these conditions penetration of electron or proton takes place.

2.32 THE RIGID ROTATOR

By a rigid rotator we mean, a two or more particle system, in which the distance between the particles is assumed to remain fixed during rotation and cannot vary with time. The theory of such a rigid rotator is useful in dealing with the rotational spectra of diatomic molecules. If the masses of the electrons and the vibration of the nuclei are ignored, a diatomic molecule may be compared to a rigid rotator.

1. Classical Treatment of Rigid Rotator

Let us consider a two-particle rigid rotator like a diatomic molecule with masses m_1 and m_2 and separated by fixed distance "r". Assume that the centre of gravity of the system is fixed at the origin of our coordinate. Let the distance of m_1 from the centre of gravity be r_1 and distance m_2 be r_2, then

$$m_1 r_1 = m_2 r_2 \qquad (2.125)$$

or $$r_1 + r_2 = r \qquad (2.126)$$

From Eq. (2.125) and (2.126)

$$m_1 r_1 = m_2 r_2$$

$$= m_2(r - r_1) \qquad (\because\ r_1 + r_2 = r)$$

$$= m_2 r - m_2 r_1$$

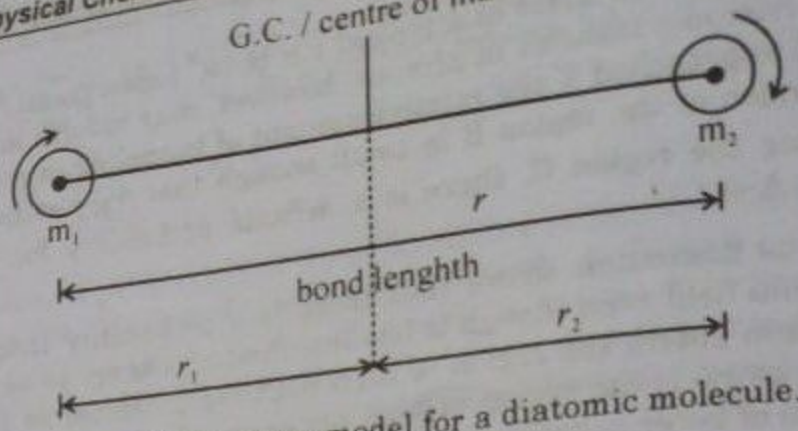

Fig.2.23 Rigid rotator model for a diatomic molecule.

or $m_1r_1 + m_2r_1 = m_2r$

$r_1(m_1 + m_2) = m_2r$

$$r_1 = \frac{m_2 r}{m_1 + m_2}$$

Similarly,

$$r_2 = \frac{m_1 r}{m_1 + m_2}$$

The moment of inertia (I) of the rotating body, about the C.G. is

$$I = m_1 r_1^2 + m_2 r_1^2 \qquad (2.127)$$

$$\left(I = \sum_{i=1}^{n} mir_i^2 \right)$$

Substituting the values of r_1 and r_2 in 2.127, we get

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

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

Taking m_1m_2 as common.

$$= m_1 m_2 \left[\frac{m_2 + m_1}{(m_1 + m_2)^2} \right] r^2$$

$$= m_1 m_2 \left[\frac{1}{m_1 + m_2} \right] r^2$$

$$= \left[\frac{m_1 m_2}{m_1 + m_2} \right] r^2$$

$$I = \mu r^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \text{reduced mass} \qquad (2.128)$$

(Reduced mass: When masses of two particles are converted into a single mass, then it is called reduced mass, because in quantum mechanics, it is easy to handle one particle system as compared to two particle.)

Since the distance between the two particle is fixed, the P.E. is treated as zero. Therefore, the rigid rotator has only K.E. The K.E. of rotation, (T) is the given by

$$T = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2$$

where v_1 and v_2 are the linear velocities of masses m_1 and m_2 respectively. Then, in terms of angular velocity, we can write

$$T = \frac{1}{2} m_1 \omega^2 r_1^2 + \frac{1}{2} m_2 \omega^2 r_2^2$$

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

$$= \frac{1}{2} \omega^2 I \qquad (2.129)$$

where ω (omega) is the angular velocity and I is the moment of inertia about an axis passing through the centre of the gravity and normal to the line through the masses.

