LECTURE #9

HYDROGEN ATOM: $V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$

RADIAL EQUATION: $$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \underbrace{\left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]}_{\text{EFFECTIVE POTENTIAL}} u = Eu$$

EFFECTIVE POTENTIAL → $\boxed{\text{SEE FIG. 7.7}}$

SEEK **BOUND STATES** $(E<0)$:

LET $K = \frac{\sqrt{-2mE}}{\hbar} \Rightarrow E = -\frac{\hbar^2 K^2}{2m}$

$$\therefore \frac{1}{K^2}\frac{d^2u}{dr^2} + \left[\frac{e^2}{4\pi\epsilon_0}\frac{2m}{\hbar^2K^2}\frac{1}{r} - \frac{1}{K^2}\frac{l(l+1)}{r^2}\right]u = u$$

LET $\rho = Kr$ (DIMENSIONLESS VARIABLE)

$$\frac{d^2u}{d\rho^2} + \left[\underbrace{\frac{e^2}{4\pi\epsilon_0}\frac{2m}{\hbar^2K}}_{\rho_0}\frac{1}{\rho} - \frac{l(l+1)}{\rho^2}\right]u = u$$

$$\therefore \frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]u$$

CONSIDER ASYMPTOTIC BEHAVIOR OF u:

$$\rho\to\infty \Rightarrow \frac{d^2u}{d\rho^2} = u \Rightarrow u \sim Ae^{-\rho} + Be^{\rho}$$

2nd TERM BLOWS UP AS $\rho\to\infty \Rightarrow B=0$

$\therefore$ AS $\rho\to\infty$, $u\sim Ae^{-\rho}$

$$\rho \to 0 \Rightarrow \frac{d^2u}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2} u \Rightarrow u \sim C\rho^{\ell+1} + D\rho^{-\ell}$$

2^{nd} TERM BLOWS UP AS $\rho \to 0 \Rightarrow D = 0$

$$\therefore \text{ As } \rho \to 0, \quad u \sim C\rho^{\ell+1}$$

THIS MOTIVATES THE CHOICE OF A NEW FUNCTION: $v(\rho)$

SUCH THAT:

$$u(\rho) = \rho^{\ell+1} e^{-\rho} v(\rho)$$

NOTE: (1) $\frac{du}{d\rho} = \rho^{\ell} e^{-\rho}\left[(\ell+1-\rho)v + \rho \frac{dv}{d\rho}\right]$

(2) $\frac{d^2u}{d\rho^2} = \rho^{\ell} e^{-\rho}\left[\left(-2\ell-2+\rho+\frac{\ell(\ell+1)}{\rho}\right)v + 2(\ell+1-\rho)\frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2}\right]$

$\therefore$ IN TERMS OF v, THE RADIAL EQUATION READS:

$$\rho \frac{d^2v}{d\rho^2} + 2(\ell+1-\rho)\frac{dv}{d\rho} + [\rho_0 - 2(\ell+1)]v = 0$$

SEEK A POWER SERIES SOLUTION: $v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$

NOTE: (1) $\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j c_j \rho^{j-1} = \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j$

(2) $\frac{d^2v}{d\rho^2} = \sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^{j-1}$

INSERTING THESE POWER SERIES INTO THE RADIAL EQUATION:

$$\sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^j + 2(\ell+1)\sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j - 2\sum_{j=0}^{\infty} j c_j \rho^j + [\rho_0 - 2(\ell+1)]\sum_{j=0}^{\infty} c_j \rho^j = 0$$

$\Rightarrow$ THE COEFFICIENTS MUST VANISH FOR EACH j

$$\therefore \left[j(j+1) + 2(l+1)(j+1)\right] c_{j+1} + \left[-2j + \rho_0 - 2(l+1)\right] c_j = 0$$

$$\Rightarrow \quad c_{j+1} = \frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} c_j \qquad \text{RECURSION RELATION}$$

NOTE: FOR LARGE j, $\quad c_{j+1} \approx \frac{2j}{j(j+1)} c_j = \frac{2}{j+1} c_j$

