Hydrogen atom – Coulomb potential

$\bullet -e$

$\oplus$
$+e$

$$U_{Coulumb} = -\frac{ke^2}{r}$$

(H-like ions $\;\; \bullet -e \;\; (+Ze) \;\; U_c = -\frac{Zke^2}{r}$)

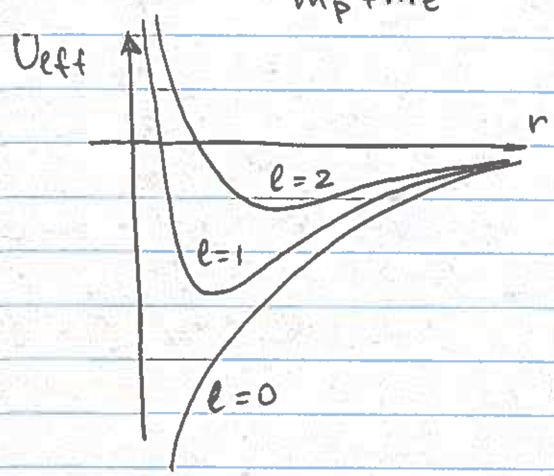
Spherically symmetric potential, angular moment conserved

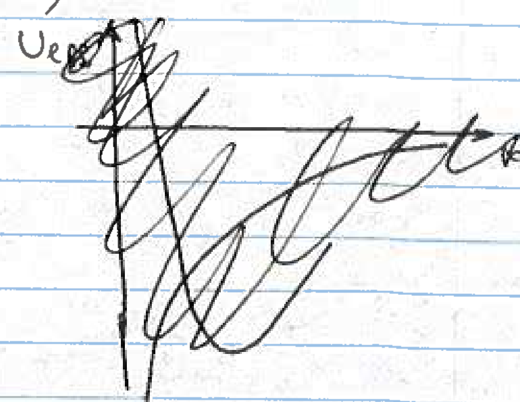
$$\psi_{n\ell m}(r,\theta,\varphi) = \frac{u(r)}{r} Y_{\ell m}(\theta,\varphi)$$

$\ell = 0 \quad U_c = -\frac{ke^2}{r}$; ~~electrons~~ $Y_{00} = \text{const}$
electron can overlap with nucleus!

$\ell > 0 \quad U_{eff} = \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} - \frac{ke^2}{r}$

$$\mu = \frac{m_p m_e}{m_p + m_e} \approx m_e$$





Higher ℓ → electron on average is farther from the nucleus

Characteristic length scale
Bohr radius

$$a = \frac{\hbar^2}{\mu k e^2} = 0.5 \cdot 10^{-10}\ m$$

Characteristic energy
Rydberg energy

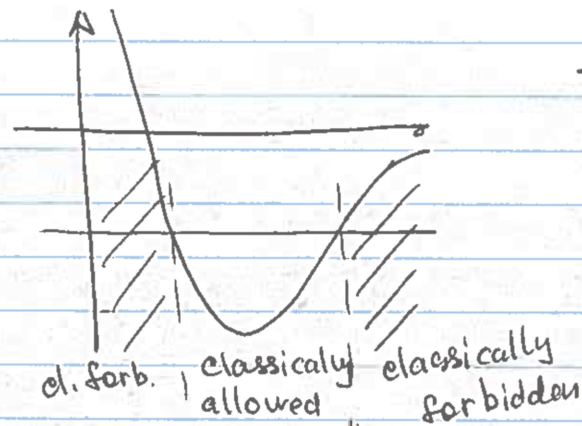
$$E = -\frac{ke^2}{2a} = -\frac{\mu (ke^2)^2}{2\hbar^2} = -E_R$$

$$E_R = 13.6\ eV$$

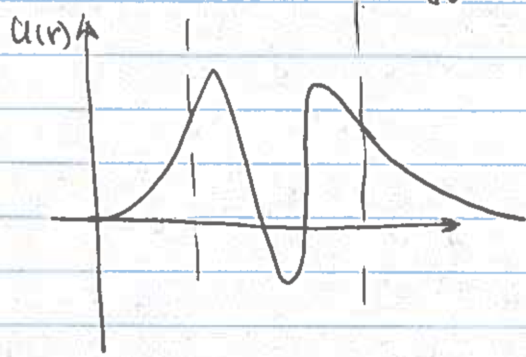
$$\boxed{E_R = \frac{1}{2} mc^2 \cdot \left(\frac{ke^2}{\hbar c}\right)^2 = -\frac{1}{2} mc^2 \cdot \alpha^2 \quad \alpha = 1/137}$$