Since the angular momentum L, is related to the moment of Inertia. I through the relation

$$L = \omega I \qquad (2.130)$$

Therefore,

$$T = \frac{L^2}{2I} = \frac{L^2}{2\mu r^2} \qquad (2.131)$$

$$\therefore \quad T = \frac{1}{2} \omega^2 I = \frac{1}{2} \frac{\omega^2 I^2}{I} = \frac{L^2}{2I}$$

Quantum Mechanical Treatment of Rigid Rotator

Now, let us consider the two particle rigid rotator from quantum-mechanical stand point.

N.B. The molecule is called rigid rotator because it is not compressed in any situation, because we are dealing with an ideal system.

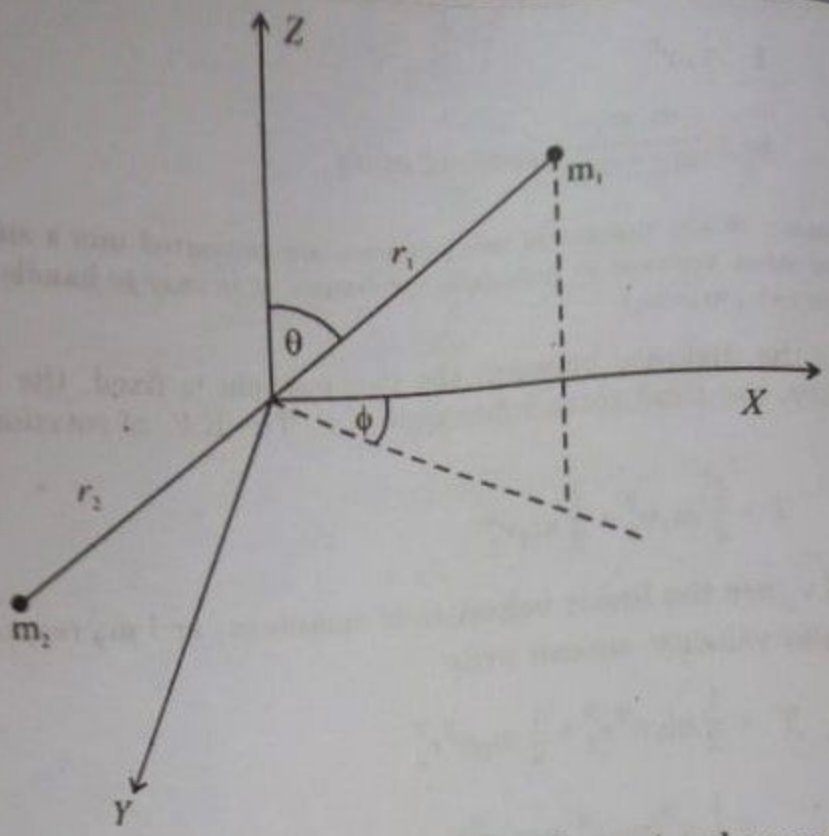

Fig.2.24 The rigid rotator in three-dimensional spaces

It will be recalled that the three-dimensional Schrodinger wave equation for a single particle is

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

The potential energy of the rigid rotator will be constant and this constant value may be conveniently taken as zero. Applying above equation to the rigid rotator and putting $V = 0$

$$\nabla^2\Psi + \frac{8\pi^2\mu}{h^2}E\Psi = 0 \qquad (2.132)$$

The Laplacian operator was given in terms of spherical polar coordinates.

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

For the rigid rotator, r has constant value. Since r is constant, factors involving $\partial/\partial r$ will be zero.

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

Substitute this value in equation (2.132), we get

$$\frac{1}{r^2\sin\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\cdot\frac{\partial\Psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\cdot\frac{\partial^2\Psi}{\partial\phi^2} + \frac{8\pi^2 IE}{h^2r^2}\Psi = 0 \qquad (2.133)$$

$$\left(\because \mu = \frac{I}{r^2}\right)$$

Multiplying both sides by "r^2". We get

$$\frac{1}{\sin\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\cdot\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\cdot\frac{\partial^2\Psi}{\partial\phi^2}+\frac{8\pi^2 I}{h^2}E\Psi=0 \qquad (2.134)$$

