Chapter 18
The Hydrogen Atom

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Chem. 4300
The Hydrogen Atom

- Hydrogen atom is simplest atomic system where Schrödinger equation can be solved analytically and compared to experimental measurements.

- Analytical solution serve as basis for obtaining approximate solutions for multi-electron atoms and molecules, where no analytical solution exists.

- Warning: Working through analytical solution of H-atom may cause drowsiness. Do not operate heavy machinery during this derivation.
Two Particle Problem

2 particles with mass \( m_p \) and \( m_e \) at \( \vec{r}_p \) and \( \vec{r}_e \).

Total mass, center of mass, and inter-particle distance vector is

\[
M = m_p + m_e, \quad \vec{R} = \frac{m_p \vec{r}_p + m_e \vec{r}_e}{M}, \quad \text{and} \quad \vec{r} = \vec{r}_e - \vec{r}_p
\]

Express \( \vec{r}_p \) and \( \vec{r}_e \) in terms of \( M, \vec{R} \) and \( \vec{r} \) as

\[
\vec{r}_p = \vec{R} - \frac{m_e}{M} \vec{r} \quad \text{and} \quad \vec{r}_e = \vec{R} + \frac{m_p}{M} \vec{r}
\]

Express individual momenta of 2 particles as

\[
\vec{p}_p = m_p \frac{d\vec{r}_p}{dt} \quad \text{and} \quad \vec{p}_e = m_e \frac{d\vec{r}_e}{dt}
\]

then in terms of \( M, \vec{R} \) and \( \vec{r} \) as

\[
\vec{p}_p = m_p \left( \frac{d\vec{R}}{dt} - \frac{m_e}{M} \frac{d\vec{r}}{dt} \right) \quad \text{and} \quad \vec{p}_e = m_e \left( \frac{d\vec{R}}{dt} + \frac{m_p}{M} \frac{d\vec{r}}{dt} \right)
\]
Two Particle Problem

Next consider total energy

\[ E = \frac{\vec{p}_p^2}{2m_p} + \frac{\vec{p}_e^2}{2m_e} + V(\vec{r}) \]

\( V(\vec{r}) \) depends only on distance between 2 particles.
Write energy in terms of \( M, \vec{R} \) and \( \vec{r} \) and obtain

\[ E = \frac{1}{2}M \left( \frac{d\vec{R}}{dt} \right)^2 + \frac{1}{2} \mu \left( \frac{d\vec{r}}{dt} \right)^2 + V(\vec{r}) \]

\( \mu \) is reduced mass, given by

\[ \frac{1}{\mu} = \frac{1}{m_p} + \frac{1}{m_e} \]

Define 2 new momenta associated with center of mass and reduced mass,

\[ \vec{p}_R = M \frac{d\vec{R}}{dt}, \text{ and } \vec{p}_r = \mu \frac{d\vec{r}}{dt} \]
Two Particle Problem

Total energy becomes

\[ E = \frac{\vec{p}_R^2}{2M} + \frac{\vec{p}_r^2}{2\mu} + V(\vec{r}) \]

1st term is *translational energy of center of mass*

2nd term is *kinetic energy due to relative motion of 2 particles*

Translating to quantum mechanics we write

time independent Schrödinger equation for 2 particle system as

\[
\left[ \frac{\vec{p}_R^2}{2M} + \frac{\vec{p}_r^2}{2\mu} + V(\vec{r}) \right] f(\vec{R}, \vec{r}) = \left[ -\frac{\hbar^2}{2M} \nabla^2_R - \frac{\hbar^2}{2\mu} \nabla^2_r + V(\vec{r}) \right] f(\vec{R}, \vec{r}) = Ef(\vec{R}, \vec{r})
\]
Two Particle Problem

\[
\left[ -\frac{\hbar^2}{2M} \nabla^2_R - \frac{\hbar^2}{2\mu} \nabla^2_r + V(\vec{r}) \right] f(\vec{R}, \vec{r}) = Ef(\vec{R}, \vec{r})
\]

Wave function can be separated into product of two wave functions

\[ f(\vec{R}, \vec{r}) = \chi(\vec{R})\psi(\vec{r}) \]

\(\chi(\vec{R})\) depending only on center of mass
\(\psi(\vec{r})\) depending only on relative motion of 2 particles

Substitute product into Schrödinger Eq above we obtain 2 wave equations

\[-\frac{\hbar^2}{2M} \nabla^2_R \chi(\vec{R}) = E_R \chi(\vec{R}) \]

and

\[-\frac{\hbar^2}{2\mu} \nabla^2_r + V(\vec{r}) \psi(\vec{r}) = E_r \psi(\vec{r}) \]

where

\[ E = E_R + E_r \]

On left is wave equation for translational motion of free particle of mass \(M\)
On right is wave equation for particle with mass \(\mu\) in potential \(V(\vec{r})\)
For electron bound positively charged nucleus we focus on PDE for \(\psi(\vec{r})\)
Schrödinger Equation in Spherical Coordinates

Focus on PDE for $\psi(\vec{r})$: Electron bound to positively charged nucleus

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 + \hat{V}(r)\right] \psi(\vec{r}) = E \psi(\vec{r})$$

Coulomb potential is

$$\hat{V}(r) = -\frac{Zq_e^2}{4\pi\varepsilon_0 r}$$

- Central potential with $1/r$ dependence.
- $V \to -\infty$ as $r \to 0$
- $V \to 0$ as $r \to \infty$
Schrödinger Equation in Spherical Coordinates

