Lecture 17

Everything you should remember about hydrogen forever

QUALITATIVE FIRST

SOLVE TISE FOR HYDROGEN

FIND eV'S $\longrightarrow$ EIGEN ENERGIES

FIND $e\vec{v}$'S $\longrightarrow$ ENERGY EIGENFCNS

STATIONARY STATES

$$|n\,l\,m\rangle \longrightarrow \psi_{nlm}(\vec{r})$$

$$E_{nlm} \longrightarrow E_n$$

TWO POV:

(1) $\nabla^2 \longrightarrow$ RADIAL ∇^2 + ANGULAR ∇^2

SOLN'S Y_{lm}'S

SEPARATE $\Rightarrow$ RADIAL EQN

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

$$H = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2} + V(r)$$

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

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

$$\frac{\vec{p}^{\,2}}{2m} = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2}$$

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

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

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

ANGULAR MOMENTUM BARRIER REPULSIVE

ATTRACTIVE COULOMB POTENTIAL

SOLUTIONS TO THE RADIAL EQUATION

$$R_{nl}(r) \sim \left(\begin{array}{c}\text{ASYMPTOTIC}\\ \text{FORM}\end{array}\right)\left(\begin{array}{c}\text{LAGUERRE}\\ \text{POLYNOMIALS}\end{array}\right)$$

$\exp(-r/na_0)$ HYDROGEN

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

Ways to solve the radial equation

(1) Solve the differential equation

- Find the asymptotic form
- Separate it
- Differential equation for each value of l
- Make the diff eq dimensionless
- Put highest derivative first
- Set its coefficient equal to 1
- Futz around
- Discover radial equation is Laguerre eqn !!!
- Declare victory
- Normalize the wave functions (caution)

