λ) is a wave concept. So the equation itself shows dual behaviour of light.

Particle aspect and wave aspect of electron:

Microscopic particles also behave a particle and wave both. For example, particle character of a sub-atomic particle like electron is evidenced by the experiment of charge determination of electron by Millikan and (e/m) of electron in Thomson experiment. The mass and momentum are the characteristics of the particle nature of electron.

Davission and Germer in 1927 showed the wave nature of electron by their famous electron diffraction experiment. A beam of electrons are made to impinge upon a Ni-crystal and diffraction maximum is obtained. They also were able to determine the wavelength (λ) of the electron-beam.



This shows a break-down of particle character in the micro world.

De – Broglie Relation:

In 1924, de-Broglie combined the wave aspect and particle aspect of light and formulated an important relation between the two conflicting aspects.

He utilized Planck's quantum theory and Einstein's theory of relativity. The energy of the smallest unit of light, called photon is given by Planck's theory as

$$\varepsilon_{photon} = h\nu \text{ , but } \nu = c/\lambda \text{, so } \varepsilon_{photon} = hc/\lambda .$$

Again, when mass of the photon is converted into energy according to Einstein's theory of relativity

$$\varepsilon_{photon} = mc^2 .$$

Combining the two relations, we have $\frac{hc}{\lambda} = mc^2$ or, $\lambda = \frac{h}{mc}$ but, mc = momentum of the photon (p).

So, $$\lambda = \frac{h}{p} .$$

This is the famous de-Broglie relation that connects the wave nature (λ) and particle nature (p) of light.

De-Broglie extended the relation for matter wave also. He suggested that every particle in motion is also associated with wave, like photon. Thus de-Broglie made a hypothesis that for sub-atomic particles in motion, the relation $\lambda = \frac{h}{p}$ also holds, where λ = wave length associated with the particle of momentum p.

It is obvious that wave character (λ) and particle character (p) are inversely related. If in a phenomenon, particle character becomes prominent, then wave character remains subdued. De-Broglie concept does not mean that matter behaves like particle at one time and wave at another time in the same experiment. Rather, wave nature is an inherent property of each dynamic particle. If in an experiment, the particle character is revealed then wave character remains concealed. Both aspects do not appear simultaneously in any one experiment. This aspects are complimentary to each other and mutually exclusive.

This relation also shows that for macroscopic bodies, p is large and so λ is so small that wave character becomes negligible. Only for sub-atomic particles like electron, proton, etc. wave character becomes important as p is small.

Davisson and Germer electron diffraction experiment:

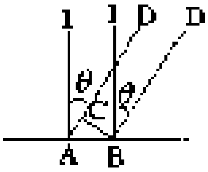
Davisson and Germer verified the relation in 1927 by their famous electron diffraction experiment. They used Ni crystal as diffraction grating for mono energetic electron beam. The surface of the crystal contains parallel rows of atoms with spacing of 2.15Å. Waves falling on the surface gets diffracted at an angle θ, the angle between the direction of incident and diffracted beam.

In the figure, I and D are the incident and diffracted beams.

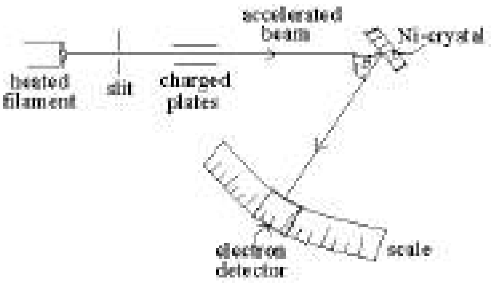
AC = the path difference between the diffracted beams

AB cos (90 – θ) = AB sin θ = d sin θ = $n\lambda$ for constructive interference.

Thus, d sin θ = $n\lambda$ is analogous to Bragg's relation of X-rays of light.



Experimental set-up:



Davisson and Germer found that diffraction of electron beam occurred at θ = 50° and 55° for electrons when accelerated by 54 volts and 181 volts respectively.

The wave length (λ) of the electron beam when accelerated by 54 volts is predicted by de-Broglie relation as

$$\lambda = \frac{h}{p}, \text{ but } \frac{1}{2}mv^2 = \frac{p^2}{2m} = eV \quad \text{or, } p^2 = 2meV$$

$$\text{or, } \quad p = \sqrt{2meV}\text{ . Thus, } \lambda = \frac{h}{\sqrt{2meV}}.$$

Putting the values, we get $\lambda = \frac{6.625\times10^{-34}\,Js}{\sqrt{2\times9.1\times10^{-31}kg\times1.6\times10^{-19}C\times54V}} = 1.67\times10^{-10}m$ = 1.67Å.

The experimental value of λ from Davisson and Germer experiment is calculated as given below:

$n\lambda = d\sin\theta$, but n = 1 when θ = 50°, d = 2.15 Å.

So, $\lambda = 2.15\text{Å} \times \sin 50°$ or, λ = 1.65 Å.

Thus de Broglie prediction of λ = 1.67 Å is in good agreement with the experimental value of λ = 1.65 Å.

Comparison between photon and electron:

In the relation $\varepsilon_{photon} = mc^2$, m is the relativistic mass of the photon. A photon has a zero rest mass, but photons always move at speed c in vacuum and are never at rest. At speed c, the photon has non-zero mass.

Similar to photon, an electron is neither a particle nor a wave. It is something that can not be adequately described in terms of a suitable model.

The significant differences between light and electrons can be made though they both show wave-particle duality. Light travels at a speed c in vacuum and photon has zero-rest mass. Electrons always travel at speed less than c and have always a non-zero rest mass.

Application of de Broglie Relation

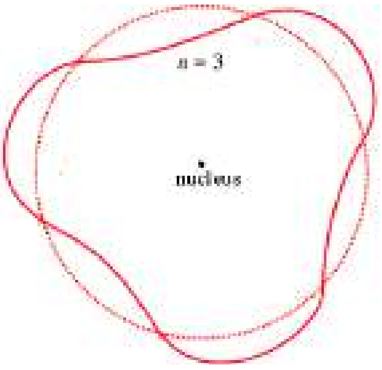
Introduction: Imposition of wave character in the moving particle brings out the quantum condition of the system. We can cite by two examples given below.

(1) Quantization of Bohr H-Atom:

De Broglie relation is, $\lambda = \frac{h}{p} = \frac{h}{mv}$ suggests that waves are associated with the electron moving in H-atom.

The wave in the stationary Bohr orbit forms standing wave whose position of maxima and minima do not change with time. A stationary wave produces a stationary pattern, its profile being fixed within the space allowed to it and it does not travel beyond the allowed space.

Thus to form standing wave, the circumference of the Bohr circular orbit ($2\pi r$) must accommodate the integral multiple of wave length ($n\lambda$) i.e. $2\pi r = n\lambda$.



The wave length (λ) associated with the moving electron in the Bohr orbit is equated with h/mv.

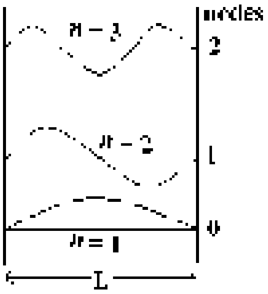
Thus, $2\pi r = n\left(\frac{h}{mv}\right)$ or, $mvr = n\left(\frac{h}{2\pi}\right)$.

de Broglie relation thus imposes quantum condition of the angular momentum (mvr) for the electron moving in Bohr orbit of H-atom.

Using the above relation, $mvr = n\left(h/2\pi\right)$, it is possible to derive the quantized value of energy of Bohr H-atom.

$$E_n = \frac{1}{n^2}\left(-\frac{2\pi^2 \mu e^4}{h^2}\right)$$, where μ = reduced mass of H-atom = $\frac{m_n m_e}{m_n + m_e}$.

(2) Quantization of Energy of a Particle in a Box



When a particle is executing to-and-fro-motion in one dimensional box, it produces standing waves.

The nodes must be at the two sides of the box and distance between the walls must be integral multiple of half wave length $\left(\lambda/2\right)$. Standing wave produces stationary energy state of the system.

Thus, $L = n\left(\lambda/2\right)$ or, $2L = n\lambda$. But de Broglie relation gives $\lambda = h/p_x$.

Putting, we get $2L = nh/p_x$ or, $p_x = n\left(h/2L\right)$.

That is x- component linear momentum of the particle in the box is quantized. The total energy of the particle in the box is, $E = KE + PE$, but for this system, PE = 0, so $E = KE = \left(p_x^2/2m\right)$. Now putting the quantum condition of p_x, we have the total energy of the particle in the box, $E_n = \frac{\left(nh/2L\right)^2}{2m}$ or, $E_n = \left(n^2\right)\frac{h^2}{8mL^2}$.

This shows that energy of the particle in the box takes discrete values only.

The number of nodes where the amplitude of the wave is zero (except the two ends of the box) = $n-1$.

Heisenberg Uncertainty (Indeterminacy) Principle

Principle:

The principle states that it is not possible to design an experiment with the help of which one can determine simultaneously the precise values of a pair of conjugate variables like position and momentum, angular momentum and azimuthal angle, energy and time, etc.

Mathematical form of the principle:

The uncertainty in position (Δx) and uncertainty in momentum (Δp_x) is given by the principle

$\Delta x \times \Delta p_x \geq (1/2)\hbar$, where $\hbar = h/4\pi$, called reduced Planck's constant.

Approximately, we can write $\Delta x \times \Delta p_x \approx h$ (Plank's constant).

Other conjugate variables follow $\Delta p_\varphi \times \Delta \varphi \approx h$ and $\Delta \varepsilon \times \Delta t \approx h$.

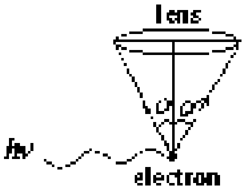
In general, the principle is $\Delta p \times \Delta q = (1/2)\hbar$, where p and q are conjugate variables in the same direction in space. Momentum (p) parallel to x and position (q) along x are complimentary and therefore can not be specified simultaneously with precision greater than allowed by the principle.

Critical comment:

However, the value of any one conjugate quantity can be determined accurately at any time though simultaneous determination of two conjugate quantities induces inaccuracy with the limit given by the principle.

Momentum perpendicular to x and position along x are not conjugate variables and for this, the principle does not hold i.e. $\Delta p_y \times \Delta x = 0$.

Approximate formulation and illustration of the principle



This principle can be approximately formulated as given below:
Let the position of the electron is detected by a microscope using light of wavelength λ. The position of the electron remains uncertain within the length λ (approximately) i.e. $\Delta x = \lambda$.
Again, when the photon of the light strikes the electron it can impart momentum
The momentum of the electron remains uncertain within the limit p_x i.e. $\Delta p_x \approx p \approx h/\lambda$ (According to de Broglie relation).
Thus the product of the uncertainty of position (Δx) and momentum (Δp_x) of the electron is

$$\Delta p_x \times \Delta x \approx \left(h/\lambda\right) \times (\lambda) \approx h.$$

This is the lowest value of the uncertainty of momentum and position. If one tries to reduce the uncertainty in position (Δx) to a negligible extent, then the principle suggests to use short λ value of light. This improves the position measurement i.e. Δx will be small but the electron recoil effect will induce large uncertainty in momentum ($\Delta p_x \approx p \approx h/\lambda$) in the measurement.

Breaking of Newtonian mechanics:

The principle breaks the Newtonian mechanics in which both position and velocity (hence momentum) can be determined very accurately and simultaneously for macro objects. Due to association of wave aspect in micro particles, Newtonian mechanics fails and uncertainty develops.

The principle does not arise due to imperfection of the experimental technique but it is the result of the interaction of the system with the measuring instrument. This uncertainty is thus a fundamental limit of nature.

Micro particles have no definite trajectory and rejection of Bohr orbit):

Since microscopic particles have no definite position and momentum, we can not draw any definite trajectory of a micro particle. Thus the principle at once invalidates Bohr-Sommerfeld theory. Since in this theory, electrons are assigned to definite orbits (tracks) with precise velocity (and hence momentum) and position. This rejection of Bohr model of having a definite trajectory (orbit) can be explained as follows:

Let the electron moving in Bohr orbit in H-atom with velocity, $v = 2\times10^{8}\,cm/\sec$ and momentum, $p = mv = 9.1\times10^{-28}\,gm\times 2\times10^{8}\,cm/\sec = 1.81\times10^{-19}\,gm\,cm/\sec$. Even we can determine momentum with error within 0.1 % (0.001), then $\Delta p = 1.81\times10^{-19}\,gm\,cm/\sec\times 0.001 = 1.81\times10^{-22}\,gm\,cm/\sec$.
Thus uncertainty in position according to the principle,

$$\Delta r \approx \frac{h}{\Delta p} \quad \text{or,} \quad \Delta r = \frac{6.626\times10^{-27}\,erg\sec}{1.81\times10^{-22}\,gm\,cm/\sec} = 3.66\times10^{-5}\,cm = 3660\,\text{Å}.$$

While the radius of the first Bohr orbit is 0.5Å, the uncertainty in radius lies 3660Å. That is, it seems that it is not even known at a given instant whether the electron is within the atom or not.
The principle thus demonstrates the inadequacy of the Bohr orbit.

Energy time uncertainty and unstable state:

For energy-time uncertainty, the principle states that $\Delta\varepsilon\times\Delta t \geq \frac{h}{4\pi}$, where Δt should not be regarded as the uncertainty in the measurement of time, rather it should be treated as the duration of the measurement or life period. If Δt is very large, $\Delta\varepsilon$ will be very small which means that the energy is determined with great accuracy. That is, if the energy of a system in a given state has a precise value, the life-time of the system in that state is infinite and we can say that the system is in a stationary state.
This is in agreement with Bohr's concept of discrete energy levels associated with stationary (infinitely long-lived) states.

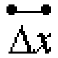
For unstable system (for dissociating molecule or atoms in excited state) whose life-time is short say, Δt, the energy levels are imprecisely defined at the extent $h/\Delta t$.

Uncertainty of the conjugate variables is their RMS deviation:

In the principle, $\Delta p_x\times\Delta x \geq \frac{h}{4\pi}$, $\Delta p_x = \sqrt{\left(\langle p_x^2\rangle - \langle p_x\rangle^2\right)}$ and $\Delta x = \sqrt{\left(\langle x^2\rangle - \langle x\rangle^2\right)}$ and so Δp_x and Δx are root-mean-square deviation of momentum, p_x and position, x of a micro particle respectively.

Simple view of the uncertainty principle:

If two spots are viewed under a microscope (given in the sketch), there is limitation on the proximity of two spots in order that these two can be detected as distinct spots. The physical principle of distance restriction is $\Delta x \geq \lambda/\sin\alpha$ or, $\Delta x \geq \lambda$ (approximately). The photon of wave length λ has momentum h/λ.



Assuming that this momentum of photon is transferred to the electron which is then having momentum uncertainty $\Delta p \approx h/\lambda$ and hence the principle is thus $\Delta p_x\times\Delta x \approx h$.

Problem: Making use of the expression, $\Delta p_x\times\Delta x \geq \frac{h}{4\pi}$, show that for a free particle $\Delta\varepsilon\times\Delta t \geq \frac{h}{4\pi}$, where $\Delta\varepsilon$ and Δt are the minimum uncertainty in energy and duration of measurement of energy and duration of measurement of velocity, respectively.

Solution: For free particle, PE = 0, so $\varepsilon = KE = p_x^2/2m$ or, $\Delta\varepsilon = \left(\frac{2p_x}{2m}\right)\Delta p_x$ or, $\Delta p_x = \left(\frac{2m}{2p_x}\right)\Delta\varepsilon$.

Again, $p_x = mv_x = m\frac{\Delta x}{\Delta t}$ or, $\Delta x = \frac{p_x}{m}\times\Delta t$. It is given that $\Delta p_x\times\Delta x \geq \frac{h}{4\pi}$,

now putting the above, we get $\left(\frac{2m}{2p_x}\times\Delta\varepsilon\right)\times\left(\frac{p_x}{m}\times\Delta t\right) \geq \frac{h}{4\pi}$ or, $\Delta\varepsilon\times\Delta t \geq \frac{h}{4\pi}$.

Bohr's correspondence principle:

Theory of micro particles is in some sense finer than those of macro particles. But in some situations, however, it is possible that some behavior in microscopic domain resembles the classical interpretation. Thus, one finds a correspondence between classical and quantum results. Bohr's principle refers to the $n \to \infty$ is the limit to bridge the results. The principle thus states that quantum results of an event must go over to classical results when the quantum number describing the system becomes very large, i.e. when $n \to \infty$ both theories merge. This is Bohr's correspondence principle.

(1) Bohr's correspondence principle and Bohr H-atom:

Let us take the Bohr's H-atom, whose energy of the nth state, $E_n = -\frac{2\pi^2 me^4}{n^2h^2} = -\frac{A}{n^2}$, where $A = \frac{2\pi^2 me^4}{h^2}$.

Thus, $\Delta E = E_{n+1} - E_n = -\frac{A}{(n+1)^2} + \frac{A}{n^2} = A\left[\frac{1}{n^2} - \frac{1}{(n+1)^2}\right]$ or, $\Delta E = A\left[\frac{2n+1}{n^2(n+1)^2}\right]$

This is energy difference between the two successive energy-levels.

But when $n \to \infty$, $2n+1 \approx 2n$ and $n+1 \approx n$, $\Delta E = \frac{2nA}{n^2 \times n^2}$ or, $\Delta E = \frac{2A}{n^3}$.

Thus for the transition of the atom from n to $n+1$ energy state, it absorbs one photon of energy $h\nu$.

Thus $h\nu = \Delta E = \frac{2A}{n^3}$ or, $\nu = \frac{2A}{n^3h}$. So the frequency of radiation absorbed by H-atom is predicted by quantum calculation. This frequency of radiation is called perturbation frequency as it disturbs the equilibrium of H-atom by promoting the energy state from n to n +1.

But classical theory states that resonance absorption or emission of radiation would occur only when the perturbation frequency matches the system frequency. In this example, the system frequency is the frequency of the electron with which it is revolving round the nucleus of the H-atom.

Thus the system frequency, $\nu_{syst} = \frac{v}{2\pi r}$ for the nth state of H-atom.

But $v = \frac{2\pi e^2}{nh}$ and $r = \frac{n^2h^2}{4\pi^2 me^2}$. Hence, $\nu_{syst} = \frac{v}{2\pi r} = \frac{4\pi^2 me^4}{n^3h^3} = \frac{2A}{n^3h} = \nu_{perturb.}$.

Therefore, when $n \to \infty$ the quantum results merge with the classical results.

[NOTE: v *and* r can have the expressions from the two equations, (I) $mvr = n\left(\frac{h}{2\pi}\right)$ and (II) $\frac{mv^2}{r} = \frac{e^2}{r^2}$]

(2) Bohr's correspondence principle and rigid rotator:

For rigid rotator, $E = n^2h^2/8\pi^2 I$. The energy difference between two consecutive energy levels is $\Delta E = (n+1)^2\, h^2/8\pi^2 I - n^2h^2/8\pi^2 I$ or, $\Delta E = (2n+1)h^2/8\pi^2 I$. If the transition is made by absorption of radiation of frequency, ν, then $h\nu = \Delta E = (2n+1)h^2/8\pi^2 I$ or, $\nu = (2n+1)h/8\pi^2 I$.

But when $n \to \infty$, $2n+1 \approx 2n$ and so $\nu = nh/4\pi^2 I$. Thus the quantum result for the frequency of radiation absorbed, called perturbation frequency ($\nu_{purturbation}$) = $nh/4\pi^2 I$.

Classical theory assumes that this perturbation frequency is equal to the frequency with which the rotator rotates (ν_{system}) which is equal to $\frac{\omega}{2\pi}$. But for rigid rotator, $E = \frac{1}{2}I\omega^2 = \frac{n^2h^2}{8\pi^2 I}$ or, $\omega^2 = \frac{n^2h^2}{4\pi^2 I^2}$

or, $\nu_{system} = \frac{\omega}{2\pi} = \frac{nh}{4\pi^2 I}$. Thus quantum result and classical result merge each other when $n \to \infty$.

This is Bohr's correspondence.

(3) Bohr’s correspondence principle and particle in 1-D box:

$\nu_{purturbation} = (2n+1)h/8mL^2$, but when $n \to \infty,\ 2n+1 \approx 2n$ and $\nu_{purturbation} = nh/4mL^2$.
On the other hand, $\nu_{system} = v/2L$. But $p = nh/2L$ or $mv = nh/2L$ or, $v = nh/2mL$.
Thus, $\nu_{system} = v/2L = nh/4mL^2$. Classical result corresponds to the quantum result when $n \to \infty$ and this is Bohr’s correspondence principle.

Problem(1): An electron with an effective mass 9×10^{-28} gm is free to move in a crystal lattice with interionic separation 10^{-5} cm. Find the various energy levels of the electron. Calculate the wave length of the absorbed photons during the transition of the electron from the level n = 1 to the level $n = 2$.

Solution: we have the expression, $E_n = (n^2)h^2/8mL^2$. Putting the values, we get

$$E_n = (n^2)(6.627\times10^{-27}erg\ \text{sec})^2\Big/\left(8\times9\times10^{-28}\ \text{gm}\ (10^{-5}\text{cm})^2\right) = n^2\times6.1\times10^{-17}erg\ .$$

The various energy levels could be found by putting n = 1, 2, 3 etc .

Thus, $E_1 = 6.1\times10^{-17}erg$, $E_2 = 4\times6.1\times10^{-17}erg$, $E_3 = 9\times6.1\times10^{-17}erg$, etc.

The energy of the photons absorbed for transition n = 1 to n = 2, $h\nu = E_2 - E_1$

or, $hc/\lambda = (4-1)\times6.1\times10^{-17}erg$. Thus, the wave length of radiation absorbed for the above transition is $\lambda = \left(6.627\times10^{-27}erg\ \text{sec}\times3\times10^{10}cm\ \text{sec}^{-1}\right)\Big/\left(3\times6.1\times10^{-17}erg\right) = 1.08\ cm$.

Problem (2): The difference in the ground state energies (kJ/mol) of an electron in one dimensional boxes of lengths 0.2 nm and 2 nm is --------------. **[GATE, 2015]**

Answer. The energy of the electron in 1-D box is given as $E_n = \dfrac{n^2h^2}{8mL^2}$. Foe ground state of the electron, $n = 1$.

When L = 0.2 nm, $E_1 = \dfrac{h^2}{8m(0.2)^2}$ and when L = 2 nm, $E_2 = \dfrac{h^2}{8m(2)^2}$.

The difference of energies of the electron in the two boxes are $\Delta E = E_1 - E_2 = \dfrac{h^2}{8m}\left[\dfrac{1}{(0.2)^2} - \dfrac{1}{(2)^2}\right]$.

Putting the values of $h = 6.625\times10^{-34}\,Js$, $m = 9.1\times10^{-31}kg$, we get $\Delta E = 1.48\times10^{-18}\,J$.

The energy per mole, we have $\Delta E = 1.48\times10^{-18}\,J\times6.02\times10^{23}\times10^{-3} = 891$ kJ/mol.

QUANTUM CHEMISTRY - MECHANICS

Introduction

Wave-particle dual nature of microscopic particles: De Broglie's suggestion of matter wave and its confirmation by Davisson and Germer's electron diffraction experiment conclusively proves that electron is not an ordinary particle. It has both the particle nature [as evidenced by the experiment of determination of mass (m) and e/m] and wave nature [as evidenced by Davisson and Germer's electron diffraction experiment]. All sub-atomic particles are found to possess both the particle and wave nature i.e., they play dual nature.
The two natures of the electron are contradictory as a particle is highly localised i.e., it could not be found more than one point at a time while wave is a kind of disturbance which varies from point to point and cannot be localised.

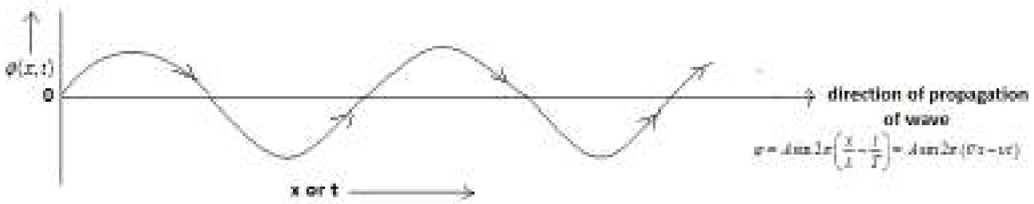
Necessity of quantum mechanical model: Therefore to describe the finer details of microscopic (sub-atomic) particles like electron, it is necessary to create a mathematical model which can reconcile both the particle nature and wave nature of the substance. Quantum mechanics is such a mathematical model.

Function used to define quantum mechanical state: In classical mechanics, position and momentum of a dynamic particle are definite and so its state is defined by position and momentum coordinates which are expressed by number only. But if the state of a microscopic particle is described by numbers, then it violates Heisenberg uncertainty principle as it states that position and momentum of a sub-atomic particle could not be known accurately and simultaneously. Therefore to incorporate the uncertainty principle, the state of sub-atomic particle should be described not by numbers but by a function. A function is more generalised way of describing a state. A continuous function refers to infinitude of numbers. These are usually functions of space coordinates (Schrodinger representation). In one dimension (x), a quantum mechanical state is thus defined by some function of x only.

Measurable properties of a quantum mechanical system: The observable properties of a dynamical particle like mass, position, velocity, momentum, energy, etc, are obtained by treating the function with an appropriate quantum mechanical operator. Each observable property has a definite quantum mechanical operator which on operation with the function gives the value of the property. Though the uncertainty in the variables are considered in quantum mechanics, the values of the observable properties of the system are obtained very accurate. This is the triumph this new model.

Classical Wave and Wave Equation

Classical wave and SHM is the simplest one: All waves originate from some kind of vibratory (oscillatory) motion. The simplest of these is simple harmonic motion (SHM). A SHM is one in which some physical quantity assumes definite value after a definite period of time. In a water wave, this quantity is the height of water and in vibration of string; it is the vertical displacement of the string from its mean position. This is sometimes called amplitude function (φ). This quantity is a function of space coordinate (x in one dimension) and time (t) i.e., $\varphi = f\left(x,t\right)$.



