SHIMMING AN NMR MAGNET

Gerald A. Pearson — Chemistry Deptartment, University of Iowa — Iowa City, IA 52252 — USA

INTRODUCTION

A few general points about magnetic field gradients and shimming are discussed in this section. In the next two sections, gradients and their associated shims are classified into various categories, and the NMR line distortions caused by each category are described; with this information, you can tell which shim(s) are most badly in need of adjustment merely by looking at the shapes of the NMR lines in a spectrum. *This information can be useful even if you never shim an NMR magnet yourself, but need to evaluate spectra obtained by other people.*   This is followed by a listing of which shims must be adjusted under various circumstances. A recommended procedure for routine shimming is then described, followed by a list of common problems. Finally, several sections are devoted to additional information needed mainly by people who manage NMR spectrometers and who are responsible for keeping them in good shape.

The variation of magnetic field with position is a **GRADIENT**. As you know, the frequency of an NMR line is directly proportional to the strength of the magnetic field. If the strength of the magnetic field varies by some percentage over an NMR sample, the resonance frequency will vary by the same percentage, which will smear out the NMR lines and possibly distort their shape. If you want to see a proton line as sharp as 0.3 Hz on a 300 MHz spectrometer, the field must vary over the sample by less than (0.3 Hz / 300,000,000 Hz), or one part in 10^9. Since the diamagnetic susceptibility of organic solvents is of the order of 10^{-7}, gradients in the NMR probe will change of the order of 100 parts in 10^9 when you remove or insert samples. Replacing one sample with another containing a different solvent (or filled to a different height -- or inserted into the spinner by a different amount -- or in a slightly different NMR tube, or changing the sample temperature, etc.) can cause a noticeable change in the NMR line shape and width. Paramagnetic samples obviously cause much larger changes.

To create a homogeneous (no variation) magnetic field over the sample, funny-shaped coils of wire (**SHIM COILS**) are placed in the vicinity of the sample, and currents (**SHIM CURRENTS**) are passed through them to create various gradients of any desired strength. The idea is to adjust the shim currents so as to cancel any gradients in the NMR sample as accurately as possible. This procedure is called **SHIMMING THE MAGNET**.

In order to obtain satisfactory spectra, any operator of an NMR spectrometer must be able to shim out the relatively small gradients caused by changing the sample and the sample temperature. This must be done fairly accurately, or lousy spectra will be produced. This routine shimming can be simple, fairly fast, and consistently accurate if done properly. It can be time consuming and produce inconsistent results if done wrong. ***PROPER SHIMMING STRATEGY IS IMPORTANT, BECAUSE IT HELPS YOU TO GET A GOOD SHIM FAST.***

Shimming is simple in principle -- just adjust the shim currents until you've cancelled out the gradients over the NMR sample as much as possible. In practice, it's a bit more complicated and tedious. Part of the problem is that the effects of many shim controls interact, so a bad setting of one shim control will prevent you from finding the exactly correct setting of another. A related problem is false optima: You can find some combinations of shim settings which are not good, but changing any one shim by a small amount actually makes things worse. The most commonly-used criterion for shimming -- the height of the lock-signal level -- is rather insensitive to some shims, almost never points the way to the best possible shim, and is just plain wrong under some conditions. It helps to be able to identify which shims need to be adjusted, how much and in what direction and in what order to adjust them, and to know when to quit.

CLASSIFICATION OF GRADIENTS AND SHIMS

Gradients can have different *shapes*. For example, if the strength of field is independent of X and Y, but increases linearly in the +Z direction, that's a Z gradient -- same shape as a P_z atomic orbital. An XY gradient is independent of Z, and has the shape of a D_{xy} atomic orbital. A **FIRST-ORDER GRADIENT** produces a linear variation of magnetic field strength with position, and it's shaped like a P atomic orbital. **SECOND-ORDER GRADIENTS** produce quadratic variations of field strength, and are shaped like D orbitals. Third-order gradients produce cubic variations, and are shaped like F orbitals, and so forth. Any 3 independent first-order gradients can be combined to produce a first-order gradient which points in an arbitrary direction. This is closely related to the fact that 3 orthogonal atomic P orbitals constitute a closed shell. Similarly, 5 independent second-order gradients can combine to produce an arbitrary second-order gradient -- and atomic D orbitals come in 5 different flavors. 7 third-order gradients form a complete set (like the F orbitals), 9 fourth-order gradients, etc.

"SPINNING" GRADIENTS vary only along the axis about which the NMR tube is rotated. (Y for an iron-core electromagnet, Z for a superconducting magnet) The NMR line distortions caused by spinning gradients do not change when you stop or start the spinner. Normally, **SPINNING GRADIENTS ARE ADJUSTED WITH THE SPINNER ON.**

"NON-SPINNING" GRADIENTS are everything else. They all depend in some way on at least one of the coordinates perpendicular to the spinning axis. The resulting line distortions are visible in all their glory when the spinner is off. When the spinner is on, these line distortions are greatly reduced, but now the non-spinning gradients produce spinning sidebands. **NON-SPINNING GRADIENTS MUST BE ADJUSTED WITH THE SPINNER OFF.**

LOW ORDER gradients are 1-st and 2-nd order. **HIGH-ORDER** means 3-rd order or higher. **ODD ORDERS** are 1-st, 3-rd, 5-th, etc. **EVEN ORDERS** are 2-nd, 4-th, etc. The 2-nd order spinning gradient is called **CURVATURE** ("C") on some older spectrometers.