(2) Use the ladder operators

(3) Type “hydrogen atom wavefunctions” into Google

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

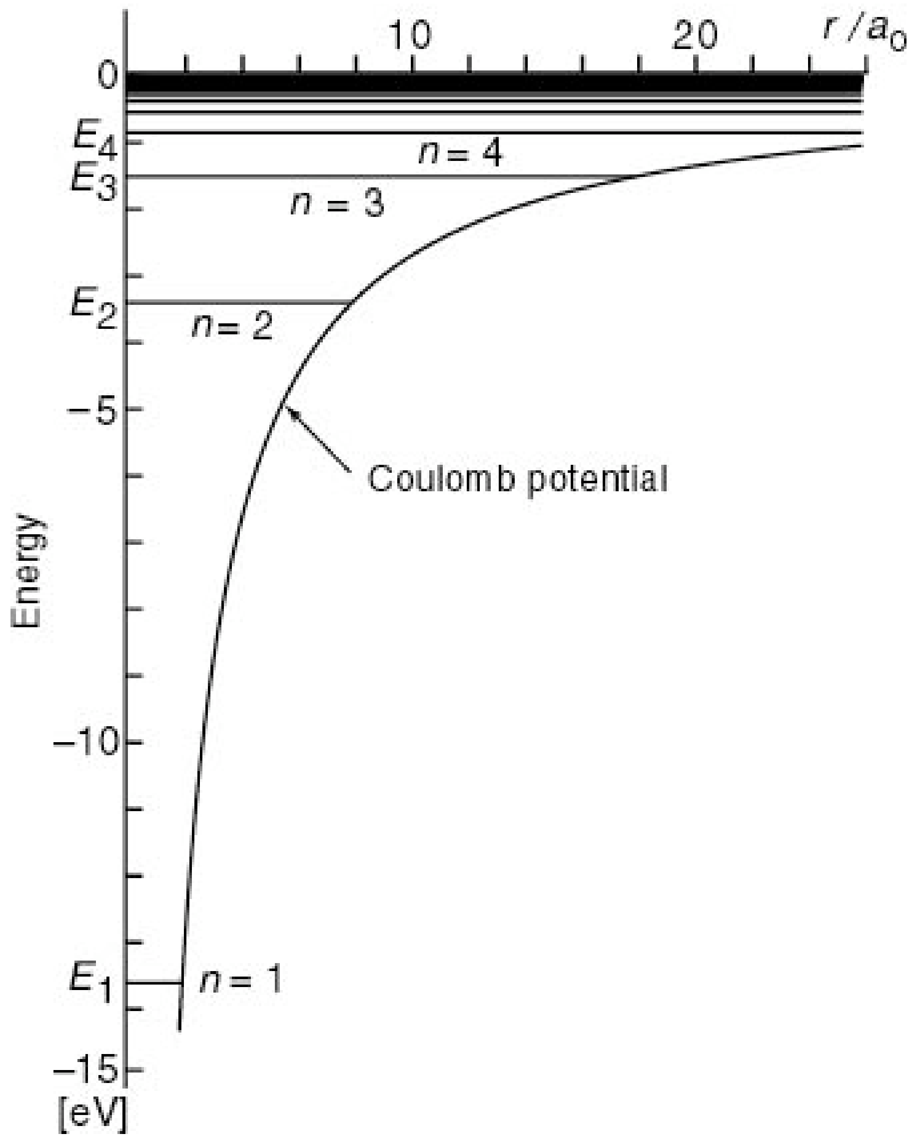
(2) USE LADDER OPERATORS

EIGENFCNS ⇒ ENERGY EIGEN FCNS

EIGENVALUES ⇒ EIGEN ENERGIES

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

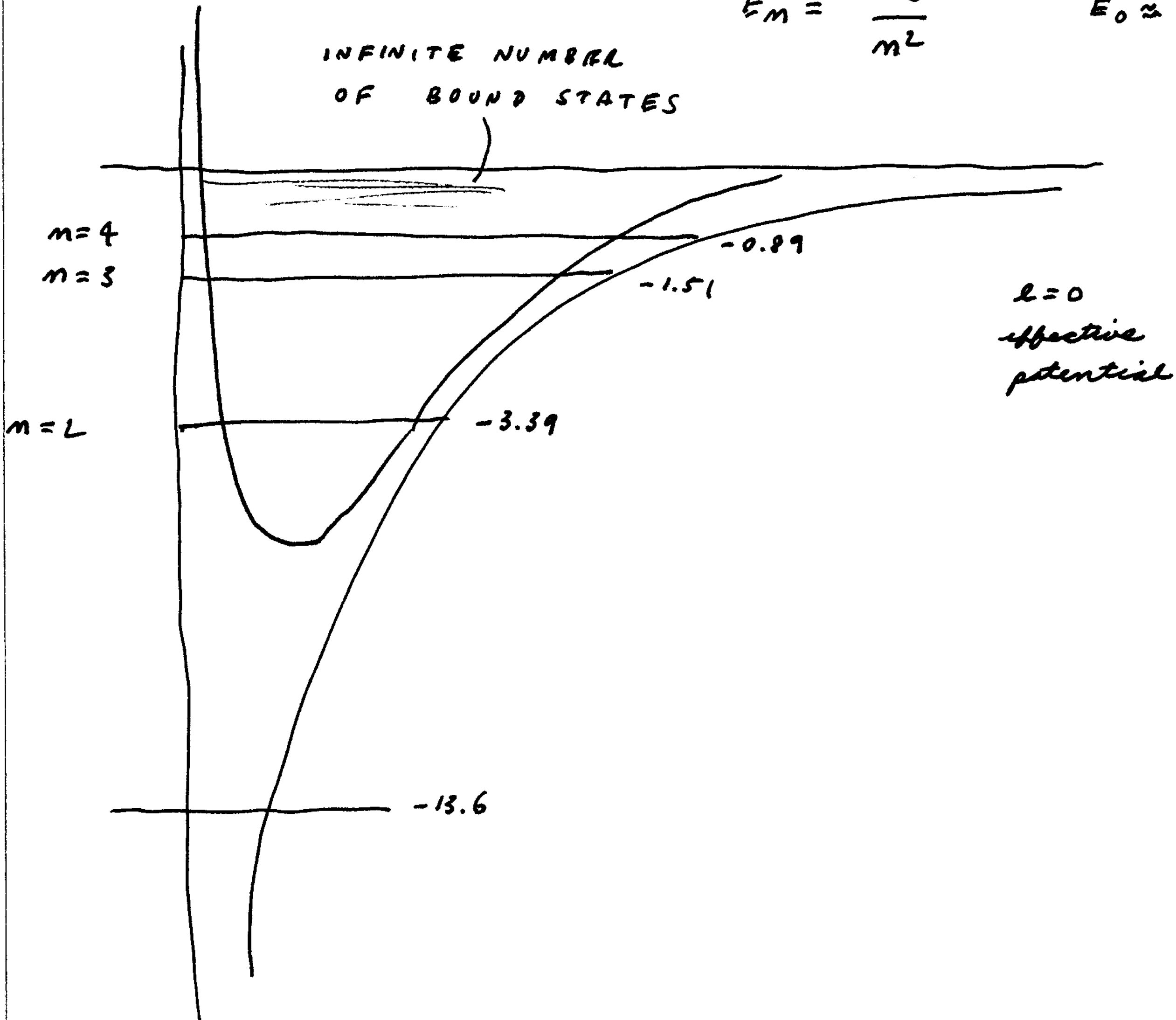
$$E_n' = -\frac{Z^2 Ry}{n^2}$$ HYDROGEN-LIKE



