Hydrogen & Hydrogen-like atoms

We'll start simple: 
- non-relativistic
- ignore spin

\[ H = \frac{p^2}{2\mu} - \frac{Ze^2}{4\pi\varepsilon_0 r} \]

\( \mu = \frac{m_e m_N}{m_e + m_N} \approx m_e \) is the reduced mass
and \( r \) is the distance of the electron from the nucleus

Let's survey the problem and make some estimates

\[ V(r) \]

- Should have bound states for \( E < 0 \)
- Unbound, scattering states for \( E > 0 \)
- 3D problem, so we'll have 3 spatial quantum numbers

Let's estimate the minimum allowed energy, based on Heisenberg Uncertainty

\[ \Delta p \Delta r \approx \hbar \]
For our lowest energy bound state, having \( \langle \mathbf{p} \rangle = 0 \), we can say \( \Delta p^2 \approx \langle p^2 \rangle \) and recast our "ground state" energy as

\[
E = \langle \hat{H}_g \rangle = \frac{\hbar^2}{2\mu r_*^2} - \frac{Z e^2}{4\pi \varepsilon_0 r_*} \tag{1}
\]

tractive Coulomb potential

due to wave function confinement.

\[\begin{array}{c}
\text{let's minimize } E \text{ w.r.t. } r_* \text{ to find extremum}
\end{array}\]

\[
\frac{\partial E}{\partial r_*} = \frac{\hbar^2}{2\mu} (-2r_*^{-3}) - \frac{Ze^2}{4\pi \varepsilon_0 } (-r_*^{-2}) = 0
\]

\[
\Rightarrow r_{*,\text{min}} = \frac{\hbar^2}{\mu e^2} \left( \frac{4\pi \varepsilon_0}{Z} \right) = a_\mu \frac{m_e}{Z}
\]

where \( a_\mu = a_0 \frac{m_e}{\mu} \)

and \( a_0 = \frac{\hbar^2}{2\mu m_e c^2} = \frac{4\pi \varepsilon_0}{2} \)

\[\begin{array}{c}
\text{average distance } \langle r \rangle \sim \Delta r = r_*
\end{array}\]

should get smaller like \( \sqrt{Z} \)

for increasing atomic #.

Energy estimate, let's plug back into \( E(r_*) \)

\[
E(r_*) = \frac{\hbar^2}{2\mu r_*^2} - \frac{Ze^2}{4\pi \varepsilon_0 r_*} = -\frac{i Z e^2}{8\pi \varepsilon_0 \, r_*} = -\frac{Z^2 m_e}{2(4\pi \varepsilon_0)^2 \hbar^2} = -\frac{Z^2 \hbar c}{R_\infty}
\]

the Rydberg unit of energy \( = -13.6 \text{ eV} \)

\[\begin{array}{c}
\text{these "estimates" are spot on, but let's do things more formally}
\end{array}\]
3. With a bit more rigor

\[ H = \frac{p^2}{2\mu} - \frac{Ze^2}{4\pi\varepsilon_0 r} \]

\[ \Psi_{n\ell m} = R_{n\ell}(r) Y_{\ell m}(\theta, \phi) \]

plug into Schrödinger Eqn.
expressed in spherical coordinates

and find it to be separable with separate expressions for radial and angular parts.

from Foot 2.1.2

Let \( P(r) = r R(r) \)

and let \( b = \ell (\ell + 1) \) be an integer \( \ell \) satisfying the eigenvalue problem.

Radial part of Schrödinger

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

\[ E = V_{\text{eff}}(r) \]

the two \( r \)-dependent terms can be incorporated into the effective radial potential

\[ V_{\text{eff}}(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{\ell (\ell + 1) \hbar^2}{2\mu r^2} \]

centrifugal term
minimum or $V_{eff}$ moves to larger $r$ values as $l$ increases, i.e., for larger centrifugal barrier term

What are the solutions that satisfy the radial Schrödinger equation for integer $l$?

