

Before we begin relativistic correction treatment
let's recall some Hydrogen properties

$$\text{Energy levels: } E_n^{(0)} = - \frac{\mu Z^2 e^4}{2 \hbar^2 n^2}$$

Introducing

Fine structure
constant

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137}$$

then

$$E_n^{(1)} = -Z^2 mc^2 \frac{1}{2n^2} \alpha^2$$

\approx rest energy of
electron mc^2

so we see
that electron
energy

$$\begin{aligned} E_n^{(1)} &\sim mc^2 \cdot \alpha^2 \\ &\sim \frac{mc^2}{137^2} \\ &\ll mc^2 \end{aligned}$$

this itself just
a "correction"
to the rest energy
of electron

Even without external fields the hydrogen-like atom energy are not what we learned in QM I!

Relativistic corrections:

We have $\hat{H}_0 = \frac{\hat{p}^2}{2\mu} - \frac{ze^2}{r}$

reduce mass \rightarrow $\frac{\hat{p}^2}{2\mu}$ Kinetic - K energy

The real kinetic energy of a particle is

actually $\hat{K} = \sqrt{(mc^2)^2 + \hat{p}^2 c^2} - mc^2$

rest mass energy \rightarrow mc^2

if 'p' is small (i.e. $v \ll c$) we can express

$$\hat{K} = (mc^2) \sqrt{1 + \frac{\hat{p}^2 c^2}{(mc^2)^2}} - mc^2$$

$\ll 1$

$$\sqrt{1+x} \approx 1 + \frac{1}{2}x - \frac{1}{8}x^2 + \dots \quad \text{Taylor series}$$

$$K = (mc^2) \left(1 + \frac{1}{2} \frac{\hat{p}^2 c^2}{(mc^2)^2} - \frac{1}{8} \left(\frac{\hat{p}^2 c^2}{(mc^2)^2} \right)^2 + \dots \right) - mc^2 = \frac{\hat{p}^2}{2m} - \frac{1}{8} \frac{\hat{p}^4}{m^3 c^2}$$

\ll since

for Hydrogen $K \sim 10\text{eV}$ but $mc^2 = 500,000\text{eV}$ non relativistic (old fashioned) kinetic energy

To derive H_0 we used $K_e + K_p$ but now we need to modify both, so

$$\hat{K} = \frac{\hat{p}_e^2}{2m_e} + \frac{\hat{p}_p^2}{8m_p^3c^2} + \frac{\hat{p}_e^2}{2m_p} + \frac{\hat{p}_p^2}{8m_p^3c^2}$$

were used in original H_0

we drop this since $m_p \gg m_e$

Now "corrected" Hamiltonian:

$$\hat{H} = \hat{H}_0 + \hat{H}_1 = \frac{\hat{p}^2}{2M} - \frac{ze^2}{r} - \frac{\hat{p}^4}{8m_e^3c^2}$$

notice $M = \frac{m_e m_p}{m_e + m_p}$ and just m_e

The rest is "easy"

$$E_{n,l,m}^{(1)} = \langle n, l, m | H_1 | n, l, m \rangle$$

What about degeneracy?

thus degeneracy in solving matrix is diagonal in $|n, l, m\rangle$ basis

$$\tilde{H}_1 = \begin{pmatrix} H_{aa} & & 0 \\ & H_{bb} & \\ 0 & & H_{cc} \end{pmatrix}$$

We are lucky $[\hat{H}_1, \hat{L}]$

and elements solutions of $\det(M_1 - E_n^{(1)}) = 0$ are given by the same eq.

We can brute force $E_{n,l,m}^{(1)}$ but *degeneracy stays due to rotational symmetry* but there are several tricks to make our life easy! *HW prove*

$$\hat{H}_1 = -\frac{(\hat{p}^2)^2}{8m_e^3 c^2} = -\left(\frac{\hat{p}^2}{2m_e}\right)^2 \frac{1}{2m_e c^2} =$$

note $\hat{H}_0 \approx \frac{\hat{p}^2}{2m_e} - \frac{ze^2}{r} \Rightarrow \frac{\hat{p}^2}{2m_e} = \hat{H}_0 + \frac{ze^2}{r}, \mu \approx m_e$

