HYDROGEN ATOM

H1 - H9
HYDROGEN ATOM

proton + electron around (and other things)

$$\hat{H} = \frac{\hat{p}_N^2}{2m_N} + \frac{\hat{p}_e^2}{2m_e} + V_{ep}(r_e - r_N)$$

New coordinates

POSITION: center of mass + distance

$$m_N \gg m_e$$ (~1850 times)

introduce effective mass $$\mu$$

COORDINATES

center of mass $$R = \frac{m_N r_N + m_e r_e}{m_N + m_e}$$

$$r = r_e - r_N$$

$$\frac{1}{\mu} = \frac{1}{m_N} + \frac{1}{m_e}$$

$$\mu = m_N + m_e$$

$$\Rightarrow \hat{H} = \frac{\hat{p}^2}{2\mu} + \frac{\hat{r}^2}{2\mu} + V(r)$$

H1
\[ \frac{\hat{p}^2}{2m} \rightarrow \text{heavy } M, \text{ do with } C.M. \]
\[ \Rightarrow \text{ electron for } t \text{ follows } M \text{ as cloud} \]

\[ \Rightarrow \hat{H} = \frac{\hat{p}^2}{2m} + V(r) \]
\[ V(r) = \text{COULOMB} \]
\[ -\frac{Z e^2}{r} \]

central potential

spherically symmetric \( \Rightarrow \psi = \)

\[ \Rightarrow \text{ go in spherical coordinates} \]

\[ \hat{H} \psi(r, \theta, \phi) = E \psi(r, \theta, \phi) \]
\[ \psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \]

\[ \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \]

\[ \Delta \psi = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \]
\[ + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \]

H2
\[
-\frac{\hbar^2}{2\mu x^2} \left[ \Theta \phi \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + R \phi \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \\
+ R \Theta \frac{1}{\sin^2 \theta} \frac{d^2 \phi}{d\phi^2} \right] - \frac{Ze^2}{(4\pi \varepsilon_0) x} \right] \cdot R \phi = E R \Theta \phi
\]

1) isolate \( \phi \) dependence.

multiply \( \frac{1}{-\frac{2\mu x^2 \varepsilon^2}{\hbar^2}} \) to both sides and rearranging

\[
\frac{\sin^2 \theta}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2\mu x^2 \varepsilon^2}{\hbar^2} \left( E + \frac{Ze^2}{(4\pi \varepsilon_0) x} \right) + \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\sin^2 \theta} \frac{d^2 \phi}{d\phi^2} = 0
\]

- \( x, \Theta \) dependence is mixed
- \( \phi \) is simple, if I rotate around \( \phi \) the stuff doesn't change

\[
\Rightarrow \quad \text{constant} + \frac{1}{\phi} \frac{d^2 \phi}{d\phi^2} = \infty \quad \Rightarrow \quad \frac{d^2 \phi}{d\phi^2} = -m^2 \phi
\]

\( \Rightarrow \) real or imaginary?

must be real and integer for boundary conditions

\( \phi \) must be normalized

\[
\phi = \frac{1}{\sqrt{2\pi}} \ e^{im\phi}
\]

\( m \) is integer, which??

H3
2) Equation becomes:

\[
\frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2 \mu r^2}{h^2} \left( E + \frac{Z e^2}{(4\pi\varepsilon_0) r} \right) + \frac{1}{\theta \sin \theta} \frac{d}{d\theta} \left( \theta \sin \theta \frac{d\Theta}{d\theta} \right) - \frac{m^2}{\sin^2 \theta} = 0
\]

\[
\text{all } \mu > 0 \quad \forall \theta
\]

\[
= \beta
\]

\[
\text{all } \mu > 0 \quad \forall \theta = \frac{\pi}{2}
\]

\[
= -\beta
\]

\[
\begin{cases}
\frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2 \mu r^2}{h^2} \left( E + \frac{Z e^2}{(4\pi\varepsilon_0) r} \right) R = \beta R
\end{cases}
\]

\[
\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \theta \sin \theta \frac{d\Theta}{d\theta} \right) - \frac{m^2}{\sin^2 \theta} = -\beta \theta
\]

