Applied
Spectroscopy

Nuclear Magnetic Resonance (NMR) Spectroscopy

cont...

Recommended Reading:

Banwell and McCash Chapter 7

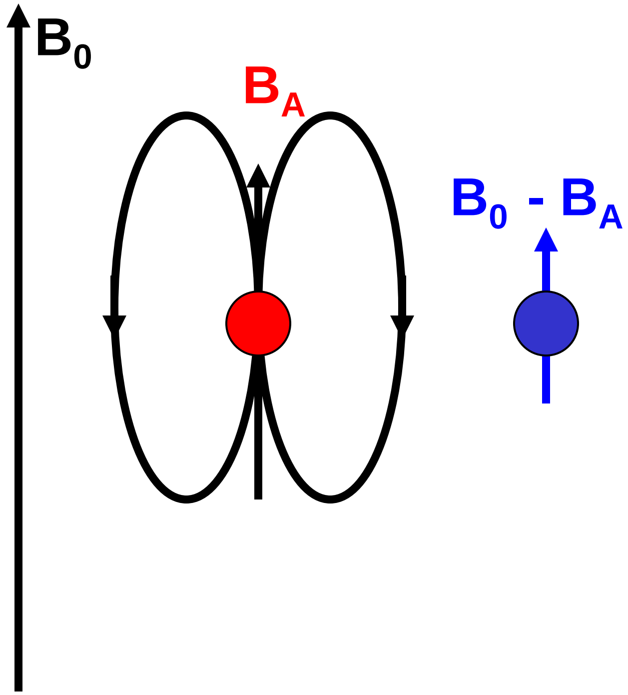
Skoog, Holler Nieman Chapter 19

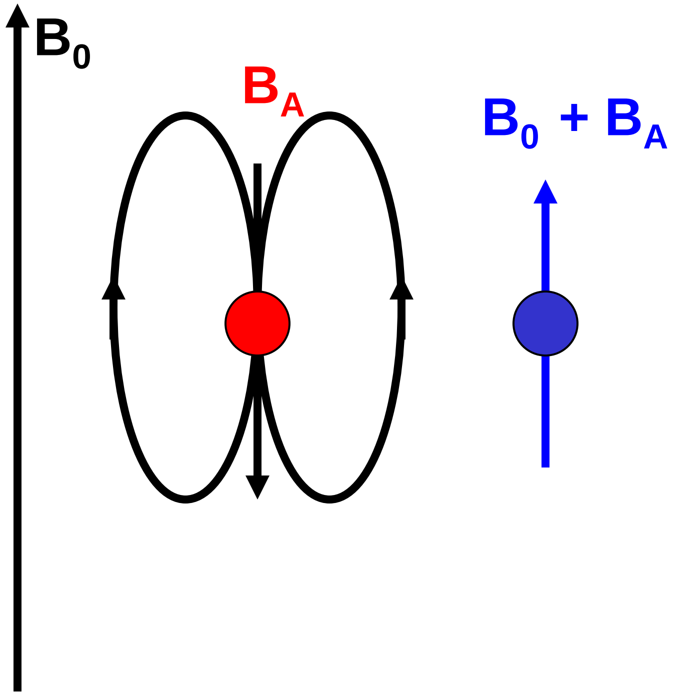
Atkins, Chapter 18

Spin-Spin Coupling

There is an additional piece of information that can be obtained from NMR spectra which arises from the fact that non-equivalent nuclei can couple to each other.

That is, the small magnetic field arising from one nucleus can influence the magnetic field experienced by another non-equivalent nucleus that is nearby on the molecule.



