LECTURE 26 8-6-09

SOLVE TISE FOR HYDROGEN

FIND EIGENVALUES $\longrightarrow$ EIGEN ENERGIES E_n

FIND EIGENVECTORS $\longrightarrow$ EIGEN FUNCTIONS $\psi_{n\ell m}$

STATIONARY STATES

TWO POV'S

(1) $\nabla^2 \rightarrow \nabla_r^2 + \nabla^2(\theta,\varphi)$ MATH

(2) $H = \dfrac{\vec{p}^{\,2}}{2m} + V(\vec{r})$ PHYSICS

$$\frac{\vec{p}^{\,2}}{2m} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$$

$$= \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

$$= \frac{-\hbar}{2m}\nabla^2$$ cartesian

SPHERICAL SYMMETRY $\quad V(\vec{r}) = V(x,y,z) = V(r)$

$$H = \frac{\vec{P}^{\,2}}{2m} + V(r)$$

$$\frac{\vec{P}^{\,2}}{2m} = \frac{P_r^2}{2m} + \frac{L^2}{2mr^2}$$

PRODUCT ANSATZ $\quad \psi = R_{nl}\, Y_{lm}$

$$\left[\frac{P_r^2}{2m} + \frac{L^2}{2mr^2} + V(r) \right] R_{nl}\, Y_{lm} = E_n\, R_{nl}\, Y_{lm}$$

$$\left[\frac{P_r^2}{2m} + \frac{l(l+1)\hbar^2}{2mr^2} + V(r) \right] R_{nl} = E_n\, R_{nl}$$

ANGULAR
MOMENTUM
BARRIER
REPULSIVE

ATTRACTIVE
COULOMB
POTENTIAL

SOLUTIONS TO THE RADIAL EQUATION

$$R_{nl}(r) \sim \begin{pmatrix} \text{ASYMPTOTIC} \\ \text{FORM} \end{pmatrix} \begin{pmatrix} \text{LAGUERRE} \\ \text{POLYNOMIALS} \end{pmatrix}$$

$\exp(-r/na_0)$
HYDROGEN

HYDROGEN-LIKE
$\exp(-Zr/na_0)$

SOLVE RADIAL EQN

TWO METHODS:

(1) DIFF EQN METHOD

FIND ASYMPTOTIC FORM

SEPARATE IT

DIFFERENTIAL EQN for each value of l

MAKE DIMENSIONLESS

ORDER ~~no.~~ HIGHEST DERIVATIVE FIRST

COEFF OF HIGHEST DERIVATIVE TERM = 1

FUTZ AROUND

DISCOVER RADIAL EQN IS EQUIVALENT TO

THE ASSOCIATED LAGUERRE EQN

DECLARE VICTORY

NORMALIZE WAVEFCNS

(2) USE LADDER OPERATORS

EIGEN FCNS $\Rightarrow$ ENERGY EIGEN FCNS

EIGEN VALUES $\Rightarrow$ EIGEN ENERGIES

$$E_n = \frac{-Ry}{n^2} = \frac{-13.6\ eV}{n^2} \qquad \text{HYDROGEN}$$

$$E_n' = -\frac{Z^2 Ry}{n^2} \qquad \text{HYDROGEN-LIKE}$$

CSCO's

$$H \, | n \, l \, m \rangle = E_n \, | n \, l \, m \rangle \qquad \text{only } n$$

$$L^2 \, | n \, l \, m \rangle = l(l+1)\hbar^2 \, | n \, l \, m \rangle \qquad \text{only } l$$

$$L_z \, | n \, l \, m \rangle = m\hbar \, | n \, l \, m \rangle \qquad \text{only } m$$

RADIAL EQUATION

$$\left[-\frac{\hbar^2}{2\mu} \nabla_r^2 + V(r) + \frac{L^2}{2\mu r^2} \right] | n \, l \, m \rangle$$

$$\left[-\frac{\hbar^2}{2\mu r} \frac{\partial^2}{\partial r^2} r - \frac{Ze^2}{r} + \frac{l(l+1)\hbar^2}{2\mu r^2} \right] R_{nl}(r) = E_n R_{nl}(r)$$

ATTRACTIVE COULOMB POTENTIAL

REPULSIVE CENTRIFUGAL BARRIER

$$V_{EFF}(l, r)$$

SOLVE BY POWER SERIES
OR BY LADDER OPERATORS $\Big\}$ $\Rightarrow$ LAGUERRE POLYNOMIALS

$$H = -\frac{\hbar^2}{2\mu r}\frac{\partial^2}{\partial r^2} r + \frac{\vec{L}^2}{2\mu r^2} + V(r)$$

coupled system of eigenequations

$$H\,\varphi_{nlm}(\vec{r}) = E_n\,\varphi_{nlm}(\vec{r})$$

$$L^2\,\varphi_{nlm}(\vec{r}) = l(l+1)\hbar^2\,\varphi_{nlm}(\vec{r})$$

$$L_z\,\varphi_{nlm}(\vec{r}) = m\hbar\,\varphi_{nlm}(\vec{r})$$

we already solved the L^2, L_z problem

$$\varphi_{nlm}(\vec{r}) = R_n(r)\,Y_{lm}(\theta,\varphi)$$

$$\left[-\frac{\hbar^2}{2\mu r}\frac{\partial^2}{\partial r^2} r - \frac{e^2}{r}\right] R_n Y_{lm}$$

$$+ \left[\frac{L^2}{2\mu r^2}\right] R_n Y_{lm} = E_n R_n Y_{lm}$$

$$l(l+1)\hbar^2$$

NEW TISE

$$\left[-\frac{\hbar^2}{2\mu r} \frac{\partial^2}{\partial r^2} r - \frac{e^2}{r} + \frac{l(l+1)\hbar^2}{2\mu r^2} \right] R_n = E_n R_n$$

