classical free rotation

2d rotor → wrap PIAB on itself

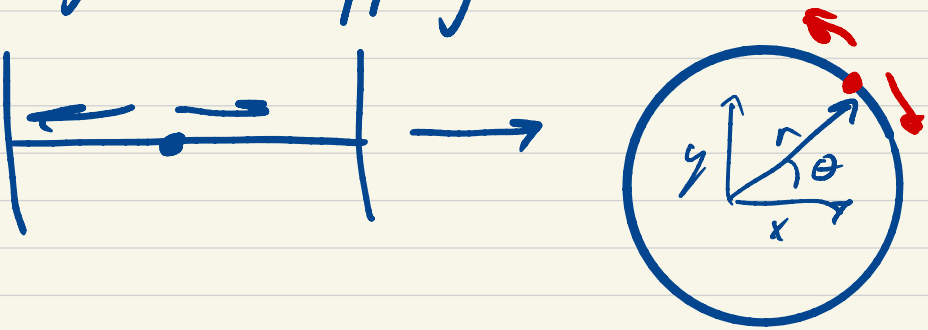
3d rotor

application to:

- rotational spectra
- fundamental particles

Centrosymmetric rotation

Imagine wrapping PIAB on itself



Particle freely going around in a circle.

Schrödinger eq

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\psi(x,y)=E\psi(x,y)$$

Not very convenient coordinate sys

$\Rightarrow$ cylindrical coords

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

r is a constant

$$\rightarrow \quad \frac{-\hbar^2}{2mr^2}\frac{d^2}{d\phi^2}\psi(\phi) = E\psi(\phi)$$

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

mr^2 common in rotational problems.

$\underline{I = mr^2}$ "moment of inertia"

$$-\frac{\hbar^2}{2I}\psi''(\phi) = E\psi(\phi)$$

$$\psi''(\phi) = -\frac{2IE}{\hbar^2}\psi(\phi)$$

$$= -m^2\psi(\phi) \qquad m = \frac{\sqrt{2IE}}{\hbar}$$

$$\psi(\phi) = e^{\pm im\phi}$$

$$= e^{\pm im(\phi+2\pi)} \quad \text{Boundary condition}$$

$$\rightarrow \quad e^{\pm im2\pi} = 1$$

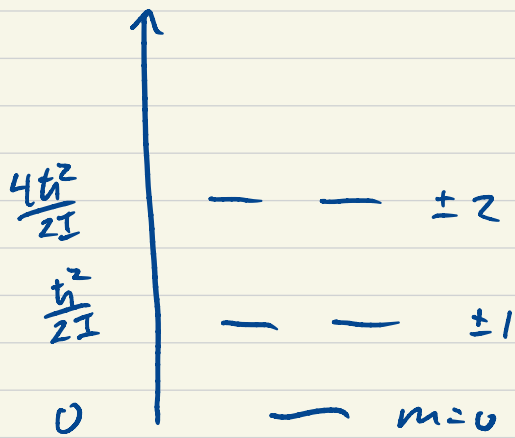
$$\rightarrow \quad m = 0, \pm 1, \cdots$$

$$\psi_m(\phi) = e^{im\phi} \qquad E = \frac{m^2\hbar^2}{2I}$$

normalize

$$N = \int_0^{2\pi} \psi_m^* \psi_m \, d\phi$$
$$= 2\pi$$

$$\psi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$ complex...



no ZPE!

degenerate levels

Object going in a circle has an angular momentum.

vector orthogonal to plane of rotation

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

In QM, becomes $\hat{L} = \hat{r} \times \hat{p}$

In cylindrical coords, becomes

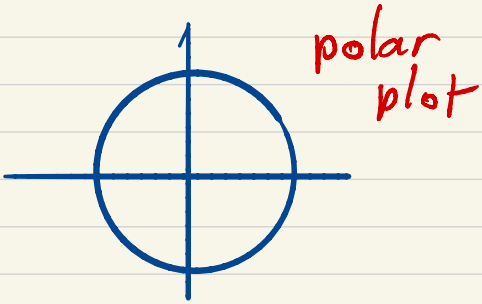
$$\hat{l}_z = -i\hbar \frac{\partial}{\partial \phi}$$

$$\hat{l}_z \tilde{\psi}_m = m\hbar \tilde{\psi}_m$$

Each m corresponds to a rate of rotation, sign corresponds to direction, cw or ccw.

