Lecture 13

spring (vibrating molecule)

ow-⊖

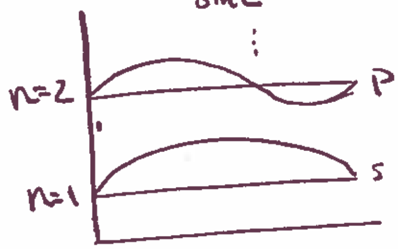
$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2$$

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

Box:
(conjugated molecule)

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + 0$$

$$E_n = \frac{h^2 n^2}{8mL^2}$$



distance b/twn energy levels increases ($E_n \propto n^2$)

Today particle in a ring

particle in a box bent on itself
$(x=0=L)$
$L = 2\pi R$
$x = \varphi \cdot R$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

$$= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial (R\cdot\varphi)^2}$$

$$= \frac{-\hbar^2}{2mR^2}\frac{\partial^2}{\partial (\varphi)^2}$$

(similar to particle in a box)

Solutions: trig functions $\sin(M\varphi)/\cos(M\varphi)/e^{iM\varphi}$

n= for translation   continuity is perserved
M= for rotation

$$\Rightarrow \hat{H}e^{iM\varphi} = \frac{-\hbar^2}{2mR^2}(iM)^2\underbrace{e^{iM\varphi}}$$

wave function returned ✓
eigen function

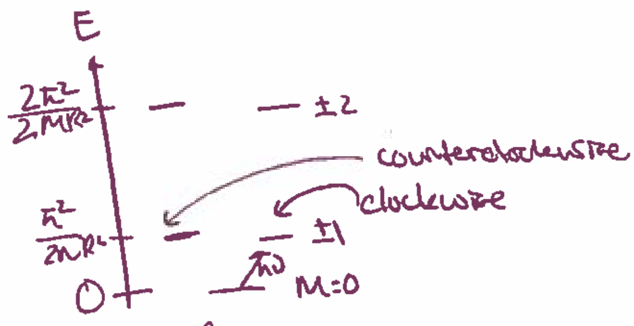
$$= \underbrace{\frac{\hbar^2 M^2}{2mR^2}}_{E} e^{iM\varphi}$$

Are all values of M allowed?
wave function must be continuous

$$\Rightarrow e^{iM\varphi} = e^{iM(\varphi+2\pi)}$$

$$= e^{iM\varphi}\cdot e^{iM2\pi} \Rightarrow \underline{M = 0, \pm 1, \pm 2, \ldots}$$

so $E_m = \frac{\hbar^2 M^2}{2mR^2}$ $\psi_m(\varphi) = \underbrace{\frac{1}{\sqrt{2\pi}}}_{\text{comes from normalization}} e^{iM\varphi}$



Origin for rotational spectroscopy

Meaning of M

CM:

$H = \frac{p^2}{2m}$

$= \frac{(mv)^2}{2m} = \frac{(mvR^2)}{2mR^2} = \frac{L_z^2}{2mR^2}$ angular momentum

QM

$E_m = \frac{(\hbar M)^2}{2mR^2}$

$\vec{L} = \hbar M$ = angular momentum

$M>0$ $M<0$

* For $n=0$ ϕ is a constant $(1/\sqrt{2})$

in POTB $n=0$ is not continuous, even though ψ is still a constant

Important facts

The combination of two degenerate eigenfunctions is also an eigenfunction

$a\cdot(\hat{H}\psi_A = E\psi_A)$

$+\; b\cdot(\hat{H}\psi_B = E\psi_B)$

$\hat{H}(a\psi_A + b\psi_B) = E(a\psi_A + b\psi_B)$ or

$\hat{H}\psi_C = E\psi_C \quad \psi_C = a\psi_A + b\psi_B$

ex: $\psi_C = \underbrace{e^{iM\phi} + e^{-iM\phi}}_{\text{complex eigenfunction}} = \underbrace{2\cos M\phi}_{\text{real eigenfunction}}$] Very important