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Atomic Physics

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Simple Harmonic Oscillation (S.H.O.)

There are many examples of Simple Harmonic Oscillations of microscopic level such as vibrations of atoms and ions in lattice. The information of motion of such tiny oscillations can be obtained by applying Schrödinger's wave equation. Schrödinger's time dependent equation (1-dimension)

$$\frac{-\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}+V(x,t)\Psi(x,t)=i\hbar\frac{\partial}{\partial t}\Psi(x,t)$$

For Simple Harmonic Oscillations, the potential function is independent of time. Hence above equation reduces to Schrödinger's time independent equation as

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}-V(x)\psi(x)=\varepsilon\psi(x)$$

For Simple Harmonic Oscillations:

$$V(x)=\frac{1}{2}kx^2=\frac{1}{2}m\omega^2x^2$$

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}+\frac{1}{2}m\omega^2x^2\psi(x)=\varepsilon\psi(x)$$

Multiplying through out by –2,

$$\frac{\hbar^2}{m}\frac{\partial^2\psi(x)}{\partial x^2}-m\omega^2x^2\psi(x)=-2\varepsilon\psi(x)$$

Right hand side has dimensions of energy, to make it dimensionless divide entire equation by $\hbar\omega$

$$\left(\frac{\hbar}{m\omega}\right)\frac{\partial^2\psi}{\partial x^2}-\left(\frac{m\omega}{\hbar}\right)x^2\psi(x)=\frac{-2\varepsilon\psi}{\hbar\omega}$$

Change of variable:

Let $\frac{E}{\hbar\omega}=t$ and $\left(\frac{m\omega}{\hbar}\right)x^2=y^2$

i.e. $\sqrt{\frac{m\omega}{\hbar}}x=y$

$$\frac{\partial\psi}{\partial x}=\frac{\partial\psi}{\partial y}\left(\frac{\partial y}{\partial x}\right)=\sqrt{\frac{m\omega}{\hbar}}\frac{\partial\psi}{\partial y}$$

$$\therefore \frac{\partial^2\psi}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{\partial\psi}{\partial x}\right) = \frac{\partial}{\partial y}\left(\frac{\partial\psi}{\partial x}\right)\left(\frac{\partial y}{\partial x}\right)$$

$$= \frac{\partial}{\partial y}\left(\sqrt{\frac{m\omega}{\hbar}}\frac{\partial\psi}{\partial y}\right)\left(\sqrt{\frac{m\omega}{\hbar}}\right)$$

$$\therefore \frac{\partial^2\psi}{\partial x^2} = \frac{m\omega}{\hbar}\frac{\partial^2\psi}{\partial y^2}$$

After substituting it in Schrödinger's wave equation Schrödinger's time independent equation becomes:

$$\frac{\partial^2\psi(y)}{\partial y^2} - y^2\psi(y) = -2\varepsilon\psi(y)$$

Operator Method:

The Schrödinger's equation for Simple Harmonic Oscillator can be solved easily by the operator method.

Show that:

$$\left(\frac{\partial}{\partial y} - y\right)\left(\frac{\partial}{\partial y} + y\right) \neq \left(\frac{\partial}{\partial y} + y\right)\left(\frac{\partial}{\partial y} - y\right)$$

L.H.S. $= \left[\left(\frac{\partial}{\partial y} - y\right)\left(\frac{\partial}{\partial y} + y\right)\right]\psi$

$$= \left(\frac{\partial}{\partial y} - y\right)\left(\frac{\partial\psi}{\partial y} + y\psi\right)$$

$$= \frac{\partial^2\psi}{\partial y^2} + y\frac{\partial\psi}{\partial y} + \psi - y\frac{\partial\psi}{\partial y} - y^2\psi$$

$$= \frac{\partial^2\psi}{\partial y^2} - y^2\psi + \psi$$

$$= \left[\frac{\partial^2}{\partial y^2} - y^2 + 1\right]\psi$$

$$\therefore \left(\frac{\partial}{\partial y} - y\right)\left(\frac{\partial}{\partial y} + y\right) = \frac{\partial^2}{\partial y^2} - y^2 + 1 \qquad (1)$$

R.H.S. $= \left(\frac{\partial}{\partial y} + y\right)\left(\frac{\partial}{\partial y} - y\right)\psi$

$$= \left(\frac{\partial}{\partial y} + y\right)\left(\frac{\partial\psi}{\partial y} - y\psi\right)$$

$$= \frac{\partial^2\psi}{\partial y^2} - y\frac{\partial\psi}{\partial y} - \psi + y\frac{\partial\psi}{\partial y} - y^2\psi$$

$$= \frac{\partial^2\psi}{\partial y^2} - y^2\psi - \psi$$

$$= \left[\frac{\partial^2}{\partial y^2} - y^2 - 1\right]\psi \qquad (2)$$

From (1) and (2) we see that $\left(\frac{\partial}{\partial y} - y\right)\left(\frac{\partial}{\partial y} + y\right) \neq \left(\frac{\partial}{\partial y} + y\right)\left(\frac{\partial}{\partial y} - y\right)$

We use the operator identities:

$$\left(\frac{\partial}{\partial y}+y\right)\left(\frac{\partial}{\partial y}-y\right)=\frac{\partial^2}{\partial y^2}-y^2-1 \qquad (1)$$

$$\left(\frac{\partial}{\partial y}-y\right)\left(\frac{\partial}{\partial y}+y\right)=\frac{\partial^2}{\partial y^2}-y^2+1 \qquad (2)$$

Let $\psi(y)$ be the solution of Schrödinger's equation for 1-dimensional simple harmonic oscillator. The operator identity number 1 operates on the solution ψ.

$$\left(\frac{\partial}{\partial y}+y\right)\left(\frac{\partial}{\partial y}-y\right)\psi=\left(\frac{\partial^2}{\partial y^2}-y^2-1\right)\psi$$

$$=\left(\frac{\partial^2\psi}{\partial y^2}-y^2\psi\right)-\psi$$

$$=-2\varepsilon\psi-\psi \qquad \text{(Since, } \psi \text{ is a solution of S.H.O. equation)}$$

$$=(-2\varepsilon-1)\psi$$

Let the operator $\left(\frac{\partial}{\partial y}-y\right)$ operates on the above equation from left.

$$\left(\frac{\partial}{\partial y}-y\right)\left(\frac{\partial}{\partial y}+y\right)\left(\frac{\partial}{\partial y}-y\right)\psi=\left(\frac{\partial}{\partial y}-y\right)(-2\varepsilon-1)\psi$$

$$=(-2\varepsilon-1)\left(\frac{\partial}{\partial y}-y\right)\psi \qquad \because -2\varepsilon-1 \text{ is a constant}$$

The operator $\left(\frac{\partial}{\partial y}-y\right)$ operating on ψ gives a new function, say, ψ_+

$$\left(\frac{\partial}{\partial y}-y\right)\left(\frac{\partial}{\partial y}+y\right)\left[\left(\frac{\partial}{\partial y}-y\right)\psi\right]=(-2\varepsilon-1)\left[\left(\frac{\partial}{\partial y}-y\right)\psi\right]$$

$$\therefore\left(\frac{\partial}{\partial y}-y\right)\left(\frac{\partial}{\partial y}+y\right)\psi_+=(-2\varepsilon-1)\psi_+$$

$$=[-2(\varepsilon+1)-1]\psi_+ \qquad (3)$$

Comparing the above equation with identity number (2) which can be simplified as

$$\left(\frac{\partial}{\partial y}-y\right)\left(\frac{\partial}{\partial y}+y\right)\Psi=(-2\varepsilon+1)\Psi \qquad (4)$$

Comparing (3) and (4) we get, that function ψ is replaced by $\psi_+$and ε is replaced by $\varepsilon+1$.

This implies that if ψ is a solution of Schrödinger's equation of one-dimensional S.H.O., with eigenvalue ε then ψ_+ is also a solution with corresponding eigenvalue $\varepsilon+1$. Similarly equation number (3) can be multiplied from left. By the operator $\left(\frac{\partial}{\partial y}-y\right)$ we get $\left(\frac{\partial}{\partial y}-y\right)\left(\frac{\partial}{\partial y}-y\right)\left(\frac{\partial}{\partial y}+y\right)\psi_+=(-2\varepsilon-1)\left(\frac{\partial}{\partial y}-y\right)\psi_+$

With little bit of algebra, we can show that the above equation reduces to

$$\left(\frac{\partial}{\partial y}-y\right)\left(\frac{\partial}{\partial y}+y\right)\left[\left(\frac{\partial}{\partial y}-y\right)\psi_+\right]=[-2(\varepsilon+2)+1]\left[\left(\frac{\partial}{\partial y}-y\right)\psi_+\right]$$

Thus if ψ is a solution with eigenvalue ε then Ψ_+ is also a solution with eigenvalue $\varepsilon+1$ and Ψ_{++} is also a solution with eigenvalue $\varepsilon+2$, and Ψ_{+++} is a solution with eigenvalue $\varepsilon+3$ and so on.

If solution ψ is known with eigenvalue E then following is a set of solution with corresponding eigenvalues.

$\psi \rightarrow \varepsilon$

$\psi_1 \to \varepsilon + 1 \qquad \psi_1 = \left(\frac{\partial}{\partial y} - y\right)\psi$

$\psi_2 \to \varepsilon + 2 \qquad \psi_2 = \left(\frac{\partial}{\partial y} - y\right)^2 \psi$

$\vdots \qquad\qquad \vdots$

$\psi_n \to \varepsilon + n \qquad \psi_n = \left(\frac{\partial}{\partial y} - y\right)^n \psi$

Consider, the 2nd operator identity with ψ as a solution of simple harmonic oscillator.

$$\left(\frac{\partial}{\partial y} - y\right)\left(\frac{\partial}{\partial y} + y\right)\psi = \left(\frac{\partial^2}{\partial y^2} - y^2 + 1\right)\psi = (2\varepsilon + 1)\psi$$

Multiply on the left to the above equation by the operator $\left(\frac{\partial}{\partial y} + y\right)$

Then we get,

$$\left(\frac{\partial}{\partial y} + y\right)\left(\frac{\partial}{\partial y} - y\right)\left[\left(\frac{\partial}{\partial y} + y\right)\psi\right] = (2\varepsilon + 1)\left[\left(\frac{\partial}{\partial y} + y\right)\psi\right]$$

Let $\psi_- = \left(\frac{\partial}{\partial y} + y\right)\psi$

$$\left(\frac{\partial}{\partial y} + y\right)\left(\frac{\partial}{\partial y} - y\right)\psi_- = (2\varepsilon + 1)\psi_-$$

$$= [2(\varepsilon - 1) + 1]\psi \qquad (5)$$

Identity number (1) can be simplified as

$$\left(\frac{\partial}{\partial y} + y\right)\left(\frac{\partial}{\partial y} - y\right)\psi = (2\varepsilon - 1)\psi \qquad (6)$$

Comparing equations (5) and (6) we say that ψ is replaced by ψ_- and ε is replaced by $\varepsilon - 1$.

Thus ψ is a solution with eigenvalue ε

Then ψ_- is a solution with eigenvalue $\varepsilon - 1$

ψ_{--} is a solution with eigenvalue $\varepsilon - 2$

Ψ_{-n} is a solution with eigenvalue $\varepsilon - n$

$\therefore$Let $\psi_- = \left(\frac{\partial}{\partial y} + y\right)\psi$

$\psi_{--} = \left(\frac{\partial}{\partial y} + y\right)^2 \psi$

$\psi_{-n} = \left(\frac{\partial}{\partial y} + y\right)^n \psi$

The operators $\left(\frac{\partial}{\partial y} - y\right)$ and $\left(\frac{\partial}{\partial y} + y\right)$ are well known raising and lowering operators in quantum mechanics.

$0_+ \equiv \left(\frac{\partial}{\partial y} - y\right)$

$0_- \equiv \left(\frac{\partial}{\partial y} + y\right)$

By operating the lowering operators various lower order solutions can be obtained. But this process ends with the ground state. If ψ_0 is a lowest solution of the ground state, then lowering operators operating on ψ_0 should give null result as no solution exist lower than ψ_0

Let Ψ_0 be the ground state

$$\left(\frac{\partial}{\partial y}+y\right)\psi_0=0$$

$$\frac{\partial\psi_0}{\partial y}+y\psi_0=0$$

Separating the variables, we get

$$\frac{d\psi_0}{\Psi_0}=-ydy$$

Integrating

$$\ln\psi_0=\frac{-y^2}{2}+C$$

$$\ln\psi_0=-\frac{y^2}{2}+\ln A_0$$

$$\psi_0=A_0e^{-\frac{y^2}{2}}$$

Thus the ground state solution is

$$\psi_0=A_0e^{-\frac{y^2}{2}}$$

By operating raising operator $\left(\frac{\partial}{\partial y}-y\right)$ several times we can get all the higher order solution.

$$\psi_0=A_0e^{-\frac{y^2}{2}}$$

$$\psi_1=A_1\left(\frac{\partial}{\partial y}-y\right)e^{-\frac{y^2}{2}}$$

$$\psi_2=A_2\left(\frac{\partial}{\partial y}-y\right)^2e^{-\frac{y^2}{2}}$$

$$\psi_n=A_n\left(\frac{\partial}{\partial y}-y\right)^ne^{-\frac{y^2}{2}}$$

The eigenfunction ψ_n can be normalised and then the values of A_n are given by

$$A_n=\frac{1}{\sqrt{\pi}2^n n!}$$

To find out the eigenvalue corresponding to the ground state ψ_0 consider, the following equation:

$$\left(\frac{\partial}{\partial y}-y\right)\left(\frac{\partial}{\partial y}+y\right)\psi_0=\blacksquare 2\varepsilon_0+1\widetilde{\psi}_0$$

The L.H.S. of above equation is zero as

$$\left(\frac{\partial}{\partial y}+y\right)\psi_0=0$$

$\Rightarrow (2\varepsilon_0 + 1)\psi_0 = 0$

$\because \Psi_0 \neq 0$

$\Rightarrow -2\varepsilon_0 + 1 = 0$

$\Rightarrow 2\varepsilon_0 = 1$

$\Rightarrow \varepsilon_0 = \frac{1}{2}$

The eigenvalue for general solution ψ_n is

$\varepsilon_n = \varepsilon_0 + n$

$= \left(n + \frac{1}{2}\right)$

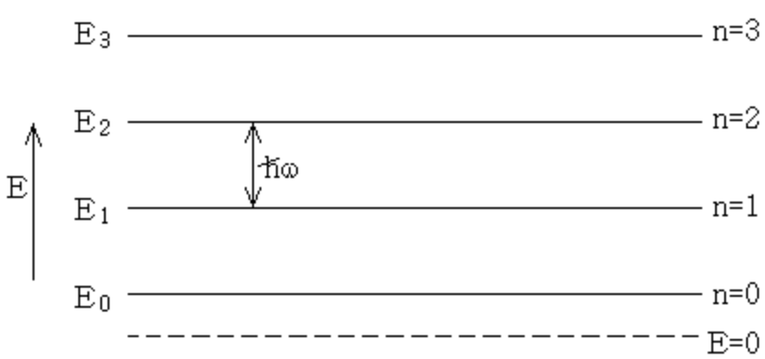
But $\varepsilon = \frac{E}{\hbar\omega}$

$\Rightarrow \varepsilon_n = \frac{E_n}{\hbar\omega} = \left(n + \frac{1}{2}\right)$

$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$

Conclusions: -

1) According to quantum mechanics the simple harmonic oscillator cannot have any arbitrary energy. It must be given by the discrete values $E_n = \left(n + \frac{1}{2}\right)\hbar\omega$



Energy possessed by 1-dimensional harmonic oscillator is quantized.

