

The Schrodinger Theory of Quantum Mechanics:

The quantity that characterises the De-broglie wave is called wavefunction $\psi(x,t)$. The Schrodinger theory tells us how to obtain the wavefunction $\psi(x,t)$ associated with a particle acted upon by a force giving the P.E. associated with force. Schrodinger developed a differential equation whose solution yield the possible wave wavefunction. There are two types of Schrodinger Equation.

(1) The time dependent Schrodinger Equation:

The wavefunction associated with the motion of free particle is $\psi(x,t) = A e^{i(kx - \omega t)}$ — (1)

or, $\psi = A e^{-\frac{i}{\hbar} (\hbar\omega t - \hbar kx)}$

or, $\psi = A e^{\frac{i}{\hbar} (Et - Px)}$ — (2)

Differentiating w.r. to x

$\frac{\partial \psi}{\partial x} = \left(-\frac{i}{\hbar}\right) (-P) A e^{\frac{i}{\hbar} (Et - Px)}$

or, $\frac{\partial \psi}{\partial x} = \frac{iP}{\hbar} \psi$ — (3)

Again diff. eq. (3) w.r. to 'x'

$\frac{\partial^2 \psi}{\partial x^2} = \left(\frac{iP}{\hbar}\right)^2 \psi$

or, $\frac{\partial^2 \psi}{\partial x^2} = -\frac{P^2}{\hbar^2} \psi$

$\Rightarrow P^2 \psi = -\hbar^2 \frac{\partial^2 \psi}{\partial x^2}$ — (4)

Now diff. eq. (2) w.r. to 't'

$\frac{\partial \psi}{\partial t} = \left(-\frac{i}{\hbar}\right) E A e^{\frac{i}{\hbar} (Et - Px)}$

or, $\frac{\partial \psi}{\partial t} = -\frac{iE}{\hbar} \psi \Rightarrow \frac{\partial \psi}{\partial t} = \frac{E\psi}{i\hbar}$

$\therefore E\psi = i\hbar \frac{\partial \psi}{\partial t}$ — (5)

Energy operator $\hat{E} = i\hbar \frac{\partial}{\partial t}$

The total energy of particle is given by $E = K.E. + P.E.$

or, $E = \frac{P^2}{2m} + V$

or, $E\psi = \frac{P^2 \psi}{2m} + V\psi$ — (6)

from eq. (4), (5) \rightarrow (6)

$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi$ — (7)

which is required time dependent Schrodinger wave equation

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

where $\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V$ is

Known as Hamiltonian operator.

② Time independent Schrodinger Equation: (SWE)

It has been observed that in many situations, potential (V) acting on the particle does not depend upon time and varies only with its position. In this case time independent Schrodinger equation is applicable.

The wavefunction associated with the motion of free particle is $\psi = A e^{\frac{i}{\hbar}(Et - Px)}$ - (1)

or, $\frac{d\psi}{dx} = -\frac{iP}{\hbar} A e^{\frac{i}{\hbar}(Et - Px)}$ or, $E = \frac{P^2}{2m} + V$

or, $\frac{d\psi}{dx} = \frac{iP}{\hbar} \psi$

$\therefore \frac{d}{dx} \left(\frac{d\psi}{dx} \right) = \frac{iP}{\hbar} \frac{d\psi}{dx}$

or, $\frac{d^2\psi}{dx^2} = \frac{iP}{\hbar} \left(\frac{iP}{\hbar} \psi \right)$

$\Rightarrow P^2 \psi = -\hbar^2 \frac{d^2\psi}{dx^2}$ - (2)

The total energy of particle is

or, $E\psi = \frac{P^2}{2m} \psi + V\psi$ - (3)

from (2) + (3), $E\psi = -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi$

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

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

$\Rightarrow \frac{d^2\psi}{dx^2} + \frac{2m(E - V)}{\hbar^2} \psi = 0$ - (4)

which is required time independent SWE (Schrodinger wave equation).

In three dimension

$\nabla^2 \psi + \frac{2m(E - V)}{\hbar^2} \psi = 0$ - (5)

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

$\nabla = \hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z}$ is nabla operator.

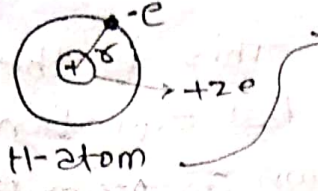
from eq. (2) + (3) $E\psi = \left(-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V \right) \psi$

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

Solution of Schrodinger Equation for H-atom:

The H-atom consist of a Proton around which the electron revolves. The P.F. function due to the Coulomb field is

$V(r) = \frac{(ze) \cdot (-e)}{4\pi\epsilon_0 r} \Rightarrow V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$ - (1) (z=1 for H-atom)



Hence time independent SWE for electron is

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

The geometrical symmetry of problem suggest that, it is more convenient to use the spherical polar co-ordinate system as shown in fig. below.

