2 NMR and energy levels

The picture that we use to understand most kinds of spectroscopy is that molecules have a set of *energy levels* and that the lines we see in spectra are due to *transitions* between these energy levels. Such a transition can be caused by a photon of light whose frequency, ν, is related to the energy gap, $\triangle E$, between the two levels according to:

$$\triangle E = h\nu$$

where h is a universal constant known as Planck's constant. For the case shown in Fig. 2.1, $\triangle E = E_2 - E_1$.

In NMR spectroscopy we tend not to use this approach of thinking about energy levels and the transitions between them. Rather, we use different rules for working out the appearance of multiplets and so on. However, it is useful, especially for understanding more complex experiments, to think about how the familiar NMR spectra we see are related to energy levels. To start with we will look at the energy levels of just one spin and them move on quickly to look at two and three coupled spins. In such spin systems, as they are known, we will see that in principle there are other transitions, called *multiple quantum transitions*, which can take place. Such transitions are not observed in simple NMR spectra, but we can detect them indirectly using two-dimensional experiments; there are, as we shall see, important applications of such multiple quantum transitions.
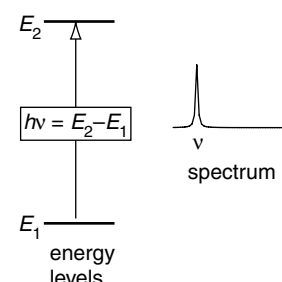
Finally, we will look at *strongly coupled spectra*. These are spectra in which the simple rules used to construct multiplets no longer apply because the shift differences between the spins have become small compared to the couplings. The most familiar effect of strong coupling is the "roofing" or "tilting" of multiplets. We will see how such spectra can be analysed in some simple cases.

Fig. 2.1 A line in the spectrum is associated with a transition between two energy levels.

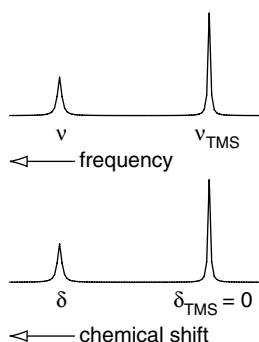## 2.1 Frequency and energy: sorting out the units

NMR spectroscopists tend to use some rather unusual units, and so we need to know about these and how to convert from one to another if we are not to get into a muddle.

Chemical shifts

It is found to a very good approximation that the frequencies at which NMR absorptions (lines) occur scale linearly with the magnetic field strength. So, if the line from TMS comes out on one spectrometer at 400 MHz, doubling the magnetic field will result in it coming out at 800 MHz. If we wanted to quote the NMR frequency it would be inconvenient to have to specify the exact magnetic field strength as well. In addition, the numbers we would have

to quote would not be very memorable. For example, would you like to quote the shift of the protons in benzene as 400.001234 MHz?

We neatly side-step both of these problems by quoting the *chemical shift* relative to an agreed *reference compound*. For example, in the case of proton NMR the reference compound is TMS. If the frequency of the line we are interested in is ν (in Hz) and the frequency of the line from TMS is ν_{TMS} (also in Hz), the chemical shift of the line is computed as:

$$\delta = \frac{\nu - \nu_{\text{TMS}}}{\nu_{\text{TMS}}}. \tag{2.1}$$

ν ν_{TMS}

◁——— frequency

δ $\delta_{\text{TMS}} = 0$

◁——— chemical shift

Fig. 2.2 An NMR spectrum can be plotted as a function of frequency, but it is more convenient to use the chemical shift scale in which frequencies are expressed relative to that of an agreed reference compound, such as TMS in the case of proton spectra.

As all the frequencies scale with the magnetic field, this ratio is independent of the magnetic field strength. Typically, the chemical shift is rather small so it is common to multiply the value for δ by 10^6 and then quote its value in *parts per million*, or ppm. With this definition the chemical shift of the reference compound is 0 ppm.

$$\delta_{\text{ppm}} = 10^6 \times \frac{\nu - \nu_{\text{TMS}}}{\nu_{\text{TMS}}}. \tag{2.2}$$

Sometimes we want to convert from shifts in ppm to frequencies. Suppose that there are two peaks in the spectrum at shifts δ_1 and δ_2 in ppm. What is the frequency separation between the two peaks? It is easy enough to work out what it is in ppm, it is just $(\delta_2 - \delta_2)$. Writing this difference out in terms of the definition of chemical shift given in Eq. 2.2 we have:

$$(\delta_2 - \delta_1) = 10^6 \times \frac{\nu_2 - \nu_{\text{TMS}}}{\nu_{\text{TMS}}} - 10^6 \times \frac{\nu_1 - \nu_{\text{TMS}}}{\nu_{\text{TMS}}}$$
$$= 10^6 \times \frac{\nu_2 - \nu_1}{\nu_{\text{TMS}}}.$$

Multiplying both sides by ν_{TMS} now gives us what we want:

$$(\nu_2 - \nu_1) = 10^{-6} \times \nu_{\text{TMS}} \times (\delta_2 - \delta_1).$$

It is often sufficiently accurate to replace ν_{TMS} with the spectrometer *reference frequency*, about which we will explain later.

If we want to change the ppm scale of a spectrum into a frequency scale we need to decide where zero is going to be. One choice for the zero frequency point is the line from the reference compound. However, there are plenty of other possibilities so it is as well to regard the zero point on the frequency scale as arbitrary.

Angular frequency

Frequencies are most commonly quoted in Hz, which is the same as "per second" or s^{-1}. Think about a point on the edge of a disc which is rotating about its centre. If the disc is moving at a constant speed, the point returns to the same position at regular intervals each time it has competed 360° of rotation. The time taken for the point to return to its original position is called the *period*, τ.

The frequency, ν, is simply the inverse of the period:

$$\nu = \frac{1}{\tau}.$$

For example, if the period is 0.001 s, the frequency is $1/0.001 = 1000$ Hz.

There is another way of expressing the frequency, which is in *angular units*. Recall that $360°$ is 2π radians. So, if the point completes a rotation in τ seconds, we can say that it has rotated though 2π radians in τ seconds. The angular frequency, ω, is given by

$$\omega = \frac{2\pi}{\tau}.$$

The units of this frequency are "radians per second" or rad s^{-1}. ν and ω are related via

$$\nu = \frac{\omega}{2\pi} \quad \text{or} \quad \omega = 2\pi\nu.$$

We will find that angular frequencies are often the most natural units to use in NMR calculations. Angular frequencies will be denoted by the symbols ω or Ω whereas frequencies in Hz will be denoted ν.

Energies

A photon of frequency ν has energy E given by

$$E = h\nu$$

where h is Planck's constant. In SI units the frequency is in Hz and h is in J s^{-1}. If we want to express the frequency in angular units then the relationship with the energy is

$$E = h\frac{\omega}{2\pi}$$
$$= \hbar\omega$$

where $\hbar$ (pronounced "h bar" or "h cross") is Planck's constant divided by 2π.

The point to notice here is that frequency, in either Hz or rad s^{-1}, is directly proportional to energy. So, there is really nothing wrong with quoting energies in frequency units. All we have to remember is that there is a factor of h or $\hbar$ needed to convert to Joules if we need to. It turns out to be much more convenient to work in frequency units throughout, and so this is what we will do. So, do not be concerned to see an energy expressed in Hz or rad s^{-1}.

2.2 Nuclear spin and spin states

NMR spectroscopy arises from the fact that nuclei have a property known as *spin*; we will not concern ourselves with where this comes from, but just take it as a fact. Quantum mechanics tells us that this nuclear spin is characterised by a nuclear spin quantum number, I. For all the nuclei that we are going
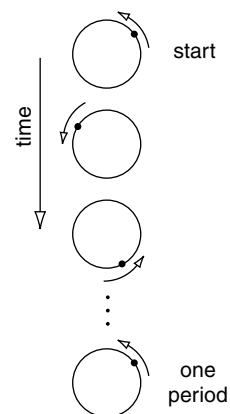
Fig. 2.3 A point at the edge of a circle which is moving at a constant speed returns to its original position after a time called the *period*. During each period the point moves through 2π radians or $360°$.

to be concerned with, $I = \frac{1}{2}$, although other values are possible. A spin-half nucleus has an interaction with a magnetic field which gives rise to two energy levels; these are characterised by another quantum number m which quantum mechanics tells us is restricted to the values $-I$ to I in integer steps. So, in the case of a spin-half, there are only two values of m, $-\frac{1}{2}$ and $+\frac{1}{2}$.

