## Lecture 15

Everything you should remember about hydrogen forever

Qualitative first

SOLVE TISE FOR HYOLOGEN

FIND CNIS $\rightarrow$ EIGEN THNERGIIF
FIND EN'S $\rightarrow$ ENERGY FIGENECNS

STATIONARY STATES

$$
\begin{aligned}
& \mid m \& m>\psi_{n \ell m}(\vec{r}) \\
& E_{m \& m} \rightarrow E_{m}
\end{aligned}
$$

Two pov:
(1) $\nabla^{2} \rightarrow$ RADIAL $\nabla^{2}+A N G U L A R \nabla^{2}$ sonn's Yem's

SEPARATE $\Rightarrow$ RADIALEQN
(2) $\quad H=\frac{\vec{P}^{2}}{2 m}+V(\Omega)$

$$
H=\frac{p_{2}^{2}}{2 m}+\frac{L^{2}}{2 m n^{2}}+V(\Omega)
$$

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

$$
\begin{aligned}
& H=\frac{\vec{P}^{2}}{2 m}+V(\Omega) \\
& \frac{\vec{P}^{2}}{2 m}=\frac{\rho_{n}^{2}}{2 m}+\frac{L^{2}}{2 m n^{2}}
\end{aligned}
$$

$$
\text { PRODVCT ANSATZ } \Psi=R_{M L} Y_{\text {LM }}
$$

$$
\left[\frac{P_{R}^{2}}{2 m}+\frac{L^{2}}{2 m n^{2}}+V(n)\right] R_{m l} Y_{\ell m}=E_{n} R_{n l} Y_{\ell m}
$$

$$
\left[\frac{P_{n}^{2}}{2 m}+\frac{\ell(\ell+1) \hbar^{2}}{2 m r^{2}}+V(\imath)\right] R_{n \ell}=E_{n} R_{n l}
$$



ANGULAR MOMENTOM
BARAER
REPULSIVE


ATTRACTIVE COOLOMB

DOTENTIAL

SOLUTIONS TO THE AADIAL EQUATION

$$
R_{m l}(r) \sim\binom{\text { ASVMPTOTIC }}{\text { fORM }}\binom{\text { LAGURLRE }}{\text { POLYNOMAALS }}
$$

$$
\begin{array}{ll}
\text { afyqupa } & \text { HYOROGEN-LIKE } \\
\text { exp }\left(-n / m a_{0}\right) & \text { exp }\left(-z r / m a_{0}\right)
\end{array}
$$

## Ways to solve the radial equation

(1) Solve the differential equation

Find the asymptotic form
Separate it
Differential equation for each value of I
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

As always, first solve the TISE
Find the eigenvalues aka the eigenenergies
Find the eigenfons aka the energy eigenfons aka the stationary states

GIGENGCNS $\Rightarrow$ ENERGY RIGOR RUNS
EIGENVALUES $\Rightarrow$ EIGEN IRNBRGIES

$$
E_{n}=\frac{-2 y}{n^{2}}=\frac{-13.6 \mathrm{eV}}{n^{2}}
$$

eigenenergies
HVOROAEN

$$
\epsilon_{m}^{\prime}=-\frac{z^{2} \angle y}{n^{2}}
$$

HYDROGEN - LIKE

The I=0 well, aka the s-well, is the pure Coulomb potential Because $\mathrm{I}=0$ there is no angular momentum barrier infinite number of bound states


NEW RISE

$$
\left[-\frac{\hbar^{2}}{2 \mu r} \frac{\partial^{2}}{\partial n^{2}} r-\frac{e^{2}}{n}+\frac{e(e+1) \hbar^{2}}{2 \mu r^{2}}\right] R_{m}=1_{n} R_{n}
$$

Id PROBLEM
with ifffrctive potential The effective potential

bNerGy degentracy
anly $n$

$$
E_{n}=\frac{E_{0}}{n^{2}}
$$

$$
E_{0} \approx-13 .
$$

INFINITE NUMBIFR
OF BOUND STATES

$$
n=L
$$



# The Effective Potential Depends on the Angular Momentum 

## => Series of Nested Wells



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

> The states in different wells line up!

## Set of nested wells

3s
2s
$1 s$


The s well
The I=0 well

The states line up!