Definition of λ, T, ν *and* $\bar{\nu}$ **:** This amplitude $\varphi(x,t)$ assumes the definite value as the wave is in progress after the distance Δx and it is the wave length $\left(\lambda\right)$ of the wave. The time interval Δt at which it takes same definite value is called time period (T). Hence the velocity of the wave, $c = \lambda/T$. But $1/T = \nu$, the frequency of the wave which is the number of waves passed at a point in unit time. Again, $1/\lambda = \bar{\nu}$, the wave number i.e., it is the number of waves in unit length. The periodic nature of the certain property suggests that the analytical expression is either a sine or cosine function of x and t. Such expression of φ is obtained by the general differential wave equation,

General Differentia Equation: $$\frac{\partial^2\varphi}{\partial x^2}=\frac{1}{c^2}\frac{\partial^2\varphi}{\partial t^2}.$$

The equation is derived from Newton's 2nd law of motion and also considering that each wave propagates along the medium continuously. The wave equation is a differential equation with a constant coefficient (c). Hence this equation has a number of solutions. Let us consider a solution in terms of sine function, as

$$\varphi = A\sin 2\pi\left(\frac{x}{\lambda}-\nu t\right),$$

where φ is a amplitude function, A is amplitude, x is displacement of the wave at time t. λ and ν are the wave length and frequency of the wave respectively. This wave equation represents a plane wave travelling from left to right starting from the origin of the wave. An equivalent wave travelling in the opposite direction is given as $\varphi = A\sin 2\pi\left(\frac{x}{\lambda}+\nu t\right)$

Formulation of Standing Wave Function: When the two waves of the above form travel with equal velocity but in opposite directions, the resultant amplitude function is obtained by the principle of superposition of waves, as

$$\varphi = A\sin 2\pi\left(\frac{x}{\lambda}-\nu t\right)+A\sin 2\pi\left(\frac{x}{\lambda}+\nu t\right)=2A\sin\frac{2\pi x}{\lambda}.\cos 2\pi\nu t$$

This resultant wave neither move forward nor backward directions and it is called **standing wave** or **stationary wave.** Mathematically, all waves whose amplitude function can be product of two functions – one dependent of space coordinate (say, x) and the other dependent of time (t) are standing wave or stationary wave.

Characteristics of Standing Wave Function: The standing wave equation shows that φ vanishes irrespective of the value of t for the points at which $\sin(2\pi x/\lambda)=0$ i.e., at the points, $x=0,\lambda/2,2\lambda/2,---n\lambda/2.$ These points are known as **nodes (**minimum amplitude**).** The distance between two successive nodes is $\lambda/2$. The mid-point between two nodes is **antinode** (maximum amplitude)

Formulation of Differential Equation of Standing Wave: The amplitude function for standing wave is

$$\varphi = 2A\sin 2\pi(x/\lambda).\cos 2\pi\nu t=\psi(x).f(t)\ ,$$

Where $\psi(x)=2A\sin 2\pi(x/\lambda)$ and $f(t)=\cos 2\pi\nu t$ or, we write simply as $\varphi=\psi.f$.

These two functions are independent of each other.

Therefore, $$\frac{\partial^2\varphi}{\partial x^2}=f\times\frac{\partial^2\psi}{\partial x^2}\ \text{ or, }\ \frac{\partial^2\varphi}{\partial x^2}=\cos 2\pi\nu t\frac{\partial^2\psi}{\partial x^2}.$$

Again, $$\frac{\partial^2\varphi}{\partial t^2}=\psi\times\left[-4\pi^2\nu^2\cos 2\pi\nu t\right]=-4\pi^2\frac{c^2}{\lambda^2}\psi\times\cos 2\pi\nu t.$$

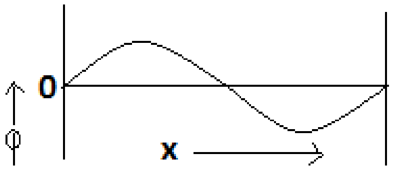
Putting these expression in the generalised differential wave equation, $\frac{\partial^2\varphi}{\partial x^2}=\frac{1}{c^2}\frac{\partial^2\varphi}{\partial t^2}$, we get

$\cos 2\pi\nu t\times\frac{\partial^2\psi}{\partial x^2}=\frac{1}{c^2}\times\left[-4\pi^2\frac{c^2}{\lambda^2}\psi\right]\cos 2\pi\nu t$. Now cancelling the like terms, we have

$\frac{d^2\psi}{dx^2}=-\left(4\pi^2/\lambda^2\right)\psi$. This is differential equation of the standing wave where t is absent.

The Schrodinger Time-independent Equation for Matter Waves :

Using the de Broglie’s wave particle duality, E. Schrodinger in 1926, argued that microscopic particles such as electrons behave like standing wave in atoms and molecules. Therefore, he proposed a wave equation analogous to that used to describe the standing wave system such as the vibrating string tied at both the ends.



[Vibration of string is given as: The analytical expression of amplitude function is $\varphi = A\sin\left(2\pi x/\lambda\right)$.

For matter wave, it is $\psi = A\sin\left(2\pi x/\lambda\right)$.

Double differentiation of ψ with respect to x gives the differential form of the standing wave,

$$\frac{d^2\psi}{dx^2} = -\left(4\pi^2/\lambda^2\right)\psi \text{ .]}$$

The equation proposes probable distribution of the electron instead of the well defined trajectory.

Schrodinger used the time-independent wave equation $\dfrac{d^2\psi}{dx^2} = -\left(4\pi^2/\lambda^2\right)\psi$, where $\psi = \psi(x)$, represents the quantity analogous to the amplitude function in classical wave.

Introducing the de Broglie relation, $\lambda = h/p_x$, we get $\dfrac{d^2\psi}{dx^2} = -\left(4\pi^2 {p_x}^2/h^2\right)\psi$,

where p_x is the $x-$component momentum .

The kinetic energy, $T = {p_x}^2/2m$ = E – V , so ${p_x}^2 = 2m\left(E-V\right)$, where E = total energy of the system and V = time-independent potential energy. Now replacing ${p_x}^2$ in the wave equation, we get x - directional Schrödinger equation, $\dfrac{d^2\psi}{dx^2} = -\dfrac{4\pi^2 \times 2m(E-V)}{h^2}\psi$ or, $\dfrac{d^2\psi}{dx^2} = -\dfrac{8\pi^2 m(E-V)}{h^2}\psi$. We may use $\hbar = h/2\pi$, called reduced Planck’s constant in the equation and then it is

$\dfrac{d^2\psi}{dx^2} + \dfrac{2m}{\hbar^2}(E-V)\psi = 0$. It is in one dimension time-independent Schrodinger equation.

However, in three-dimensions, the equation is $\dfrac{\partial^2\psi}{\partial x^2} + \dfrac{\partial^2\psi}{\partial y^2} + \dfrac{\partial^2\psi}{\partial z^2} + \dfrac{2m}{\hbar^2}(E-V)\psi = 0$.

But, $\dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2} = \nabla^2$ (del squared), Laplacian operator. So the Schrodinger equation in 3-D

is $\nabla^2\psi + \dfrac{2m}{\hbar^2}(E-V)\psi = 0$ or, $-\dfrac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$ or, $\left[-\dfrac{\hbar^2}{2m}\nabla^2 + V\right]\psi = E\psi$

or, $\hat{H}\psi = E\psi$, where $\hat{H} = -\dfrac{\hbar^2}{2m}\nabla^2 + V$ and is called Hamiltonian operator is an energy operator.

Schrodinger equation is an energy eigen value equation. It is, in fact, the quantum mechanical analogue of the classical standing wave equation. It describes the finer details of the particle in motion in atoms and molecules. Predictions of this equation have been confirmed without exception.

Schrodinger Equation for different systems: The Schrodinger equation

(1) For particle in one dimensional box: For system, the potential energy (V) = 0, hence

$\dfrac{d^2\psi}{dx^2} + \dfrac{2mE}{\hbar^2}\psi = 0$, where m = mass of the particle moving in the box.

(2) For particle in three dimensional box: $\nabla^2\psi + \dfrac{2mE}{\hbar^2}\psi = 0$, where $\nabla^2 = \dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}$.

(3) For simple harmonic oscillator in 1D motion: $\frac{d^2\psi}{dx^2}+\frac{2m}{\hbar^2}\left[E-\left(1/2\right)kx^2\right]\psi=0$, as $V=\frac{1}{2}kx^2$

(4) For H – atom: $\nabla^2\psi+\frac{2\mu}{\hbar^2}\left(E+e^2/r\right)\psi=0$, as $V=-\frac{e^2}{r}$ and r is distance of the electron from the nucleus and μ = reduced mass of the atom. Laplacian operator in polar coordinates is $\nabla^2=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$, where θ = zenith angle and φ = azimuthal angle. Thus the Schrodinger equation for H – atom in polar coordinates is

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}+\frac{2\mu}{\hbar^2}\left(E+\frac{e^2}{r}\right)\psi=0 .$$

(5) For rigid rotator: The particle of mass m is rotating on the XY plane along the Z axis and V = 0. $\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\psi+\frac{2mE}{\hbar^2}\psi=0$. For the system in polar coordinates, r is constant, θ = 90^{o} and φ is varying from 0 to 2π. When it is changed in polar coordinates, $\sin\theta=1, \frac{\partial}{\partial r}=0$ and $\frac{\partial}{\partial\theta}=0$, so the equation is $\frac{1}{r^2}\frac{d^2\psi}{d\varphi^2}+\frac{2\mu E}{\hbar^2}\psi=0$ or, $\frac{d^2\psi}{d\varphi^2}+\frac{2\left(\mu r^2\right)E}{\hbar^2}\psi=0$.

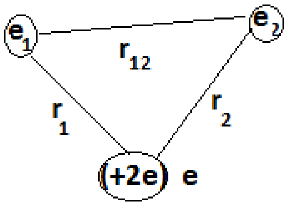
But $\mu r^2=I$, moment of inertia of the system. So the equation is $\frac{d^2\psi}{d\varphi^2}+\frac{2IE}{\hbar^2}\psi=0$.

(6) For He atom: The atom contains two electrons and one nucleus of charge $+2e$.

$$\left(\nabla_1{}^2+\nabla_2{}^2\right)\psi+\frac{2\mu}{\hbar^2}\left(E+\frac{2e^2}{r_1}+\frac{2e^2}{r_2}-\frac{e^2}{r_{12}}\right)\psi=0$$

where, $\nabla_1{}^2=\frac{\partial^2}{\partial x_1{}^2}+\frac{\partial^2}{\partial y_1{}^2}+\frac{\partial^2}{\partial z_1{}^2}$ and $\nabla_2{}^2=\frac{\partial^2}{\partial x_2{}^2}+\frac{\partial^2}{\partial y_2{}^2}+\frac{\partial^2}{\partial z_2{}^2}$.

One electron has the coordinates $\left(x_1,y_1,z_1\right)$ and the other electron has the coordinate $\left(x_2,y_2,z_2\right)$. This is shown pictorially as :



Interpretation of Wave Function (ψ)

Introduction: The Schrodinger time-independent wave equation is the best mathematical model to describe the motions of the particles in an isolated atom or molecule. The acting forces among the charged particles depend on the space coordinates only and do not depend on time. The potential energy (V) coming out from these forces is also time-independent. For one particle in 3D motions, the Schrodinger equation is

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

Here, ψ is called quantum mechanical wave function and it is the function of space coordinates only i.e. $\psi=f\left(x,y,z\right)$.

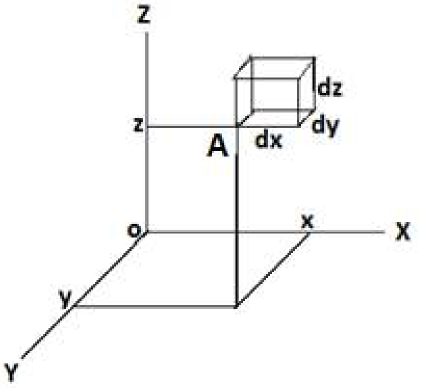
Interpretation of ψ : (1) The wave function in quantum mechanics is the analogue of amplitude function in classical wave mechanics. However, amplitude function in wave mechanics can be determined experimentally and hence a **physical quantity**. But wave function (ψ) is not to be thought of a physical wave but an **abstract mathematical entity** and has no experimental bearing.

(2) It is supposed that all the information of a state of the system is mysterically hidden within the expression of ψ and so it is often called **state function** of the system. Any observable property of the system can be obtained by the mathematical treatment of the wave function of that system. If any property or information could not be obtained from ψ, it is believed that this property or information is not at all present in the system.

(3) Though ψ has no physical meaning as such, ψ^2 bears a meaningful physical concept.

Max Born in 1926, postulated that ψ^2 gives **probability density** for finding the particle at a point in space, hence it must be a real quantity. When ψ is a complex function, $\psi\psi^*$ is used as a measure of probability of finding the particle at the point in space. In general it is written as $|\psi|^2$ (modulus square of ψ). Thus classical mechanics is a **deterministic theory** but quantum mechanics fails to give exact trajectory or path of the particle like classical mechanics. It gives probable positions of the particle at different locations in space, hence it is **probabilistic theory**.

(4) Let P is the probability of finding the particle at the point, A in space within range x to $x+dx$, y to $y+dy$ and z to $z+dz$, then it is the probability of finding the particle in a tiny rectangular box-shaped region located at point (x, y, z) in space having edges dx, dy and dz. Born's postulates is then probability (P) = $|\psi(x, y, z)|^2\, dxdydz$ = $|\psi|^2\, d\tau$, where $d\tau$ is infinitesimal volume element equal to $dxdydz$ in space at the point (x, y, z).



$|\psi|^2$ is called probability density of finding the particle at the point (x, y, z) and $|\psi|^2\, d\tau$ is called probability of finding the particle within the volume element $d\tau$.

Similarly, if the wave function of a particle has a value of ψ at some point A located at x within range dx, the probability (P) of finding the particle between this infinitesimal distance range is

$$P = |\psi|^2\, dx$$

(5) Probability idea also imposes that total probability of finding the particle in all available range must be unity. i.e., $\int_{\text{all space}} |\psi|^2\, d\tau = 1.$

(6) If the particle is smeared into cloud, then often $|\psi|^2$ denotes the particle density. If the particle is charged, then it denotes the charge density at the given point. This concept arises for the particle like electron due to their wave character and are delocalised.

Conditions of Accepted (Well-behaved) Wave Function

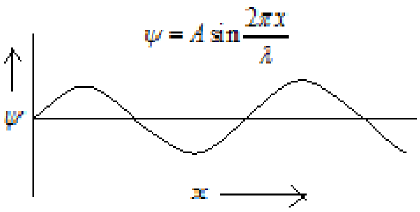
The Schrodinger wave equation is a double differential equation and so it produces a number of solutions of ψ. But all the expressions of ψ are not quantum mechanically accepted. The quantum mechanical restrictions for ψ being well-behaved originate from the following two considerations.

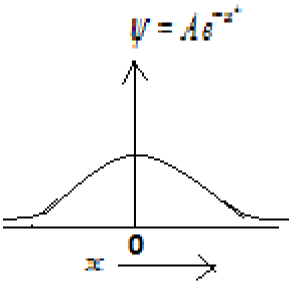
(a) The Schrodinger equation must be finite at every point within the system and

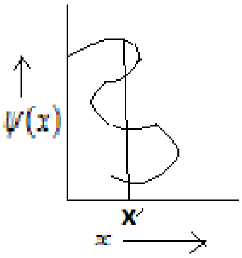
(b) $|\psi|^2$ measures the probability density at a point and hence it must be finite

These above conditions put some restrictions of ψ for being quantum mechanically accepted.

(1) The accepted wave function must be **single-valued**.

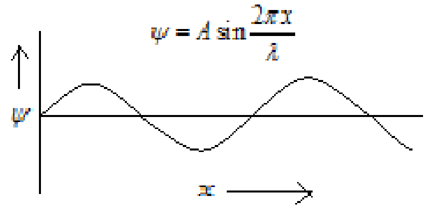


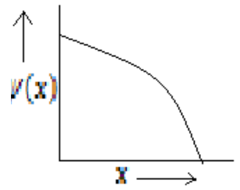




$\psi(x)$ assumes single-valued at a given point. But it is possible for ψ to have same value at different values of x as for the function $\psi = A\sin\frac{2\pi x}{\lambda}$ viz. $\psi(x) = \psi(x+\lambda)$ or at different value of θ for the function $\psi(\theta) = \psi(2\pi n + \theta)$. But this function is not acceptable as it assumes more than one value at $x = x'$

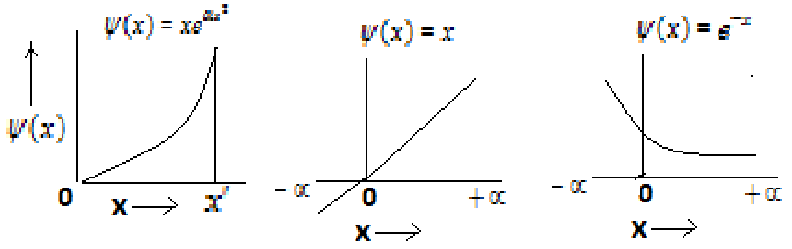
(2) The accepteble wave function must be **finite**.





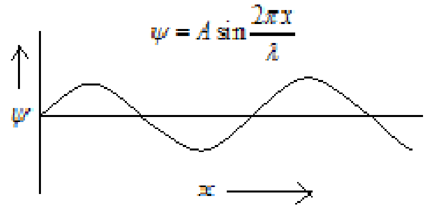
These functions, $\psi(x)$ are acceptable since at any point x the function is finite including zero.

But these functions given below are not acceptable.



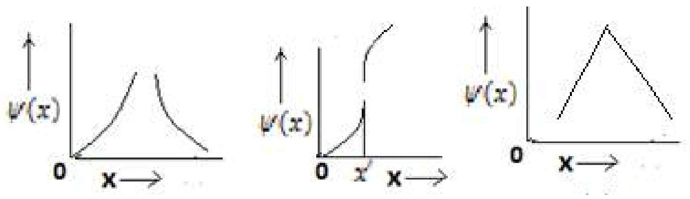
This also arises from the probability idea that $|\psi|^2$ never be infinity and in that case probability density would be infinity which is not possible.

(3) The acceptable wave function must be **continuous.**



This ψ is acceptable since it varies continuously with the change of x. The probability of finding the particle must be continuous. It means that the probability density at x must not differ to large extent at a point $x+dx$. For example, if the probability at x were 90%, and that at the adjacent point $x+dx$ only 10%, it would be highly absurd situation

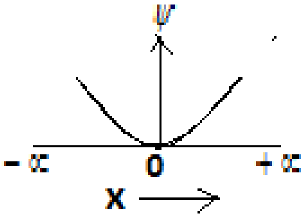
Not only ψ is continuous, $\frac{\partial\psi}{\partial x}, \frac{\partial\psi}{\partial y}, \frac{\partial\psi}{\partial z}$ must also be continuous, otherwise double differentiation of ψ, $\nabla^2\psi$ must be infinite. But the Schrodinger equation is finite at every point of the system.



In (a) and (b), ψ functions are not acceptable since they assume sudden change with x. In (c), ψ is continuous but the slope $\frac{d\psi}{dx}$ is not continuous.

(4) ψ must be quadratically integrable. Otherwise the probability id becomes untenable as

$\int \psi^2 d\tau$ is finite. For example, $\int_{-\infty}^{+\infty} x^4 dx$ is equal to infinity hence x^2 function is not quadratically integrable.



Problem: Indicate which of the functions are acceptable as wave functions?

(i) $\psi = x$, (ii) $\psi = x^2$ (iii) $\psi = \sin x$ (iv) $\psi = e^{x}$ (v) $\psi = e^{-x}$ (vi) $\psi = e^{-x^2}$
(vii) $\psi = \tan x$. **[Ans. (iii) and (vi) are acceptable]**

Problem: Show whether the following functions belong to the well-behaved class in the range given:

(a) $\psi = e^{-x}(0,\propto)$ (b) $\psi = e^{-x}(-\propto,+\propto)$ (c) $\psi = \sin^{-1} x(-1,+1)$
(d) $\psi = e^{-x^2}(-\propto,+\propto)$ (e) $\psi = e^{x}(0,\propto)$ (f) $\cos|x|$ (g) $\psi = e^{i\theta}(0,2\pi)$ (h) $\psi = e^{|x|}$.
[Ans. (a), (d), (g)]

Illustration: (a) $\psi = e^{-x}(0,\propto)$ acceptable. (b) not acceptable as when $x = -\propto$, $e^{-x} \to \propto$.
(c) not acceptable, as it leads to multi-valued. (d) acceptable (e) not acceptable as when $x = \propto$, $e^{x} \to \propto$ (f) not acceptable, ψ is continuous but $\frac{d\psi}{dx}$ is not continuous.
(g) acceptable as $\psi = e^{i\theta} = \cos\theta + i\sin\theta$.

Some Important Properties of Wave Function

(1) Normalised Wave Function: If $|\psi|^2\, d\tau$ is the probability of finding a particle in the volume element $d\tau$, then the sum of such probabilities over the entire space must be unity. Mathematically, it is expressed as

$$\int\limits_{all\ space} |\psi|^2\, d\tau = 1.$$

When a wave function satisfies this condition, it is said to be a **normalised wave function.**
If a wave function is not normalised, then it can be normalised by multiplying the function by a constant A, called normalised constant so that

$$\int\limits_{all\ space} |A\psi|^2\, d\tau = 1.$$ The value of A can be calculated by $$A^2 = \frac{1}{\int\limits_{all\ space} |\psi|^2\, d\tau}.$$

If ψ is a solution of the Schrodinger equation, it could be shown that $A\psi$ is also a solution of the equation.

For a particle in one dimensional box, the normalisation condition is $\int_0^L |\psi|^2\, dx = 1$, if the particle is constraint to move within a distance L.
This condition of normalisation arises from the fact that total probability of finding the particle within the all available space must be unity.

Mathematically, we can write the normalisation condition as, $\int_{-\propto}^{+\propto} \psi_i \psi_j\, d\tau = 1$, when $i = j$.

Exercise:

(1) The wave function of a particle moving within a box of length L is given by $\psi_n = A\sin^2 \frac{n\pi x}{L}$.

Find the normalisation constant A.

Answer: Putting the normalisation condition, $\int_0^L \psi_n{}^2 dx = 1$ or, $A^2 \int_0^L \sin\frac{n\pi x}{L}\, dx = 1$

or, $\frac{A^2}{2}\int_0^L 2\sin^2\frac{n\pi x}{L}\, dx = 1$ or, $\frac{A^2}{2}\int_0^L \left(1-\cos\frac{2n\pi x}{L}\right) dx = 1$ or, $\frac{A^2}{2}\int_0^L dx - \frac{A^2}{2}\int_0^L \cos\frac{2n\pi x}{L}\, dx = 1$

or, $\frac{A^2}{2} \times L = 1$, since $\int_0^L \cos\frac{2n\pi x}{L}\, dx = 0$, hence $A = \sqrt{\frac{2}{L}}$.

(2) The wave function for the ground state of H-atom is proportional to e^{-r/a_0}, where a_0 = constant.

Find the normalisation constant, N such that $\psi(r) = Ne^{-r/a_0}$ is normalised to unity.

Answer: Using normalisation condition, we have $\int\limits_{all\ space} |\psi(r)|^2 \, d\tau = 1$, but $d\tau = dxdydz$

$$= r^2 dr \sin\theta d\theta d\varphi .$$

Therefore, $\int\limits_{r=0}^{\infty} \left(Ne^{-r/a_0} \right)^2 r^2 dr \int\limits_{\theta=0}^{2\pi} \sin\theta d\theta \int\limits_{\varphi=0}^{2\pi} d\varphi = 1$ or, $N^2 \times \dfrac{a_0^3}{4} \times 2 \times 2\pi = 1$ or, $N = \left(\pi a_0^3\right)^{-1/2}$.

(3) Normalise the wave function $\cos\dfrac{n\pi x}{L}$ over the integral $-L \le x \le L$. **[Answer:** $\dfrac{1}{\sqrt{L}}\cos\dfrac{n\pi x}{L}$**]**

(4) A system is defined by the wave function, $\psi = Axe^{-x^2/2}$. Calculate the value of A if the wave function is normalised. [**Ans.** $A = \left(4/\pi\right)^{1/4}$]

(2) Orthogonal Wave Functions:

The functions f and g are said to be orthogonal if $\int f^* g \, d\tau = 0$.

In quantum mechanics, there may be many acceptable wave functions to Schrodinger equation

$\widehat{H}\psi = E\psi$ for a particular system.

Each wave function ψ has a corresponding energy value E. For any two wave functions ψ_i and ψ_j corresponding to the energy values E_i and E_j respectively, they are orthogonal to each other.

That is, $\int\limits_{all\ space} \psi_i \psi_j d\tau = 0$, when $i \ne j$.

It means that two wave functions that correspond to different energy values of a quantum mechanical system are orthogonal. [In geometry, orthogonal means perpendicular to each other.]

Orthogonal wave functions are completely independent functions and one can not be expressed in terms of other. It implies also that the energy levels corresponding to the orthogonal functions are not overlapping or interacting each other.

Exercise: Check whether the wave functions of a particle in one-dimensional box, $\psi_n = A\sin\dfrac{n\pi x}{L}$ within box length L are orthogonal.

Answer: We have to show $\int\limits_0^L \psi_i \, \psi_j \, dx = 0$. Now for the system,

$$A^2\int\limits_0^L \sin\frac{n_i\pi x}{L}\sin\frac{n_j\pi x}{L}dx = \frac{A^2}{2}\int\limits_0^L 2\sin\frac{n_i\pi x}{L}\sin\frac{n_j\pi x}{L}dx = \frac{A^2}{2}\int\limits_0^L\left[\cos\frac{\left(n_i - n_j\right)\pi x}{L} - \cos\frac{\left(n_i + n_j\right)\pi x}{L}\right]dx$$

$$= \frac{A^2}{2}\int\limits_0^L \cos\frac{\left(n_i - n_j\right)\pi x}{L}dx - \frac{A^2}{2}\int\limits_0^L \cos\frac{\left(n_i + n_j\right)\pi x}{L}dx$$

$$= \frac{A^2}{2}\times\frac{L}{\pi}\left(\frac{1}{n_i - n_j}\right)\left[\sin\frac{\left(n_i - n_j\right)\pi x}{L}\right]_0^L - \frac{A^2}{2}\times\frac{L}{\pi}\left(\frac{1}{n_i + n_j}\right)\left[\sin\frac{\left(n_i + n_j\right)\pi x}{L}\right]_0^L$$

$$= \frac{A^2L}{2\pi}\left(\frac{1}{n_i - n_j}\right)(0-0) - \frac{A^2L}{2\pi}\left(\frac{1}{n_i + n_j}\right)(0-0) = 0 .$$

This shows that wave functions of the system are orthogonal to each other.

