Angular momentum and rotation

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

$$\hat{L}_x = (\hat{y}\hat{p}_z - \hat{z}p_y)$$

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

Commutator relations

$$[\hat{L}_x, \hat{L}_y] = i\hbar L_z, \quad [\hat{L}_y, \hat{L}_z] = i\hbar L_x, \quad [\hat{L}_z, \hat{L}_x] = i\hbar L_y$$

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0$$

Definition of L^2 in spherical coordinates

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

Rigid rotor confined to a plane

$$\hat{H} = \frac{\hat{L}^2}{2I} = -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\varphi^2}$$

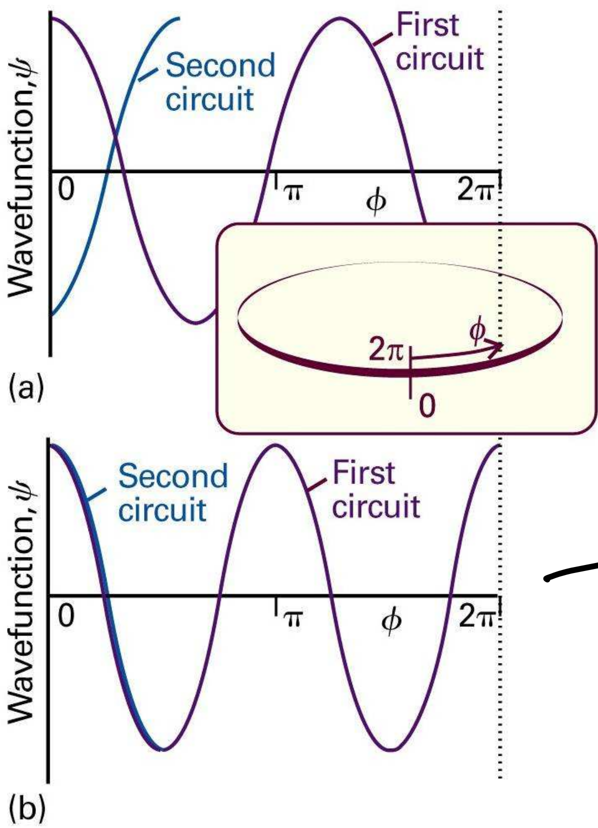

Figure 9-28
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$$\hat{H}\psi = E\psi$$

$$\to \psi = A e^{im\varphi} \qquad m = \sqrt{\frac{2IE}{\hbar^2}}$$

$$\psi(\varphi) = \psi(\varphi + 2\pi)$$

Restricts

$$m = 0, \pm 1, \pm 2$$

$$E = \frac{m^2 \hbar^2}{2I} \qquad m = 0, \pm 1, \pm 2, \cdots$$

E

$\frac{4\hbar^2}{2I}$

$\pm 1 \quad \frac{\hbar^2}{2I}$

0

$$L^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} - \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right]$$

Power series solution

$$L^2 \psi = k \psi \qquad L^2 (L_z \psi) = L_z L^2 \psi$$

$$L_z \psi = c \psi \qquad\qquad = L_z k \psi$$

simultaneous eigenfunctions $= k (L_z \psi)$

of L_z and L^2

Rotor confined to the plane

$$L^2 = L_z^2 = -\hbar^2 \frac{d^2}{d\varphi^2}$$

$$\Phi(\varphi) = A e^{im\varphi} \qquad A = \frac{1}{\sqrt{2\pi}}$$

$$\psi(\theta,\varphi) = \Theta(\theta)\,\Phi(\varphi)$$

$$L_z^2\,\Phi(\varphi) = -\hbar^2 \frac{d^2}{d\varphi^2} A e^{im\varphi}$$

$$= m^2 \hbar^2 A e^{im\varphi}$$

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

$$\lambda\hbar^2$$

$$L^2\psi = \lambda\hbar^2\,\psi$$

"Associated Legendre equation"

