ENTRI

FINE STRUCTURE OF HYDROGEN - RELATIVISTIC CORRECTION

One of the main applications of perturbation theory is the study of the fine structure of the hydrogen atom spectrum. There are several effects that cause adjustments to the energy levels, so we'll look at some of them in the next few posts.

One adjustment arises from relativity. This is a bit problematical, since the Schrödinger equation is designed to be a non-relativistic model, and if we want to study relativistic quantum mechanics we should really use a proper relativistic model like the Dirac equation. However, when the effects of relativity are small, as they are expected to be in the case of the hydrogen atom, since the electron's kinetic energy is quite small, we can get some idea of the correction due to relativity from perturbation theory. The argument goes as follows.

The kinetic energy term in the non-relativistic theory is

$$T = \frac{p^2}{2m} \tag{1}$$

where the momentum operator is $p = -i\hbar\nabla$.

In relativity, the total energy of a free particle (no potential energy) is

$$E = \frac{mc^2}{\sqrt{1 - v^2/c^2}} \equiv \gamma mc^2 \tag{2}$$

where m is the rest mass and v is the particle's speed. The kinetic energy is then the total energy minus the rest energy:

$$T = (\gamma - 1)mc^2 \tag{3}$$

Relativistic (3-d) momentum is defined as

$$p = \gamma mv \tag{4}$$

so

$$
\begin{aligned}
\left(T+mc^2\right)^2 &= \gamma^2 m^2 c^4 && (5)\\
&= \gamma^2\left[(mvc)^2-(mvc)^2+\left(mc^2\right)^2\right] && (6)\\
&= p^2c^2+\gamma^2\left(mc^2\right)^2\left(1-v^2/c^2\right) && (7)\\
&= p^2c^2+\left(mc^2\right)^2 && (8)
\end{aligned}
$$

The relativistic kinetic energy is then

$$
\begin{aligned}
T &= \sqrt{p^2c^2+(mc^2)^2}-mc^2 && (9)\\
&= mc^2\left[\sqrt{1+(pc/mc^2)^2}-1\right] && (10)
\end{aligned}
$$

If the momentum is small compared to the rest mass, we can expand the square root in a Taylor series:

$$T=\frac{p^2}{2m}-\frac{p^4}{8m^3c^2}+\ldots \qquad (11)$$

The lowest order perturbation is then

$$T_1=-\frac{p^4}{8m^3c^2} \qquad (12)$$

There is a technical point here which I've not seen addressed anywhere I've found this topic covered. At this point it is usually asserted (or sometimes just glossed over without comment) that the p in this expression can be represented by the same operator $-i\hbar\nabla$ as in the non-relativistic case. In our original argument in which this identification was made, we arrived at the formula by computing the mean velocity $\langle v\rangle$ and then saying that $\langle p\rangle = m\langle v\rangle$. Perhaps the assumption that p still has this form in the relativistic equation is another approximation, but it's not clear. In any event, it appears that when the correct Dirac equation is applied, we do get the same answer, so the results appear to be valid.

In any case, we can now apply perturbation theory to get the relativistic energy correction. Since the energy levels of the hydrogen atom are degenerate (the energy depends only on the quantum number n so the energy is the same for all values of l and m), we might think we need to apply degenerate perturbation theory. However, we can recall a theorem that we proved earlier which states that if we can find an operator that commutes with the unperturbed hamiltonian and the perturbation, then the eigenvectors of that operator can be used as the 'special' states and we can get away with using the non-degenerate theory. In this case, the stationary states ψ_{nlm} are eigenstates of the angular momentum operators L^2 and L_z and these two operators commute with p^2 and p^4, so the ψ_{nlm} functions are already the special states and we can just apply non-degenerate theory using these functions directly.

That is, we can write

$$E_{n1} = -\frac{1}{8m_e^3c^2}\langle nlm| p^4 |nlm\rangle \tag{13}$$

where we've denoted the electron mass by m_e to distinguish it from the L_z quantum number m.

At this point, we might be tempted to use the fact that p^2 is hermitian when applied to hydrogen wave functions to write

$$E_{n1} = -\frac{1}{8m_e^3c^2}\langle p^2nlm| p^2nlm\rangle \tag{14}$$

However, as we saw in the last post, this is not true in general since p^4 is not hermitian in the case $l = 0$. This is because $p^2\psi_{nlm}$ is not a hydrogen wave function.

