Applications of perturbation theory to the hydrogen atom

The Hamiltonian of an electron in the hydrogen atom is

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} - \frac{q^2}{r} \qquad (1)$$

where

$$q^2 = \frac{e^2}{4\pi\varepsilon_0} \qquad (2)$$

This Hamiltonian represents only the brute part of the whole story. In reality there are several additional terms to be included. However, these terms are all much smaller than typical energies of Eq (1), so they may be treated as perturbations

The energy levels of $\hat{H}_0$ are

$$E_n = -\frac{mq^4}{2n^2\hbar^2} = -\frac{q^2}{2n^2a_0} \qquad (3)$$

The typical energies involved are of the order of

$$E_1 \simeq -13.6\ eV \qquad (4)$$

It is convenient to define the the fine structure constant

$$\boxed{\alpha = \frac{q^2}{\hbar c} \simeq \frac{1}{137}} \qquad (5)$$

this dimensionless constant is commonly used in particle physics. In terms of α, Eq (3) becomes

$$E_n = -\frac{\alpha^2 mc^2}{2n^2} \qquad (6)$$

So the typical energies are of order $\alpha^2 mc^2$. For an electron

$$mc^2 \simeq 511\ \text{keV} \qquad (7)$$

there are a series of corrections to Eq (6) which are all of order $\alpha^4 mc^2$ these are called the fine structure of hydrogen and will be discussed next. then there is another correction which is of order $\alpha^5 mc^2$ related to the quantization of the electromagnetic field. this is called the Lamb shift and requires a more sofisticated theory called quantum electrodynamics. then there is also a correction of the order $\alpha^6 mc^2$ called the hyperfine structure and related to the interaction between the spin of the electron and the spin of the proton

Bohr energies	$\alpha^2 mc^2$
Fine structure	$\alpha^4 mc^2$
Lamb shift	$\alpha^5 mc^2$
Hyperfine structure	$\alpha^6 mc^2$.

Review of the Hydrogen atom

The unperturbed Hydrogen atom with Hamiltonian $\hat{H}_0$ is usually attributed to have 3 quantum numbers

$$\begin{aligned} n &= 1, 2, 3, \ldots \\ \ell &= 0, 1, \ldots, n-1 \\ -\ell \leqslant m_\ell &\leqslant \ell \qquad \Delta m_\ell = 1 \end{aligned} \tag{8}$$

However, the energy happens to depend only on n.

In fact, there are 4 quantum numbers because we must also consider the spin. So the correct basis is

$$|n \, \ell \, m_\ell \, m_s\rangle \tag{9}$$

where $m_s = \pm 1/2$. If you want to be very rigorous, there is actually a fifth quantum number, which is the total spin $s = 1/2$. But since this is always fixed we don't bother writting it. In fact, recall that

$$\hat{S}^2 = \frac{1}{4}\left(\hat{\sigma}_x^2 + \hat{\sigma}_y^2 + \hat{\sigma}_z^2\right) = \frac{3}{4} \tag{10}$$

which matches with $s(s+1) = \frac{1}{2}\left(\frac{1}{2}+1\right) = \frac{3}{4}$.

If a problem does not involve spin, we may simply write $|n, \ell, m_\ell\rangle$.

e Hamiltonian H_0 is invariant under rotations since e potential is central. It is also independent of spin. Thus

$$[\hat{H}_0, \hat{L}_z] = [\hat{H}_0, \hat{L}^2] = [\hat{H}_0, \hat{S}_z] = 0 \qquad (11)$$

oreover, $\hat{S}_z$, $\hat{L}_z$ and $\hat{L}^2$ all commute among themselves. In fact, the eigenvectors $|n\,\ell\,m_\ell\,m_s\rangle$ <u>simultaneously</u> diagonalize 5 operators :

$$\hat{H}_0 \,|n\,\ell\,m_\ell\,m_s\rangle = E_n \,|n\,\ell\,m_\ell\,m_s\rangle \qquad (12a)$$

