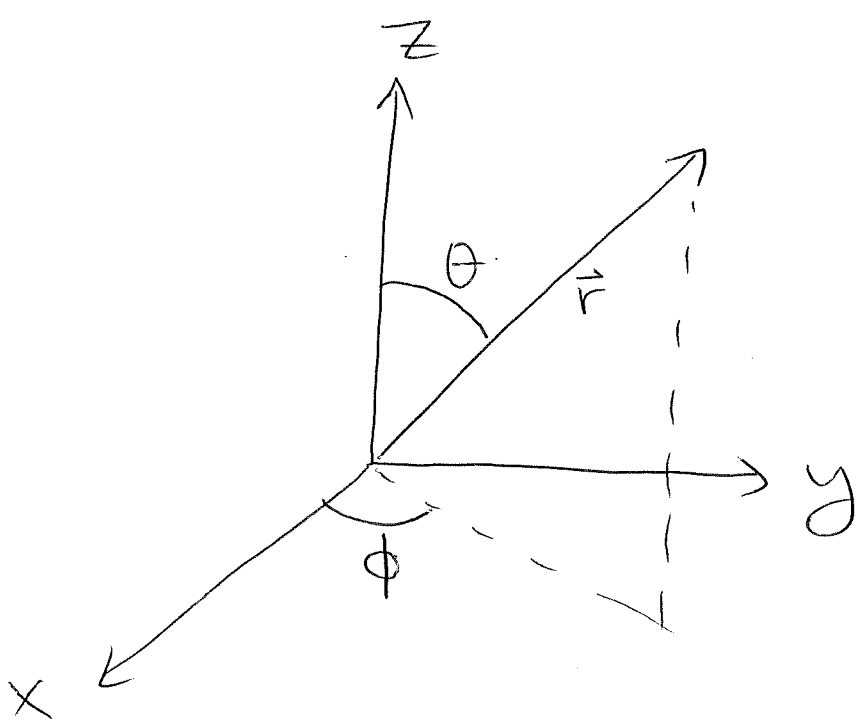
Physics 570A Lecture 27

Angular momentum wavefunctions

$$\vec{L} = \vec{r} \times \vec{p} = \frac{\hbar}{i} \vec{r} \times \vec{\nabla}$$

It is most convenient to work in spherical polar coordinates:

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



$r = |\vec{r}|$

Expressed in terms of θ + ϕ, the Cartesian components of $\vec{L}$ are:

$$\boxed{\begin{aligned} L_x &= i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \\ L_y &= -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \\ L_z &= -i\hbar\frac{\partial}{\partial\phi} \qquad \text{(c.f. Lecture 7)} \end{aligned}}$$

see pp. 168-169 Griffiths

By convention, the angular momentum eigenfunctions in polar coordinates are written

$$\psi_{\ell m} \equiv Y_{\ell m}(\theta, \phi).$$

The eigenvalue problem

$$L_z Y_{\ell m} = m\hbar Y_{\ell m}$$

can thus be expressed as

$$\frac{\hbar}{i}\frac{\partial}{\partial\phi}Y_{\ell m}(\theta,\phi) = m\hbar\, Y_{\ell m}(\theta,\phi)$$

$$\frac{\partial}{\partial\phi}Y_{\ell m} = im\, Y_{\ell m}$$

$$\boxed{\Rightarrow\ Y_{\ell m}(\theta,\phi) = e^{im\phi}\, Y_{\ell m}(\theta,0)}$$

$Y_{\ell m}$ must be single-valued under $\phi \to \phi + 2\pi$ in order for the wavefunction to be continuous.

$$\Rightarrow\ e^{im2\pi} = 1\,,\qquad m \in \mathbb{Z}\,.$$

This implies, in particular,

that $l \equiv m_{max} \in \mathbb{Z}$. The orbital angular momentum quantum # is a non-negative integer.

