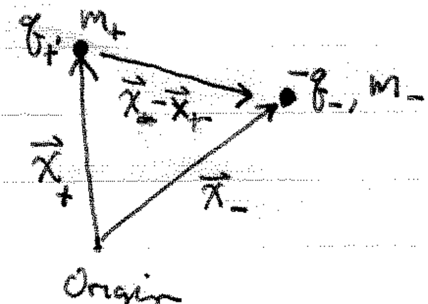
Lecture 10a : Hydrogenic Atoms (I)

- **Simplest atoms:** Two oppositely charged particles bound together

Examples:

- Hydrogen — electron + proton
- He^+ — electron + α-nucleus
- Li^{++} — electron + ($Z=3$ nucleus)
- Positronium — electron + positron
- Muonium — muon + proton

- Geometry



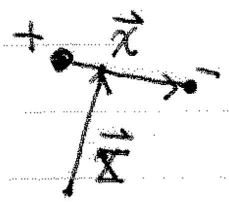
$$\hat{H} = \hat{T}_+ + \hat{T}_- + \hat{V}_{+-}$$

$$\hat{H}_\pm = \frac{\hat{P}_\pm^2}{2m_\pm} \qquad \hat{V}_{+-} = \frac{-q_+ q_-}{|\vec{x}_- - \vec{x}_+|}$$

(c.g.s. units)

Not separable in $\pm$ coordinates

Separable in Center of mass and relative coordinates



Center of mass coördinate

$$\vec{X} \equiv \frac{m_+ \vec{x}_+ + m_- \vec{x}_-}{M} \qquad (M = m_+ + m_-)$$

relative coordinate: $\vec{x} \equiv \vec{x}_- - \vec{x}_+$

$$\vec{x}_- = \vec{X} + \frac{m_+}{M}\vec{x} \qquad \vec{x}_+ = \vec{X} - \frac{m_-}{M}\vec{x}$$

For future: Define "reduced mass"

$$\mu \equiv \frac{m_+ m_-}{M} \qquad \left(\begin{array}{c}\text{Smaller mass}\\ \text{dominates}\end{array}\right)$$

Classical mechanics of two-body problem

$$\vec{p}_\pm = m_\pm \dot{\vec{x}}_\pm = m_\pm \dot{\vec{X}} \pm \frac{\mu}{M} \dot{\vec{x}}$$

$\Rightarrow$ Center of mass momentum: $\vec{P} \equiv (m_+ + m_-)\dot{\vec{X}} = M\dot{\vec{X}}$

Relative coordinate momentum:

$$\vec{p} = \frac{m_+}{M}\vec{p}_- - \frac{m_-}{M}\vec{p}_+ = \mu\dot{\vec{x}}$$

$\vec{P}$ and $\vec{p}$ are canonical conjugates of $\vec{X}$ and $\vec{x}$

Total kinetic energy

$$\hat{T}_+ + \hat{T}_- = \frac{\vec{P}_+^2}{2m_+} + \frac{\vec{P}_-^2}{2m_-} = \frac{\vec{P}^2}{2M} + \frac{\vec{p}^2}{2\mu}$$

$$= \hat{T}_{CM} + \hat{T}_{rel}$$

$$\hat{V}_{+-} = -\frac{q_+ q_-}{r} \quad \text{where } r = |\vec{x}_- - \vec{x}_+|$$

(depends only on relative coördinate)

$\therefore$

$$\boxed{\begin{aligned} \hat{H} &= \hat{H}_{cm} + \hat{H}_{rel} \quad \text{separable!} \\ \hat{H}_{cm} &= \frac{\hat{P}^2}{2M} \\ \hat{H}_{rel} &= \frac{\hat{p}^2}{2\mu} - \frac{q_1 q_2}{r} \end{aligned}}$$

