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More On Quantum Rotation

Rotation-Vibration Spectroscopy (3D Rotation)

$$E_{n,j} = \hbar\omega(n+\tfrac{1}{2}) + Bj(j+1) \qquad n: 0 \to 1$$
$$j: j \to j \pm 1$$

$$h\nu = \Delta E = E_{n=1,j+1} - E_{n=0,j} \qquad \text{(R-branch)}$$
$$= \hbar\omega + B[(j+1)(j+2) - j(j+1)]$$
$$= \hbar\omega + B[(\cancel{j^2} + 3j + 2) - (\cancel{j^2} + j)]$$
$$= \hbar\omega + B(2j+2) = \boxed{\hbar\omega + 2B(j+1)}$$
$$j = 0, 1, 2, 3, \ldots$$

P-branch $(j \to j-1)$

$$h\nu = \Delta E = E_{n=1,j-1} - E_{n=0,j}$$
$$= \hbar\omega + B[(j-1)(j) - j(j+1)]$$
$$= \hbar\omega + B[(\cancel{j^2} - j) - (\cancel{j^2} + j)]$$
$$= \hbar\omega + B(-2j) = \boxed{\hbar\omega - 2Bj}$$
$$j = 1, 2, 3, \ldots$$

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Table of Absorbances

	Initial j	Degeneracy $= 2j+1$	ΔE
			$\vdots$
P-branch	5	11	$\hbar\omega - 10B$
	4	9	$\hbar\omega - 8B$
	3	7	$\hbar\omega - 6B$
	2	5	$\hbar\omega - 4B$
	1	3	$\hbar\omega - 2B$
R-branch	0	1	$\hbar\omega + 2B$
	1	3	$\hbar\omega + 4B$
	2	5	$\hbar\omega + 6B$
	3	7	$\hbar\omega + 8B$
	4	9	$\hbar\omega + 10B$
	5	11	$\hbar\omega + 12B$
	6	13	$\hbar\omega + 14B$
			$\vdots$

4B

equally spaced $\rightarrow 2B$

Works - although spacings do shrink for larger initial j values - why?

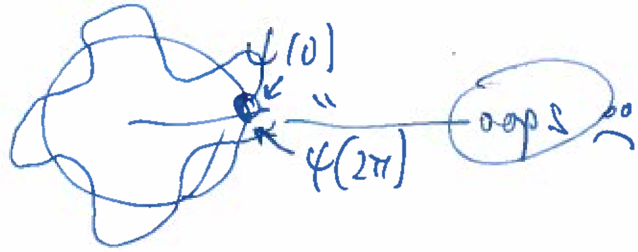
Rigid rotor approximation breaks down.

$j \uparrow \quad r \uparrow \quad B \downarrow$ Aha!

$\boxed{\text{Speak Spectra!}}$

$$\psi(\phi) = c\, e^{iJ\phi/\hbar}$$

$c \in \mathbb{R}$



$$\psi(0) = c e^{0} = c$$

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

$$\frac{J\cdot \cancel{2\pi}}{\hbar} = m\cdot \cancel{2\pi}$$

$$\boxed{J = m\hbar}$$

Angular momentum is quantized!

$\cos(\theta) = 1$ at $0, \pm 2\pi, \pm 4\pi \cdots$ guarantees both

$\sin(\theta) = 0$ at $0, \pm\pi, \pm 2\pi, \cdots$

$$\frac{J\cdot 2\pi}{\hbar} = 0, \pm 2\pi, \pm 4\pi \equiv m\cdot 2\pi$$

$m = 0, \pm 1, \pm 2, \cdots$ integers

ccw

cw take ± ✓

NOT Mass

spin → magnetic

$$\psi_m(\phi) = c\, e^{i(m\cancel{\hbar})\phi/\cancel{\hbar}}$$

$$\boxed{= c\, e^{im\phi}}$$

c = normalization coef (assume real)

