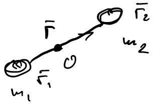
Rotation: concept, wavefunctions and energies

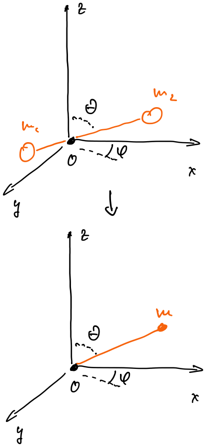
For single particle (single atom) it will predict the properties very nicely, but not for or more:



We place center of mass at O

$$\bar{O} = \frac{m_1}{m_1+m_2}\bar{r}_1 + \frac{m_2}{m_1+m_2}\bar{r}_2$$

$$\bar{r} = \bar{r}_2 - \bar{r}_1$$



To prepare for SE:

$$E_k = \frac{1}{2}mV_1^2 + \frac{1}{2}mV_2^2$$

$$\Downarrow$$

$$E_k = \frac{1}{2}mV^2 \quad m = \frac{m_1 m_2}{m_1+m_2}$$

reduced mass

This is the model of rigid rotator – $r = \text{const}$

Changing r → vibration $\overset{\nabla}{0}$

SE:

$$-\frac{h^2}{8\pi^2 m}\nabla^2\Psi(\theta,\varphi) + \cancelto{0}{V(\theta,\varphi)}\,\Psi(\theta,\varphi) = E\Psi(\theta,\varphi)$$

$$-\frac{h^2}{8\pi^2 m}\nabla^2\Psi = E\Psi$$

It is almost like for PIB, but in polar coordinates and with different boundary conditions!

$$\begin{cases} \psi(\theta,\varphi) = \psi(\theta, \varphi + 2\pi) \\ \psi(\theta,\varphi) = \psi(\theta + 2\pi, \varphi) \end{cases}$$

Little help:

Cartesian: $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

Polar: $\nabla^2 = \underbrace{\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r}}_{\substack{0 \\ (\text{rigid})}} + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\sin\theta\frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2\theta}\cdot\frac{\partial^2}{\partial \varphi^2}$

Finally SE for rigid rotor specifically:

$$-\frac{h^2}{8\pi^2 m r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)\psi = E\psi$$

Let's take first simple case $\psi = \cos\theta$

$$\frac{\partial^2}{\partial\varphi^2} \rightarrow 0$$

$$\frac{1}{\sin\theta}\cdot\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\cos\theta = -2\cos\theta$$

$$\Downarrow$$

$$-\frac{h^2}{8\pi^2 m r^2}(-2\cos\theta) = E\cos\theta \Rightarrow \boxed{E = \frac{h^2}{4\pi^2 m r^2}}$$

What about $\sin\theta$?

$$\psi(\theta,\varphi) = \sin\theta \Rightarrow \frac{\partial\psi}{\partial\varphi} = 0$$

$$\sin\theta\frac{\partial\psi}{\partial\theta} = \sin\theta\cos\theta \Rightarrow \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) = \cos^2\theta - \sin^2\theta$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) = -\sin\theta + \frac{\cos^2\theta}{\sin\theta}$$

$$\frac{\cos^2\theta}{\sin\theta} - \sin\theta \neq E\sin\theta$$

Solutions:

$$\Psi(\theta,\varphi) = \left\{ \begin{array}{l} N \\ N\cos\theta \\ N\sin\theta\, e^{\pm i\varphi} \xrightarrow{\quad} \text{adding phase} \\ \vdots \end{array} \right.$$

Let's check it for $\psi = N\sin\theta\, e^{i\varphi}$:

$$\hat{H}\psi = -\frac{h^2}{8\pi^2 r^2 m}\left(\frac{1}{\sin\theta}\cdot\frac{\partial}{\partial\theta}\underbrace{\sin\theta\frac{\partial\psi}{\partial\theta}}_{\underbrace{N\cos\theta\sin\theta\, e^{i\varphi}}_{-N\sin^2\theta\, e^{i\varphi} + N\cos^2\theta\, e^{i\varphi}}} + \frac{1}{\sin^2\theta}\cdot\underbrace{\frac{\partial^2\psi}{\partial\varphi^2}}_{\underbrace{N i\sin\theta\, e^{i\varphi}}_{-N\sin\theta\, e^{i\varphi}}}\right) = E\psi$$