2) The lower energy possessed by Simple Harmonic Oscillator is <u>not</u> zero.

$E_0 = \frac{1}{2}\hbar\omega$

This lowest energy is called zero point energy quantum mechanically no oscillator can ever be at rest. This is in agreement with Heisenberg's uncertainty principle $\Delta x.\Delta p \geq \hbar/2$.

If energy were zero, then position and momentum can be determined exactly which violates the uncertainly principle. The various eigen functions as a function of y can be plotted as follows.

[Diagram]

2. Hydrogen Atom

An electron revolves around the nucleus in a hydrogen atom. The electron is acted upon by electrostatic force of attraction between electron and proton in the nucleus. The potential energy of the system (Hydrogen atom)

$$V(r) = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r}$$

$$= \frac{1}{4\pi\varepsilon_0}\frac{(e)(-e)}{r}$$

$$V(r) = \frac{1}{4\pi\varepsilon_0}\frac{-e^2}{r}$$

Schrödinger's time independent equation is:
1-dimension:

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi = \varepsilon\psi$$

3 dim.

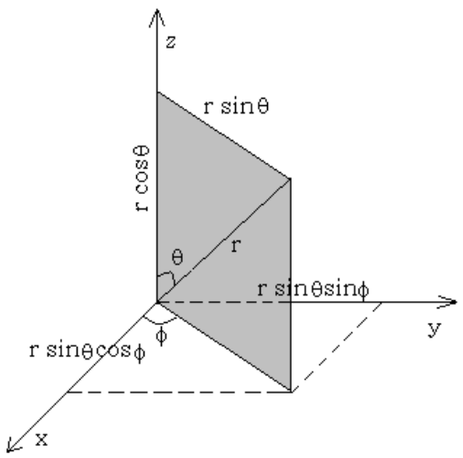
$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2\psi(x,y,z)}{\partial x^2} + \frac{\partial^2\psi(x,y,z)}{\partial y^2} + \frac{\partial^2\psi(x,y,z)}{\partial z^2}\right) + V(x,y,z)\psi(x,y,z) = \varepsilon\psi(x,y,z)$$

$$\frac{-\hbar^2}{2m}\nabla^2\psi(x,y,z) + V\psi = E\psi$$

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

$$\nabla^2\psi\frac{-2m}{\hbar^2}[V - E]\psi = 0$$

This Schrödinger's equation for hydrogen atom cannot be solved in Cartesian co-ordinate system. We use spherical polar co-ordinate system.



$x = r\sin\theta\cos\phi$ $\qquad$ $r = \sqrt{x^2 + y^2 + z^2}$

$y = r\sin\theta\cos\phi$ $\qquad$ $\theta = \cos^{-1}\left(\frac{z}{\sqrt{x^2 + y^2 + z^2}}\right)$

$z = r\cos\theta$ $\qquad$ $\phi = \tan^{-1}\left(\frac{y}{x}\right)$

The Laplacian operator can now be expressed in spherical polar co-ordinates.

$$\nabla^2 \equiv \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

$$\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}$$

∴Schrödinger's time independent equation for hydrogen atom becomes;

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{2m}{\hbar^2}\left[E-V(r)\right]\psi = 0$$

Method of separation of variables is employed to solve the above 2nd-order partial differential equation.

Let $\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$

$$\Rightarrow \frac{\partial\psi}{\partial r} = \Theta\Phi\frac{dR}{dr}$$

$$\frac{\partial\psi}{\partial\theta} = R\Phi\frac{d\Theta}{d\theta}$$

$$\frac{\partial\psi}{\partial\phi} = R\Theta\frac{d\Phi}{d\phi}$$

Substituting these in Schrödinger's equation, we get,

$$\Phi\Theta\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{R\Phi}{r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{R\Theta}{r^2\sin^2\theta}\frac{d^2\Phi}{d\phi^2}+\frac{2m}{\hbar^2}\left[E-V(r)\right]R\Theta\Phi = 0$$

Divide above equation throughout by $R\Theta\Phi$

$$\frac{1}{Rr^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{1}{\Theta r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{1}{\Phi r^2\sin^2\theta}\frac{d^2\Phi}{d\phi^2}+\frac{2m}{\hbar^2}\left[E-V(r)\right] = 0$$

Multiply the above equation by $r^2\sin^2\theta$.

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}+\frac{2mr^2\sin^2\theta}{\hbar^2}\left[E-V(r)\right] = 0$$

$$\therefore \frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\forall}\right)+\frac{2mr^2\sin^2\theta}{\hbar^2}\left[E-V(r)\right] = -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}$$

L.H.S. of above equation is a function of r and θ, whereas, *R.H.S.* is a function of only independent variable ϕ. Since r, θ, ϕ are independent variables, thus both the order should be independently equal to const (m_l^2)

Therefore, we get two equations:

$$-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = m_l^2 \qquad (1)$$

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{2mr^2\sin^2\theta}{\hbar^2}\left[E-V(r)\right] = m_l^2 \qquad (2)$$

Divide equation (2) $\sin^2\theta$

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{1}{\sin\theta\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{2mr^2}{\hbar^2}\left[E-V(r)\right] = \frac{m_l^2}{\sin^2\theta}$$

∴Rearranging,

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2mr^2}{\hbar^2}\left[E-V(r)\right]=\frac{m_l^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)$$

The L.H.S. of above equation is a function of independent variable '*r*' whereas R.H.S. is a function of independent variable θ. Therefore, both the sides must be equal to some constant. We take constant in the form $l(l+1)$. Thus, we get the two differential equations corresponding R,θ:

$$\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+l(l+1)-\frac{m_l^2}{\sin^2\theta}=0$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left[l(l+1)-\frac{m_1^2}{\sin^2\theta}\right]\Theta=0 \qquad (1)$$

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2mr^2}{\hbar^2}\left[E-V(r)\right]R-l(l+1)R=0 \qquad (2)$$

$$-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=ml^2 \qquad (3)$$

Equation (3) can be solved easily as following:

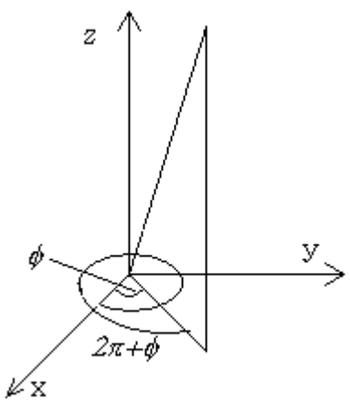
$$-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=m_l^2$$

$$\frac{d^2\Phi}{d\phi^2}=-m_l^2\Phi$$

$$\frac{d^2\Phi}{d\phi^2}+m_l^2\Phi=0$$

$$\Phi=Ae^{\pm im_l\phi}$$

The azimuth angle ϕ can change from 0 to 2π. Therefore, the function Φ should be a periodic function with period '2π' so that function Φ is physically meaningful.



$$\Phi(\phi)=\Phi(\phi+2\pi n);\ n=1,2,3\ldots$$
$$\therefore Ae^{im_l\phi}=Ae^{im_l(\phi+2\pi n)}$$
$$Ae^{im_l\phi}=Ae^{im_l 2\pi n}$$
$$\therefore e^{i2\pi m m_l}=1$$
$$\therefore \cos(2\pi m_l n)+i\sin(2\pi m_l n)=1$$
$$\Rightarrow 2\pi m_l n=2\pi k;\ k=0,\pm1,\pm2,\pm3,..$$
$$\Rightarrow m_l n=k$$

This implies m_l should be integer as n is an integer
eg. $m_l = 0, \pm1, \pm2,\ldots$
So m_l cannot take any arbitrary value, it takes only integral value.

The θ equation can be solved to obtain the solution known as associated "Legendre polynomials". These solution are possible if l can take integer values $0,1,2,\ldots$ and $l \geq |m_l|$

'r' equation can also be solved by higher order mathematics to obtain the solution called as associated 'Laguare polynomials'. The solution are possible only if energy of the system is quantized with the quantum number *n* taking values as *1,2,3,….* etc. with one more condition that *n>l.*

Quantum Numbers that arise in the solution of Schrödinger's equation of hydrogen atom can be summarised as follows:-

1) Principal Quantum Number $n = 1,2,3,4,\ldots$
2) Orbital quantum No. $l = 0,1,2,\cdots,n-1$
3) Magnetic Quantum number $m_l = -l,-(l-1),\cdots,-1,0,1,\cdots,(l-1),l$

Principal (Total) Quantum No: -
The result of application of Schrödinger's equation to *H*-atom is as follows:
The electron in the H-atom can have any positive energy but then it is not bound to the nucleus. If electron is bound to the nucleus, then it has negative energy and according to solution of Schrödinger's equation of *H*-atom, the electron cannot have any arbitrary negative energy. It is quantized and given by.

$$E_n = \frac{-me^4}{8\varepsilon_0^{\,2}h^2n^2}; n = 1,2,3,\cdots$$

'n' is called principal quantum number because it decides total energy of the electron.
The above result is also true for macroscopic particles as well but then the quantum number is so large that there is hardly any change is in energy as quantum number changes by unity.

1) Orbital Quantum Number: -
Consider *'r'* equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{\hbar^2}\left[E-V(r)\right]R=\frac{l(l+1)}{r^2}R$$

We have, potential energy experienced by the electron is due to electrostatic interaction between electron and positively charged nucleus.

$$V(r)=\frac{-e^2}{4\pi\varepsilon_0 r}$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}-\frac{\hbar^2 l(l+1)}{2mr^2}\right)R=0$$

$E = T_{(radial)} + T_{(orbital)} + V(r)$

The above ordinary differential equation is radial differential equation and it governs the motion of the electron along the radial direction. All the terms in the above equation are involving radial part except the total energy *E.* This total energy involves two types of *K.E.* namely radial *K.E.* and orbital *K.E.*

$$\therefore E = T_{radial} + T_{orbital} + V(r)$$

Substituting this we get

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{\hbar^2}\left(T_{radial}+T_{rotational}-\frac{e^2}{4\pi\varepsilon_0 r}+\frac{e^2}{4\pi\varepsilon_0 r}-\frac{\hbar^2 l(l+1)}{2mr^2}\right)R=0$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{\hbar^2}\left(T_{radial}+T_{rotational}-\frac{\hbar^2 l(l+1)}{2mr^2}\right)R=0$$

Above equation involves one term which is not radial i.e. $T_{orbital}$. If the above differential equation is radial equation, there should not be any component

related to orbital motion. In the above equation, it is possible to have pure or only radial components if $T_{orbital}$ cancels with the last term in bracket i.e.

$$\frac{\hbar^2 l(l+1)}{2mr^2}$$

$$\Rightarrow T_{orbital} = \frac{l(l+1)\hbar^2}{2mr^2}$$

$$T_{orbital} = \frac{1}{2} m v_{orbital}^2$$

& orbital angular momentum $L = mv_{orbital}\, r$ of the electron.

$$\Rightarrow T_{orbital} = \frac{1}{2} m \left[\frac{L}{mr}\right]^2$$

$$= \frac{L^2}{2mr^2}$$

$$\Rightarrow \frac{L^2}{2mr^2} = \frac{l(l+1)\hbar^2}{2mr^2}$$

$$L^2 = l(l+1)\hbar^2$$

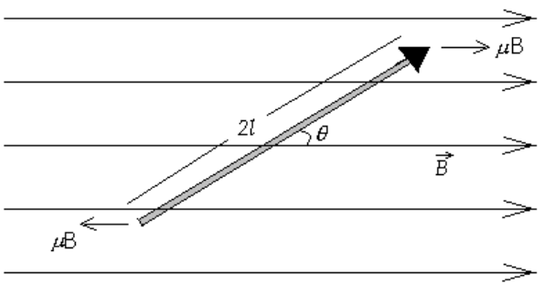
$$L = \sqrt{l(l+1)}\hbar$$

Thus the magnitude of orbital angular momentum of the electron is given by the above relation and it is obvious that angular momentum is quantized since l is quantized and can take values $l=0,1,2,..,(n-1)$

$l=0$	$L=0$
$l=1$	$L=\sqrt{2}\hbar$
$l=2$	$L=\sqrt{6}\hbar$
$l=3$	$L=\sqrt{12}\hbar$
$l=4$	$L=\sqrt{20}\hbar$

2) Magnetic Quantum Number: -

In order to consider the significance of magnetic quantum number we first discuss the effect of external magnetic field on a magnetic dipole. An electron revolving around the nucleus has magnetic dipole momentum (μ)



The magnetic dipole has magnetic potential energy due to its position with respect to the direction of magnetic field. We take the reference direction of the zero magnetic potential such that the magnet is at right angles to the external field.

$$dV_m = \tau d\theta$$

$$V_m = \int_0^{\theta} \mu B \sin\theta d\theta = \mu B \int_0^{\theta} \sin\theta d\theta$$

$$V_m = -\vec{\mu}\cdot\vec{B}$$

Case I If the dipole is parallel with $\vec{B}$ i.e. $\theta = 0 \Rightarrow \cos\theta = 1$

$$\therefore V_m = -\mu B$$

Case II If the dipole is antiparallel with $\vec{B}$ i.e. $\theta = 180° \Rightarrow \cos\theta = -1$

$V_m = \mu B$

Case III If the dipole is perpendicular to $\vec{B}$ i.e. $\theta = 90° \Rightarrow \cos\theta = 0$

$V_m = 0$

Note: When a dipole changes its position from antiparallel to parallel to the external magnetic field, change in magnetic potential increases.

It is known that current carrying coil produces magnetic field in the surrounding region. The direction is given by right hand screw rule. The magnetic dipole moment μ associated with the current carrying loop is defined as

$\mu = iA$

Where, i – current in the loop

A – Area of cross section of loop

Electron revolving around the nucleus is analogous to current carrying loop. The dipole moment associated with revolving electron is given by

$\mu = iA$

$\mu = (-e\nu)\pi r^2$

where, ν is the frequency with which the electron revolves around the nucleus and r - radius of the orbit

$\mu = -e\pi\nu r^2$ (1)

The angular momentum of the electron is given by

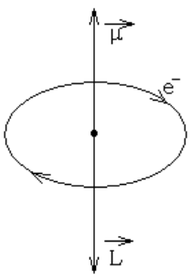
$L = mvr = m\left(\frac{2\pi r}{T}\right)r$

$L = 2m\pi r^2\nu$ (2)

$\therefore$comparing equations (1) and (2)

$\frac{\mu}{L} = \frac{-e}{2m}$

$\therefore \mu = \left(\frac{-e}{2m}\right)L$



Taking into account the directions of dipole moment and angular momentum

$\vec{\mu} = \left(\frac{-e}{2m}\right)\vec{L}$

$\vec{\mu}_L = \left(\frac{-e}{2m}\right)\vec{L}$

The constant $\frac{-e}{2m}$ is called "Gyromagnetic Ratio". The magnitude of μ_L is given by

$\mu_L = -\left(\frac{e}{2m}\right)\sqrt{l(+1)}\hbar$

$= -\left(\frac{e\hbar}{2m}\right)\sqrt{l(+1)}$

Let (Bohr magneton) $\mu_B = \frac{e\hbar}{2m} = 9.27 \times 10^{-24}$ J/Wb/m^2

Since the orbital quantum number (l) is quantized, the magnetic dipole moment is also quantized. The values that it can take are

$l = 0;$ $\mu_L = 0$

$l=1;$ $\mu_L = \sqrt{2}\mu_B$

l=2; $\mu_L = \sqrt{6}\mu_B$

l=3; $\mu_L = \sqrt{12}\mu_B$

The magnitude of the orbital angular momentum is quantized.