(Later we'll prove $c = \frac{1}{\sqrt{2\pi}}$ for all m)

$$\hat{J}\psi_m(\phi) = \frac{\hbar}{i}\frac{d}{d\phi} c e^{im\phi} = \frac{\hbar c}{i}\frac{d e^{im\phi}}{d\phi} = \frac{\hbar c}{\cancel{i}}(\cancel{i}m) e^{im\phi}$$

$$= (\hbar m)(c e^{im\phi}) = J_m \psi_m(\phi)$$

eigenvalue of angular momentum $= \hbar m$

$$\hat{H}\psi_m(\phi) = \frac{\hat{J}^2}{2I}\psi_m(\phi) \overset{?}{=} \qquad \hat{J}^2\psi_m = \hat{J}(\hat{J}\psi_m) = \hat{J}(\hbar m)\psi_m = (\hbar m)\hat{J}\psi_m = (\hbar m)(\hbar m)\psi_m$$

$$= (\hbar m)^2\psi_m$$

$I = \mu r^2$, r = constant (rigid rotor approx) HCl $r = 1.27\,\text{Å} = r_e$

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

$$E_m = \frac{\hbar^2 m^2}{2\mu r^2} \qquad m = 0, \pm 1, \pm 2, \ldots \quad (\text{depends on } |m|)$$

$B = E_0 =$ fundamental energy scale (like $\frac{\hbar^2\pi^2}{2mL^2}$, $\hbar\omega$)

$\frac{\hbar^2\pi^2}{2mL^2} \rightarrow$ PIAB, $\hbar\omega \rightarrow$ QHO

HCl $\mu \sim m_H$

$$= \frac{(1.05 \cdot 10^{-34}\ \mathrm{J\,s})^2}{2\,(1.67 \cdot 10^{-27}\ \mathrm{kg})(1.27 \cdot 10^{-10}\ \mathrm{m})^2}$$

$$= \frac{1.05^2}{2 \cdot 1.67 \cdot 1.27^2} \cdot \underbrace{\frac{10^{-68}}{10^{-27} \cdot 10^{-20}}}_{10^{-21}} = 0.209 \times 10^{-21}\ \mathrm{J} \equiv B$$

(rot const)

$$\bar{B} = \frac{B}{hc} = \frac{0.205 \cdot 10^{-21}\ \cancel{\mathrm{J}}}{6.63 \cdot 10^{-34}\ \cancel{\mathrm{J\,s}} \cdot 3.0 \cdot 10^{10}\ \frac{\mathrm{cm}}{\cancel{\mathrm{s}}}} = \frac{0.209}{6.63 \cdot 3.0} \cdot \underbrace{\frac{10^{-21}}{10^{-34} \cdot 10^{10}}}_{10^{3}}$$

$$= 0.0103 \cdot 10^{3}\ \mathrm{cm}^{-1} = \boxed{10.5\ \mathrm{cm}^{-1}}$$

$\boxed{\text{VIB } 2885\ \mathrm{cm}^{-1}}$

$\boxed{E_m = Bm^2}$ — KE

$m = -2$ $m = +2$ $E_2 = 4B^2$, $g_2 = 2$

$3B$

$m = -1$ $m = +1$ $E_1 = B \cdot 1^2 = B$, $g_1 = 2$

$\Delta E = E_1 - E_0 = B$

$m = 0$ $E_0 = 0$, deg $= g = 1$

no zero pt vib energy

b/c no VIB —

no "confinement" $\psi \not\to 0$ except at nodes

IR Spectrum?

$$\boxed{\begin{array}{l} \Delta x \, \Delta p \geq \hbar/2 \\ \downarrow \\ \Delta\phi \, \Delta J \geq \hbar/2 \quad ? \end{array}}$$

(PIAB, QHO ✓)

Conjecture

$\psi_m(\phi) = \frac{1}{\sqrt{2}} e^{im\phi}$ — Eigenfunction of BOTH $\hat{J}$ and $\hat{H}$

