Quantum Physics 1
Class 23

Class 23

Hydrogen Atom

Last time:

Consider central force problem:

$$\hat{H} = \frac{\hat{p}^2}{2M_0} + V(r)$$

$$\Rightarrow \left(\frac{\hat{p}_r^2}{2M_0} + \frac{\hat{L}^2}{2M_0 r^2}\right)\psi(r,\theta,\phi) = (E - V(r))\psi(r,\theta,\phi)$$

where $\psi(r,\theta,\phi) = R(r)\underbrace{Y_{\ell m}(\theta,\phi)}_{\text{angular part}}$

$$\left.\begin{aligned} \hat{L}^2 Y_{\ell,m}(\theta,\phi) &= \ell(\ell+1)\hbar^2 Y_{\ell m}(\theta,\phi) \\ \hat{L}_z^2 Y_{\ell,m}(\theta,\phi) &= m^2\hbar^2 Y_{\ell,m}(\theta,\phi) \\ L_z \Phi(\phi) &= m\hbar\,\Phi(\phi) \end{aligned}\right\}$$

Radial part:

$$\left(\frac{\hat{p}_r^2}{2M_0} + \underbrace{\frac{\ell(\ell+1)\hbar^2}{2M_0 r^2}}_{\hat{L}^2}\right)R(r) = [E - V(r)]R(r)$$

Now consider the hydrogen-like atoms:

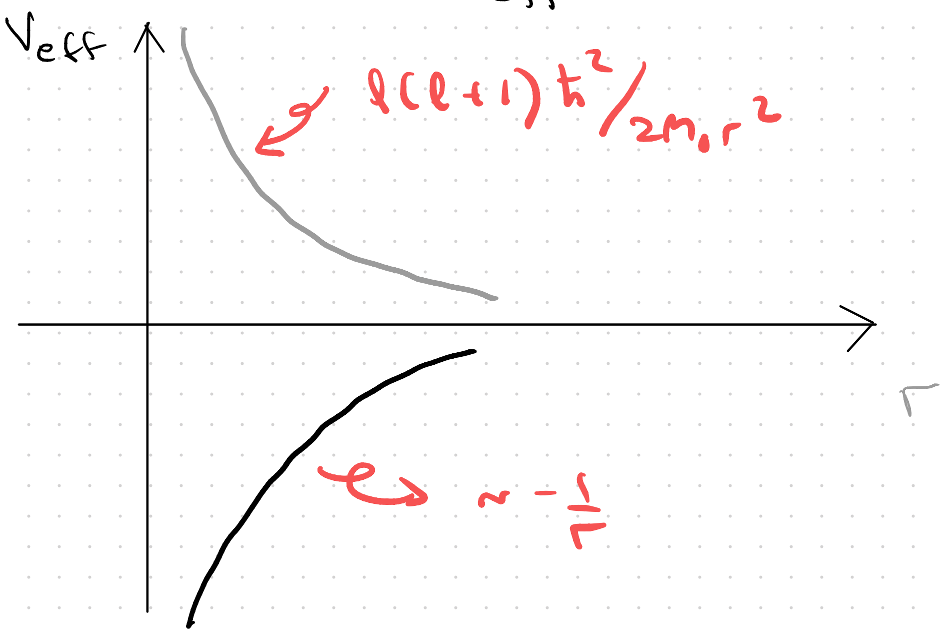
$$\boxed{V = \frac{-Ze^2}{4\pi\varepsilon_0 r}}$$

