

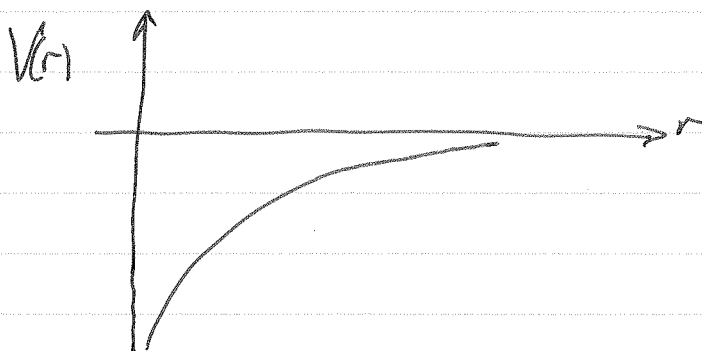
Hydrogen I

1.

We'll start by quickly reviewing the gross structure of the Hydrogen atom. The Hamiltonian is

$$H = \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r}, \quad m = \text{reduced mass} = \frac{m_e m_p}{m_e + m_p}$$

Note that the potential is negative



This means that we expect bound states to have negative energy - to knock the electron out so that it can get, just, to $r = \infty$ we have to supply the ionisation energy to take the total energy of the electron up to 0.

Energy eigenstates $|E\rangle$ satisfy

$$H |E\rangle = E |E\rangle$$

or $H |n, l, m\rangle = E_n |n, l, m\rangle$
quantum numbers label states

A. Wavefunctions

2.

As you know the wavefunctions are most conveniently written in spherical polar coordinates

$$\psi_{nlm} = R_{nl}(r) Y_{l,m}(\theta, \phi)$$

↙ not to be confused with m the mass!

where the spherical harmonics $Y_{l,m}$ are angular momentum eigenfunctions

$$L^2 Y_{l,m}(\theta, \phi) = \hbar^2 l(l+1) Y_{l,m}(\theta, \phi)$$

$$L_z Y_{l,m}(\theta, \phi) = \hbar m Y_{l,m}(\theta, \phi)$$

with $l = 0, 1, \dots$ $m = -l, -l+1, \dots, l-1, l$

and $\int |Y_{l,m}(\theta, \phi)|^2 d\Omega = 1$

↑ solid angle

The radial wave equation is then

$$+\frac{\hbar^2}{2m} \left(-\frac{1}{r^2} \frac{d}{dr} r^2 \frac{dR}{dr} + \frac{l(l+1)}{r^2} R \right) - \frac{e^2}{4\pi\epsilon_0 r} R = ER$$

or

$$\frac{1}{r^2} \frac{d}{dr} r^2 \frac{dR}{dr} + \frac{2R}{a_0 r} = -\frac{2mE}{\hbar^2} R$$

where $a = \left(\frac{me^2}{\hbar^2 4\pi\epsilon_0} \right)^{-1}$ is (and is, in fact, the "Bohr radius") when $m = m_e$

In order that ψ be properly normalized ~~we~~

$$\int_0^{\infty} |R_{n,l}|^2 r^2 dr = 1$$

We can easily get a feel for the behaviour of R as follows:

1. When r is very large drop all terms in the wave equation which have inverse powers of r in them - we're left with

$$R'' = -\frac{2mE}{\hbar^2} R$$

R must be normalizable so

$$R = \exp\left(-\sqrt{\frac{-2mE}{\hbar^2}} r\right)$$

(remember that E is negative so this is exponential fall-off).

2. When r is very small keep only the $\frac{1}{r^2}$ terms

so

$$\frac{1}{r^2} \frac{d}{dr} r^2 \frac{dR}{dr} - \frac{l(l+1)}{r^2} R = 0$$

which gives $R = r^l$

(the alternative $r^{-(l+1)}$ is not normalizable for $l \neq 0$ and in fact not a solution of the Sch. eqn for $l=0$).