Example: The rigid rotor

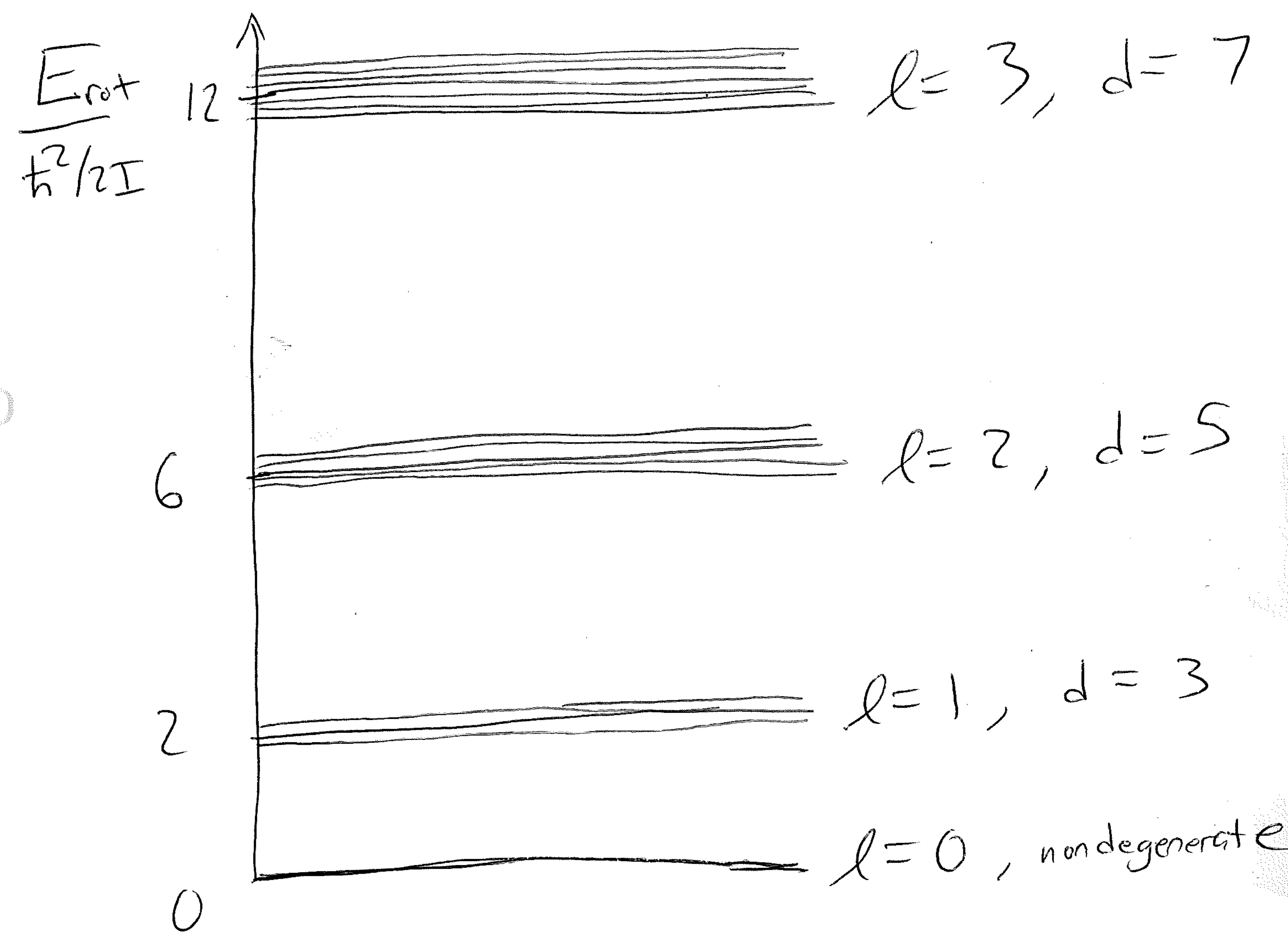
Consider a diatomic molecule in the form of two identical atoms of mass M, separated by a rigid rod (bond) of length a.

$$I_{cm} = \frac{Ma^2}{2} = I$$

$$\hat{H} = \hat{H}_{cm} + \hat{H}_{rot}, \quad \hat{H}_{rot} = \frac{\vec{L}^2}{2I}$$

$$E_{rot} = \frac{\hbar^2}{2I} l(l+1), \quad l = 0, 1, 2, \ldots$$

For each value of ℓ, there are $2\ell + 1$ degenerate energy levels $-\ell \le m \le \ell$:



Now, for the dependence on θ

$$L_+ Y_{\ell\ell}(\theta,\phi) = 0$$

$$L_+ = L_x + i L_y = \hbar e^{i\phi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)$$

$$\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right) Y_{\ell\ell}(\theta,\phi) = 0$$

$$Y_{\ell\ell}(\theta,\phi) = e^{i\ell\phi} P_\ell^\ell(\theta),$$

where $P_\ell^\ell(\theta) \equiv Y_{\ell\ell}(\theta,0)$

$$\left(\frac{\partial}{\partial\theta} - \ell\cot\theta\right) P_\ell^\ell(\theta) = 0$$

$$\frac{d P_\ell^\ell(\theta)}{d\theta} = \ell\cot\theta\, P_\ell^\ell(\theta)$$

$$\frac{d P_\ell^\ell}{P_\ell^\ell} = \ell\,\frac{d\sin\theta}{\sin\theta}$$

$$\ln P_\ell^\ell = \ell \ln(\sin\theta) + c'$$

$$P_\ell^\ell(\theta) = C(\sin\theta)^\ell$$

$$\boxed{\Rightarrow \quad Y_{\ell\ell}(\theta,\phi) = C\sin^\ell\theta\, e^{i\ell\phi}}$$

Normalization

$$1 = \langle \ell\ell | \ell\ell \rangle = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta\, |Y_{\ell\ell}(\theta,\phi)|^2$$

$$= 2\pi |C|^2 \int_0^{\pi} (\sin\theta)^{2\ell+1}\, d\theta$$

$$= 2\pi |C|^2 \frac{2^{2\ell+1}(\ell!)^2}{(2\ell+1)!}$$

$$\boxed{\Rightarrow \quad C = \frac{1}{2^\ell \ell!}\sqrt{\frac{(2\ell+1)!}{4\pi}}}$$

The remaining wavefunctions may be obtained from $Y_{\ell\ell}(\theta,\phi)$ using L_- :

$$L_- = L_x - iL_y = \hbar e^{-i\varphi}\left(-\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right)$$

$$Y_{\ell,\ell-1}(\theta,\varphi) = \frac{L_- Y_{\ell\ell}(\theta,\varphi)}{\hbar\sqrt{\ell(\ell+1)-\ell(\ell-1)}} = \frac{L_-}{\hbar}\frac{Y_{\ell\ell}}{\sqrt{2\ell}}$$

$$\vdots$$

$$Y_{\ell m} = \left(\frac{1}{\hbar}\right)^{\ell-m}\sqrt{\frac{(\ell+m)!}{(2\ell)!\,(\ell-m)!}}\; L_-^{\ell-m}\, Y_{\ell\ell}$$

$$Y_{\ell m}(\theta,\varphi) = \frac{(-1)^m}{2^\ell\,\ell!}\sqrt{\frac{2\ell+1}{4\pi}}\sqrt{\frac{(\ell+m)!}{(\ell-m)!}}\; P_\ell^m(\cos\theta)\, e^{im\varphi},$$

where $P_\ell^m(u)$ is an <u>associated Legendre function</u>, defined by $P_\ell^m(\eta) = (-1)^m \left(\frac{1}{1-\eta^2}\right)^{m/2} \left(\frac{d}{d\eta}\right)^{\ell-m} (\eta^2-1)^\ell$.

$P_0^0 = 1$

$P_1^0 = 2\cos\theta$

$P_1^1 = \sin\theta$

$P_2^0 = 4(3\cos^2\theta - 1)$

$P_2^1 = 4\sin\theta\cos\theta$

$P_2^2 = \sin^2\theta$

$\vdots$

The first few angular momentum wavefunctions are:

$$Y_{00} = \frac{1}{2\sqrt{\pi}}$$

$$Y_{10} = \frac{1}{2}\sqrt{\frac{3}{\pi}} \cos\theta$$

$$Y_{1,\pm 1} = \mp \frac{1}{2}\sqrt{\frac{3}{2\pi}} \sin\theta \, e^{\pm i\varphi}$$

$$Y_{20} = \frac{1}{4}\sqrt{\frac{5}{\pi}} \left(3\cos^2\theta - 1\right)$$

$$Y_{2,\pm 1} = \mp \frac{1}{2}\sqrt{\frac{15}{2\pi}} \sin\theta\cos\theta \, e^{\pm i\varphi}$$

$$Y_{2,\pm 2} = \frac{1}{4}\sqrt{\frac{15}{2\pi}} \sin^2\theta \, e^{\pm 2i\varphi}$$

$$\vdots$$

These are known as <u>spherical harmonics</u>.