Equation (2.134) contains two angular variable θ and ϕ. It is solved once again by the method of separation of variables. It is assumed that Ψ is a product of two functions, each of which is a function of only one of the variables. It is assumed therefore, that

$$\Psi(\theta, \phi) = Y(\theta)\cdot Z(\phi) \qquad (2.135)$$

which means that Ψ(which is a function of θ and ϕ) is equal to the product of two functions "Y" and "Z" where "Y" is a function only of θ and "Z" is a function only of ϕ. Equation (2.135) may be written more simply as

$$\Psi = YZ \qquad (2.135)$$

Since the function Z is independent of θ, differentiation of equation (2.135) w.r.t. θ yields

$$\frac{\partial\Psi}{\partial\theta} = Z\cdot\frac{dY}{d\theta} \qquad (2.136)$$

Similarly, differentiation w.r.t. ϕ gives

$$\frac{\partial\Psi}{\partial\phi} = Y\frac{dZ}{d\phi}$$

and further differentiation w.r.t. ϕ yields,

$$\frac{\partial^2\Psi}{\partial\phi^2} = Y\cdot\frac{d^2Z}{d\phi^2} \qquad (2.137)$$

Substituting from Eq. (2.136) and (2.137) into (2.134) gives

$$\frac{Z}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dY}{d\theta}\right)+\frac{Y}{\sin^2\theta}\cdot\frac{d^2Z}{d\phi^2}+\frac{8\pi^2 IE}{h^2}YZ=0$$

Multiplying by $\sin^2\theta/YZ$

$$\frac{\sin\theta}{Y}\cdot\frac{d}{d\theta}\left(\sin\theta\cdot\frac{dY}{d\theta}\right)+\frac{1}{Z}\cdot\frac{d^2Z}{d\phi^2}+\frac{8\pi^2 IE}{h^2}\cdot\sin^2\theta=0 \qquad (2.138)$$

or
$$\frac{\sin\theta}{Y}\cdot\frac{d}{d\theta}\left(\sin\theta\cdot\frac{dY}{d\theta}\right)+\frac{8\pi^2 IE}{h^2}\cdot\sin^2\theta=-\frac{1}{Z}\cdot\frac{d^2Z}{d\phi^2} \qquad (2.139)$$

Each side of equation (2.139) contains only one variable. The L.H.S. has only terms in the variable θ and the R.H.S. has only a term in the variable ϕ. As the equation must hold for all values of θ and ϕ, each side of the equation must be a

constant. Representing this constant value by m^2 allows each side of equation (2.139) to be written

$$-\frac{1}{Z}\cdot\frac{d^2Z}{d\phi^2} = m^2$$

or $$\frac{1}{Z}\cdot\frac{d^2Z}{d\phi^2} + m^2 = 0$$

or $$\frac{d^2Z}{d\phi^2} + m^2Z = 0 \qquad (2.140)$$

and $$\frac{\sin\theta}{Y}\cdot\frac{d}{d\theta}\left(\sin\theta\cdot\frac{dY}{d\theta}\right) + \frac{8\pi^2IE}{h^2}\cdot\sin^2\theta = m^2$$

or $$\frac{\sin\theta}{Y}\cdot\frac{d}{d\theta}\left(\sin\theta\cdot\frac{dY}{d\theta}\right) + \beta\sin^2\theta = m^2$$

Putting $\beta = \frac{8\pi^2IE}{h^2}$

or $$\frac{\sin\theta}{Y}\cdot\frac{d}{d\theta}\left(\sin\theta\cdot\frac{dY}{d\theta}\right) + \beta\sin^2\theta - m^2 = 0$$

Multiply by $Y/\sin^2\theta$

$$\frac{1}{\sin\theta}\cdot\frac{d}{d\theta}\left(\sin\theta\cdot\frac{dY}{d\theta}\right) + \left(\beta - \frac{m^2}{\sin^2\theta}\right)Y = 0$$

Carrying out the differentiation indicated in the first term and remembering that $(\sin\theta)\left(\frac{dY}{d\theta}\right)$ must be differentiated as a product.

$$\frac{1}{\sin\theta}\cdot\left(\sin\theta\cdot\frac{d^2Y}{d\theta^2} + \cos\theta\cdot\frac{dY}{d\theta}\right) + \left(\beta - \frac{m^2}{\sin^2\theta}\right)Y = 0$$

The variable in the equation is now changed by putting.

