Weak Coupling Limit: First-Order Spectra

$\nu_j - \nu_k \gg |J_{jk}|$

- In the limit as $B_0 \to \infty$, all spectra are first-order, but it was not always this way!

\[
\begin{align*}
7\text{ppm} & \quad \rightarrow \quad 800\text{Hz} \\
60\text{MHz} & \quad \rightarrow \quad 60\text{Hz}
\end{align*}
\]

- First order spectra:
  
  i) n equivalent spins alter fine structure of coupled spin, producing n+1 components
  
  ii) relative intensities of multiplet components follow Pascal's triangle

\[
\begin{array}{ccccccc}
1 & & & & & & \\
1 & 1 & & & & & \\
1 & 2 & 1 & & & & \\
1 & 3 & 3 & 1 & & & \\
1 & 4 & 6 & 4 & 1 & & \\
1 & 5 & 10 & 10 & 5 & 1 & \\
\end{array}
\]
iii) nuclei with same chemical shift, e.g. three proton in a methyl group, do not generate fine structure in one another

iv) frequency displacements in each/every component of multiplet reflect $J$

\[ 1:3:3:1 \]

- Fine structure splitting symmetrical about uncoupled frequency
The NMR spectrum corresponding to an AX system might appear as shown below:

**AX Spin System**

A

A-resonance; X \( \uparrow \text{ or } \downarrow \)

Mutual Coupling

\( J_{AX} \)

X

X-resonance; A \( \uparrow \text{ or } \downarrow \)

Note that this same pattern could also represent two spins separated by two or three bonds.
The following spectrum represents one A-type nucleus coupled to two identical X-type nuclei:

**AX₂ Spin System**

**Mutual Coupling**

- $J_{AX}$
- 1:1
- A-resonance; $X \uparrow \uparrow$ or $\uparrow \downarrow$ or $\uparrow \downarrow$ or $\downarrow \downarrow$

- $J_{AX}$
- 1:1
- X-resonance; $A \uparrow$ or $\downarrow$
In the following spectrum, one two identical A-type nuclei are coupled to three X-type nuclei:

\[ A_2X_3 \text{ Spin System} \]

\[ J_{AX} \quad 1:3:3:1 \quad J_{AX} \quad 1:2:1 \]

A-resonance;
\[ X \uparrow\uparrow\uparrow \text{ or } \uparrow\uparrow\downarrow \text{ or } \uparrow\downarrow\uparrow \]
\[ \text{or } \downarrow\uparrow\uparrow \text{ or } \uparrow\downarrow\downarrow \text{ or } \downarrow\uparrow\downarrow \text{ or } \downarrow\downarrow\downarrow \]

X-resonance;
\[ A \uparrow\uparrow \text{ or } \uparrow\downarrow \text{ or } \uparrow\downarrow \text{ or } \downarrow\downarrow \]
Using $^1H$ NMR to Monitor 1st-Order Kinetics

- Recall what for a process...

\[ A \rightarrow B \]

- We may write that

\[ \frac{d[A]}{dt} = k[A] \quad \Rightarrow \quad \frac{d[A]}{[A]} = -kdt \]

- Integration leads to:

\[ \ln[A] = -kt + \ln[A]_0 \]

\[ \ln[A] - \ln[A]_0 = -kt \]

\[ \ln \left( \frac{[A]}{[A]_0} \right) = -kt \]

\[ \frac{[A]}{[A]_0} = e^{-kt} \]

\[ [A] = [A]_0 e^{-kt} \]
• To monitor \([A]_t\) using NMR, we need to record spectra at (regular) time intervals.

• Arrays

• Virtually any variable in NMR can be arrayed

• We can evaluate \([A]_t\) if we can
  1) Identify a resonance in molecule A that decreases in intensity as \([A]_t\) decreases
  2) Record identical NMR spectra over time

• There are at least two ways to array acquisition parameters:
  \[pw = 1, 2, 3, 4, 5, \ldots\]
  \[\text{array ('pw', 40, 1, 1)} \rightarrow pw = 1, 2, 3, 4, 5, \ldots\]
  Note: increasing