

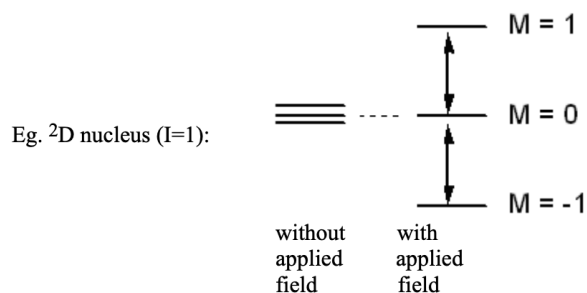
1.4: Introduction to NMR Spectroscopy

Chemical Shift

A nucleus of spin quantum number I can have an angular momentum M of

$$M = I, I - 1, I - 2, \dots -I + 1, -I \text{ (in units of } h/2\pi) \quad (1.4.1)$$

Therefore, every nucleus has a spin degeneracy of $2I+1$ (i.e. the energy level of the nucleus is independent of the value of M). In an NMR experiment, one places a sample inside a strong magnetic field. Inside such a magnetic field the degeneracy is lifted (i.e. the energy level of the nucleus does depend on the value of M).



Scheme 1. The effect of applied magnetic field on the energy levels of a nucleus

Transitions between these levels ($\Delta M=1$ only) can be detected by spectroscopy at frequency ν , where

$$\nu = \frac{\gamma H_{eff}}{2\pi} \quad (1.4.2)$$

$$\gamma = \text{magnetogyric ratio for that isotope} \quad (1.4.3)$$

$$H_{eff} = \text{applied magnetic field as experienced by the nucleus} \quad (1.4.4)$$

However, the applied magnetic field as experienced by the nucleus may be slightly lower than the magnetic field put out by the magnet of the spectrometer because the nucleus may be shielded from the main field by electron density. Therefore, we must modify the equation to take such shielding into account.

$$H_{eff} = H_0(1 - \sigma) \quad (1.4.5)$$

$$\nu = \frac{\gamma H_0(1 - \sigma)}{2\pi} = \frac{\gamma H_{eff}}{2\pi} \quad (1.4.6)$$

or

$$\frac{\nu}{H_0} = \frac{\gamma(1 - \sigma)}{2\pi} \quad (1.4.7)$$

$$H_0 = \text{applied magnetic field} \quad (1.4.8)$$

$$\sigma = \text{screening constant, which decreases the effective magnetic field} \quad (1.4.9)$$

If one keeps the frequency constant and scans H , one can plot intensity versus H . One will then observe an intensity peak when absorption occurs, at the H value which allows equation 3 (and 4) to be true (see figure below). On the other hand, one may choose to keep the magnetic field constant and scan frequency instead. This is experimentally easier to do. The positions of the peaks are described in terms of their distance from a chosen standard.

$$\delta = \frac{\nu - \nu_{ref}}{\nu_0} * 10^6 \text{ ppm} = \frac{(H - H_{ref})}{H_0} * 10^6 \text{ ppm} \quad (1.4.10)$$

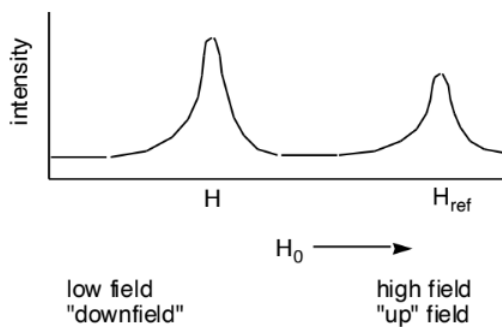


Figure 1

Usually, downfield is referred to as being positive; a nucleus that appears downfield of the reference will have a positive δ . The reference is usually assigned a chemical shift of zero. The reference for ^1H and ^{13}C NMR spectra is SiMe_4 (TMS). The reference for ^{31}P NMR is 85% H_3PO_4 in water.

