5.3 Spin-Spin Splitting  J-Coupling

The actual local magnetic field encountered by a nucleus is affected by neighboring magnetic nuclei (spin-spin splitting) as a result of perturbation of the electron distribution. The principal magnetic nuclei are other protons, the 100% abundant spin ½ nuclei $^{19}$F and $^{31}$P, and some spin 1 or greater (quadrupolar) nuclei such as $^{14}$N, $^2$H, $^{11}$B, and $^{12}$B. Although Br, Cl, and I all have isotopes with spin $>\frac{1}{2}$, coupling is not seen because of relaxation effects. This will be discussed in more detail in Section 7.

Note: vertical scale of the couplings is grossly exaggerated

### Sign of Coupling Constants

Coupling constants can be either positive or negative. These are defined as shown below:

- $J_{AX} < 0$
- $J_{AX} > 0$

Coupling constants are positive if the spin state in which A and X have opposite spins ($\alpha\beta$) is lower in energy than the one in which they have the same spin ($\beta\beta$).

The signs of couplings shows some consistency:
- $^1J_{C-H}$ and most other one-bond couplings are positive.
- $^2J_{H-H}$ in $sp^3$ CH$_2$ groups are almost all negative, some others are positive.
- $^3J_{H-H}$ is always positive.

For first order patterns the signs of the couplings have no effect on the appearance of the spectrum, and so cannot be determined by observation. However, decoupling experiments (spin tickling) can provide the relative signs. For second-order patterns (e.g. ABX or AA'BB'), the relative signs of coupling constants often have dramatic effects on the appearance of the spectrum, and relative signs can be determined by proper analysis of the multiplets.
Two Different Couplings to one Proton

Consider the NMR spectrum of 3,4-dichlorobenzoyl chloride below.

The proton-proton couplings in benzene are typically 7-9 Hz for $J_{\text{ortho}}$, 2-3 Hz for $J_{\text{meta}}$ and <1 Hz for $J_{\text{para}}$. The substitution pattern can be derived from examination of each of the three aromatic protons. For example, the doublet at $\delta \approx 8.2$ with $J = 2.5$ Hz is interpreted as follows: this proton has no protons ortho to it, and only one proton meta to it. Structure A summarizes the structural information. For the doublet of doublets at $\delta \approx 7.95$ ($J = 8.5, 2.3$ Hz), formed by coupling of one proton to both an ortho and a meta proton, the two structures B and C are possible. The doublet at $\delta \approx 7.6$ ($J = 8.5$ Hz) defines the substitution pattern of structure D. In each case the position marked by ? is undefined since the para coupling is usually too small to resolve.
A slightly more complicated case is 1,1,2-trichloropropane. A simulated spectrum is shown below.

The C-2 proton is coupled to one proton at C-1 and three protons of the methyl group at C-3. Naively, one might expect a pentet (p), as shown in the left spectrum below. Although pentets are, in fact, often observed in such situations, this occurs only if $J_{1-2}$ and $J_{2-3}$ are identical. When they are not (as is actually the case in this example), then we get a quartet of doublets (qd). It is customary to quote the larger coupling first (q) and then the smaller coupling (d). A proper text description of the multiplet is: $\delta 4.30, 1H, qd, J = 6.6, 3.8 \text{ Hz}$.

**Exercise:** what would a dq, $J = 6.6, 3.8 \text{ Hz}$ look like?
1. Nuclei must be chemical shift nonequivalent to show obvious coupling to each other. Thus the protons of CH₂Cl₂, Si(CH₃)₄, Cl-CH₂-CH₂-Cl, H₂C=CH₂ and benzene are all singlets. Equivalent protons are still coupled to each other, but the spectra do not show it.

2. J coupling is mutual, i.e. $J_{AB} = J_{BA}$ always. Thus there is never just one nucleus which shows J splitting - there must be two, and they must have the same splitting constant J. However, both nuclei need not be protons - fluorine ($^{19}$F) and phosphorus ($^{31}$P) are two other common nuclei that have spin $\frac{1}{2}$ and 100% abundance, so they will couple to all nearby protons. If these nuclei are present in a molecule, there are likely to be splittings which are present in only one proton multiplet (i.e. not shared by two multiplets).