Strictly, α is the low energy state for nuclei with a positive gyromagnetic ratio, more of which below.

By tradition in NMR the energy level (or *state*, as it is sometimes called) with $m = \frac{1}{2}$ is denoted α and is sometimes described as "spin up". The state with $m = -\frac{1}{2}$ is denoted β and is sometimes described as "spin down". For the nuclei we are interested in, the α state is the one with the lowest energy.

If we have two spins in our molecule, then each spin can be in the α or β state, and so there are four possibilities: $\alpha_1\alpha_2$, $\alpha_1\beta_2$, $\beta_1\alpha_2$ and $\beta_1\beta_2$. These four possibilities correspond to four energy levels. Note that we have added a subscript 1 or 2 to differentiate the two nuclei, although often we will dispense with these and simply take it that the first spin state is for spin 1 and the second for spin 2. So $\alpha\beta$ implies $\alpha_1\beta_2$ etc.

We can continue the same process for three or more spins, and as each spin is added the number of possible combinations increases. So, for example, for three spins there are 8 combinations leading to 8 energy levels. It should be noted here that there is only a one-to-one correspondence between these spin state combinations and the energy levels in the case of weak coupling, which we will assume from now on. Further details are to be found in section 2.6.

2.3   One spin

There are just two energy levels for a single spin, and these can be labelled with either the m value of the labels α and β. From quantum mechanics we can show that the energies of these two levels, E_α and E_β, are:

$$E_\alpha = +\tfrac{1}{2}\nu_{0,1} \quad \text{and} \quad E_\beta = -\tfrac{1}{2}\nu_{0,1}$$

where $\nu_{0,1}$ is the *Larmor frequency* of spin 1 (we will need the 1 later on, but it is a bit superfluous here as we only have one spin). In fact it is easy to see that the energies just depend on m:

$$E_m = m\nu_{0,1}.$$

You will note here that, as explained in section 2.1 we have written the energies in frequency units. The Larmor frequency depends on a quantity known as the *gyromagnetic ratio*, γ, the chemical shift δ, and the strength of the applied magnetic field, B_0:

This negative Larmor frequency for nuclei with a positive γ sometimes seems a bit unnatural and awkward, but to be consistent we need to stick with this convention. We will see in a later chapter that all this negative frequency really means is that the spin precesses in a particular sense.

$$\nu_{0,1} = -\frac{1}{2\pi}\gamma_1(1 + \delta_1)B_0 \tag{2.3}$$

where again we have used the subscript 1 to distinguish the of nucleus. The magnetic field is normally given in units of Tesla (symbol T). The gyromagnetic ratio is characteristic of a particular kind of nucleus, such as proton or carbon-13; its units are normally rad s^{-1} T^{-1}. In fact, γ can be positive or negative; for the commonest nuclei (protons and carbon-13) it is positive. For such nuclei we therefore see that the Larmor frequency is negative.

To take a specific example, for protons $\gamma = +2.67 \times 10^8$ rad s^{-1} T^{-1}, so in a magnetic field of 4.7 T the Larmor frequency of a spin with chemical shift zero is

$$\begin{aligned}
\nu_0 &= -\frac{1}{2\pi}\gamma(1+\delta)B_0 \\
&= -\frac{1}{2\pi} \times 2.67 \times 10^8 \times 4.7 = -200 \times 10^6 \text{ Hz.}
\end{aligned}$$

In other words, the Larmor frequency is -200 MHz.

We can also calculate the Larmor frequency in angular units, ω_0, in which case the factor of $1/2\pi$ is not needed:

$$\omega_0 = -\gamma(1+\delta)B_0$$

which gives a value of 1.255×10^9 rad s^{-1}.

Spectrum

As you may know from other kinds of spectroscopy you have met, only certain transitions are *allowed* i.e. only certain ones actually take place. There are usually rules – called *selection rules* – about which transitions can take place; these rules normally relate to the quantum numbers which are characteristic of each state or energy level.

In the case of NMR, the selection rule refers to the quantum number m: only transitions in which m changes by one (up or down) are allowed. This is sometimes expressed as

$$\begin{aligned}
\triangle m &= m(\text{initial state}) - m(\text{final state}) \\
&= \pm 1.
\end{aligned}$$

Another way as saying this is that one spin can flip between "up" and "down" or vice versa.

In the case of a single spin-half, the change in m between the two states is $(+\frac{1}{2} - (-\frac{1}{2})) = 1$ so the transition is allowed. We can now simply work out the frequency of the allowed transition:

$$\begin{aligned}
\nu_{\alpha\beta} &= E_\beta - E_\alpha \\
&= -\tfrac{1}{2}\nu_{0,1} - (+\tfrac{1}{2}\nu_{0,1}) \\
&= -\nu_{0,1}.
\end{aligned}$$

Note that we have taken the energy of the upper state minus that of the lower state. In words, therefore, we see one transition at the minus the Larmor frequency, $-\nu_{0,1}$.

You would be forgiven for thinking that this is all an enormous amount of effort to come up with something very simple! However, the techniques and ideas developed in this section will enable us to make faster progress with the case of two and three coupled spins, which we consider next.
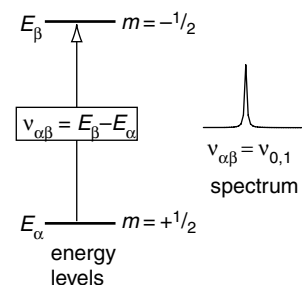
Fig. 2.4 The transition between the two energy levels of a spin-half is allowed, and results in a single line at the Larmor frequency of the spin.

2.4 Two spins
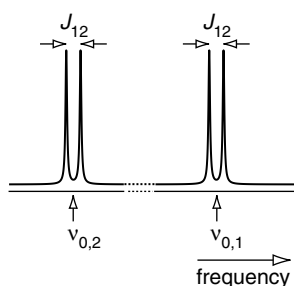
Fig. 2.5 Schematic spectrum of two coupled spins showing two doublets with equal splittings. As indicated by the dashed lines, the separation of the Larmor frequencies is much larger than the coupling between the spins.

We know that the spectrum of two coupled spins consists of two doublets, each split by the same amount, one centred at the chemical shift of the first spin and one at the shift of the second. The splitting of the doublets is the scalar coupling, J_{12}, quoted in Hz; the subscripts indicate which spins are involved. We will write the shifts of the two spins as δ_1 and δ_2, and give the corresponding Larmor frequencies, $\nu_{0,1}$ and $\nu_{0,2}$ as:

$$\nu_{0,1} = -\frac{1}{2\pi}\gamma_1(1+\delta_1)B_0$$

$$\nu_{0,2} = -\frac{1}{2\pi}\gamma_2(1+\delta_2)B_0.$$

If the two nuclei are of the same type, such a proton, then the two gyromagnetic ratios are equal; such a two spin system would be described as *homonuclear*. The opposite case is where the two nuclei are of different types, such as proton and carbon-13; such a spin system is described as *heteronuclear*.

Energy levels

As was already described in section 2.2, there are four possible combinations of the spin states of two spins and these combinations correspond to four energy levels. Their energies are given in the following table:

number	spin states	energy
1	$\alpha\alpha$	$+\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} + \frac{1}{4}J_{12}$
2	$\alpha\beta$	$+\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} - \frac{1}{4}J_{12}$
3	$\beta\alpha$	$-\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} - \frac{1}{4}J_{12}$
4	$\beta\beta$	$-\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} + \frac{1}{4}J_{12}$

The second column gives the spin states of spins 1 and 2, in that order. It is easy to see that these energies have the general form:

$$E_{m_1 m_2} = m_1\nu_{0,1} + m_2\nu_{0,2} + m_1 m_2 J_{12}$$

where m_1 and m_2 are the m values for spins 1 and 2, respectively.