Since $\hat{V}(r)$ only depends on $r$ we adopt spherical coordinates

$$\begin{align*}
-\frac{\hbar^2}{2\mu} \left[ \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \right] \psi + \hat{V}(r)\psi &= E\psi \\
\end{align*}$$

Take term in parentheses as $-\hat{L}^2/\hbar^2$, rearrange, and simplify to

$$r^2 \frac{\partial^2 \psi(r, \theta, \phi)}{\partial r^2} + 2r \frac{\partial \psi(r, \theta, \phi)}{\partial r} + \frac{2\mu r^2}{\hbar^2} (E - \hat{V}(r)) \psi(r, \theta, \phi) = \frac{1}{\hbar^2} \hat{L}^2 \psi(r, \theta, \phi)$$

To solve PDE use separation of variables

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$
Schrödinger Equation in Spherical Coordinates

Substitute $\psi(r, \theta, \phi)$ into PDE and dividing both sides by $\psi(r, \theta, \phi)$

$$\frac{r^2}{R(r)} \frac{\partial^2 R(r)}{\partial r^2} + \frac{2r}{R(r)} \frac{\partial R(r)}{\partial r} + \frac{2\mu r^2}{\hbar^2} \left( E - \hat{V}(r) \right) = \frac{1}{Y(\theta, \phi)} \frac{1}{\hbar^2} \hat{L}^2 Y(\theta, \phi)$$

Left side depends only on $r$
Right side depends only on $\theta$ and $\phi$.
We have turned one PDE into two ODEs.

1. We know eigenfunctions and eigenvalues of $\hat{L}^2$ on right side,

$$\hat{L}^2 Y_{\ell, m}(\theta, \phi) = \ell (\ell + 1) \hbar^2 Y_{\ell, m}(\theta, \phi)$$

2. Define $\ell (\ell + 1)$ as separation constant and obtain ODE for radial part

$$\frac{r^2}{R(r)} \frac{d^2 R(r)}{dr^2} + \frac{2r}{R(r)} \frac{dR(r)}{dr} + \frac{2\mu r^2}{\hbar^2} \left( E - \hat{V}(r) \right) = \ell (\ell + 1)$$
Schrödinger Equation in Spherical Coordinates

Expanding and rearranging ODE for radial part we obtain

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

Looks like 1D time independent Schrödinger Eq with effective potential

\[
\hat{V}_{\text{eff}}(r) = \frac{\hbar^2}{2\mu} \frac{\ell(\ell + 1)}{r^2} - \frac{Zq_e^2}{4\pi\epsilon_0 r}
\]

Centrifugal Term

Total angular momentum, \(\sqrt{\ell(\ell + 1)}\hbar\), creates centrifugal force that pushes electron away from nucleus.

Notice 2 terms in \(\hat{V}_{\text{eff}}(r)\) always have opposite signs.
\( \hat{V}_{\text{eff}}(r) \): Effective Potential of H-Like Atom

Switching to Atomic Units: Convenient units for atomic physics

*Atomic unit of length*, also called Bohr radius, is defined as

\[
a_0 \equiv \frac{4\pi\varepsilon_0\hbar^2}{q_e^2 m_e} = 52.9177210526763 \text{ pm}
\]

*Atomic unit of energy* is

\[
1\text{E}_h \equiv \frac{\hbar^2}{m_e a_0^2} = \frac{q_e^2}{4\pi\varepsilon_0 a_0} = 27.21138602818051 \text{ eV}
\]

Dividing effective potential by \( E_h \), set \( Z = 1 \), \( \mu \approx m_e \), and obtain

\[
\hat{V}_{\text{eff}}(r)/E_h = \frac{\ell(\ell + 1)}{2} \frac{m_e a_0^2}{\mu r^2} - \frac{a_0}{r} \approx \frac{\ell(\ell + 1)}{2\varphi^2} - \frac{1}{\varphi}
\]

Define dimensionless radius as \( \varphi = r/a_0 \)
Plot of $V_{\text{eff}}$ for $\ell = 0, 1, 2, \text{ and } 3$.

Note: potential minimum shifts to higher radii with increasing angular momentum (i.e., centrifugal force).
Solving the Wave Equation for the Radial Part

\[
\left[ -\frac{\hbar^2}{2\mu} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + \frac{\hbar^2}{2\mu} \frac{\ell(\ell + 1)}{r^2} - \frac{Zq_e^2}{4\pi\epsilon_0 r} \right] R(r) = ER(r)
\]

pour yourself a third cup of coffee...
Solving the Radial Wave Equation

To obtain radial wave function, $R(r)$, we must solve

$$\left[ -\frac{\hbar^2}{2\mu} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + \frac{\hbar^2}{2\mu} \frac{\ell(\ell+1)}{r^2} - \frac{Zq_e^2}{4\pi\epsilon_0 r} \right] R(r) = ER(r)$$

Begin by dividing and both sides by $E$ and obtain

$$-\frac{\hbar^2}{2\mu E} \left[ \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right] R(r) + \left( \frac{\hbar^2}{2\mu E} \frac{\ell(\ell+1)}{r^2} - \frac{Zq_e^2}{4\pi\epsilon_0 rE} - 1 \right) R(r) = 0$$