Looking at equation 4 you will understand why the direction of increasing field and the direction of increasing frequency are opposite. A nucleus with negligible shielding ($\sigma \approx 0$) will need a large ν or a small H_0 and therefore will have a downfield shift. Acidic protons such as RCO_2H fit this description. In contrast, a nucleus with a lot of shielding ($0 < \sigma$) will need a small ν or a large H_0 and therefore will have an upfield shift. Hydrogen atoms attached to electropositive atoms or groups will fit this description. For example, $\text{Si}(\text{CH}_3)_4$.

All nuclei can be observed on the same scale of field vs intensity, but the distance on the scale between the signals for H and P, for example, is so large that they are usually shown separately. A table of some of the magnetically active nuclei is shown below. A larger table is in Appendix 7 of the textbook.

The strength of a magnet is usually measured in Tesla, but NMR magnets are more often described in terms of the resonance frequency for ^1H NMR. This can be misleading if you are planning to use a nucleus other than ^1H . For example, a 7.0 Tesla magnet has a resonance frequency of 300 MHz for ^1H (and will be referred to as a 300 MHz NMR magnet) but the resonance frequency for ^{31}P NMR on the same instrument will be 121 MHz. You can calculate the resonance frequency for any isotope from the magnetic field strength using equation 1.

Use a modification of equation 5 to convert between Hz and ppm units. For example, if two peaks are 106 Hz apart in a ^1H NMR spectrum on an NMR with a proton resonance frequency of 60 MHz, how many ppm apart are they?

$$\delta = \frac{\Delta\nu}{\nu_0} * 10^6 \text{ ppm} = \frac{106 \text{ Hz}}{60 * 10^6 \text{ Hz}} * 10^6 \text{ ppm} = 1.77 \text{ ppm} \quad (1.4.11)$$

| Nucleus | Spin | γ^a (1.4.12) | nat. abund. % | relative sensitivity ^b | Reference |
|-------------------|------|---------------------|----------------------|-----------------------------------|--------------------------------------|
| ^1H | 1/2 | 26.75 | 99.99 | 1.00 | SiMe_4 |
| ^2H | 1 | 4.11 | 1.5×10^{-2} | 9.7×10^{-3} | $\text{Si}(\text{CD}_3)_4$ |
| ^{13}C | 1/2 | 6.73 | 1.1 | 1.6×10^{-2} | SiMe_4 |
| ^{15}N | 1/2 | -2.71 | 0.37 | 1.0×10^{-3} | MeNO_2 or NO_3^- |
| ^{19}F | 1/2 | 25.17 | 100 | 0.833 | CFCl_3 |
| ^{31}P | 1/2 | 10.83 | 100 | 6.6×10^{-2} | $\text{H}_3\text{PO}_4(\text{aq})$ |
| ^{35}Cl | 3/2 | 2.62 | 76 | 4.7×10^{-3} | $\text{NaCl}(\text{aq})$ |
| ^{51}V | 7/2 | 7.04 | 99 | 0.382 | VOCl_3 |
| ^{55}Mn | 5/2 | 6.62 | 100 | 0.175 | $\text{KMnO}_4(\text{aq})$ |
| ^{59}Co | 7/2 | 6.35 | 100 | 0.277 | $\text{K}_3[\text{Co}(\text{CN})_6]$ |
| ^{103}Rh | 1/2 | -0.852 | 100 | 3.1×10^{-5} | $\text{RhCl}_3(\text{SMe}_2)_3$ |

| | | | | | |
|-------------------|-----|-------|------|----------------------|-----------------|
| ^{115}Sn | 1/2 | -8.75 | 0.35 | 3.5×10^{-2} | SnMe_4 |
| ^{117}Sn | 1/2 | -9.53 | 7.6 | 4.5×10^{-2} | SnMe_4 |
| ^{119}Sn | 1/2 | -9.98 | 8.6 | 5.2×10^{-2} | SnMe_4 |

^a magnetogyric ratio ($10^7 \text{ rad T}^{-1} \text{ s}^{-1}$)

^b for equivalent numbers of nuclei at constant field

Quadrupolar nuclei are those with $I > 1/2$. They have non-symmetrical nuclear charge distribution. They often relax far more quickly than other nuclei and therefore can have very broad signals or might not be observed, and they can have the same effect on nuclei with which they are coupled. For this reason, usually ^{35}Cl and ^{14}N ($I=1$) NMR are not possible due to excessive broadening.

