Now we can discuss rotational motion:

We must still assume that rotation & vibration are independent of each other (i.e. bond length is the same).

To describe the rotation of a particle, we need the following relations:

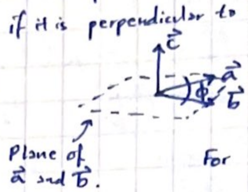
$\vec{p} = m\vec{v}$, $K = \frac{\vec{p}^2}{2m}$

$I = mr^2$, $\vec{\omega} = \frac{\vec{r} \times \vec{v}}{r^2}$

$\vec{v} = \vec{\omega} \times \vec{r}$, $\vec{l} = \vec{r} \times \vec{p}$

$(\vec{l} = I\vec{\omega})$

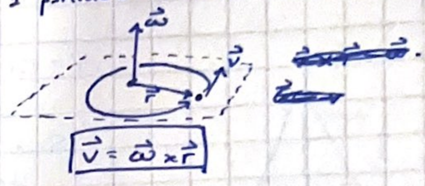
Cross product refresher: vector $\vec{c}$ is a cross product of $\vec{a}$ and $\vec{b}$ if it is perpendicular to both vectors:



$|\vec{c}| = |\vec{a}||\vec{b}| \sin(\phi)$,

$\vec{c} = \vec{a} \times \vec{b}$.

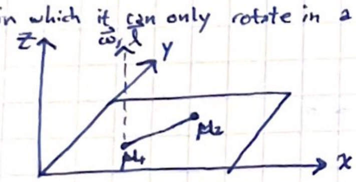
For a particle's rotation, this is:



$\boxed{\vec{v} = \vec{\omega} \times \vec{r}}$

$K = \frac{I\vec{\omega}^2}{2} = \frac{\vec{l}^2}{2I}$

Consider the rotation of a ~~particle~~ diatomic molecule on a surface, in which it can only rotate in a 2D space, and not in 3-D.

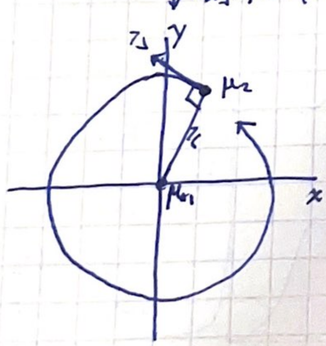


$\vec{\omega}$ and $\vec{l}$ will always be along the z-axis due to

$\vec{l} = \vec{r} \times \vec{p}$

$\vec{v} = \vec{\omega} \times \vec{r}$

Recenter μ_1 to origin, view from above:



Since $\vec{v}$ will always be tangential to $\vec{r}$, (since we assume $\vec{r}$ to be constant throughout rotation) $\sin(\phi) = 1$. This simplifies

$\vec{v} = \vec{\omega} \times \vec{r} \rightarrow v = \omega r$.

"Particle on a ring"

How would we describe the energy of this particle in the classical sense?

$E = K + U$, $U = 0$, no force pushing particle in or out (we disregard centripetal force)

$E = K = \frac{p_x^2}{2\mu} + \frac{p_y^2}{2\mu} = \frac{\vec{l}^2}{2I}$, where $I = \mu r^2$.

Translate into quantum case:

① Write hamiltonian

$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial y^2}$. If the wave function is in 2-D space, then $\Psi(x,y)$.

State Schrödinger Equation:

$\hat{H}\Psi = E\Psi$, $-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\Psi = E\Psi$

Recall that for a single particle in 3-D space, we separated these variables since they are independent of each other. However, in a rotating model, x depends on y.

x depends on y and y depends on x.

$\Psi(x,y) \rightarrow \Psi(r,\phi)$

→ We should use polar coordinates instead of cartesian coordinates.

This way, when μ_2 moves, only ϕ changes.

$\{x, y\} \rightarrow \{r, \phi\}$ since r is constant.

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

$x^2 + y^2 = r^2$

Arc length $= r\phi$

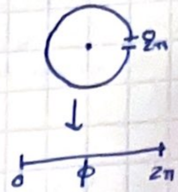
Restrictions

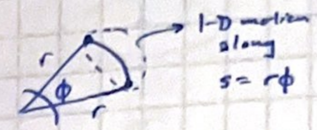
Since $\Psi(x,y) \rightarrow \Psi(r,\phi)$, ~~and r is~~ in general and r is constant in our case, $\Psi(\phi)$.