1d PROBLEM

WITH EFFECTIVE POTENTIAL

$$V_{eff}(r) = -\frac{e^2}{r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

COULOMB ATTRACTION

CENTRIFUGAL ~~POTENTIAL~~ BARRIER

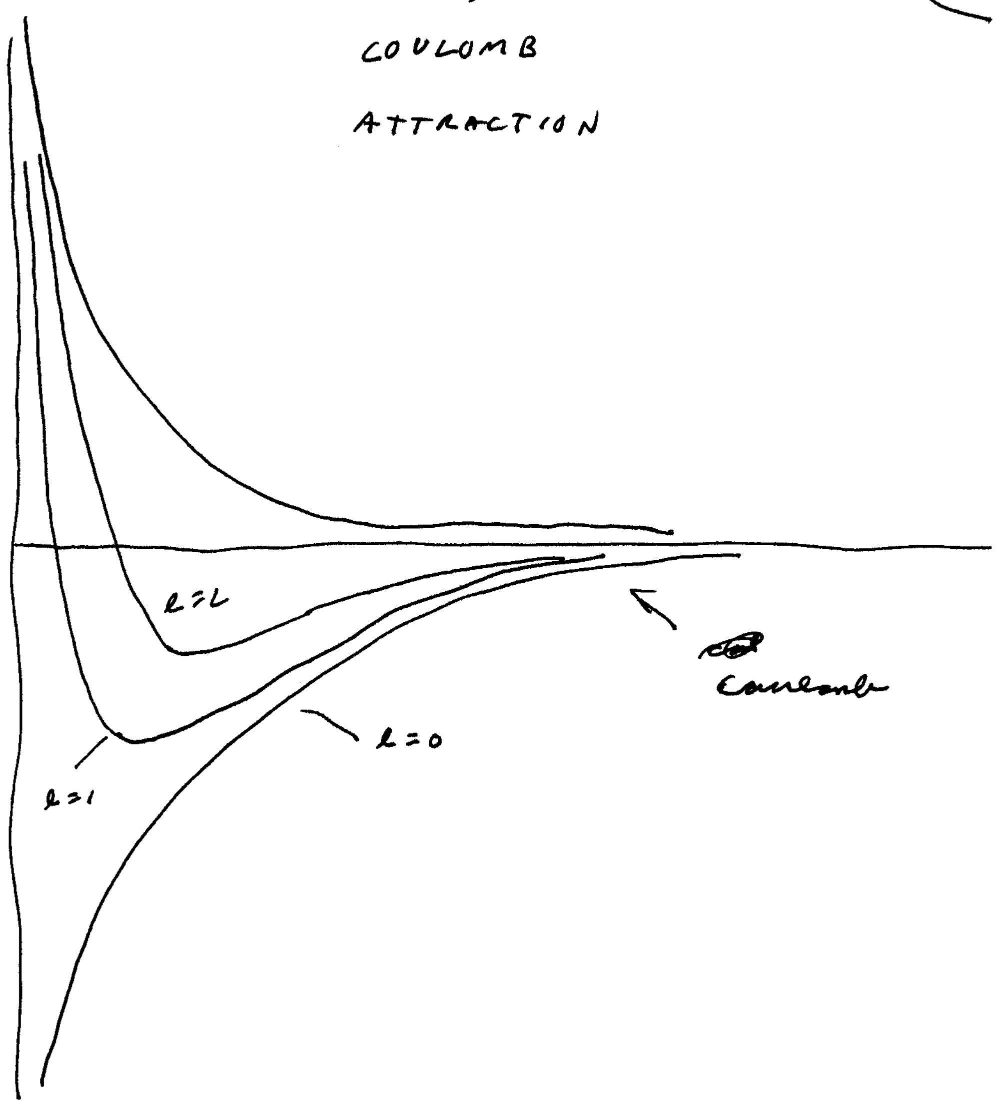
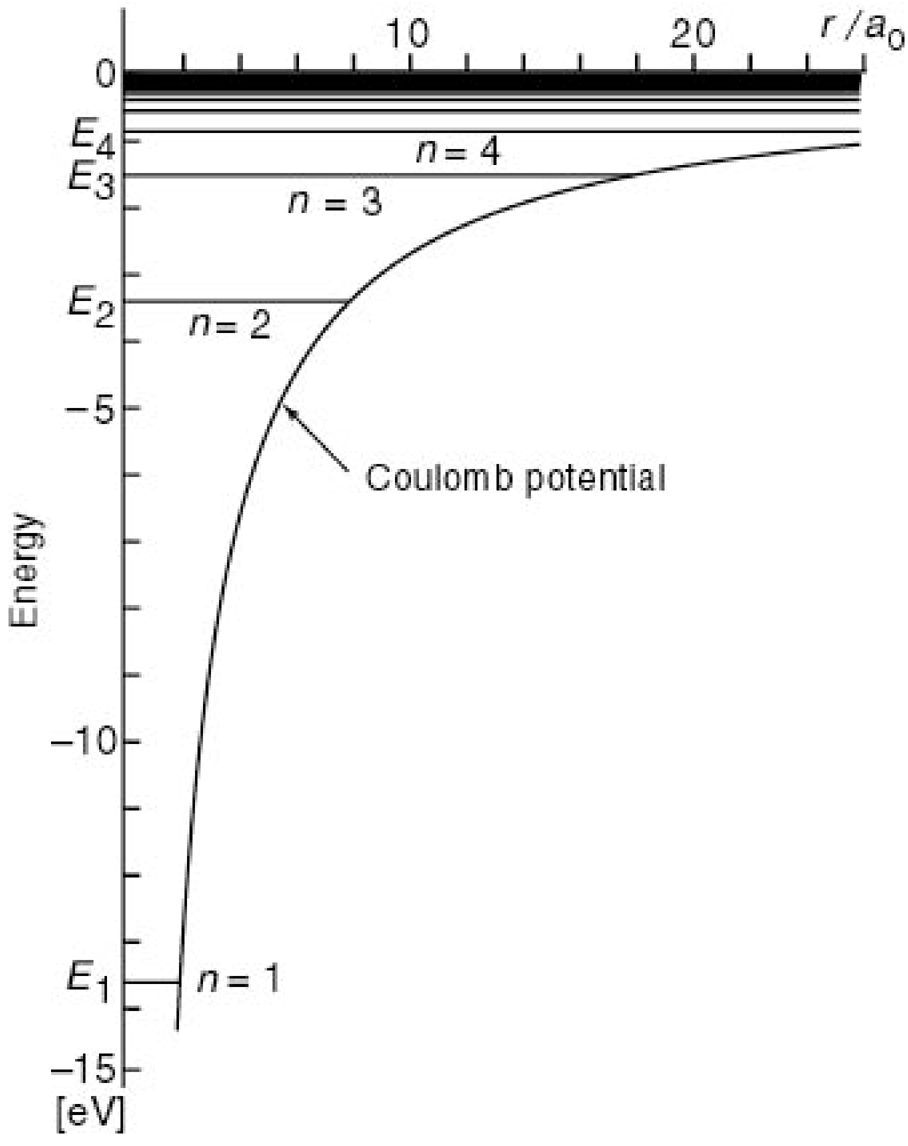