The Energy Degeneracy

$$
E_{n}=-z^{2} \frac{E_{0}}{n^{2}}
$$

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

$$
\text { or ease } l: m=-l, \ldots,+l
$$

n = the principal quantum number



I = the orbital angular momentum quantum number

$$
l=0
$$

$l=1$
$l=2$
$l=3$
$l=4$ spectroscopic notation for I
$d$
$f$
$g$
hi ok

5
7
9

## Table 8.5 Spectroscopic Notation for Atomic Shells and Subhells

| $\boldsymbol{n}$ | Shell Symbol | $\boldsymbol{\ell}$ | Shell Symbol |
| :--- | :---: | :---: | :---: |
| 1 | $K$ | 0 | $s$ |
| 2 | $L$ | 1 | sharp |
| 3 | $M$ | 2 | $d$ principal |
| 4 | $N$ | 3 | $d$ diffuse |
| 5 | $O$ | 4 | $f$ |
| 6 | $P$ | 5 | $g$ |
| $\cdots$ | $\cdots$ | $h$ |  |

FIRST FEW RADiAL WAVEFUNCTIONS

$$
R_{10}(n)=2 z^{3 / 2} e^{-32}
$$

$$
m=2
$$

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

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

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

$$
\begin{aligned}
& R_{31}(n)=\frac{8}{27 \sqrt{6}} z^{5 / 2}\left(3 \pi-\frac{1}{6} 3^{2} n^{2}\right) e^{-3 \pi / 3} \\
& \left.R_{32}(n)=\frac{4}{81 \sqrt{30}}\right\}^{7 / 2}\left(n^{2}\right) e^{-3 r / 3}
\end{aligned}
$$

general

$$
(N O R M)(\text { POCYNOMIAC }) e^{-z R / n a_{0}}
$$ form

WHAT DO THE RADIAL WAVEFCNS LOOK LIKE? III

| $*$ | $"$ | $"$ | RADIAL | "ROB DISS |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $"$ | $"$ | $"$ | $3 d$ | $"$ | $"$ | $"$ | 4 |



The R_n 0's


ANOTHER NOTATION MAS IS 25 IS tS...

$$
\begin{array}{ll}
h=0 & s \\
L=1 & p \\
L=2 & d
\end{array} \quad \exp (-r / n \text { a_o })
$$



2 NODES 2 zero crossings
$R_{20}$ AKA LS ANODE 1 zero crossing
$R_{1 O}$ AKA IS NO NODES 0 zero crossings
 wants

$$
l=1 \quad W A V E R C N S
$$

## The R_n 1's

$$
R_{m l} \rightarrow R_{m l}
$$




## <r> increases as $n$ increases <br> (for fixed I)


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Fig. 8-11b, p. 285

## <r> decreases as I increases (for fixed $\mathbf{n}$ )



To put it all together we need to multiply the radial dependence by the angular dependence
radial times angular

TOTAL SOLUTION


PROB DENSITIES
The probability density to find within XV of $\mathbf{r}$

$$
\begin{gathered}
|\psi(\vec{i})|^{2} d V \quad \text { PROB TO FIND ELECTED AT } \\
\text { POINT } \vec{i}
\end{gathered}
$$

PROB TO FIND ELECTRON AT DISTANCELAI FROM ORIGIN The probability density to find within dr of $\mathbf{r}$

$$
\begin{aligned}
& \left|R_{m L}(\alpha) y_{e_{m}}(\theta, \varphi)\right|^{2} d V \\
& \left|R_{n e}(n)\right|^{2}\left|Y_{\operatorname{Lm}}(\theta, \varphi)\right|^{2} n^{2} d r d \Omega \\
& \left(\left|R_{m e}(n)\right|^{2} r^{2} d r\right)\left(\left|Y_{\operatorname{lam}}(\theta, \varphi)\right|^{2} d \Omega\right) \\
& \text { radial times angular } \\
& P_{n \ell}(\sim) \quad P_{\ell}(\theta) \\
& \text { depends on } \\
& \text { n, I, and r } \\
& \text { depends on } \\
& \text { I and theta }
\end{aligned}
$$

Angular dependence

$$
\left|y_{e m}(\theta, \varphi)\right|^{2}=\Theta(\theta) e^{\operatorname{im\varphi }} \Theta^{*}(\theta) e^{-i m \varphi}
$$

phase changes se you fo pound $z$ aria bluet the prob does not change

$$
|\oplus(\theta)|^{2}
$$

## no phi dependence

only depends on theta
polar peat


> Figure of revolution ascend $t$ afc

The s state probabilities do not depend on the angles
p 271272 Eisbung


Click on the symbol for any state to show radial probability and distribution.