From fig. co-ordinate transformation

equations are

$$\begin{cases} x = r \sin \theta \cos \phi \\ y = r \sin \theta \sin \phi \\ z = r \cos \theta \end{cases} \quad \text{--- (3)}$$

where, 'r' is radius vector
 'θ' is polar angle
 'φ' is azimuthal angle

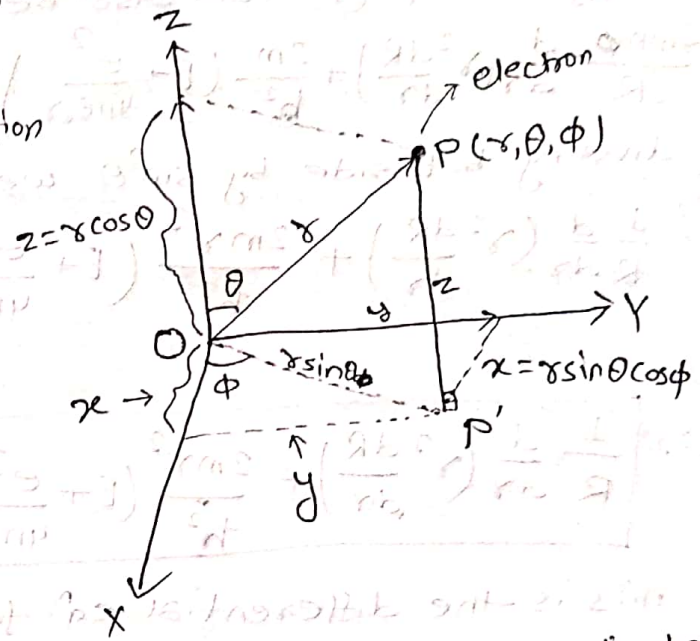


fig. spherical polar co-ordinate

Hence SWE in spherical polar co-ordinate system is

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \theta} \left(\sin^2 \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2 \psi}{\partial \phi^2} \right) + \frac{2m}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) \psi = 0 \quad \text{--- (4)}$$

This equation is the partial differential equation for the wavefunction 'ψ' of the electron in H-atom.

Equation (4) can be solved by separation of variables method of the form

$$\psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \quad \text{--- (5)}$$

From (4) + (5),

$$\Theta \Phi \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{R \Phi}{r^2 \sin^2 \theta} \frac{d}{d\theta} \left(\sin^2 \theta \frac{d\Theta}{d\theta} \right) + \frac{R \Theta}{r^2 \sin^2 \theta} \frac{d^2 \Phi}{d\phi^2} + \frac{2m}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) R \Theta \Phi = 0 \quad \text{--- (6)}$$

multiplying eq. (6) by $\frac{r^2 \sin^2 \theta}{R \Theta \Phi}$, we get

$$\frac{\sin^2 \theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin^2 \theta}{\Theta} \frac{d}{d\theta} \left(\sin^2 \theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} + \frac{2m}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) r^2 \sin^2 \theta = 0$$

$$\frac{\sin^2 \theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin^2 \theta}{\Theta} \frac{d}{d\theta} \left(\sin^2 \theta \frac{d\Theta}{d\theta} \right) + \frac{2m}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) r^2 \sin^2 \theta = -\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = m^2 \quad \text{--- (7)}$$

$$-\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = m_l^2 \Rightarrow \boxed{\frac{d^2 \Phi}{d\phi^2} + m_l^2 \Phi = 0} \quad (8)$$

This is the differential equation for Φ known as Azimuthal equation

and ' m_l ' is known as Azimuthal quantum no. or magnetic quantum no.

Again eq. (7) can also be written as

$$\frac{\sin\theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) r^2 \sin^2\theta = m_l^2 - \frac{\sin\theta}{\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\theta}{d\theta} \right)$$

dividing bothside by $\sin^2\theta$ we get

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m r^2}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) = \frac{m_l^2}{\sin^2\theta} - \frac{1}{\theta \sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\theta}{d\theta} \right)$$

= $\lambda(\lambda+1)$ say

$$\boxed{\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m r^2}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) = \lambda(\lambda+1)} \quad (9)$$

this is the differential eq. for 'R' known as radial equation.

and $\boxed{\frac{m_l^2}{\sin^2\theta} - \frac{1}{\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\theta}{d\theta} \right) = \lambda(\lambda+1)} \quad (10)$ this is the differential equation for

' θ ' known as polar equation.

Hence the SWE for H-atom can be separated into three differential equation (8), (9) & (10)

(1) The solution of Azimuthal eq. (8) is of the form $\Phi(\phi) = A e^{im_l \phi}$
 for this function $\Phi(\phi)$ to be single valued, $\Phi(\phi) = \Phi(\phi + 2\pi)$
 i.e. $e^{im_l \phi} = A e^{im_l(\phi + 2\pi)}$

$\Rightarrow m_l = 0, \pm 1, \pm 2, \pm 3 \dots$ known as magnetic orbital quantum no. of H-atom.

(2) The solution of radial eq. (9) are given by the standard mathematical function known as Laguerre polynomials. The solution for 'R' remains finite every where for which $E = E_n = -\frac{me^4}{8\epsilon_0^2 \hbar^2} \left(\frac{1}{n^2} \right) = -\frac{13.6}{n^2} \text{ eV}$ where $n = 1, 2, 3 \dots$ are known as principle quantum no.