(3) Orthonormal wave functions: Two wave functions are said to be Orthonormal when the following two conditions are simultaneously satisfied.

$$\int\limits_{all\ space} \psi_i \psi_j d\tau = 1, \text{ when } i = j \text{ and } \int\limits_{all\ space} \psi_i \psi_j d\tau = 0, \text{ when } i \neq j.$$

The integration is known as Kronecker delta, δ_{ij} and for orthonormal conditions,

$$\delta_{ij} = 1, \text{ when } i = j \text{ and } \delta_{ij} = 0, \text{ when } i \neq j.$$

Example: Show that the wave functions of a particle in one-dimensional box, $\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$ are orthonormal.

(4) Degenerate Wave Functions: When two wave functions ψ_i and ψ_j correspond to the same energy E, the wave functions are said to be in a degenerate state.

However, the degenerate wave functions will not necessarily be orthogonal. The p - orbitals are three-fold degenerate since they have same energy.

Operators

Formal treatment of quantum mechanics requires the idea of the operator algebra, eigen values, eigen functions and a set of postulates called quantum mechanical laws. Let us start with quantum mechanical operators.

An operator is a mathematical instruction to be applied to a function or a number to give a new function or number. For example, $\sqrt{\ }$ is an operator which itself does not mean anything, but if a quantity is put under it, it transforms that quantity into square root, another quantity i.e. $\sqrt{4} = 2$.

Similarly, $\frac{d}{dx}$ is an operator which operates on $(\cos x)$ gives $(-\sin x)$ i.e., $\frac{d \cos x}{dx} = -\sin x$.

In general, $\hat{A} f(x) = g(x)$, where $\hat{A}$ is an operator operating on the function $f(x)$ giving a new function $g(x)$. Let $\hat{A} = \frac{d}{dx}$ and $f(x) = 5x^2$, then $\hat{A} f(x) = \frac{d(5x^2)}{dx} = 10x = g(x)$.

A list of mathematical operators is given below:

Operation	Operator	Result of operation on x^3
taking square	$(\ )^2$	x^6
taking square root	$\sqrt{\ }$	$x^{3/2}$
multiplication by a constant k	k	kx^3
differential with respect to x	$\frac{d}{dx}$	$3x^2$
integration with respect to x	$\int dx$	$\frac{1}{4}x^4 + c$

Algebra of Operator:

Although the operators do not have any physical meaning, they can be added, subtracted, multiplied and have some other properties.

Addition and Subtraction:

The addition or subtraction of operators yields new operators. As for example,

$$\left(\hat{A} \pm \hat{B}\right) f(x) = \hat{A} f(x) \pm \hat{B} f(x).$$

If $\hat{A} = \log_e$, $\hat{B} = \frac{d}{dx}$, then sum or difference yields new operators, $\left(\log_e \pm \frac{d}{dx}\right)$. When operated on the function x^2, we get $\left(\log_e \pm \frac{d}{dx}\right) x^2 = \log_e x^2 \pm \frac{d(x^2)}{dx} = 2\log_e x \pm 2x$.

Problem: $\left[-\frac{h^2}{\left(8\pi^2 m\right)}\frac{d^2}{dx^2}+\frac{h^2\alpha^2x^2}{\left(2\pi^2 m\right)}\right]e^{-\alpha x^2}=c\frac{h^2}{\left(4\pi^2\right)}e^{-\alpha x^2}$, where h, π and m are constants.

Then c is (A) $2\alpha/m$ (B) $\alpha/2m$ (C) α/m (D) α^2/m. **[GATE, 2014]**

Ans. (C).

Multiplication: Multiplication of two operators means operations by two operators one after the other, the order of operation being from right to left. For example, $\hat{A}\hat{B}f(x)$ means that the function $f(x)$ is first operated on by $\hat{B}$ to yield a new function $g(x)$ which is then operated on by $\hat{A}$ to yield function $h(x)$.

i.e. $$\hat{A}\hat{B}f(x)=\hat{A}\left[\hat{B}f(x)\right]=\hat{A}g(x)=h(x).$$

Let $\hat{A}=4x^2$, $\hat{B}=\frac{d}{dx}$ and $f(x)=ax^3$ then $\hat{A}\hat{B}f(x)=4x^2.\frac{d}{dx}\left(ax^3\right)=4x^2.3ax^2=12ax^4$.

If the order of operation is changed, the result of operation may be or may not be different.

The square of an operator means that the same operator is applied successively twice

i.e. $$\hat{A}^2f(x)=\hat{A}\left[\hat{A}f(x)\right]=\hat{A}g(x)=h(x).$$

Let $\hat{A}=\frac{d}{dx}$ and $f(x)=\sin x$, then $\hat{A}^2f(x)=\left(\frac{d}{dx}\right)^2\sin x=\frac{d}{dx}\left[\frac{d}{dx}\sin x\right]=\frac{d}{dx}(\cos x)=-\sin x$.

Rules for Quantum Mechanical Operators:

(1) **Linear Operators:** An operator is said to be linear if its application on the sum of two functions gives the result which is equal to the sum of operations of the two functions separately.

i.e. $\hat{A}\left[f(x)+g(x)\right]=\hat{A}f(x)+\hat{A}g(x)$ and $\hat{A}cf(x)=c\hat{A}f(x)$, where c is constant.

Examples: (i) $\frac{d}{dx}$ is a linear operator since $\frac{d}{dx}\left(ax^m+bx^n\right)=\frac{d}{dx}\left(ax^m\right)+\frac{d}{dx}\left(bx^n\right)$.

(ii) Square root $\left(\sqrt{\ }\right)$ operator is not linear operator, as $\sqrt{f(x)+g(x)}\neq\sqrt{f(x)}+\sqrt{g(x)}$.

$\log, \sin, \cos,$ etc are not linear operators.

All quantum mechanical operators are linear operators.

Commutator Operator: For two operators $\hat{A}$ and $\hat{B}$, the difference $\left(\hat{A}\hat{B}-\hat{B}\hat{A}\right)$ is called "commutator operator" . This commutator operator of $\hat{A}$ and $\hat{B}$ is simply denoted by $\left[\hat{A},\hat{B}\right]$.

If $\hat{A}$ and $\hat{B}$ commute, then $\left[\hat{A},\hat{B}\right]=0$, where 0 is called zero operator which means multiplying a function with zero. For example, $\hat{A}=\frac{d}{dx}$, $\hat{B}=3x^2$ and $f(x)=\sin x$, the commutator operator is obtained as:

$$\left[\hat{A},\hat{B}\right]f(x)=\left(\hat{A}\hat{B}-\hat{B}\hat{A}\right)f(x)=\frac{d}{dx}.\left(3x^2\sin x\right)-3x^2.\frac{d}{dx}(\sin x)$$

$$=\left(6x.\sin x+3x^2\cos x\right)-3x^2\cos x=6x\sin x=(6x)f(x).$$

The commutator operator of $\frac{d}{dx}$ and $3x^2$ is $6x$. The value of commutator of two operators is same irrespective of function. If we consider the function e^x, then the commutator of the above two operators will be the same i.e. $6x$.

Commutative property: If $\left[\hat{A},\hat{B}\right]$ = 0 then the operators $\hat{A}$ and $\hat{B}$ are commuting and

when $\left[\hat{A},\hat{B}\right]\neq 0$, then the operators $\hat{A}$ and $\hat{B}$ are not commuting.

Example: $\left[x,\hat{p}_x\right]\neq 0$ i.e. x and $\hat{p}_x$ are not commuting but $\left[y,\hat{p}_x\right]=0$ i.e. y and $\hat{p}_x$ are commuting.

Every physical property of a system has its quantum mechanical operator. If the two operators are not commuting, and in these cases, physical properties (such as x and p_x) they represent, cannot be determined accurately and simultaneously beyond a certain limit.
If the two operators are commuting, then their corresponding physical properties (such as y and p_x) can be determined accurately and simultaneously.

Two physical properties position (x) and x-component momentum (p_x) have operators $\hat{x}$ and $\frac{h}{2\pi i}\frac{d}{dx}$.

These operators are not commuting i.e. $\left[\hat{x},\ \frac{h}{2\pi i}\frac{d}{dx}\right] \neq 0$, hence x and p_x of a system cannot be determined accurately at the same time. It is to be noted that operators representing physical quantities must be linear.

To show that $\hat{x}$ and $\hat{p}_x$ are not commuting. Let the function is taken as $\psi(x)$, then

$$[\hat{x}, \hat{p}_x] = \left[\hat{x},\ \frac{h}{2\pi i}\frac{d}{dx}\right]\psi(x) = \left(x.\frac{h}{2\pi i}\frac{d}{dx} - \frac{h}{2\pi i}\frac{d}{dx}.x\right)\psi(x) = x\frac{h}{2\pi i}\frac{d\psi(x)}{dx} - \frac{h}{2\pi i}\frac{d}{dx}\left[x\,\psi(x)\right]$$

$$= \frac{h}{2\pi i}x\frac{d\psi(x)}{dx} - \frac{h}{2\pi i}\psi(x) - \frac{h}{2\pi i}x\frac{d\psi(x)}{dx} = -\frac{h}{2\pi i}\psi(x) \neq 0.$$

Hence the commutator operator is $-\frac{h}{2\pi i}$ and the operators are not commuting.

Eigen Values and Eigen Functions: If an operator $\hat{A}$ operates on a well-behaved (i.e., finite, continuous and single-valued) function f to give the same function but multiplied by a constant, then the function f is called the 'eigen function' and the constant is called 'eigen value'. The equation is called 'eigen value equation'. [Eigen means characteristic, a German word].

For example, if the function $f = e^{-ax}$ is acted upon by the operator $\frac{d}{dx}$, the result is

$$\frac{d}{dx}\left(e^{-ax}\right) = -a\left(e^{-ax}\right).$$

Therefore, $\left(e^{-ax}\right)$ is the eigen function of the operator $\frac{d}{dx}$ with eigen value $(-a)$. An eigen function does not have any absolute meaning, it always refers to an operator.

Example: (1) Show that $\sin 2x$ is not an eigen function of the operator $\frac{d}{dx}$ but of $\frac{d^2}{dx^2}$;
What is the eigen value?

Answer: $\frac{d}{dx}(\sin 2x) = 2(\cos 2x)$, hence $\sin 2x$ is not eigen function of the $\frac{d}{dx}$ operator.

Again, $\frac{d^2}{dx^2}(\sin 2x) = -4(\sin 2x)$, hence $\sin 2x$ is an eigen function of the $\frac{d^2}{dx^2}$ operator and the eigen value is (-4).

Example: (2) Show that if ψ is an eigen function of a linear operator $\hat{A}$ with an eigen value λ, then $c\psi$, where c is constant, is also an eigen function of $\hat{A}$ with same eigen value λ.

Answer: $\hat{A}\psi = \lambda\psi$, but $\hat{A}$ is linear, so $\hat{A}(c\psi) = c\hat{A}\psi = c\lambda\psi = \lambda(c\psi)$, here c and λ are just the numbers.

Example: (3) Show that e^{ax} is an eigen function of the operator $\frac{d^n}{dx^n}$. What is the eigen value? **Answer:** When e^{ax} is operated n times, $\frac{d^n}{dx^n}\left(e^{ax}\right) = a^n\left(e^{ax}\right)$, so e^{ax} is an eigen function of $\frac{d^n}{dx^n}$ and the eigen value is a^n.

The Schrodinger wave equation $\hat{H}\psi = E\psi$ is also an eigen value equation. ψ is the eigen function of the Hamiltonian operator $\hat{H}$ with eigen value E.

Both $\cos kx$ and $\sin kx$ are the eigen functions of the operator $\frac{d^2}{dx^2}$ with same eigen value $\left(-k^2\right)$. Such eigen functions are called degenerate functions. The 3 p-orbitals are also three-fold degenerate wave functions.

Operator algebra differs from ordinary algebra. From $\hat{H}\psi = E\psi$, one cannot conclude that $\hat{H} = E$. $\hat{H}$ is an operator and E is a property and two are not equal. Thus, $\frac{d}{dx}\left(e^{-2x}\right) = 2\left(e^{-2x}\right)$, but $\frac{d}{dx} \neq 2$

Exercise: (1) Which of the functions $\sin 3x$, $6\cos 4x$, $5x^2$, $\frac{1}{x}$, $3\,e^{-5x}$ are eigen functions of $\frac{d^2}{dx^2}$? For each eigen function, state the eigen value. (2) Show the function $f(y) = y(6-y)e^{-y/3}$ is an eigen function of the operator $\hat{A} = -\left(\frac{d^2}{dy^2}\right) - \frac{2}{y}\left(\frac{d}{dy}\right) - \left(\frac{2}{y}\right) + \left(\frac{2}{y^2}\right)$. Find the eigen value. $\left[-\frac{1}{3}\right]$.

Hermitian Operator: If a linear operator, $\hat{A}$ has two eigen functions ψ and φ with eigen value, and if it satisfies the following condition, then $\hat{A}$ is called Hermitian operator. The condition is,

$$\int \psi\left(\hat{A}\varphi\right)d\tau = \int \varphi\left(\hat{A}\psi\right)d\tau, \quad \text{when } \psi \text{ and } \varphi \text{ are real and}$$

$$\int \psi^*\left(\hat{A}\varphi\right)d\tau = \int \varphi\left(\hat{A}\psi\right)^* d\tau, \quad \text{when } \psi \text{ and } \varphi \text{ are complex, } \psi^* \text{ is the complex}$$

conjugate of ψ. $d\tau$ is the infinitesimal volume element of space in which the functions are defined.

Example: Check $\frac{d^2}{dx^2}$ as Hermitian operator of the eigen functions $\psi = e^{ix}$ and $\varphi = \sin x$.

$$\int \psi^*\left(\hat{A}\varphi\right)d\tau = \int e^{-ix}\left(\frac{d^2}{dx^2}\sin x\right)dx = -\int e^{-ix}\sin x\,dx \text{ and}$$

$$\int \varphi\left(\hat{A}\psi\right)^* d\tau = \int \sin x\left(\frac{d^2}{dx^2}e^{ix}\right)^* dx = -\int e^{-ix}\sin x\,dx.$$

The two integrals are same, hence $\frac{d^2}{dx^2}$ is Hermitian operator

There are three important properties of the Hermitian operator.

(1) The eigen values of the Hermitian operator are real.

It can be easily proved. Let $\hat{A}$ is Hermitian operator for the eigen function with eigen value λ.

Then $\int \psi^*\left(\hat{A}\psi\right)d\tau = \int \psi^*\left(\lambda\psi\right)d\tau = \lambda\int \psi^*\psi\,d\tau$, since $\hat{A}\psi = \lambda\psi$.

And $\int \psi\left(\hat{A}\psi\right)^* d\tau = \int \psi\left(\lambda^*\psi^*\right)d\tau = \lambda^*\int \psi^*\psi\,d\tau$, since $\left(\hat{A}\psi\right)^* = \left(\lambda\psi\right)^* = \lambda^*\psi^*$.

But $\hat{A}$ is Hermitian operator, hence $\int \psi^*\left(\hat{A}\psi\right)d\tau = \int \psi\left(\lambda\psi\right)^* d\tau$, so $\lambda = \lambda^*$, i.e., λ is real.

(2) Eigen functions of a Hermitian operator corresponding to different eigen values are orthogonal.

Let ψ_1 and ψ_2 are the two eigen functions of a Hermitian operator $\hat{A}$ with different eigen values λ_1 and λ_2, then $\hat{A}\psi_1 = \lambda_1\psi_1$ and $\hat{A}\psi_2 = \lambda_2\psi_2$. If complex conjugate of ψ_2 is used,

Then $\hat{A}\psi_2^* = \lambda_2^*\psi_2^* = \lambda_2\psi_2^*$, since λ_2 is always real.

Now, $\int \psi_2^*\left(\hat{A}\psi_1\right)d\tau = \lambda_1\int \psi_2^*\psi_1\,d\tau$ and $\int \psi_1\left(\hat{A}\psi_2\right)^* d\tau = \lambda_2\int \psi_2^*\psi_1\,d\tau$.

From these two equations, it follows that $\int \psi_2^*\left(\hat{A}\psi_1\right)d\tau - \int \psi_1\left(\hat{A}\psi_2\right)^* d\tau = \left(\lambda_1 - \lambda_2\right)\int \psi_2^*\psi_1\,d\tau$

But left hand side is zero since $\hat{A}$ is Hermitian operator, hence $\left(\lambda_1 - \lambda_2\right)\int \psi_2^*\psi_1\,d\tau = 0$, but $\lambda_1 - \lambda_2 \neq 0$, hence $\int \psi_2^* \psi_1 d\tau = 0$ i.e., ψ_1 and ψ_2 are orthogonal.

(3) The eigen functions φ_i of a Hermitian operator form a complete set of functions if it is possible to expand any function, ψ that obeys the same boundary conditions as the eigen function.

$$\psi = c_1\varphi_1 + c_2\varphi_2 + c_3\varphi_3 + -- \qquad \textbf{i.e., } \psi = \Sigma c_i\, \varphi_i \textbf{ or,}$$

This is an important method of expanding a function in terms of a set of eigen functions.

Basic Postulates of Quantum Mechanical

Introduction:

Quantum mechanical calculations of observable properties are based on four postulates. These postulates cannot be derived or proved rather these are taken as **axioms.** However, these postulates form the basic format of quantum mechanics.

Postulate I: (Construction of quantum mechanical operators)

Examples of Physical Properties: Every physical property (observable) of a system has a corresponding quantum mechanical operator. These operators are **linear** and **Hermitian**. The physically measurable properties of a system are position (q), momentum (p), kinetic energy (T), potential energy (V), total energy (E), angular momentum (L), etc.

Rules for Setting Quantum Mechanical Operators: Rules for setting up a quantum mechanical operator for a physical property are given below:

(1) First, the physical property is to be expressed as a function of Cartesian coordinates and corresponding momenta i.e., the property is expressed in terms of position coordinates (x, y, z) and corresponding momenta (p_x, p_y, p_z).

(2) These position coordinates and momenta are then replaced by corresponding operators.

(3) Operator for a position coordinate (say, q) is multiplied by that variable itself i.e., $\hat{q} = q$.

(4) Operator for a momentum p_q, say $\hat{p}_q = \frac{h}{2\pi i}\frac{d}{dq} = -i\hbar\frac{d}{dq}$. $\frac{d}{dq}$ in the operator is the 1st derivative with respect to q.

Formulation of $\hat{p}_q$: The formulation of $\hat{p}_q$ operator can be obtained from the differential equation of standing wave along q- axis (as for example, q- axis can be taken as x- axis).

The wave equation is $\frac{d^2\psi(x)}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi(x)$. But de Broglie relation is, $\lambda = \frac{h}{p_x^2}$,

so, $\frac{d^2\psi(x)}{dx^2} = -\frac{4\pi^2 p_x^2}{h^2}\psi(x) = \frac{i^2 p_x^2}{\hbar^2}\psi(x)$ or, $\frac{\hbar^2}{i^2}\frac{d^2}{dx^2}\psi(x) = p_x^2\psi(x)$. This shows that p_x^2 is the eigen value of the operator $\frac{\hbar^2}{i^2}\frac{d^2}{dx^2}$ for the eigen function $\psi(x)$. Thus the operator of p_x is $\frac{\hbar}{i}\frac{d}{dx}$ But $(-) = i^2$, so the operator, $\hat{p}_x = -i\hbar\frac{d}{dx}$ in the (+ve) direction.

Other linear momentum operators are $\hat{p}_y = -i\hbar\frac{d}{dy}$ and $\hat{p}_z = -i\hbar\frac{d}{dz}$.

(1) Construction of Hamiltonian operator (energy operator)

[The Hamiltonian reflects the contribution made by Sir William Rowan Hamilton to the formulation of mechanics during the nineteenth century (1805 – 1865)] can be made by using the above rules.

Energy of the system, E = KE + PE = $\frac{p_x^2}{2m} + V(x)$, when the system acts along x- axis.

Replacing by operators, $\hat{H} = \frac{1}{2m}\left(-i\hbar \, {}^{d}\!/_{dx}\right)^2 + \hat{V}(x)$ or, $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \hat{V}(x)$.

In three dimensions, the Hamiltonian operator is $\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \hat{V}(x, y, z)$

or, $\hat{H} = -\dfrac{\hbar^2}{2m}\nabla^2 + \hat{V}(x,y,z)$

(a) For one-dimensional box, $V(x)$ = 0, so $\hat{H} = -\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2}$.

(b) For one-dimensional simple harmonic oscillator, $\hat{V} = \dfrac{1}{2}kx^2$, so $\hat{H} = -\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2} + \dfrac{1}{2}kx^2$.

(c) For H-atom, $\hat{H} = -\dfrac{\hbar^2}{2\mu}\nabla^2 - \dfrac{e^2}{r}$, where μ is reduced mass of H-atom and PE, $\hat{V} = -\dfrac{e^2}{r}$.

In polar coordinates, $\hat{H} = -\dfrac{\hbar^2}{2\mu}\left[\dfrac{1}{r^2}\dfrac{\partial}{\partial r}\left(r^2\dfrac{\partial}{\partial r}\right) + \dfrac{1}{r^2\sin\theta}\dfrac{\partial}{\partial\theta}\left(\sin\theta\dfrac{\partial}{\partial\theta}\right) + \dfrac{1}{r^2\sin^2\theta}\dfrac{\partial^2}{\partial\varphi^2}\right] - \dfrac{e^2}{r}$.

(d) For rigid rotator (PE = 0), $\hat{H} = -\dfrac{\hbar^2}{2\mu}\left(\dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2}\right)$.

In polar coordinates, $\hat{H} = -\dfrac{\hbar^2}{2\mu r^2}\dfrac{d^2}{d\varphi^2} = -\dfrac{\hbar^2}{2I}\dfrac{d^2}{d\varphi^2}$, where $I = \mu r^2$, moment of inertia.

(e) For He-atom (two-electron system), $\hat{H} = -\dfrac{\hbar^2}{2\mu}\left[\nabla_1^2 + \nabla_2^2\right] - \dfrac{2e^2}{r_1} - \dfrac{2e^2}{r_2} + \dfrac{e^2}{r_{12}}$.

(f) For a system of n particles, $\hat{H} = -\dfrac{h^2}{8\pi^2}\Sigma\dfrac{1}{m_i}\nabla_i^2 + \hat{V}(x,y,z) = -\dfrac{\hbar^2}{2}\Sigma\dfrac{1}{m_i}\nabla_i^2 + \hat{V}(x,y,z)$,

where m_i is the mass and ∇_i^2 the Laplacian operator of the i th particle.

(2) Construction of kinetic energy operator in one dimension is given as

$$T = \frac{p_x^2}{2m} \text{ so, } \hat{T} = \frac{1}{2m}\left(-i\hbar\, {d}/{dx}\right)^2 \text{ or, } \hat{T} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}.$$

(3) Construction of Angular momentum operators $\left(\hat{L}_x, \hat{L}_y, \hat{L}_z\right)$.

Angular momentum (L) is very important physical quantity for rotating system.

Classically, it is obtained by the cross vector product of position $\left(\vec{r}\right)$ and linear momentum $\left(\vec{p}\right)$.

i.e., $\vec{L} = \vec{r} \times \vec{p}$. If $\vec{i}, \vec{j}, \vec{k}$ are the unit vectors along x, y and z respectively, then we have $\vec{r} = \vec{i}\,x + \vec{j}\,y + \vec{k}\,z$, $\vec{p} = \vec{i}\,p_x + \vec{j}\,p_y + \vec{k}\,p_z$ and $\vec{L} = \vec{i}\,L_x + \vec{j}\,L_y + \vec{k}\,L_z$.

So, $\vec{L} = \vec{i}\,L_x + \vec{j}\,L_y + \vec{k}\,L_z = \left(\vec{i}\,x + \vec{j}\,y + \vec{k}\,z\right) \times \left(\vec{i}\,p_x + \vec{j}\,p_y + \vec{k}\,p_z\right)$. Thus $L = \begin{vmatrix} i & j & k \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$

$$= \vec{i}\left(yp_z - zp_y\right) + \vec{j}\left(zp_x - xp_z\right) + \vec{k}\left(xp_y - yp_x\right).$$

Equating, we get the formulation of the angular momentum in classical coordinates, as

$$L_x = yp_z - zp_y,\ L_y = zp_x - xp_z \text{ and } L_z = xp_y - yp_x.$$

Replacing by the corresponding operators of position and momentum, we have the angular momentum operators as

$$\hat{L}_x = \frac{h}{2\pi i}\left(y.\frac{\partial}{\partial z} - z.\frac{\partial}{\partial y}\right),\ \hat{L}_y = \frac{h}{2\pi i}\left(z.\frac{\partial}{\partial x} - x.\frac{\partial}{\partial z}\right) \text{ and } \hat{L}_z = \frac{h}{2\pi i}\left(x.\frac{\partial}{\partial y} - y.\frac{\partial}{\partial x}\right) = \frac{h}{2\pi i}\frac{\partial}{\partial\varphi}$$

or, $\hat{L}_x = -i\hbar\left(y.\dfrac{\partial}{\partial z} - z.\dfrac{\partial}{\partial y}\right)$, $\hat{L}_y = -i\hbar\left(z.\dfrac{\partial}{\partial x} - x.\dfrac{\partial}{\partial z}\right)$ and $\hat{L}_z = -i\hbar\left(x.\dfrac{\partial}{\partial y} - y.\dfrac{\partial}{\partial x}\right) = -i\hbar\dfrac{\partial}{\partial\varphi}$.

Commutator of angular momenta is given as

$$\left[\hat{L}_x,\hat{L}_y\right]=\left(\hat{L}_x\hat{L}_y-\hat{L}_y\hat{L}_x\right)=-i\hbar\left[\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)-\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)\right]$$

$$-i\hbar\left[\left(y\frac{\partial}{\partial z}.z\frac{\partial}{\partial x}-y\frac{\partial}{\partial z}.x\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}.z\frac{\partial}{\partial x}+z\frac{\partial}{\partial y}.x\frac{\partial}{\partial z}\right)-\left(z\frac{\partial}{\partial x}.y\frac{\partial}{\partial z}-z\frac{\partial}{\partial x}.z\frac{\partial}{\partial y}-x\frac{\partial}{\partial z}.y\frac{\partial}{\partial z}+x\frac{\partial}{\partial z}.z\frac{\partial}{\partial y}\right)\right]$$

$$=-i\hbar\left[y\frac{\partial}{\partial x}+yz\frac{\partial^2}{\partial z\partial x}-0-xy\frac{\partial^2}{\partial z^2}-0-z^2\frac{\partial^2}{\partial y\partial x}+0+xz\frac{\partial^2}{\partial y\partial z}-0-yz\frac{\partial^2}{\partial x\partial z}+0+z^2\frac{\partial^2}{\partial x\partial y}+0+xy\frac{\partial^2}{\partial z^2}-x\frac{\partial}{\partial y}-xz\frac{\partial^2}{\partial z\partial x}\right]$$

$$=i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)=i\hbar\hat{L}_z.$$

list of operators corresponding to the physical properties of the system is given here.