↳ 1-D motion along the circumference of the circle with radius r (to be proved)

→ $\int |\Psi|^2 d\phi = 1$, save for later

→ Periodicity: $\Psi(\phi) = \Psi(\phi + 2\pi) = \Psi(\phi + 4\pi) = \cdots$





↳ Note however, that once the particle reaches 2π and increases, it jumps back to 0 due to circular symmetry.

Keep these in mind as we solve for the Schrödinger's Equation:

We need to convert

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\Psi = E\Psi$$ to polar coordinates.

Use LaPlace's operator in place: $\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\Psi$ becomes

$$\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\right)$$

Recall, however, that Ψ does not depend on r. Therefore, $\frac{\partial^2}{\partial r^2}$ and $\frac{\partial}{\partial r} = 0$.

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\Psi = -\frac{\hbar^2}{2\mu}\left(\frac{1}{r^2}\frac{d^2}{d\phi^2}\right) = \hat{\mathcal{H}}.$$ Recall that $\mu r^2 = I$, so $\underline{\hat{\mathcal{H}} = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}}$

Note that this is functionally the same as a particle in a 1-D motion, where $\hat{\mathcal{H}} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ for KE.

Solve Schrödinger's Equation

$-\frac{\hbar^2}{2\mu}\frac{d^2}{d\phi^2}\Psi = E\Psi$ → We already have solutions to this, from the movement of a particle in 1-D: $-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}\Psi = E\Psi$, where $\Psi = ce^{ikx}$. Instead of x however, we will get $\Psi = ce^{ik\phi}$.

$$-\frac{\hbar^2}{2\mu}\frac{d^2}{d\phi^2}\left(ce^{ik\phi}\right) = E\left(ce^{ik\phi}\right) \rightarrow E = \frac{\hbar^2 k^2}{2I}, \quad k = \pm\frac{\sqrt{2IE}}{\hbar}$$

(Note similarity to 1-D case, where $k = \frac{\sqrt{2mE}}{\hbar}$)

→ Let's solve the boundary condition that $\Psi(\phi) = \Psi(\phi + 2\pi) = \Psi(\phi + 4\pi)$

$$\underbrace{e^{ik\phi} = e^{ik(\phi+2\pi)}} = e^{ik(\phi+4\pi)} = \cdots$$

$$e^{ik\phi} = e^{ik\phi}e^{ik2\pi}$$

$$1 = e^{ik2\pi}$$ → Euler's identity, $\cos 2\pi k + i\sin 2\pi k = 1$, Either $\cos 2\pi k = 1$, $i\sin 2\pi k = 0$ or $\cos 2\pi k = 0$, $i\sin 2\pi k = 1$,

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

$\Psi_{m_l} = ce^{im_l\phi}$ where $m_l = 0, \pm 1, \pm 2, \pm 3, \cdots$ <u>Quantization.</u>

↳ $E_{m_l} = \frac{\hbar^2}{2I}m_l^2$

Since $E_{m_l} = \frac{\hbar^2}{2I}m_l$ and $I = mr^2$,

$$E_{m_l} = \frac{h^2}{8mr^2\pi^2}m_l^2$$

...

$m_l = \pm 2$ — $\frac{\hbar^2}{2I}\cdot 4$ ----> $\pm 2\,m_l$, two states

$m_l = \pm 1$ — $\frac{\hbar^2}{2I}$ ----> $\pm m_l$, two states

↳ Note that when $m_l = 1$, $e^{i\phi}$ and when $m_l = -1$, $e^{-i\phi}$

Not the same

$m_l = 0$ — 0

$\boxed{\text{Unlike in a 1-D system, where } n \neq 0 \text{ in } \frac{h^2}{8ma^2}n^2,\ m_l = 0 \text{ actually makes physical sense. When } m_l = 0,\ \Psi = 1, \text{ and the wave function still exists.}}$

Normalizing Ψ:

$$P = |\Psi|^2 = |c|^2 \cdot 1$$ ↲ $|e^{im_l\phi}|^2 = (e^{im_l\phi})(e^{-im_l\phi}) = 1$

$$\int_0^{2\pi} P\,d\phi = |c|^2 \cdot \int_0^{2\pi} d\phi = |c|^2 \cdot 2\pi = 1$$

(For normalization)

$$c = \frac{1}{\sqrt{2\pi}}.$$

For PIR problem,

$$\boxed{\Psi = \frac{1}{\sqrt{2\pi}}e^{im_l\phi}}$$

$\psi = \frac{1}{\sqrt{2\pi}} e^{im_\ell \phi}$, when $m_\ell = 1$ $e^{i\phi}$ when $m = -1$ $-e^{-i\phi}$: $\psi(x) = e^{ikx}$ for 1-D motion; left or right motion.

