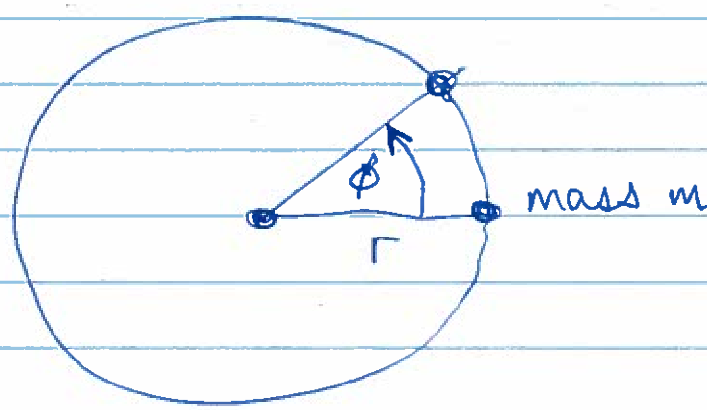
Quantum Theory of Rotation

Particle-on-a-Ring

(POAR)



Mechanical Concepts – Linear – Rotation

	Linear / Translation / Vibration	Rotation
mass	m (or μ)	I = moment of inertia
position	x	ϕ
velocity	$v = \frac{dx}{dt}$	$\omega = \frac{d\phi}{dt}$
momentum	$p = mv$	$J = I\omega = mvr$ = angular momentum
Kinetic Energy	$\frac{1}{2}mv^2 = \frac{p^2}{2m}$	$\frac{1}{2}I\omega^2 = \frac{J^2}{2I}$
$\hat{p}$	$\frac{\hbar}{i}\frac{d}{dx}$	$\hat{J} = \frac{\hbar}{i}\frac{d}{d\phi}$
$\hat{K}$	$\frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$	$\frac{\hat{J}^2}{2I} = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}$

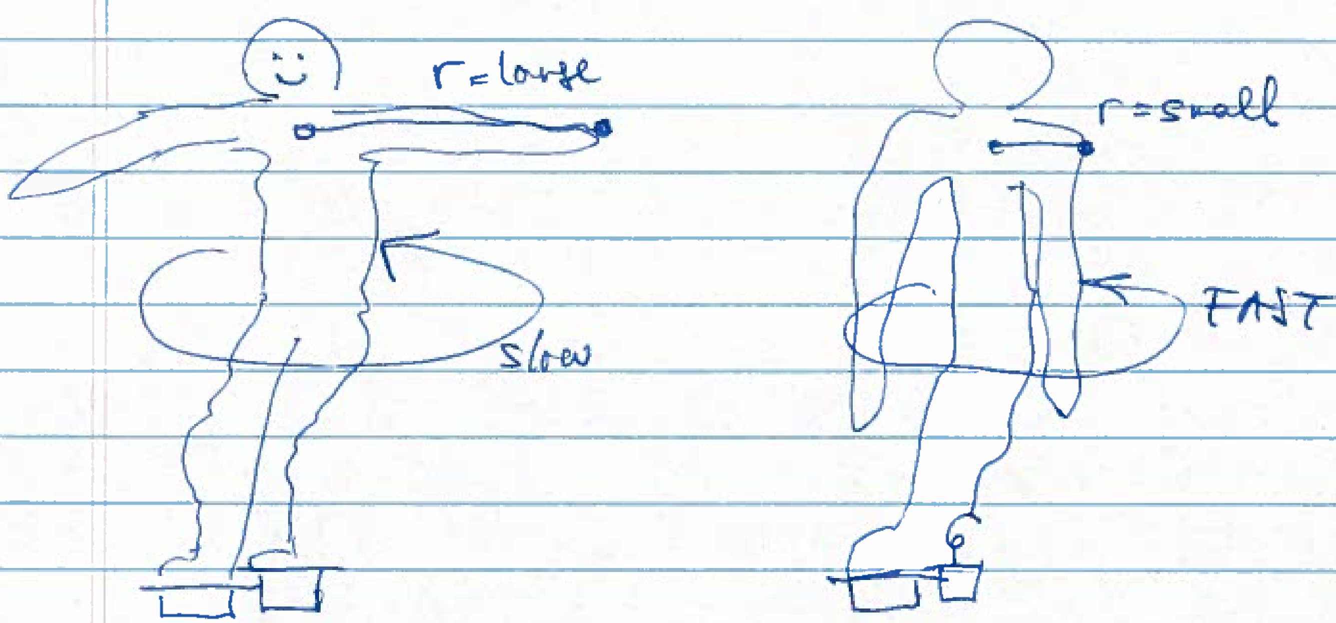
Connection between Linear & Rotational KE:

