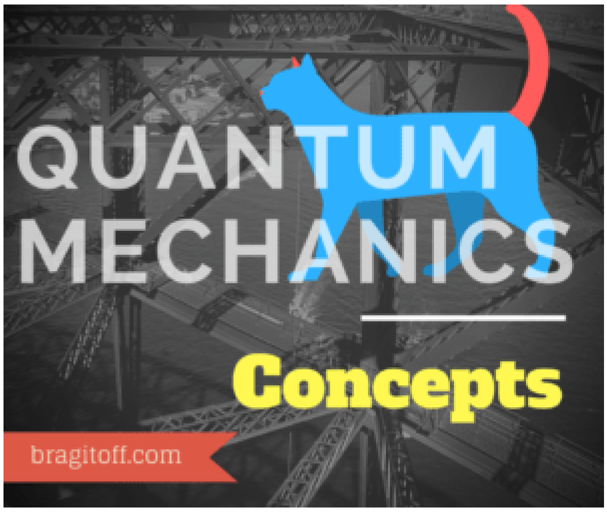
In this post, I will use the stationary(time-independent) first order perturbation theory, to find out the relativistic correction to the Energy of the nth state of an Hydrogen Atom.



In order to find out the relativistic correction to the Energy, we would need to consider and use relativistic relations. The relativistic Kinetic Energy is given as:

$$T = \sqrt{p^2c^2 + m^2c^4} - mc^2$$

The first term in the above equation is the total energy of a relativistic particle and the second term is the rest mass energy of a particle. So we get the Kinetic energy by subtracting those.

$$\implies T = mc^2\sqrt{1 + \frac{p^2c^2}{m^2c^4}} - mc^2$$

Now, using the binomial expansion on the Kinetic energy we can write it as:

$$T = mc^2(1 + \frac{1}{2}\frac{p^2c^2}{m^2c^4} - \frac{1}{8}\left(\frac{p^2c^2}{m^2c^4}\right)^2 + ...) - mc^2$$

Note Binomial Expansion: $(1+x)^n = 1 + nx + n(n-1)\frac{x^2}{2} + \ldots$

$$\implies T = (mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3c^4} + ...) - mc^2$$

If we ignore the rest of the higher order terms and take only the first three terms of the Binomial expansion, then

$$\implies T = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2}$$

We can now see that the Kinetic Energy is actually modified and not just $\frac{p^2}{2m}$ as in the classical case. Since the second term would be very small due to c^2 in the denominator, we can take it as a perturbation, and use the time-independent perturbation theory to find out the correction to the energy levels.

Let perturbation, $H' = -\frac{p^4}{8m^3c^2}$

Then the first order energy correction to the nth level is given as:

$$E_n^1 = \langle\psi_n|\, H' \,|\psi_n\rangle$$
$$\implies E_n^1 = -\frac{1}{8m^3c^2}\langle\psi_n|\, p^4 \,|\psi_n\rangle$$

From Schrodinger's Equation:

$\frac{p^2}{2m}\left|\psi_n\right\rangle + V\left|\psi_n\right\rangle = E_n\left|\psi_n\right\rangle$
$\implies p^2\left|\psi_n\right\rangle = 2m(E_n - V)\left|\psi_n\right\rangle$

Using the above relation,

$$\implies E_n^1 = -\frac{1}{8m^3c^2}\left\langle\psi_n\right|\left(2m(E_n - V)\right)^2\left|\psi_n\right\rangle$$
$$\implies E_n^1 = -\frac{1}{2mc^2}\left\langle\psi_n\right|\left(E_n^2 + V^2 - 2E_nV\right)\left|\psi_n\right\rangle$$
$$\implies E_n^1 = -\frac{1}{2mc^2}\left(E_n^2 + \left\langle V^2\right\rangle - 2E_n\left\langle V\right\rangle\right)$$

From Virial Theroem for Hydrogen atom, we know that the expectation value of V:

$$\left\langle V\right\rangle = 2E_n$$
$$\implies E_n^1 = -\frac{1}{2mc^2}\left(E_n^2 + \left\langle V^2\right\rangle - 4E_n^2\right)$$
$$\implies E_n^1 = -\frac{1}{2mc^2}\left(\left\langle V^2\right\rangle - 3E_n^2\right)$$

So it all boils down to finding the expectation value of V^2.

To do that we would need to use the following relations, from the Harmonic Oscillator:

$$V = -\frac{e^2}{4\pi\epsilon_0 r}$$
$$\implies V^2 = \left(\frac{e^2}{4\pi\epsilon_0 r}\right)^2$$
$$\implies \left\langle V^2\right\rangle = \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle$$

So we need to find the expectation value of $\frac{1}{r^2}$ for H-atom.

We already did this in this post, using the Hellmann-Feynman Theorem and found that:

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

Substituting this back in equation

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

We know that,

$$E_n = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{1}{n^2}$$

and, $a = \frac{4\pi\epsilon_0\hbar^2}{mc^2}$

Therefore,

$$\implies E_n^1 = -\frac{1}{2mc^2}\left(\frac{-E_n 2\hbar^2}{mn^2a^2(l+\frac{1}{2})} - 3E_n^2\right)$$

$$\implies E_n^1 = -\frac{1}{2mc^2}\left(\frac{-E_n 2\hbar^2}{m(l+1/2)n}\left(\frac{mc^2}{4\pi\epsilon_0\hbar^2}\right)^2 - 3E_n^2\right)$$

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

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

If you have any questions or doubts regarding the above proof, feel free to post a comment down below.

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