Define

$$\kappa^2 \equiv -\frac{2\mu E}{\hbar^2} \quad \text{or} \quad E = -\frac{\hbar^2 \kappa^2}{2\mu}$$

$kappa$ is in wave numbers. Rearrange potential energy expression to

$$-\frac{Zq_e^2}{4\pi\epsilon_0 rE} = \frac{Zq_e^2}{4\pi\epsilon_0 r} \frac{2\mu}{\hbar^2 \kappa^2} = \frac{Zq_e^2 \mu}{2\pi\epsilon_0 \hbar^2 \kappa} \frac{1}{\kappa r} = \frac{2\rho_0}{\kappa r}$$

$\rho_0$ is a dimensionless quantity: $\rho_0 \equiv \frac{Zq_e^2 \mu}{2\pi\epsilon_0 \hbar^2 \kappa}$
Solving the Radial Wave Equation

Substitute expression for potential energy into ODE

\[
\frac{1}{\kappa^2} \left[ \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right] R(r) - \left( 1 + \frac{\ell(\ell + 1)}{(\kappa r)^2} + \frac{2\rho_0}{\kappa r} \right) R(r) = 0
\]

Define dimensionless variable: \( \rho \equiv 2\kappa r \)

Rewrite radial part as function of \( \rho \) as

\[
\left[ \frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} \right] R(\rho) - \left( 1 + \frac{\ell(\ell + 1)}{\rho^2} + \frac{2\rho_0}{\rho} \right) R(\rho) = 0
\]

Further simplify ODE by defining

\[
u(\rho) = \rho R(\rho), \quad \frac{d\nu(\rho)}{d\rho} = \rho \frac{dR(\rho)}{d\rho} + R(\rho), \quad \frac{d^2\nu(\rho)}{d\rho^2} = \rho \frac{d^2R(\rho)}{d\rho^2} + 2 \frac{dR(\rho)}{d\rho}
\]

Re-express ODE as

\[
\frac{d^2\nu(\rho)}{d\rho^2} - \left( \frac{1}{4} - \frac{\rho_0}{2\rho} + \frac{\ell(\ell + 1)}{\rho^2} \right) \nu(\rho) = 0
\]

\( \rho \) varies from 0 to \( \infty \). 1st look at asymptotic solutions: (1) \( \rho \to \infty \) and (2) \( \rho \to 0 \)
Solving the Radial Wave Equation, $\rho \to \infty$

Starting with

$$\frac{d^2 u(\rho)}{d\rho^2} - \left( \frac{1}{4} - \frac{\rho_0}{2\rho} + \frac{\ell(\ell + 1)}{\rho^2} \right) u(\rho) = 0$$

(1) $\rho \to \infty$. At large values of $\rho$ approximate ODE as

$$\frac{d^2 u(\rho)}{d\rho^2} - \frac{u(\rho)}{4} \approx 0$$

Solutions to this ODE have form

$$u(\rho) \sim A e^{-\rho/2} + B e^{\rho/2}$$

Reject positive exponent since require that solution be finite everywhere,

$$u(\rho) \sim A e^{-\rho/2} \quad \text{in limit that } \rho \to \infty$$
Solving the Radial Wave Equation, $\rho \rightarrow 0$

Starting with

$$\frac{d^2 u(\rho)}{d\rho^2} - \left( \frac{1}{4} - \frac{\rho_0}{2\rho} + \frac{\ell(\ell + 1)}{\rho^2} \right) u(\rho) = 0.$$  

(2) $\rho \rightarrow 0$. At small values of $\rho$ approximate ODE as

$$\frac{d^2 u(\rho)}{d\rho^2} - \frac{\ell(\ell + 1)}{\rho^2} u(\rho) \approx 0.$$  

Solutions to this ODE have form

$$u(\rho) \sim A \rho^{\ell+1} + B \rho^{-\ell}.$$  

Reject B term again because require that solution be finite at $\rho = 0$.

$$u(\rho) \sim A \rho^{\ell+1} \quad \text{in limit that } \rho \rightarrow 0$$
Solving the Radial Wave Equation

\[ u(\rho) \sim A e^{-\rho/2} \quad \text{in limit that } \rho \to \infty \]

\[ u(\rho) \sim A \rho^{\ell+1} \quad \text{in limit that } \rho \to 0 \]

Now, back to

\[
\frac{d^2 u(\rho)}{d\rho^2} - \left( \frac{1}{4} - \frac{\rho_0}{2\rho} + \frac{\ell(\ell+1)}{\rho^2} \right) u(\rho) = 0
\]

we propose general solution of form

\[ u(\rho) = \rho^{\ell+1} L(\rho) e^{-\rho/2} \]

This has correct behavior in two limits.