The shim controls on spectrometers can be divided into eight different classes, depending on the type of distortion which each gradient produces in the NMR lines, and depending on whether or not spinning the sample reduces the distortion.
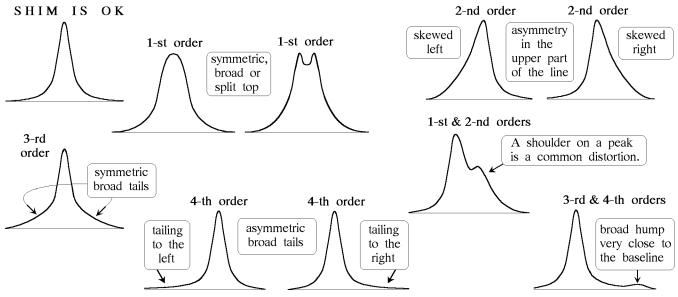
SHIM CONTROLS ON THE SPECTROMETERS					spinning/ non-spin	high/ low	odd/ even	order
FX-90Q	WM-360	MSL-300	AC-300	AMX-600				
Y	Z	Z	Z	Z	spinning	low	odd	1-st
C	Z^2	Z^2	Z^2	Z^2	spinning	low	even	2-nd
Y^3	Z^3	Z^3	Z^3	Z^3	spinning	high	odd	3-rd
				Z^5	spinning	high	odd	5-th
F	Z^4	Z^4	Z^4	Z^4	spinning	high	even	4-th
Z	X	X	X	X	non-spin	low	odd	1-st
X	Y	Y	Y	Y	non-spin	low	odd	1-st
ZX	XY	XY	XY	XY	non-spin	low	even	2-nd
XY	YZ	YZ	YZ	YZ	non-spin	low	even	2-nd
YZ	XZ	XZ	XZ	XZ	non-spin	low	even	2-nd
	X^2-Y^2	X^2-Y^2	X^2-Y^2	X^2-Y^2	non-spin	low	even	2-nd
X^2-Y^2					non-spin	low	even	2-nd
X^3	X^3	X^3	X^3	X^3	non-spin	high	odd	3-rd
Z^3	Y^3	Y^3	Y^3	Y^3	non-spin	high	odd	3-rd
		XZ^2	XZ^2	XZ^2	non-spin	high	odd	3-rd
		YZ^2	YZ^2	YZ^2	non-spin	high	odd	3-rd
				ZXY	non-spin	high	odd	3-rd
				$Z(X^2-Y^2)$	non-spin	high	odd	3-rd
				XZ^3	non-spin	high	even	4-th
				YZ^3	non-spin	high	even	4-th
Y	Z				<--- spinning axis for NMR tubes			

All of the spectrometers have complete sets of first-order shims (3 of them) and second-order shims (5 of them), so all gradients through second order can be cancelled. The AMX-600 also has a complete set of 7 third-order shims and can therefore shim out all gradients through third order. On this instrument, it is possible to get narrow lines with good shape without the necessity of spinning the sample.

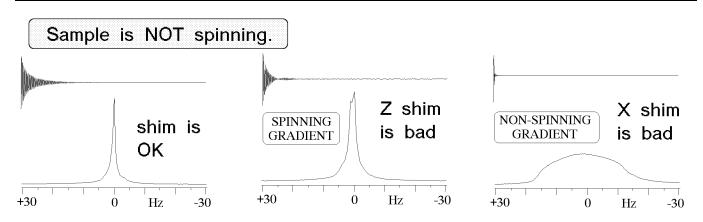# DISTORTIONS PRODUCED BY MAGNETIC-FIELD GRADIENTS

From the shape of the NMR line(s), you can get a good idea of which gradients are bad. In general, odd-order gradients cause symmetrical distortions of NMR lines, and even-order gradients produce skew distortions. Low-order gradients distort the entire NMR line, while high-order gradients distort mainly the bottoms ("feet" or "tails") of the lines. The higher the order of the gradient, the lower down on the line you have to look to see the distortion.

In the case of even-order gradients, the shape of the NMR line will tell you which direction you want to move the shim-control knob to improve things. The skew (or "tailing") moves from one side of the NMR line to the other as an even-order shim is moved from a bad setting, through the correct setting, and further on to a bad setting on the other side. On the Bruker spectrometers, the correct direction to move the control knob is toward the offending "tailing" in the line for both the Z^2 and Z^4 shims. On the FX-90Q, you need to move the C (2-nd order) knob in the opposite direction. On any given spectrometer, the "line-skew" response to a particular even-order shim will always be in the same direction.
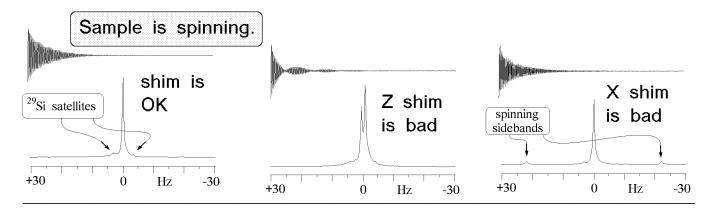
S H I M   I S   O K

1-st order

symmetric,
broad or
split top

1-st order

2-nd order

skewed
left

2-nd order

asymmetry
in the
upper part
of the line

skewed
right

3-rd
order

symmetric
broad tails

4-th order

tailing
to the
left

asymmetric
broad tails

4-th order

tailing
to the
right

1-st & 2-nd orders

A shoulder on a peak
is a common distortion.

3-rd & 4-th orders

broad hump
very close to
the baseline

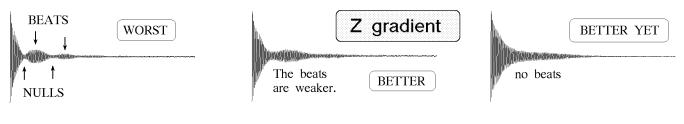**SKETCHES OF LINE DISTORTIONS CAUSED BY VARIOUS GRADIENTS**

The remaining figures are actual proton NMR data acquired on a Bruker WM-360 with a 5 mm BB probe. The FID's in this particular section are from the trimethylsilyl peak from DSS dissolved in D2O. They were obtained using the setup file SHIMD2O.JOBP. SI = TD = 2K and SW = 200 Hz, which gives AQ = 5.12 sec. The FID's were processed into spectra using LB = 0, and expanded sections were plotted.

Sample is NOT spinning.

shim is
OK

+30   0   Hz   -30

SPINNING
GRADIENT

Z shim
is bad

+30   0   Hz   -30

NON-SPINNING
GRADIENT

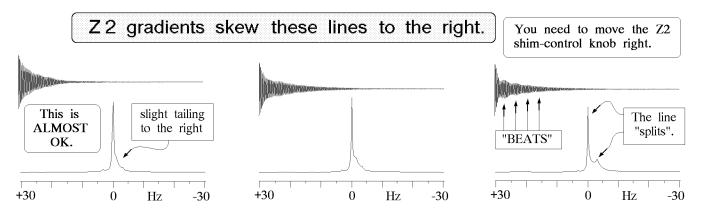X shim
is bad

+30   0   Hz   -30

EFFECT OF SAMPLE SPINNING: Distortions of the FID and of the lineshape which are caused by spinning gradients are not changed, but distortions caused by non-spinning gradients are greatly reduced. *Some of the third-order non-spinning gradients cannot be shimmed out on the WM-360, and they cause the base of the NMR line to broaden slightly when the spinner is stopped.*

Sample is spinning.