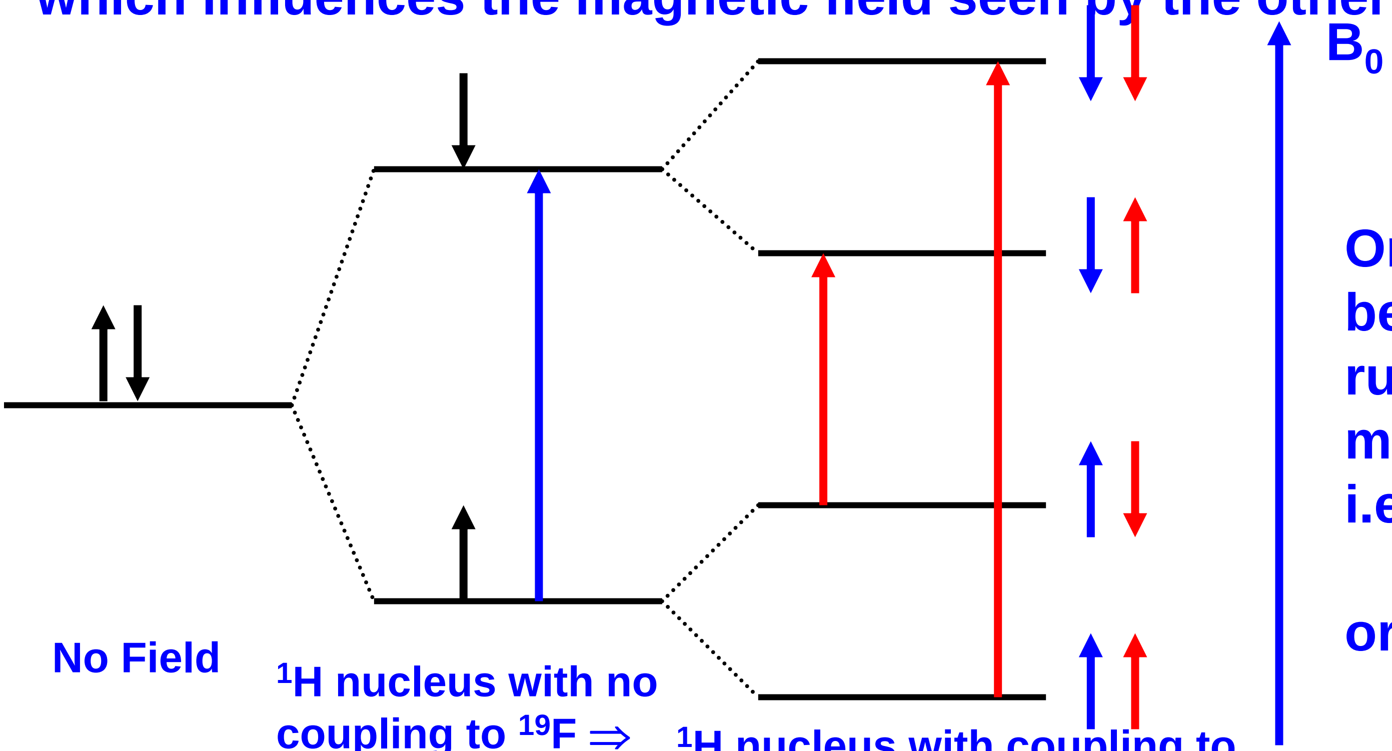


Example

In $^{1}H^{19}F$ the ^{1}H-NMR spectrum consist of two lines and the ^{19}F-NMR spectrum also consists of two lines. Only one proton and one F nucleus so we cannot have two different chemical environments for each nucleus. So, the two lines are not due to chemical shift! What is going on???

Explanation

Both ^{1}H and ^{19}F have spin 1/2 nuclei which each act as a small magnet which influences the magnetic field seen by the other nucleus.



No Field

^{1}H nucleus with no coupling to ^{19}F ⇒ singlet

^{1}H nucleus with coupling to ^{19}F ⇒ doublet

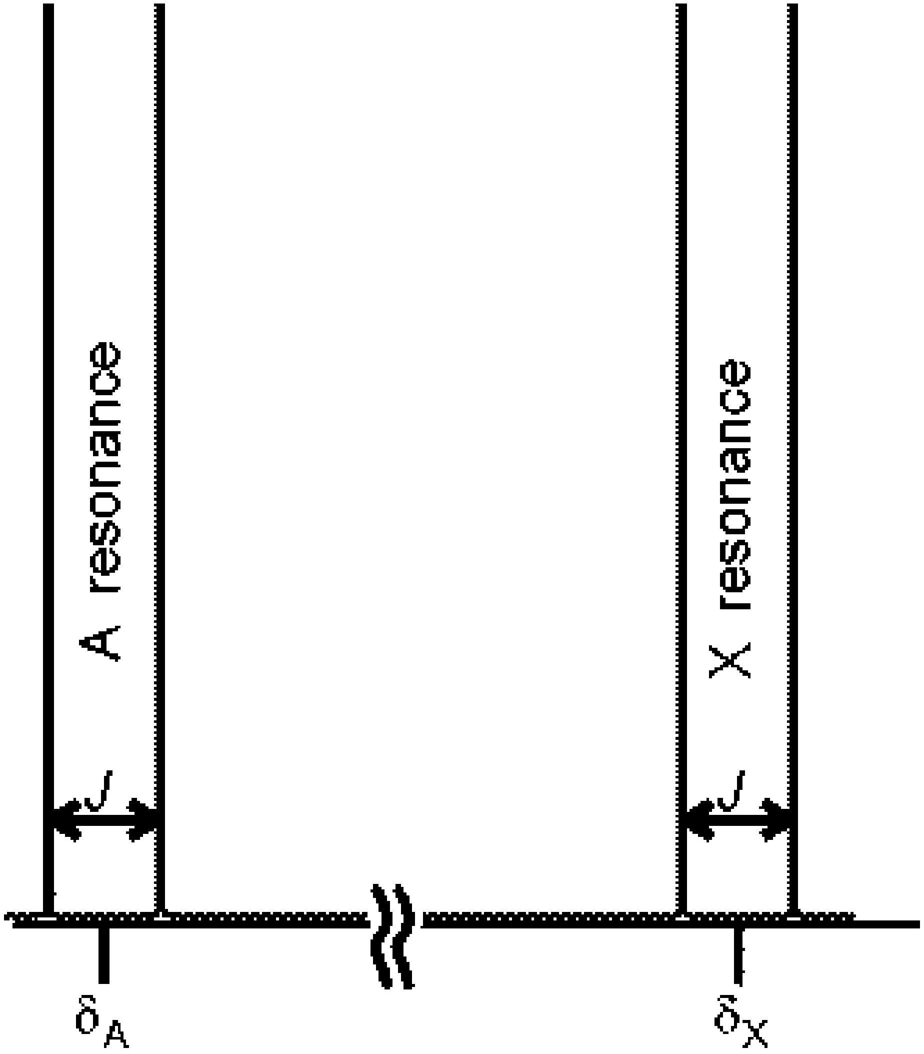
Only two lines because of selection rule, Spin of ^{1}H (or ^{19}F) must flip in transition, i.e.

