Shimming: Adjusting Magnetic Field Homogeneity

General Considerations:

In order to produce a high resolution spectrum with good lineshape, the static magnetic field must be very homogeneous throughout the volume of the sample. If you want to see a proton line as sharp as 0.3 Hz on a 300 MHz spectrometer, the field must vary no more than $1/10^9$. If the magnetic field is inhomogeneous, the magnetic field varies as a function of position, creating a magnetic field gradient. When you insert your sample, different parts of the sample experience different values of the magnetic field. These parts will have slightly different resonance frequencies, and could result in broader lines or broad hump(s) at the baseline.

Adjusting the magnetic field homogeneity is called "shimming." There are shim coils surrounding the area where the sample sits inside of the magnet. Currents run through the coils, producing local magnetic field gradients that minimize the magnetic field gradients present in and around the sample.

In the facility, there are two main factors that contribute to line broadening due to magnetic field inhomogeneity:

1. Probe Contributions (the hardware): Contributions from the probe are determined with the use of a standard sample. The NMR staff regularly check the probe and write shim files for each probe at each spectrometer. These shim files produce reasonable homogeneity with a clean sample of at least 4 cm in length (for the Brukers) and 5 cm in length (for the Varian). You can check the date of the last shim file on the whiteboard in the NMR lab.

2. User Contributions (your sample): Every sample will distort the magnetic field slightly differently compared to another sample, even the standard sample used for writing the shim files. Magnetic field gradients will change if you remove or insert samples with different solvents, different tubes, changes in sample temperature, paramagnetic samples, etc. Shimming should be carried out on each sample prior to data acquisition.

- To minimize sample contributions to field inhomogeneity, we strongly suggest using high-quality NMR tubes (especially for high-field instruments), filtering your sample to remove any particles, and making sure the outside of the NMR tube is clean and free of grease.
- Whenever possible, make the column of liquid in the NMR tube comparable to the size of the radiofrequency (rf) coil of the probe (i.e., ≥ 4 cm). When shorter samples are required, make sure to center the sample around the line marking the center of the rf coils when using the depth gauge.

How Good is "Good" Homogeneity?

In solution (without spinning), proton linewidths should be less than 2 Hz, and ≤1 Hz can be easily achieved. If you look at the TMS peak in the standard samples, they should

show clearly resolved ^{29}Si satellites. For routine samples, it is more important to have good line shape rather than the sharpest linewidth. This is because routine samples contain dissolved oxygen, which is paramagnetic. This broadens the lines by a few tenths of a Hz. Also in routine experiments, line broadening is applied in an exponential apodization step to improve the signal to noise ratio (SNR), further broadening the proton linewidth by 0.3 Hz. Thus, shimming for the narrow linewidth (0.2 Hz or less) that you achieve with the standard sample does not typically improve the spectra of routine samples. However, proper adjustment of the shims is important because it improves NMR sensitivity.

General Shimming Methods:

There are several ways to carry out the shimming process, i.e., to determine whether the adjustments of the shim currents make the magnetic field homogeneity better or worse.

1. Lock Level Signal: good for routine shimming.

- Recall that the lock level corresponds to the intensity of the deuterium signal. An inhomogeneous field will lead to a broad line. This broad line corresponds to a low intensity of the deuterium lock signal, i.e., the ^{2}H peak is short. If the homogeneity is improved, the ^{2}H line would be narrower and therefore taller. This corresponds to a high lock level.
- Adjusting the shim currents in response to changes in the lock level is a simple way to shim and usually produces a magnetic field sufficiently homogeneous for routine work.

2. Free induction decay (FID) shape: can often produce much better shimming than just observing the lock level.

- The FID should be an exponential decay. The magnitude of the decay constant of the FID determines the width of the lines; a larger decay constant corresponds to narrower NMR lines.
- Fast decaying signals at the beginning of the FID correspond to broadness at the base of peaks. These peaks might still be narrow at full-width half max (FWHM). However, the integrated intensity of this broadness could be quite significant and reduce the total intensity of the peaks. For low SNR resonances, this could be problematic. Additionally, for water suppression experiments, the water resonance can be problematic.