$$\hat{L}^2 \,|n\,\ell\,m_\ell\,m_s\rangle = \ell(\ell+1)\,|n\,\ell\,m_\ell\,m_s\rangle \qquad (12b)$$

$$\hat{L}_z \,|n\,\ell\,m_\ell\,m_s\rangle = m_\ell \,|n\,\ell\,m_\ell\,m_s\rangle \qquad (12c)$$

$$\hat{S}^2 \,|n\,\ell\,m_\ell\,m_s\rangle = \frac{3}{4}\,|n\,\ell\,m_\ell\,m_s\rangle \qquad (12d)$$

$$\hat{S}_z \,|n\,\ell\,m_\ell\,m_s\rangle = m_s \,|n\,\ell\,m_\ell\,m_s\rangle \qquad (12e)$$

Fine structure : relativistic correction

The first correction to the hydrogen energies is relativistic. We used a kinetic energy

$$T = \frac{p^2}{2m} \qquad (13)$$

But the correct formula is actually

$$T = \sqrt{m^2c^4 + p^2c^2} - mc^2 \qquad (14)$$

Quick review : the energy is

$$E = \frac{mc^2}{\sqrt{1-(v/c)^2}}$$

Since $E = mc^2$ if $v = 0$, the remainder must be kinetic energy. Thus

$$T = \frac{mc^2}{\sqrt{1-(v/c)^2}} - mc^2$$

We also define momentum as

$$p = \frac{mv}{\sqrt{1-(v/c)^2}}$$

With a little algebra we then get to Eq (14) the electron in a hydrogen atom is not very relativistic

$\supset$ $$p^2c^2 << m^2c^4$$

thus we may expand

$$T = mc^2\sqrt{1+\left(\frac{p}{mc}\right)^2} - mc^2$$

$$= mc^2\left[1 + \frac{1}{2}\left(\frac{p}{mc}\right)^2 - \frac{1}{8}\left(\frac{p}{mc}\right)^4 + \cdots\right] - mc^2$$

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

Thus, the first correction due to relativistic motion may be described by the perturbation

$$V_r = -\frac{p^4}{8m^3c^2} \qquad (15)$$

Now note that $\hat{p}^4$ is a scalar operator, so it commutes with L^2 and L_z. This means that the basis $|n\,\ell\,m_\ell\rangle$ (or $|n\,\ell\,m_\ell\,m_s\rangle$ if you want) is a good basis for the problem; we may use non-degenerate perturbation theory. Thus

$$E_r^1 = \langle n\,\ell\,m_\ell|\,\hat{V}_r\,|n\,\ell\,m_\ell\rangle \tag{16}$$

Please note the huge simplification that this is. Otherwise we would have to use degenerate perturbation theory, which is much more complicated.

From Eq (1) we know that

$$\left(\frac{\hat{p}^2}{2m} - \frac{q^2}{r}\right)|n\,\ell\,m_\ell\rangle = E_n\,|n\,\ell\,m_\ell\rangle$$

thus

$$\hat{p}^2\,|n\,\ell\,m_\ell\rangle = 2m\,(E_n + q^2/\hat{r})\,|n\,\ell\,m_\ell\rangle$$

We may use this trick to write

$$E_r^1 = -\frac{1}{8m^3c^2}\,\langle n\,\ell\,m_\ell|\,\hat{p}^4\,|n\,\ell\,m_\ell\rangle$$

$$= -\frac{1}{8m^3c^2}\,(2m)^2\,\langle n\,\ell\,m_\ell|\,(E_n + q/\hat{r})^2\,|n\,\ell\,m_\ell\rangle$$

Here we used the fact that $\hat{p}^2$ is Hermitian so we may also act with it on the left. In Griffith's book there is a confusion about $\hat{p}^4$ being Hermitian or not. Of course it is

$$(\hat{p}^4)^\dagger = \hat{p}^\dagger\,\hat{p}^\dagger\,\hat{p}^\dagger\,\hat{p}^\dagger = \hat{p}^4$$