③ The solution of polar equation (10) ~~are~~ ^{is} given by standard mathematical function known as Legendre polynomials. The solution for Θ remain finite everywhere for which $l = 0, 1, 2, 3, \dots, (n-1)$ known as orbital quantum no. here, $n \geq (l+1)$

Significance of various quantum number:

(1) The principle quantum number (n):

The radial wave equation for H-atom can be solved only when 'E' has continuous range of +ve values ~~and~~ or discrete set of -ve values (i.e. bound state)

Given by $E = \frac{-me^4}{8\epsilon_0^2 h^2} \left(\frac{1}{n^2}\right) = \frac{-13.6}{n^2} \text{ eV}$ where

$n = 1, 2, 3, 4, \dots$ are integers.

Hence principle quantum no. 'n' describes the quantization of electron energy in H-atom.

(2) The orbital quantum no. (l):

The total energy of electron is $E = \text{K.E.} + \text{P.E.}$

$E = (E_r + E_o) + \left(-\frac{e^2}{4\pi\epsilon_0 r}\right) = \text{①}$ where, E_o is orbital K.E. E_r is radial K.E.

The radial equation is

$\frac{1}{r} \frac{d}{dr} \left(r^2 \frac{dR}{dr}\right) + \frac{2m r^2}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r}\right) = l(l+1) = \text{②}$

Putting value of 'E' from eq. ① into eq. ②

$\frac{1}{r} \frac{d}{dr} \left(r^2 \frac{dR}{dr}\right) + \frac{2m r^2}{\hbar^2} \left[E_r + E_o - \frac{e^2}{4\pi\epsilon_0 r} + \frac{e^2}{4\pi\epsilon_0 r}\right] - l(l+1) = 0$

⇒ multiplying by $\left(\frac{R}{r^2}\right)$

$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr}\right) + \frac{2m}{\hbar^2} \left[E_r + E_o - \frac{\hbar^2 l(l+1)}{2m r^2}\right] R = 0 = \text{③}$

Equation (3) is completely radial only if

$$E_0 - \frac{\hbar^2 l(l+1)}{2m r^2} = 0 \rightarrow L^2 = \hbar^2 l(l+1)$$

$$\therefore E_0 = \frac{\hbar^2 l(l+1)}{2m r^2}$$

$$\therefore \frac{1}{2} m v_0^2 = \frac{\hbar^2 l(l+1)}{2m r^2}$$

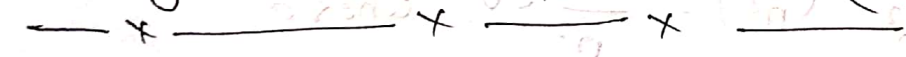
$$\therefore m^2 v_0^2 r^2 = \hbar^2 l(l+1)$$

$L = \hbar \sqrt{l(l+1)}$ is angular momentum of electron in its orbital motion.

here $l = 0, 1, 2, \dots (n-1)$.

Hence orbital quantum no. describe the quantization of angular momentum. i.e. orbital quantum no. 'l' determines the magnitude of angular momentum of electron.

③ Magnetic orbital quantum no. (m_l):



Due to electron current in the loop uniform m.f.

\vec{B} parallel to z-axis is developed as shown in fig. (1). The component of 'L' in the z-axis is quantized and given by

$$L_z = m_l \hbar \quad \text{--- (1)}$$

where $m_l = 0, \pm 1, \pm 2, \dots, \pm l$

given value of 'l', possible value of

' m_l ' is $(2l+1)$. Hence angular momentum vector ' \vec{L} '

can have $(2l+1)$ discrete orientation

w.r. to m.f. This quantization of ~~orbital~~ angular momentum of atom in space is

known as "space quantization". The space quantization of orbital angular momentum of electron is shown in fig. (2)

for $l=2$ $\cos \theta = \frac{L_z}{L} = \frac{m_l \hbar}{\hbar \sqrt{l(l+1)}} = \frac{m_l}{\sqrt{l(l+1)}}$

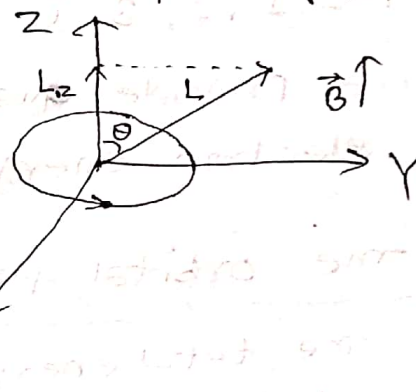


fig. electron revolving around nucleus.

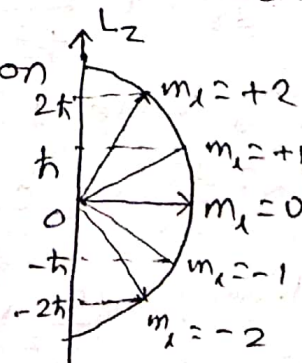


fig. (2) orientation of \vec{L} of electron in H-atom

Degeneracy of Energy Levels of H-atom.

The phenomenon in which there are a number of independent quantum states of a system each having same energy level is called degeneracy. Total no. of quantum state is called degree of degeneracy and corresponding energy is called degenerate energy.

We know energy eigen value of n^{th} energy state of H-atom is $E_n = \frac{-m^2 e^4}{8 \epsilon_0^2 h^2} \left(\frac{1}{n^2} \right) = -\frac{13.6}{n^2} \text{ eV}$

where $n = 1, 2, 3, 4, \dots$ is principle quantum no.

