Relativistic Corrections to Hydrogen

For hydrogen, $\hat{H} = \hat{p}^2/2m + U(r)$ w/ $\hat{\vec{p}} \to \frac{\hbar}{i}\nabla$.
Coulomb

The Hamiltonian here comes from the non-relativistic

$$E = p^2/2m + U$$

The relativistic energy of a (classical) particle is:

$$E = \frac{mc^2}{\sqrt{1-v^2/c^2}} + U \qquad (*)$$

which can be written in terms of the relativistic momentum:

$$\vec{p} = \frac{m\vec{v}}{\sqrt{1-v^2/c^2}} \longrightarrow p^2(1-v^2/c^2) = m^2v^2$$

or

$$v^2(m^2 + p^2/c^2) = p^2 \text{ so that } v^2 = \frac{(p/m)^2}{1+(p/mc)^2}$$

we want

$$1 - v^2/c^2 = \frac{1}{(1+(p/mc)^2)} \Rightarrow \frac{1}{\sqrt{1-v^2/c^2}} = \sqrt{1+\left(\frac{p}{mc}\right)^2}$$

the Hamiltonian form of $(*)$ is:

$$E = mc^2\sqrt{1+(p/mc)^2} + U \qquad (\circ)$$

What happens if we try to make this eqn. into a quantum Hamiltonian operator?

$$E\psi = mc^2\left(1 - \frac{\hbar^2}{m^2c^2}\nabla^2\right)^{1/2}\psi + U\psi \quad \ldots ?$$

Instead, let's Taylor expand $(\circ)$ for $p \ll (mc)$ (non-relativistic limit) first,

$f(\epsilon) = \sqrt{1+\epsilon}$ for $\epsilon \equiv (p/mc)^2$, has

$$\begin{aligned} &\doteq 1 + \epsilon f'(0) + \tfrac{1}{2}\epsilon^2 f''(0) + \cdots \\ &= 1 + \frac{\frac{1}{2}\epsilon}{\sqrt{1+\epsilon}}\Big|_{\epsilon=0} - \frac{(\frac{1}{2}\epsilon^2)\frac{1}{4}}{(1+\epsilon)^{3/2}}\Big|_{\epsilon=0} + \cdots \\ &= 1 + \tfrac{1}{2}\epsilon - \tfrac{1}{8}\epsilon^2 + \cdots \end{aligned}$$

then $(\circ)$ becomes:

$$E \approx mc^2\left(1 + \frac{p^2}{2m^2c^2} - \frac{1}{8}\frac{p^4}{m^4c^4}\right) + U$$

$$\doteq mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + U$$

constant offset to U is irrelevant ... ?

as a Hamiltonian operator, we have:

$$\hat{H} = \underbrace{\frac{\hat{p}^2}{2m} + U}_{\hat{H}^0} \underbrace{- \frac{\hat{p}^4}{8m^3c^2}}_{\hat{H}'}$$

w/ $\hat{H}^0$ the hydrogen Hamiltonian, & $\hat{H}'$ a new, perturbing, piece.

The hydrogen states have "a lot" of degeneracy, so we need to find a Hermitian op. $\hat{A}$ w/

$$[\hat{H}^0, \hat{A}] = 0 \quad \& \quad [\hat{H}', \hat{A}] = 0$$

w/ $\hat{A}|n\ell m\rangle$ producing distinct e-vals for energy-degenerate states.

candidate: $\hat{L}_z$ - that's Hermitian, commutes w/ $\hat{H}^0$ (spherically symmetric potential), commutes w/ $\hat{p}^2$ ($\hat{p}$ is a vector op.) & therefore $\hat{p}^4$, so

$$[\hat{H}^1, \hat{L}_z] = 0$$

and has: $\hat{L}_z|n\ell m\rangle = \hbar m|n\ell m\rangle$

$$\hat{L}_z|n\ell m'\rangle = \hbar m'|n\ell m'\rangle$$

(distinct e-vals for states w/ the same energy)

Similarly for $\hat{L}^2$, we have $[\hat{H}^0, \hat{L}^2] = 0 = [\hat{H}^1, \hat{L}^2]$ w/

$$\hat{L}^2|n\ell m\rangle = \hbar^2 \ell(\ell+1)|n\ell m\rangle$$

$$\hat{L}^2|n\ell' m\rangle = \hbar^2 \ell'(\ell'+1)|n\ell' m\rangle$$

& the hydrogenic states are already the "good" linear combinations for this perturbation.

