Physics 492: Quantum Mechanics II

Lecture 10: Hydrogenic Energy Spectrum and Eigenfunctions (continued)

Last lecture we solved the T.I.S.E. for the bound states of hydrogen

relative motion: $\hat{H}_{\ell} = \frac{\hat{p}_r^2}{2m_e} + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} - \frac{e^2}{r}$

$$\hat{H}\, \psi_{n_r,\ell,m} = E_{n_r,\ell}\, \psi_{n_r,\ell,m}$$

$$E_{n_r,\ell} = \frac{-\mathbb{R}}{(n_r+\ell+1)^2} \equiv \frac{-\mathbb{R}}{n^2}$$

$$\mathbb{R} = 13.6 \text{ eV}, \quad n \equiv n_r + \ell + 1 = 1, 2, 3, \ldots$$

$$\psi_{n_r,\ell,m} = R_{n_r,\ell}(r)\, Y_\ell^m(\theta,\phi)$$

Radial wave function $R_{n_r,\ell}(r) = \frac{u_{n_r,\ell}(r)}{r}$

In dimensionless units $\bar{r} \equiv r/a_0$ $\quad \bar{E}_b = E_b/E_0$

$$\bar{u}_{n_r,\ell}(\bar{r}) = \bar{r}^{\ell+1} e^{-\bar{\kappa}_n \bar{r}}\, F_{n_r,\ell}(2\bar{\kappa}\bar{r})$$

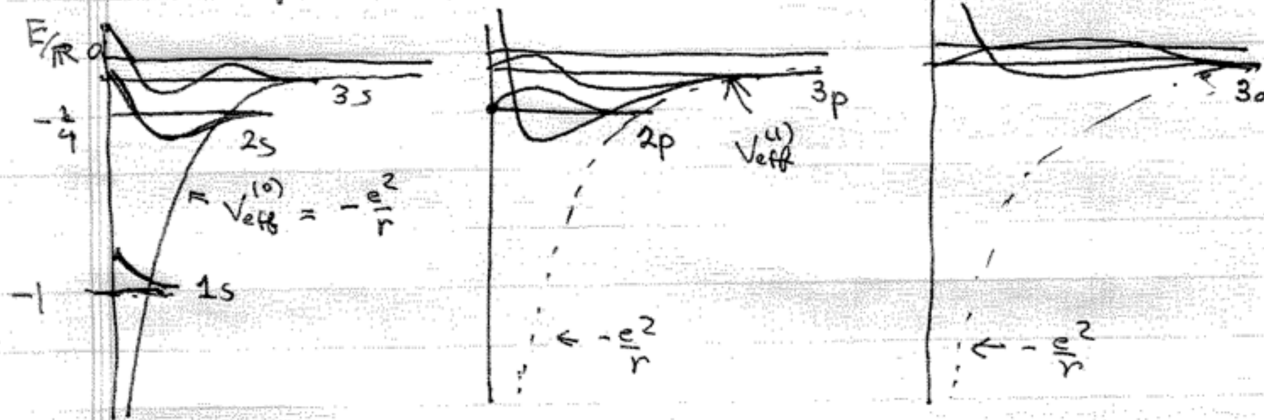
$$\bar{\kappa} \equiv \sqrt{2|\bar{E}_n|} = \frac{1}{n}$$

$$\bar{F}_{n_r,\ell}(2\bar{\kappa}\bar{r}) = \underset{\text{norm}}{N_{n_r,\ell}}\, \mathcal{L}_{n_r}^{2\ell+1}(2\bar{\kappa}\bar{r}) \quad \text{(associated Laguerre)}$$

Laguerre polynomial, order p, $\mathcal{L}_p(x) = e^x \frac{d^p}{dx^p}\left(x^p e^{-x}\right)$

