Lecture 3 Summary

Classically the electron Kinetic Energy can be written as $T = \frac{p_{rad}^2}{2m} + \frac{p_\perp^2}{2m}$, where p_{rad} is the radial component and $p_\perp$ is the perpendicular to $\vec{r}$ component of momentum. The total kinetic energy is made up of a radial part and a rotational part. This becomes an operator in quantum mechanics: $T = \frac{p_{rad}^2}{2m} + \frac{L^2}{2mr^2}$. Comparing to the Schrödinger equation separated into radial and angular pieces we see that the angular momentum squared operator is: $L^2 = \frac{-\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{-\hbar^2}{\sin\theta}\frac{\partial^2}{\partial\phi^2}$. The angular equation part of the Schrödinger equation for the Hydrogen atom can be written as an eigenvalue problem: $L^2 Y = \hbar^2 \alpha Y$, with eigenvalue $\hbar^2\alpha$ and eigenfunction Y.

The angular equation, after introducing the separation constant α, becomes: $\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right) + \frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2} = -\alpha\sin^2\theta\, Y(\theta,\phi)$. Now separate variables again using $Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$ and a separation constant m^2. This yields two 2nd-order linear ordinary differential equations:

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\,\frac{d\Theta(\theta)}{d\theta}\right) + \ell(\ell+1)\sin^2\theta\,\Theta(\theta) = m^2\Theta(\theta)$$

And $$\frac{d^2\Phi(\phi)}{d\phi^2} = -m^2\Phi(\phi)$$

The latter equation has solutions of the form $\Phi(\phi) = e^{im\phi}$, where m is equal to zero or a positive or negative integer. The correct argument to show that m can take on only positive or negative integers, or zero, will come later when we study the angular momentum ladder operators.

The Θ equation is simplified with the change of variables $x = \cos\theta$ and $y(x) = \Theta(\theta)$ to yield the associated Legendre differential equation:

$$(1-x^2)\frac{d^2y}{dx^2} - 2x\frac{dy}{dx} + \left[\alpha - \frac{m^2}{1-x^2}\right]y = 0$$

From a series solution ansatz one finds that the infinite series must be terminated to keep the solution finite at $x = \pm 1$ ($\theta = 0, \pi$). The resulting general solution is the associated Legendre function $P_\ell^m(x)$. However to recover this finite solution it is required that $\alpha = \ell(\ell+1)$, where ℓ is either zero or a positive integer. One finds from inspection of the associated Legendre function that is zero unless $\ell \ge |m|$. Another solution to this equation is discarded because it diverges at $x = \pm 1$ ($\theta = 0, \pi$) no matter what is done (see Griffiths [4.4]).

The final result for the original angular partial differential equation is the 'spherical harmonic':

$$Y_\ell^m(\theta,\phi) = \varepsilon\sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}}e^{im\phi}P_\ell^m(\cos\theta)\text{, where } \varepsilon = \begin{cases}(-1)^m & m \geq 0 \\ 1 & m \leq 0\end{cases},$$

where $\ell = 0,1,2,3,\ldots$ and $\ell \geq |m|$. The spherical harmonics are orthonormal in angle-space:

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \, Y_\ell^{m*}(\theta,\phi) \, Y_{\ell'}^{m'}(\theta,\phi) = \delta_{\ell\ell'}\delta_{mm'}$$

In other words, the inner product of these two functions on the unit sphere is either zero (if either of the two indices ℓ, ℓ' or m, m' is different), or equal to 1 when they are the same ($\ell = \ell'$ and $m = m'$).