ASSUME THIS IS THE EXACT RESULT.

$$\Rightarrow \quad c_{j+1} = \underbrace{\left(\frac{2}{j+1}\right)\left(\frac{2}{j}\right)\left(\frac{2}{j-1}\right)\cdots}_{j+1 \text{ FACTORS}} c_0 = \frac{2^{j+1}}{(j+1)!} c_0$$

$$\Rightarrow \quad c_j = \frac{2^j}{j!} c_0 \quad \Rightarrow \quad v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho}$$

$$\Rightarrow \quad u(\rho) = \rho^{l+1} e^{-\rho} v(\rho) = c_0 \rho^{l+1} e^{\rho},$$ WHICH BLOWS UP AS $\rho \to \infty$

$\therefore$ THE SERIES MUST TERMINATE $\Rightarrow$ $c_{j_{max}+1} = 0$

FROM THE RECURSION RELATION,

$$2(j_{max} + l + 1) - \rho_0 = 0$$

DEFINE: $\quad n = j_{max} + l + 1 \qquad$ "PRINCIPAL QUANTUM NUMBER"

SINCE $j_{max} = 0, 1, 2, \ldots$ AND $l = 0, 1, 2, \ldots$

$$\Rightarrow \boxed{n = 1, 2, 3, \ldots}$$

NOTE: $\rho_0 = 2n \Rightarrow c_{j+1} = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)} c_j$

BUT, $\rho_0 = \frac{e^2}{4\pi\epsilon_0} \frac{2m}{\hbar^2 K}$, $K = \frac{\sqrt{2m(-E)}}{\hbar}$

$$\therefore \boxed{E_n = -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{m}{2\hbar^2} \frac{1}{n^2} = \frac{E_1}{n^2}, \quad E_1 = -13.61\,eV}$$

BOHR FORMULA

SINCE $n = j_{max} + l + 1$, THE MAXIMUM l IS RESTRICTED FOR A GIVEN n.

FOR EXAMPLE, $n=1$: $j_{max} = 0 \Rightarrow l = 0$

$n = 2$: $j_{max} = 0 \Rightarrow l = 1$

$j_{max} = 1 \Rightarrow l = 0$

$$\therefore \boxed{l \leq n-1} \qquad \boxed{m = -l, -l+1, \ldots 0, \ldots l-1, l}$$

IN SUMMARY, $R(r) = \frac{u(r)}{r}$

$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho)$, $\rho = Kr$

$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$, $n = j_{max} + l + 1$, $c_{j_{max}+1} = 0$

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

$a = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$ = BOHR RADIUS = 0.529 Å

DEGENERACY: $d(n) = \sum_{l=0}^{n-1} (2l+1) = 2\,\frac{1}{2}(n)(n-1) + n = n^2$

GROUND STATE: $n=1$

SINCE $n = j_{max} + l + 1 \Rightarrow j_{max} = 0,\ l = 0 \Rightarrow c_1 = c_2 = \cdots = 0$

$$\therefore\ v(\rho) = c_0 \Rightarrow u(\rho) = c_0\, \rho\, e^{-\rho} \quad (l = 0)$$

$$\Rightarrow u(r)\ \ c_0 \frac{r}{a} e^{-r/a}$$

NORMALIZE: $\int_0^\infty |u(r)|^2 dr = \frac{|c_0|^2}{a^2} \int_0^\infty r^2 e^{-2r/a} dr = 1$

NOTE: $\int_0^\infty r^n e^{-2r/a} dr = n! \left(\frac{a}{2}\right)^{n+1}$

$$\therefore \int_0^\infty |u(r)|^2 dr = 2 \frac{|c_0|^2}{a^2} \left(\frac{a}{2}\right)^3 = 1 \Rightarrow \frac{c_0}{a} = 2a^{-3/2}$$

$$\therefore\ R_{10}(r) = \frac{u(r)}{r} = 2a^{-3/2} e^{-r/a}$$

$n \nearrow \ \nwarrow l$

$$\psi_{100}(\vec{r}) = R_{10}(r)\, \underset{\frac{1}{\sqrt{4\pi}}}{\underset{\uparrow}{Y_0^0(\theta, \phi)}} = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

$n \nearrow \ \uparrow l \ \nwarrow m$

EXCITED STATES CAN BE DERIVED IN A SIMILAR FASHION.