$$KE = \left(\frac{1}{2} m v^2\right)\frac{mr^2}{mr^2} = \frac{1}{2}\,\frac{mv^2 \cdot mr^2}{mr^2} = \frac{(mvr)^2}{2mr^2}$$

but $J = mvr$ so $KE = \dfrac{J^2}{2mr^2} = \dfrac{J^2}{2I}$

thus $\boxed{I = mr^2}$ = rotational mass

E.g. Think of a figure skater



So when r gets small, $I = mr^2$ = rotational mass gets small, and higher rotational speeds can be obtained. ✓

$$\hat{H}\psi = E\psi$$

$$\hat{H} = \hat{K} = \frac{\hat{J}^2}{2I} = -\frac{\hbar^2}{2mr^2}\frac{d^2}{d\phi^2} \quad \text{(no Potential)}$$

Diatomic $m = \mu = \frac{M_A M_B}{M_A + M_B}$

r = equil. bond length = r_e or r_0

$$\boxed{\hat{H}\psi = -\frac{\hbar^2}{2\mu r_e^2}\frac{d^2}{d\phi^2}\psi(\phi) = E\,\psi(\phi)}$$

Looks like Particle-in-a-Box with $x \to \phi$

Recall how we solved PIAB:

$$\psi(x) = c_+ e^{ikx} + c_- e^{-ikx}$$

moving to the RIGHT — moving to the LEFT

$$p = \frac{h}{\lambda} = \frac{h}{2\pi}\cdot\frac{2\pi}{\lambda} = \hbar k$$

Thus $k = p/\hbar$

px

$$= c_+ e^{ipx/\hbar} + c_- e^{-ipx/\hbar}$$

$$\boxed{\begin{array}{l}\psi(x=0)=0\\ \psi(x=L)=0\end{array}}$$

Boundary Conditions

$\downarrow$

$J\phi$

$$\psi(\phi) = c_+ e^{iJ\phi/\hbar} + c_- e^{-iJ\phi/\hbar}$$

positive J — $\boxed{\text{counter-clockwise}}$ (right hand rule) — $\boxed{\text{clockwise}}$

$$\boxed{\psi(\phi=0) = \psi(\phi=2\pi)}$$

"Periodic Boundary Conditions"

Note difference in Boundary Conditions

PIAB $\psi(x=0) = 0 = C_+ e^{ik\cdot 0} + C_- e^{-ik\cdot 0} = C_+ + C_- = 0$

Destructive Interference
Need 2 waves!

PDAR $\psi(\phi=0) = \psi(\phi=2\pi)$ No Need to $\rightarrow 0$
No Need for destructive interference

Thus can take $\boxed{e^{iJ\phi/\hbar}}$ and $\boxed{e^{-iJ\phi/\hbar}}$
as two separate states
(clockwise) (counter-clockwise)

Consider $\psi(\phi) = C_+ e^{iJ\phi/\hbar}$ $\boxed{e^{i\theta} = \cos\theta + i\sin\theta}$

$\psi(\phi=0) = C_+ e^{iJ\cdot 0/\hbar} = C_+ \cdot 1 = \boxed{\cancel{C_+}}$

$\psi(\phi=2\pi) = C_+ e^{iJ2\pi/\hbar} = \boxed{\cancel{C_+}\left(\cos(J\cdot 2\pi/\hbar) + i\sin(J\cdot 2\pi/\hbar)\right)}$

