07/01/15

The hyperfine splitting in hydrogen

Feynman, vol 3, chap 12

We now begin our study of systems with more than one particle. As a warm up, I thought it would be nice to start with a useful example.

If you remember the Bohr model of the hydrogen atom, then you know that the electron has energy

$$E_n = -\frac{13.6\ eV}{n^2} \qquad (1)$$

(If you don't remember this it is fine; we will derive it later). People can measure these energy levels using atomic spectroscopy and what they find is that Eq (1) is not entirely correct. In fact, some levels are split in more than one

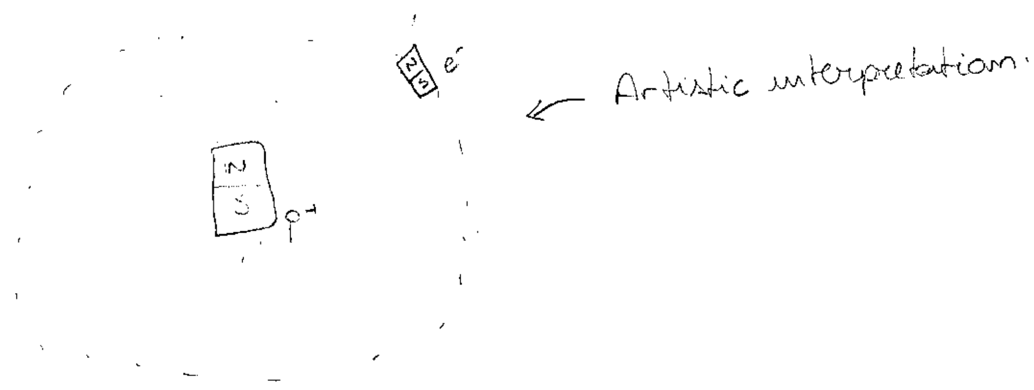
These splittings are physically very interesting because they show that there is more physics which must be taken into account.

It turns out that the majority of these splittings is due to an effect called the <u>spin-orbit</u> coupling. Namely, there is a certain interaction between the spin of the electron and its orbital angular momentum (from the fact that it is orbiting around the nucleus).

This effect is called the <u>fine structure</u> of <u>hydrogen</u> and we will deal with it later when we learn about perturbation theory.
The ground state, however, does <u>not</u> have a fine structure. This is verified experimentally and also predicted by the theory. However, if we look at it really really closely we actually see a splitting! It is tiny but it is there. To give you an idea, the magnitude of the splitting is

$$\Delta E \approx 5.87432593 \times 10^{-6} \ eV \qquad (2)$$

Yes, this quantity can be measured <u>very</u> precisely). Compare this value with ~ 13.6 eV and you see that it is very small indeed.
This tiny splitting of the ground state is called the <u>hyperfine splitting</u>. We will now discuss it in detail. It's physical origin lies in a <u>coupling</u> between the spin of the electron and the spin of the proton. It makes sense: spins are like dipole moments or little magnets. So there is some interaction between the two magnetic moments.
Here is how you can imagine this



We now have a problem with two spin 1/2 particles and we want to find its Hamiltonian. The first thing we must notice is that each particle will have its own spin operators.

$$\text{Spin operators of } e^- : \quad \hat{\sigma}_1{}^x, \hat{\sigma}_1{}^y, \hat{\sigma}_1{}^z$$
$$\text{Spin operators of } p^+ : \quad \hat{\sigma}_2{}^x, \hat{\sigma}_2{}^y, \hat{\sigma}_2{}^z \qquad (3)$$

(I use labels 1 and 2 just for simplicity)

The main point is now this:

$$\boxed{\text{"Operators pertaining to different particles commute"}} \qquad (4)$$

that is

$$[\hat{\sigma}_1{}^z, \hat{\sigma}_2{}^x] = 0 \qquad \text{etc.}$$

Reason: one particle has <u>nothing</u> to do with the other. Why on earth should they <u>not</u> commute!

The idea in (4) is always true. So you can trust it. If it were not true, operators of different particles would not be compatible so measuring one would affect the other.

Now what about states? Remember that what we put inside
> is just a label for something with physical meaning.
For instance, if we have a single spin 1/2 we normally use
as basis the states $|z+\rangle$ and $|z-\rangle$. They are defined as

$$\hat{\sigma}^z |z\pm\rangle = \pm |z\pm\rangle \tag{5}$$

Thus, when we have two spins, we can define the basis states
as

$$|z+z+\rangle, \; |z+z-\rangle, |z-z+\rangle, \; |z-z-\rangle \tag{6}$$

There are 4 states because there are 4 possibilities

up, up

up, down

down, up

down, down.

For simplicity, however, we will henceforth omit the "z"
and write our base states simply as

$$\boxed{|++\rangle, \; |+-\rangle, \; |-+\rangle, \; |--\rangle} \tag{7}$$

The base states (7) are defined such that $\hat{\sigma}_1{}^3$ acts only on the first symbol and $\hat{\sigma}_2{}^3$ only on the second. That is,

$$\hat{\sigma}_1{}^3 |+\square\rangle = +|+\square\rangle \tag{8}$$

for $\square$ being anything you want: $\sigma_1{}^3$ doesn't even look at the other part. It just looks at the first.

