Lecture 2

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H atom continued

Normalization:

$$d^3r = r^2 \sin\vartheta \, dr \, d\vartheta \, d\phi$$

$$\int |\psi|^2 r^2 \sin\vartheta \, dr \, d\vartheta \, d\phi = \int |R|^2 r^2 dr \int |Y|^2 \sin\vartheta \, d\vartheta \, d\phi = 1$$

$$\int_0^\infty |R|^2 r^2 dr = 1$$

$$\int_0^{2\pi} \int_0^\pi |Y|^2 \sin\vartheta \, d\vartheta \, d\phi = 1$$

$$Y_\ell^m(\vartheta, \phi) = \varepsilon \sqrt{\frac{(2\ell+1)}{4\pi} \frac{(\ell-|m|)!}{(\ell+|m|)!}} \, e^{im\phi} P_\ell^m(\cos\vartheta)$$

$$\begin{cases} \varepsilon = (-1)^m & ; m > 0 \\ \varepsilon = 1 & ; m \leq 0 \end{cases}$$

$\boxed{\text{spherical harmonics}}$

They are orthogonal:

$$\int_0^{2\pi} \int_0^\pi \left[Y_\ell^m(\vartheta, \phi)\right]^* \left[Y_{\ell'}^{m'}(\vartheta, \phi)\right] \sin\vartheta \, d\vartheta \, d\phi = \delta_{\ell\ell'} \delta_{mm'}$$

$\ell \equiv$ azimuthal quantum number

$m \equiv$ magnetic quantum number

<u>Solve the radial equation</u>

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

change variables

$$u(r) \equiv rR(r) \Rightarrow R = \frac{u}{r} \quad ; \int_0^\infty |u|^2 dr = 1$$

$$\frac{dR}{dr} = \left[r\left(\frac{du}{dr}\right) - u\right]/r^2 \quad ; \left(\frac{d}{dr}\right)\left[r^2\left(\frac{dR}{dr}\right)\right] = r\frac{d^2u}{dr^2}$$

$$\Downarrow$$

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

1-D equation with effective potential

$$V_{eff} = V + \underbrace{\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}}_{\text{centrifugal term}} = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$$

; pushes electrons outward

<u>Solve the radial equation</u>

There are both continuum states: ionization and discrete bound states: hydrogen atom

Define $\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}$ $\quad E<0$ (bound states)

Divide (1) by $E$:

$$\frac{1}{\kappa^2}\frac{d^2u}{dr^2} = \left[1 - \frac{me^2}{2\pi\varepsilon_0\hbar^2\kappa}\frac{1}{(\kappa r)} + \frac{(\ell+1)\ell}{(\kappa r)^2}\right]u$$

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

$$\Downarrow$$

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

confluent Hypergeometric equation ⇒ hypergeometric function

- For $r\to\infty$, $\rho\to\infty$ ⇒ $\frac{d^2u}{d\rho^2} \sim u$

$$u(\rho) = Ae^{-\rho} + Be^{\rho} \quad ; \quad e^{\rho} \text{ diverges} \Rightarrow B=0$$

$$\Downarrow$$

$$u(\rho) \sim Ae^{-\rho} \quad \text{for } \rho\to\infty$$

- For $r\to 0$, $\rho\to 0$ the centrifugal term dominates

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

$$u(\rho) = C\rho^{\ell+1} + D\rho^{-\ell} \quad ; \rho^{-\ell} \to \infty, \ \rho \to 0 \Rightarrow D = 0$$

$$\Downarrow$$

$$u(\rho) = C\rho^{\ell+1}, \quad \rho \to 0$$

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

$$\Downarrow$$

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

Assume $v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$, i.e. a power series

Determine $c_j$s by differentiating term by term

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j c_j \rho^{j-1} \overset{\text{rename } j \to j+1}{=} \sum_{j=0} (j+1) c_{j+1} \rho^j$$

$$\frac{d^2 v}{d\rho^2} = \sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^{j-1}$$

Putting into $*$ we obtain the recursion formula

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

For large $j$ $\quad c_{j+1} \sim \dfrac{2c_j}{j+1}$

If we iterate

$$C_j = \frac{2^j}{j!} c_0$$

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

$$\Downarrow$$

$$u(\rho) = c_0 \rho^{\ell+1} e^{\rho} \to \infty \text{ for } \rho \to \infty$$

There has to be a $j_{max}$ such that

$$C_{j_{max}+1} = 0$$

From the recurrence formula

$$2(\underbrace{j_{max} + \ell + 1}_{\equiv n \,\equiv\, \text{principal quantum number}}) - \rho_0 = 0$$

$$\Downarrow$$

$$\rho_0 = 2n \Rightarrow E = \frac{-\hbar^2 k^2}{2m} = -\frac{me^4}{8\pi^2 \varepsilon_0^2 \hbar^2 \rho_0^2}$$

Allowed energies:

Bohr formula $\rightarrow$ $E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2}$ ; $n = 1, 2, 3, \ldots$

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