FIRST EXCITED STATES: $n = 2$

$$\begin{array}{cccc}
 & n=2 & & \\
l=0 & & l=1 & \\
\downarrow & \swarrow & \downarrow & \searrow \\
m=0 & m=1 & m=0 & m=-1 \\
\downarrow & \downarrow & \downarrow & \downarrow \\
\psi_{200} & \psi_{211} & \psi_{210} & \psi_{21-1}
\end{array}$$

$$\ell=0: \quad R_{20}(r) = \frac{1}{\sqrt{2a^3}}\left(1-\frac{r}{2a}\right)e^{-r/2a}$$

$$\ell=1: \quad R_{21}(r) = \frac{1}{\sqrt{24a^3}}\frac{r}{a}e^{-r/2a}$$

$$E_2 = \frac{1}{4}E_1$$

$$\psi_{200} = R_{20}(r)\,Y_0^0(\theta,\phi) \qquad Y_0^0 = \frac{1}{\sqrt{4\pi}}$$

$$\psi_{210} = R_{21}(r)\,Y_1^0(\theta,\phi) \qquad Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$$

$$\psi_{21\pm1} = R_{21}(r)\,Y_1^{\pm1}(\theta,\phi) \qquad Y_1^{\pm1} = \mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{\pm i\phi}$$

→ NOTE: WAVEFUNCTIONS FOR $\ell=1$ ARE NOT SPHERICALLY SYMMETRIC

FOR HIGHER ORDER RADIAL FUNCTIONS, $\boxed{\text{SEE FIG. 7.9}}$

CONSIDER THE SPECTRUM OF HYDROGEN:

UPON TRANSITION FROM AN EXCITED STATE TO A LOWER ENERGY STATE, ENERGY CAN BE CONSERVED THROUGH THE EMISSION OF A PHOTON WITH ENERGY E_γ:

$$E_\gamma = E_i - E_f = -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{m}{2\hbar^2}\left(\frac{1}{n_i^2}-\frac{1}{n_f^2}\right)$$