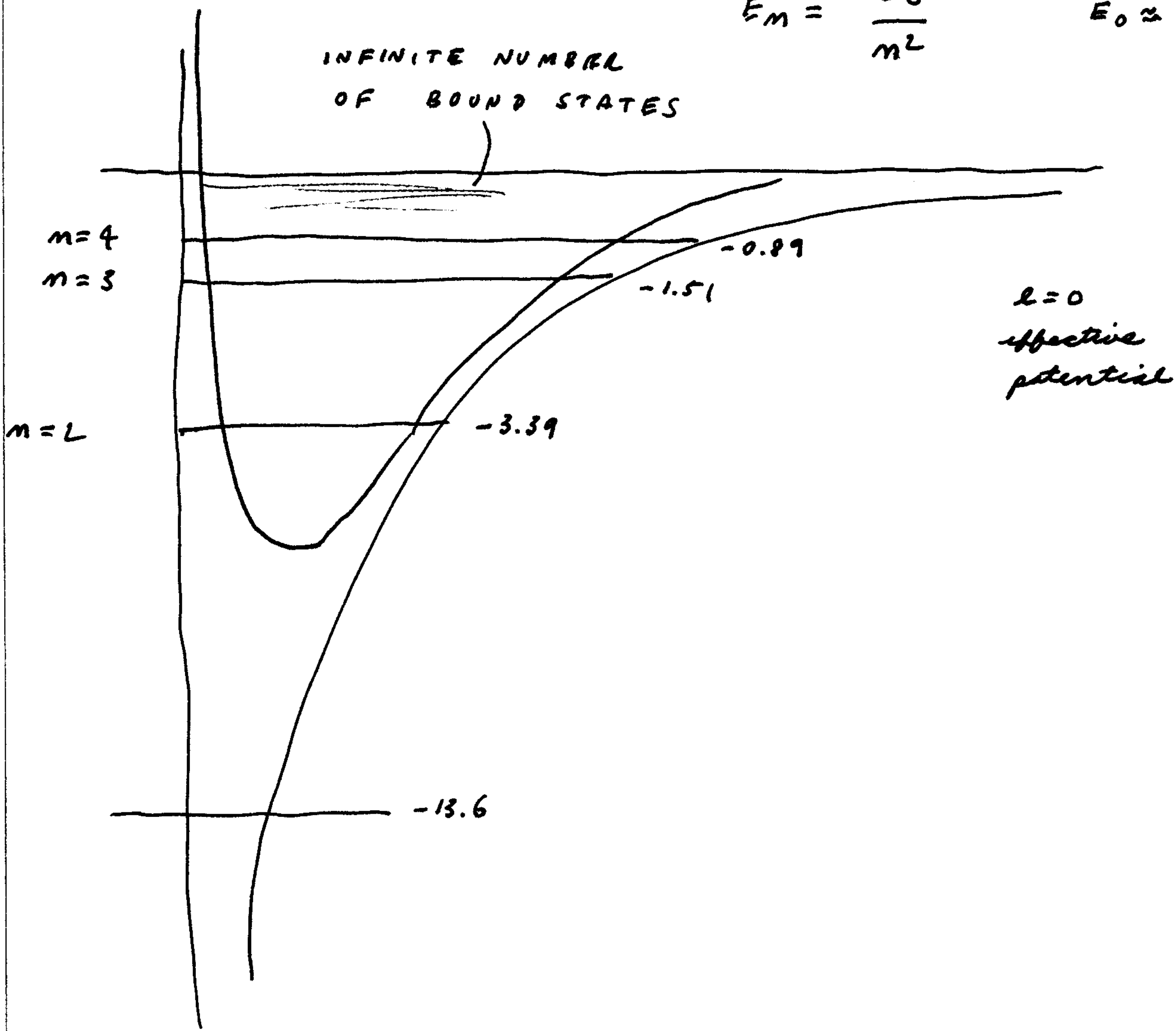
Fig. (B)



