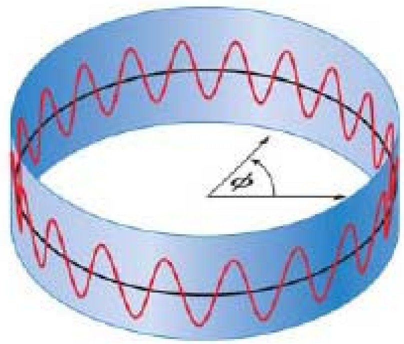
Particle on a ring

Particle on a Ring: Eigenfunction

$$\Phi_+(\phi) = A_{+\phi} e^{im_l\phi}$$

$$\Phi_-(\phi) = A_{-\phi} e^{-im_l\phi}$$

$$m_l = \left(\frac{2IE}{\hbar^2}\right)^{1/2} \quad E_m = \frac{m^2\hbar^2}{2I}$$



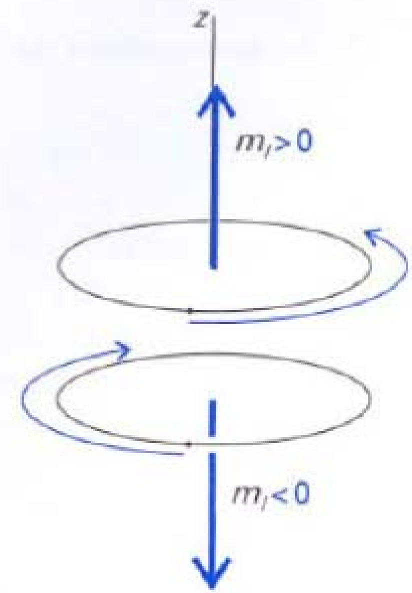


Fig. 3.2 The vector representation of angular momentum of a particle (or an effective particle) confined to a plane. Note the right-hand screw convention for the orientation of the vector.

Normalization

$$\int_0^{2\pi} \Phi^* \Phi \, d\phi = |A|^2 \int_0^{2\pi} e^{-im_l\phi} e^{im_l\phi} \, d\phi = |A|^2 \int_0^{2\pi} d\phi = 2\pi|A|^2$$

$$A_{+\phi} = A_{-\phi} = \frac{1}{\sqrt{2\pi}}$$

<u>Final Solutions: Eigenstates of a Free Particle on a Ring</u> $\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \; E_m = \frac{m^2\hbar^2}{2I}$

Particle on a Ring: Boundary Condition

Wave functions must be single-valued: $\Phi_m(\phi) = \Phi_m(\phi + 2\pi)$

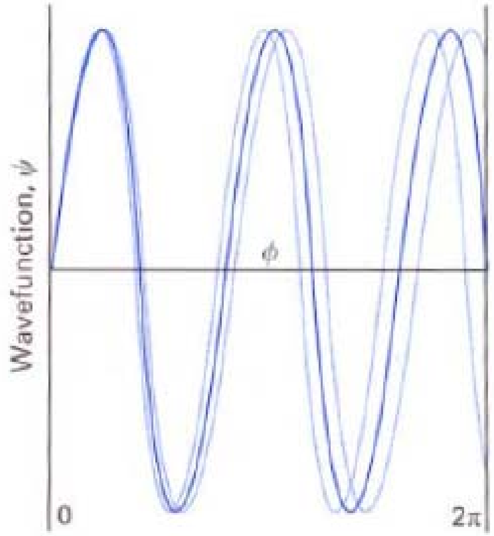
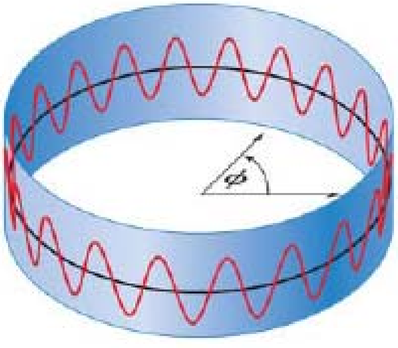
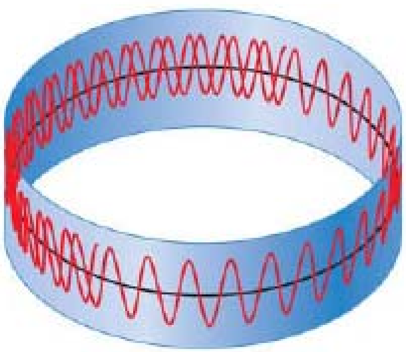


Fig. 3.3 The wavefunction must satisfy cyclic boundary conditions; only the dark curve of these three is acceptable. The horizontal coordinate corresponds to an entire circumference of the ring, and the end points should be considered to be joined.