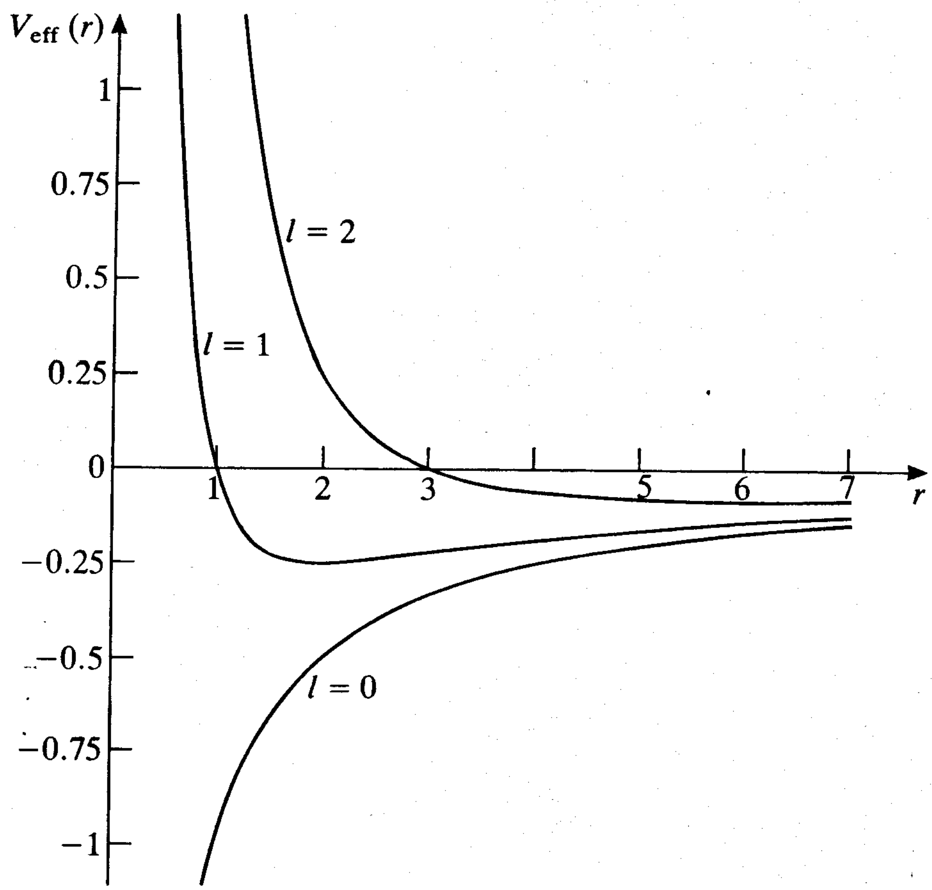
SINCE $E_\gamma = \frac{hc}{\lambda}$,

$$\frac{1}{\lambda} = \underbrace{\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{m}{4\pi\hbar^3 c}}_{R}\left(\frac{1}{n_f^2}-\frac{1}{n_i^2}\right)$$

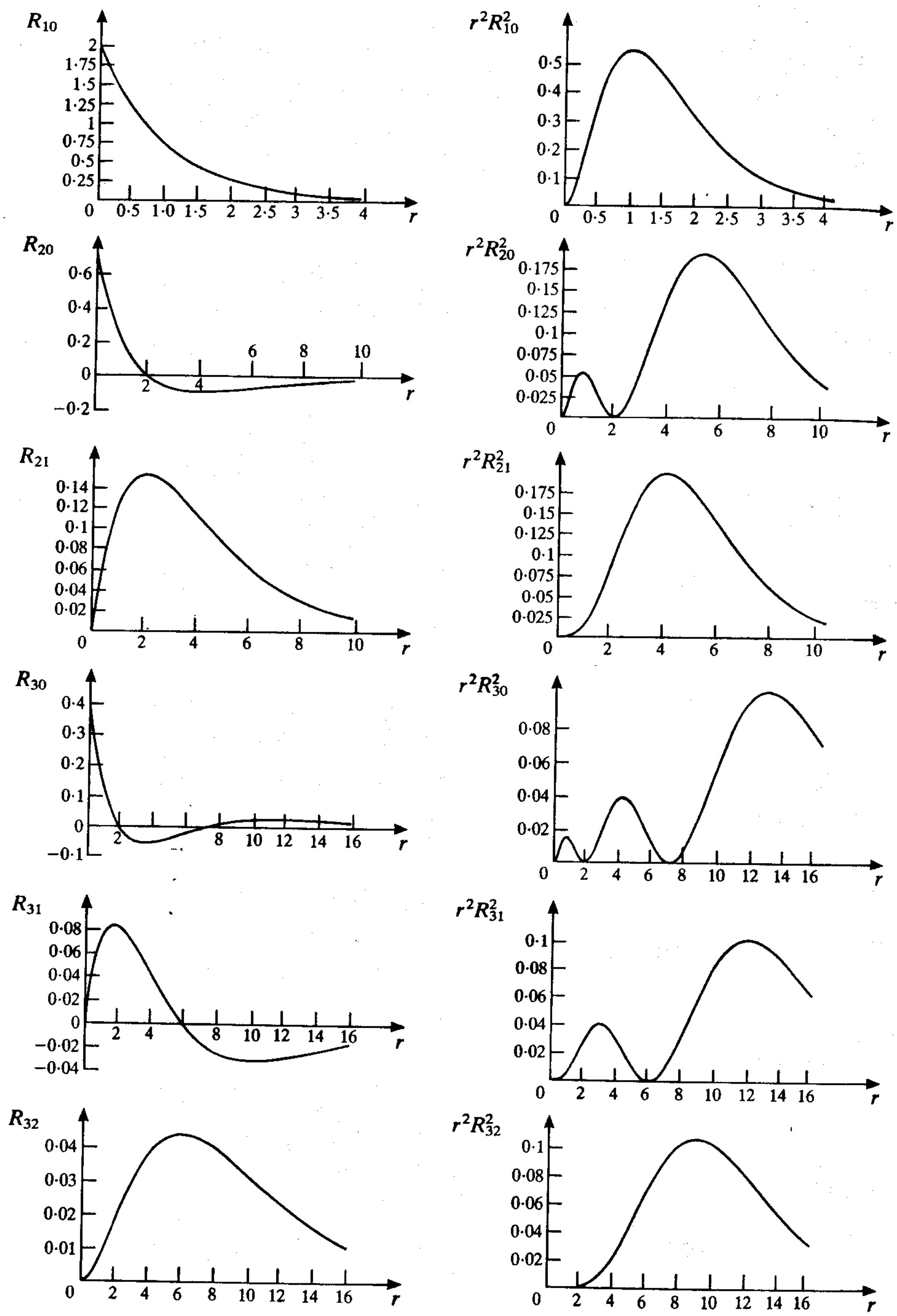
→ R = RYDBERG CONSTANT = $1.097\times10^{7}\ m^{-1}$