So it makes sense to guess that

$$R = r^l (\text{something}) \exp\left(-\sqrt{\frac{-2mE}{\hbar^2}} r\right)$$

It's always a good idea to arrange things

as much as possible in terms of dimensionless

quantities — from the physics point of view

these are just numbers ~~which~~ whose value is

independent of the units you're using. In

this case it helps to write the exponential

as

$$\exp\left(-\sqrt{\frac{-2mEa^2}{\hbar^2}} \left(\frac{r}{a}\right)\right)$$

and call $\sqrt{\frac{-2mEa^2}{\hbar^2}} = \lambda$ so $\exp(-\lambda \frac{r}{a})$

If we now write

(something) as $F(2\lambda r/a)$ then

$F(y)$ satisfies

$$y F'' + F' (2(l+1) - y) - (l+1 - \frac{1}{2}) F = 0$$

This is the generalized Laguerre equation and you

can read about it in books. The solutions are polynomials if $\lambda = \frac{1}{n}$ and $n > l$; otherwise they are functions which lead to a non-normalizable wavefunction.

So we have

$$\sqrt{\frac{-2m E_n a^2}{\hbar^2}} = \frac{1}{n} \quad \begin{array}{l} \text{Rydberg} \\ \text{constant} \end{array}$$

$$\text{or } E_n = -\frac{\hbar^2}{2ma^2} \cdot \frac{1}{n^2} = -\frac{Rhc}{n^2}$$

$$\text{and } R_{n,l} = \text{const } r^l \times \left(1 + \dots + \left(\frac{r}{a}\right)^{n-l-1} \right) \\ \times \exp\left(-\frac{1}{n} \cdot \frac{r}{a}\right)$$

$$\text{for } l = 0 \dots n-1$$

When you need these functions look them up in a book.

B. Scales and Scaling

Let's look at the Rydberg constant a little more closely

$$\begin{aligned} hcR &= \frac{\hbar^2}{2ma^2} = \frac{\hbar^2}{2m} \left(\frac{me^2}{\hbar^2 4\pi\epsilon_0} \right) \\ &= \frac{m}{2} \left(\frac{e^2}{4\pi\epsilon_0 \hbar} \right)^2 \\ &= \frac{mc^2}{2} \left(\frac{e^2}{4\pi\epsilon_0 \hbar c} \right)^2 \end{aligned}$$

[Why did we bring c into a non-relativistic system?
We'll see next week!]

The combination $\frac{e^2}{4\pi\epsilon_0\hbar c} = \alpha$ is called the "fine-structure constant"; it is dimensionless and takes the value $\approx \frac{1}{137}$; $\alpha^{-1} = 137.036$

This ~~formula~~ tells us that ionization energies in hydrogen are of order

$$\left(\begin{array}{l} \text{rest mass energy} \\ \text{of the electron} \end{array} \right) \times \alpha^2$$

This is the characteristic energy scale of the gross structure of hydrogen.

If we look at a we see

$$a = \left(\frac{mc^2}{\hbar c} \frac{e^2}{4\pi\epsilon_0\hbar c} \right)^{-1}$$

$$= \frac{\hbar c}{mc^2} \cdot \frac{1}{\alpha}$$

$\frac{1}{2\pi} \times$ Compton wavelength of free electron

Now of course a is the characteristic distance scale for the motion of the electron in a hydrogen

atom. For example in the ground state

$$\langle r \rangle = \frac{\int_0^{\infty} r e^{-2r/a} r^2 dr}{\int_0^{\infty} 1 e^{-2r/a} r^2 dr} = \frac{3a}{2}$$

$$\langle r^{-1} \rangle = a^{-1}$$

→ Finally note that we can also consider what happens for a central charge Ze (ie we strip off all the electrons bar one from a bigger atom). Then

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

so the only change is

$$e^2 \rightarrow Ze^2$$

and that means wherever we have a factor of α we replace it by αZ .