He later put a correction to this in his website.

o

$$E_r^1 = -\frac{4m^2}{8m^3c^2}\langle n\ell m_\ell|\left[E_n^2 + \frac{2E_n q^2}{\hat r} + \frac{q^4}{\hat r^2}\right]|n\ell m_\ell\rangle$$

ext we use some results about the hydrogen atom

$$\langle n\ell m_\ell|\frac{1}{\hat r}|n\ell m_\ell\rangle = \frac{1}{a_0 n^2}$$

$$\langle n\ell m_\ell|\frac{1}{\hat r^2}|n\ell m_\ell\rangle = \frac{1}{a_0^2 n^3(\ell+1/2)}$$

here

$$a_0 = \hbar^2/mq^2$$

us

$$2E_n q^2\langle n\ell m_\ell|1/\hat r|n\ell m_\ell\rangle = \frac{2E_n q^2}{n^2 a_0} = 2E_n\left[-2E_n\right]$$

$$= -4(E_n)^2$$

$$q^4\langle n\ell m_\ell|1/\hat r^2|n\ell m_\ell\rangle = \frac{q^4}{a_0^2}\frac{1}{n^3}\frac{1}{\ell+1/2} = \left[\frac{q^2}{n^2 a_0}\right]^2\frac{n}{\ell+1/2}$$

$$= \frac{4(E_n)^2 n}{\ell+1/2}$$

Combining everything

$$E_r^1 = -\frac{(E_n)^2}{mc^2}\left[1 - 4 + \frac{4n}{\ell+1/2}\right]$$

or

$$\boxed{E_r^1 = \frac{(E_n)^2}{mc^2}\left[3 - \frac{4n}{\ell+1/2}\right]} \qquad (17)$$

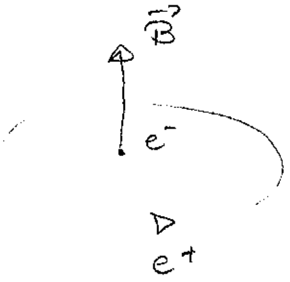
Fine - structure : spin - orbit coupling

The total magnetic moment of the electron has 2 parts: orbital and spin

$$\vec{\mu} = \mu_B \left[\vec{L} + g_e \vec{S} \right] \qquad (18)$$

where $g_e \approx 2$. But notice that both are quite different if you look up close because the spin is well localized around the electron whereas $\vec{L}$ is spread around the whole orbit.

The spin is a permanent magnetic moment of the electron, so it is like having a magnet orbiting around a charged particle (the nucleus). Now let us look at this from the reference frame of the electron. It is like the proton is orbiting around him



The proton orbiting around the electron produces a magnetic field $\vec{B}$ which interacts with the spin of the electron.

I will give here a semi-classical discussion.

we can find this field using the Biot-Savart law

$$B = \frac{\mu_0 I}{2r}$$

the current is $I = e/T$, where T is the period of the rbit, which is

$$\frac{1}{T} = \frac{v}{2\pi r}$$

Thus

$$B = \frac{\mu_0 c}{4\pi r^2} v = \frac{\mu_0 e}{4\pi r^3} \frac{m v r}{\hbar} \frac{\hbar}{m}$$

we now recognize $\frac{mvr}{\hbar}$ as the angular momentum of the electron. the directions of $\vec{L}$ and $\vec{B}$ are also the same so we may finally write

$$\vec{B} = \frac{\hbar \mu_0 c}{4\pi m r^3} = \frac{\hbar e \vec{L}}{4\pi(\epsilon_0 c^2) m r^3}$$

where I used that $c = \frac{1}{\sqrt{\epsilon_0 \mu_0}}$

This field $\vec{B}$ interacts with the spin of the electron by means of

$$V_{SO} = -\vec{\mu}\cdot\vec{B} = \mu_B g_e \vec{S}\cdot\vec{B}$$

$$= \frac{e\hbar}{2m} g_e \frac{e\hbar}{4\pi(\epsilon_0 c^2) m r^3} \vec{S}\cdot\vec{L}$$

$$= g_e \underbrace{\frac{e^2}{4\pi\epsilon_0}}_{q^2} \frac{\hbar^2}{m^2c^2} \frac{1}{2r^3} \vec{S}\cdot\vec{L}$$