Physical properties	QM operators
Position (x)	x
$x-$comp. momentum (p_x)	$-i\hbar\frac{d}{dx}$
momentum (p)	$-i\hbar\nabla$
kinetic energy (T)	$-\frac{\hbar^2}{2m}\nabla^2$
$x-$component KE (T_x)	$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$

Physical properties	QM operators
potential energy (V)	$\hat{V}$
total energy (E)	$-\frac{\hbar^2}{2m}\nabla^2+\hat{V}\left(x,y,z\right)$ or, $-i\hbar\frac{d}{dt}$
$x-$comp. angular momentum	$-i\hbar\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$
$y-$comp. angular momentum	$-i\hbar\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)$
$z-$comp. angular momentum	$-i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$

Expressions of Some Operators:

(1) Expansion of the operator, $\left(x\frac{d}{dx}\right)^2$. Let the wave function be $\psi(x)$. Then

$$\left(x\frac{d}{dx}\right)^2\psi(x)=\left(x\frac{d}{dx}\right)x\frac{d\psi(x)}{dx}=x\left[\frac{d}{dx}\left\{x\frac{d\psi(x)}{dx}\right\}\right]=x\left[x\frac{d^2\psi(x)}{dx^2}+\frac{d\psi(x)}{dx}\right]$$

$$=x^2\frac{d^2\psi(x)}{dx^2}+x\frac{d\psi(x)}{dx}=\left[x^2\frac{d^2}{dx^2}+x\frac{d}{dx}\right]\psi(x)$$. Thus $\left(x\frac{d}{dx}\right)^2=x^2\frac{d^2}{dx^2}+x\frac{d}{dx}$.

(2) Expansion of the operator, $\left(\frac{d}{dx}.x\right)^2$. Let the wave function be $\psi(x)$.

Then $\left(\frac{d}{dx}.x\right)^2\psi(x)=\left(\frac{d}{dx}.x\right)\left(\frac{d}{dx}.x\right)\psi(x)=\left(\frac{d}{dx}.x\right)\frac{d\left\{x\psi(x)\right\}}{dx}=\left(\frac{d}{dx}.x\right)\left[x\frac{d\psi(x)}{dx}+\psi(x)\right]$

$$=\frac{d}{dx}\left[x^2\frac{d\psi(x)}{dx}+x\psi(x)\right]=x^2\frac{d^2\psi(x)}{dx^2}+2x\frac{d\psi(x)}{dx}+x\frac{d\psi(x)}{dx}+\psi(x)$$

$$=\left[x^2\frac{d^2}{dx^2}+3x\frac{d}{dx}+1\right]\psi(x)$$. Thus, $\left(\frac{d}{dx}.x\right)^2=x^2\frac{d^2}{dx^2}+3x\frac{d}{dx}+1$.

(3) Expansion of the operator $\left(x\frac{d}{dx}\right)^2$: Let the function be ψ that depends on x.

Then $\left(\frac{d}{dx}+x\right)^2\psi=\left(\frac{d}{dx}+x\right)\left(\frac{d}{dx}+x\right)\psi=\left(\frac{d}{dx}+x\right)\left(\frac{d\psi}{dx}+x\psi\right)=\frac{d}{dx}\left(\frac{d\psi}{dx}+x\psi\right)+x\frac{d\psi}{dx}+x^2\psi$

$$= \frac{d^2\psi}{dx^2} + x\frac{d\psi}{dx} + \psi + x\frac{d\psi}{dx} + x^2\psi = \left(\frac{d^2}{dx^2} + 2x\frac{d}{dx} + x^2 + 1\right)\psi .$$

So, Thus $\left(\frac{d}{dx} + x\right)^2 = \frac{d^2}{dx^2} + 2x\frac{d}{dx} + x^2 + 1$.

Non-commuting Operators: When a physical quantity contains a product of a Cartesian coordinate and its conjugate momentum (such as $x p_x$), we face the problem of non-commutativity in constructing the correct quantum mechanical operator. Several different rules have been proposed to solve this problem.
Construction of quantum mechanical operator is difficult for the physical property that contains non-Cartesian coordinates.

Postulate II:

The exact or precise value of physical quantities (like energy, momentum, angular momentum, etc) of a given state of the system is obtained by the eigen value of the operator equation.
This is called **eigen value equation** and it is

$$\hat{A}\psi_i = \lambda_i \psi_i \ ,$$

where $\hat{A}$ is the operator of the physical quantity λ_i . For the quantum mechanical system, the operator $\hat{A}$ must be linear and Hermitian and the wave function is well-behaved.
λ_i is the eigen value of the physical property of the i th state of the system.

When the eigen value equation is satisfied, the physical quantity obtained is exact and precise. The eigen function and the operator may be real or imaginary but the eigen value is always real since the operator is Hermitian in nature. The eigen value represents the magnitude of the physical property.

If the eigen value equation is not satisfied for a physical quantity, then we get a spread jin the measured values of the property. In that case, we remain satisfied with the average value of the property.

Example: The wave function of the ground state of 1D simple harmonic oscillator (SHO) is given by

$$\psi(x) = Ae^{-\beta x^2/2} \text{ and } \beta = \hbar^{-1}\sqrt{\mu k} .$$

Show that the KE of the system does not satisfy the eigen value equation. But the total energy (E) satisfies the equation. The operator of KE ($\hat{T}$) is $-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}$, hence

(i) $\hat{T}\psi(x) = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}\left(Ae^{-\beta x^2/2}\right) = -\frac{\hbar^2}{2\mu}\frac{d}{dx}\left[Ae^{-\beta x^2/2}\left(-\frac{2\beta x}{2}\right)\right] = \frac{\hbar^2\beta}{2\mu}\left[\frac{d}{dx}\left(xAe^{-\beta x^2/2}\right)\right]$

$$= \frac{\hbar^2\beta}{2\mu}\left[Ae^{-\beta x^2/2} + xAe^{-\beta x^2/2}\left(-\frac{2\beta x}{2}\right)\right] = \frac{\hbar^2\beta}{2\mu}\left(1-\beta x^2\right)Ae^{-\beta x^2/2}$$

$= \frac{\hbar^2\beta}{2\mu}\left(1-\beta x^2\right)\psi(x) \neq \text{constant } \times\psi(x)$. The eigen value equation is not satisfied.

(ii) The energy operator, $\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$,

so $\hat{H}\psi(x) = \left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right)\psi(x) = -\frac{\hbar^2}{2\mu}\frac{d^2\psi(x)}{dx^2} + \left(\frac{1}{2}kx^2\right)\psi(x)$

$$= \frac{\hbar^2}{2\mu}\beta\left(1-\beta x^2\right)\psi(x) + \frac{1}{2}kx^2\psi(x) = \left[\frac{\hbar^2}{2\mu}\left(\beta - \beta^2 x^2\right) + \frac{1}{2}kx^2\right]\psi(x)$$

$$= \left[\frac{\hbar^2}{2\mu}\left\{\hbar^{-1}\sqrt{\mu k} - \hbar^{-2}(\mu k)x^2\right\} + \frac{1}{2}kx^2\right]\psi(x)$$

$$= \left[\frac{\hbar^2}{2\mu}\times\hbar^{-1}\sqrt{\mu k} - \frac{\hbar^2}{2\mu}\times\hbar^{-2}(\mu k)x^2 + \frac{1}{2}kx^2\right]\psi(x)$$

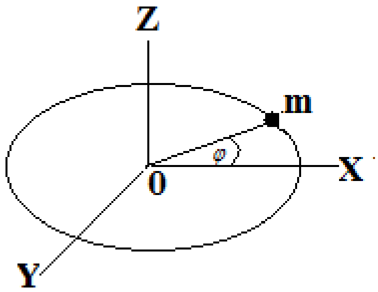
$$= \left[\frac{\hbar}{2}\sqrt{k/\mu} - \frac{1}{2}kx^2 + \frac{1}{2}kx^2\right]\psi(x) = \left[\frac{1}{2}\frac{h}{2\pi}\sqrt{\frac{k}{\mu}}\right]\psi(x) = \left(\frac{1}{2}h\nu_0\right)\psi(x).$$

This shows that the total energy of 1D SHO is constant and the eigen value equation is satisfied.

Its value in the ground state is $E_0 = \frac{1}{2}h\nu_0$. But the KE (T) of the system does not yield constant value. Its value varies with x.

One example of solving eigen value equation: When the eigen value equation is constructed for a given property of the system, the eigen function and eigen value can be obtained by solving the eigen value equation.

As for example, let us consider a rotating system. A particle is rotating in the xy plane along the fixed z - axis. Let us consider L_z (z - component angular momentum), the property of the system.



The eigen value equation if the property is $\hat{L}_z\psi(\varphi) = L_z\psi(\varphi)$.

But the operator of L_z is $\hat{L}_z = -i\hbar\frac{d}{d\varphi}$. φ is the azimuthal angle which is changing with the rotation of the particle and its limit is 0 to 2π. Thus the eigen value equation for L_z is $-i\hbar\frac{d\psi(\varphi)}{d\varphi} = L_z\psi(\varphi)$ or,

$\frac{d\psi(\varphi)}{\psi(\varphi)} = -\frac{L_z}{i\hbar}d\varphi$. Integrating, we get $\int\frac{d\psi(\varphi)}{\psi(\varphi)} = -\frac{L_z}{i\hbar}\int d\varphi = \frac{iL_z}{\hbar}\int d\varphi$

or, $ln\psi(\varphi) = (iL_z/\hbar)\varphi + ln A$ (integration constant) or, $\psi(\varphi) = Ae^{(iL_z/\hbar)\varphi}$.

Let $(L_z/\hbar) = m$ so, $\psi(\varphi) = Ae^{im\varphi}$. The value of A is obtained from the normalisation condition,

$\int_0^{2\pi}|\psi(\varphi)|^2 d\varphi = 1$ or, $\int_0^{2\pi}\psi(\varphi)\psi(\varphi)^* d\varphi = 1$ or, $A^2\int_0^{2\pi}e^{im\varphi}\times e^{-im\varphi}d\varphi = 1$ or, $A^2\int_0^{2\pi}d\varphi = 1$

or, $A = \left(1/\sqrt{2\pi}\right)$. Thus the normalised eigen function of the system is $\psi(\varphi) = \left(1/\sqrt{2\pi}\right)e^{im\varphi}$.

Again, $(L_z/\hbar) = m$ or, $L_z = m\hbar$. The values of m can be obtained from the condition $\psi(\varphi) = \psi(2\pi + \varphi)$, hence $Ae^{im\varphi} = Ae^{im(2\pi+\varphi)} = Ae^{im\varphi}\times e^{2\pi im}$ or, $e^{2\pi im} = 1$

or, $\cos 2\pi m + i\sin 2\pi m = 1$. This equation is satisfied when $m = 0, \pm1, \pm2, \pm3$, etc.

Therefore solving the L_z - eigen value equation, we get the eigen function, $\psi(\varphi) = \left(1/\sqrt{2\pi}\right)e^{im\varphi}$ and the eigen value, $L_z = m\hbar$, where $m = 0, \pm1, \pm2, \pm3$, etc.

For total energy of the system, the eigen value equation is $\hat{H}\psi(\varphi) = E\psi(\varphi)$, where $\hat{H}$ is the Hamiltonian operator of the rigid rotator and $\hat{H} = -\frac{\hbar^2}{2mr^2}\frac{d^2}{d\varphi^2}$ Using the above normalised function of the system,

$\psi(\varphi) = \left(1/\sqrt{2\pi}\right)e^{im\varphi}$, we can get the energy of the rigid rotator, $E = \left(m^2\right)\frac{\hbar^2}{2mr^2}$ or, $E = \left(m^2\right)\frac{\hbar^2}{2I}$, where I = moment of inertia of the system = mr^2.

Other examples:

(1) Calculate the energy of a particle in 1D box of length L if the wave function is $\psi = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$.

(2) A certain system is described by the Hamiltonian operator $\hat{H} = -\frac{d^2}{dx^2} + x^2$. If $\psi = Axe^{-x^2/2}$, calculate the energy value of the system. **[Ans. 3]**

Problem: A solution of a free particle Schrodinger equation $-\dfrac{h^2}{8\pi^2 m}\dfrac{d^2\psi(x)}{dx^2} = E\psi(x)$ is $\psi(x) = e^{ikx} = \cos kx + i\sin kx$.

(a) Derive the expression for energy 'E' and momentum 'p' of the particle.

(b) Using the above relations, show that the wave length (λ) is h/p. **[IIT-JAM, 2012]**

Solution: Putting the expression of $\psi(x)$ in the Schrodinger equation, we have

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\left(e^{ikx}\right)}{dx^2} = E\psi(x) \quad \text{or,} \quad -\frac{h^2}{8\pi^2 m}\frac{d^2\left(e^{ikx}\right)}{dx^2} = -\frac{h^2}{8\pi^2 m}\left(i^2k^2\right)e^{ikx} = \left(k^2\right)\frac{h^2}{8\pi^2 m}\psi(x).$$

Equating with the Schrodinger equation, we have $E = \left(k^2\right)\dfrac{h^2}{8\pi^2 m}$. Again, E = KE + PE

but for the free particle, PE = 0. So E = KE = $\dfrac{p^2}{2m}$. Thus, $\dfrac{p^2}{2m} = \left(k^2\right)\dfrac{h^2}{8\pi^2 m}$ or, $p = k\left(\dfrac{h}{2\pi}\right)$.

(b) Condition for $\psi(x)$ is that $\psi(x) = \psi(\lambda + x)$ or, $e^{ikx} = e^{ik(\lambda+x)} = e^{ikx}\times e^{ik\lambda}$ or, $e^{ik\lambda} = 1$.

or, $\cos k\lambda + i\sin k\lambda = 1$. This is possible only when $k\lambda = 2\pi$ or, $k = 2\pi/\lambda$. But $p = k\left(\dfrac{h}{2\pi}\right)$

so, putting the expression of k, we have $p = \left(\dfrac{2\pi}{\lambda}\right)\times\left(\dfrac{h}{2\pi}\right)$ or, $\lambda = \left(\dfrac{h}{p}\right)$.

Postulate III

Introduction: The second postulate states that $\hat{A}\psi = \lambda\psi$. However, the eigen value (λ) can not be written as $\lambda = \dfrac{\hat{A}\psi}{\psi}$, because $\dfrac{\hat{A}\psi}{\psi}$ is the function of coordinates (x, y, z) of the system so its value varies from point to point of the system and it cannot be equated to a constant, λ.

But if the numerator and denominator on the right hand side are multiplied by ψ^* and integrated over the entire space accessible to the system, then the expression $\int\psi^*\hat{A}\psi\,d\tau \Big/ \int\psi^*\psi\,d\tau$ is no longer a function of coordinates (as it is definite integral). It is approximated to the average value of the property λ.

This leads to the third postulate when a great many measurements of any observable represented by the operator, $\hat{A}$ are made on a certain system defined by the function, ψ, the average value obtained as $\bar{\lambda} = \dfrac{\int\psi^*\hat{A}\psi\,d\tau}{\int\psi^*\psi\,d\tau}$, the bar over λ is used to indicate the average value of the property.

When λ is the eigen value to the operator $\hat{A}$ for the system characterised by the wave function, ψ, $\bar{\lambda}$ becomes λ.

$$\bar{\lambda} = \frac{\int\psi^*\left(\hat{A}\psi\right)d\tau}{\int\psi^*\psi\,d\tau} = \frac{\int\psi^*\left(\lambda\psi\right)d\tau}{\int\psi^*\psi\,d\tau} = \lambda\frac{\int\psi^*\psi\,d\tau}{\int\psi^*\psi\,d\tau} = \lambda.$$

Dirac has introduced bracket notation as $\langle\lambda\rangle = \dfrac{\langle\psi|\hat{A}|\psi\rangle}{\langle\psi|\psi\rangle}$. $\hat{A}$ is sandwiched between ψ^* and ψ. It may be read as bracketed ψ^* bar $\hat{A}$ bar ψ. When the wave function is normalised $\langle\psi|\psi\rangle = 1$ and the postulate is written as $\langle\lambda\rangle = \langle\psi|\hat{A}|\psi\rangle$. $\langle\lambda\rangle$ denotes the expectation value of the property represented by the operator $\hat{A}$ when a series of measurements carried out on the system or a single measurement carried out on some identical systems described by the same state function ψ.

When the physical property of the system does not produce exact or precise value, its expectation or average value is determined by the use of this postulate.

Examples:

(1) Let us take the physical quantity, position (x) in a 1D box system. This quantity varies from place to place while moving within the box and we can calculate the average value of the position only.

$\langle x\rangle = \int_0^L \psi\hat{x}\psi dx$. This function ψ is normalised and its expression, $\psi = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$.

Thus, $\langle x\rangle = \frac{2}{L}\int_0^L x\sin^2\frac{n\pi x}{L}dx = \frac{1}{L}\int_0^L x\left(1-\cos\frac{2n\pi x}{L}\right)dx = \frac{1}{L}\int_0^L xdx - \frac{1}{L}\int_0^L x\cos\frac{2n\pi x}{L}dx$

$= \frac{1}{L}\times\left[\frac{x^2}{2}\right]_0^L - 0 = \frac{L}{2}$. That is $\langle x\rangle = L/2$. This show that the expectation location of the particle is at the middle point of the box.

(2) A rotating system is defined by a function, $\psi = \left(1/\sqrt{\pi}\right)\cos 2\varphi$. Find the average value of the angular momentum, p_φ which is defined by the operator is $\hat{p}_\varphi = \frac{h}{2\pi i}\frac{d}{d\varphi}$.

$$\langle p_\varphi\rangle = \int_0^{2\pi}\psi\hat{p}_\varphi\psi d\varphi = \int_0^{2\pi}\frac{1}{\sqrt{\pi}}\cos 2\varphi\left(\frac{h}{2\pi i}\frac{d}{d\varphi}\right)\frac{1}{\sqrt{\pi}}\cos 2\varphi d\varphi = \frac{h}{2\pi^2 i}\int_0^{2\pi}\cos 2\varphi(-2\sin 2\varphi)d\varphi$$

$$= -\frac{h}{2\pi^2 i}\int_0^{2\pi}2\sin 2\varphi\cos 2\varphi d\varphi = \frac{ih}{2\pi^2}\int_0^{2\pi}\sin 4\varphi d\varphi = \frac{ih}{2\pi^2}\left[-\frac{\cos 4\varphi}{4}\right]_0^{2\pi}$$

$= -\frac{ih}{8\pi^2}\left[\cos 8\pi - \cos 0\right]_0^{2\pi} = 0$. The average angular momentum of the system, $\langle p_\varphi\rangle = 0$.

(3) Find the expectation value of KE (T) of 1D SHO given by the state function $\psi(x) = Ae^{-\beta x^2/2}$ and $\beta = \hbar^{-1}\sqrt{\mu k}$.

The expectation value of KE, $\langle T\rangle = \frac{\langle\psi|\hat{T}|\psi\rangle}{\langle\psi|\psi\rangle}$ and KE operator, $\hat{T} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}$.

First we calculate $\langle\psi|\psi\rangle = \int_{-\infty}^{+\infty}A^2e^{-\beta x^2}dx = A^2\times 2\int_0^{+\infty}e^{-\beta x^2}dx = 2A^2\times\frac{\Gamma(1/2)}{2\beta^{1/2}} = A^2\sqrt{\frac{\pi}{\beta}}$. Then

$$\langle\psi|\hat{T}|\psi\rangle = \int_{-\infty}^{+\infty}Ae^{-\beta x^2/2}\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}\left(Ae^{-\beta x^2/2}\right)\right]dx = A^2\left(-\frac{\hbar^2}{2\mu}\right)\int_{-\infty}^{+\infty}e^{-\beta x^2/2}\left[\frac{d}{dx}\left\{\frac{d}{dx}\left(e^{-\beta x^2/2}\right)\right\}\right]dx$$

$$= A^2\left(-\frac{\hbar^2}{2\mu}\right)\int_{-\infty}^{+\infty}e^{-\beta x^2/2}\left[\frac{d}{dx}e^{-\beta x^2/2}(-\beta x)\right]dx = A^2\left(\frac{\hbar^2\beta}{2\mu}\right)\int_{-\infty}^{+\infty}e^{-\beta x^2/2}\left[\frac{d}{dx}\left(xe^{-\beta x^2/2}\right)\right]dx$$

$$= A^2\left(\frac{\hbar^2\beta}{2\mu}\right)\int_{-\infty}^{+\infty}e^{-\beta x^2/2}\left[e^{-\beta x^2/2} + xe^{-\beta x^2/2}(-\beta x)\right]dx = A^2\left(\frac{\hbar^2\beta}{2\mu}\right)\left[\int_{-\infty}^{+\infty}e^{-\beta x^2/2}dx - \beta\int_{-\infty}^{+\infty}x^2e^{-\beta x^2/2}dx\right]$$

$$= A^2\left(\frac{\hbar^2\beta}{2\mu}\right)\left[2\times\int_0^{+\infty}e^{-\beta x^2}dx - 2\beta\int_0^{+\infty}x^2e^{-\beta x^2}dx\right] = A^2\left(\frac{\hbar^2\beta}{2\mu}\right)\left[2\times\frac{\Gamma(1/2)}{2\beta^{1/2}} - 2\beta\times\frac{\Gamma(3/2)}{2\beta^{3/2}}\right]$$

$$= A^2\left(\frac{\hbar^2\beta}{2\mu}\right)\left[\sqrt{\frac{\pi}{\beta}} - \frac{1}{2}\sqrt{\frac{\pi}{\beta}}\right] = A^2\left(\frac{\hbar^2\beta}{2\mu}\right)\times\frac{1}{2}\sqrt{\frac{\pi}{\beta}} = A^2\left(\frac{\hbar^2\beta}{4\mu}\right)\sqrt{\frac{\pi}{\beta}}.$$

Now, $\langle T\rangle = \frac{\langle\psi|\hat{T}|\psi\rangle}{\langle\psi|\psi\rangle} = A^2\left(\frac{\hbar^2\beta}{4\mu}\right)\sqrt{\frac{\pi}{\beta}}\Big/A^2\sqrt{\pi/\beta} = \frac{\hbar^2\beta}{4\mu} = \frac{\hbar^2}{4\mu}\times\hbar^{-1}\sqrt{\mu k} = \frac{\hbar}{4}\sqrt{\frac{k}{\mu}}$

$$= \frac{1}{4} h \times \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{4} h\nu_0 .$$ Hence, $\langle T \rangle = \frac{1}{4} h\nu_0$. Total energy $E = \frac{1}{2} h\nu_0$.

Thus the average PE, $V = E - \langle T \rangle = \frac{1}{2} h\nu_0 - \frac{1}{4} h\nu_0 = \frac{1}{4} h\nu_0$.

Problem: Calculate the expectation value of the potential energy for a H-atom in the ground state. Show that the average KE is equal to the total energy with the change in sign.

[Given, $\psi_{1s}(H) = \left(\pi a_0^3\right)^{-1/2} e^{-r/a_0}$] **[Burdwan Univ. 2012]**

Solution: The average PE, $\langle V \rangle = \int \psi_{1s} \hat{V} \psi_{1s} d\tau = \left(\pi a_0^3\right)^{-1} \int e^{-r/a_0} \left(-\frac{e^2}{r}\right) e^{-r/a_0} \, r^2 dr \sin\theta d\theta d\varphi$

$$= \left(\pi a_0^3\right)^{-1}\left(-e^2\right) \int_0^{\infty} e^{-2r/a_0} \, r dr \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\varphi = \left(\pi a_0^3\right)^{-1}\left(-e^2\right) \frac{\Gamma(2)}{\left(2/a_0\right)^2} \times 2 \times 2\pi$$

$$= -\frac{1}{\pi a_0^3} \times e^2 \times \frac{a_0^2}{4} \times 4\pi = -\frac{e^2}{a_0}$$. Thus, expectation value of PE, $\langle V \rangle = -\frac{e^2}{a_0}$.

Again, total energy, $E = -\frac{e^4 m}{2\hbar^2}$, but $a_0 = \frac{\hbar^2}{e^2 m}$.

Putting, $E \times a_0 = -\frac{e^4 m}{2\hbar^2} \times \frac{\hbar^2}{e^2 m} = -\frac{e^2}{2}$ so, $E = -\frac{e^2}{2a_0}$.

Thus, $\langle T \rangle = E - \langle V \rangle = -\frac{e^2}{2a_0} + \frac{e^2}{a_0} = \frac{e^2}{2a_0}$. Hence $\langle T \rangle = \frac{e^2}{2a_0}$.

This proves that average KE is equal to total energy with change in sign.

Example (4):

The average value of a physical quantity (say, E) of a state obtained by mixing two states defined by wave functions ψ_1 and ψ_2 can be calculated by the use of this postulate III.

The resultant wave function of the mixed up state is obtained by linear combination of ψ_1 and ψ_2,

$$\psi = c_1 \psi_1 + c_2 \psi_2 ,$$

where c_1 and c_2 are the contributing factors of ψ_1 and ψ_2 towards the mixed-up state function ψ.

