Quantum Mechanics and Atomic Physics

Lecture 17:
Hydrogen Atom Probability Distribution

http://www.physics.rutgers.edu/ugrad/361

Prof. Eva Halkiadakis
Last time: the Radial Equation with the Coulomb Potential

\[ \frac{d^2 u(r)}{dr^2} + \frac{2\hbar}{\hbar^2} \left[ E - V(r) - \frac{l(l+1)}{r^2} \cdot \frac{\hbar^2}{2m} \right] u(r) = 0 \]

Where \( u(r) = r R(r) \)

Recall \( \psi(r, \theta, \varphi) = R(r) \ Y(\theta, \varphi) \)

For \( V(r) = -\frac{e^2}{4\pi\varepsilon_0 r} \)

Note: \( E < 0 \), since we are seeking bound states, and \( V \) is negative.
Last time: Asymptotic Behavior $r \to 0$

The term that dominates is $\frac{1}{r^2}$ term so,

$$\frac{d^2 U}{dr^2} - \frac{\ell(\ell+1)U}{r^2} \to 0 \quad U(r) = A r^\kappa$$

$$\kappa (\kappa-1) A r^{\kappa-2} = \ell (\ell+1) A r^{\kappa-2}$$

$$\kappa (\kappa-1) = \ell (\ell+1)$$

$k = -\ell$ or $\kappa = \ell + 1$

But $\ell \geq 0$ so, $\kappa = \ell + 1$

$U(r) \propto r^{\ell+1}$

or

$R(r) \propto r^k$ as $r \to 0$
Asymptotic Behavior $r \to \infty$

$r \to \infty$

$\frac{1}{r}$ and $\frac{1}{r^2}$ terms $\to 0$

$$\frac{d^2 u}{dr^2} = -\frac{2\mu}{\kappa^2} E \cdot u$$

So,

$$u(r) \propto e^{-\sqrt{\frac{-2\mu}{\kappa^2} E}} r$$

as $r \to \infty$

$$\Rightarrow u(r) \propto r^{e+1} e^{-\sqrt{\frac{-2\mu}{\kappa^2} E} r}$$

or

$$r(r) \propto r^e e^{-\sqrt{\frac{-2\mu}{\kappa^2} E} r}$$

(Note: number inside the square root is positive, since $E<0$)
Look at term in exponential

- This has units of $1/r$
- Let’s call it $1/a_0$
- And let’s note that we expect $E \propto 1/n^2$ (and $E<0$, since we are seeking bound states, and $V$ is negative.)
- So,

$$\sqrt{-\frac{2\mu}{\hbar^2} E} = \frac{1}{a_0 \cdot n}$$

$$\Rightarrow R(r) \propto r^n e^{-r/a_0}$$

- See your book for full derivation using a power series solution
Let’s try a solution

- Let’s try a solution to S.E. for the ground state \( n=1 \) and zero angular momentum \( \ell = 0 \)

- Therefore, we can assume the ground state is spherically symmetric so: \( \Psi(r,\theta,\phi) = \Psi(r) \)

- So, let’s try this solution:

\[
R(r) = C e^{-r/a_0}
\]
Look familiar?

It should! This is the Bohr radius!
- Let's put this expression for $a_0$ back into equation above:

$$-\frac{h^2}{2\mu a_0^2} = \varepsilon$$

$$\Rightarrow \varepsilon = -\frac{h^2}{2\mu} \frac{\mu^2 e^4}{\varepsilon_0^2} = -\frac{\mu e^4}{32\pi^2 h^2 \varepsilon_0^2}$$

- Again, does this look familiar?