$L = \sqrt{l(l+1)}\hbar$; l = 0,1,2,...

Similarly the *Z* component of angular momentum is also quantized and is given by

$L_Z = m_l \hbar$ where m_l can take values from $-l$ to l in integral steps.

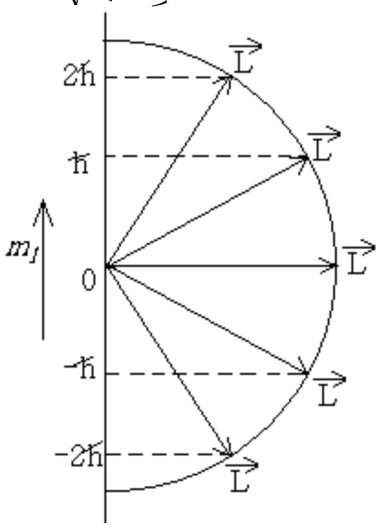
$m_l = -l,-(l-1),..,-1, 0, 1, .., (l-1),l$

The above discussion implies that the projection of orbital angular momentum along some arbitrary direction say z-axis is also quantized. This quantum number is the magnetic quantum number m_l.

It is obvious that the orbital angular momentum cannot take any arbitrary orientations with respect to Z-axis. It should have certain specific orientations only. This phenomenon is known as space quantization.

The orbital angular momentum can be parallel or antiparallel with the Z axis as

$m_l \neq \sqrt{l(l+1)}$



The angle θ between the orientation of orbital angular momentum and Z-axis is given by.

$$\cos\theta = \frac{m_l}{\sqrt{l(l+1)}}$$

$$\theta_1 = \cos^{-1}\left(\frac{2}{\sqrt{6}}\right)$$

$$\theta_2 = \cos^{-1}\left(\frac{1}{\sqrt{6}}\right)$$

$$\theta_3 = \frac{\pi}{2}$$

Z-axis is arbitrary but when external magnetic field is applied, the direction of the field becomes automatically *Z*-axis. The dipole gains energy due to magnetic interaction with the external field. Thus, gain in energy is dissipated easily in the processional motion of the dipole.

In this case, the *Z* component is fixed but the *X* and *Y* components are, all the time changing and on an average, they are zero.

The magnetic energy gained by the dipole is

$$V_m = -\vec{\mu}_L \cdot \vec{B}$$

$$= -\mu_L B\cos\theta$$

$$= -\left(\frac{-e}{2m}\right) LB\cos\theta$$

$$= \left(\frac{e}{2m}\right)\sqrt{l(l+1)}\hbar B\cos\theta$$

$$= \left(\frac{e\hbar}{2m}\right)\sqrt{l(l+1)}B\frac{m_l}{\sqrt{l(l+1)}}$$

$$= \left(\frac{e\hbar}{2m}\right)m_l B$$

$$V_m = m_l \mu_B B$$

Thus, the magnetic energy possessed by the dipole is quantized as m_l is quantized.

Angular momentum

The angular momentum of an electrum as it revolves around the nucleus is an important parameter to be discussed in the light of quantum mechanics *with respect to H*-atom.

Angular momentum of an electron performing orbital portion is given by

$$\vec{L} = \vec{r} x \vec{p}$$

Where, $\vec{r}$ is the position vector of electron and $\vec{p}$ is the momentum

In quantum mechanics, each physical variable is represented by mathematical operators. The solutions of Schrödinger's equation are generally complex. Hence, in order to co-relate with the real motion of the particle, the complex solutions must be manipulated with the help of appropriate operators to obtain suitable information about the motion of the particle.

$$\vec{L} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$= \hat{i}(yp_z - zp_y) + \hat{j}(zp_x - xp_z) + \hat{k}(xp_y - yp_x)$$

Let $\vec{L} = \hat{i}L_x + \hat{j}L_y + \hat{k}L_z$

Comparing

$L_x = yp_z - zp_y$

$L_y = zp_x - xp_z$

$L_z = xp_y - yp_x$

In quantum mechanics, position and momentum components are represented by x and $-i\hbar\frac{\partial}{\partial x}$ respectively

$$p_x \to -i\hbar\frac{\partial}{\partial x}$$

$$p_y \to -i\hbar\frac{\partial}{\partial y}$$

$$p_z \to -i\hbar\frac{\partial}{\partial z}$$

Thus, the angular momentum components have the following operator representation.

$$L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$L_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

Transforming above operator representations of angular momentum components in terms of spherical polar co-ordinates

$$L_x = -i\hbar\left[-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right]$$

$$L_y = -i\hbar\left[\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right]$$

$$L_z = -i\hbar\frac{\partial}{\partial\phi}$$

The operator representation of L^2 is given by

$$L^2 = L_x{}^2 + L_y{}^2 + L_z{}^2$$

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

The solution ψ of Schrödinger's equation of hydrogen atom is expressed as:

$$\psi(r,\theta,\phi) = R_{nl}(r)\Theta_{lm_l}(\theta)\Phi_{m_l}(\phi)$$

Consider, $L_z\psi = L_z R_{nl}\Theta_{lm_l}\Phi_{m_l}$

$$= -i\hbar\frac{\partial}{\partial\phi} R_{nl}\Theta_{lm_l}\Phi_{m_l}$$

$$= -i\hbar R_{nl}\Theta_{lm_l}\frac{\partial}{\partial\phi}\Phi_{m_l}$$

$$= -i\hbar R_{nl}\Theta_{lm_l}\frac{\partial}{\partial\phi}Ae^{im_l\phi}$$

$$= -i\hbar R_{nl}\Theta_{lm_l}Aim_l e^{im_l\phi}$$

$$= -i^2 m_l\hbar R_{nl}\Theta_{lm_l}\Phi_{m_l}$$

$$L_z\psi = m_l\hbar\psi$$

Above equation is an eigenvalue equation hence, the magnitude of physical variable represented by the operator is always equal to the eigenvalue. In this case, the magnitude of the Z component of orbital angular momentum must be $m_l\hbar$.

Thus, the Z component of angular momentum is quantized as m_l can take only values $0,\pm1,+2,\cdots,\pm l$

Consider the operator representation of L^2 and its effect as the eigenfunction ψ.

$$L^2\psi = L^2 R_{nl}\Theta_{lm_l}\Phi_{m_l}$$

$$= -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]R_{nl}\Theta_{lm_l}\Phi_{m_l}$$

$$= -\hbar^2 R_{nl}\left[\frac{\Phi_{m_l}}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{\Theta_{lm_l}}{\sin^2\theta}\frac{d^2\Phi_{m_l}}{d\phi^2}\right]$$

But $\Phi_{m_l} = Ae^{im_l\phi}$

$$\frac{d^2\Phi_1}{d\phi^2} = A(m_l)^2 e^{im_l\phi}$$

$$= -m_l{}^2 Ae^{im_l\phi}$$

$$= -m_l{}^2\Phi_{m_l}$$

Using this result

$$L^2\psi = -\hbar^2 R_{nl}\left[\frac{\Phi_{m_l}}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) - \frac{m_l{}^2\Theta_{lm_l}\Phi_{m_l}}{\sin^2\theta}\right]$$

$$= -\hbar^2 R_{nl}\Phi_{m_l}\left[\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{m_l{}^2\Theta_{lm_l}}{\sin^2\theta}\right]$$

Consider the θ equation of Schrödinger's equation from H-atom:

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{\partial\theta}\right) + \left[l(l+1) - \frac{m_l{}^2}{\sin^2\theta}\right]\Theta = 0$$

$$\therefore \frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta_{lm_l}}{d\theta}\right) - \frac{m_l{}^2\Theta_{lm_l}}{\sin^2\theta} = -l(l+1)\Theta_{lm_l}$$

Substituting the result in the above relation:

$$-\hbar^2 R_{nl}\Phi_{m_l}\left[-l(l+1)\Theta_{lm_l}\right]$$

$$= l(l+1)\hbar^2 R_{nl}\Phi_{nl}\Theta_{lm_l}$$

$$L^2\psi = l(l+1)\hbar^2\psi$$

Thus the operator L^2 satisfies the eigenvalue equation hence the magnitude of L^2 must be $l(l+1)\hbar^2$ and therefore the magnitude of orbital angular momentum is $\sqrt{l(l+1)}\hbar$.

Convert $L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$ in terms of spherical polar co-ordinates.

$x = r\sin\theta\cos\phi$

$y = r\sin\theta\sin\phi$

$z = r\cos\theta$

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

$$\theta = \cos^{-1}\left(\frac{z}{\sqrt{x^2 + y^2 + z^2}}\right)$$

$$\phi = \tan^{-1}\left(\frac{y}{r}\right)$$

$$\frac{\partial\psi(r,\theta,\phi)}{\partial x} = \frac{\partial\psi}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial\psi}{\partial\theta}\frac{\partial\theta}{\partial x} + \frac{\partial\psi}{\partial\phi}\frac{\partial\phi}{\partial x}$$

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

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

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

$$= \frac{r\sin\theta\cos\phi}{r}$$

$$\frac{\partial r}{\partial x} = \sin\theta.\cos\phi$$

Similarly $\frac{\partial r}{\partial y} = \sin\theta\sin\phi$

$$\frac{\partial\theta}{\partial x} = \frac{\partial}{\partial x}\left[\cos^{-1}\left(\frac{z}{\sqrt{x^2 + y^2 + z^2}}\right)\right]$$

Let $Y = \cos^{-1} x$ $\qquad \dfrac{dY}{dx} = ?$

$x = \cos Y$

$$1 = -\sin Y \frac{dY}{dx}$$

$$\frac{dY}{dx} = \frac{-1}{\sin Y} = \frac{-1}{\sqrt{1-x^2}}$$

$$\therefore \frac{\partial\theta}{\partial x} = -\frac{1}{\sqrt{1-\dfrac{z^2}{x^2+y^2+z^2}}} \frac{\partial}{\partial x}\left(\frac{z}{\sqrt{x^2+y^2+z^2}}\right)$$

$$= \frac{-1}{\sqrt{1-\dfrac{z^2}{x^2+y^2+z^2}}} z\left(-\frac{1}{2}\right)\left(x^2+y^2+z^2\right)^{-3/2} 2x$$

$$= \frac{zx\left(x^2+y^2+z^2\right)^{-3/2}}{\sqrt{\dfrac{x^2+y^2}{x^2+y^2+z^2}}}$$

$$\therefore \frac{\partial\theta}{\partial x} = \frac{zx}{\sqrt{x^2+y^2}\left(x^2+y^2+z^2\right)}$$

Similarly, $\dfrac{\partial\theta}{\partial y} = \dfrac{zy}{\left(\sqrt{x^2+y^2}\right)\left(x^2+y^2+z^2\right)}$

$$\frac{\partial\phi}{\partial x} = \frac{\partial}{\partial x}\left[\tan^{-1}\left(\frac{y}{x}\right)\right]$$

$$= \frac{1}{1+\left(\dfrac{y}{x}\right)^2} \frac{\partial}{\partial x}\left(\frac{y}{x}\right)$$

$$= \frac{y}{1+\left(\dfrac{y}{x}\right)^2}\left(-\frac{1}{x^2}\right)$$

$$\therefore \frac{\partial\phi}{\partial x} = \frac{-y}{x^2\left[1+\left(\dfrac{y}{x}\right)^2\right]} = \frac{-y}{x^2+y^2}$$

$$\frac{\partial\phi}{\partial y} = \frac{\partial\phi}{\partial y}\left[\tan^{-1}\left(\frac{y}{x}\right)\right] = \frac{1}{1+\left(\dfrac{y}{x}\right)^2} \frac{\partial}{\partial y}\left(\frac{y}{x}\right) = \frac{1}{1+\left(\dfrac{y}{x}\right)^2}\left(\frac{1}{x}\right) = \frac{x}{x^2+y^2}$$

Electron Probability Density:-

The basic difference between Bohr's theory and quantum theory of H-atom is as follows. Bohr's theory predicts well-defined circular orbits around the nucleus whereas quantum theory doesn't produce well-defined orbits.
In quantum mechanics, the position of the electron around the nucleus is always specified in terms of probability density of locating the electron around the nucleus. This probability density is given by:

$$\psi^*\psi = \left(R_{nl}\Theta_{lm_l}\Phi_{m_l}\right)^*\left(R_{nl}\Theta_{lm_l}\Phi_{m_l}\right)$$

$$= \left|R_{nl}\right|^2\left|\Theta_{lm_l}\right|^2\left|\Phi_{m_l}\right|^2$$

Consider,

$$\Phi^*_{m_l}\Phi_{m_l} = \left|\Phi_{m_l}\right|^2 = \left(Ae^{im_l\phi}\right)^*\left(Ae^{im_l\phi}\right)$$

Complex conjugate of a function means replace 'i' by '-i'

$$\therefore \Phi^*_{m_l}\Phi_{m_l} = A^2e^{-im_l\phi}e^{im_l\phi} = A^2$$

We know that probability of locating the electron somewhere in the universe must be one.

$$\Rightarrow \int_{\phi=0}^{2\pi}\Phi^*\Phi d\phi = 1$$

$$A^2\int_{\phi=0}^{2\pi}d\phi = 1$$

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

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

[Diagram]

Thus the normalised function is

$$\Phi_{m_l}(\phi) = \frac{1}{\sqrt{2\pi}}e^{im_l\phi}$$

Probability of locating the electron is the neighbourhood of nucleus is basically given by

$\left|R_{nl}(r)\right|^2$ Where R is a function of distance of electron from the nucleus

The function R for various quantum numbers is as shown in the following graph:

[Diagram]

3. Electron spin

It is seen that the quantum theory of H-atom gives rise to three quantum numbers: Principal quantum number, orbital quantum number and magnetic quantum number. The theory was successful is explaining the existence of line spectra of H-like elements. But experimentally it is observed that most of the spectral lines are doublet for e.g. The Balmer series of H-atom consist of all doublets. The first line in the series has wavelength 6563Å and the other line in the doublet has a separation only 1.4Å from this line. The existence of this doublet was not explained by the quantum theory.

Under the application of external magnetic field a single spectral line observed to split into three lines. This phenomenon is known as 'normal Zeeman effect'. Some elements produce 'anomalous Zeeman effect' i.e. single spectral line may split into 3, 4, 5, 6, 8, etc. spectral lines under the application of even weak magnetic field. There is no explanation for this anomalous Zeeman effect.

In order to overcome these practical discrepancies, it was suggested by Ulhenbeck and Goudsmit that there is an intrinsic property attached with electron in addition to its extrinsic property.

An electron can revolve around the nucleus, it can also spin about its own axis. Hence, there is extrinsic spin angular momentum associated with the electron. This spin angular momentum lead to the fourth quantum number called as spin quantum number.

Normal Zeeman Effect: -

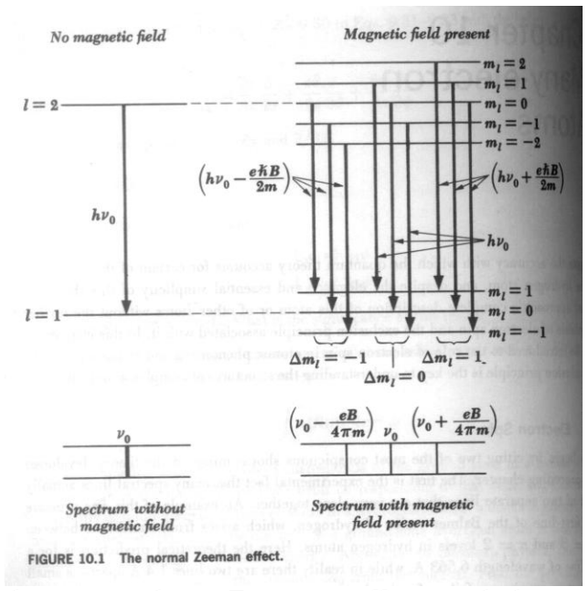


FIGURE 10.1 The normal Zeeman effect.