$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

$$a_m e^{im\phi} = a_m e^{im(\phi+2\pi)} = a_m e^{im\phi} e^{i2\pi m}$$

$$e^{i2\pi m} = 1$$

$$m_l = 0, \ \pm 1, \pm 2, \pm 3, \ldots$$

must be integer!

Final Solutions

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \ E_m = \frac{m^2\hbar^2}{2I}$$

$$(m = 0, \pm 1, \pm 2, \cdots)$$

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}}\, e^{im\phi}$$

.

and can be verified to satisfy the normalization condition containing the complex conjugate

$$\int_0^{2\pi} \psi_m^*(\phi)\, \psi_m(\phi)\, d\phi = 1$$

where we have noted that $\psi_m^*(\phi) = (2\pi)^{-1/2}\, e^{-im\phi}$. The mutual orthogonality of the functions (13) also follows easily, for

$$\int_0^{2\pi} \psi_{m'}^*\, \psi_m(\phi)\, d\phi = \frac{1}{2\pi} \int_0^{2\pi} e^{i(m-m')\phi}\, d\phi$$

$$= \frac{1}{2\pi} \int_0^{2\pi} [\cos(m-m')\phi + i\, \sin(m-m')\phi]\, d\phi = 0$$

$$\text{for } m' \neq m$$

Particle on a sphere: Spherical harmonics

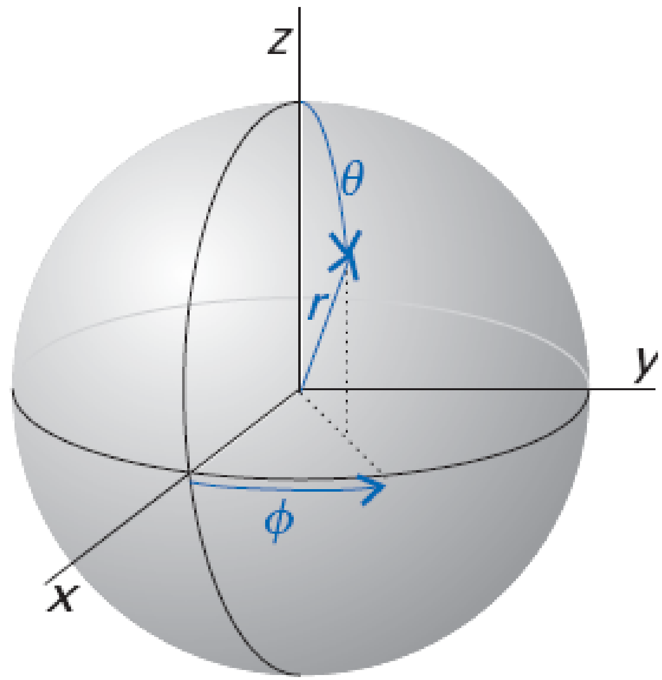


Fig. 3.7 Spherical polar coordinates. The angle θ is called the colatitude and the angle ϕ is the azimuth.

Solutions to the Rigid Rotor

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

$$\hat{H}Y(\theta,\phi)=EY(\theta,\phi)$$

After Rearranging:

$$\underbrace{\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{2IE}{\hbar^2}\sin^2\theta\right]}_{\text{only }\theta}Y(\theta,\phi)=-\underbrace{\frac{\partial^2}{\partial\phi^2}}_{\text{only }\phi}Y(\theta,\phi)$$

Try $Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$ as a solution

Define $\beta \equiv \dfrac{2IE}{\hbar^2}$

$$\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\beta\sin^2\theta\right]\Theta(\theta)\Phi(\phi) = -\frac{\partial^2}{\partial\phi^2}\Theta(\theta)\Phi(\phi)$$

Dividing by $\Theta(\theta)\Phi(\phi)$ and simplifying

$$\underbrace{\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta)+\beta\sin^2\theta}_{\text{only }\theta} = \underbrace{-\frac{1}{\Phi(\phi)}\frac{\partial^2}{\partial\phi^2}\Phi(\phi)}_{\text{only }\phi}$$

