Lecture 5

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- Associated Legendre Functions
  - For $l = 0, 1, 2, 3\cdots$

$$\left[(1-z^2)\frac{d^2}{dz^2} - 2z\frac{d}{dz} + l(l+1) - \frac{m^2}{1-z^2}\right]P(z)0$$

  - With:

$$P_l^m(z) = P_l^{-m}(z) = (1-z^2)^{m/2}\frac{d^m}{dz^m}P_l(z)$$

  - Since $P_l(z)$ is an l-th order polynomial, then $P_l^m(z)$ vanishes if $m > l$
  - Properties of $P_l^m(z)$:
    * $P_l^m(z) = 0$ if $|m| > l$
    * $P_l^m(z) = P_l^{-m}(z)$
    * $P_l^m(\pm 1) = 0$ for $m \neq 0$
    * $P_l^m(-z) = (-1)^{l-m}P_l^m(z)$
    * $\displaystyle\int_{-1}^{1} P_l^m(z)P_q^m(z)\,dz = \frac{2}{2l+2}\cdot\frac{(l+m)!}{(l-m)!}\delta_{lq}$
  - We can obtain our $\Theta(\theta)$ function as:

$$\Theta_l^m(\theta) = (-1)^m\frac{(2l+1)}{2}\frac{(l-m)!}{(l+m)!}P_l^k(\cos(\theta)), \quad m \geq 0$$

  And:

$$\Theta_l^{-m}(\theta) = (-1)^m\Theta_l^m(\theta)$$

– Here, we arrive at a point where the associated Legendre Functions are needed:

$$P_o^o = 1$$
$$P_1^o = \cos(\theta)$$
$$P_1^1 = \sin(\theta)$$
$$P_2^o = \frac{1}{2}(3\cos^3(\theta) - 1)$$
$$P_3^o = \frac{1}{2}(5\cos^5(\theta) - 3\cos(\theta))$$

– Spherical Harmonics

$$Y_l^m(\theta, \phi) = (-1)^{(m+|m|)/2}\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}P_l^m(\cos(\theta))e^{im\phi}$$
$$Y_l^m(\theta, \phi) = (-1)(Y_l^m(\theta, \phi))^*$$

Our first few values may be written as:

$$Y_o^o(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$$
$$Y_1^o(\theta, \phi) = \sqrt{\frac{3}{4\pi}}\cos(\theta)$$
$$Y_1^{\pm 1}(\theta, \phi) = \mp\sqrt{\frac{3}{8\pi}}\sin(\theta)e^{\pm i\phi}$$

– Important Properties:

* Orthonormality:

$$\langle l_1 m_1 | l_2 m_2 \rangle = \delta_{l_1 l_2}\delta_{m_1 m_2}$$

* Completeness:

$$\psi(\theta, \phi) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} C_{lm} Y_l^m(\theta, \phi)$$
$$C_{lm} = \langle lm | \psi \rangle = \int_0^{2\pi}\int_0^{\pi} (Y_l^m(\theta, \phi))^* \psi(\theta, \phi)\, d\Omega$$

* Parity:

$$Y_l^m(\pi - \theta, \phi + \pi) = (-1)^l Y_l^m(\theta, \phi)$$

- The Radial Component

- We may consider a general case:

$$R_n(\rho) = \rho^l H(\rho) e^{-\gamma\rho}$$

  * Where $\rho = r/a$ with r as the radial distance and a as some scaling factor
  * Furthermore, we have:

$$\gamma^2 = \frac{E}{\left(\frac{\hbar^2}{2\mu a^2}\right)} \Rightarrow E_n = -\frac{1}{2n^2}\left(\frac{Ze^2}{4\pi\varepsilon_o}\right)^2 \frac{\mu}{\hbar^2}$$

  * Our constraints then become:

$$n = 1, 2, \cdots, \infty$$
$$l = 0, 1, \cdots, n-1$$
$$m = -l, -l+1, \cdots, l-1, l$$

- Hydrogen Energies and Spectrum
  - The principal quantum number, n, is also called the shell number
  - We may observe that, as $n \to \infty$ we find the ionization limit
    * Note, E does not depend on m
  - For an electron (with a rest energy of 511[keV]), we may find:

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

  - The Bohr Radius becomes:

$$a_o = \frac{4\pi\varepsilon_o\hbar^2}{m_e e^2}$$

  - We may write the energy scale as:

$$E_n = -\frac{1}{2n^2}\left(\frac{e^2}{4\pi\varepsilon_o a_o}\right)$$

  - Noteworthy Features:
    * Infinite number of bound states since the Coulomb potential falls of slowly for $r \to \infty$ (finite square well in 3D has only a finite number of bound states)
    * We compute the degeneracy of E_n by counting up all possible values:

$$\sum_{l=0}^{n-1}(2l+1) = 2\sum_{l=0}^{n-1} l + \sum_{l=0}^{n-1} 1$$
$$\sum_{l=0}^{n-1}(2l+1) = n(n-1) + n$$

$$\sum_{l=0}^{n-1}(2l+1) = n^2$$

- If one includes the spin of the e^- atom, the total degeneracy is $2n^2$
- m degeneracy is a result of spherical symmetry, and is removed if an electric field or magnetic field is applied
- l degeneracy is a result of the $1/r$ potential and is removed if this changes
- The energies of emitted or absorbed light can be obtained as:

$$E_{photon} = \Delta E_{fi} = |E_f - E_i|$$

$$|E_f - E_i| = \frac{1}{2}(m_e c^2)\left(\frac{e^2}{4\pi\varepsilon_o\hbar c}\right)^2 \left|\frac{1}{n_i^2} - \frac{1}{n_f^2}\right|$$

- Furthermore, we know:

$$E_{photon} = \hbar\omega = hv = \frac{hc}{\lambda}$$

- We may thus conclude:

$$\frac{1}{\lambda} = \frac{m_e}{4\pi\hbar^3 c}\left(\frac{e^2}{4\pi\varepsilon_o}\right)^2 \left|\frac{1}{n_i^2} - \frac{1}{n_f^2}\right|$$

- Not all transitions are allowed in the hydrogen atom; transitions require a non-zero value of $\langle n_f l_f m_f | V_{int} | n_i l_i m_i \rangle$
- For electromagnetic interactions, the selection rules, which follow from conservation of angular momentum, are:

$$\Delta l = l_f - l_i = \pm 1$$

$$\Delta m = m_f - m_i = 0, \pm 1$$

- The Radial Wave Functions
  - Using:

$$a = \frac{4\pi\varepsilon_o\hbar^2}{m_e Z e^2} = \frac{a_o}{Z}$$

$$\gamma = \frac{1}{n}$$

$$\rho = \frac{r}{a} = \frac{Zr}{a_o} \Rightarrow R_{nl}(r) = \left(\frac{Zr}{a_o}\right)^l e^{-Zr/na_o} H\left(\frac{Zr}{a_o}\right)$$

- The Overall Hydrogen Wave Function

$$|nlm\rangle = \psi_{nlm}(r,\theta,\phi) = R_{nl}(r) Y_l^m(\theta,\phi)$$

– We then establish the following relationships:

$$H\left|nlm\right\rangle = -\frac{13.6}{n^2}\left|nlm\right\rangle$$
$$\vec{L}^2\left|nlm\right\rangle = l(l+1)\hbar^2\left|nlm\right\rangle$$
$$L_z\left|nlm\right\rangle = m\hbar\left|nlm\right\rangle$$