Accurate wave function solutions

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



$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left(\frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{ke^2}{r}\right)u =$$
$$= Eu$$



wave function will decay in classically forbidden regions, can oscillate in the classically allowed region

To find solution, convert eqn in the dimentionless units

position $\quad r \to \rho = \sqrt{\dfrac{2\mu|E|}{\hbar^2}}\, r \qquad (E<0)$

$$\lambda = \frac{ke^2}{\hbar}\sqrt{\mu/2|E|}$$

$$\frac{d^2u}{d\rho^2} - \frac{l(l+1)}{\rho^2}u(\rho) + \left(\frac{\lambda}{\rho} - \frac{1}{4}\right)u(\rho) = 0$$

assimptotics : $\quad \rho \to \infty \qquad u \to 0$

dominant contribution

$$\frac{d^2u}{d\rho^2} - \frac{1}{4}u(\rho) = 0 \qquad u(\rho) \propto e^{-\rho/2} \quad \text{for } \rho \to \infty$$

$\rho \to 0 \qquad u(\rho) \to 0$

$$\frac{d^2u}{d\rho^2} - \frac{\ell(\ell+1)}{\rho^2}u(\rho) = 0 \qquad\qquad u(\rho) \propto \rho^{\ell+1}$$

General solution for all ρ values

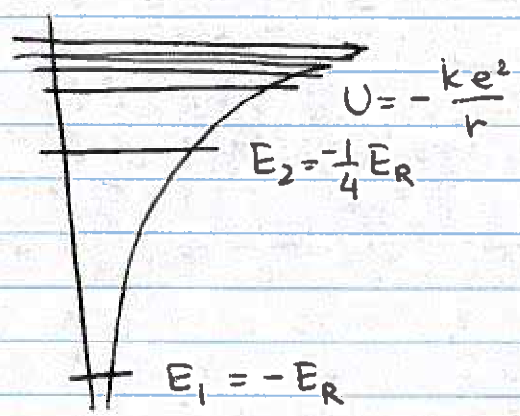
$$u(\rho) = \rho^{\ell+1} e^{-\rho/2} L(\rho) \leftarrow \text{looking for a polinomial solution}$$

One can show that solution exists if
$\lambda = n$ — positive integer number
and $\ell < n$ $(\ell = 0, 1 \ldots n-1)$

$$u_{\ell n}(\rho) = \rho^{\ell+1} e^{-\rho/2} \underbrace{L^{2\ell+1}_{n-\ell-1}(\rho)}_{\text{associate Laguerre polinomials}}$$

$$\lambda = n \qquad E_n = -\frac{\mu(ke^2)^2}{2\hbar^2 n^2} = -\frac{E_R}{n^2} \qquad E_R = 13.6\,eV$$

This is unexpected that energy values of Coulumb potential eigenstates do not depend on angular momentum



Each state has massive degeneracy
for each n: $(n-1)$ values of ℓ
each ℓ has $2\ell+1$ values of m

$$\text{degeneracy} \quad \sum_{\ell=0}^{n-1}(2\ell+1) = \frac{1+(2n-1)}{2}\cdot n = n^2$$

Selection rules: no restrictions for Δn values

$\Delta \ell = \pm 1$, $\Delta m = 0, \pm 1$

Possible electron transitions

$$\hbar \omega_{if} = \frac{2\pi \hbar c}{\lambda_{if}} = E_{in} - E_f = E_R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad n_f < n_i$$

Because for small n energies are so different, the emission / absorption lines are usually divided into series

$n_{fin} = 1$ Lyman series

$$\hbar\omega = E_R\left(1 - \frac{1}{n^2}\right) \qquad n = 2, 3 \ldots$$

$$\hbar\omega_{min} = \frac{3}{4} E_R \sim 10\,eV \qquad \text{deep UV light}$$
$$\hbar\omega_{max} = E_R$$