Since θ and ϕ are independent variables, each side of the equation must be equal to a constant $\equiv m^2$.

$$\Rightarrow \quad \boxed{\frac{1}{\Phi(\phi)}\frac{\partial^2}{\partial\phi^2}\Phi(\phi) = -m^2} \qquad \text{I}$$

and $$\Rightarrow \quad \boxed{\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta) + \beta\sin^2\theta = m^2} \qquad \text{II}$$

$$\frac{\partial^2\Phi(\phi)}{\partial\phi^2} = -m^2\Phi(\phi)$$

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi} \qquad m = 0,\ \pm 1,\ \pm 2,\ \pm 3, \ldots$$

Particle on a ring

Now let's look at $\Theta(\theta)$.

$$\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta)+\beta\sin^2\theta=m^2$$

Change variables: $x=\cos\theta$ $\Theta(\theta)=P(x)$ $\frac{dx}{-\sin\theta}=d\theta$

Since $0\le\theta\le\pi$ $\Rightarrow$ $-1\le x\le+1$

Also $\sin^2\theta=1-\cos^2\theta=1-x^2$

After some rearrangement we obtain the ***Legendre*** equation ……

$$\left(1-x^2\right)\frac{d^2}{dx^2}P(x)-2x\frac{d}{dx}P(x)+\left[\beta-\frac{m^2}{1-x^2}\right]P(x)=0$$

$$\beta = l\left(l+1\right) \qquad \text{where} \qquad l = 0,\ 1,\ 2,\ldots$$

$$\text{and} \qquad m = 0,\ \pm 1,\ \pm 2,\ldots,\pm l$$

$$\beta = \frac{2IE}{\hbar^2} \quad \Rightarrow \quad E = \frac{\hbar^2}{2I}\beta$$

(Energy is quantized)

$$E = \frac{\hbar^2}{2I}l\left(l+1\right) \qquad l = 0,\ 1,\ 2,\ldots$$

Spherical harmonics

$$Y_l^m(\theta,\phi) = \Theta_l^{|m|}(\theta)\Phi_m(\phi)$$

$$Y_l^m(\theta,\phi) = \left[\left(\frac{2l+1}{4\pi}\right)\frac{(l-|m|)!}{(l+|m|)!}\right]^{\frac{1}{2}} P_l^{|m|}(\cos\theta)e^{im\phi}$$

$$l = 0,\ 1,\ 2,\ldots \qquad m = 0,\ \pm 1,\ \pm 2,\ \pm 3,\ldots \pm l$$

$$P_l^{|m|}(x) = P_l^{|m|}(\cos\theta)$$

$$P_0^0(\cos\theta) = 1$$

$$P_1^0(\cos\theta) = \cos\theta$$

$$P_1^1(\cos\theta) = \sin\theta$$

$$P_2^0(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$$

$$P_2^1(\cos\theta) = 3\cos\theta\sin\theta$$

$$P_2^2(\cos\theta) = 3\sin^2\theta$$

Y_l^m's are the eigenfunctions to $\hat{H}\psi = E\psi$ for the rigid rotor problem.

$$Y_0^0 = \frac{1}{(4\pi)^{1/2}}$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \cos\theta$$

$$Y_1^1 = \left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin\theta e^{i\phi}$$

