NMR Tips for Shimming, Part I

Computerized Shimming with the Tuning Algorithm

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Introduction

The efficiency of automation with large numbers of individual samples and the quality of the acquired spectra depend heavily on the efficiency and quality of adjustments made to the B_0 field homogeneity (shimming) after each sample change. The adjustments required depend mainly on sample properties such as bulk magnetic susceptibility of the solvent, volume, and position within the rf coil. The influence of these parameters increases as the volume is reduced and B_0 is increased. Part I of this report presents some basic information and practical advice which should help to minimize the effort and increase the quality and consistency of field homogeneity adjustment for high sample throughput. In particular, the computerized shimming algorithms called *Tuning*, which is available with XWIN-NMR and AVANCE spectrometers will be explained in some detail. These methods were originally developed for AM and AC spectrometers with the Aspect 3000 data system (*TX* subroutine) so that much of the information in this article will be useful for spectroscopists who still have an "oldtimer" in the laboratory. In Part II of this article (in the next SpinReport) the *Simplex* iteration method and the field mapping procedure *GradShim*, which uses gradient echoes to actually measure the inhomogeneity of B_0, will be examined in detail.

Note, the english noun "shim" refers to a thin, often tapered, piece of some material that is inserted between two larger objects to adjust their relative positions or angles. In the early days of NMR with iron-core magnets, coarse field homogeneity was adjusted by the equivalent of mechanical shims, i.e., by turning large bolts which shifted the relative positions of the iron cores and their pole caps. This so-called "shimming" procedure (verb: "to shim") has now been generalized to include the electronic fine adjustment of field homogeneity for all types of magnet via field gradients produced by so-called shim coils contained within a shim system. About 30 years ago, the author actually had the dubious pleasure of working with a 60 MHz electromagnet which had a paltry number of electronic shims (needing constant attention) as well as an imposing hand-crank mounted on the magnet yoke that was regularly used as a coarse mechanical shim.

Sample Preparation

The use of a constant standarized sample tube, volume, and position does a great deal to minimize the amount of shim adjustment needed from sample to sample. Furthermore, it is advantageous to group samples together according to solvent when using a sample changer. Even for constant volumes, significantly different settings for the family of Zn shims will be required for samples in $CDCl_3$ vs. D_2O, for example. These differences can be largely accounted for by maintaining for each solvent a standard shim file which can be read in as initial shim settings. Although "long" samples (such as the test samples delivered with the spectrometer) are generally easier to shim than the "short" samples often encountered in daily work, there are reasons for keeping sample volumes to a minimum: deuterated solvents are expensive, decreased volume means higher sample concentration within the rf coil and higher sensitivity, smaller volumes reach temperature equilibrium faster and exhibit smaller temperature gradients. Note: for a constant amount of solute, reducing the volume from 0.5 to 0.35 ml decreases the measurement time for a given S/N by a factor of 2.

In practice, samples with a liquid height equal to twice the height of the rf coil give excellent results, but this sample height (ca. 35 mm for current 5-mm probeheads (0.46 ml), ca. 28 mm (0.38 ml) for older AM/AC designs) must be conscientiously maintained to minimize shimming effort. Longer samples are less critical with respect to positioning, spinning vortex, and readjustment of shims, but they simply waste sample and solvent and cannot be maintained at a uniform temperature. Thus, 5-mm samples longer than about 40 mm should be avoided.

Short samples should be carefully positioned in the sample spinner to align the sample center with the center of the rf coil (Z symmetry). This minimizes all odd-order Zn gradients (n = 1,3,5). As the sample volume decreases (sample length approaches rf coil length), the even-order Zn gradients (n = 2,4,6) produced by the sample itself will increase dramatically. This effect is consistent and reproducible, i.e., the direction in which a given shim setting must be changed will be the same, but the amplitude of the correction will increase as sample length decreases. With some effort it is even possible to get reasonably good lineshapes for samples that are only 10-20% longer than the rf coil, but rather large Z2,Z4,Z6 shim corrections will be needed.

High-order gradients are produced at the sample-air and glass-air interfaces at the top and bottom of short samples. This effect can be minimized through the use of susceptibility-matched NMR tubes, as introduced by Shigemi and now available from other companies. The short sample is placed between plugs of material with a magnetic susceptibility closely matching that of the sample solvent. This configuration behaves like a long sample in terms of B_0 homogeneity and the required shim settings while maintaining the sample of interest in a minimum volume within the rf coil.

