Pulsed-Field Gradient Shimming With VNMR

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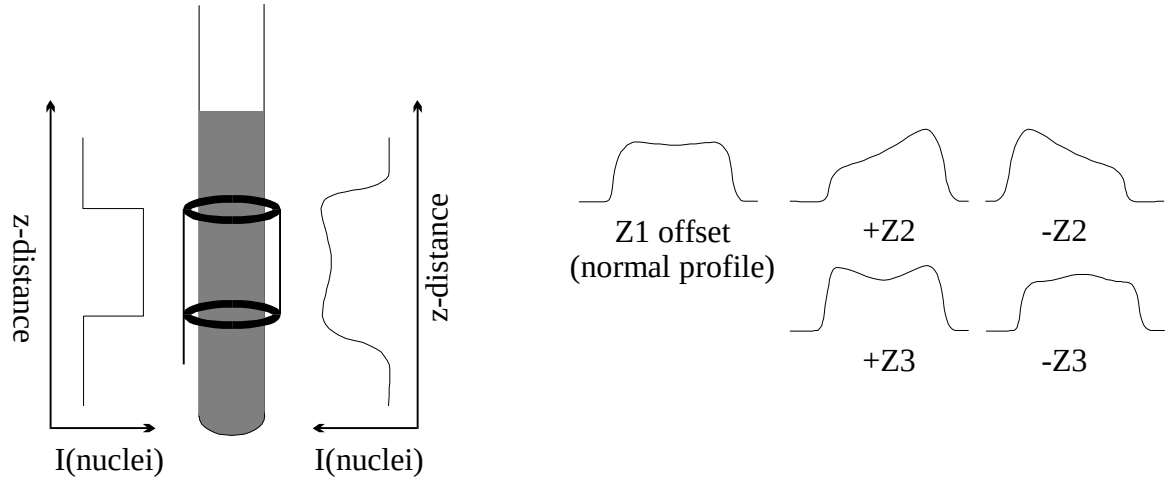
I. General Discussion

Pulsed-field gradients allow analytically accurate, automated adjustments of shims. The technique uses "gradient profiles," more pictorially described as 1-dimensional images of the atomic density of either protons or deuterons [see Section III below for a description of how the profile is experimentally generated]. The picture below shows a sample tube with solvent (in gray), and a crude picture of a standard rf coil about the tube. On the left side of the tube, the density (intensity) of observed nuclei (either ^{1}H or ^{2}H) is shown as a function of position along the z-direction, with the assumption that the rf coil observes nuclei at equal intensities at all positions inside the coil boundaries and observes nothing outside the coil. The profile to the right is a depiction closer to the real case, where the rf coil loses intensity slowly outside its boundaries, and has a slight loss of intensity in the center of the coil compared to the intensity closer to the horizontal wires.



The normal profile is observed in the presence of a large Z1 shim offset, produced by the pulsed-field gradients (but otherwise identical in nature to the RT shim's Z1 shim setting). When higher order Z shims are misset from the "perfectly shimmed" case (denoted as the normal profile above), identifyable changes occur in the profiles. Exagerated changes are shown for Z2 and Z3 missets. The gradient shimming software analytically expresses these changes when a ***shim map*** is made; each RT z-axis shim is changed independently, providing data upon which an analytical expression can be calculated for each Z shim. From this shim map, analytically accurate changes to the Z shims can be performed to minimize shim missets—getting as close to a perfect shim as possible in the presence of noise and inaccurate non-radial (X,Y) shims.

☞ Keep in mind that linewidths are ***sample dependent***. PFG, or gradient, shimming cannot overcome aggregating or suspended samples, solvent bubbles, too little solvent height (use susceptibility inserts!!), scratched sample tubes, etc. And many samples simply will not shim to better than 1 (or even 2 or higher) Hz linewidths due to their intrinsic relaxation properties in the solvent and temperature being used; i.e. their natural linewidths are >1 or 2 Hz.

☞ ***Students needing to perform PFG shimming must make a commitment to learning the proper procedures and pitfalls involved with this method; facility staff will not entertain extended questioning or training sessions to assist students beyond a brief introduction. Moreover, it is my opinion (cg fry) that PFG shimming is not as efficient for shimming as standard methods for most samples. I and the facility staff, therefore, will not answer any questions about PFG shimming unless students can provide a good reason as to why they are not manually shimming their sample in. Some common reasons for needing PFG shimming:***

1. When working with a wide range of temperatures; PFG shimming in my experience is very helpful in adjusting to the changes in Z shims when temps change >40 degrees.

2. When working with D2O or DMSO (or similar deuterated solvent) that simply will not lock-shim well; students might (should) be FID shimming in these cases. Anyone FID shimming should look into PFG shimming, as large time savings in getting to good line shapes are likely.