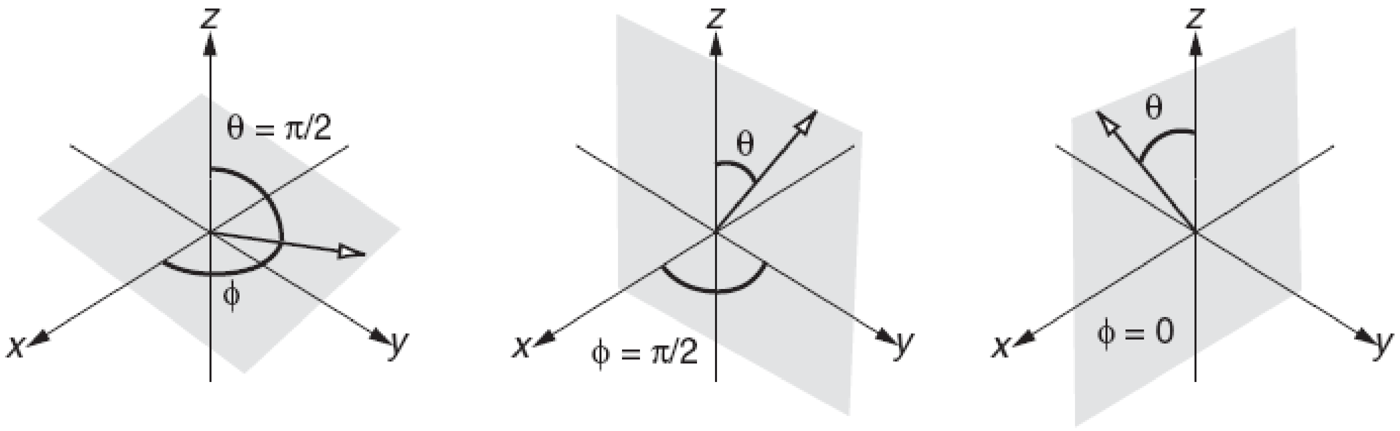
$$Y_1^{-1} = \left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin\theta e^{-i\phi}$$

$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{\frac{1}{2}} \left(3\cos^2\theta - 1\right)$$

$$Y_2^{\pm 1} = \left(\frac{15}{8\pi}\right)^{\frac{1}{2}} \sin\theta\cos\theta e^{\pm i\phi}$$

$$Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{\frac{1}{2}} \sin^2\theta e^{\pm 2i\phi}$$

Angular parts of Hydrogen atom orbitals



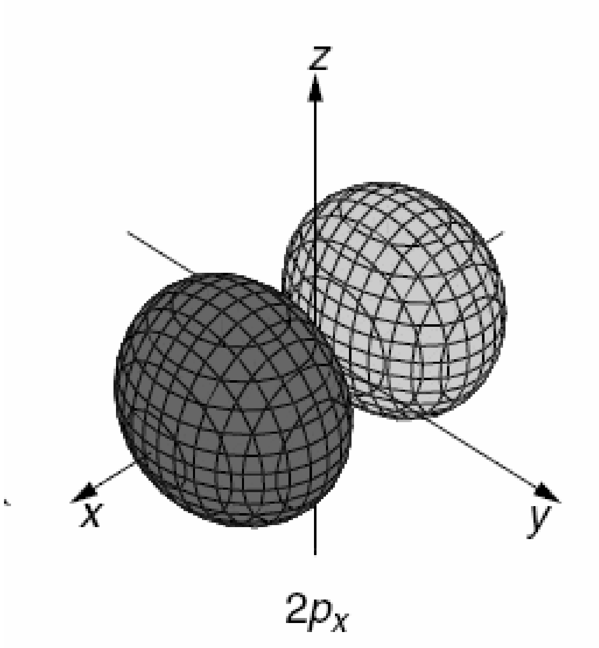
xy-plane *yz*-plane *xz*-plane

xy –plane corresponds to $\theta = \pi/2$ and any value of φ

yz-plane corresponds to $\varphi = \pi/2$ and any value of θ

xz-plane corresponds to $\varphi = 0$ and any value of θ

The specified plane is shown tinted in each case

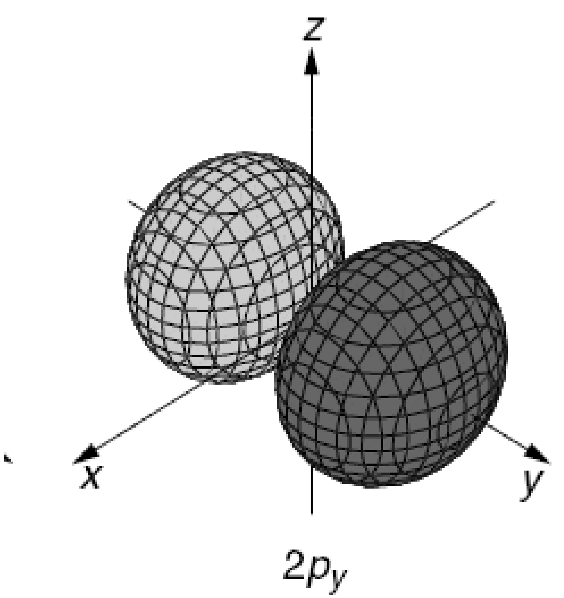


Angular part of the $2p_x$ orbital is:

$$\sin\theta \times \cos\phi$$

for all values of *θ*, the function is zero when *φ* = *π*/2

this range of angles corresponds to the *yz*-plane, which therefore is the angular node