$$\hat{H}_1 = \frac{-1}{2m_e c^2} \left(\hat{H}_0 + \frac{ze^2}{r} \right)^2 =$$

$$= \frac{-1}{2m_e c^2} \left(\hat{H}_0^2 + 2\hat{H}_0 \frac{ze^2}{r} + \frac{z^2 e^4}{r^2} \right)$$

$$\langle n,l,m | \hat{H}_1 | n,l,m \rangle = \frac{-1}{2m_e c^2} \left(\left(E_n^{(0)} \right)^2 + 2E_n^{(0)} \left\langle \frac{1}{r} \right\rangle ze^2 + z^2 e^4 \left\langle \frac{1}{r^2} \right\rangle \right)$$

where $\left\langle \frac{1}{r} \right\rangle$ and $\left\langle \frac{1}{r^2} \right\rangle$

are averaged over $|n,l,m\rangle$, e.g. $\langle n,l,m | \frac{1}{r} | n,l,m \rangle$

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a_0} = -\frac{2E_n^{(0)}}{ze^2}$$

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{z^2}{(l+1/2)n^3 a_0^2} = -\frac{2E_n^{(0)}}{(l+1/2)n}$$

$$E_n^{(0)} = -\frac{\mu z^2 e^4}{2\hbar^2 n^2}, \quad a_0 = \frac{\hbar}{\mu c \alpha}$$

$\alpha = e^2/\hbar c = 1/137$
H₀ solution fine-structure const

combining terms

$$E_{n,l}^{(1)} = \frac{-1}{2m_e c^2} \left(\left(\frac{M z^2 e^4}{2 \hbar^2 n^2} \right)^2 + 2(-) \left(\frac{M z^2 e^4}{2 \hbar^2 n^2} \right) \cdot 2 + \frac{z^4 e^4}{(l + \frac{1}{2}) n^3 a_0^2} \right)$$

$$= \frac{-1}{2m_e c^2} \left[-\frac{3 M z^4}{4 n^4} \left(\frac{e^2}{\hbar c} \right)^4 \cdot c^4 + \frac{z^4 e^4}{(l + \frac{1}{2}) n^3} \left(\frac{M c d}{\hbar} \right)^2 \right]$$

$$= \frac{-1}{2m_e c^2} z^4 M^2 c^4 d^2 \left[-\frac{3}{4} \frac{d^2}{n^4} + \frac{1}{(l + \frac{1}{2}) n^3} \frac{e^4}{c^2 \hbar^2} \right]$$

$m_e \approx \mu$

$$E_{n,l}^{(1)} = \frac{z^4 d^4 M c^2}{2} \left[\frac{3}{4} \frac{1}{n^4} - \frac{1}{(l + \frac{1}{2}) n^3} \right]$$

resolve
degeneracy
in l !

recall $E_n^{(0)} = -\frac{M z^2 e^4}{2 \hbar^2 n^2} \cdot \frac{c^2}{c^2} = -\frac{z^2 d^2}{2 n^2} M c^2 = E_n^{(0)}$

thus for
Hydrogen
 $z=1$

$$\frac{E_n^{(1)}}{E_n^{(0)}} \sim d^2 = \left(\frac{1}{137} \right)^2 \ll 1, \quad \frac{E_n^{(0)}}{M c^2} \sim d^2 \ll 1$$

Notes about how to attack $\langle \frac{1}{r} \rangle$ and $\langle \frac{1}{r^2} \rangle$.

Feynman-Hellmann Theorem if $\hat{H}(\lambda)$, i.e. Hamiltonian is function of λ where λ is some variable and $\hat{H}(\lambda) |\psi(\lambda)\rangle = E(\lambda) |\psi(\lambda)\rangle$

then
$$\frac{\partial E(\lambda)}{\partial \lambda} = \langle \psi(\lambda) | \frac{\partial \hat{H}(\lambda)}{\partial \lambda} | \psi(\lambda) \rangle$$