a. $\Theta(\theta) = \text{constant}$

$\lambda = 0, \quad m = 0$

$\psi(x,y) = \psi_x \psi_y$

$\psi(\theta,\phi) = \Theta(\theta)\Phi(\phi)$

b. $\Theta(\theta) = \sin\theta$

$\lambda = 2, \quad m = \pm 1$

c. $\Theta(\theta) = \cos\theta$

$\lambda = 2, \quad m = 0$

d $\Theta(\theta) = \cos^2\theta - \frac{1}{3}$

$\lambda = 6, \quad m = 0$

$\lambda = 0, \qquad m = 0$

$\lambda = 2, \qquad m = 0, \pm 1$

$\lambda = 6, \qquad m = 0, \pm 1, \pm 2$

$\lambda = l(l+1) \qquad l = 0, 1, 2, 3 \ldots$

$m = 0, \pm \ldots \pm l$

$L^2 \psi_{l,m}(\theta, \varphi) = l(l+1)\hbar^2 \psi_{lm}(\theta, \varphi)$

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

$L_z \psi_{lm}(\varphi, \theta) = m\hbar \psi_{lm}$

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

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

length $= \sqrt{6}\,\hbar$

z projection

$2\hbar, 1\hbar, 0\hbar, -1\hbar, -2\hbar$

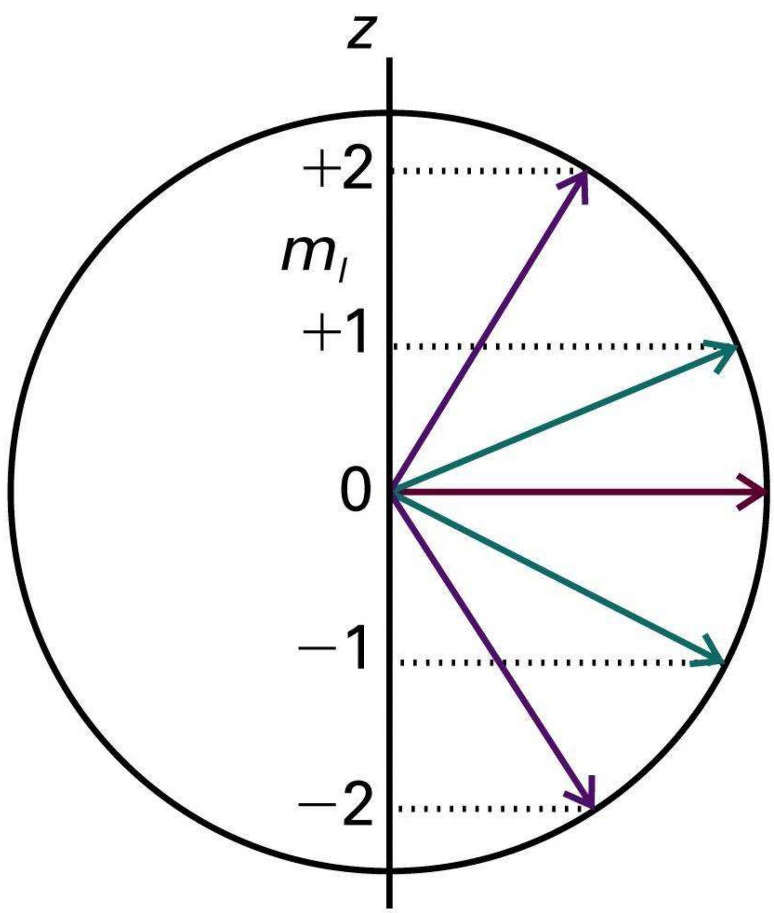

Figure 9-40a

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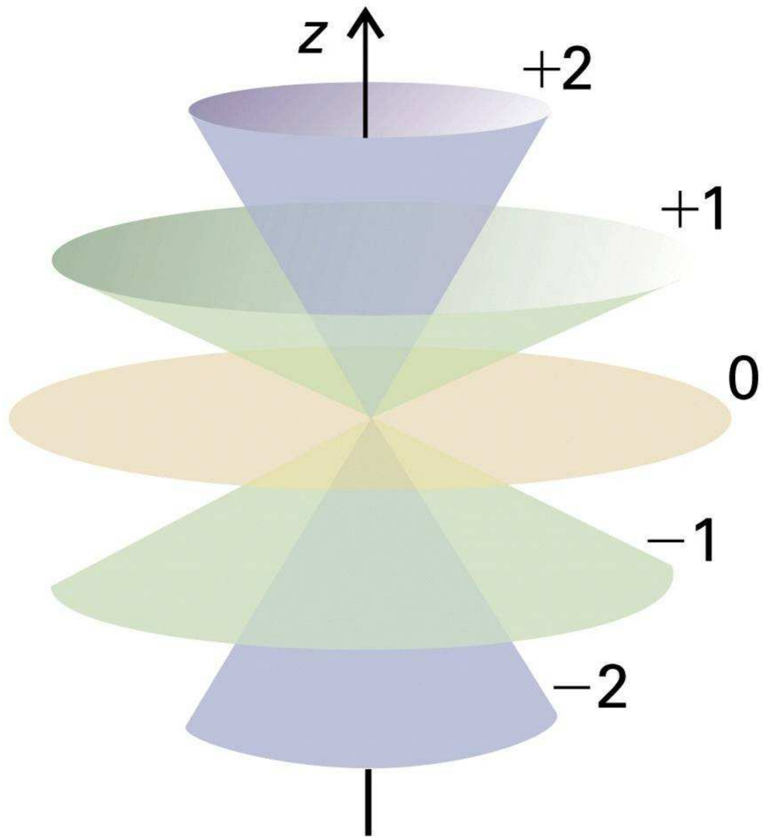

