

Relativistic correction in hydrogen

The electron in light hydrogen-like atoms (Z is small) does not move very fast. Indeed, if we take the ground state ($n=1$), in which the average kinetic energy is

$$\langle T \rangle = -\frac{1}{2} \langle V \rangle = -E_{n=1} = \frac{m}{2\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2}$$

and interpret it classically as $T = \frac{mv^2}{2}$ (where v is the "speed" of the electron), we will find that

$$v = \frac{Ze^2}{4\pi\epsilon_0\hbar} = \frac{Ze^2}{4\pi\epsilon_0\hbar c} c = \alpha Zc \quad (c \text{ is the speed of light})$$

The dimensionless quantity α has a special place in physics

$$\alpha = \begin{cases} \frac{e^2}{4\pi\epsilon_0\hbar c} & (\text{SI units}) \\ \frac{e^2}{\hbar c} & (\text{Gauss units}) \\ \frac{1}{c} & (\text{atomic units}) \end{cases} \approx \frac{1}{137}$$

and is called the fine structure constant. α is considerably smaller than 1. Therefore, the non-relativistic description of the electron in hydrogen by means of the Schrödinger equation with the Hamiltonian

$$H_0 = \frac{p^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r}$$

should be adequate for many practical purposes. Still, one may ask how relativism affects the energy spectrum of hydrogen. An investigation of this kind can be attempted at different levels of theory. A more systematic (and more complicated) treatment would start from the Dirac equation. A more practical

way, however, is to use the perturbation theory. This is the approach we will adopt below.

In general, there are three equally important physical effects that cause shifting and/or splitting of the energy levels in hydrogen: 1) correction to the kinetic energy formula due to finite value $\frac{v}{c}$ 2) interaction of the electron spin with its orbital angular momentum 3) rapid trembling motion of the electron (zitterbewegung) that smears out its Coulomb interaction with the nucleus. All these give rise to the so-called fine structure of the energy levels. Because the shifts of the energies caused by the above effects are small, the use of the perturbation theory is justified.

In general we can represent the total Hamiltonian as a series in powers of α :

$$H = H_0 + \alpha^2 H_2 + \alpha^3 H_3 + \alpha^4 H_4 + \dots$$

It turns out the terms proportional to α^1 are absent in this expansion (we will see why). Then the energy can be written as a series in powers of α as well:

$$E = E^{(0)} + \alpha^2 E_2^{(1)} + \dots$$

where $E_2^{(1)}$ is the expectation value of H_2 with proper zero-order wave functions.

Let us now focus on the relativistic correction to the kinetic energy formula. In our original non-relativistic Hamiltonian we had the following expression for the kinetic energy

$$T = \frac{p^2}{2m}$$

This expression, however, is purely non-relativistic. The relativistic formula that connects the kinetic energy (which is the total energy minus the rest energy) to the momentum of a particle is

$$p^2 c^2 + m^2 c^4 = E_{\text{tot}}^2 = (T + mc^2)^2$$

Solving for T we obtain

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

If $\frac{p}{mc} \ll 1$ then we can Taylor expand the last expression:

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

(here we used the fact that $(1+x)^{\alpha} = 1 + \alpha x + \frac{\alpha(\alpha-1)x^2}{2!} + \dots$)

$$= \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2} + \dots$$

With that we can identify the lowest order relativistic perturbation:

$$H'_{\text{rel}} = -\frac{p^4}{8m^3 c^2}$$

It should be noted that in the above formulae \vec{p} is the relativistic momentum. It is the former that we now associate with the operator $-i\hbar \nabla$. Now we can proceed further and use the first order perturbation theory to evaluate the corrections to the energy levels of hydrogen. Since the eigenstates of H_0 are highly degenerate (the degeneracy of E_n is n^2) we need to employ the perturbation theory for degenerate levels. It turns out, however, that the matrix of the perturbation Hamiltonian is diagonal in $\psi_{n\ell m}$, i.e. the hydrogenic wave functions already form a proper zero-order basis.

Let us prove a more general statement now:

If operator A commutes with both H_0 and H' then the eigenfunctions of A (and, simultaneously, H_0) that correspond to distinct eigenvalues form a proper zero-order basis (i.e. the basis in which H' is diagonal).

We will do it for the case of q -fold degenerate states (that is $\psi_1, \psi_2, \dots, \psi_q$ correspond to the same energy value). Suppose ψ_i and ψ_j are degenerate eigenfunctions of H_0 and are at the same time non-degenerate eigenfunctions of A :

$$A\psi_i = a_i\psi_i \quad A\psi_j = a_j\psi_j \quad a_i \neq a_j \quad i, j = 1 \dots q$$

Then since $[A, H'] = 0$ we can write

$$0 = \langle \psi_i | [A, H'] | \psi_j \rangle = \langle \psi_i | AH' - H'A | \psi_j \rangle = \langle A\psi_i | H' | \psi_j \rangle - \langle \psi_i | H' | A\psi_j \rangle = (a_i - a_j) \langle \psi_i | H' | \psi_j \rangle \Rightarrow H'_{ij} = 0 \text{ for } i \neq j \quad i, j = 1 \dots q$$

