Hydrogen: The simplest atom, binding an electron to a proton (the nucleus). In the last lecture we saw that $m_p \approx 2000 \, m_e$, so the center-of-mass is essentially at the proton. The relative coordinate is then essentially the electron coordinate, with the proton at rest
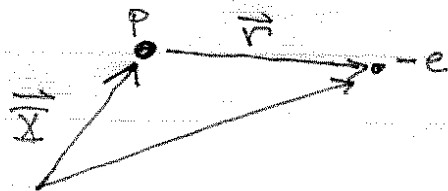
reduced mass
$$\mu = \frac{m_e m_p}{m_e + m_p} \approx m_e$$

Atomic units: The first step in any physics problem is to identify the characteristic units (scales). For our problem we have three fundamental constants, $\hbar$, m_e, e. Putting these together yields the so called "atomic units".

We seek a characteristic length a_0, and Energy E_0

We know $\frac{\hbar}{a_0}$ is a momentum

$$\Rightarrow \frac{(\hbar/a_0)^2}{m} = \frac{\hbar^2}{m a_0^2} = E_0 \quad \left(\begin{array}{c}\text{characteristic}\\\text{energy}\end{array}\right)$$

We also know $\frac{e^2}{a_0} = E_0$

$$\Rightarrow \frac{e^2}{a_0} = \frac{\hbar^2}{m a_0^2} \Rightarrow \boxed{a_0 = \frac{\hbar^2}{m e^2} = 0.5 \, \text{Å}}$$
Bohr Radius

$$\Rightarrow \boxed{\frac{e^2}{a_0} = \frac{m e^4}{\hbar^2} = 27.2 \, eV}$$
Hartree

Historic reasons
$$R = \frac{e^2}{2 a_0} = 13.6 \, eV$$

Schrödinger Equation (for electron, with proton at origin)

$$\hat{H} = \frac{\hat{P}^2}{2m} + V(r) = \frac{\hat{P_r}^2}{2m} + \left(\frac{\hat{L}^2}{2mr^2} - \frac{e^2}{r}\right)$$
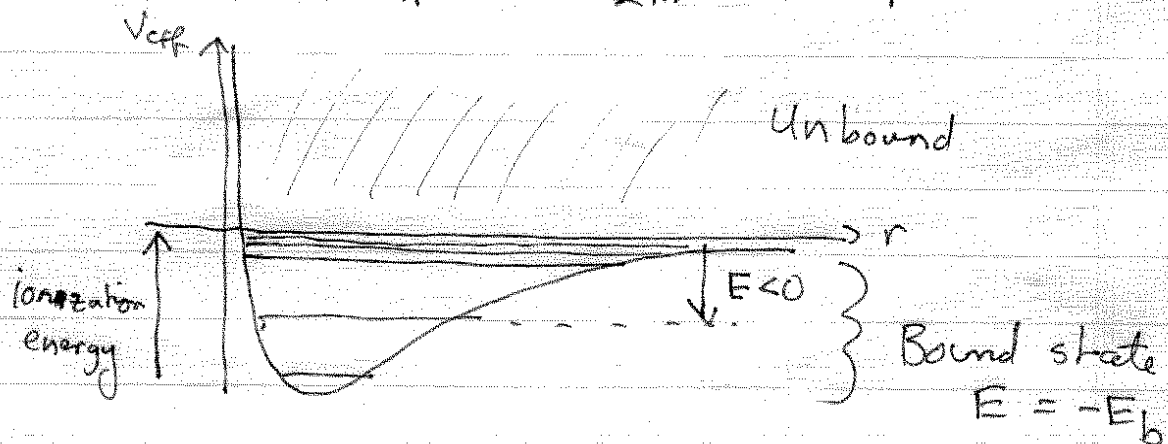
(central potential)

$$\hat{H}\psi = E\psi \qquad \text{T.I.S.E.}$$

$$\psi(r,\theta,\phi) = \frac{u_\ell(r)}{r} Y_\ell^m(\theta,\phi)$$

$\Rightarrow$ Radial equation

$$-\frac{\hbar^2}{2m}\frac{d^2 u_\ell}{dr^2} + V_{eff}^{(\ell)}(r)\, u_\ell(r) = E\, u_\ell(r)$$

$$V_{eff}^{(\ell)}(r) = \frac{\hbar^2 \ell(\ell+1)}{2mr^2} - \frac{e^2}{r}$$

Now remove the characteristic units

Let $\quad r = a_0 \bar{r}, \qquad E_b = E_0 \bar{E}_b$

dimensionless

$$\Rightarrow \frac{\hbar^2}{2ma_0^2}\left(-\frac{1}{2}\frac{d^2 u_\ell}{d\bar{r}^2} + \frac{\ell(\ell+1)}{2\bar{r}^2}u\right) - \frac{e^2}{a_0}\frac{u_\ell}{\bar{r}} = E_0 \bar{E}_b u_\ell$$

Remembering $E_0 = \dfrac{\hbar^2}{m_e a_0^2} = \dfrac{e^2}{a_0}$

$$\Rightarrow \left[-\frac{1}{2} \frac{d^2}{d\bar{r}^2} + \frac{\ell(\ell+1)}{2\bar{r}^2} - \frac{1}{\bar{r}} \right] \mathcal{U}_\ell(\bar{r}) = -\bar{E}_b \, \mathcal{U}_\ell(\bar{r})$$

Nature of solutions (asymptotic properties)

- Near origin

How fast does $\mathcal{U}_\ell(r) \to 0$ near $r=0$?