Only need to determine \( L(\rho) \) to get behavior for all \( \rho \).
Solving the Radial Wave Equation

Plug $u(\rho) = \rho^{\ell+1} L(\rho) e^{-\rho/2}$, where $\rho \equiv 2\kappa r$, into

$$\frac{d^2u(\rho)}{d\rho^2} - \left( \frac{1}{4} - \frac{\rho_0}{2\rho} + \frac{\ell(\ell + 1)}{\rho^2} \right) u(\rho) = 0$$

gives

$$\rho \frac{d^2L(\rho)}{d\rho^2} + \frac{dL(\rho)}{d\rho} \left( 2(\ell + 1) - \rho \right) + \left( \frac{\rho_0}{2} - (\ell + 1) \right) L(\rho) = 0$$

Set $j = \rho_0/2 - \ell - 1$, and $k = 2\ell + 1$ and this ODE is recognized as

$$\rho \frac{d^2L^k_j(\rho)}{d\rho^2} + (k + 1 - \rho) \frac{dL^k_j(\rho)}{d\rho} + jL^k_j(\rho) = 0,$$

associated Laguerre differential equation

Has nonsingular solutions only if $j$ is non-negative integers, $j = 0, 1, 2, \ldots$

These solutions, $L^k_j(\rho)$, are called the associated Laguerre polynomials.
Selected associated Laguerre polynomials

<table>
<thead>
<tr>
<th>n</th>
<th>\ell</th>
<th>\frac{\ell+1}{n-\ell-1}(\rho)</th>
<th>Polynomial Roots</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>$L_0^1(\rho)$</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>$L_1^1(\rho)$</td>
<td>2 - \rho</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>$L_3^1(\rho)$</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>$L_2^2(\rho)$</td>
<td>$\frac{1}{2}(6 - 6\rho + \rho^2)$</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>$L_1^3(\rho)$</td>
<td>4 - \rho</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>$L_5^1(\rho)$</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>$L_3^2(\rho)$</td>
<td>$\frac{1}{6}(24 - 36\rho + 12\rho^2 - \rho^3)$</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>$L_2^3(\rho)$</td>
<td>$\frac{1}{2}(20 - 10\rho + \rho^2)$</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>$L_1^5(\rho)$</td>
<td>6 - \rho</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>$L_7^1(\rho)$</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>$L_4^2(\rho)$</td>
<td>$\frac{1}{24}(120 - 240\rho + 120\rho^2 - 20\rho^3 + \rho^4)$</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>$L_3^3(\rho)$</td>
<td>$\frac{1}{6}(120 - 90\rho + 18\rho^2 - \rho^3)$</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>$L_2^5(\rho)$</td>
<td>$\frac{1}{2}(42 - 14\rho + \rho^2)$</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>$L_1^7(\rho)$</td>
<td>8 - \rho</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>$L_9^1(\rho)$</td>
<td>1</td>
</tr>
</tbody>
</table>

Associated Laguerre polynomials following definition where $L_j^k(x) = (-1)^k \frac{d^k}{dx^k} L_{j+k}(x)$.

Laguerre polynomial $L_j(x)$ is defined by Rodrigues formula: $L_j(x) = \frac{1}{n!} e^x \frac{d^j}{dx^j} \left(x^j e^{-x}\right)$. 

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Chapter 18: The Hydrogen Atom
Solving the Radial Wave Equation

- Since $\ell = 0, 1, 2, \ldots$, and $j = 0, 1, 2, \ldots$, then
  \[
  \frac{\rho_0}{2} = j + \ell + 1
  \]
  can only take on integer values of $\rho_0/2 = 1, 2, \ldots$.
- We define this as the principal quantum number
  \[
  n \equiv \frac{\rho_0}{2} = j + \ell + 1,
  \]
  which can only take on values of
  \[
  n = 1, 2, 3, \ldots.
  \]
- Wave functions with same $n$ value form set called a shell.
- Special letters are sometimes assigned to each $n$ value
  \[
  n = 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad \leftarrow \text{numerical value} \\
  K \quad L \quad M \quad N \quad O \quad \leftarrow \text{symbol}
  \]
Solving the Radial Wave Equation

\( \ell \) is called the azimuthal quantum number

Rearranging \( n = j + \ell + 1 \) for \( \ell \) gives

\[
\ell = n - j - 1
\]

and we find that \( \ell \) cannot exceed \( n - 1 \) (since lowest value of \( j \) is zero).

Range of \( \ell \) is

\[
\ell = 0, \ldots, n - 1.
\]

Recall that azimuthal quantum number, \( \ell \), defines total angular momentum of \( \sqrt{\ell(\ell + 1)} \hbar \).

\( m_\ell \) is called the magnetic quantum number.

\( m_\ell \) has positive and negative integer values between \(-\ell\) and \( \ell \).

When \( x, y, \) or \( z \) component of the electron’s angular momentum is measured only values of \( m_\ell \hbar \) are observed.
Solving the Radial Wave Equation

Wave functions with same value of $n$ and $\ell$ form set called a sub-shell. Special letters are assigned to sub-shell with given $\ell$ value,

$$\ell = 0 \ 1 \ 2 \ 3 \ 4 \ 5 \ 6 \ 7 \ 8 \ 9 \ 10 \ 11 \ 12 \ 13 \ \leftarrow \text{ numerical value}$$

$$\text{s p d f g h i k l m o q r t} \ \leftarrow \text{ symbol}$$

and continue afterwards in alphabetical order.

- 1st four letters arose in pre-quantum atomic spectroscopy for classifying emission lines and stand for *sharp*, *principal*, *diffuse*, and *fine*.
- Shorthand $n\ell$ notation uses principal quantum number with $\ell$ symbol,
- Wave function with
  - $n = 1, \ell = 0$ is referred to as 1s state
  - $n = 2, \ell = 1$ is referred to as 2p state
- Number of roots of $L_{n-\ell-1}^{2\ell+1}$ is $n - \ell - 1$. Thus, number of radial nodes is equal to $n - \ell - 1$.
- Recall for Spherical Harmonics that number of angular nodes is $\ell$
- Thus, total number of nodes is $(n - \ell - 1) + \ell = n - 1$. 