$m=0$ $\quad \psi_0 = \frac{1}{\sqrt{2\pi}}$

constant



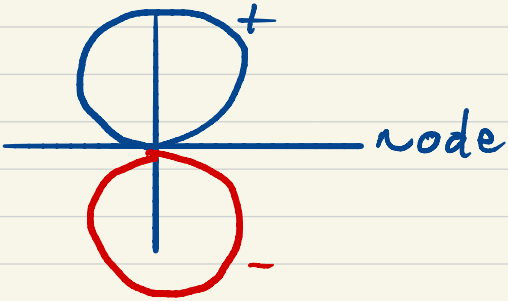
$m=\pm 1$ complex

$\psi_1 + \psi_{-1} \propto \cos\phi$

$\psi_1 - \psi_{-1} \propto \sin\phi$

polar plot

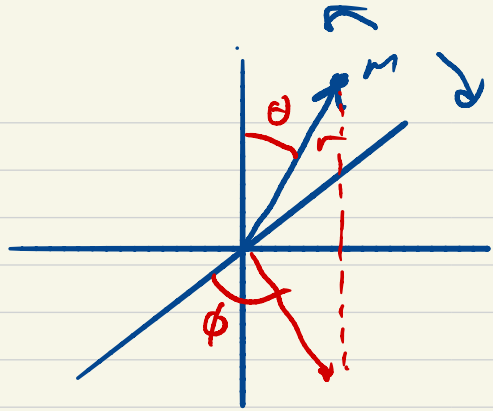
angular "shape"



...

Same idea 3D

spherical coords



Something rotating in 3d on a fixed dope.

$$I = mr^2 \qquad V(\theta,\phi) = 0$$

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

$$\frac{\hat{L}^2}{2I}\psi(\theta,\phi) = E\psi(\theta,\phi)$$

$$\psi(\theta+\pi,\phi) = \psi(\theta,\phi) \qquad \text{B.C.}$$

$$\psi(\theta,\phi+2\pi) = \psi(\theta,\phi)$$

(Separate variables. $\Phi \to e^{\pm im_\ell\phi}$.
Assoc. Legendre polynomials for θ)

Solutions called the spherical harmonics. Standing waves on surface of a sphere.

$Y_{\ell m}(\theta, \phi)$ $\quad \ell = 0, 1, 2, \cdots$

$m_\ell = -\ell, -\ell+1, \cdots 0, \cdots, \ell$

$$E_\ell = \frac{\hbar^2}{2I}\,\ell(\ell+1)$$

$$\ell_z = m_\ell \hbar \qquad |\vec{\ell}| = \hbar\sqrt{\ell(\ell+1)}$$

Shapes reminiscent of s, p, d, ...

degeneracy $2\ell+1$

						nodes
$\frac{6\hbar^2}{2I}$	2	1	0	−1	−2	2
$\frac{2\hbar^2}{2I}$	1	0	−1			1
	0					0

applications

- electrons in an atom
- fundamental particles
  "spin" angular momentum
  s analogous to l

fermions: s $1/2$ integer
(matter)