In order to explain the anomalous Zeeman effect and the existence of doublets, in various series of hydrogen spectrum, the concept of intrinsic spin of electron was introduced by Goudsmit and Ulhenbeck.

Intrinsic Electron Spin: -

Goudsmit and Ulhenbeck proposed the hypothesis that as electron can have orbital angular momentum so it can also have spin angular momentum. It is supposed to be independent of orbital motion. Analogous to orbital angular momentum, a dipole moment is associated with spin angular momentum; experimentally it is observed that the dipole moment due to spin motion of electrons is given to.

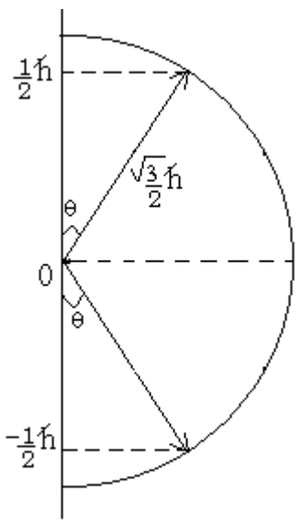
$$\vec{\mu}_s = \left(\frac{e}{m}\right)\vec{s}$$

Here, the Gyromagnetic Ratio is twice that in case of orbital motion of an electron. The magnitude of spin angular momentum is quantized is given by

$$|\vec{s}| = \sqrt{s(s+1)}\,\hbar$$

Where '*s*' is the spin quantum number, empirically it is observed that the quantum number '*s*' can take only one possible value i.e. s = $\frac{1}{2}$

$$\therefore |\vec{s}| = \frac{\sqrt{3}}{2}\hbar$$

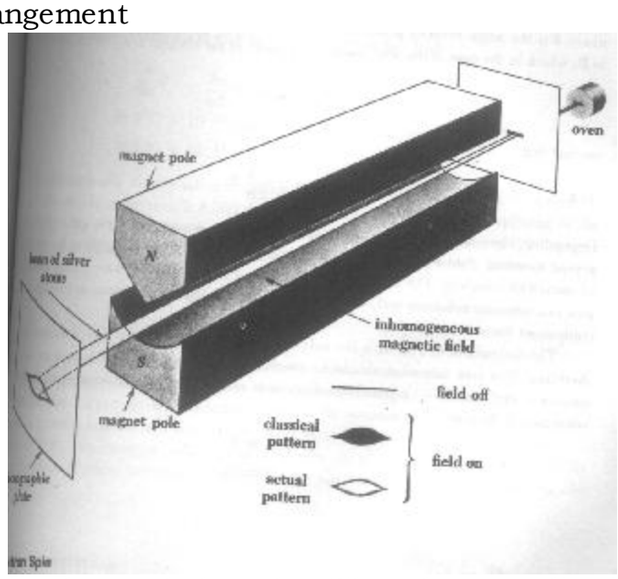


Similar to orbital angular momentum spin angular momentum also can have certain fixed orientations in space with respect to Z-axis. This is known as space quantization of spin. i.e. $s_z = m_s\hbar$ where, m_S –magnetic spin quantum number. It can take values from –*s* to +*s* in integrals steps i.e. in all 2*s*+1 states. Since the values of *s* is fixed as $\frac{1}{2}$, it means m_S can be only $-\frac{1}{2}, +\frac{1}{2}$

*Stern-Gerlach Experiment: -

The experiment performed by stern and Gerlach demonstrated clearly that there exists spin quantum number with unique value *s* = ½. Element silver is chosen for the experimental purpose, as it has only one electron in the outermost shell in 's' state i.e. *l=0*

Experimental Arrangement



Experimentally it is observed that the Silver beam splits into 2 components (rather than broadening the beam)
This suggests that the dipole moment of silver atom must have only two orientations *with respect to* the field. Hence the multiplicity is 2.
$\Rightarrow 2s+1 = 2$
$\Rightarrow s = ½$

The projection of s on Z axis has defined variations +½ and –½

Exclusion Principle: -

The distribution of electrons in many electron atoms is governed by Pauli's Exclusion Principle. It states that, "No two electrons can have the same set of four quantum numbers (n, l, m_l, m_s). In other words, no two electrons can occupy same quantum state.
The physical justification for the exclusion principle can be given on the basis of quantum mechanics as follows.
The complete information about the motion of electron is given by the wave function ψ. As ψ can be expressed as product of three functions where each function being a function of only one independent variable r, θ, ϕ respectively. Similarly, the wave function of a system of many particles can be expressed as product of wave function of individual particles i.e. $\psi_{1,2,..,n} \rightarrow \psi(1)\ \psi(2)\ ..\psi(n)$
Consider a system of 2 identical particles and let there be 2 quantum states for particles to occupy.

b state	(2)	(1)	(-)	(1,2)
a state	(1)	(2)	(1,2)	(-)

The two identical particles can be distributed in 2 steps as shown above. Since, the two particles are identical the exchange of particles should leave the system unchanged. This implies $|\psi(2,1)|^2 = |\psi(1,2)|^2$

But $\psi_S(2,1) = \psi(1,2)$ _____Symmetric function

$\psi_A(2,1) = -\psi(1,2)$ _____Anti-symmetric function

We may have a situation in which particle 1 is in state (a) and particle 2 in state (b) or vice versa. Both these possibilities are equally probable i.e. 50% time the system spends in 1st state and remaining 50% time in the 2nd state.

Therefore, the system on an average is correctly described by the following function.

$\psi_I(1,2) = \psi_a(1)\psi_b(2)$

$\psi_{II}(1,2) = \psi_a(2)\psi_b(1)$

$\Rightarrow \psi_S(1,2) = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)]$

$\psi_A(1,2) = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)]$

Thus, there exist two different kinds of system of identical particles. One system is described by symmetric wave function and the other is described by Anti symmetric function.

Show that, $\Theta_{20}(\theta) = \frac{\sqrt{10}}{4}(3\cos^2\theta - 1)$ is the solution θ equation

θ equation is $\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta_{lm_l}}{\partial\theta}\right) + \left[l(l+1) - \frac{m_l^2}{\sin^2\theta}\right]\Theta_{lm_l} = 0$

For the given function Θ_{20} can be compared with general function Θ_{lm_l} ; this gives $l = 2$ and $m_l = 0$.

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta_{20}}{\partial\theta}\right) + 6\Theta_{20} = 0$$

To prove:

Consider,

$$\text{L.H.S.} = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta_{20}}{\partial\theta}\right) + 6\Theta_{20}$$

$$= \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\frac{\sqrt{10}}{4}(3\cos^2\theta - 1)\right] + 3\frac{\sqrt{10}}{2}(3\cos^2\theta - 1)$$

$$= \frac{\sqrt{10}}{4\sin\theta}\frac{\partial}{\partial\theta}[\sin\theta(\cdot 2\cos\theta(-\sin\theta))] + \frac{3\sqrt{10}}{2}(3\cos^2\theta - 1)$$

$$= \frac{3\sqrt{10}}{2\sin\theta}\frac{\partial}{\partial\theta}[-\sin^2\theta.\cos\theta] + \frac{3\sqrt{10}}{2}(3\cos^2\theta - 1)$$

$$= \frac{3\sqrt{10}}{2\sin\theta}[-\sin^2\theta(-\sin\theta) - \cos\theta(2\sin\theta\cdot\cos\theta)] + \frac{3\sqrt{10}}{2}(3\cos^2\theta - 1)$$

$$= \frac{3\sqrt{10}}{2\sin\theta}[\sin^3\theta - 2\sin\theta\cos^2\theta] + \frac{3\sqrt{10}}{2}(3\cos^2\theta - 1)$$

$$= \frac{3\sqrt{10}}{2}[\sin^2\theta - 2\cos^2\theta + 3\cos^2\theta - 1]$$

$$= \frac{3\sqrt{10}}{2}[\sin^2\theta + \cos^2\theta - 1]$$

$$= \frac{3\sqrt{10}}{2}[-1 + 1] = 0$$

= R.H.S.

1) A beam of electrons enters a uniform magnetic field of strength 1.2 Wb/m^2. Find the energy difference between electrons whose spins are parallel and antiparallel to the field.

→ The magnetic energy gained is

$V_m = m_s\mu_B B.$

$= \pm 1/2\,\mu_B B$

$$\Delta V_m = \mu_B B$$
$$= 9.27x10^{-24} x1.2$$
$$= 11.124x10^{-24}$$

1) The ground state wave function of H atom is given by $\psi = \frac{re^{-r/a_0}}{a_0^{3/2}\sqrt{\pi}}$ where a_0 is Bohr Radius (0.53A°). Show that the most probable value of the electrons radial co-ordinate is a_0 itself.

$\rightarrow$ In quantum mechanics, the probability of finding the electron in the given state can be obtained by taking the product $\psi^*\psi$.

This probability is maximum if the derivative of this probability *with respect to* '*r*' vanishes.

$$\frac{d}{dr}(\psi^*\psi) = \frac{d}{dr}\left(\frac{r^2 e^{-2r/a_0}}{\pi a_0^{\ 3}}\right)$$
$$\frac{1}{\pi a_0^{\ 3}}\left[\left(\frac{-2}{a_0}\right)r^2 e^{-2r/a_0} + (2r)e^{-2r/a_0}\right] = 0$$
$$\frac{2re^{-2r/a_0}}{\pi a_0 3}\left[\frac{-r}{a_0}+1\right] = 0$$
$$\frac{-r}{a_0}+1 = 0$$
$$\frac{-r}{a_0} = -1$$
$$r = a_0$$

1b) Using raising operator $0_+ = \left(\frac{\partial}{\partial y} - y\right)$ obtain $u_1(y)$ and $u_2(y)$.

Given $y_0(y) = e^{-y^2/2}$

$y_1(y) = ?$

$y_2(y) = ?$

$$y_1(y) = 0_+ y_0(y)$$
$$= \left(\frac{0}{dy} - y\right)e^{-y^2/2}$$
$$= e^{-y^2/2} - y - ye^{-y^2/2}$$
$$y_1(y) = -2ye^{-y^2/2}$$
$$y_2(y) = \left(\frac{\partial}{\partial y} - y\right)^2 y_0$$
$$= \left(\frac{\partial}{\partial y} - y\right)\left[\left(\frac{\partial}{\partial y} - y\right)y_0\right]$$
$$= \left(\frac{\partial}{\partial y} - y\right)(-2ye^{-y^2/2})$$
$$= -2(y.e^{-y^2/2} + e^{-y^2/2}(-y)) + 2y^2e^{-y^2/2}$$
$$= +2y^2e^{-y^2/2} - 2e^{-y^2/2} + 2y^2e^{-y^2/2}$$
$$y_2(y) = -4y^2e^{-y^2/2} - 2e^{-y^2/2}$$
$$= 2e^{-y^2/2}(2y^2 - 1)$$

Vector Atom Model

According to Bohr's model of an atom, electrons revolve around heavy nucleus in various orbits. This model is inadequate to explain various spectral properties such as existence of fine structure. According to quantum mechanics extra properties are assigned to the electron in the atom such as principal quantum number (*n*), orbital quantum number (*l*), magnetic quantum number m_l and spin quantum number m_s. Different types of angular momenta are associated with the motions of the electrons and there exist magnetic dipole moment corresponding to each type of angular momentum. Thus, angular momentum follows the vector addition laws. Hence, this model is generally known as vector atom model. In this model, all the spectral properties of the material are tried to be explained through these vector quantities.
Orbital angular momentum is *quantized*.

$L = |\vec{L}| = \sqrt{l(l+1)}\hbar$ $\quad l=0,1,2,..,(n-1)$

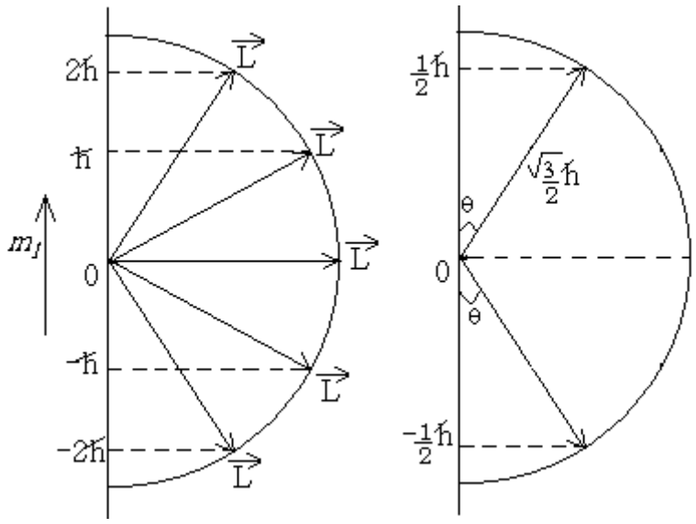
Similarly $S = |\vec{S}| = \sqrt{s(s+1)}\hbar$

$$s = \frac{1}{2}$$

Not only the magnitude of orbital angular momentum is quantized but its orientation in space is also quantized. In other words, it can take only definite orientation with respect to *Z*-axis.

$L_z = m_l\hbar$; $\quad m_l = -l,-(l-1),..,-1, 0, 1, .., (l-1),l$

$S_z = m_s\hbar$; $\quad m_s = -\frac{1}{2},+\frac{1}{2}$



There are many electrons in an atom. The vector addition of the orbital angular momentum of various electrons are performed using the vector addition laws. Similarly, spin angular momenta are also added. There are two important ways or schemes under which the addition of such vectors is carried out. They are
1) *L–S* coupling (also known as Russell Saunders coupling)
2) *j–j* coupling

<u>*L–S* coupling</u>: Under this *L–S* coupling the orbital angular momenta of all the electrons are added together to give the resultant orbital angular momentum.

$\vec{L} = \vec{l}_1 + \vec{l}_2 + \vec{l}_3 + ---$

Similarly, all the spin angular momenta of the electrons are added vectorially to obtain the resultant spin angular momentum

$\vec{S} = \vec{S}_1 + \vec{S}_2 + \vec{S}_3 + ---$

Finally, the resultant orbital angular momentum $\vec{L}$ & resultant spin angular momentum $\vec{S}$ are related together to get the total angular momentum $\vec{J}$ of the atom.

$\vec{J} = \vec{L} + \vec{S}$

The resultant orbital and spin angular momenta are quantized in similar ways.

$L = |\vec{L}| = \sqrt{L(L+1)}\hbar$; $L = |l_1 - l_2|,..., |l_1 + l_2|$ in integral steps

$S = \sqrt{s(s+1)}\hbar$; $S = |s_1 - s_2|,..., |s_1 + s_2|$

Analogously the magnitude of the total angular momentum J is also quantized.

$J = \sqrt{J(J+1)}\hbar$ $J = |L-S|, \ldots, |L+S|$ in integral steps

The Z components of these angular momenta are also quantized. They are given by,

$L_Z = m_L \hbar$; $m_L = -L$ to $+L$

$S_Z = m_S \hbar$; $m_S = -s$ to $+s$

$J_Z = m_J \hbar$; $m_J = -J$ to $+J$

Example: 1) consider two electrons each having spin $\frac{1}{2}\hbar$

$\vec{S} = \vec{S}_1 + \vec{S}_2$

[Diagram]

2) Consider three electrons.