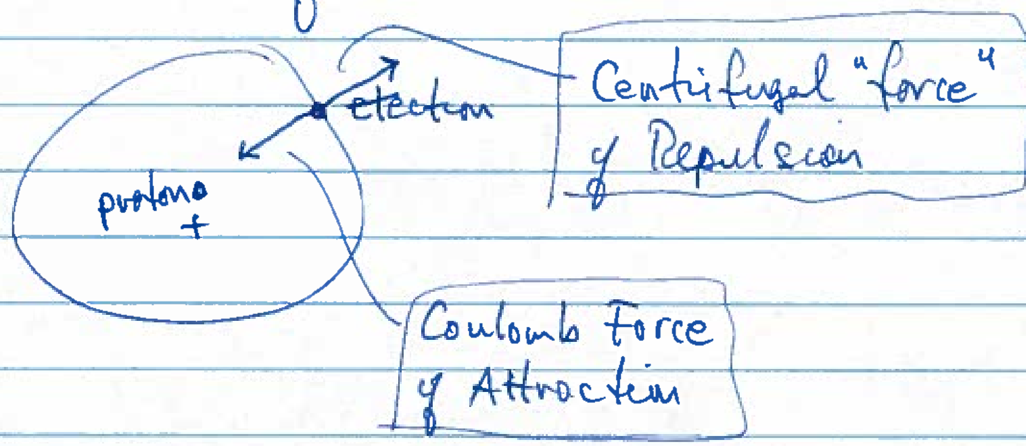
$1 = \underbrace{\cos\left(J\cdot 2\pi/\hbar\right)}_{=1} + i\,\underbrace{\sin\left(J\cdot 2\pi/\hbar\right)}_{=0}$

must destroy!

$\boxed{\text{when is } \cos\theta = 1 \text{ and } \sin\theta = 0 \text{ ?}}$

... **WAIT!** - NEED HISTORICAL CONTEXT ...

Bohr Model of Hydrogen (1913) → Nobel Prize (1922)



Bohr Balanced these to find the Radius (r) of stable orbits (math later) - he found:

$$r = \left(\frac{4\pi\varepsilon_0}{\mu e^2}\right) J^2$$

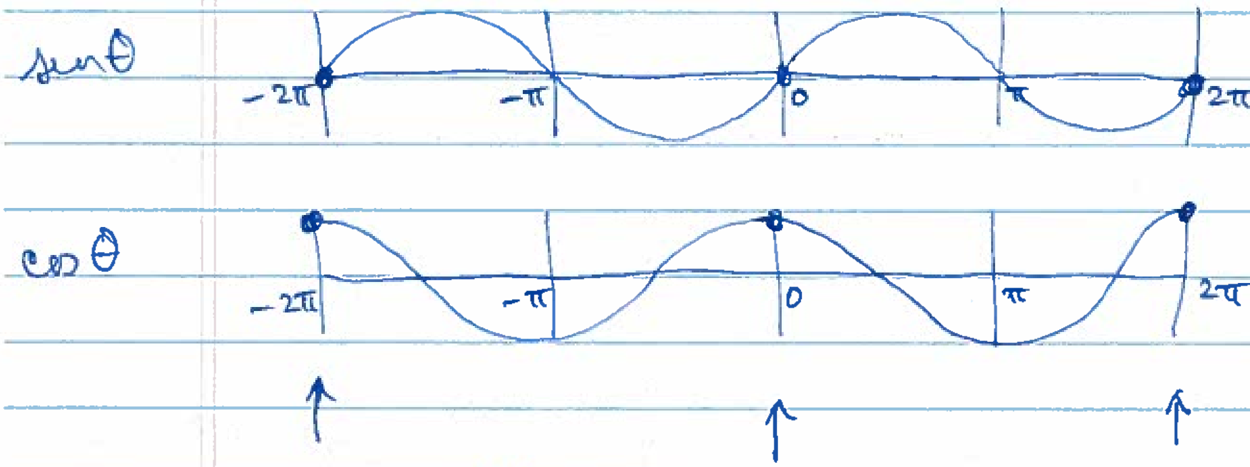
bunch of Known constants

but what is J ?

- Bohr set $\boxed{J = n\hbar}$, $n = 1, 2, 3, \ldots$
- He gave no good reason :(
- People were impressed b/c this gave great agreement w/ spectra;

But People were Upset b/c there was no justification for setting $J = n\hbar$, ... till now!

Back to POAR: $\cos\theta = 1$ and $\sin\theta = 0$



$\theta = (2\pi)(\text{integer})$ ← call this $m = 0, \pm 1, \pm 2, \pm 3, \ldots$ (magnetic q.n.)