- This is the same expression as the Bohr model energy in the ground state!

$$\varepsilon = -13.6\,\text{eV} \quad \text{for} \quad n=1$$
Normalization of the ground state

Note that $\Psi = \Psi_{100}$

After two integrations by parts, or just look in the appendix of your book:

Ground state eigenfunction for Hydrogen. Same energy as Bohr model, but $r$ is not fixed at $a_0$!
Not a circular orbit - something like an electron cloud around nucleus.
Hydrogen Radial Wavefunctions

- Complete radial function solutions are:

\[
R(r) = e^{-r/\alpha_0} \left( \frac{r}{\alpha_0} \right)^l \, L_n^l \left( \frac{r}{\alpha_0} \right)
\]

\[
\alpha_0 = \frac{\hbar^2}{2 ME^2}
\]

\[
L_n^l \left( \frac{r}{\alpha_0} \right)
\]

\(n\) is called the principal quantum number and must be an integer with \(n > l\).

These are called Associated Laguerre Polynomials

\[
\text{Table 7.1 Hydrogen Radial Wavefunctions } R_n^l(r).
\]

\[
R_{10}(r) = \frac{2}{a_0^{3/2}} e^{-r/a_0}
\]

\[
R_{20}(r) = \frac{1}{(2a_0)^{3/2}} (2 - r/a_0) e^{-r/2a_0}
\]

\[
R_{21}(r) = \frac{1}{\sqrt{3}(2a_0)^{3/2}} (r/a_0) e^{-r/2a_0}
\]

\[
R_{30}(r) = \frac{2}{(3a_0)^{3/2}} \left[ 1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2} \right] e^{-r/3a_0}
\]

\[
R_{31}(r) = \frac{4\sqrt{2}}{9(3a_0)^{3/2}} (r/a_0) \left[ 1 - \frac{r}{6a_0} \right] e^{-r/3a_0}
\]

\[
R_{32}(r) = \frac{2\sqrt{2}}{27\sqrt{5}(3a_0)^{3/2}} (r/a_0)^2 e^{-r/3a_0}
\]

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Hydrogen Radial Wavefunctions

http://phet.colorado.edu/simulations/sims.php?sim=Quantum_Bound_States
Summary of Hydrogen Atom Solutions

- $\Psi$ is a product of
  - $\Phi$ which is oscillatory
  - $\Theta$ which is a polynomial in $\cos\theta$
  - $R$ which is a product of a decaying exponential and a polynomial in $r$

- $\Psi$ depends on 3 quantum numbers
  - Principal quantum number $n = 1, 2, 3, \ldots$
  - Orbital angular momentum quantum number $\ell = 0, 1, 2, \ldots (n-1)$
  - Magnetic quantum number $m_\ell = 0, \pm 1, \ldots \pm \ell$ or $m_\ell = -\ell, -\ell+1, \ldots \ell-1, \ell$
Hydrogen Atom Wavefunctions

This is the one we derived. Ground state wavefunction

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Energy Degeneracy

- Energy only depends on $n$
- For each $n$, there are $n$ values of $\ell$
- For each $\ell$, there are $(2\ell+1)$ values of $m_{\ell}$
- So, for each $n$, the degeneracy is:

\[
\begin{align*}
\sum_{\ell=0}^{n-1} (2\ell+1) &= 2 \sum_{\ell=0}^{n-1} \ell + \sum_{\ell=0}^{n-1} 1 \\
&= 2 \left( \frac{(n-1)n}{2} \right) + n \\
&= n^2 - n + n = n^2 
\end{align*}
\]
Quantum numbers and Degeneracy

<table>
<thead>
<tr>
<th>n</th>
<th>l</th>
<th>m_l</th>
<th>((2l+1))</th>
<th>Degeneracy</th>
<th>(n^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0, \pm 1</td>
<td>3</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0, \pm 1</td>
<td>3</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0, \pm 1, \pm 2</td>
<td>5</td>
<td>9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **Question:** So if energy is the same, what’s different about the various degenerate states?

- **Answer:** The probability distribution of the electron around the nucleus, i.e. the shape of the electron cloud.
Spectroscopic Notation

For historical reasons, all states with same quantum number $n$ are said to form a shell.

And states having the same value of both $n$ and $\ell$ are said to form a subshell (s, p, d, f, …)

The probability distributions for these different states have important features, which we will cover next time.