10
20
r / a0
0
E4
n = 4
E3
n = 3
E2
n = 2
−5
Coulomb potential
Energy
−10
E1
n = 1
−15
[eV]

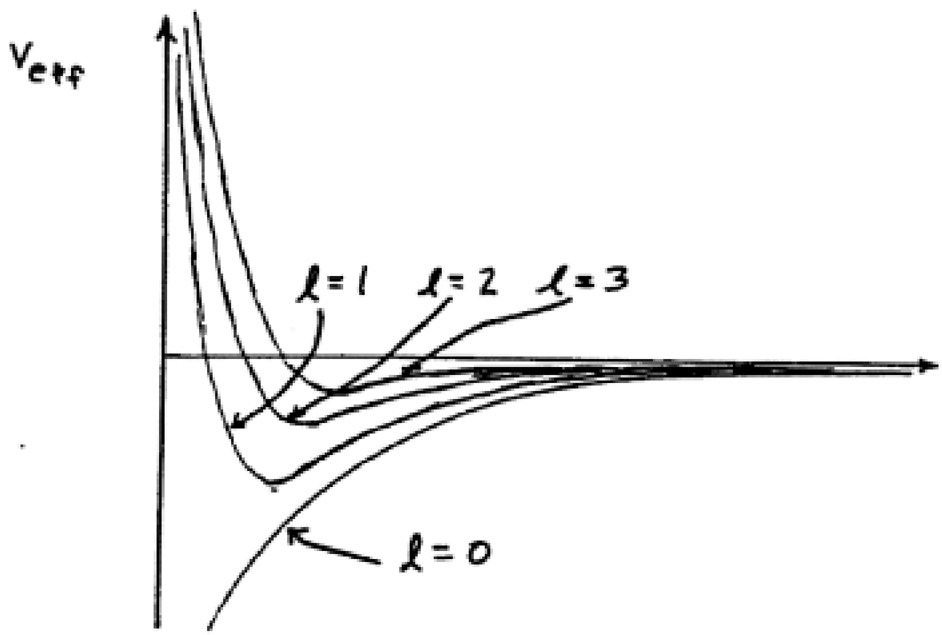
ENERGY DEGENERACY only n

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

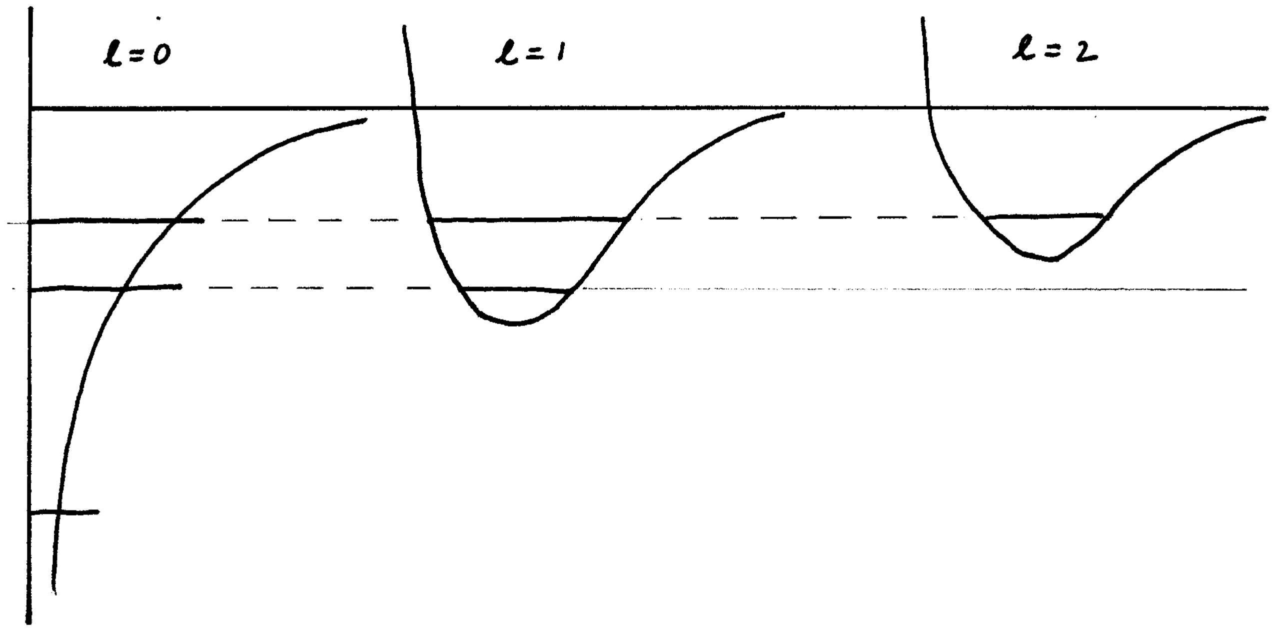


The Effective Potential Depends on the Angular Momentum

=> Series of Nested Wells



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



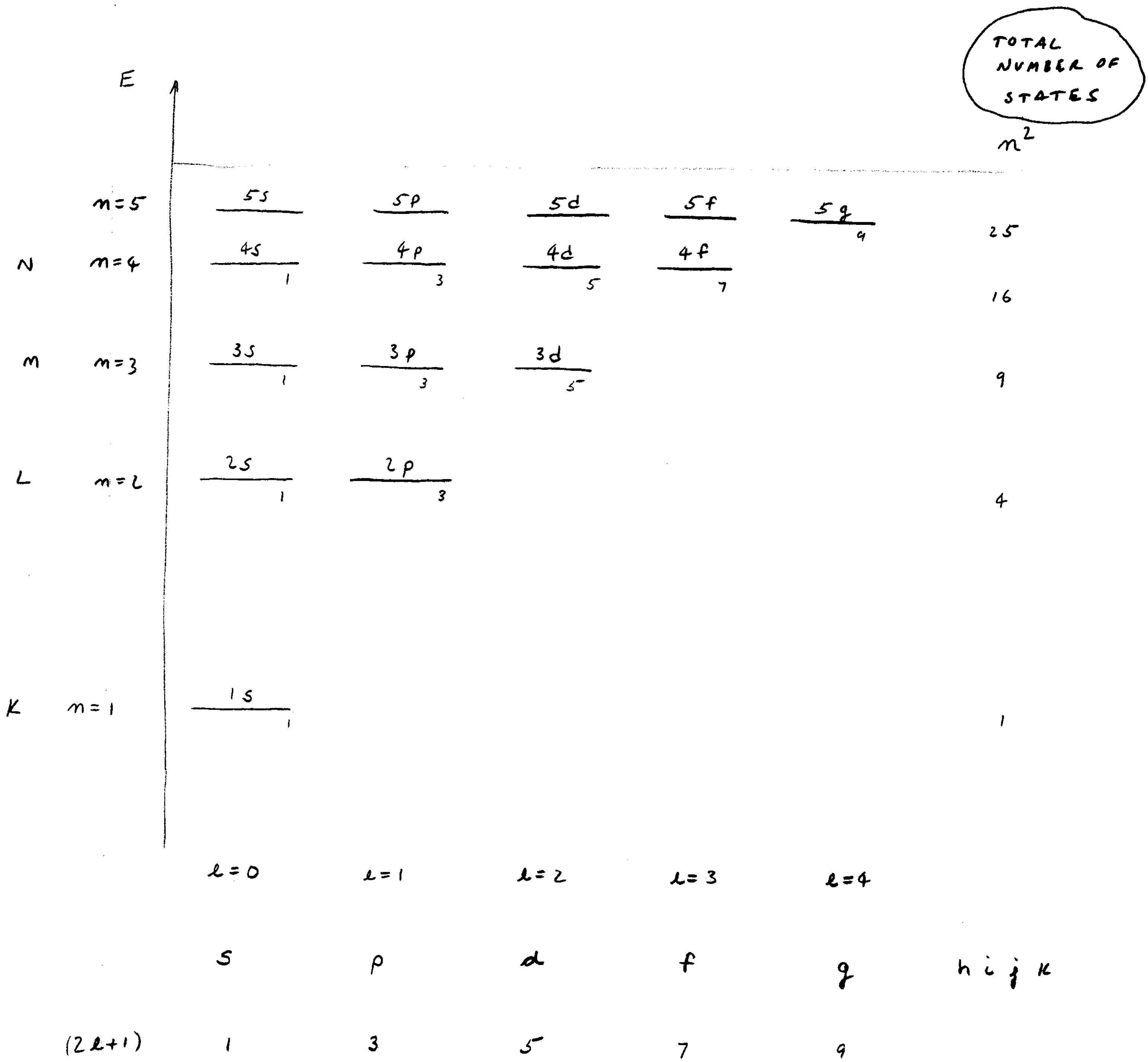
$\ell = 0$
$\ell = 1$
$\ell = 2$

Energy
Degeneracy

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

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

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



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

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

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

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

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

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

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

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

WHAT DO THE RADIAL WAVEFCNS LOOK LIKE?