This has the useful consequence
that in the ground state

$$\begin{aligned}\langle V \rangle_{\text{g.s.}} &= -\frac{e^2}{4\pi\epsilon_0 a} \\ &= -\frac{e^2}{4\pi\epsilon_0 \hbar c} \cdot \frac{\hbar c}{a} \\ &= -\alpha^2 mc^2 \\ &= 2 E_1\end{aligned}$$

and therefore

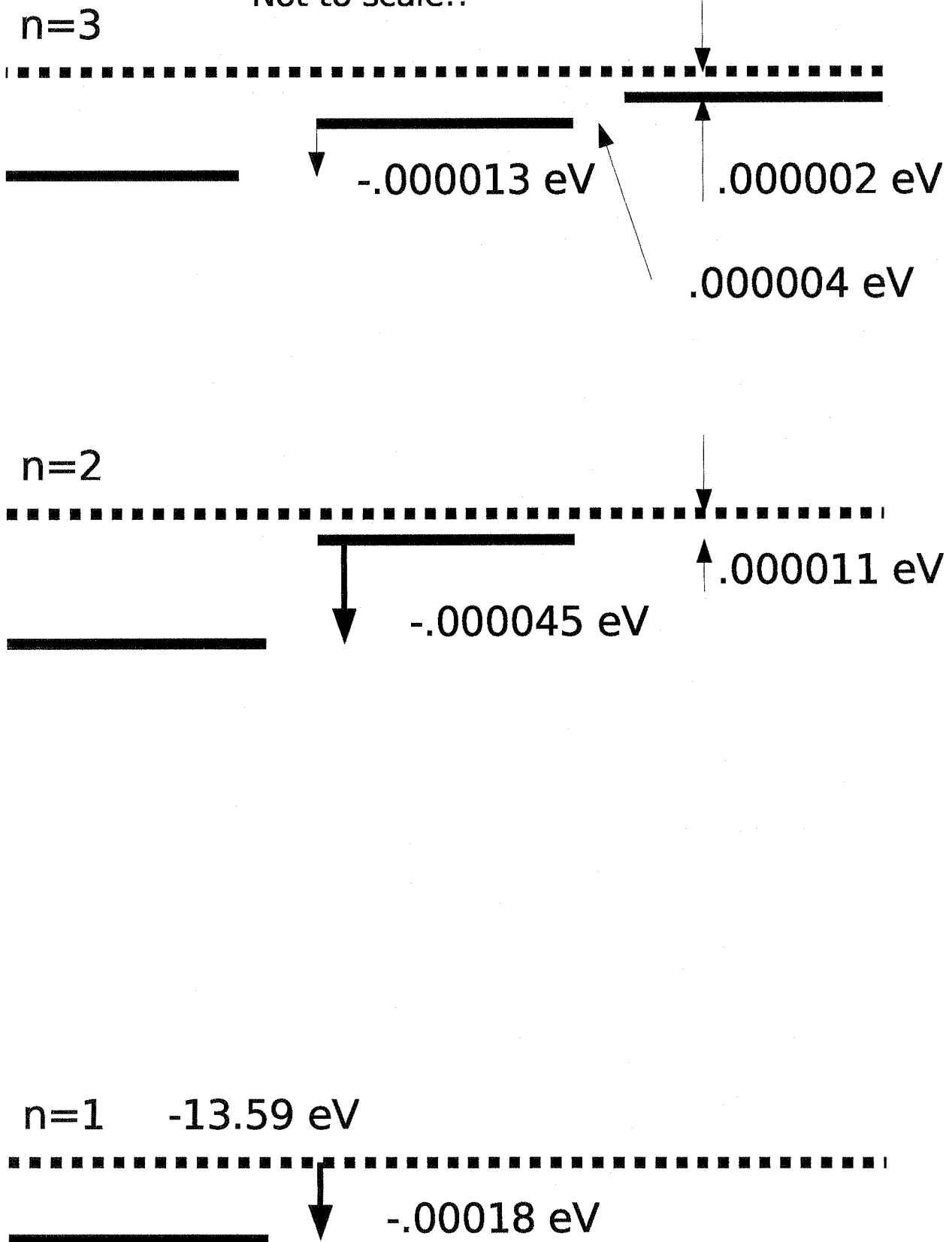
$$\langle T \rangle_{\text{g.s.}} = -E_1$$

This is a special case of the virial theorem which states that

$$0 = \langle V \rangle + 2\langle T \rangle$$

Hydrogen Spectrum

Not to scale!!