We can now find the matrix elements of $\hat{\sigma}_1{}^3$ in the basis (7). This matrix will be 4×4 since there are 4 basis vectors. Let us try and see what we find

$$\begin{aligned}
\hat{\sigma}_1{}^3|++\rangle &= |++\rangle & \langle ++|\hat{\sigma}_1{}^3|++\rangle &= 1 \\
\hat{\sigma}_1{}^3|+-\rangle &= |+-\rangle & \langle +-|\hat{\sigma}_1{}^3|+-\rangle &= 1 \\
\hat{\sigma}_1{}^3|-+\rangle &= -|-+\rangle & \langle -+|\hat{\sigma}_1{}^3|-+\rangle &= -1 \\
\hat{\sigma}_1{}^3|--\rangle &= -|--\rangle & \langle --|\hat{\sigma}_1{}^3|--\rangle &= -1
\end{aligned} \tag{9}$$

On the right I only wrote the matrix elements which are non-zero. All others are zero. We thus see that $\hat{\sigma}_1{}^3$ is diagonal, as of course it must

$$\hat{\sigma}_1{}^3 = \begin{array}{c c}
\begin{array}{cccc} |++\rangle & |+-\rangle & |-+\rangle & |--\rangle \end{array} & \\
\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} & \begin{array}{c} \langle ++| \\ \langle +-| \\ \langle -+| \\ \langle --| \end{array}
\end{array} \tag{10}$$

The order I used doesn't matter. But once you choose an order, stick to it until the end!

ry doing the same for $\hat{\sigma}_2^3$. You will conclude that

$$\hat{\sigma}_2^3 = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \tag{11}$$

But how about other operators. For instance, let us start with $\sigma_{1,2}^x$. We first learn what σ^x does on the space of a single spin 1/2

$$\hat{\sigma}^x |+\rangle = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \end{bmatrix} = |-\rangle$$

Thus, we conclude that

$$\hat{\sigma}^x |+\rangle = |-\rangle \tag{12}$$
$$\hat{\sigma}^x |-\rangle = |+\rangle$$

the operator $\hat{\sigma}^x$ simply flips the spin. Now we can work out $\hat{\sigma}_1^x$ and $\hat{\sigma}_2^x$. We simply need to recall that σ_1^x will only act on the first symbol and $\hat{\sigma}_2^x$ only in the second.

For instance

$$\hat{\sigma}_1^x |++\rangle = |-+\rangle \qquad \langle -+|\hat{\sigma}_1^x|++\rangle = 1$$

$$\hat{\sigma}_1^x |+-\rangle = |--\rangle \qquad \langle --|\hat{\sigma}_1^x|+-\rangle = 1$$

$$\hat{\sigma}_1^x |-+\rangle = |++\rangle \qquad \langle ++|\hat{\sigma}_1^x|-+\rangle = 1 \tag{13}$$

$$\hat{\sigma}_1^x |--\rangle = |+-\rangle \qquad \langle +-|\hat{\sigma}_1^x|--\rangle = 1$$

I know it seems confusing. But do it patiently. We now have

$$\hat{\sigma}_1^x = \begin{array}{cc} \begin{array}{cccc} |++\rangle & |+-\rangle & |-+\rangle & |--\rangle \end{array} & \\ \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix} & \begin{array}{c} \langle ++| \\ \langle +-| \\ \langle -+| \\ \langle --| \end{array} \end{array} \tag{14}$$

Note how you see two identities in each corner. This is not a coincidence. We will learn more about it later.

Let us also work out σ_2^x

$$\hat{\sigma}_2^x |++\rangle = |+-\rangle \qquad \langle +-|\hat{\sigma}_2^x|++\rangle = 1$$

$$\hat{\sigma}_2^x |+-\rangle = |++\rangle \qquad \langle ++|\hat{\sigma}_2^x|+-\rangle = 1$$

$$\hat{\sigma}_2^x |-+\rangle = |--\rangle \qquad \langle --|\hat{\sigma}_2^x|-+\rangle = 1 \tag{15}$$

$$\hat{\sigma}_2^x |--\rangle = |-+\rangle \qquad \langle -+|\hat{\sigma}_2^x|--\rangle = 1$$

thus

$$\hat{\sigma}_2^x = \begin{array}{c} |++\rangle \; |+-\rangle \; |-+\rangle \; |--\rangle \\ \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \end{array} \begin{array}{l} \langle ++| \\ \langle +-| \\ \langle -+| \\ \langle --| \end{array} \qquad (16)$$

Finally, we can work out σ_1^y and σ_2^y. For this we go back to a single spin and find that

$$\hat{\sigma}^y |+\rangle = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = -i |-\rangle$$

$$\hat{\sigma}^y |-\rangle = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = i |+\rangle$$

thus

$$\begin{aligned} \hat{\sigma}^y |+\rangle &= -i |-\rangle \\ \hat{\sigma}^y |-\rangle &= i |+\rangle \end{aligned} \qquad (17)$$

I will leave it for you as an (incredibly fun) exercise to work out that

$$\hat{\sigma}_1^y = \begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{bmatrix} \qquad \hat{\sigma}_2^y = \begin{bmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{bmatrix} \qquad (18)$$

Two spins in a magnetic field

Before we tackle our main problem, let us first suppose that the e^- and the p^+ do not interact, but are both in the presence of a magnetic field B. The energy of interaction between a spin 1/2 and a magnetic field in the z-direction

$$-\mu B \hat{\sigma}^3 \qquad (19)$$

where μ is a constant.

