III

Practical Liquid State NMR

Lecture notes by Assaf Tal

Lectures 1 & 2 were aimed at understanding how an NMR spectrum is formed. In this chapter we will address several practical issues which we've glossed over, including interpreting NMR spectra and setting acquisition parameters.

1. Understanding NMR Spectra

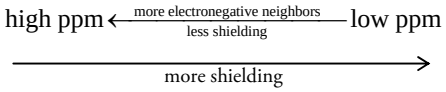
The current course is aimed at an understanding of the basic principles of MR, and not at understanding and deciphering NMR spectra. However, it would be amiss without discussing at least the basics of understanding NMR spectra and where the variability in chemical shifts come from. Being able to "understand" a spectrum – i.e., to tell which peak corresponds to which group in a molecule – is an artform that results from an amalgam of experience and rules-of-thumb. We attempt to outline some basic concepts in this section. We discuss liquids only.

1.1 "Local" Shielding

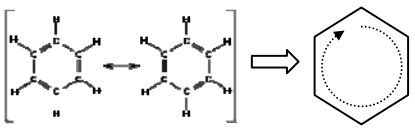
This is the "simplest" kind of shielding that results from electron currents surrounding the nucleus. Here the main factor influencing the amount of shift for different groups is the electron density around the nucleus. Nearby groups will withdraw electrons from a nucleus, an effect known as **electronegativity**. Some groups/atoms do so more than others. For example, consider what happens to the chemical shift of the protons of a CH_3 group as we attach different atoms to the remaining C bond:

X atom (CH_3X)	Predicted ppm	Electronegativity
H	0.23	2.3
I	2.16	2.4
Br	2.68	2.7
Cl	3.05	2.7
OH	3.4	O=3.6
F	4.26	4.2

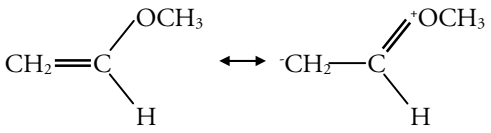
The higher the electronegativity the more it "draws" electrons, the less shielded the methyl H nuclei become, the higher their resonance frequency (and ppm).



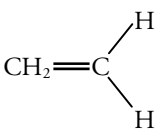
Another form of local shielding comes from **resonance** (aka mesomerism). Here, electrons are delocalized and withdrawn from an atom. This is a non-local effect (although the shielding is local, because the effect is directly applied to the electrons orbiting the nucleus in question). An example of this is a benzene ring in which there are two resonant structures which alternate between them and cause an electron current in the ring:



Another example is of vinyl ether:



Here the electron density at the CH_2 group increases (it becomes more negative) which then leads to a decrease in the field and the ppm of their resonance to about 4.1 ppm. Compare this to ethene, in which the protons in the CH_2 group resonate at 5.28 ppm:

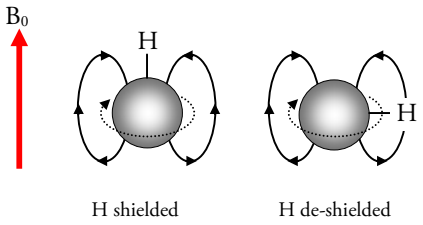


Note that you cannot ascribe this change to the difference in attached groups (H vs. OCH_3). If anything, the more electronegative OCH_3 of vinyl ether would drive the resonance frequency **up**, not **down**!

A third effect is **hybridization**, in which orbitals change their shape upon being combined in molecules, making electrons move closer or farther away from the nucleus and changing their effective shielding.

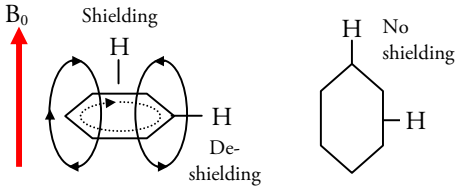
1.2 Nonlocal Shielding

Non isotropic electron distributions can also affect the chemical shift of far-away nuclei. Let's first think about an isotropic electron distribution. The diamagnetic shielding currents induced by the external magnetic field to not change as we rotate the molecule because, well, it's isotropic! However, if we think about what happens to an attached nucleus – say, a proton – then this proton is occasionally shielded and occasionally deshielded:



On average, as the molecule tumbles through the liquid, these shielding-deshielding effects will be averaged to zero. Thus, it will not be directly observable in liquid state, but **will** contribute to relaxation. It will also be visible in solid state.

When dealing with non-isotropic current distributions, the averaging doesn't yield a zero effect. The simplest example is that of a benzene ring. When it is perpendicular to B_0, the aromatic electrons go around in a circle and create a magnetic field, while when it is parallel to B_0 no such current exists:



When the molecule tumbles now it the average shielding is not zero but some non-zero number.

