Lecture #18

The radial equation

The angular part of the wave function $Y_l^m(\theta, \phi)$ is the same for all spherically symmetric potentials. To solve the radial equation, we need the know V(r).

$$\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}(V(r) - E)R = \ell(\ell+1)R$$

To simplify this equation, we change variables

$$u(r) \equiv r R(r), \qquad R = u/r$$

$$\frac{dR}{dr} = \frac{d}{dr}\left(\frac{u}{r}\right) = \frac{1}{r}\frac{du}{dr} - \frac{1}{r^2}u$$

$$\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) = \frac{d}{dr}\left\{ r\frac{du}{dr} - u \right\} = \cancel{\frac{du}{dr}} + r\frac{d^2u}{dr^2} - \cancel{\frac{du}{dr}}$$

$$= r\frac{d^2u}{dr^2} \implies$$

$$r\frac{d^2u}{dr^2} - \frac{2mr^{\cancel{2}}}{\hbar^2}(V - E)\frac{u}{\cancel{r}} = \ell(\ell+1)\frac{u}{r}$$

$$\frac{d^2u}{dr^2} - \frac{2m}{\hbar^2}Vu + \frac{2m}{\hbar^2}Eu = \ell(\ell+1)\frac{u}{r^2}$$

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + Vu + \ell(\ell+1)\frac{u}{r^2}\frac{\hbar^2}{2m} = Eu$$

Radial equation

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \underbrace{\left[V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]}_{V_{eff} = V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}} u = Eu}$$

This equation looks exactly like time-independent Schrödinger equation $H\psi = E\psi$

with $V \to V_{eff}$.

The normalization condition $\int_0^\infty |R|^2 r^2 \, dr = 1$ becomes

$$\boxed{\int_0^\infty |u|^2 \, dr = 1}.$$

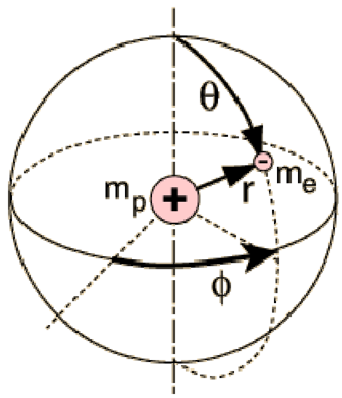
Summary for radial equation:

$$u(r) = rR(r)$$

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

$$\int_0^\infty |u|^2 \, dr = 1$$

The hydrogen atom



Heavy proton (put at the origin), charge e and much lighter electron, charge -e.

Potential energy, from Coulomb's law

$$\boxed{V(r) = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}}$$

Radial equation:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu$$

Our mission is to find the allowed energies E and the corresponding functions $u(r)$. The approach is essentially the same as in the case of analytical solution for harmonic oscillator. While there are both continuum (E> 0) and bound (E < 0) states for the Coulomb potential, we will only consider bound states now.

Step 1. First, we introduce some designations to put this equation in a bit "cleaner" form.

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}$$

← Remember, E< 0 for the bound states so κ is real.

$$\rho \equiv \kappa r \qquad \rho_0 \equiv \frac{me^2}{2\pi\varepsilon_0\hbar^2\kappa}$$

Substituting the above notations into our equation gives

$$\boxed{\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]u}$$

Step 2. Study the asymptotic form of the solutions.

(a) $\rho \to \infty \Rightarrow$

$$\frac{d^2u}{d\rho^2} = \left[1 - \cancel{\frac{\rho_0}{\rho}} + \cancel{\frac{\ell(\ell+1)}{\rho^2}}\right]u$$

constant term dominates

$$\frac{d^2u}{d\rho^2} = u \quad \text{and} \quad u(\rho) = Ae^{-\rho} + \cancel{Be^{\rho}}$$

This term blows up at $\rho \to \infty \Rightarrow$ get rid of it. $B = 0$

Therefore, for large ρ $\boxed{u = Ae^{-\rho}}$.

(b) $\rho \to 0 \Rightarrow$

$$\frac{d^2u}{d\rho^2} = \left[\cancel{1} - \cancel{\frac{\rho_0}{\rho}} + \frac{\ell(\ell+1)}{\rho^2}\right]u$$

this term dominates

$$\frac{d^2u}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2}u$$

The general solution of this equation is $u(\rho) = C\rho^{\ell+1} + \cancel{D\rho^{-\ell}}$

This solution blows up at $\rho \to 0 \Rightarrow D = 0$

Therefore, for small ρ $\boxed{u(\rho) = C\rho^{\ell+1}}$.