Prove

$$\frac{\partial}{\partial \lambda} \left(\langle \psi(\lambda) | E(\lambda) | \psi(\lambda) \rangle = \langle \psi(\lambda) | \hat{H}(\lambda) | \psi(\lambda) \rangle \right)$$

$$\begin{aligned} & \left(\langle \frac{\partial \psi}{\partial \lambda} | E_\lambda | \psi_\lambda \rangle + \langle \psi | \frac{\partial E(\lambda)}{\partial \lambda} | \psi \rangle + \langle \psi | E_\lambda | \frac{\partial \psi}{\partial \lambda} \rangle \right) = \\ & = \left(\langle \frac{\partial \psi}{\partial \lambda} | \hat{H} | \psi \rangle + \langle \psi | \frac{\partial \hat{H}}{\partial \lambda} | \psi \rangle + \langle \psi | \hat{H} | \frac{\partial \psi}{\partial \lambda} \rangle \right) \end{aligned}$$

Annotations:

- Blue arrow: "just a number" pointing to $\frac{\partial E(\lambda)}{\partial \lambda}$.
- Green circles: $\langle \frac{\partial \psi}{\partial \lambda} | E_\lambda | \psi_\lambda \rangle$ and $\langle \frac{\partial \psi}{\partial \lambda} | \hat{H} | \psi \rangle$.
- Pink circles: $\langle \psi | E_\lambda | \frac{\partial \psi}{\partial \lambda} \rangle$ and $\langle \psi | \hat{H} | \frac{\partial \psi}{\partial \lambda} \rangle$.
- Blue annotations in pink circles: $\langle \psi | \hat{H} | \frac{\partial \psi}{\partial \lambda} \rangle = \langle \psi | E_\lambda | \frac{\partial \psi}{\partial \lambda} \rangle$.

$$\frac{\partial E(\lambda)}{\partial \lambda} = \langle \psi(\lambda) | \hat{H}(\lambda) | \psi(\lambda) \rangle$$

Application of R-M theorem

When solving $H_0 |\psi\rangle = E(\psi) |\psi\rangle$ we decompose

$$\hat{H}_0 = \hat{H}_r + H_{\theta,\varphi} \Rightarrow |\psi\rangle = |R_{n,l}\rangle \cdot |Y_{l,m}\rangle$$

$\Rightarrow \hat{H}_r |R_{n,l}\rangle = E_{n,l} |R_{n,l}\rangle$ exact form of it

$$\hat{H}_r = -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{\hbar^2}{2\mu} \frac{l(l+1)}{r^2} - \frac{ze^2}{r}$$

$$\ast E_{N,l} = -\frac{\mu e^4 z^2}{2\hbar^2 (N+l)^2}$$

note that familiar 'n' for full E_n solution is $n = N+l$
 ↗ radial quantum number

case $\langle \frac{1}{r} \rangle$: we see that $\frac{\partial H_r}{\partial z} = -\frac{e^2}{r}$

z is λ in R-M theorem
 thus $\langle \psi | -\frac{e^2}{r} | \psi \rangle = \frac{\partial E_{n,l}}{\partial z}$

$$\Rightarrow -e^2 \langle \frac{1}{r} \rangle = -\frac{\mu e^4 z}{\hbar^2 (N+l)^2} \Rightarrow$$

$$\langle \frac{1}{r} \rangle = \frac{\mu e^2 z}{\hbar^2 (N+l)^2}$$

compare with \ast

$$= -\frac{2E_n}{ze^2} \therefore$$

Similar idea to get $\langle \frac{1}{r^2} \rangle$ $\lambda \leftrightarrow l$

$$\frac{\delta M_r}{\delta l} = \frac{2l+1}{r^2}$$

$$\Rightarrow (2l+1) \langle \frac{1}{r^2} \rangle = \frac{\delta E_{n,l}}{\delta l} = \underbrace{-\frac{\mu e^4 z^2}{2\hbar^2}}_{-C} \frac{\partial}{\partial l} \left(\frac{1}{N+l} \right)^2$$

$$= -C (-2) (N+l)^{-3} = E_{n,l} \underbrace{\frac{(-2)}{(N+l)}}_{\sim}$$

$$\Rightarrow \langle \frac{1}{r^2} \rangle = \frac{-2 E_n}{(2l+1) \cdot n} = -\frac{E_n}{(l+\frac{1}{2}) \cdot n}$$