3. When filter of the sample is not possible; so cloudy solutions, or some suspension, etc. are present that substantially pushes the shims away from the facility settings.

4. When forced (usually by cost) to reduced solvent quantities, such that air-solvent interfaces get close enough to the rf coil such that shims are pushed well away from the facility settings. I recommend in these cases that students try susceptibility inserts; in some cases, these cannot be used and PFG shimming will assist in obtaining optimimum lineshape [for very small solvent quantities, "good" line shapes will not be feasible].

5. When performing water suppression. I have not had great success with having PFG shimming always improve my water suppression, but Varian (and Bruker for their systems) insist PFG shimming can do better than the best spectroscopists even for these most demanding samples. So it is worth trying and experimenting with.

II. Normal PFG Shimming Procedure

1. Save your shims if they are important (use **svs<enter>** or click **FILE SAVESHIMS**).

2. Type **gmapsys** to start the gradient mapping system in the software.

   If you "lose" the **gmapsys** buttons at anytime (as happens, for example, after a **wft** or **ds**), simply re-enter the **gmapsys** command to get them back.

☞ You can run gmapsys from any experiment, but you ***must*** end the session by clicking on **QUIT** to properly exit back to your original data set/parameters.

3. Check that the parameters are setup correctly for your solvent:
   e.g., if you are working in a deuterated solvent, **tn='lk'** (INOVA) or **tn='H2'** (UNITY);
   for a protonated solvent (90%:10% H_2O:D_2O), **tn='H1'**

☞ See Section III below for **1ST-TIME USE** and a detailed explanation of parameter setup.

4. *If you are using a deuterated solvent on the UNITY only*: disconnect the lock cable at the bottom of the 2nd lock filter (attached to the back of the magnet preamp box), and connect it to the X Observe BNC. No cable switching is needed on the INOVA, or for protonated solvents on the UNITY.

5. *If you are using a different deuterated solvent than the last time you PFG shimmed*, run the macro to setup parameters for the solvent you are now using. E.g., for $CDCl_3$ enter **gmapcdcl3**, or for acetone enter **gmapacetone**.

   To see a list of available macros for various solvents and temperatures, type the following in the UNIX terminal window: **ls /vnmr/maclib/gmap*** . Parameters for deuterated solvents will be very temperature dependent. See Section III below for a detailed discussion of how to setup parameters for individual cases.

6. Click on **SETUP** on the gmapsys menu, and then on **FIND GZWIN**. gzwin is a very important parameter for proper PFG shimming; see item 8 below. gzwin is the percentage of the spectral width that contains usable data (so it would ~70 in the schematic shown above).

7. If you have a recent Shim Map in place for the probe you are using, skip to step 8 [Shim Maps done on protonated solvents will *not* work for deuterated solvents, and vice-versa. A Shim Map made with DMSO will work for $CDCl_3$, however. Since DMSO provides much better S/N with ^2H than $CDCl_3$, it is a much better choice for making a Shim Map for all deuterated solvents].

   Otherwise, click on **SHIMMAP MAKE SHIMMAP** . Depending on the solvent, the shim map will take 2 to 10 mins to create. [As noted above, it is often best to use a DMSO-d_6 sample to make the shim map.] You should check the quality of the map after it finishes by clicking on **RETURN DISPLAY DISPLAY SHIMMAP**. Each shim should show its characteristic polynomial dependence, and less noise is of course better.

8. Click on **AUTOSHIM ON Z** and wait for the procedure to finish. Do this at least once more to ensure that the autoshim procedure has converged on good shims.

☞ I have found that nearly every time the procedure fails to run (i.e., get an error message and it doesn't even start), it is because **gzwin** has been set slightly too large. For example, if **gzwin=63.2**, and the autoshim fails to run, setting **gzwin=61** will nearly always work.

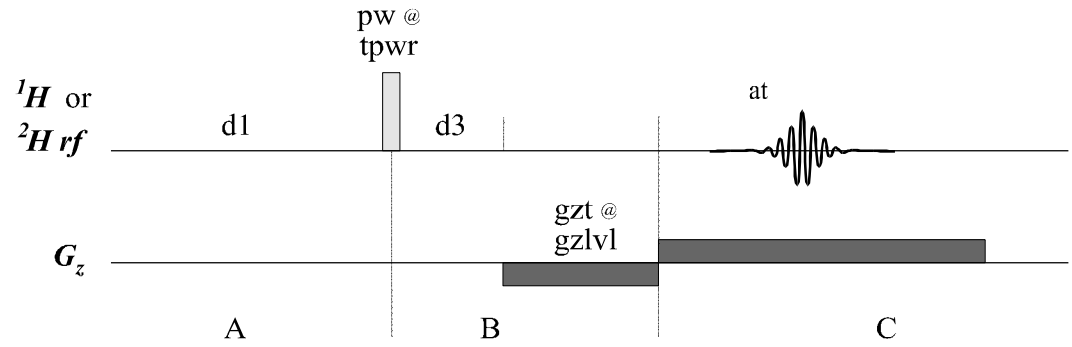
☞ If the autoshim fails to converge (i.e., the convergence factor simply will not get < 1.00), it is usually because the XY shims are very poor (re-read in the facility shim file), or because your sample/tube quality is poor: check the tube quality, especially for scratches; check solvent clarity and filter if needed; check solvent height—PFG shimming can help a lot with solvent amounts less than recommended, but cannot necessarily achieve a good shim for solvent heights < 3.5 cm (< 0.45 ml).