^{29}Si satellites

shim is
OK

+30   0   Hz   -30

Z shim
is bad

+30   0   Hz   -30

spinning
sidebands

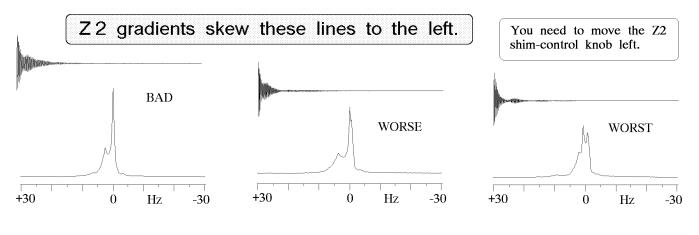X shim
is bad

+30   0   Hz   -30

A bad FIRST-ORDER gradient is easiest to see in the FID. Beats in a FID mean small line splittings in the spectrum, and the signal from a single NMR line should not have any! Multiplet splittings will also produce beats in a FID, but these beats will not be affected by shim adjustments. Nulls arising from a bad Z shim, however, can be made to move to the right and disappear off the right end of the FID as you adjust the shim control.

BEATS

WORST

Z gradient

BETTER YET

NULLS

The beats are weaker.

BETTER

no beats

Z2 gradients skew these lines to the right.

You need to move the Z2 shim-control knob right.

This is ALMOST OK.

slight tailing to the right

"BEATS"

The line "splits".

+30   0   Hz   -30   +30   0   Hz   -30   +30   0   Hz   -30
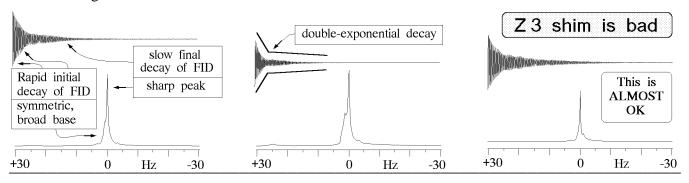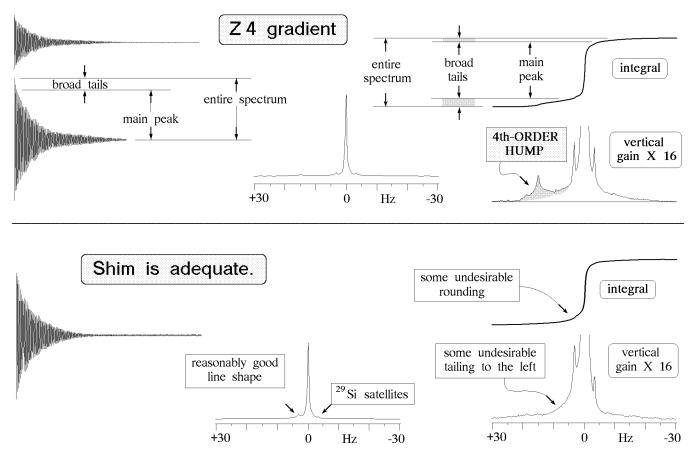
SECOND-ORDER GRADIENTS produce SKEW distortions visible in the UPPER PART of the line. They cause the early part of the FID to decay more rapidly than the later part, which is seen as a double-exponential decay if the first-order gradients are adjusted to remove the beats in the FID. The shape of the line is the most sensitive and unambiguous indicator of an imperfectly-adjusted second-order shim, and it tells you which direction to move the knob. Neither the FID nor the lock level are as good at detecting a slight error, or at distinguishing between a second-order shim error from a third-order shim error. The beats in the FID and the splitting of the line are caused by interaction with a first-order gradient -- Z, in this case.

Z2 gradients skew these lines to the left.

You need to move the Z2 shim-control knob left.

BAD

WORSE

WORST

+30   0   Hz   -30   +30   0   Hz   -30   +30   0   Hz   -30

THIRD-ORDER GRADIENTS produce SYMMETRIC broadening at the BOTTOM of the NMR line. The rapid initial decay of the FID can be easily mistaken for the distortion produced by a second- or fourth-order gradient.

slow final
decay of FID

sharp peak

Rapid initial
decay of FID
symmetric,
broad base

double-exponential decay

Z 3 shim is bad

This is
ALMOST
OK

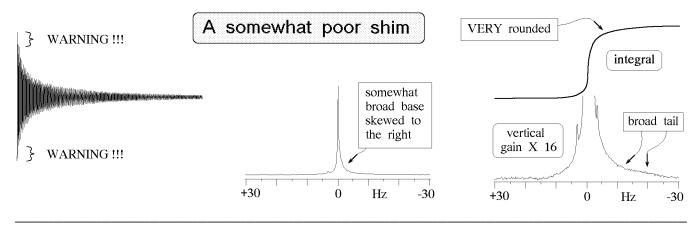+30   0   Hz   -30   +30   0   Hz   -30   +30   0   Hz   -30

FOURTH-ORDER gradients produce SKEW distortions of the "tails" or "feet" of the NMR line. If the first- and second-order shims are optimized, the broad 4-th order hump can be so close to the baseline that it's difficult to see unless one observes the integral or uses high vertical gain. The FID shows an extremely sudden initial drop, followed by a nice-looking decay. This particular line has a fourth-order hump on the left, which has been shaded for clarity. It also appears to have some symmetrical fifth-order broadening (very close to the baseline).

Z 4 gradient

broad tails

main peak

entire spectrum

entire
spectrum

broad
tails

main
peak

integral

4th-ORDER
HUMP

vertical
gain X 16

+30   0   Hz   -30

Shim is adequate.

some undesirable
rounding

integral

reasonably good
line shape

^{29}Si satellites

some undesirable
tailing to the left

vertical
gain X 16

+30   0   Hz   -30   +30   0   Hz   -30

IN MOST CASES, IT IS FAR MORE IMPORTANT TO HAVE A GOOD LINE SHAPE THAN TO HAVE THE UPPER PART OF THE LINE BE AS NARROW AS POSSIBLE. The advantages of good line shape are better sensitivity (in most cases), the ability to accurately compare integrals of lines which are closer together, and the ability to apply resolution-enhancement techniques.

A large, extremely sudden initial decay of the FID is a warning that the tails of the NMR line are very intense and broad.   It's rather easy to get extremely good homogeneity over perhaps 70% of the volume of the sample, and lousy homogeneity over the rest of the sample. The consequences of this mistake are shown below. Don't be deceived by the very slow ring-down at the end of the FID and the corresponding impressive sharpness of the tops of the NMR lines.   **Sensitivity is lost** by the "leakage" of part of the integral of the signal into the broad base and tails of the line, and it's **impossible to accurately compare integrals** of closely-spaced lines, because the tails overlap. (Looking at it another way, notice that the integral of the line doesn't level off until it's about 25 Hz to the right of the center of the line.) The   **Gaussian resolution enhancement** technique presupposes that the line shape is pure Lorenzian, and it   **does not work well** with badly distorted line shapes such as this one.