[Diagram]

It can be generalised as follows.

If spins of odd number of electrons are added together, the resultant spin will be in odd integral multiple of $\frac{1}{2}\hbar$ such $\frac{1}{2}\hbar, \frac{3}{2}\hbar, \frac{5}{2}\hbar$ etc.

If spins of even number of electrons are added together, the resultant spin will be zero or integral multiple of $\hbar$.

3) Consider two electrons with $l_1=1$ (p sub shell), $l_2=2$ (d sub shell)

[Diagram]

4) Consider two electrons with $l_1=1$, $l_2=3$

[diagram]

Question:

Given $l_1 = 2$, $s_1 = \frac{1}{2}$

$l_2 = 2$, $s_2 = \frac{1}{2}$

$\vec{L} = \vec{l}_1 + \vec{l}_2$

$|\vec{L}| = \sqrt{L(L+1)}\hbar$

Where $L=|l_1-l_2|$ to $|l_1+l_2|$

$L=0,1,2,3,4$

Sum $\vec{S} = \vec{s}_1 + \vec{s}_2$

$|\vec{S}| = \sqrt{s(s+1)}\hbar$

Where S=0,1

Total angular momentum

$\vec{J} = \vec{L} + \vec{S}$

$|\vec{J}| = \sqrt{J(J+1)}\hbar$

J=|L-S| to |L+S| (Total angular moment Quest no.)

Term Symbol	L	S	J	Remark
$^1S_0$	0	0	0	singlet State
$^1P_1$	1	0	1	
$^1D_2$	2	0	2	
$^1F_3$	3	0	3	
$^1G_4$	4	0	4	
$^3S_1$	0	1	1	singlet state *(2L+1)
$^3P_{(0,1,2)}$	1	1	0,1,2	

$^3D_{(1,2,3)}$	2	1	1,2,3	triplet (2 S+1)
$^3F_{(2,3,4)}$	3	1	2,3,4	
$^3G_{(3,4,5)}$	4	1	3,4,5	

Whenever $S < L$, the number of J states i.e. multiplicity of the state is given by the formula $(2S+1)$.
Whenever $L < S$, the multiplicity of J states is given by $(2L+1)$
For
1) L=3, S=1; J=3
2) L=4, S=1; J=4

(Diagram)

L=0,1,2,3
Symbol = S,P,D,F

Term Symbol
$^{(2S+1)}L_J$

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Q. Find the values of S, L, and J in the following states:
$^2F_{5/2}$, $^2D_{5/2}$, $^3P_0$, $^3D_3$

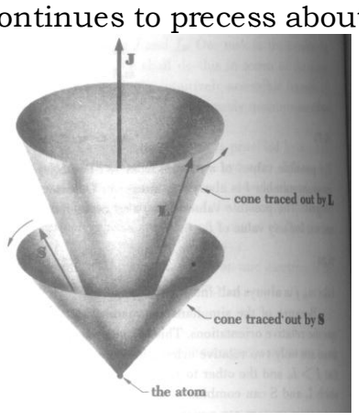
Sr. number	States (Term Symbol)	L	S	J
1	$^2F_{5/2}$	3	+1/2	5/2
2	$^2D_{5/2}$	2	+1/2	5/2
3	$^3P_0$	1	1	0
4	$^3D_3$	2	1	3

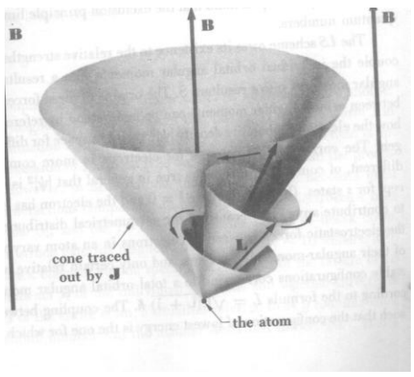
L-S Coupling (origin):
The orbital angular momenta combine together to give the resultant orbital momentum.
$\vec{L} = \vec{l}_1 + \vec{l}_2 + - - -$
Similarly, spin angular momenta of all the electrons combine together to give the resultant spin angular momentum.
$\vec{S} = \vec{S}_1 + \vec{S}_2 + - - -$
The resultant orbital spin angular momenta combine to produce total angular momentum J.
$\vec{J} = \vec{L} + \vec{S}$

The orbital angular momenta of various electrons are coupled together because of very strong electrostatic interaction between the electrons and the nucleus and weak repulsive interaction between electrons. If two electrons are there in the same sub shell then they try to have parallel spin because the electrons with parallel spin must occupy states with different m_l values (according to Pauli's exclusion principle). Due to this, the average distance between the electrons becomes more and hence its electrostatic energy is less.
The coupling between the spins is entirely due to quantum mechanical results. There is no classical analogue.
Electrons are fermions. Hence the many electron system is described by antisymmetric wave function $\psi(1,2,3,---)$. This total wave function can be split into many particle orbital wave functions u(1,2,3,---) and many particle spin wave functions $s(1,2,3,---)$
The product of $u(1,2,3,---)$ and $s(1,2,3,---)$ must be antisymmetric. This implies that if orbital function is symmetric, then spin function must be antisymmetric and if the orbital function becomes antisymmetric then the spin wave function

must transform itself into symmetric wave function. Thus, the orbital coupling makes indirect changes is the spin orientations.

In *L–S* coupling $\vec{S}$ precesses around $\vec{L}$ and $\vec{L}$ precesses about J. When weak magnetic field is applied then the total angular momentum $\vec{J}$ precesses about the direction of magnetic field. $\vec{S}$ continues to precess about $\vec{L}$ and $\vec{L}$ continues to precess about $\vec{J}$. In other words, L-S coupling is still valid.





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j–j Coupling

In most of the heavier atoms, it is observed that *j-j* coupling prevails. In many electron system, the orbital angular momentum and spin angular momentum of individual electron couple together to give resultant total angular momentum of an electron. This way each electron has the total angular momentum and finally these individual total angular momenta combine to give the total angular momentum of the many electron system.

$\vec{j}_1 = \vec{l}_1 + \vec{s}_1 \qquad j_1 = |l_1 - s_1| \text{ to } |l_1 + s_1|$

$\Rightarrow |\vec{j}_1| = \sqrt{j_1(j_1+1)}\hbar$

Finally

$\vec{J} = \vec{j}_1 + \vec{j}_2 + \vec{j}_3 + ---$

Example:

$l_1 = 1, s_1 = 1/2 \Rightarrow j_1 = 1/2, 3/2$

Spin Orbit Interaction

Experimentally, it is observed that the 'Balmer Series' of Hydrogen spectrum exhibits doublet structure. Especially the first line which corresponds to the transition of electron from *n*=3 to *n*=2 has wavelength of 6563A°. It is a doublet with a separation 1.4A°. This separation or existence of doublet can be explained on the basis of intrinsic spin property of the electron and the interaction between the spin motion and the orbital motion of the electron.

In the electron's frame of reference nucleus revolves around it and produces magnetic field $\vec{B}$ at the position of electron. This is due to the orbital motion of the electron. The electron also has spin angular momentum and the corresponding dipole moment μ_s. This spin dipole moment μ_s is now kept in the field produced by the orbital motion. Due to the interaction of the spin dipole moment with the field produced by the orbital motion i.e. due to spin orbit interaction gives rise to change in energy.

$\Delta E = -\vec{\mu}_s \cdot \vec{B}$

$= -\mu_s B \cos\theta$

$= -(\mu_s \cos\theta) B$

$\Delta E = -\mu_{sz} B$

But we have

$$\mu_{sz} = \left(\frac{-e}{m}\right) s_z$$

$$= \left(\frac{-e}{m}\right)\left(\pm\frac{1}{2}\hbar\right)$$

$$= \pm\frac{e\hbar}{2m}$$

$$= \pm\mu_B$$

Thus $\Delta E = \pm\mu_B B$

[Diagram]

The field produced by the revolving nucleus at the position of electron

$$B = \frac{\mu_0 I}{2r}$$

$$= \frac{\mu_0 ef}{2r}$$

For 1st Bohr orbit r = 0.53Å

$\mu_0 = 4\pi x10^{-7}$ S.I.units

$e = 1.6x10^{-19} C$

$f = 10^{15} H_Z$

$B = 1.8968T$

$\therefore \Delta E = \mu_B B$

$\mu_B = 9.28x10^{-24}$ A-m^2

$\Delta E = 1.14x10^{-22}$ J

$$\Rightarrow \Delta\lambda = 2\text{Å} \quad \left(\lambda(\text{Å}) = \frac{12400}{E(ev)}\right)$$

Experimentally observed difference in wavelength is of the order of 1.4Å. Wherever the difference estimated on the basis of spin-orbit interaction is 2Å, the discrepancy can be accounted as follows.

The field B is calculated for the ground state of the H-atom whereas the spectral line corresponds to transition between excited states and the field produced for the excited states is higher and therefore small separation in wavelength.

Origin of Spectral Lines

According to Bohr's theory of H-atom, it has been postulated that the atom emits radiation only when an electron jumps from the excited state having energy E_m to the ground state having energy E_n and the frequency of radiation is given by,

$$\nu = \frac{E_m - E_n}{h}$$

Quantum mechanically this postulate can be derived easily. According to classical electrodynamics, it has been observed that whenever a charge particle has acceleration it looses its energy. But Bohr's postulate assumes that if the electron revolves in certain orbits then it does not emit any energy. Such orbits are called 'Stationary Orbit'.

The state of the electron in quantum mechanics is described by the wave function.

$$\Psi_n = \psi_n e^{-i\left(\frac{E_n}{\hbar}\right)t}$$

Where the eigenfunction ψ_n is $\psi_n = R_{nl}(r)\Theta_{lm_l}(\theta)\Phi_{m_l}(\phi)$

Let the electron be described by single eigenfunction Ψ_n. The average position of the electron around the nucleus can be estimated as follows and if the average position $\bar{x}$ is independent of time then there is no acceleration involved and hence the electron is in the stationary orbit and no emission of radiation.

$$\bar{x} = \int_{-\infty}^{\infty} \Psi_n^* [x] \Psi_n dx$$

$$= \int_{-\infty}^{\infty} \left[\psi_n e^{-i\left(\frac{E_n}{\hbar}\right)t} \right] x \left[\psi_n e^{-i\left(\frac{E_n}{\hbar}\right)t} \right] dx$$

$$= \int_{-\infty}^{\infty} x \psi_n^* \psi_n e^{i\left(\frac{En}{\hbar}\right)t} e^{-i\left(\frac{En}{\hbar}\right)t} dx$$

$$\bar{x} = \int_{-\infty}^{\infty} x \psi_n^* \psi_n dx$$

It is time independent hence stationary states.

Now consider a situation in which electron makes a transition from the excited state having energy E_m to the ground state having energy E_n.

The wave function of the electron during this transition is described by the linear combination of the wave function of the two states.

$$\Psi = a\Psi_n + b\Psi_m$$

Where 'a' is the probability amplitude that the electron exists in the state 'n' and 'b' is probability amplitude that the electron exists in state 'm'.

If a = 0 and $|b|^2 = b^*b = 1$ then the electron is definitely in the excited state ψ_m i.e. initial state.

If b = 0 and $|a^2| = a^*a = 1$ then the electron is in the ground state ψ_n i.e. final state.

The average value of the position of the electron during the transition is given by

$$\bar{x} = \int_{-\infty}^{\infty} \Psi^* x \Psi dx$$

$$= \int_{-\infty}^{\infty} [a\Psi_n + b\Psi_m]^* x [a\Psi_n + b\Psi_m] dx$$

$$= a^*a \int_{-\infty}^{\infty} x \Psi_n \Psi_n dx + a^*b \int_{-\infty}^{\infty} x \Psi_n{}^* \Psi_m dx + b^*a \int_{-\infty}^{\infty} x \Psi_m{}^* \Psi_n dx + b^*b \int_{-\infty}^{\infty} x \Psi_m{}^* \Psi_m dx$$

Where $\Psi_m = \psi_m e^{-i\left(\frac{Em}{\hbar}\right)t}$

$$\Psi_n = \psi_n e^{-i\left(\frac{En}{\hbar}\right)t}$$

$$= a^*a \int_{-\infty}^{\infty} x \psi_n{}^* \psi_n dx + b^*b \int_{-\infty}^{\infty} x \psi_m{}^* \psi_m dx + a^*b \int_{-\infty}^{\infty} x \psi_n{}^* e^{i\left(\frac{E_n}{\hbar}\right)t} \psi_m e^{-i\left(\frac{E_m}{\hbar}\right)t} dx + b^*a \int_{-\infty}^{\infty} x \psi_m{}^* e^{i\left(\frac{E_m}{\hbar}\right)t} \psi_n e^{-i\left(\frac{E_n}{\hbar}\right)t} dx$$

Due to homogeneity and symmetry of the states we have,

$$\psi_n{}^* \psi_m = \psi_m{}^* \psi_n$$

and $a^*b = b^*a$

Hence, we get

$$\bar{x} = a^*a \int_{-\infty}^{\infty} x \psi_n{}^* \psi_n dx + b^*b \int_{-\infty}^{\infty} x \psi_m{}^* \psi_m dx + a^*b \int_{-\infty}^{\infty} x \psi_n{}^* \psi_m dx \left[e^{-i\left(\frac{E_m - E_n}{\hbar}\right)t} + e^{i\left(\frac{E_m - E_n}{\hbar}\right)t} \right]$$

$$\bar{x} = a^*a \int_{-\infty}^{\infty} x \psi_n{}^* \psi_n dx + b^*b \int_{-\infty}^{\infty} x \psi_m{}^* \psi_m dx + 2a^*b \cos\left(\frac{E_m - E_n}{\hbar}\right)t \int_{-\infty}^{\infty} x \psi_n{}^* \psi_m dx$$

Using De Movier Theorem

$$e^{i\theta} + e^{-i\theta} = 2\cos\theta$$

$$\bar{x} = a^* a \int_{-\infty}^{\infty} x\psi_n{}^* \psi_n dx + b^* b \int_{-\infty}^{\infty} x\psi_m{}^* \psi_m dx + 2a^* b \cos 2\pi \left(\frac{E_m - E_n}{h} \right) t \int_{-\infty}^{\infty} x\psi_n{}^* \psi_m dx$$

$$\bar{x} = a^* a \int_{-\infty}^{\infty} x\psi_n{}^* \psi_n dx + b^* b \int_{-\infty}^{\infty} x\psi_m{}^* \psi_m dx + 2a^* b \cos 2\pi\nu t \int_{-\infty}^{\infty} x\psi_n{}^* \psi_m dx$$

where $\nu = \dfrac{E_m - E_n}{h}$

The first two terms in the above equation are time independent. The last term depends on time through '*cos* $2\pi\nu t$' it means the average position of the electron oscillates with frequency ν.

$$\nu = \frac{E_m - E_n}{h}$$

Thus, the electron has acceleration and the frequency of radiation emitted is the same as the frequency with which electron oscillates. The Bohr's frequency postulate is thus proved without any assumption but only the mathematical analysis. There is no need to know the exact form of the eigenfunction ψ_n and ψ_m

Selection Rule

In the derivation of $\bar{x}$ the last term is time dependent. It is

$$2a^* b \cos 2\pi\nu t \int_{\infty}^{\infty} x\psi_n{}^* \psi_m dx$$

If the integration $\int_{\infty}^{\infty} x\psi_n{}^* \psi_m dx$ is zero, then the transition does not exist, in other words, it is forbidden transition [corresponding spectral line is absent.]