3. Gradient Shimming: similar to methods in magnetic resonance imaging, however, it requires the appropriate hardware.

- The simplest way is to image the sample and look at the shape of the sample profile. From there, the software calculates the appropriate shim currents to improve it and sets the shims accordingly. The shape of the NMR peak is then observed after setting the shim currents. The software does this iteratively to determine the best peak shape before setting the final shim values.

Shimming at UO NMR Facility

1. Shimming based on lock level can be done at all spectrometers.

Manual adjustment is generally fast and easy, but can be challenging for high field instruments (i.e., > 500 MHz).

Bruker: Manually Shimming on Lock Level

- Launch the **bsmsdisp**
- On-Axis Shims: Make sure the **ON AXIS** button is turned on at the BSMS panel. Adjust Z_1, Z_2, and then Z_1 again to obtain a maximum lock level. The LOCK GAIN may need to be reduced to keep the signal on scale.
- Off-Axis Shims: Hit the **Z0** button on the BSMS panel. Adjust X and Y to obtain a maximum lock level. Then hit the **ON AXIS** button and re-adjust Z.
- Press STD BY when finished to prevent accidental change of the last selected shim value.

Varian: Manually Shimming on the Lock Level

- In the Shim submenu, adjust Z_1, Z_2, and then Z_1 again to obtain a maximum lock level. The LOCK GAIN may need to be reduced to keep the signal on scale.
- Off-Axis Shims: adjust X and Y to obtain a maximum lock level. Then go back and reoptimize Z1.

2. Shimming based on FID is available on all spectrometers.

If you would like to learn this method, the NMR staff can show you what to look for and what parameters are important.

3. Gradient Shimming is available on ALL spectrometers.

Bruker: Gradient Shimming with topshim

- Use **topshim**. Topshim has a variety of different options and functions. They are useful but add extra time to the shimming procedure. You can read the topshim manual for more information, but briefly:
    - **topshim rga** performs a receiver gain adjustment before running
    - **topshim convcomp** utilizes a convection compensated sequence for gradient shimming. This is useful when you run Variable Temperature (VT) NMR.
    - **topshim tuneb** will quickly adjust the field gradients Z-X-Y-XZ-YZ before gradient shimming.

  - **topshim tunebxyz** will quickly adjust the field gradients Z-X-Y before gradient shimming. This is slightly faster than **topshim tuneb**.
  - **topshim lockoff 1H o1p=[peak]** is used for no-deuterium NMR. See below.

- Using **topshim** with proteo solvents in a no deuterium experiment: this technique can be an extremely useful alternative to using expensive deuterated solvents (e.g. THF-d8). The sample can be shimmed by using the ^{1}H peak from the proteo solvent. However, there are several limitations. The lock will be turned off without the deuterated solvent; extraneous changes to chemical shifts, e.g. magnet drift, temperature change, etc., will broaden the resonances. Also, solvent peak(s) will be very strong, and can overlap with peaks of interest, making it difficult to analyze the sample qualitatively and/or quantitatively. Moreover, large signal(s) from the solvent will create a large dynamic range for sample peaks. It will be difficult to observe peaks with smaller intensity especially if the sample is of limited concentration. If these limitations are not an issue, no-D NMR can save a lot of time and minimize costs. To shim your sample without a deuterated solvent:
  - Type **lock_off;ii** in the command line. Wait for it to finish.
  - Type **topshim lockoff 1H o1p=[peakcenterppm] selwid=0.1**. Here **[peakcenterppm]** is the center of the solvent peak on which you want to shim reported in ppm. If you don't know where your solvent peak will appear, load the proton parameter set, set ns=1, and execute **rga;zg;ef;apk**, and note down the location of the solvent peak.

Varian: Gradient Shimming

- Hit the **Gradient Shim** button and gradient shimming will automatically run.
- There are additional options, but the default works well for most people.