$\frac{\partial}{\partial\varphi}$

$\frac{\partial^2}{\partial\varphi^2}$

$$-N\sin\theta\, e^{i\varphi} + N\frac{\cancel{1-}\sin^2\theta}{\sin\theta}e^{i\varphi} \qquad -N\cancel{\frac{1}{\sin\theta}}e^{i\varphi}$$

that is why we need $e^{i\varphi}$

$$\Downarrow$$

$$\frac{h^2}{8\pi^2 r^2 m}\cdot 2N\cancel{\sin\theta}\, e^{i\varphi} = EN\cancel{\sin\theta}\, e^{i\varphi}$$

$$\boxed{E = 2\cdot\frac{h^2}{8\pi^2 r^2 m}}$$

$\psi = N\sin\theta\, e^{i\varphi}$ → the complexity will be cancelled for probability $P = \psi\psi^*$.

We need one more thing — N.

$$\Psi(\theta,\varphi) = \left\{ \begin{array}{l} N \\ N\cos\theta \\ N\sin\theta\, e^{i\varphi} \\ \vdots \end{array} \right.$$

$$P = \psi^*\psi \rightarrow \iint P(\theta,\varphi)\sin\theta\, d\theta\, d\varphi = 1$$

$$\psi = N\sin\theta\, e^{i\varphi}$$

$$1 = \int_0^{2\pi}\int_0^{\pi} N^*\sin\theta\, e^{i\varphi}\, N\sin\theta\, e^{-i\varphi}\,\sin\theta\, d\theta\, d\varphi =$$

$$= N^2\iint \sin^3\theta\, d\theta\, d\varphi = 2\pi|N|^2\int_0^{\pi}\sin^3\theta\, d\theta =$$

$u = \cos\theta$
$du = -\sin\theta \, d\theta$ $\Big\}$ $\sin^3\theta = (1-u^2)\,du$

$$= 2\pi N^2 \int_1^{-1} (1-u^2)\,du = 2\pi N^2 \left(u - \frac{u^3}{3}\right)\Bigg|_1^{-1} =$$

$$= 2\pi N^2 \cdot \frac{4}{3} \Rightarrow \boxed{N = \sqrt{\frac{3}{8\pi}}}$$

$\Psi(\theta,\varphi)$:

1) normalization constant (for each Ψ)
2) polynomial in $\sin / \cos\theta$
3) $e^{im\varphi}$

This allows to introduce quantum numbers!

$\sqrt{\frac{1}{4\pi}}$	$l=0$	$m=0$
$\sqrt{\frac{3}{8\pi}} \sin\theta \, e^{-i\varphi}$		$m=-1$
$\sqrt{\frac{3}{4\pi}} \cos\theta$	$l=1$	$m=0$
$\sqrt{\frac{3}{8\pi}} \sin\theta \, e^{i\varphi}$		$m=1$
$\sqrt{\frac{15}{32\pi}} \sin^2\theta \, e^{-2i\varphi}$		$m=-2$
$\sqrt{\frac{15}{8\pi}} \sin\theta\cos\theta \, e^{-i\varphi}$		$m=-1$
$\sqrt{\frac{15}{16\pi}} (3\cos^2\theta - 1)$	$l=2$	$m=0$
$\sqrt{\frac{15}{8\pi}} \sin\theta\cos\theta \, e^{i\varphi}$		$m=1$
$\sqrt{\frac{15}{32\pi}} \sin^2\theta \, e^{2i\varphi}$		$m=2$

1) l - angular momentum
order of polynomial
number of oscillations θ !