Most derivations push ahead with this equation in any case and, as luck would have it, the resulting analysis actually does give the right answer. We know this because the relativistic Dirac equation can be solved exactly for hydrogen and gives the same answer. It's worth remembering, however, that the derivation given here is flawed.

In any case, proceeding from the last equation, we can use the fact that

$$\frac{p^2}{2m_e}|nlm\rangle = (E_{n0} - V)|nlm\rangle \tag{15}$$

so

$$E_{n1} = -\frac{1}{2m_ec^2}\langle nlm|(E_{n0} - V)^2|nlm\rangle \tag{16}$$

$$= -\frac{1}{2m_ec^2}\left(E_{n0}^2 - 2E_{n0}\langle V\rangle + \langle V^2\rangle\right) \tag{17}$$

At this point, it's worth making a comment on something Griffiths says in his derivation in his section 6.3.1. He says that the derivation up to this

point is 'entirely general', whereas it isn't really, since it relies on two things: first, that we can use non-degenerate perturbation theory (which is true in this case only because the wave functions happen to be the 'special' functions) and second, we have been lucky with our assumption that we can shift the operator p^2 from ket to bra and thus get an expression in terms of
E_{n0} and V.

Carrying on from above, we can now plug in the hydrogen potential

$$V = -\frac{e^2}{4\pi\epsilon_0 r} \tag{18}$$

and we get

$$E_{n1} = -\frac{1}{2m_e c^2}\left(E_{n0}^2 + 2\frac{e^2}{4\pi\epsilon_0}E_{n0}\left\langle\frac{1}{r}\right\rangle + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle\right) \tag{19}$$

We can get the first average from the virial theorem applied to hydrogen, since we found that (using the Bohr radius $a = 4\pi\epsilon_0\hbar^2/m_e e^2$)

$$\langle V \rangle = 2E_{n0} \tag{20}$$

$$-\frac{e^2}{4\pi\epsilon_0}\left\langle\frac{1}{r}\right\rangle = -2\frac{m_e}{2\hbar^2 n^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 = -\frac{\hbar^2}{m_e}\frac{1}{a^2 n^2} \tag{21}$$

$$-\frac{\hbar^2}{m_e a}\left\langle\frac{1}{r}\right\rangle = -\frac{\hbar^2}{m_e}\frac{1}{a^2 n^2} \tag{22}$$

$$\left\langle\frac{1}{r}\right\rangle = \frac{1}{an^2} \tag{23}$$

The derivation of the second average can be done using the FeynmanHellmann theorem:

$$\left\langle\frac{1}{r^2}\right\rangle = \frac{1}{\left(l+\frac{1}{2}\right)n^3 a^2} \tag{24}$$

The first order relativistic correction is then

$$E_{n1} = -\frac{1}{2m_e c^2}\left(E_{n0}^2 + 2\frac{e^2}{4\pi\epsilon_0}E_{n0}\frac{1}{an^2} + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{1}{\left(l+\frac{1}{2}\right)n^3 a^2}\right) \tag{25}$$

Substituting for a we get

$$E_{n1} = -\frac{1}{2m_e c^2}\left(E_{n0}^2 + 2\frac{m_e}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 E_{n0}\frac{1}{n^2} + \left[\frac{m}{\hbar}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]^2 \frac{1}{\left(l+\frac{1}{2}\right)n^3}\right) \tag{26}$$

Finally, using

$$E_{n0} = -\frac{m_e}{2\hbar^2 n^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \tag{27}$$

we get

$$E_{n1} = -\frac{1}{2m_e c^2}\left(E_{n0}^2 - 4E_{n0}^2 + \frac{4nE_{n0}^2}{l+\frac{1}{2}}\right) \tag{28}$$

$$= -\frac{E_{n0}^2}{2m_e c^2}\left(\frac{4n}{l+\frac{1}{2}} - 3\right) \tag{29}$$

Note that the degeneracy in l has been split, since the relativistic correction depends on l, whereas the original energy E_{n0} depended only on n. The degeneracy on the L_z quantum number m remains however.

PINGBACKS

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