$\dfrac{1}{\bar{r}^2} \gg \dfrac{1}{\bar{r}}$ for $\bar{r} \ll 1$ $\Rightarrow \left[-\dfrac{1}{2}\dfrac{d^2}{d\bar{r}^2} + \dfrac{\ell(\ell+1)}{2\bar{r}^2} \right] \mathcal{U}_\ell \approx 0$

$\Rightarrow$ Near origin $\mathcal{U}_\ell(\bar{r}) \sim C r^{\ell+1}$

$$\left(\text{Note } R_\ell = \frac{\mathcal{U}_\ell}{r} \sim C r^\ell \right)$$

- Boundary condition as $r \to \infty$ $\quad \mathcal{U}_\ell \to 0$

Larger r, $V_{eff} \to 0 \Rightarrow -\dfrac{1}{2}\dfrac{d^2 \mathcal{U}_\ell}{d\bar{r}^2} \approx -\bar{E}_b \, \mathcal{U}_\ell$

$\Rightarrow$ As $\bar{r} \to \infty$, $\mathcal{U}_\ell \to C e^{-\sqrt{2\bar{E}_b}\, r} + D e^{+\sqrt{2\bar{E}_b}\, r}$

reject

$\Rightarrow \bar{r} \to \infty$, $\mathcal{U}_\ell \to C e^{-\kappa r}$ $\quad \kappa = \sqrt{2\bar{E}_b}$

$\Rightarrow$ Thus we can take into account these asymptotic properties in an ansatz

(Next Page)

<u>Ansatz</u>: $u_{E,\ell}(\bar{r}) = \bar{r}^{\ell+1} e^{-K\bar{r}} F_{E,\ell}(\bar{r})$

where $K \equiv \sqrt{2E_b}$, $F_{E,\ell}(\bar{r})$ is constant as $r\to 0$ and $r \to \infty$

Plug into the radial equation

$\Rightarrow \bar{r}\dfrac{d^2 F}{d\bar{r}^2} + (2\ell+2 - 2K\bar{r})\dfrac{dF}{d\bar{r}} + 2(1 - K(\ell+1))F = 0$

The boundary conditions of F as $r\to 0$ & $r\to \infty$ restrict the possible values of K, and thus the binding energy. One can use the method of power series to solve this. Please refer to a standard text, like Griffiths. Here we will massage the equation into a standard form to find the energy eigenvalues.

Let $x = 2K\bar{r} \quad \Rightarrow \quad \dfrac{d}{d\bar{r}} = 2K\dfrac{d}{dx}$

$\Rightarrow (2K)x\dfrac{d^2 F}{dx^2} + (2\ell+2 - x)(2K)\dfrac{dF}{dx} + 2K\left(\dfrac{1}{K} - (\ell+1)\right)F = 0$

$\Rightarrow \dfrac{d^2 F}{dx^2} + (2\ell+2 - x)\dfrac{dF}{dx} + \left(\dfrac{1}{K} - (\ell+1)\right)F = 0$

This has the form of the Generalized Laguerre equation

$x\dfrac{d^2\mathcal{L}_p^q(x)}{dx^2} + (q+1 - x)\dfrac{d\mathcal{L}_p^q}{dx} + p\mathcal{L}_p^q(x) = 0$

where p and q must be integer is $\mathcal{L}_p^q(x)$ does not blow up

$\mathcal{L}_p(x) = e^x \dfrac{d^p}{dx^p}(x^p e^{-x})$, $\mathcal{L}_p^q(x) = (-1)^q \dfrac{d^q}{dx^q}\mathcal{L}_{p+q}(x)$

↑   ↑
Laguere polynomial   Associate Laguerre polynomial:
     Both are polynomials of order p.