3. Two closely spaced lines can be either chemically shifted or coupled. It is not always possible to distinguish $J$ from $\delta$ by the appearance of the spectrum (see Item 4 below). For tough cases (e.g. two closely spaced singlets in the methyl region) there are several possibilities:
   - decouple the spectrum
   - obtain it at a different field strength (measured in Hz, coupling constants are field independent, chemical shifts are proportional to the magnetic field)
   - measure the spectrum a different solvent (chemical shifts are usually more solvent dependent than coupling constants, benzene and chloroform are a good pair of solvents).

   For multiplets with more than two lines, areas, intensities, symmetry of the pattern and spacing of the lines generally make it easy to distinguish chemical shift from coupling.

   For a simple example see the spectrum of 3-acetoxy-2-butanone below. Here it is pretty easy to identify one of the doublets as the 4-methyl group, the other “doublet” (with a separation of 9 Hz, which could easily be a coupling) actually corresponds to the two CH₃C(=O) groups.

4. Chemical shifts are usually reported in $\delta$ (units: ppm) so that the numeric values will not depend on the spectrometer frequency (field-independent units), coupling constants are always reported in Hz (cycles per second). Chemical shifts are caused by the magnetic field, couplings are field-independent, the coupling is inherent in the magnetic properties of the molecule. However, all calculations on NMR spectra are done using Hz (or, more precisely, in radians per sec).
5. Protons two ($^2J$, geminal) or three bonds ($^3J$, vicinal) apart are usually coupled to each other, more remote protons ($^4J$, $^5J$) may be if geometry is right, or if $\pi$-systems (multiple bonds) intervene. Long range couplings ($^4J$ or greater) are usually small, typically $<$0.5 Hz, but up to 3 Hz in some cases where there are intervening $\pi$ bonds.

6. Multiplicity for first order patterns follows the "doubling rule". If all couplings to a particular proton are the same there will be $2nI+1$ lines, where $I$ is the spin and $n$ is the number of neighboring nuclei ($n + 1$ for $^1H$ $I = 1/2$). The intensities will follow Pascal's triangle.

<table>
<thead>
<tr>
<th>$n$</th>
<th>Intensities</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>1 1</td>
</tr>
<tr>
<td>2</td>
<td>1 2 1</td>
</tr>
<tr>
<td>3</td>
<td>1 3 3 1</td>
</tr>
<tr>
<td>4</td>
<td>1 4 6 4 1</td>
</tr>
<tr>
<td>5</td>
<td>1 5 10 10 5 1</td>
</tr>
<tr>
<td>6</td>
<td>1 6 15 20 15 6 1</td>
</tr>
</tbody>
</table>

7. If all couplings are different, then the number of peaks is $2^n$ for $^1H$, and the intensities are 1:1:1:... Thus a proton coupled to two others by different couplings gives a dd (doublet of doublets, see Figure). This pattern is never called a quartet. As the number of couplings gets larger, accidental superpositions of lines will sometimes occur, so that the 1:1:1... intensity ratio no longer applies. The intensities are also often distorted by leaning effects, as seen in several examples below.

8. More typically, some of the couplings are the same, others different, so get a variety of patterns. In favorable cases, these patterns can be analyzed and all couplings extracted. The number and size of couplings ($J$-values) provide important structural information.
Second Order Effects

1. Protons or groups of protons form simple multiplets only if the chemical shift differences between the protons ($\Delta \nu$) are large compared to the coupling constants between them ($J$). If $\Delta \nu / J$ (all in Hz) is <5 then second order effects appear (see 5.8) which complicate the analysis:

(a) A universally observed effect is that the intensities of the lines no longer follow simple integer ratios - the multiplets "lean" towards each other: the lines away from the chemical shift of the other proton (outer lines) become smaller and lines closer (inner lines) become larger (see the triplets below). The leaning becomes more pronounced as the chemical shift difference between the coupled multiplets becomes smaller.

(b) Additional lines over that predicted by simple coupling rules appear. A nice example is provided by the compound below. For the BrCH$_2$CH$_2$O group the two methylenes at $\delta$ 3.48 and $\delta$ 3.81 have a relatively large chemical shift separation, and they form recognizable triplets, although with a little leaning. For the MeOCH$_2$CH$_2$O group the chemical shift between the CH$_2$ groups is small, and the signals are a complicated multiplet with only a vague resemblance to a triplet. There is likely an additional complication from variability in the size of the two different vicinal couplings in the two patterns (see section 5-HMR-15 for more on this).
(c) Coupling constants and chemical shifts can no longer be easily determined from the spectrum. The sign of the coupling constant is significant. "Virtual coupling" effects (apparent coupling to protons that are actually not coupled) may appear (see Section 5.16).