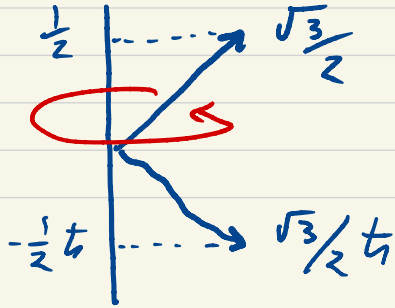
bosons: s integer
(force carrying particles)

p^+, e^-, n^0 $\quad s = 1/2$
$m_s = \pm 1/2$ up & down spin

impart magnetic moment,
probed in NMR / MRI & EPR

$$|\vec{S}| = \hbar\sqrt{\frac{1}{2}\cdot\frac{3}{2}} = \frac{\sqrt{3}}{2}\hbar$$

$$S_z = \pm\frac{1}{2}\hbar$$



- molecular rotations

ex $^1H - ^{35}Cl$ $\quad d = 1.27455\ \text{Å}$

(1) $\mu = 0.9796$

$$I = \mu d^2 = 1.5913\ \text{amu}\cdot\text{Å}^2$$

(2) rotational constant

$$\frac{\hbar^2}{2I} = 2.104 \times 10^{-22}\ \text{J} \qquad \text{"B"}$$

$$= 0.1267\ \text{kJ/mol}$$

(3) $$\frac{P(l=1)}{P(l=0)} = \frac{3}{1}\,\frac{e^{-2B/kT}}{e^{-0/kT}}$$

$$= 2.708\ !!$$

⋮

— — — 2.708

— 1

Many rotational states occupied at room temperature

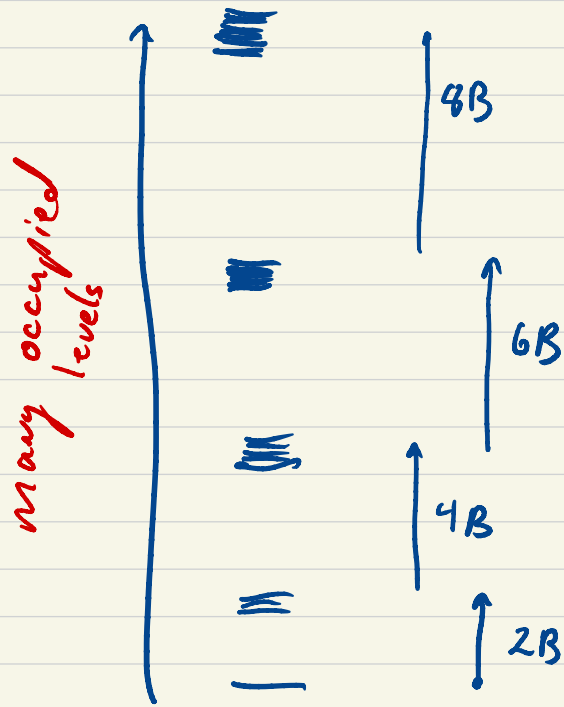
spectroscopy selection rules

$$\langle Y_{\ell m} | \hat{r} | Y_{\ell' m'} \rangle = 0 \quad \text{unless}$$

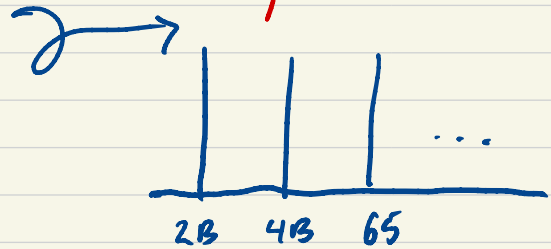
$$\Delta \ell = \pm 1 \quad (\Delta m_\ell = 0, \pm 1)$$

$$E_{\ell+1} - E_\ell = B(\ell+1)(\ell+2) - B\ell(\ell+1)$$

$$= 2B(\ell+1) = h\nu_{light} = hc\tilde{\nu}$$



HCl rotational spectrum



$$2B = 0.2534 \text{ kJ/mol}$$

$$\frac{2B}{hc} = 21.2/\text{cm}$$

$$\lambda = 0.0472 \text{ cm}$$

microwave

- way to measure I & thus bond length
- basis of μwave heating