Lecture 8
3D Rigid Rotor

- Quiz next Saturday 27/01/2018 $\leftarrow$ starting of the H – atom problem.

Last lecture we saw that for a particle of mass on a ring of radius R,

$$\psi_{m_l}(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_l\phi} \quad ; \quad m_l = 0, \pm 1, \pm 2, \ldots.$$

squared =>independent of direction

and, $E_{m_l} = \dfrac{m_l^2 \hbar^2}{2I}$; $I = mR^2$

$L_z = m_l \hbar$

Both energy and angular mom. are quantized.

$$E = \frac{1}{2I} L_z^2$$

Since, L_z and ϕ are conjugate variables we have:

$$\Delta L_z . \Delta\phi \geq \frac{\hbar}{2}; \qquad \text{Uncertainty principle.}$$

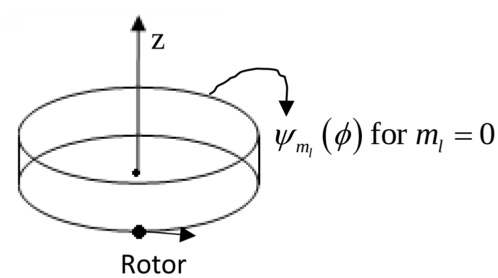
It is important to note that for the quantum state $\psi_{me}(\phi)$ both energy and L_z are known with certainty, i.e.,

$\Delta E = 0$ *and* $\Delta L_z = 0$; because eigenstate of $\hat{H}$ and $\hat{L}_z$.

$\Rightarrow \Delta\phi = \infty$; Complete Uncertainty in angle ϕ.

$\Rightarrow$Consistent with the fact that

$|\psi_{m_l}(\phi)|^2 = \dfrac{1}{2\pi}$; Uniform probability density independent of ϕ.



(Quite similar to what happens for a free particle in 1-dim.)

$$\Delta p_x = 0 \quad \& \quad \Delta x = \infty \quad , \quad |\psi(x)|^2 = |c|^2 \text{ independent of x.}$$

Particle in box case – Zero-point energy is finite since position has to be definite, so Energy cannot be simultaneously definite (zero).

Angular Momentum: ϕ can be indefinite, Energy can be definite (zero).

Armed with this, we can think about the QM of a particle of mass m constrained to be a sphere, where: ϕ: again specifies rotation in a plane about Z - axis & θ: specifies the "plane".

Now, we have to think of, $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$

In analogy, we must also have $E = \frac{1}{2I}L^2$

But now $\hat{L}^2$ (operator) have a term corresponding to the θ degree of freedom also.

Then the quantum state is going to be: $\psi(\theta,\phi)$

But, what is the form of $\hat{L}^2$?

Turns out that, as one might expect, the best coordinates to express the operator $\hat{L}^2$ is the one in the (θ,ϕ) coordinates (given that Radial part is fixed) is:

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

(Note, with θ fixed at $\pi/2$ we get back the $\hat{L}_z^2$ result)

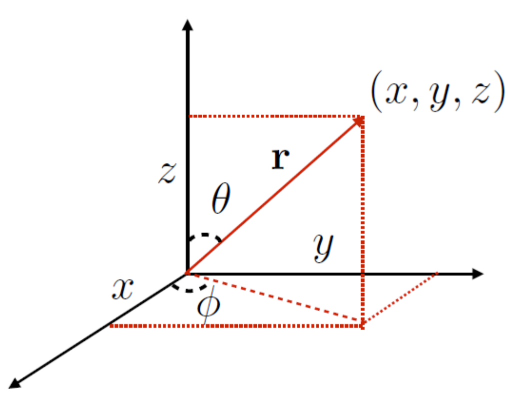
Let us now go on with a more rigorous look into the 3D rigid rotor.

Let us consider a particle confined to move in three dimensions, but on a sphere of radius r. Let there be no external potential acting on the system. The Hamiltonian operator of the system is

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

The boundary condition for this problem is

$$\psi(\theta,\phi) = \phi(\theta,\phi+2\pi) = \phi(\theta+\pi,\phi)$$



Thus, it is convenient to work in spherical polar coordinate system (where θ and ϕ are part of the coordinates) than in cartesian coordinate system. In spherical polar coordinate system:

$$z = r\cos\theta, \quad x = r\sin\theta\cos\phi, \quad y = r\sin\theta\sin\phi$$

where $r = \sqrt{x^2 + y^2 + z^2}$. Also,

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

where

$$\Lambda^2 = \left(\frac{\partial^2}{\partial \theta^2} + \cot\theta\frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right)$$

Here Λ^2, called as Legendrian, has the angular part. The volume element is

$$r^2 dr\, d\theta \sin\theta\, d\phi \ .$$

Note also that,

$$\theta \in [0, \pi], \quad \phi \in [0, 2\pi]$$

As r is fixed for our problem, terms containing the derivatives of the radial parts (i.e. $\partial/\partial r$ or $\partial^2/\partial r^2$) can be dropped from the Hamiltonian operator. Thus,

$$\hat{H} = -\frac{\hbar^2}{2mr^2}\Lambda^2 \ = -\frac{\hbar^2}{2I}\Lambda^2$$

Schrödinger equation for the problem is

$$\begin{aligned} -\frac{\hbar^2}{2I}\Lambda^2\psi(\theta, \phi) &= E\psi(\theta, \phi) \\ \Lambda^2\psi &= \frac{-2IE}{\hbar^2}\psi(\theta, \phi) \end{aligned}$$

Solution for the above equation can be obtained by separation of variables:

$$\psi(\theta, \phi) = S(\theta)T(\phi)$$

Boundary conditions are

$$S(\theta) = S(\theta + \pi)$$

$$T(\phi) = T(\phi + 2\pi)$$

Derivation of the solutions is beyond the scope of this course. What is important for here is to appreciate the features of its solutions. In fact, a part of the solution

$$T_{m_l}(\theta) = \frac{1}{\sqrt{2\pi}} e^{i m_l \phi}, \ \ m_l = 0, \pm 1, \cdots, \pm l, \quad l = 0, 1, \cdots$$

is identical to the wave function of particle in a circle. Note that $2l + 1$ values are possible for the m_l quantum number.