$\boxed{\text{Note: } \mu_e < 0,\ \mu_p > 0,\ |\mu_e| >> \mu_p}$

$$\boxed{\begin{array}{l} \mu_e \approx -5.79 \times 10^{-5} \text{ eV/T} \\ \mu_p \approx 8.80 \times 10^{-8} \text{ eV/T} \end{array}}$$

Thus, the energy of interaction of the electron with a magnetic field is

$$\hat{H}_1 = -\mu_e B \hat{\sigma}_1^3 \qquad (20a)$$

and for the proton

$$\hat{H}_2 = -\mu_p B \hat{\sigma}_2^3 \qquad (20b)$$

If we consider the electron and the proton as a single system, then since energy is additive, the total Hamiltonian is

$$\hat{H} = \hat{H}_1 + \hat{H}_2 = -\mu_e B \hat{\sigma}_1^3 - \mu_p B \hat{\sigma}_2^3 \qquad (21)$$

This is how it must be: if two systems do not interact, the total energy must be the sum of the individual energies ow we may ask, what are the eigenvalues and eigenvectors of $\hat{H}$? well, the answer is sort of obvious: they are the basis elements (7). For instance

$$\hat{H}|++\rangle = -\mu_e B \hat{\sigma}_z^3 |++\rangle - \mu_p B \hat{\sigma}_z^3 |++\rangle = (-\mu_e B - \mu_p B)|++\rangle \qquad (22)$$

nd similarly for the other 3 vectors.

This result is obvious for the following reason. Since the two systems do not interact, one has nothing to do with the other. Suppose you have an electron and a hairy physicist eating a hamburger. If they do not interact, the eigenstates of the electron cannot depend on the physicist. So the energies are sums and the states are "products"

$$|\text{states of } e^-, \text{ states of hairy physicist}\rangle \qquad (23)$$

In summary, we conclude that when two systems do not interact, the total energy is just the sum and the eigenvectors of the individual particles continue to be eigenvectors of the composite system.

For instance, if we have N spin 1/2 particles that do not interact, the total Hamiltonian is

$$\hat{H} = -\mu B \sum_{i=1}^{N} \sigma_i^3 \qquad (24)$$

The eigenstates of this system have the form

$$|++\dots+-++\dots\rangle \qquad (25)$$

etc.

Electron-proton interaction

The hyperfine structure is due to an interaction between the electron and the proton. This interaction involves operators of both particles. Thus, our total Hamiltonian will look like this:

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{12} \qquad (26)$$

$\hat{H}_1$ and $\hat{H}_2$ involve only operators of the electron and the proton respectively, but $\hat{H}_{12}$ will involve a mixture of both. Our task is now to figure out what is the interaction term $\hat{H}_{12}$. This interaction turns out to be different if we are in the ground state of hydrogen or not. Since the most interesting case is the ground state, we shall henceforth focus only on this case, ie, the 1s state.

You may remember from chemistry that the orbital of the electron in the 1s state is spherically symmetric. This means that there are no preferred orientations in space and $\hat{H}_{12}$ must reflect this.

Thus, $\hat{H}_{12}$ must depend on $\hat{\sigma}_1^x$, $\hat{\sigma}_1^y$, $\hat{\sigma}_1^z$, $\hat{\sigma}_2^x$, $\hat{\sigma}_2^y$ and $\hat{\sigma}_2^z$ in a way which does not favour any spatial directions. I want to convince you that the only possibility is

$$\boxed{\hat{H}_{12} = A\,(\hat{\sigma}_1 \cdot \hat{\sigma}_2) = A\,(\sigma_1^x\sigma_2^x + \sigma_1^y\sigma_2^y + \sigma_1^z\sigma_2^z)} \qquad (27)$$

where A is a constant.

Here the notation $\hat{\sigma}_1 \cdot \hat{\sigma}_2$ is just an abbreviation. I'm thinking $\hat{\sigma}_1$ as a vector of operators, $\hat{\sigma}_1 = (\hat{\sigma}_1^x, \hat{\sigma}_1^y, \hat{\sigma}_1^z)$.

The interaction in (27) is called a Heisenberg interaction and it is very important. It is also the interaction which explains ferromagnetism (for instance in iron).

Now, to convince ourselves that Eq (27) is correct, we can proceed by elimination. Consider just a single spin 1/2 with operators $\hat{\sigma}^x$, $\hat{\sigma}^y$ and $\hat{\sigma}^z$. Previously you have shown that

$$(\hat{\sigma}^x)^2 = (\hat{\sigma}^y)^2 = (\hat{\sigma}^z)^2 = 1 \tag{28}$$

So our interaction can have no terms with the same σ squared, since this would only add a constant to the energy, which is not important. Similarly you may recall that products of σ's give other σ's. For instance

$$\hat{\sigma}^x \hat{\sigma}^y = i\, \hat{\sigma}^z \tag{29}$$

Thus, if our interaction has a term $\hat{\sigma}^x\hat{\sigma}^y$, that is not really anything new. It is just $\hat{\sigma}_z$. All of this would not be true if the e^- and the p^+ were spin 1 particles, for example. But it is true for spin 1/2.