The magnitude of ring current effects can be quite sizable, around 1 ppm in real life applications. It will depend on where the proton is: protons above the center of a ring will experience shielding and a reduction in ppm. Protons in the plane will experience an increase in ppm. The effect of the ring can be modeled as a dipole in its center, and the shift can be calculated by modeling it as a dipole at the ring's center:

$$\sigma = IB\frac{1-3\cos^2\theta}{r^3}$$

In this equation by Pople et. al., B=25 ppm, I the ring-current factor which depends on the ring's geometry (e.g. I=1 for a phenyl group), θ is the angle between the normal to the ring and the vector that joins the nucleus to the ring's center, and r is the distance of the nucleus from the ring's center.

2. Setting Up the Acquisition

2.1 Tuning and Matching

Ohm's law states that V=IR, where R is the resistance between two points A and B, V the voltage, and I the current flowing between them. In electronics, voltage and current both have a magnitude and a phase:

$$I = I_0\cos\left(\omega t + \varphi_I\right)$$
$$V = V_0\cos\left(\omega t + \varphi_V\right)$$

One often recasts them in complex notation as

$$I = I_0 e^{i(\omega t+\varphi_I)}$$
$$V = V_0 e^{i(\omega t+\varphi_V)}$$

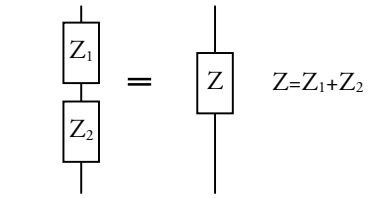
with the understanding that their real part represents the actual physical signal. One can then generalize Ohm's law to the form

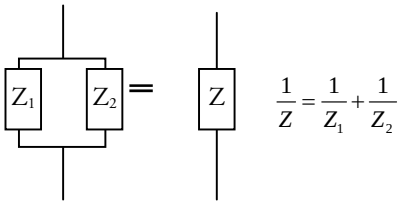
$$V=IZ.$$

In this new form, Z is called the *impedance* and can be a complex quantity, as follows:

Resistor:	Z=R
Capacitor:	Z=1(iωC)
Inductor:	Z=iωL

Capacitors and inductors are seen to change the phase of the signal because they are imaginary quantities. Impedances follow the same addition rules as resistors: impedances in series add up, while in parallel their inverses add up:





For example, the impedance of a capacitor and resistor in series is

$$Z = \frac{1}{i\omega C} + R$$

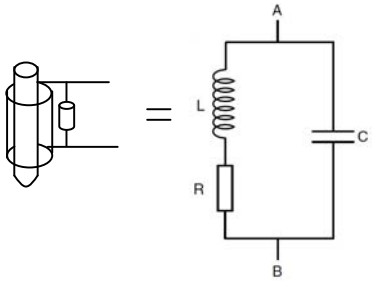
We can then say that the voltage and current obey the relation:

$$V = I \cdot \left(\frac{1}{i\omega C} + R \right)$$

Since the impedance is a complex quantity, it will affect both the relative magnitude and phase of V and I.

An important theorem in electrical engineering states that any circuit made out of passive linear components (resistors, capacitors, inductors, etc) can be represented using a voltage source and an impedance in series. Even active nonlinear components such as transistors and diodes, can often be approximated using this simple reduction.

The NMR acquisition apparatus and sample can be thought of in terms of electrical components: The sample is a resistor and the coil is an inductor, and there is additional resistance and capacitance in the probe electronics. Thus, it can be analyzed in terms of its impedance.



The probe+sample system is equivalent to an LRC circuit – a circuit which has an inductor L, capacitor C and resistor R. This system has a certain **resonant frequency**, given by

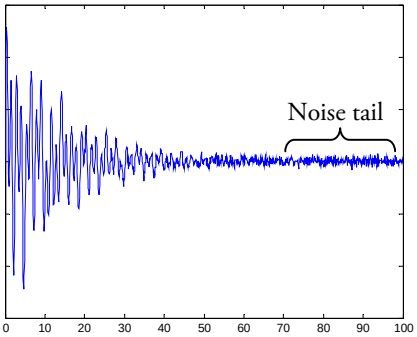
$$\omega_{LRC} = \frac{1}{\sqrt{LC}}.$$

This means the greatest current will be created when the circuit is driven with a sinusoidal voltage at a frequency ω_{LRC}. In our experiment, the voltage source is the sample itself – that is, the spins that precess and create the FID! We can change ω_{LRC} to match the resonant frequency of the spins by adjusting the value of the capacitor C (often chosen to be a variable capacitor). You don't need to re-tune often if you're just doing simple ^{1}H spectra, but if you have a broadband probe or looking at an unusual frequency range you should probably retune.

One can then consider the **coupling** between the NMR probe and the spectrometer's electronics. It is possible to prove that when the resistive part of the impedance of the source (NMR probe + sample) equals that of the spectrometer's electronics, which is usually set at 50 Ω, power transfer is optimal between the system. Since the sample has some unknown a-priori resistance, it is necessary to play around with the Probe+Sample impedance to **match** its impedance to 50 Ω, which is achieved by attaching a variable capacitor or inductor and playing around with its capacitance until the impednace is matched.