1st order energy corrections are:

$$E_n^1 = \langle n\ell m|\hat{H}^1|n\ell m\rangle = -\frac{1}{8m^3c^2}\langle n\ell m|\hat{p}^4|n\ell m\rangle$$

$$= -\frac{1}{8m^3c^2}\langle \hat{p}^2 n\ell m|\hat{p}^2|n\ell m\rangle \quad (\hat{p}^4 \text{ is Hermitian})$$

& we need $\hat{p}^2|n\ell m\rangle$ - go back to the unperturbed problem:

$$\frac{\hat{p}^2}{2m}|n\ell m\rangle + U|n\ell m\rangle = E_n^0|n\ell m\rangle \Rightarrow$$

$$\hat{p}^2|n\ell m\rangle = 2m(E_n^0 - U)|n\ell m\rangle$$

& $E_n^1 = -\frac{1}{2mc^2}\langle n\ell m|(E_n^0 - U)^2|n\ell m\rangle$

$$= -\frac{1}{2mc^2}\left(E_n^{0\,2} - 2E_n^0\langle U\rangle + \langle U^2\rangle\right)$$

(expectation values taken w.r.t. $|n\ell m\rangle$)

w/ $\langle U\rangle \sim \langle \frac{1}{r}\rangle$ & $\langle U^2\rangle \sim \langle \frac{1}{r^2}\rangle$.

<u>Virial Theorem</u> & <u>$\langle U\rangle$</u>

In CM, for a potential energy U that can sustain UCM:

$$\frac{mv^2}{r} = \frac{dU}{dr} \Rightarrow \underbrace{2T}_{\text{kinetic energy.}} = r\frac{dU}{dr}$$

& for $U = U_c = \frac{-e^2}{4\pi\epsilon_0 r}$, $r\frac{dU_c}{dr} = \frac{e^2}{4\pi\epsilon_0 r} = -U_c$

so that $2T = -U$ in this case.

Then in the Ehrenfest-ian way, we expect

$$2\langle T\rangle = -\langle U\rangle$$

& going back to the base Hamiltonian:

$$E_n^0|n\ell m\rangle = \hat{T}|n\ell m\rangle + U|n\ell m\rangle$$

so

$$E_n^0 = \langle \hat{T}\rangle + \langle U\rangle \quad (\text{hitting both sides w/ } \langle n\ell m|)$$

$$= \tfrac{1}{2}\langle U\rangle \Rightarrow \boxed{\langle U\rangle = 2E_n^0}$$

Feynman-Hellman Theorem to $\langle \frac{1}{r^2} \rangle$

For a Hamiltonian w/ parameter μ, $\hat{H}(\mu)$, suppose you have:

$$\hat{H}(\mu)|\psi(\mu)\rangle = E(\mu)|\psi(\mu)\rangle \quad (*)$$

take the derivative of $(*)$ w.r.t. μ,

$$\frac{\partial \hat{H}}{\partial \mu}|\psi\rangle + \hat{H}\frac{\partial|\psi\rangle}{\partial \mu} = \frac{\partial E}{\partial \mu}|\psi\rangle + E\frac{\partial|\psi\rangle}{\partial \mu}$$

& hit both sides w/ $\langle\psi|$ (& $\langle\psi|\psi\rangle = 1$)

$$\langle\psi|\frac{\partial \hat{H}}{\partial \mu}|\psi\rangle + \underbrace{\langle\psi|\hat{H}\cdot\frac{\partial|\psi\rangle}{\partial \mu}}_{=E\langle\psi|\frac{\partial|\psi\rangle}{\partial\mu}} = \frac{\partial E}{\partial \mu} + E\langle\psi|\frac{\partial|\psi\rangle}{\partial \mu}$$

$\leftarrow$ cancels

we get

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

that's the Feynman-Hellman theorem.

For the hydrogen Hamiltonian & energies:

$$\hat{H}^0 = \frac{\hat{p}_r^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2 l(l+1)}{2mr^2}$$

$$E_n^0 = -\frac{\hbar^2}{2ma^2}\cdot\frac{1}{(N+l)^2}$$

$\leftarrow$ Bohr radius

If we take $\mu = l$ as the parameter,

we get: $\frac{\partial \hat{H}^0}{\partial l} = \frac{\hbar^2}{2m}\cdot\frac{(2l+1)}{r^2}$ $\leftarrow$ oh!

& $\frac{\partial E_n^0}{\partial l} = \frac{\hbar^2}{ma^2}\cdot\frac{1}{n^3}$.

& then $(\circ)$ gives:

$$\frac{\hbar^2}{ma^2 n^3} = \frac{\hbar^2(2l+1)}{2m}\left\langle\frac{1}{r^2}\right\rangle \Rightarrow \boxed{\left\langle\frac{1}{r^2}\right\rangle = \frac{2}{a^2 n^3(2l+1)} = \frac{1}{a^2 n^3(l+1/2)}}$$

Putting it all together!

$$E_n^1 = -\frac{1}{2mc^2}\left((E_n^0)^2 - 2E_n^0\langle u\rangle + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle\right)$$

$$= -\frac{1}{2mc^2}\left((E_n^0)^2 - 2E_n^0(2E_n^0) + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\cdot\frac{1}{a^2(l+1/2)n^3}\right)$$

$$= -\frac{(E_n^0)^2}{2mc^2}\left(\frac{4n}{l+1/2} - 3\right)$$