2. For a given molecule $\Delta \nu / J$ increases as the magnetic field increases, hence spectra are usually simpler at higher field (better dispersion).

3. Second order effects will appear even if $\Delta \delta / J$ is large when groups of magnetically non-equivalent protons with identical chemical shifts are coupled to each other (see Section 5.8). Thus Me$_3$Si-CH$_2$-CH$_2$-Cl (an AA'XX' system, see Section 5.15) is not just two triplets. These patterns do not get simpler at higher field strengths.

These effects will be dealt with in some detail in subsequent sections on the various coupling patterns. 01/39
5.3.7 Rules for Analyzing First Order Multiplets

A first order multiplet can be expected when both of the following criteria are met:

First, the chemical shift of the observed proton must be far away from any of the protons it is coupled to (far away means $\Delta \nu >> J$). In practice, multiplets can be treated in a first order fashion if $\Delta \nu > 3J$, although the substantial leaning distortions can complicate analysis. The leaning will have almost completely disappeared by the time $\Delta \nu = 10J$.

Second, if more than one proton is coupled to the observed one, then these protons must not be "strongly coupled." In other words, if they are coupled to each other and very close in chemical shift then the observed proton multiplet will not yield true coupling constants on analysis, even though it looks first order. See the section on Virtual Coupling.

Structure of First Order Multiplets. The fundamental rule governing multiplet intensities for spin 1/2 nuclei with all couplings identical is Pascal's triangle ($n =$ number of equivalent couplings).

<table>
<thead>
<tr>
<th>$n$</th>
<th>$2^n$</th>
<th>Multiplet Intensities</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>1 1</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
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<td>8</td>
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<td>Pentet 1 4 6 4 1</td>
</tr>
<tr>
<td>5</td>
<td>32</td>
<td>Sextet 1 5 10 10 5 1</td>
</tr>
<tr>
<td>6</td>
<td>64</td>
<td>Septet 1 6 15 20 15 6 1</td>
</tr>
<tr>
<td>7</td>
<td>128</td>
<td>Octet 1 7 21 35 35 21 7 1</td>
</tr>
<tr>
<td>8</td>
<td>256</td>
<td>Nonet 1 8 28 56 70 56 28 8 1</td>
</tr>
</tbody>
</table>

A first order multiplet consists of the product (not the sum) of several such multiplets. In other words, a single line will first be split into one of the symmetrical multiplets (1:1 d, 1:2:1 t, 1:3:3:1 q, etc), then each line of this multiplet will be again split into d, t, q, or higher multiplet.
Recognizing a First Order Multiplet.

1. All truly first order multiplets are centrosymmetric - there is a mirror plane in the middle (in real spectra, this is usually not strictly true because of leaning and other distortions). However, the reverse is not true: not all symmetrical multiplets are first order.

2. If the small outermost peaks are assigned intensity 1, then all other peaks must be an integral multiple intensity of this one (1x, 2x, 3x, 4x in height), and the total intensity of all peaks must be a power of 2 (2, 4, 8, 16, 32, etc). The intensity of each of the two outermost lines is \(1/2^n\) of the total multiplet intensity, where \(n\) is the number of protons which are coupled with the proton signal being analyzed. There can be no lines smaller than the outermost one. Note, however, that if \(n\) is large, the outermost peaks may not be distinguishable from noise. Intensity assignments and determination of \(n\) cannot be easily made for such multiplets.

3. There is a strict regularity of spacing in a first order multiplet: if you have correctly identified a coupling constant \(J\), then every peak in the multiplet must have a partner \(J\) Hz away to the left or to the right of it.

4. Most first order multiplets integrate to a single proton, a few may be 2 or 3 protons in area. It is rare to have more than 3 protons, unless there is symmetry in the molecule (e.g., \((\text{CH}_3)_2\text{CH}^-\) gives a 6-proton doublet for the methyl groups). Thus a 4-proton symmetrical multiplet is usually not a first-order pattern (it is more likely to be the very common AA'BB' pattern).