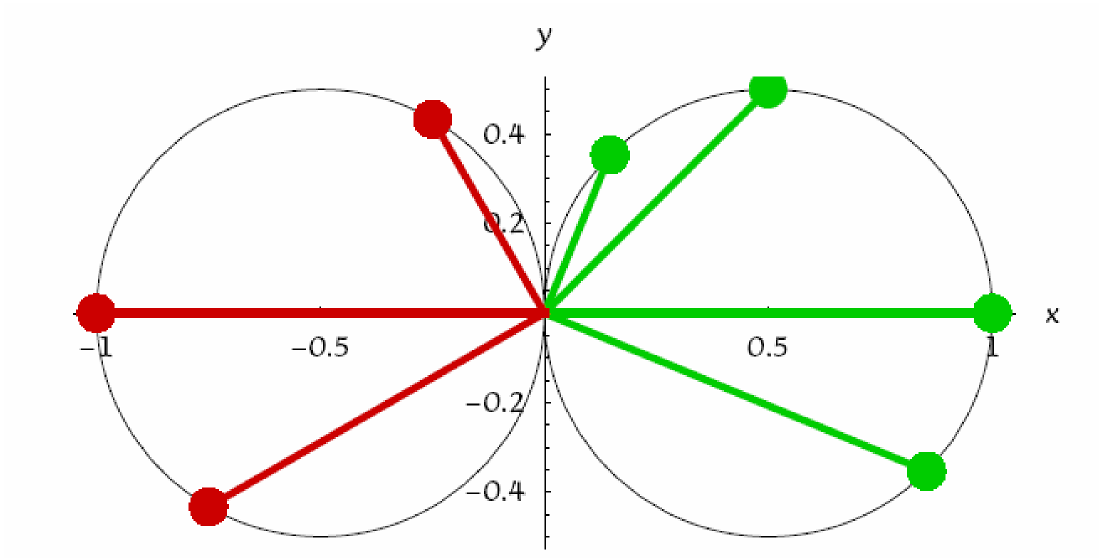
Angular part of the $2p_y$ orbital is:

$$\sin\theta \times \sin\phi$$

zero, for all values of *θ*, when *φ* = 0

this specifies the *xz* plane which is therefore a nodal plane for this orbital

Angular dependence of the p_x spherical harmonic



$$\sin\theta \times \cos\phi$$

in the *xy* plane for $\theta = \pi/2$

The right lobe corresponds to positive values and the left lobe corresponds to negative values

The length of each line terminating in a point is the value of $\cos\phi$ for the corresponding value of ϕ

Angular Momentum Operators

$$\hat{L}_x = -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

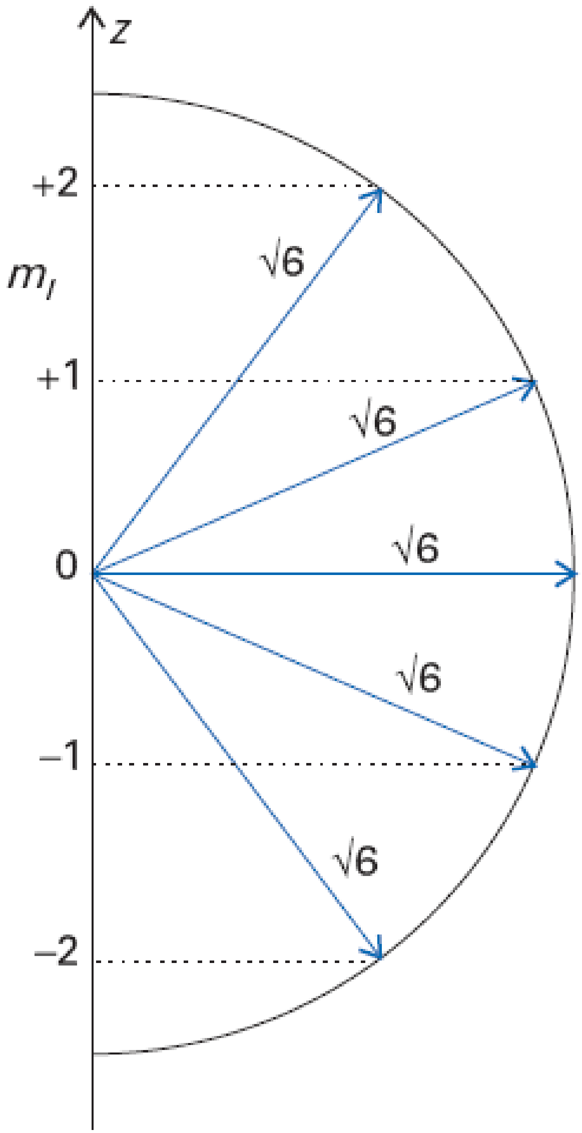
$$\hat{L}_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_Y^2 + \hat{L}_z^2 \quad \Rightarrow \quad \hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