$W/P = \frac{Z}{n} \frac{r}{a_n}$, in terms of $R_{nl}$ (i.e., $n^l P_l(r) = r R_{nl}$)

$$R_{nl} = \sqrt{\frac{(2Z)^3}{n a_n}} \frac{(n-l-1)!}{2n [(n+l)]^3} e^{-\frac{\rho}{2}} (\frac{2l+1}{n-l-1})^{L_{2l+1}}$$

a few things:
- no radial solutions for $l \geq n$
- associated (generalized) Laguerre polynomials

For $n = 1$, only $l = 0 \Rightarrow R_{1,0} \propto e^{-\rho}$

For $n = 2$, $l = 0$ solution $\Rightarrow R_{2,0}(r) \propto (1-\rho)e^{-\rho}$
  $l = 1$ solution $\Rightarrow R_{2,1}(r) \propto pe^{-\rho}$

see table ii Foot (Table 2.2) for more
Some key properties

At small $r$ (small $p$)

$R_{nl} \propto p^l$ vanishes unless $l = 0$

At very large $r$ (large $p$)

$R_{nl} \propto r^{n-1} e^{-r}$

Normalization

\[
\int_0^{2\pi} \int_0^\pi |Y_{lm}|^2 \sin \theta \, d\theta \, d\phi = \frac{4\pi}{2l+1}
\]

\[
\int_0^\infty R_{nl}^2 r^2 \, dr = 1
\]

Other key quantities related to radial wave functions

Radial probability density

\[
\frac{\int |R_{nl}(r)|^2 |Y_{lm}(\theta, \phi)|^2 \, r^2 \sin \theta \, d\theta \, d\phi}{\int |Y_{lm}|^2 \, d\theta \, d\phi}
\]

Some helpful expectation values

\[
\langle r \rangle = \frac{\langle n, l | \hat{r} | n, l \rangle}{Z} = a_\mu \frac{n^2}{Z} \left[ 1 + \frac{1}{2} \left( 1 - \frac{l(l+1)}{n^2} \right) \right]
\]

\[
\langle r^2 \rangle = a_\mu^2 \frac{n^4}{Z^2} \left[ 1 + \frac{3}{2} \left( 1 - \frac{l(l+1)-\frac{1}{3}}{n^2} \right) \right]
\]

\[
\langle r^3 \rangle = a_\mu^3 \frac{n^6}{Z^3} \left[ 1 + \frac{27}{8} \left( 1 - \frac{(35/27 + 10 (2l+1)(l-1)/2)}{n^2} \right) + \frac{(l+2)(l+1)l(l-1)}{9n^4} \right]
\]

\[
\langle \frac{1}{r} \rangle = \frac{Z}{a_\mu n^2}
\]

\[
\langle \frac{1}{r^2} \rangle = \frac{Z^2}{a_\mu^2 n^3 (l+\frac{1}{2})}
\]

\[
\langle \frac{1}{r^3} \rangle = \frac{Z^3}{a_\mu^3 n^4 l(l+\frac{1}{2})(l+1)}
\]
Energy \[ E_n \rightarrow \text{ind. of } l, m \] due to non-radiation result for \( \frac{1}{r} \) potential

\[ E_n = -\frac{1}{2n^2} \left( \frac{Z e^2}{4\pi \varepsilon_0} \right)^2 \frac{\mu}{k^2} = -\frac{Z^2}{n^2} hc R_0 x \left( \frac{\mu}{m_e} \right) \]

can also be expressed as

\[ E_n = -\frac{1}{2} \mu c^2 \left( \frac{Z \alpha}{n} \right)^2 \]

where \( \alpha = \frac{e^2}{4\pi \varepsilon_0 hc} = \frac{1}{137} \)

is the fine structure constant

\[ \alpha = \left( \frac{\frac{e^2}{4\pi \varepsilon_0 d}}{hc} \right) \text{ for } \lambda = 2\pi d \]

also, compare energy of elementary dipoles (magnetic + electric) at equivalent distance

\[ \alpha^2 = \left( \frac{M_0 M_0}{4\pi} \right)^2 \left( \frac{\alpha_0^2}{\varepsilon_0^2} \right) \text{ with } \mu_0 = \frac{e^2}{2m_e} \]
Angular wfs

