Week 8

The Hydrogen Atom

8.1 Hydrogen Atom II

2/19: - Review of the hydrogen atom.
  - The potential is given by
$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$
    - This is an important case of motion in a central potential in quantum mechanics.
  - We go to polar coordinates because they are most convenient for motion in a central potential.
  - We achieve separation of variables via
$$\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)Y_{\ell m}(\theta,\phi)$$
  - This leads into the spherical harmonics
$$\begin{aligned}\hat{\vec{L}}^2 Y_{\ell m}(\theta,\phi) &= \hbar^2\ell(\ell+1)Y_{\ell m}(\theta,\phi)\\ \hat{L}_z Y_{\ell m}(\theta,\phi) &= \hbar m Y_{\ell m}(\theta,\phi)\end{aligned}$$
    - Additionally, the quantum number m satisfies $-\ell \leq m \leq \ell$, giving us $2\ell+1$ solutions for each ℓ.
  - With the spherical harmonics, the main question becomes how to find $R_{n\ell}$.
    - We do this via the change of variables
$$U_{n\ell}(r) = rR_{n\ell}(r)$$
yielding a function that satisfies the analogous one-dimensional effective system
$$-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2}{\mathrm{d}r^2}[U_{n\ell}(r)] + \underbrace{\left[V(r) + \frac{\hbar^2\ell(\ell+1)}{2Mr^2}\right]}_{V_{\text{eff}}(r)} U_{n\ell}(r) = E_{n\ell}U_{n\ell}(r)$$
  - We analyze such systems using their asymptotic behavior as $r \to 0$ and $r \to \infty$.
    - See Figure 7.2. We are looking for bound states $E_{n\ell}$.
    - When the energy is positive, we have continuous solutions; it's only when the energy is negative that we have quantized bound states.
  - Performing such analyses, we propose an ansatz
$$U_{n\ell}(r) = f_{n\ell}(r)r^{\ell+1}\mathrm{e}^{-k_{n\ell}r}$$
where
$$E_{n\ell} = -\frac{\hbar^2k_{n\ell}^2}{2M}$$

- We suppose that f is a polynomial function

$$f_{n\ell}(r) = \sum_j a_j r^j$$

  and solve for it using the differential equation

$$f''_{n\ell}(r) + f'_{n\ell}(r)\left[\frac{2(\ell+1)}{r} - 2k_{n\ell}\right] + f_{n\ell}(r)\left[-\frac{2k_{n\ell}(\ell+1)}{r} + \frac{2}{a_{\text{B}}r}\right] = 0$$

- This analysis leads us to the recursion relation

$$a_{j+1} = \frac{2k_{n\ell}(j+\ell+1) - \frac{2}{a_{\text{B}}}}{(j+1)(j+2\ell+2)}a_j$$

- We then choose $j_{\max} = N$, yielding

$$k_{n\ell} = \frac{1}{a_{\text{B}}\underbrace{(N+\ell+1)}_{n}}$$

  where we canonically call n the **principal quantum number**.
  - This is a divergence from last time's notation, but one made for good reason, as we will see shortly.
  - Note that we did not introduce this notation last time because we didn't want to have to discuss its subtleties then, as we will today.
- Thus, the energy depends only on this value n via

$$E_{n\ell} = -\frac{\hbar^2}{2m_e a_{\text{B}}^2(N+\ell+1)^2} = -\frac{\text{Ry}}{n^2}$$

  where Ry is the Rydberg constant defined last time.
  - Essentially, the energy depends on this value n which in turn has a hidden dependence on ℓ.

- We now begin on new content, continuing from above however.
- The energy spacing versus n.

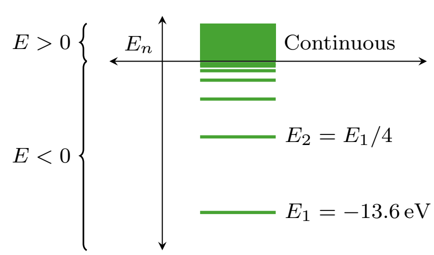

Figure 8.1: ^{1}H energy spacing vs. n.