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Chapter 18: The Hydrogen Atom
Energy of the Hydrogen-Like Atom

Given the constraint that $\rho_0/2 = n$ we go back to

$$\rho_0 \equiv \frac{Zq_e^2 \mu}{2\pi e_0 \hbar^2 \kappa} = 2n$$

and rearrange to

$$\kappa_n = \frac{Zq_e^2 \mu}{4\pi e_0 \hbar^2 n}$$

From

$$\kappa^2 \equiv -\frac{2\mu E}{\hbar^2}$$

rearranges to

$$E_n = -\frac{\hbar^2 \kappa_n^2}{2\mu} = -\frac{Z^2 q_e^4 \mu}{32\pi^2 e_0^2 \hbar^2 n^2} = -\frac{Z^2 q_e^4 \mu}{8e_0^2 \hbar^2 n^2}$$

$$E_n = -\frac{Z^2 q_e^4 \mu}{8e_0^2 \hbar^2 n^2}$$

Energy of H-like atom
Energy of the Hydrogen-Like Atom

\[ E_n = -\frac{Z^2 q_e^4 \mu}{8\epsilon_0^2 h^2 n^2} \]

- e\(^-\) bound to nucleus with charge Z energy only depends on \( n \) and \( Z \)
- If \( Z \) increases (holding \( n \) constant) then \( E_n \) decreases—becomes more negative. Higher \( Z \) means nucleus holds e\(^-\) more tightly
- In limit that \( n \to \infty \) then \( E \to 0 \) and e\(^-\) is unbound
Energy of the Hydrogen-Like Atom

With $\mu \approx m_e$, the $n = 1$ energy is called Rydberg unit of energy (Ry)

$$1 \text{Ry} = -E_1 = \frac{q_e^4 m_e}{8e_0^2 h^2} = 13.60569301218355 \text{ eV}$$

With $\mu \approx m_e$ approximation

$$E_n = -\frac{1}{n^2} \text{ Ry} \quad \text{Energy of H atom}$$

Can also divide by atomic unit of energy, $E_h$, to obtain

$$E_n = -\frac{1}{2n^2} E_h \quad \text{Energy of H atom}$$

Given $n$, energy is identical for each $\ell$. Given $\ell$ energy is identical for $2\ell + 1$ values of $m_\ell$.

Degeneracy of $n$th energy level is

$$g_n = \sum_{\ell=0}^{n-1} (2\ell + 1) = n + 2 \sum_{\ell=0}^{n-1} \ell = n + n(n - 1) = n^2$$
Energy levels of single electron bound to proton

\[
\begin{array}{c|cc}
\text{n} & \text{orbitals} & \text{degeneracy} \\
\infty & 5s, 5p, 5d, 5f, 5g & g_5 = 25 \\
5 & 4s, 4p, 4d, 4f & g_4 = 16 \\
4 & 3s, 3p, 3d & g_3 = 9 \\
3 & 2s, 2p & g_2 = 4 \\
2 & 1s & g_1 = 1 \\
1 & & \\
\end{array}
\]
Energy of the Hydrogen-Like Atom

Remember Balmer series for hydrogen emission spectra obeys relation:

$$\frac{1}{\lambda} = R_H \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \quad \text{where} \quad R_H = 1.097 \times 10^7 \text{ /m}$$

Followed by Bohr’s theory of atom which gave

$$\frac{1}{\lambda} = \left( \frac{1}{4\pi\epsilon_0} \right)^2 \left( \frac{m_e q_e^4}{4\pi\hbar^3 c_0} \right)^2 Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

perfect agreement with $R_H$

- Taking $h\nu = \frac{h\nu}{\lambda} = \Delta E = E_f - E_i$ and solving for $1/\lambda$ from H-like atom energy gives exact same result as Bohr’s theory for $R_H$.
- At this point Schrödinger knew wave equation approach was working.
- After determining full wave function for H-like atom next step is solutions for multi-electron atoms where Bohr’s theory had failed.
Normalizing the Radial Wave Function

Solutions, $L_j^k(\rho)$, are called associated Laguerre polynomials.

From these we construct radial part of wave function.

Need to retrace steps from $u(\rho)$ back to $R(r)$ starting with

$$u_{n,\ell}(\rho_n) = \rho_n^{\ell+1} L_{n-\ell-1}^{2\ell+1}(\rho_n) e^{-\rho_n/2}$$

going back through

$$R_{n,\ell}(\rho_n) = \frac{u_{n,\ell}(\rho_n)}{\rho_n} = \rho_n^{\ell} L_{n-\ell-1}^{2\ell+1}(\rho_n) e^{-\rho_n/2}$$

and finally with $\rho = 2\kappa r$ returning to

$$R_{n,\ell}(r) = (2\kappa_n r)^{\ell} L_{n-\ell-1}^{2\ell+1}(2\kappa_n r) e^{-\kappa_n r}$$
Normalizing the Radial Wave Function

To normalization radial part we define $x = 2\kappa_n r$ and express radial part as

$$ R_{n,\ell}(x) = A_{n,\ell} x^\ell L_{n-\ell-1}^{2\ell+1}(x) e^{-x/2} $$

$A_{n,\ell}$ is to-be-determined normalization constant. Normalization integral is

$$ \int_0^\infty R_{n,\ell}^*(r) R_{n,\ell}(r) r^2 dr = \frac{1}{(2\kappa_n)^3} \int_0^\infty R_{n,\ell}^*(x) R_{n,\ell}(x) x^2 dx = 1 $$