$n_{fin} = 2$ Balmer series

$$\hbar\omega = E_R\left(\frac{1}{4} - \frac{1}{n^2}\right) \qquad n = 3, 4, \ldots$$

$$\hbar\omega_{max} = \frac{1}{4} E_R = \cancel{4}\ 3.4\,eV \qquad \text{VIS-UV light}$$
$$\hbar\omega_{min} = \frac{5}{36} E_R = 1.8\,eV$$

$n_{fin} = 3$ Paschen series

$$\hbar\omega = E_R\left(\frac{1}{9} - \frac{1}{n^2}\right) \qquad n = 4, 5, \ldots$$

$$\hbar\omega_{max} = 1.5\,eV = \frac{1}{9} E_R$$
$$\hbar\omega_{min} = \frac{7}{144} E_R = 0.66\,eV \qquad \text{IR} \to \text{VIS light}$$

n	l	m	$\psi_{n,l,m}(r,\theta,\phi)$
1	0	0	$\frac{1}{\sqrt{\pi}a_0^{3/2}}e^{-r/a_0}$
2	0	0	$\frac{1}{4\sqrt{2\pi}a_0^{3/2}}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$
2	1	0	$\frac{1}{4\sqrt{2\pi}a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}cos\ \theta$
2	1	±1	$\frac{1}{8\sqrt{3\pi}a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}sin\ \theta\ e^{\pm i\phi}$
3	0	0	$\frac{1}{81\sqrt{3\pi}a_0^{3/2}}\left(27-18\frac{r}{a_0}+2\frac{r^2}{a_o^2}\right)e^{-r/2a_o}$
3	1	0	$\frac{1}{81\sqrt{3\pi}a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}\ cos\ \theta$
3	1	±1	$\frac{1}{81\sqrt{3\pi}a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}\ sin\ \theta\ e^{\pm i\phi}$
3	2	0	$\frac{1}{81\sqrt{6\pi}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\ \left(3\ cos^2\ \theta-1\right)$
3	2	±1	$\frac{1}{81\sqrt{\pi}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\ sin\ \theta\ cos\ \theta\ e^{\pm i\phi}$
3	2	±2	$\frac{1}{162\sqrt{\pi}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\ sin^2\ \theta\ e^{\pm 2i\phi}$