We thus conclude that $\hat{H}_{12}$ can only contain terms linear in σ's. The fact that Eq. (27) is isotropic in space is a little more subtle and we will only be able to discuss it later on when we understand the theory of angular momentum. But it sort of makes sense since it involves a dot product of 2 "vectors" $\sigma_1 \cdot \sigma_2$, and the dot product is isotropic

What about the constant A in (27). Our analysis cannot say anything about it. But it can be shown that

$$A = \frac{\mu_0 g_p e^2 \hbar^2}{12\pi m_p m_e a^3} \tag{30}$$

where $g_p = 5.59$ and a is the Bohr radius, $a = \frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2} \simeq 0.5 \,\text{Å}$.

You don't need to worry too much about this formula. I just wanted you to know that it exists. The calculation which shows this is done Griffiths, Sec 6.5. But it requires some more advanced material which we haven't seen yet.

To summarize, we now know the formula for the interaction between the spins of the proton and the electron. It is given by Eq (27). I tried to argue as to why it must have this shape, but if you didn't like my arguments, know that this formula can be derived rigorously.

Energy levels

Our next task is now clear. Suppose there is no magnetic field, then the total energy between the proton and the electron is

$$\boxed{\hat{H} = A\, \hat{\sigma}_1 \cdot \hat{\sigma}_2 = A(\hat{\sigma}_1{}^x\hat{\sigma}_2{}^x + \hat{\sigma}_1{}^y\hat{\sigma}_2{}^y + \hat{\sigma}_1{}^z\hat{\sigma}_2{}^z} \qquad (31)$$

Now we do what we always do: we find the eigenvalues and eigenvectors of $\hat{H}$.

This can be done in two ways. One is to multiply the pairs $\sigma_1{}^x\sigma_2{}^x$, etc and then add them. This is straightforward because we know all the matrices: Eqs (10), (11), (14), (16), (18). I will leave this for you as an exercise.

The other way to do it is to directly apply $\hat{H}$ to our basis vectors (7). For this, all we need to recall is that

$$\begin{aligned} &\hat{\sigma}^z|+\rangle = |+\rangle \qquad &&\hat{\sigma}^x|+\rangle = |-\rangle \qquad &&\hat{\sigma}^y|+\rangle = -i|-\rangle \\ &\hat{\sigma}^z|-\rangle = -|-\rangle \qquad &&\hat{\sigma}^x|-\rangle = |+\rangle \qquad &&\hat{\sigma}_y|-\rangle = i|+\rangle \end{aligned} \qquad (32)$$

Now we apply the operators sequentially

$$\begin{aligned} \hat{H}|++\rangle &= A\{\hat{\sigma}_1{}^x\hat{\sigma}_2{}^x|++\rangle + \hat{\sigma}_1{}^y\hat{\sigma}_2{}^y|++\rangle + \hat{\sigma}_1{}^z\hat{\sigma}_2{}^z|++\rangle\} \\ &= A\{\hat{\sigma}_1{}^x|+-\rangle + \hat{\sigma}_1{}^y(-i)|+-\rangle + \hat{\sigma}_1{}^z|++\rangle\} \\ &= A\{|--\rangle + (-i)(-i)|--\rangle + |++\rangle\} \\ &= A|++\rangle \end{aligned} \qquad (33a)$$

ws $\qquad \langle ++|\hat{H}|++\rangle = A$ (33b)

next: (I'm getting tired of all the hats in the σ's)

$$\hat{H}|+-\rangle = A\{\sigma_1^x\sigma_2^x|+-\rangle + \sigma_1^y\sigma_2^y|+-\rangle + \sigma_1^z\sigma_2^z|+-\rangle\}$$

$$= A\{|-+\rangle + (-i)(i)|-+\rangle - |+-\rangle\}$$

$$= A\{2|-+\rangle - |+-\rangle\} \qquad (34a)$$

ws

$$\langle +-|\hat{H}|+-\rangle = -A \qquad (34b)$$

$$\langle -+|\hat{H}|+-\rangle = 2A \qquad (34c)$$

Next:

$$\hat{H}|-+\rangle = A\{\sigma_1^x\sigma_2^x|-+\rangle + \sigma_1^y\sigma_2^y|-+\rangle + \sigma_1^z\sigma_2^z|-+\rangle\}$$

$$= A\{|+-\rangle + (i)(-i)|+-\rangle - |-+\rangle\} \qquad (35a)$$

So

$$\langle -+|\hat{H}|-+\rangle = -A \qquad (35b)$$

$$\langle +-|\hat{H}|-+\rangle = 2A \qquad (35c)$$

Finally

$$\hat{H}|--\rangle = A\{\sigma_1^x\sigma_2^x|--\rangle + \sigma_1^y\sigma_2^y|--\rangle + \sigma_1^z\sigma_2^z|--\rangle\}$$

$$= A\{|++\rangle + (i)(i)|++\rangle + (-1)(-1)|--\rangle\} \qquad (36a)$$

$$= A|--\rangle$$

$$\langle --|\hat{H}|--\rangle = A \qquad (36b)$$

$\therefore$

Phew! We are done

$$
\hat{H} = \begin{array}{c} \\ \\ \\ \\ \\ \end{array}
\begin{array}{cccc|c}
|++\rangle & |+-\rangle & |-+\rangle & |--\rangle & \\
\hline
A & 0 & 0 & 0 & \langle ++| \\
0 & -A & 2A & 0 & \langle +-| \\
0 & 2A & -A & 0 & \langle -+| \\
0 & 0 & 0 & A & \langle --|
\end{array}
$$