Going back to our perturbation, $H'_{\text{rel}} = -\frac{p^4}{8m^3c^2}$, where $p^2 = p_r^2 + \frac{L^2}{r^2}$ and

$$p_r^2 = \hbar^2 \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \quad L^2 = \hbar^2 \left(\frac{1}{\sin^2 \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \quad L_z = -i\hbar \frac{\partial}{\partial \phi}$$

We can easily see that

$$[p^2, L^2] = [p_r^2, L^2] + \left[\frac{L^2}{r^2}, L^2 \right] = 0$$

$$[p^2, L_z] = [p_r^2, L_z] + \left[\frac{L^2}{r^2}, L_z \right] = 0$$

and, further,

$$[p^4, L^2] = 0 \quad [p^4, L_z] = 0$$

Now we can relate this to our general statement above. In this case our A is the set of operators

L^2 and L_z . They commute with both H_0 and H' . Additionally, L^2, L_z and H_0 have mutual eigenfunctions. While eigenfunctions H_0 are degenerate (except for the ground states) these same eigenfunctions correspond to distinct sets of eigenvalues of L^2, L_z ($\hbar^2 l(l+1)$ & $\hbar m$)

Therefore we can conclude that H'_{rel} is diagonal in the basis of hydrogenic wave functions $\Psi_{n\ell m}$ that correspond to the same value of the principle quantum number n . For example, for the first excited state ($n=2$) we have a four-fold degeneracy:

$$1. \quad n=2 \quad n_r=1 \quad \ell=0 \quad m=0$$

$$2. \quad n=2 \quad n_r=0 \quad \ell=1 \quad m=1$$

$$3. \quad n=2 \quad n_r=0 \quad \ell=1 \quad m=0$$

$$4. \quad n=2 \quad n_r=0 \quad \ell=1 \quad m=-1$$

$$\langle \Psi_{n\ell m} | H'_{rel} | \Psi_{n\ell' m'} \rangle = A_{n\ell m} \delta_{\ell\ell'} \delta_{mm'}$$

As a result of H'_{rel} being diagonal in the $\Psi_{n\ell m}$ basis we can use the formulae for the non-degenerate perturbation theory.

$$E_{n\ell m}^{(1)} = \langle \Psi_{n\ell m} | H'_{rel} | \Psi_{n\ell m} \rangle = -\frac{1}{8m^3c^2} \langle \Psi_{n\ell m} | p^4 | \Psi_{n\ell m} \rangle =$$

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

[Note: the Hermiticity of operator p^2 does not take place in the case $\ell=0$. However, it turns out the final result for the energy correction is correct even for $\ell=0$ states]

From the Schrödinger equation we know that

$$p^2 \Psi = 2m(E^{(0)} - V)\Psi$$

So

$$E_{n\ell m}^{(1)} = -\frac{1}{2mc^2} \langle \Psi_{n\ell m} | (E_n^{(0)} - V)^2 | \Psi_{n\ell m} \rangle = -\frac{1}{2mc^2} [E_n^{(0)2} - 2E_n^{(0)} \langle V \rangle + \langle V^2 \rangle]$$

where $V = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}$. We can also write it as

$$E_{n\ell m}^{(1)} = -\frac{1}{2mc^2} \left[E_n^{(0)2} + 2E_n^{(0)} \frac{Ze^2}{4\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle_{n\ell m} + \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle_{n\ell m} \right]$$

The expectation values of $\langle \frac{1}{r} \rangle$ and $\langle \frac{1}{r^2} \rangle$ with hydrogenic wave functions can be easily evaluated or found in tables/textbooks:

$$\langle \Psi_{n\ell m} | \frac{1}{r} | \Psi_{n\ell m} \rangle = \frac{1}{n^2 a} \quad \text{where } a = \frac{4\pi\epsilon_0 \hbar^2}{m e^2 Z} \text{ is the Bohr radius}$$

$$\langle \Psi_{n\ell m} | \frac{1}{r^2} | \Psi_{n\ell m} \rangle = \frac{1}{(l + \frac{1}{2}) n^3 a^2}$$

With that the corrections to the hydrogen energy levels due to relativistic effect become

$$E_{n\ell}^{(1)} = -\frac{1}{2mc^2} \left[E_n^{(0)2} + 2E_n^{(0)} \left(\frac{Ze^2}{4\pi\epsilon_0} \right) \frac{1}{n^2 a} + \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2 \frac{1}{(l + \frac{1}{2}) n^3 a^2} \right]$$

We can rearrange this formula by noting that

$$E_n^{(0)} = -\frac{m}{2\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2} \quad \frac{e^2 Z}{4\pi\epsilon_0} = \frac{\hbar^2}{ma^2} \quad E_n^{(0)} = -\frac{\hbar^2}{2m} \frac{1}{a^2 n^2}$$

the formula becomes, after reduction

$$E_{n\ell}^{(1)} = -\frac{E_n^{(0)2}}{2mc^2} \left[\frac{4n}{l + \frac{1}{2}} - 3 \right] < 0$$

Alternatively we can use the fact that $E_n^{(0)} = -\frac{1}{2n^2} mc^2 \alpha^2$ and

rewrite it as

$$E_{n\ell}^{(1)} = -\frac{1}{8n^4} \left[\frac{4n}{l + \frac{1}{2}} - 3 \right] mc^2 \alpha^4$$

We can see that the n^2 -degeneracy is partially lifted due to the relativism ($E^{(1)}$ depends not only on n but also on l). However, the levels corresponding to the same value of m quantum number remain intact.