Stationary states: $\hat{H}|\Psi\rangle = E|\Psi\rangle$

$$|\Psi\rangle = |\Phi_{CM}\rangle \otimes |\psi_{rel}\rangle$$

$$E = E_{CM} + E_{rel}$$

where $\hat{H}_{CM}|\Phi_{CM}\rangle = E_{CM}|\Phi_{CM}\rangle$

$$\hat{H}_{rel}|\psi_{rel}\rangle = E_{rel}|\psi_{rel}\rangle$$

If there is no confining potential for the center of mass $\Rightarrow$ CM is a free particle

$$\Rightarrow E_{CM} = \frac{P^2}{2M} \quad : \text{Continuous}$$

Relative coordinate dynamics:

$$\left(\frac{\hat{p}^2}{2\mu} + V(\hat{r})\right)|\psi_{rel}\rangle = E_{rel}|\psi_{rel}\rangle$$

$$V(\hat{r}) = -\frac{q_+ q_-}{r}$$

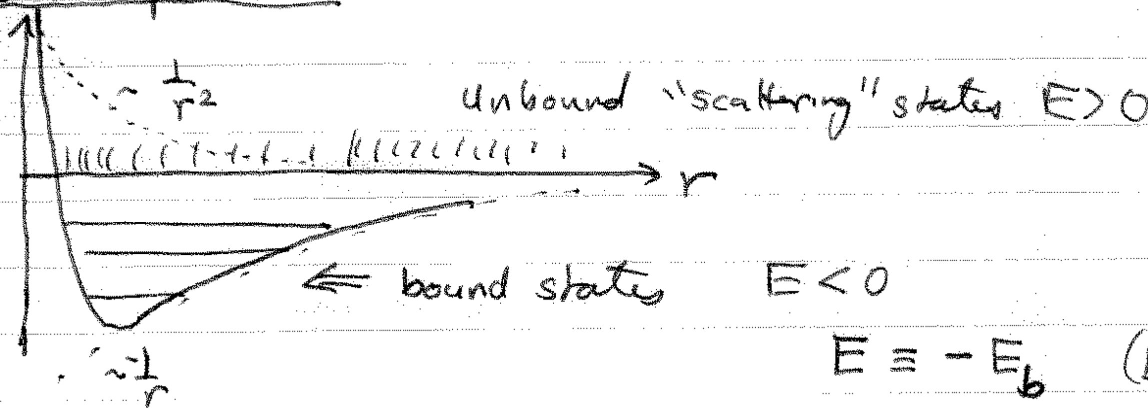
Central potential for reduced mass. Separate radial and angular motion:

$$\left[\frac{\hat{p}_r^2}{2\mu} - \frac{q_+ q_-}{r} + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}\right]|n_r, \ell, m\rangle = E_{n_r,\ell}|n_r, \ell, m\rangle$$

$\Rightarrow$ Radial equation for $u_{n_r\ell}(r) = r\langle r|n_r\ell\rangle = r R_{n_r,\ell}(r)$

$$\Rightarrow \boxed{\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} - \frac{q_+ q_-}{r} + \frac{\hbar^2 \ell(\ell+1)}{2mr^2}\right]u = E_{n_r,\ell}\, u}$$

Effective potential



$$E \equiv -E_b \quad (E_b > 0)$$

Solving the radial equation

- Characteristic units

Let $\bar{r} = \dfrac{r}{a_0}$, $\quad \mathcal{E} = \dfrac{-E_b}{E_0}$, $\quad U_{n,l} = \sqrt{a_0}\, u_{n_r,l}$

$$\Rightarrow \left[\left(\frac{\hbar^2}{\mu a_0^2}\right)\left(-\frac{1}{2}\frac{d^2}{d\bar{r}^2}\right) - \left(\frac{q_+ q_-}{a_0}\right)\frac{1}{\bar{r}} + \left(\frac{\hbar^2}{\mu a_0^2}\right)\frac{l(l+1)}{2\bar{r}^2}\right] U = -E_0\, \mathcal{E}\, U$$

Choose: $E_0 \equiv \dfrac{q_+ q_-}{a_0} = \dfrac{\hbar^2}{\mu a_0^2}$

$$\Rightarrow a_0 = \frac{\hbar^2}{\mu q_+ q_-} \qquad E_0 = \frac{\mu (q_+ q_-)^2}{\hbar^2}$$

Case of Hydrogen: $q_+ = -q_- = e = 4.8 \times 10^{-10}$ esu

$m_e \cong 0.5$ MeV $\quad m_p \cong 1$ GeV

$$\Rightarrow \mu = \frac{m_e m_p}{M} \approx m_e \qquad M \approx m_p$$

$\Rightarrow$ C of M $\approx$ proton $\quad$ relative $\approx$ electron to proton