\[ Y_{lm}(\theta, \phi) = P^m_l(\cos \theta) e^{im\phi} \]

for some explicit \( Y_{lm} \) wfs

\[ \text{eigenstate of } \hat{L}^2, \hat{L}_z \]

associated Legendre polynomial of degree \( l \) and order \( m \) (generalized)

parity transformation

\[ \hat{r} \rightarrow -\hat{r}, \text{ such that } \theta \rightarrow \pi - \theta \text{ and } \phi \rightarrow \phi + \pi \]

under parity transformation

\[ Y_{lm}(\pi - \theta, \phi + \pi) = (-1)^l Y_{lm}(\theta, \phi) \]

parity of the states \( Y_{nle} \) is given by \((-1)^l\)

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A note on notation

principal quantum number \( n = 1, 2, 3, \ldots \)

orbital quantum number \( l = 0, \ldots, n-1 \)

\( \text{w/ } l = 0 \Rightarrow \text{"s" orbital} \)

\( l = 1 \Rightarrow \text{"p" orbital} \)

\( l = 2 \Rightarrow \text{"d" orbital} \)

\( l = 3 \Rightarrow \text{"f" orbital} \)

\( l = 4 \Rightarrow \text{"g" orbital} \)

Taking into account the spin of the electron \( (S=\frac{1}{2}) \)

\[ 2S+1 \]

\( L^J \)

is the common atomic orbital notation, where we typically use \( L \) in place of \( l \), where possible angular momentum values run from \( J = L + S \) to \( J = L - S \), and the "2S+1" term is often dropped.

\[ \text{principal quantum number} \quad n = 1, 2, 3, \ldots \]

\[ \text{orbital quantum number} \quad l = 0, \ldots, n-1 \]
A note on units

I'll try to use SI units throughout the course, but you may find that some of the course reference materials use alternate unit systems, such as Gaussian Cgs or atomic units.

Atomic units, in particular, show up in many atomic physics references:

- Unit of length = the Bohr radius, \( a_0 \approx 0.5 \, \text{\AA} \)
- Unit of energy = the Hartree energy, \( E_h = 2 \, \text{Ry} = 2 \, h \, c \, \alpha_0 \)

easy: \( m_e = 1, e = 1, k = 1, \alpha = 1, \, c = \frac{1}{\alpha} \approx 137 \)

at times, may use technical units (mostly w/ energy + frequencies)

e.g. \( \mu_B = \frac{e^2}{2m_e} = 9.27 \times 10^{-24} \, \text{J/T} \)

but \( \frac{\mu_B}{h} = \frac{2\pi \times 1.46 \, \text{MHz}}{6} \)

is more convenient for determining how a transition frequency will change with an applied magnetic field.

Note: Also, spectroscopy folks love wave numbers (cm\(^{-1}\))

\( \tilde{v} = \frac{\omega}{2\pi c} \), expressed in inverse centimeters.
To solve this problem, we must specify the potential energy of the electron. In an atom, the Coulomb force binds the electron to the nucleus.

This problem does not separate in Cartesian coordinates, because we cannot write \( U(x,y,z) = U_x(x)+U_y(y)+U_z(z) \). However, we can separate the potential in spherical coordinates \((r,\theta,\phi)\), because:

\[
U(r,\theta,\phi) = U_r(r) + U_\theta(\theta) + U_\phi(\phi)
\]

\[
= -\frac{\kappa e^2}{r} + 0 + 0
\]

Therefore, we will be able to write:

\[
\psi(r,\theta,\phi) = R(r) \Theta(\theta) \Phi(\phi)
\]
Supplement: Potential Energy in the Hydrogen Atom

Time Independent Schrodinger’s Equation

\[
\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{\kappa e^2}{r}\right] \psi(\vec{r}) = E\psi(\vec{r})
\]

In Cartesian Coordinates:

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

In Spherical Coordinates:

\[
\left[-\frac{\hbar^2}{2m} \frac{1}{r^2}\left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2}\right) - \frac{\kappa e^2}{r}\right] \psi(\vec{r}) = E\psi(\vec{r})
\]

