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P1

sec 5.2. H-atom

If we consider the Hamiltonian for H-atom

$$H = \frac{P_p^2}{2m_p} + \frac{P_e^2}{2m_e} + V(\vec{r}_p - \vec{r}_e)$$

we can decoupled this two-body problem into two one-body problems. If we use the C.O.M frame.

(i) free particle (COM)

(ii) single particle of reduced mass in the potential $V(r)$

In C.O.M frame

$$r_{cm} = \frac{m_p r_p + m_e r_e}{m_p + m_e}$$

$$\vec{r} = \vec{r}_p - \vec{r}_e$$

reduced mass $\mu = \frac{m_p m_e}{m_e + m_p}$; Total mass $M = m_e + m_p$

but $\left.\begin{aligned} m_e &= 0.91 \times 10^{-30} \text{ kg} \\ m_p &= 1.67 \times 10^{-27} \text{ kg} \end{aligned}\right\} \Rightarrow \frac{m_e}{m_p} \ll 1$

using binomial expansion

$$(1+\delta)^{\alpha} = 1 + \alpha\delta + \frac{\alpha(\alpha-1)}{2!}\delta^2 + \cdots + \frac{(\alpha)(\alpha-1)\cdots(\alpha-n+1)}{n!}\delta^n$$

$$\mu = m_e\left(1 + \frac{m_e}{m_p}\right)^{-1} \simeq m_e\left(1 - \frac{m_e}{m_p}\right) \simeq m_e$$

Hamiltonian

$$H = \frac{P_{cm}^2}{2M} + \frac{\bar{P}_{rel}^2}{2\mu} + V(\vec{r})$$

If we write TISE

$$i\hbar \frac{\partial}{\partial t} \psi(r_{cm}, r_{rel}, t) = \left[\frac{P_{cm}^2}{2M} + \frac{P_{rel}^2}{2\mu} + U(\vec{r}) \right] \psi(r_{cm}, r_{rel}, t)$$

for H-atom $V(r) = -\frac{e^2}{r}$ in Gaussian units.

$\Rightarrow$ $V(r)$ time independent.

The time dependance can be seperate from the spacial part and then the spacial part can be seperated into "product functions of $\vec{r}_{cm}$ & $\vec{r}_{rel}$

Now we are considering the case of single particle of reduced mass in the potential $V(r)$
$\llcorner \!\!\to \sim m_e$ = say m

From eq^n (5.24) in last section.
the radial Shrodinger eq^n:

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

$$\Rightarrow \left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + 2\frac{me^2}{\hbar^2 r} + \frac{2mE_{kl}}{\hbar^2} \right] u_{kl}(r) = 0 \quad \text{——①}$$

(↳ has dimentions of (length)$^{-1}$

$\frac{me^2}{\hbar^2}$ define as $\frac{1}{a_0}$

where a_0 is define as Bohr radius

$$\Rightarrow a_0 = \frac{\hbar^2}{me^2}$$

Now let us change our variables as $\rho = r/a_0$

then ① $\Rightarrow$

$$\left[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{2}{\rho} + \underbrace{\frac{2ma_0^2}{\hbar^2} E_{kl}}_{\text{let us define this term as } -\lambda_{kl}^2} \right] u_{kl}(\rho) = 0 \quad \text{——②}$$

$$\Rightarrow -\lambda_{kl}^2 = \frac{2m}{\hbar^2} \left(\frac{\hbar^2}{me^2} \right)^2 E_{kl}$$

$$= \frac{2\cancel{m}}{\cancel{\hbar^2}} \frac{\hbar^{\cancel{4}\,2}}{m^{\cancel{2}}e^4} E_{kl}$$

$$= \frac{2\hbar^2}{me^4} E_{kl}$$

$$\Rightarrow E_{kl} = -\frac{me^4}{2\hbar^2} \lambda_{kl}^2 \quad \text{——③}$$

Goal: find the value for λ_{kl}.

If we consider the asymptotic behavior of eq^n (2) we can write a general solution for that.

General sol^n: $u_{kl}(\rho) = e^{-\lambda_{kl}} y_{kl}(\rho)$

by expanding $y_{kl}(\rho)$ in the powers of ρ

$$y_{kl}(\rho) = \rho^s \sum_{k=0}^{\infty} C_k \rho^k.$$

$$\Rightarrow u_{kl}(\rho) = e^{-\lambda_{kl}} \sum_{k=0}^{\infty} C_k \rho^{k+s} \quad \text{—— (4)}$$

Now we assume this solution is true for every where (i.e not only when $\rho \to \infty$)

by sub (4) in (2) an equating the coefficients of both sides we can get a relation ship as follows

$$C_k = \frac{2\left[\lambda_{kl}(k+l) - 1\right]}{k^2 + 2kl + k} C_{k-1}$$

If we consider $\dfrac{C_k}{C_{k-1}} \xrightarrow[k \to \infty]{} \dfrac{2\lambda_{kl} \cancel{k}}{k\cancel{k}} \to \dfrac{2\lambda_{kl}}{k} \to 0$

$\Rightarrow$ This can't be happen

$\Rightarrow$ q - should be finite.

$\Rightarrow$ series should terminate for physically acceptable solutions

for terminating value

$$2[a_{kl}(k+l)-1]=0$$

$$\Rightarrow a_{kl}=\frac{1}{(k+l)}$$ we found a value for a_{kl}.

$\Rightarrow$ sub in ③

$$E_{kl}=-\frac{me^4}{2\hbar^2}\frac{1}{(k+l)^2}$$

we define the principle quantum no. n as

$$n=(k+l)$$

$$\Rightarrow E_n=-\frac{me^4}{2\hbar^2}\frac{1}{n^2}. \quad \text{—⑤}$$

Now let us consider the degeneracy of E_n.

For H-atom, shells characterised by n and it contain n subshells corresponding to each l value. where l can vary $l=0,1,2,\ldots,(n-1)$

Each sub shell contain $(2l+1)$ distinct states corresponding to possible values of m.

$$m=-l,-l+1,\ldots\ldots,l-1,l.$$

$$1, 2, 3 \ldots n = \frac{n(n+1)}{2}.$$

this is due to radial w.f. is independent of quantum number m.

=> total degeneracy

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

$$= \cancel{2}\frac{(n-1)(n)}{\cancel{2}} + n$$

$$= n^2.$$

$$\Rightarrow g_n = n^2. \quad — (6)$$

Now let us discuss about the quantized energy levels of H - atom.
we analyse this by means of wave length of emitted or absorbe photons from transitions.

It is clear that photons carry the difference in energy in initial & final states

from Planck formula

$$E_{photon} = h\nu = E_i - E_n = -\frac{me^4}{2\hbar^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

but we know that $c = \nu\lambda$

$\hbar = \frac{h}{2\pi}$

$$\Rightarrow \frac{1}{\lambda} = \frac{me^4c}{4\pi\hbar^3}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \quad \text{- Rydberg formula.}$$

In page 150 fig 5.1 we can see the spectrum of H atom.

here $n_i = 1$ —> $n_f = 2, 3 ....$ – Lyman series in ultraviolet region

$n_i = 2$ —> $n_f = 3, 4, ...$ Balmer series in visible region.

$n_i = 3$ —> $n_f = 4, 5 ....$ Paschen series infrared.

Brackett.
far infrared

Pfund
far infrared

Humphreys
far infrared.