- In Schrodinger theory, different $\ell$ states for same $n$ have same energy
  - Called $\ell$-degeneracy
- Energy level diagram omits different $m_\ell$ states - independent of $m_\ell$ due to spherical symmetry of the atom.
  - This is for no external magnetic field!
- We treat this in the next chapter
Probability Distribution

- What is the probability of finding the electron in a volume of space dV?

\[ \text{Probability} = \Psi \Psi^* \, dV = \Psi \Psi^* r^2 \sin \theta \, dr \, d\theta \, d\phi \]

\[ \text{Probability density} = \Psi \Psi^* \]

Remember that the probability is independent of \( \Phi \) - rotationally symmetric around the z-axis

\[ \Phi^* \Phi \propto e^{-im\phi} e^{im\phi} = 1 \]

Volume dV associated with radial interval dr is a shell of radius r and thickness dr

We have an electron cloud around the nucleus.
Example

What is the probability of finding the electron at a distance \( r < r_0 \)? Assume \( n=1, \ell=0, m_\ell=0 \).

\[
P(r < r_0) = \int_0^{r_0} \int_0^{2\pi} \int_0^{\pi} y^2 \psi^* \psi r^2 \sin \theta \, dr \, d\theta \, d\phi
\]

\[
= \int_0^{r_0} \frac{1}{\kappa a_0^3} e^{-2\kappa r/a_0} \, 4\pi r^2 \, dr
\]

\[
= 1 - \int_0^{\infty} \frac{1}{\kappa a_0^3} e^{-2\kappa r/a_0} \, 4\pi r^2 \, dr
\]

\[
= 1 - \frac{4}{a_0^3} \int_0^{\infty} e^{-2\kappa r/a_0} \, r^2 \, dr
\]

\[
= 1 - e^{-2r/a_0} \left( 2 \frac{r_0^2}{a_0^2} + 2 \frac{r_0}{a_0} + 1 \right)
\]

(Hint: change variables from \( r \) to \( z = 2r/a_0 \))
Use this to determine the probability of finding the electron inside the first Bohr radius \((r<a_0)\)? Or \(r<2a_0\) or \(r<3a_0\)?
Cumulative Probability Density

- For the ground state \((1,0,0)\) of Hydrogen:
- As \(r \to \infty\), \(P(\leq r) \to 1\)

The probability of finding the electron beyond 10 Bohr radii is about 0.003, in other words, very small!

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Ground State of Hydrogen

- Wave function of the ground state \((1,0,0)\)

\[ \psi_{100} = \frac{1}{\sqrt{\pi}} a_0^{3/2} e^{-r/a_0} \]

- Probability density is:

\[ p_{100} = \psi_{100}^* \psi_{100} = \frac{1}{\pi a_0^3} e^{-2r/a_0} \]

- What is the position of the highest probability density?
  - We can see from the expression above that it’s for \(r=0\)

- What about the most likely radius?
  - Recall that for an infinite spherical well the expectation value (or average value) of \(r\) was \(\langle r \rangle = a/2\)
Radial Probability

To determine probability of finding the electron within a shell of radius \( r \)

Imagine the nucleus is surrounded with concentric spherical shells each of thickness \( \Delta r \)

Volume of each shell is \( 4\pi r^2 \Delta r \)

So,

\[
P(\text{electron in shell @ radius } r) = P_{1s} (\text{volume of shell}) = \frac{4}{a_0^3} \left( r^2 e^{-2r/a_0} \right) \Delta r
\]
Most Probable Radius

- In what shell are we most likely to find the electron?
- Maximize $P$ with respect to $r$:

$$\left(\frac{dp}{dr}\right)_{r=r_{mp}} = 0$$

$$\frac{d}{dr}(r^2 e^{-2r/a_0}) = 2re^{-2r/a_0} - \left(\frac{2}{a_0}\right)r^2 e^{-2r/a_0} = 0$$

$$\Rightarrow 1 = \frac{1}{a_0} \frac{r_{mp}}{r} \Rightarrow r_{mp} = a_0$$

- $r_{mp}$ in the ground state of Hydrogen is exactly one Bohr radius!
- We will check: is $(r_{mp})_{n,\ell,m_\ell} = n^2 a_0$? (hint: we will find that this is not always true)
Radial Probability Distribution

