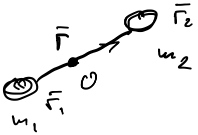
Rotation: concept, wavefunctions and energies

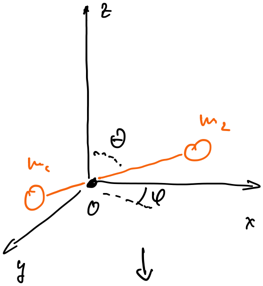
For single particle (single atom) it will predict the properties very nicely, but not for or more:



We place center of mass at O

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

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



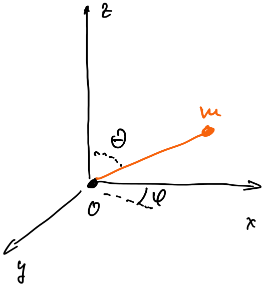
To prepare for SE:

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

$$\Downarrow$$

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

reduced mass



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

SE:

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

0

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

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

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 $\psi = \cos\theta$

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

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

$$\Downarrow$$

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

What about $\sin\theta$?

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

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

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

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

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Solutions !

$$\psi(\theta,\varphi) = \begin{cases} N \\ N\cos\theta \\ N\sin\theta\, e^{\pm i\varphi} \longrightarrow \text{adding phase} \\ \vdots \end{cases}$$

Let's check it !

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

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

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

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

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.

$$\psi(\theta,\varphi) = \begin{cases} N \\ N\cos\theta \\ N\sin\theta e^{i\varphi} \\ \vdots \end{cases}$$

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

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

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

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

$$\left.\begin{array}{l} u = \cos\theta \\ du = -\sin\theta \, d\theta \end{array}\right\} \sin^3\theta = (1-u^2)\,du$$

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

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

That now allow us to introduce

quantum numbers

$\Psi(\theta, \varphi)$

$\sqrt{\frac{1}{4\pi}}$ $\quad l=0 \quad m=0$

$\sqrt{\frac{3}{8\pi}} \sin\theta \, e^{-i\varphi}$ $\quad m=-1$

$\sqrt{\frac{3}{4\pi}} \cos\theta$ $\quad l=1 \quad m=0$

$\sqrt{\frac{3}{8\pi}} \sin\theta \, e^{i\varphi}$ $\quad m=1$

1) l - angular momentum
order of $\underline{P}$

2) m - magnetic number
order of $e^{im\varphi}$

$\sqrt{\frac{15}{32\pi}} \sin^2\theta \, e^{-2i\varphi}$ $\quad m=-2$

$\sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta \, e^{-i\varphi}$ $\quad m=-1$

$\sqrt{\frac{15}{16\pi}} \left(3\cos^2\theta - 1\right)$ $\quad l=2 \quad m=0$

$\sqrt{\frac{15}{8\pi}} \sin\Theta \cos\Theta \; e^{i\varphi}$ $\quad m = 1$

$\sqrt{\frac{15}{32\pi}} \sin^2\Theta \; e^{2i\varphi}$ $\quad m = 2$

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

Legendre polynomial

Little help

$$P_l^0(x) = \frac{1}{2^l\, l!}\frac{d^l}{dx^l}(x^2-1)^l$$

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

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

Recursion:

$$(l+1)\, P_{l+1}^0 = (2l+1)\, P_l^0(x) - l\, P_{l-1}^0(X)$$

Finally:

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

Important property of Ψ's is they are orthogonal!

$$\int \Psi^*_{lm}\, \Psi_{l'm'} = 0 \qquad \begin{matrix} l \neq l' \\ m \neq m' \end{matrix}$$

why?

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

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

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

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

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

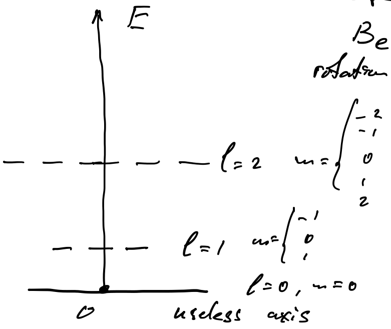
$$\Psi_{20}(\theta,\varphi) = N\left(3\cos^2\theta - 1\right) \rightarrow E_{20} = \frac{h^2}{8\pi^2 r^2 m} 6$$

$$\vdots$$

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

$\underbrace{\qquad}_{B_e}$

rotation constant.


E
$l=2$
$m=\begin{cases}-2\\-1\\0\\1\\2\end{cases}$
$l=1$
$m=\begin{cases}-1\\0\\1\end{cases}$
$l=0,\ m=0$
0
useless axis

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

Selection rules:

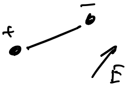
We have to skip here a lot of QM:

$$I_{\psi\to\psi'} \sim \underset{\textcircled{1}}{\frac{\sin^2(\Delta E-\hbar\Omega)}{(\Delta E-\hbar\Omega)^2}} \underset{\textcircled{2}}{\int \psi\,\mu_z\,\psi'}$$

FGR

μ_z is dipole moment

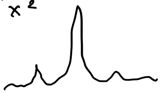
$$\bar{\mu}=q\cdot\bar{r}$$



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 ...

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 $\int e^{i\Delta m\varphi} d\varphi = \int d\varphi \neq 0$

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

$$= \frac{1}{i\Delta m}\Big(\underset{\substack{\downarrow \\ 1}}{e^{2\pi i \Delta m}} - 1\Big) = 0$$

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.

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

$$\Downarrow$$

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

$$\Downarrow$$

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

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

$$\Delta l = \pm 1$$