For a homonuclear system $\nu_{0,1} \approx \nu_{0,2}$; also both Larmor frequencies are much greater in magnitude than the coupling (the Larmor frequencies are of the order of hundreds of MHz, while couplings are at most a few tens of Hz). Therefore, under these circumstances, the energies of the $\alpha\beta$ and $\beta\alpha$ states are rather similar, but very different from the other two states. For a heteronuclear system, in which the Larmor frequencies differ significantly, the four levels are all at markedly different energies. These points are illustrated in Fig. 2.6.

Spectrum

The selection rule is the same as before, but this time it applies to the quantum number M which is found by adding up the m values for each of the spins. In this case:

$$M = m_1 + m_2.$$

The resulting M values for the four levels are:

ββ ———— 4

ββ ———— 4

αβ ———— 2

αβ ———— 2   βα ———— 3

βα ———— 3

αα ———— 1

αα ———— 1

^{1}H–^{1}H ^{13}C–^{1}H
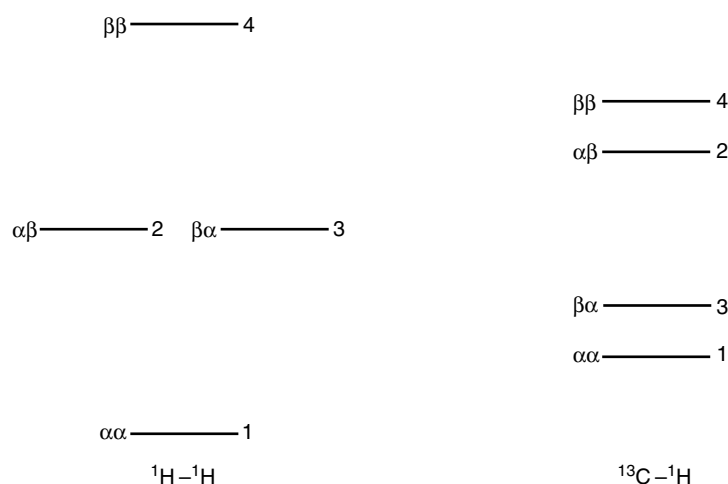
Fig. 2.6 Energy levels, drawn approximately to scale, for two spin systems. On the left is shown a homonuclear system (two protons); on this scale the $\alpha\beta$ and $\beta\alpha$ states have the same energy. On the right is the case for a carbon-13 – proton pair. The Larmor frequency of proton is about four times that of carbon-13, and this is clear reflected in the diagram. The $\alpha\beta$ and $\beta\alpha$ states now have substantially different energies.

number	spin states	M
1	$\alpha\alpha$	1
2	$\alpha\beta$	0
3	$\beta\alpha$	0
4	$\beta\beta$	-1

The selection rule is that $\triangle M = \pm 1$, i.e. the value of M can change up or down by one unit. This means that the allowed transitions are between levels 1 & 2, 3 & 4, 1 & 3 and 2 & 4. The resulting frequencies are easily worked out; for example, the 1–2 transition:
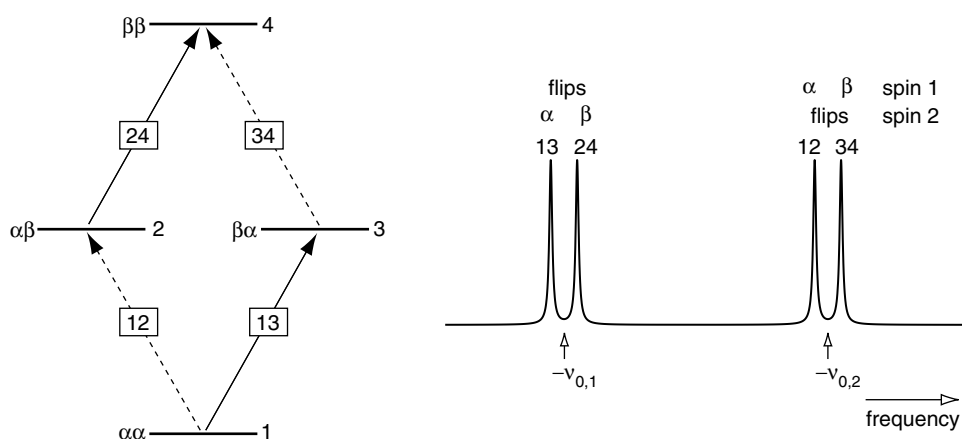
$$\nu_{12} = E_2 - E_1$$
$$= +\tfrac{1}{2}\nu_{0,1} - \tfrac{1}{2}\nu_{0,2} - \tfrac{1}{4}J_{12} - (\tfrac{1}{2}\nu_{0,1} + \tfrac{1}{2}\nu_{0,2} + \tfrac{1}{4}J_{12})$$
$$= -\nu_{0,2} - \tfrac{1}{2}J_{12}.$$

Throughout we will use the convention that when computing the transition frequency we will take the energy of the upper state minus the energy of the lower: $\triangle E = E_{\text{upper}} - E_{\text{lower}}$.

The complete set of transitions are:

transition	spin states	frequency
$1 \to 2$	$\alpha\alpha \to \alpha\beta$	$-\nu_{0,2} - \tfrac{1}{2}J_{12}$
$3 \to 4$	$\beta\alpha \to \beta\beta$	$-\nu_{0,2} + \tfrac{1}{2}J_{12}$
$1 \to 3$	$\alpha\alpha \to \beta\alpha$	$-\nu_{0,1} - \tfrac{1}{2}J_{12}$
$2 \to 4$	$\alpha\beta \to \beta\beta$	$-\nu_{0,1} + \tfrac{1}{2}J_{12}$

The energy levels and corresponding schematic spectrum are shown in Fig. 2.7. There is a lot we can say about this spectrum. Firstly, each allowed transition corresponds to one of the spins flipping from one spin state to the other, while the spin state of the other spin remains fixed. For example, transition 1–2 involves a spin 2 going from α to β whilst spin 1 remains in the α state. In this transition we say that spin 2 is *active* and spin 1 is *passive*. As

Fig. 2.7 On the left, the energy levels of a two-spin system; the arrows show the allowed transitions: solid lines for transitions in which spin 1 flips and dotted for those in which spin 2 flips. On the right, the corresponding spectrum; it is assumed that the Larmor frequency of spin 2 is greater in magnitude than that of spin 1 and that the coupling J_{12} is positive.

spin 2 flips in this transition, it is not surprising that the transition forms one part of the doublet for spin 2.

Transition 3–4 is similar to 1–2 except that the passive spin (spin 1) is in the β state; this transition forms the second line of the doublet for spin 2. This discussion illustrates a very important point, which is that the lines of a multiplet can be associated with different spin states of the coupled (passive) spins. We will use this kind of interpretation very often, especially when considering two-dimensional spectra.

The two transitions in which spin 1 flips are 1–3 and 2–4, and these are associated with spin 2 being in the α and β spin states, respectively. Which spin flips and the spins states of the passive spins are shown in Fig. 2.7.

What happens is the coupling is negative? If you work through the table you will see that there are still four lines at the same frequencies as before. All that changes is the labels of the lines. So, for example, transition 1–2 is now the right line of the doublet, rather than the left line. From the point of view of the spectrum, what swaps over is the spin state of the passive spin associated with each line of the multiplet. The overall appearance of the spectrum is therefore independent of the sign of the coupling constant.

Multiple quantum transitions

There are two more transitions in our two-spin system which are not allowed by the usual selection rule. The first is between states 1 and 4 ($\alpha\alpha \rightarrow \beta\beta$) in which both spins flip. The $\triangle M$ value is 2, so this is called a *double-quantum* transition. Using the same terminology, all of the allowed transitions described above, which have $\triangle M = 1$, are *single-quantum* transitions. From the table of energy levels it is easy to work out that its frequency is $(-\nu_{0,1} - \nu_{0,2})$ i.e. the sum of the Larmor frequencies. Note that the coupling has no effect on the frequency of this line.

