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

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

Introducing

Fine structure constant $\boxed{\alpha = \frac{e^2}{\hbar c} = \frac{1}{137}}$

then $\boxed{E_n^{(0)} = -Z^2 \mu c^2 \frac{1}{2n^2} \alpha^2}$

$\approx$ rest energy of electron $m_e c^2$

so we see that electron energy

$E_n^{(0)} \sim m_e c^2 \cdot \alpha^2$

$\sim \frac{m_e c^2}{137^2}$

$\ll m_e c^2$

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 V!

Relativistic corrections:

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

reduce mass

Kinetic energy - K

The real kinetic energy of a particle is actually $\hat{K} = \sqrt{(mc^2)^2 + \hat{p}^2c^2} - mc^2$

rest mass energy

if "p" is small (i.e. $v << c$) we can express

$$\hat{K} = (mc^2)\sqrt{\left(1 + \underbrace{\frac{\hat{p}^2c^2}{(mc^2)^2}}_{<<1}\right)} - mc^2$$

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

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

$x <<$ since for Hydrogen $K \sim 10\,eV$ but $m_ec^2 \simeq 500'000\,eV$

non relativistic (old fashion) kinetic energy

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

$$\hat{K} = \frac{\hat{p}_e^2}{2m_e} + \frac{\hat{p}_e^4}{8m_e^3c^2} + \frac{\hat{p}_p^2}{2m_p} + \cancel{\frac{\hat{p}_4^2}{8m_p^3c^2}} \to 0$$

we drop this since $m_p \gg m_e$

were used in original H_0

Now "corrected" Hamiltonian:

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

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

The rest is "easy" $\boxed{E^{(1)}_{n,\ell,m} = \langle n,\ell,m | H_1 | n,\ell,m \rangle}$

What about degeneracy? We are lucky $[\hat{H}_1, \hat{L}]$ $[\hat{H}_1, L_z]$

thus degeneracy involving matrix is diagonal in $|n,\ell,m\rangle$ basis

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

and elements solutions of $\det(H_1 - E_n^{(1)}) = 0$ are given by the same eq.

We can brute force $E^{(1)}_{n,l,\cancel{m}}$ but there are several tricks to make our life easy

degeneracy stays due to rotational symmetry

HW prove

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

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

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

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

$$\langle n,l,m|H_1|n,l,m\rangle = \frac{-1}{2m_e c^2}\left(\left(E_n^{(0)}\right)^2 + 2E_n^{(0)}\left\langle\frac{1}{r}\right\rangle Ze^2 + Z^2 e^4\left\langle\frac{1}{r^2}\right\rangle\right)$$

wrere $\left\langle\frac{1}{r}\right\rangle$ and $\left\langle\frac{1}{r^2}\right\rangle$ are averaged over $|n,l,m\rangle$, e.g. $\langle n,l,m|\frac{1}{r}|n,l,m\rangle$

$$\boxed{\begin{aligned} \left\langle\frac{1}{r}\right\rangle &= \frac{1}{n^2 a_0} = -\frac{2E_n^{(0)}}{Ze^2} \\ \left\langle\frac{1}{r^2}\right\rangle &= \frac{Z^2}{(l+1/2)n^3 a_0^2} = -\frac{2E_n^{(0)}}{(l+\frac{1}{2})n} \end{aligned}}$$

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

$\hat{H}_0$ solution

fine-structure const $\alpha = e^2/\hbar c = \frac{1}{137}$

combining terms

$$E^{(1)}_{n,\ell} = \frac{-1}{2m_e c^2}\left(\left(\frac{\mu z^2 e^4}{2\hbar^2 n^2}\right)^2 + 2(-)\left(\frac{\mu z^2 e^4}{2\hbar^2 n^2}\right)\cdot 2 + \frac{z^4 e^4}{(\ell+\frac{1}{2})n^3 a_0^2}\right)$$

$$= \frac{-1}{2m_e c^2}\left[-\frac{3}{4}\frac{\mu^2 z^4}{n^4}\underbrace{\left(\frac{e^2}{\hbar c}\right)^4}_{\alpha^4}\cdot c^4 + \frac{z^4 e^4}{(\ell+\frac{1}{2})n^3}\left(\frac{\mu c\alpha}{\hbar}\right)^2\right]$$

$$= \frac{-1}{2m_e c^2} z^4 \mu^2 c^4 \alpha^2\left[-\frac{3}{4}\frac{\alpha^2}{n^4} + \frac{1}{(\ell+\frac{1}{2})n^3}\underbrace{\frac{e^4}{c^2\hbar^2}}_{\alpha^2}\right]$$

$m_e \simeq \mu$

$$\boxed{E^{(1)}_{n,\ell} = \frac{z^4\alpha^4\mu c^2}{2}\left[\frac{3}{4}\frac{1}{n^4} - \frac{1}{(\ell+\frac{1}{2})n^3}\right]}$$

resolve degeneracy in ℓ !

recall $E^{(0)}_n = -\frac{\mu z^2 e^4}{2\hbar^2 n^2}\cdot\frac{c^2}{c^2} = \boxed{-\frac{z^2\alpha^2}{2n^2}\mu c^2 = E^{(0)}_n}$ ($=\alpha^2$)

thus for Hydrogen $z=1$

$$\frac{E^{(1)}_n}{E^{(0)}_n} \sim \alpha^2 = \left(\frac{1}{137}\right)^2 \ll 1, \quad \frac{E^{(0)}_n}{\mu c^2} \sim \alpha^2 \ll 1$$

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

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

Prove

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

Just a number

$$\cancel{\langle \tfrac{\partial \psi}{\partial \lambda} | E_\lambda | \psi_\lambda \rangle} + \langle \psi | \frac{\partial E(\lambda)}{\partial \lambda} | \psi \rangle + \cancel{\langle \psi | E_\lambda | \tfrac{\partial \psi}{\partial \lambda} \rangle} =$$

$$= \cancel{\langle \tfrac{\partial \psi}{\partial \lambda} | \underbrace{H|\psi\rangle}_{E(\lambda)|\psi\rangle}} + \langle \psi | \frac{\partial H}{\partial \lambda} | \psi \rangle + \cancel{\underbrace{\langle \psi | H}_{\substack{\langle \psi | H^\dagger \\ E(\lambda)\langle \psi |}} | \tfrac{\partial \psi}{\partial \lambda} \rangle}$$

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

Application of F-H theorem

when solving $H_0|\psi\rangle = E|\psi\rangle$ we decompose

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

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

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

$$* \quad E_{N,\ell} = -\frac{\mu e^4 Z^2}{2\hbar^2(N+\ell)^2}$$

, note that familiar 'n' for full E_n solution is $n = N+\ell$

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 F-H theorem

thus $\langle\psi| -\frac{e^2}{r}|\psi\rangle = \frac{\partial E_{N,\ell}}{\partial Z}$

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

compare with *

$$= -\frac{2E_n}{Ze^2}$$

$\therefore$

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

$$\frac{\partial H_r}{\partial \ell} = \frac{2\ell + 1}{r^2}$$

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

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

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