Lecture 10b : Hydrogenic Atoms (II)

Eigenfunctions for bound states of Hydrogen

$$\psi_{n_r,\ell,m}(r,\theta,\phi) = \frac{U_{n_r,\ell}(\bar{r})}{\sqrt[3]{a_0}\,\bar{r}}\, Y_{\ell,m}(\theta,\phi) \quad , \quad \bar{r} \equiv \frac{r}{a_0}$$

$$U_{n_r,\ell}(\bar{r}) = \bar{r}^{\,\ell+1}\, e^{-\frac{\bar{r}}{n}}\, F_{n_r,\ell}(\bar{r}) \qquad \left(\begin{array}{c}\text{Having used} \\ \kappa = \frac{1}{n}\end{array}\right)$$

First few polynomials

$n=1,\ \ell=0 \Rightarrow n_r=0$ $\boxed{1s}$: $F_{0,0}(\bar{r}) = \text{constant} = c_{00}$ (normalization)

$n=2\ \ell=0 \Rightarrow n_r=1$ $\boxed{2s}$: $F_{1,0}(\bar{r}) = c_{10}\left(1-\frac{\bar{r}}{2}\right)$

$n=2,\ \ell=1 \Rightarrow n_r=0$ $\boxed{2p}$: $F_{0,1}(\bar{r}) = c_{01}$

$n=3,\ \ell=0 \Rightarrow n_r=2$ $\boxed{3s}$: $F_{2,0}(\bar{r}) = c_{2,0}\left(2\bar{r}^2 - 2\bar{r} + 3\right)$

These are known as the associated Laguerre polynomial

satisfies: $$\left[x\frac{d^2}{dx^2} + (q+1-x)\frac{d}{dx}\right]\mathcal{L}_p^q(x) = -p\,\mathcal{L}_p^q(x)$$

where p, q are integers

Note: $$\mathcal{L}_p(x) \equiv \mathcal{L}_p^0(x) = e^{x}\frac{d^p}{dx^p}\left(e^{-x}x^p\right)$$

$$\mathcal{L}_p^q(x) = (-1)^q\frac{d^q}{dx^q}\mathcal{L}_{p+q}(x)$$

Radial eqn gives Laguerre diff'eqn:

$$\bar{r}F'' + (2\ell+2-2\kappa\bar{r})F' + 2(1-\kappa(\ell+1))F = 0$$

Let $x = 2\kappa\bar{r}$

$$\Rightarrow xF'' + (2\ell+2-x)F' = -\underbrace{\left(\frac{1}{\kappa}+\ell+1\right)}_{\text{Integer } n_r}F$$

$$\Rightarrow F_{n_r,\ell}(\bar{r}) = \mathcal{L}^{2\ell+1}_{n_r}(2\kappa\bar{r}) = \mathcal{L}^{2\ell+1}_{n_r}\left(\frac{2r}{na_0}\right)$$

Final solution

$$\psi_{n_r,\ell,m}(\theta,\phi) = \frac{N_{n\ell}}{(a_0)^{3/2}}\,\bar{r}^{\ell}e^{-\frac{\bar{r}}{n}}\,\mathcal{L}^{2\ell+1}_{n_r}\left(\frac{2\bar{r}}{n}\right)Y_{\ell,m}(\theta,\phi)$$

$$n = n_r+\ell+1,\quad \bar{r} = \frac{r}{a_0},\quad N_{n\ell} = \frac{2^{\ell+1}}{n^{\ell+2}}\sqrt{\frac{(n-\ell-1)!}{(n+\ell)!}}$$

$$a_0 = \frac{\hbar^2}{\mu q_+ q_-}\quad \left(= \frac{\hbar^2}{m_e e^2}\ \text{Hydrogen}\right)$$

bound energy $\quad E = -\frac{\mathbb{R}}{n^2} \qquad \mathbb{R} = 13.6\ \text{eV}$