Or, more suscintly

$$
\boxed{\hat{H} = A \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}} \tag{37}
$$

We now have $\hat{H}$, so the next step is to diagonalize it. This is a slightly harder problem, because the matrix is 4×4. But it will teach us an important lesson: if a matrix is divided in blocks, we can diagonalize each block supparately. Look again at $\hat{H}$: I see 3 independent blocks

$$
\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}
$$

This looks like

$$
\begin{bmatrix} B & 0 & 0 \\ 0 & C & 0 \\ 0 & 0 & D \end{bmatrix}
$$

where B, C, D are matrices

In fact, just by looking really hard at $\hat{H}$, we can already figure out 2 eigenvectors

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$$

This is great: we have two eigenvalues and eigenvectors

$$\hat{H}|++\rangle = A|++\rangle \tag{38a}$$

$$\hat{H}|--\rangle = A|--\rangle \tag{38b}$$

You shouldn't be surprised! Look at (33a) and (36a).

We now need only 2 more eigenvectors. They <u>must</u> come from the middle block. This block is related to the vectors $|+-\rangle$ and $|-+\rangle$ only. That's why we call it a block in the first place: it does not interact with the other parts.

Thus, we can look only at this 2×2 block

$$\begin{bmatrix} -1 & 2 \\ 2 & -1 \end{bmatrix}$$

We find its eigenvectors and eigenvalues and then relate the vectors to $|+-\rangle$ and $|-+\rangle$. For instance, if we find an eigenvector $\begin{bmatrix} a \\ b \end{bmatrix}$, then the actual eigenvector will be

$$a|+-\rangle + b|-+\rangle .$$

It is important that you practice laziness. Instead of doing the full procedure for diagonalizing a matrix, relate it to something you know:

$$\begin{bmatrix} -1 & 2 \\ 2 & -1 \end{bmatrix} = -1 + 2\hat{\sigma}^x$$

The eigenvectors of $\hat{\sigma}^x$ are $\frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ 1 \end{bmatrix}$ and $\frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -1 \end{bmatrix}$, with eigenvalues $+1$ and -1 respectively. Thus the eigenvalues and eigenvectors of our matrix are

$$-1 + 2 = 1 \qquad \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

$$-1 - 2 = -3 \qquad \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -1 \end{bmatrix}$$

Now we go back to the full 4×4 $\hat{H}$. Remember that we have to put on an A in front of the eigenvalues. Thus

$$\boxed{\begin{aligned} E_1 &= -3A & |1\rangle &= \frac{1}{\sqrt{2}}\left(|+-\rangle - |-+\rangle\right) \\ E_2 &= A & |2\rangle &= \frac{1}{\sqrt{2}}\left(|+-\rangle + |-+\rangle\right) \\ E_3 &= A & |3\rangle &= |++\rangle \\ E_4 &= A & |4\rangle &= |--\rangle \end{aligned}}$$

(39a)

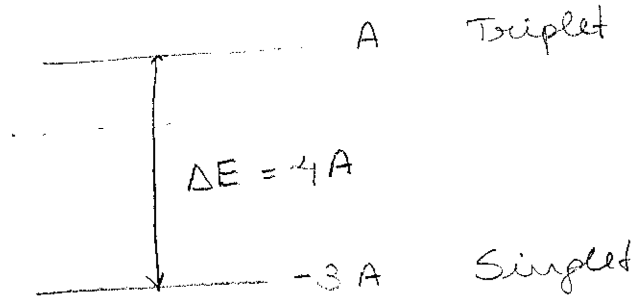
(39b)

(39c)

(39d)

For reasons that will become clearer later on, the state $|1\rangle$ is called a <u>singlet</u> and the states $|2\rangle$, $|3\rangle$ and $|4\rangle$ are called a <u>triplet</u>

We thus find that there are 3 degenerate levels. So the splitting is actually between the level $-3A$ and the levels with energy A.



The total change in energy is

$$\Delta E = 4A \tag{40}$$

Now we can check this because we know ΔE experimentally, Eq (2), and we know A, Eq (30). Substituting the values we obtain

$$4A = 5.87744 \times 10^{-6}\ eV$$

compare with Eq (2)

$$\Delta E_{exp} = 5.874 \times 10^{-6}\ eV.$$

Great match!

In terms of Frequency of the photon emitted in this transition, we have

$$\nu = \frac{\Delta E}{h} = 1420.40 \text{ MHz}$$

Or, in terms of wavelength

$$\boxed{\lambda = 21.106 \text{ cm}} \qquad (41)$$

This line is very famous. It is called the <u>21 cm line</u> or the "<u>Hydrogen line</u>".

Astronomists and cosmologists love this because this type of radiation is emitted by hydrogen gas in the galaxy. Moreover, since this line falls in the microwave region, it penetrates interstellar cosmic dust, which is usually opaque for visible light.

