Physics 3313 - Lecture 14

Monday March 22, 2010
Dr. Andrew Brandt

1. Hydrogen Atom
2. HW 6 on Ch. 7 to be assigned Weds 3/24 for 3/31
3. Return test at end of class
7.1 Application of the Schrödinger Equation to the Hydrogen Atom

7.2 Solution of the Schrödinger Equation for Hydrogen

7.3 Quantum Numbers

The atom of modern physics can be symbolized only through a partial differential equation in an abstract space of many dimensions. All its qualities are inferential; no material properties can be directly attributed to it. An understanding of the atomic world in that primary sensuous fashion...is impossible.

- Werner Heisenberg
7.1: Application of the Schrödinger Equation to the Hydrogen Atom

To a good approximation the potential energy of the electron-proton system is electrostatic:

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

Rewrite the three-dimensional time-independent Schrödinger Equation:

\[
-\frac{\hbar^2}{2m}\frac{1}{\psi(x,y,z)} \left[ \frac{\partial^2 \psi(x,y,z)}{\partial x^2} + \frac{\partial^2 \psi(x,y,z)}{\partial y^2} + \frac{\partial^2 \psi(x,y,z)}{\partial z^2} \right] = E - V(r)
\]

For Hydrogen-like atoms (He\(^+\) or Li\(^{++}\))

- Replace \(e^2\) with \(Ze^2\) (Z is the atomic number).
- Use appropriate reduced mass \(\mu\).
- Solving this equation will specify behavior of electron
- 3 dimensions implies 3 quantum numbers (for now)
Application of the Schrödinger Equation

• The potential (central force) $V(r)$ depends on the distance $r$ between the proton and electron.

• Transform to spherical polar coordinates because of the radial symmetry.

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu}{\hbar^2} (E - V) \psi = 0
\]
Application of the Schrödinger Equation

The wave function \( \psi \) is a function of \( r, \theta, \phi \).

Equation is separable.

Solution may be a product of three functions.

\[ \psi(r, \theta, \phi) = R(r) f(\theta) g(\phi) \]  

Equation 7.4

We can separate Equation 7.3 into three separate differential equations, each depending on one coordinate: \( r, \theta, \) or \( \phi \).
7.2: Solution of the Schrödinger Equation for Hydrogen

Substitute Eq (7.4) into Eq (7.3) and separate the resulting equation into three equations: \( R(r) \), \( f(\theta) \), and \( g(\phi) \).

**Separation of Variables**

The derivatives from Eq (7.4)

\[
\frac{\partial \psi}{\partial r} = fg \frac{\partial R}{\partial r} \quad \frac{\partial \psi}{\partial \theta} = Rg \frac{\partial f}{\partial \theta} \quad \frac{\partial^2 \psi}{\partial \phi^2} = Rf \frac{\partial^2 g}{\partial \phi^2}
\]

Substitute them into Eq (7.3)

\[
\frac{fg}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{Rg}{r^2 \sin^2 \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial f}{\partial \theta} \right) + \frac{Rf}{r^2 \sin^2 \theta} \frac{\partial^2 g}{\partial \phi^2} + \frac{2\mu}{h^2} (E - V) Rfg = 0
\]

Multiply both sides of Eq (7.6) by \( r^2 \sin^2 \theta / Rfg \)

\[
- \frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) - \frac{2\mu}{h^2} r^2 \sin^2 \theta (E - V) - \frac{\sin \theta}{f} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial f}{\partial \theta} \right) = \frac{1}{g} \frac{\partial^2 g}{\partial \phi^2}
\]
Solution of the Schrödinger Equation

• Only \( r \) and \( \theta \) appear on the left side and only \( \phi \) appears on the right side of Eq (7.7)
• The left side of the equation cannot change as \( \phi \) changes.
• The right side cannot change with either \( r \) or \( \theta \).