The second transition is between states 2 and 3 ($\alpha\beta \rightarrow \beta\alpha$); again, both

spins flip. The $\triangle M$ value is 0, so this is called a *zero-quantum* transition, and its frequency is $(-\nu_{0,1} + \nu_{0,2})$ i.e. the difference of the Larmor frequencies. As with the double-quantum transition, the coupling has no effect on the frequency of this line.

In a two spin system the double- and zero-quantum spectra are not especially interesting, but we will see in a three-spin system that the situation is rather different. We will also see later on that in two-dimensional spectra we can exploit to our advantage the special properties of these multiple-quantum spectra.

2.5 Three spins

If we have three spins, each of which is coupled to the other two, then the spectrum consists of three doublets of doublets, one centred at the shift of each of the three spins; the *spin topology* is shown in Fig. 2.9. The appearance of these multiplets will depend on the relative sizes of the couplings. For example, if $J_{12} = J_{13}$ the doublet of doublets from spin 1 will collapse to a 1:2:1 triplet. On the other hand, if $J_{12} = 0$, only doublets will be seen for spin 1 and spin 2, but spin 3 will still show a doublet of doublets.

Energy levels

Each of the three spins can be in the α or β spin state, so there are a total of 8 possible combinations corresponding to 8 energy levels. The energies are given by:

$$E_{m_1 m_2 m_3} = m_1 \nu_{0,1} + m_2 \nu_{0,2} + m_3 \nu_{0,3} + m_1 m_2 J_{12} + m_1 m_3 J_{13} + m_2 m_3 J_{23}$$

where m_i is the value of the quantum number m for the ith spin. The energies and corresponding M values ($= m_1 + m_2 + m_3$) are shown in the table:

| number	spin states	M	energy
1	$\alpha\alpha\alpha$	$\frac{3}{2}$	$+\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} + \frac{1}{2}\nu_{0,3} + \frac{1}{4}J_{12} + \frac{1}{4}J_{13} + \frac{1}{4}J_{23}$
2	$\alpha\beta\alpha$	$\frac{1}{2}$	$+\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} + \frac{1}{2}\nu_{0,3} - \frac{1}{4}J_{12} + \frac{1}{4}J_{13} - \frac{1}{4}J_{23}$
3	$\beta\alpha\alpha$	$\frac{1}{2}$	$-\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} + \frac{1}{2}\nu_{0,3} - \frac{1}{4}J_{12} - \frac{1}{4}J_{13} + \frac{1}{4}J_{23}$
4	$\beta\beta\alpha$	$-\frac{1}{2}$	$-\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} + \frac{1}{2}\nu_{0,3} + \frac{1}{4}J_{12} - \frac{1}{4}J_{13} - \frac{1}{4}J_{23}$
5	$\alpha\alpha\beta$	$\frac{1}{2}$	$+\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} - \frac{1}{2}\nu_{0,3} + \frac{1}{4}J_{12} - \frac{1}{4}J_{13} - \frac{1}{4}J_{23}$
6	$\alpha\beta\beta$	$-\frac{1}{2}$	$+\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} - \frac{1}{2}\nu_{0,3} - \frac{1}{4}J_{12} - \frac{1}{4}J_{13} + \frac{1}{4}J_{23}$
7	$\beta\alpha\beta$	$-\frac{1}{2}$	$-\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} - \frac{1}{2}\nu_{0,3} - \frac{1}{4}J_{12} + \frac{1}{4}J_{13} - \frac{1}{4}J_{23}$
8	$\beta\beta\beta$	$-\frac{3}{2}$	$-\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} - \frac{1}{2}\nu_{0,3} + \frac{1}{4}J_{12} + \frac{1}{4}J_{13} + \frac{1}{4}J_{23}$

We have grouped the energy levels into two groups of four; the first group all have spin 3 in the α state and the second have spin 3 in the β state. The energy levels (for a homonuclear system) are shown schematically in Fig. 2.10.

Spectrum

The selection rule is as before, that is M can only change by 1. However, in the case of more than two spins, there is the additional constraint that *only*
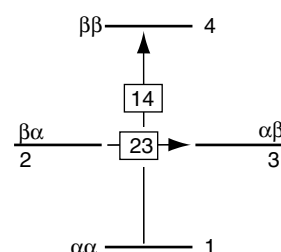
Fig. 2.8 In a two-spin system there is one double quantum transition (1–4) and one zero-quantum transition (2–3); the frequency of neither of these transitions are affected by the size of the coupling between the two spins.
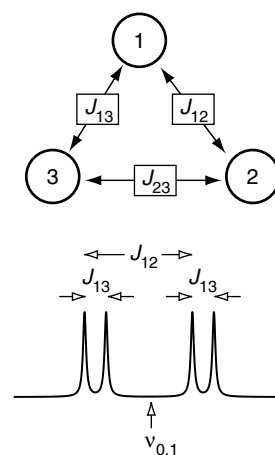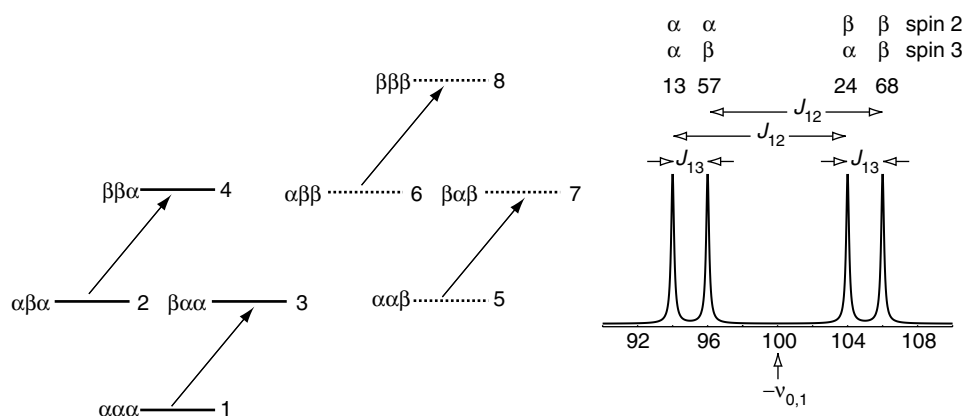
Fig. 2.9 The *topology* – that is the number of spins and the couplings between them – for a three-spin system in which each spin is coupled to both of the others. The resulting spectrum consists of three doublets of doublets, a typical example of which is shown for spin 1 with the assumption that J_{12} is greater than J_{13}.
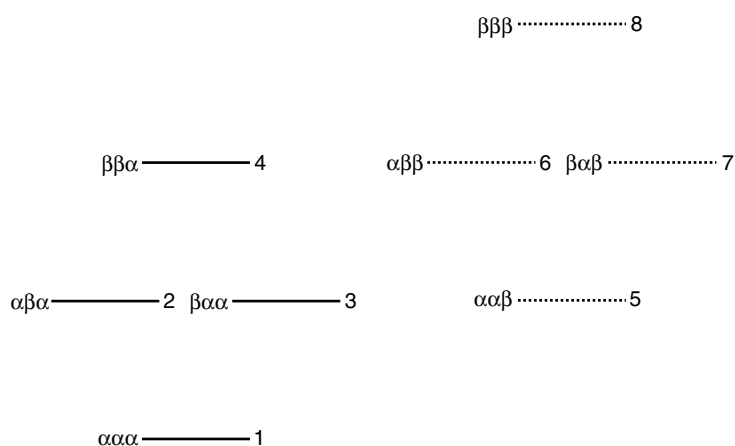
Fig. 2.10 Energy levels for a homonuclear three-spin system. The levels can be grouped into two sets of four: those with spin 3 in the α state (shown on the left with solid lines) and those with spin 3 in the β state, shown on the right (dashed lines).

one spin can flip. Applying these rules we see that there are four allowed transitions in which spin 1 slips: 1–3, 2–4, 5–7 and 6–8. The frequencies of these lines can easily be worked out from the table of energy levels on page **2–9**. The results are shown in the table, along with the spin states of the passive spins (2 and 3 in this case).