- The probability of finding an electron in the ground state at radius $r$ is proportional to:

$$P(r) \propto r^2 e^{-r/a_0}$$

- And more generally:

$$P(r) = 4\pi r^2 R_{n2}(r)$$

- $P(r)$ vs. $r$:

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Expectation value $\langle r_{100} \rangle$

We found the most probable radius so now let’s find the expectation value of $r$ in ground state:

$$\langle r_{100} \rangle = \langle \psi_{100} | r | \psi_{100} \rangle = \int_0^\infty \int_0^{2\pi} \int_0^\pi \psi_{100}^* r \psi_{100} r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$= \int_0^\infty \psi_{100}^* r \psi_{100} 4\pi r^2 \, dr$$

$$= \frac{4}{a_0^3} \int_0^\infty e^{-2r/a_o} r^3 \, dr$$

Useful integral (or look in Appendix of your book):

$$\int_0^\infty e^{-ax} x^n \, dx = \frac{n!}{a^{n+1}}$$

$$\Rightarrow \langle r_{100} \rangle = \frac{4}{a_0^3} \frac{3!}{(2a_0)^4} = \frac{24 a_0}{16} = \frac{3 a_0}{2}$$
Does this make sense?

- So, $<r> > r_{mp}$

- The average value of observations of the radial positions of electrons in many ground-state Hydrogen atoms would be $3a_0/2$ from the nucleus.
The “first excited state” (2,0,0)

- The wavefunction is:
  \[ \Psi_{200} = \frac{1}{\sqrt{32\pi a_0^3}} (2 - n/a_0) e^{-r/a_0}. \]

- Let’s test the hypothesis that:
  \[ (r_{mp})_{n,\ell,m_\ell} = n^2 a_0 = 4a_0? \]

- We do this by maximizing \( 4\pi r^2 R^2_{200} \)
Quadratic equation gives two solutions:

\[ r = 2 \left( \frac{3}{2} \pm \frac{\sqrt{5}}{2} \right) a_0 \]

or

\[ r = 2 \left( \frac{3}{2} - \frac{\sqrt{5}}{2} \right) a_0 \]
Solution that maximizes the probability density is:

\[(r_{mp})_{200} = 5.236a_o\]

Turns out:

\[r_{mp} = n^2a_o \text{ only for } l = n-1\]
Other Hydrogen States

- $P(r)$ for $(n,\ell)$ states ($m_\ell$ does not affect these functions)
- There are a number of radii where $P(r)$ is zero
  - Nodes - where we never expect to find the electron
  - Number of nodes is $n - \ell - 1$
- $R_{n\ell}(0) = 0$ for $\ell \neq 0$
- $R_{n\ell}(0) \neq 0$ for $\ell = 0$
- Electron will reside closest to the nucleus when $\ell = n-1$, for a given $n$.
  - More on this later.

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Plotting $|\Psi|$ 

- $\Psi_{nlm}$ also have an angular dependence
- Plot $|\Psi|$ in a plane cutting through the nucleus
  - Usually taken to be $\phi=0$ plane or the xz-plane
  - Remember $|\Psi|$ is rotationally symmetric about the z-axis.
- Since we are representing something that is in 3D onto a 2D surface, think of the figures rotating about the z-axis

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Wave-functions

No radial nodes
But one angular node

Radial node (but non-central)

Two radial nodes (including a central one)
And three angular nodes.

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FIGURE 7.9 Flowchart for Analysis of $|\phi|$ $(x, z)$ Plots.
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- http://phet.colorado.edu/simulations/sims.php?sim=Quantum_Bound_States
Figure 7-19: 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.
Summary/Announcements

- Next time:
  Angular Momentum Raising and Lowering Operators
  And setting the stage for applying an external magnetic field

- Next homework due on Monday Nov 11.

- Quiz on Monday Nov 11 on Chapters 5/6.