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 $\sin 2\theta$.

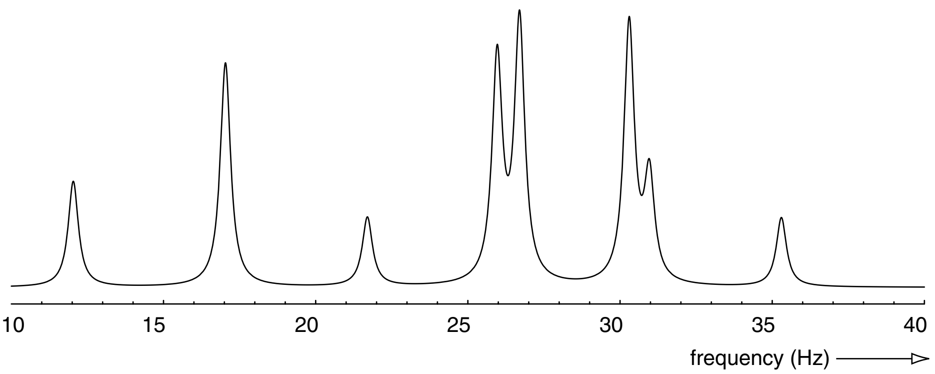

Fig. 2.18 The AB part of an ABX spectrum

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.