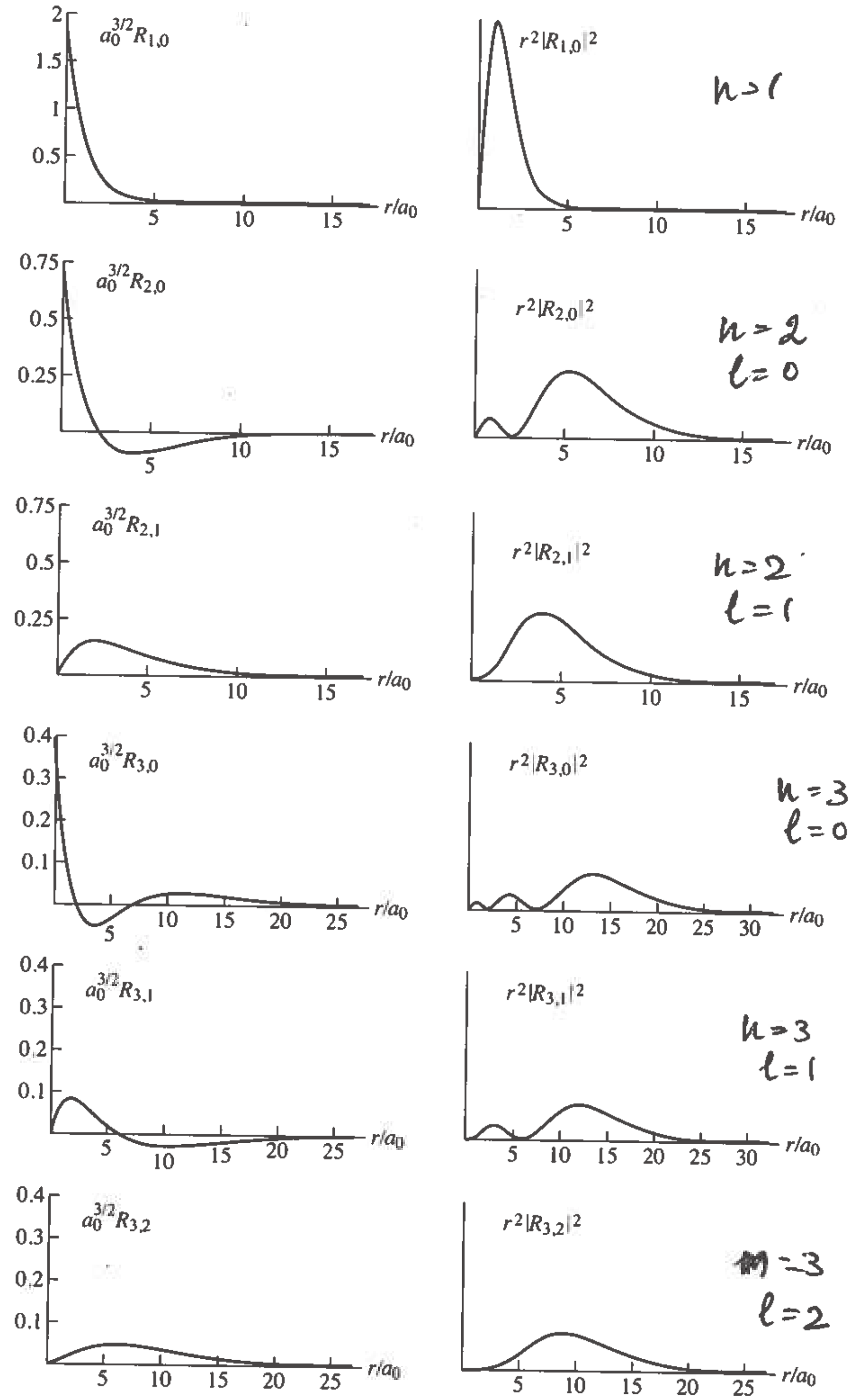
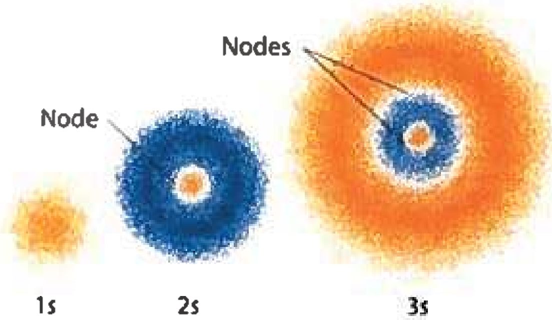
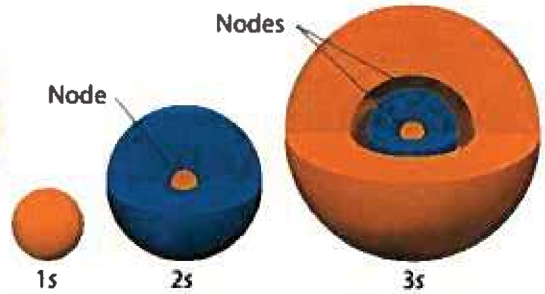


Figure 10.5 Plots of the radial wave function $R_{n,l}(r)$ and the radial probability density $r^2|R_{n,l}(r)|^2$ for the wave functions in (10.43), (10.44), and (10.45).

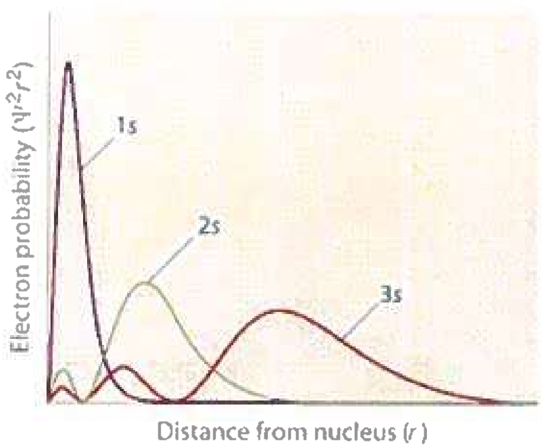
$$\int |\psi(\vec{r})|^2 dV = \int \underbrace{|R|^2 r^2}\, dr$$



(a) Electron probability



(b) Contour probability



(c) Radial probability