" " " RADIAL PROB DISTS " " ?

" " " 3d " " " " ?

$l = 0$ WAVE FCNS

R_{nl}

energy — orbital angular momentum

$l=0$ R_{n0}'s

ANOTHER NOTATION ns 1s 2s 3s 4s ...

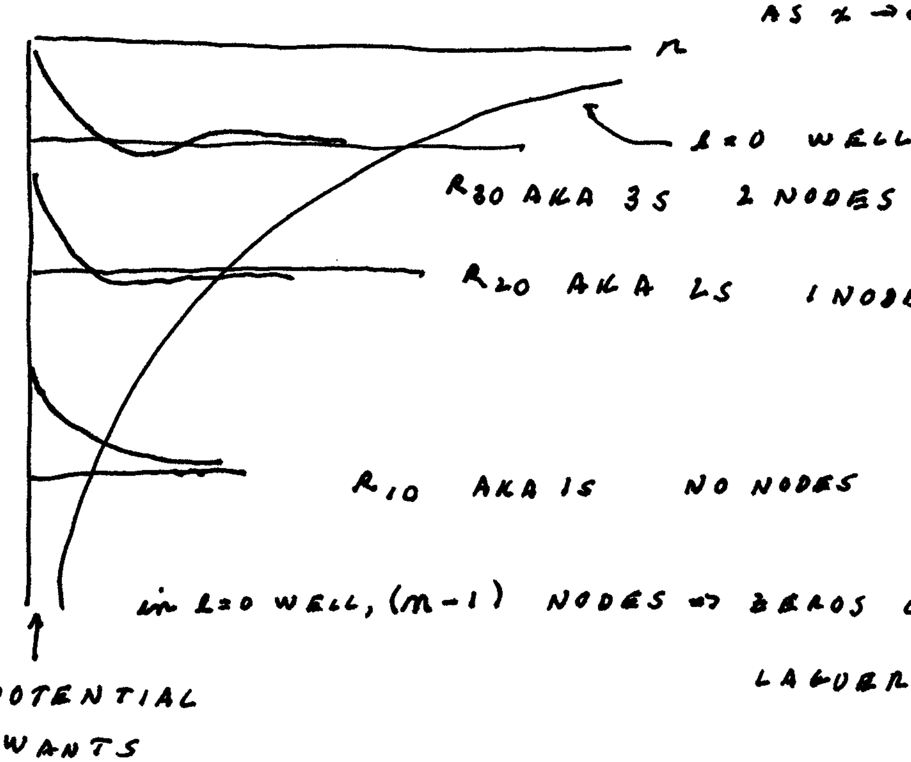
$l=0$ s

$l=1$ p

$l=2$ d

ASYMPTOTIC FORM

AS $r \to \infty$ $\psi \to e^{-r/a_0}$

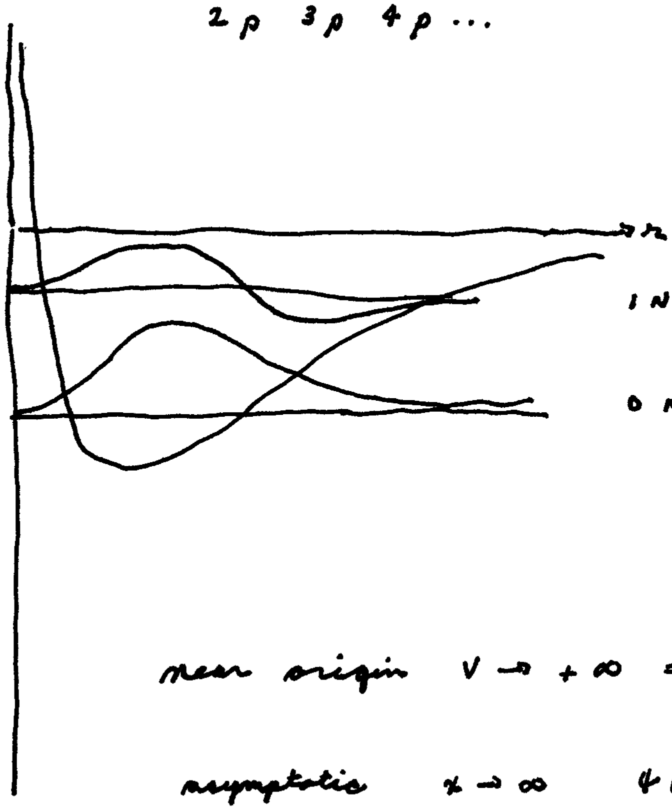


in $l=0$ WELL, $(n-1)$ NODES $\Rightarrow$ ZEROS OF THE LAGUERRE POLY

$\ell = 1$ WAVE FCNS

$R_{n\ell} \rightarrow R_{n1}$

2p 3p 4p ...



