Multiple spins systems

We recall that in coupled spins we have

$$\nu_A^* = \nu_A + m_X J_{AX} \qquad (1)$$

It comes that

$$\nu_A^+ = \nu_A + \tfrac{1}{2} J_{AX} \qquad (2)$$
$$\nu_A^- = \nu_A - \tfrac{1}{2} J_{AX} \qquad (3)$$

It means that one spin that couples with another is splited and the extent of coupling is J.

Remember that J_{AX} may be positive but also negative.
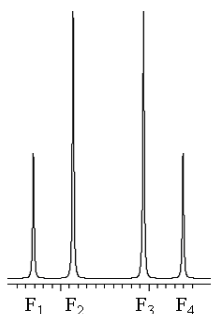
AX system

As the two lines of an AX doublet are equal, we cannot tell from a simple NMR experiment, which is which. Therefore we cannot find the sign of J_{AX} directly for an AX system. An AX spin system is called a 'first order system'.

At an operating frequency of 121.499 MHz, the $^{31}P\{1H\}$ spectrum of Ph_3PSe shows a satellite spectrum of two equal peaks at 4795.997 and 4035.354 Hz, caused by coupling to ^{77}Se (*i.e.* an AX system). (There is also a much larger peak at 4415.673 Hz, the main ^{31}P spectrum, due to molecules which contain any of the other isotopes of selenium which do not have $I = \tfrac{1}{2}$ and therefore do not show coupling to phosphorus.)

1. Calculate the coupling constant $^1J(^{31}P^{77}Se)$ to one decimal place, the chemical shift in Hz of phosphorus in molecules containing ^{77}Se, and this shift in ppm, to two decimal places.

AB system

In the first order AX system, the molecule can be thought to be in two different separate states, depending on the value of m_X: we can analyse the spectrum of A as the superposition of two different sub-spectra, + and –, for the two values $+\tfrac{1}{2}$ or $-\tfrac{1}{2}$ of m_X. We say that m_X is a 'good quantum number', because it can vary independently of the other quantum numbers. In an AB system, this is not so: if we wanted to analyse the effect of the AB pair on another nucleus X, we would have to take a combined quantum number for A and B together.

An AB system consists of four lines, $F_1...F_4$, as in the diagram. There are two equal splittings, equal to the coupling constant:

$$|J_{AB}| = F_1 - F_2 = F_3 - F_4 \qquad (4) \text{ Slide #19}$$

This is the same as for an AX spin system: if you take the X-approximation for an AB system, you still get the correct coupling constant. You still cannot find the sign of J. The intensities of the four lines are $I_1...I_4$ and

$$I_2/I_1 = I_3/I_4 = (F_1 - F_4)/(F_2 - F_3) \qquad (5)$$

$F_1 \quad F_2 \qquad F_3 \quad F_4$

Be careful on the calculation of the chemical shifts. The midpoint of the AB spectrum is the average of ν_A and ν_B:

$$\nu_M = (\nu_A + \nu_B)/2 = (F_1 + F_4)/2 = (F_2 + F_3)/2 \qquad (6)$$

The difference between ν_A and ν_B is given by:

$$\delta_{AB} = \nu_A - \nu_B = \sqrt{((F1 - F4)(F2 - F3))} \qquad (7)$$
$$\text{Since } 2C = \sqrt{((\nu_A - \nu_B)^2 + (J)^2)}$$

Make sure you understood!! And demonstrate that
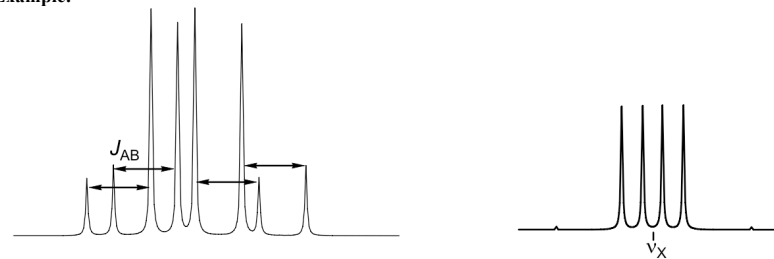
$$\nu_A = \nu_M + \delta_{AB}/2 \qquad (8)$$
$$\nu_B = \nu_M - \delta_{AB}/2 \qquad (9)$$

Question: The four lines of the ^{31}P AB spectrum shown above are at

18906.223, 18679.424, 18280.477, 18053.680 Hz.

1. Calculate ν_A, ν_B and J_{AB} in Hz, all to one decimal place.

ABX system

Example:

Problem:

Chemical shift of the AB systems

121.2 ; 115.7 ; 108.1 ; 102.7 ; 99.3 ; 89.8 ; 86.3 ; 76.7

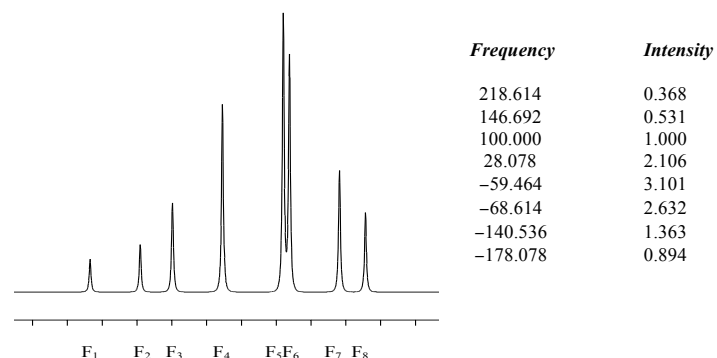An ABX system will consists in two superimposed AB sub-spectra, with the same J_{AB}

All you need to do is to find the two AB sub-spectra + and –

1. Find the value of $^2J_{AB}$
2. Solve the AB system for each quartet.
3. Compare the two solution you have found.
4. Cite some arguments to choose between both.