2) m - magnetic number
order of $e^{im\varphi}$
will behave differently in magnetic field !
$m = -l, -l+1, \dots, l-1, l$

$$\Psi(\theta,\varphi) = N_{lm} \cdot P_l^m(\cos\theta)\, e^{im\varphi}$$

Legendre polynomial

Little help

$$P_\ell^0(x) = \frac{1}{2^\ell \ell!} \frac{d^\ell}{dx^\ell} (x^2-1)^\ell$$

For example: $P_2^0(x) = \frac{1}{2^2} \cdot \frac{1}{2!} \cdot \frac{d^2}{dx^2} (x^2-1)^2 =$

$$= \frac{1}{2}(3x^2-1)$$

Recursion:

$$(\ell+1) P_{\ell+1}^0 = (2\ell+1) P_\ell^0(x) - \ell P_{\ell-1}^0(x)$$

Finally:

$$P_\ell^m(x) = (1-x^2)^{\frac{m}{2}} \frac{d^m}{dx^m} P_\ell^0(x)$$

Important property of Ψ's is they are orthogonal!

$$\int \Psi_{\ell m}^* \Psi_{\ell' m'} = 0 \qquad \begin{matrix} \ell \neq \ell' \\ m \neq m' \end{matrix}$$

Why?

$$0 = \int \Psi_{\ell m}^* \Psi_{\ell' m'} = \iint N_{11}^* \sin\theta \, e^{-i\varphi} N_{00} \sin\theta \, d\theta \, d\varphi =$$

$$= N_{11}^* N_{00} \int_0^\pi \sin^2\theta \, d\theta \underbrace{\int_0^{2\pi} e^{-i\varphi} d\varphi}_{0} = 0$$

Physical meaning of orthogonality!

If we need to produce transition from Ψ_1 to Ψ_2, they cannot be orthogonal. The particle must be able to exist in both Ψ_1 and Ψ_2, meaning $P = \int \Psi_1 \Psi_2 \neq 0$

Now we determined all functions and are ready to see energy structure!

$$\Psi_{00}(\theta,\varphi) = N \rightarrow E_{00} = 0$$

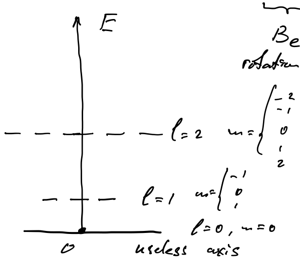
$$\left\{ \begin{aligned} &\Psi_{1-1}(\theta,\varphi) = N\sin\theta\, e^{-i\varphi} \rightarrow E_{1-1} = \frac{h^2}{8\pi^2 r^2 m}\cdot 2 \\ &\Psi_{10}(\theta,\varphi) = N\cos\theta \rightarrow E_{10} = \frac{h^2}{8\pi^2 r^2 m}\cdot 2 \\ &\Psi_{11}(\theta,\varphi) = N\sin\theta\, e^{i\varphi} \rightarrow E_{11} = \frac{h^2}{8\pi^2 r^2 m}\cdot 2 \end{aligned} \right.$$

$$\Psi_{20}(\theta,\varphi) = N(3\cos^2\theta - 1) \rightarrow E_{20} = \frac{h^2}{8\pi^2 r^2 m}\, 6$$

$$\vdots$$

$$\Psi_{lm}(\theta,\varphi) = N_{lm} P_l^m(\cos\theta)\, e^{im\varphi} \rightarrow E = \underbrace{\frac{h^2}{8\pi^2 r^2 m}}_{B_e} l(l+1)$$

rotation constant.



Now the question is from which to which energy states we can produce transitions.

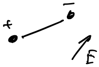
Selection rules:

We have to skip here a lot of QM:

$$I_{\Psi \to \Psi'} \sim \underset{\textcircled{1}}{\frac{\sin^2(\Delta E - h\nu)}{(\Delta E - h\nu)^2}} \underset{\textcircled{2}\ \text{FGR}}{\int \Psi \mu_e \Psi'}$$

μ_z is dipole moment

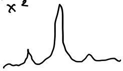
$$\bar{\mu} = q \cdot \bar{r}$$



① This is basically resonance condition!

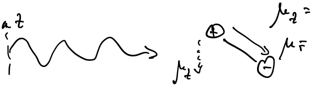
$$\lim_{\hbar\omega \to \Delta E} \frac{\sin^2(\Delta E - \hbar\omega)}{(\Delta E - \hbar\omega)^2} = \infty$$

$\frac{\sin^2 x}{x^2}$ → fast function



② Molecule have to have μ_z, i.e. CO ...