↑ to ↓

or

↓ to ↑

AX-type Spin-Spin Coupling



In NMR, letters far apart in the alphabet (typically A and X) are used to denote nuclei with very different chemical shifts;

Letters close together (typically A and B) are used for nuclei that have similar chemical shifts.

This figure shows the effect of spin coupling on an AX spectrum (e.g. HF)
Each resonance line is split into two lines separated by J (the coupling constant)
The pairs of resonances are centred on the chemical shifts of the A and X species in the absence of spin-spin coupling

Back to $^{1}H^{19}F$ - Because of Boltzmann distribution, all four states will have almost equal populations (to within a few ppm), so line intensities will be equal.

Because coupling is mutual, the effect of the ^{1}H nucleus on the ^{19}F is the same as the effect of the ^{19}F nucleus on the ^{1}H ⇒ The separation of the peaks in the ^{1}H doublet is the same as the separation of the peaks in the ^{19}F doublet. This separation is called the Coupling Constant J

J gives two pieces of information:

1) it allows us to be sure that the doublets in the ^{1}H and ^{19}F arise from the same species since they have the same J (separation)

2) The magnitude of J can provide structural information (depends on how close the nuclei are on the molecule

What happens if there are two chemically equivalent, spin-active nuclei coupling to a third spin active nuclei, e.g. HF_2? (this would be referred to as an AX_2 type molecule).

The two F atoms are chemically equivalent and there are four possible arrangements of the ^{19}F nuclei,

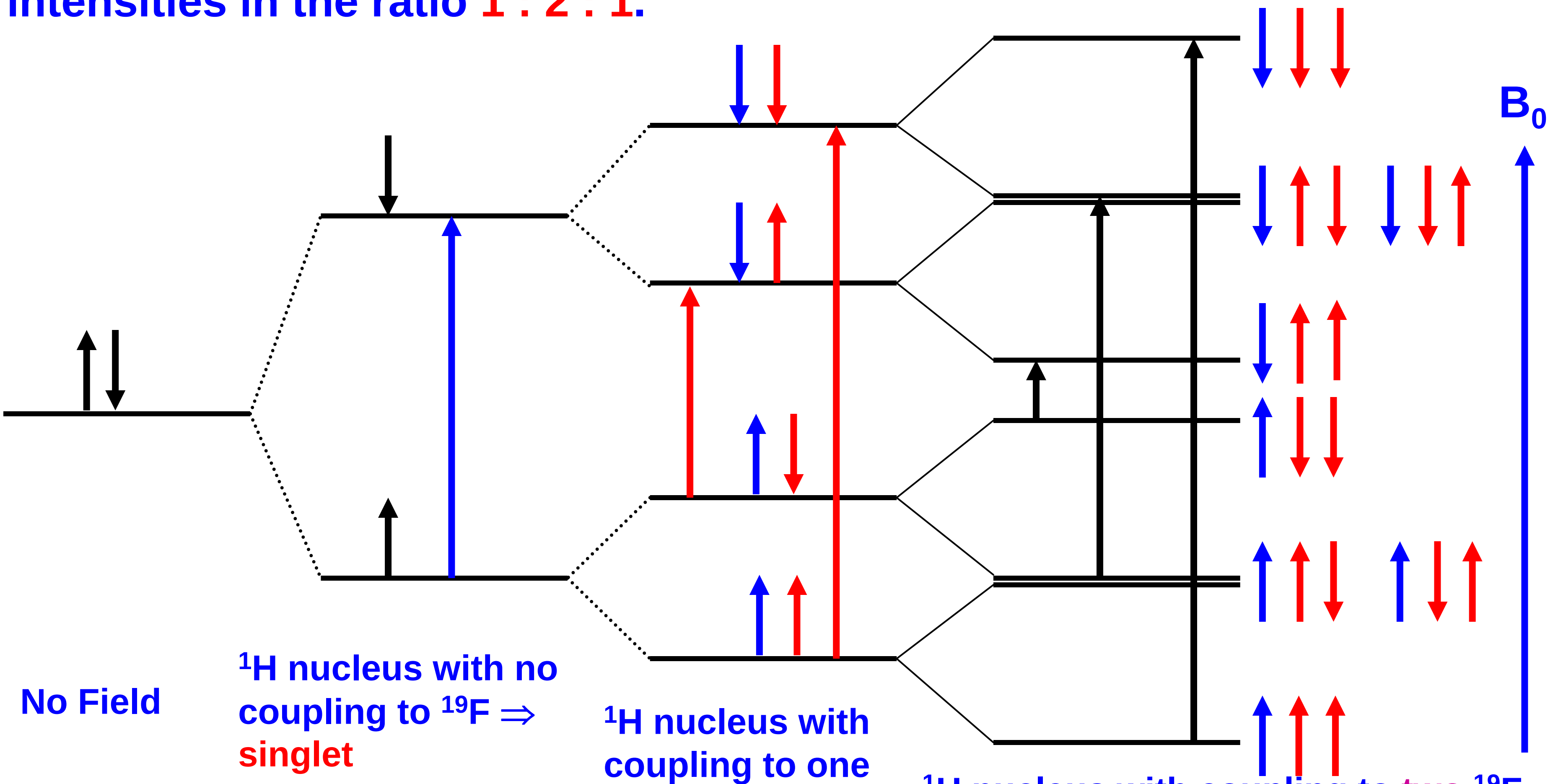
$\uparrow\uparrow \quad \uparrow\downarrow \quad \downarrow\uparrow \quad \downarrow\downarrow$