The average energy value of the mixed-up state is $\bar{E} = \frac{\int \psi \hat{H} \psi d\tau}{\int \psi \psi d\tau}$,

Let E_1 and E_2 are the energy eigen values of the two states defined by ψ_1 and ψ_2,

so $\hat{H}\psi_1 = E_1 \psi_1$ and $\hat{H}\psi_2 = E_2 \psi_2$. $\hat{H}$ is also a Hermitian operator, so $\int \psi_1 \hat{H} \psi_2 d\tau = \int \psi_2 \hat{H} \psi_1 d\tau$

and ψ_1 and ψ_2 are orthonormal so $\int \psi_1^2 d\tau = 1$ and $\int \psi_2^2 d\tau = 1$, and $\int \psi_1 \psi_2 d\tau = 0$.

$$\bar{E} = \frac{\int \left(c_1 \psi_1 + c_2 \psi_2\right) \hat{H} \left(c_1 \psi_1 + c_2 \psi_2\right) d\tau}{\int \left(c_1 \psi_1 + c_2 \psi_2\right)^2 d\tau}$$

$$= \frac{c_1^2 \int \psi_1 \hat{H} \psi_1 d\tau + c_1 c_2 \int \psi_1 \hat{H} \psi_2 d\tau + c_1 c_2 \int \psi_2 \hat{H} \psi_1 d\tau + c_2^2 \int \psi_2 \hat{H} \psi_2 d\tau}{c_1^2 \int \psi_1^2 d\tau + 2c_1 c_2 \int \psi_1 \psi_2 d\tau + c_2^2 \int \psi_2^2 d\tau}$$

$$= \frac{c_1^2 \int \psi_1 E_1 \psi_1 d\tau + 2c_1 c_2 \int \psi_1 \hat{H} \psi_2 d\tau + c_2^2 \int \psi_2 E_2 \psi_2 d\tau}{c_1^2 + c_2^2}$$

$$= \frac{c_1^2 E_1 \int \psi_1 \psi_1 d\tau + 2c_1 c_2 \int \psi_1 E_2 \psi_2 d\tau + c_2^2 E_2 \int \psi_2 \psi_2 d\tau}{c_1^2 + c_2^2} = \frac{c_1^2 E_1 + 2c_1 c_2 E_2 \int \psi_1 \psi_2 d\tau + c_2^2 E_2}{c_1^2 + c_2^2}$$

This average energy of the mixed-up state, $\bar{E}=\left(\frac{c_1^2}{c_1^2+c_2^2}\right)E_1+\left(\frac{c_2^2}{c_1^2+c_2^2}\right)E_2$, where

$\frac{c_1^2}{c_1^2+c_2^2}$ and $\frac{c_2^2}{c_1^2+c_2^2}$ are the contributing factors of E_1 and E_2 respectively of the energy of the resulting mixed-up state.

(4) Find the expectation value of x for the state described by $\psi = Axe^{-x^2/2}$. **[Ans. 0]**

Postulate IV

Time-dependent Schrodinger equation is considered as one postulate. The equation is,

$$\hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t}\ ,$$

where $\hat{H}=-\frac{\hbar^2}{2m}\nabla^2+\hat{V}$ and ψ is a function of $(x, y, z \textit{ and } t)$ i.e., ψ is a function of space coordinate (q) and time (t). The PE (V) is a function of space coordinate only and assumed to be time-independent. However, if the force existing in the system varies with time then V will also vary with time. When x is taken the space coordinate and t the time, the time-dependent Schrodinger equation is

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+\hat{V}(x)\right]\psi(x,t)=i\hbar\frac{\partial\psi(x,t)}{\partial t}.$$

Schrodinger equation is a quantum mechanical analog of Newton's 2nd law of motion:

Time-dependent Schrodinger equation contains the first derivative of ψ with respect to t, $(\partial\psi/\partial t)$.
Thus, single integration with respect to time yields the value of ψ at another time for the system.
That is, if one knows the value of ψ at one time, with also the knowledge of V, he can find the value of ψ at another time for the system. The future state o the system can be predicted from the value of a given state.
This time-dependent Schrodinger equation is the quantum mechanical analog of the Newton's second law.
However quantum mechanics predicts the probable state while classical mechanics predicts the state definitely.

Separation of $\psi(x)$ and $\psi(t)$:

Time-dependent Schrodinger equation can be resolved into time-dependent and space-dependent Schrodinger equation when potential energy (V) does not vary with time.
Let the wave function is $\psi(x,t)=\psi(x)\times\psi(t)$. Putting in the time-dependent Schrodinger equation, and differentiating, we get $-\frac{\hbar^2}{2m}\psi(t)\frac{\partial^2\psi(x)}{\partial x^2}+\hat{V}(x)\psi(x)\times\psi(t)=i\hbar\,\psi(x)\frac{\partial\psi(t)}{\partial t}$

Dividing by $\psi(x)\times\psi(t)$, we have $\left[-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\partial^2\psi(x)}{\partial x^2}+\hat{V}(x)\right]=i\hbar\frac{1}{\psi(t)}\frac{\partial\psi(t)}{\partial t}$ = E (say).

Left hand side is independent of t and right hand side is independent of x, hence to satisfy such condition, each side of the equation may be equal to constant which does not depend on either x or t.
The dimension consideration shows that this constant is energy term (E) of the system.
Separating the two equations, we get

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2}+\hat{V}(x)=E \quad \text{or,} \quad \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\hat{V}(x)\right]\psi(x)=E\psi(x).$$

The other equation is $i\hbar\frac{1}{\psi(t)}\frac{d\psi(t)}{dt}=E$ or, $i\hbar\frac{d\psi(t)}{dt}=E\psi(t)$.

This shows that $i\hbar\frac{d}{dt}$ is also an energy operator for the eigen value equation, i.e. $\hat{E}=i\hbar\frac{d}{dt}$.

Solution of time-dependent equation: On solving the equation, we get the expression of $\psi(t)$.

$\int \frac{d\psi(t)}{\psi(t)} = \frac{E}{i\hbar}\int dt$ or, $ln\psi(t) = \frac{E}{i\hbar}t + ln\, A$ (integration constant) or, $\psi(t) = Ae^{Et/i\hbar}$.

Therefore, the wave function, $\psi(x,t) = \psi(x)Ae^{Et/i\hbar}$.

Stationary state: A stationary state is defined by wave function, $\psi(x,t)$ which is the product of two factors – one dependent of space coordinate and other dependent of time i.e.,

$$\psi(x,t) = \psi(x)\times\psi(t).$$

By stationary state we do not mean that particle or particles of the system are at rest but it implies that the probability density $|\psi|^2$ and the energy are independent of time at any point.

The probability density $|\psi(x,t)|^2 = \psi(x,t).\psi^*(x,t) = \psi(x,t) = A\psi(x)e^{Et/i\hbar}\times A^*\psi^*(x)e^{-Et/i\hbar}$

$= AA^*\psi(x)\psi^*(x)$ and this is time-independent.

The factor $e^{-Et/i\hbar}$ is of no significance and the essential part of the wave function, $\psi(x,t)$ is the time-independent wave function, $\psi(x)$.

Problem: Calculate the energy eigen value of the system defined by $\psi(x,t) = A\psi(x)e^{Et/i\hbar}$.

Solution: $\hat{E}\psi(x,t) = i\hbar\frac{\partial\psi(x,t)}{\partial t} = i\hbar\times A\psi(x).\frac{d}{dt}e^{Et/i\hbar} = i\hbar\times A\psi(x).\frac{d}{dt}e^{Et/i\hbar}\times\frac{E}{i\hbar}$

$= E\left[A\psi(x)e^{Et/i\hbar}\right] = E\,\psi(x,t)$. This energy value E is thus time-independent.

Problem: If ψ_1 and ψ_2 are the eigen functions of the operator, $\hat{H}$ with eigen values E_1 and E_2 respectively, then show that $\psi = c_1\psi_1 + c_2\psi_2$ is not an eigen function of $\hat{H}$ unless $E_1 = E_2$.

Solution: Given, $\hat{H}\psi_1 = E_1\psi_1$ and $\hat{H}\psi_2 = E_2\psi_2$. Now, $\hat{H}\psi = \hat{H}(c_1\psi_1 + c_2\psi_2) = c_1\hat{H}\psi_1 + c_2\hat{H}\psi_2$

or, $\hat{H}\psi = c_1E_1\psi_1 + c_2E_2\psi_2 \neq$ constant $\times(c_1\psi_1 + c_2\psi_2)$.

But, when $E_1 = E_2$, $\hat{H}\psi = c_1E\psi_1 + c_2E\psi_2 = E(c_1\psi_1 + c_2\psi_2) = E\psi$ and thus $\hat{H}\psi = E\psi$.

Thus, if ψ_1 and ψ_2 are the degenerate eigen functions of $\hat{H}$ then $(c_1\psi_1 + c_2\psi_2)$ is also the eigen function of $\hat{H}$ with same eigen value.

Problem: If ψ_1 and ψ_2 are solutions of Schrodinger equation, then show that $\psi = c_1\psi_1 + c_2\psi_2$ is also a solution when c_1 and c_2 are constant coefficients.

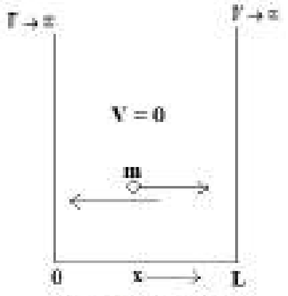
Solution: Let us consider time-dependent Schrodinger equation, then $\hat{H}\psi_1 = i\hbar\frac{\partial\psi_1}{\partial t}$ and $\hat{H}\psi_2 = i\hbar\frac{\partial\psi_2}{\partial t}$ as ψ_1 and ψ_2 are the solutions of the Schrödinger equation.

Now, $\hat{H}\psi = \hat{H}(c_1\psi_1 + c_2\psi_2) = c_1\hat{H}\psi_1 + c_2\hat{H}\psi_2 = c_1\times i\hbar\frac{\partial\psi_1}{\partial t} + c_2\times i\hbar\frac{\partial\psi_2}{\partial t}$

$= i\hbar\frac{\partial(c_1\psi_1)}{\partial t} + i\hbar\frac{\partial(c_2\psi_2)}{\partial t} = i\hbar\frac{\partial(c_1\psi_1 + c_2\psi_2)}{\partial t} = i\hbar\frac{\partial\psi}{\partial t}$.

Thus $\hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t}$. It proves that ψ is also a solution of the Schrodinger equation.

Particle in One-dimensional Box



Sketch of the system

Description of the system: Let us take a particle of mass m executing to-and –fro motion along x-axis in one-dimensional box of length L. The potential energy (V) within the box is zero i.e., no force is acting on the particle within the box except during the collision at the walls from which it rebounds elastically. The potential energy outside the box is very high $(V \to \propto)$. In other words, the particle is confined to move in the length L. The model is also called particle in a potential well as is compared with a frog in a deep well.
Since the potential is discontinuous (suddenly rises) at $x = 0$ and $x = L$, it is convenient to consider the Schrodinger equation inside and outside the box separately.
Schrodinger equation for the particle outside the box: Outside the box potential energy, $V \to \propto$, so the Schrodinger equation for the particle is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - \propto)\psi = 0 \text{ or, } \frac{d^2\psi}{dx^2} - \propto \psi = 0 \text{ or, } \psi = \frac{1}{\propto}.\frac{d^2\psi}{dx^2} \text{ or, } \psi = 0.$$

This means that the value of ψ outside the box is always zero. Hence probability density of finding the particle $|\psi|^2$ is also zero.

Schrodinger equation for the particle inside the box: Inside the box where $V = 0$, the Schrodinger equation is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - 0)\psi = 0 \text{ or, } \frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \text{ or, } \frac{d^2\psi}{dx^2} + k^2\psi = 0\text{, where } k^2 = \frac{2mE}{\hbar^2}.$$

The general solution of this differential equation is $\psi = A\sin kx + B\cos kx$, here A and B are arbitrary constants. However there are other solutions of the equation are e^{ikx}, e^{-ikx}, etc.
Now putting the boundary conditions, exact wave function for the system can formulated.
(i) when $x = 0$, $\psi = 0$, then the above general solution reduces to $0 = A\sin 0 + B\cos 0$
or, $0 = 0 + B$ or, $B = 0$.
Thus putting the 1st boundary condition, we get the expression of $\psi = A\sin kx$.
(ii) Now when $x = L$, again $\psi = 0$, hence the solution becomes $0 = A\sin kL$. Two possibilities may be considered , either $A = 0$ or, $\sin kL = 0$. But when $A = 0$, $\psi = 0$ at everywhere of the box and this indicates the probability density $|\psi|^2 = 0$ within the box irrespective of the value of x. This is not acceptable and called trivial solution. It is rejected. The other possibility is $\sin kL = 0 = \sin n\pi$,
where $n = 0, 1, 2, 3,$ etc, any positive integer including zero. But again n cannot be zero, because if n were to be zero and ψ would become zero everywhere.
So we get $kL = n\pi$ or $k = n\pi/L$. Putting the value of k, we get the appropriate wave function of the system

$$\psi_n = A\sin\frac{n\pi x}{L}.$$

Normalised wave function of the system: The value of A can be obtained from the use of normalisation condition, $\int_0^L \psi_n^2 dx = 1$. Thus $A^2\int_0^L \sin^2\frac{n\pi x}{L}dx = 1$ or, $\frac{A^2}{2}\int_0^L\left(1 - \cos\frac{2n\pi x}{L}\right)dx = 1$

$$\text{or, } \frac{A^2}{2}\int_0^L dx - \frac{A^2}{2}\int_0^L \cos\frac{2n\pi x}{L}dx = 1 \text{ or, } \frac{A^2}{2}[x]_0^L - \frac{A^2}{2}\left[\sin\frac{2n\pi x}{L}\right]_0^L \times \frac{L}{2n\pi} = 1 \text{ or, } \frac{A^2}{2} \times L - 0 = 1 \text{ or,}$$

$A = \sqrt{\frac{2}{L}}$. The normalised wave function of the system is thus $\psi_n = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$

The value of $n = 1, 2, 3$,etc i.e., any positive integer excluding zero. If n is taken equal to 0, then $\psi_n = 0$ in everywhere within the box(independent of position of x). But it is not acceptable as in that case ($n = 0$), the probability density becomes zero everywhere within the box. .

Energy of the system (E_n): We have the relation, $k = n\pi/L$ or, $k^2 = (n\pi/L)^2$,

but $k^2 = 2mE_n/\hbar^2$. Equating, we get $2mE_n/\hbar^2 = (n\pi/L)^2$.

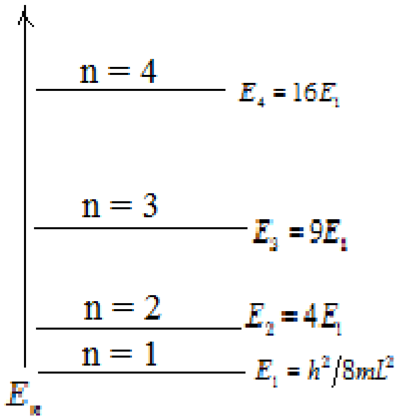
Thus the energy of the system, $E_n = n^2\left(\dfrac{\pi^2\hbar^2}{2mL^2}\right)$ or, $E_n = n^2\left(\dfrac{h^2}{8mL^2}\right)$.

We can extract some important information of the system from the above energy expression.

(1) The energy-value is seen to be independent of x. This means that in a given state (n = fixed), E_n will be same for every value of x. It refers that the particle has 'constant motion' in a given state. This E_n is KE only and so $E_n = p_x^2/2m$, so p_x is constant and v_x thus is same for any position x for fixed n.

(2) Again, E_n is independent of time. This means that in a given state (n = fixed), the energy of the particle remains constant at any time. This refers 'conservative motion' of the particle.

(3) The expression shows that energy of the system is quantised and the energy levels are not equispaced.



The quantisation is more prominent in the higher energy levels i.e. for higher value of n.

The energy spacing between two successive levels

$$\Delta E = E_{n+1} - E_n = (n+1)^2\frac{h^2}{8mL^2} - n^2\left(\frac{h^2}{8mL^2}\right)$$

or, $$\Delta E = (2n+1)\frac{h^2}{8mL^2}.$$

(4) **Zero-point energy (ZPE)** of the system can be obtained by putting $n=1$ (lowest value of n),

$$E_{Zero-point} = \frac{h^2}{8mL^2}.$$

This concludes that even at absolute zero temperature, the particle will be in motion, though in classical mechanics, the particle is at rest at 0K temperature.

Non-zero value of ZPE is in conformity with the Heisenberg uncertainty principle, $\Delta p_x \times \Delta x \approx h$.

If the particle would have zero energy, then its momentum (p_x) would be zero as $E = p_x^2/2m$.

With p_x having zero, $\Delta p_x = 0$ and so $\Delta x = h/\Delta p_x \to \propto$. But the particle must be somewhere within the box of length L.

Uncertainty Principle from ZPE: The particle may remain anywhere within the box. The error involved in a single measurement of position is thus L i.e., $\Delta x = L$.

Again, $E_{Zero-point} = \dfrac{h^2}{8mL^2} = \dfrac{p_x^2}{2m}$ or, $p_x = \pm\dfrac{h}{2L}$ i.e., p_x can have any value between $+p_x$ to $-p_x$, so $\Delta p_x = p_x - (-p_x) = 2p_x = 2\times\dfrac{h}{2L} = \dfrac{h}{L}$. Thus $\Delta p_x \times \Delta x = \dfrac{h}{L}\times L = h$.

ZPE from Uncertainty Principle: Conversely, we can arrive at the ZPE from uncertainty principle.

The principle is $\Delta p_x \times \Delta x = h$. But $\Delta p_x = 2p_x$ and $\Delta x = L$. So $2p_x \times L = h$ or, $p_x = \dfrac{h}{2L}$.

Thus lowest energy, $E = \dfrac{p_x^2}{2m} = \dfrac{(h/2L)^2}{2m} = \dfrac{h^2}{8mL^2}$ or, ZPE $= \dfrac{h^2}{8mL^2}$.

(5) **Free particle** suffers no quantisation of energy. This can be shown as follows:

ΔE = Energy-gap for two consecutive energy levels = $(2n+1)\dfrac{h^2}{8mL^2}$.

But for free particle, $L \to \propto$, so $\Delta E \to 0$. That is energy of the free particle changes continuously, it can have all values of energy. But when it is confined within a certain range of space, the energy values are quantised. The greater the localisation, the higher is the energy quantisation.

(6) The energy of the **macroscopic bodies** also changes continuously and suffers no quantisation of energy. We have $\Delta E = \left(2n+1\right)\dfrac{h^2}{8mL^2}$, but for macroscopic body, m is very high and ΔE becomes very small. Thus quantisation of energy is important only for microscopic particles. So quantum mechanics need not apply for the motion of macroscopic bodies.

Problem: Calculate the spacing between energy levels for

(i) electron (mass $\approx 10^{-30}$ kg) in 1D box of 1.0 Å length and

(ii) a ball bearing (mass= 1 gm) in a box of 10 cm length.

Comment on the energy gaps in the two cases.

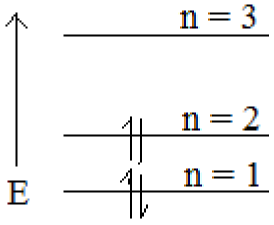
Solution: (i) $\Delta E = 102ev$ and (ii) $\Delta E = 10.2\times10^{-44}ev$. In case (i) energy-gap is large so quantisation of energy occurs while in (ii) it is too small for quantisation to be observed.

(7) **The spectra of conjugated polyenes** can be explained by this particle in 1D box model. The simplest conjugated polyene is butadiene (1,3but-diene)

$$CH_2 = CH - CH = CH_2 \text{ or, } CH_2 - CH - CH - CH_2.$$

The π electrons are considered to be delocalised over the almost entire length of the molecule. This is known free electron molecular orbital (FEMO) model. The electrons will transit from highest molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO).

In the example of butadiene, there are 4 π electrons and the length of the molecule is taken the box length. The π electrons are arranged in the molecule as



The electrons will jump from the energy level, 2 (HOMO) to the level, 3 (LOMO).

The energy required for such transition is

$$\Delta E = \left(2n+1\right)\frac{h^2}{8mL^2} = \left(2\times2+1\right)\frac{h^2}{8mL^2} = \frac{5h^2}{8mL^2}.$$

The energy is supplied by the absorption of photon of energy $h\nu$ by the molecule.

Thus, $$h\nu = \frac{5h^2}{8mL^2} \quad \text{or,} \quad \frac{hc}{\lambda} = \frac{5h^2}{8mL^2} \quad \text{or,} \quad \lambda = \frac{8mL^2c}{5h}.$$

L = chain length of butadiene = 2 double bond distance + 1 single bond distance + end correction = $\left(2\times1.34+1\times1.54+1.54\right)$ Å = 5.76 Å. [One single bond distance is taken as end correction]

Putting the values, we get

$$\lambda = \frac{8\times9.1\times10^{-28}\,gm\times(5.76\times10^{-8}\,cm)^2\times3\times10^{10}\,cm\sec^{-1}}{5\times6.627\times10^{-27}\,erg\sec} = 207\times10^{-7}\,cm = 207\times10^{-9}\,m = 207nm.$$

This is the wavelength of radiation required for transition in butadiene.

Experimentally, it is found that the radiation absorbed by the molecule has $\lambda = 217\,nm$.

Thus this simple model can explain approximately the spectra of butadiene.

[Note: Selection rule for the particle in 1D box is $n=1$ to $n=2$ or 4, etc but cannot be from $n=1$ to $n=3$ or 5]

Problem: Linear polyenes have general formula, $CH_2 = CH\left(CH = CH\right)_m CH = CH_2$.

Predict the smallest value of m which should make a polyene coloured, treating the electrons according to the 'particle in a box' model. Assume a value of $0.15\,nm$ for the $C-C$ bond length and neglect the end correction. (The visible region of the electromagnetic spectrum extends from 400 – 750 nm). **[Burdwan Univ, 2007]**

Solution: For the linear polyenes, when m = 0, the number of bonds = 3,

when m = 1, the number of bonds = 5,

when m = 2, the number of bonds = 7,

when m = 3, the number of bonds = 9, etc.

Thus the general expression of the number of bonds in the molecule = 2 m + 3.
The length of the molecule = $(2m+3)\times 0.15\ nm$. For the lowest value of m, the molecular chain length will be minimum and this gives the least value of λ in the visible range 400 to 750 nm. So λ = 400 nm.

We have the relation of the wave length absorbed by the molecule is $\lambda = \dfrac{8mL^2c}{(2n+1)h}$.

Number of double bonds = $m+2$, so the electron shifts from $m+2$ to $m+3$.
Thus $n = m+2$ and $2n+1 = 2(m+2)+1 = 2m+5$.

Now putting the values, $400\times10^{-7} = \dfrac{8\times9.1\times10^{-28}(2m+3)^2\times(0.15\times10^{-7})^2\times3\times10^{10}}{(2m+5)\times6.627\times10^{-27}}$

or, $\dfrac{(2m+3)^2}{(2m+5)} = \dfrac{400\times10^{-7}\times6.627\times10^{-27}}{8\times9.1\times10^{-28}\times(0.15\times10^{-7})^2\times3\times10^{10}} = \dfrac{4\times6.627}{8\times9.1\times(0.15)^2\times3} = 5.4$.

Now, when m = 1, $\dfrac{(2m+3)^2}{(2m+5)} = \dfrac{5^2}{7} = 3.57$, when $m=2$, $\dfrac{(2m+3)^2}{(2m+5)} = \dfrac{7^2}{9} = 5.44$,

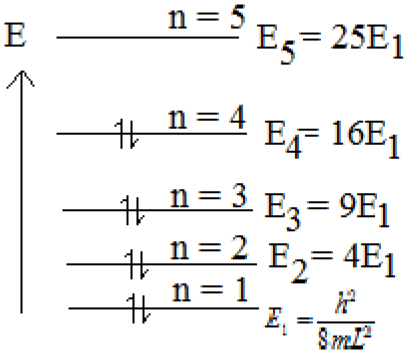
$m=3$, $\dfrac{(2m+3)^2}{(2m+5)} = \dfrac{9^2}{11} = 9$. So the value matches the result when $m=2$.

Problem: Calculate the energy levels of the π-network in octatetraene, C_8H_{10}, using particle in a 1- d box model. To calculate the box length, assume that the molecule is linear and use the values 135 pm and 154 pm for C = C and C – C bonds. What is the wavelength of the light required to induce a transition from the ground state to first excited state?

[Burdwan Univ. 2015]

Solution: The formula of octatetraene is $CH_2=CH-CH=CH-CH=CH-CH=CH_2$.

The number of π electrons = $4\times2=8$. The energy levels of the molecule are given as:
The transition occurs from $n=4$ (ground level) to $n=5$ (first excited level).



$\Delta E = E_5 - E_4 = 25E_1 - 16E_1 = 9E_1 = \dfrac{9h^2}{8mL^2}$.

This energy is supplied by the absorption of one photon of energy of $h\nu = \dfrac{hc}{\lambda}$. Thus, $\dfrac{hc}{\lambda} = \dfrac{9h^2}{8mL^2}$

or, $\lambda = \dfrac{8mcL^2}{9h}$. The length of the molecule is

$L = 4\times135+3\times154+165$ (end correction)
= 1156 pm = 1156×10^{-12} m.

Putting the values, we get

$$\lambda = \frac{8mcL^2}{9h} = \frac{8\times9.1\times10^{31}kg\times(1156\times10^{-12}m)^2\times3\times10^8 ms^{-1}}{9\times6.627\times10^{-34}Js} = 8.895\times10^{-7}m = 489.5\ nm.$$

Wave Function of the System (ψ_n): The normalised wave function of the particle in 1-d box is

$$\psi_n = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}.$$

It is supposed that all the possible properties of the system could be obtained from the use of the wave function. That is, all the information of the system remain hidden within the expression of ψ_n.

(1) **Non-degenerate system:** Each quantum state of the system as a specific energy value and a specific wave function. It means that this system is non-degenerate and wave function is non-degenerate one.

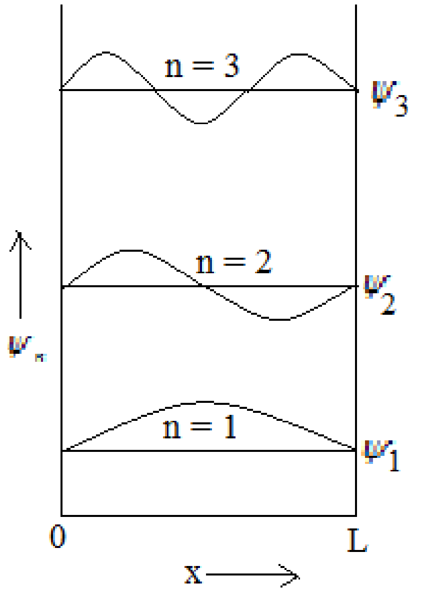
(2) **Orthogonal wave function:** The wave functions of the different quantum states of the system are orthogonal and so the states they represent are not interacting and independent of each other.

$$\int_0^L \psi_i \psi_j dx = \frac{2}{L}\int_0^L \sin\frac{n_i \pi x}{L}\sin\frac{n_j \pi x}{L}dx = \frac{1}{L}\left[\int_0^L \cos\left(n_i - n_j\right)\frac{\pi x}{L}dx - \int_0^L \cos\left(n_i + n_j\right)\frac{\pi x}{L}dx\right]$$

$$= \frac{1}{L}\times\frac{L}{\pi}\left(\frac{1}{n_i - n_j}\right)\left[\sin\left(n_i - n_j\right)\frac{\pi x}{L}\right]_0^L - \frac{1}{L}\times\frac{L}{\pi}\left(\frac{1}{n_i + n_j}\right)\left[\sin\left(n_i + n_j\right)\frac{\pi x}{L}\right]_0^L$$

$$= \frac{1}{\pi}\left(\frac{1}{n_i - n_j}\right)\left(0-0\right) - \frac{1}{\pi}\left(\frac{1}{n_i + n_j}\right)\left(0-0\right) = 0.$$ i.e., ψ_i and ψ_j are orthogonal.

