LECTURE #10

WE HAVE SHOWN THAT THE STATES OF THE HYDROGEN ATOM CAN BE SPECIFIED WITH QUANTUM NUMBERS.

(1) n: PRINCIPAL QUANTUM NUMBER : $n = 1, 2, 3, \ldots$
↳ THIS SPECIFIES THE ENERGY LEVEL

(2) ℓ: AZIMUTHAL QUANTUM NUMBER: $\ell \leq n-1$

NOMENCLATURE:

$\ell = 0 \rightarrow$ "s" $\rightarrow$ SHARP
$\ell = 1 \rightarrow$ "p" $\rightarrow$ PRINCIPAL
$\ell = 2 \rightarrow$ "d" $\rightarrow$ DIFFUSE
$\ell = 3 \rightarrow$ "f" $\rightarrow$ FUNDAMENTAL
$\ell = 4 \rightarrow$ "g"
$\ell = 5 \rightarrow$ "h"
$\vdots$

(3) m_ℓ: MAGNETIC QUANTUM NUMBER, $|m_\ell| \leq \ell$

WHAT DO ℓ AND m_ℓ REPRESENT PHYSICALLY?

RECALL: CLASSICAL NOTION OF ANGULAR MOMENTUM

$$\vec{L} = \vec{r} \times \vec{p} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$\therefore L_x = y p_z - z p_y, \quad L_y = z p_x - x p_z, \quad L_z = x p_y - y p_x$$

$\Rightarrow$ QUANTUM MECHANICALLY, WE CAN DEFINE ANGULAR MOMENTUM OPERATORS.

$$L_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right), \quad L_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right), \quad L_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

CONSIDER THE COMMUTATION RELATION FOR L_x, L_y:

$$[L_x, L_y] = [yp_z - zp_y, \; zp_x - xp_z]$$

$$= [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z]$$

FROM THE CANONICAL COMMUTATION RELATIONS
$\left[\text{i.e., } [r_i, p_j] = -[p_i, r_j] = i\hbar\delta_{ij}, \; [r_i, r_j] = [p_i, p_j] = 0\right]$

WE KNOW THAT THE ONLY OPERATORS THAT FAIL TO COMMUTE ARE x WITH p_x, y WITH p_y, AND z WITH p_z.

$$\therefore [L_x, L_y] = yp_x[p_z, z] + xp_y[z, p_z] = i\hbar(xp_y - yp_x) = i\hbar L_z$$

$\Rightarrow$ <u>FUNDAMENTAL COMMUTATION RELATIONS FOR ANGULAR MOMENTUM</u>:

$$[L_x, L_y] = i\hbar L_z \; ; \; [L_y, L_z] = i\hbar L_x \; ; \; [L_z, L_x] = i\hbar L_y$$

<u>NOTE</u>: L_x, L_y, AND L_z ARE INCOMPATIBLE OBSERVABLES

HOWEVER, CONSIDER $L^2 = L_x^2 + L_y^2 + L_z^2$

$$\begin{aligned}
[L^2, L_x] &= [L_x^2, L_x] + [L_y^2, L_x] + [L_z^2, L_x] \\
&= L_y[L_y, L_x] + [L_y, L_x]L_y + L_z[L_z, L_x] + [L_z, L_x]L_z \\
&= L_y(-i\hbar L_z) + (-i\hbar L_z)L_y + L_z(i\hbar L_y) + (i\hbar L_y)L_z \\
&= 0
\end{aligned}$$

SIMILARLY, $[L^2, L_y] = 0$ AND $[L^2, L_z] = 0$

OR MORE COMPACTLY, $[L^2, \vec{L}] = 0$

i.e., L^2 IS COMPATIBLE WITH EACH COMPONENT OF $\vec{L}$

$\Rightarrow$ WE CAN FIND SIMULTANEOUS EIGENSTATES OF L^2 AND L_z:

$$L^2 f = \lambda f \quad \text{AND} \quad L_z f = \mu f$$

INTRODUCE <u>ANGULAR MOMENTUM LADDER OPERATOR</u>:

$$L_\pm = L_x \pm i L_y$$

$$[L_z, L_\pm] = [L_z, L_x] \pm i [L_z, L_y]$$
$$= i\hbar L_y \pm i(-i\hbar L_x) = \pm\hbar (L_x \pm i L_y) = \pm \hbar L_\pm$$

$$\therefore \quad [L_z, L_\pm] = \pm \hbar L_\pm$$

OF COURSE, $[L^2, L_\pm] = 0$

$$L^2 (L_\pm f) = L_\pm (L^2 f) = L_\pm (\lambda f) = \lambda (L_\pm f)$$

$\Rightarrow$ IF f IS AN EIGENFUNCTION OF L^2 AND L_z, THEN SO IS $L_\pm f$ WITH THE SAME EIGENVALUE λ.

$$\therefore \quad L_z (L_\pm f) = (L_z L_\pm - L_\pm L_z) f + L_\pm L_z f = \pm \hbar L_\pm f + L_\pm (\mu f)$$
$$= (\mu \pm \hbar)(L_\pm f)$$

