12/11/2025 Lecture 35: The QM Rigid Rotor

Particle on a sphere of radius R

Coordinate transforms can be used to derive the Laplacian in spherical polar coordinates

$$\boxed{\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}(r) + \frac{1}{r^2}\overbrace{\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right]}^{\hat{L}^2/-\hbar^2}} \quad -(1)$$

We just saw an expression for $\hat{L}^2$ which can be identified in (1).

$$\Rightarrow \boxed{\nabla^2 = \frac{1}{r^2}\frac{\partial^2}{\partial r^2}(r) - \frac{1}{\hbar^2}\frac{\hat{L}^2}{r^2}} \quad -(2)$$

Consider a particle moving freely on the surface of a sphere of radius R. The Schrödinger equ. on the surface is:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(R,\theta,\varphi) = E\,\psi(R,\theta,\varphi) \quad — (3)$$

Since r is restricted to be R, the first term in (1)/(2) drop out and we can leave out mentioning R in ψ.

∴ we get:

$$\frac{\hat{L}^2}{2mR^2}\psi(\theta,\varphi) = E\,\psi(\theta,\varphi) \quad — (4)$$

$$\Rightarrow \left.\begin{array}{l}[\hat{H},\hat{L}^2] = 0 \;\; \& \;\; [\hat{H},\hat{L}_z] = 0 \\ [\hat{L}^2,\hat{L}_z] = 0\end{array}\right\} (5)$$

$\Rightarrow$ l, m_l are good quantum numbers.

$\therefore$ the energy eigenfunctions are the same as eigenfunction of $\hat{L}^2$ & $\hat{L}_z$. Namely, the spherical Harmonics

$$\Rightarrow \psi_{l m_l}(\theta,\varphi) = Y_{l,m_l}(\theta,\varphi) \quad \text{—} ⑥$$

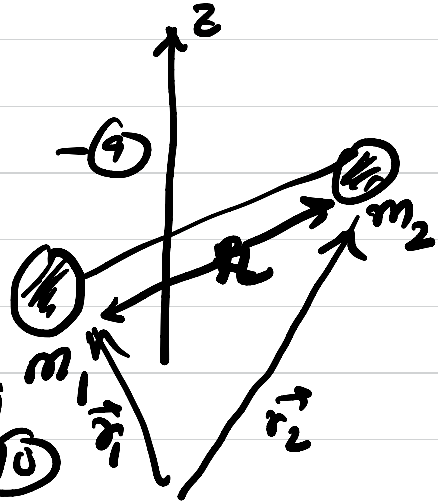
$$E_l = \frac{l(l+1)\hbar^2}{2mR^2} \quad \text{—} ⑦$$

$$\left.\begin{array}{l} l = 0, 1, 2, \cdots \\ m_l = 0, \pm 1, \pm 2, \cdots, \pm l \end{array}\right\} ⑧$$

Since the energy does not depend on m_l, for a given l we have a $(2l+1)$-fold degeneracy in energy.

QM Rigid Rotor:

This is a model used to describe rotational motion of diatomic molecules.



$$\hat{H} = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 \quad \text{— (9)}$$

where $\vec{\nabla}_i = \hat{i}\frac{\partial}{\partial x_i} + \hat{j}\frac{\partial}{\partial y_i} + \hat{k}\frac{\partial}{\partial z_i}$ — (10)

We first perform a coordinate transform.

Let $$\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2} \quad \text{— (11)}$$

→ location of centre of mass

& $$\vec{r} = \vec{r}_2 - \vec{r}_1 \quad \text{— (12)}$$

→ relative coord.

Each component depends only on the corresponding components across the sets of coordinates.

For eg.

$$\left.\begin{aligned} x &= x_2 - x_1 \\ X &= \frac{m_1 x_1 + m_2 x_2}{M} \end{aligned}\right\} \quad (13)$$

$$M = m_1 + m_2 \quad — (14)$$

$$\Rightarrow \frac{\partial}{\partial x_1} = \frac{\partial x}{\partial x_1}\frac{\partial}{\partial x} + \frac{\partial X}{\partial x_1}\frac{\partial}{\partial X}$$

$$= -\frac{\partial}{\partial x} + \frac{m_1}{M}\frac{\partial}{\partial X} \quad — (15)$$

$$\Rightarrow \frac{\partial^2}{\partial x_1^2} = \left(-\frac{\partial}{\partial x} + \frac{m_1}{M}\frac{\partial}{\partial X}\right)^2$$

$$= \frac{\partial^2}{\partial x^2} + \left(\frac{m_1}{M}\right)^2\frac{\partial^2}{\partial X^2} - \frac{2m_1}{M}\frac{\partial^2}{\partial x \partial X} \quad — (16)$$

|||ly

$$\frac{\partial^2}{\partial x_2^2} = \frac{\partial^2}{\partial x^2} + \left(\frac{m_2}{M}\right)^2\frac{\partial^2}{\partial X^2} + \frac{2m_2}{M}\frac{\partial^2}{\partial x \partial X} \quad — (17)$$

$$\Rightarrow \frac{1}{m_1}\frac{\partial^2}{\partial x_1^2} + \frac{1}{m_2}\frac{\partial^2}{\partial x_2^2}$$

$$= \left(\frac{1}{m_1} + \frac{1}{m_2}\right)\frac{\partial^2}{\partial x^2} + \frac{1}{M}\frac{\partial^2}{\partial X^2} \quad — (18)$$

Similar relations are easily derived for the other components as well. Putting all together we get. Laplacians.

$$\hat{H} = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial \vec{R}^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial \vec{r}^2} \quad — (19)$$

where $\mu = \left(\frac{1}{m_1} + \frac{1}{m_2}\right)^{-1} = \frac{m_1 m_2}{M}$ — (20)

is called the reduced mass of the system.