The $\uparrow\uparrow$ configuration gives an decrease in the magnetic field at the ^{1}H nucleus.

The ↓↓ configuration gives an increase in the magnetic field at the ^{1}H nucleus, and

the ↑↓ and ↓↑ configuration give no overall change in the effective magnetic field at the ^{1}H nucleus, (because their fields cancel out)

So, the ^{1}H NMR spectrum splits into three equally spaced lines with intensities in the ratio 1 : 2 : 1.



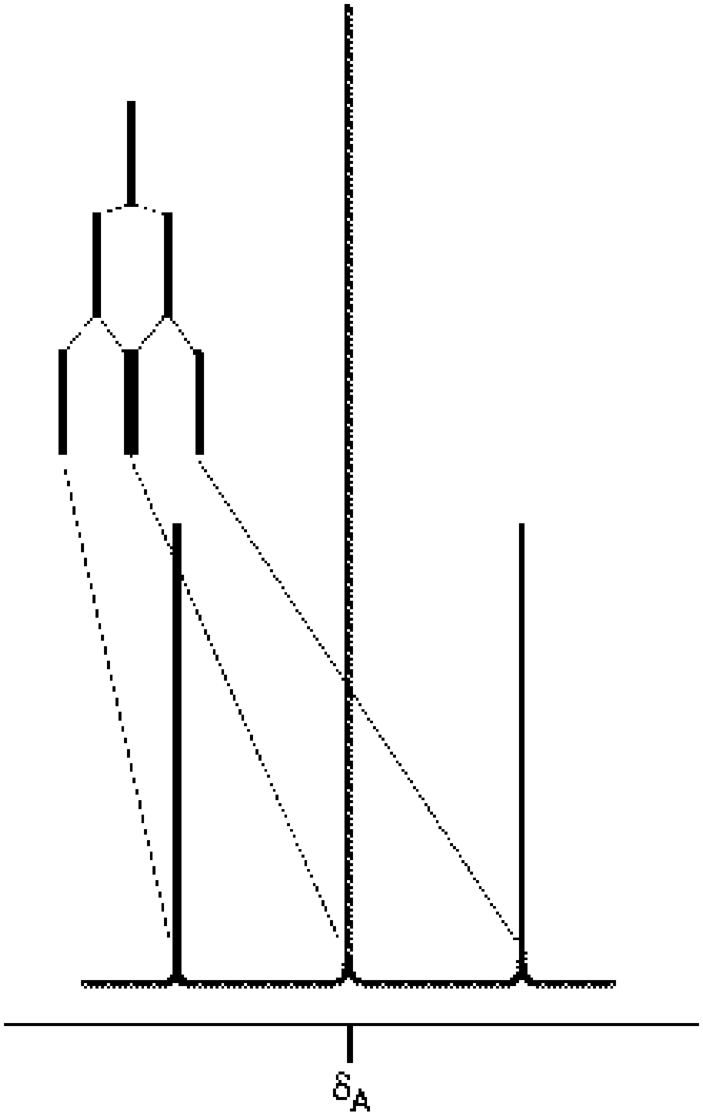
No Field

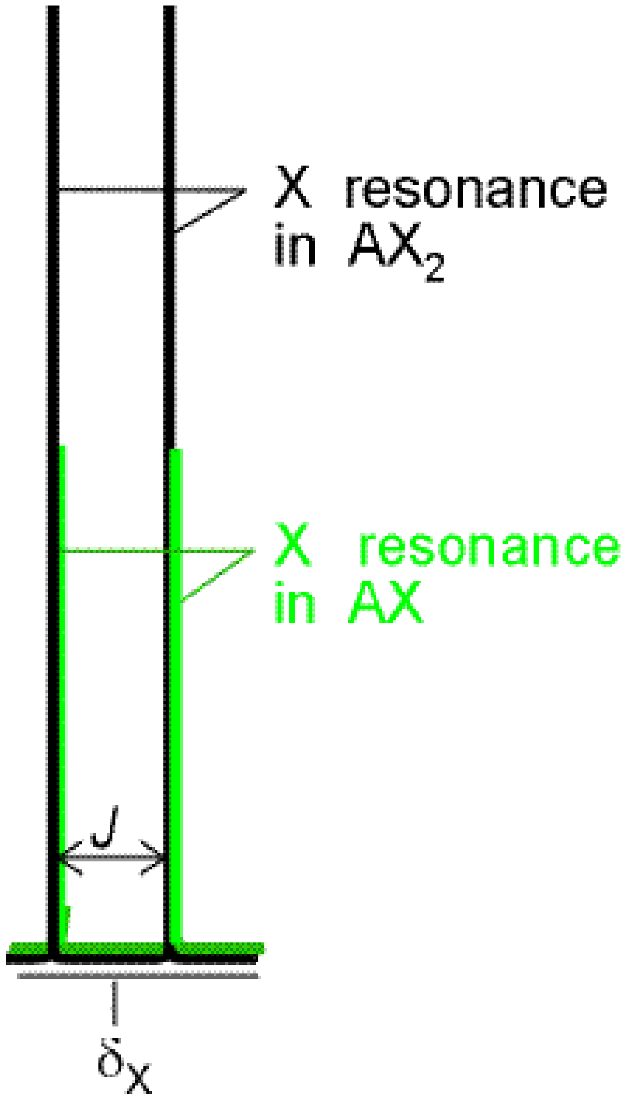
^{1}H nucleus with no coupling to ^{19}F ⇒ singlet

^{1}H nucleus with coupling to one ^{19}F ⇒ doublet

^{1}H nucleus with coupling to two ^{19}F nuclei ⇒ triplet 1 : 2 : 1 intensity

AX_2-type Spin-Spin Coupling





Subtle point here!!!

Note the splitting of the X species in AX_2!! **Still a doublet - Why?**

The X resonance line in an AX_n species (AX_2, AX_3 …) is a doublet with splitting J.