Hydrogen II

The energy eigenstates for the Hamiltonian

$$H = \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r}$$

are $|n, l, m\rangle$ with

$$H |n, l, m\rangle = E_n |n, l, m\rangle, \quad E_n = -\frac{Rhc}{n^2}$$

$$L^2 |n, l, m\rangle = \hbar^2 l(l+1) |n, l, m\rangle$$

$$L_z |n, l, m\rangle = \hbar m |n, l, m\rangle$$

But is H really the correct Hamiltonian for the hydrogen atom? We should compare the spectrum we have calculated with the energy levels deduced from observations on real hydrogen.

→ transparency of idealised spectrum

→ transparency of experimentally determined spectrum

So, what have we forgotten? Let's look at the assumptions we've made.

A. Kinetic Energy

We have used

$$K.E. = \frac{p^2}{2m}$$

which is true non-relativistically but we know that this is an approximation.

For a free particle the relativistic energy is given by

$$\begin{aligned} E^2 &= p^2 c^2 + m^2 c^4 \\ &= (mc^2)^2 \left(1 + \frac{p^2}{m^2 c^2} \right) \end{aligned}$$

taking the square root

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

$$= \underset{\substack{\uparrow \\ \text{rest mass} \\ \text{energy}}}{mc^2} + \frac{p^2}{2m} - \frac{1}{2mc^2} \left(\frac{p^2}{2m} \right)^2$$

\uparrow non-rel. K.E. \uparrow first rel. correction to non-rel. K.E.

Let's estimate the size of this correction in the case of hydrogen.

$$\Delta_{\text{K.E.}} \sim \left(\frac{1}{mc^2} \frac{p^2}{2m} \right) \cdot \frac{p^2}{2m}$$

Now $\frac{p^2}{2m}$ is the original K.E. and it's reasonable to suppose that its magnitude is roughly the energy scale for the motion of the electron i.e. $\frac{p^2}{2m} \sim \alpha^2 mc^2$. Therefore

$$\Delta_{\text{K.E.}} \sim \left(\frac{\alpha^2 mc^2}{mc^2} \right) \cdot \frac{p^2}{2m}$$

$$\sim \alpha^2 \times (\text{non-rel. K.E.})$$

So it's roughly a 0.01% shift. Perhaps we should take ^{another} look at the real hydrogen spectrum!

B. Potential Energy

We have used

$$P.E. = - \frac{e^2}{4\pi\epsilon_0 r}$$

for all r . This is not quite right because the proton has a finite size $r_0 \approx 10^{-15} \text{ m}$. If we assume that the charge density is constant (which is roughly right) then using Gauss law tells us that inside the proton

$$E_r(r) = \frac{1}{4\pi r^2} \frac{e}{\epsilon_0} \cdot \frac{\frac{4}{3}\pi r^3}{\frac{4}{3}\pi r_0^3}$$

