Lecture 13: Hydrogen Atom

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QM I _ Fall 2019

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There are 2 DOF.

$$\psi(\vec{r}_p, \vec{r}_e), \quad H = \frac{\hat{P}_e^2}{2m_e} + \frac{\hat{P}_p^2}{2m_p} - \frac{e^2}{|r_e - r_p|^2}$$

The first thing we do is to rewrite H in terms of two indep. variables

$$\vec{r}_\mu = \vec{r}_e - \vec{r}_p \qquad \vec{R}_{cm} = \frac{m_e \vec{r}_e + m_p \vec{r}_p}{m_e + m_p}$$

Ⓐ Show that

$$\frac{\hat{\vec{P}}_e^2}{m_e} + \frac{\hat{\vec{P}}_p^2}{m_p} = \frac{1}{m_e + m_p} \hat{\vec{P}}_{cm}^2 + \frac{1}{\mu} \hat{\vec{P}}_\mu^2$$

$$\text{with } \mu = \frac{m_e m_p}{m_e + m_p}$$

$$H = H_{cm} + H_\mu : \quad H_{cm} = \frac{\hat{\vec{P}}_{cm}^2}{2(m_e + m_e)} \Rightarrow \hat{H}_{cm}|\phi\rangle = E|\phi\rangle$$

$$H_\mu = \frac{\hat{\vec{P}}_\mu^2}{2\mu} - \frac{e^2}{|r|} \Rightarrow \hat{H}_\mu |\psi\rangle = E' |\psi\rangle$$

$$H |\phi\rangle \otimes |\psi\rangle = (E + E') |\phi\rangle |\psi\rangle$$

$$\Rightarrow \psi(\vec{r}, \vec{R}) = \phi(\vec{R}) \psi(\vec{r})$$

It's easy to check that $\hat{H}_{cm}$ is a free particle ($V = 0$) and $\phi(R)$ are plane waves.

For $|\psi\rangle$, we need to solve the radial sch. eq.

Radial Sch. eq. for the Hydrogen atom

$$\frac{-\hbar^2}{2\mu}\frac{d^2}{dr^2} rR_{n\ell}(r) + \left[\frac{\ell(\ell+1)\hbar^2}{2\mu r^2} - \frac{e^2}{r}\right] rR_{n\ell}(r) = E\, rR_{n\ell}(r)$$

Step 1. Asymptotic behavior

$r \to 0 \qquad E \gg \frac{1}{r^2}, \frac{1}{r}$

$$\frac{-\hbar^2}{2\mu}\frac{d^2}{dr^2} U^0_{n\ell}(r) = E\, U^0_{n\ell}(r) \Rightarrow U^0_{n\ell}(r) \sim e^{-kr}$$

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

$r \to \infty \qquad \frac{1}{r^2} \gg \frac{1}{r}, E$

$$\frac{-\hbar^2}{2m}\frac{d^2}{dr^2} U^\infty_{n\ell}(r) + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} = 0 \Rightarrow U^\infty_{n\ell}(r) \sim r^{\ell+1}$$

Step 2: Guessing the Solution

$$U_{n\ell}(r) = f_{n\ell}(r)\, r^{\ell+1}\, e^{-kr}$$

Next we need to rewrite the Sch. eq for $f(r)$:

$$\frac{d^2 U}{dr^2} = r^{\ell+1} e^{-kr} \frac{d^2 f}{dr^2} \qquad \left[\frac{d}{dr} r^{\ell+1} e^{-kr} = (\ell+1) r^{\ell} e^{-kr} - k r^{\ell+1} e^{-kr}\right]$$

$$+ \frac{df}{dr}\left[\frac{2(\ell+1)}{r} - 2k\right] r^{\ell+1} e^{-kr}$$

$$+ f(r)\left[\frac{\ell(\ell+1)}{r^2} + k^2 - \frac{2k(\ell+1)}{r}\right] r^{\ell+1} e^{-kr}$$

$$\Rightarrow \frac{d^2f}{dr^2} + \frac{df}{dr}\left[\frac{2(\ell+1)}{r} - 2k\right] + \left[-\frac{2k(\ell+1)}{r} + \frac{2\mu e^2}{\hbar^2 r}\right] f(r) = 0$$