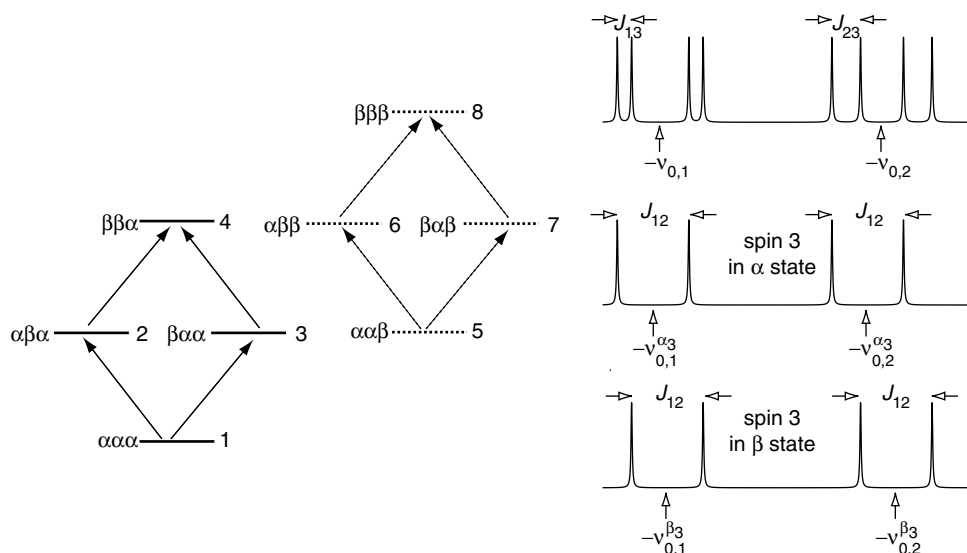| transition	state of spin 2	state of spin 3	frequency
1–3	α	α	$-\nu_{0,1} - \frac{1}{2}J_{12} - \frac{1}{2}J_{13}$
2–4	β	α	$-\nu_{0,1} + \frac{1}{2}J_{12} - \frac{1}{2}J_{13}$
5–7	α	β	$-\nu_{0,1} - \frac{1}{2}J_{12} + \frac{1}{2}J_{13}$
6–8	β	β	$-\nu_{0,1} + \frac{1}{2}J_{12} + \frac{1}{2}J_{13}$

Fig. 2.11 Energy levels for a three-spin system showing by the arrows the four allowed transitions which result in the doublet of doublets at the shift of spin 1. The schematic multiplet is shown on the right, where it has been assuming that $\nu_{0,1} = -100$ Hz, $J_{12} = 10$ Hz and $J_{13} = 2$ Hz. The multiplet is labelled with the spin states of the passive spins.

These four transitions form the four lines of the multiplet (a doublet of doublets) at the shift of spin 1. The schematic spectrum is illustrated in Fig. 2.11. As in the case of a two-spin system, we can label each line of the

multiplet with the spin states of the passive spins – in the case of the multiplet from spin 1, this means the spin states of spins 2 and 3. In the same way, we can identify the four transitions which contribute to the multiplet from spin 2 (1–2, 3–4, 5–6 and 7–8) and the four which contribute to that from spin 3 (1–5, 3–7, 2–6 and 4–8).

Subspectra

Fig. 2.12 Illustration of the division of the two multiplets from spins 1 and 2 into subspectra according to the spin state of spin 3. The transitions associated with spin 3 in the α state (indicated by the full lines on the energy level diagram) give rise to a pair of doublets, but with their centres shifted from the Larmor frequencies by half the coupling to spin 3. The same is true of those transitions associated with spin 3 being in the β state (dashed lines), except that the shift is in the opposite direction.

One was of thinking about the spectrum from the three-spin system is to divide up the lines in the multiplets for spins 1 and 2 into two groups or *subspectra*. The first group consists of the lines which have spin 3 in the α state and the second group consists of the lines which have spin 3 in the α state. This separation is illustrated in Fig. 2.12.

There are four lines which have spin-3 in the α state, and as can be seen from the spectrum these form two doublets with a common separation of J_{12}. However, the two doublets are not centred at $-v_{0,1}$ and $-v_{0,2}$, but at $(-v_{0,1} - \frac{1}{2}J_{13})$ and $(-v_{0,2} - \frac{1}{2}J_{23})$. We can define an *effective* Larmor frequency for spin 1 with spin 3 in the α spin state, $v_{0,1}^{\alpha_3}$, as

$$v_{0,1}^{\alpha_3} = v_{0,1} + \tfrac{1}{2}J_{13}$$

and likewise for spin 2:

$$v_{0,2}^{\alpha_3} = v_{0,2} + \tfrac{1}{2}J_{23}.$$

The two doublets in the sub-spectrum corresponding to spin 3 being in the α state are thus centred at $-v_{0,1}^{\alpha_3}$ and $-v_{0,2}^{\alpha_3}$. Similarly, we can define effective Larmor frequencies for spin 3 being in the β state:

$$v_{0,1}^{\beta_3} = v_{0,1} - \tfrac{1}{2}J_{13} \qquad v_{0,2}^{\beta_3} = v_{0,2} - \tfrac{1}{2}J_{23}.$$

The two doublets in the β sub-spectrum are centred at $-\nu_{0,1}^{\beta_3}$ and $-\nu_{0,2}^{\beta_3}$.

We can think of the spectrum of spin 1 and 2 as being composed of two subspectra, each from a two spin system but in which the Larmor frequencies are effectively shifted one way of the other by half the coupling to the third spin. This kind of approach is particularly useful when it comes to dealing with strongly coupled spin systems, section 2.6

Note that the separation of the spectra according to the spin state of spin 3 is arbitrary. We could just as well separate the two multiplets from spins 1 and 3 according to the spin state of spin 2.

Multiple quantum transitions

There are six transitions in which M changes by 2. Their frequencies are given in the table.

transition	initial state	final state	frequency
1–4	$\alpha\alpha\alpha$	$\beta\beta\alpha$	$-\nu_{0,1} - \nu_{0,2} - \frac{1}{2}J_{13} - \frac{1}{2}J_{23}$
5–8	$\alpha\alpha\beta$	$\beta\beta\beta$	$-\nu_{0,1} - \nu_{0,2} + \frac{1}{2}J_{13} + \frac{1}{2}J_{23}$
1–7	$\alpha\alpha\alpha$	$\beta\alpha\beta$	$-\nu_{0,1} - \nu_{0,3} - \frac{1}{2}J_{12} - \frac{1}{2}J_{23}$
2–8	$\alpha\beta\alpha$	$\beta\beta\beta$	$-\nu_{0,1} - \nu_{0,3} + \frac{1}{2}J_{12} + \frac{1}{2}J_{23}$
1–6	$\alpha\alpha\alpha$	$\alpha\beta\beta$	$-\nu_{0,2} - \nu_{0,3} - \frac{1}{2}J_{12} - \frac{1}{2}J_{13}$
3–8	$\beta\alpha\alpha$	$\beta\beta\beta$	$-\nu_{0,2} - \nu_{0,3} + \frac{1}{2}J_{12} + \frac{1}{2}J_{13}$

These transitions come in three pairs. Transitions 1–4 and 5–8 are centred at the sum of the Larmor frequencies of spins 1 and 2; this is not surprising as we note that in these transitions it is the spin states of both spins 1 and 2 which flip. The two transitions are separated by the *sum* of the couplings to spin 3 ($J_{13} + J_{23}$), but they are unaffected by the coupling J_{12} which is between the two spins which flip.
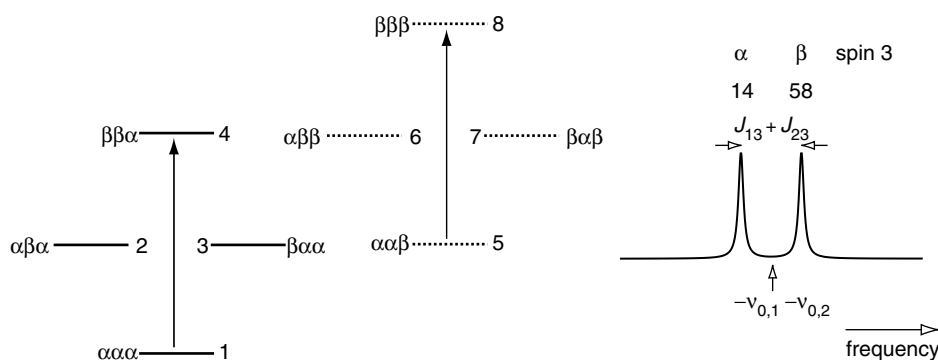
Fig. 2.13 There are two double quantum transitions in which spins 1 and 2 both flip (1–4 and 5–8). The two resulting lines form a doublet which is centred at the sum of the Larmor frequencies of spins 1 and 2 and which is split by the sum of the couplings to spin 3. As with the single-quantum spectra, we can associate the two lines of the doublet with different spin states of the third spin. It has been assumed that both couplings are positive.