If $\int_{\infty}^{\infty} x\psi_n{}^* \psi_m dx \neq 0$, then the transition is allowed. The rules called as 'Selection Rules' under which the integration does not vanish can be obtained as follows:

In quantum mechanics $\psi_n = R_{nl}(r)\Theta_{lm_l}(\theta)\Phi_{m_l}(\phi)$

Where $\Phi_{m_l} = \dfrac{1}{\sqrt{2\pi}} e^{im_l\phi}$

Consider the general integral of the form $I = \int u\psi^*_{nlm_l}\psi_{n'l'm_l'} d\tau$

Where $u = x$ or $u = y$ or $u = z$ as the case may be. Here the integration is taken over real 3-D space and in spherical polar co-ordinates.

We have $d\tau = r^2 \sin\theta dr d\theta d\phi$

$x = r\sin\theta\cos\phi$

$y = r\sin\theta\sin\phi$

$z = r\cos\theta$

Thus our integral now becomes taking $u = x$

$$I = \int_{r=0}^{\infty} \int_{0}^{\pi} \int_{0}^{2\pi} [\sin\theta\cos\phi] R_{nl}{}^* \Theta_{lm_l}{}^* \Phi_{m_l}{}^* R_{n'l'} \Theta_{l'm_l'} \Phi_{m_l'} r^2 \sin\theta dr d\theta d\phi$$

$$I = \int_{r=0}^{\infty} r^3 R_{n_l}{}^* R_{n'l'} dr \int_{\theta=0}^{\pi} \sin^2\theta \Theta_{lm_l}{}^* \Theta_{l'm_l'} d\theta \int_{\phi=0}^{2\pi} \cos\phi \Phi_{m_l}{}^* \Phi_{m_l'} d\phi$$

Consider third part of the integral

$$\int_{\phi=0}^{2\pi} \cos\phi \Phi_{m_l}{}^* \Phi_{m_l'} d\phi$$

We have $\Phi_{m_l}{}^* = \dfrac{1}{\sqrt{2\pi}} e^{-im_l\phi}$

$$\Phi_{m'_l} = \frac{1}{\sqrt{2\pi}} e^{im'_l\phi}$$

$$e^{i\phi} = \cos\phi + i\sin\phi$$

$$e^{-i\phi} = \cos\phi - i\sin\phi$$

$$\cos\phi = \frac{e^{i\phi} + e^{-i\phi}}{2}$$

$$\int_0^{2\pi} \left(\frac{e^{i\phi} + e^{-i\phi}}{2} \right) \frac{1}{\sqrt{2\pi}} e^{-im_l\phi} \frac{1}{\sqrt{2\pi}} e^{im'_l\phi} d\phi$$

$$= \frac{1}{4\pi} \int_0^{2\pi} e^{i\phi} e^{-im_l\phi} e^{im'_l\phi} d\phi + \frac{1}{4\pi} \int_0^{2\pi} e^{-i\phi} e^{-im_l\phi} e^{im'_l\phi} d\phi$$

$$= \frac{1}{4\pi} \int_0^{2\pi} e^{i[m_l' - m_l + 1]\phi} d\phi + \frac{1}{4\pi} \int_0^{2\pi} e^{i[m'_l - m_l - 1]\phi} d\phi$$

We have

$m_l' - m_l \pm 1 = 0, \pm 1, \pm 2, \pm 3, \ldots = k$ (say) $\qquad (\because m_l \text{ and } m_l' \text{ are quantised})$

Then the above integration is of the form

$$\int_0^{2\pi} e^{ik\phi} d\phi$$

It is obvious that the integration

$$\int_0^{2\pi} e^{ik\phi} d\phi = 0 \quad \text{For } k = \pm 1, \pm 2, \pm 3, \ldots$$

The integration is not equal to zero when $k = 0$

But $k = 0$

$$\Rightarrow m'_l - m_l \pm 1 = 0$$

$$\Rightarrow m'_l - m_l = \pm 1$$

$$\Rightarrow \Delta m_l = \pm 1$$

Thus, when the magnetic quantum number of the two states differs by +1 or –1, then the integral is non-zero and hence the transition is allowed otherwise the transition is forbidden.

Similarly, the integration over θ co-ordinate can be carried out and it is observed than whenever, $\Delta l = \pm 1$ then only the transitions are allowed otherwise forbidden.

The integration over R co-ordinate does not give any restriction on principal quantum number 'n'.

In the above discussion, the general co-ordinate u was taken as 'x'. Even if one takes u=y, the same result is obtained. But for the co-ordinate u = z the integration for ϕ co-ordinate is different. It can be obtained as follows:

$$\int_{\phi=0}^{2\pi} \Phi_{m_l}^{*} \Phi_{m'_l} d\phi$$

$$\int_0^{2\pi} \frac{1}{\sqrt{2\pi}} e^{-im_l\phi} \frac{1}{\sqrt{2\pi}} e^{im'_l\phi} d\phi$$

$$= \frac{1}{2\pi} \int_0^{2\pi} e^{-im_l\phi} e^{im'_l\phi} d\phi$$

$$= \frac{1}{2\pi} \int_0^{2\pi} e^{i[m_l' - m_l]\phi} d\phi$$

$$m'_l - m_l = k$$

$$\int_0^{2\pi} e^{ik\phi} d\phi = 0 \quad \text{if } k = \pm 1, \pm 2, \pm 3, - - -$$

$\neq 0$ if $k = 0$

Thus integration is not equal to zero, when $k = 0$.

$\Rightarrow m'_l - m_l = 0$

$\Delta m_l = 0$

Thus, the selection rules for the allowed atomic transitions corresponding to spectral lines can be summarised as follows:

$\Delta m'_l = 0, \pm 1$

$\Delta l = \pm 1$

$\Delta n =$ no restriction

Q. Say whether transition Ψ_{210}-Ψ_{100} is allowed for *L-S* group?

$\psi_{n,l,m_l} \rightarrow \psi_{n',l',m'_l}$ $n = 2$ $n' = 1$

$l = 1$ $l' = 0$

$m_l = 0$ $m'_l = 0$

$\Delta m_l = 0$

$\Delta l = 1$ Thus, it is allowed transition.

$\Delta n = 1$

Q. For $^3P_1$ state find values of *S,L,J* calculate the angle between $\vec{L}$ & $\vec{S}$

$^3P_1$ compare with $^{2S+1}L_J$

$2S+1=3$

$\Rightarrow S=1$

For *P* state $L=1$

And $J=1$

$S=1$, $L=1$, $J=1$

[Diagram]

$$\cos(\vec{L},\vec{s}) = \frac{L^2 + s^2 - J^2}{2Ls}$$

$$= \frac{L(L+1)\hbar^2 + S(S+1)\hbar^2 - J(J+1)\hbar^2}{2\sqrt{L(L+1)}\hbar\sqrt{S(S+1)}\hbar}$$

Substituting value of S, L, J

$$= \frac{S(S+1)}{2\sqrt{S(S+1)}\sqrt{L(L+1)}} \qquad \because L = S = J$$

$$= \frac{1}{2}\frac{S}{S} \qquad \because L = S = J$$

$$\cos(\vec{L},\vec{S}) = \frac{1}{2}$$

$$\angle(\vec{L},\vec{S}) = \cos^{-1}\frac{1}{2}$$

$$= \underline{\underline{60^0}}$$

H-Like atomic spectra

Hydrogen has only one electron. It has a characteristic atomic line spectrum. Similarly alkali elements *Li, Na, K* has exactly one electron in the outermost shell.

e.g. Na^{11}. The sodium has 11 electrons, as its atomic number is 11. Electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^1$

The last electron is unpaired and the orbital angular momentum of the electron is same as the orbital angular momentum of the atom. Similarly, the resultant spin angular momentum of the atom is the same as that of the electron. Therefore, the total angular momentum is given by,

$\vec{j} = \vec{l} + \vec{s}$

Where $j = |l-s|$ to $|l+s|$ in integral steps

$j = ½$

$m_j = -½ + ½$

$|\vec{j}| = \sqrt{j(j+1)}\hbar$

$= \frac{\sqrt{3}}{2}\hbar$

The excitation energy level diagram for sodium can be drawn as follows:
The excitation energy measured in eV is the amount of energy required to excite an electron to higher energy states.
[Diagram]

The principle series of sodium is produced by transitions from $2p$ states to the lowest $3\ ^2S_{1/2}$ state.
The lines are all doublet because the p states are doublet (*). The well known sodium yellow doublet corresponds to the following transitions:
[Diagram]

Anomalous Zeeman Effect

When weak magnetic field is applied to certain elements emitting spectral lines such as sodium, it is observed the sodium doublet splits into six lines. It is not possible to explain the splitting on the basis of classical physics. Therefore, it is known as anomalous Zeeman effect. The energy level diagram corresponding to splitting of sodium doublet is shown in the following diagram:

[Diagram]

Lande 'g' factor: (12 Marks)

We know that the dipole moment $\vec{\mu}_l$ associated with orbital angular momentum of the electron is given by:

$\vec{\mu}_l = g_l\left(\frac{-e}{2m}\right)\vec{L}$

Where $g_l = 1$ = Gyromagnetic Ratio

Similarly for the spin angular momentum, we can write

$\vec{\mu}_s = g_s\left(\frac{-e}{2m}\right)\vec{S}$

Where $g_s = 2$

Analogously, the magnetic dipole moment associated with the total angular momentum $\vec{J}$ g the atom can be written as

$\vec{\mu}_J = g_J\left(\frac{-e}{2m}\right)\vec{J}$

Where, 'g_J' is called 'Lande 'g' factor'. It depends on values of L, S, and J.

Definition: Lande 'g' factor: It is defined as the ratio of dipole moment associated with total angular momentum expressed in (terms) units of Bohr magneton to the magnitude of total angular momentum expressed in units of $\hbar$

$$g_J = \frac{|\vec{\mu}_J|/\mu_B}{|\vec{J}|/\hbar}$$

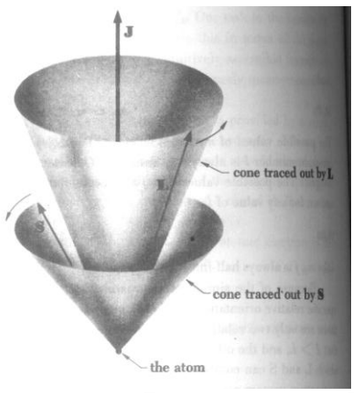
Expression for g_J Lande 'g' factor

The orbital angular momentum $\vec{L}$ precesses around $\vec{J}$. Similarly, spin angular momentum $\vec{S}$ processes around $\vec{J}$. Analogously their dipole moments also precess around $\vec{\mu}_J$. The projections of $\vec{\mu}_L$ and $\vec{\mu}_S$ along $\vec{\mu}_J$ survive whereas the components of $\vec{\mu}_L$ & $\vec{\mu}_S$ perpendicular to $\vec{\mu}_J$ keep on processing and hence average out to zero. Therefore effectively $\vec{\mu}_g$ is made up of the projections of $\vec{\mu}_L$ & $\vec{\mu}_S$ along $\vec{\mu}_J$

$$\mu_J = \mu_L \cos(\vec{L}, \vec{J}) + \mu_S \cos(\vec{S}, \vec{J})$$

$$= \mu_B \sqrt{L(L+1)} \cos(\vec{L}, \vec{J}) + 2\mu_B \sqrt{S(S+1)} \cos(\vec{S}, \vec{J})$$

Using cosine rule



$$= \mu_B \sqrt{L(L+1)} \left[\frac{L(L+1) + J(J+1) - S(S+1)}{2\sqrt{L(L+1)}\sqrt{J(J+1)}} \right] + 2\mu_B \sqrt{S(S+1)} \left[\frac{S(S+1) + J(J+1) - L(L+1)}{2\sqrt{S(S+1)}\sqrt{J(J+1)}} \right]$$

$$= \frac{\mu_B}{2\sqrt{J(J+1)}} \left[3J(J+1) + S(S+1) - L(L+1) \right]$$

Multiply and Divide J(J+1)

$$= \mu_B \sqrt{J(J+1)} \left[\frac{2J(J+1) + J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right]$$

$$= \mu_B \sqrt{J(J+1)} \left[1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right]$$

=Comparing with $\mu_J = g_J \mu_B \sqrt{J(J+1)}$

$$\Rightarrow g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Normal Zeeman Effect: (Quantum Theory)

Consider an atom with s = 0; i.e. there must be an even number of electrons, at least two. Let us consider an atom with two electron s_1 = ½ and s_2 = ½

$\Rightarrow S$ = 0,1

$\Rightarrow \vec{J} = \vec{L}$

Total Dipole moment associated with the atom is just the total orbital dipole moment and is given by,

$$\vec{\mu}_L = \left(\frac{-e}{2m} \right) \vec{L}$$

The gain in energy when the dipole moment is kept in external magnetic field, is given by,

$$\Delta E = \vec{\mu}_L \cdot \vec{B}$$
$$= \left(\frac{-e}{2m}\right)\vec{L}.\vec{B}$$
$$= \frac{e}{2m} LB\cos\theta$$
$$= \frac{e}{2m} BL\cos\theta$$
$$= \frac{eB}{2m} L_Z$$
$$= \frac{eB}{2m} m_l \hbar$$
$$= m_l \frac{e\hbar}{2m} B$$
$$\Delta E = m_l \mu_B B$$

In absence of the magnetic field; i.e. B = 0 we have

[diagram]

i.e. $h\nu_0 = E_0^i - E_0^f$

As soon as the field is applied i.e. B ≠ 0 we have

$$E^i = E_0^i + \Delta E = E_0^i + m_l \mu_B B$$
$$E^f = E_0^f + \Delta E^1 = E_0^f + m_l' \mu_B B$$

When field is applied electrons make transitions from excited state to the lower energy state and frequency is given by

$$h\nu = E^i - E^f$$
$$= \left(E_0^i - E_0^f\right) + \left(m_l - m_{l'}\right)\mu_B B$$
$$h\nu = h\nu_0 + \Delta m_l \mu_B B$$
$$\Rightarrow \nu = \nu_0 + \frac{\Delta m_l \mu_B B}{h}$$

But according to selection rule, only the transitions with $\Delta m_l = 0, \pm 1$ are allowed and all other transitions are forbidden

$$\Rightarrow \nu = \nu_0 \qquad \Delta m_l = 0$$
$$\nu = \nu_0 - \frac{\mu_B B}{h} \quad \Delta m_l = -1$$
$$\nu = \nu_0 + \frac{\mu_B B}{h} \quad \Delta m_l = \pm 1$$

Thus, quantum mechanics explains correctly the Normal Zeeman Effect i.e. when field is applied a single spectral line splits into three spectral lines. With middle line having the same frequency as the original one and two adjacent spectral line equally spaced on either side.