3) The \( \Theta(\theta) \) equation can be solved (poor):

a) change variables

b) express solution in power series and get recursive solution

c) keep only square summable solutions: \( \int \Theta^2 \, d\theta = 1 \)
d) solution = series \( \rightarrow \) to terminate (no divergences)

\[ \Rightarrow \beta = \ell (\ell + 1) \quad \ell = \text{integer} \]

d) truncated series = Legendre polynomial \( P_\ell^m (\cos \theta) \)

e) return to angular frame:

\[ \Theta_{\ell m} (\theta) = \left[ \frac{(2\ell + 1)}{2} \frac{(\ell - |m|)!}{(\ell + |m|)!} \right]^{1/2} \text{ associated Legendre polynomial} \]

H 4)
\[ P_0(x) = 1 \quad P_1(x) = x \quad P_2(x) = \frac{1}{2} (3x^2 - 1) \quad \ldots \]

\[ P_1'(x) = (1-x^2)^{\frac{1}{2}} \quad P_2'(x) = 3(1-x^2)^{\frac{3}{2}} \quad \ldots \]

\[ P_{e-1}^{(m)}(x) = 0 \text{ if } |m| > e \]

\[ \Rightarrow m = -e, -e+1, \ldots, |e|, e \]

A) The \textit{R} equation \textit{(pam)}:

a) \( E \) is negative banded state

b) plug \( \beta = e(e+1) \) from \( \Theta \)

c) change variables

d) Find asymptotic solution for large \( R = \text{asymptotic}(r) \)

e) guess \( R \) as product \( \text{asymptotic}(r) \times \text{unknown}(r) \)

express \( R \) equation in the unknown solution and get power series of unknown \( (r) \)

f) get recursive solution of coefficients of unknown \( (r) \)

\[ \int R^2\, dx = 1 \Rightarrow \text{convergence} \Rightarrow \text{series must be truncated at } m \text{ step} \quad \text{(with } m > e) \]

g) series becomes Laguerre polynomials

\[ R_{me}(x) = -\left[ \frac{(2\pi)^3}{(m-1)!} \frac{(m-e-1)!}{2^m (m+2)!} \right]^{1/2} \exp\left(-\frac{r^2}{2}\right) \quad \text{for } L_{m+e}(\beta) \]

\[ \beta = \frac{2z}{ma_0} \quad a_0 = \frac{E_0h^2}{m^2e^2} \approx 0.5 \text{ Å} \quad \text{H Hund's} \]
\[ L_1'(\rho) = 1 \quad L_2'(\rho) = 2\rho - 4 \quad L_3'(\rho) = 3\rho^2 + 18\rho - 18 \]

\[ \text{Plot } / \text{get } \psi = R(\rho) \Theta(\theta) \Phi(\phi) \]

\[ E = -\frac{\mu Z e^2}{r} \quad \frac{1}{(4\pi\varepsilon_0)^2} \frac{2\hbar^2 n^2}{m^2} = -13.6 \quad \text{eV} \]

\[ m = \text{integer} = 0, 1, 2, \ldots \]
\[ l = \text{integer} \quad 0 < l \leq m \Rightarrow l = 0, 1, \ldots, m-1 \]
\[ m = \text{integer} \quad m = -\ell, 0, \ldots, \ell \quad (\ell = \frac{1}{2}) \]

**TABLE 7-2. Some Eigenfunctions for the One-Electron Atom**

<table>
<thead>
<tr>
<th>Quantum Numbers</th>
<th>Eigenfunctions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )</td>
<td>( l )</td>
</tr>
</tbody>
</table>

\[ \psi_{100} = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} \]

\[ \psi_{200} = \frac{1}{4\sqrt{2\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \left( 2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0} \]

\[ \psi_{210} = \frac{1}{4\sqrt{2\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos \theta \]

\[ \psi_{21\pm1} = \frac{1}{8\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin \theta e^{\pm i\varphi} \]

\[ \psi_{300} = \frac{1}{81\sqrt{3\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \left( 27 - 18 \frac{Zr}{a_0} + 2 \frac{Z^2 r^2}{a_0^2} \right) e^{-Zr/3a_0} \]

\[ \psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \left( 6 - \frac{Zr}{a_0} \right) \frac{Zr}{a_0} e^{-Zr/3a_0} \cos \theta \]

\[ \psi_{31\pm1} = \frac{1}{81\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \frac{Zr}{a_0} e^{-Zr/3a_0} \sin \theta e^{\pm i\varphi} \]