2.2 Setting the Acquisition Time

A typical FID looks like this:



ms

How long should you acquire for? On the one hand, if you acquire for too long you might end up just wasting time and acquiring unnecessary noise. If you don't acquire for long enough you might lose out on important signal. The rule of thumb is to *acquire until your signal decays away*, which happens around $5T_2$ ms. This means you should have an idea of when the signal decays by running a preliminary experiment or knowing something about your sample. In the example above, T_2 was about 15 ms.

2.3 Dwell Time and Acquisition Time

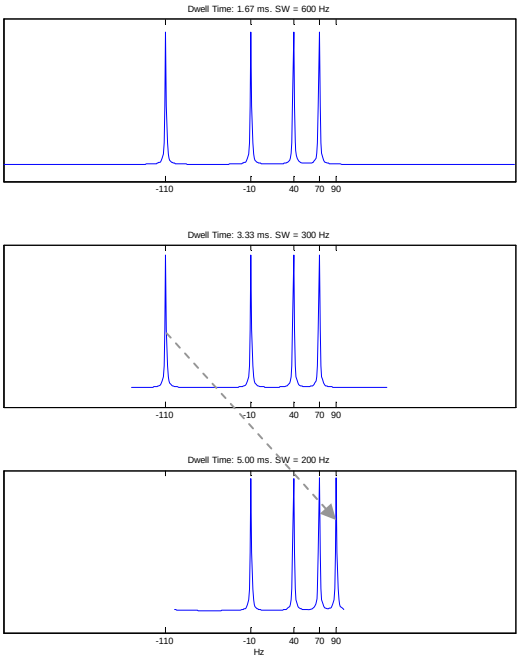
The acquired signal is digitized and we record not the continuous analog signal, but a set of points acquired at equidistant time intervals. This time interval is called the *dwell time* and usually denoted dt or Δt.

If one acquires for a time T and a dwell time dt, then they will end up with

$$N = \left\lfloor \frac{T}{dt} \right\rfloor$$

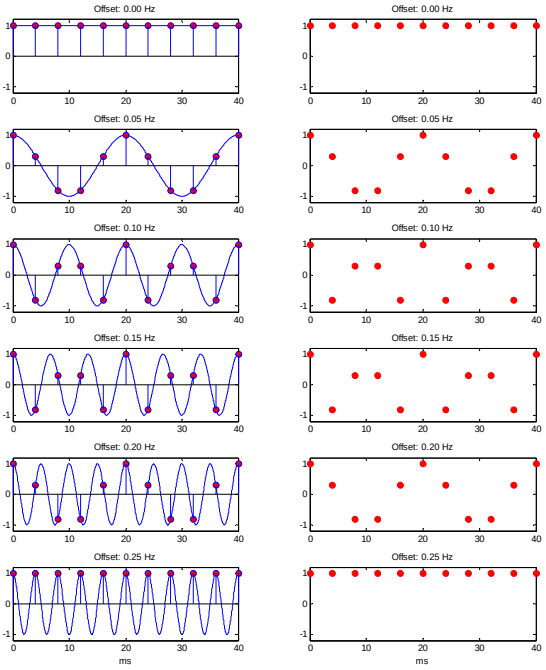
at times 0, dt, 2dt, 3dt, ... Consequently, the fourier transform the occurs in the computer is called the *discrete fourier transform*. The MATLAB command that carries it out is called fft.

The effect of the dwell time is to cause **aliasing** in the spectrum: imagine the spectrum not as a linear graph, but as a sheet of paper wrapped around a cylinder of length 1/dt. If the cylinder is too short, the paper will "wrap" onto itself and will make it difficult to read the spectrum. As long as 1/dt is bigger than the length of the sheet of paper you should be ok. This is demonstrated in the next example, in which there are four peaks at -110, -10, 40 and 70 Hz:



In the third case, dt=5 ms and 1/dt = 200 Hz. The peak at -110 then "folds" back onto 90 Hz (90 = -110+1/dt = -110 + 200).

The reason for aliasing can be understood by looking at the following example, in which the signal $\cos(2\pi\nu t)$ is digitized for different offsets ν at a dwell time of 4 ms (total acquisition time 40 ms):



We see that once we progress by 1/dt=0.25 kHz from ν=0, we once again acquire a constant set of points, making it impossible for us to distinguish between ν=0 and ν=0.25 kHz (or ν=0.5 kHz, 0.75 kHz, etc ...). Think of the ADC as a stroboscopic party light: we only observe the scene at equidistant time points (0, dt, 2dt, 3dt, ...), but have no way of knowing what happened between those time points. If we tried to view something that had a periodicity of the stroboscopic light we wouldn't see anything and mistake it for being constant.

The range of non aliased frequencies we observe is called the **spectral width** (denoted SW), and we have just shown that:

$$\mathrm{SW} = \frac{1}{dt}.$$

Q: Why not sample really really fast (use tiny Δt) and make the SW really big so we don't have to worry about aliasing?
A: First, all ADCs have a maximal sampling rate, which may or may not allow fast sampling. Second, most ADCs tend to use really small dwell times "behind the scenes", and actually NMR spectrometers tend to *oversample* (use small Δts) and then digitally *downsample*. This is a slightly complex process which is done because it makes it possible to build simpler analog low pass filters in the ADC. We won't go into the reasons in this course (but you can come and ask me if you're curious).