The only real problem with short samples in normal NMR tubes is the sensitivity of shim settings to small changes in sample length, position, and spinning rate (vortex), requiring more precision in sample handling. For volatile solvents such as $CDCl_3$, solvent evaporation from a standard capped tube will change the volume and produce noticeable effects on B_0 homogeneity in just a few hours. If caps that are impermeable to solvent are not available, one can insert one or two teflon vortex plugs into the top of the tube to restrict the cross-section available for evaporation.

The Mathematics of Shimming

Most NMR novices consider shimming, like piano tuning, to be some sort of black magic or an art form requiring something like "perfect pitch". Actually both procedures are highly systematic and mathematical and can be learned by any patient individual with the aid of some basic knowledge of the fundamental principles or "laws" of shimming. Computers are infinitely patient and can also be taught to shim NMR magnets.

Shimming is just the solution of a linear equation

$$B_0^* = B_0(x,y,z) + \Sigma_i \, c_i \, S_i(x,y,z) \qquad (1)$$

$$\Sigma_i \, c_i \, S_i(x,y,z) = B_0^* - B_0(x,y,z) = -\Delta B_0(x,y,z) \qquad (2)$$

where B_0^* is the desired *constant* or homogeneous field (independent of x,y,z) within a cylindrical volume, $B_0(x,y,z)$ is the inhomogeneous field that we are confronted with, and the summation is taken over the shim gradient functions S_i multiplied by their amplitudes or shim settings c_i. Note that the shim functions S_i simply represent a basis set of (ideally orthogonal) spatial functions that can be summed to reproduce (cancel) ΔB_0, the 3D variation in B_0 (Eq. 2).

The spectrometer's shim system contains a precisely designed set of coils or conductor geometries which, individually or in appropriate combinations, produce the various spatially dependent field profiles S_i, i.e., the shim gradients that we know by the names X, Y, Z, XY, X2Y2, Z2, etc. The strength of a shim gradient is proportional to the digital shim setting viewed on the BSMS panel, which controls the current flowing in the shim conductors via a high-resolution DAC. By twiddling knobs in a more or less intelligent manner, we try to find the best set of c_i (shim currents) to correct for inhomogeneities and solve Eq. 2. So, why not let the computer carry out the drudgery for us?

Shim Geometry

Modern cryomagnets are not just simple homogeneous solenoids containing many kilometers of wire; a solenoid of finite length creates even-order Zn gradients that are undesirable for NMR. Actually, a typical high-field magnet is built up from several concentric sections, and some of these will have a nonuniform distribution of conductive windings (notches or gaps) which are

calculated to cancel out the natural gradients of a solenoid, e.g., a magnet might be designated as a sixth-order corrected solenoid. In addition, one of the sections or cylinders composing the complete magnet system will contain a set of superconducting shim coils which are energized after the magnet has stabilized at field. Today, magnets for AVANCE NMR systems have 8 cryoshims covering the first-order (X,Y,Z) and second-order gradients (Z2, XZ, YZ, XY, X2-Y2). The cryoshims provide the main field corrections necessary to create a large homogeneous field volume with ΔB_0 typically <5 ppm. The adjustment of the cryoshims is what one can truly think of as "shimming the magnet" but also provides correction of static environmental influences. The room-temperature shim system is used mainly for "shimming the sample", i.e., it corrects the fixed residual gradients left over after cryoshimming, the fixed local field gradients produced by the probehead materials, and the variable gradients produced by the sample itself.

Depending on magnet type and bore diameter, Bruker offers various BOSS shim systems with larger or smaller sets of shim gradients. The individual shims are named according to the terms in the S_i that describe their functional form and can be arranged in three basic groups (on-axis, off-axis, and 3D shims) with various orders n. The on-axis shims are the group of Zn shims that create field profiles depending only on the z coordinate (the bore and sample axis in cryomagnets). These shims have no x,y dependency and can be adjusted with or without sample spinning. The off-axis shims will be considered here to be those with only x,y but no z dependence. Finally, the group which we call 3D shims represents all product combinations of the on- and off-axis shims, i.e., depends on all three coordinates x,y,z. The *order* of a given shim is defined by the exponents of the coordinates involved.

Over the years the number of shims available on NMR spectrometers has increased from 8 to 12 to 17 and now over 30. Thus, shimming has become more complicated but also more rewarding since the additional higher-order shims allow correction of the higher-order inhomogeneities that are responsible for poor lineshape (hump). In particular, the increased number of 3D shims allows excellent lineshape and resolution to be obtained *without* sample spinning, as desired for multidimensional NMR and ultra-high-field applications. Table 1 summarizes the 34 shim gradients now available with a BOSS II™ shim system typically used for the standard-bore AVANCE 500 or higher-field systems. The BOSS I™ system for lower-field magnets uses a subset of these shims (20 gradients), while for wide-bore magnets BOSS WB™ shim systems are available with 18 or 28 shim gradients. The complete set of available shims and their settings in a stored shim file can be viewed and printed with the keyboard command *vish*.