(3) Wave function (ψ_n) varies with x as sine function. ψ_n vs. x can be plotted for the different quantum states of the system.



(a) For the quantum state, $n = 1$, the wave function

$$\psi_1 = \sqrt{\frac{2}{L}}\sin\frac{\pi x}{L}.$$

When $x = 0$, $\psi_1 = 0$, $x = \frac{L}{2}$, $\psi_1 = \sqrt{\frac{2}{L}}$ (max^{m}.)

and $x = L$, $\psi_1 = 0$. Thus, ψ_1 starts from zero, attains maximum and again drops to zero.

(b) For state, $n = 2$, $\psi_2 = \sqrt{\frac{2}{L}}\sin\frac{2\pi x}{L}$.

When $x = 0, \psi_2 = 0$; $x = \frac{L}{4}, \psi_2 = \sqrt{\frac{2}{L}}$ (max^{m}.);

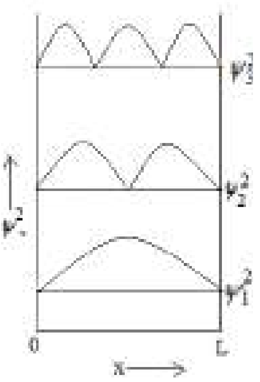
$x = \frac{L}{2}$, $\psi_2 = 0$; it is called nodal point.

$x = \frac{3L}{4}$, $\psi_2 = -\sqrt{\frac{2}{L}}$ (minimum). (c) For state $n = 3$, $\psi_3 = \sqrt{\frac{2}{L}}\sin\frac{3\pi x}{L}$.

When $x = 0$, $\psi_3 = 0$; $x = \frac{L}{6}$, $\psi_3 = \sqrt{\frac{2}{L}}$ (maxi^{m}.); $x = \frac{L}{3}$, $\psi_3 = 0$; $x = \frac{L}{2}$, $\psi_3 = -\sqrt{\frac{2}{L}}$ (minimum); $x = L$, $\psi_3 = 0$.

From the schematic diagram of ψ_n vs. x, it is seen that ψ_1, ψ_3 or wave functions of odd quantum states are symmetrical. If a mirror is placed at the middle point of the box, one half of the wave function is mirror image of the other half.

ψ_2, ψ_4.. or wave functions of even quantum states are antisymmetrical.



(4) Probability density $\left(\psi_n^2\right)$ of the particle in the box is $\psi_n^2 = \frac{2}{L}\sin^2\frac{n\pi x}{L}$.

ψ_n^2 can also be plotted vs. x for different quantum states.

(a) For the quantum state, $n = 1$, $\psi_1^2 = \frac{2}{L}\sin^2\frac{\pi x}{L}$. When $x = 0$ and L, $\psi_1^2 = 0$ (probability density zero); $x = \frac{L}{2}$, $\psi_1^2 = \frac{2}{L}$, maximum probability density.

(b) For the quantum state, $n = 2$, $\psi_2^2 = \frac{2}{L}\sin^2\frac{2\pi x}{L}$. When $x = 0$ and L, $\psi_2^2 = 0$;

$x = \frac{L}{4}$ and $\frac{3L}{4}$, $\psi_2^2 = \frac{2}{L}$, maximum probability density; $x = \frac{L}{2}$, $\psi_2^2 = 0$, no chance of finding the particle at the middle point of the box. This is the nodal point.

(c) For the quantum state, $n = 3$, $\psi_3^2 = \frac{2}{L}\sin^2\frac{3\pi x}{L}$. When $x = 0$ and L, $\psi_3^2 = 0$ these are end points; when $x = \frac{L}{6}$, $\frac{L}{2}$ and $\frac{5L}{6}$, $\psi_3^2 = \frac{2}{L}$ maximum probability densities and these positions are antinodes. When $x = \frac{L}{3}$ and $\frac{2L}{3}$, $\psi_3^2 = 0$, these points are nodal points.

[The wave functions besides being zero at the walls of the box, also have zero at various points within the box. These points are called nodes of the wave function. The number of nodes = ($n-1$)].

ψ_n^2 spreads out but measurement gives definite location: Wave function (ψ) and probability density (ψ^2) are spread out over the length of the box, much like a wave. However, quantum mechanics does not assert that the particle itself is spread out like a wave. A measurement of position will give a definite location for the particle. It is the probability function (ψ) that spread out in space and obeys a wave equation. (Measurement paradox).

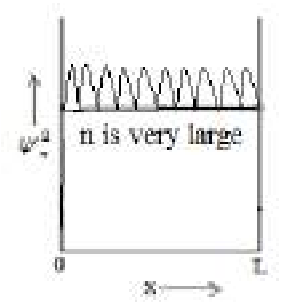
Special comment on ψ_2^2 vs. x plot: In the quantum state, $n = 2$, there is finite probability (though varying) of finding the particle at all points on either side of the middle point of the box, but there is no chance at all to find the particle at the middle point. Does it mean that the particle can move to and fro from one end to the other end without even touching the middle point? Though it is not realisable, but it happens in quantum mechanical calculation.

It can be explained if we consider the particle is smeared into dust forming cloud of varying density. There is zero density at the idle an maximum on either side of it. The behaviour of microscopic particle cannot be realised in terms of visualizable model.

Quantum mechanical result corresponds to the classical result when n is large: The probability density is not uniform at all positions of the box. It is more pronounced when n is small. But the distribution becomes more and more uniform as n increases. This becomes completely uniform for the very large value of n.

The result attains the predictions of classical mechanics which states that all locations of the particle is equally likely. This fact is in agreement with Bohr correspondence principle.

Further, $$E = n^2\left(\frac{h^2}{8mL^2}\right) \quad \text{or,} \quad \frac{8mL^2E}{h^2} = n^2.$$



For macroscopic bodies, m, L and E are large and h is small so n is very large for macroscopic bodies in classical mechanics and the probability of finding the particle becomes uniform within the box.

Problem(1): Using particle in a box model, find the positions of maximum electron density in the molecule of butadiene, giving that the average C – C distance is 0.140 nm.
Show graphically the variation of electron density in the molecule.

Solution: For the molecule, $C_1 = C_2 - C_3 = C_4$, $L = 4\times 0.140 = 0.560\ nm$ (taking $C-C$ bond length as end correction). In the ground state, the four π electrons are accommodated in the first two energy levels, $n = 1$ and $n = 2$.

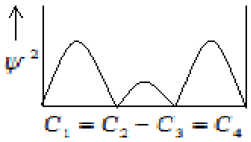
The corresponding wave functions are $\psi_1 = \sqrt{\frac{2}{L}}\sin\frac{\pi x}{L}$ and $\psi_2 = \sqrt{\frac{2}{L}}\sin\frac{2\pi x}{L}$.

At $x = L/2$ i.e. between C_2 and C_3, $\psi_1^2 = 2/L$, max$^{\text{m}}$. and $\psi_2^2 = 0$.

On the other hand, at $L/4$ and $3L/4$, $\psi_2^2 = 2/L$, max$^{\text{m}}$. but ψ_1^2 is not zero.

Therefore π electron density, $\psi^2 = \psi_1^2 + \psi_2^2$ is maximum in $C_1 - C_2$ and $C_3 - C_4$ bonds but minimum in $C_2 - C_3$ bond.

Graphical variation of the electron density of the molecule is shown here.



Problem(2): For a particle in the state $n = 1$ of a 1 – d box of length L, find the probability that the particle is in the region $0 \le x \le L/4$.

Solution: The wave function for the state $n=1$ of a 1 – d box is $\psi_1 = \sqrt{\frac{2}{L}}\sin\frac{\pi x}{L}$.

The probability of the particle to be found within the range $0 \le x \le L/4$

$$P = \int_0^{L/4} \psi_1^2 dx = \frac{2}{L}\int_0^{L/4} \sin^2\frac{\pi x}{L}dx = \frac{1}{L}\int_0^{L/4}\left(1-\cos\frac{2\pi x}{L}\right)dx = \frac{1}{L}\int_0^{L/4}dx - \frac{1}{L}\int_0^{L/4}\cos\frac{2\pi x}{L}dx$$

$$= \frac{1}{L}\left[x\right]_0^{L/4} - \frac{1}{L}\times\frac{L}{2\pi}\left[\sin\frac{2\pi x}{L}\right]_0^{L/4} = \frac{1}{L}\times\frac{L}{4} - \frac{1}{2\pi}\left[\sin\frac{\pi}{2} - \sin 0\right] = \frac{1}{4} - \frac{1}{2\pi}\times(1-0)$$

or, probability, $P = \frac{1}{4} - \frac{1}{2\pi} = 0.0908$.

Problem(3): A particle of mass 2.00×10^{-26} g is in 1 – d box of length 4.00 nm. Find the frequency and wave length of the photon emitted when the particle goes from $n=3$ to $n=2$ level.

[Ans. $\nu = 1.29\times10^{12}s^{-1}$, $\lambda = 2.32\times10^{-4}m$ **].**

Calculation of Physical Properties of the System

(1) Energy eigen value: $\psi_n = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$ and $\hat{H} = -\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}$ are the wave function and the energy operator of the system since the potential energy of the system is zero.

The energy eigen value equation is $\hat{H}\psi_n = E_n\psi_n$.

Thus, $-\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}\left(A\sin\frac{n\pi x}{L}\right) = -\frac{h^2}{8\pi^2 m}\times\left(-\frac{n^2\pi^2}{L^2}\right)A\sin\frac{n\pi x}{L} = \left(\frac{n^2h^2}{8mL^2}\right)\psi_n = E_n\psi_n$.

Hence the energy of the particle in 1 – d box for the nth state is $E_n = n^2\left(\frac{h^2}{8mL^2}\right)$.

Since the eigen value equation is satisfied, it is possible to find E_n of the system very precisely.

(2) **Square of linear momentum eigen value (** p_x^2 **):** The corresponding quantum mechanical operator for the property is $\hat{p}_x^2 = \left(\frac{h}{2\pi i}\frac{d}{dx}\right)^2 = -\frac{h^2}{4\pi^2}\frac{d^2}{dx^2}$.

Now the x-component linear momentum square eigen value equation is $\hat{p}_x^2\,\psi_n = p_x^2\psi_n$.

Thus, $-\frac{h^2}{4\pi^2}\frac{d^2}{dx^2}\left(A\sin\frac{n\pi x}{L}\right) = -\frac{h^2}{4\pi^2}\left(-\frac{n^2\pi^2}{L^2}\right)\left(A\sin\frac{n\pi x}{L}\right) = \frac{n^2h^2}{4L^2}\psi_n$ or, $p_x^2 = \frac{n^2h^2}{4L^2}$.

This x-component linear momentum square of the system is quantised and takes discrete values.

(3) x**-component linear momentum (** p_x **):** The corresponding operator $\hat{p}_x = \frac{h}{2\pi i}\frac{d}{dx}$.

The wave function $\psi_n = A\sin\frac{n\pi x}{L}$ is not an eigen function of the operator $\hat{p}_x$. It means that this value is not a characteristic property of the system and it can not produce precise value, rather the value of p_x spreads over the different observations. Hence we can find out the average value of p_x of the system. That is, $\langle p_x\rangle = \int_0^L \psi_n\hat{p}_x\psi_n\,dx$, where $\psi_n = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$, normalised wave function of the particle in 1 – d box system.

So, $\langle p_x\rangle = \frac{2}{L}\int_0^L \sin\frac{n\pi x}{L}\left(\frac{h}{2\pi i}\frac{d}{dx}\right)\sin\frac{n\pi x}{L}dx = \frac{2}{L}\int_0^L\sin\frac{n\pi x}{L}\left(\frac{h}{2\pi i}\right)\times\frac{n\pi}{L}\cos\frac{n\pi x}{L}dx$

$$= \frac{2}{L}\times\frac{h}{2\pi i}\times\frac{n\pi}{L}\int_0^L \sin\frac{n\pi x}{L}\cos\frac{n\pi x}{L}dx = \frac{nh}{2L^2 i}\int_0^L \sin\frac{2n\pi x}{L}dx$$

$$= \frac{nh}{2L^2 i}\left[-\cos\frac{2n\pi x}{L}\right]_0^L \times\frac{L}{2n\pi} = -\frac{h}{4L\pi i}\left[\cos 2n\pi - \cos 0\right] = -\frac{h}{4L\pi i}(1-1) = 0 .$$

The zero value of p_x signifies that the value of p_x oscillate within the value $\pm {}^{nh}\!/_{2L}$ $\left(as\ p_x^2 = \frac{n^2h^2}{4L^2}\right)$. The average value of the property is thus equal to zero. $p_x = +\frac{nh}{2L}$ when the particle moves from left to right and $p_x = -\frac{nh}{2L}$ when it moves from right to left, so for one complete oscillation of the particle, $\langle p_x\rangle = 0$.

(4) Average position of the particle, $\langle x\rangle$: Position of the particle varies within the box from 0 to L. So it has no precise value. The average position can be calculated by using postulate III.

$$\langle x\rangle = \int_0^L \psi_n \hat{x}\psi_n dx = \frac{2}{L}\int_0^L x\sin^2\frac{n\pi x}{L}dx = \frac{1}{L}\int_0^L x\left(1-\cos\frac{2n\pi x}{L}\right)dx$$

$$= \frac{1}{L}\int_0^L x dx - \frac{1}{L}\int_0^L x\cos\frac{2n\pi x}{L}dx = \frac{L}{2} - \frac{1}{L}\times\frac{L}{2n\pi}\left[x\sin\frac{2n\pi x}{L}\right]_0^L + \frac{1}{L}\times\left(\frac{L}{2n\pi}\right)^2\left[-\cos\frac{2n\pi x}{L}\right]_0^L$$

$$= \frac{L}{2} - \frac{1}{2n\pi}\left[L\sin 2n\pi - 0\sin 0\right] - \frac{L}{(2n\pi)^2}\left[\cos 2n\pi - \cos 0\right]$$

$$= \frac{L}{2} - \frac{1}{2n\pi}(0-0) - \frac{L}{(2n\pi)^2}(1-1) = \frac{L}{2}$$. The expected location of the particle $\langle x\rangle = \frac{L}{2}$.

(5) Average square position of the particle $\langle x^2\rangle$: We have $\langle x^2\rangle = \int_0^L \psi_n \hat{x}^2\,\psi_n dx$

or, $$\langle x^2\rangle = \frac{2}{L}\int_0^L x^2\sin^2\frac{n\pi x}{L}dx = \frac{1}{L}\int_0^L x^2\left(1-\cos\frac{2n\pi x}{L}\right)dx = \frac{1}{L}\int_0^L x^2 dx - \frac{1}{L}\int_0^L x^2\cos\frac{2n\pi x}{L}dx$$

$$= \frac{L^2}{3} - \frac{1}{L}\left[x^2\int_0^L \cos\frac{2n\pi x}{L}dx - \int_0^L 2x\left(\sin\frac{2n\pi x}{L}\right)\times\left(\frac{L}{2n\pi}\right)dx\right]$$

$$= \frac{L^2}{3} - \frac{1}{L}\times\left(\frac{L}{2n\pi}\right)\left[x^2\sin\frac{2n\pi x}{L}\right]_0^L + \frac{2}{L}\times\frac{L}{2n\pi}\int_0^L x\sin\frac{2n\pi x}{L}dx$$

$$= \frac{L^2}{3} - \frac{1}{2n\pi}\left[L^2\sin 2n\pi - 0\sin 0\right] + \frac{1}{n\pi}\int_0^L x\sin\frac{2n\pi x}{L}dx$$

$$= \frac{L^2}{3} - \frac{1}{2n\pi}(0-0) + \frac{1}{n\pi}\left[x\int_0^L \sin\frac{2n\pi x}{L}dx + \int_0^L\left(\cos\frac{2n\pi x}{L}\right)\times\frac{L}{2n\pi}dx\right]$$

$$= \frac{L^2}{3} + \frac{1}{n\pi}\left[-\left(\frac{L}{2n\pi}\right)x\cos\frac{2n\pi x}{L}\right]_0^L + \frac{1}{n\pi}\left(\frac{L}{2n\pi}\right)^2\left[\sin\frac{2n\pi x}{L}\right]_0^L$$

$$= \frac{L^2}{3} - \frac{L}{2n^2\pi^2}\left(L\cos 2n\pi - 0\times\cos 0\right) + \frac{L^2}{4n^3\pi^3}\left(\sin 2n\pi - \sin 0\right)$$

$$= \frac{L^2}{3} - \frac{L}{2n^2\pi^2}(L-0) = \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2}$$. Thus, $\langle x^2\rangle = \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2}$.

Related Problems:

(1) Using particle in 1 – d box, verify Heisenberg Uncertainty Principle, $\Delta p_x \times \Delta x > \frac{1}{2}\hbar$,

where Δp_x = root mean square momentum uncertainty = $\left(\langle p_x^2\rangle - \langle p_x\rangle^2\right)^{1/2}$

Δx = root mean square position uncertainty = $\left(\langle x^2\rangle - \langle x\rangle^2\right)^{1/2}$

and $\langle p_x^2\rangle = \frac{n^2h^2}{4L^2}$, $\langle p_x\rangle = 0$, $\langle x^2\rangle = \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2}$ and $\langle x\rangle = \frac{L}{2}$.

Solution: Using the above data, we have $\Delta p_x \times \Delta x = \left(\frac{n^2h^2}{4L^2} - 0\right)^{1/2}\left(\frac{L^2}{3} - \frac{L^2}{2n^2\pi^2} - \frac{L^2}{4}\right)^{1/2}$

or, $\Delta p_x \times \Delta x = \frac{nh}{2L} \times L\left(\frac{1}{3} - \frac{1}{4} - \frac{1}{2n^2\pi^2}\right)^{1/2} = \frac{nh}{2}\left(\frac{1}{12} - \frac{1}{2n^2\pi^2}\right)^{1/2}$

$= \frac{h}{4\pi}\left(\frac{n^2\pi^2}{3} - 2\right)^{1/2}$, but n = 1, 2, 3, etc, so $\Delta p_x \times \Delta x > \frac{h}{4\pi}$

or, $\Delta p_x \times \Delta x > \frac{1}{2}\hbar$.

(2) By use of expression, $\Delta p_x \times \Delta x \geq h/4\pi$, show that for particle in 1 – d box, $\Delta E \times \Delta t \geq h/4\pi$.

Solution: For particle in 1 – d box, E = KE + PE = KE = $\frac{p_x^2}{2m}$, so $\Delta E = \frac{2p_x}{2m}\Delta p_x = \frac{p_x}{m}\Delta p_x$,

or, $\Delta p_x = \frac{m}{p_x}\Delta E$. Again, $p_x = mv_x = m\frac{\Delta x}{\Delta t}$ or, $\Delta x = \frac{\Delta t}{m}.p_x$.

Thus $\Delta p_x \times \Delta x = \frac{m}{p_x}\Delta E \times \frac{\Delta t}{m}.p_x = \Delta E \times \Delta t$, but $\Delta p_x \times \Delta x \geq h/4\pi$, so $\Delta E \times \Delta t \geq h/4\pi$.

This shows that making use of $\Delta p_x \times \Delta x \geq h/4\pi$, it is possible to show that $\Delta E \times \Delta t \geq h/4\pi$.

(3) A particle of mass m is confined to a 1 – d box with origin at the centre of the box. The box extends from $-L/2$ to $+L/2$.

The potential energy is $V(x) = 0;\ -L/2 \leq x \leq +L/2$ and $V(x) = \propto;\ |x| > L/2$.

(a) Write the Schrodinger equation for the system showing separate equations for the inside and outside of the box.

(b) Assume a solution (inside the box) of the form, $\psi(x) = A\sin kx + B\cos kx$, find out the correct form by making use of boundary conditions. (c) Derive the energy expression of the particle.

Solution: (a) Schrodinger equation is $\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$.

(i) Outside the box, $V = \propto$, hence the equation is $\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - \propto)\psi = 0$ or, $\frac{d^2\psi}{dx^2} - \propto\psi = 0$.

(ii) Inside the box, $V = 0$, hence the equation is $\frac{d^2\psi}{dx^2} + \frac{8\pi^2 mE}{h^2}\psi = 0$ or, $\frac{d^2\psi}{dx^2} + k^2\psi = 0$.

(b) General solution of the equation inside the box is given as $\psi(x) = A\sin kx + B\cos kx$.

The boundary conditions are: when $x = -L/2$, $\psi = 0$, so $0 = -A\sin(kL/2) + B\cos(kL/2)$ ---(i)

and when $x = L/2, \psi = 0$, so $0 = A\sin(kL/2) + B\cos(kL/2)$ -------(ii)

Adding (i) and (ii), $0 = 2B\cos(kL/2)$, but $B \neq 0$, so $\cos(kL/2) = 0 = \cos(n\pi/2)$, when n = odd values, 1, 3, 5, etc. . Again subtracting (i) from (ii), $0 = 2A\sin(kL/2)$, but $A \neq 0$, so $\sin(kL/2) = 0 = \sin(n\pi/2)$ for even values of n = 2, 4, 6, etc. So, $(kL/2) = (n\pi/2)$ or, $k = (n\pi/L)$ Thus for the same value of k, both sine and cosine functions cannot be zero. Thus we obtain two sets of solutions

$$\psi = A\sin(n\pi x/L) \text{, when } n = \text{even} \quad \text{and} \quad \psi = B\cos(n\pi x/L)\text{, when } n = \text{odd.}$$

[Extra comments: With respect to x = 0, at the middle point of the box, the cosine functions are symmetrical and sine functions are antisymmetrical].

(c) The energy expression can be obtained from energy eigen value equation, $\hat{H}\psi = E\psi$ or,

$$-\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}\left(A\sin\frac{n\pi x}{L} + B\cos\frac{n\pi x}{L}\right) = -\frac{h^2}{8\pi^2 m}\left[-\left(\frac{n\pi}{L}\right)^2 A\sin\frac{n\pi x}{L} - \left(\frac{n\pi}{L}\right)^2 B\cos\frac{n\pi x}{L}\right]$$

$$= \frac{n^2h^2}{8mL^2}\left(A\sin\frac{n\pi x}{L} + B\cos\frac{n\pi x}{L}\right) \text{. Thus, } E = \frac{n^2h^2}{8mL^2}.$$

(4) A particle of mass 10^{-6} kg is rolling on a smooth floor of a 1×10^{-4} m wide box with a speed 3.3313×10^{-3} ms^{-1}. Applying particle in a box problem, calculate the quantum number (n) corresponding to the translational energy of a ball. Will you consider the energy to be quantised in a practical sense?

Solution: KE , T = E_n since PE = 0 in the box. So $T = \frac{1}{2}mv_x^2 = \frac{n^2h^2}{8mL^2}$ or, $n^2 = \frac{4m^2L^2}{h^2}\left(v_x^2\right)$,

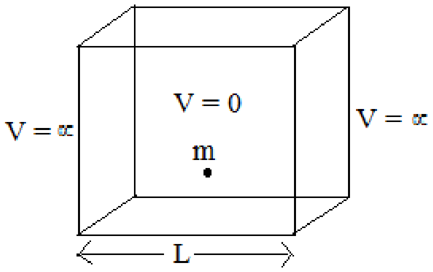
or, $n = \frac{2mL}{h}(v_x)$. Putting values, $n = \frac{2\times\left(10^{-6}kg\right)\times\left(1\times10^{-4}m\right)}{\left(6.626\times10^{-34}Js\right)}\left(3.3313\times10^{-3}ms^{-1}\right) = 10^{21}$.

Large value of n indicates that translational energy of the ball changes continuously and not quantised according to Bohr correspondence principle.

Again, $\Delta E = 1.098\times10^{-32}$ J and this confirms the conclusion.

Particle in Three- Dimensional (3 – d) Box

Let a particle of mass m is confined to move within a cube of edge length L. The potential energy (V) is zero within the box and infinity out-side the box. The particle can move without any restriction along X-axis, Y-axis and Z-axis. It is sometimes called 3 – d potential well.



Schrodinger equation of the particle inside the box $\left(\frac{\partial^2}{\partial x}\right.$ nce PE = 0.

Here, ψ is a function of x, y, z.

Let $\psi(x,y,z) = X(x)\times Y(y)\times Z(z)$ or, simply, $\psi = XYZ$, where X is a function of x, Y is a function of y and Z is a function of z. Putting the value of $\psi = XYZ$ in the Schrodinger equation, we have

$YZ\frac{\partial^2 X}{\partial x^2} + XZ\frac{\partial^2 Y}{\partial y^2} + XY\frac{\partial^2 Z}{\partial z^2} + \frac{8\pi^2 m}{h^2}\left(E_x + E_y + E_z\right)XYZ = 0$. Dividing by XYZ and separating the variables, we get $\left(\frac{1}{X}\frac{d^2X}{dx^2} + \frac{8\pi^2 mE_x}{h^2}\right) + \left(\frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{8\pi^2 mE_y}{h^2}\right) + \left(\frac{1}{Z}\frac{d^2Z}{dz^2} + \frac{8\pi^2 mE_z}{h^2}\right) = 0$.

The sum of three independent terms is zero, hence each term is then separately equal to zero. Thus,

$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{8\pi^2 mE_x}{h^2} = 0 \quad \text{or,} \quad \frac{d^2X}{dx^2} + \left(\frac{8\pi^2 mE_x}{h^2}\right)X = 0.$$

Similarly, the other equatio are given as $\frac{d^2Y}{dy^2} + \left(\frac{8\pi^2 mE_y}{h^2}\right)Y = 0$ and $\frac{d^2Z}{dz^2} + \left(\frac{8\pi^2 mE_z}{h^2}\right)Z = 0$.

Each of the equations has a form similar to the Schrodinger equation for a particle in 1 – d box with similar boundary conditions. This is equivalent to one of three particles in three separate 1 – d boxes of lengths L_x, L_y and L_z. But for cubical box, $L_x = L_y = L_z = L$.