10
20
r/a_0
0
E_4
$n = 4$
E_3
$n = 3$
E_2
$n = 2$
−5
Coulomb potential
Energy
−10
E_1
$n = 1$
−15
[eV]

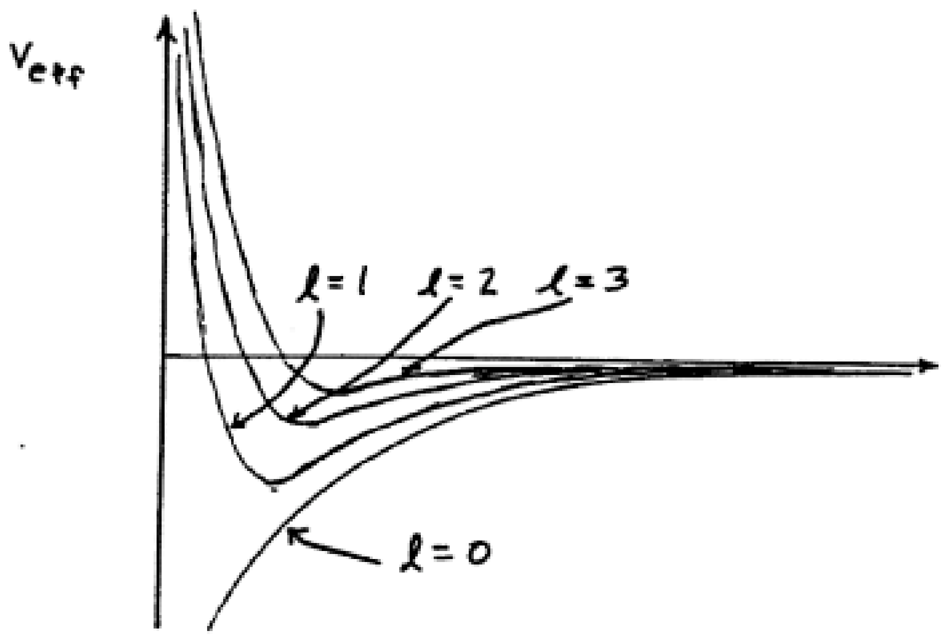
ENERGY DEGENERACY only n

$$E_n = \frac{E_0}{n^2} \qquad E_0 \approx -13.$$



The Effective Potential Depends on the Angular Momentum

=> Series of Nested Wells



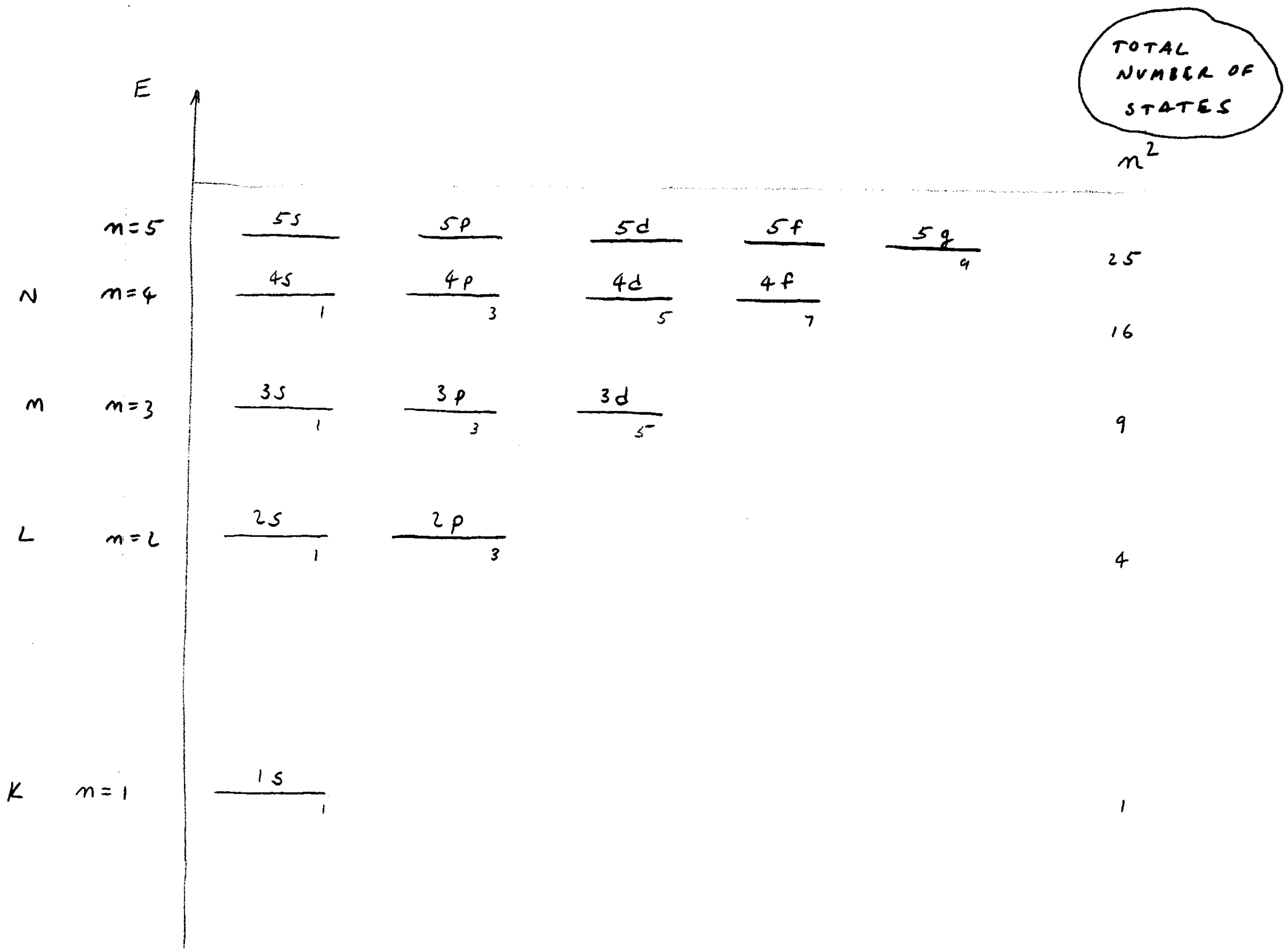
Series of States in each Well
Ground, 1st, 2nd, 3rd, ... excited

