Proton NMR Spectroscopy: Signal Splitting

- **Chemical Shift**: The position of a signal in an NMR spectrum.
- **Nuclear Spin Flip**: Change in orientation of the nuclear spin axis upon energy absorption (excitation) or energy release (relaxation).
- **Splitting**: In NMR spectroscopy, the division of an NMR signal into two or more lines, closely spaced, due to spin-spin coupling.
- **Spin-Spin Coupling**: In NMR spectroscopy, it is the effect of one nuclei’s magnetic field on other nuclei within the molecule, causing splitting of the NMR signals.
- **Magnetic Environment**: Determined by magnetic induction. Some atomic nuclei possess a magnetic moment (nuclear spin), which gives rise to different energy levels and resonance frequencies in a magnetic field.
  - **Magnetic Induction**: Magnetic field generation due to the presence of another magnetic field. In NMR spectroscopy, application of an external magnetic field $B_0$ to a pi electron cloud causes these pi electrons to circulate. Because electrons bear an electric charge and are moving, they create their own magnetic field.
- **Coupling constant ($J$)**: Spacing between lines in a splitting pattern.

**What are the implications of signal splitting?**
- The splitting pattern of each signal indicates that neighboring hydrogen atoms are coupling.
- Each line in the signal:
  - Represents a hydrogen atom with a slightly different chemical shift.
  - Represents a slightly different spin flip energy due to excitation or relaxation.
    - When $H_a$ and $H_b$ are parallel, they feel a stronger magnetic field, whereas when they are antiparallel, they feel a weaker field. The difference in how the magnetic field affects the protons causes two, closely placed signals.
What are the rules and restrictions for proton-proton spin-spin coupling?

The signal for a proton with \( n \) neighbors is split into \( n+1 \) signals (lines).

No coupled hydrogens: \( \text{C—C—C—H} \)
One coupled Hydrogen:

\[
\begin{align*}
\text{C} & \quad \text{C} \quad \text{C} \quad \text{H} \\
\text{C} & \quad & & \\
\text{C} & \quad \text{H}
\end{align*}
\]

A Doublet

Two coupled Hydrogen:

\[
\begin{align*}
\text{C} & \quad \text{C} \quad \text{C} \quad \text{H} \\
\text{H} & & & & \\
\text{H}
\end{align*}
\]

1. Only nonequivalent protons couple. Equivalent protons cannot couple because they have the same chemical shift, spin flip energy, and are in the same magnetic environment. Only nonequivalent protons can split signals.

- \(H_a\) and \(H_b\): Don't couple because equivalent
- \(H_c\) and \(H_d\): Don't couple because equivalent
- \(H_a\) and \(H_c\): Couple
- \(H_b\) and \(H_c\): Couple

2. Protons separated by more than three \(\sigma\) bonds usually do not couple. Protons that are more than 3 \(\sigma\) bonds away don’t couple because the signal from their neighbor is too insignificant to affect their overall spin.
   a. \(\pi\) bonds don’t count toward this “three-bond limit” and are thus counted as free spacers. \(\pi\) bonds don’t count because the electron density around the bond is much higher than that of a \(\sigma\) bond.
b. Due to resonance, all hydrogen’s attached to the benzene ring couple, while the ring itself counts as a free spacer. However, only hydrogen’s directly attached to the benzene ring couple—those attached to other atoms cannot couple with these hydrogen’s even if they are within the three-bond limit.

All hydrogen’s bonded to the benzene ring are nonequivalent and therefore couple. However, the hydrogen’s bonded to the benzene ring cannot couple with they hydrogen’s bonded to the methyl group.

3. Signals for O-H and N-H usually do not couple with other protons and therefore remain as singlets.

**Exceptions to the n+1 rule?**

So far, we have gone over normal, what we call, first order splitting. First order splitting occurs when the coupling constant, J, are equal (ex. \( J_{ab} = J_{ac} \)). However, when J values are not equal, the nucleus spin-couples with 2 or more sets of neighboring nuclei that have different J values, producing more complex splitting patterns such as doublets of doublets. For non-first order splitting, the n+1 rule cannot predict the splitting pattern of the signal.

\[
\begin{align*}
J_{ab} &= J_{ac} \\
\text{First Order Triplet} \\
J_{ab} &
e J_{ac} \\
\text{Non First Order Triplet}
\end{align*}
\]
Works Cited


Hardinger, S. Proton NMR Spectroscopy. Chem 14C Lecture Supplement, pp. 149-152.


   <http://www.chemistry.jhu.edu/NMR/NMR>.