Spin-Spin Coupling

You may have already studied the coupling of ^1H nuclei in organic chemistry courses. In this course you will be required to understand NMR coupling. The following

is a very brief introduction to the topic. If there is a proton (H_A) which is close (i.e. fewer than 4 bonds away) in the molecule to another proton H_B , then the NMR spectrum of H_A will appear to be a doublet (two peaks of equal height). This occurs because the magnetic field around H_A is influenced by the spin of H_B . The neighboring proton H_B could be in a spin 1/2 or spin -1/2 state, causing the observed nucleus H_A to have two different energy levels. Therefore there will be two lines for the observed nucleus.

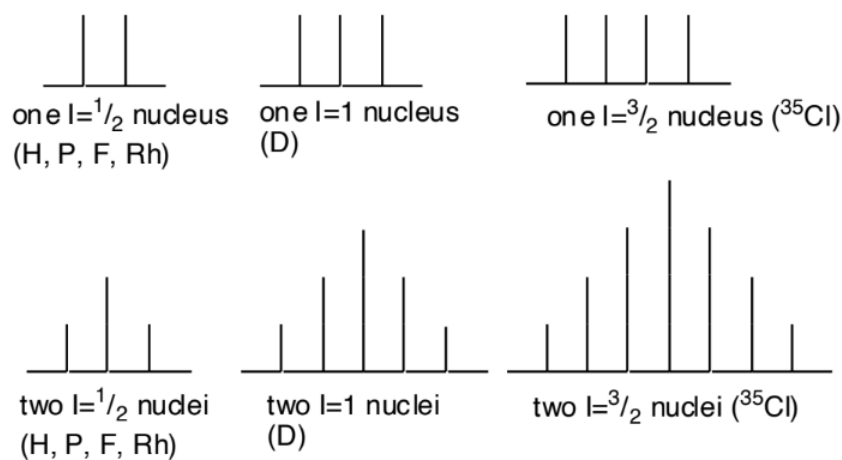
However, coupling of a proton H_A to a neighboring ^2H (deuterium) atom ($I = 1$) will generate three lines of equal intensity because the neighboring deuterium nucleus could be in 1, 0 or -1 spin states.

In order to predict the number of lines that the spectrum of a nucleus (let's call it A) will have, one has to know the number of nuclei (B) it is coupled to and the spin of those nuclei. We shall assume, for now, that the "other nuclei" are all equivalent to each other. We can then use the following rule: In general, for any nucleus A coupled to n_B equivalent neighboring nuclei B of spin I_B , the number of peaks in the NMR spectrum of the nucleus A is:

$$\# \text{ of peaks} = 2n_\text{B}I_\text{B} + 1 \quad (1.4.13)$$

Notice that the spin I_A of the nucleus we are observing does not appear in the equation. It doesn't matter what nucleus you are observing, the coupling pattern observed only depends on the isotope and number of neighboring nuclei.

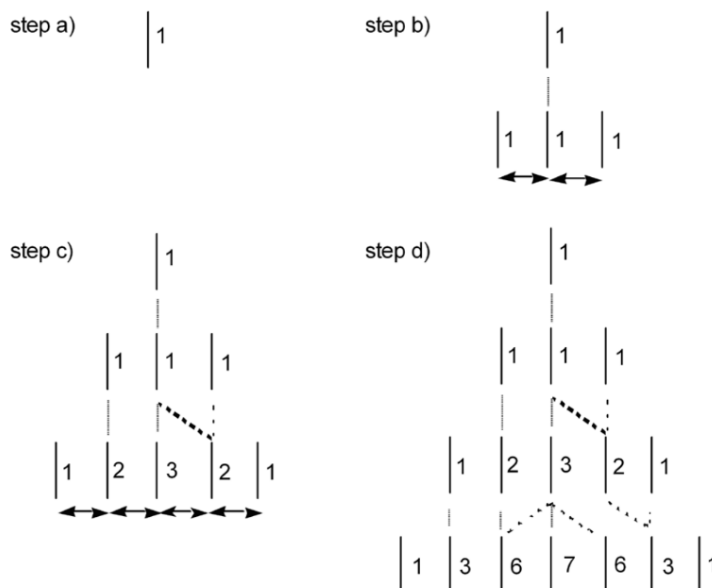
For example, coupling of a nucleus A to two equivalent neighboring ^2H (deuterium) atoms ($I = 1$) will generate five lines (# of peaks = $2n_\text{B}I_\text{B} + 1 = 2 \times 2 + 1 = 5$). This answer is correct no matter what element nucleus A is (as long as it is NMR observable, of course).