Thus

$$V_{SO} = g_e \frac{q^2\hbar^2}{2m^2c^2r^3} \vec{S}\cdot\vec{L}$$

However, this was all done in the reference frame of the electron, which is not inertial! There is a correction to this called the Thomas precession which turns out to be a multiplication by 1/2. Since $g_e \approx 2$ anyway, we may write

$$\boxed{V_{SO} = \frac{q^2\hbar^2}{2mc^2r^3} \vec{S}\cdot\vec{L}} \qquad (19)$$

This is called the <u>spin-orbit interaction</u>, and it is very important in atomic physics, as well as condensed matter physics. This coupling was historically very important because in certain atoms, such as sodium, the relativistic correction was not capable of explaining the experimentally observed splittings of the energy levels (the yellow color of the street lamp is actually a doublet).

this led Uhlenbeck and Goudsmit to propose in 1925 he spin of the electron as an intrinsic magnetic moment.

The perturbation $\vec{L}\cdot\vec{S}$ does not commute with S_z or L_z. Hence the eigenvectors $|m\ell\, m_\ell\, m_s\rangle$ are no longer the good basis.

But $\vec{S}\cdot\vec{L}$ is a scalar operator and therefore should be invariant under rotations. However, the generator of rotation must be the total angular momentum

$$\vec{J} = \vec{L} + \vec{S} \tag{20}$$

Indeed, you may check that

$$[\vec{L}\cdot\vec{S}, J_z] = [\vec{L}\cdot\vec{S}, J^2] = 0$$

Moreover, since $\hat{H}_0$ also commutes with $\vec{J}$ (since it commutes with $\vec{L}$ and $\vec{S}$), we may use as a good basis the vectors $|m\ell\, j\, m_j\rangle$ which simultaneously diagonalize $\hat{H}_0, \hat{L}^2, \hat{J}^2, \hat{J}_z$:

$$\hat{H}_0|m\ell\, j\, m_j\rangle = E_m|m\ell\, j\, m_j\rangle \tag{21a}$$

$$\hat{L}^2|m\ell\, j\, m_j\rangle = \ell(\ell+1)|m\ell\, j\, m_j\rangle \tag{21b}$$

$$\hat{J}^2|m\ell\, j\, m_j\rangle = j(j+1)|m\ell\, j\, m_j\rangle \tag{21c}$$

$$\hat{J}_z|m\ell\, j\, m_j\rangle = m_j\, |m\ell\, j\, m_j \tag{21d}$$

The allowed values of j are determined as follows. Consider two vectors $\vec{u}$ and $\vec{v}$. The smallest and largest possible magnitudes of $\vec{w} = \vec{u} + \vec{v}$ is $|\vec{u} - \vec{v}|$ and $|\vec{u} + \vec{v}|$, which is obtained when they are either anti-parallel or parallel.

-lore it is no different. the smallest and largest values of j are

$$|l - 1/2| \leq j \leq l + 1/2 \qquad (22)$$

Since $\hat{J}^2$ is an angular momentum operator, we know that j will always move in integer steps.

