Lecture 9
Recap of Toy problems & Introducing H-atom

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

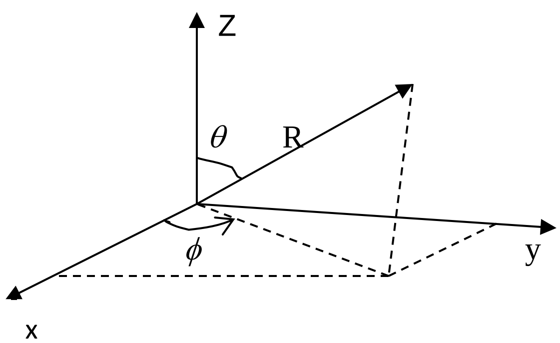
Angular Momentum : ϕ can be indefinite, Energy can be definite (zero).

Armed with this, we can think about the QM of a particle of mass m constrained to be a sphere. Now we have to think of,

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

$$\hat{H} = \frac{1}{2I}\hat{L}^2 \qquad ; \qquad I = \text{moment of inertia}$$

Clearly, quantum state now $\psi(\theta, \phi)$



Also, bound motion so we expect E to be quantized and two quantum numbers

$$\begin{cases} \theta : -\pi, +\pi \leftarrow \\ \phi : \quad 0, 2\pi \end{cases}$$

due to symmetry we only need to consider 0 to π

One quantum number is associated with ϕ : m_l => precession about z-axis.
What is the other one? xy plane rotation (θ), for that,

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

$\Uparrow$

L_z^2 part.

(This is written in spherical polar coordinates)

Thus the Schrödinger equation that we have to solve is :

$$\frac{-\hbar^2}{2I}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial}{\partial\phi^2}\right\}\psi(\theta,\phi)=E\,\psi(\theta,\phi)$$

This is a partial differential equation. The solutions are known,

$\psi(\theta,\phi)\equiv Y_{lm_l}(\theta,\phi)$; Spherical Harmonics.

Separation of variables :

$$\psi(\theta,\phi)\equiv Y_{l m_l}(\theta,\phi) = S(\theta).T(\phi)$$

$$S(\theta)=S(\theta+\pi) \quad \& \quad \underline{T(\phi)=T(\phi+2\pi)}$$

$$T_{m_l}(\phi)=\frac{1}{\sqrt{2\pi}}\exp(i m_l \phi) \quad ; \quad m_l = 0, \pm 1, \pm 2, \dots \pm l, \dots$$

$$l = 0, 1, 2 \dots$$

$S_{l m_l}(\theta)$ = Associated Legendre polynomials.

$$\hat{L}^2 \longleftarrow \hat{L}_z^2 + \hat{L}_x^2 + \hat{L}_y^2$$

$$Y_{lm_l}(\theta,\phi) \;=\; N_{lm_l}\;\underbrace{P_{l|m_l|}(\cos\theta)}_{\Downarrow}\;\; e^{im_l\phi}$$

Polynomial in $\cos\theta$

Normalization Constant. our L_z eigenfunctions

Now, l is the other quantum number apart from m_l .

What one obtains is that the spherical harmonics satisfy :

$$\hat{H}\ Y_{l\ m_l}(\theta,\phi) = \left(\frac{\hbar^2 l(l+1)}{2I}\right)\ Y_{l\ m_l}(\theta,\phi)$$

$$\hat{L}^2 Y_{l\ m_l}(\theta,\phi) = \left[\hbar^2 l(l+1)\right]\ Y_{l\ m_l}(\theta,\phi)$$

$$\hat{L}_Z\ Y_{l\ m_l}(\theta,\phi) = (\hbar\ m_l)\ Y_{l\ m_l}(\theta,\phi)$$

$\therefore$ They are eigenfuctions of $\hat{H}, \hat{L}^2$ *and* $\hat{L}$.

$\Rightarrow \Delta E = 0, \quad \Delta L_Z = 0$ and Square of Ang. Mom. is known with certainty.

* But Y_{lm_l} are not eignfunctions of $\hat{L}_x$ and $\hat{L}_y$.

Also, $l = 0,1,2,....$ (integer)

But $m_l = 0, \pm 1, \pm 2, ..., \pm l \quad i.e, \quad |m_l| \le l$.

These restrictions on quantum numbers have been logically discussed. Restriction on m_l arise to satisfy the condition of simultaneous eigenfunction of $\hat{H}, \hat{L}^2$ *and* $\hat{L}$

Now, note that Energy does not depend on m_l!

$$E_{l\ m_l} = \frac{\hbar^2}{2I} l(l+1) \quad ; \quad \text{independent of } m_l.$$

Why

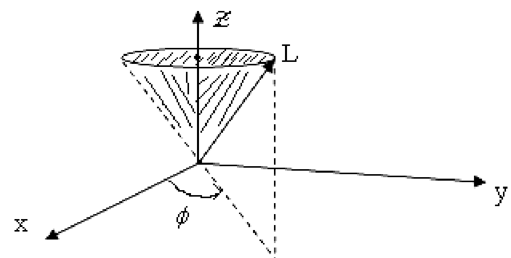
In fact, since $m_l = 0, \pm 1, \pm 2, ..., \pm l$ there is a degeneracy of $(2l+1)$.