near origin $V \rightarrow +\infty \Rightarrow \psi(0) = 0$

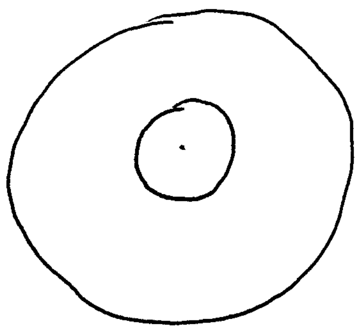
asymptotic $x \rightarrow \infty$ $\psi(x) \rightarrow e^{-r/na_0}$

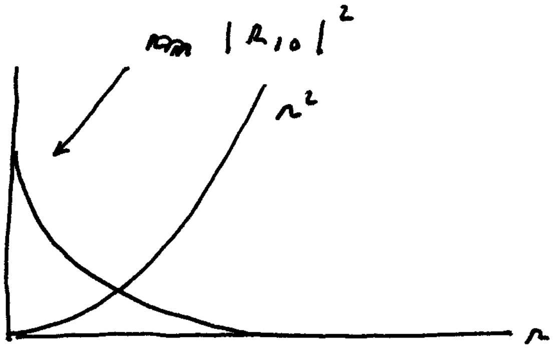
KNOW R_{ml}'s

FIND P_{ml}'s

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

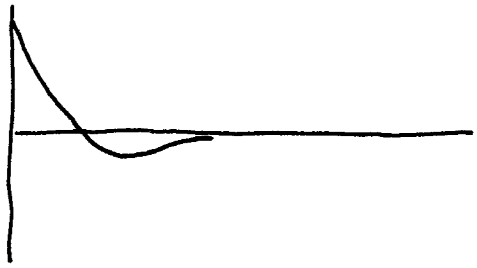
$$P_{ml}(r) = |R_{ml}(r)|^2\, r^2\, dr$$