\[ \psi_{320} = \frac{1}{81\sqrt{6\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \left( \frac{Z^2 r^2}{a_0^2} \right) e^{-Zr/3a_0} (3 \cos^2 \theta - 1) \]

\[ \psi_{32\pm1} = \frac{1}{81\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \left( \frac{Z^2 r^2}{a_0^2} \right) e^{-Zr/3a_0} \sin \theta \cos \theta e^{\pm i\varphi} \]

\[ \psi_{32\pm2} = \frac{1}{162\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \left( \frac{Z^2 r^2}{a_0^2} \right) e^{-Zr/3a_0} \sin^2 \theta e^{\pm 2i\varphi} \]
s orbital  \( l=0 \)  \( m=0 \)  \( e(l+1) = 0 \)  spherical
p orbital  \( l=1 \)  \( m=\pm \frac{1}{2} \)  \( e(l+1) = 2 \)  6
d orbital  \( l=2 \)  \( m=\pm \frac{2}{2} \)  \( e(l+1) = 6 \)  10
f orbital  \( l=3 \)  \( m=\pm \frac{3}{2} \)  \( e(l+1) = 12 \)  14

\[ \Rightarrow L = 0, \sqrt{2} \hbar, \sqrt{6} \hbar, \sqrt{12} \hbar \]

draw rooting  \( L = \frac{\sqrt{2} \hbar}{2} \)

\[ \Rightarrow S_0 = \pm \frac{\sqrt{2}}{8} \hbar \]

\[ S_2 = 5(5+1) \hbar \]

\[ \frac{3 \hbar^2}{4} \]

\[ \text{System with } 2e... \]

\[ \text{and } \cdots \text{ on } \]
# Relationship between Quantum Numbers

**TABLE 7-1.** Possible Values of $l$ and $m_l$ for $n = 1, 2, 3$

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>$l$</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>$m_l$</td>
<td>0</td>
<td>0</td>
<td>$-1, 0, +1$</td>
</tr>
<tr>
<td>Number of degenerate eigenfunctions for each $l$</td>
<td>1</td>
<td>1</td>
<td>3</td>
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Origin of the periodic table
# Hydrogen Wavefunctions

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Physical Nature of Orbitals ($\Psi^2$)

$\psi^2 = \psi^* \psi = P(r, l, m_l)$ Probability density

Radial Probability Density = $R*R4\pi r^2 dr$

Look at only probability of finding electron in a shell of thickness $dr$ at $r$ from the nucleus

$\Psi$ can be negative; cross over is 0 in $\Psi^2$

Compare to Bohr

$\bar{r} = \int_0^\infty rP(r, l, m_l)dr = \int_0^\infty rR*R4\pi r^2 dr$

$\bar{r} = \frac{n^2a_o}{Z} \left[ 1 + \frac{1}{2} \left[ 1 - \frac{l(l+1)}{n^2} \right] \right]$

$r_{Bohr} = \frac{n^2a_o}{Z} ; a_o = \frac{\hbar^2}{\mu e^2} = 0.52 A$
Review of H atom

\[ \psi = R(r) \Theta(\theta) \Phi(\phi) \]

\[ H\psi = E\psi \]

Do separation of variables; each variable gives a separation constant

φ separation yields \( m_\ell \)
θ gives \( \ell \)
r gives \( n \)

After solving, the energy \( E \) is a function of \( n \)

\[ E = \frac{-\mu Z^2 e^4}{(4\pi \varepsilon_0)^2 2\hbar^2 n^2} = \frac{-13.6eV}{n^2} \]

\( m_\ell \) and \( \ell \) in \( \Phi \) and \( \Theta \) give \( \Psi \) the shape
(i.e. orbital shape)

The relationship between the separation constants (and therefore the quantum numbers are:)

\[ n=1,2,3,... \]
\[ \ell = 0,1,2,...,n-1 \]
\[ m_\ell = -\ell, -\ell+1,...,0,...,\ell-1, \]
\[ (m_s = + \text{ or } -1/2) \]
Neon Lights

The sum and difference of these two solutions can be formed if we wish them to represent \( p_x \) and \( p_y \) specifically (Fig. 9.4):

\[
\psi_{2p_x}(r) = A(r/a_0)e^{-r/2a_0} \sin \theta \cos \phi \\
\psi_{2p_y}(r) = A(r/a_0)e^{-r/2a_0} \sin \theta \sin \phi
\]

The angular dependence of \( d \) functions (Fig. 9.4) includes an additional node. The simplest to represent mathematically is the 3d wave function for \( m = 0 \):

\[
\psi_{3d_m=0}(r) = A(r/a_0)^2e^{-r/3a_0}(3 \cos^2 \theta - 1)
\]

The nodes for this function are two cones with \( \theta = \cos^{-1}(\pm 1/\sqrt{3}) \).