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

Sketch of radial wave function $R(r) = \frac{u(r)}{r}$



Spectroscopic Notation	Several Normalized Time-Independent Eigenstates of Hydrogen
1S	$\varphi_{100} = \frac{2}{a_0^{3/2}} e^{-r/a_0} Y_0^0(\theta, \phi)$
2S	$\varphi_{200} = \frac{2}{(2a_0)^{3/2}} (1 - r/2a_0) e^{-r/2a_0} Y_0^0(\theta, \phi)$
2P	$\begin{pmatrix} \varphi_{211} \\ \varphi_{210} \\ \varphi_{21-1} \end{pmatrix} = \frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \begin{pmatrix} Y_1^1(\theta, \phi) \\ Y_1^0(\theta, \phi) \\ Y_1^{-1}(\theta, \phi) \end{pmatrix}$
3S	$\varphi_{300} = \frac{2}{3(3a_0)^{3/2}} [3 - 2r/a_0 + 2(r/3a_0)^2] e^{-r/3a_0} Y_0^0(\theta, \phi)$
3P	$\begin{pmatrix} \varphi_{311} \\ \varphi_{310} \\ \varphi_{31-1} \end{pmatrix} = \frac{4\sqrt{2}}{9(3a_0)^{3/2}} \frac{r}{a_0} (1 - r/6a_0) e^{-r/3a_0} \begin{pmatrix} Y_1^1(\theta, \phi) \\ Y_1^0(\theta, \phi) \\ Y_1^{-1}(\theta, \phi) \end{pmatrix}$
3D	$\begin{pmatrix} \varphi_{322} \\ \varphi_{321} \\ \varphi_{320} \\ \varphi_{32-1} \\ \phi_{32-2} \end{pmatrix} = \frac{2\sqrt{2}}{27\sqrt{5}(3a_0)^{3/2}} \left(\frac{r}{a_0}\right)^2 e^{-r/3a_0} \begin{pmatrix} Y_2^2(\theta, \phi) \\ Y_2^1(\theta, \phi) \\ Y_2^0(\theta, \phi) \\ Y_2^{-1}(\theta, \phi) \\ Y_2^{-2}(\theta, \phi) \end{pmatrix}$

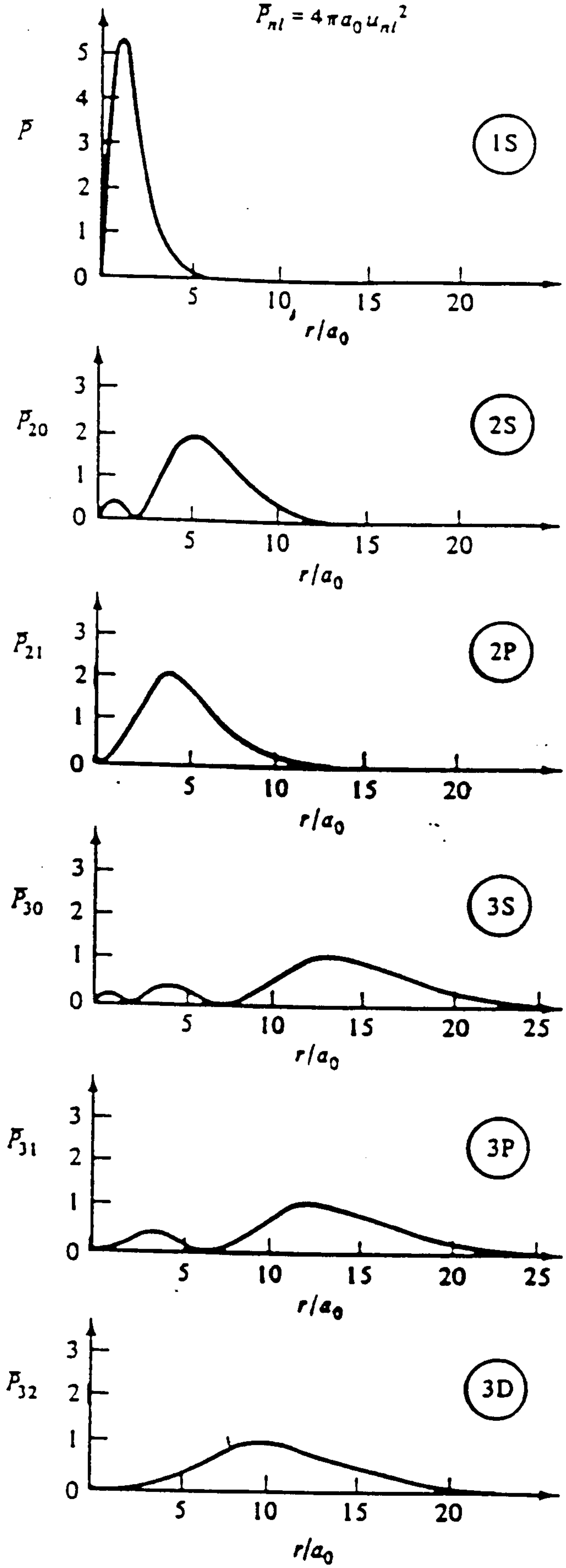


FIGURE 12-5.