Atomic units

$$a_0 = \frac{\hbar^2}{m_e e^2} \cong 0.5 \mathring{A} = 0.5 \times 10^{-10}\ m$$

"Bohr radius"

$$E_0 = \frac{e^2}{a_0} = \frac{m_e e^4}{\hbar^2} = 27.2\ eV \quad \text{"Hartree"}$$

$$\text{Rydberg} \quad \mathbb{R} = \tfrac{1}{2} E_0 = 13.6\ eV$$

Radial equation in dimensionless units for bound states

$$\left[-\frac{1}{2}\frac{d^2}{d\bar{r}^2} - \frac{1}{\bar{r}} + \frac{\ell(\ell+1)}{\bar{r}^2}\right] U_{n_r,\ell}(\bar{r}) = -\varepsilon\, U_{n_r,\ell}(\bar{r})$$

Solution: theory of ODE

- Boundary condition at origin:

$$\Longrightarrow \text{ as } \bar{r} \Rightarrow 0 \quad U \Rightarrow \bar{r}^{\,\ell+1}$$

- Boundary condition at ∞ $\quad U \Rightarrow 0$

Large $\bar{r}$, $V(r) \to 0$

$$-\frac{1}{2}\frac{d^2 U_\infty}{d\bar{r}^2} = -\varepsilon U_\infty \Longrightarrow U_\infty = \cancel{A_+ e^{\sqrt{2\varepsilon}\,\bar{r}}} + A_- e^{-\sqrt{2\varepsilon}\,\bar{r}}$$

~~pdfelse~~ reject

$$\Rightarrow U_\infty \sim A e^{-\kappa \bar{r}} \qquad \kappa \equiv \sqrt{2\varepsilon}$$

Thus we can express the reduced radial wave function using the Ansatz:

$$\bar{U}(\bar{r}) = \bar{r}^{\ell+1} e^{-K\bar{r}} F(\bar{r})$$

where $K \equiv \sqrt{2\epsilon}$, $F(\bar{r})$ is constant as $\bar{r} \to 0$ or $\bar{r} \to \infty$

<u>Plug in Ansatz:</u>

$$\bar{r} F'' + (2\ell+2-2K\bar{r}) F' + 2(1-K(\ell+1))F = 0$$

(prime denotes $\frac{d}{d\bar{r}}$)

Assume a power series solution

$$F(\bar{r}) = \sum_{j=0}^{\infty} a_j \bar{r}^j$$

Plug into diff 'eqn and equate powers:

$$F'(\bar{r}) = \sum_{j=0}^{\infty} j a_j \bar{r}^{j-1} = \sum_{j=0}^{\infty} (j+1) a_{j+1} \bar{r}^j$$

$$F''(\bar{r}) = \sum_{j=0}^{\infty} j(j-1) a_j \bar{r}^{j-2}$$

$$\bar{r} F''(\bar{r}) = \sum_{j=0}^{\infty} j(j-1) a_j \bar{r}^{j-1} = \sum_{j=0}^{\infty} (j+1) j \, a_{j+1} \bar{r}^j$$

$$\Rightarrow j(j+1) a_{j+1} + (2\ell+2)(j+1) a_{j+1} - 2Kj a_j + 2(1-K(\ell+1)) a_j = 0$$

$\Rightarrow$ Recursion relation

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

Asymptotic behavior for $\bar{r} \to \infty$ dominated by large j terms

$$j \to \infty \quad a_{j+1} \cong \frac{2\kappa}{j} a_j \Rightarrow a_j \sim \frac{(2\kappa)^j}{j!} a_0$$

$$\Rightarrow F(\bar{r}) \sim e^{\kappa \bar{r}} \text{ diverges!}$$

$\Rightarrow$ Boundary condition at infinity $\Longrightarrow$ series is <u>finite</u>.