We can describe these transitions as a kind of double quantum doublet. Spins 1 and 2 are both active in these transitions, and spin 3 is passive. Just as

we did before, we can associate one line with spin 3 being in the α state (1–4) and one with it being in the β state (5–8). A schematic representation of the spectrum is shown in Fig. 2.13.

There are also six zero-quantum transitions in which M does not change. Like the double quantum transitions these group in three pairs, but this time centred around the *difference* in the Larmor frequencies of two of the spins. These zero-quantum doublets are split by the *difference* of the couplings to the spin which does not flip in the transitions. There are thus many similarities between the double- and zero-quantum spectra.

In a three spin system there is one triple-quantum transition, in which M changes by 3, between levels 1 ($\alpha\alpha\alpha$) and 8 ($\beta\beta\beta$). In this transition all of the spins flip, and from the table of energies we can easily work out that its frequency is $-\nu_{0,1} - \nu_{0,2} - \nu_{0,3}$, i.e. the sum of the Larmor frequencies.

We see that the single-quantum spectrum consists of three doublets of doublets, the double-quantum spectrum of three doublets and the triple-quantum spectrum of a single line. This illustrates the idea that as we move to higher orders of multiple quantum, the corresponding spectra become simpler. This feature has been used in the analysis of some complex spin systems.

Combination lines

There are three more transitions which we have not yet described. For these, M changes by 1 but all three spins flip; they are called *combination lines*. Such lines are not seen in normal spectra but, like multiple quantum transitions, they can be detected indirectly using two-dimensional spectra. We will also see in section 2.6 that these lines may be observable in strongly coupled spectra. The table gives the frequencies of these three lines:

transition	initial state	final state	frequency
2–7	$\alpha\beta\alpha$	$\beta\alpha\beta$	$-\nu_{0,1} + \nu_{0,2} - \nu_{0,3}$
3–6	$\beta\alpha\alpha$	$\alpha\beta\beta$	$+\nu_{0,1} - \nu_{0,2} - \nu_{0,3}$
4–5	$\beta\beta\alpha$	$\alpha\alpha\beta$	$+\nu_{0,1} + \nu_{0,2} - \nu_{0,3}$

Notice that the frequencies of these lines are not affected by any of the couplings.

2.6 Strong coupling

So far all we have said about energy levels and spectra applies to what are called *weakly coupled* spin systems. These are spin systems in which the differences between the Larmor frequencies (in Hz) of the spins are much greater in magnitude than the magnitude of the couplings between the spins.

Under these circumstances the rules from predicting spectra are very simple – they are the ones you are already familiar with which you use for constructing multiplets. In addition, in the weak coupling limit it is possible to work out the energies of the levels present simply by making all possible combinations of spin states, just as we have done above. Finally, in this limit all of the lines in a multiplet have the same intensity.

We need to be careful here as Larmor frequencies, the differences between Larmor frequencies and the values of couplings can be positive or negative! In deciding whether or not a spectrum will be strongly coupled we need to compare the *magnitude* of the difference in the Larmor frequencies with the *magnitude* of the coupling.

If the separation of the Larmor frequencies is not sufficient to satisfy the weak coupling criterion, the system is said to be *strongly coupled*. In this limit *none* of the rules outlined in the previous paragraph apply. This makes predicting or analysing the spectra much more difficult than in the case of weak coupling, and really the only practical approach is to use computer simulation. However, it is useful to look at the spectrum from two strongly coupled spins as the spectrum is simple enough to analyse by hand and will reveal most of the of the crucial features of strong coupling.

You will often find that people talk of two spins being *strongly coupled* when what they really mean is the coupling between the two spins is *large*. This is sloppy usage; we will always use the term strong coupling in the sense described in this section.

It is a relatively simple exercise in quantum mechanics to work out the energy levels and hence frequencies and intensities of the lines from a strongly coupled two-spin system[1]. These are given in the following table.

transition	frequency	intensity
1–2	$\frac{1}{2}D - \frac{1}{2}\Sigma - \frac{1}{2}J_{12}$	$(1 + \sin 2\theta)$
3–4	$\frac{1}{2}D - \frac{1}{2}\Sigma + \frac{1}{2}J_{12}$	$(1 - \sin 2\theta)$
1–3	$-\frac{1}{2}D - \frac{1}{2}\Sigma - \frac{1}{2}J_{12}$	$(1 - \sin 2\theta)$
2–4	$-\frac{1}{2}D - \frac{1}{2}\Sigma + \frac{1}{2}J_{12}$	$(1 + \sin 2\theta)$

In this table Σ is the sum of the Larmor frequencies:

$$\Sigma = \nu_{0,1} + \nu_{0,2}$$

and D is the *positive* quantity defined as

$$D^2 = (\nu_{0,1} - \nu_{0,2})^2 + J_{12}^2. \tag{2.4}$$

The angle θ is called the *strong coupling parameter* and is defined via

$$\sin 2\theta = \frac{J_{12}}{D}.$$

The first thing to do is to verify that these formulae give us the expected result when we impose the condition that the separation of the Larmor frequencies is large compared to the coupling. In this limit it is clear that

$$D^2 = (\nu_{0,1} - \nu_{0,2})^2 + J_{12}^2$$
$$\approx (\nu_{0,1} - \nu_{0,2})^2$$

and so $D = (\nu_{0,1} - \nu_{0,2})$. Putting this value into the table above gives us exactly the frequencies we had before on page **2**–7.

When D is very much larger than J_{12} the fraction J_{12}/D becomes small, and so $\sin 2\theta \approx 0$ ($\sin \phi$ goes to zero as ϕ goes to zero). Under these circumstances all of the lines have unit intensity. So, the weak coupling limit is regained.

Figure 2.14 shows a series of spectra computed using the above formulae in which the Larmor frequency of spin 1 is held constant while the Larmor frequency of spin 2 is progressively moved towards that of spin 1. This makes the spectrum more and more strongly coupled. The spectrum at the bottom is almost weakly coupled; the peaks are just about all the same intensity and where we expect them to be.