Moreover,

$$-j \leq m_j \leq j \qquad \Delta m_j = 1 \qquad (23).$$

hich is always true for an angular momentum operator thus, in the $|n l j m_j\rangle$ basis the quantum numbers vary as

$$\begin{aligned} & n = 1, 2, 3, \ldots \\ & l = 0, 1, \ldots, n-1 \\ & j = l + 1/2 \text{ or } l - 1/2 \\ & -j \leq m_j \leq j \qquad \Delta m_j = 1 \end{aligned} \qquad (24)$$

Now we may compute the perturbation using the non-degenerate formula

$$E_{so}^{1} = \langle n \ell j m_j | \hat{V}_{so} | n \ell j m_j \rangle$$

$$= \frac{q^2 \hbar^2}{2m^2c^2} \langle n \ell j m_j | \frac{\vec{S}\cdot\vec{L}}{r^3} | n \ell j m_j \rangle$$

But

$$\hat{J}^2 = \hat{L}^2 + \hat{S}^2 + 2\,\vec{S}\cdot\vec{L}$$

$$\Rightarrow \quad \vec{S}\cdot\vec{L} = \frac{\hat{J}^2 - \hat{L}^2 - \hat{S}^2}{2} = \frac{\hat{J}^2 - \hat{L}^2 - 3/4}{2}$$

thus $\vec{S}\cdot\vec{L}$ is diagonal in the $|n \ell j m_j\rangle$ basis

$$\vec{S}\cdot\vec{L}\,|n \ell j m_j\rangle = \left[\frac{j(j+1) - \ell(\ell+1)}{2} - 3/4\right] |n \ell j m_j\rangle$$

Moreover,

$$\langle n \ell j m_j | \frac{1}{r^3} | n \ell j m_j \rangle = \frac{1}{a_0^3 n^3} \frac{1}{\ell(\ell+1)(\ell+1/2)}$$

So

$$E_{so}^{1} = \frac{q^2 \hbar^2}{2m^2c^2} \frac{1}{n^3} \left(\frac{m q^2}{\hbar^2}\right)^3 \frac{1}{2} \cdot \frac{j(j+1) - \ell(\ell+1) - 3/4}{(\ell+1)(\ell+1/2)}$$

Simplifying:

$$\frac{m^3 q^8 \hbar^2}{2m^2c^2 n^3 \hbar^6} \frac{1}{2} = \frac{1}{mc^2} \left[\frac{m^2 q^8}{\hbar^4} \frac{1}{4n^4}\right] n = \frac{n\,(E_n)^2}{mc^2}$$

NJS

$$\boxed{E_{so}^{1} = \frac{(E_n)^2}{mc^2} \; \frac{n\left[j(j+1) - \ell(\ell+1) - 3/4 \right]}{\ell(\ell+1)(\ell+1/2)}} \qquad (25)$$

this is the spin - orbit contribution to the fine structure.

Fine-structure: combining the two results

We now add Eq's (17) and (25)

$$E^1_{fs} = \frac{(E_n)^2}{mc^2}\left\{ \frac{4n}{l+1/2} - 3 + \frac{n[j(j+1) - l(l+1)]}{l(l+1)(l+1/2)} \right\}$$

In order to simplify we must recall that $j = l+1/2$ or $l-1/2$

The final result is

$$\boxed{E^1_{fs} = \frac{(E_n)^2}{2mc^2}\left[3 - \frac{4n}{j+1/2} \right]} \qquad (26)$$

Since $mc^2 \sim 500\,\text{keV}$ and $E_1 \sim 13.6\,\text{eV}$, we get

$$\frac{E_1}{mc^2} \sim \alpha^2 \sim 10^{-5}$$

This shows that these corrections are indeed much smaller than the typical energies of the Hydrogen atom.

