Magnetic vs. Chemical Equivalence

Today:
Magnetic equivalence
Non-first-order spectra

First order vs. second order spectra

• Causes of 2nd order splitting:
  Strong coupling:

  – If Δν between two signals is near J between two signals, then second order spectra result, Δν/J > 10
  – On 60 MHz, Δν = 1.5 ppm, J = 7 Hz
  – Δν = 1.5 ppm (60 Hz/ppm) = 90 Hz
  – Δν/J = 90 Hz/7 Hz = 13 → 1st order spectrum
First order vs. second order spectra

• Causes of 2nd order splitting:

  **Strong coupling:**
  - On 60 MHz, \( \Delta \nu = 0.3 \) ppm, \( J = 7 \) Hz
  - \( \Delta \nu = 0.3 \) ppm (60 Hz/ppm) = 18 Hz
  - \( \Delta \nu/J = 18 \text{ Hz}/7\text{ Hz} = 2.6 \) → 2nd order spectrum

  - On 400 MHz, \( \Delta \nu = 0.3 \) ppm, \( J = 7 \) Hz
  - \( \Delta \nu = 0.3 \) ppm (400 Hz/ppm) = 120Hz
  - \( \Delta \nu/J = 120 \text{ Hz}/7\text{ Hz} = 17 \) → 1st order spectrum

What are second order spectra?

One uses ABX nomenclature to differentiate between the proton signals.
  - AX and all other first order systems (AX\(_2\), AMX, A\(_3\)X\(_2\), etc.)
  - AB (line intensities start to lean, \( J \) can be measured, \( \delta \) has to be calculated)
  - AB\(_2\) (extra lines, both \( J \) and \( \delta \) have to be calculated)
  - ABX, ABX\(_2\), ABX\(_3\), \( J_{AB} \) can be measured, others require a simple calculation
  - ABC (both \( J \) and \( \delta \) can only be obtained by computer simulation)
  - AA'XX' (these do not become first order even at higher fields)
  - AA'BB'
  - AA'BB'X (etc)
Chemical Equivalence?

- **Chemical equivalence** = two nuclei that are interchangeable by a symmetry operation or a rapid mechanism (rapid on the NMR timescale, $\pm 10^{-3}$ sec)

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H     H
   X—CH2CH2—Y
H     H
```
Magnetic Equivalence?

- **Magnetic equivalence** = when two nuclei have identical relations with all the same identical partners (presupposes chemical equivalence).

Two nuclei are ME when they have:

1. The same chemical shift
2. The same coupling constant
3. ...with the same partners!

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Magnetic Equivalence?

- **Compare these two molecules:**

- If the nuclei are not magnetically equivalent, the designations AA', XX', etc. are used.
Magnetic Equivalence?

• *Try more examples:*

![Molecular Structure 1](image1)

![Molecular Structure 2](image2)

Magnetic Equivalence?

• *Try more examples:*

![Molecular Structure 3](image3)

![Molecular Structure 4](image4)
The splitting patterns of a three-proton system \( \text{CH}_3 - \text{CH}_2 - \) for various ratios of \( \Delta v/\Delta \).

1st order

not 1st order

singlet when \( \Delta \delta = 0 \)

The splitting patterns of a four-proton system \( \text{CH}_3 - \text{CH}_2 - \) for various ratios of \( \Delta v/\Delta \).

1st order

not 1st order