~~magnetic~~ orbital quantum no. $l = 0, 1, 2, \dots, (n-1)$

magnetic orbital quantum no. $m_l = 0, \pm 1, \pm 2, \dots, \pm l$

Hence wavefunction of H-atom is ψ_{nlm}

of $n=1$, $l=0$ and $m_l=0 \Rightarrow$ only one state ψ_{100}

of $n=2$, $l=0 \Rightarrow m_l=0$
or $l=1 \Rightarrow m_l = +1, 0, -1$

Four state

- ψ_{200}
- ψ_{211}
- ψ_{210}
- ψ_{21-1}

i.e. Four fold degeneracy

as shown in fig. below

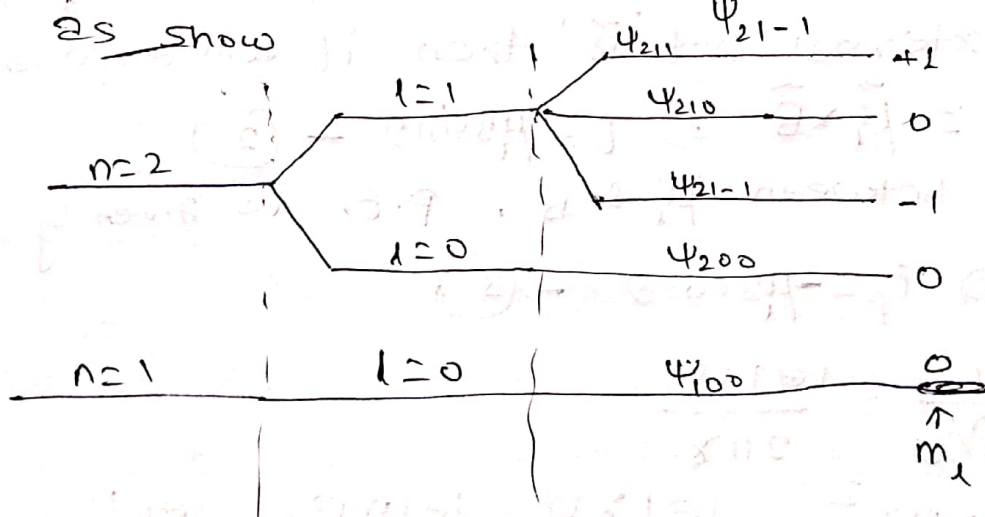


fig. Degeneracy of energy levels of H-atom.

The Spin (S): Due to the spinning motion of electron, it has an intrinsic spin angular momentum (S). and spin magnetic dipole moment $\mu_s = \frac{-e\hbar}{m} S$

z-component of S is $S_z = m_s \hbar$ which is quantized

also, $S = \hbar \sqrt{s(s+1)}$ where $s = \frac{1}{2}$
 $\Rightarrow m_s = \pm \frac{1}{2}$ is called magnetic spin quantum no.

The Zeeman effect and space quantization:

Let us consider an electron of mass 'm' and charge 'e' is revolving around the nucleus of charge +e in the

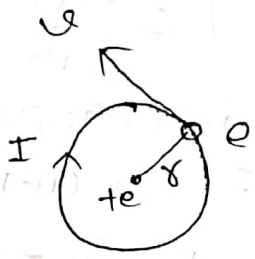


fig (1) An electron revolving the nucleus

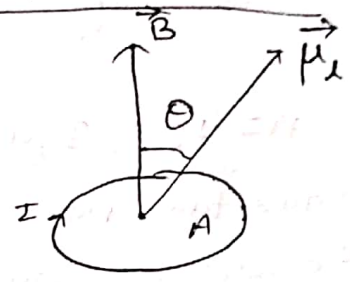


fig (2) magnetic dipole moment $\mu = IA$ in mt B

charge +e in the circular orbit of radius 'r' with velocity 'v'. Due to current 'I' in the loop of area 'A', magnetic dipole moment $\mu = IA$ is associated with electron. If this dipole is placed in external mt. 'B' then it will experience torque

$$\vec{\tau} = \vec{\mu} \times \vec{B} \Rightarrow \tau = \mu B \sin \theta \quad (2)$$

where 'theta' is angle between μ & 'B'. P.E. is given by

$$E_p = -\vec{\mu} \cdot \vec{B} \Rightarrow E_p = -\mu B \cos \theta \quad (3)$$

$$I = \frac{|e|}{t} = \frac{|e|}{2\pi r/v} = \frac{|e|v}{2\pi r}$$

$$\mu = IA = \frac{|e|v}{2\pi r} \cdot \pi r^2 = \frac{|e| r v}{2} = \frac{|e| m v r}{2m} = \frac{|e| L}{2m}$$

$\Rightarrow \mu = -\frac{|e| L}{2m}$ (-ve sign indicate that direction of 'I' is opposite to direction of motion of electron (v))

Putting value of μ in eqn (3) we get $E_p = \frac{|e|}{2m} B L \cos \theta$

or $E_p = \frac{|e|\hbar}{2m} B L_z$ — (4)

The total energy of atom $E_{total} = E_n + E_p$

or, $E_T = E_n + \frac{|e|\hbar}{2m} B L_z$

put $L_z = m_l \hbar$

$E_T = E_n + \frac{|e|\hbar}{2m} B m_l \hbar$ — (5)