Step 3: Polynomial Expasion

$$f(r) = \sum_{i=0}^{\infty} a_i r^i$$

$$\Rightarrow \sum_i \left(i(i-1)\, a_i r^{i-2} + 2(\ell+1)\, i\, a_i r^{i-2} - 2ki\, a_i r^{i-1} - 2k(\ell+1) a_i r^{i-1} + \frac{2\mu e^2}{\hbar^2} a_i r^{i-1} \right) = 0$$

$$\underbrace{i(2\ell + i + 1)\, a_i \, r^{i-2}}_{\substack{i \to i+1 \\ (i+1)(2\ell+i+2)\, a_{i+1}\, r^{i-1}}} + \left(\frac{2\mu e^2}{\hbar^2} - 2k(\ell+i+1) \right) a_i \, r^{i-1}$$

$$a_{i+1} = \frac{-\frac{2\mu e^2}{\hbar^2} + 2k(\ell+i+1)}{(i+1)(2\ell+i+2)}\, a_i$$

$$\lim_{i\to\infty} \frac{a_{i+1}}{a_i} = \frac{2k}{i+1} \rightsquigarrow \text{Exponential series}$$

$$\Rightarrow \sum_i a_i r^i \sim e^{2kr}$$

$$U_{n\ell}(r) \sim r^{\ell+1} e^{kr} \xrightarrow{r\to\infty} \infty$$

It diverges for large r

This could only work if the serie terminates at some finite i.

$\longrightarrow$ Quantization of energy.

$$\underline{E_n} \leftarrow \begin{cases} a_i \neq 0 \\ a_{i+1} = 0 \Rightarrow \end{cases}$$

$$\frac{2\mu e^2}{\hbar^2} = 2k\,(l+i+1)$$

$$\Rightarrow k = \frac{\mu e^2}{\hbar^2 (l+i+1)} \quad , \; k = \sqrt{\frac{-2\mu E}{\hbar^2}}$$

$$\boxed{\Rightarrow E_{i,l} = \frac{-\mu e^4}{2\hbar^2 (l+i+1)^2}}$$

$*$ $\begin{cases} n = l+i+1 \Rightarrow E_n = \dfrac{-E_0}{n^2} \\ E_0 = \dfrac{\mu e^4}{2\hbar^2} \end{cases}$

$*$ $n = l+i+1 \quad , \; i = 0, 1, \cdots$

$n = 1, 2, \cdots$

g_n: $\quad n$: $\; l = 0, 1, \cdots n-1$

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

$*$ $n = 1 \;,\; l = 0$

$n = 2 \;,\; l = 0 \longrightarrow a_2 = 0$

$l = 1 \longrightarrow a_1 = 0$

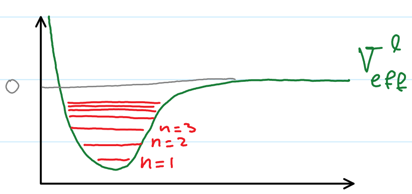
$n = 3, \; l = 0$

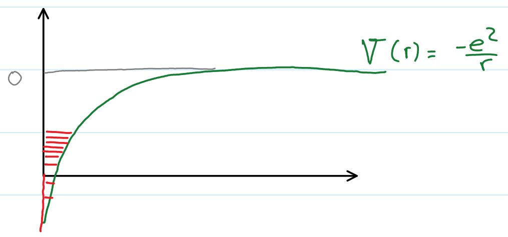
$l = 1$

$l = 2$

$*$

The schematic picture





$*$ $\longrightarrow$ Bohr radius $a_o = \frac{\hbar^2}{\mu e^2}$

$$\Rightarrow E_n = -\frac{e^2}{2a_o} \frac{1}{n^2}$$

$*$ $Z > 1$. $E_o \longrightarrow \frac{\mu Z^2 e^4}{2\hbar^2}$

Wave Function

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

$$R_{n\ell}(r) = A_{n\ell}\, r^{\ell}\, e^{-\frac{r}{na_o}} \sum_{i}^{n-\ell-1} a_i r^i$$