A somewhat poor shim

} WARNING !!!

} WARNING !!!

somewhat broad base skewed to the right

+30   0   Hz   -30

VERY rounded

integral

vertical gain X 16

broad tail

+30   0   Hz   -30

WHO NEEDS TO SHIM WHICH GRADIENTS? WHEN?

THE FIRST- AND SECOND-ORDER SPINNING SHIMS NEED TO BE ADJUSTED FOR EACH SAMPLE. FOR ROUTINE USE OF MOST NMR SPECTROMETERS, THIS IS ALL THAT IS NECESSARY. A crude adjustment can be done in a couple of minutes, and a careful, accurate adjustment should require about 5 minutes. Operators should become very familiar and comfortable with this procedure before attempting to adjust any additional gradients.

IN ADDITION TO THE FIRST- AND SECOND-ORDER SPINNING SHIMS, SOME HIGHER-ORDER SPINNING GRADIENTS FREQUENTLY NEED TO BE ADJUSTED IN THOSE SITUATIONS WHERE THE BEST POSSIBLE PROTON RESOLUTION IS REQUIRED -- WHEN IT'S VERY IMPORTANT TO MAKE THE BROAD FEET AROUND PROTON LINES NARROWER. These adjustments -- when they're required -- really do have to be made on each individual sample. On the 300 MHz and 360 MHz spectrometers, you'll need to adjust the first 3 spinning shims (Z, Z^2, and Z^3), which should take about 15 minutes or less. On the AMX-600, you'll need to adjust the first 4 spinning shims -- the first 3 will not be enough.

IT IS SOMETIMES DESIRABLE TO RUN A SAMPLE WITH THE SPINNER OFF. 2D experiments in particular tend to give better results when run non-spinning. IN THIS CASE, YOU NEED TO ADJUST *ALL* OF THE FIRST-ORDER GRADIENTS AS WELL AS THE SECOND-ORDER SPINNING GRADIENT. All 4 of these gradients must be adjusted with the spinner off. This can usually be done in well under 10 minutes.

Spinning sidebands in spectra probably indicate that the first-order non-spinning shims require adjustment. This can be done by any experienced operator who is familiar with the procedure.

Ordinary users of the spectrometers will not need to shim any other gradients. The sample-to-sample changes in the high-order gradients are negligible, and they drift only very slowly with time. People who maintain an instrument, however, must be able to shim out the high-order gradient changes caused by any magnet drift with time, and to shim out gradient changes caused by probe repairs, probe modifications, and adjustment of the cryoshims. This involves adjusting all gradients while monitoring the NMR signals from test samples. This is more complicated and tedious than routine shimming by at least one order of magnitude; it usually requires 2 to 5 hours by an experienced operator, but the procedure can burn up a day or more. Shimming a new probe from scratch is more difficult yet, and shimming a newly-energized superconducting NMR magnet is best left to people who do this for a living.

ROUTINE SHIMMING

KEY POINTS ARE PRINTED BOLDFACE, supporting information is in normal type,   *and side comments are in italics.*

The general idea is to adjust the Z and Z2 shims as you monitor both the lock-signal amplitude and the shape of the FID of a single sharp proton NMR line in your sample. The lock signal responds more quickly to shim changes, but the FID is more accurate and sensitive near the optimum shim settings. After getting the "best" shim, check the line shape for second-order asymmetry. If there is none, you're done. Otherwise make a small change in Z2, re-optimize Z while monitoring the FID and the lock signal, and check the line shape again. Repeat until the NMR line is sharp and symmetrical.

PRELIMINARY STUFF: Put your sample in the spectrometer.   Turn on the spinner.   Find the deuterium lock signal & phase it.   Press the lock button, wait until the lock engages, and reduce the lock-receiver gain ("lock gain" or "lock amplitude") so that the lock signal is seen a few centimeters below the top of the graphics display.   Don't start adjusting the shims yet.   Use *Ctrl*/**L** as necessary to make sure the graphics screen shows both the lock signal and the data.

RJ *setup-filename*, **PJ**, and **II** — where *setup filename* is a setup parameter file to put a narrow window (SW = 200 Hz or less) around a single sharp line in your sample. Currently, the standard files for this purpose are:
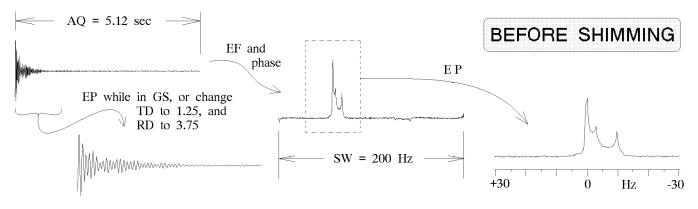   **SHIMACE.JOBP** — for monitoring TMS, with acetone-d6 lock solvent — WM-360 and AC-300
     SHIMD2O.JOBP — for monitoring the trimethylsilyl peak from DSS or TSP, with D_2O lock solvent
         — WM-360 and AC-300
     SHIMDMSO.JOBP — for monitoring TMS, with DMSO-d6 lock solvent — WM-360
     SHIMCHL.JOBP — for monitoring TMS, with chloroform-d lock solvent — WM-360 and AC-300
These files set SI = TD = 2K and SW = 200 Hz, which gives an acquisition time of AQ = 5.12 sec. Please check with Mr. Snyder or Dr. Pearson if you need any other job-parameter setup files for your samples.

GS and change the receiver gain **RG** as needed so that the FID doesn't clip.

*From time to time during the following procedures, you might want to examine the early part of the FID more closely. If so, just make the acquisition time **AQ** shorter (1, 2, or 3 sec, for example), and increase the relaxation delay **RD** so that AQ + RD 5 sec. The real+imaginary display is sometimes convenient for examining the tail of a FID; Ctrl/Y toggles it on and off.*

At this point, you would not normally have any reason to bother EF'ing the FID and phasing it to look at the spectrum. The following figure illustrates just how bad the starting shim settings can be. The shim settings in this case were exactly right for the previous sample!