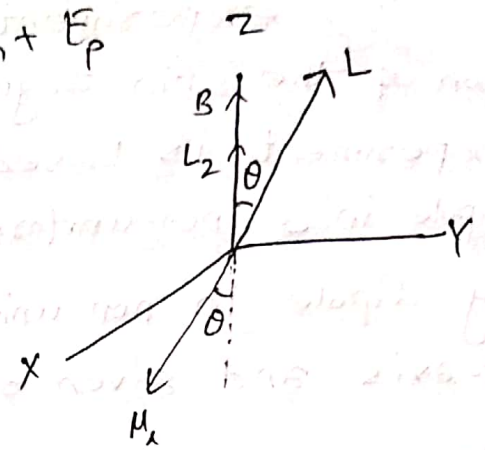


fig. (3) relative orientation of L & M_z

since $m_l = 0, \pm 1, \pm 2 \dots \pm l$ then

given energy level of quantum states with orbital quantum no. $l > 0$

splits into several discrete sublevels as shown in fig. below.

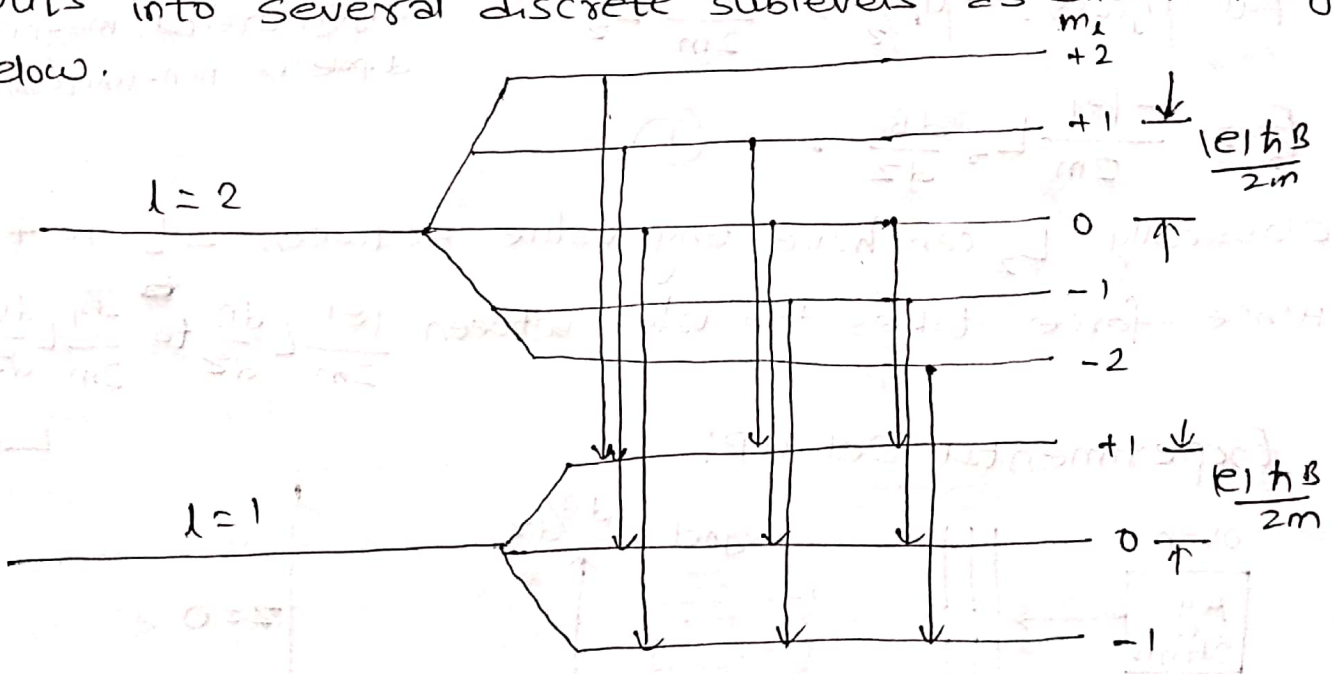


fig. (4) Energy level splitting in normal zeeman effect

The allowed transitions are those for which $m_l = 0$ or ± 1 known as selection rule. The difference between adjacent level is $\frac{(e)\hbar B}{2m}$ and is independent of 'l' known as normal zeeman effect. But experimentally more than three lines are observed for transition from $n=2$ to $n=1$ of H-atom. Known as anomalous zeeman effect. Thus, the experiment shows the idea of space quantization of orbital angular momentum 'L'

② Stern-Gerlach Experiment :

This experiment shows the idea of space quantization of the spin angular momentum of an electron. This experiment is based on the behaviour of a orbital magnetic dipole in a non-uniform m.f. The net force experience by dipole in non-uniform m.f. is along z-axis and given by $F_z = \vec{\mu}_l \cdot \frac{d\vec{B}}{dz}$

As shown in fig ①

$$\text{or, } F_z = \mu_l \frac{dB}{dz} \cos\theta$$

$$\text{put } \mu_l \cos\theta = (\mu_l)_z = \frac{-|e|}{2m} L_z$$

$$F_z = \frac{-|e|}{2m} L_z \frac{dB}{dz} \quad \text{--- (1)}$$

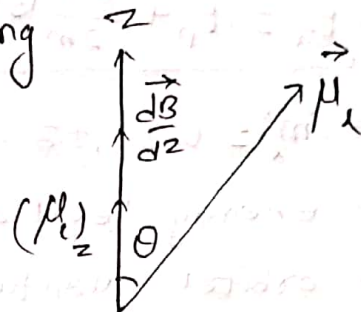


fig. ① orbital magnetic dipole in non-uniform m.f.