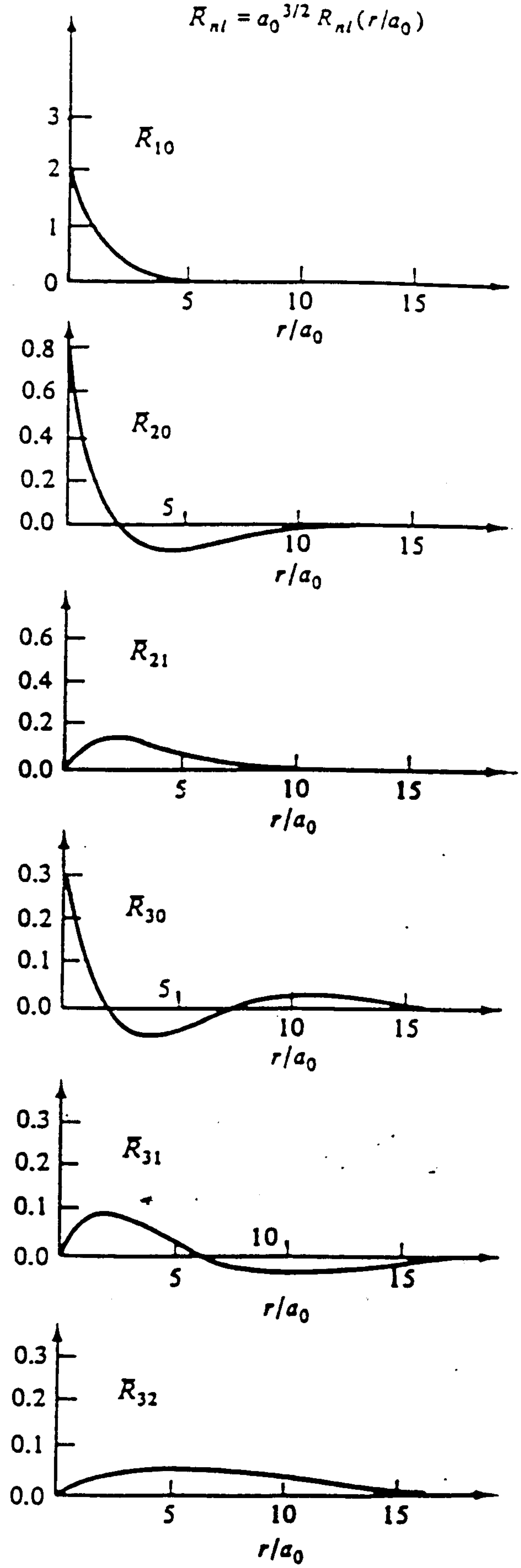


FIG. 12-4

Normalization: $\int d^3r \, |\psi_{n_r,\ell,m}|^2 = 1$

$$\Rightarrow \underbrace{\int dr\, r^2 |R_{n_r,\ell}(r)|^2}_{\|} \underbrace{\int d\Omega\, |Y_\ell^m|^2}_{1} = 1$$

$P(r)$ = probability density to find electron in radius $r \to r+dr$

$$P(r) = r^2 |R_{n_r,\ell}(r)|^2 = |u_{n_r,\ell}(r)|^2$$

units $= \frac{1}{(\text{Length})}$

Dimensionless connection: $r = a_0 \bar{r}$

$$\int dr\, r^2 |R(r)|^2 = \int dr\, |u(r)|^2$$

$$\text{Define } u(r) \equiv \frac{1}{\sqrt{a_0}} \bar{u}\left(\bar{r} = \frac{r}{a_0}\right)$$

Putting it all together

$$\boxed{u_{n_r,\ell}(r) = N_{n_r,\ell} \left(\frac{2r}{na_0}\right)^{\ell+1} e^{-\frac{r}{na_0}} \mathcal{L}_{n_r}^{2\ell+1}\left(\frac{2}{n}\frac{r}{a_0}\right) \qquad N_{n_r,\ell} = \left(\frac{2}{na_0}\right)^{3/2} \sqrt{\frac{n_r!}{2n\left[(n+\ell)!\right]^3}}, \quad n = n_r + \ell + 1}$$