$+$ → ccw motion

$-$ → cw motion

Thus, $\dfrac{J \cdot \cancel{2\pi}}{\hbar} = \theta = \cancel{2\pi} m$

$\dfrac{J}{\hbar} = \text{integer } m \rightarrow \boxed{J = m\hbar}$ Voila!

The Bohr quantization mystery was solved in 1926 by Schrödinger himself!

↳ Nobel (1933)

1926 → 1933 (7yrs)

Bohr 1913 → 1922 (9yrs)

Note that J can be NEGATIVE (direction)

Thus $\psi(\phi) = c_+ e^{iJ\phi/\hbar} = c_+ e^{i(\cancel{\hbar} m)\phi/\cancel{\hbar}}$

$$\boxed{\psi_m(\phi) = c_+ e^{im\phi}}$$

$$\hat{J}\psi_m = \frac{\hbar}{i}\frac{d}{d\phi} c_+ e^{im\phi}$$

$$= \frac{\hbar c_+}{i}\frac{d}{d\phi} e^{im\phi}$$

$$= \frac{\hbar c_+}{\cancel{i}}(\cancel{i}m)\, e^{im\phi}$$

$$= (\hbar m)(c_+ e^{im\phi}) = (\hbar m)\psi_m$$

Eigenvalue of Angular Momentum

$$\hat{H}\psi_m = \frac{\hat{J}^2}{2I}\psi_m = \frac{1}{2I}\hat{J}(\hat{J}\psi_m) = \frac{1}{2I}\hat{J}((\hbar m)\psi_m)$$

$$= \frac{\hbar m}{2I}(\hat{J}\psi_m) = \frac{\hbar m}{2I}(\hbar m\psi_m) = \left(\frac{\hbar^2 m^2}{2I}\right)\psi_m$$

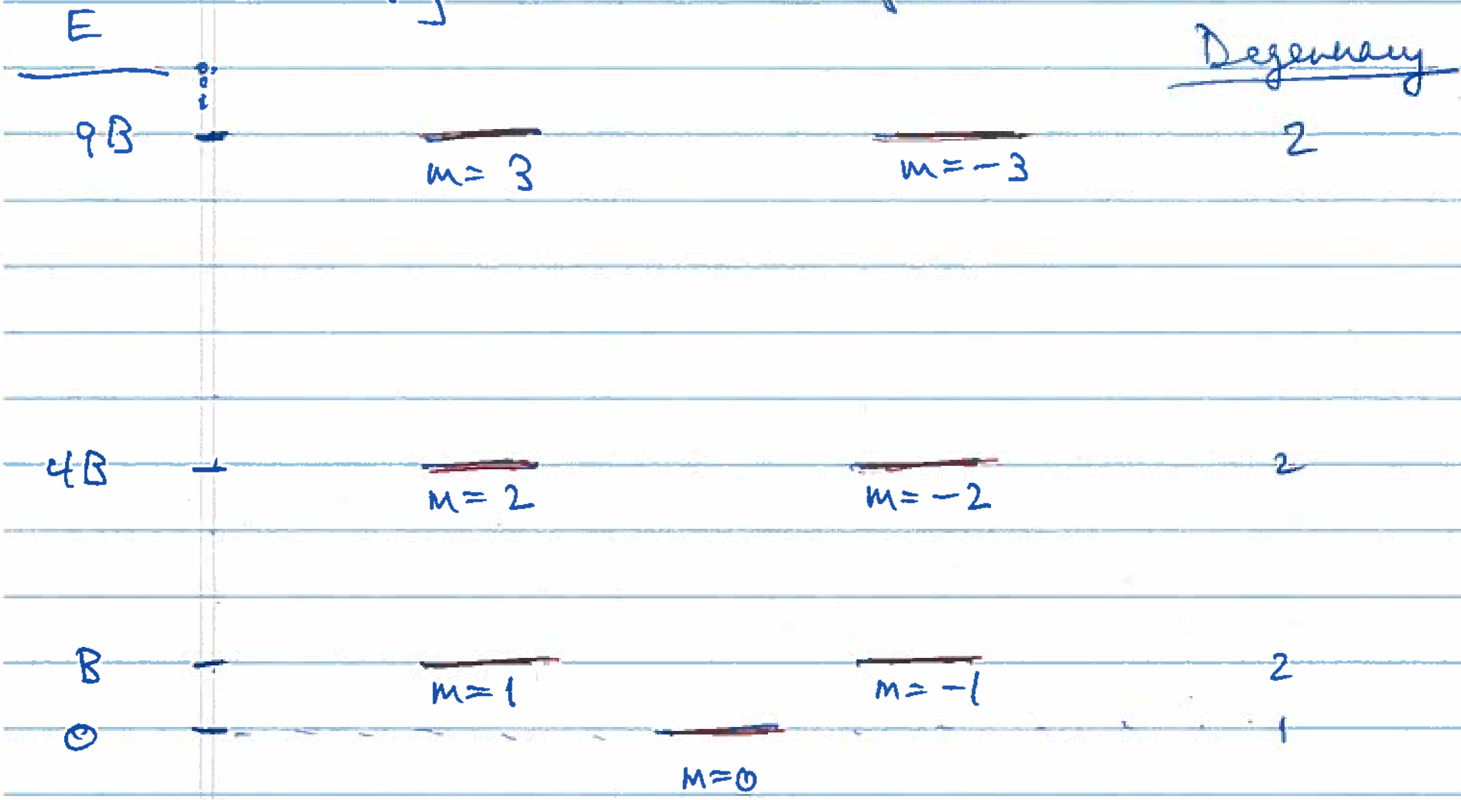
$$= E_m\psi_m \qquad E_m = \frac{\hbar^2 m^2}{2I} = \boxed{\frac{\hbar^2 m^2}{2\mu r_e^2}}$$