Classically L_z can have any value between $-L$ to $+L$.

Hence force takes the value between $\frac{|e|}{2m} L \frac{dB}{dz}$ to $\frac{-|e|}{2m} L \frac{dB}{dz} = F_z$

L (2)

Experimental Set up:

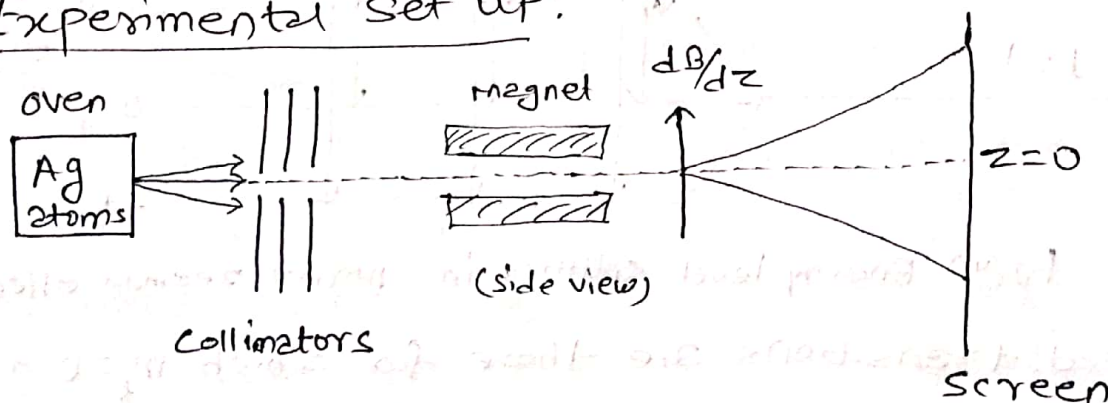


fig. ② Stern-Gerlach experiment.

Silver atoms from heated oven are well collimated and pass through non-uniform m.f. ($\frac{dB}{dz}$). Silver atoms are collected on the screen. Although the atoms were uncharged, they did not possess a magnet dipole. The only force acting on atoms was due to non-uniform m.f. ($\frac{dB}{dz}$).

Depending on the magnitude of this force, the atomic dipoles will be deflected as shown in fig. above i.e. force varies between two values.

In silver atom outermost electron is in '2s' state. For s-state $l=0 \Rightarrow \mu_l = 0$. Hence electron has only one spin magnetic dipole moment μ_s . This leads the space quantization of the spin angular momentum.

Atomic Wavefunctions (Probability densities of electrons)

Atomic wavefunction is the solution of Schrödinger wave equation in spherical polar co-ordinate system which is used to calculate the probability density $P(r, \theta, \phi)$ i.e. probability of finding any electron of an atom in unit volume around a given point. Hence, Atomic wave function is

$$\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r) \Theta_{lm}(\theta) \Phi_m(\phi) \quad \text{--- (1)}$$

$$\therefore P(r, \theta, \phi) = \Psi \Psi^* = |\Psi|^2 = |R_{nl}(r)|^2 |\Theta_{lm}(\theta)|^2 |\Phi_m(\phi)|^2 \quad \text{--- (2)}$$

$$\begin{aligned} |\Phi(\phi)|^2 &= \Phi \Phi^* \\ &= \frac{1}{\sqrt{2\pi}} e^{im\phi} \cdot \frac{1}{\sqrt{2\pi}} e^{-im\phi} \\ &= \frac{1}{2\pi} \end{aligned}$$

$$\therefore P(r, \theta, \phi) = \frac{1}{2\pi} |R_{nl}(r)|^2 |\Theta_{lm}(\theta)|^2 \quad \text{--- (3)}$$

which shows that probability density is independent upon azimuthal co-ordinate ' ϕ ' i.e. electron distribution in an atom is symmetric about z-axis as shown in fig. below for lowest energy state of H-atom.

Soln. of Azimuthal eqn. $\frac{d^2\Phi}{d\phi^2} + m_l^2\Phi = 0$ is $\Phi = A e^{im_l\phi}$ --- (1)

The normalizing condition for the wavefunction ' Φ ' is

$$\int_0^{2\pi} |\Phi|^2 d\phi = 1$$

$$\int_0^{2\pi} \Phi \Phi^* d\phi = 1$$

$$\int_0^{2\pi} A e^{im_l\phi} \cdot A e^{-im_l\phi} d\phi = 1$$

$$A^2 \int_0^{2\pi} d\phi = 1$$

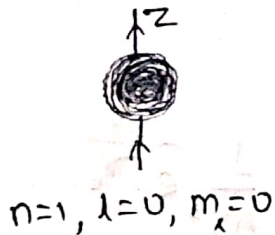
$$A^2 [2\pi] = 1$$

$$A^2 \cdot 2\pi = 1$$

$$A^2 = \frac{1}{2\pi}$$

$$A = \frac{1}{\sqrt{2\pi}}$$

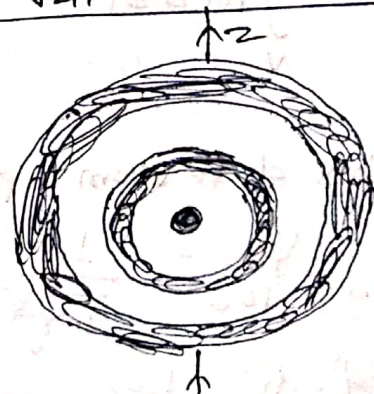
\therefore Normalized wave function is $\Phi = \frac{1}{\sqrt{2\pi}} e^{im_l\phi}$