i.e. there is a $j_{max} \equiv n_r$ (radial quantum #)

$$a_{n_r+1} = 0 \Rightarrow \kappa(n_r+\ell+1) - 1 = 0$$

$$\Longrightarrow n_r = \frac{1}{\kappa} - (\ell+1)$$

$$\Longrightarrow \kappa = \frac{1}{n_r+\ell+1} \equiv \frac{1}{n} \quad (n \equiv n_r+\ell+1)$$

$$\kappa \equiv \sqrt{2\varepsilon'} = \frac{1}{n_r+\ell+1}$$

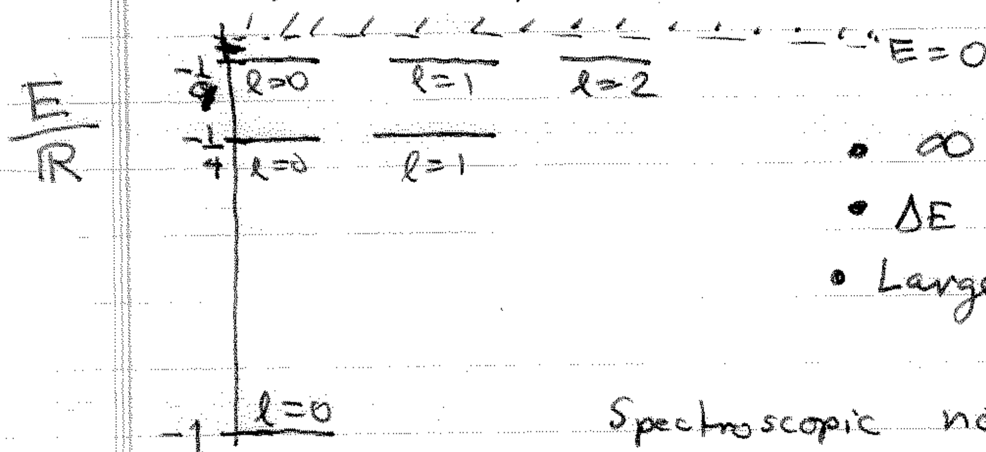
$$\Longrightarrow \boxed{\varepsilon = \frac{1}{2(n_r+\ell+1)^2}}$$

Bound-state eigenvalues

$$\boxed{\begin{aligned} E_{n_r,\ell} &= -\frac{E_0}{2(n_r+\ell+1)^2} = -\frac{E_0}{2n^2} \\ \text{Hydrogen} &= -\frac{\mathbb{R}}{n^2} = -\frac{1}{n^2}(13.6\,\text{eV}) \quad \text{Balmer series} \end{aligned}}$$

Principle quantum # $n \equiv n_r + \ell + 1$

For given n, $\ell = 0, 1, 2, \ldots, n-1$ since $n_r = 0, 1, \ldots$



- ∞ # of bound-states
- ΔE gets smaller near $E=0$
- Large $n \Rightarrow$ "Rydberg states"

Spectroscopic notation

$\ell=0$: s-states ("sharp")
$\ell=1$: p-states ("principle")
$\ell=2$: d-states ("distinct")
$\ell=3$: f-states ("fine")

<u>Degeneracy:</u> Given n (excluding spin)

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

<u>Including</u> electron spin $g_n = 2n^2$

"Accidental degeneracy"

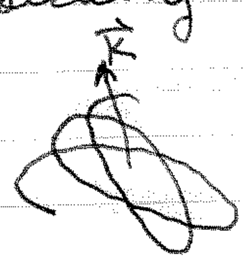
E_n depends only on $n_r + l$ and not on n_r and l independently:

Hidden symmetry: The Runge-Lenz vector

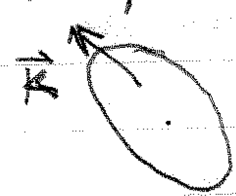
$$\hat{\vec{K}} = \frac{1}{2me^2}\left(\hat{\vec{L}} \times \hat{\vec{p}} - \hat{\vec{p}} \times \hat{\vec{L}}\right) + \frac{\hat{\vec{x}}}{r}$$

$\hat{\vec{K}}$ is a conserved quantity

Classically $\Rightarrow$ no precession of orbit for $-\frac{1}{r}$ potential



$V(r) \neq \frac{-1}{r}$



$V(r) = -\frac{1}{r}$

New symmetry $\Rightarrow$ Another set of commuting operators

$\Rightarrow$ Can separate in parabolic coordinates

Suppose we add a small potential $V_{int} = \frac{\lambda}{r^2}$

$$\Rightarrow E_{n_r, l} \cong \frac{-E_0}{2\left(n_r + \frac{1}{2} + \sqrt{(l+\frac{1}{2})^2 + \lambda^2}\right)^2}$$

"Breaks" the degeneracy