Relativistic correction in hydrogen

The electron in light hydrogen-like atoms (Z is small) is not very fast and the non-relativistic description in terms of the Schrödinger equation with the Hamiltonian

$$H^0 = \frac{p^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}$$

is quite appropriate. Still, one may ask how relativistic effects affect the energy spectrum. 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, which we will be adopting in this lecture.

It turns out there are three equally important effects that cause shifts of the energy levels in hydrogen: 1) correction to the kinetic energy formula; 2) the interaction of the electron's spin with its orbital angular momentum 3) rapid trembling motion of the electron (zitterbewegung). All these give rise to the so-called fine structure of the energy levels. Because the shifts of the energies caused by the above effect are small, the use of the perturbation theory is justified. The small perturbations are smaller than the Bohr (i.e. nonrelativistic) energy by a factor of α^2. Here

$$\alpha = \begin{cases} \dfrac{e^2}{4\pi\varepsilon_0\hbar c} & (\mathrm{SI}) \\ \dfrac{e^2}{\hbar c} & (\mathrm{Gauss}) \end{cases} \approx \frac{1}{137}$$

In general, we can look for the energies as a series in terms of the powers of α:

$$E_n = E_n^{(0)} + \alpha^2 E_n^{(2)} + \alpha^3 E_n^{(3)} + \ldots$$

While the Hamiltonian is given by

$$H = H^{0} + \alpha^{2} H^{(2)} + \alpha^{3} H^{(3)} + \ldots$$

It turns out the terms proportional to α^{1} are absent in this expansion.

Let us first consider the relativistic correction to the motion of the electron in hydrogen.

In our original Hamiltonian we had the following expression for the kinetic energy

$$T = \frac{p^2}{2m} \quad \left(\begin{array}{l}\text{if we could talk about the "velocity" that} \\ \text{would be } T = \frac{mv^2}{2}\end{array}\right)$$

This expression, however, is classical. The relativistic formula that connects the kinetic energy (which is the total energy minus the rest energ) is

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

or, solving for T:

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

If we introduce a small parameter $\frac{p}{mc} << 1$ then we can Taylor expand the last expression:

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

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

$$= \frac{p^2}{2m} - \frac{1}{8m^3c^2}p^4 + \ldots$$

With that we can see that the lowest order relativistic perturbation is

$$H^{1}_{rel} = -\frac{p^4}{8m^3c^2}$$

It should be noted that in the above formulae p is the relativistic momentum. It is the former that we now associate with the operator $-i\hbar\nabla$.

Now we can use the first order perturbation theory to evaluate the corrections to the energy levels. Since the eigenstates of H^0 are highly degenerate (the degeneracy of E_n is n^2) we need to use the perturbation theory for degenerate levels. It turns out, however, that the matrix of the perturbation Hamiltonian is diagonal in ψ_{nlm}, i.e. hydrogenic wave functions already form a correct 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 H_0) that correspond to distinct eigenvalues form the correct zero-order basis (i.e. the basis in which H' is diagonal). We will do it for a case of two-fold degenerate levels.

Suppose ψ_i and ψ_j are degenerate eigenfunctions of H^0 and are at the same time nondegenerate eigenfunctions of A:

$$A\psi_i = a_i\psi_i \qquad A\psi_j = a_j\psi_j \qquad a_i \neq a_j$$

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

$$0 = \langle\psi_i|[A,H']|\psi_j\rangle = \langle\psi_i|AH'-H'A|\psi_j\rangle = \langle A\psi_i|H'|\psi_j\rangle -$$

$$-\langle\psi_i|H'|A\psi_j\rangle = (a_i - a_j)\langle\psi_i|H'|\psi_j\rangle$$

Hence $H'_{ij} = 0 \quad i \neq j$

Going back to our perturbation, $H'_{rel} = -\frac{p^4}{8m^3c^2}$,

where $p^2 = p_r^2 + \frac{L^2}{r^2}$

$$p_r^2 = \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \qquad L^2 = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

$$L_z = -i\hbar\frac{\partial}{\partial\phi}$$

we can easily see that $[p^2, L^2] = 0$ $[p^2, L_z] = 0$

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

Thus, H'_{rel} is diagonal in the basis of the eigenfunctions of L^2 and L_z (which the hydrogenic wave functions are) that correspond to the same n quantum number. For example for the first excited state ($n=2$) we have four-fold degeneracy:

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

$$\langle \psi_{n\ell m} | p^4 | \psi_{n\ell' m'} \rangle = A_{n\ell m}\delta_{\ell\ell'}\delta_{mm'}$$

As a result we can use the formulae for the nondegenerate perturbation theory. Hence,

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

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

From the Schrödinger equation we know that

$$p^2\psi = 2m(E^{(0)} - V)\psi \quad , \text{ so}$$

$$E^{(1)}_{n\ell m} = -\frac{1}{2mc^2}\langle \psi_{n\ell m} | (E^{(0)}_n - V)^2 | \psi_{n\ell m} \rangle = -\frac{1}{2mc^2}\left[E^{(0)2}_n - 2E^{(0)}_n\langle V\rangle + \langle V^2\rangle\right]$$

Now since for hydrogen $V = -\frac{1}{4\pi\varepsilon_0}\frac{Z}{r}$ we get

$$E_n^{(1)} = -\frac{1}{2mc^2}\left[E_n^{(0)2} + 2E_n^{(0)}\frac{e^2}{4\pi\varepsilon_0}\left\langle\frac{Z}{r}\right\rangle + \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\left\langle\frac{Z}{r^2}\right\rangle\right]$$

The expectation values of $\langle\frac{1}{r}\rangle$ and $\langle\frac{1}{r^2}\rangle$ can be found in tables:

$$\langle\psi_{nlm}|\frac{1}{r}|\psi_{nlm}\rangle = \frac{1}{n^2a}$$

$a = \frac{4\pi\varepsilon_0\hbar^2}{me^2Z}$ - Bohr radius

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

With that the corrections to the energy levels become

$$E_{nl}^{(1)} = -\frac{1}{2mc^2}\left[E_n^{(0)2} + 2E_n^{(0)}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\frac{1}{n^2a} + \left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\frac{1}{(l+\frac{1}{2})n^3a^2}\right]$$

since $E_n^{(0)}$ can be expressed through a:

$$E_n^{(0)} = -\frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\frac{1}{n^2} \qquad \frac{e^2Z}{4\pi\varepsilon_0} = \frac{\hbar^2}{ma}$$

$$E_n^{(0)} = -\frac{\hbar^2}{2m}\frac{1}{a^2n^2}$$

we can rewrite the expression for $E_{nl}^{(1)}$ as

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

We can see that the degeneracy is partially lifted due to the relativistic correction ($E^{(1)}$ depends not only on n but also on l)