Ψ_{100}



Ψ_{200}

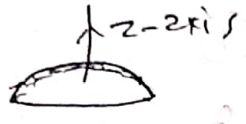


Ψ_{300}



$n=2, l=1, m_l = \pm 1$

$\psi_{21\pm 1}$



$n=2, l=1, m_l = 0$

ψ_{210}

The important feature is that, except for s-state (i.e. $l=0$), $|\psi|^2$ does not have spherical symmetry.

The sum of all the wavefunction of a subset of states having the same 'n' and is spherically symmetric not only for H-atom wavefunctions but for those for multielectron atoms as well. It explains partially why the rare gases 'He', 'Ne', 'Ar' are inert. It also explains why atoms such as 'Li', 'Na', 'K' are Hydrogen like.

Radial Probability density $P(r) dr$:

It is defined as the Probability of finding the electron between 'r' and 'r+dr'.

We know that probability of finding the electron in small volume 'dv' is

$$P(r, \theta, \phi) dv = |\psi(r, \theta, \phi)|^2 dv = |\psi(r, \theta, \phi)|^2 r^2 \sin \theta dr d\theta d\phi$$

$$P(r) dr = \int_v P(r, \theta, \phi) dv = |\psi(r, \theta, \phi)|^2 r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \quad \text{--- (1)}$$

For G.S. of H-atom $n=1, l=0, m_l=0$

$$\therefore \psi_{nlm} = \psi_{100} = \frac{1}{\sqrt{\pi r_0^3}} e^{-\frac{r}{r_0}} \Rightarrow |\psi_{(r, \theta, \phi)}|^2 = |\psi_{100}|^2 = \frac{1}{\pi r_0^3} e^{-\frac{2r}{r_0}}$$

\therefore Eq. (1) becomes where $r_0 = 0.53 \text{ \AA}$ is Bohr's radius

$$P(r) dr = \frac{1}{\pi r_0^3} e^{-\frac{2r}{r_0}} \cdot r^2 dr \cdot [\cos \theta]_0^\pi [\phi]_0^{2\pi}$$

$$\therefore P(r) dr = |\Psi_{100}|^2 \cdot r^2 dr \cdot [-\{\cos r - \cos 0\}]_r (2\pi - 0)$$

$$P(r) dr = |\Psi_{100}|^2 r^2 dr (-(-1-1)) + 2\pi$$

$$P(r) dr = |\Psi_{100}|^2 \underbrace{4\pi r^2 dr}_{\text{vol. element}} \quad \text{--- (2)}$$

$$\therefore P(r) dr = \frac{1}{\pi r_0^3} e^{-\frac{2r}{r_0}} 4\pi r^2 dr \quad \text{--- (3)}$$

$$\Rightarrow \boxed{P(r) dr = \frac{4}{r_0^3} e^{-2r/r_0} \cdot r^2} \quad \text{--- (4) which is required expression for radial probability density,}$$

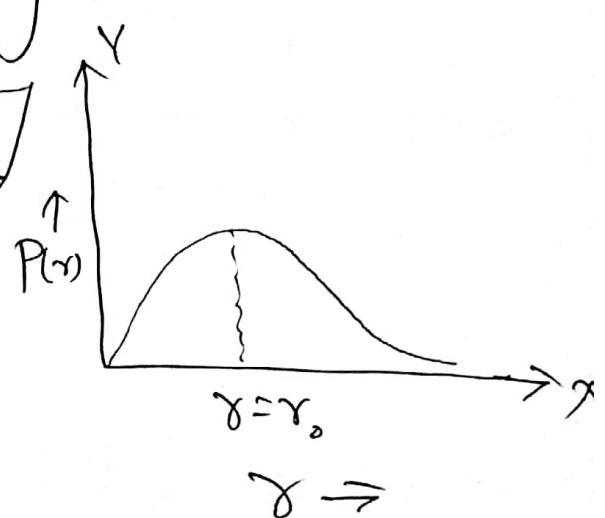
For maximum value of $P(r)$

$$\frac{dP(r)}{dr} = 0$$

$$\therefore \frac{4}{r_0^3} \left[e^{-2r/r_0} (2r) + r^2 e^{-2r/r_0} \left(-\frac{2}{r_0}\right) \right] = 0$$

$$\Rightarrow 2r + r^2 \left(-\frac{2}{r_0}\right) = 0 \Rightarrow \boxed{r = r_0}$$

Hence graph of $P(r)$ against ' r ' is most probable distance of electron from nucleus (r_0) is obtained.



Hence for $n=1$, the electron is found at r_0 .