So radio telescopes tune into the 21 cm wavelength and may then observe the location of large concentrations of hydrogen (ie stars) within the galaxy. The intensity is proportional to the concentration and the Dopler shift to the velocities. So it can also tell how these things are moving about the galaxy.

he Pauli spin exchange operator

Define $\hat{P}$ as the operator which exchanges the spins of the wo particles.

$$\hat{P}\,|++\rangle = |++\rangle$$

$$\hat{P}\,|+-\rangle = |-+\rangle$$

$$\hat{P}\,|-+\rangle = |+-\rangle$$

$$\hat{P}\,|--\rangle = |--\rangle$$

This is called the Pauli spin exchange operator. However, it was actually inventend by Dirac! You see, Dirac was very modest and frequently named things he discovered after other people.

Looking back at (33)-(36) we see that

$$(\hat{\sigma}_1 \cdot \hat{\sigma}_2)\,|++\rangle = |++\rangle$$

$$(\hat{\sigma}_1 \cdot \hat{\sigma}_2)\,|+-\rangle = 2|-+\rangle - |+-\rangle$$

$$(\hat{\sigma}_1 \cdot \hat{\sigma}_2)\,|-+\rangle = 2|+-\rangle - |-+\rangle$$

$$(\hat{\sigma}_1 \cdot \hat{\sigma}_2)\,|--\rangle = |--\rangle$$

we see that we can relate the two operators

$$\boxed{\hat{\sigma}_1 \cdot \hat{\sigma}_2 = 2\hat{P} - 1} \quad \leftrightarrow \quad \boxed{\hat{P} = \frac{1 + \hat{\sigma}_1 \cdot \hat{\sigma}_2}{2}}$$

This formula will be important for us later on, when we talk about spin waves and magnons. Please keep it in mind.

The Zeeman effect

Whenever you hear or read the word "Zeeman" (named after Pieter Zeeman), always think of a splitting of the energy levels due to a magnetic field.

We will show that if we apply a magnetic field the 3 degenerate states in (39) are again split. We know the Hamiltonian already. It will be

$$\boxed{\hat{H} = -\mu_e B \hat{\sigma}_{1}^{z} - \mu_p B \hat{\sigma}_{2}^{z} + A(\hat{\sigma}_1 \cdot \hat{\sigma}_2)} \tag{42}$$

Writing it as a matrix is very easy because we already know the individual parts. Using (10), (11) and (37), we get

$$\hat{H} = -\mu_e B \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} - \mu_p B \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} + A \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

So

$$\hat{H} = \begin{bmatrix} -B(\mu_e + \mu_p) + A & 0 & 0 & 0 \\ 0 & -B(\mu_e - \mu_p) - A & 2A & 0 \\ 0 & 2A & -B(-\mu_e + \mu_p) - A & 0 \\ 0 & 0 & 0 & B(\mu_e + \mu_p) + A \end{bmatrix} \tag{43}$$

ow remember that $\mu_e < 0$, $\mu_p > 0$ and $|\mu_e| >> \mu_p$. Let us
en define

$$\mu = -(\mu_e + \mu_p) \tag{44a}$$

$$\mu' = -(\mu_e - \mu_p) \tag{44b}$$

Since $|\mu_e| >> \mu_p$ and $\mu_e < 0$, both of these terms are positive
nd very similar. Then

$$\hat{H} = \begin{bmatrix} A + B\mu & 0 & 0 & 0 \\ 0 & -A + B\mu' & 2A & 0 \\ 0 & 2A & -A - B\mu' & 0 \\ 0 & 0 & 0 & A - B\mu \end{bmatrix} \tag{45}$$

we are again lucky because this matrix still factors as 3
blocks. The states $|++\rangle$ and $|--\rangle$ continue to be eigenvectors,
but with eigenvalues $A + B\mu$ and $A - B\mu$.

As for the 2×2 block in the middle, we have no choice.
Let us find its eigenvalues the usual way

$$\begin{bmatrix} -A + B\mu' & 2A \\ 2A & -A - B\mu' \end{bmatrix}$$

the characteristic Eq is

$$(-A + B\mu' - \lambda)(-A - B\mu' - \lambda) - 4A^2 = 0$$

$$\lambda^2 - \lambda[-A + B\nu' - A - B\nu'] + (-A + B\nu')(-A - B\nu') - 4A^2 = 0$$

$$\lambda^2 + 2A\lambda + A^2 - B^2\nu'^2 - 4A^2 = 0$$

$$\lambda^2 + 2A\lambda - 3A^2 - B^2\nu'^2 = 0$$

$$\lambda = -\frac{2A}{2} \pm \sqrt{\frac{(2A)^2}{4} + 3A^2 + B^2\nu'^2}$$

$$= -A \pm \sqrt{4A^2 + B^2\nu'^2}$$

$$\boxed{\lambda = -A\left\{1 \pm \sqrt{4 + \frac{B^2\nu'^2}{A^2}}\right\}} \qquad (46)$$