When planning or performing shimming operations, it is important to realize that shims that share a given coordinate in their names can be expected to show some degree of interdependence, i.e., the setting in one shim will affect the required setting in the other, and errors in one shim will force errors in related shims. Only the linear shims X,Y,Z can be considered independent and can be optimized directly via the Lock Level, for example. In general, higher-order shims cannot be directly optimized individually but only in iteration with their lower-order "partners". For example, the complete set of Zn shims must be adjusted together since any significant errors in the setting of one shim will lead to apparently "optimal" but incorrect settings of other shims in the group (the local optimum problem). This can easily be observed by simply setting one or more Zn shims to zero; adjustment of the other shims will lead to a certain "local" optimum in homogeneity but with different shim settings compared to those obtained when all Zn are active. Similarly, a third-order shim such as XYZ may influence the required settings for X, Y, XY, XZ, YZ, and Z. These interdependences between various shims can only be sorted out by an interative process. Since shimming is much like performing a least-squares fit in n dimensional space, it is clear that if one parameter (shim value) is held at an incorrect value, then the fitting procedure will force other "interacting" parameters to false values in order to achieve a "best" fit.

Another complication in shimming can be caused by direct physical interactions between shims due to "impurities" in the generated shim gradients themselves, i.e., when shims generate additional gradients other than those intended or when there is misalignment of the gradient axes for various shims. For example, a Z5 shim might generate small amounts of Z3 and Z gradients. The problem of purity or orthogonality of shim gradients has been progressively reduced over the years through the increased use of computer-assisted design strategies and simulations as well as improved construction techniques. Thus, the current generation of BOSS shim systems not only provide more shims but also more accurate gradient geometries of highest purity.

Computerized Shimming Methods

There are three basic methods in XWIN-NMR which can be used to perform computerized shimming. In order of increasing sophistication these are: (i) the so-called "Tuning" method, which can use the deuterium Lock Level or the area under the ^{1}H FID as quality parameter; (ii) the "Simplex" method, which also uses the lock signal or the FID area; (iii) a field profiling or mapping procedure, often referred to as "gradient shimming" (the *GradShim* routine in XWIN-NMR), which uses a *gradient-echo* data acquisition sequence, similar to simple imaging methods, and either the ^{2}H signal of a deuterated solvent or the ^{1}H signal(s) of the sample.

The Tuning and Simplex methods in XWIN-NMR are closely related to the shimming algorithms originally developed for the AM/Aspect 3000 spectrometer series. These methods require only the standard spectrometer hardware and can be used with virtually any probehead and sample and for any selection of shim gradients with or without spinning.

In the Tuning procedure described below a user-defined group of shims is examined in an iterative cycle; each shim in succession is adjusted *individually* to maximize the chosen "quality" parameter (Lock DC Level or FID area). This is essentially a linear procedure which works well when only small adjustments are needed on low-order shims. Mutual dependencies (iteractions) between various shims and high-order effects, especially within the group of Zn shims, will generally not be handled well, and the method may converge only to a local optimum in shim space.

The Simplex algorithm (next SpinReport)is slower but more robust than Tuning and generally more successful at handling high-order shims. All shims within a user-defined group are varied in *simultaneous* steps using a special search technique, and interactions between shims can be better accounted for.

The GradShim algorithm (next SpinReport) is, in principle, the most efficient method; however, field profiling via gradient echos requires a probehead equipped with field gradient coils (Z or XYZ) and corresponding hardware for generating pulsed field gradients.

Finally, the "AutoShim" firmware function of the AVANCE BSMS shim control unit can be turned on or off via the BSMS buttons panel, via the keyboard command *autoshim on* or *autoshim off*, in automation sequences via AUTOSHIM_ON or AUTOSHIM_OFF, and via the script used to control the Tuning method (see below). With the BSMS panel the operator can use menu *5. ShimAmpl.* to dial in a *small* nonzero current increment for any desired shim (typical candidates are: Z1, Z2, Z3, X, Y, XZ, YZ). When AutoShim is activated, the BSMS unit

Table 1. BOSS II™ shim gradients.