- The energies get closer and closer together as n increases until they become continuous for positive values of energy.
- The equations and figure imply that $-E_1 = \text{Ry}$ is the minimum energy necessary to remove the electron from the hydrogen atom.
- If we don't have this much energy, a lesser amount will still affect the electron, just moving it to an **excited state**.

        - In particular, $E_m - E_1$ is the amount of energy necessary to move the electron to an excited state E_m of higher energy than E_1.
    - What is also interesting is that if the electron is in an excited state of energy E_m, then it will *not* stay there forever.
        - Experimentally, even in this time independent potential, the electron can jump back down to a lower state by emitting electromagnetic radiation of energy $E_\gamma = E_m - E_1$.
        - This is evidence that the vacuum in which we assume the hydrogen atom lies is not really *vacuum*! Rather, the vacuum contains something called the EM field, and there are fluctuations in this EM field that can push the electron down energy states.
        - This is discussed more in Quantum Mechanics II, but is ignored in our present formalism of the hydrogen atom.
- Now for every fixed n, the equation $n = N + \ell + 1$ implies that $\ell = 0, 1, \dots, n-1$.
    - But for every ℓ, there are $2\ell + 1$ solutions with the same energy.
    - Thus, for every n, there are

$$\sum_{\ell=0}^{n-1}(2\ell+1) = 2\sum_{\ell=0}^{n-1}\ell + \sum_{\ell=0}^{n-1}1 = 2\cdot\frac{n(n-1)}{2} + n = n^2$$

    different states with the same energy.
- Aside: A fun application of this stuff to cosmology.
    - The universe started as a hot plasma that cooled down as the universe expanded.
    - The early universe contained a lot of crap, including photons.
    - When early protons and electrons tried to combine at hot temperatures, the huge amount of EM radiation would kick the electrons out.
    - Thus, stable atoms could not form.
    - The specific temperatures at which this would occur were

$$k_\text{B}T > 13.6\,\text{eV}$$

    - At temperatures $k_\text{B}T < 13.6\,\text{eV}$, protons and electrons bind together, and the universe becomes transparent to radiation.
    - Evidence that this happened: Cosmic microwave background.
        - When the universe became transparent, it was at microwave temperatures.
        - This was when the universe was about 13 000 years old.
- Now back to math.
- Since we now have an explicit definition for $k_{n\ell}$, we may rewrite the solutions as

$$U_{n\ell}(r) = f_{n\ell}(r)r^{\ell+1}\mathrm{e}^{-r/a_\text{B}n}$$

    - Notationally, do remember that n gives energy, ℓ gives angular momentum, and $N = n - \ell - 1$ gives the polynomial degree of $f_{n\ell}(r)$.
- Thus, if $N = 0$, then $n = \ell + 1$ and the radial probability density of finding the particle at a given r is

$$r^2|R_{n\ell}(r)|^2 = |U_{n\ell}(r)|^2 = r^{2n}\mathrm{e}^{-2r/a_\text{B}n}$$

- What is the maximum, i.e., the most probable distance from the nucleus?

  - Differentiate the probability density with respect to r and determine where it equals zero.

$$\begin{aligned}
0 &= 2nr^{2n-1}\mathrm{e}^{-2r/a_{\mathrm{B}}n} - \frac{2r^{2n}}{a_{\mathrm{B}}n}\mathrm{e}^{-2r/a_{\mathrm{B}}n} \\
\frac{2r^{2n}}{a_{\mathrm{B}}n} &= 2nr^{2n-1} \\
r_{\mathrm{max}} &= a_{\mathrm{B}}n^2
\end{aligned}$$

- What happens if you have an ion of charge Ze?
  - Then

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

  - Thus,

$$E_n = -\frac{\mathrm{Ry}\,Z^2}{n^2}$$

    and the Bohr radius halves.