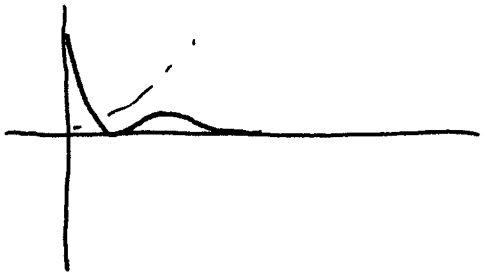
R_{nl}

R_{20}



$|R_{nl}|^2$

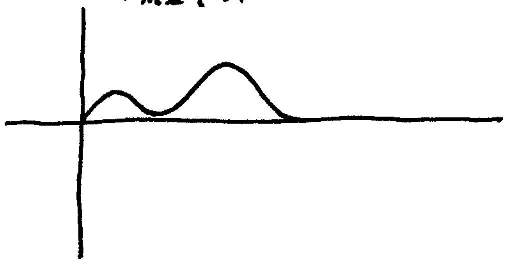
$|R_{20}|^2$



$r^2 |R_{20}|$

RADIAL PROB DIST

$P_{nl}(r)$



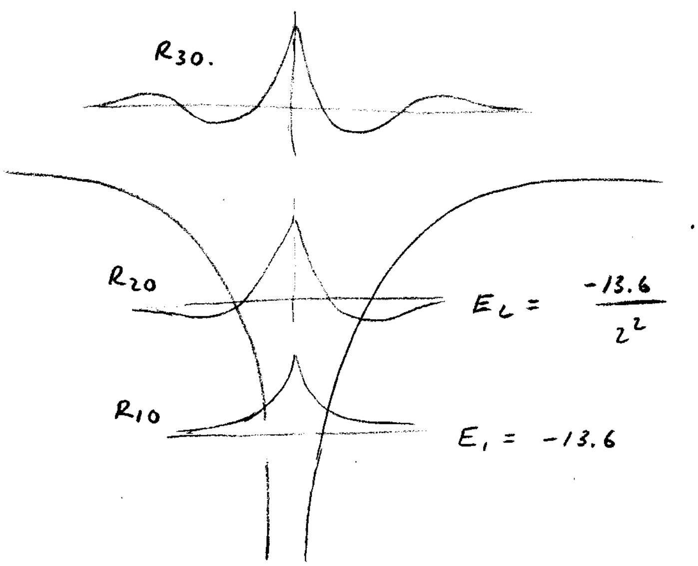
Probability distributions

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

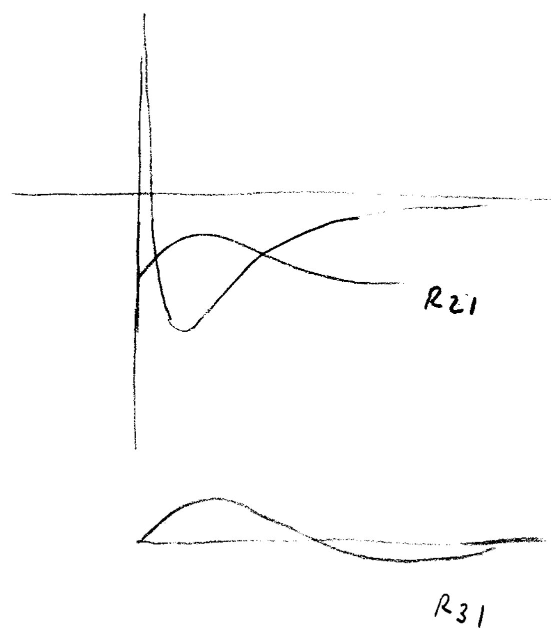
$$|R_{n\ell}(r)|^2 \, r^2 \, dr$$

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

$\ell = 0$



$\ell = 1$



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

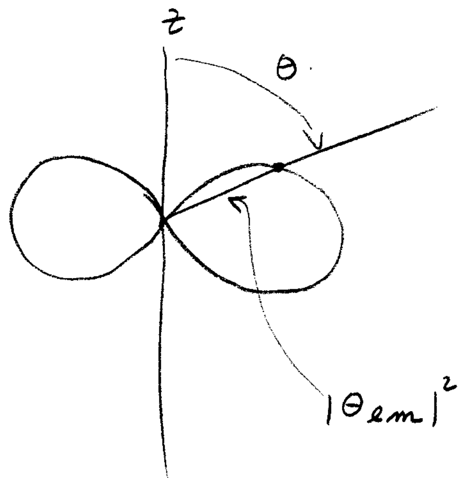


Figure of revolution around z axis

p 271 272 Eisberg

The Functional Form
http://panda.unm.edu/Courses/Finley/P262/Hydrogen/WaveFcns.html

The Radial Components
http://hyperphysics.phy-astr.gsu.edu/Hbase/hydwf.html#c1

The Angular Components
http://oak.ucc.nau.edu/jws8/dpgraph/Yellm.html

Radial times Angular
http://www.falstad.com/qmatom/
http://webphysics.davidson.edu/faculty/dmb/hydrogen/intro_hyd.html

The Story Continues
http://www.pha.jhu.edu/~rt19/hydro/

Associated Laguerre Polynomials

Some wag once said the nice thing about standards is that there are so many to choose from. I have been trying to come to grips with the difference between what I presented in class and the formulae in Sakurai. It is easy to explain the differences on the basis of different conventions about the associated Laguerre polynomials.

If you want to skip details, a main result is that Sakurai and *Mathematica* use different conventions. If we call $\mathcal{L}_n^q(\rho)$ the convention of Sakurai and $L_p^{(q)}(\rho)$ the convention of *Mathematica*, we have

$$\mathcal{L}_{p+q}^q(\rho) = (p+q)!(-1)^q L_p^{(q)}(\rho) \ .$$

Below are the details. They are presented somewhat in the order of my investigation and not according to the shorted derivation of the above result.

Differential equation

I have consulted two well known books on mathematical functions that adhere to the same index convention, but have different normalization conventions. The first book that I consulted by Abramowitz & Stegun states on pg 778, Eqs. (22.5.16) and (22.5.17):

$$L_n^{(0)}(x) = L_n(x)$$

$$L_n^{(m)}(x) = (-1)^m \frac{d^m}{dx^m}[L_{n+m}(x)]$$

Also, on pg 781, in Eq. (22.6.15), the differential equation is given.

$$x\frac{d^2}{dx^2}L_n^{(\alpha)}(x) + (\alpha+1-x)\frac{d}{dx}L_n^{(\alpha)}(x) + nL_n^{(\alpha)}(x) = 0 \ .$$

The differential equation is very valuable, but being linear, does not tell us anything about the normalization.