$\mu_z = \mu\cos\Theta = q r \cos\Theta$



H_2 and N_2 cannot have it.

As long as we bring light at energy resonance, it is all about $\int \psi \mu \psi'$

$$\iint \psi^*_{lm}\, \mu \cos\theta\, \psi_{l'm'} \sin\theta \, d\theta \, d\varphi \begin{cases} = 0 & \text{forbidden} \\ \neq 0 & \text{allowed} \end{cases}$$

$$\begin{cases} \psi^*_{lm} = N^*_{lm} P_l^m e^{-im\varphi} \\ \psi_{l'm'} = N_{l'm'} P_{l'}^{m'} e^{im'\varphi} \end{cases}$$

Pulling all constants outside integral:

$$N^*_{lm} N_{l'm'} \mu \underbrace{\int P_l^m P_{l'}^{m'} \cos\theta \sin\theta \, d\theta}_{\Delta l} \underbrace{\int e^{-im\varphi} e^{im'\varphi} d\varphi}_{\Delta m}$$

① $\Delta m = ?$

if $\Delta m = 0$, then $\int e^{i\Delta m\varphi} dp = \int d\varphi \neq 0$

if $\Delta m \neq 0$, then $\int_0^{2\pi} e^{i\Delta m\varphi} d\varphi = \frac{1}{i\Delta m} e^{i\Delta m\varphi}\Big|_0^{2\pi} =$

$$= \frac{1}{i\Delta m}\left(\underset{\overset{\Downarrow}{1}}{e^{2\pi i \Delta m}} - 1\right) = 0$$

Δm has to be 0 !

② $\Delta l = ?$

This is little bit more complex.

Let's first make preparations!

$$x = \cos\theta \Rightarrow dx = -\sin\theta \, d\theta$$

$$\int_{1}^{-1} P_l^m(x)\, P_{l'}^{m'}(x)\, x \, dx$$

To remind, recursion for LP!

$$(l-m+1)\, P_{l+1}^m = (2l+1)\, x\, P_l^m - (l+m)\, P_{l-1}^m$$

The constants are not important, what is important is if integral is 0 or not.

$$C\, P_{l+1}^m = A\, x\, P_l^m - B\, P_{l-1}^m$$

$$\Downarrow$$

$$A\, x\, P_l^m = C\, P_{l+1}^m + B\, P_{l-1}^m$$

$$\Downarrow$$

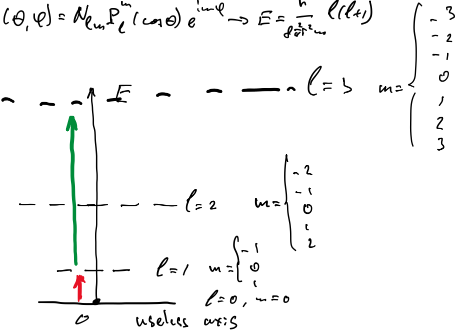
$$\int_{1}^{-1} P_l^m(x)\, P_{l'}^{m'}(x)\, x\, dx = \int \left(P_{l+1}^m + P_{l-1}^m\right) P_{l'}^{m'}\, dx =$$

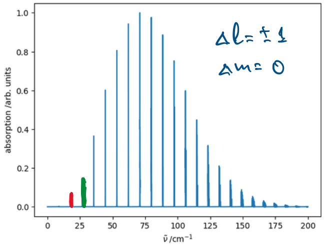
$$= \underbrace{\int P_{l+1}^m P_{l'}^{m'}\, dx}_{\substack{=0 \\ \text{unless } l' = l+1}} + \underbrace{\int P_{l-1}^m P_{l'}^{m'}\, dx}_{\substack{=0 \\ \text{unless } l' = l-1}} \quad \Delta m = 0 \,!$$

$$\Delta l = \pm 1$$

Carbon monoxide:

$$\Psi_{lm}(\theta,\varphi) = N_{lm} P_l^m(\cos\theta)\, e^{im\varphi} \rightarrow E = \frac{h^2}{8\pi^2 r^2 m} l(l+1)$$





$\Delta l = \pm 1$

$\Delta m = 0$