AQ = 5.12 sec

EF and phase

E P

BEFORE SHIMMING

EP while in GS, or change TD to 1.25, and RD to 3.75

SW = 200 Hz

+30   0   Hz   -30

ALTERNATELY ADJUST Z, Z2, Z, Z2, ETC. YOU WANT TO MAXIMIZE THE AMPLITUDE OF THE LOCK SIGNAL, as indicated by its height on the graphics display screen. Reduce the lock receiver gain as needed to keep the lock-signal display a few cm down from the top of the screen. If the FID looks very bad, then the shims are very far out of adjustment and the lock-signal response to the shims might "feel" vague.

After the lock-signal amplitude is maximized with respect to the Z and Z2 shims,   **ADJUST THE LOCK PHASE SO AS TO MAXIMIZE THE LOCK-SIGNAL AMPLITUDE.**   *This is normally a small adjustment, but it's very important. It makes the lock-signal amplitude a more reliable indicator of a good shim setting.*
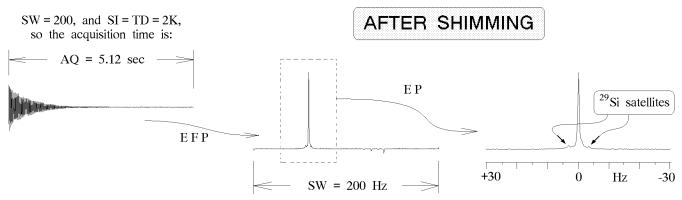
Again, **ALTERNATELY ADJUST Z AND Z2 TO MAXIMIZE THE AMPLITUDE OF THE LOCK SIGNAL.**   After you can get no further improvement in lock-signal amplitude,   **USE THE SHAPE OF THE FID AS A GUIDE TO FINAL SHIM ADJUSTMENTS.**   The FID should show dramatic improvements as the optimum shim settings are approached, and get noticeably worse as a shim setting is moved slightly away from its optimum setting. If you see beats in the FID, use the Z shim to move them to the right and off the end of the FID. If the shim settings are good, then   **THE FID SHOULD RING AS LONG AS POSSIBLE, CONSISTENT WITH THE REQUIREMENT THAT THE ENVELOPE BE A SIMPLE EXPONENTIAL DECAY,** with no nulls, double-exponential kinks, or a sudden initial decay followed by a slowly-decaying exponential.

*You might not need an especially good shim for this particular sample. If you don't, then you can stop the GS at this point, and set up & acquire your data. If you want to be sure that the shim is good, then spend an extra few minutes and complete the next few steps. It's a good idea to   **always** do this whenever you plan to use a data-acquisition time of more than a half hour for your NMR experiment(s) on a sample.*
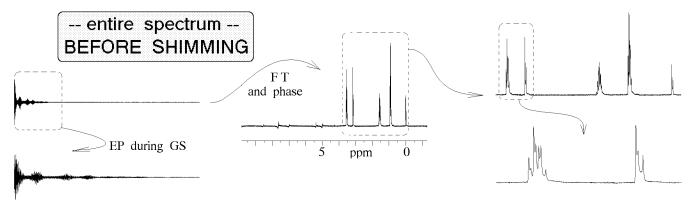
Ctrl/H TO HALT THE GS. THEN   EF, EP, AND PHASE THE SPECTRUM. CHECK THE LINE SHAPE FOR ASYMMETRY. *In EP, the   9   key will toggle between vector and dots display. The dots display is sometimes convenient for evaluating asymmetry.*   If the line shape is OK, then you're done. If not, then proceed as follows.

MOVE THE Z2 KNOB IN THE DIRECTION OF THE SKEW OF THE LINE SHAPE, RE-START THE GS, AND USE THE Z SHIM ONLY   TO OPTIMIZE THE SHAPE OF THE FID.
How much should you move the Z2 shim knob? That depends on how much skew you see in the NMR line. Try turning the knob by   1/10-th   of a turn, and see how much change it causes in the line skew. With a little practice, you should be able to judge this reasonably well.

Ctrl/H TO HALT THE GS, AND   EFP TO GET THE SPECTRUM.   EP AND CHECK FOR ASYMMETRY IN THE LINE SHAPE. Keep repeating these last two steps — alternately moving Z2 and optimizing with Z — until the line shape looks OK. *If the phase needs a slight adjustment, enter the phasing routine with the A key (instead of the P_ key) to ADD a small phase correction for use by future EFP's.*

After shimming, the NMR line should narrow and symmetrical, and have a relatively narrow base. The ^{29}Si satellites of a trimethylsilyl or TMS peak should be clearly resolved.   *The first few times that you follow this shimming procedure, you might require several iterations to get a good shim. With practice, an average of two iterations should be sufficient.*

SW = 200, and SI = TD = 2K,
   so the acquisition time is:

AFTER SHIMMING

AQ = 5.12 sec

E P

^{29}Si satellites

E F P

SW = 200 Hz

+30   0   Hz   -30

If you don't have TMS or any other isolated, sharp peak in the proton spectrum of your sample, at least look at the proton FID for the entire spectrum as you adjust the shims. It doesn't cost you any extra time to do this, and you will almost always get more information on your shimming progress than you would have gotten if you had monitored only the lock-signal amplitude.

-- entire spectrum --
BEFORE SHIMMING

F T
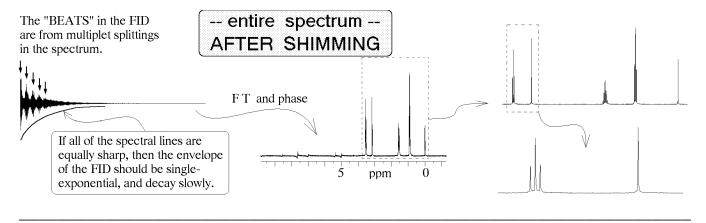and phase

EP during GS

5   ppm   0

The main advantage of monitoring the FID of a   *single, sharp* NMR line rather than the FID of an entire spectrum is that the envelope should be a simple, decaying exponential. You can be sure that any deviations from this ideal shape must arise from the magnetic field gradients which you are trying to cancel with the shims.

If the proton NMR spectrum contains lines of different widths, then the start of the FID will always decay faster than later parts. Depending on the distribution of line widths, you might see multiple-exponential "kinks", or an extremely fast decay at the very beginning of the FID. These can mask small shim errors which you might easily see in the FID of a single line.

Closely-spaced lines such as those found in spin multiplets will produce beats in the FID. The only way you can distinguish them from beats caused by a bad shim is that the "multiplet beats" never move as you change the shims. The "multiplet beats" also make it more difficult to see the envelope of the FID, since your eye must interpolate between the peaks of the beats.

In spite of these problems, you can almost always get a great deal of information on shimming progress by noticing how the shape of the the FID changes as you adjust the shims.