Any group of equivalent nuclei resonates like a single nucleus.

The only difference for the X resonance of an AX_n species is that the intensity is n times as great as that for an AX species. The A-resonance in an AX species is very different from the A-resonance in an AX_n species.

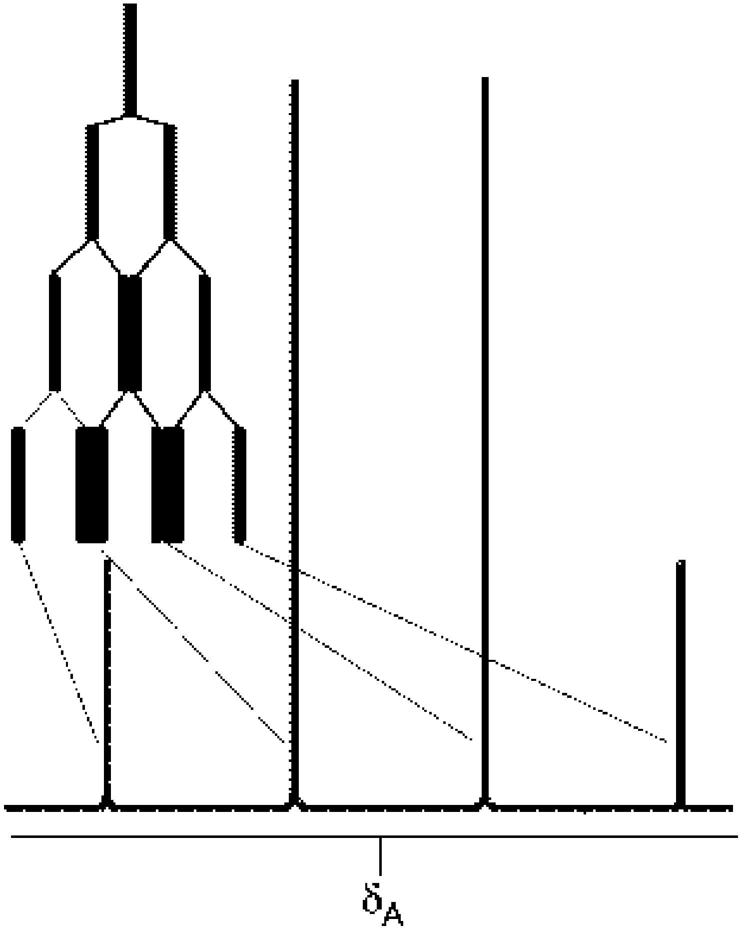
In the AX_2 species the A-resonance is split into a doublet of separation J by one X, and each line of that doublet is split again by the same amount (J) by the second X. This splitting results in three lines in the intensity ratio 1 : 2 : 1 (because the central line can be obtained in two ways).

The A resonance of an A_nX_2 species will also be split into a 1:2:1 triplet of splitting J, the only difference being that the intensity of the lines would be n times as great as that of AX_2, (remember the A_n atoms are equivalent and behave like a single nucleus).