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[1]See, for example, Chapter 10 of *NMR: The Toolkit*, by P J Hore, J A Jones and S Wimperis (Oxford University Press, 2000)
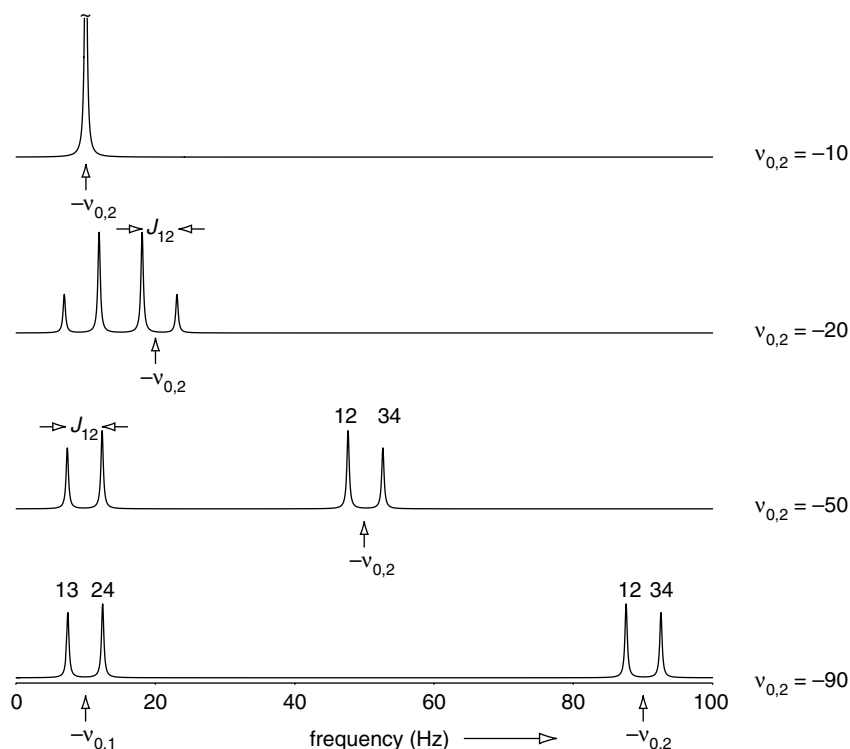
Fig. 2.14 A series of spectra of a two spin system in which the Larmor frequency of spin 1 is help constant and that of spin 2 is moved in closer to spin 1. The spectra become more and more strongly coupled showing a pronounced roof effect until in the limit that the two Larmor frequencies are equal only one line is observed. Note that as the "outer" lines get weaker the "inner" lines get proportionately stronger. The parameters used for these spectra were $\nu_{0,1} = -10$ Hz and $J_{12} = 5$ Hz; the peak in the top most spectrum has been truncated.
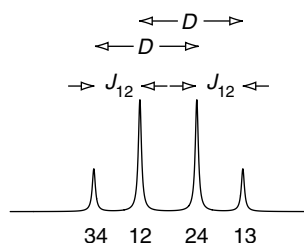
However, as the Larmor frequencies of the two spins get closer and closer together we notice two things: (1) the "outer" two lines get weaker and the "inner" two lines get stronger; (2) the two lines which originally formed the doublet are no longer symmetrically spaced about the Larmor frequency; in fact the stronger of the two lines moves progressively closer to the Larmor frequency. There is one more thing to notice which is not so clear from the spectra but is clear if one looks at the frequencies in the table. This is that the two lines that originally formed the spin 1 doublet are always separated by J_{12}; the same is true for the other doublet.

These spectra illustrate the so-called *roof* effect in which the intensities of the lines in a strongly coupled multiplet tilt upwards towards the multiplet from the coupled spin, making a kind of roof; Fig. 2.15 illustrates the idea. The spectra in Fig 2.14 also illustrate the point that when the two Larmor frequencies are identical there is only one line seen in the spectrum and this is at this Larmor frequency. In this limit lines 1–2 and 2–4 both appear at the Larmor frequency and with intensity 2; lines 1–3 and 3–4 appear elsewhere but have intensity zero.

The "take home message" is that from such strongly coupled spectra we can easily measure the coupling, but the Larmor frequencies (the shifts) are no longer mid-way between the two lines of the doublet. In fact it is easy
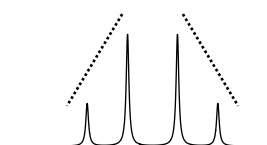
Fig. 2.15 The intensity distributions in multiplets from strongly-coupled spectra are such that the multiplets "tilt" towards one another; this is called the "roof" effect.

enough to work out the Larmor frequencies using the following method; the idea is illustrated in Fig. 2.16.

If we denote the frequency of transition 1–2 as ν_{12} and so on, it is clear from the table that the frequency separation of the left-hand lines of the two multiplets (3–4 and 2–4) is D

$$\nu_{34} - \nu_{24} = (\tfrac{1}{2}D - \tfrac{1}{2}\Sigma + \tfrac{1}{2}J_{12}) - (-\tfrac{1}{2}D - \tfrac{1}{2}\Sigma + \tfrac{1}{2}J_{12})$$
$$= D.$$

Fig. 2.16 The quantities J_{12} and D are readily measurable from the spectrum of two strongly coupled spins.

The separation of the other two lines is also D. Remember we can easily measure J_{12} directly from the splitting, and so once we know D it is easy to compute $(\nu_{0,1} - \nu_{0,2})$ from its definition, Eqn. 2.4.

$$D^2 = (\nu_{0,1} - \nu_{0,2})^2 + J_{12}^2$$
$$\text{therefore } (\nu_{0,1} - \nu_{0,2}) = \sqrt{D^2 - J_{12}^2}.$$

Now we notice from the table on **2–**14 that the sum of the frequencies of the two stronger lines (1–2 and 2–4) or the two weaker lines (3–4 and 2–4) gives us $-\Sigma$:

$$\nu_{12} + \nu_{24} = (\tfrac{1}{2}D - \tfrac{1}{2}\Sigma - \tfrac{1}{2}J_{12}) + (-\tfrac{1}{2}D - \tfrac{1}{2}\Sigma + \tfrac{1}{2}J_{12})$$
$$= -\Sigma.$$

Now we have a values for $\Sigma = (\nu_{0,1} + \nu_{0,2})$ and a value for $(\nu_{0,1} - \nu_{0,2})$ we can find $\nu_{0,1}$ and $\nu_{0,2}$ separately:

$$\nu_{0,1} = \tfrac{1}{2}(\Sigma + (\nu_{0,1} - \nu_{0,2})) \quad \nu_{0,2} = \tfrac{1}{2}(\Sigma - (\nu_{0,1} - \nu_{0,2})).$$

In this way we can extract the Larmor frequencies of the two spins (the shifts) and the coupling from the strongly coupled spectrum.

Notation for spin systems

There is a traditional notation for spin systems which it is sometimes useful to use. Each spin is given a letter (rather than a number), with a different letter for spins which have different Larmor frequencies (chemical shifts). If the Larmor frequencies of two spins are widely separated they are given letters which are widely separated in the alphabet. So, two weakly coupled spins are usually denoted as A and X; whereas three weakly coupled spins would be denoted AMX.

If spins are strongly coupled, then the convention is to used letters which are close in the alphabet. So, a strongly coupled two-spin system would be denoted AB and a strongly coupled three-spin system ABC. The notation ABX implies that two of the spins (A and B) are strongly coupled but the Larmor frequency of the third spin is widely separated from that of A and B.