$$E_l = \frac{\hbar^2}{2I}l\left(l+1\right) \qquad l = 0,\ 1,\ 2,\ldots$$

Space Quantization



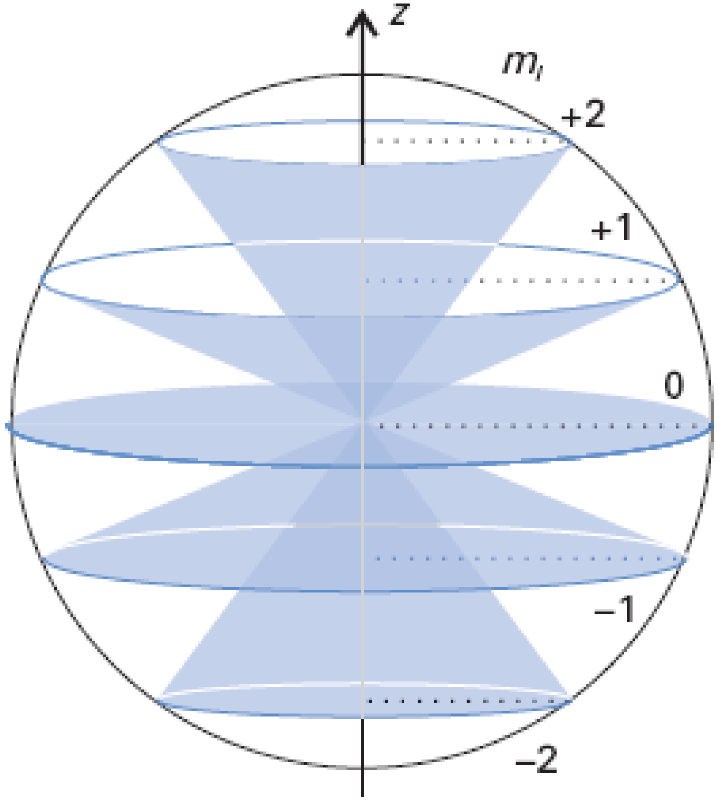
The five (that is, $2l+1$) allowed orientations of the angular momentum with $l=2$.

The length of the vector is $\{l(l+1)\}^{1/2}$, which in this case is $6^{1/2}$.

m_l is restricted to certain values; hence the z-component of the angular momentum is also restricted to $2l+1$ discrete values for a given value of l

This restriction of the component of angular momentum is called space quantization

The vector can adopt only $2l+1$ orientations in contrast to the classical description in which the orientation of the rotating body is continuously variable



The figure represents the fact that if the z-component of angular momentum is specified, the x- and y-components cannot in general be specified, the angular momentum vector is supposed to lie at an indeterminate position on one of the cones shown here (for l=2)

Rigid Rotor

One confusing point about angular momentum is that for different kinds of angular momentum, we use different letters.