## Hydrogen 2s Radial Probability



Click on the symbol for any state to show radial probability and distribution.

## Hydrogen 3s Radial Probability



## No angular

dependence

$\mathrm{Y}_{0,0}$
<r> goes up as n goes up (for fixed I)


# Hydrogen 3s Radial Probability 



Click on the symbol for any state to show radial probability and distribution.

## Hydrogen 3p Radial Probability



Click on the symbol for any state to show radial probability and distribution.

## Hydrogen 3d Radial Probability


<r> goes down as I goes up (for fixed $n$ )

$Y_{1,1}$

$\mathrm{Y}_{2,2}$


## The Associated

## Laguerre Polynomials

constant

## The Radial Wavefunctions



Fig. 13.14. Radial eigenfunctions $R_{n \ell}(\rho)$ for the electron in the hydrogen atom. Their zeros are the $n-\ell-1$ zeros of the Laguerre polynomials $L_{n-\ell-1}^{2 \ell+1}(2 \rho / n)$. Here the argument of the Laguerre polynomial is $2 \rho / n$ with $n$ being the principal quantum number and $\rho=r / a$ the distance between electron and nucleus divided by the Bohr radius $a$.


1s, 2s, 3s, 4s, 5s


## 2p, 3p, 4p, 5p



## 3d, 4d, 5d



L = 0 well is
not shown


Fig. 13.15. Radial eigenfunctions $R_{n \ell}(r)$, their squares $R_{n \ell}^{2}(r)$, and the functions $r^{2} R_{n \ell}^{2}(r)$ for the lowest eigenstates of the electron in the hydrogen atom and the lowest angular-momentum quantum numbers $\ell=0,1,2$. Also shown are the energy eigenvalues as horizontal dashed lines, the form of the Coulomb potential $V(r)$, and, for $\ell \neq 0$, the forms of the effective potential $V_{\ell}^{\text {eff }}(r)$. The eigenvalue spectra are degenerate for all $\ell$ values, except that the minimum value of the principal quantum number is $n=\ell+1$.

# The Radial Wavefunctions Times the Angular Wavefunctions in Three-Dimensions 



## Three-dimensional representations

## (1) The Cut Solid Representation

Two Representations of the Hydrogen 1s, 2s, and 3s Orbitals25

(a)


## (2) The Computer Generated Dot Representation

Figure 37-5 Computer-generated dot picture of the probability density $\phi^{2}$ for the ground state of hydrogen The quantity $e \psi^{2}$ can be thought of as the electron charge density in the atom. The density is spherically symmetric, is greatest at the origin, and decreases exponentially with $r$.


## spectroscopic notation



## | $\mathbf{n}$ I m > notation

(3) The Shaded Picture with a Plot Representation

Probability Distribution for the 1s Wave Function

(a)

(b)
(3) The Shaded Picture with a Plot Representation

Radial Probability Distribution

where's the node?
(a)


Distance from nucleus ( $r$ )


When L = 0


Fig. 8-9, p. 282
(4) Electron density contours


## Electron density contours



Electron density contours for hydrogen


## Old Fashioned and New Fangled

## Artists' Conceptions





## More figures


(a)


(c)

Mpure 7-10 An artist's conception of the three-dimensional appearance of several one-electron atom probability density functions. For each of the drawings a line represents the $z$ axis. If all the probability densities for a given $n$ and $t$ are combined, the result is spherically symmetrical.



## Beware

# Beware continued 

## Essence of Optimal Human Movement Recognitions

Hydrogen atom wave functions.
When Optimal Human Movement first started almost one year ago, the
Statement of Purpose included 23
"recognitions."
Decided to look for the
"essence" of those recognitions, for simplicity and ease of review.

The term "recognition" is used for they are truths that one needs simply to recognize. They're not handed down from any authority.

Original Statement of Purpose can still be found on this page, and in "Notes" of Facebook page.