Step 3. Separate out the asymptotic behavior.

$$u(\rho) = \rho^{\ell+1} e^{-\rho} v(\rho)$$

Plugging this expression back into the radial equation $\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right]u$

yields the equation for the function v:

$$\boxed{\rho \frac{d^2 v}{d\rho^2} + 2(\ell + 1 - \rho)\frac{dv}{d\rho} + [\rho_0 - 2(\ell+1)]v = 0} \quad (1)$$

Step 4. Look for the solutions of the above equation in the form of a power series.

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j \qquad \text{need to find } c_0, c_1, c_2, \ldots$$

Substituting this expansion into equation (1) gives the formula for determining the coefficients c. The resulting recursion formula is:

$$\boxed{c_{j+1} = \left\{\frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2\ell+2)}\right\} c_j}$$

How to use this formula?
Start with c_0 (j = 0), determine c_1. Next, get c_2 from c_1 and so on.
The overall coefficient c_0 becomes normalization constant.

Step 5. Study how these coefficients look for large j. We must ensure that the solution does not blows up for large ρ.

$$c_{j+1} = \left\{\frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2\ell+2)}\right\} c_j \xrightarrow[\text{large } j]{} c_{j+1} \cong \frac{2j}{j(j+1)} c_j = \frac{2}{j+1} c_j$$

If this formula were exact it would give

$$c_j = \frac{2^j}{j!} c_0 \Rightarrow v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho}$$

$$u(\rho) = c_0 \rho^{l+1} e^{\rho} \quad \leftarrow \text{blow up at large } \rho.$$

Solution: the power series must terminate.

Therefore, for some maximal integer j_{max}

$$\boxed{c_{j_{max}+1} = 0}.$$

This will obviously terminate the entire series, since all other higher coefficients will be zero as well.

From equation

$$c_{j+1} = \left\{ \frac{\boxed{2(j+l+1) - \rho_0}}{(j+1)(j+2l+2)} \right\} c_j$$

must be zero for j_{max}

$$\boxed{2(j_{max}+l+1) - \rho_0 = 0}$$

We define $n \equiv j_{max} + l + 1$ and call it **principal quantum number**.

$$\boxed{2n = \rho_0}$$

Now, we remember what ρ_0 was: $\rho_0 \equiv \dfrac{me^2}{2\pi\varepsilon_0 \hbar^2 k}$, $k \equiv \dfrac{\sqrt{-2mE}}{\hbar}$

$$k^2 = -\frac{2mE}{\hbar^2} \Rightarrow E = -\frac{\hbar^2 k^2}{2m}$$

$$E = -\frac{\hbar^2 k^2}{2m} \qquad k^2 = \frac{m^2 e^4}{4\pi^2 \varepsilon_0^2 \hbar^4 \rho_0^2} \qquad \rho_0^2 = 4n^2$$

$$E = -\frac{\cancel{\hbar^2}}{2\cancel{m}} \frac{m^{\cancel{2}} e^4}{4\pi^2 \varepsilon_0^2 \hbar^{\cancel{4}2} 4n^2} = \underbrace{-\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]}_{E_1} \frac{1}{n^2}$$

$$\boxed{E = \frac{E_1}{n^2} \, , \; n = 1, 2, 3, \ldots}$$

Famous Bohr formula

$\boxed{n=1}$

$$E_1 = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right] = -13.6 \text{ eV}$$

Ground state energy

$\boxed{n=2}$

$$E_2 = \frac{E_1}{2^2} = \frac{-13.6 \text{ eV}}{4} = -3.4 \text{ eV}$$

Next energy state[s]. [Degenerate]

Summary:

$$\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)\, Y_\ell^m(\theta,\phi)$$

$$R_{n\ell} = \frac{1}{r}\rho^{\ell+1} e^{-\rho} v(\rho) \qquad \rho = kr$$

$$v(\rho) = \sum_{j=0}^{j_{max}} c_j \rho^j, \qquad j_{max} = n - \ell - 1$$

$$c_{j+1} = \frac{2(j+\ell+1-n)}{(j+1)(j+2\ell+2)} c_j$$

Note: need to normalize functions to get c_0.