Group	Z Order	Shim Names[a]		
on-axis	1 - 6	Z, Z2, Z3, Z4, Z5, Z6		
		X,Y Order 1	2	3
off-axis	0	X, Y	XY, X2Y2	X3, Y3
3D	1	XZ, YZ	XYZ, X2Y2Z	X3Z, Y3Z
	2	XZ2, YZ2	XYZ2, X2Y2Z2	
	3	XZ3, YZ3	XYZ3, X2Y2Z3	
	4	XZ4, YZ4	XYZ4, X2Y2Z4	
	5	XZ5, YZ5	XYZ5, X2Y2Z5	

[a] the letters X,Y,Z refer to the spatial coordinates x,y,z; the numbers are the corresponding exponents; X2Y2 = (x^2-y^2).

automatically cycles through each of the shims for which a nonzero increment has been defined and uses this increment to check for possible improvement in the Lock Level (takes a few seconds per shim). The AutoShim increments should be large enough to just barely affect the Lock Level, and the cycle is repeated indefinitely to improve/maintain B_0 homogeneity for long-term experiments where, for example, changes in sample height due to solvent evaporation would require readjustment of shims. The AutoShim function is *not* recommended for high-order shims or for experiments where gradient pulses are used which disturb the lock signal level.

Regardless of which shimming method is employed, the efficiency and the quality of the results will depend to some extent on a variety of parameters which must be defined when setting up the method. In the following we provide some suggestions for optimizing the performance of computerized shimming.

The *tunefile* Script

File Organization

The setup and execution of both the Tuning and Simplex methods is controlled by an ASCII text file or script, the so-called *tunefile*. There are two basic directory paths that are used for the storage of scripts for computer-controlled shimming. The subdirectory

.../exp/stan/nmr/lists/group/

within the XWIN-NMR home directory is used by the *edtune* or *tune* commands, which are usually entered on the keyboard command line. This directory initially contains a sample tunefile called *example* which is not linked to any specific probehead. With *edtune* this file can be viewed and edited, and a variety of scripts for shimming different sets of shims with the tuning or simplex methods can be created and stored with user-defined names via the *save as...* procedure. The *tune* command shows the list of tunefile scripts currently stored in the .../group/ subdirectory and allows one to be selected for immediate execution.

Note that in the .../group/ subdirectory one special tunefile name, *mytunefile*, has been reserved for use by ICON-NMR (see below). An updated version of *example* and some additional scripts for specific shimming procedures will be made available via the Bruker Website.

To support shimming under automation program control (*xau*) or ICON-NMR, the XWIN-NMR subdirectory

.../conf/instr/<spectrometer>/prosol/<probe id>/

is used to link a specific tunefile with a specific probehead defined by <probe id>. Initially this subdirectory contains as default the script named *tunefile*, which can be accessed via *edprosol* for the selected probehead with the setting *solvent* = All by using the menu *file* → *edit tunefile*. Changes made in *tunefile* will be stored in the above subdirectory, and this script can serve as a master copy for generating an initial tunefile for any specific solvent using the corresponding subdirectory

.../prosol/<probe id>/<solvent>/.

For example, when *solvent* = CDCL3 has been selected in *edprosol*, the *edit tunefile* routine will look for a script named *tunefile* in the CDCL3 subdirectory for the current probehead. If the file is not found (e.g., initial state of XWIN-NMR), an error message will prompt the user to execute the *save* command (button) in *edprosol*; this causes the *tunefile* stored in the parent <probe id> directory to

be copied to the current <solvent> subdirectory. The next time *edit tunefile* is called from *edprosol* for this solvent, the *tunefile* script located in the <solvent> subdirectory will be opened and made available for editing. For example, the optimum values for parameters such as DELAY or *initstep* (see below) may depend on solvent.

Note: the user must ensure that, for the probeheads and solvents to be handled under automation, an appropriate *tunefile* script is present in *each* solvent directory. This can be done by editing each script via *edprosol* and *edit tunefile* or by copying and renaming (to *tunefile*) a particular script from the .../group/ subdirectory used by *edtune* to the correct <solvent> subdirectory in the .../prosol/... path.

Tunefile Editing and Execution

The tunefile scripts delivered with XWIN-NMR contain explanatory descriptive text and comments, whereby these lines of text are marked with a leading symbol #. The explanatory text can be deleted from user-edited tunefiles, if desired. Unmarked text lines will be interpreted as parameter settings or command code lines, according to the command syntax described in Table 2, and will be executed sequentially as they appear.