"Circular" orbits: No radial excitation $n_r = 0$

$$\Rightarrow n = \ell + 1 \quad , \quad \ell = n - 1 = \ell_{max}$$

Radial probability density

$$P(r) = r^2 |R_{0,\ell_{max}}(r)|^2 = |u_{0,n-1}(r)|^2$$

$$\propto \Big| r^n e^{-\frac{r}{a_0 n}} \underbrace{\mathcal{L}_0^{n-1}\left(\frac{2r}{a_0 n}\right)}_{\text{constant, } 0^{th} \text{ order poly}} \Big|^2$$

$$\Rightarrow P(r) \propto r^{2n} e^{-2r/a_0 n}$$

Peak probability: $\frac{dP}{dr} = \left(2n\, r^{2n-1} - \frac{2}{a_0 n} r^{2n}\right) e^{-\frac{2r}{a_0 n}} = 0$

$$\Rightarrow \boxed{r_{peak} = n^2 a_0}$$

Expectation value $\langle r \rangle_{n,\ell,m} = \int d^3x \; r \; |\psi_{n,\ell,m}(\vec{x})|^2$

$$= \int_0^\infty dr \; r^3 |R_{n,\ell}|^2 = \int_0^\infty dr \; r \; |u_{n,\ell}|^2$$

$$\Rightarrow \langle r \rangle_{n,\ell} = a_0 \int_0^\infty d\bar{r} \; \bar{r} \; |\bar{u}_{n,\ell}(\bar{r})|^2 \quad \text{(independent of } m\text{)}$$

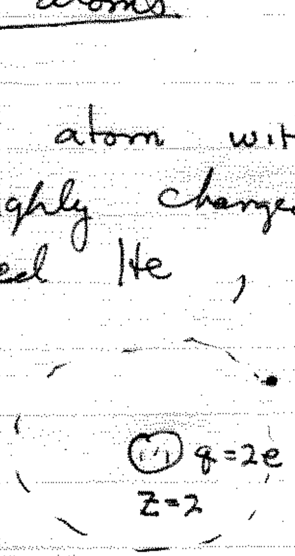
Example: Ground state $\bar{u}_{1s}(\bar{r}) = 2\bar{r}\, e^{-\bar{r}}$

$$\Rightarrow \langle r \rangle_{1s} = a_0 \Big[\underbrace{4\int_0^\infty d\bar{r} \; \bar{r}^3 e^{-2\bar{r}}}_{= \frac{3}{2}}\Big] = \frac{3 a_0}{2}$$

Generally $\boxed{\langle r \rangle_{n\ell} = a_0 \left[\frac{3}{2} n^2 - \ell(\ell+1)\right]}$, $\boxed{\langle r \rangle_{n,\ell_{max}} = a_0 \left(n^2 + \frac{n}{2}\right)}$

"Hydrogenic" atoms

Consider an atom with one electron, but a more highly charged nucleus, e.g. singly ionized He, atomic number $Z=2$



The Hamiltonian is the same except the Coulomb potential

$$V(r) = \frac{q_1 q_2}{r} = \frac{Z e^2}{r}$$

The characteristic scales of length and energy now changes, but how?

Recall $p_c \equiv \frac{\hbar}{a_c}$ $\quad E_c = \frac{\hbar^2}{a_c^2 m_e} = \frac{q_1 q_2}{a_c} = \frac{Z e^2}{a_c}$

$$\boxed{\begin{aligned} &\Rightarrow a_c = \frac{\hbar^2}{Z m_e e^2} = \frac{a_0}{Z} \\ &\Rightarrow E_c = Z^2 \frac{e^2}{a_0} = Z^2 E_0 \end{aligned}}$$

Thus the solutions to the hydrogen atom can now be directly used with this scaling

$$\boxed{E_n = -Z^2 \frac{\mathbb{R}}{n^2}}$$

More generally, we can consider a "hydrogenic" atom consisting of the bound states of two arbitrary charges with arbitrary masses. Such atoms are called "hydrogenic" because they have the same universal form of hydrogen, but just a different scaling.

Now we must consider the <u>reduced mass</u>

$$E_c = \frac{p_c^2}{\mu} = \frac{\hbar^2}{\mu a_c^2} = \frac{q_1 q_2}{a_c}$$

$$\Rightarrow \boxed{a_c = \frac{\hbar^2}{\mu q_1 q_2}}$$

$$\Rightarrow \boxed{E_c = \frac{\mu (q_1 q_2)^2}{\hbar^2}}$$

Energy levels of bound states: $E_n = -\frac{E_c}{2n^2}$

Energy eigenfunctions $\psi_{n,\ell,m} = R_{n,\ell}(r)\, Y_\ell^m(\theta,\phi)$

$$R_{n,\ell}(r) = N_{n,\ell} \left(\frac{2r}{na_c}\right)^\ell e^{-\frac{r}{na_c}} \mathcal{L}_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na_c}\right)$$