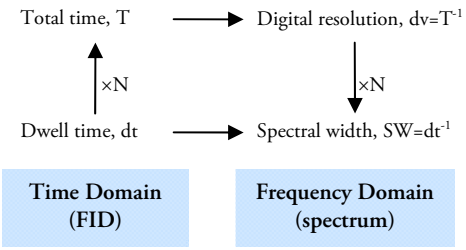
A complementary parameter to the dwell time is the total acquisition time, T. If we have N points and a dwell time dt, then

$$T = N \cdot dt\,.$$

The total acquisition time determines the digital resolution: the smallest frequency range one can observe in the Fourier transformed spectrum:

$$\frac{1}{T} = d\nu\,.$$

Thus we have an "inverse" relationship between the time and frequency domains:



Where does the relation T=1/dν come from? We can understand this by examining the FT of a complex exponent, $f(t)=e^{i2\pi\nu t}$. We have seen in the previous lecture that

$$\hat{f}(\nu) = \int_{-\infty}^{\infty} f(t) e^{-2\pi i \nu t} dt = \delta(\nu - \nu_0)$$

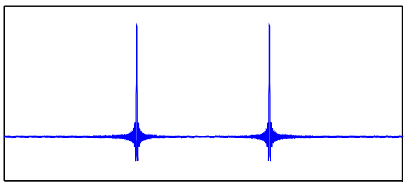
and, if we zero out the function outside [-T/2, T/2],

$$\hat{f}_T(\nu) = \int_{-\infty}^{\infty} f(t) e^{-2\pi i \nu t} dt = T \cdot \mathrm{sinc}(\pi \nu T)\,.$$

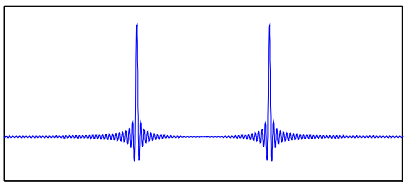
As $T\to\infty$ we have $\hat{f}_T(\nu) \to \delta(\nu - \nu_0)$. However, for a finite T – that is, for a finite acquisition time – we obtain a **broadening** of the signal on the order of $d\nu=T^{-1}$. This means that anything thinner than $d\nu=T^{-1}$ (say, a delta function) will "fatten up" and get a width of $d\nu=T^{-1}$ simply because we

acquire for a finite amount of time, T. This can be seen in the following example, in which two chemical shifts at 0 Hz and 200 Hz were simulated with different acquisition times, 512 acquisition points and $T_2=\infty$. Ideally for an acquisition time of $T=\infty$ we should get a perfect delta function. For $T<\infty$ the delta function is replaced with sinc-like functions. The real part of the spectrum is displayed after 15-fold zero filling of the FID (See below for what zero filling is):

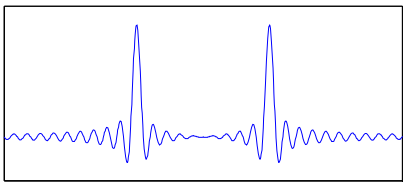
Acq. time: 500 ms



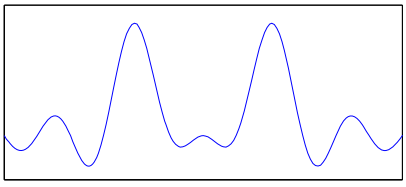
Acq. time: 200 ms



Acq. time: 50 ms



Acq. time: 10 ms



In general, the width of each peak behaves as 1/T (approximately).

The example highlights another interesting feature: **ringing**, which refers to the sinc-like wiggles accompanying each peak. This comes whenever we truncate our signal, which is the case here, since we suddenly stop acquiring after a time T. Ringing is avoided if the FID decays smoothly to zero, which is the case if $T>>T_2$. Even if $T<T_2$ the FID can be multiplied by a function that has a smooth decay, such as $\exp(-t/T_{smooth})$. This will make the ringing go away.

The digital resolution is not the only factor affecting resolution. We have already remarked that the width of a Lorentzian peak is determined by T_2 and given by approximately $1/T_2$. This means that even if we acquire for an infinite amount of time ($T=\infty$), our spectral peaks will still be broadened by their natural T_2 decay which also limits our resolution. So the following should be kept in mind: **The fastest decay factor of our signal determines our ultimate resolution**. If $T_2<T$ then our resolution will be $1/T_2$. If $T<T_2$ then our resolution will be $1/T$. If there is some other factor causing our signal to decay even faster than T, T_2 then that will determine our peaks' widths and, hence, our resolving power.

2.4 Lock

NMR samples are prepared in a solvent. Many of these are sold in deuterated forms. For example, D_2O instead of H_2O. This is done for two reasons: to reduce the very large signal from the solvent, which is often at a much larger concentration than the solute and might overpower it; and to provide a signal from the deuterium atoms to "lock" the spectrometer's frequency.