$\Rightarrow$ Radial equation for F has the form of the Generalized Laguerre equation with $q = 2\ell+1$, $p = \dfrac{1}{K} - (\ell+1) \equiv n_r$ (radial quantum)
                                                          ≠
                                 $n_r = 0, 1, 2, \cdots$

$\Rightarrow$ Energy eigenvalue $\overline{E}_{n_r, \ell} = -\overline{E}_b = -\frac{1}{2\kappa^2}$

$n_r = \frac{1}{\kappa} - \ell + 1 \quad \Rightarrow \quad \kappa = \frac{1}{n_r + \ell + 1}$

$\not\Rightarrow$ Bound states of hydrogen.

$$E_{n_r, \ell} = -\frac{\overset{\text{Hartree}}{E_0}}{2(n_r + \ell + 1)^2} = -\frac{\overset{\text{Rydberg}}{R}}{(n_r + \ell + 1)} = -\frac{13.6 \text{ eV}}{(n_r + \ell + 1)^2}$$

Note: The energy does <u>not</u> depend independently on radial and angular momentum quantum numbers. It depends only on the <u>sum</u>

Define "principle quantum number" $\boxed{n \equiv n_r + \ell + 1 \quad = 0, 1, 2, \ldots}$

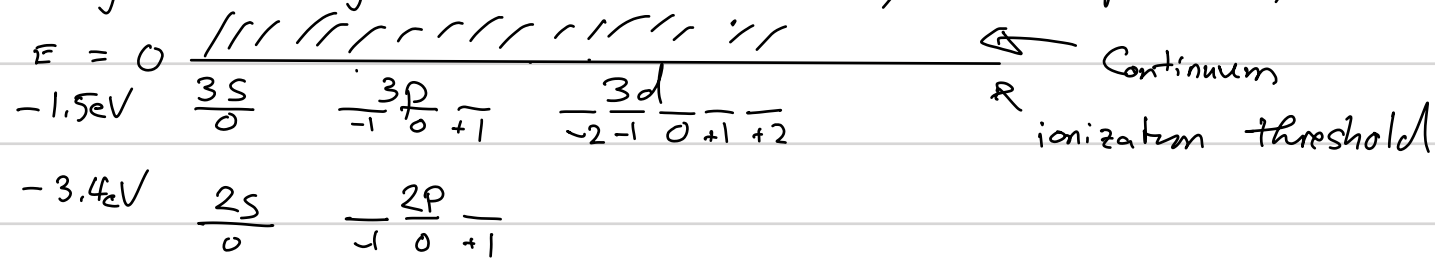$$\boxed{E_n = \frac{-13.6 \text{ eV}}{n^2}} \quad , \qquad n = 0, 1, 2, \ldots \quad \text{Binding energies of hydrogen}$$

Degeneracy: For a given principle quantum number, n, the value of ℓ can range from $\ell = 0$, in which case $n_r = n-1$, to $\ell = n-1$ if which case $n_r = 0$ (no radial energy). This degeneracy may seem like an "accident" but in fact it is a manefestation of a "hidden" symmetry, that is special for a $\frac{1}{r}$ podential. In multielectron atoms, the potential seen by the valence electrons is no longer $\frac{1}{r}$. The different ℓ's have vastly different energy due to the difference in the angular momentum barrier.

For hydrogen with $V(r) = -\frac{e^2}{r}$
- There are $n-1$ different ℓ values that are degenerate, for given n
- As is always, for spherical symmetry, for each level there are $2\ell + 1$ different m-states that have the same energy

$\Rightarrow$ Total degeneracy: $g_n = \sum_{\ell = 0}^{n-1} (2\ell+1) = n^2$

(ignoring spin)

Energy level diagram: ($\ell = 0$ "s-state", $\ell = 1$ "p-state", $\ell = 2$ "d-state"

$E = 0$ ━━━━━━━━━━━━━━━━━━━━━━━━━━━━━━━━━   ← Continuum

$-1.5eV$ $\underline{3S}$ $\underline{3p}$ $\overline{}$ $\underline{3d}$ $\overline{}\,\overline{}$ R ionization threshold
          0 $-1\ \ 0\ +1$ $-2\ -1\ \ 0\ +1\ +2$

$-3.4eV$ $\underline{2s}$ $\underline{2p}$ $\overline{}$
          0 $-1\ \ 0\ +1$

$-13.6\ eV$ $\underline{1S}$
            $m=0$

Note: There are an _infinite_ number of bound states, but they bunch up very close near the ionization threshold.

Eigen functions: $|n, m, \ell\rangle \doteq R_{n,\ell}(r)\, Y_{\ell,m}(\theta, \phi)$

$$R_{n,\ell}(r) = \frac{u_{n,\ell}(r)}{r}, \qquad u_{n,\ell}(r) = \bar{r}^{\ell+1}\, e^{-\kappa\bar{r}}\, \mathcal{L}_{n_r}^{2\ell+1}(2\kappa\bar{r}), \qquad \begin{array}{l} \bar{r} = \dfrac{r}{a_0} \\[6pt] \kappa = \dfrac{1}{n} \\[6pt] n_r = n-1-\ell \end{array}$$

$$\Rightarrow |n,m,\ell\rangle \doteq A_{n,\ell}\left(\frac{r}{a_0}\right)^{\ell} e^{-\frac{r}{na_0}}\, \mathcal{L}_{n-\ell-1}^{2\ell+1}\left(2\frac{r}{na_0}\right)$$