Quantum Mechanics and Atomic Physics

Lecture 17: Hydrogen Atom Probability Distribution

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

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Last time

- We solved S.E. for the Coulomb Potential!
- We found the Hydrogen Atom wavefunctions to be:

\[ \psi_{n\ell m_k}(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \]

| Table 7.2 | Hydrogen Atom Wavefunctions $\psi_{n\ell m_k}(r, \theta, \phi)$.
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>$\psi_{10}$</td>
<td>$\frac{1}{\sqrt{\pi} a_0^2} e^{-r/a_0}$</td>
</tr>
<tr>
<td>$\psi_{20}$</td>
<td>$\frac{1}{4\sqrt{2\pi} a_0^2} (r/a_0) e^{-r/a_0} \cos \theta$</td>
</tr>
<tr>
<td>$\psi_{211}$</td>
<td>$\frac{1}{8\sqrt{\pi} a_0^2} (r/a_0) e^{-r/a_0} \sin \theta e^{i\phi}$</td>
</tr>
<tr>
<td>$\psi_{n\ell m_k}$</td>
<td>$\frac{1}{81\sqrt{\pi} a_0^2} (r/a_0) (6 - r/a_0) e^{-r/a_0} \cos \theta$</td>
</tr>
<tr>
<td>$\psi_{n\ell \pm 1}$</td>
<td>$\frac{1}{81\sqrt{\pi} a_0^2} (r/a_0)^2 e^{-r/a_0} \sin \theta \cos \phi e^{i\phi}$</td>
</tr>
<tr>
<td>$\psi_{30}$</td>
<td>$\frac{1}{81\sqrt{\pi} a_0^2} (r/a_0)^2 e^{-r/a_0} (3\cos^2 \theta - 1)$</td>
</tr>
<tr>
<td>$\psi_{n\ell \pm 1}$</td>
<td>$\frac{1}{81\sqrt{\pi} a_0^2} (r/a_0)^2 e^{-r/a_0} \sin \theta \sin \phi e^{i\phi}$</td>
</tr>
</tbody>
</table>

Reed Chapter 7
Last time

- We found that the probability of finding the electron in a volume of space $dV$

\[
\text{Probability} = 4\pi \Psi^2 \ dV = 4\pi r^2 \sin \theta \ dr \ d\theta \ d\phi
\]

\[
\text{Probability density} = \Psi^2
\]

- We also found that the probability of finding the ground state electron at a distance $r < a_0$, $r < 2a_0$, $r < 3a_0$ was increasing....

We have an electron cloud around the nucleus.
Cumulative Probability Density

- For the ground state (1,0,0) of Hydrogen:

- As $r \rightarrow \infty$, $P(\leq r) \rightarrow 1$

Reed Chapter 7

- The probability of finding the electron beyond 10 Bohr radii is about 0.003, in other words, very small!
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?
  \(r=0\)

- What about the most likely radius?
  Recall that for an infinite spherical well the expectation value of \(r\) was \(<r> = a/2\)
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,

$$P(\text{electron in shell @ radius } r) = P_{100}(\text{volume of shell}) \approx \frac{4}{a_0^3} (r^2 e^{-2r/a_0}) \Delta r$$
Most Probable Radius

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

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

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

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

- $r_{mp}$ in the ground state of Hydrogen is exactly one Bohr radius!
- We will check if:

$$Is \ (r_{mf})_{n=1,m=1} = n^2 a_0 ?$$
Radial Probability Distribution

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

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

- And more generally:

$$P(r) = 4\pi r^2 \tilde{R}(r \lambda)$$

Reed is confused between probability and probability density, $P(r)$ is radial probability density here.