The spectrometer's field is not constant over time but slowly diminishes due to tiny dissipative losses in the superconducting wire. A typical magnet might drift by 10^{-7} Tesla/hour. This might not sound like a lot, but in reality it translates to

$$\gamma \times 10^{-7} T \sim 1-10 \ \frac{\text{Hz}}{\text{Hour}}.$$

Some NMR experiments are left overnight for many hours to increase the SNR or simply because they are complicated and take a lot of time (see the lecture about 2D NMR). This amounts to drifts much larger than the linewidth and can lead to severe spectral issues.

To overcome this, the signal from the deuterium – which is completely independent from the hydrogen/carbon/nitrogen/phosphorous

signals one usually measures in NMR – is acquired in rapid pulses and used to track the field's drift by looking at the frequency of the deuterium nuclei of the solvent. When the spectrometer "sees" this changes, it adjusts the current through a ring which creates a homogeneous main field much like B_0, only not superconducting. This is fine because the changes this ring needs to make are very small, so we don't need it to be superconducting. Samples without any deuterium cannot "lock" the spectrometer's frequency and this should be kept in mind when running long experiments.

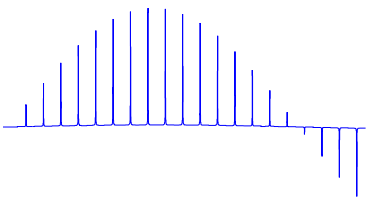
2.5 Calibrating the Pulse

As an experimentalist, we can only vary the voltage on the transmitter. How does one give a 90° pulse? That is, how does one know which voltage corresponds to such a pulse? The answer is we need to calibrate it.

The flip angle α is proportional to the B_1 field:

$$\gamma B_1 t_p = \alpha$$

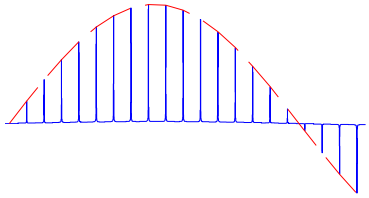
and B_1 is proportional to the applied voltage by the fundamental equations of electrodynamics, known as Maxwell's equations. We now fix t_p at a very short duration and start increasing the voltage in constant steps, looking at a particular peak in the sample. Often this is the solvent which gives off the strongest value when unsuppressed. What we'll get is something that looks like this:



Each peak represents a separate experiment with a different B_1 (which you don't know). The peak amplitude is modeled by

$$A \cdot \sin(\alpha) = A \cdot \sin(\gamma B_1 t_p).$$

By fitting the maxima of the peaks with this function you can easily find both A (which is meaningless) and B_1, and determine which voltage corresponds to it:

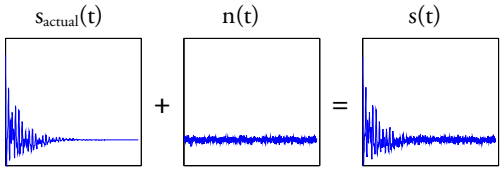


2.6 Averaging and SNR

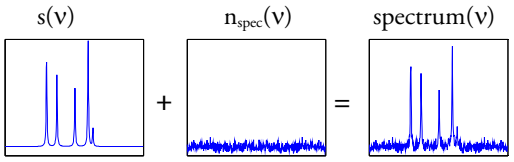
The **signal to noise ratio** (SNR) of an NMR spectrum is one of its most important aspects, particularly because peak strengths are so weak in NMR and often get swallowed up in the noise, becoming unobservable. This is mainly because nuclear paramagnetism is a very weak effect. Because we (usually) can't control the paramagnetic polarization, we have to average over many measurements. The idea is that each measurement has a signal and noise:

$$s(t) = s_{actual}(t) + n(t)$$

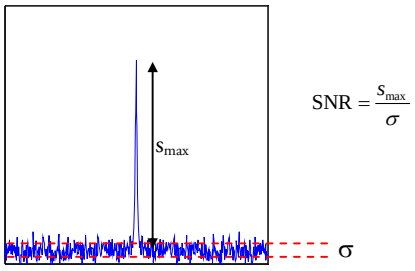
where n(t) is some random noise term:



Because the Fourier transform is linear, the same thing happens in the spectral domain (the noise term there will be the FT of the noise term in the time domain, which is ... also noise!):



The SNR of a given peak is defined as the ratio of its amplitude to the standard deviation of the noise:



Two independent measurements will have exactly the same signal $s_{actual}(t)$ but the noise term will be different. What happens when we add them together? The signal doubles in intensity. What happens to the noise? Noise + noise still equals noise, but remember these are random signals: some of the time the signals will cancel out, some of the times they will add constructively, so we won't really get a factor of ×2 in the standard deviation. What we actually get is a factor of $\sqrt{2}$, so the SNR grows by $\sqrt{2}$ as well:

$$\text{SNR} = \frac{S_{max}}{\sigma} \xrightarrow{\text{avg. 2 signals}} \frac{2 \cdot S_{max}}{\sqrt{2}\sigma} = \sqrt{2} \cdot \text{SNR} .$$

In general, for N averages, the SNR will increase by a factor of $\sqrt{N}$. This is the principal of signal averaging. It's not very efficient. For example, if we repeat the same experiment 100 times, we only get ×10 SNR but have to spend ×100 time. Unfortunately, it's often the best we can do.