Energy
Degeneracy

$$E_n = - Z^2 \frac{E_0}{n^2}$$

for each n: $\ell = 0, 1, \ldots, n$

for each ℓ: $m = -\ell, \ldots, +\ell$



	$\ell=0$	$\ell=1$	$\ell=2$	$\ell=3$	$\ell=4$	
	s	p	d	f	g	h i j k
$(2\ell+1)$	1	3	5	7	9	

FIRST FEW RADIAL WAVEFUNCTIONS $\quad \mathfrak{z} = Z/a_0$

$n=1 \qquad R_{10}(r) = 2\,\mathfrak{z}^{3/2}\,e^{-\mathfrak{z}r}$

$n=2 \qquad R_{20}(r) = \frac{1}{\sqrt{2}}\,\mathfrak{z}^{3/2}\left(1-\frac{1}{2}\mathfrak{z}r\right)e^{-\mathfrak{z}r/2}$

$$R_{21}(r) = \frac{1}{2\sqrt{6}}\,\mathfrak{z}^{5/2}\,(r)\,e^{-\mathfrak{z}r/2}$$

$n=3 \qquad R_{30}(r) = \frac{2}{3\sqrt{3}}\,\mathfrak{z}^{3/2}\left(1-\frac{2}{3}\mathfrak{z}r+\frac{2}{27}\mathfrak{z}^2r^2\right)e^{-\mathfrak{z}r/3}$

$$R_{31}(r) = \frac{8}{27\sqrt{6}}\,\mathfrak{z}^{5/2}\left(\mathfrak{z}r-\frac{1}{6}\mathfrak{z}^2r^2\right)e^{-\mathfrak{z}r/3}$$

$$R_{32}(r) = \frac{4}{81\sqrt{30}}\,\mathfrak{z}^{7/2}\,(r^2)\,e^{-\mathfrak{z}r/3}$$

general form $\qquad (\text{NORM})\,(\text{POLYNOMIAL})\,e^{-Zr/na_0}$

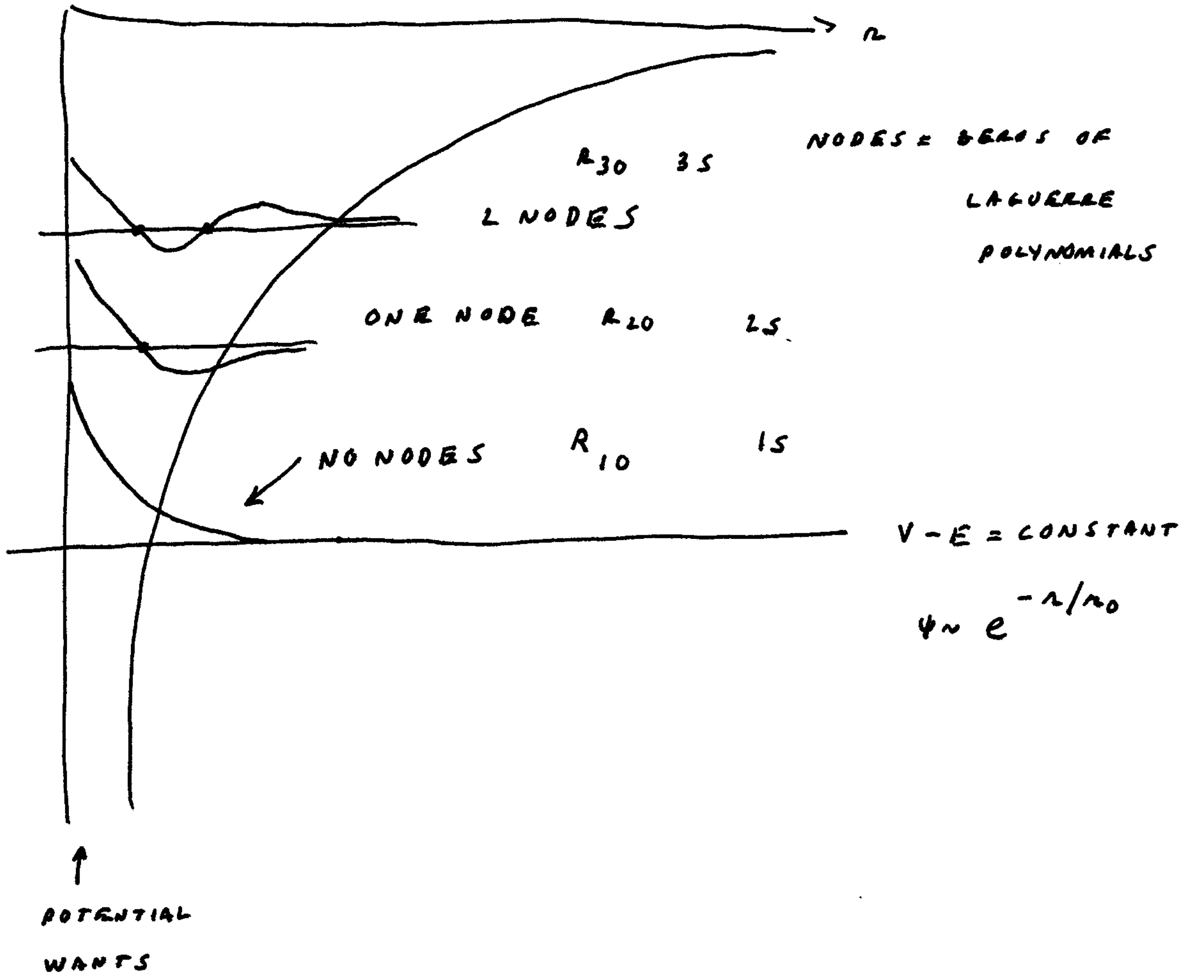
WHAT DO THE RADIAL WAVEFCNS LOOK LIKE?