Solving the equations, $X = \sqrt{\frac{2}{L}}\sin\frac{n_x \pi x}{L}$, $Y = \sqrt{\frac{2}{L}}\sin\frac{n_y \pi y}{L}$ and $Z = \sqrt{\frac{2}{L}}\sin\frac{n_z \pi z}{L}$,

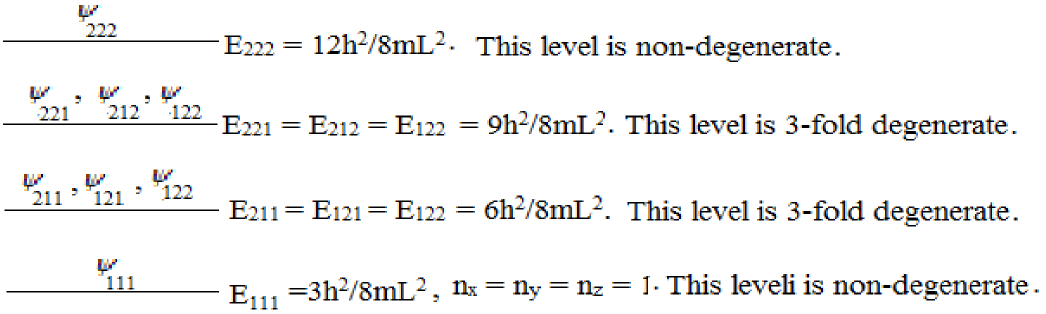
here n_x, n_y and n_z are the quantum numbers along x, y and z directional motion of the particle. They have values 1, 2, 3, etc any positive integer excluding zero. Total wave function is given as

$$\psi = \left(\frac{2}{L}\right)^{3/2}\sin\frac{n_x \pi x}{L}\sin\frac{n_y \pi y}{L}\sin\frac{n_z \pi z}{L} \quad \text{and}$$

the total energy of the system, $E = n_x^2\left(\frac{h^2}{8mL^2}\right) + n_y^2\left(\frac{h^2}{8mL^2}\right) + n_z^2\left(\frac{h^2}{8mL^2}\right) = \left(n_x^2 + n_y^2 + n_z^2\right)\frac{h^2}{8mL^2}$

The total energy and wave function of the particle depends on the value of n_x, n_y and n_z.

Zero-point energy is $E_{111} = \frac{3h^2}{8mL^2}$ and $\psi_{111} = \left(\frac{2}{L}\right)^{3/2}\sin\frac{\pi x}{L}\sin\frac{\pi y}{L}\sin\frac{\pi z}{L}$.



$E_{222} = 12h^2/8mL^2$. This level is non-degenerate.

$E_{221} = E_{212} = E_{122} = 9h^2/8mL^2$. This level is 3-fold degenerate.

$E_{211} = E_{121} = E_{122} = 6h^2/8mL^2$. This level is 3-fold degenerate.

$E_{111} = 3h^2/8mL^2$, $n_x = n_y = n_z = 1$. This leveli is non-degenerate.

E levels and corresponding wave functions are shown below. Some levels are degenerate and some are nc generate.

In e cases, there are degenerate levels, each is defined by a particular wave function but all the wave functions have same energy value. The degeneracy is developed when the quantum numbers are are not equal, i.e., $n_x \neq n_y \neq n_z$. The degeneracy can be lifted by slight distortion of edge of the box, i.e., the edges of the box are not equal, $L_x \neq L_y \neq L_z$.

Problem(1): Calculate the number of degeneracy of the energy level $14h^2/8mL^2$ for a particle moving in a cube with zero potential energy.

Solution: Six-fold degeneracy.

n_x	n_y	n_z
1	2	3
1	3	2
2	1	3
2	3	1
3	1	2
3	2	1

Problem(2): Determine the degree of degeneracy of the level $38h^2/8mL^2$ of a particle in a cubical box with PE = 0.

Solution: 9 – fold degeneracy. [1,1,6 → 3 – fold and 2, 3, 5 → 6 – fold].

Problem(3): If benzene is regarded as square box of side 0.4 nm containing 6π electrons, then calculate the wave length of light to promote a π electron to the first excited state.

Solution: The energy of the benzene in the ground state

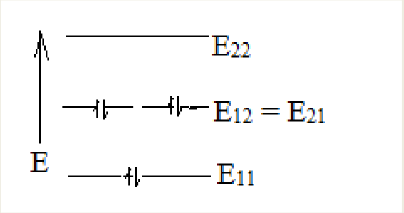
$E_{GS} = 2\times\left(2h^2/8mL^2\right) + 4\times\left(5h^2/8mL^2\right) = 24h^2/8mL^2$, since $E = \left(n_x^2 + n_y^2\right)h^2/8mL^2$.

The energy in the excited state,

$$E_{ES} = 2\times\left(2h^2/8mL^2\right) + 3\times\left(5h^2/8mL^2\right) + 1\times\left(8h^2/8mL^2\right) = 27h^2/8mL^2.$$

The difference of energy levels is equal to the energy of the photon absorbed to promote the electron to the excited state. That is, $h\nu = hc/\lambda = E_{ES} - E_{GS}$

or, $hc/\lambda = 27h^2/8mL^2 - 24h^2/8mL^2 = 3h^2/8mL^2$



or, $\lambda = 8mL^2c/3h$. Putting the values,

$$\lambda = \frac{8\times 9.1\times 10^{-28}\,g\times\left(0.4\times 10^{-7}\,cm\right)^2\times 3\times 10^{10}\,cm\sec^{-1}}{3\times 6.626\times 10^{-27}\,erg\sec} = 175.8\times 10^{-7} = 175\,nm.$$

Hydrogen-atom Problem

H-atom is the simplest of all chemical elements. Solution of non – relativistic and time – independent Schrodinger equation of H – atom produces the expression of wave functions which are called atomic orbitals. These are labelled as 1s, 2s, 2p, etc. The atomic orbitals are the building blocks for the construction of molecular orbitals, which, in turn, play a very important role in the understanding of chemical bonding, electronic structure and spectrum of molecules.

Thus, the quantum mechanical study of H-atom constitutes the most important problem in quantum chemistry. H-atom is composed of one electron and one nucleus. The nucleus again contains only one proton. We may consider two types of motion of H-atom.

(1) **Translatory motion of the atom as a whole in 3-d space.** This motion is like that of free particle and energy for this motion changes continuously. Therefore, this motion need not require quantum mechanical treatment.

(2) **Internal motion of the electron and nucleus within the H-atom.** But nucleus is about 1836 times heavier than the electron. So, we may consider the nucleus is at rest (fixed nucleus approximation or infinite nuclear mass approximation).

The spatial rotation of an electron around the nucleus in the H-atom can be described in terms of electron's two angular variables, θ (zenith angle) and φ (azimuthal angle), and its radial distance r from the nucleus. The nucleus is at rest at the origin of the co-ordinate system. Schrodinger equation for electron's 3-d motion within the H-atom is $\nabla^2\psi + \frac{2\mu}{\hbar^2}(E-V)\psi = 0$, where

∇^2 = Laplacian operator = $\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$ and μ = reduced mass of H-atom = $\frac{m_n\times m_e}{m_n+m_e}\approx m_e$.

Since mass of the nucleus is much greater than that of electron so $\mu\approx m_e$. But we shall continue to write μ instead of m_e.

V is the potential energy of the electron in the atom. This energy originates due to Coulombic force of attraction ($-e^2/r^2$) of the electron from the nucleus. Thus potential energy,

$$V = -\int_{\infty}^{r} F dr \quad \text{but,}\quad F = -\frac{e^2}{r^2} \quad \text{so,}\quad V = -\int_{\infty}^{r}\left(-\frac{e^2}{r^2}\right)dr = -\frac{e^2}{r}.$$

This shows that the PE of the electron is spherically symmetrical and V is inversely proportional to r and it is known as central field problem (the force $-e^2/r^2$ acts towards the centre). The electron experiences the same potential energy due to nucleus at any point on the surface of sphere of radius r.

Hence the name is spherically symmetrical.

Schrodinger equation in polar co-ordinates:

Since the Schrodinger equation of H-atom contains radial distance (r), it is better to write the equation in polar co-ordinates. In polar co-ordinates

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}.$$

Thus the Schrodinger equation is given as

$$\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi+\frac{2\mu}{\hbar^2}\left(E+\frac{e^2}{r}\right)\psi = 0 .$$

The wave function, ψ depends on r,θ and φ. Thus we can write $\psi(r\,\theta\,\varphi) = R(r)\times P(\theta)\times F(\varphi)$, where R, P and F are the functions of r,θ and φ respectively .

In brief, we can write $\psi = RPF$ and the functions R, P, F are independent of each other.

Separation into three equations – each containing one variable:

Now replacing ψ in the Schrodinger equation and differentiating, we get

$$\frac{PF}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{RF}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial P}{\partial\theta}\right)+\frac{RP}{r^2\sin^2\theta}\frac{\partial^2 F}{\partial\varphi^2}+\frac{2\mu}{\hbar^2}\left(E+\frac{e^2}{r}\right)RPF=0\ .$$

Dividing by RPF and multiplying by r^2 and rearranging, we have

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{1}{P\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial P}{\partial\theta}\right)+\frac{1}{F\sin^2\theta}\frac{\partial^2 F}{\partial\varphi^2}+\frac{2\mu r^2}{\hbar^2}\left(E+\frac{e^2}{r}\right)=0$$

or, $\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}\left(E+\frac{e^2}{r}\right)=-\left[\frac{1}{P\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial P}{\partial\theta}\right)+\frac{1}{F\sin^2\theta}\frac{\partial^2 F}{\partial\varphi^2}\right]=l(l+1)$.

Each side of the equation must be a constant, as LHS depends on r while RHS depends on θ and φ.
l is constant and called azimuthal quantum number, having values 0, 1, 2, 3, etc.
Now Schrodinger equation is separated into radial part that depends on r and angular part that depends on angles θ and φ.

Radial part is $$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\frac{2\mu r^2}{\hbar^2}\left(E+\frac{e^2}{r}\right)-l(l+1)\right]R=0$$

and angular part is $\frac{1}{P\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial P}{\partial\theta}\right)+\frac{1}{F\sin^2\theta}\frac{\partial^2 F}{\partial\varphi^2}+l(l+1)=0$.

Again the angular part could be separated into two – one depending on θ and other depending on φ.
Multiplying by $\sin^2\theta$ and separating into two sides depending on θ and φ, we have

$$\frac{\sin\theta}{P}\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right)+l(l+1)\sin^2\theta=-\frac{1}{F}\frac{d^2F}{d\varphi^2}=m^2 \text{ (say).}$$

Each part is constant and m is called magnetic quantum number that depends on the value of l.
Thus, three separate equations are given here:

(1) r - dependent equation, $$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\frac{2\mu r^2}{\hbar^2}\left(E+\frac{e^2}{r}\right)-l(l+1)\right]R=0$$

(2) θ - dependent equation, $$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right)+\left[l(l+1)\sin^2\theta-m^2\right]P=0 \quad \text{and}$$

(3) φ - dependent equation, $\frac{d^2F}{d\varphi^2}+m^2F=0$.

Energy eigen value (E_n): Solving the radial part equation (1), the expression of the energy of the system is obtained. $E_n=-\left(\frac{1}{n^2}\right)\frac{\mu e^4}{2\hbar^2}$ or, $E_n=-\left(\frac{1}{n^2}\right)\frac{2\pi^2\mu e^4}{h^2}$.

The energy is found to be identical with the value calculated from the Bohr model of H-atom. Thus, this expression of energy can explain the spectrum of H-atom successfully.

The potential energy, $V=-e^2/r$ and it is (-ve) always. E = KE + PE and KE is always (+ve).

As the total energy (E) is (-ve), hence numerical value of PE is greater than the KE of the electron.
The electron is thus remains bound within the atom and energy is required to separate it from nucleus.

Quantum numbers (n, l and m): When the three differential equations of the Schrodinger equation are solved, the solutions contain three quantum numbers – principle quantum number (n), azimuthal quantum number (l) and magnetic quantum number (m).
The radial function, R contains n and l, angular function, P contains l and m, and F contains m only. Thus the wave functions of the H-atom is

$$\psi_{nlm}(r\theta\varphi)=R_{nl}(r)\times P_{lm}(\theta)\times F_m(\varphi).$$

This wave function of the electron in atom constitutes what we call **atomic orbital**.

Principal quantum number (n): We have $E_n=-\left(\frac{1}{n^2}\right)\frac{2\pi^2\mu e^4}{h^2}$.

Thus, this quantum number (n) determines the energy of the electron in the atom. Higher the value of n, higher will be its energy value. The value of n = 1, 2. 3, ..., any (+ve) integer excluding zero.
It also determines the distance of the electron from the nucleus. For state n = 2, the electron is at higher distance from the nucleus than for state n = 1.

Azimuthal quantum number (l) : The angular momentum (L) eigen value equation is,

$$\hat{L}P = \left(\sqrt{l(l+1)}\,\frac{h}{2\pi}\right)P \text{ and the angular momentum of the electron is } L = \sqrt{l(l+1)}\,\frac{h}{2\pi}.$$

Thus this quantum number (l) determines the quantised value of angular momentum (L) of the electron. The value of l depends on n and it is 0, 1, 2, 3, ...(n - 1). l specifies the orbitals.
These are usually expressed by the symbols $s\,(l=0),\ p\,(l=1), d\,(l=2),\ f\,(l=3).$

The degeneracy of the of the orbitals is given by $(2l+1)$. Thus s - orbital is non-degenerate, p - orbitals are 3-fold degenerate, d - orbitals are 5-fold degenerate and f - orbitals are 7-fold degenerate.

Magnetic quantum number (m): It determines the spatial orientation of the angular momentum, L_z.
z - component angular momentum eigen value equation is $\hat{L}_z F = \left(m\frac{h}{2\pi}\right)F$, where $\hat{L}_z = \frac{h}{2\pi i}\frac{\partial}{\partial\varphi}$.

On solving the equation, it possible to find the function, $F = \frac{1}{\sqrt{2\pi}}e^{\pm im\varphi}$ and magnitude of the property, $L_z = m\frac{h}{2\pi}$. The value of m depends on the value of l. It is $-l, -(l-1)....0....(l-1), l$. The value of m is $(2l+1)$. It means that there are $(2l+1)$ orientations of angular momentum vector in space with respect to Z-axis. For l = 1, $m = -1, 0, +1$ and total orientations of p - orbitals are 3.

Problem: Calculate the magnitude of ground state orbital angular momentum of the electron in a H-atom , according to the (a) quantum mechanics and (b) Bohr theory.

Answer: (a) $L = \sqrt{l(l+1)}\,\frac{h}{2\pi}$, but for ground state orbital, $l = 0$ (s - orbital) and so, $L = 0$.

(b) $L = n\frac{h}{2\pi}$ and for ground state of H-atom, $n = 1$, so $L = \frac{h}{2\pi}$.

Wave function of H-atom and its normalisation condition: The wave function of H-atom is represented as $\psi_{nlm}(r\theta\varphi)$. The normalisation condition of the function is given as

$$\int_{all\ space} |\psi_{nlm}(r\theta\varphi)|^2 d\tau = 1, \text{ but } d\tau = r^2 dr \sin\theta d\theta d\varphi \text{ (small element of volume) or,}$$

$\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} |\psi_{nlm}(r\theta\varphi)|^2 r^2 dr \sin\theta d\theta d\varphi = 1$. The probability density of finding the electron at a point defined by r, θ and φ is $\psi_{nlm}(r\theta\varphi)\times\psi^*_{nlm}(r\theta\varphi)$ and the probability of finding the electron within small element of volume, $d\tau$ at r, θ and φ is given as $|\psi_{nlm}(r\theta\varphi)|^2 d\tau$.

Expression of different orbitals: The wave functions of H-atom, ψ_{nlm} is called atomic orbitals. The expression of different orbitals is given below:

(1) $\psi_{100}(=\psi_{1s}) = (\pi a_0^3)^{-1/2} e^{-r/a_0}$, where a_0 = Bohr first orbit radius = 0.53Å

(2) $\psi_{200}(=\psi_{2s}) = \left(32\pi a_0^5\right)^{-1/2}\left(2a_0 - r\right)e^{-r/2a_0}$.

(3) $\psi_{210}(=\psi_{2p_z}) = \left(32\pi a_0^5\right)^{-1/2} e^{-r/2a_0}\ r\cos\theta = \left(32\pi a_0^5\right)^{-1/2} e^{-r/2a_0}\ z$

(4) $\psi_{211}(=\psi_{2p_y}) = \left(32\pi a_0^5\right)^{-1/2} e^{-r/2a_0}\ r\sin\theta\sin\varphi = \left(32\pi a_0^5\right)^{-1/2} e^{-r/2a_0}\ y$

(5) $\psi_{21\bar{1}}(=\psi_{2p_x})=\left(32\pi a_0^5\right)^{-1/2} e^{-r/2a_0}\, r\sin\theta\cos\varphi=\left(32\pi a_0^5\right)^{-1/2} e^{-r/2a_0}\, x$.

Atomic Orbitals

For hydrogen-like (i.e. one electron) atoms, the wave functions are called 'atomic orbitals'.

Is orbital (ψ_{100}): For this orbital, $n=1, l=0, m=0$. The analytical expression of this orbital is obtained from the solution of the radial part of the Schrodinger equation of H-atom.

The expression of this orbital, $\psi_{1s}=Ae^{-r/a_0}$, where A is normalisation constant.

The value of A is obtained from the normalisation condition, $\int\limits_{all\ space} |\psi|^2 d\tau=1$,

or, $A^2\int\limits_0^{\infty} e^{-2r/a_0}\, r^2dr\int\limits_0^{\pi}\sin\theta\, d\theta\int\limits_0^{2\pi} d\varphi=1$ [since $d\tau$ = small element of volume = $r^2dr\sin\theta d\theta d\varphi$].

or, $A^2\times\dfrac{\Gamma(2+1)}{(2/a_0)^{2+1}}\times\left[-\cos\theta\right]_0^{\pi}\times\left[\varphi\right]_0^{2\pi}=1$ or, $A^2\times\dfrac{a_0^3}{4}\times 2\times 2\pi=1$ or, $\left(\pi a_0^3\right)^{-1/2}$.

Thus, the normalised wave function of 1s orbital is $\psi_{1s}=\left(\pi a_0^3\right)^{-1/2} e^{-r/a_0}$.

This is the ground state of the electron in H-atom. The electron remains in the 1s orbital at this ground state. For this state, $n=1, l=0, m=0$. So the total energy (zero-point energy), ZPE = $-\dfrac{\mu e^4}{2\hbar^2}$, the angular momentum, $L=\sqrt{l(l+1)}\,\hbar=0$, since $l=0$ and the z - component of angular momentum, $L_z=m\hbar=0$ as m = 0. a_0 = Bohr radius = $\hbar^2/\mu e^2$ = 0.53 Å. ψ_{1s} is independent of the angular variables (θ *and* φ) and depends on the radial distance (distance of the electron from the nucleus), r . ψ_{1s} takes shapes of spherical symmetrical. At every point on the surface of a sphere of fixed radius (r), the value of ψ is same.

Calculation of energy value of 1s orbital : The eigen energy value of 1s orbital is obtained by solving the eigen value equation, $\hat{H}\psi_{1s}=E_1\psi_{1s}$.

The energy operator, $\hat{H}=-\dfrac{\hbar^2}{2\mu}\nabla^2+V$. But $\nabla^2=\dfrac{1}{r^2}\dfrac{d}{dr}\left(r^2\dfrac{d}{dr}\right)$, $V=-\dfrac{e^2}{r}$ and $\psi_{1s}=Ae^{-r/a_0}$.

[ψ_{1s} is independent of θ and φ so, θ and φ part of the equation is zero]. Putting in $\hat{H}\psi_{1s}=E\psi_{1s}$,

$$\hat{H}\psi_{1s}=-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dAe^{-r/a_0}}{dr}\right)\right]-\left(\frac{e^2}{r}\right)\psi_{1s}=-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\left(-\frac{A}{a_0}\right)e^{-r/a_0}\right)\right]-\left(\frac{e^2}{r}\right)\psi_{1s}$$

or, $$\hat{H}\psi_{1s}=-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\left\{\left(r^2\left(\frac{A}{a_0^2}\right)e^{-r/a_0}+2r\left(-\frac{A}{a_0}\right)e^{-r/a_0}\right)\right\}\right]-\left(\frac{e^2}{r}\right)\psi_{1s}$$

$$=-\frac{\hbar^2}{2\mu}\left[\frac{A}{a_0^2}e^{-r/a_0}-\frac{2}{ra_0}\left(Ae^{-r/a_0}\right)\right]-\left(\frac{e^2}{r}\right)\psi_{1s}=\left[-\frac{\hbar^2}{2\mu a_0^2}+\frac{\hbar^2}{2\mu}\frac{2}{ra_0}-\frac{e^2}{r}\right]\psi_{1s}$$

$$=\left[-\frac{\hbar^2}{2\mu\left(\hbar^2/\mu e^2\right)^2}+\frac{\hbar^2}{2\mu}\frac{2}{r\left(\hbar^2/\mu e^2\right)}-\frac{e^2}{r}\right]\psi_{1s}$$

$$=\left[-\frac{\hbar^2}{2\mu}\times\frac{\mu^2e^4}{\hbar^4}+\frac{2}{r}\times\frac{\hbar^2}{2\mu}\times\frac{\mu e^2}{\hbar^2}-\frac{e^2}{r}\right]\psi_{1s}=\left[-\frac{\mu e^4}{2\hbar^2}+\frac{e^2}{r}-\frac{e^2}{r}\right]\psi_{1s}$$

or, $\hat{H}\psi_{1s} = \left(-\frac{\mu e^4}{2\hbar^2}\right)\psi_{1s} = E_1\psi_{1s}$. Thus the energy of 1s orbital is $E_1 = -\frac{\mu e^4}{2\hbar^2}$ or, $E_1 = -\frac{2\pi^2\mu e^4}{h^2}$.

The energy value is independent of t and r, so the energy remains constant for infinite time of duration at this state. Heisenberg uncertainty principle states that $\Delta E \times \Delta t \geq (1/2)\hbar$, thus $\Delta E = 0$, hence $\Delta t \to \infty$. E also remains constant at any point though KE and PE will vary from point to point within 1s state of the H-atom.

The energy value is (-ve) and hence the electron remains within this state and energy is required to remove the electron from the influence of nucleus of the atom. The ionisation potential (IP) of H-atom

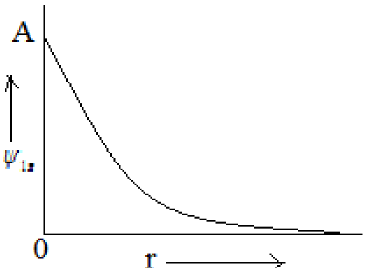
$$IP = \frac{2\pi^2\mu e^4}{h^2} = \frac{2\times(3.14)^2\times 9.1\times 10^{-31}kg\times(1.6\times 10^{-19}C)^4}{(6.626\times 10^{-34}J\ s)^2} = 21.69\times 10^{-19}J = 13.56\,eV.$$

Shapes of H-like atomic orbitals: There are two fundamentally different ways of depicting orbitals.

Method 1 is to draw graphs of the function and

Method 2 is to draw contour surfaces of constant probability density.

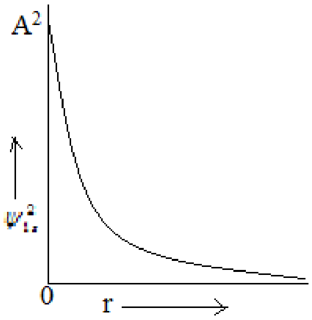
Shape of 1s orbital: The wave function, $\psi_{1s} = \left(1/\sqrt{\pi a_0^3}\right)e^{-r/a_0} = Ae^{-r/a_0}$.



Method 1: If ψ_{1s} is plotted against radial distance (r), the curve is given as,

At $r = 0$ (near the nucleus), ψ_{1s} = A (maximum) and as r increases, ψ_{1s} decreases exponentially, and $\psi_{1s} = 0$ at $r \to \infty$. Practically, ψ_{1s} almost vanishes at $r = 2a_0$. Since ψ_{1s} is only dependent of r and independent of θ and φ, so 3 – d picture of the orbital is obtained by drawing spheres of equal value ψ_{1s} around the nucleus. The shape of the orbital becomes spherically symmetrical.

The value of ψ_{1s} becomes maximum near the nucleus (which is at the centre of the sphere) and fading away as r increases from the nucleus. ψ_{1s} extends up to $r = 2a_0$.

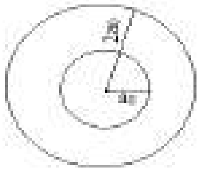


Method 2: Again the probability density is $\psi_{1s}^2 = A^2 e^{-2r/a_0}$, where $A^2 = 1/(\pi a_0^3)$.

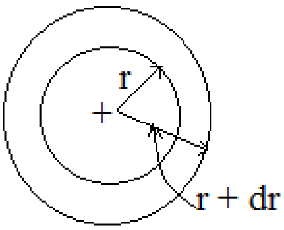
When ψ_{1s}^2 is plotted against r, the curve will be steeper than ψ_{1s} vs. r.

At r = 0, ψ_{1s}^2 = A^2 (maximum). This means that probability density of finding the electron is maximum near the nucleus and it decreases very rapidly as r increases.

We can connect the points of equal probability density and get spherical shape of contour within which there is definite probability of finding the electron. Thus, the shape of 1s orbital is spherically symmetrical.



Radial Probability Density, $P(r)$: If we consider a spherical shell of radius ne is $4\pi r^2 dr$ and probability of finding the electron within the shell is $4\pi r^2 dr \times \psi_{1s}^2 = 4\pi r^2 \psi_{1s}^2 dr = P(r)dr$.



$P(r)$ is also called radial distribution function. It is obtained also by integrating $\psi^2 d\tau$ over all angles of θ and φ but not over r and then putting dr = 1. Thus probability of finding the electron within radial distance r to $r + dr$ irrespective of θ and φ,

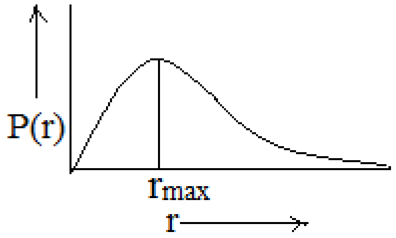
$$P(r)dr = \int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\psi_{1s}^2 d\tau = \int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}A^2 e^{-2r/a_0} r^2 dr \sin\theta d\theta d\varphi$$

$$= A^2 e^{-2r/a_0} r^2 dr \int_{\theta=0}^{\pi} \sin\theta \, d\theta \int_{\varphi=0}^{2\pi} d\varphi \; = \; 4\pi r^2 \left(A^2 e^{-2r/a_0} \right) dr = 4\pi r^2 \psi_{1s}^2 dr \, .$$

$P(r)dr$ is the probability of finding electron within the spherical shell of radius r and thickness dr and nucleus is at the centre.

