Hydrogen Atom / Coulomb Potential

— Basics:

- The potential is $V(r) = \frac{-e^2}{4\pi\epsilon_0}\frac{1}{r}$ and is central

  Therefore we know angular wave function is spherical harmonic $Y_l^m(\theta,\phi)$

- Radial equation is (recall $u = rR(r)$)

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[\frac{-e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu$$

(As argued on HW, m = electron mass) should be replaced by μ = reduced mass)

- The energy eigenvalues will be (bound states)

$$E_n = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{1}{n^2}$$

radial scale set by Bohr radius $a = \frac{4\pi\epsilon_0\hbar^2}{me^2}$

+ States are therefore

$$|n, l, m; s=1/2, m_s\rangle$$ counting electron spin (add $|s=1/2, m_s\rangle_p$ for proton in nucleus)

or $|n, \underbrace{j, m}, l, s=1/2\rangle$ → total angular momentum

+ Energy is independent of m, m_s due to invariance under rotations
  But it is also independent of l (or j). Special to Coulomb potential

— Radial Equation (bound states only $E<0$)

- Dimensionless form

  + Define $\kappa = \sqrt{-2mE}/\hbar$, as before. Then $\rho = \kappa r$ is dimensionless
  + Radial equation is

$$\frac{d^2u}{d\rho^2} = \left[1 - \left(\frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}\right)\frac{1}{\rho} + \frac{l(l+1)}{\rho^2}\right]u$$

You can simplify a bit by calling $\rho_0 \equiv me^2/2\pi\epsilon_0\hbar^2\kappa \equiv 2/\kappa a$

- Asymptotics

  + As $\rho \to 0$, we recall $u \propto \rho^{l+1}$ for normalizability (centrifugal term dominates at $l \geq 1$).

+ As $\rho \to \infty$, $d^2u/d\rho^2 = u \Rightarrow u \sim e^{-\rho}$ for normalizable behavior
up to polynomial corrections

- Series solution for $v(\rho)$
  + Guess at form $u(\rho) = \rho^{l+1} e^{-\rho} v(\rho)$ (even for $l=0$)
  + Radial equation becomes
$$\rho \frac{d^2v}{d\rho^2} + 2(l+1-\rho)\frac{dv}{d\rho} + (\rho_0 - 2(l+1))v = 0$$
(Please check the book for yourself)
  + Set $v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$ (cannot have - powers b/c of $\rho \to 0$ asymptotics)
After some algebra (see text again), get recursion relation
$$c_{j+1} = \frac{2(j+l+1)-\rho_0}{(j+1)(j+2l+2)} c_j$$
  + The series must terminate (or it changes $e^{-\rho}$ form of $\rho \to \infty$ asymptotic)
This means some j_0 is largest w/nonzero coeff.
$$\Rightarrow 2j_0 + 2l + 2 = \rho_0 = 2n \quad \text{where } n = 1,2,3,\ldots, \; n \geq l+1$$

- Alternate solutions b/c we don't want to use recursion all day
  + The differential eqn $x v'' + (\nu+1-x)v' + \lambda v = 0$ is associated Laguerre eqn
By comparison, this is our radial eqn if
$$\rho = x/2, \quad \nu = 2l+1, \quad \lambda = n-l-1$$
The normalizable solution is associated Laguerre polynomial $L^{2l+1}_{n-l-1}(2\rho)$
See text for some properties; In particular, $\lambda \geq 0$, integer for normalizable
  + May also use an algebraic procedure similar to harmonic oscillator but more complicated + less illuminating.
See Ohanian.

– Wavefunctions + Spectra.

- Bohr radius + Bohr energy
  - + Normalizability requires $\rho_0 = 2n \implies \kappa = 1/na$, $a = \dfrac{4\pi\epsilon_0 \hbar^2}{me^2}$
  - + The definition of κ gives the Bohr formula

$$E = -\frac{\hbar^2}{2ma^2}\frac{1}{n^2} = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{1}{n^2}$$

  - + Transitions from n_i to n_f produce light of wavelength (near visible) by $\frac{hc}{\lambda} = E_{n_i} - E_{n_f}$ or $\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$, R = Rydberg constant
- The wave function assembles all the parts
  - + $\rho = \kappa r = r/na$, so $R = u/r \propto (r/na)^l e^{-r/na} L^{2l+1}_{n-l-1}(2r/na)$
  - + The angular parts are spherical harmonics (and spin stuff)
  - +

$$\psi_{nlmm_s} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\, e^{-r/na}\left(\frac{2r}{na}\right)^l L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right) Y_l^m(\theta,\phi)\,|m_s\rangle$$

  - + Energy depends only on principal quantum number n, but wave functions depend on all of them.