• Each side needs to be equal to a constant for the equation to always be true.
  Set the constant \(-m_\ell^2\) equal to the right side of Eq (7.7)
  \[
  \frac{d^2g}{d\phi^2} = -m_\ell^2 g
  \]
  azimuthal equation
• Solutions then have the form: \( e^{im_\ell\phi} \)
Solution of the Schrödinger Equation

- $e^{im_\ell \phi}$ satisfies Eq (7.8) for any value of $m_\ell$.
- The solution must be single valued in order to have a valid solution for any $\phi$ implying: $g(\phi) = g(\phi + 2\pi)$
  $g(\phi = 0) = g(\phi = 2\pi) \Rightarrow e^0 = e^{2\pi im_\ell}$
- $m_\ell$ must be zero or an integer (positive or negative) for this to be true.

- Set the left side of Eq (7.7) equal to $-m_\ell^2$ and rearrange it.
  $$\frac{1}{\sqrt{R}} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} R \right) + \frac{2\mu r^2}{\hbar^2} (E - V) = \frac{m_\ell^2}{\sin^2 \theta} - \frac{1}{f \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial f}{\partial \theta} \right)$$
- Everything depends on $r$ on the left side and $\theta$ on the right side of the equation.
Solution of the Schrödinger Equation

• Set each side of Eq (7.9) equal to constant \( \ell(\ell + 1) \).

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2\mu}{\hbar^2} \left[ E - V - \frac{\hbar^2}{2\mu} \frac{\ell(\ell + 1)}{r^2} \right] R = 0 \quad \text{Radial equation}
\]

\[
\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{df}{d\theta} \right) + \left[ \ell(\ell + 1) - \frac{m_e^2}{\sin^2 \theta} \right] f = 0 \quad \text{Angular equation}
\]

• Schrödinger equation has been separated into three ordinary second-order differential equations [Eq (7.8), (7.10), and (7.11)], each containing only one variable.
Solution of the Radial Equation

• The radial equation is called the **associated Laguerre equation** and the **solutions** \( R \) that satisfy the appropriate boundary conditions are called **associated Laguerre functions**.

• Assume the ground state has \( \ell = 0 \) and this requires \( m_{\ell} = 0 \). Eq (7.10) becomes

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2\mu}{\hbar^2} (E - V)R = 0
\]

• The derivative of \( r^2 \frac{dR}{dr} \) yields two terms. Write those terms and insert Eq (7.1)

\[
\frac{d^2R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \frac{2\mu}{\hbar^2} \left( E + \frac{e^2}{4\pi\varepsilon_0 r} \right)R = 0
\]
Quantum Numbers

• The appropriate boundary conditions to Eq (7.10) and (7.11) leads to the following restrictions on the quantum numbers \( \ell \) and \( m_\ell \):
  
  - \( \ell = 0, 1, 2, 3, \ldots \)
  - \( m_\ell = -\ell, -\ell + 1, \ldots, -2, -1, 0, 1, 2, \ldots, \ell - 1, \ell \)
  - \( |m_\ell| \leq \ell \) and \( \ell < n \).

• The predicted energy levels are given by:

\[
E_n = -\frac{E_0}{n^2}
\]
Hydrogen Atom Radial Wave Functions

- First few radial wave functions $R_{n\ell}$

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\ell$</th>
<th>$R_{n\ell}(r)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>$\frac{2}{(a_0)^{3/2}}e^{-r/a_0}$</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>$\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>$\frac{r}{a_0}\frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>$\frac{1}{(a_0)^{3/2}}\frac{2}{81\sqrt{3}}\left(\frac{27}{a_0} - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right)e^{-r/3a_0}$</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>$\frac{1}{(a_0)^{3/2}}\frac{4}{81\sqrt{5}}\left(6 - \frac{r}{a_0}\right)e^{-r/3a_0}$</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>$\frac{1}{(a_0)^{3/2}}\frac{4}{81\sqrt{30}}\frac{r^2}{a_0^2}e^{-r/3a_0}$</td>
</tr>
</tbody>
</table>

- Subscripts on $R$ specify the values of $n$ and $\ell$. 