Scheme 2. The NMR spectrum of nucleus A will look like this if the proton is coupled to.

Now that we know how to calculate how many lines there will be, how do we calculate how tall each line will be? Build a splitting tree, using the following steps. The process is illustrated in Scheme 3.

- Draw a vertical line for the observed nucleus. This represents what the spectrum would look like in the absence of splitting to any neighboring nuclei. Put a "1" beside the line.
- To represent splitting with the first neighboring *B*, draw $2I_B + 1$ lines centered below the first line. This is row #2. The spacing between the lines represents J_{AB} , the coupling constant in Hertz (see double headed arrows in the diagram). Write a 1 beside each of these lines. Draw dashed lines from row one to the lines on row #2.
- To represent splitting with the second neighbor *B*, draw $2I_B + 1$ lines below centered below *each* of the lines in row #2 and spaced J_{AB} apart. This is row #3. Note that some of the lines coincide. Draw dashed lines from the lines on row #2 to the corresponding lines on row #3. Write a number beside each of these lines, the number being the sum of the numbers from the lines in row #2 to which the line in row #3 is connected.
- Repeat this process until you have accounted for all of the neighbors.



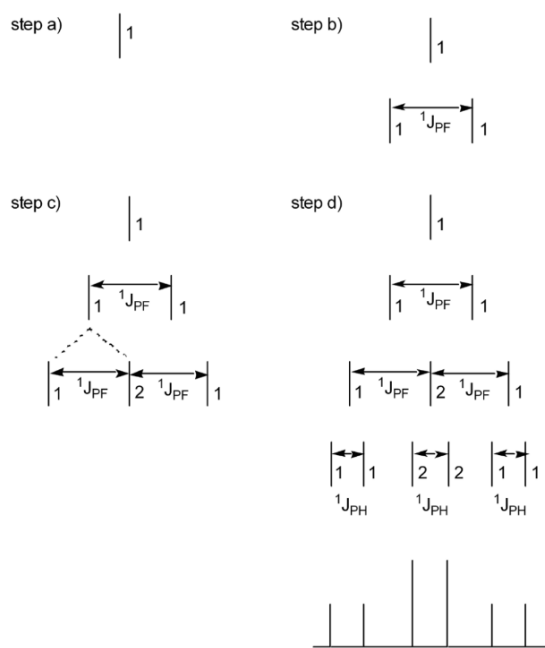
Scheme 3. What would the ^1H NMR spectrum of HCD_3 look like? The H is coupled to 3 equivalent nuclei of spin 1.

What if the neighboring nuclei are not all equivalent? For example, what if the observed nucleus A is split by *two* sets of nuclei B (total spin $n_B I_B$) and C (total spin $n_C I_C$)? The number of peaks in the spectrum of A = $(2n_B I_B + 1)(2n_C I_C + 1)$.

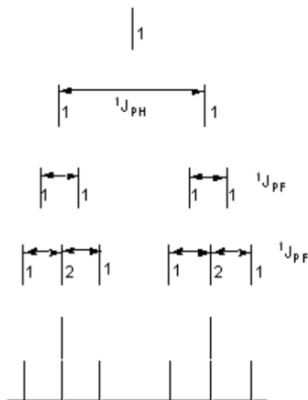
For example, the ^{31}P NMR spectrum of HPF_2 (F, P, and H have $I = 1/2$) would have six peaks.

$$\# \text{ of peaks} = (2n_F I_F + 1)(2n_H I_H + 1) = (2 \times 2 \times \frac{1}{2} + 1)(2 \times 1 \times \frac{1}{2} + 1) = 3 \times 2 = 6 \quad (1.4.14)$$

In order to predict the intensities in the peaks, you have to draw another splitting tree, using the same rules as before. However, this time the lines might not overlap.