For e.g. $E_{10} = E_{1,+1} = E_{1,-1} = \dfrac{\hbar^2}{I}$ (3 fold deg.).

Reason that Energy is independent of m_l is because our choice of Z -axis is arbitrary. We could have chosen L_x or L_y to describe our projections and the system does not care about our convention / choice. Thus, Energy cannot depend on m_l!

Since $Y_{l\,m_l}$ is an eigenfn. of $\hat{H}, \hat{L}^2$ *and* $\hat{L}_Z$ this means we can determine there values simultaneously with arbitrary precision. At the same time we cannot observe the precise values of $\hat{L}_x$ or $\hat{L}_y$!

Again, this has to do with uncertainity principle. Since $\Delta L_Z = 0 \quad \Rightarrow \quad \Delta\phi = \infty$. This, in turn, means that the angular mom. vector can lie anywhere on a cone!



Completely Uncertain

(a) Orbital angular momentum vectors for $l = 1$ and $m_l = 0, \pm 1$. The magnitude of these vectors ($\sqrt{2}\hbar$) are the same, but they orient at different angles from the z axis with different projections (0, $\pm\hbar$) to the z-axis.

(b) Visualizing angular momentum vectors lying on a cone about the z–axis(picture taken from Atkins, Physical Chemistry)

It may be noted that, specifying l and m_l only defines the orientation of the angular momentum vector (and the z component), but it doesn't define x and y component of the angular momentum. Due to this reason, we may visualize the angular momentum vector as some vectors lying on a cone about the z–axis, with unspecified positions (see Figures above.

For a classical rotor, the rotational energy

$$E = \frac{L^2}{2I}$$

where L is the classical angular momentum, and I is the inertia. Comparing this with the quantum mechanical result, we can interpret that the magnitude of the angular momentum of the quantum mechanical oscillator is

$$|\mathbf{L}| = \hbar\sqrt{l\,(l+1)}$$

where $\mathbf{L}$ is the angular momentum vector. Clearly, in quantum mechanics, angular momentum is quantized. l quantum numbers are called angular momentum quantum numbers, as they dictate the angular momentum.

Now,

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

corresponds to the quantum mechanical operator for the z–component of the orbital angular momentum. You can easily prove that Y_{l,m_l}s are eigenfunctions of the $\hat{L}_z$ operator, and the eigenvalue is $m\hbar$:

$$\hat{L}_z Y_{l,m_l} = m\hbar Y_{l,m_l}, \quad m_l = 0, \pm1, \cdots, \pm l$$

Pictorially, we can interpret $m\hbar$ as the projection of the orbital angular momentum on the z–axis, as shown in Figure 7.5a.

Let us take a simple example to illustrate the concept:

Suppose, $\quad l = 1 \;\Rightarrow\; m_l = 0, \pm1$

Clearly, $\quad \psi \rightarrow Y_{10}(\theta,\phi), Y_{1,+1}(\theta,\phi), Y_{1,-1}(\theta,\phi)$

$N_{10}P_{10}(\cos\theta) \qquad N_{1,1}\;P_{11}(\cos\theta)\,l^{i\phi} \qquad N_{1,1}\;P_{1,1}(\cos\theta)\,e^{-i\phi}$

Also, $\quad \hat{H}\;Y_{1,\substack{0\\ \pm1\}}}(\theta,\phi) = \left(\frac{\hbar^2}{I}\right)\;Y_{1,\substack{0\\ \pm1\}}}(\theta,\phi)$

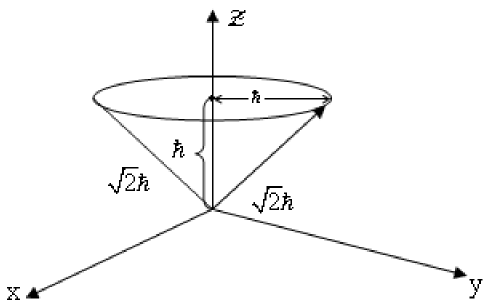
and $\quad \hat{L}^{\,2}\,Y_{1,\substack{0\\ \pm1\}}}(\theta,\phi) = 2\hbar^2\;Y_{1,\substack{0\\ \pm1\}}}(\theta,\phi)$

But, $\hat{L}_z \; Y_{10}(\theta,\phi) = 0.Y_{10}(\theta,\phi)$

$$\hat{L}_z \; Y_{1,\pm 1}(\theta,\phi) = (\pm\hbar) Y_{1,\pm 1}(\theta,\phi)$$

Since, $\hat{L}^2$ has eigenvalue $2\hbar^2$, the magnitude,

$|L| = \sqrt{2}\hbar$; Since $|L|$ > max. value of L_z (projection)



$\Rightarrow$ L and L_z cannot in same direction!