This is SEPARABLE! (thankfully!!)
Supplement: Potential Energy in the Hydrogen Atom

In Spherical Coordinates:

\[
-\frac{\hbar^2}{2mr^2} \left( \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) - \frac{\kappa e^2}{r} \right] \psi(\vec{r}) = E\psi(\vec{r})
\]

Let's separate the \( r \) dependence from the \( \theta \) and \( \phi \) dependences. Write

\[
\psi(\vec{r}) = R(r) Y(\theta, \phi)
\]

Plug this into TI-SEQ. Divide by \( RY \). Multiply by \(-\frac{2mr^2}{\hbar^2}\)

\[
\left[ \frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2m^2}{\hbar^2} \left( \frac{\kappa e^2}{r} + E \right) \right] = -\frac{1}{Y} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial Y}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right]
\]

Only depends on \( r \)  

Only depends on \( \theta \) and \( \phi \)

Therefore each side equals a constant, \( l(l+1) \), \( l \) must be 0, 1, 2, ...

This comes from solving diff eq for \( Y \).
Supplement: Potential Energy in the Hydrogen Atom

\[
\left[ \frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} \left( \frac{\kappa e^2}{r} + E \right) \right] = -\frac{1}{Y} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial Y}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right]
\]

Only depends on \( r \)

Only depends on \( \theta \) and \( \phi \)

Therefore each side equals a constant, \( l(l + 1) \), \( l \) must be 0, 1, 2, ...

This comes from solving diff eq for \( Y \).
Effective radial potential

\[ V_{\text{eff}}(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2} \]
Radial wave functions $R_{nl}$

Radial wave function

$$
R_{nl}(\rho) \propto \left(\frac{\rho}{r}\right)^{3/2} e^{-\rho} \rho^l L_{n-l-1}^{2l+1}(2\rho)
$$

Radial probability density

$$\rho \equiv Zr / na_{\mu}
$$

$$\int_0^\infty |R_{nl}|^2 r^2 dr = 1$$
Radial wave functions $R_{nl}$

Radial wave function

$\propto e^{-\rho}$

Radial probability density

$n = 1$
$l = 0$

$n = 1$
$l = 0$

$n = 2$
$l = 0$

$n = 2$
$l = 0$

$n - l$ nodes
(wf zero crossings)

$\propto (1 - \rho)e^{-\rho}$
Radial wave functions $R_{nl}$

Radial wave function

Radial probability density

$n = 3$
$l = 0$

$n = 4$
$l = 0$
Radial wave functions $R_{nl}$

Radial wave function

Radial probability density

$n = 4$, $l = 0$

$n = 4$, $l = 1$
Radial wave functions $R_{nl}$

For increasing $l$:

1. $n = 4$, $l = 2$
2. $n = 4$, $l = 3$

Radial wave function

Radial probability density
Angular wave function - $Y_{lm}$

http://mathworld.wolfram.com/SphericalHarmonic.html
The Angular Wave Function, $Y_{lm}(\theta, \varphi)$

$l = 0$

$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$

$l = 1$

$|Y_{1,0}| \propto |\cos \theta|$

$|Y_{1,\pm 1}| \propto |\sin \theta|$

Length of the dashed arrow is the magnitude of $Y_{lm}$ as a function of $\theta$.

$\Psi_{1,+1} \propto e^{i(\varphi - \omega t)}$

$\Psi_{1,-1} \propto e^{i(-\varphi - \omega t)}$

Positive $L_z$
The Angular Wave Function, $Y_{lm}(\theta, \phi)$

$l = 2$

$|Y_{2,0}| \propto |(3\cos^2 \theta - 1)|$

$Y_{2,\pm 1} \propto \sin \theta \cos \theta$

$\propto e^{\pm i\phi}$

$|Y_{2,\pm 2}| \propto |\sin^2 \theta|$

$\propto e^{\pm 2 i\phi}$
$n$ = “principal quantum number”

$l$ = “total orbital angular momentum”  \( L = \mathbf{r} \times \mathbf{p} \)

\( m \) = projection of the angular momentum along z-axis

“magnetic quantum number”