Quantized energy of POAR.

Rotational Energy

$$\frac{\hbar^2}{2\mu r_e^2} = B \quad \text{(tradition)}$$

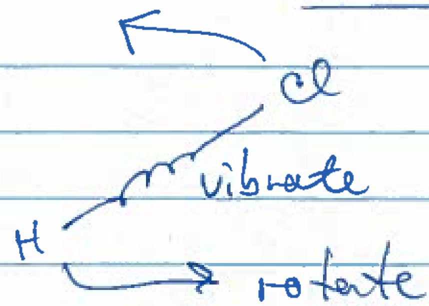
Energy Level Diagram



Why degenerate states? Clockwise + Counter CW have same energy!

> Later – Normalize $\psi(\phi)$ so we can compute Expectation Values to check Heisenberg Uncertainty Principle

Now – HCl spectroscopy – does this 2D model work?



$$\psi(r,\phi) \cong \underbrace{R(r)\ \Phi(\phi)}_{\text{approximately independent}}$$

$$E = E_{vib} + E_{rot}$$

$$= \hbar\omega\left(n+\tfrac{1}{2}\right) + Bm^2 \qquad n = 0, 1, 2, 3, \ldots \quad m = 0, \pm 1, \pm 2, \pm 3, \ldots$$

Allowed transitions

only VIB state populated

VIB $\quad n: 0 \to 1 \qquad \Delta n = 1$

ROT $\quad |m| \to |m| \pm 1 \qquad \Delta m = \pm 1$

many initial ROT states populated

"R-branch"

"P-branch"

Consider these separately

R-branch ($|m| \to |m|+1$): Gain ROT energy

$$h\nu = \Delta E = E_{n=1,m+1} - E_{n=0,m}$$

$$= \left[\hbar\omega\left(1+\cancel{\tfrac{1}{2}}\right) + B(m+1)^2\right] - \left[\hbar\omega\left(0+\cancel{\tfrac{1}{2}}\right) + Bm^2\right]$$

$$= \hbar\omega + B(m+1)^2 - Bm^2 = \hbar\omega + B(\cancel{m^2} + 2m + 1) - \cancel{Bm^2}$$

$$\boxed{h\nu = \Delta E = \hbar\omega + B(2m+1)} \quad \text{odd \#s}$$

Table of R-branch Absorptions

$\lvert m_{init} \rvert$	degeneracy	ΔE
0	1	$\hbar\omega + B$
1	2	$\hbar\omega + 3B$
2	2	$\hbar\omega + 5B$
3	2	$\hbar\omega + 7B$
4	2	$\hbar\omega + 9B$
5	2	$\hbar\omega + 11B$