$$= \frac{e r}{4\pi\epsilon_0 r_0^3}$$

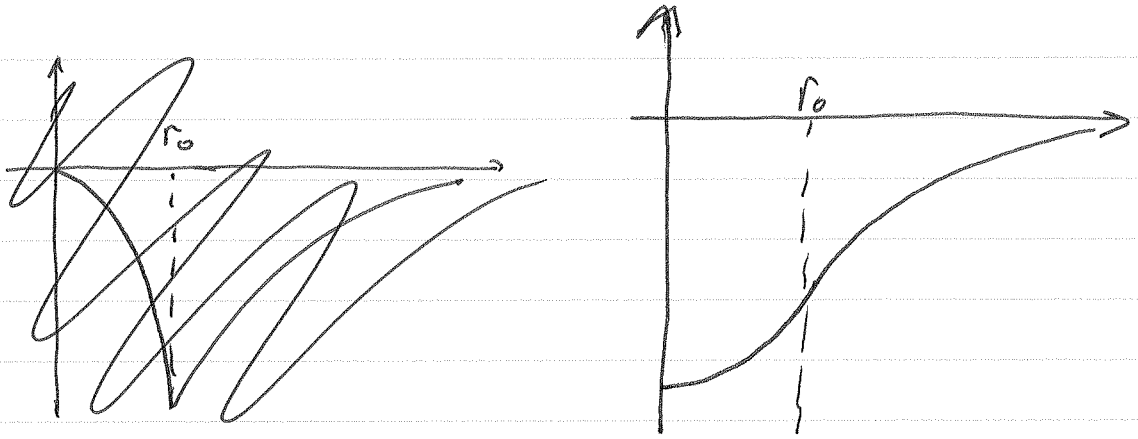
but this is $-\frac{\partial V}{\partial r}$ ← electrostatic potential so

$$-\frac{\partial V}{\partial r} = \frac{e r}{4\pi\epsilon_0 r_0^3}$$

$$- [V(r) - V(r_0)] = \frac{1}{2} (r^2 - r_0^2) \frac{e}{4\pi\epsilon_0 r_0^3}$$

$$V(r) = + \frac{e}{4\pi\epsilon_0 r_0} - \frac{1}{2} (r^2 - r_0^2) \frac{e}{4\pi\epsilon_0 r_0^3}$$

so $P.E. = - \frac{1}{2} \frac{e^2 (3r_0^2 - r^2)}{4\pi\epsilon_0 r_0^3}$ if $r \leq r_0$



The effect of this on energy levels is not immediately obvious. The difference between the true potential energy and $-\frac{e^2}{4\pi\epsilon_0 r}$ is very large when $r \ll r_0$ but on the other hand it's not very probable that the electron will be in that region. So we could guess that it would be something like

$$\Delta E \sim \frac{e^2}{4\pi\epsilon_0 r_0} \cdot \frac{r_0^3}{a^3}$$

↑
shift in energy level

↑
typical size of differences in potential

↑
Probability of finding electron inside $r = r_0$

$$\sim \frac{e^2}{4\pi\epsilon_0 a} \cdot \frac{r_0^2}{a^2}$$

↑
same order as Rhc + ionization energy

↑
 10^{-10}

so it looks as though this effect will be rather small.

We'll calculate it properly in a later lecture, so we'll be able to check that.

C. Electron Spin

We know from the Stern-Gerlach experiment that the electron has spin $\frac{1}{2}$ and a magnetic dipole moment. On the other hand it is charged and moving in the atom (at least on a classical picture) and moving charges generate magnetic fields.

So we should expect there to be an interaction potential energy $-\underline{\mu} \cdot \underline{B}$ between the dipole and the field.

The magnetic dipole moment of the electron is given by

$$\underline{\mu} = -\frac{e}{2m_e} g_s \underline{S} \quad (1)$$

There are classical "explanations" for this but I don't like these at all because there is no classical analogue for the spin of a point-like particle such as the electron.

It's better to look at like this:

1. It is an experimental fact. The dipole moment has been measured very accurately and the number g_s is known to high precision

$$g_s = 2 \times (1.0011596 \dots \dots)$$

ie it is very close to 2.

2. The theoretical understanding comes from the Dirac equation which is the ~~relata~~ relativistic wave equation for the electron. This gives the formula (1) with $g_s = 2$. Even the Dirac equation is not the whole story; the discrepancy from $g_s = 2$ can be calculated in Quantum Electrodynamics which gives

$$\frac{g_s - 2}{2} \stackrel{\text{theory}}{=} 1.159652 \left\{ \begin{array}{l} 095 \\ 379 \end{array} \right\} \times 10^{-12}$$

~~$$g_s = 2 \times 2$$~~

$$\frac{g_s - 2}{2} \stackrel{\text{expt}}{=} 1.159652187.9 (4.3) \times 10^{-12}$$

[You can read more about this in Rev. Mod. Phys. 71, S133 (1999)]