The ABX spin system

We noted in section 2.5 that we could think about the spectrum of three coupled spins in terms of sub-spectra in which the Larmor frequencies were replaced by effective Larmor frequencies. This kind of approach is very useful for understanding the AB part of the ABX spectrum.
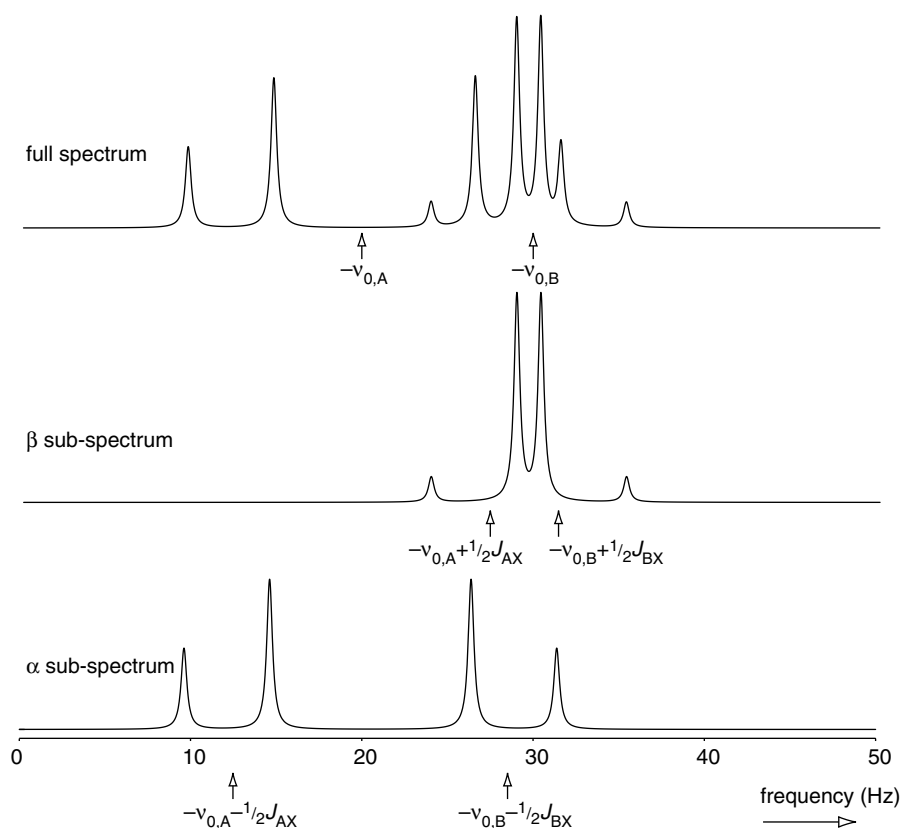
Fig. 2.17 AB parts of an ABX spectrum illustrating the decomposition into two sub-spectra with different effective Larmor frequencies (indicated by the arrows). The parameters used in the simulation were $\nu_{0,\mathrm{A}} = -20$ Hz, $\nu_{0,\mathrm{B}} = -30$ Hz, $J_{\mathrm{AB}} = 5$ Hz, $J_{\mathrm{AX}} = 15$ Hz and $J_{\mathrm{BX}} = 3$ Hz.

As spin X is weakly coupled to the others we can think of the AB part of the spectrum as two superimposed AB sub-spectra; one is associated with the X spin being in the α state and the other with the spin being in the β state. If spins A and B have Larmor frequencies $\nu_{0,A}$ and $\nu_{0,B}$, respectively, then one sub-spectrum has effective Larmor frequencies $\nu_{0,A} + \frac{1}{2}J_{\mathrm{AX}}$ and $\nu_{0,B} + \frac{1}{2}J_{\mathrm{BX}}$. The other has effective Larmor frequencies $\nu_{0,A} - \frac{1}{2}J_{\mathrm{AX}}$ and $\nu_{0,B} - \frac{1}{2}J_{\mathrm{BX}}$.

The separation between the two effective Larmor frequencies in the two subspectra can easily be different, and so the degree of strong coupling (and hence the intensity patterns) in the two subspectra will be different. All we can measure is the complete spectrum (the sum of the two sub-spectra) but once we know that it is in fact the sum of two AB-type spectra it is usually possible to disentangle these two contributions. Once we have done this, the two sub-spectra can be analysed in exactly the way described above for an AB system. Figure 2.17 illustrates this decomposition.

The form of the X part of the ABX spectrum cannot be deduced from this simple analysis. In general it contains 6 lines, rather than the four which would be expected in the weak coupling limit. The two extra lines are combination lines which become observable when strong coupling is present.

2.7   Exercises

E 2–1

In a proton spectrum the peak from TMS is found to be at 400.135705 MHz. What is the shift, in ppm, of a peak which has a frequency of 400.136305 MHz? Recalculate the shift using the spectrometer frequency, ν_{spec} quoted by the manufacturer as 400.13 MHz rather than ν_{TMS} in the denominator of Eq. 2.2:

$$\delta_{\text{ppm}} = 10^6 \times \frac{\nu - \nu_{\text{TMS}}}{\nu_{\text{spec}}}.$$

Does this make a significant difference to the value of the shift?

E 2–2

Two peaks in a proton spectrum are found at 1.54 and 5.34 ppm. The spectrometer frequency is quoted as 400.13 MHz. What is the separation of these two lines in Hz and in rad s^{-1}?

E 2–3

Calculate the Larmor frequency (in Hz and in rad s^{-1}) of a carbon-13 resonance with chemical shift 48 ppm when recorded in a spectrometer with a magnetic field strength of 9.4 T. The gyromagnetic ratio of carbon-13 is $+6.7283 \times 10^7$ rad s^{-1} T^{-1}.

E 2–4

Of course in reality the Larmor frequencies out to be tens or hundreds of MHz, not 100 Hz! However, it makes the numbers easier to handle if we use these unrealistic small values; the principles remain the same, however.

Consider a system of two weakly coupled spins. Let the Larmor frequency of the first spin be -100 Hz and that of the second spin be -200 Hz, and let the coupling between the two spins be -5 Hz. Compute the frequencies of the lines in the normal (single quantum) spectrum.

Make a sketch of the spectrum, roughly to scale, and label each line with the energy levels involved (i.e. 1–2 etc.). Also indicate for each line which spin flips and the spin state of the passive spin. Compare your sketch with Fig. 2.7 and comment on any differences.

E 2–5

For a three spin system, draw up a table similar to that on page **2**–10 showing the frequencies of the four lines of the multiplet from spin 2. Then, taking $\nu_{0,2} = -200$ Hz, $J_{23} = 4$ Hz and the rest of the parameters as in Fig. 2.11, compute the frequencies of the lines which comprise the spin 2 multiplet. Make a sketch of the multiplet (roughly to scale) and label the lines in the same way as is done in Fig. 2.11. How would these labels change if $J_{23} = -4$ Hz?

On an energy level diagram, indicate the four transitions which comprise the spin 2 multiplet, and which four comprise the spin 3 multiplet.

E 2–6

For a three spin system, compute the frequencies of the six zero-quantum

transitions and also mark these on an energy level diagram. Do these six transitions fall into natural groups? How would you describe the spectrum?

E 2–7
Calculate the line frequencies and intensities of the spectrum for a system of two spins with the following parameters: $\nu_{0,1} = -10$ Hz, $\nu_{0,2} = -20$ Hz, $J_{12} = 5$ Hz. Make a sketch of the spectrum (roughly to scale) indicating which transition is which and the position of the Larmor frequencies.

E 2–8
The spectrum from a strongly-coupled two spin system showed lines at the following frequencies, in Hz, (intensities are given in brackets): 32.0 (1.3), 39.0 (0.7), 6.0 (0.7), 13.0 (1.3). Determine the values of the coupling constant and the two Larmor frequencies. Show that the values you find are consistent with the observed intensities.

Make sure that you have your calculator set to "radians" when you compute $\sin 2\theta$.
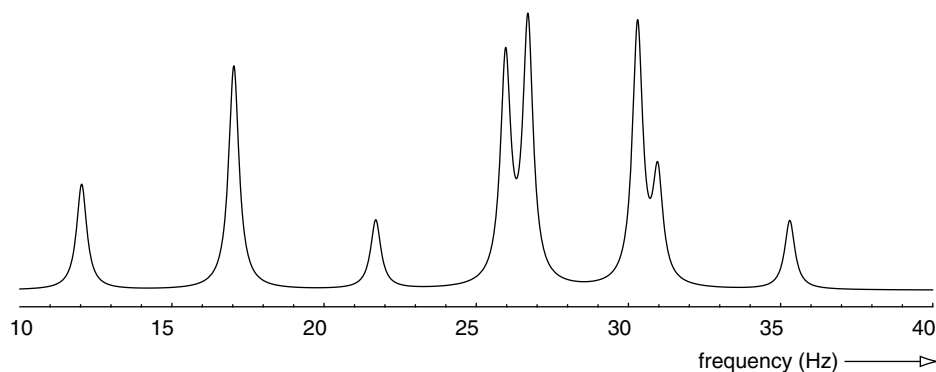
Fig. 2.18 The AB part of an ABX spectrum

E 2–9
Figure 2.18 shows the AB part of an ABX spectrum. Disentangle the two subspectra, mark in the rough positions of the effective Larmor frequencies and hence estimate the size of the AX and BX couplings. Also, give the value of the AB coupling.