This process can be applied continuously to obtain the splitting pattern and intensities for any number of **equivalent nuclei**.

E.g: three equivalent nuclei (and AX_3 species) split the A-resonance into four lines of intensity ration 1 : 3 : 3 : 1 and separation J.

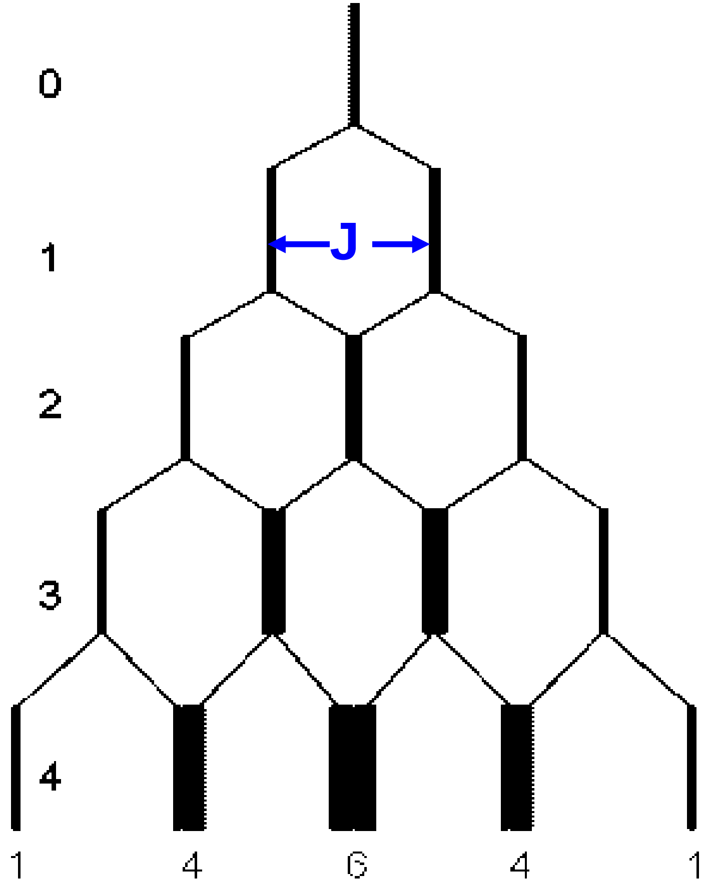
In general n equivalent **spin-1/2** nuclei split the resonance of a nearby line into **n + 1 lines** with an intensity distribution given by **Pascal's Triangle**



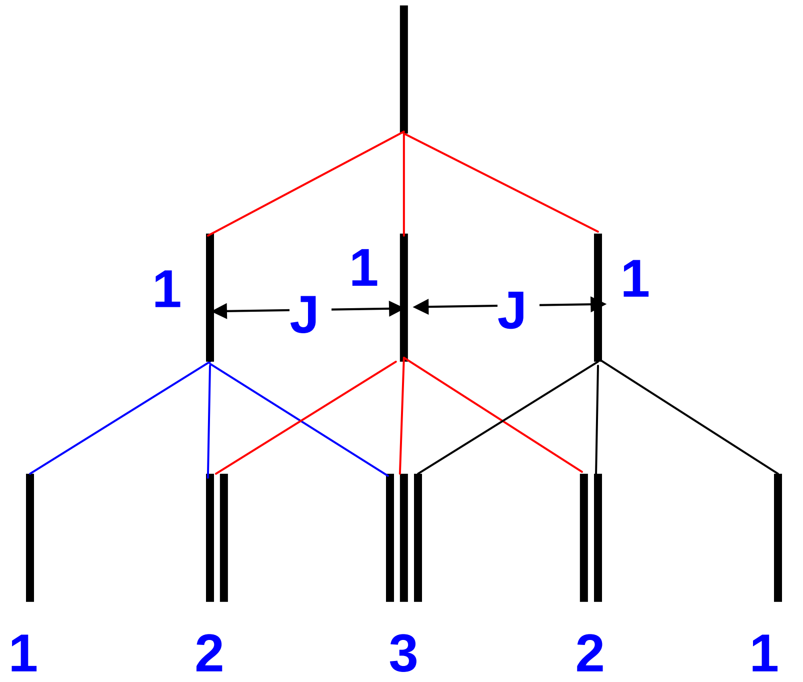
	n
1	0
1 1	1
1 2 1	2
1 3 3 1	3
1 4 6 4 1	4
1 5 10 10 5 1	5

This process can be extended to systems containing nuclei with spins I > 1/2

Stick Diagrams, used to show the splittings of a single energy level with n equivalent nuclei.