Similarly, for $n=2, l=0, m_l=0$

$$\Psi_{200} = \frac{1}{4\sqrt{(2\pi r_0^3)}} \left(2 - \frac{r}{r_0}\right) e^{-\frac{r}{2r_0}}$$

The electron is found at $4r_0$.

extra

Exa: 20.1 Evaluate the constant 'B' for the ground state wave function of a particle in one-dimensional well, i.e., for the wave function

$$\Psi_1(x,t) = B \sin\left(\frac{\pi x}{a}\right) \exp\left(-\frac{iE_0 t}{\hbar}\right) \cdot \text{obtain normalized wave function}$$

Exa: 20.2 Consider the particle in the ground state is represented by a wave function $\Psi(x) = B \sin\left(\frac{\pi x}{a}\right)$ within $0 < x < a$ where $B = \sqrt{\frac{2}{a}}$. What is (a) the average position (b) the average momentum (c) the average energy of such particle?

Problem 20.1 show by direct substitution that the wave function $\Psi(x,t) = A \cos kx \cdot e^{-i\omega t}$ satisfies the time dependent Schrödinger equation for the free particle.

Problem 20.1 show by direct substitution into the time dependent Schrödinger equation for the free particle that $\Psi(x,t) = A \cos(kx - \omega t)$ is not solution.

Problem 20.3 Explain why the following eigenfunctions are not acceptable solutions of the Schrödinger equation

(a) $\chi(x) = 0$ for $x \leq 0$ (b) $\chi(x) = A e^{ikx}$
 $\chi(x) = A \cos kx$ for $x > 0$ (c) $\chi(x) = A \ln kx$

Problem 20.12 what is the probability of finding a particle in a well of width 'a' at position $\frac{a}{4}$ from the wall if $n=1$, if $n=2$ & if $n=3$. Use normalized wave function $\Psi(x,t) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} e^{-iEt/\hbar}$.

extra

Problem 20.7 (a) under quantum conditions, what is the minimum energy that a 100kg person can have when confined to a closet 1m long? (b) if the person moves with

a speed of 10^4 m/s, what would be his quantum number n ?

(Ans. (a) 5.4×10^{-70} (b) 3×10^{31})

extra

Problem 20.13

calculate the expectation value for the coordinate x , momentum P , and energy E of a particle in an infinite potential well represented by wave function

$$\psi = \sqrt{\frac{2}{a}} \sin \frac{2\pi x}{a} e^{-iE_2 t/\hbar}$$

(Ans $\frac{a}{2}, 0, E_2$)

Problem 21.2 extra

~~Problem 21.1~~

The differential equation for $\Phi(\phi)$ is given $\frac{d^2 \Phi}{d\phi^2} + m_l^2 \Phi = 0$ with solution of the form $\Phi(\phi) = A e^{im_l \phi}$. Normalize the wave function and show that the value of m_l can only be $0, \pm 1, \pm 2, \pm 3, \dots$

Exa 21.1

calculate the normal Zeeman splitting of the calcium 4226 \AA line when the atoms are placed in a magnetic field of 1.2 T .

Exa 21.2

A beam of H-atom is used in Stern-Gerlach type experiment. The atom emerges from the oven with a velocity 10^4 m/s. They enter a region 20 cm long where there is a magnetic field gradient $3 \times 10^4 \text{ T/m}$. The field gradient is perpendicular to the incident velocity of the atoms. The mass of the hydrogen atom is $1.67 \times 10^{-27} \text{ kg}$. What is the separation of the two components of the beam as they emerge from the magnet?

Exa 21.3

Let us assume Na -atom is Hydrogen like atom. The electron configuration of $\text{Na} (Z=11)$ is $1s^2 2s^2 2p^6 3s^1$

(a) what would be the expected energy needed to remove the $3s$ electron? (b) Ionization energy of Na is 5.14 eV what is the effective +ve charge seen by $3s$ electron.

(Ans. -1.51 eV & 1.85)

Problem 21.3 In the Bohr model of H-atom, the electron is assumed to move in circular orbits around the protons, that is motion takes place in a plane that we call the xy-plane. Use the uncertainty principle in z-direction, i.e. $\Delta p_z \geq \frac{h}{4\pi}$ and the fact that $p^2 \geq (\Delta p_z)^2$ to show that the motion of the electron can not be planar motion.

extra

Problem 21.4 Singly ionized Helium behaves as a H-atom but with twice the nuclear charge of the H-atom. What is G.S. energy of the remaining electron in singly ionized 'He'? (Ans @ 54.24 eV)

- Problem 21.6**
- (a) How many atomic states are there in Hydrogen with $n=3$?
 - (b) How are they distributed among the sub shells? Label each state with appropriate set of quantum no. n, l, m, m_s
 - (c) Show that the no. of states in a shell, i.e., states having the same 'n' is given by $2n^2$

extra

Problem 21.12 A beam of H-atoms emerges from an oven with a velocity $v = 10^4$ m/s. The beam of atoms passes through a region 5cm long with a magnetic field gradient $\frac{dB}{dz} = 10^5$ T/m. The direction of the field gradient is perpendicular to the incident velocity. The atoms then continue through a field-free region for another 20cm before being deposited on the screen. What is the separation between the two lines on the screen? (Ans. 12.5cm)

extra

Problem 21.14 The radial probability function for the G.S. of H-atom is $P(r) = Ar^2 e^{-2r/\gamma_0}$. For what value of 'r' $P(r)$ is maximum? 'A' is const.