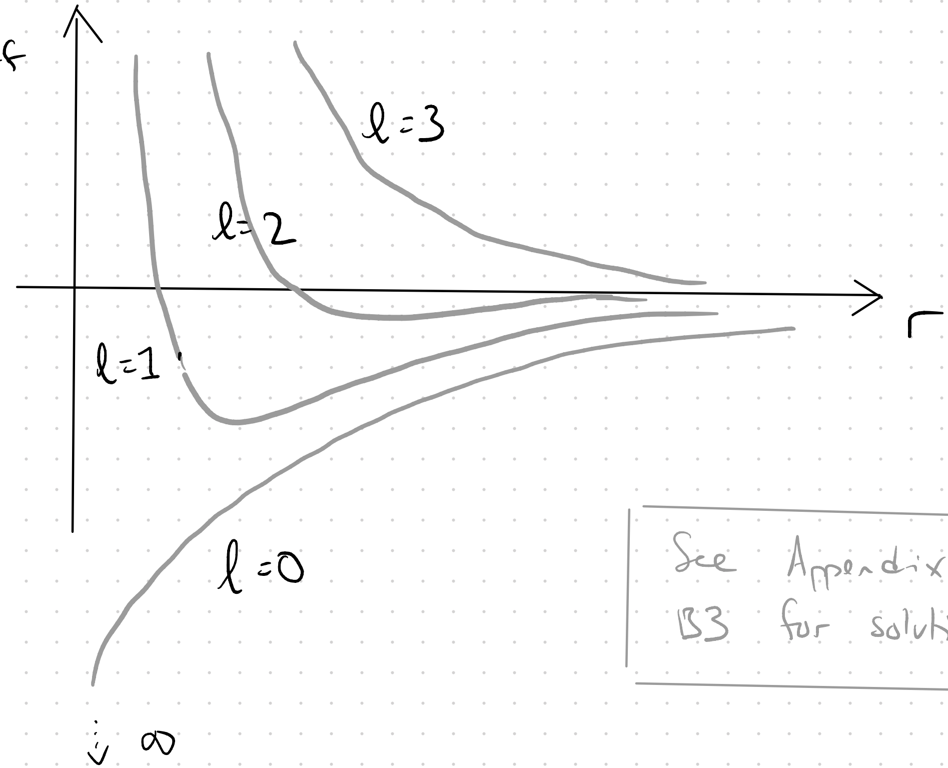
where hydrogen: $Z = 1$

Δ variables to simplify

$$u(r) \equiv r R(r)$$

$$\Rightarrow \quad -\frac{\hbar^2}{2m_0}\frac{d^2u}{dr^2} + \underbrace{\left[\frac{l(l+1)\hbar^2}{2m_0 r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}\right]}_{V_{eff}} u(r) = E\,u(r)$$



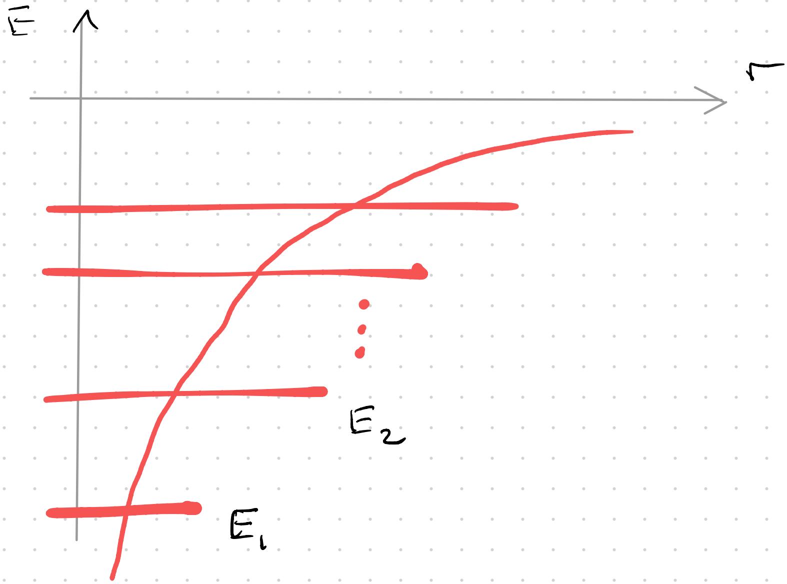


See Appendix B3 for solution

$$u_{n,l} = r^{l+1} \underbrace{F_n(r)}_{\text{Associate Leguerre Polynomials}} e^{-\sqrt{2m_0E/\hbar^2}\, r}$$

$$\therefore \boxed{R(r)_{n,l} = r^{l} F_n(r) e^{-\sqrt{2m_0E/\hbar^2}\, r}}$$

w/t $E_n = \dfrac{-m_0 Z^2 e^4}{(4\pi\varepsilon_0)^2 2\hbar^2 n^2} = \dfrac{-(13.6\,eV) Z^2}{n^2}$; $n = 1, 2, 3, \ldots$
$l = 0, 1, 2, \ldots n-1$