2.7 Shimming

The quality of the spectrum depends greatly on the macroscopic homogeneity of the B_0 field. In inhomogeneous field will lead to a spatial distribution of larmor frequencies (say, for one chemical shift):

$$\omega(\mathbf{r}) = (1-\sigma)\gamma B_0(\mathbf{r}) .$$

Our spectrum will therefore contain an integral over all these peaks:

$$s(t) = \int_{\text{sample}} e^{i\omega(\mathbf{r})t - t/T_2} d\mathbf{r} .$$

Its Fourier transform will consequently look distorted. When is B_0 inhomogeneity an issue? When the range of frequencies it creates is wider than a linewidth, which is about 1 Hz in liquid state NMR. Think about what sort of amazing feat it is to achieve this level of homogeneity: we require that

$$\Delta\omega = 1\text{Hz}$$
$$\omega = \gamma B_0 = 500 \text{ MHz}$$
$$\frac{\Delta\omega}{\omega} \sim 10^{-9}$$

We require the field to be homogeneous to about 1 part per billion! Think of building a wall 10 cm thick that is so straight it does not deviate (say, by shear forces) by even 10^{-9} of its thickness, which is 1 Å! This is an amazing feat of engineering. While today's modern B_0 main coils can produce a field that's homogeneous to about 10^{-6} over the sample size, further improvements are achieved via **shims**. There are two types of shims:

- **Passive shims** are small ferromagnetic (e.g. iron) elements placed inside the magnet's bore during construction to cancel out spatial inhomogeneities. The shims produce spatial fields which are specifically engineered to cancel out imperfections in the main coil.
- **Active shims** are conducting loops of wire placed around the sample. Current passed through them will generate spatially varying magnetic fields. By adjusting the levels of current we can build spatial patterns that cancel out (some of) the remaining spatial inhomogeneity.

Q: Why do we need active shims? Why aren't passive shims enough?
A: Very simple. Most samples have bulk atomic diamagnetism which will depend on (i) the sample's shape and (ii) composition. This means our magnetic field will be distorted **by the sample itself** and we can't account for it beforehand because we don't know what sort of samples the user will want to test! Active shims let the user fix those sample-specific effects.

Most active shims produce spatial fields which approximate linear combinations of spherical harmonics $Y_{lm}(\phi,\theta)$. The first few are:

Order (l)	Deg. (m)	Polar function	Cartesian function	Symbol
0	0	1	1	Z^0
1	0	$r\cos\theta$	z	Z
1	1'	$r\sin\theta\cos\phi$	x	X
1	1	$r\sin\theta\sin\phi$	y	Y
2	0	$r^2(3\cos^2\theta-1)$	$2z^2-(x^2+y^2)$	Z^2
2	1	$r^2\sin\theta\cos\theta\sin\phi$	zx	ZX
2	1'	$r^2\sin\theta\cos\theta\cos\phi$	zy	ZY
2	2	$r^2\sin^2\theta\cos2\phi$	x^2-y^2	X^2-Y^2
2	2'	$r^2\sin^2\theta\sin2\phi$	2xy	XY
3	0	$r^3(5\cos^3\theta-3\cos\theta)$	$2z^3-3z(x^2+y^2)$	Z^3
...	...	...	...	...

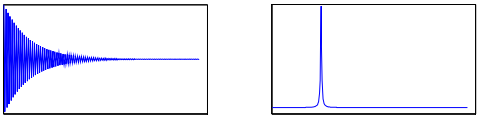
There are 2l+1 shims of degree l, which are linear combinations of spherical harmonic functions. In theory, if we had an infinite number of shims of orders l=0 until ∞ we could approximate **any** spatial inhomogeneity. In reality:

- We only have a limited number of orders. NMR spectrometers usually have shims up until orders 5 or so, and often not the full set (it might be missing degrees).
- We are limited with the amount of current we can pass through the shim coils.
- Actual shim coils' fields deviate from the perfect spherical harmonics, which complicates things a bit.

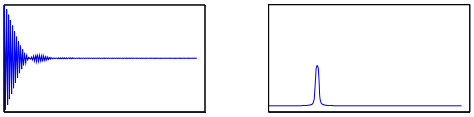
Shimming however is a major preliminary part of any NMR experiment, in which one adjusts the active shims to minimize B_0 inhomogeneity. There are many ways to assess the level of B_0 inhomogeneity, but on the most basic level we adjust the shim currents until our peak looks lorentzian and narrow.

The effects of different "types" of field inhomogeneity are shown below.