So while *l* is the letter chosen for an electron moving around the nucleus, J is the chosen letter for the rotation of a diatomic molecule

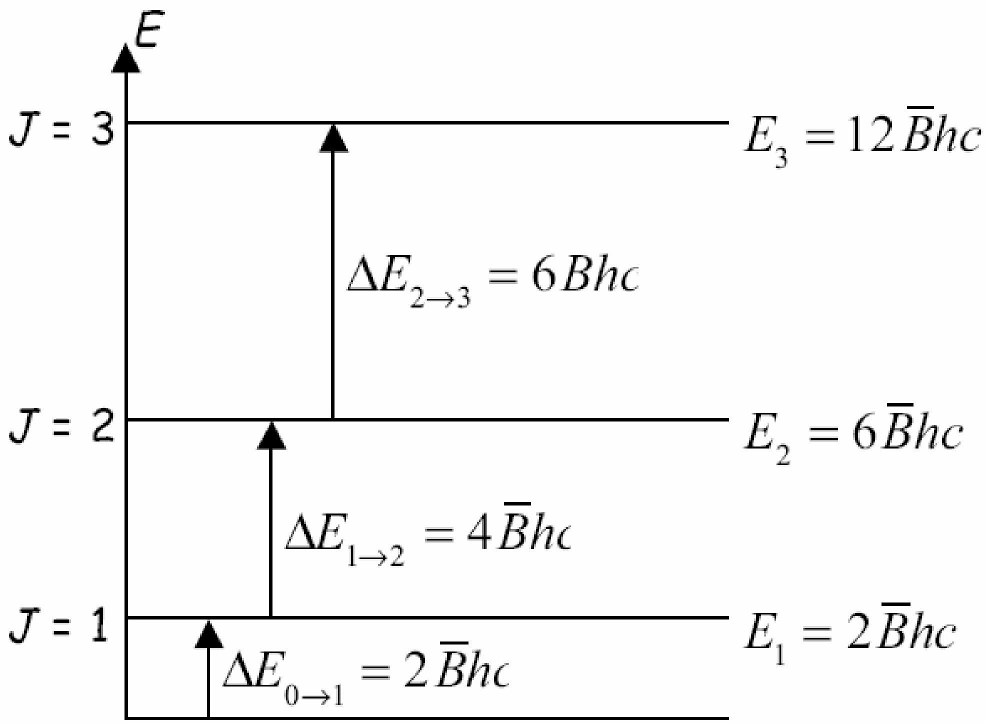
$$E_J = \frac{\hbar^2}{2I} J\left(J+1\right) \qquad J = 0,\ 1,\ 2, \ldots$$

$$E_{\substack{photon \\ J\to J+1}} = h\nu_{\substack{photon \\ J\to J+1}} = \Delta E_{rot} = E_{J+1} - E_J = \frac{\hbar^2}{I}(J+1) \qquad \nu_{\substack{photon \\ J\to J+1}} = \frac{h}{4\pi^2 I}(J+1)$$

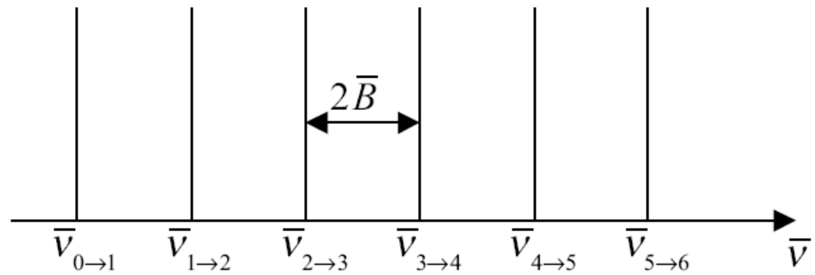
Define the rotational constant B

$$B \equiv \frac{h}{8\pi^2 I} \quad \text{(Hz)} \qquad \text{or} \qquad \overline{B} \equiv \frac{h}{8\pi^2 cI} \quad (\text{cm}^{-1})$$

$$\therefore \qquad \nu_{J\to J+1}\ (\text{Hz}) = 2B(J+1) \qquad \overline{\nu}_{J\to J+1}\ (\text{cm}^{-1}) = 2\overline{B}(J+1)$$



This gives rise to a rigid rotor absorption spectrum with <u>evenly spaced</u> lines.



Spacing between transitions is $\boxed{2B\ (\text{Hz})\ \text{or}\ 2\overline{B}\ (\text{cm}^{-1})}$

$$\overline{\nu}_{J+1\to J+2} - \overline{\nu}_{J\to J+1} = 2\overline{B}\left[\left(J+1\right)+1\right] - 2\overline{B}\left(J+1\right) = 2\overline{B}$$

Use this to get microscopic structure of diatomic molecules directly from the absorption spectrum!