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

$$\hat{J}\psi_m = (\hbar m)\psi_m \quad \text{(same)}$$

$$\Delta\phi = \sqrt{\langle\hat{\phi}^2\rangle - \langle\hat{\phi}\rangle^2}$$

$$\Delta J = \sqrt{\langle\hat{J}^2\rangle - \langle\hat{J}\rangle^2}$$

$$\langle\hat{A}\rangle = \int_0^{2\pi} d\phi\, \psi_m^*(\phi)\,\hat{A}\,\psi_m(\phi)$$

$$\langle\hat{\phi}\rangle = \int_0^{2\pi} d\phi \left(\frac{1}{\sqrt{2\pi}}\cancel{e^{-im\phi}}\right)\phi\left(\frac{1}{\sqrt{2\pi}}\cancel{e^{im\phi}}\right) \qquad m = 0, \pm1, \pm2, \pm3, \dots$$

$$= \frac{1}{2\pi}\int_0^{2\pi} d\phi \cdot \phi = \frac{1}{2\pi}\frac{\phi^2}{2}\Big|_0^{2\pi} = \frac{1}{4\pi}\left((2\pi)^2 - 0\right) = \frac{4\pi^2}{4\pi} = \pi$$

Make sense? $\phi \in [0, 2\pi]$ $\langle\hat{\phi}\rangle = \frac{0 + 2\pi}{2} = \pi$ ✓

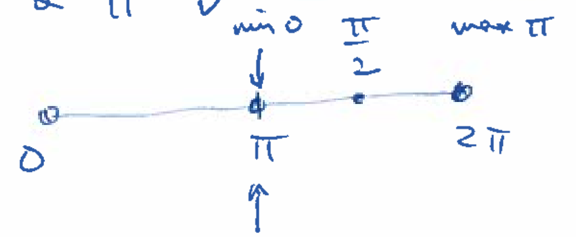
Probability distribution $= |\psi|^2 = \psi^*\psi = \left(\frac{1}{\sqrt{2\pi}}\cancel{e^{-im\phi}}\right)\left(\frac{1}{\sqrt{2\pi}}\cancel{e^{im\phi}}\right) = \frac{1}{2\pi}$

independent of ϕ
all angles equally likely

$$\langle\hat{\phi}^2\rangle = \int_0^{2\pi} d\phi\, \psi_m^*(\phi)\cdot\phi^2\cdot\psi_m(\phi) = \int_0^{2\pi} d\phi \left(\frac{1}{\sqrt{2\pi}}\cancel{e^{-im\phi}}\right)\phi^2\left(\frac{1}{\sqrt{2\pi}}\cancel{e^{im\phi}}\right)$$

$$= \frac{1}{2\pi}\int_0^{2\pi} d\phi\,\phi^2 = \frac{1}{2\pi}\frac{\phi^3}{3}\Big|_0^{2\pi} = \frac{1}{6\pi}\left(8\pi^3 - 0\right) = \frac{4}{3}\pi^2 \propto \pi^2 \quad ✓$$

$$\Delta\phi = \sqrt{\tfrac{4}{3}\pi^2 - \pi^2} = \sqrt{\tfrac{1}{3}\pi^2} = \frac{\pi}{\sqrt{3}} \propto \pi \checkmark \quad \frac{\pi}{1.7}$$



$$\langle \hat{J} \rangle = \int_0^{2\pi} d\phi \; \psi_m^*(\phi)\, \hat{J}\, \psi_m(\phi)$$

$$= \int_0^{2\pi} d\phi \left(\frac{1}{\sqrt{2\pi}} e^{-im\phi}\right)\left(\frac{\hbar}{i}\frac{d}{d\phi}\right)\left(\frac{1}{\sqrt{2\pi}} e^{im\phi}\right)$$

$$= \frac{\hbar}{2\pi i}\int_0^{2\pi} d\phi \; e^{-im\phi}\, \frac{d e^{im\phi}}{d\phi} = \frac{\hbar}{2\pi \cancel{i}} \int_0^{2\pi} d\phi \; \cancel{e^{-im\phi}}\, (\cancel{i}m)\, \cancel{e^{im\phi}}$$

$$= \frac{\hbar m}{2\pi}\int_0^{2\pi} d\phi = \frac{\hbar m}{2\pi}\, \phi \Big|_0^{2\pi} = \frac{\hbar m}{\cancel{2\pi}} \cdot (\cancel{2\pi - 0}) = \hbar m$$