5. The symmetry and intensities of an otherwise first-order multiplet can be distorted by leaning effects (see Section 5-HMR-9). Many such multiplets can still be correctly analyzed by first-order techniques, but you have to mentally correct for the intensity distortions. However, the coupling constants extracted may not be perfectly accurate.
• **Analyzing a First Order Multiplet.** First order multiplets are analyzed by constructing a reverse coupling tree, by "removing" each of the couplings in turn, starting with the smallest.

1. "Take out" the smallest couplings first. The separation between the two lines at the edge of the multiplet is the smallest coupling. Each time you remove a coupling you generate a new, simpler multiplet, which can then be analyzed in turn. Remember that each line of the multiplet participates in each coupling.

2. Watch line intensities (i.e., peak areas or peak heights) carefully--when you "take out" a coupling, the intensities of the newly created lines should be appropriate (i.e., each time you "take out" a coupling, also "take out" the proper intensity). When a coupling has been taken out completely, all intensity should be accounted for. Keep track of your analysis by using a "coupling tree".

3. The couplings may be removed one at a time as doublets, or as triplets, quartets and higher multiplets. The intensity ratio of the first two lines signals the number of protons involved in the coupling: 1:1 means there is only one proton, 1:2 means that there is a triplet splitting (2 protons), etc. Be especially careful to keep track of intensities when you "take out" triplets (1:2:1) or quartets (1:3:3:1). Each time you completely remove a coupling you generate a new multiplet which follows first order rules, and can be analyzed in turn.

When you have finished your analysis, all peaks in the multiplet must be accounted for. You can check the analysis as follows: the separation of the two outermost peaks of the multiplet is the sum of all the $J$s (i.e., for a dt, $J = 8, 3 \text{ Hz}$ the outermost lines are separated by $8 + 3 + 3 = 14 \text{ Hz}$).

• **Reporting a First Order Multiplet.** Multiplets are reported starting with the largest coupling, and the symbols must be in the order of the reported numbers: $\delta 2.10, 1\text{H, qt, } J = 10, 6 \text{ Hz}$ means: a single proton q of 10 Hz, t of 6 Hz with a chemical shifts of 2.10 ppm.

• **Quartets.** Keep clear in your mind the distinction between a simple q (one proton equally coupled to 3 others, with an intensity 1:3:3:1), an ABq (2 protons coupled to each other, see Sect 5-HMR-9), and the quartet formed by coupling with a spin 3/2 nucleus (e.g., $^7\text{Li, intensity 1:1:1:1, see Sect 7-MULTI-2.4}$). Only the first of these should be referred to by just a "q" symbol. The early NMR literature (and even modern novices) sometimes call doublets of doublets "quartets" (there are four lines, after all).
First Order Analysis

The separation between the first and second lines is the smallest coupling in the multiplet ($J_1$). They are in an intensity ratio of 1:1, so that coupling appears only once (i.e., it is a doublet splitting).

"Remove" the first coupling. Keep track of line intensities, and draw a child multiplet with positions at the center of each doublet. Each unit of line intensity can only be used once, and all line intensity must be accounted for.

Repeat the process - the first and second lines now represent the next largest coupling. Remove this in turn, and repeat the process until you get a singlet.

This is ddd, $J = 12, 10, 4$ Hz

Here again the separation of the first two lines is the smallest coupling in the multiplet ($J_1$). However, they are in an intensity ratio of 1:2, so this coupling appears twice (i.e., it is a triplet splitting).

"Remove" the triplet coupling. Keep track of line intensities, and draw a child multiplet with positions at the center of each triplet. Note that the central two lines of intensity 3 are the sum of two lines - one of intensity 1 and the other intensity 2.

This is a ddt, $J = 16, 10, 6$ Hz
Simple Multiplets

Assign the protons where structure and chemical shift scale are given.
Note the leaning, indicating that the coupled partner is close by.

Doublet of doublets (dd)

Triplet of doublets or doublet of triplets (dt, td)

Doublet of doublet of doublets (ddd)

Doublet of quartets (dq)

The multiplet below integrates to two protons. Using the chemical shift (δ 5.8) and coupling identify the structural fragment.
Symmetrical Multiplets which are NOT First Order

Only ONE of the multiplets below is first order

Some criteria to use:
- Pattern must be centrosymmetric (true of all of these)
- Intensity of lines - patterns must be repeated, especially examine outer lines
- Be wary if \( #H > 1 \), especially if \( 4H \)
- Consider size of possible couplings

(a)

(b)

(c)

(d)

(e)

(f)
The accurate measurement of $J$ coupling constants requires that the multiplets be correctly analyzed. In the following pages are described techniques for performing such analyses. The procedures are summarized below.