$\Rightarrow$ $L_\pm f$ IS AN EIGENFUNCTION OF L_z WITH NEW EIGENVALUE $\mu \pm \hbar$

L_+ IS A "RAISING OPERATOR" THAT INCREASES THE EIGENVALUE OF L_z BY $\hbar$
L_- IS A "LOWERING OPERATOR" THAT DECREASES THE EIGENVALUE OF L_z BY $\hbar$

NOTE: WE CANNOT RAISE L_z INDEFINITELY SINCE EVENTUALLY THE Z-COMPONENT WOULD EXCEED THE TOTAL

$\therefore$ THERE MUST EXIST A "TOP RUNG" SUCH THAT

$$L_+ f_+ = 0$$

LET $\hbar l$ BE THE EIGENVALUE OF L_z AT THE TOP RUNG:

$$\therefore \quad L_z f_+ = \hbar l f_+ \; ; \; L^2 f_+ = \lambda f_+$$

NOTE: $L_\pm L_\mp = (L_x \pm i L_y)(L_x \mp i L_y) = L_x^2 + L_y^2 \mp i(L_x L_y - L_y L_x)$
$= L^2 - L_z^2 \mp i(i\hbar L_z)$

$$\Rightarrow L^2 = L_\pm L_\mp + L_z^2 \mp \hbar L_z$$

$$\therefore L^2 f_+ = (L_- L_+ + L_z^2 + \hbar L_z) f_+ = (0 + \hbar^2 l^2 + \hbar^2 l) f_+ = \lambda f_+$$

$$\Rightarrow \lambda = \hbar^2 l(l+1)$$

SIMILARLY, THERE MUST EXIST A "BOTTOM RUNG" SUCH THAT:

$$L_- f_b = 0$$

LET $\hbar \bar{l}$ BE THE EIGENVALUE OF L_z AT THE BOTTOM RUNG.

$$L_z f_b = \hbar \bar{l} f_b \quad ; \quad L^2 f_b = \lambda f_b$$

$$\therefore L^2 f_b = (L_+ L_- + L_z^2 - \hbar L_z) f_b = (0 + \hbar^2 \bar{l}^2 - \hbar^2 \bar{l}) f_b = \lambda f_b$$

$$\Rightarrow \lambda = \hbar^2 \bar{l}(\bar{l} - 1)$$

$$\therefore \quad l(l+1) = \bar{l}(\bar{l}-1)$$

$\Rightarrow \quad \bar{l} = l + 1$ (WHICH IS ABSURD SINCE THE BOTTOM RUNG WOULD BE HIGHER THAN THE TOP RUNG)

OR $\quad \bar{l} = -l$

$\Rightarrow$ THE EIGENVALUES OF L_z ARE $m\hbar$ WHERE m RUNS FROM $-l$ TO $+l$ IN N INTEGER STEPS

$\therefore \quad l = -l + N \Rightarrow l = \frac{N}{2} \Rightarrow l$ MUST BE AN INTEGER OF HALF INTEGER

IN SUMMARY, $\boxed{L^2 f_l^m = \hbar^2 l(l+1) f_l^m \; ; \; L_z f_l^m = \hbar m f_l^m}$

WHERE $l = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots \; ; \; m = \underbrace{-l, -l+1, \ldots, l-1, l}_{2l+1 \text{ RUNGS ON THE LADDER}}$

TO DETERMINE THE EIGENFUNCTIONS, WE NEED TO EXPRESS L_z AND L^2 IN SPHERICAL COORDINATES:

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

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

* THIS IS PRECISELY THE ANGULAR EQUATION!

$$L_z f_\ell^m = \frac{\hbar}{i}\frac{\partial}{\partial\phi} f_\ell^m = \hbar m f_\ell^m$$

* THIS IS EQUIVALENT TO THE Φ EQUATION!

$\Rightarrow f_\ell^m = Y_\ell^m(\theta, \phi) \rightarrow$ THE SPHERICAL HARMONICS ARE THE EIGENFUNCTIONS OF L^2 AND L_z

$\therefore$ WHEN WE SOLVED THE SCH. EQ. FOR SPHERICALLY SYMMETRIC POTENTIALS BY SEPARATION OF VARIABLES, WE INADVERTENTLY CONSTRUCTED SIMULTANEOUS EIGENFUNCTIONS OF THREE COMMUTING OPERATORS H, L^2, AND L_z:

$$H\psi = E\psi \quad , \quad L^2\psi = \hbar^2\ell(\ell+1)\psi \quad , \quad L_z\psi = \hbar m\psi$$

<u>NOTE</u>: FROM SEPARATION OF VARIABLES, WE FOUND THAT ℓ (AND ALSO m) COULD ONLY BE INTEGER VALUED. HOWEVER, THE LADDER OPERATORS YIELDED HALF-INTEGER VALUES. WHAT IS THE PHYSICAL SIGNIFICANCE OF THE HALF-INTEGER VALUES?