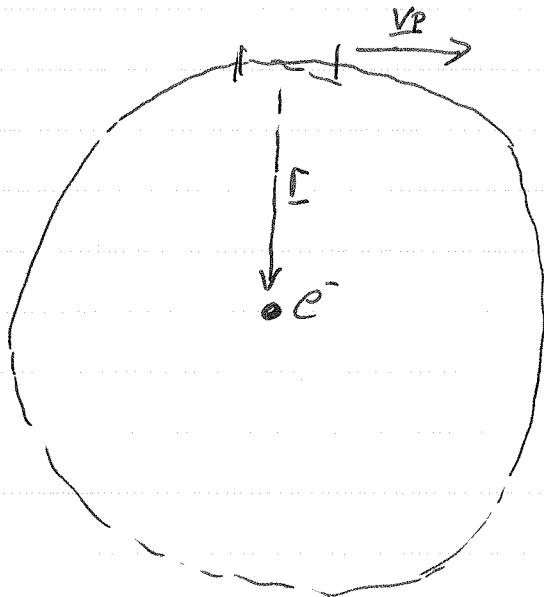
We can see from (1) that the z-component can take values

$$\mu_z = - \left(\frac{e \hbar}{2m_e} \right) \left(g_s x \pm \frac{1}{2} \right) \quad \sim \mp \mu_B$$

Bohr magneton μ_B

9. at the position of the electron

Now we need to calculate the magnetic field. There are several ways to do this. Here is one. Sit in the electron's ^{instantaneous} rest frame; then the proton is orbiting it and creating a current loop



$$\underline{I} = \frac{e v_p}{2\pi r}$$

so by Biot-Savart law

$$\begin{aligned} \underline{B} &= \frac{\mu_0}{4\pi} \frac{\underline{I} \times \hat{r}}{r^2} 2\pi r \\ &= \frac{\mu_0 e v_p \times r}{4\pi r^3} \end{aligned}$$

~~Remember that~~ Now we can ~~express this in quantities in~~ express this in quantities in

the proton's rest frame, and remembering that the relative velocities are opposite in the two rest frames, get

$$\begin{aligned} \underline{B} &= -\frac{\mu_0 e v_p \times r}{4\pi r^3} \\ &= -\frac{\mu_0 e}{4\pi r^3 m_p} m_p v_p \times r \\ &= \frac{e}{c^2 \epsilon_0} \frac{\underline{L}}{m_e 4\pi r^3} \end{aligned}$$

$$\mu_0 = \frac{1}{\epsilon_0 c^2}$$

Now you should be a little uneasy about

the hopping between frames and in particular about the fact the electron's rest frame is not a fixed frame but changes with time. Indeed, this is a problem and in fact the answer we have obtained is wrong by a factor of 2 due to the Thomas precession (so called after L.H. Thomas who discovered it). The correct \underline{B} field is (again this is what we would find from the Dirac eqn)

$$\underline{B} = \frac{1}{2} \frac{e}{c^2 \epsilon_0 m_e} \frac{\underline{L}}{4\pi r^3}$$

and so the dipole interaction energy is

$$-\underline{\mu} \cdot \underline{B} = \frac{e}{2m_e} g_s \underline{S} \cdot \frac{e}{2c^2 \epsilon_0 m_e} \frac{\underline{L}}{4\pi r^3}$$

$$= \frac{1}{2} \frac{e^2}{4\pi \epsilon_0} \frac{\underline{S} \cdot \underline{L}}{m_e^2 c^2 r^3} \quad (\text{where we've put } g_s = 2)$$

Now we can estimate its size to be

$$\sim \frac{e^2}{4\pi \epsilon_0 a} \cdot \frac{\hbar^2}{m_e^2 c^2} \frac{1}{a^2}$$

but $a = \frac{\hbar}{mc} \cdot \frac{1}{\alpha}$ so we get

$$\sim \alpha^2 \times (\text{non-rel PE})$$

So it's the same size as the relativistic KE correction and the discrepancies in the spectra that we were looking at. Our next problem is how to calculate these effects accurately?