For first order multiplets a simple "tree" analysis as described in Section 5-HMR-3.9 can directly yield coupling constants within the accuracy of the digital resolution of the spectrum. This includes AB spectra, where $J_{AB}$ can be measured directly. See section 5-HMR-7 for a description of the ABC.. nomenclature for spin systems.

For AB$_2$ spectra both the coupling constant $J_{AB}$ and the chemical shifts can be obtained by simple arithmetic manipulations, provided that line assignments can be made correctly. For ABX spectra the $J_{AB}$ is accurately measurable by inspection. An approximate analysis, which treats the peaks as AMX, will give values for $J_{AX}$ and $J_{BX}$ that will be in error by varying amounts, depending on the relative size of $\nu_{AB}$, the relative size of $J_{AX}$ and $J_{BX}$ and the size of $J_{AB}$ (the smaller $\nu_{AB}$ the larger the error). To get accurate values for the $J_{AX}$ and $J_{BX}$ coupling constants a proper ABX analysis as described in Section 5-HMR-12 is required.

For many simple compounds the symmetry is such that protons are homotopic or enantiotopic, and no coupling constants can be measured directly (e.g., the $^2$J coupling in methane or dichloromethane; the ortho, meta, and para couplings in benzene; the cis, trans and gem couplings in ethylene, etc). For such compounds the following techniques are used to measure $J_{HH}$:

**Analysis of Complex Spin Systems.** In molecules where the chemical shift-equivalent protons are of the AA' type (part of an AA'XX', AA'X'X' or similar system), complete analysis of the spectrum system can, in favorable circumstances, give the value of $J_{AA'}$. An example is 1,3-butadiene, an AA'B'B'C'C' system in which all protons are coupled to all other ones. Analysis of the complex NMR spectrum gave, among numerous other couplings, values for the following couplings between chemical shift equivalent nuclei: $^3J_{AA'}$, $^5J_{BB'}$ and $^5J_{CC'}$ (Hobgood, R. T., Jr.; Goldstein, J. H. J. Mol. Spectr. 1964, 12, 76).

![Butadiene NMR spectrum](image)

**Isotopic Substitution.** Replacing one of the protons by deuterium (or even tritium) breaks the symmetry of the coupled system and allows measurement of $J_{HD}$ (or $J_{HT}$). The value of $J_{HH}$ can then be calculated from the gyromagnetic ratios. In the example below, the 60 MHz NMR spectrum of a mixture of undeuterated (s), monodeuterated (1:1:1 triplet, the spin of D is 1, see Sect. 7-MULTI-2.1) and dideuterated (1:2:3:2:1 quintet) acetonitrile is shown. Note the isotopic shifts. (Grant, D. M.; Barfield, M. JACS 1961, 83, 4727)

![Acetonitrile NMR spectrum](image)
**Analysis of $^{13}$C Satellite Spectra.** Vicinal couplings between homotopic or enantiotopic protons $^{3}J_{HH}$ can often be obtained by analysis of the $^{13}$C satellites. The $^{1}$H NMR signal for the vinyl protons of dimethyl maleate is a singlet. However, the $^{13}$C satellites are doublets, with a splitting that is equal to $^{3}J_{HH}$. In effect, the A$_{2}$ spin system of the $^{12}$C isotopomer has become an ABX pattern in the mono-$^{13}$C labelled compound, where X is the $^{13}$C nucleus, and A and B are the two vinyl protons, one on $^{13}$C and the other on $^{12}$C.

For systems of the X-CH$_{2}$-CH$_{2}$-X type, the mono-$^{13}$C isotopomer is an AA'BB'X pattern, which can be solved to obtain $J_{AA'} (= J_{BB'})$ as well as $J_{AB}$ and $J_{AB'}$. 

![Diagram of $^{13}$C Satellite Spectra](image)

2.2% of the molecules have $^{13}$C at one of the vinyl carbons.

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**5-HMR-3.16**
Below is an example of the measurement of a $^4J_{HH}$ in a symmetric tricyclic system using the $^{13}$C satellite method.