Substituting $R_{n,\ell}(x)$ into integral gives

$$ \frac{A_{n,\ell}^2}{(2\kappa_n)^3} \int_0^\infty x^{2\ell+2} [L_{n-\ell-1}^{2\ell+1}(x)]^2 e^{-x} dx = 1 $$

Look up the general integral for associated Laguerre polynomials

$$ \int_0^\infty x^{k+1} [L_j^k(x)]^2 e^{-x} dx = (2j + k + 1) \frac{(j + k)!}{j!} $$

we find

$$ \frac{A_{n,\ell}^2}{(2\kappa_n)^3} \frac{2n(n + \ell)!}{(n - \ell - 1)!} = 1 \quad \text{or} \quad A_{n,\ell} = (2\kappa_n)^{3/2} \sqrt{\frac{(n - \ell - 1)!}{2n(n + \ell)!}} $$

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Chapter 18: The Hydrogen Atom
Radial Wave Function

To further simplify \( R_{n,\ell}(r) \) we introduce quantity analogous to Bohr radius,

\[
a_\mu \equiv \frac{4\pi e_0 \hbar^2}{q_e^2 \mu}
\]

then we obtain

\[
\kappa_n = \frac{Z}{na_\mu}
\]

and express \( \rho_n \) as

\[
\rho_n = 2\kappa_n r = \frac{2Zr}{na_\mu}
\]

Finally, we obtain radial part of wave function of hydrogen-like atom

\[
R_{n,\ell}(r) = \left( \frac{2Z}{na_\mu} \right)^{\ell+3/2} \sqrt{\frac{(n-\ell-1)!}{2n(n+\ell)!}} L_{n-\ell-1}^{2\ell+1} \left( \frac{2Z}{na_\mu} r \right) r^\ell e^{-Zr/(na_\mu)}
\]
Radial part of H-like wave functions for $n = 1$ to $n = 4$.

\[ R_{1,0} = 2 \left( \frac{Z}{a_\mu} \right)^{3/2} e^{-Zr/a_\mu} \]

\[ R_{2,0} = \frac{1}{2\sqrt{2}} \left( \frac{Z}{a_\mu} \right)^{3/2} \left( 2 - \frac{Zr}{a_\mu} \right) e^{-Zr/(2a_\mu)} \]

\[ R_{2,1} = \frac{1}{2\sqrt{6}} \left( \frac{Z}{a_\mu} \right)^{5/2} r e^{-Zr/(2a_\mu)} \]

\[ R_{3,0} = \sqrt{\frac{2}{81}} \left( \frac{Z}{a_\mu} \right)^{3/2} \left( 6 - 6 \left( \frac{2Zr}{3a_\mu} \right) + \left( \frac{2Zr}{3a_\mu} \right)^2 \right) e^{-Zr/(3a_\mu)} \]

\[ R_{3,1} = \frac{1}{27} \sqrt{\frac{2}{3}} \left( \frac{Z}{a_\mu} \right)^{5/2} \left( 4 - \left( \frac{2Zr}{3a_\mu} \right) \right) e^{-Zr/(3a_\mu)} \]

\[ R_{3,2} = \frac{2}{81} \sqrt{\frac{2}{15}} \left( \frac{Z}{a_\mu} \right)^{7/2} r^2 e^{-Zr/(3a_\mu)} \]

\[ R_{4,0} = \frac{1}{16} \left( \frac{Z}{a_\mu} \right)^{3/2} \frac{1}{6} \left( 24 - 36 \left( \frac{Zr}{2a_\mu} \right) + 12 \left( \frac{Zr}{2a_\mu} \right)^2 - \left( \frac{Zr}{2a_\mu} \right)^3 \right) e^{-Zr/(4a_\mu)} \]

\[ R_{4,1} = \frac{1}{32} \sqrt{\frac{1}{15}} \left( \frac{Z}{a_\mu} \right)^{5/2} \frac{1}{2} \left( 20 - 10 \left( \frac{Zr}{2a_\mu} \right) + \left( \frac{Zr}{2a_\mu} \right)^2 \right) r e^{-Zr/(4a_\mu)} \]

\[ R_{4,2} = \frac{1}{384} \sqrt{\frac{1}{35}} \left( \frac{Z}{a_\mu} \right)^{7/2} \left( 6 - \left( \frac{Zr}{2a_\mu} \right) \right) r^2 e^{-Zr/(4a_\mu)} \]

\[ R_{4,3} = \frac{1}{768} \sqrt{\frac{1}{5}} \left( \frac{Z}{a_\mu} \right)^{9/2} r^3 e^{-Zr/(4a_\mu)} \]
Wave function extends further out in $r$, away from the nucleus, as $n$ increases.

As with harmonic oscillator classically excluded positions are displacements where $E > V(r)$.

For hydrogen atom classically excluded radii are $r/a_\mu > 2n^2$.