Extreme limits of r:

1. for $r \longrightarrow \infty$; $V_{eff} \rightarrow 0$

$$\Rightarrow \quad -\frac{\hbar^2}{2m_0}\frac{d^2u(r)}{dr^2} = E\,u(r) \; ; \quad u = e^{-\sqrt{2m_0E/\hbar^2}\, r}$$

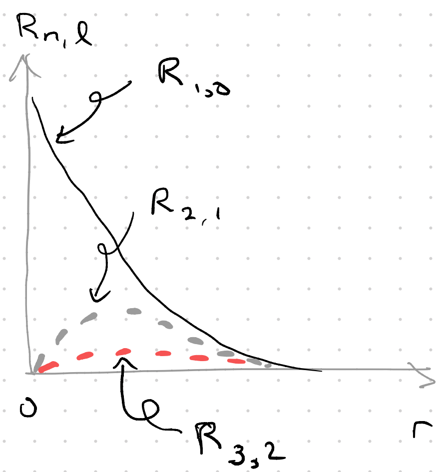
$$R = u/r$$

2. for $r \longrightarrow 0$

$$\Rightarrow \quad \frac{d^2u(r)}{dr^2} = \frac{l(l+1)}{r^2}u(r)$$

$$u \sim r^{l+1}$$

$$R = \frac{u}{r} = r^l$$



In general (arbitrary r)

eg) $n=1,\ l=0,\ m=0$

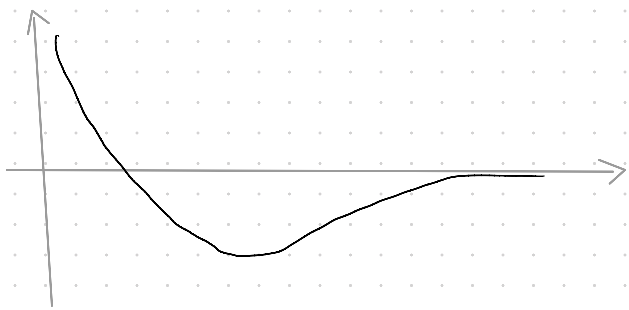
$$R_{1,0} = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$a_0 \equiv \frac{4\pi\varepsilon_0 \hbar^2}{m_0 e^2}, \quad \text{Bohr Radius}$$

$a_0 \approx 0.53\ \text{Å}$ for Hydrogen.

eg) $n=2 \begin{cases} l=1, & m=\pm 1, 0 \\ l=0, & m=0 \end{cases}$

$$R_{2,0}(r) = 2\left(\frac{Z}{2a_0}\right)^{3/2}\left(1-\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$



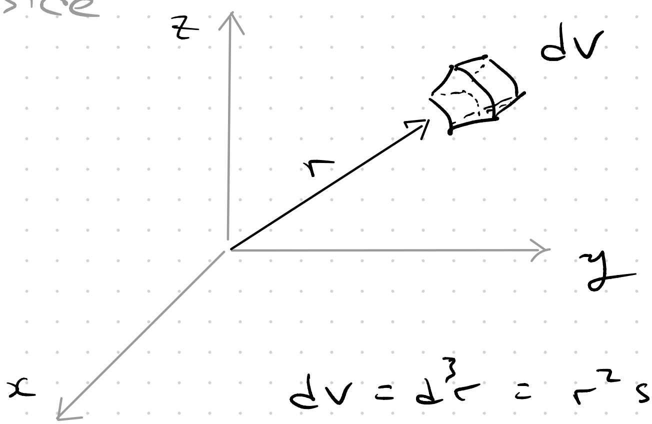
<u>NB</u> Are normalizable!

$$\int \Psi^*_{n,l,m}(r,\theta,\phi)\, \Psi_{n,l,m}(r,\theta,\phi)\, \underbrace{d^3r}_{dV} = 1$$

$$\Rightarrow \int \psi^*_{n,l,m} \psi_{n,l,m} \, r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$\Rightarrow \iiint dr \, r^2 R^*_{n,l} R_{n,l} Y^*_{l,m}(\theta,\phi) Y_{l,m}(\theta,\phi) \sin\theta \, d\theta \, d\phi = 1$$