$z = \cos\theta$

$z^2 = \cos^2\theta$

$\sin^2\theta + \cos^2\theta = 1$

$\sin^2\theta = 1 - \cos^2\theta = 1 - z^2$

$$\frac{1}{\sin\theta}\cdot\frac{d}{d\theta}\left(\sin\theta\cdot\frac{dY}{d\theta}\right) + \left(\beta - \frac{m^2}{1-z^2}\right)Y = 0$$

$$\frac{1}{\sin\theta}\cdot\frac{d}{d\theta}\left(\sin\theta\cdot(-\sin\theta)\frac{dY}{dz}\right) + \left(\beta - \frac{m^2}{(1-z^2)}\right)Y = 0$$

$$\frac{dz}{d\theta} = -\sin\theta$$

$$\frac{dY}{d\theta} = \frac{dY}{dz}\cdot\frac{dz}{d\theta}$$

$$= \frac{dY}{dz}(-\sin\theta)$$

$$\frac{d}{d\theta} = \frac{dz}{d\theta}\cdot\frac{d}{dz}$$

$$= -\sin\theta\cdot\frac{d}{dz}$$

$$\frac{1}{\sin\theta}\cdot\frac{d}{d\theta}\left(-\sin^2\theta\cdot\frac{dY}{dz}\right)+\left(\beta-\frac{m^2}{1-z^2}\right)Y=0$$

$$\frac{d}{d\theta}(\sin^2\theta)=2\sin\theta\cos\theta$$

$$\frac{1}{\sin\theta}\left[-2\sin\theta\cdot\cos\theta\cdot\frac{dY}{dz}-\sin^2\theta\,\frac{d}{d\theta}\cdot\frac{dY}{dz}\right]$$

$$\frac{1}{\sin\theta}\left[-2\sin\theta\cdot\cos\theta\cdot\frac{dY}{dz}-\sin^2\theta\,\frac{d}{d\theta}\cdot\frac{dY}{dz}\right]$$

$$-2\cos\frac{dY}{dz}-\sin\theta\cdot\frac{d}{d\theta}\cdot\frac{dY}{dz}+\left(\beta-\frac{m^2}{1-z^2}\right)Y=0$$

$$-2\cos\cdot\frac{dY}{dz}-\sin\theta\cdot\left(-\sin\theta\frac{d}{dz}\right)\cdot\frac{dY}{dz}+\left(\beta-\frac{m^2}{1-z^2}\right)Y=0$$

$$-2\cos\frac{dY}{dz}+\sin^2\theta\cdot\frac{d}{dz}\cdot\frac{dY}{dz}+\left(\beta-\frac{m^2}{1-z^2}\right)Y=0$$

$$\sin^2\theta\cdot\frac{d^2Y}{dz^2}-2\cos\theta\frac{dY}{dz}+\left(\beta-\frac{m^2}{1-z^2}\right)Y=0$$

$$(1-z^2)\cdot\frac{d^2Y}{dz^2}-2z\cdot\frac{dY}{dz}+\left(\beta-\frac{m^2}{(1-z^2)}\right)Y=0 \qquad (2.143)$$

$$(1-z^2)\cdot\frac{d^2Y}{dz^2}-2z\cdot\frac{dY}{dz}+\left(l(l+1)-\frac{m^2}{(1-z^2)}\right)Y=0 \qquad (2.144)$$

$\therefore \quad \beta = l(l+1)$

Equation (2.144) is similar to *Associated Legender Equation* and the function $P_l^m(z) = P_l^m(\cos\theta) = Y(\theta)$ is called *Associated Legendre* Polynomial of degree "l" and order "m"

$$(1-z^2)\cdot\frac{d^2P_l^m(z)}{dz^2}-2z\frac{d}{dz}P_l^m(z)+\left(l(l+1)-\frac{m^2}{(1-z^2)}\right)P_l^m(z)=0$$

It is a well known equation of physics.

$$\beta=\frac{8\pi^2IE}{h^2}$$

$$l(l+1)=\frac{8\pi^2IE}{h^2}$$

$$E_{rot}=\frac{h^2l(l+1)}{8\pi^2I}$$

While considering the rotational spectra of diatomic molecules, the quantum number is usually written J rather than *l*

$$E_J = E_{rot} = \frac{h^2}{8\pi^2 I} \cdot J(J+1) \qquad (2.145)$$

This relationship gives the eigen values of the energy of the rotator and J is known as the *rotational quantum number*.