- $P(r) \int_0^\infty P(r) \, dr = 1$
We found the most probable radius so now let’s find the expectation value of $r$ in ground state:

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

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

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

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

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

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

- So, $\langle r \rangle > r_{mp}$

- 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:

  \[
  \psi_{2,0,0} = \frac{1}{\sqrt{32\pi}} a_0^{-\frac{3}{2}} (2 - n a_0) e^{-\frac{r}{2a_0}}
  \]

- Let’s test the hypothesis that:

  \[
  r_{mp} = n^2 a_0 = 4 a_0 \gtrless?
  \]

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

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

\[ 2r \left( 2 - r \frac{r}{a_0} \right) e^{-r/a_0} - \frac{2r^2}{a_0} \left( 2 - r \frac{r}{a_0} \right) e^{-r/a_0} - \frac{r^2}{a_0^2} \left( 2 - r \frac{r}{a_0} \right) e^{-r/a_0} = 0 \]

Divide by \( r \left( 2 - r \frac{r}{a_0} \right) e^{-r/a_0} \)

\[ 2 \left( 2 - r \frac{r}{a_0} \right) - \frac{2r}{a_0} - \frac{r}{a_0} \left( 2 - r \frac{r}{a_0} \right) = 0 \]

\[ y - \frac{2y}{a_0} - \frac{2r}{a_0} - \frac{r^2}{a_0^2} = 0 \]

\[ \left( \frac{r}{a_0} \right)^2 + \frac{y}{a_0} - 2 = 0 \]

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

Quadratic equation gives two solutions:
Inner shell nested within a shell of higher probability density

Solution that maximizes the probability density is:

\[(r_{mp})_{200} = 0.764\ a_0\]

or

\[5.236\ a_0\]

So, \(r_{mp} \neq n^2 a_0\)

**Solution that maximizes the probability density is:**

\[(r_{mp})_{200} = 5.236\ a_0\]

**Turns out:**

\[r_{mp} = n^2 a_0\] only for \(l = n-1\)
Other Hydrogen States

- \( P( r) \) for \((n,\ell)\) states \((m_\ell \text{ does not affect these functions})\)

- 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.
Plotting $|\Psi|$ 

- $\Psi_{n\ell ml}$ 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.
Wavefunctions

No radial node
one angular node

One radial node
(but non-central)

One radial node excluding
the central one
And three angular nodes.

Reed Chapter 7
This table is a little confusing. See the examples in the next slide. Do not include the origin (r=0) when counting radial nodes; it is confusing.
Probability Densities

\# of radial nodes (excluding r=0) in blue
\[ = n - l - 1 \]

\# of angular nodes
\[ \begin{cases} \ell - m + 1, & \text{if } m \neq 0 \\ \ell, & \text{if } m = 0 \end{cases} \]

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Try to count the number of radial and angular nodes yourself on these figures and find the relationship with $n$, $l$, $m$ values.
Figure 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.
The Effective Potential

Recall the radial equation with the Coulomb Potential:

\[
\frac{k^2}{2\mu} \frac{d^2 U(r)}{dr^2} + \left( E - V(r) - \frac{e^2}{2\mu r^2} \right) U(r) = 0
\]

With \( V_{\text{eff}}(r) \equiv V(r) + \frac{e^2}{2\mu r^2} \)

\[
\Rightarrow \frac{k^2}{2\mu} \frac{d^2 U(r)}{dr^2} + \left( E - V_{\text{eff}}(r) \right) U(r) = 0
\]

\[
\Rightarrow \frac{k^2}{2\mu} \frac{d^2 U(r)}{dr^2} + V_{\text{eff}}(r) U(r) = E U(r)
\]

This looks like the 1D S.E.!
\[ V_{\text{eff}} \]

- \( V_{\text{eff}} \) vs. \( \rho \), where \( \rho = r/a_0 \)
- Striking difference between \( \ell = 0 \) and \( \ell \neq 0 \)
  - When \( \ell \neq 0 \) the combination of the two terms in the effective potential leads to potential wells with infinite walls as \( r \to 0 \)
    (see that the wavefunction is zero for \( \ell \neq 0 \) in Fig. 7.10)
- \( V_{\text{eff}} = 0 \) as \( r \to \infty \)
  - Bohr energy levels get closer together as \( n \to \infty \)

Reed Chapter 7
The $\ell(\ell+1)/r^2$ term is known as the “centrifugal” term. It contributes a repulsive potential that drives the electron away from the nucleus. Stronger repulsion occurs as $\ell$ increases, and we expect to find the electron further from the nucleus.
Summary/Announcements

- Next time:
  Angular Momentum Raising and Lowering Operators

- Time for Quiz.