Lecture #17 Rigid Rotor Eigenvalues and spectroscopy

I. **Rigid Rotor:2-body Problem**
II. **Rigid Rotor Eigenfunction Problems**

I. Rigid Rotor:2-body Problem

In a plane 2: m_1, m_2, →μ, and r_1, r_2, →r=internal coord (relative)

$$H = \frac{l_z^2}{2I} = -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial q^2} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$$ where $I = m_1 r_1^2 + m_2 r_2^2 = \mu r^2$: (1)

NOTE: The above step is proved by problem 5-30 of Mcquarrie:

$$\frac{1}{r^2}\frac{\partial^2}{\partial q^2} = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) \qquad (2)$$

S.E. $$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 y}{\partial x^2} + \frac{\partial^2 y}{\partial y^2}\right) = Ey \qquad (3)$$

Rigid Rotor S.E. for 2 bodies in 3 dimensions (nonplanar):

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 y}{\partial x^2} + \frac{\partial^2 y}{\partial y^2} + \frac{\partial^2 y}{\partial z^2}\right) = Ey \qquad (4)$$

we want to transfrom this equation (4) into one using spherical coordinates instead of x,y,z.

$$x = r\sin q\,\cos f \quad or \quad r = \sqrt{x^2 + y^2 + z^2}$$

$$y = r\sin q\,\sin f \quad or \quad \cos q = \frac{z}{\sqrt{x^2 + y^2 + z^2}}$$

$$z = r\cos q \quad or \quad \tan f = \frac{y}{x}$$

$$d t = r^2 \sin q dq d f dr \quad = volume \quad element \;\; will\; be\, used \;\; for\; H - like atom$$

For the rigid rotor, since r is constant the dt =sinqdqdf

Note: Int limits® 0£Q£p, 0£f£2p, 0£r£¥

to finally arrive at the **Internal Motion Hamiltonian in Spherical Coordinates:**

$r = r_0$ for rigid (fixed distance between bodies) rotor.

$$H\text{Y} = -\frac{\hbar^2}{2\mu r_0^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\text{Y} = E\text{Y} \qquad (5)$$

$$= -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\text{Y} = E\text{Y}$$

$$= \frac{\hat{L}^2}{2I} = E\text{Y}$$

The eigenfunctions **L²** and hence **H** of this are written as Y instead of Ψ, and are called **Spherical Harmonics:** $\mathbf{Y_l^m} = \Phi(\phi)\Theta(\theta)$**.**

$$Y_0^0 = \frac{1}{(4\pi)^{\frac{1}{2}}}$$

$$Y_1^0 = (\frac{3}{4\pi})^{\frac{1}{2}}\cos\theta$$

$$Y_1^1 = (\frac{3}{8\pi})^{\frac{1}{2}}\sin\theta\, e^{i\phi}$$

$$Y_1^{-1} = (\frac{3}{8\pi})^{\frac{1}{2}}\sin\theta\, e^{-i\phi}$$

$$Y_2^0 = (\frac{5}{16\pi})^{\frac{1}{2}}(3\cos^2\theta - 1)$$

$$Y_2^1 = (\frac{15}{8\pi})^{\frac{1}{2}}\sin\theta\cos\theta\, e^{i\phi}$$

$$Y_2^{-1} = (\frac{15}{8\pi})^{\frac{1}{2}}\sin\theta\cos\theta\, e^{-i\phi}$$

$$Y_2^2 = (\frac{15}{32\pi})^{\frac{1}{2}}\sin^2\theta\, e^{2i\phi}$$

$$Y_2^{-2} = (\frac{15}{32\pi})^{\frac{1}{2}}\sin^2\theta\, e^{-2i\phi}$$

II. Rigid Rotor Eigenfunction Problems

Be able to (1) Prove orthogonality of $\mathbf{Y_l^m}$ (2) normalization of $\mathbf{Y_l^m}$ (3) Expectation values of an observable with $\mathbf{Y_l^m}$ basis functions (4) most probable value of θ and ϕ. (5) and the probability of θ and ϕ in an interval. For $0 \le \theta \le \pi,\ 0 \le \phi \le 2\pi,\ 0 \le r \le \infty$

Use the following two integrals to solve the 3 problems below.

$$\int x\, sinx dx = -xcosx + sinx$$

$$\int x\sin^3 x dx = \frac{3}{4}sinx - \frac{1}{36}\sin 3x - \frac{3}{4}xcosx + \frac{x}{12}\cos 3x$$

1. Prove the normalization of $Y_0^0 = \frac{1}{(4p\ )^{\frac{1}{2}}}$

$$\int_0^{2p}\int_0^{p} Y_0^0 Y_0^0 \sin q dq df = \frac{1}{4p}\int_0^{2p} df \int_0^{p} \sin q dq = \frac{1}{4p} f\Big|_0^{2p} - \cos q\Big|_0^{p} = \frac{1}{4p}(2p\ )(-\cos p - (-\cos 0))$$

$$= \frac{1}{4p}(2p\ )(1+1) = 1$$

2. For *l* =0, m=0, determine the expectation value of θ, which intuitively one would guess as π/2.

$$\langle q \rangle = \int_{f=0}^{2p}\int_{q=0}^{p} Y_0^0 q\, Y_0^0 \sin q\, dq\, dj = \int_{f=0}^{2p}\int_{q=0}^{p} \frac{1}{\sqrt{4p}} q \frac{1}{\sqrt{4p}} \sin q\, dq\, dj = \frac{1}{4p}\int_{f=0}^{2p} dj \int_{q=0}^{p} q \sin q\, dq$$

$$\frac{1}{4p}\int_{f=0}^{2p} dj \int_{q=0}^{p} q \sin q\, dq = \frac{1}{4p}\left[f\Big|_0^{2p} \int_{q=0}^{p} q \sin q\, dq \right] = \frac{1}{4p}(2p\ )\left(\left(-xcosx + sinx\Big|_0^{p}\right)\right) =$$

$$\frac{1}{4p}(2p\ )((-pcosp\ + sinp\ ) - (-0cos0 + sin0)) = \frac{1}{2} - p(-1) = \frac{p}{2}$$

3. Similarly show that for *l* =0, m=0, the expectation value of ϕ is π.

4. For *l* =1, m=0, determine the expectation value of θ..

$$Y_{1,0} = (\frac{3}{4p})^{1/2}(\cos q\ )$$

$$< q > = \int_{f=0}^{f=2p} df \int_{q=0}^{q=p} Y_{1,0}^{*}\, q\ Y_{1,0} \sin q\ dq$$

$$= 2p\, [\frac{3}{4p}\int_0^{p} (\cos^2 q\ )q \sin q dq\ ]$$

$$= \frac{3}{2}\int_0^{p} q(1 - \sin^2 q\ )\sin q dq$$

$$= \frac{3}{2}\int_0^{p} q \sin q - q \sin^3 q dq$$

$$= \frac{3}{2}[\{-q \cos q + \sin q\ \}\Big|_0^{p} - \{-\frac{3}{4} q \cos q + \frac{q}{12}\cos 3q\ \}\Big|_0^{p}\ ]$$

$$= \frac{3}{2}[p\quad - \quad (\frac{3}{4}p - \frac{p}{12})] = \frac{p}{2} radians = 90°$$