Quantum Theory of Anomalous Zeeman effect

Consider an atom such as Sodium in which the spin angular momentum is non zero. This gives the total angular momentum J according L-S coupling

$$\vec{J} = \vec{L} + \vec{S}$$

When magnetic field is applied, the gain in energy due to field is given by:

$$\Delta E = -\vec{\mu}_j.\vec{B}$$
$$= g_j m_j \mu_B B$$

where g_j is Lande g factor given by:

$$g_j = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

For the sodium doublet D_1 and D_2 lines the Lande g factor for various states can be calculated as follows:

i] For the ground state $3\ ^2S_{1/2}$ g_j factor can be obtained as follows *(j=½,s=½,l=0)*

$$\therefore g_j = 1 + \frac{\frac{1}{2}\left(\frac{1}{2}+1\right) + \frac{1}{2}\left(\frac{1}{2}+1\right)}{2\frac{1}{2}\left(\frac{1}{2}+1\right)}$$

$$g_j = 2$$

$$\Delta m_j = -\frac{1}{2} + \frac{1}{2} \qquad \textit{(-j to j)}$$

$$\Rightarrow g_j m_j = 2\left(-\frac{1}{2}\right) or 2\left(+\frac{1}{2}\right)$$

$$g_j m_j = -1, +1$$

$$\therefore \Delta E = \pm \mu_B B$$

ii] For the $3^2p_{1/2}$ state g_j can be calculated as follows:

$$j = \frac{1}{2} \quad s = \frac{1}{2} \quad l = \frac{1}{2}$$

$$g_j = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

$$= 1 + \frac{\frac{1}{2}\left(\frac{1}{2}+1\right) + \frac{1}{2}\left(\frac{1}{2}+1\right) - 1(1+1)}{2\frac{1}{2}\left(\frac{1}{2}+1\right)}$$

$$g_j = \frac{2}{3}$$

$$m_j = -\frac{1}{2} + \frac{1}{2}$$

$$\Rightarrow g, m_j = \frac{2}{3}\left(\frac{1}{2}\right)\frac{2}{3}\left(\frac{1}{2}\right)$$

$$g_j m_j = -\frac{1}{3}, \frac{1}{3}$$

$$\Delta E = -\frac{1}{3}\mu_B B$$

iii] For the $3^2p_{3/2}$ state g_j can be calculated as follows:

$$j = \frac{3}{2} \quad s = \frac{1}{2} \quad l = 1$$

$$g_j = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

$$= 1 + \frac{\frac{3}{2}\left(\frac{3}{2}+1\right) + \frac{1}{2}\left(\frac{1}{2}+1\right) - 1(1+1)}{2\frac{3}{2}\left(\frac{3}{2}+1\right)}$$

$$= 1 + \frac{\left(\frac{3}{2}\right)\left(\frac{5}{2}\right) + \frac{1}{2}\left(\frac{3}{2}\right) - 2}{\frac{5}{2}}$$

$$= 1 + \frac{\frac{15}{4} + \frac{3}{4} - 2}{\frac{15}{2}}$$

$$= 1 + \frac{\frac{9}{2} - 2}{\frac{15}{2}}$$

$$= 1 + \frac{1}{3}$$

$$g_j = \frac{4}{3}$$

$$m_j = -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}$$

$$\therefore g_j m_j = -2, -\frac{2}{3}, +\frac{2}{3}, +2$$

$$\Rightarrow \Delta E = -2\mu_B B, -\frac{2}{3}\mu_B, +\frac{2}{3}\mu_B, +2\mu_B$$

Paschen-Back Effect

In many electron atoms, the orbital angular momenta and spin angular momenta combine under *LS* coupling or *jj* coupling schemes. When magnetic field is applied, it is observed that the resultant orbital angular momentum $\vec{L}$ and spin angular momentum $\vec{S}$ precess around total angular momentum $\vec{J}$ and total angular momentum J precesses slowly about $\vec{B}$ i.e. external magnetic field. The interaction energy between $\vec{J}$ & $\vec{B}$ is small as compared to the interaction energy between $\vec{L}$ & $\vec{S}$

When magnetic field strength is increased $\vec{L}$ & $\vec{S}$ independently precess around the direction of external field $\vec{B}$. This effect is called 'Paschen Back Effect'.

Even in 'Paschen Back Effect' the resultant orbital angular momentum $\vec{L}$ is still given by vector sum of individual orbital angular momenta of the electrons.

$$\vec{L} = \Sigma \vec{l}_i$$

Similarly, the resultant spin angular momentum is given by

$$\vec{S} = \Sigma \vec{s}_i$$

According to vector atom model, the vector diagrams under *L-S* coupling and *jj* coupling for the Paschen Back effect are shown in the following diagram.

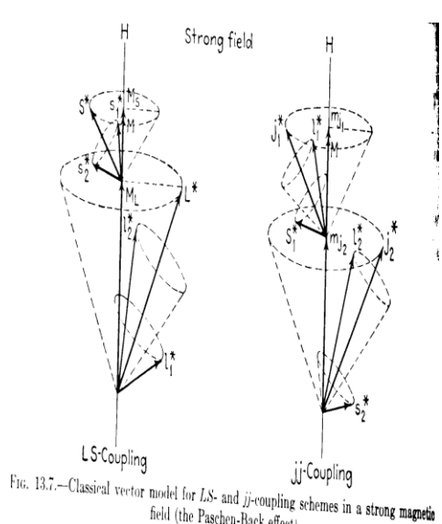


FIG. 13.7.—Classical vector model for *LS*- and *jj*-coupling schemes in a strong magnetic field (the Paschen-Back effect).

Selection rule for Paschen Back effect:

When strong magnetic field is applied the resultant orbital and spin angular momenta i.e. $\vec{L}\,\&\,\vec{S}$ precess almost independently about the direction of the field. The total angular momentum has no significance. Therefore, the selection rules are the same as for orbital and spin angular momenta. The selection rules are stated as follows:

$\Delta m_l = 0, \pm 1$

$\Delta m_s = 0$

Spectra of Diatomic Molecules

IMP.

1) Rotational spectra of diatomic molecules: Consider simple structure of diatomic molecules in the form of dumbbell shape for e.g. molecule of carbon monoxide [CO], HCl etc. A bond is formed between the atoms is the diatomic molecule. The atoms can rotate about an axis passing through the C.M. of the two atoms and perpendicular to line joining two masses. This rotational kinetic energy of the molecule is also quantized. When a molecule makes a transition between these rotational energy states it gives out energy in the form of rotation and the spectrum obtained of these radiation is called rotational spectrum of diatomic molecules.

Expression of moment of inertia of the diatomic molecule can be obtained as follows:

Origin is takes at C.M.

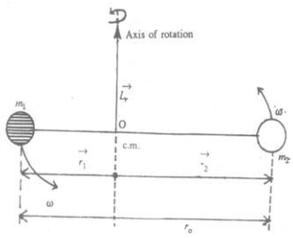


Fig. 6.1 Rotational motion of a diatomic molecule about an axis passing through its centre of mass and perpendicular to the line joining the two atoms

By definition of C.M.

$$\frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2} = 0$$

$$m_1\vec{r}_1 = -m_2\vec{r}_2$$

$$\Rightarrow m_1 r_1 = m_2 r_2 \qquad \text{(in magnitude)}$$

M.I. of the molecule about normal axis passing through C.M. i.e. perpendicular to line joining the molecule

$$I = m_1 r_1^{\,2} + m_2 r_2^{\,2}$$

$$I = \frac{m_1 (m_1 + m_2)}{(m_1 + m_2)} r_1^{\,2} + \frac{m_2 (m_1 + m_2)}{m_1 + m_2} r_2^{\,2}$$

$$= \frac{1}{(m_1 + m_2)} \left(m_1^{\,2} r_1^{\,2} + m_1 m_2 r_1^{\,2} + m_1 m_2 r_2^{\,2} + m_2^{\,2} r_2^{\,2} \right)$$

$$= \frac{m_1 m_2}{(m_1 + m_2)} \left(\frac{m_1 r_1^{\,2}}{m_2} + \frac{m_2 r_2^{\,2}}{m_1} + r_1^{\,2} + r_2^{\,2} \right)$$

$$= \frac{m_1 m_2}{(m_1 + m_2)} \left(\frac{m_2 r_2 \, r_1}{m_2} + \frac{m_1 r_1 \, r_2}{m_1} + r_1^{\,2} + r_2^{\,2} \right)$$

$$= \frac{m_1 m_2}{(m_1 + m_2)} \left(r^2 + 2 r_1 r_2 + r_2^{\,2} \right)$$

$$= \frac{m_1 m_2}{(m_1 + m_2)}(r_1 + r_2)^2$$

$$\frac{m_1 m_2}{m_1 + m_2} = \mu \quad r_1 + r_2 = r_0$$

$$I = \mu r_0^2$$

There is angular momentum associated with rotational motion of the diatomic molecule. Analogues to the orbital angular momentum of the electron even the angular momentum of the diatomic molecule is also quantized. We have,

$$L_r = I\omega$$

$$L_r = \sqrt{J(J+1)}\hbar \qquad \text{Where } J=0,1,2$$

J is called rotational quantum number.

Thus, the rotational K.E. of the diatomic molecule is given by

$$E_r = \frac{1}{2} I\omega^2$$

$$= \frac{(\omega)^2}{2I}$$

$$E_r = \frac{L_r^2}{2I}$$

$$E_r = \frac{J(J+1)\hbar^2}{2I}$$

The various rotational energy states are shown in the following energy level diagram. It is assumed that it is a rigid rotator i.e. the bond length does not change.

[diagram]

In above discussion the diatomic molecule was assumed to be rigid rotator but in fact, the bond length is flexible. If there is a small change in the distance between the atoms then the restoring force is developed which tries to bring back the atom to its equilibrium position. This restoring force is given by

$$F = -k(r - r_0)$$

Where k is force constant or spring constant representing bond between the atoms. This restoring force provides the necessary centripetal force for the rotation of the diatomic molecule.

C.P.F = Restore force.

$$\Rightarrow \mu\omega^2 r = k(r - r_0)$$

$$\Rightarrow r = \frac{kr_0}{(k - \mu\omega^2)}$$

Thus, the diatomic molecule has the rotational kinetic energy as well as the potential energy due to the stretching or the compression of the bond length between the atoms. Thus the total energy of the diatomic molecule

$$E = \frac{1}{2} I\omega^2 + \frac{1}{2} k(r - r_0)^2$$

$$= \frac{L_r^2}{2I} + \frac{1}{2} k\left[\frac{k}{(k - \mu\omega^2)} - 1\right]^2 r_0^2$$

$$= \frac{J(J+1)\hbar^2}{2I} + \frac{1}{2} k r_0^2 \left[1 - \frac{2k}{(k - \mu\omega^2)} + \frac{2 \cdot 3k^2}{2!(k - \mu\omega)}\right]$$

As an approximation, the higher order terms can be neglected. The above expression gives the modified rotational energy states of the diatomic molecule. It can also be expressed as

$$E = \frac{J(J+1)\hbar^2}{2I} + \frac{1}{2} k(r - r_0)^2$$

$$= \frac{J(J+1)\hbar^2}{2I} + \frac{1}{2}k\left[\frac{\mu\omega^2 r}{k}\right]^2$$

$$= \frac{J(J+1)\hbar^2}{2I} + \frac{(\mu r)^2\omega^4}{2k}$$

$$= \frac{J(J+1)\hbar^2}{2I} + \frac{\mu I^2\omega^4}{2kI}$$

$$= \frac{J(J+1)\hbar^2}{2I} + \frac{2\mu}{kI}\left(\frac{1}{2}I\omega^2\right)^2$$

$$\frac{J(J+1)\hbar^2}{2I} + \frac{2\mu}{kI}\left(\frac{L^2}{2I}\right)^2$$

$$= \frac{J(J+1)\hbar^2}{2I} + \frac{2\mu}{4kI^3}J(J+1)^2\hbar^4$$

Thus, the modified energy levels are found to be different from those of rigid rotator. From small value of J there is not much change in the energy level. But as rotational quantum number J increases the difference in energy level also increases. It is as shown in the previous graph.

Problem 1) The force constant between the nucleus of H-molecule is $4.8\text{x}10^2$N/m. Calculate the frequency of oscillation and wavelength and wave number of the vibrational emission line obtained. Mass of H-atom is $1.67\text{x}10^{-27}$kg.

Frequency of oscillation of $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

But $m_1=m_2=m$ (say)

$$\mu = \frac{m^2}{2m}$$

$$\mu = \frac{1}{2}m$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{2k}{m}}$$

$$= \frac{1}{2\pi}\sqrt{\frac{2x4.8x10^2}{1.6x10^{-27}}}$$

$$\nu = 1.21x10^{14}\,\text{Hz}$$

Frequency of oscillation is same as the frequency of emission.

$\therefore$Wavelength of emission line $\lambda = \frac{c}{\nu}$

$$= \frac{3x10^8}{1.21x10^{14}}$$

$$= 2.4^8 x10^{-6} m$$

$$\lambda = 2.4800\,\text{Å}$$

Wave number $\nu = \frac{1}{\lambda} = 103225$

2) What is a force constant of HCl molecule given that its vibration frequency is $9\text{x}10^{13}$ Hz. What is its zero point energy? Mass of H=$1.67\text{x}10^{-27}$ kg; Cl=$5.81\text{x}10^{-26}$ kg.

Zero point energy $E_0 = \frac{1}{2}\hbar\omega$ (1^{st} lesson S.H.O. vibration)

Vibration energy $E_\nu\left(\nu+\frac{1}{2}\right)\hbar\omega$

ν – Vibration quantum number

$\nu = 0,1,2,3$

$$E_\nu = \left(\nu+\frac{1}{2}\right)h\nu$$

$$E_0 = \frac{1}{2}h\nu$$

$$= \frac{1}{2}x667x10^{-34}\,x9x10^{13} = 3x10^{-20}\,\text{J}$$

In Q.M. Lowest possible energy is not zero but it has some value called as zero point energy.

Vibration spectra of diatomic molecule

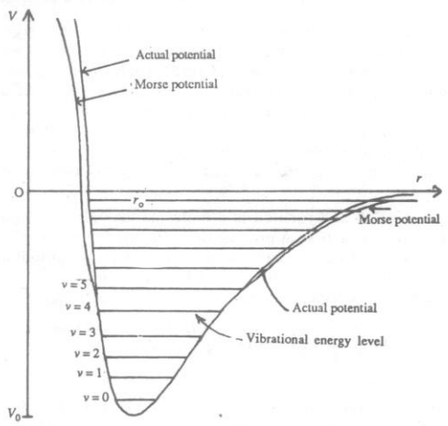


Fig. 6.6 Morse potential

The above figure shows variation of potential energy of a molecule as a function of *r*. The equilibrium configuration of molecule is minimum of this curve. In this region, the shape of the curve is nearly parabola, hence we write

$$V = V_0 + \frac{1}{2}K(r-r_0)^2$$

The force responsible for this p.t. is given by

$$F = -\frac{dV}{dr}$$

$$\therefore F = -K(r-r_0)$$

This equation is same as for simple harmonic oscillator where the frequency of oscillation is given by

$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{m}}$ K is spring constant

Let's consider vibrations of a diatonic role value.

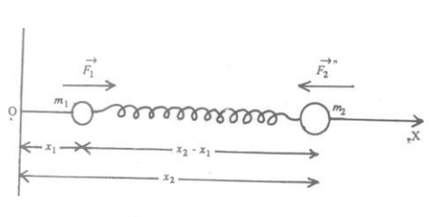


Fig. 6.5 A two-body oscillator

Here two atoms of masses m_1 and m_2 are joined by means of a spring as shown in figure. The masses m_1 and m_2 move back and forth relative to centre of mass in the opposite direction. The length of spring when it is displaced from its

mean position is $x_2 - x_1$, which is same as the equilibrium length *(l)* of the spring plus the extension produced.

