Lecture 15

Everything you should remember about hydrogen forever

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 eigenfcns aka the energy eigenfcns aka the stationary states

EIGENFONS => ENGREY RIGEN RONS

BIGENVALUES => EIGEN ENERGIES

$$E_{M} = \frac{-2q}{m^{2}} = \frac{-13.6 \text{ eV}}{m^{2}}$$
if $V O R O A E N$

$$E_{m}^{\prime} = -\frac{2^{-}L_{y}^{\prime}}{m^{2}} \qquad HYDLOGEN - LIKE$$

The I=0 well, aka the s-well, is the pure Coulomb potential Because I=0 there is no angular momentum barrier

infinite number of bound states



$$\int \frac{d}{dt} \frac{d}{dt} = \frac{d}{dt} - \frac{d}{dt} = \frac{d}{dt} + \frac{d}{dt}$$

ENERGY DEGENERACY only n $E_m = \frac{E_0}{m^2}$ Eo 2 - 13. INFINITE NUMBER BOUND STATES OF m=4 0.89 m=3 1.51 L=0 Affective potential -3.39 M=L I=1 potential

-13.6

| n l m >

I=0 potential

The energy only depends on n It does not depend on I or m Why is this?

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



Emergy O egeneracy

The Energy Degeneracy

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

n = the principal quantum number



the number of m states for each value of I

Table 8.5Spectroscopic Notation forAtomic Shells and Subhells

n	Shell Symbol	l	Shell Symbol	
1	K	0	\$ sharp	
2	L	1	p principal	
3	M	2	d diffuse	
4	N	3	f fine	
5	0	4	g	
6	P	5	$\stackrel{\scriptstyle \leftrightarrow}{h}$	

@ 2005 Brooks/Cole - Thorsen

Table 8-5, p.280









<r> increases as n increases

(for fixed I)



@ 2005 Brooks/Cole - Thomson

Fig. 8-11b, p.285

<pr> <r> decreases as I increases (for fixed n)







 $|\forall e_m(\theta, \varphi)|^2 = \Theta(\theta) e^{im\varphi} \Theta^*(\theta) e^{-im\varphi}$

phase changes so you go sound 2 spice but the prob does not change no phi dependence |@(e)|²

only depends on theta

Polar plat



Figure of revolution around & apic

The s state probabilities do not depend on the angles

p 271 272 Eisberg



No angular dependence



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







The Associated Laguerre Polynomials



no zero1 zero2 zero3 zerocrossingscrossingcrossingscrossings

The Radial Wavefunctions



distance between electron and nucleus divided by the Bohr radius a.

From The Picture Book of Quantum Mechanics, S. Brandt and H.D. Dahmen, 3rd ed., © 2001 by Springer-Verlag New York.



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



2p, 3p, 4p, 5p



the L = 0 well

3d, 4d, 5d



not shown

All Together



Fig. 13.15. Radial eigenfunctions $R_{n\ell}(r)$, their squares $R_{n\ell}^2(r)$, and the functions $r^2 R^2_{n\ell}(r)$ 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 ℓ values, except that the minimum value of the principal quantum number is $n = \ell + 1$.

From The Picture Book of Quantum Mechanics, S. Brandt and H.D. Dahmen, 3rd ed., © 2001 by Springer-Verlag New York.

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 Orbitals



(2) The Computer Generated Dot Representation



spectroscopic notation



200> 210>

| n l m > notation

(3) The Shaded Picture with a Plot Representation

(a)

Probability Distribution for the 1s Wave Function



(3) The Shaded Picture with a Plot Representation

Radial Probability Distribution







(4) Electron density contours



Electron density contours



Electron density contours for hydrogen















Old Fashioned and New Fangled Artists' Conceptions







More figures



Pigure 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 l are combined, the result is spherically symmetrical.









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.

 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.

Read more »

1. 2.1



(2,0,0)	(3,0,0)	Hydrogen $\psi_{nlm}(r, \vartheta, \varphi) = \sqrt{\left(\frac{2}{na_0}\right)^2}$	n Wave \mathbf{F}_{Prot} $\overline{\Big)^{\frac{n-l-1}{2n[(n+l)!]}}}e^{-\rho/2}\rho^{l}L_{p}^{2}$	ability density plots. $M_{n-l-1}^{l+1}(\rho) \cdot Y_{lm}(\vartheta, \varphi)$
(2,1,0)	8 (3,1,0)	(3,1,1)		-
(2,1,1)	(3,2,0)	(3,2,1)	(3,2,2)	
(4,0,0)	3 (4,1,0)	(4,1,1)	(4,2,0)	(4,2,1)
(4,2,2)	(4,3,0)	(4,3,1)	(4,3,2)	(4,3,3)









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):

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

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:

$$\mathcal{L}_{p+q}^q(
ho) = rac{d^q}{d
ho^q} L_{p+q}(
ho) = (-1)^q L_p^{(q)}(
ho)$$
 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

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

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,q,x]. They were in agreement.

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