$n = N + \ell + 1$, $A_{n\ell}$: normalization factor

$k_n = \frac{1}{na_o}$

$$a_i = \delta_i a_{i-1} \Rightarrow a_i = \prod_{j=0}^{i} \delta_j \; a_o$$

$$\delta_i = \frac{-\frac{2\mu e^2}{\hbar^2} + 2k_n(\ell+1)}{i(2\ell+i+1)}$$

For $R_{n\ell}(r)$: $\frac{2\mu e^2}{\hbar^2} = 2k_n n$, $n = \ell + 1$

$$\Rightarrow \delta_i = 2k_n \frac{(-n+\ell+i)}{i(2\ell+i+1)}$$

Use with caution, indices may be off

$$\prod_{j=0}^{n-\ell-1} \delta_j = (2k_n)^{n-\ell-1} \frac{(-1)^{n-\ell-1}\,(n-\ell)!\,(2\ell+2)!}{(n-\ell-1)!\,(n+\ell)!}$$

$\underline{n=1} \longrightarrow N=0,\ l=0$

$$R_{10}(r) = A_{10}\, e^{-r/a_0}$$

a_0 not the Bohr radius.

(A) Show that $A_{10}\, a_0 = 2\,(a_0)^{-3/2}$

(A) Find $R_{20}(r)$ & $R_{21}(r)$.

The radial functions R_{nl} can be expressed in terms of "Associated Laguerre" functions:

$$R_{nl}(r) = \underset{\substack{\downarrow \\ \text{Normalization factor}}}{N_{nl}} \left(\frac{2r}{na_0}\right)^{l} e^{-\frac{r}{na_0}}\, L^{2l+1}_{n+l}\left(\frac{2r}{na_0}\right)$$

Magnetic Field

Now we consider application of uniform magnetic field $\vec{B}$:

$$\vec{A} = \frac{1}{2}\left(\vec{B}\times\vec{r}\right)$$

$$H = \left(\vec{P} - \frac{q\vec{A}}{c}\right)^2 \Big/ 2\mu + V(\vec{r}) \longrightarrow \text{Hamiltonian with the vector potential.}$$

...

$$H = H_0 - \frac{q}{2\mu c}\boxed{\vec{A}.\vec{P}} + \boxed{\frac{q^2}{2\mu c^2}}\,\vec{A}^2$$

Too small

Coulomb gauge $\vec{A}.\vec{P} = \vec{P}.\vec{A}$

(A) Show this!

(A) $\vec{A}.\vec{P} = \dfrac{\vec{B}.\vec{L}}{2}$

$$\boxed{H = H_0 - \frac{q}{2\mu c}\,\vec{B}\cdot\vec{L} = H_0 - \vec{\mu}_L\cdot\vec{B}}$$

$$\mu_L = \frac{q}{2\mu c}\vec{L} = \frac{\mu_B}{\hbar}\vec{L} \quad : \mu_B \text{ Bohr magneton.}$$

Zeeman Effect

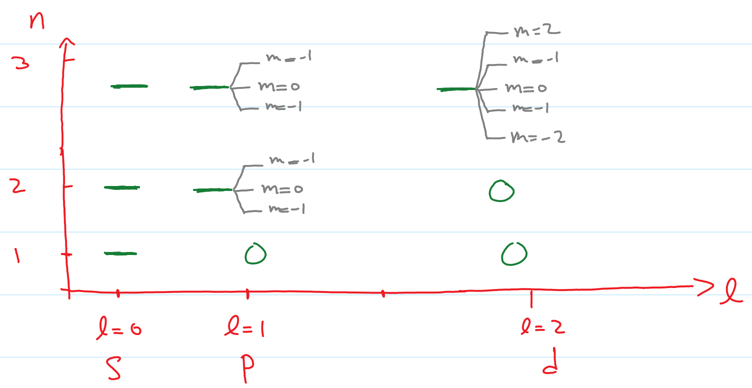
Take $B = B_z$:

$$H = H_0 - \left(\frac{q}{2\mu c} B_z\right) L_z \quad , \; q = -e$$

$$= H_0 + \frac{B_z e}{2\mu c} L_z \longrightarrow \text{Breaks the symmetry}$$

$$|n\ell m\rangle \longrightarrow E_{n,m} = \frac{-E_0}{n^2} + (\mu_B B_z)\, m$$

$$\mu_B = \frac{e\hbar}{2\mu c}$$



We still have degeneracy for ℓ.