Equally spaced lines

Spacing = $2B$

P-branch ($\lvert m \rvert \to \lvert m \rvert - 1$) : Lose ROT Energy

$$h\nu = \Delta E = E_{n=1, m-1} - E_{n=0, m}$$

$$= \left(\frac{3}{2}\hbar\omega + B(m-1)^2\right) - \left(\frac{1}{2}\hbar\omega + Bm^2\right)$$

$$= \hbar\omega + B(\cancel{m^2} - 2m + 1) - \cancel{Bm^2}$$

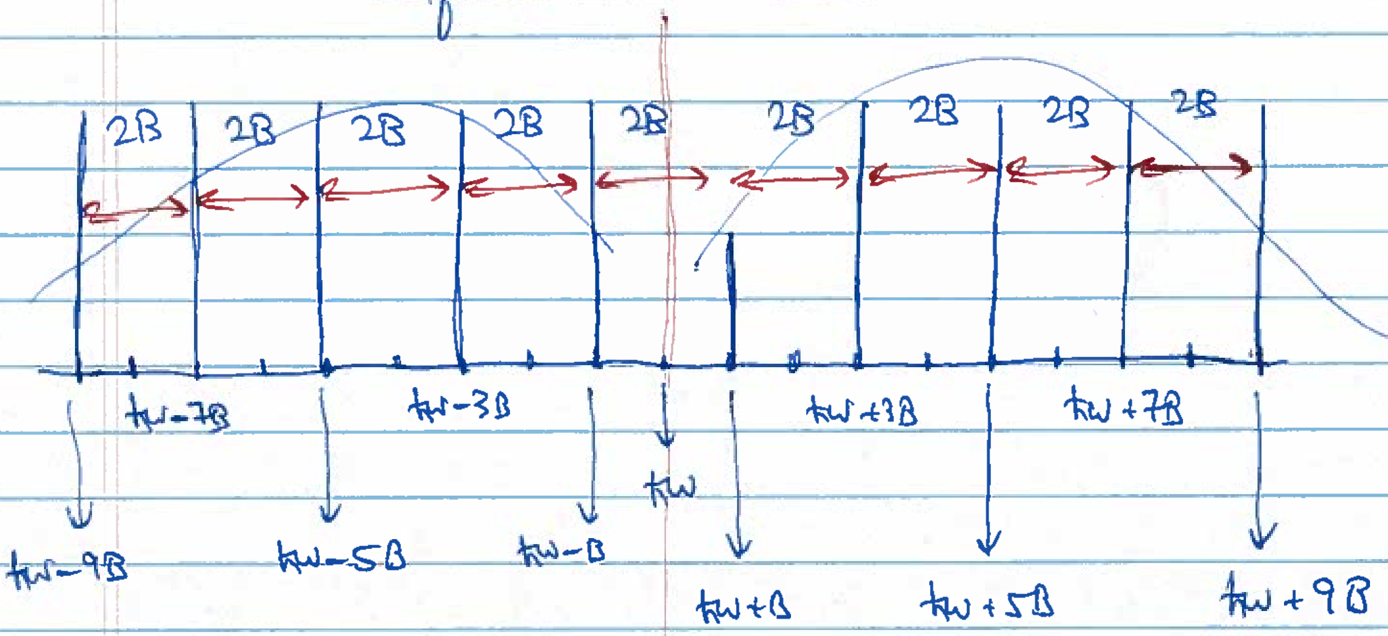
$$\boxed{h\nu = \Delta E = \hbar\omega - B(2m-1)}$$

$\lvert m_{init} \rvert$	deg	ΔE
1	2	$\hbar\omega - B$
2	2	$\hbar\omega - 3B$
3	2	$\hbar\omega - 5B$
4	2	$\hbar\omega - 7B$
5	2	$\hbar\omega - 9B$

Also Equally Spaced ... Spacing $= 2B$

Lect 18 – Pg 11

Prediction of Spectrum (Rigid 2D Rotor – Harmonic Osc)



Agree? NO :(

Need 3D Angular Momentum ...

Punchline

$$E = B j (j+1)$$

$j = 0, 1, 2, 3$ = magnitude of angular momentum

degeneracy $= 2j+1$ (3D effect)

Now see if 3D model works!