The state of the system however, requires the specification of two quantum number J and m. It will be remembered that the relationship between two quantum numbers is

$$J \geq |m|$$

when J = 2, for example, then m = +2, +1, 0, −1, −2. There are thus five possible states of the system for J = 2. As the energy is determined solely by the value of J in equation (2.145) there are thus five different states of the system with the same energy. In general for any value of J, there are (2J + 1) degenerate states. It may be mentioned here that this degeneracy is removed if the molecule, is placed in a magnetic field, and hence in the presence of a magnetic field extra lines appear in the rotational spectrum. It should be noted that J can have the value zero, therefore, it is once again seen that a rotational motion can have zero energy. The rigid rotator serves as an approximate model for the rotational spectra of diatomic molecules. If two energy levels are defined by rotational quantum numbers J and J', then the energy difference between then ΔE, is given by

$$\Delta E_J = \frac{h^2}{8\pi^2 I}[J'(J'+1) - J(J+1)] \quad \text{Joules} \qquad (2.146)$$

There is a selection rule in rotational spectroscopy

$$\Delta J = \pm 1$$

We need only those transitions in which J changes by one unit, all other transitions, being spectroscopically *forbidden*.

Equation (2.145) expresses the allowed energy in joules. In rotational region spectra are usually discussed in terms of wave number,

$$\bar{\upsilon} = \Delta E/hc$$

or $$\epsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 Ic} \cdot J(J+1)\text{cm}^{-1} \qquad (J = 0, 1, 2, \ldots)$$

or $$\bar{\upsilon} = BJ(J+1)\ \text{cm}^{-1}$$

where B, the *rotational constant*, is given by

$$B = \frac{h}{8\pi^2 Ic}$$

where

h = Planck, constant

c = Velocity of light, cm s^{-1}

I = moment of Inertia

when $J = 0$, ground rotational state where no rotation occurs.

After absorption of radiation $J = 1$

The energy absorbed will be

$$\epsilon_{J=1} - \epsilon_{J=0} = 2B - 0 = 2B \text{ cm}^{-1}$$

and therefore,

$$\bar{\upsilon}_{J=0 \to J=1} = 2B \text{ cm}^{-1}$$

The absorption line appears at $2B \text{ cm}^{-1}$.

If now ,the molecule is raised $J = 1$ to $J = 2$ level of absorption of more energy, we see

$$\bar{\upsilon}_{J=1 \to J=2} = \epsilon_{J=2} - \epsilon_{J=1} = 6B - 2B = 4B \text{ cm}^{-1}$$

In general

$$\bar{\upsilon}_{J \to J+1} = 2B\,(J + 1) \text{ cm}^{-1}$$

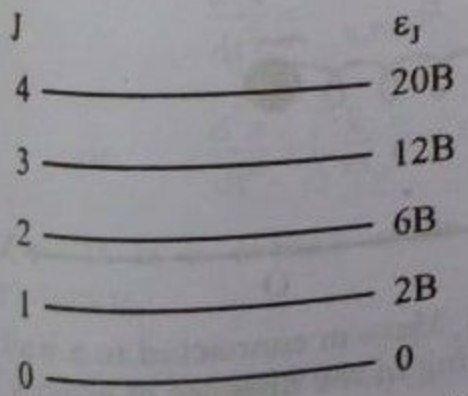

Fig. 2.25 the allowed rotational energy levels

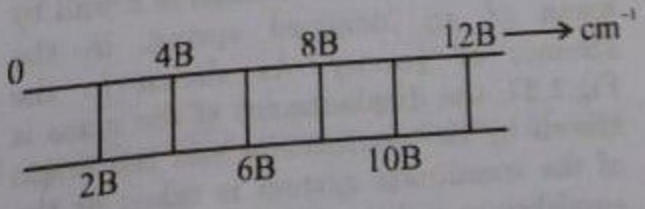

Fig. 2.26 Allowed transitions and observed rotational spectrum.