It *will* cost you extra time to examine the NMR lines for asymmetry. On a slow computer such as the Aspect 2000 on the WM-360 spectrometer, EFP will take nearly a half minute longer with the entire spectrum than it would have if you had used the small array size provided by one of the shimming setup files SHIM*.JOBP. If you really do need a good shim, then you'll just have to bite the bullet and spend the time to do this.

The "BEATS" in the FID are from multiplet splittings in the spectrum.

-- entire spectrum --
AFTER SHIMMING

F T and phase

If all of the spectral lines are equally sharp, then the envelope of the FID should be single-exponential, and decay slowly.

5   ppm   0

_____

COMMON PROBLEMS

Neglecting to touch up the lock phase before making final shim adjustments produces unreliable results from a lock-level shim. It's simply not possible to set the lock phase consistently with sufficient accuracy while while looking at the sweep pattern; furthermore, the lock phase will change whenever the lock transmitter power is changed, which happens automatically in many spectrometers when the lock in engaged. Inconsistencies in the phase settings produce inconsistencies in lock-level shimming results. Sometimes the NMR lines are symmetrical and ‰   Hz wide, sometimes they tail off to the right or left, and sometimes the lines are 1 Hz wide or broader. Even if you do your final shimming on the proton FID and line shape, a very misleading lock-level response will make the shimming process unnecessarily tedious and time-consuming.

The ultimate criterion for a good shim is the observed nucleus, not the deuterium lock signal. The highest possible deuterium lock-signal level is usually *__not__* obtained at the same shim settings as the best shape and narrowest width of a ^{1}H or ^{13}C line in the same sample. The difference is small for many samples, moderate for some samples, and spectacularly huge for a few unusual samples. For adjusting high-order gradients, the lock-signal-level criterion is particularly likely to give misleading indications, which can lead to very artistic results.

Changing a probe produces strong, complicated gradient changes, so it's necessary to "dial in" the appropriate "standard" shim settings for each probe before using it. Forgetting to do this is actually a very uncommon problem, but it's mentioned here because you can waste a huge amount of time and be very frustrated while trying to get a good shim if the high-order gradients are off. If you ever have serious trouble getting a good shim within a few minutes, then stop, re-set the shims to their "standard" values, and proceed from there.

Different magnets do respond differently, depending on such things as manufacturing details, the initial adjustments which were made when the spectrometer was installed, and on sample characteristics. People who have only run one particular type of sample on one particular instrument sometimes find that they can't get a good shim on some other instrument. Frequently, the problem is that the particular shimming strategy that they had been using is not generally optimum, even though it happens to work very well most of the time with a particular class of samples on one particular spectrometer.

HOW FREQUENTLY SHOULD SHIMS BE ADJUSTED?

The first- and second-order spinning shims need to be adjusted for each sample.

Spinning sidebands in spectra probably indicate that the first-order non-spinning shims require adjustment.

In a stable superconducting NMR spectrometer, the non-spinning gradients and all the high-order gradients will indeed drift very slowly, but it takes several months for this drift to be noticeable. it is usually sufficient to carefully adjust all shims once or twice a year. If probe repairs or modifications are made in the vicinity of the sample coil(s), the shim should be checked carefully. If necessary, the probe should be shimmed completely in order to determine the new correct "standard" values for the shim settings. If the cryoshims are ever adjusted, then all the probes for that magnet must be re-shimmed.

The shim settings in an iron-core electromagnet NMR, such as a JEOL FX90Q, drift much more rapidly and erratically than in a supercon. Because the lower-order gradients will exhibit the fastest drift, it's desirable to routinely adjust all low-order shims every week. The high-order shims don't change much under normal conditions so a complete shim adjustment every few months is normally more than sufficient. Abnormally large drifts can occur when the chiller for the magnet-cooling water malfunctions in any way, and when you open the cover over the magnet and allow "cold" (room temperature) air to spill into the magnet housing.

When an iron-core electromagnet is re-energized (*e.g.*   after a power failure), the gradients will drift severely during the first half hour. After the magnet has stopped drifting, the correct shim settings will frequently differ from what they were before the magnet was turned off. Wait about an hour before shimming the low-order gradients and using the spectrometer for routine survey spectra. Don't touch the high-order gradients yet, or try any fancy NMR experiment. Wait about 24 hours, and then do a complete shim adjustment.

TEST SAMPLES

Most shim adjustments are made while monitoring a sharp, intense single ^{1}H line. 10% CHCl3 in acetone-d6 is convenient, but you could also use the TMS signal in such samples as o-dichlorobenzene (ODCB) and TMS in acetone-d6 or CH $_3$CHO/TMS/C $_6$D$_6$.

Final adjustment of the high-order spinning gradients is most easily done while looking at a complicated multiplet. The tails of the lines overlap, so high-order gradients produce a highly visible, broad hump under the multiplet. 15% ODCB and 3% TMS in acetone-d6 is best monitoring the forest of aromatic lines from the ODCB. For low-field spectrometers (JEOL FX-90Q, etc.), you could use 15% CH $_3$CO and 5% TMS in C $_6$D$_6$, monitoring the aldehyde quartet.

NMR standard samples can be purchased from Wilmad. If you make them yourself, you'll need NMR tubes at least 8" long, a high-vacuum line, a special O-ring seal from Kontes, a hand torch with a very fine tip, and enough glassblowing experience to properly seal off the NMR tube. Degas (3 or 4 freeze/pump/thaw cycles) and seal the samples, preferably with about 1/4 atmosphere partial pressure of N $_2$ or Ar gas. It is important to use pure reagents, high-quality NMR tubes, and a lock solvent with a loud, sharp deuterium signal. It is also important to remove any traces of paramagnetic impurities (such as oxygen from dissolved air), and to seal off the NMR tube evenly and neatly so that it will spin OK in the probe.

An air-saturated sample of D $_2$O contaminated with about 1 atom % hydrogen (1% HDO, or 0.5 % added H $_2$O) is useful for initial shim adjustments when the homogeneity is extremely poor.

HOW GOOD IS "GOOD" HOMOGENEITY?

Proton line widths in a standard sample should be less than 0.5 Hz with the spinner on. 0.2 to 0.3 Hz is not too difficult to achieve. Lines from tetramethylsilane or trimethylsilyl groups should show clearly resolved ^{29}Si satellites.

Non-spinning proton line widths in a 5 mm probe can be easily adjusted to about 2 Hz. As long as the spinning sidebands are weak, the intensities of the first sidebands will be proportional to the SQUARE of the non-spinning line width. The reason for this is that the second moment of an NMR line is unchanged by ample spinning. Non-spinning gradients begin to contribute noticeably to spinning sidebands when the non-spinning line width is approximately 5 Hz.