When $P(r)$ is plotted against r, the curve is obtained as

$$P(r) = 4\pi A^2 r^2 e^{-2r/a_o} = A' r^2 e^{-2r/a_o} \, .$$



When $r = 0$, $P(r) = 0$ i.e., though ψ_{1s}^2 is maximum at $r = 0$ but the $P(r) = 0$ i.e., there is no probability of finding the electron within the spherical shell of radius r near to the nucleus. As r increases, $P(r)$ increases due to factor r^2, then attains maximum at some value of r and then decreases due to factor e^{-2r/a_o}. $P(r) \to 0$ as $r \to \infty$.

For small value of r, non-exponential factor dominates and at high value of r, exponential factor dominates.

Calculation of $r_{\max}$ value: We have $P(r) = A' r^2 e^{-2r/a_o}$, but for extreme value of $P(r)$, $\frac{P(r)}{dr} = 0$.

so, $\frac{P(r)}{dr} = \frac{d}{dr}\left(A' r^2 e^{-2r/a_o} \right) = A' \left[2r e^{-2r/a_o} + r^2 e^{-2r/a_o} \left(-\frac{2}{a_o} \right) \right] = 0$ or $2A' r e^{-2r/a_o} \left(1 - \frac{r}{a_o} \right) = 0$.

But for $r = 0$ and $e^{-2r/a_o} = 0$ ($r \to \infty$), $\frac{P(r)}{dr} = 0$, the curve shows minima, hence at $1 - \frac{r}{a_o} = 0$, $P(r)$ attains maximum and so $r_{\max} = a_o$. This means that in the sphere of radius a_o will have the maximum radial probability density.

It seems very interesting to see that the electron density (ψ_{1s}^2) is maximum just near the nucleus while the electron is most probable to be found at a distance of a_0 from the nucleus. This apparent inconsistency may be explained by considering a number of concentric rings of same thickness but different radii and made of materials of decreasing density with increasing radius.

Mass = volume (dv) × density (ρ).

The ring closest to the centre has smallest mass though it has highest density but its volume is smallest. Again, the ring of very large radius may not have the highest mass as volume is high but the density is very small. For a certain ring of intermediate value of radius, the mass may be maximum although the density of the ring near the centre has maximum value.

This result is consistent with the Bohr's calculation of H-atom. But the result differs in the concept. In the quantum concept, electron is most likely to be found at a distance of a_o from the nucleus in any direction but there is definite chance for the electron to be found beyond the distance, a_o.

But Bohr concept gives the certainty of the position of the electron. It is rotating round the nucleus in a circular path of radius a_o.

Calculation of average value of r in 1s orbital: We have $\langle r \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{1s} \hat{r} \psi_{1s} d\tau$,

when ψ_{1s} is normalised $= \left(1/\sqrt{\pi a_0^3} \right) e^{-r/a_o}$. Thus, $\langle r \rangle = \left(\pi a_0^3 \right)^{-1} \int_0^r e^{-2r/a_0} r^3 dr \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\varphi$

or, $\langle r \rangle = \frac{1}{\pi a_o^3} \times \frac{\underline{|3}}{(2/a_o)^4} \times 2 \times 2\pi = \frac{3}{2} a_o$. Thus the average distance of finding the electron is $\frac{3}{2} a_o$.

This shows that there is definite probability of the electron to be found in the spherical shell of radius greater than a_o.

Calculation of average value of x in 1s orbital:

$$\langle x\rangle = \int_{-\infty}^{+\infty}\psi_{1s}\,\hat{x}\psi_{1s}d\tau = \int_{0}^{\infty}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\frac{1}{\pi a_o^3}e^{-2r/a_0}\left(r\sin\theta\cos\varphi\right)r^2dr\sin\theta d\theta d\varphi$$, [since $x = r\sin\theta\cos\varphi$]

$$= \frac{1}{\pi a_o^3}\int_0^\infty e^{-2r/a_0}r^3dr\int_0^\pi\sin^2\theta d\theta\int_0^{2\pi}\cos\varphi d\varphi = 0$$. Since $\int_0^{2\pi}\cos\varphi d\varphi = \left[\sin\varphi\right]_0^{2\pi} = \sin 2\pi - \sin 0 = 0$.

Because ψ_{1s} and ψ_{1s}^2 are spherically symmetrical, there is equal chances of the electron being found at $+x$ and $-x$ distances from the nucleus leading to average value of x equal to zero.

2s orbital (ψ_{200}): For this 2s orbital, $n = 2, l = 0$ and $m = 0$. Thus it is designated as ψ_{200}.

The total energy of the orbital, $E_2 = -\frac{1}{4}\left(\frac{\mu e^4}{2\hbar^2}\right)$, as $n = 2$, the angular momentum,

$L = \sqrt{l(l+1)}\,\hbar = 0$ as $l = 0$ and z - component angular momentum, $L_z = m\hbar = 0$ as $m = 0$.
On solving the radial part of the Schrodinger equation, the expression of 2s orbital is obtained as

$$\psi_{2s} = \psi_{200} = A\left(2a_o - r\right)e^{-r/2a_o},$$ where A is normalisation constant.

Normalisation of ψ_{2s} orbital: The value of A is obtained from the condition, $\int_{all\ space}\psi_{2s}^2 d\tau = 1$.

So, $A^2\int_0^\infty\left(2a_o - r\right)^2 r^2e^{-r/a_o}dr\int_0^\pi\sin\theta d\theta\int_0^{2\pi}d\varphi = 1$ or, $A^2\int_0^\infty\left(4a_o^2 - 4ra_o + r^2\right)r^2e^{-r/a_o}dr\times 2\times 2\pi = 1$

or, $4\pi A^2\left[4a_0^2\int_0^\infty r^2e^{-r/a_o}dr - 4a_o\int_0^\infty r^3e^{-r/a_o}dr + \int_0^\infty r^4e^{-r/a_o}dr\right] = 1$

or, $4\pi A^2\left[4a_o^2\times\frac{\underline{|2}}{\left(1/a_o\right)^3} - 4a_o\times\frac{\underline{|3}}{\left(1/a_o\right)^4} + \frac{\underline{|4}}{\left(1/a_o\right)^5}\right] = 1$ or, $4\pi A^2\left[8a_o^5 - 24a_o^5 + 24a_o^5\right] = 1$

or, $4\pi A^2 8a_o^5 = 1$ or, $A^2 = \left(32\pi a_o^5\right)^{-1}$ or, $A = \left(32\pi a_o^5\right)^{-1/2}$.

So normalised wave function of the2s orbital is $\psi_{2s} = \left(32\pi a_0^5\right)^{-1/2}\left(2a_o - r\right)e^{-r/2a_o}$.
This wave function depends only on r hence it is also spherically symmetrical in shape.
Energy eigen value of ψ_{2s} orbital: The energy eigen value equation of 2s orbital is $\hat{H}\psi_{2s} = E_2\psi_{2s}$.

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 + V = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)\right] - \frac{e^2}{r}$$ and $\psi_{2s} = A\left(2a_o - r\right)e^{-r/2a_o}$.

So the energy eigen value equation is $-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_{2s}}{dr}\right)\right] - \frac{e^2}{r}\psi_{2s} = E_2\psi_{2s}$.

Solving the equation, we have the energy eigen value of 2s orbital $E_2 = -\frac{1}{4}\left(\frac{\mu e^4}{2\hbar^2}\right)$.

The energy of this orbital is precise value and energy remains conserved for infinite period of time in state. [Heisenberg uncertainty principle, $\Delta E_2\times\Delta t \geq \frac{1}{2}\hbar$, but $\Delta E_2 = 0$ and so $\Delta t \to \infty$, i.e., duration or life time of the electron at this state is infinite.]

Shape of 2s orbital: The expression of the function of 2s orbital is $\psi_{2s} = \psi_{200} = A\left(2a_o - r\right)e^{-r/2a_o}$.

The function consists of three terms (i) $A = \left(32\pi a_o^5\right)^{-1/2}$ (ii) non-exponential term $\left(2a_o - r\right)$ and

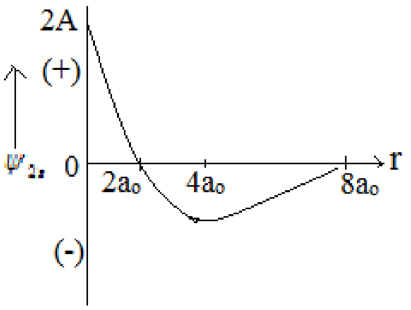
(iii) exponential term $e^{-r/2a_o}$. The exponential term ($e^{-r/2a_o}$) is just the square root of that in ψ_{1s} (e^{-r/a_o}). For this exponential term, ψ_{2s} will decreases more slowly with increase of r than ψ_{1s} function. This means that this orbital will spread more around the nucleus than ψ_{1s} orbital.

The sign of ψ_{2s} depends on the term $(2a_o - r)$.

(i) ψ_{2s} (+ve) when $r < 2a_o$ i.e., at smaller distance than $2a_o$.

(ii) ψ_{2s} = 0, when $r = 2a_o$, this is the nodal point of the orbital ψ_{2s}.

(iii) ψ_{2s} = (-ve), when $r > 2a_o$, at large distance from the nucleus.



Method 1 for depicting ψ_{2s}: When ψ_{2s} is plotted against r the following plot is obtained

At r = 0, ψ_{2s} = 2A a_o (maximum value). Now as r increases, ψ_{2s} sharply decreases due to decreasing value of $(2a_o - r)$ and $e^{-r/2a_o}$.

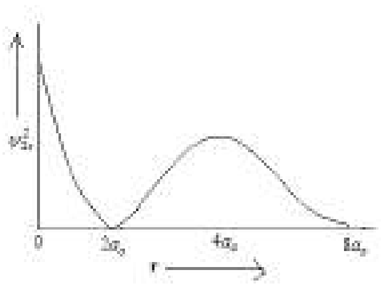
The value of ψ_{2s} becomes zero at $r = 2a_o$ (nodal point).

When $r > 2a_o$, ψ_{2s} becomes (-ve) and with increase of r, $(2a_o - r)$ is more negative and increases. The value dominates over the decreasing nature of the exponential term, $e^{-r/2a_o}$ as at this value of $r > 2a_o$,.

With further increase of r, ψ_{2s} attains minimum value and then becomes zero at large distance i.e., $r \to \infty$, $\psi_{2s} \to 0$.

There occurs nodal point at $r = 2a_o$. The sphere practically extends up to $r = 8a_o$ with (-ve) sign at $r > 2a_o$.

Method 2 for depicting 2s orbital : We have $\psi_{2s}^2 = A^2(2a_o - r)^2 e^{-r/a_o}$, where $A^2 = (32\pi a_o^5)^{-1}$.



ψ_{2s}^2 is the probability density of finding the electron in 2s orbital, and it is always (+ve).

ψ_{2s}^2 decreases from 4A^2 a_0^2 (when r = 0) more rapidly than ψ_{2s} with increase of r and becomes zero at $r = 2a_o$ and again attains maximum at $r = 4a_o$ and then decreases to asymptotic at $r \to \infty$.

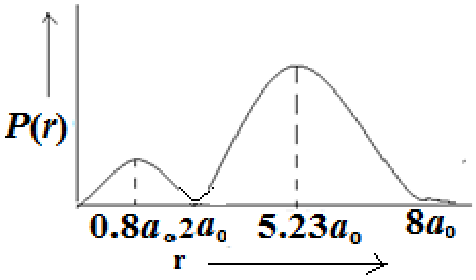
Since $(2a_o - r)^2$ = (+ve) always so ψ_{2s}^2 is also (+ve).

This nature of variation of ψ_{2s}^2 with r can be explained by the values of non-exponential term $(2a_o - r)^2$ and exponential term e^{-r/a_o}. When $r < 2a_o$ both the terms decreases with increase of r, so ψ_{2s}^2 decreases more sharply than ψ_{2s}. At $r = 2a_0$, ψ_{2s}^2 = 0 i.e., there is no probability of finding the electron at this distance (nodal point). With further increase of r at $r > 2a_o$, $(2a_o - r)^2$ increases and e^{-r/a_o} decreases but former is dominating. Again for further increase of r, exponential term dominates. So, the curve attains maximum and then decreases to $\psi_{2s} \to 0$ as $r \to \infty$.

Radial distribution function [$P(r)$ **]:** It is defined as $P(r) = 4\pi r^2 \psi_{2s}^2$, but $\psi_{2s} = A(2a_o - r)e^{-r/2a_o}$. Thus,

$$P(r) = 4\pi r^2 \times A^2 (2a_o - r)^2 e^{-r/a_o} = A' r^2 (2a_o - r)^2 e^{-r/a_o}, \text{ where } A' = 4\pi A^2.$$

$$P(r)dr = \int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} \psi_{2s}^2 d\tau$$ can also be used to find the expression of $P(r)$.



If $P(r)$ is plotted against r, we get the following curve.
When $r = 0$, $P(r) = 0$. As r increases, first term (r^2) increases, but second factor $(2a_o - r)^2$ and third term e^{-r/a_o} both decrease. For smaller value of r, first term dominates and so $P(r)$ increases. As r is further increased, second and third terms dominate, and so $P(r)$ attains maximum at certain value of r and then decreases and finally becomes zero at $r = 2a_o$. With further increase of r beyond the value of $2a_o$, second term also increase. Now first and second terms increase but the third term decreases as usual. So, $P(r)$ increases and attains maximum with greater value than the first maximum value. Again for further increase of r, $P(r)$ decreases and becomes zero when $r \rightarrow \infty$.

The values of r at which $P(r)$ attains max^{m}. : The distance (r) from the nucleus, at which $P(r)$ attains maximum, can be calculated by using the condition of extrema.

$$\frac{dP(r)}{dr} = \frac{d}{dr}\left[A'r^2(2a_o - r)^2 e^{-r/a_o}\right] = A'\frac{d}{dr}\left[\left(4a_o^2r^2 - 4a_or^3 + r^4\right)e^{-r/a_o}\right]$$

$$= A'\left[\left(8a_o^2r - 12a_or^2 + 4r^3\right)e^{-r/a_o} + \left(4a_o^2r^2 - 4a_or^3 + r^4\right)\left(-\frac{1}{a_o}\right)e^{-r/a_o}\right]$$

$$= A'e^{-r/a_o}\left(8a_o^2r - 16a_or^2 + 8r^3 - \frac{r^4}{a_o}\right) = A're^{-r/a_o}\left(8a_o^2 - 16a_or + 8r^2 - \frac{r^3}{a_o}\right) = 0.$$

So, (i) $r = 0$ and (ii) $e^{-r/a_o} = 0$ or, $r \rightarrow \infty$ correspond to the minimal points of $P(r)$ in the graph.

and (iii) $8a_o^2 - 16a_or + 8r^2 - \frac{r^3}{a_o} = 0$, but $r = 2a_o$ is the nodal point so $(2a_o - r) = 0$ is also a factor of the equation. Thus, $8a_o^2 - 16a_or + 8r^2 - \frac{r^3}{a_o} = 8a_o^2 - 4a_or - 12a_or + 6r^2 + 2r^2 - \frac{r^3}{a_o} = 0$

or, $4a_o(2a_o - r) - 6r(2a_o - r) + \frac{r^2}{a_o}(2a_o - r) = 0$ or, $(2a_o - r)\left(4a_o - 6r + \frac{r^2}{a_o}\right) = 0$.

Then $4a_o - 6r + \frac{r^2}{a_o} = 0$ or, $r^2 - 6a_or + 4a_o^2 = 0$, so $r = \frac{6a_o \pm \sqrt{36a_o^2 - 16a_o^2}}{2} = 3a_o \pm \sqrt{5}a_o$ $= \left(3 \pm \sqrt{5}\right)a_o$. The values of r, at which $P(r)$ attains maximum, are $r = 0.8a_o$ and $r = 5.23a_o$.

The shape of 2s orbital is spherical with nucleus at the centre. When a spherical shape orbital rotates, its angular momentum (L) becomes zero.

At $r = 0.8a_o$, $P(r)$ is maximum (1st), at $r = 2a_o$, there is nodal point and at $r = 5.23a_o$, $P(r)$ again attains maximum (2nd). The orbital contour extends up to $r = 8a_o$.

The number of nodal points = $(n-1) = 1$.

Calculation of average distance, $\langle r \rangle$: Average distance of the electron from the nucleus of H-atom in the 2s state is calculated by the use of the quantum theorem.

$$\langle r \rangle = \int\limits_{all\ space} \psi_{2s}\,\hat{r}\,\psi_{2s}\,d\tau = \left(32\pi a_o^5\right)^{-1} \int\limits_{all\,space} r\left(2a_o - r\right)^2 e^{-r/a_o} r^2 dr \sin\theta d\theta d\varphi$$

$$= \left(32\pi a_o^5\right)^{-1}\int_0^\infty r^3\left(4 - \frac{4r}{a_o} + \frac{r^2}{a_o^2}\right)e^{-r/a_o}dr\int_0^\pi \sin\theta d\theta\int_0^{2\pi} d\varphi$$

$$= \left(32\pi a_o^5\right)^{-1}\int_0^\infty r^3\left(4a_o^2-4a_o r+r^2\right)e^{-r/a_o}dr\times 2\times 2\pi$$

$$\text{or, } \langle r\rangle = \left(32\pi a_o^5\right)^{-1}\times 4\pi\left[4a_o^2\int_0^\infty r^3 e^{-r/a_o}dr-4a_o\int_0^\infty r^4 e^{-r/a_o}dr+\int_0^\infty r^5 e^{-r/a_o}dr\right]$$

$$= \left(8a_o^5\right)^{-1}\left[4a_o^2\times\frac{\lfloor 3}{\left(1/a_o\right)^4}-4a_o\times\frac{\lfloor 4}{\left(1/a_o\right)^5}+\frac{\lfloor 5}{\left(1/a_o\right)^6}\right]=\left(8a_o^5\right)^{-1}\left[24a_o^6-96a_o^6+120a_o^6\right]$$

$$=\left(8a_o^5\right)^{-1}\times 48a_o^6=6a_o .$$

Thus the average distance of the electron in the 2s state of H-atom is $6a_o = 6\times 0.53$Å = 3.18 Å.

Value of $\langle x\rangle$: Using the same quantum theorem, it is possible to calculate the average distance of the electron along the x- axis.

$$\langle x\rangle = \int_{all\ space}\psi_{1s}\,\hat{x}\,\psi_{2s}d\tau = \left(32\pi a_o^5\right)^{-1}\int_{all\ space}\left(2a_o-r\right)^2 e^{-r/a_o}r\sin\theta\cos\varphi\times r^2 dr\sin\theta d\theta d\varphi$$

$$= \left(32\pi a_o^5\right)^{-1}\int_0^\infty r^3\left(2a_o-r\right)^2 e^{-r/a_o}dr\int^\pi\sin^2\theta d\theta\int_0^{2\pi}\cos\varphi d\varphi = 0.$$

[since $\int_0^{2\pi}\cos\varphi d\varphi=\left[\sin\varphi\right]_0^{2\pi}=\left(\sin 2\pi-\sin 0\right)=0-0=0$]

Because ψ_{2s} and ψ_{2s}^2 are spherically symmetrical, there is equal chances of the electron to be found at $+x$ and $-x$ distances from the nucleus leading to the average value of x equal to zero.

2p-orbitals: For this orbitals, $n=2$, $l=1$ and $m=-1,0,+1$. Thus 2p-orbitals are of three in number and these are degenerate. These p-orbitals are $\psi_{21\bar{1}}\left(\psi_{2p_x}\right),\psi_{211}\left(\psi_{2p_y}\right)$ and $\psi_{210}\left(\psi_{2p_z}\right)$.

For H-atom, the state $n=2$ are four-fold degenerate, $2s, 2p_x, 2p_y$ and $2p_z$ since the number of degeneracy of a given state (n) in H-atom is n^2.

The angular momentum of the 2p-orbital is $=\sqrt{l(l+1)}\hbar=\sqrt{2}\hbar$ and z - component angular momentum, $L_z=m\hbar=-\hbar$, 0 and $+\hbar$ for $2p_x, 2p_y$ and $2p_z$ orbitals respectively.

2p$_x$ orbital: The wave function of 2p$_x$ orbital is $\psi_{2p_x}=\psi_{21\bar{1}}=Ae^{-r/2a_o}\left(r\sin\theta\cos\varphi\right)$,

but $x=r\sin\theta\cos\varphi$, thus $\psi_{2p_x}=Ae^{-r/2a_o}x$, where A = normalisation constant.

Putting the normalisation condition, $\int_{all\ space}\left|\psi_{2p_x}\right|^2 d\tau=1$, the value of A can be determined.

Thus $A^2\int_{all\ space}e^{-r/a_o}r^2\sin^2\theta\cos^2\varphi\times r^2 dr\sin\theta d\theta d\varphi=1$ or, $A^2\int_0^\infty r^4 e^{-r/a_o}dr\int_0^\pi\sin^3\theta d\theta\int_0^{2\pi}\cos^2\varphi d\varphi=1$ or,

$$A^2\times\frac{\lfloor 4}{\left(1/a_o\right)^5}\times\frac{4}{3}\times\pi=1 \text{ or, } A^2\times 32\pi a_o^5=1$$

or, $A=\left(32\pi a_o^5\right)^{-1/2}$. Thus the normalised wave function of 2p$_x$ orbital is $\left(32\pi a_o^5\right)^{-1/2}e^{-r/2a_o}x$.

[Integration: $\int_0^\pi\sin^3\theta d\theta=\int_0^\pi\sin\theta\times\sin^2\theta d\theta=\int_0^\pi\sin\theta\left(1-\cos^2\theta\right)d\theta=-\int_0^\pi\left(1-\cos^2\theta\right)d\left(\cos\theta\right)$

$$=-\int_0^\pi d\left(\cos\theta\right)+\int_0^\pi\cos^2\theta d\left(\cos\theta\right)=\left[-\cos\theta\right]_0^\pi+\frac{1}{3}\left[\cos^3\theta\right]_0^\pi$$

$$= [-\cos\pi + \cos 0] + \frac{1}{3}\left[\cos^3\pi - \cos^3 0\right] = 2 + \frac{1}{3}\times(-2) = \frac{4}{3}\,.$$

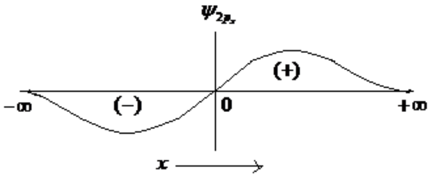
And $\int_0^{2\pi}\cos^2\varphi d\varphi = \frac{1}{2}\int_0^{2\pi}(1+\cos 2\varphi)\,d\varphi = \frac{1}{2}\int_0^{2\pi}d\varphi + \frac{1}{2}\int_0^{2\pi}\cos 2\varphi d\varphi = \pi + \frac{1}{4}\left[sin2\varphi\right]_0^{2\pi} = \pi$].

Shape of $2p_x$ orbital: We have $\psi_{2p_x} = \left(32\pi a_o^5\right)^{-1/2} e^{-r/2a_o} x$, and $r = \sqrt{x^2+y^2+z^2}$

but along the x - axis, $y = 0$ and $z = 0$, thus $r = |x|$, hence $\psi_{2p_x} = \left(32\pi a_o^5\right)^{-1/2} e^{-|x|/2a_o} x$

or, $\psi_{2p_x} = Ae^{-|x|/2a_o} x$. **The plot of ψ_{2p_x} vs.** x is a Gaussian type in both sides of the origin.

When x = 0, ψ_{2p_x} = 0. As x increases within the range 0 to $+\infty$, ψ_{2p_x} increases, attains maximum and then decreases to zero at $x \to +\infty$. ψ_{2p_x} is (+ve) in sign in this range of x.



But when x increases within the range 0 to $-\infty$, ψ_{2p_x} is (-ve) and decreases, attains minimum and then increases to zero at $x \to -\infty$.

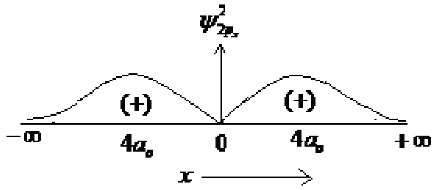
When the ψ_{2p_x} is rotated by 360° along the x - axis, two lobes are obtained on the both sides of origin. The right lobe is (+ve) in sign while left lobe is (-ve). The shape of ψ_{2p_x} orbital is of dumb-bell shape. ψ_{2p_x} = 0 at x = 0. Thus the orbital has a nodal plane in the yz - plane.

$\psi^2_{2p_x}$ **vs.** x **plot:** $\psi^2_{2p_x}$ is the probability of finding the electron in the $2p_x$ orbital.

$\psi^2_{2p_x} = A^2 e^{-|x|/a_o} x^2$,   where $A^2 = \left(32\pi a_o^5\right)^{-1}$.

When $\psi^2_{2p_x}$ is plotted against x, the curve is given as:

If $\psi^2_{2p_x}$ is rotated by 360° along x - axis, we get two lobes of equal probability at a given value of x on both sides of origin. The probability density extends along the x - axis only.



Radial distribution function, $P(r)$:

$$P(r)dr = \int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\left|\psi_{2p_x}\right|^2 d\tau = A^2 e^{-r/a_o} r^4 dr \int_0^{\pi}\sin^3\theta d\theta \int_0^{2\pi}\cos^2\varphi d\varphi = \left(32\pi a_o^5\right)^{-1} e^{-r/a_o} r^4 dr \times \frac{4}{3}\times\pi$$

$= \left(24a_o^5\right)^{-1} e^{-r/a_o} r^4 dr$. Thus radial distribution function, $P(r) = \left(24a_o^5\right)^{-1} e^{-r/a_o} r^4$.

$$\frac{dP(r)}{dr} = A'\frac{d}{dr}\left(e^{-r/a_o} r^4\right) = A'\left[4r^3 e^{-r/a_o} + r^4 e^{-r/a_o}\left(-1/a_o\right)\right] = A'\left[4r^3 e^{-r/a_o} - r^4/a_o\, e^{-r/a_o}\right]$$

$= A' r^3 e^{-r/a_o}\left(4 - r/a_o\right)$ = 0. Thus, at r = 0 and e^{-r/a_o} = 0 or, $r = \infty$, $P(r)$ attains minimum.

But for $\left(4 - r/a_o\right)$ = 0 or, $r = 4a_o$, $P(r)$ attains maximum.

Problem: Find the most probable distance from the nucleus of 2p state of H-atom.

Given, $R_{2,1} = \frac{1}{\sqrt{3}}\left(\frac{1}{2a_o}\right)^{3/2}\left(r/a_o\right)e^{-r/2a_o}$. **(SKB Univ., 2014)** **[Ans.** $r = 4a_o$ **].**

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