These positive or negative versions represent counter-clockwise or clockwise motion respectively:

Proof that $m_\ell = +1$ is ~~cloc~~ counter clockwise and $m_\ell = -1$ is clockwise:

The operator for angular momentum in the z-component is defined as:

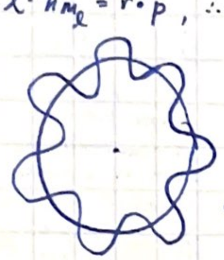
$$\hat{l}_z = -i\hbar \frac{d}{d\phi} \rightarrow \text{note similarity to } \hat{p} = -i\hbar \frac{d}{dx}$$

$$\psi = \frac{1}{\sqrt{2\pi}} e^{im_\ell \phi}, \quad \hat{l}_z \psi = -i\hbar \frac{d}{d\phi}\left(\sqrt{\tfrac{1}{2\pi}}\, e^{im_\ell \phi}\right) = \underbrace{-i\hbar \frac{1}{\sqrt{2\pi}}\left(im_\ell e^{im_\ell \phi}\right)}$$

$\boxed{\text{If } m_\ell \text{ is } (-),\ l_z \text{ is } (-) \text{ in z-direction, } m_\ell \text{ is } (+),\ l_z \text{ is } (+) \text{ in z-direction}}$ $\leftarrow$ $l_z = \pm \frac{\hbar m_\ell}{\sqrt{2\pi}} e^{im_\ell \phi}$

→ Relating this all to waves on a ring:

$l = \hbar m_\ell = r \cdot p$, $\therefore$ $l = r\left(\frac{h}{\lambda}\right)$, $\lambda = \frac{h}{p}$, $p = \frac{h}{\lambda}$: Relate λ to length of box (r):

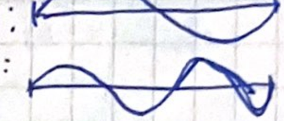


Integer (m_ℓ) number of wavelengths feeding into the circle.

$r\left(\frac{h}{\hbar}\right) = \cancel{\ }\ m_\ell \lambda$. $2\pi r = \lambda m_\ell$
$\hookrightarrow 2\pi$

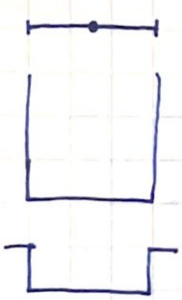
When $m_\ell = 1$:

$m_\ell = 2$:



SUMMARY OF KNOWN MODELS OF QM

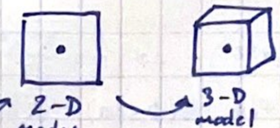
Particle in a box:



→ Particle on a line

→ Particle in a box with infinitely high walls

→ Particle in a box with finitely high walls.

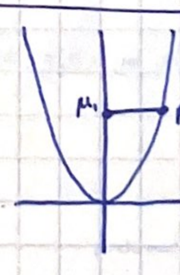


$$\boxed{\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi n x}{a}\right) \qquad E_n = \frac{h^2}{8ma^2} \cdot n^2 \text{ where } n = 1, 2, 3, \ldots}$$

$n=9$
$n=4$
$n=1$
} Unequal spacing

Harmonic Oscillator:

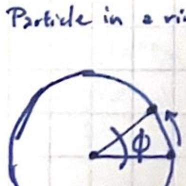
Note that the n for the Energy equation is not the same as the one in the PIB model.



$$\boxed{E_n = (n + \tfrac{1}{2})h\nu \quad n = 0, 1, 2, 3, \ldots \qquad \psi_n(x) = A_n H_n(x\sqrt{a}) e^{\frac{-ax^2}{2}}}$$

$\frac{5}{2}h\nu$
$\frac{3}{2}h\nu$
$\frac{1}{2}h\nu$
} Equal spacing

Particle in a ring:



$$\boxed{\psi_{m_\ell}(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_\ell \phi} \qquad E_{m_\ell} = \frac{\hbar^2}{2I}(m_\ell)^2 \qquad m_\ell = 0, \pm 1, \pm 2, \ldots}$$