Classically excluded regions are indicated by gray regions.
$R_{n, \ell}(r)$ for $n = 5$ and all possible values of $\ell$

- Radial function at origin, $r = 0$, is non-zero only for $s$ states, where $\ell = 0$.
- Maximum in wave function at constant $n$ is pushed further away from nucleus as $\ell$ increases. This is consequence of centrifugal term in effective potential.

\[
\hat{V}_{\text{eff}}(r) = \frac{\hbar^2}{2\mu} \frac{\ell (\ell + 1)}{r^2} - \frac{Z q_e^2}{4\pi \epsilon_0 r}
\]

Centrifugal Term
Hydrogen-Like Atom Wave Functions

In summary, solutions to Schrödinger equation for single electron bound to positive charge nucleus are

\[
\psi_{n,\ell,m_\ell}(r, \theta, \phi) = R_{n,\ell}(r)Y_{\ell,m_\ell}(\theta, \phi).
\]

- \(R_{n,\ell}(r)\) is radial part of wave function and depends on quantum numbers \(n\) and \(\ell\).
- \(Y_{\ell,m_\ell}(\theta, \phi)\) is angular part of wave function and depends on quantum numbers \(\ell\) and \(m_\ell\).
- Radial part combined with spherical harmonics give full wave function, also called \textit{orbital} since wave function describes electron’s “orbit” around nucleus.
Hydrogen wave functions for \( n = 1 \) to \( n = 3 \)

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Wave Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1s )</td>
<td>( \psi_{1,0,0} = \frac{2}{\sqrt{4\pi}} \left( \frac{Z}{a_\mu} \right)^{3/2} e^{-Zr/a_\mu} )</td>
</tr>
<tr>
<td>( 2s )</td>
<td>( \psi_{2,0,0} = \frac{1}{\sqrt{32\pi}} \left( \frac{Z}{a_\mu} \right)^{5/2} \left( 2 - \frac{Zr}{a_\mu} \right) e^{-Zr/(2a_\mu)} )</td>
</tr>
<tr>
<td>( 2p_0 )</td>
<td>( \psi_{2,1,0} = \frac{1}{\sqrt{32\pi}} \left( \frac{Z}{a_\mu} \right)^{5/2} r e^{-Zr/(2a_\mu)} \cos \theta )</td>
</tr>
<tr>
<td>( 2p_{\pm 1} )</td>
<td>( \psi_{2,1,\pm 1} = \mp \frac{1}{\sqrt{64\pi}} \left( \frac{Z}{a_\mu} \right)^{5/2} r e^{-Zr/(2a_\mu)} \sin \theta \ e^{\pm i\phi} )</td>
</tr>
<tr>
<td>( 3s )</td>
<td>( \psi_{3,0,0} = \frac{1}{\sqrt{162\pi}} \left( \frac{Z}{a_\mu} \right)^{3/2} \left( 6 - 6 \left( \frac{2Zr}{3a_\mu} \right) + \left( \frac{2Zr}{3a_\mu} \right)^2 \right) e^{-Zr/(3a_\mu)} )</td>
</tr>
<tr>
<td>( 3p_0 )</td>
<td>( \psi_{3,1,0} = \frac{1}{27} \frac{1}{\sqrt{2\pi}} \left( \frac{Z}{a_\mu} \right)^{5/2} \left( 4 - \left( \frac{2Zr}{3a_\mu} \right) \right) r e^{-Zr/(3a_\mu)} \cos \theta )</td>
</tr>
<tr>
<td>( 3p_{\pm 1} )</td>
<td>( \psi_{3,1,\pm 1} = \mp \frac{1}{27} \frac{1}{\sqrt{2\pi}} \left( \frac{Z}{a_\mu} \right)^{5/2} \left( 4 - \left( \frac{2Zr}{3a_\mu} \right) \right) r e^{-Zr/(3a_\mu)} \sin \theta \ e^{\pm i\phi} )</td>
</tr>
<tr>
<td>( 3d_0 )</td>
<td>( \psi_{3,2,0} = \frac{2}{81} \frac{1}{\sqrt{6\pi}} \left( \frac{Z}{a_\mu} \right)^{7/2} r^2 e^{-Zr/(3a_\mu)} \frac{1}{2} (3 \cos^2 \theta - 1) )</td>
</tr>
<tr>
<td>( 3d_{\pm 1} )</td>
<td>( \psi_{3,2,\pm 1} = \mp \frac{1}{243} \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_\mu} \right)^{7/2} r^2 e^{-Zr/(3a_\mu)} 3 \cos \theta \sin \theta \ e^{\pm i\phi} )</td>
</tr>
<tr>
<td>( 3d_{\pm 2} )</td>
<td>( \psi_{3,2,\pm 2} = \pm \frac{1}{486} \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_\mu} \right)^{7/2} r^2 e^{-Zr/(3a_\mu)} 3 \sin^2 \theta \ e^{\pm 2i\phi} )</td>
</tr>
</tbody>
</table>
Hydrogen-Like Atom Wave Functions

2D cross sections through $x$-$z$ plane of 3D probability density of selected hydrogen atom wave functions.
Probability density for finding $e^-$ in given volume element, $d\tau$, is

$$|\psi(r, \theta, \phi)|^2 d\tau = |R_{n,\ell}(r)|^2 |Y_{\ell,m_\ell}(\theta, \phi)|^2 r^2 dr \sin \theta d\theta d\phi$$

Integrate over all values of $\theta$ and $\phi$ to calculate probability of finding $e^-$ inside spherical shell of thickness $dr$ at distance $r$ from origin

$$|\psi(r, \theta, \phi)|^2 d\tau = |R_{n,\ell}(r)|^2 \int_0^\pi \int_0^{2\pi} |Y_{\ell,m_\ell}(\theta, \phi)|^2 r^2 dr \sin \theta d\theta d\phi = r^2 R_{n,\ell}^2 (r) dr.$$ 

Recall that spherical harmonic functions are already normalized.