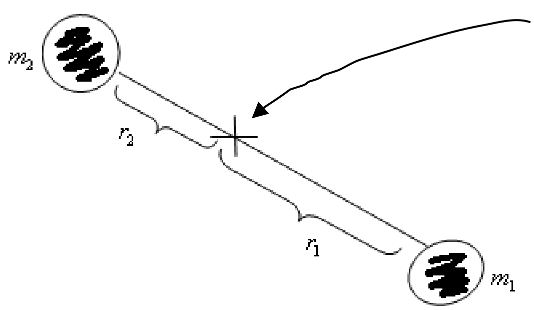
$$L_x^2 + L_y^2 + L_z^2 = L^2 = 2\hbar^2$$

$$\therefore \; L_x^2 + L_y^2 = \hbar^2$$

* Projected Motion in x-y plane is circular with Radius $\hbar$.

Classically we can interpret this as ang. mom. vector precessing about Z -axis.

Now, for any 2-particle system undergoing rotational motion,



$$m_1 r_1 = m_2 r_2$$

moment of inertia, $I = \mu r^2$; $r = r_1 + r_2$

and $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$; reduced mass

$\therefore$ Think of a particle of mass μ on a sphere of radius r !
The C.M. is associated with translational motion of a body of mass $(m_1 + m_2)$.

* Thus, what we have just discussed can be applied to diatomic molecules and the Hydrogen atom.

Now, let us discuss the Hydrogen atom. Hydrogen atom is an exactly solvable problem in Quantum Mechanics. The solutions of H atoms are the basis for us to solve many electron atoms and molecules.
We now have to deal with electronic motion which is much faster as compared to the nuclear.

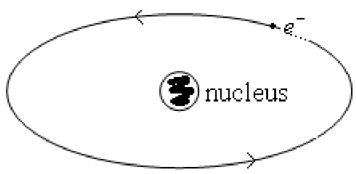
Also, the H-atom spectrum was one of the prime motivation for Quant. Mech. From the point of view of chemistry, the H-atoms (the lightest ones around in a molecule) are crucial in chemical reactions—including our vision process: The initial process of our vision is triggered by a proton motion in about 6 fs timescale !!

The emission spectrum of H, was noted as early as 1885 (by Balmer), 1890 (Rydberg) : Long before QM (~1925) !

Discrete spectrum.

Bohr, introduced the concept of quantization, Energy in terms of a integer.

(Rutherford, before that, argued the ‘planetary model’)



Problems with classical Interpretation.

Bohr : Certain orbits stable.

Why QM provides the answer.

Schrödinger was the first to solve. $\hat{H}\psi = E\psi$

Only case where we can solve the Schrödinger equation exactly.

As soon as we consider He atom with ($2e^-$ + nucleus), we have to resort to approximations / computations.

The Hamiltonian for – H-atom can be written as:

$$H = K.E \text{ of } e^- + K.E \text{ of nucleus} + \overbrace{\text{Coulomb attraction.}}^{\text{Potential}}$$

$$\frac{1}{2_{m_e}} p_e^2 \qquad\qquad \frac{1}{2_{m_N}} p_N^2 \qquad\qquad \frac{-e^2}{4\pi\varepsilon_0 r}$$

$$r^2 = (x_N - x_e)^2 + (y_N - y_e)^2 + (Z_N - Z_e)^2$$

In QM approach:

$$\hat{H} = \frac{1}{2m_e}\hat{p}_e^2 + \frac{1}{2m_N}\hat{p}_N^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

$$\hat{p}_e = -i\hbar\left(\hat{i}\,\frac{\partial}{\partial x_e} + \hat{j}\,\frac{\partial}{\partial y_e} + \hat{k}\,\frac{\partial}{\partial z_e}\right)$$

Similarly,

$$\hat{p}_N = -i\hbar\left(\hat{i}\,\frac{\partial}{\partial x_N} + \hat{j}\,\frac{\partial}{\partial y_N} + \hat{k}\,\frac{\partial}{\partial z_N}\right)$$

$$\therefore\ \hat{p}_e^2 \to -\hbar^2\left(\frac{\partial}{\partial x_e^2} + \frac{\partial}{\partial y_e^2} + \frac{\partial}{\partial z_e^2}\right) \equiv -\hbar^2\ \underset{\Uparrow}{\nabla_e^2}$$

“Laplacian”

As usual, we are interested in the internal is electronic motion and not the translation part of the atom.

$\therefore$ let’s go to center of mass and relative co-ordinates

$$\Downarrow$$

$$\boxed{r = r_N - r_e}$$

Then motion (internal) described by reduced mass μ,

$$\mu = \frac{m_e m_N}{m_e + m_N} \approx m_e$$

Then,

$$\boxed{\hat{H}_{relative} = \frac{-\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\ \varepsilon_0 r}}$$

We will be discussing the solution to the Schrödinger equation for the hydrogen atom.
We will solve $\hat{H}\psi = E\psi$ to get quantized energies as:

$$E_n = \frac{-13.6}{n^2}eV$$