The spherical harmonics can also be found by solving the P.D.E.:

$$\vec{L}^2 Y_{\ell m}(\theta,\varphi) = \hbar^2 \ell(\ell+1)\, Y_{\ell m}(\theta,\varphi)$$

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

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \ell(\ell+1) \right] Y_{\ell m}(\theta,\phi) = 0$$

$$0 = \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right) - \frac{m^2}{\sin^2\theta} + \ell(\ell+1) \right] P_\ell^m(\cos\theta)$$

$$\frac{d}{d\eta}(1-\eta^2)\frac{dP_\ell^m(\eta)}{d\eta} + \left[\ell(\ell+1) - \frac{m^2}{1-\eta^2} \right] P_\ell^m(\eta) = 0$$

Parity of the angular momentum eigenfunctions

$$\vec{L} = \vec{r} \times \vec{p} = \frac{\hbar}{i}(\vec{r} \times \nabla)$$

$$\hat{P}\vec{L}\psi = \frac{\hbar}{i}\left(-\vec{r} \times \frac{\partial}{\partial(-\vec{r})}\right)\hat{P}\psi$$

$$= \frac{\hbar}{i}(\vec{r} \times \nabla)\hat{P}\psi$$

$$= \vec{L}\hat{P}\psi$$

$$\Rightarrow [\hat{P}, \vec{L}] = 0$$

$$[\hat{P}, L_\pm] = 0, \quad [\hat{P}, L_z] = 0$$

$$[\hat{P}, \vec{L}^2] = 0.$$

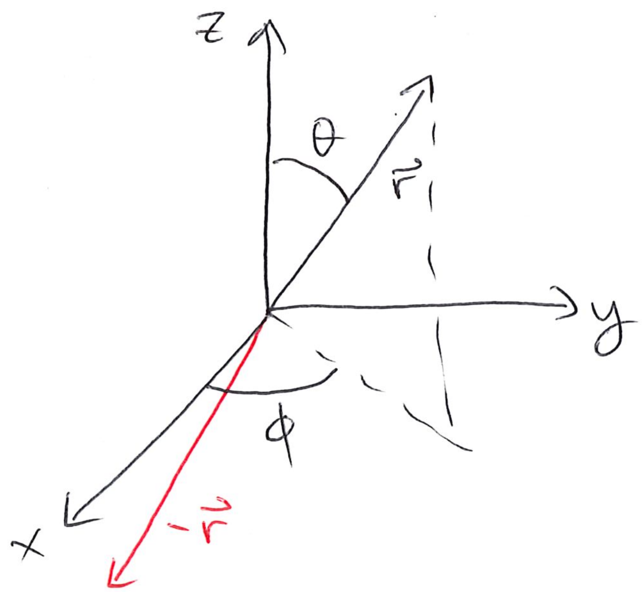
These relations imply that the eigenfunctions of $\vec{L}^2$ are also eigenfunctions of $\hat{P}$ = parity. Moreover, since $L_\pm$ commute with $\hat{P}$, the eigenvalue of parity cannot depend on $m = L_z/\hbar$, but only on ℓ, the total angular momentum quantum #:

$$\hat{P}\, Y_{\ell m} = P(\ell)\, Y_{\ell m}$$

Now $\hat{P}\,\psi(\vec{r}) = \psi(-\vec{r})$.

In polar coordinates,

$$\hat{P}\,\psi(r,\theta,\phi) = \psi(r, \pi-\theta, \phi+\pi)$$



$\hat{P}$: $r \to r$

$\theta \to \pi - \theta$

$\phi \to \phi + \pi$

$$\hat{P}\, Y_{\ell m}(\theta,\phi) = Y_{\ell m}(\pi-\theta,\, \phi+\pi)$$

We can thus determine $P(\ell)$

from

$$Y_{\ell\ell}(\theta,\phi) = C \sin^{\ell}\theta\, e^{i\ell\phi}$$

$$\sin(\pi-\theta) = \sin\theta, \quad e^{i\ell\pi} = (-1)^{\ell}$$

$$\Rightarrow \boxed{P(\ell) = (-1)^{\ell}}$$