Wait - we could have guessed that:

$$\hat{J}\psi_m(\phi) = (\hbar m)\,\psi_m(\phi) \qquad (\text{see} \star \text{ pg } 1)$$

$$\underset{\text{const}}{\uparrow} \quad \underset{\therefore\ \text{eigenfunction of } \hat{J}}{\uparrow}$$

$$\langle \hat{J} \rangle = \int_0^{2\pi} d\phi \; \psi_m^*(\phi)\, \underbrace{\hat{J}\, \psi_m(\phi)}_{(\hbar m)\psi_m(\phi)} = (\hbar m) \boxed{\int_0^{2\pi} d\phi \; \psi_m^*(\phi)\, \psi_m(\phi)}^{\,1} = (\hbar m) \propto \hbar \checkmark$$

$$\langle \hat{J}^2 \rangle \overset{?}{=} \int_0^{2\pi} d\phi \; \psi_m^*(\phi)\, \hat{J}^2 \psi_m(\phi) = \int_0^{2\pi} d\phi \; \psi_m^*(\phi)\, (\hbar m)^2\, \psi_m(\phi) = (\hbar m)^2 \boxed{\int_0^{2\pi} d\phi \; \psi_m^*(\phi)\psi_m(\phi)}^{\,1}$$

$$\hat{J}^2\psi_m = \hat{J}(\underbrace{\hat{J}\psi_m}_{(\hbar m)\psi_m}) = (\hbar m)(\underbrace{\hat{J}\psi_m}_{(\hbar m)\psi_m}) = (\hbar m)^2\psi_m$$

$$= (\hbar m)^2 \propto \hbar^2 \checkmark$$

$$\Delta J = \sqrt{\langle \hat{J}^2\rangle - \langle \hat{J}\rangle^2} = \sqrt{\hbar^2 m^2 - (\hbar m)^2} = \sqrt{\hbar^2 m^2 - \hbar^2 m^2} = 0 \quad \left(\begin{array}{c}\text{Eigenfunction —}\\ \text{NO UNCERTAINTY}\end{array}\right)$$

Thus $\Delta\phi \, \Delta J = \left(\frac{\pi}{\sqrt{3}}\right)(0) = 0 \not\geq \frac{\hbar}{2}$?

What went wrong?

– 2D rotation – constrains molecule to xy plane
thus we know both $\underset{=0}{z}$ and $\underset{=0}{p_z}$ at the same time!

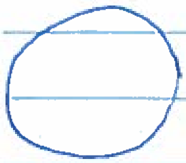
$\boxed{\text{Solve by going to 3D}}$ (yes and No)

– Should be able to apply Heisenberg Uncertainty Principle to a reduced-dimensional model (we applied it successfully in 1D!)

But how?

> "A" on a test of your choice
> if anyone can solve this CONUNDRUM

Visualizing Orbitals



(all same sign)

$m=0$ $\quad \psi_{m=0}(\phi) = \frac{1}{\sqrt{2\pi}}\, \underbrace{e^{i\cdot 0\cdot\phi}}_{1} = \frac{1}{\sqrt{2\pi}} = \text{const.}$

counter cw

$m=\pm 1$ $\quad \psi_{m=\pm1}(\phi) = \frac{1}{\sqrt{2\pi}}\, e^{\pm i\phi}$

cw

Complex functions – hard to visualize

Chemistry – symmetrize!

$$\boxed{\begin{array}{ll} \text{Even symmetry} & \psi_{+1} + \psi_{-1} \\ \text{Odd Symmetry} & \psi_{+1} - \psi_{-1} \end{array}}$$

Even (e) $\quad \psi_{1,e}(\phi) = A\left(e^{i\phi} + e^{-i\phi}\right) = 2A\,\boxed{\cos(\phi)}$

ODD (o) $\quad \psi_{1,o}(\phi) = A\left(e^{i\phi} - e^{-i\phi}\right) = 2iA\,\boxed{\sin(\phi)}$

e) which is which?

$$\boxed{\begin{array}{l} \psi_{1,e} \text{ looks like } P_x \\ \psi_{1,o} \text{ looks like } P_y \end{array}}$$

linear combos of Angular Momentum Eigenfunctions!