Aside



$$dV = d^3r = r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$\int \underbrace{dr \, r^2 R^*_{nl} R_{n,l}}_{} = 1$$

$p(r) \sim$ probability density at r

In-class 23.1

Degeneracy:

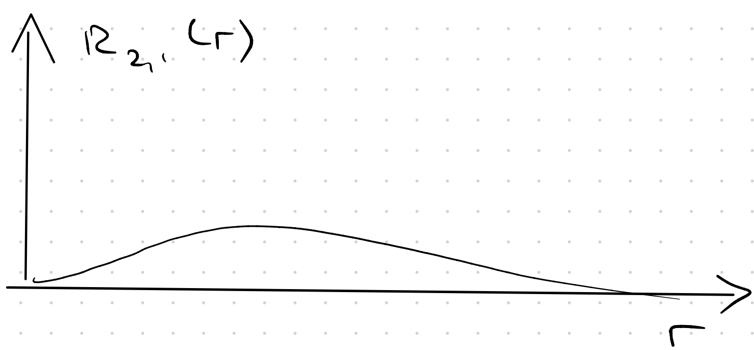
$n=1$, $l=0$, $m=0$ NO Degeneracy

$$n=2 \begin{cases} l=0, & m=0 \\ l=1, & m=0, \pm 1 \end{cases} \rightarrow 4 \text{ fold degeneracy}$$

$$n=3 \begin{cases} l=0, & m=0 \\ l=1, & m=0, \pm 1 \\ l=2, & m=0, \pm 1, \pm 2 \end{cases} \rightarrow 9$$

example: $n=2$, $l=1$

$$R_{2,1}(r) = \frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$



Now, Total Solution:

$$\psi_{nlm}(r,\theta,\phi) = R_{nl} Y_{lm}(\theta,\phi)$$

$(n\ l\ m)$: example, $(1\,0\,0)$

$1s_{l=0}$ $\quad \psi_{1,0,0} = \frac{2}{a_0^{3/2}} e^{-r/a_0} Y_{0,0}(\theta,\phi)$

$2s_{l=0}$ $\quad \psi_{2,0,0} = \frac{2}{(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0} Y_{0,0}(\theta,\phi)$

$2p_{l=1}$ $\quad \begin{pmatrix} \psi_{2,1,1} \\ \psi_{2,1,0} \\ \psi_{2,1,-1} \end{pmatrix} = \frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \begin{pmatrix} Y_{1,1} \\ Y_{1,0} \\ Y_{1,-1} \end{pmatrix}$

In-class 23-2

Atomic orbitals: ** can construct real functions out of $\psi^r_{n,l,m}$, which can have both real and imaginary parts.

P; $l=1$

$$\psi^r_{n,1,0} = \sqrt{\frac{3}{4\pi}} R_{n,1} \cos\theta$$

$$\psi_{n,1,1} = -\sqrt{\frac{3}{8\pi}} R_{n,1} \sin\theta\, e^{i\phi}$$

$$\psi_{n,1,-1} = \sqrt{\frac{3}{8\pi}} R_{n,1} \sin\theta\, e^{-i\phi}$$

eg)

** these are reel functions

$$
\left.
\begin{aligned}
p_z &= \sqrt{\frac{3}{4\pi}}\, R_{n,1} \cos\theta \\
p_x &= -\frac{1}{\sqrt{2}}\left[\psi_{n,1,1} - \psi_{n,1,-1}\right] = \sqrt{\frac{3}{4\pi}}\, R_{n,1}\, \frac{x}{r} \\
p_y &= \frac{i}{\sqrt{2}}\left[\psi_{n,1,1} + \psi_{n,1,-1}\right] = \sqrt{\frac{3}{4\pi}}\, R_{n,1}\, \frac{y}{r}
\end{aligned}
\right\} **
$$

also have s-p hybrid orbitals etc.

In-class 23.3

In-class 23.4