Another well known book by Morse & Feshbach on pg 784, in an unnumbered equation three lines from the bottom of the page gives their convention for the associated Laguerre polynomials.

$$L_n^m(z) = (-1)^m \frac{d^m}{dx^m}[L_{n+m}^0(z)] \ .$$

The differential equation is also given a few lines above:

$$z\frac{d^2}{dz^2}L_n^a(z) + (a+1-z)\frac{d}{dz}L_n^a(z) + nL_n^a(z) = 0 \ .$$

Morse & Feshbach do not put the upper index in parentheses, otherwise, it looks like these conventions might agree. We can be pretty certain that in these two books the $L_n^{(a)}$ is a polynomial of degree n. However, we will soon see that the normalizations don't agree in the two books.

Sakurai convention

Now, let's turn to Sakurai. On pg 454 in Eq. (A.6.4), we find

$$L_p^q(\rho) = \frac{d^q}{d\rho^q} L_p(\rho) \ .$$

This leads us to conclude that L_p^q is of degree $p-q$, and makes the result above plausible. In fact, if the normalizations were the same, we would expect:

$$\mathcal{L}_{p+q}^q(\rho) = \frac{d^q}{d\rho^q} L_{p+q}(\rho) = (-1)^q L_p^{(q)}(\rho) \qquad \textbf{Not quite correct!} \ .$$

Class Derivation

In class, I presented the differential equation for the associated Laguerre polynomials as stated by *Mathematica*,

$$xy'' + (a+1-x)y' + ny = 0 \ .$$

This is the same convention as Abramowitz & Stegun and Morse & Feshbach.

In class, we found we needed to solve this differential equation:

$$\rho L'' + (2(l+1) - \rho)L' + (\lambda - l - 1)L = 0 \ ,$$

but $\lambda = n$, the total quantum number, and $n - l - 1 = n'$ the radial quantum number. So, we have

$$\rho L'' + (2l + 1 + 1 - \rho)L' = n' L = 0 \ .$$

In the notation of Abramowitz & Stegun, *Mathematica* or the Morse & Feshbach index convention, the solution to the differential equation is

$$L_{n'}^{(2l+1)}(\rho) = L_{n-l-1}^{(2l+1)}(\rho) \ .$$

In Sakurai notation, $L_{n-l-1}^{(2l+1)}(\rho) = (-1)^{2l+1}\mathcal{L}_{n+l}^{2l+1} = -\mathcal{L}_{n+l}^{2l+1}$. This explains the indices for R_{nl} in Sakurai in the equation above (A.6.3).

Pinning Down the Normalizations

We still need to consider normalization conventions, and that can be done from the generating function or from what is know as Rodrigues' formula. In fact, in retrospect, it seems that just looking at the Rodrigues' formulae in the three books might have been the easiest way to proceed.

In Abramowitz & Stegun, we find on pg 785, Eq. (22.11.6)

$$L_n^{(\alpha)}(x) = \frac{1}{n!} e^x x^{-\alpha} \frac{d^n}{dx^n}[x^{n+\alpha} e^{-x}] \ .$$

On pg 784 of Morse & Feshbach, we find

$$L_n^a(z) = \frac{\Gamma(a+n+1)}{\Gamma(n+1)} \frac{e^z}{z^\alpha} \frac{d^n}{dz^n}[z^{a+n}e^{-z}] \ .$$

If we set α and a to zero, we can compare with Sakurai, which states in Eq. (A.6.5)

$$L_p(\rho) = e^\rho \frac{d^p}{d\rho^p}(\rho^p e^{-\rho}) \ .$$

We immediately see that Sakurai agrees in normalization with Morse & Feshbach, at least for the Laguerre polynomials, if not for the associated Laguerre polynomials. However, the two books on mathematical methods differ by a factor of $(n+a)!$ in their normalizations with Abramowitz & Stegun convention being smaller by division by that factor. Morse & Feshbach include a small table of associated Laguerre polynomials at the bottom of page 784. They have $L_0^n = n!$, whereas Abramowitz & Stegun according to Eq. (22.4.7) have $L_0^{(\alpha)} = 1$. The only remaining mystery is which normalization convention *Mathematica* obeys. With this command

$$\mathrm{Table}[\{\mathrm{n}, \mathrm{LaguerreL}[0,\mathrm{n},\mathrm{x}]\}, \{\mathrm{n}, 0, 6\}]$$

you will easily find that all results are 1 and *Mathematica* follows the Abramowitz & Stegun normalization.

Further, I coded up the Rodrigues' formula with the Sakurai convention and compared with $(p+q)!(-1)^q L_p^{(q)}$ where the I used the *Mathematica* function `LaguerreL[p,q,x]`. They were in agreement.

Mystery solved! Quantum mechanics and children can now sleep soundly at night.