5. The two lines having small intensity are combination lines and decrease in intensity as $\nu_A-\nu_B$ increases. Their intensity is $\sin^2(\phi+-\phi-)$ for an intensity of 1 for the external lines of the X system.

    a. $\phi+$ and $\phi-$ can be calculated from the formula $\sin^2\phi = J/2C$ (see slide #18)

    b. Give the calculated intensity of the two combinations lines considering the two solutions obtained before and conclude.

AB$_2$ system

This is much easier! Here atom A sits on an element of symmetry (*e.g.* a C_2 axis or more often a mirror plane), which relates the two atoms B, so that A couples equally to each B. The B atoms are chemically and magnetically equivalent. In the X limit we have an AX$_2$ system, which consists of a 1:2:1 triplet for A and a 1:1 doublet for X. When J_{AB}/δ_{AB} is small, there are more peaks (eight + one combination line with 0 intensity) and the spectrum is no longer recognisable as a triplet and doublet. However, the appearance depends only on J/δ, so by simulating several values using a computer program (or looking up pictures in a textbook) it is usually possible to assign the peaks. Here is the picture for $J/\delta=0.5$, with $\nu_A>\nu_B$. If $\nu_A<\nu_B$, it would be back to front, because, unlike an AB spectrum, it is not symmetrical.

Frequency	Intensity
218.614	0.368
146.692	0.531
100.000	1.000
28.078	2.106
−59.464	3.101
−68.614	2.632
−140.536	1.363
−178.078	0.894

F_1 F_2 F_3 F_4 F_5F_6 F_7 F_8

To find the parameters, use the following equations:

$$\nu_A = F_3 \tag{10}$$
$$\nu_B = (F_5 + F_7)/2 \tag{11}$$
$$|J_{AB}| = (F_1 - F_4 + F_6 - F_8)/3 \tag{12}$$

1. Give ν_A

2. ν_B and J_{AB}
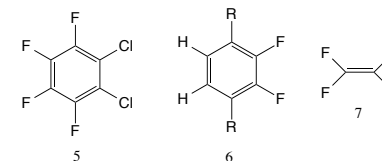
3. **Make sure you understand!**

AA′XX′ system

In A$_2$X$_2$ and A$_2$B$_2$ patterns the two A nuclei and the two X (B) nuclei are magnetically equivalent: they have the same chemical shift by symmetry, and each A proton is coupled equally to the two X (or B) protons. True A$_2$X$_2$ patterns are quite rare. Both the A and X protons are identical triplets. More complicated patterns are seen when the chemical shift difference approaches or is smaller than the J_{AB} coupling. However, both A$_2$B$_2$ and AABB' always give centrosymmetric patterns (A$_2$ part mirror image of the B$_2$ part).
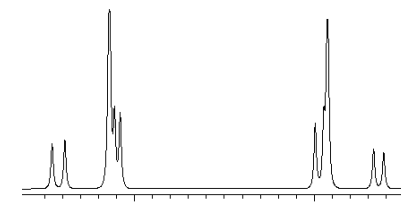
Some molecule with such system are listed as followed:

In strict AA'XX' systems spectra are given by pairs of different species:

For these systems we define

$\|K\| = \|J_{AA'} + J_{XX'}\|$	"J" of one ab quartet
$\|L\| = \|J_{AX} - J_{AX'}\|$	"δ"of both ab quartet
$\|M\| = \|J_{AA'} - J_{XX'}\|$	"J" of other ab quartet
$\|N\| = \|J_{AX} + J_{AX'}\|$	"J" of doublet

For the molecule 7, the ^{19}F spectrum shows 10 lines with the following chemical shifts in Hz at:
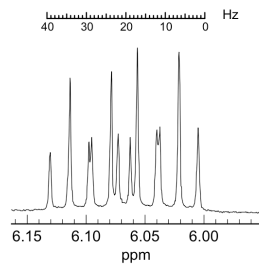
276.2 ; 268.1 ; 247.0 ; 236.4 ; 235.0 ; 222.7 ; 221.8 ; 211.7 ; 189.8 ; 181.3.

1. Determine N.

2. Measure K and M.

3. Calculate L from the formulae given in equation 7.

4. Calculate $J_{AA'}$ and $J_{XX'}$ by summing and subtracting K and M.

5. Calculate J_{AX} and $J_{AX'}$ by summing and subtracting L and N.

6. Give your awsers on a scheme and comment on J signs.

Exercices:

Analyze the multiplet below and report in standard format.

Suggest a part structure that fits the multiplet, indicate which proton is being observed, and label the structure with J values

Analyze the multiplets below. Identify the patterns (e.g., ABXYZ - underline the observed nuclei). If they are first order, report them in the standard format (δ 0.00, dqt, J = 0.0, 0.0, 0.0, 2H). Provide part structure(s) defined by these protons.