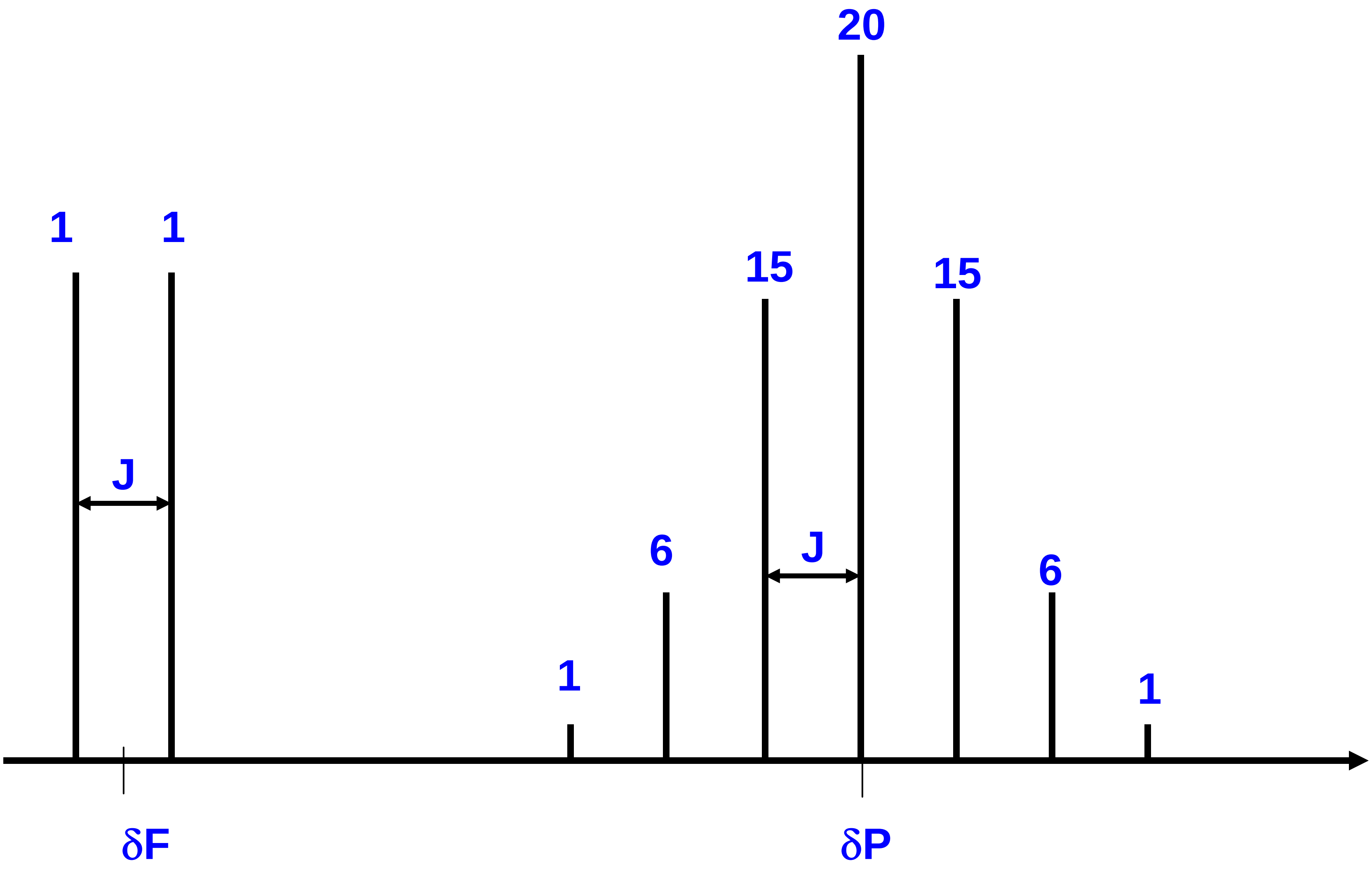
Splittings for spin-1/2 nuclei



Splittings for spin-1 nuclei

In general, any nucleus will couple with every other magnetically active nucleus in the molecule provided they are chemically non-equivalent to give rise to a pattern consisting of (2nI + 1) lines. For spin-1/2 nuclei this reduces to (n+1) lines.

The ^{31}P and ^{19}F NMR spectra of an ion of the type $[P_xF_y]^-$ are shown in figure. What is the simplest formula for the ion?



The ^{19}F spectrum shows two peaks of equal intensity - i.e. a doublet. ⇒ one or more equivalent fluorine nuclei is coupling with one phosphorus atom to yield the doublet

$$(2nI + 1 = 2 \times 1 \times 1/2 + 1 = 2)$$

in the NMR spectrum

The ^{31}P NMR spectrum exhibits a seven-line pattern with a 1 : 6 : 15 : 20 : 15 : 6 : 1 intensity pattern.

Since the fluorine is a spin-1/2 nucleus this intensity pattern is most likely to arise from coupling to six equivalent fluorine nuclei,

$$(2nI + 1 = 2 \times 6 \times 1/2 + 1 = 7).$$

So we have one phosphorus nucleus coupling to six equivalent fluorine nuclei to give a septet in the ^{31}P NMR spectrum and the six equivalent fluorine nuclei coupling with the single phosphorus nucleus resulting in a doublet in the ^{19}F NMR spectrum.