This transformation can always be used to separate the centre of mass motion from any internal (relative) motion.

Note that x & X are independent. $\therefore \left[\frac{\partial}{\partial x}, X\right] = 0$

$$\left[\frac{\partial}{\partial x}, \frac{\partial}{\partial X}\right] = 0, \quad \left[\frac{\partial}{\partial X}, x\right] = 0$$

$\therefore$ The Hamiltonian above is separable into $\vec{r}$-only and $\vec{R}$-only dependent wavefunction

$$\Psi(\vec{r}_1, \vec{r}_2) = \Psi(\vec{r}, \vec{R}) = \chi(\vec{R})\, \psi(\vec{r}) \quad \text{— (21)}$$

$\therefore \quad \hat{H}\Psi = E^{tot}\Psi \implies$

$$\psi(\vec{r})\left(-\frac{\hbar^2}{2M}\right)\frac{\partial^2}{\partial \vec{R}^2}\chi(\vec{R}) + \chi(\vec{R})\left(\frac{-\hbar^2}{2\mu}\right)\frac{\partial^2}{\partial \vec{r}^2}\psi(\vec{r})$$

$$= E^{tot}\chi(\vec{R})\,\psi(\vec{r}) \quad \text{— (22)}$$

$\div$ both sides by $\chi\psi$ gives

$$-\frac{\hbar^2}{2M}\frac{1}{\chi(\vec{R})}\frac{\partial^2}{\partial \vec{R}^2}\chi(\vec{R})$$

$$-\frac{\hbar^2}{2\mu}\frac{1}{\psi(\vec{r})}\frac{\partial^2}{\partial \vec{r}^{\,2}}\psi(\vec{r}) = E^{tot} \quad -(23)$$

Each term on LHS must be a constant. So we get,

$$-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial \vec{R}^{\,2}}\chi(\vec{R}) = E^{CM}\chi(\vec{R}) \quad -(24)$$

&

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial \vec{r}^2}\psi(\vec{r}) = E\,\psi(\vec{r}) \quad -(25)$$

$$\& \quad E^{tot} = E^{CM} + E \quad -(26)$$

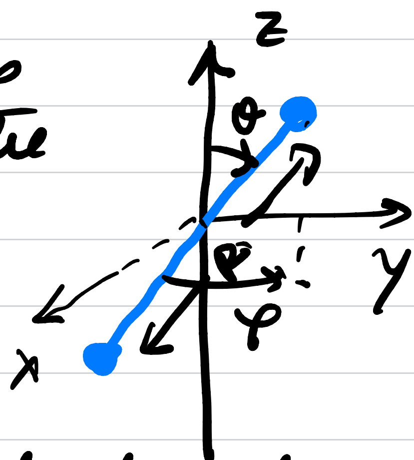
(24) is just the 3-d free particle equation. It describes the states involved in the motion of the rotor as a whole. We will focus on (25)

(26) can be written in spherical polar form as

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2} - \frac{1}{\hbar^2}\frac{\hat{L}^2}{r^2}\right]\psi(r,\theta,\varphi)$$

$$= E\,\psi(r,\theta,\varphi) \quad \text{— (27)}$$

Since the rotor is rigid $(r=R)$, the equation above is only valid for $r=R$.



$\Rightarrow$ radial derivs. drop out & ψ only depends on θ,φ)

$$\Rightarrow \quad \frac{\hat{L}^2}{\underbrace{2\mu R^2}_{I \,=\, \text{moment of inertia}}}\psi(\theta,\varphi) = E\,\psi(\theta,\varphi) \quad \text{— (28)}$$

This is just like free-particle on sphere equation. Therefore, orbital A.M. is conserved and provides the good quantum numbers. Conventionally, these are denoted as J, M_J.

Solution:

$$\left.\begin{aligned} & Y_J^{M_J}(\theta, \varphi) \\ & E_J = \frac{J(J+1)\hbar^2}{2I} \\ & J = 0, 1, 2, \cdots \\ & M_J = 0, \pm 1, \pm 2, \cdots, \pm J \end{aligned}\right\} \quad (29)$$

Once again there is a $(2J+1)$-fold degeneracy of every level.

E_J's are often given in cm^{-1}

$$E_J\,(cm^{-1}) = J(J+1)\left(\frac{h}{8\pi^2 I \underbrace{c}_{\text{in } cm/s}}\right) \quad (30)$$

where $B \equiv \dfrac{h}{8\pi^2 Ic}$ cm^{-1}

is called the rotational constant of the rotor.

Rotational transitions of a diatomic are described by these levels.