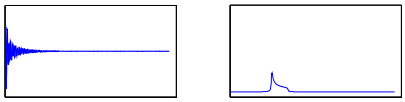
1. A homogeneous B_0 field and a perfect lorentzian (left: real part of FID; right: real part of spectrum):



2. A linear inhomogeneity $B_0=\alpha z$: this yields a "beating" in the FID and a loss of signal:



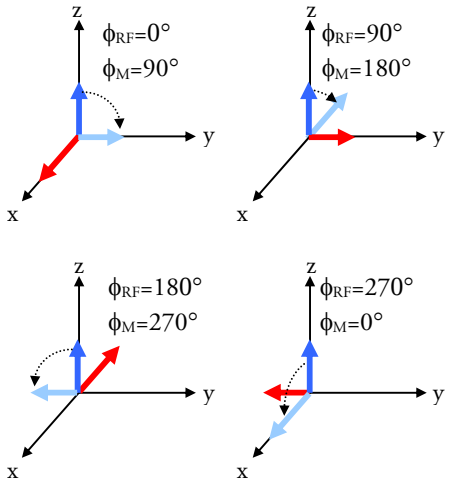
3. A quadratic inhomogeneity, $B_0=\alpha z^2$, will lead to an asymmetric spectral lineshape:



All types of B_0 inhomogeneity lead to **loss of SNR and spectral resolution**, and are extremely detrimental to spectroscopy!

2.8 Phase Cycling

Any pulse has a **phase** as well as an amplitude, determining its position in the transverse plane and, as a result, the phase of the excited magnetization:



The above drawings show that the phase of the excited magnetization, ϕ_M, merely satisfies:

$$\phi_M=\phi_{RF}+90°.$$

This opens up some very interesting opportunities for improving the final signal. For example, consider an ADC which is imperfect and adds a DC component to the acquired signal; that is, instead of s(t) it gives

$$s(t)+\eta$$

where η is some constant (this was common in the early days of NMR; today's ADCs are much better and DC offsets are rarely a problem). By repeating the experiment twice, with RF phases ϕ_{RF}, $\phi_{RF}+180°$, we obtain two signals:

$$s_1(t) = s(t) + \eta$$
$$s_2(t) = -s(t) + \eta$$

By subtracting both measurements we can cancel out the DC offset:

$$s_1(t) - s_2(t) = 2s(t).$$

There are more complicated phase cycles we'll meet down the road, but this should give you a preliminary idea of the concept.

2.9 Filter Bandwidth

Before the ADC there is a low pass filter (LPF) which cuts off high frequencies. Why? Because if it didn't the high frequencies – which contain only noise – would alias into the spectrum and increase its noise level. The width of this filter is called the filter bandwidth. For the types of electronic/white noise present in the NMR bands, one can say with great precision that

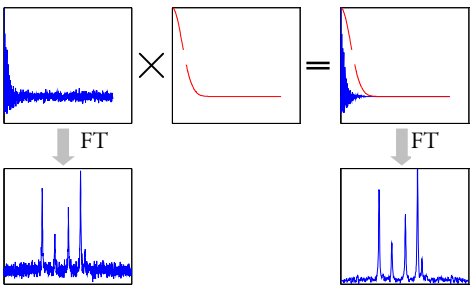
$$\text{FID noise levels} \propto \sqrt{\text{fbw}}\ .$$

The filter bandwidth is directly related to the spectral bandwidth, and in some spectrometers they are implicitly set to be equal.

3. Processing NMR Spectra

3.1 Apodization

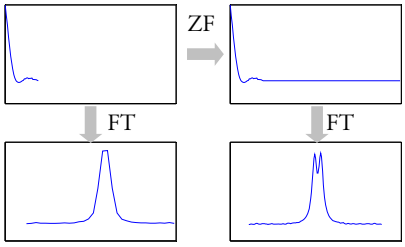
Apodization means multiplying the FID by a decaying envelope before performing the FT:



Apodization has two effects: it decreases the noise and hence increases the SNR, since it "kills off" the tail of the FID which is usually more dominated by noise than signal; but it also widens the peaks, because it makes the signal decay faster, meaning in increases the effective T_2, reducing spectral resolution.

3.2 Zero-filling

Another trick used in NMR post processing is known as zero filling: adding zeros to the end of the FID. This seemingly innocent ***extrapolation in the time domain*** action is quite useful, and can be shown mathematically to be equivalent to ***interpolation in the frequency domain***. Note that zero filling does not change the ADC dwell time and therefore does not change the spectral width.



In the above example there were two frequencies present at -0.5 Hz and 2.5 Hz with T_2=125 ms, acquisition time of 512 ms and 32 points. We miss out on the two frequencies not because of T_2 but because of the total acquisition time, i.e. our digital resolution. Zero filling magically made them appear! ZF is no regular linear interpolation in which we "connect the dots" but a special type of interpolation known as "Dirichlet interpolation" which on some mathematical level is ideal for NMR. This magical property increases the resolution by up to several percent to several tens of percent. We won't go into the math of why this happens, but it's almost always a good idea to zero fill a spectrum to twice its size before applying a FT. Zero filling of more than a factor of 2-4 is usually meaningless and should be avoided.