As with the box and the harmonic oscillator, confining a matter wave in the hydrogen atom leads to quantized energy levels and a series of corresponding wave functions that develop more nodes with increasing energy. The three-dimensionality of the problem leads to three quantum numbers (plus the spin quantum number). Although the \( s, p, d, \) and \( f \) functions all have very different shapes, the energy, as given in (9.10), depends only on the principal quantum number \( n \). Thus, in addition to the twofold spin degeneracy of each solution, there is additional degeneracy in the hydrogen atom: the 2s and 2p levels are degenerate, the 3s, 3p, and 3d levels are degenerate, and so on. This degeneracy is related to the spherical symmetry of the potential energy function (9.3). We shall see later that some of this degeneracy is removed in multielectron atoms and in molecules.

Although quantum mechanics and the solutions of Schrödinger’s equation tell us that Bohr’s model of particle-like electrons traveling in orbits around the nucleus was naïve, we retain the name orbital for electron wave functions like those in

\[
n=n, l=2, \; m=2, \; m_s=\pm \frac{1}{2}
\]

\[
n=3, \; l=3, \; m=3, \; m_s=\pm \frac{1}{2}
\]

\[
n=3, \; l = 2, \; m = 0, \; m_s = \pm \frac{1}{2}
\]

\[
n=3, \; l = 2, \; m = -2, \; m_s = \pm \frac{1}{2}
\]

\[
n=3, \; l = 2, \; m = -1, \; m_s = \pm \frac{1}{2}
\]

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\]

\[
n=3, \; l = 2, \; m = 2, \; m_s = \pm \frac{1}{2}
\]

Figure 9.4. Shapes of \( p \) and \( d \) wave functions.
COMMUTATIONS

We have seen \([\hat{H}, \hat{L}_z] = 0 \quad \text{and} \quad \hat{L}_z, \hat{L}_z = 0\)

and \(\hat{H}, \hat{L}_z, \hat{L}_z\) share a common

basis of eigenvectors:

\[ \psi(t) = \text{time evolution operator} \]

\[ U(t) = e^{\frac{iHt}{\hbar}} \]

\[ U(t) = U(t) \quad \text{and} \quad U^{-1}(t) = U(-t) \]

\[ U(ST) = 1 + \frac{HST}{\hbar} \Rightarrow \psi(t) = \psi(0) + \frac{ST}{\hbar} \hat{H} \psi(0) \]

\[ [H, f] = 0 \iff [e^{\frac{iHt}{\hbar}}, f] = 0 \quad \forall t = [U, f] = 0 \]

\[ f(t) = \int \psi^*(t) f \psi(t) \, dv = \int \psi^* U^* U \psi_0 \, dv = 0 = \int \psi^* U^* U \psi_0 \, dv \]

\[ \psi_0 \Rightarrow U \psi_0 = \psi(t) \]

\[ U(t) \psi(t) = U(t) \psi(t) \]

\[ U^*(t) \psi(t) = U(t) \psi(t) \]

\[ f(t) = f(0) \iff = \int \psi(0) \psi(0) \, dv = \psi(0) \]

**Conservation of motion** \( \implies [f, H] = 0 \)
MULTI-ELECTRONS

- Previous wavefunctions \( \psi \) make single electron

- 2 electrons? repulsion: \( \Rightarrow \) screening: how?

- \( E = -\frac{13.6Z^2}{m^2} \) does not work well \( \Rightarrow Z_{eff} \)

- Technique SCF (self-consistent field): starts from
  a guessed \( \psi(r_1, r_2) \Rightarrow \rho = \psi \psi^* \) and \( \psi \) modifies
  to minimize \( E \Rightarrow \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \Rightarrow \delta \psi \Rightarrow \min(E) \)