1) We recognize that at the commencement of the 21st century, with exponential growth of communications and global economic systems, that all human beings are interdependently connected.
2) We recognize that the greatest strength of the human species is the ability to reason, and every human being has the moral obligation to develop optimal levels of reasoning for their own benefit and the benefit of others.




* 

$\mathrm{m}=\mathbf{0}$

2

3
(0)


4




## 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/
http://webphysics.davidson.edu/faculty/dmb/hydrogen/
http://hyperphysics.phy-astr.gsu.edu/Hbase/quantum/hydcn.html\#c1
http://cronodon.com/Atomic/AtomTech4.html
http://www.evilmadscientist.com/article.php/atomiccookies
http://mareserinitatis.livejournal.com/tag/food

## Spherical Harmonics

## The Meaning of the Spherical Harmonics

http://infovis.uni-konstanz.de/research/projects/SimSearch3D/images/harmonics img.jpg

## The Spherical Harmonics

http://oak.ucc.nau.edu/jws8/dpgraph/Yellm.html
http://www.bpreid.com/applets/poasDemo.html
http://www.du.edu/~jcalvert/math/harmonic/harmonic.htm

## Encyclopedia

http://en.wikipedia.org/wiki/Spherical harmonics http://en.wikipedia.org/wiki/Table of spherical harmonics http://mathworld.wolfram.com/SphericalHarmonic.html

## Applications of Spherical Harmonics

http://www.falstad.com/qmrotator/
http://www.falstad.com/qmatom/
http://www.falstad.com/qmatomrad/
http://www.falstad.com/qm2dosc/
http://www.falstad.com/qm3dosc/

## Legendre Polynomials

## The Meaning of the Legendre Polynomials

http://physics.unl.edu/~tgay/content/multipoles.html

## Encyclopedia

http://en.wikipedia.org/wiki/Legendre polynomials http://mathworld.wolfram.com/LegendrePolynomial.html

## Wolfram Demonstrations

http://demonstrations.wolfram.com/SphericalHarmonics/ http://demonstrations.wolfram.com/VisualizingAtomicOrbitals/ http://demonstrations.wolfram.com/HydrogenOrbitals/ http://demonstrations.wolfram.com/PlotsOfLegendrePolynomials/ http://demonstrations.wolfram.com/PolarPlotsOfLegendrePolynomials/ http://demonstrations.wolfram.com/DipoleAntennaRadiationPattern/




## 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):

$$
\begin{gathered}
L_{n}^{(0)}(x)=L_{n}(x) \\
L_{n}^{(m)}(x)=(-1)^{m} \frac{d^{m}}{d x^{m}}\left[L_{n+m}(x)\right]
\end{gathered}
$$

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

$$
x \frac{d^{2}}{d x^{2}} L_{n}^{(\alpha)}(x)+(\alpha+1-x) \frac{d}{d x} L_{n}^{(\alpha)}(x)+n L_{n}^{(\alpha)}(x)=0 .
$$

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.

$$
L_{n}^{m}(z)=(-1)^{m} \frac{d^{m}}{d x^{m}}\left[L_{n+m}^{0}(z)\right]
$$

The differential equation is also given a few lines above:

$$
z \frac{d^{2}}{d z^{2}} L_{n}^{a}(z)+(a+1-z) \frac{d}{d z} L_{n}^{a}(z)+n L_{n}^{a}(z)=0
$$

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:

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

## Class Derivation

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

$$
x y^{\prime \prime}+(a+1-x) y^{\prime}+n y=0 .
$$

This is the same convention as Abramowitz \& Stegun and Morse \& Feshbach.
In class, we found we needed to solve this differential equation:

$$
\rho L^{\prime \prime}+(2(l+1)-\rho) L^{\prime}+(\lambda-l-1) L=0,
$$

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

$$
\rho L^{\prime \prime}+(2 l+1+1-\rho) L^{\prime}=n^{\prime} L=0
$$

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

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

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

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

On pg 784 of Morse \& Feshbach, we find

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

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

$$
L_{p}(\rho)=e^{\rho} \frac{d^{p}}{d \rho^{p}}\left(\rho^{p} e^{-\rho}\right)
$$

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

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

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, $\left.\mathrm{q}, \mathrm{x}\right]$. They were in agreement.

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