3.3 Phasing

Due to hardware constraints, the peaks can have a zero or first order phase. A zero-order phase is a term of the form: $s(t)e^{i\phi}$. Without it, the FID

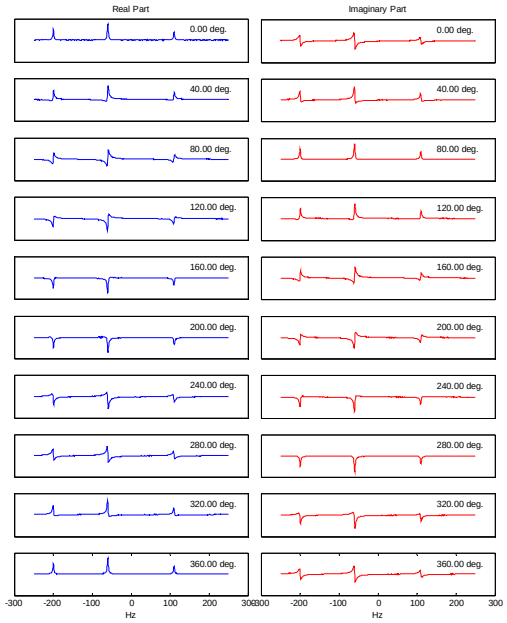
transforms into absorptive (lorentzian) and dispersive parts:

$$s(t) \xrightarrow{FT} A(\nu) + iD(\nu)$$

With it, the two parts “mix”:

$$\begin{aligned} s(t)e^{i\phi} \xrightarrow{FT} & \left[A(\nu) + iD(\nu)\right]e^{i\phi} \\ & = \left[A(\nu)\cos(\phi) - D(\nu)\sin(\phi)\right] \\ & + i\left[A(\nu)\sin(\phi) + D(\nu)\cos(\phi)\right] \end{aligned}$$

This looks like this:

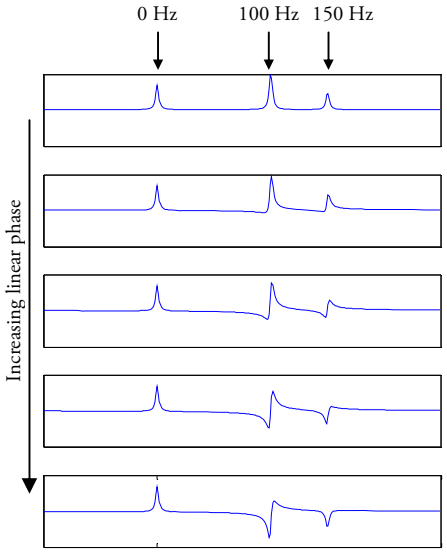


Luckily, 0th order phase is easy to correct: just multiply the spectrum by $e^{-i\phi}$. The phase ϕ is not known a-priori so the correction is usually done manually, and terminated when the operator deems his real spectrum "looks absorptive". Alternatively, sophisticated algorithms can do a pretty good job of automating this correction.

First order phases come about due to electronic imperfections as well as finiteness of the RF pulses. Here, a frequency-dependent phase gets added to the peaks. For example, if you have N peaks with frequencies ω_j then your FID will be:

$$s(t)=\sum_{j=1}^{N}A_j e^{i\omega_j t}e^{i\alpha\omega_j}e^{-t/T_2}=\sum_{j=1}^{N}A_j e^{i\omega_j(t+\alpha)}e^{-t/T_2}\ .$$

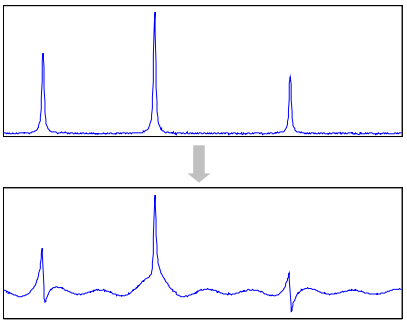
This seems almost trivial to correct: why not multiply the FID by $e^{-i\alpha\omega}$? But wait: what is ω? We don't know our frequencies a-priori, and even if we did, we can't "access" each summand and fix it independently of the others. When we look at the effects of 1st order phase in the frequency domain, is will look something like this:



You see the phase at 0 Hz is not affected at all, because its frequency is ω=0 and therefore its linear phase is always $\omega\cdot\alpha$=0 regardless of α. The effect becomes more and more pronounced for peaks farther away from 0 Hz.

Q: Why can't we fix the linear phase by multiplying the spectrum by $e^{i\omega\alpha}$ for some α?

A: Each peak has a constant phase that increases linearly with frequency. This is **not** the same as having a linear phase for the entire spectrum. To illustrate this, just look at what happens to (the real part of) the spectrum when we multiply it by $e^{i\omega\alpha}$:



Quite horrible! This happens because $e^{i\alpha\omega}$ affects **the entire lineshape** and not that lineshape's overall phase! You're trying to fix a problem that looks like this:

$$L(\omega-\omega_j)e^{i\alpha\omega_j}$$

by doing this:

$$L\left(\omega-\omega_j\right)e^{i\alpha\omega_j}e^{-i\alpha\omega}$$

where L(ω) is a lorentzian peak.

Of course, a real spectrum will have both 0^{th} and 1^{st} order phase issues, and good luck telling them apart! It takes skill, or a good computerized algorithm.