Figure 9-40b
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Table 9.3 The spherical harmonics

l	m_l	$Y_{l,m_l}(\theta,\varphi)$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
	±1	$\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\,e^{\pm i\phi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$
	±1	$\mp\left(\frac{15}{8\pi}\right)^{1/2}\cos\theta\sin\theta\,e^{\pm i\phi}$
	±2	$\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta\,e^{\pm 2i\phi}$
3	0	$\left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta-3\cos\theta)$
	±1	$\mp\left(\frac{21}{64\pi}\right)^{1/2}(5\cos^2\theta-1)\sin\theta\,e^{\pm i\phi}$
	±2	$\left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta\,e^{\pm 2i\phi}$
	±3	$\mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta\,e^{\pm 3i\phi}$

Table 9-3
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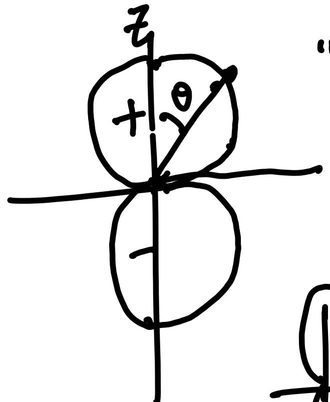
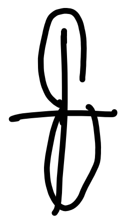
$l = 1, \quad m = 0$

$Y_{lm}(\theta, \varphi) = Y_{10}$

$= \cos\theta \qquad \cos\theta = 1$



"p_z" orbital



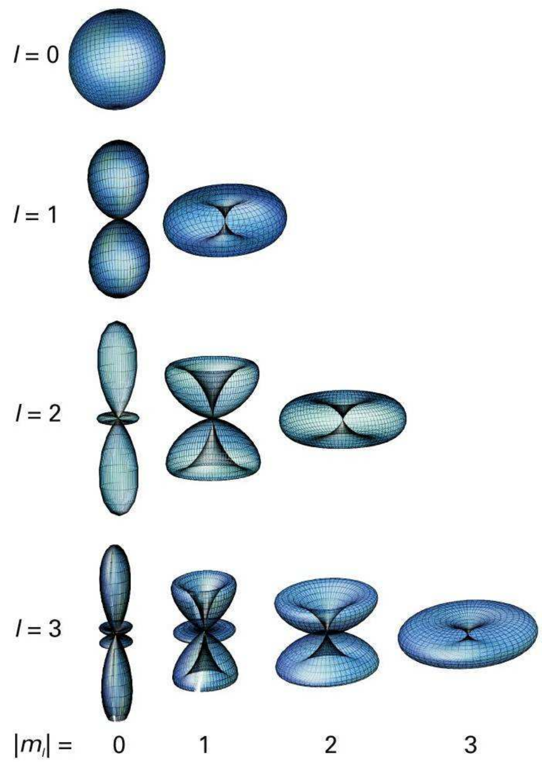


Figure 9-37
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p_x & p_y orbitals → not eigenfunctions of the $\hat{L}_z$ operator

$$Y_{11} = \cos\theta \, e^{i\varphi}$$

$$Y_{1-1} = \cos\theta \, e^{-i\varphi}$$

$$p_x = Y_{11} + Y_{1-1}$$

$$p_y = Y_{11} - iY_{1-1}$$

Rotational spectroscopy

$$\hat{H} = \frac{\hat{L}^2}{2I}$$

$$\hat{L}^2 \, Y_{lm}(\theta,\varphi) = l(l+1)\hbar^2 \, Y_{lm}$$

Rotational energies

$$E_l = \frac{l(l+1)\hbar^2}{2I} \qquad l = 0, 1, 2, 3, \ldots$$

$\frac{6\hbar^2}{2I}$

$\frac{2\hbar^2}{2I}$

0

$\Delta l = \pm 1$

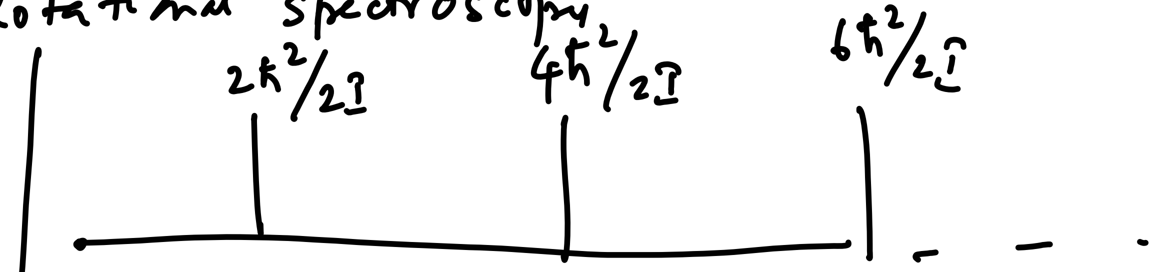
$l=0 \rightarrow l=1$

$\Delta E = \frac{2\hbar^2}{2I}$

$l=1 \rightarrow l=2$

$\Delta E = \frac{4\hbar^2}{2I}$

Rotational spectroscopy



Microwave spectroscopy

$I = \mu r^2$

determine the bond length r

Vibration – Infra red

Rotation – Microwave