For most routine samples, it is far more important to have a good line shape than the highest possible line sharpness. The reason for this is that such samples contain dissolved oxygen from the air, which broadens the ^{1}H NMR lines by a few tenths of a Hz. Shimming for the extremely narrow line widths which you can get with a test sample simply does not improve the spectra of most samples. Proper adjustment of the high-order spinning shims *is* important, however, because this improves sensitivity. Bad high-order spinning gradients allow a large amount of the integral of an NMR line to "leak" into the "feet", thus reducing the peak height.

With some samples, the 10 mm BB probe for the WM-360 can't be shimmed much better than 6 Hz non-spinning.

STRATEGY FOR ADJUSTING ALL SHIMS— INTRODUCTION

Ask 10 NMR service engineers the question "How do you go about shimming a magnet?", and you'll probably get at least 6 different answers. Sometimes, the answers are logically inconsistent or long lists of apparently unrelated rules-of-thumb. An experienced operator can use any one of dozens of strategies to do at least an acceptable job of shimming a magnet. Some of the methods will be faster than others, some will be easier to use, some will be more generally reliable, etc.

The shimming strategy described here is logically consistent, reliable, and works well both on spectrometers with iron-core electromagnets and on spectrometers with superconducting solenoids. For the low-order shims, it is easy and reliable. For the high-order shims, it is probably also the fastest method.

The basic idea is to simultaneously use both the deuterium NMR lock signal and a ^{1}H NMR signal in order to monitor progress in shimming. As usual, one maximizes the amplitude of the lock signal to optimize the low-order shims. The response of the lock signal is fast, but it is frequently unreliable for high-order shims and is occasionally misleading for the low-order shims. Occasional examination of a single line or cluster of lines in the proton spectrum shows you how you're progressing with the high-order gradients, and also warns you about "FALSE MAXIMA" in the lock-signal response.

Shim adjustments must be done iteratively. A "bad" setting of one shim control will prevent you from finding very "good" settings for the others. One of the major advantages of the real-time ^{1}H NMR display on the FX-90Q is that you can see which shim control(s) is/are in need of your most immediate attention.

In order to get the ^{1}H NMR signal(s) fairly frequently and quickly, it's necessary to use a small array size so the Fourier transform and phase correction is fast. You therefore set the transmitter frequency very close to the desired signals, and use a narrow spectrum width. As usual, you control the acquisition time by varying the array size. Remember that the digital resolution is the reciprocal of the acquisition time for the FID, and that you should set the line broadening (LB on the Bruker spectrometers, EX on the JEOL FX-90Q) to this digital resolution.

You can save time by using the shortest acquisition time that will give you the digital resolution which you need to see an improvement in the line width/shape. It would be a waste of time to spend 20 seconds getting a display with 0.05 Hz resolution while you're trying to shim the linewidth down from 20 Hz to 1 Hz. During final adjustments, however, you'll need those long acquisition times to be able to see small changes in the shape and width of the line(s).

When the starting shim is extremely bad, you need a sample with an intense lock signal which will not easily saturate. Use an air-saturated sample of D$_2$O which contains enough HDO impurity to provide a good ^{1}H NMR signal. Use this sample to shim the spinning line width down to 1 Hz, and the non-spinning line width down to 4 Hz or less. Then switch to a degassed organic sample.

COMPLETE SHIMMING — DETAILED OUTLINE

1. INTERNAL DEUTERIUM LOCK on a sample which has a SINGLE INTENSE PROTON LINE which is at least 200 Hz from any other ^{1}H signals in the sample. You will need to use a lower lock transmitter power than normal to avoid saturating the deuterium lock signal in the degassed test samples used for shimming. If you can lock OK, then proceed directly to step 2. If the starting shim is so bad that you can't even lock, then do the following preliminary shimming on the field-sweep display of the lock signal.
    1.1. DISPLAY THE LOCK SIGNAL WITH MAGNET FIELD SWEEP ON. (preferably triangular, but a sawtooth sweep will work)
    1.2. SPINNER ON. OPTIMIZE THE LOW-ORDER SPINNING SHIMS. You are really after good "ringing" of the "wiggles." If the shim is so poor that you don't see wiggles, then just shim for maximum peak height. With a triangular sweep, you've got a better handle on the 2-nd order gradient; the wiggles will ring the same in both sweep directions if and only if the 2-nd order shim is OK.
    1.3. SPINNER OFF. OPTIMIZE THE 1-st ORDER NON-SPINNING SHIMS.
    1.4. ITERATE TWO OR THREE TIMES ON STEPS 1.2. AND 1.3.
    1.5. SPINNER ON, AND LOCK TO THE DEUTERIUM SIGNAL.
    1.3. ITERATE TWO OR THREE TIMES ON STEPS 1.2 AND 1.3.

2. SET ACQUISITION PARAMETERS for initial, rough shimming -- NMR lines 0.5 Hz wide and broader.
    2.1. GET A PROTON SPECTRUM of the sample, using some standard set of parameters. Set the desired number of scans to one (1).
    2.2. SET THE OBSERVE FREQUENCY so that the transmitter is 10 to 20 Hz away from the isolated ^{1}H NMR line which you will monitor. (OBSET on the JEOL FX-90Q, O1 on Bruker spectrometers.)
    2.3. Verify that you set the frequency OK by getting another single-pulse spectrum with the standard spectrum width. The desired signal should be very close to the center of the spectrum.
    2.4. Set a narrow SPECTRUM WIDTH, between 0.5 and 1.0 ppm wide. (100 Hz on an iron-core machine, 200 to 400 Hz is usually OK on a supercon.)
    2.5. Set a small ARRAY SIZE, so that the FID acquisition time will be around 2.5 seconds.
    2.6. GET A FID with the new parameters.
    2.7. Set exponential smoothing for a line broadening equal to the reciprocal of the acquisition time you got in step 2.5.
    2.8. Get the spectrum and phase it up. Zoom in on he desired line(s) to get a convenient display.

3. SET UP TO LOOK AT THE SPECTRUM QUICKLY AND CONVENIENTLY
    3.2. On the bruker WM-360, AC-300, or MSL-300, do an **AU ZGEFP.ACQ** to get the first look at the spectrum. After that, merely typing an **AU** command without the microprogram file name will be sufficient to get a look at the current spectrum. Do an **EP** if you need a closer look at the ^{1}H NMR line(s).
    3.1. On the JEOL FX-90Q, set PD*** to 4 or 5 seconds, and then **E** (-->>FTNMR) **LINE** (-->>LINE) **PHAS** (-->>PHAS) to start the real-time display. Every (ACQTM + PD***) seconds, a FID will be acquired, apodized, FT'd, phase-corrected, and then displayed for approximately (PD*** - [POINT/1000]) seconds.