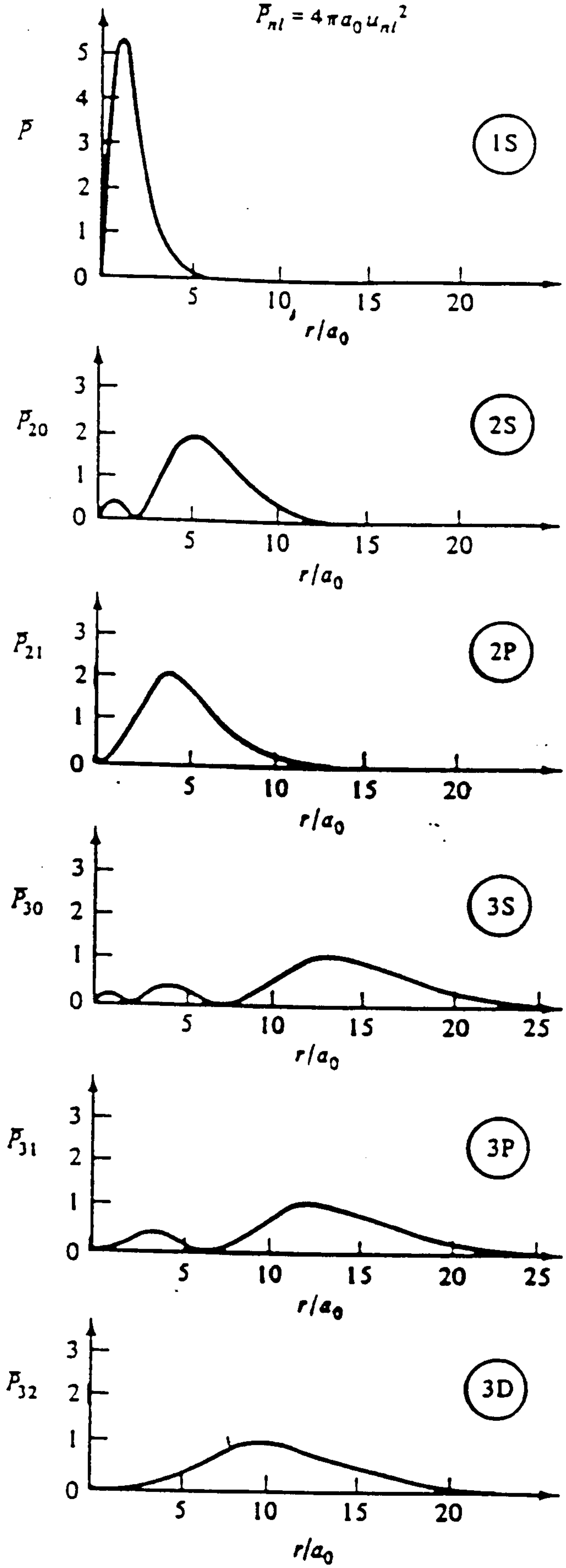

FIGURE 12-5.