" " " RADIAL PROB DISTS " " ?

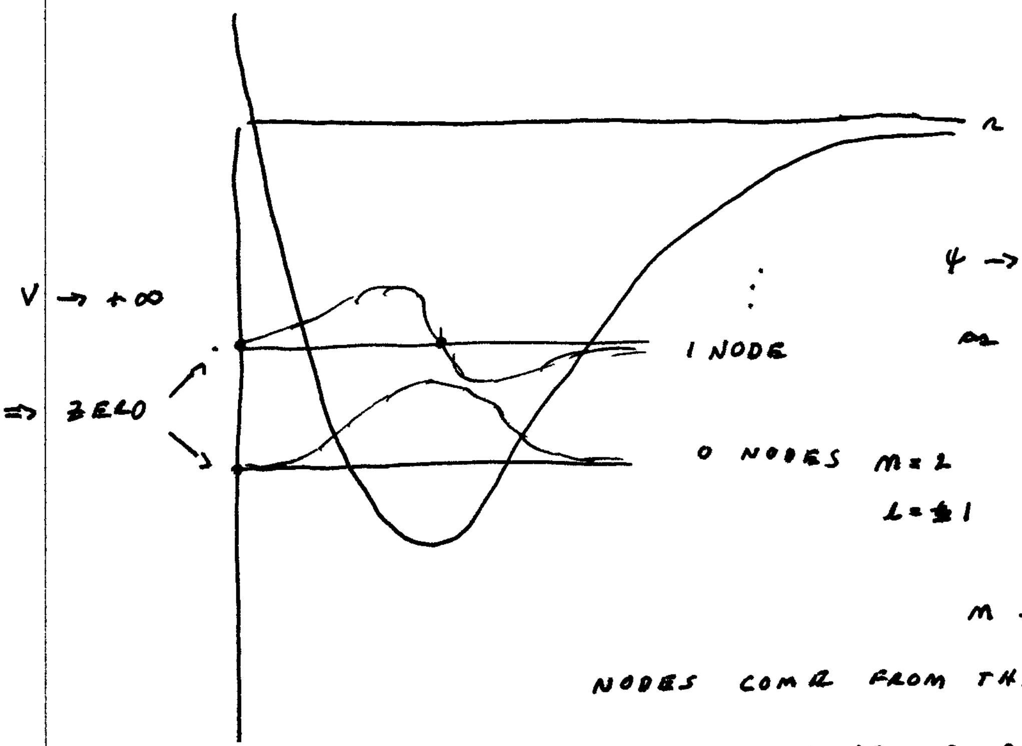
" " " 3d " " " " ?

$\ell = 0$ WAVE FCNS

$R_{n\ell} \Rightarrow R_{n0}$'s $= nS$ energy $\ell = 0$ WELL   1S 2S 3S 4S...