$n_f = 1$ → LYMAN SERIES (UV)
$n_f = 2$ → BALMER SERIES (VISIBLE)
$n_f = 3$ → PASCHEN SERIES (IR)

→ $\boxed{\text{SEE FIG. 4.5}}$



7.7 The effective potential $V_{eff}(r)$ given by [7.95b] for the case $Z = 1$ and for the values $l = 0, 1, 2$. The unit of length is $a_\mu = (m/\mu)a_0$ where a_0 is the Bohr radius [1.66]. The unit of energy is $e^2/(4\pi\varepsilon_0 a_\mu)$.



7.9 Radial functions $R_{nl}(r)$ and radial distribution functions $r^2R^2_{nl}(r)$ for atomic hydrogen. The unit of length is $a_\mu=(m/\mu)a_0$, where a_0 is the first Bohr radius [1.66].

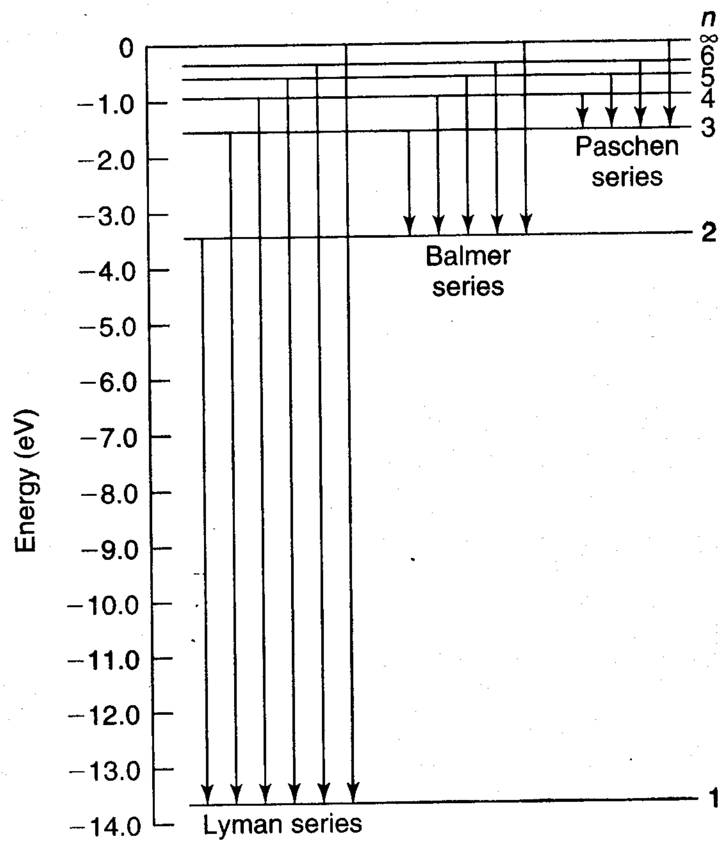


Figure 4.5: Energy levels and transitions in the spectrum of hydrogen.