The entire energy of the Hydrogen atom will now depend on 2 quantum numbers: n and j. The final formula s neatly written as

$$\boxed{E_{nj} = -\frac{13.6\,\text{eV}}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)\right]} \qquad (27)$$

he ordering is the following:

$n = 1 \rightarrow l = 0 \rightarrow j = 1/2$ ($-1/2$ is not allowed because $j > 0$)

this is called a $1S_{1/2}$ state and the energy is $E_{1,1/2}$

$n = 2 \rightarrow l = 0 \rightarrow j = 1/2$, $2S_{1/2}$ with $E_{2,1/2}$

$\quad \hookrightarrow l = 1 \rightarrow j = 1/2$, $2P_{1/2}$ with $E_{2,1/2}$

$\quad\quad \hookrightarrow j = 3/2$, $2P_{3/2}$ with $E_{2,3/2}$

tc. This notation is commonly used in spectroscopy.

$$\boxed{\underset{n}{2}\;\underset{l}{P}\;\underset{j}{{}_{1/2}}}$$

Note how the fine structure does not split the ground tate, but only the excited states.

Hyperfine Structure

The hyperfine structure corresponds to the interaction between the magnetic moment of the proton's spin and the magnetic moment of the electron (spin + orbital). The magnetic moment of the proton is

$$\vec{\mu}_p = g_p \mu_N \vec{S}_p \qquad (28)$$

where $\mu_N = e\hbar/2m_p$ is the nuclear magneton and $g_p = 5.59$ is the gyromagnetic ratio of the proton.

This magnetic moment generates a magnetic field, which we know from magnetostatics to be

$$\vec{B} = \frac{\mu_0}{4\pi r}\left[3(\vec{\mu}_p \cdot \hat{r})\hat{r} - \vec{\mu}_p\right] + \frac{2\mu_0}{3}\delta(\vec{r})\vec{\mu}_p \qquad (29)$$

We will consider only the case of the ground-state, since it is the only one without a fine structure splitting. For the ground state $l=0$ so we only need to worry about spin. The energy of interaction is then

$$V = -\vec{\mu}_e \cdot \vec{B} = -\frac{\mu_0}{4\pi r}\left[3(\vec{\mu}_p\cdot\hat{r})(\vec{\mu}_e\cdot\hat{r}) - \vec{\mu}_p\cdot\vec{\mu}_e\right] + \\ - \frac{2\mu_0}{3}\delta(\vec{r})\,\vec{\mu}_p\cdot\vec{\mu}_e$$

In the ground state the wave functions are spherically symmetrical so the average of $(\vec{\mu}_p \cdot \vec{r})(\vec{\mu}_e \cdot \vec{r})$ will e zero. Thus

$$E^1 = -\frac{2\mu_0}{3} \langle \delta(\vec{r}) \vec{\mu}_p \cdot \vec{\mu}_e \rangle$$

$$= -\frac{2\mu_0}{3} [\mu_N g_p \vec{S}_p] \cdot [-\mu_B g_e \vec{S}_e] \langle \delta(\vec{r}) \rangle$$

But

$$\langle \delta(\vec{r}) \rangle = \int \delta(\vec{r}) \, |\psi_{100}(r)|^2 \, dV$$

$$= |\psi_{100}(0)|^2 = \frac{1}{\pi a_0^3}$$

Hence

$$E^1 = \frac{2\mu_0}{3} \frac{\mu_N g_p \mu_B g_e}{\pi a_0^3} \vec{S}_p \cdot \vec{S}_e$$

Now:

$$\vec{S} = \vec{S}_e + \vec{S}_p$$

$$S^2 = S_e^2 + S_p^2 + 2 \vec{S}_e \cdot \vec{S}_p$$

$$\vec{S}_e \cdot \vec{S}_p = \frac{S^2 - 3/2}{2} = \frac{S^2}{2} - \frac{3}{4}$$

If the spin is 1, S^2 has eigenvalue 2, and if it is 0, it has eigenvalue 0. Thus

$$\frac{S^2}{2} - \frac{3}{4} = \begin{cases} 1/4 & (\text{triplet}) \\ -3/4 & (\text{singlet}) \end{cases}$$

Hence the energy difference is

$$\boxed{\Delta E = \frac{2\mu_0}{3} \frac{\mu_N \mu_B g_e g_p}{\pi a_0^3} \simeq 5.88 \times 10^{-6}\,\text{eV}.} \tag{30}$$