$\ell = 1$ WAVE FCNS



$\psi \to e^{-r/r_0}$

as $r \to \infty$

$n = 2$

$\ell = 1$

R_{21}

2p

3p

$n \to$ 4p $\leftarrow \ell$

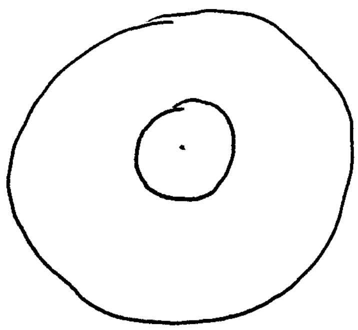
NODES COME FROM THE ZEROS OF THE LAGUERRE POLYNOMIALS

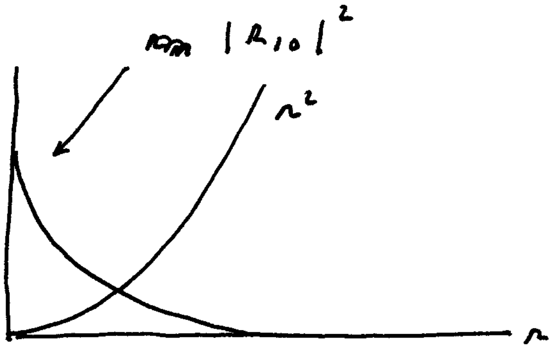
KNOW $R_{n\ell}$'s

FIND $P_{n\ell}$'s

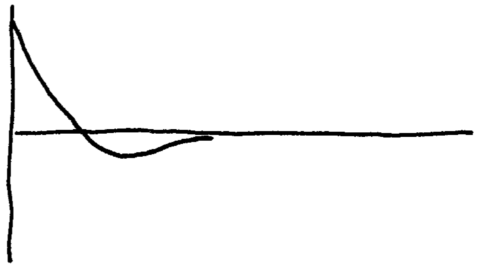
$$P(x)\,dx = |\Psi(x)|^2\,dx$$

$$P_{n\ell}(r) = |R_{n\ell}(r)|^2\, r^2\,dr$$

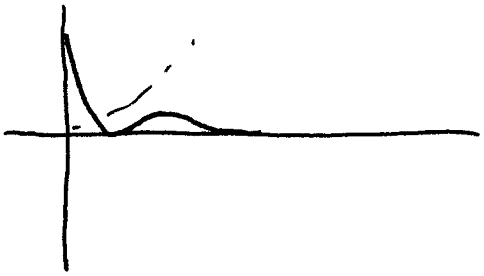




R_{nl} $\qquad$ R_{20}

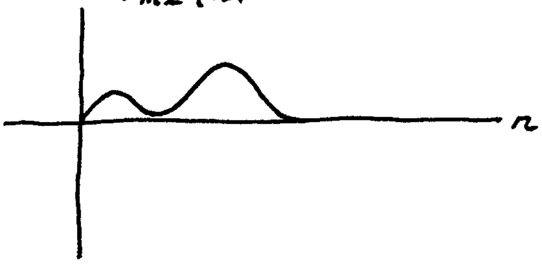


$|R_{nl}|^2$ $\qquad$ $|R_{20}|^2$



$r^2 |R_{20}|$

$P_{nl}(r)$ $\qquad$ RADIAL PROB DIST



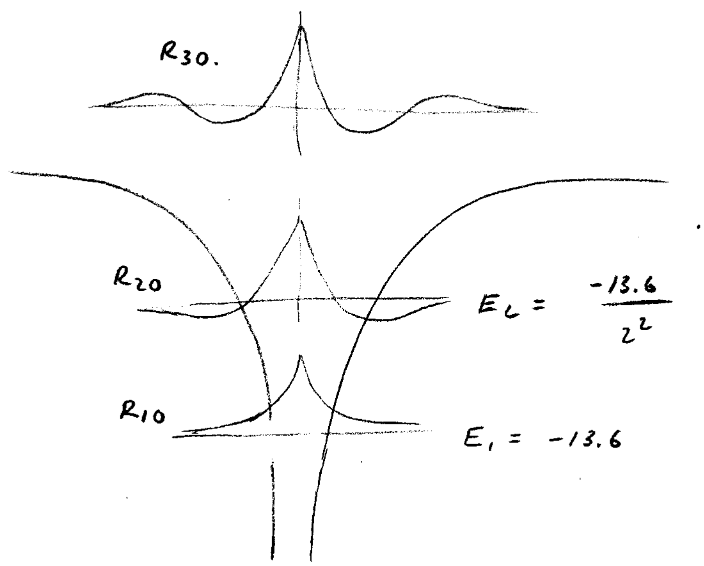
Probability distributions

$$P(\vec{r}) = |\psi_{n\ell m}(\vec{r})|^2 \, d^3r.$$

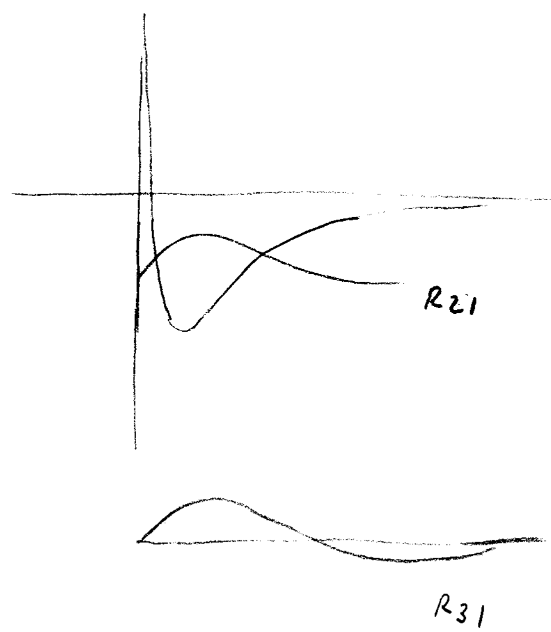
$$|R_{n\ell}(r)|^2 \, r^2 \, dr$$

$$|Y_{\ell m}(\theta, \varphi)|^2 \, d\Omega$$

$\ell = 0$



$\ell = 1$



p 142 pauling

p 266 Eisberg.

Angular dependence

$$|Y_{\ell m}(\theta,\varphi)|^2 = \Theta(\theta)\, e^{im\varphi}\, \Theta^*(\theta)\, e^{-im\varphi}$$