4. ADJUST THE LOW-ORDER SHIMS. Every time you turn off the spinner, you need to increase the lock receiver gain to avoid losing lock and to maintain a fairly strong lock-level response. On the JEOL FX-90Q, 2 or 3 steps (6 to 9 dB) on the gain switches is usually adequate. You will also need to appropriately reduce the lock receiver gain whenever you turn the spinner back on. On the Bruker WM-360, do not turn the spinner knob all the way off; turn it down (clockwise) just enough to reduce the spinning speed to zero (0).
    4.1. FIRST ITERATION
        4.1.2. SPINNER ON. Optimize low-order spinning shims.
        4.1.2. SPINNER OFF. Optimize low-order non-spinning shims.
        4.1.3. SPINNER ON. Optimize low-order spinning shims again.
        4.1.4. On the JEOL FX-90Q only, re-adjust the lock receiver gain toe the appropriate level for locking.
            (3 steps up from bare minimum.)
        4.1.5. RE-ADJUST THE LOCK PHASE very carefully to maximize the lock-level response.
    4.2. SUBSEQUENT ITERATIONS
        4.2.1. SPINNER OFF. Optimize low-order non-spinning shims.
        4.2.2. SPINNER ON. Optimize low-order spinning shims.
        4.2.3. REPEAT STEPS 4.2.1. AND 4.2.2. until the last non-spinning shim adjustment was negligible.

5. HIGH-ORDER SHIMS -- GENERAL   A different procedure is needed with these. The problem is that they interact so strongly with some of the low-order shims that "false maxima" are very difficult to avoid. It's possible to have bad high-order shims even when any adjustment of any single shim control makes the homogeneity worse. The way around this is to systematically search for the global optimum.
    5.1. START OUT WITH THE LOW-ORDER SHIMS OK. Note how good the homogeneity is. (both lock signal amplitude and line shape) Also make a note of the present values of the shim settings.
    5.2. PICK ONE HIGH-ORDER SHIM TO ADJUST.
    5.3. MAKE SOME CHANGE in the chosen high-order shim, and re-optimize the low-order shims. If you're working on a high-order spinning shim, then you only need to re-optimize the low-order spinning shims. If you're working on a high-order non-spinning shim, you should re-optimize the low-order non-spins with every change in high-order, and occasionally re-optimize the low-order spinning shims as well. Use the lock-signal response to re-optimize the low-order shims.
    5.4. IS THE RESULT BETTER, WORSE, OR THE SAME as before you changed the high-order shim? For high-order spinning gradients, look for minimum distortion/broadening of the "feet" of the ^{1}H NMR line(s). For high-order non-spinning gradients,   use the lock signal amplitude as a criterion for "good", as long as this agrees with the shape/width response of the "feet" of the ^{1}H signal(s); the fast response of the lock signal will allow you to make adjustments more rapidly.
        5.4.1. IF THE RESULT IS BETTER, try moving farther in the same direction.
        5.4.2. IF THE RESULT IS WORSE, try moving in the opposite direction.
        5.4.3. IF THE RESULT IS ABOUT THE SAME, then you didn't make a large enough change. Try moving in the same direction, but with a larger change in the high-order shim.
        5.4.4. KEEP MAKING CHANGES UNTIL YOU'VE FOUND THE BEST SETTING FOR THE HIGH-ORDER SHIM which you're adjusting. The final few stepsizes will be small, but don't try this until you've definitely bracketed the optimum by actually going past it. Don't forget to re-optimize the appropriate low-order shims at each step.

6. HIGH-ORDER NON-SPINNING SHIMS   First do one, and then another. Repeat the process if the second one changes significantly.

7. HIGH-ORDER SPINNING SHIMS   As with the non-spinning shims, do them separately and repeat if there was any significant change. You may find it helpful to shim on a ^{1}H multiplet. Use an array size and sweep width to give a digital resolution of about 0.1 Hz, and an exponential apodization function to give a line broadening of 0.1 Hz.

8. Repeat steps 6. and 7. if the high-order spinning gradients were very bad before you adjusted them.

COMPUTER SHIMMING

CHARACTERISTICS
>can remove much of the drudgery from shimming
>
>slower than an experienced human, but the computer doesn't get bored by tedious work -- even after several hours
>
>cannot take advantage of line-shape-skew information to determine which way to move even-order shims
>
>DOES determine the interactions between the shims, and makes use of this information.
>
>is particularly well suited to final optimization of a shim that's already fairly good
>
>DOES FREQUENTLY MAKE BAD MISTAKES if the starting shim is bad, unless used very carefully

RECOMMENDATIONS
>Shim on the FID of a single sharp line. Do not shim on a multiplet or on the lock signal level.
>
>Don't immediately try full optimization with a long AQ. First try an AQ of a few tenths of a second, then successively longer AQ's — increase by about a factor of 4 each time. The computer algorithm can easily be fooled into thinking that a sharp central peak sitting on a large broad hump is better than a somewhat broader line sitting on a very small, narrow hump. The purpose of using short AQ's is to prevent the computer program from seeing extremely sharp tops on the peak, thereby forcing it to pay attention to the feet and tails of the line.
>
>For each value of AQ, try the following sequence:
>>1. spinner on   — computer-shim the low-order spinning gradients
>>2. spinner off   — computer-shim the low-order non-spins
>>3. spinner on   — computer-shim all spinning gradients
>>4. spinner off   — computer-shim all non-spins
>>5. spinner on   — computer-shim all spinning gradients
>
>It will take one or two days before the process is done, but it's VERY LIKELY that you'll have an extremely good shim at the end of that time.

About the figures and text

Raw FID's were transferred from the NMR spectrometer to a PC with FASTRAN. The FID's were then processed and "plotted" to disk with PCNMR. The vector-graphics HPGL-format files were converted to .PCX raster-graphics format with HiJaak (Inset Systems, Inc.), "pasted up" and edited with the use of PC Paintbrush (Microsoft), and the results converted from .PCX to .PCL format by HiJaak. The "LaserJet-graphics" .PCL files were then further converted to TIFF-data-compressed files suitable for printing on a LaserJet III by PCL3.EXE, a program which I wrote. The PC WRITE word processor was used to create, format, and print the text, and to merge it with the figures.