We thus have our four eigenvalues

$$E_1 = A\left\{-1 - \sqrt{4 + (B\nu'/A)^2}\right\} \qquad (47a)$$

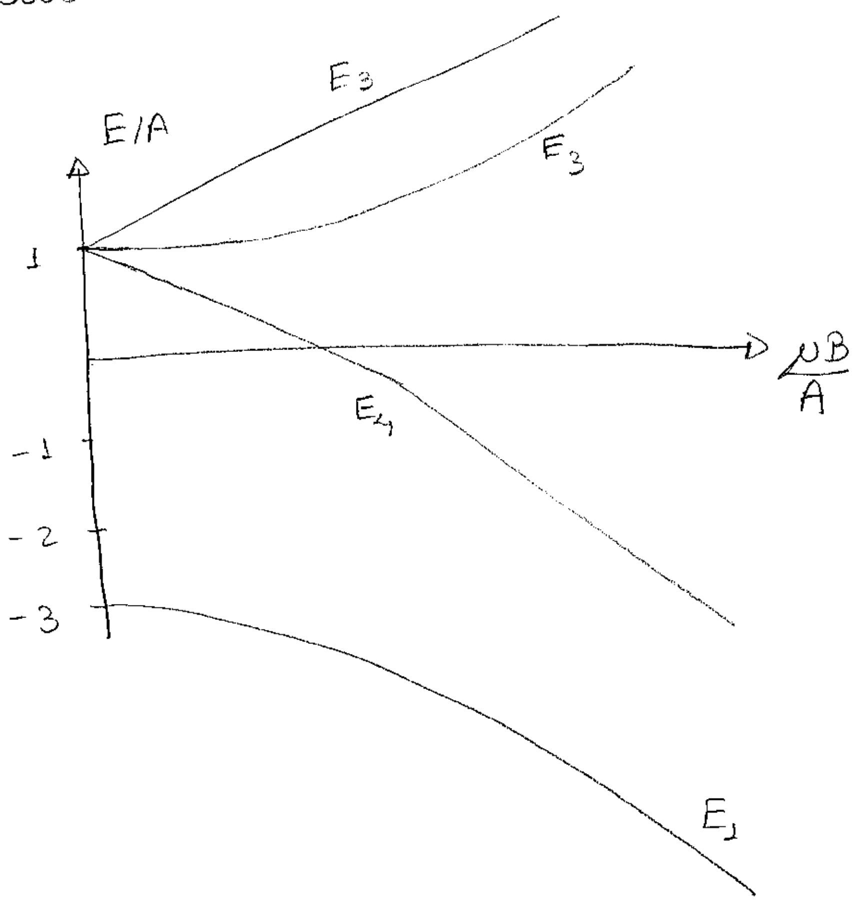
$$E_2 = A\left\{-1 + \sqrt{4 + (B\nu'/A)^2}\right\} \qquad (47b)$$

$$E_3 = A + B\nu \qquad (47c)$$

$$E_4 = A - B\nu \qquad (47d)$$

We have only found the eigenvalues. The eigenvectors are not given by (39) anymore. They will be different. You can find them if you want. It is not hard.

To plot these curves we can assume $\mu' = \mu$. Then we graph $\frac{E}{A}$ vs $\frac{\mu B}{A}$.



Note that when we have a magnetic field there can be all sorts of transitions, not just one with energy $4A$. This is what makes the presence of the magnetic field detectable.

To give you a feeling of the numbers, using the values of μ_e in page 9 and the fact that $A \simeq 1.47 \times 10^{-6}$ eV, we get

$$\frac{\mu}{A} \approx 40. \qquad (48)$$

So 1 T would mean a huge field. On the other hand, the magnetic field of the earth is $B_{earth} \approx 4 \times 10^{-5}\,T = 40\,\mu T$ (it actually varies from place to place between 25 and 65 μT. Maybe in the island of LOST it is larger).

whenever we find a nice result such as that in Eq (47), it is important to analyze certain limits.

Low field limit

When the quantity $\frac{\mu B}{A}$ is small we can expand the square root in a Taylor series. For this I recommend that you memorize the following formula

$$\boxed{\begin{gathered}(1+x)^n \approx 1 + nx \\ \text{when } x \text{ is small}\end{gathered}} \tag{49}$$

In our case $n=1/2$ because it is a square root. Thus

$$\sqrt{4+(\mu B/A)^2} = 2\sqrt{1+(\mu B/2A)^2} \approx 2\left[1+\frac{1}{2}(\mu B/2A)^2\right]$$

$$= 2 + (\mu B/2A)^2 \tag{50}$$

Thus, our 4 energies in (47) became

$$\frac{E_1}{A} \approx -3 - (\mu B/2A)^2 \tag{51a}$$

$$\frac{E_2}{A} \approx 1 + (\mu B/2A)^2 \tag{51b}$$

$$\frac{E_3}{A} = 1 + \mu B/A \tag{51c}$$

$$\frac{E_4}{A} = 1 - \mu B/A \tag{51d}$$

f $\mu B/A$ is indeed very tiny $(\mu B/2A) << \mu B/A$ so we may
encentrate only on those terms up to first order in $\mu B/A$.