phase changes as you go around z axis but the prob does not change

$$|\Theta(\theta)|^2$$

Polar plot

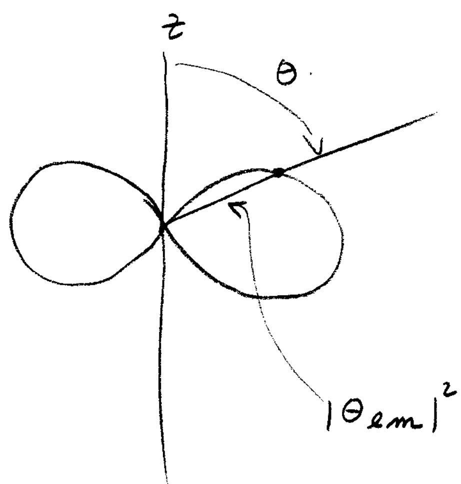
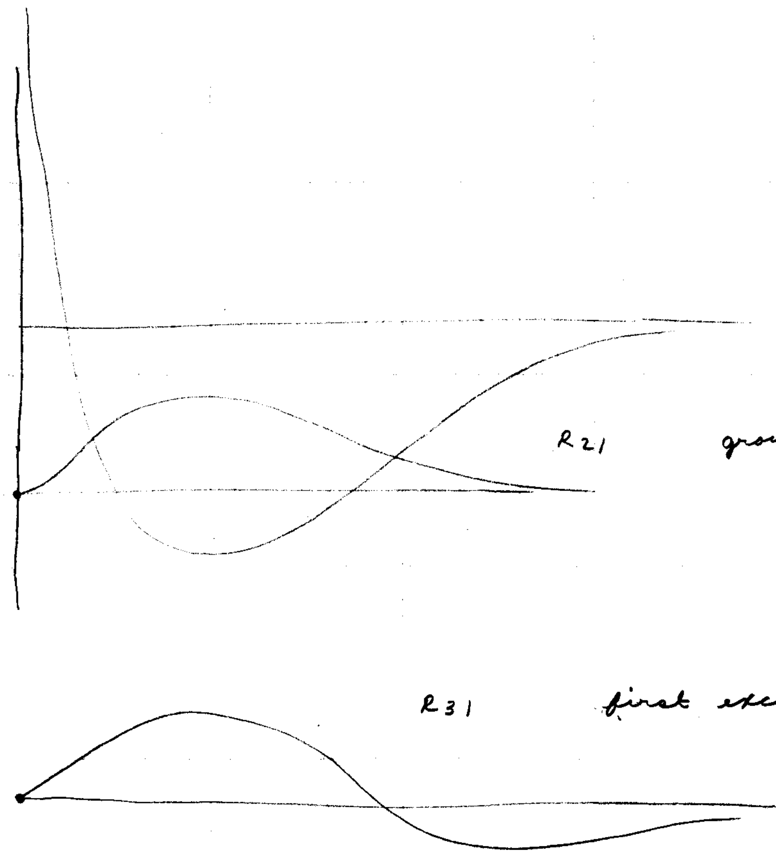


Figure of revolution around z axis

p 271 272 Eisberg

$\ell = 1$ well



ZERO AT ORIGIN

$V = \infty \Rightarrow$

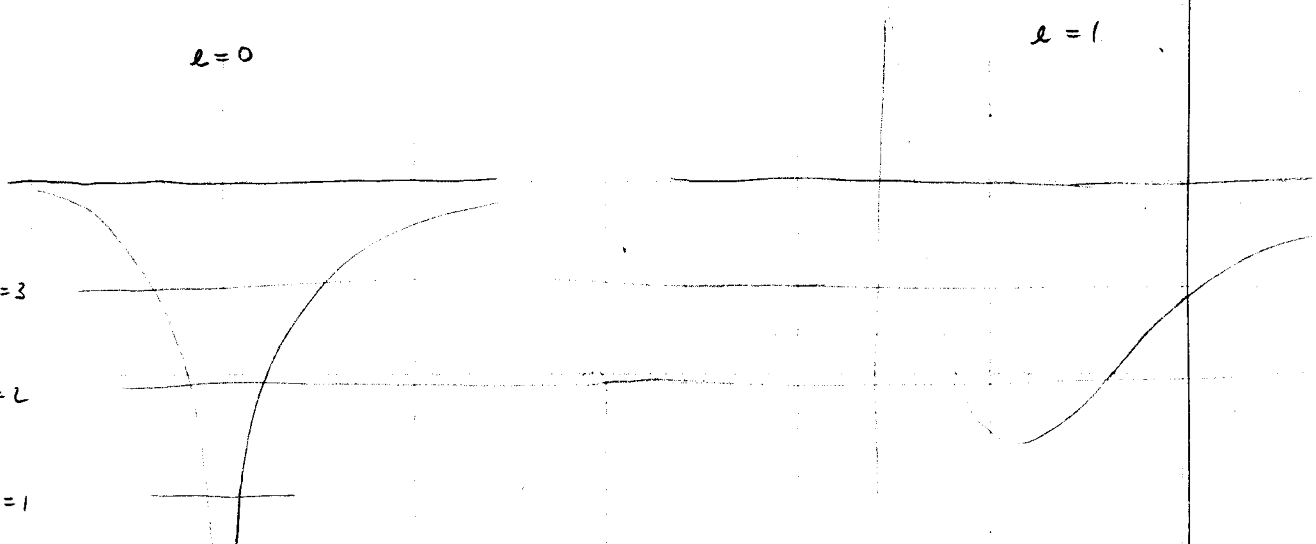
R_{21} ground state of $\ell = 1$ well

R_{31} first excited state of $\ell = 1$ well.

degeneracy :

$\ell = 0$

$\ell = 1$



$n = 3$

$n = 2$

$n = 1$

R_{20} has same energy as R_{21}

all $R_{n\ell}$'s have same energy.

$$R_{30} = \frac{2}{3\sqrt{3}} Z^{3/2} \left(1 - \tfrac{2}{3} Zr + \frac{2}{27} Z^2 r^2\right) e^{-Zr/3}$$

$$R_{31} = \frac{8}{27\sqrt{6}} Z^{3/2} \left(Zr - \frac{1}{6} Z^2 r^2\right) e^{-Zr/3}$$

$$R_{32} = \frac{4}{81\sqrt{30}} Z^{7/2} r^2 e^{-Zr/3}$$

$\vdots$

for each n: $\quad \ell = 0, \ldots, n-1$

$$e^{-Zr/n a_0}$$

$\ell = 1$