Quantum Mechanics

- **Brief review of hydrogen atom**

— The time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]+V(r)\psi=E\psi$$

- This is separable. We can write $\psi(r,\theta,\phi)=R(r)Y(\theta,\phi)$

+ Then we get

$$\frac{-\hbar^2}{2mr}\frac{\partial^2}{\partial r^2}(rR)+(V(r)-E)R=\frac{-\hbar^2}{2m}\frac{l(l+1)}{r^2}R$$

+ The $l(l+1)$ is the eigenvalue of the angular equation. $l=0,1,2,\dots$ is a non-negative integer (more later)

- If we re-write in terms of $u(r)=rR(r)$,

$$\frac{-\hbar^2}{2m}\frac{d^2u}{dr^2}+V_{eff}(r)\,u=Eu$$

+ Effective Potential $V_{eff}(r)=V(r)+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$ ← centrifugal term

+ For hydrogen $V(r)=\frac{-1}{4\pi\epsilon_0}\frac{e^2}{r}$ = Coulomb potential

— The Solution for hydrogen

- Look at the asymptotic behavior $(r\to\infty)$

$$\frac{d^2u}{dr^2}\approx\frac{-2mE}{\hbar^2}u \Rightarrow u\approx Ae^{-r/b}+Be^{+r/b}$$

We keep only the dying exponential for normalizability

- We use a power series (Frobenius) method for the full solution

+ $u(r)\equiv v(r)\exp\left[-\sqrt{-2mE}\,r/\hbar\right]$

+ Then

$$\frac{d^2v}{dr^2}-\frac{2}{\hbar}\sqrt{-2mE}\frac{dv}{dr}+\frac{e^2}{4\pi\epsilon_0}\frac{2m}{\hbar^2}\frac{v}{r}-\frac{l(l+1)}{r^2}v=0$$

(can work out)

+ A guess $v(r) = \sum_{p=0}^{\infty} A_p r^p$ gives

$$\sum_p \left[p(p+1) A_p r^{p-2} - \frac{2}{\hbar}\sqrt{-2mE}\, p A_p r^{p-1} + \frac{e^2}{4\pi\epsilon_0}\left(\frac{2m}{\hbar^2}\right) A_p r^{p-1} - l(l+1) A_p r^{p-2} \right] = 0$$

- How do we find the series?
  + Each power of r must vanish separately for solution at all r

So $$-l(l+1) A_0 r^{-2} = 0 \Rightarrow A_0 = 0$$

$$\left[\left(\frac{e^2}{4\pi\epsilon_0}\right)\left(\frac{2m}{\hbar^2}\right) A_0 - l(l+1) A_1\right] r^{-1} = 0 \Rightarrow \begin{array}{l} l=0 \\ \text{or } A_1 = 0 \end{array}$$

$$\left[\left(p(p+1) - l(l+1)\right) A_{p+1} + \left(\left(\frac{e^2}{4\pi\epsilon_0}\right)\left(\frac{2m}{\hbar^2}\right) - \frac{2}{\hbar}\sqrt{-2mE}\, p\right) A_p\right] r^{p-1} = 0, \quad p \geq 1.$$

  + The last equation means $A_{p=l} = 0$. Then every $A_{p<l} = 0$ also.
  + Furthermore, $v(r)$ must have a finite # of terms to avoid messing up the asymptotic behavior. $\Rightarrow$ there must be some integer n such that $A_{p \geq n} = 0$. That requires

$$\frac{2}{\hbar}\sqrt{-2mE}\, n = \left(\frac{e^2}{4\pi\epsilon_0}\right)\left(\frac{2m}{\hbar^2}\right) \Rightarrow E = -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{m}{2\hbar^2} \frac{1}{n^2}$$

  + Therefore

$$v(r) = A_{l+1} r^{l+1} + \cdots + A_n r^n$$

- The overall wavefunction takes the form

$$\psi_{nlm}(\vec{x}) = \frac{v(r)}{r} e^{-r/na_0} Y_l^m(\theta, \phi)$$

$$a_0 = \left(\frac{4\pi\epsilon_0}{e^2}\right)\frac{\hbar^2}{m} = \text{Bohr radius} = \text{"size" of hydrogen}$$

$$E = -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{m}{2\hbar^2}\frac{1}{n^2} = -\frac{(13.6\,\text{eV})}{n^2}$$

$n = 1, 2, 3, \ldots$ = principal quantum #

$l = 0, 1, \ldots, n-1$

$m = -l, -l+1, \ldots, l-1, l$

See specific wavefunctions in the text