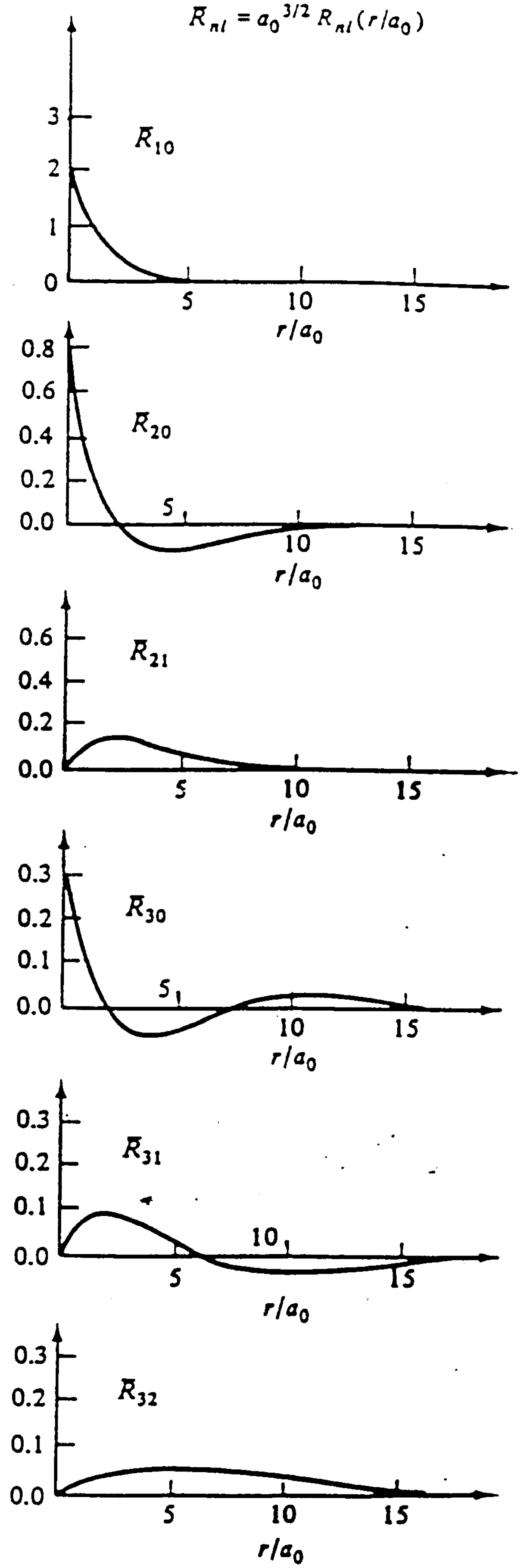

FIG. 12-4

Calculating radial integrals

$$\langle r^k \rangle_{n,\ell,m} = \langle \psi_{n\ell m} | r^k | \psi_{n\ell m} \rangle$$

$$= a_0^k \int_0^\infty \bar{r}^k \, |u_{n,\ell}(\bar{r})|^2 \, d\bar{r} \quad \left(\begin{matrix}\text{independent}\\ \text{of } m\end{matrix}\right)$$

Example: $\boxed{\langle r \rangle_{n,\ell} = a_0 \left(\frac{3}{2} n^2 - \frac{\ell(\ell+1)}{2} \right)}$

"Circular orbit": $n_r = 0$ (all kinetic energy is angular)

$$\Rightarrow \quad n = \ell + 1 \quad \Rightarrow \quad \ell = n - 1$$

$$\Rightarrow \langle r \rangle_{n=\ell+1,\, \ell=n-1} = a_0 \left(\frac{3n^2 - n(n-1)}{2} \right)$$

$$= \left(n^2 + \frac{n}{2} \right) a_0$$

Bohr's result: $\langle r \rangle = n^2 a_0$ $\left(\begin{matrix}\text{valid for}\\ \text{large } n\end{matrix}\right)$

Feynman-Hellman method

Our Hamiltonian is a function of various parameters

$$m, \; e^2, \; \ell \; \equiv \; \xi$$

$$\hat{H}(\xi) = \frac{\hat{P}_r^2}{2m} + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} - \frac{e^2}{r}$$

Energy eigenvalue $E_{n_r}(\xi) = \langle n_r, \xi | \hat{H}(\xi) | n_r, \xi \rangle$

$$= -\frac{me^4}{2\hbar^2} \frac{1}{(n_r + \ell + 1)^2}$$

Let ξ be a continuous parameter

$$\Rightarrow \frac{\partial E_{n_r}}{\partial \xi} = \langle n_r, \xi | \frac{\partial \hat{H}}{\partial \xi} | n_r, \xi \rangle + \left(\frac{\partial \langle n_r, \xi |}{\partial \xi} \right) \hat{H}(\xi) | n_r, \xi \rangle + \langle n_r, \xi | \hat{H}(\xi) \left(\frac{\partial}{\partial \xi} | n_r, \xi \rangle \right)$$