Probability density $r^2 R_{n,\ell}^2 (r) dr$ is called radial distribution function.
Cartesian (real) wave functions

$m_\ell \neq 0$ complex wave function are hard to visualize. Sometimes easier to work with real wave functions by taking sum and difference of $|m_\ell|$ wave functions,

$$\psi^{(\pm)} = c \left( \psi_{|m_\ell|} \pm \psi_{-|m_\ell|} \right)$$

Since $\psi^*_{|m_\ell|} = \psi_{-|m_\ell|}$ coefficient $c$ is adjusted to make $\psi^{(\pm)}$ real and normalized.

$$\psi_{p_x} = \frac{1}{\sqrt{2}} \left( \psi_{p+1} + \psi_{p-1} \right)$$

$$\psi_{p_y} = \frac{1}{\sqrt{2i}} \left( \psi_{p+1} - \psi_{p-1} \right)$$

Superposition principle tells us that these are also solutions to same wave equation.
Cartesian (real) wave functions: $n = 2, \ell = 1$

$2p_x, 2p_y, 2p_z$

Orbitron Web Site
Cartesian (real) wave functions

Can also form real wave functions with d orbitals

\[ nd_{z^2} = \psi_{n,2,0} \]

\[ nd_{xz} = \frac{1}{\sqrt{2}} (\psi_{n,2,1} + \psi_{n,2,-1}) \quad nd_{yz} = \frac{1}{\sqrt{2}} (\psi_{n,2,1} - \psi_{n,2,-1}) \]

\[ nd_{x^2-y^2} = \frac{1}{\sqrt{2}} (\psi_{n,2,2} + \psi_{n,2,-2}) \quad nd_{xy} = \frac{1}{\sqrt{2}} i (\psi_{n,2,2} - \psi_{n,2,-2}) \]

As long as 2 wave functions are degenerate they will also be stationary states.

Numerous illustrations of shape of the Cartesian H-orbitals can be found in elementary chemistry texts.
Cartesian (real) wave functions: \( n = 3, \ell = 2 \)

Top: \( 2d_{x^2-y^2} \) and \( 2d_{z^2} \)
Bottom \( 2d_{xy}, 2d_{xz}, \) and \( 2d_{yz} \)

Orbition Web Site
Hydrogen atom orbitals
H-like Atom Transition Selection Rules

For transitions between H-like atom energy states through absorption and emission of light we require non-zero electric dipole transition moment,

\[
\langle \vec{\mu} \rangle_{n,\ell,m_\ell,n',\ell',m'_{\ell}} = \int_{V} \psi_{n,\ell,m_\ell}^*(r, \phi, \theta) \vec{\mu} \psi_{n',\ell',m'_{\ell}}(r, \phi, \theta) d\tau
\]

For H-like atom electric dipole moment is

\[
\vec{\mu} = \sum_i q_i \vec{r} = Z q_e \vec{r}_p - q_e \vec{r}_e
\]

Since \( \vec{r}_e = \vec{r} + \vec{r}_p \) we can write

\[
\vec{\mu} = Z q_e \vec{r}_p - q_e (\vec{r} + \vec{r}_p) = (Z - 1) q_e \vec{r}_p - q_e \vec{r}
\]

Substituting this into transition moment integral gives

\[
\langle \vec{\mu} \rangle_{n,\ell,m_\ell,n',\ell',m'_{\ell}} = \int_{V} \psi_{n,\ell,m_\ell}^*(r, \phi, \theta) (Z - 1) q_e \vec{r}_p \psi_{n',\ell',m'_{\ell}}(r, \phi, \theta) d\tau
\]

\[
- \int_{V} \psi_{n,\ell,m_\ell}^*(r, \phi, \theta) q_e \vec{r} \psi_{n',\ell',m'_{\ell}}(r, \phi, \theta) d\tau
\]
H-like Atom Transition Selection Rules

\[
\langle \vec{\mu} \rangle_{n,\ell,m, n', \ell', m'} = \int_V \psi^{*}_{n,\ell,m}(r, \phi, \theta) (Z - 1) q_e \vec{r}_p \psi_{n',\ell',m'}(r, \phi, \theta) d\tau
\]

\[
- \int_V \psi^{*}_{n,\ell,m}(r, \phi, \theta) q_e \vec{r} \psi_{n',\ell',m'}(r, \phi, \theta) d\tau
\]

- 1st integral involving \( \vec{r}_p \) goes to zero for all transitions
- 2nd integral gives transition dipole moment
- Convenient to express \( \vec{r} \) in spherical coordinates

\[
-q_e \vec{r} = -q_e \hat{r} \left( \sin \theta \cos \phi \hat{e}_x + \sin \theta \sin \phi \hat{e}_y + \cos \theta \hat{e}_z \right)
\]

- Using H-like wave functions find that \( \Delta n \) can have any value and

\[
\Delta \ell = \pm 1, \quad \Delta m_\ell = 0 \text{ for } \hat{\mu}_z, \quad \Delta m_\ell = \pm 1 \text{ for } \hat{\mu}_x \text{ and } \hat{\mu}_y
\]
Atomic dipole transitions