un

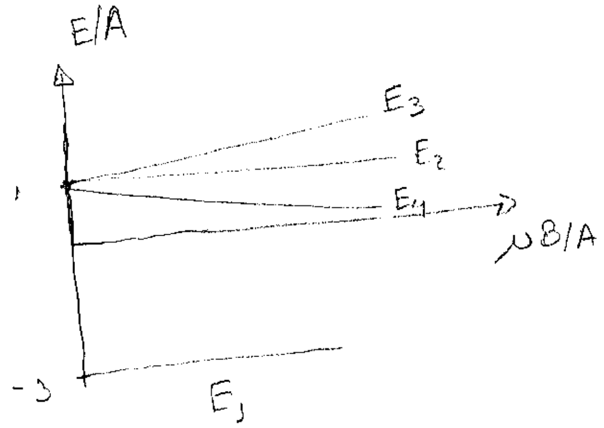
$$\frac{E_1}{A} \approx -3 \quad (52a)$$

$$\frac{E_2}{A} \approx 1 \quad (52b)$$

$$\frac{E_3}{A} = 1 + \frac{\mu B}{A} \quad (52c)$$

$$\frac{E_4}{A} = 1 - \frac{\mu B}{A} \quad (52d)$$

Think of this as a zoom in the figure of pg 26 near the
region $\mu B/A \sim 0$



High field limit

When $\mu B/A$ is very large, the interaction term $\hat{\sigma}_1 \cdot \hat{\sigma}_2$ becomes negligible in comparison with the field terms. We now have

$$\sqrt{1 + (\mu' B/A)^2} \approx \sqrt{(\mu' B/A)^2} = \mu B/A \qquad (53)$$

Thus, the energy levels in (47) become

$$E_1 \approx -\mu' B = (\mu_e - \mu_p) B \qquad (54a)$$

$$E_2 \approx \mu' B = -(\mu_e - \mu_p) B \qquad (54b)$$

$$E_3 \approx \mu B = -(\mu_e + \mu_p) B \qquad (54c)$$

$$E_4 \approx -\mu B = (\mu_e + \mu_p) B \qquad (54d)$$

These states have a simple physical interpretation. If we can neglect the interaction term $\hat{\sigma}_1 \cdot \hat{\sigma}_2$ in Eq. (42) we get

$$\hat{H} = -\mu_e B \sigma_1{}^3 - \mu_p B \sigma_2{}^3$$

We already know the eigenvalues and eigenvectors of this Hamiltonian: they are our basis vectors (7). Thus we have 4 possibilities

$$\uparrow\uparrow, \ \uparrow\downarrow \quad \downarrow\uparrow \ \text{ and } \downarrow\downarrow$$

these give the energies in (54). So everything makes sense. Everything is consistent.

Singlets and triplets

To finish I want to explain in a bit more detail the physical meaning of the states (39) [maybe this could have been discussed right after page 22].

What I want to do is convince you that the singlet state $|1\rangle$ is a state with total spin 0 and $|2\rangle, |3\rangle$ and $|4\rangle$ have a total spin 1. This is the first example of something we will do in much more detail later, called "addition of angular momentum".

To do this let me recall that the actual spin 1/2 operators are

$$\hat{S}_1 = \frac{1}{2}\hat{\sigma}_1 \qquad (55)$$
$$\hat{S}_2 = \frac{1}{2}\hat{\sigma}_2$$

the total spin is

$$S = \hat{S}_1 + \hat{S}_2 \qquad (56)$$

What I am going to do is apply $\hat{S}^2$ in $|1\rangle, \ldots, |4\rangle$. I do this because later on we will show that the eigenvalues of $\hat{S}^2$ are of the form $S(S+1)$ for S being either an integer or a half integer. So we start with 2 spin 1/2 particles and we may end up either with a spin 0 or a spin 1. Makes sense!

Just to check that this makes sense, if we have a single spin 1/2 particle, say $\hat{S}_1$, then

$$\hat{S}_1^2 = \frac{1}{4}\hat{\sigma}_1^2 = \frac{1}{4}\left[(\hat{\sigma}_1 x)^2 + (\hat{\sigma}_1 y)^2 + (\hat{\sigma}_1 z)^2\right]$$
$$= \frac{1}{4}(1+1+1)$$
$$= \frac{3}{4}$$

his is consistent with $s = 1/2$ because $1/2(1/2+1) = 3/4$.

ow for the two spins

$$\hat{S}^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_1 \cdot \hat{S}_2 = \frac{3}{4} + \frac{3}{4} + 2 \times \frac{1}{2} \times \frac{1}{2}\, \hat{\sigma}_1 \cdot \hat{\sigma}_2$$

so

$$\boxed{\hat{S}^2 = \frac{3}{2} + \frac{1}{2}\hat{\sigma}_1 \cdot \hat{\sigma}_2} \tag{57}$$

ince $\hat{\sigma}_1 \cdot \hat{\sigma}_2 |1\rangle = -3|1\rangle$ we get

$$\hat{S}^2 |1\rangle = 0$$

o $|1\rangle$ indeed represents a state with total spin 0. Similarly
$\hat{\sigma}_1 \cdot \hat{\sigma}_2 |2\rangle = 1|2\rangle$ (and similarly for $|3\rangle$ and $|4\rangle$) so

$$\hat{S}^2 |2\rangle = \left(\frac{3}{2} + \frac{1}{2}\right)|2\rangle = 2|2\rangle$$

his gives $s = 1$ because $s(s+1) = 1(1+1) = 2$. So we conclude
hat $|2\rangle$ corresponds to a total spin 1. The same is true of
$|3\rangle$ and $|4\rangle$

In summary we conclude that when we combine 2 spin 1/2 particles it is possible to make a state with spin 0, which we call the singlet, or 3 states of spin 1, which we call the triplets. Of course, not all Hamiltonian give these types of states. The reason why we got this in the present example is really related to Eq (57) [our Hamiltonian is proportional to $\hat{S}^2$].