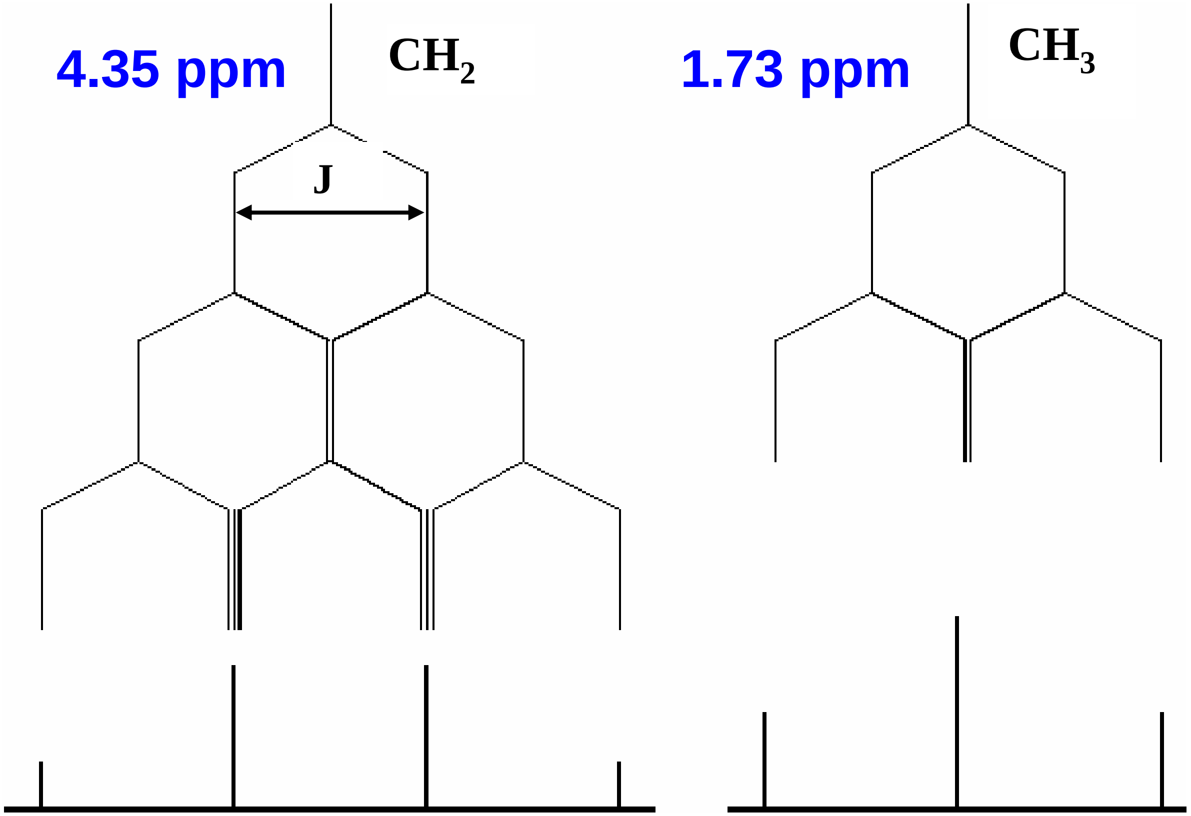
The simplest ion accounting for these observations is $[PF_6]^-$ with the fluorides being octahedrally arranged so that they are equivalent.

We can confirm that these two nuclei are coupling with each other by measuring the coupling constants in both spectra which should be the same.

The coupling described above (AX_n) between two different nuclei is called heteronuclear coupling,

but coupling can also arise from the same nuclei in different environments in which case it is referred to as homonuclear coupling.

This figure shows the 200 MHz ^1H NMR spectrum recorded for a sample of the tetrahedrally-based molecule $Si(OCH_2CH_3)_4$



The two CH_2 protons are chemically non-equivalent to the three CH_3 protons because they are in two different chemical environments. We therefore expect two sets of peaks as above.

The triplet signal is at 1.73 p.p.m and the quartet centred at 4.35 p.p.m. Since the two sets of protons are chemically non-equivalent they will couple with each other. The CH_2 protons will couple with the three methyl protons resulting in a quartet and the three CH_3 protons will couple with the two CH_2 protons to yield a triplet.

So the signal at 1.73 ppm is due to the CH_3 protons

and that at 4.35 ppm corresponds to the CH_2 protons.

This fits with idea of increasing chemical shift correlating with greater deshielding of the nucleus involved. The CH_2 protons are nearer the electronegative oxygen atom and therefore these protons will be more deshielded than the CH_3 protons.

The coupling constant, J, between these two nuclei can be determined by measuring the separation between any two peaks within a particular multiplet.

The difference in ppm is converted to the Hertz scale by multiplying by the spectrometer operating frequency for the nucleus under investigation (in this case 200 MHz).

In this case the separation between the lines is 0.035ppm so the coupling constant is

$$J = 0.035\text{ppm} \times 200\ \text{MHz} = 7\ \text{Hz}$$