Physics 371 Lecture 29

- ## Hydrogenic atoms

$$\frac{d^2u}{dr^2} + \frac{2\mu}{\hbar^2}\left(E - V_{eff}(r)\right)u(r) = 0,$$

$$u(r) = r\psi(r), \qquad \Psi(r,\theta,\phi) = \psi(r)\,Y_{\ell m}(\theta,\phi)$$

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

Coulomb attraction between electron and nucleus of charge Ze.

centrifugal barrier

$$\lim_{r\to\infty} V_{eff}(r) = 0$$

- B.C.s:

$$u(r) \xrightarrow[r\to 0]{} 0 \qquad u(r) \xrightarrow[r\to\infty]{} 0$$

(for bound states)

$\underline{r \to \infty}$ $\quad \dfrac{d^2u}{dr^2} \cong -\dfrac{2\mu}{\hbar^2} E\, u(r)$

For bound states, $E < 0$:

$$\frac{d^2u}{dr^2} \simeq \frac{2\mu|E|}{\hbar^2}\, u$$

$$\boxed{u(r) \underset{r\to\infty}{\sim} A e^{-\lambda r} \qquad \lambda = \frac{1}{\hbar}\sqrt{2\mu|E|}}$$

($e^{+\lambda r}$ does not obey B.C.s)

$\underline{r \to 0}$ $\quad \dfrac{d^2u}{dr^2} \simeq \dfrac{\ell(\ell+1)}{r^2}\, u(r)$

Try $u(r) \sim B r^p$

$$B p(p-1) r^{p-2} \simeq \frac{\ell(\ell+1)}{r^2} B r^p$$

$$p(p-1) = \ell(\ell+1)$$

$\Rightarrow p = -\ell$ or $p = \ell + 1$

- $u(r) \sim r^{-\ell}$ would violate B.C. for $r \to 0$, so we must choose

$$\boxed{u(r) \underset{r \to 0}{\sim} B r^{\ell+1}.}$$

- <u>Change to dimensionless variable</u>

Let $\rho = 2\lambda r$

$$\Rightarrow \frac{d^2 u}{d\rho^2} - \left[\frac{\ell(\ell+1)}{\rho^2} - \frac{n}{\rho} + \frac{1}{4}\right] u(\rho) = 0,$$

where $n = \dfrac{\mu Z e^2}{\hbar^2 \lambda}$.

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Power series solution

Factoring out the known asymptotic behavior, let us try for a solution of the form

$$u(\rho) = e^{-\rho/2} \rho^{l+1} \sum_{j=0}^{\infty} a_j \rho^j$$

$$= e^{-\rho/2} \sum_{j=0}^{\infty} a_j \rho^{j+l+1}$$

$$\frac{du}{d\rho} = -\frac{1}{2} u + e^{-\rho/2} \sum_{j=0}^{\infty} (j+l+1) a_j \rho^{j+l}$$

$$\frac{d^2u}{d\rho^2} = \frac{1}{4} u - e^{-\rho/2} \sum_{j=0}^{\infty} (j+l+1) a_j \rho^{j+l}$$

$$+ e^{-\rho/2} \sum_{j=0}^{\infty} (j+l+1)(j+l) a_j \rho^{j+l-1}$$

- $$\sum_{j=0}^{\infty} \left\{ [(j+\ell+1)(j+\ell) - \ell(\ell+1)]\, a_j \rho^{j+\ell-1} - (j+\ell+1-n)\, a_j \rho^{j+\ell} \right\} = 0$$

$$\sum_{j=0}^{\infty} \left\{ j(j+2\ell+1)\, a_j \rho^{j+\ell-1} - (j+\ell+1-n)\, a_j \rho^{j+\ell} \right\} = 0$$

- $$\sum_{j=0}^{\infty} \rho^{j+\ell} \left\{ (j+1)(j+2\ell+2)\, a_{j+1} - (j+\ell+1-n)\, a_j \right\} = 0$$

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

- $$\frac{a_{j+1}}{a_j} \underset{j\to\infty}{\sim} \frac{1}{j}$$

- Note that the series expansion of $e^{\rho} = \sum_{j=0}^{\infty} \frac{\rho^j}{j!}$ has

$$\frac{a_{j+1}}{a_j} = \frac{j!}{(j+1)!} = \frac{1}{j+1}.$$

- Thus, if the series does not terminate at some finite power $\rho^{j_{max}}$, we will have

$$u(\rho) \underset{\rho\to\infty}{\sim} e^{-\rho/2} \rho^{l+1} e^{\rho} = e^{\rho/2} \rho^{l+1} \longrightarrow \infty$$

this is just the discarded
- diverging solution. Only a finite

order power series is allowed. 7

$$0 = \frac{a_{j_{max}+1}}{a_{j_{max}}} = \frac{j_{max} + \ell + 1 - n}{- - - \,.}$$

$$j_{max} = n - \ell - 1$$

$\ell \in \mathbb{Z}$ and $j_{max} \in \mathbb{Z}$

$\Rightarrow$ series only terminates if

$$n = \frac{\mu Z e^2}{\hbar^2 \lambda} \in \mathbb{Z}$$

$$n = j_{max} + \ell + \underline{1}, \quad j_{max} = 0, 1, 2, \ldots \infty$$

= "principal quantum #"

- $$\lambda = \frac{\mu Z e^2}{\hbar^2 n}$$

$$E = -\frac{\hbar^2 \lambda^2}{2\mu}$$

Energy levels

- $$E_n = -\frac{\mu e^4}{2\hbar^2}\frac{Z^2}{n^2}, \quad n = 1, 2, \ldots, \infty$$

$$\frac{\mu e^4}{2\hbar^2} = 13.6\ \text{eV}$$

(independent of quantum #s ℓ and m)

Degeneracy For a given n, ℓ can take the values $0, 1, 2, \ldots, n-1$.

- For each value of ℓ, m can take the values $-\ell, -\ell+1, \ldots, \ell$.

$$d(n) = \sum_{l=0}^{n-1} (2l+1)$$

$$= 1 + 3 + 5 + \cdots + 2n - 1$$

$$= n \frac{2n}{2} = n^2$$

The $(2l+1)$-fold degeneracy of each l-value holds for any spherically symmetric potential, while the n-fold degeneracy of the l-values is special to the coulomb potential, for which the Hamiltonian possesses $O(4)$ symmetry.

Relation to Bohr

- These are the same energy levels derived by Bohr from the condition

$mvr = n\hbar$ for circular orbits.

- For such an orbit lying in the xy-plane, one would have $L_z = \ell\hbar = n\hbar$,

or $\ell = n$, whereas from the full quantum solution, we find

- $\ell \leq n - 1$

Furthermore, Bohr's model does not allow for orbits with $l = 0$. Thus Bohr's model does not correctly describe the physics of Hydrogenic atoms, and it is something of a coincidence that his model led to the correct energy levels.