Scheme 4. The splitting tree for the ^{31}P NMR spectrum for HPF_2 , assuming $^1J_{\text{PF}} > ^1J_{\text{PH}}$. Note that we do the larger coupling first. Prediction: a triplet of doublets (td)



Scheme 5. The splitting tree for the ^{31}P NMR spectrum for HPF_2 , assuming $^1J_{\text{PF}} > ^1J_{\text{PH}}$. Note that we do the larger coupling first. Prediction: a doublet of triplets (dt).

If $^1J_{\text{PF}} > ^1J_{\text{PH}}$ then some peaks will overlap and the # of peaks observed will be given by first formula above (answer = 4).

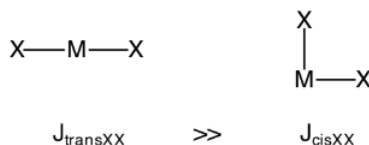
Coupling will **not be observed** if:

- the neighboring nucleus is too far away (4 bonds or more)
- the neighboring nucleus is NMR inactive ($I = 0$)
- the neighboring nucleus is NMR dilute (eg most C atoms are ^{12}C ($I = 0$), only very few are ^{13}C ($I = 1/2$), so in ^{13}C NMR one doesn't see J_{CC} coupling).
- the neighboring nucleus is decoupled (such as $^{31}\text{P}\{^1\text{H}\}$ NMR), or
- the neighboring nucleus is equivalent to the observed nucleus

Decoupling is used to simplify the spectrum if too much coupling is being observed. The nucleus which is decoupled is usually indicated by curly brackets. For example, a ^{31}P NMR spectrum acquired with the hydrogen atoms decoupled would be referred to as a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum.

Coupling constants can vary from very small (essentially 0 Hz) to very large (thousands of Hz). Coupling constants can also be negative, but that is a subject more appropriate for an advanced course. The relative size of the observed coupling constant can tell us about the relationship between the observed nucleus and the neighbor. The number of bonds between the observed nucleus and the neighboring nucleus is indicated by a superscript before the "J". For example, $^3J_{HH}$ refers to the coupling constant between two protons which are three bonds apart.

Coupling between two atoms bound to a metal center is often particularly strong if the two atoms are trans (i.e. 180° apart) and much weaker if they are cis (i.e. 90° apart).



| Coupling | J | Hz Range |
|--|-------------|----------------|
| CH_aH_b | $^2J_{HH}$ | 0 to 30 |
| $\text{CH}_a\text{-CH}_b$ | $^3J_{HH}$ | 6 to 8 |
| $\text{CH}_a\text{-CR}_2\text{-CH}_b$ | $^4J_{HH}$ | 0 to 1 |
| $\text{C}_6\text{R}_4\text{H}_a\text{H}_b$ ortho | $^3J_{HH}$ | 6 to 10 |
| $\text{C}_6\text{R}_4\text{H}_a\text{H}_b$ meta | $^4J_{HH}$ | 1 to 3 |
| $\text{C}_6\text{R}_4\text{H}_a\text{H}_b$ para | $^5J_{HH}$ | 0 to 1 |
| M-H | $^1J_{MH}$ | 40 to 1400 |
| M-P (M=Si, Sn, Se, Te) | $^1J_{MP}$ | -ve |
| M-P (M=Pt) | $^1J_{PtP}$ | +2000 to +6000 |
| $\text{P}_a\text{-M-P}_b$ trans | $^2J_{PP}$ | +300 to +1300 |
| $\text{P}_a\text{-M-P}_b$ cis | $^2J_{PP}$ | -70 to +80 |

Table: Relative strengths of coupling constants.

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