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Solution of the Angular and Azimuthal Equations

• The solutions for Eq (7.8) are $e^{im_\ell \phi}$ or $e^{-im_\ell \phi}$
• Solutions to the polar angle and azimuthal angle equations are linked because both have $m_\ell$.
• Group these solutions together into functions.

$$Y(\theta, \phi) = f(\theta)g(\phi) \quad \text{spherical harmonics}$$
# Normalized Spherical Harmonics

<table>
<thead>
<tr>
<th>$\ell$</th>
<th>$m_\ell$</th>
<th>$Y_{\ell m_\ell}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>$\frac{1}{2\sqrt{\pi}}$</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>$\frac{1}{2\sqrt{\pi}} \cos \theta$</td>
</tr>
<tr>
<td>1</td>
<td>$\pm 1$</td>
<td>$\pm \frac{1}{2}\sqrt{\frac{3}{2\pi}} \sin \theta e^{\pm i\phi}$</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>$\frac{1}{4\sqrt{\pi}} (3 \cos^2 \theta - 1)$</td>
</tr>
<tr>
<td>2</td>
<td>$\pm 1$</td>
<td>$\pm \frac{1}{2}\sqrt{\frac{15}{2\pi}} \sin \theta \cos \theta e^{\pm i\phi}$</td>
</tr>
<tr>
<td>2</td>
<td>$\pm 2$</td>
<td>$\frac{1}{4\sqrt{\pi}} \sin^2 \theta e^{\pm 2i\phi}$</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>$\frac{1}{4\sqrt{\pi}} (5 \cos^3 \theta - 3 \cos \theta)$</td>
</tr>
<tr>
<td>3</td>
<td>$\pm 1$</td>
<td>$\pm \frac{1}{8}\sqrt{\frac{21}{\pi}} \sin \theta (5 \cos^2 \theta - 1) e^{\pm i\phi}$</td>
</tr>
<tr>
<td>3</td>
<td>$\pm 2$</td>
<td>$\frac{1}{4\sqrt{\pi}} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$</td>
</tr>
<tr>
<td>3</td>
<td>$\pm 3$</td>
<td>$\pm \frac{1}{8}\sqrt{\frac{35}{\pi}} \sin^3 \theta e^{\pm 3i\phi}$</td>
</tr>
</tbody>
</table>
Solution of the Angular and Azimuthal Equations

• The radial wave function $R$ and the spherical harmonics $Y$ determine the probability density for the various quantum states. The total wave function $\psi(r, \theta, \phi)$ depends on $n$, $\ell$, and $m_\ell$. The wave function becomes

$$\psi_{n\ell m_\ell}(r, \theta, \phi) = R_{n\ell}(r)Y_{\ell m_\ell}(\theta, \phi)$$
7.3: Quantum Numbers

The three quantum numbers:

– $n$ Principal quantum number
– $\ell$ Orbital angular momentum quantum number
– $m_\ell$ Magnetic quantum number

The boundary conditions:

– $n = 1, 2, 3, 4, \ldots$ Integer
– $\ell = 0, 1, 2, 3, \ldots, n - 1$ Integer
– $m_\ell = -\ell, -\ell + 1, \ldots, 0, 1, \ldots, \ell - 1, \ell$ Integer

The restrictions for quantum numbers:

– $n > 0$
– $\ell < n$
– $|m_\ell| \leq \ell$
Principal Quantum Number $n$

- It results from the solution of $R(r)$ in Eq (7.4) because $R(r)$ includes the potential energy $V(r)$.

The result for this quantized energy is

$$E_n = \frac{-\mu}{2} \left( \frac{e^2}{4\pi\epsilon_0 \hbar} \right)^2 \frac{1}{n^2} = -\frac{E_0}{n^2}$$

- The negative means the energy $E$ indicates that the electron and proton are bound together.
Orbital Angular Momentum Quantum Number $\ell$

- It is associated with the $R(r)$ and $f(\theta)$ parts of the wave function.

- Classically, the orbital angular momentum $\vec{L} = \vec{r} \times \vec{p}$ with $L = m_v \text{orbital} \cdot r$.

- $\ell$ is related to $L$ by $L = \sqrt{\ell(\ell + 1)}\hbar$.

- In an $\ell = 0$ state, $L = \sqrt{0(1)} \hbar = 0$

This disagrees with Bohr’s semi-classical “planetary” model of electrons orbiting a nucleus $L = n\hbar$. 