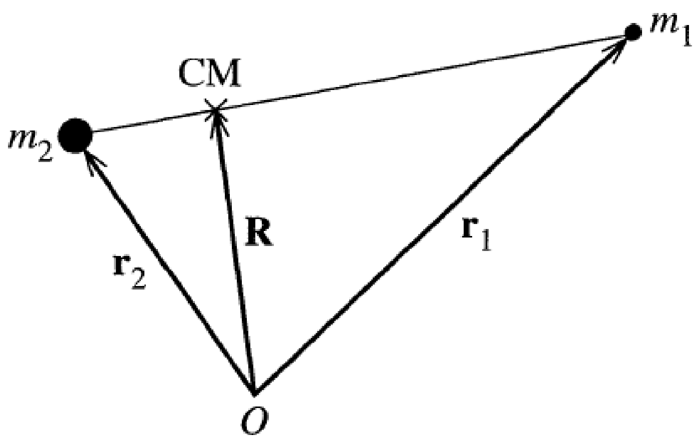
Get $\overline{B}$ directly from the separation between lines in the spectrum.

Use its value to determine the bond length r_0 !

$$2\overline{B} = \frac{h}{4\pi^2 cI} \qquad I = \mu r_0^2 \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\therefore \quad \boxed{r_0 = \left[\frac{h}{8\pi^2 c\overline{B}\mu}\right]^{\frac{1}{2}} \ (\overline{B}\text{ in cm}^{-1}) \quad \text{or} \quad r_0 = \left[\frac{h}{8\pi^2 B\mu}\right]^{\frac{1}{2}} \ (B\text{ in Hz})}$$

Central Force Problem



$$\mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{M},$$

$$M = m_1 + m_2$$

$$\mathbf{r}_1 = \mathbf{R} + \frac{m_2}{M}\mathbf{r} \qquad \text{and} \qquad \mathbf{r}_2 = \mathbf{R} - \frac{m_1}{M}\mathbf{r}$$

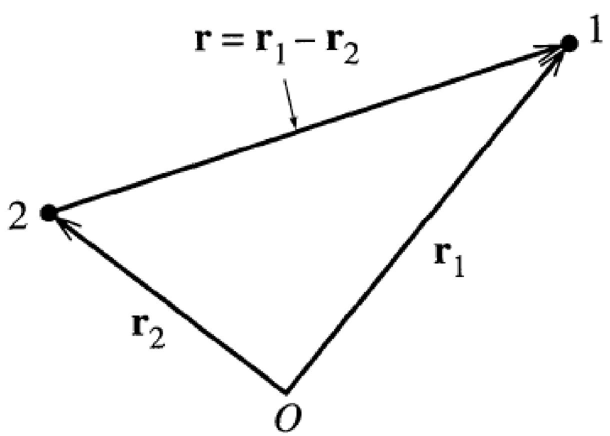
$$\begin{aligned} T &= \tfrac{1}{2}\left(m_1\dot{\mathbf{r}}_1^2 + m_2\dot{\mathbf{r}}_2^2\right) \\ &= \tfrac{1}{2}\left(m_1\left[\dot{\mathbf{R}} + \frac{m_2}{M}\dot{\mathbf{r}}\right]^2 + m_2\left[\dot{\mathbf{R}} - \frac{m_1}{M}\dot{\mathbf{r}}\right]^2\right) \\ &= \tfrac{1}{2}\left(M\dot{\mathbf{R}}^2 + \frac{m_1 m_2}{M}\dot{\mathbf{r}}^2\right). \end{aligned}$$

$$\mu = \frac{m_1 m_2}{M} \equiv \frac{m_1 m_2}{m_1 + m_2} \qquad \text{[reduced mass]}$$

$$T = \tfrac{1}{2} M \dot{\mathbf{R}}^2 + \tfrac{1}{2} \mu \dot{\mathbf{r}}^2.$$

$\frac{1}{2} M \dot{\mathbf{R}}^2$: **This term is the kinetic energy due to translational motion of the whole system of mass M, with the hypothetical particle being located at the center of mass**

$\frac{1}{2} \mu \dot{\mathbf{r}}^2$: **This term is the kinetic energy of internal (relative) motion of the two particles**



The relative position r = r_l - r_2 is the position of body 1 relative to body 2