Aside: $\hat{H} | n_r, \xi \rangle = E_{n_r} | n_r, \xi \rangle = \left(\langle n_r, \xi | \hat{H} \right)^{\dagger}$

$$\Rightarrow \boxed{\frac{\partial E_{n_r}}{\partial \xi} = \langle n_r, \xi | \frac{\partial \hat{H}}{\partial \xi} | n_r, \xi \rangle} + E_{n_r} \underbrace{\cancel{\frac{\partial}{\partial \xi} \langle n_r \xi | n_r \xi \rangle}}_{0}$$

This useful trick allows us ~~to~~ easily calculate many expection values:

Examples:

- Let $\xi = \ell$ $\Rightarrow \frac{\partial \hat{H}}{\partial \ell} = \left[\frac{(2\ell+1) \hbar^2}{2m} \right] \frac{1}{r^2}$ $\quad \frac{\partial E}{\partial \ell} = \frac{+\frac{me^4}{\hbar^2}}{(n_r + \ell + 1)^3}$

$$\therefore \left\langle \frac{\partial \hat{H}}{\partial \ell} \right\rangle_{n,\ell,m} = \frac{(2\ell+1)}{2m} \hbar^2 \left\langle \frac{1}{r^2} \right\rangle_{n\ell m} = + \frac{me^4}{\hbar^2 n^3}$$

$$\Rightarrow \left\langle \frac{1}{r^2} \right\rangle_{n,\ell,m} = \left(\frac{m^2 e^4}{\hbar^4} \right) \frac{1}{n^3 (\ell + \frac{1}{2})} =$$

$$\boxed{\left\langle \frac{1}{r^2} \right\rangle_{n,\ell,m} = \frac{1}{a_0^2} \frac{1}{n^3 (\ell + \frac{1}{2})}}$$

No integral needed to be evaluated!

Other examples

- $\xi = e^2 \Rightarrow \frac{\partial \hat{H}}{\partial \xi} = -\frac{1}{r}, \quad \frac{\partial E}{\partial \xi} = -\frac{me^2}{\hbar^2 n^2}$

$$\Rightarrow \boxed{\left\langle \frac{1}{r} \right\rangle_{n,\ell} = \frac{1}{a_0 n^2}}$$

- $\Rightarrow \langle \hat{V} \rangle_{n\ell} = -e^2 \left\langle \frac{1}{r} \right\rangle = \frac{-e^2}{a_0} \frac{1}{n^2} = -2\frac{R}{n^2}$

$$\boxed{\langle \hat{V} \rangle_{n,\ell} = 2 E_n}$$

$$\Rightarrow \langle \hat{T} \rangle_{n\ell} = \left\langle \frac{\hat{p}^2}{2m} \right\rangle = \langle \hat{H} - \hat{V} \rangle = -E_n = \frac{e^2}{2a_0 n^2}$$

Virial theorem: $2 \langle \hat{T} \rangle_n = -\langle \vec{x} \cdot \vec{F} \rangle_n = -\langle \vec{x} \cdot \vec{\nabla} V \rangle_n$

Another way: let $\xi = m$

$$\Rightarrow \frac{\partial \hat{H}}{\partial m} = -\frac{1}{m} \hat{T} \qquad \frac{\partial E_n}{\partial m} = \frac{E_n}{m}$$

$$\Rightarrow \boxed{\langle \hat{T} \rangle_n = -E_n} \quad \checkmark$$

Final radial integral of much use

$$\boxed{\left\langle \frac{1}{r^3} \right\rangle_{n,\ell} = \frac{1}{a_0^3 n^3 (\ell + \frac{1}{2}) \ell (\ell+1)} = \frac{1}{\ell(\ell+1)} \frac{1}{a_0} \left\langle \frac{1}{r^2} \right\rangle_{n\ell}}$$

trick: Consider $\left\langle \left[\frac{\partial}{\partial r}, \hat{H} \right] \right\rangle_{n,\ell} = 0$

$$\left\langle \left[\frac{\partial}{\partial r}, \hat{H} \right] \right\rangle_{n,\ell} = \left\langle \frac{+e^2}{r^2} - \frac{\hbar^2 \ell(\ell+1)}{r^3} \right\rangle_{n,\ell}$$