

12.3.3: Kinetic Energy Corrections

Before claiming that this formula explains the fine structure of the hydrogen atom, however, one needs to be careful. The correction is of the order α^4 , which means it is of the order v^4 , where v is the electron speed. The kinetic energy used in the Hamiltonian when solving the Schrödinger equation was just $p^2/2m$, which contributed to order α^2 . However, the next term in the expansion of the true relativistic kinetic energy is of order p^4 and hence will contribute to order α^4 . So if one wishes to quote the energy splittings of the hydrogen atom accurate to order α^4 , one had better include the contribution from this further correction.

The relativistic kinetic energy of the electron can be expanded in terms of momentum as

$$T = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \dots \quad (12.3.3.1)$$

Therefore, the correction to the Hamiltonian is

$$\Delta H_{rel} = -\frac{1}{8m^3c^2}p^4. \quad (12.3.3.2)$$

At first sight, this looks quite complicated, since it involves the operator $p^4 = \hbar^4 \nabla^4$. However, one can make use of the fact that

$$\frac{p^2}{2m} = E_n - V \quad (12.3.3.3)$$

to get

$$\Delta H_{rel} = -\frac{1}{2mc^2} (E_n^2 - 2E_n V + V^2). \quad (12.3.3.4)$$

With $V = -Ze^2/r$, applying first-order perturbation theory to this Hamiltonian reduces to the problem of finding the expectation values of r^{-1} and r^{-2} . This can be done with some effort, and the result is

$$\Delta E_{rel} = -(Z\alpha)^4 mc^2 \frac{1}{2n} \left[\frac{1}{(l + \frac{1}{2})} - \frac{3}{4n} \right]. \quad (12.3.3.5)$$

Combining this equation with

$$\Delta E_{so} = (Z\alpha^4) mc^2 \frac{[j(j+1) - l(l+1) - \frac{3}{4}]}{4n^3 l (l + \frac{1}{2}) (l + 1)}, \quad (12.3.3.6)$$

from the previous page and using the fact that $j = l - 1/2, l + 1/2$, the complete energy correction to order $(Z\alpha)^4$ may be written

$$\Delta E_{fs} = \Delta E_{rel} + \Delta E_{so} = -(Z\alpha)^4 mc^2 \frac{1}{2n} \left[\frac{1}{(j + \frac{1}{2})} - \frac{3}{4n} \right]. \quad (12.3.3.7)$$

This energy correction depends only on j and is called the fine structure of the hydrogen atom, since it is of order $\alpha^2 \sim 10^{-4}$ times smaller than the principle energy splittings. This is why α is known as the fine-structure constant. The fine structure of the hydrogen atom is illustrated in figure 4. Note that all levels are shifted down from the Bohr energies, and that for every n and l there are two states corresponding to $j = l - 1/2$ and $j = l + 1/2$, except for s states. Also note that states with the same n and j but different l have the same energies, though this will be shown later not to be true due an effect know as the Lamb shift. As an aside, these fine structure splittings were derived by Sommerfeld by modifying the Bohr theory to allow elliptical orbits and then calculating the energy differences between the different states due to differences in the average velocity of the electron. By using the wrong method he got exactly the right answer, a coincidence which caused much confusion at the time.

Strictly speaking, the last equation has only been shown to be correct for $l \neq 0$ states, although it turns out to be correct for all l . To do the calculation correctly for $l = 0$, one needs to include the effect of an additional term in the Hamiltonian known as the Darwin term, which is purely an effect of relativistic quantum mechanics and can only be understood in the context of the Dirac theory. It is therefore appropriate to discuss the Dirac theory to achieve a more complete understanding of the fine structure of the hydrogen atom.

Contributors and Attributions

- Randal Telfer (JWST Astronomical Optics Scientist, Space Telescope Science Institute)

This page titled [12.3.3: Kinetic Energy Corrections](#) is shared under a [CC BY-NC-SA 2.0](#) license and was authored, remixed, and/or curated by [Niels Walet](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.