$\therefore x_2 - x_1 = l + x$

$\Rightarrow x = (x_2 - x_1) - l$

x is positive when spring is stretched

x is negative when it is compressed

Due to extension and compression of the spring, the spring exerts a restoring force on each of two masses. The restoring forces are given by:

$F_1 = +Kx$

$F_2 = -Kx$ (F_1 and F_2 are in opposite direction)

By Newton's 2nd law of motion

$$m_1 \frac{d^2 x_1}{dt^2} = Kx \qquad (1)$$

$$m_2 \frac{d^2 x_2}{dt^2} = -Kx \qquad (2)$$

Multiply (1) by m_2 and (2) by m_1 and (2) – (1)

$$m_1 m_2 \frac{d^2 x_2}{dt^2} - m_1 m_2 \frac{d^2 x_1}{dt^2} = -K(m_1 + m_2)x$$

$$\frac{m_1 m_2}{m_1 + m_2}\left[\frac{d^2}{dt^2}(x_2 - x_1)\right] = -Kx$$

$$\mu \frac{d^2 x}{dt^2} = -Kx$$

$$\frac{d^2 x}{dt^2} + \left(\frac{K}{\mu}\right)x = 0$$

The solution of this equation gives the frequency of vibration as

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$$

But when the same problem is solved quantum mechanically, the energy of oscillation is found to be quantized

$$E_\nu = \left(\nu + \frac{1}{2}\right)\hbar\omega$$

Where υ – vibrational quantum number

$\upsilon = 0,1,2\ldots$

Thus, vibration energy levels of a diatomic molecule are given by

$$E_\nu = \left(\nu + \frac{1}{2}\right)\hbar\sqrt{\frac{K}{\mu}}$$

With the increasing value of υ, the curve for V vs. r is no longer a parabola but is approximated by a Morse potential as

$$V(r) = D\left[1 - e^{-a(r - r_0)}\right]^2$$

a – width of the potential well

D – Dissociation energy

On solving the Schrödinger 's equation with Morse potential, the vibration energy states are obtained as

$$E_\nu = \left(\nu + \frac{1}{2}\right)\hbar\sqrt{\frac{K}{\mu}} - \left(\nu + \frac{1}{2}\right)^2 \frac{\hbar^2 K}{4D\mu}$$

This indicates that the space between the successive levels decreases with increasing υ.

The vibrational transitions occur only in diatomic molecules, which have permanent electric dipole moment. The selection rule for the transitions between states is

$\Delta\nu = \pm 1$

Vibration rotation spectra

If a molecule has a rotational motion in addition to the vibration motion of its constituents then the resulting frequency gets modified and the corresponding spectra are called the vibration rotation spectra.

When the vibration levels are excited, the rotational energy levels also get excited. This means that as to each vibration level, many rotational levels are associated. The spectra thus obtained do not show isolated lines corresponding to each vibration transition but instead show a large number of closely spaced lines due to transition between the various rotational states of one vibration between rotational states of the other. The closely spaced lines appeal as a streak called a vibration rotation band. The vibration and rotation of a molecule take place independent of each other to a first approximation. Thus, energy of a diatonic molecule is the sum of the rotational and vibration energy.

$$E_{\nu,g} = \left(\nu + \frac{1}{2}\right)\hbar\sqrt{\frac{K}{\mu}} + \frac{J(J+1)\hbar^2}{2I}$$

When *J=0,1,2,--*

υ= 0,1,2,

The transition between the energy levels give rise to vibration rotation spectra. The corresponding selection rules are

$\Delta J = \pm 1$ and $\Delta\nu = \pm 1$

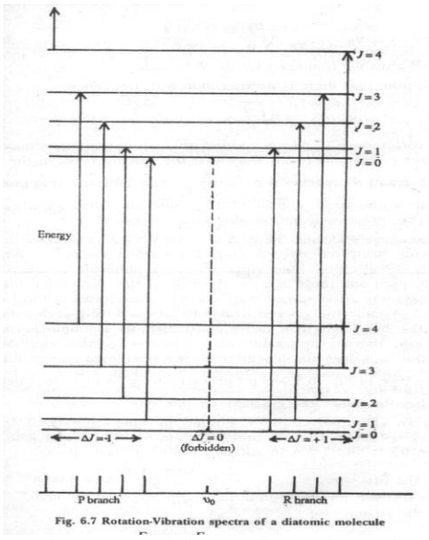


Fig. 6.7 Rotation-Vibration spectra of a diatomic molecule

Figure shows two vibration levels with *υ=0* and *υ=1*. With each of these levels, we have shown five rotational levels with *J=0,1,2,3,4*. The *υ=0→υ=1* transitions fall into two categories:

1) *ΔJ= −1* corresponds to *P* branch (i.e *J→J-1)*

The frequencies of the spectral lines corresponding to *P* branch can be calculated as

$$\nu_p = \frac{E_{1,J-1} - E_{0,J}}{h}$$

$$= \frac{1}{h}\left\{\left[\left(1+\frac{1}{2}\right)\hbar\sqrt{\frac{K}{\mu}} + \frac{J(J-1)\hbar^2}{2I}\right] - \left[\frac{1}{2}\hbar\sqrt{\frac{K}{\mu}} + \frac{J(J+1)\hbar^2}{2I}\right]\right\}$$

$$= \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} - \frac{J\hbar}{2\pi I}$$

2) *ΔJ=+1* corresponds to *R* branch (i.e. J→*J+1*). The frequencies of the spectral lines corresponding to *R* branch can be calculated as follows:

$$\nu_R = \frac{E_{R,J+1} - E_{0,J}}{h}$$

$$= \frac{1}{h}\left\{\left[\left(1+\frac{1}{2}\right)\hbar\sqrt{\frac{K}{\mu}} + \frac{(J+1)(J+2)\hbar^2}{2I}\right] - \left[\frac{1}{2}\hbar\sqrt{\frac{K}{\mu}} + \frac{J(J+1)\hbar^2}{2I}\right]\right\}$$

$$= \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} + \frac{(J+1)\hbar}{2\pi I}$$

This shows that spacing between lines for both P and R branches is $\Delta\nu = \hbar/2\pi I$

Frank Condon Principle

The time taken for the electronic transitions to occur is a small fraction of the time required for the vibrating molecule to complete a vibration. Such transitions are so rapid that we can consider the instantaneous nuclear distance in a molecule to remain constant during such a transitions. This is known as Frank Condon Principle.

We assume that the electronic, vibration and rotational energies of the electron are independent of each other. Therefore the total energy of a molecule (E_t) is

$E_t = E_e + E_\nu + E_r$

E_e – electronic energy

E_υ – Vibration energy

E_r – rotational energy

$\therefore \Delta E_t = \Delta E_e + \Delta E_\nu + \Delta E_r$

Normally $\Delta E_e >> \Delta E_\nu >> \Delta E_r$ thus if we neglect ΔE_r in comparison with ΔE_e and ΔE_ν we get the vibration. Thus, we have

$E_t = E_e + E_\nu$

But, $E_\nu = \left(\nu+\frac{1}{2}\right)\hbar\sqrt{\frac{K}{\mu}} - \left(\nu+\frac{1}{2}\right)^2\frac{\hbar^2 K}{4D\mu}$

$\therefore E_t = E_e + \left(\nu+\frac{1}{2}\right)\hbar\sqrt{\frac{K}{\mu}} - \left(\nu+\frac{1}{2}\right)^2\frac{\hbar^2 k}{4D\mu}$ (1)

[Diagram]

The above figure shows various energy levels and transitions from lowest vibration state of lower electronic state to the vibration states corresponding to a higher electronic state. Since these transitions are from a lower level to higher levels, the resulting spectrum is an absorption spectrum which is shown as below:

[Diagram]

In the absorption spectrum, the line becomes more crowded as wave number increases. This is because vibrations of real diatomic molecules are unharmonic. Since all transitions are not equally probable, the bands are not equally intense.

We have from equation (1)

$E_t' = E_e' + \left(\nu'+\frac{1}{2}\right)\hbar\sqrt{\frac{K'}{\mu}} - \left(\nu'+\frac{1}{2}\right)^2\frac{\hbar^2 K'}{4D\mu}$

is the higher electronic–vibration state.

$E_t'' = E_e'' + \left(\nu''+\frac{1}{2}\right)\hbar\sqrt{\frac{K''}{\mu}} - \left(\nu''+\frac{1}{2}\right)^2\frac{\hbar^2 K''}{4D\mu}$

in the lower electronic vibration state.

$\therefore$ The wave number of the resulting spectral line is

$$\bar{\nu} = \frac{E_t' - E_t''}{hc} \qquad \Delta E = h\nu = \frac{hc}{\lambda} \qquad \therefore \frac{1}{\lambda} = \frac{\Delta E}{hc}$$

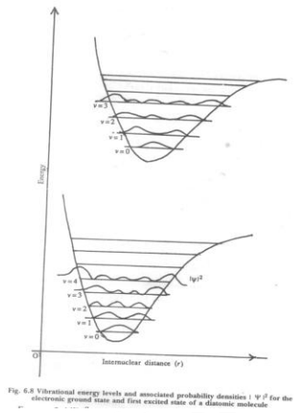


Fig. 6.8 Vibrational energy levels and associated probability densities $|\psi|^2$ for the electronic ground state and first excited state of a diatomic molecule

The above figure shows the curves of the P.E. verses the internuclear distance for the electronic ground state and the first excited state. For each of these states the vibration energy levels are shown with $\upsilon=0,1,2\ldots$ Superimposed upon these levels, the graphs of the corresponding harmonic oscillation probability density $|\psi|^2$ are shown.

Only these transitions are favoured which connect an initial configuration with high probability density $|\psi|^2$ with a final state of high probability density.

We will consider the transitions between electronic states in a diatomic molecule. Transitions occur in accordance with Frank Condon Principle.

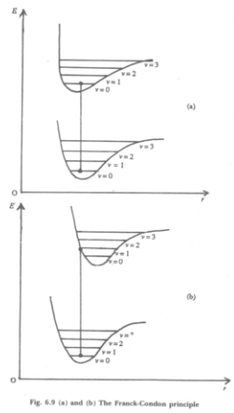


Fig. 6.9 (a) and (b) The Franck-Condon principle

In figure *(a)* average inter-nuclear distance is the same in both states. It shows the transitions to the level υ=0 of the upper state. It is favoured as it connects the states of high probability transitions to other vibration states. $\upsilon=1,2,3\ldots$ also occur but results in weak line.

In figure (*b*) average intermolecular distance is slightly greater in upper state. It shows the transitions from $\upsilon=0$ *to* $\upsilon=1$ of the upper state. It takes place as $|\psi|^2$ is maximum at the end of the motion for $\upsilon=1$.

[Diagram]

Figure (*c*) shows the transition, which is most likely to dissociate a molecule. This is because the vertical line for $\upsilon=0$ of the lower state intersects the upper curve at a point where no bound state is possible.

A curve corresponds to two excited states intersect as shown in figure (*d*), a phenomenon called pre-disassociation occurs.

Raman Effect

Though the liquids do not absorb the incident radiation, there are some frequencies in the scattered radiation, which are different from the frequency of incident radiation. Also, the observed frequency difference is a characteristic of the given medium. This effect is known as Raman Effect.

Quantum Explanation

When a photon from incident monochromatic radiation hits a molecule of the medium three things may happen:

1) The molecule merely deviate the photon without absorbing the energy. This results in intense line at the original frequency called Rayleigh line i.e. it is a elastic scattering where there is no exchange of energy.

2) The molecule might absorb part of the energy of the incident photon leading to the molecule in excitation to higher vibration energy level. Thus scattered photon will have less energy and i.e. radiation will have lower frequency, and the corresponding line is called 'Stokes line'.

3) If the molecule is already in the higher vibration energy level, it may give up this extra energy to the incident photon. In this case, the scattered photon will have higher energy i.e. high frequency. The corresponding line is called 'Anti-Stokes' line'.

[Diagram]

Transition probability for the stokes and Anti-Stokes line is the same but anti-Stokes line is much weaker as compared to the Stokes line because the Stokes line is accompanied by an increase in molecular energy while anti Stokes line involves decrease in molecular energy. Also the ground state population under normal conditions is much greater than the excited state population.

We treat the process of the Raman scattering as a collision between incident photon and the molecule. Then by principle of conservation of energy,

$$E_p + \frac{1}{2}mv^2 + h\nu_0 = E_q + \frac{1}{2}mv'^2 + h\nu'$$

When E_p, E_q rest mass energy of the molecule before and after collision, v, v' be its speed before and after the effect.

ν_0, ν' be the Frequency of incident and scattered photons respectively.

As collision does not cause appreciable change in temperature of solution i.e. kinetic energy of molecule remain practically unaltered.

$$\therefore E_p + h\nu_0 = E_q + h\nu'$$

$$h(\nu_0 - \nu') = E_q - E_p$$

$$\therefore \nu' = \nu_0 + \frac{E_p - E_q}{h}$$

If $E_p = E_q \Rightarrow \nu' = \nu_0$ Rayleigh line

$E_p < E_q \Rightarrow \nu' < \nu_0$ Stock line

$E_p > E_q \Rightarrow \nu' > \nu_0$ Anti stock line

The change in the energy of the molecule is related to vibrational frequency as

$E_p - E_q = nh\nu_v$ n = 1,2…

For $n=1$

$$\nu' = \nu_0 - \nu_v$$

Thus, Raman lines are symmetrically situated on either side of original line.

Classical Theory

When a molecule is placed in a static electric field, it gets polarised. This is because the positively charged nucleus and negatively charged electrons are acted upon by electrical force. This produces separation of the centres of the positive charge and negative charge. It leads to an induced electric dipole

moment in the molecule. If E is the magnitude of the applied field then the magnitude of electric dipole moment is related to E as

$\mu = \alpha E$

α -Polarizability of molecule

Polarizability α is not same in all directions i.e. it is anisotropic and it is indicated by making use of polarizability ellipsoid. Polarizability ellipsoid is three-dimensional surface such that distance of a point on its surface from the electric centre of the molecule is proportional to $1/\sqrt{\alpha_i}$ where α_i polarizability along the line joining the point i on the ellipsoid and electric centre. Ellipsoid has a circular cross section as it all the directions at right angle to bond axis, the polarizability is same.

[Diagram]

When a beam of frequency ν is incident on a sample containing diatomic or linear poly-atomic molecule, each molecule is subjected to an oscillating electric field due to incident beam. This is given:

$E = E_0 \sin 2\pi\nu t$

$\mu = \alpha E$

$= \alpha E_0 \sin 2\pi\nu t$

This shows that the induced electric dipole oscillates with frequency ν.

A molecule may undergo some internal motion such as vibration or rotation, which changes the polarizability of a molecule with a definite period. Hence an oscillating dipole will have an additional frequency superimposed upon it.

Let's assume that the polarizability changes due to an additional vibration motion of the molecule. If the vibration is ν_υ then

$\alpha = \alpha_0 + \beta \sin 2\pi\nu_\upsilon t$

α_0 – equilibrium polarizability

β- measure of the change of polarizability with the vibration

Hence we have,

$\mu = \alpha E$

$= (\alpha_0 + \beta \sin 2\pi\nu_\upsilon t)\ (E_0 \sin 2\pi\nu t)$

$= (\alpha_0 E_0 \sin 2\pi\nu t + \beta E_0 \sin 2\pi\nu_\upsilon t \sin 2\pi\nu t)$

$$= \alpha_0 E_0 \sin 2\pi\nu t + \frac{\beta E_0}{2}\left[\cos 2\pi(\nu - \nu_\upsilon)t - \cos 2\pi(\nu + \nu_\upsilon)t\right]$$

This shows that the oscillating dipole has frequency $\nu+\nu_\upsilon$ and $\nu-\nu_\upsilon$ as well as the exciting frequency ν.

If a molecular vibration is such that it does not cause any change in the polarizability the $\beta = 0$ and we have only one frequency ν.

Thus, the substance to be Raman Active, the rotational vibration motion of a molecule must cause a change in the polarizability of the molecule.