   In cases where autoshim fails to converge, enter **aa** or click on **ABORTACQ** to stop the acquisition. **QUIT** out of the gmapsys system, and shim the XY shims (make sure the spinner is turned off!). Then go back into **gmapsys**, remake your shimmap, and retry the autoshim. Repeat this—quit gmapsys and manually XY shim, go back in and remake shimmap and autoshim—until the shims are optimum.

III. First-Time Use and Detailed Explanation of Parameters

The pulse sequence used in the gmapsys system is gmapz, and is shown schematically below. This sequence performs a "gradient echo." Magnetization isochromats are dephased in frequency space according to the z-location of the nucleus. Assuming translational diffusion is small during the time gzt, the dephasing of the isochromats will be refocused by the opposite signed gradient a time gzt later, producing an echo. The Fourier transform of the echo, with absolute value processing, will produce intensity versus frequency: since the frequency is directly related to the z-location, the frequency axis is directly mapped to the z-location. This experiment is one example of how human and small animal images are obtained with MRI.

Gradient Echo Experiment - gmapz



A. Critical Parameters

d1 – experiment repitition rate; should be set 2-3×T_1 of the solvent ^1H or ^2H nuclei

d3 – arrayed to two values; the 2nd value should produce ~ 0.8 to 0.4 the intensity of the 1st arrayed value; use the **SETUP GO DSSH** buttons to see if **d3** is arrayed correctly; usually the 1st value = 0, but see below for more explanation

ss – usually **ss**=0, but in cases where T_1 is quite long, it may be preferable to set **ss**=-2 and **pw=30 °**

gain – reduce the gain until the baseline portion is flat

nt – increase if the signal-to-noise is poor

The following should be setup correctly by a gmap*solvent* macro:

pw – a 30-90° pulse; use smaller angles for solvents having large T_1, 90° if T_1 is short

tpwr – it is absolutely critical tpwr not be > 50 when using the lock channel to shim on ^2H solvents; normal values of pw, tpwr can be used for ^1H shimming

gzlvl – ~4000 works quite well for most situations

sw – 100 kHz for ^1H shimming, ~15 kHz for ^2H shimming

gzt – actually set as **at/2 + d2** where d2 appears to be a gradient recovery time of ~1ms (not sure why it is needed)

B. Details of Correct Parameter Setup

pw, tpwr – in cases where the solvent T_1 is not known, you must first obtain a calibrated 90° pulsewidth; this is exactly the same as for other nuclei (see, for example, Experiments on the UNITY-500, Section D: ^1H pw90 Calibration, pg 26 of this manual);

When using the lock channel

- call in a standard ^2H parameter set using **MAIN MENU SETUP**
- make sure you are on-resonance to the ^2H signal
- set **tpwr** ≤ 50 if using the lock channel, and array **pw** through a 360° rotation; change tpwr such that **pw90** ~ 400-500μs on the lock channel

d1 – after determining a correct 90° pulsewidth, set **p1=2*pw90**, **pw=pw90**, **d2=0.1** , take 1 scan and make sure the magnetization is inverted; increase **d2** until the magnetization nulls (further increase in **d2** make the magnetization go positive); $T_1 \sim 1.4 \times d2_{null}$; set **d1 = 2-3** $\times T_1$

d3 – start with **d3 = 0 , 0.6** $\times T_1$; then click in gmapsys **SETUP GO DSSH** ; if the ratio of intensities is 1:(0.8 to 0.4), the d3 array is ok. Increase **d3** if the 2nd profile is > 0.8 × the 1st; decrease **d3** if the 2nd profile is < 0.4 × the 1st, or if the 2nd profile is severely distorted compared to the first.

☞ sometimes for solvents with different ^2H nuclei (e.g., pentane-d_{12}), chemical shift and/or J-coupling of the ^2H cause intensities for d3 > 0 to be bigger than d3=0; if these cases, you just have to experiment with different d3 values to select the "best" (most sensitive) array