1) Tunefile scripts located in the path .../exp/stan/nmr/lists/group/ <script_name> can have any name, can be edited via *edtune*, and can be executed with the *tune* command from the keyboard or within macros using the command line

tune script_name.

The special filename *mytunefile* can also be used for a script in the .../group/ path and the command

tune mytunefile

can be executed as a command line or selected as the automatic shimming command for ICON-NMR (see Configuration menu: Shimming Controls, drop-down menu Automatic Shim Program).

The simple keyboard command

tune

will show all files available in the .../group/ subdirectory and allow selection for execution.

2) Tunefile scripts located in the .../prosol/<probe id>/<solvent>/ path must all have the uniform name *tunefile*. The currently defined probehead and solvent (*edhead*, *solvent*, or *edprosol* commands) specify then exactly which tunefile script will be used by the keyboard or macro command line

tune .sx

where the designator .sx means that a solvent-specific *tunefile* script will be used.

The same script will be used by the (upper case) command

TUNESX

which can be entered as a command line in automation programs (*edau*: path .../exp/stan/nmr/au/src/) that are executed by the *xau* command. This command can also be selected as the automatic shim command for ICON-NMR (Configuration menu: Shimming Controls).

Finally, the execution of any tunefile script can be halted at any time with the keyboard commands

tune halt or *tune stop*,

leaving the shims at their current settings.

Tunefile Parameters and Commands

Table 2 summarizes the parameter settings and commands that can be included in the *tunefile* script. Both the Tuning and Simplex methods can be implemented, either alone or in combination, in a single script. Many of the commands involve the setting up of parameters or definition of shim criteria; these commands can appear in any order in the script before the actual shim execution commands, which then must appear in the desired order. Furthermore, a loop construction is available for repetition of any set of statements for iteration purposes.

The Tuning and Simplex methods require a number of parameters such as delays and shim stepsizes which cannot be universally defined since they depend on the type of magnet, probehead, sample diameter, solvent, shim current ranges defined in the BSMS, etc. The default settings provided with the example script in XWIN-NMR may work well under some conditions but are intended more as a guideline for optimization by the user.

The Tuning procedure is the simplest method and is typically applied to a selected subset of shims using the deuterium Lock Level (DC signal) as the *quality parameter* (QP). Each individual shim is adjusted (optimized) by making positive or negative increments to achieve a *maximum* in QP. This *optimization* is repeated for each shim in a list, one at a time, and several cycles through the list can be made in an attempt to handle the interdependences between shims (see above). This procedure is strictly correct only for first-order shim gradients (X,Y,Z); its applicability decreases as the shim order increases, e.g., from $Z2$ to $Z3$ to $Z4$, or when large higher-order shim corrections for off-axis or 3D shims are needed, since the optimization of shims individually on the basis of the quality parameter alone will usually lead to a local rather than a global optimum.

As long as the required shim corrections are small, e.g., a series of similar samples with similar volumes, the Tuning method is reasonably dependable. However, we recommend that Tuning be applied only to shims up to a total order of 3 (Table 1). Sample rotation is useful for isolating the effects of the pure on-axis gradients (which are unchanged by spinning) from the off-axis and 3D shims whose X,Y components will be averaged out by spinning. Thus, several iterations between spinning and nonspinning states may be necessary when shimming both on- and off-axis shims. However, if the NMR measurements are to be performed *without* spinning, then at least the final pass through the Zn shims should be made without spinning.

Note: the *AutoShim* firmware routine in the BSMS unit operates in a "tuning" manner, except that the shim increments are small and constant values since the routine only needs to maintain the field homogeneity already achieved.

The Tuning Algorithm

The Tuning algorithm is executed when command lines of the form

shim_name initstep iter

are encountered in the tunefile script (see Table 2).

Optimizing Parameters

The DELAY time parameter represents a response time for stabilization of QP after a shim increment has been applied. For the Lock Level this time is related to the relaxation time of the lock nucleus and time constants in the lock channel electronics. Response can be tested manually by making an appropriate steplike shim change and observing the Lock

Tuning Algorithm

1. Measure quality parameter (QP) with current shim settings; for shim with name *shim_name*, set current_step to *initstep*.

2. Change the setting or value of the shim gradient (as viewed on the BSMS panel) with name *shim_name* by the amount defined by current_step; shim_value(current) = shim_value(last) + current_step.

3a. After a time defined by the condition DELAY, sample the Lock DC Level) n times as defined by LOCKDWELL, *or*

3b. Acquire FID using *gs* mode with corresponding delay.

4. Calculate mean and std. dev. of QP and compare with a noise parameter (stability check).

5a. If std. dev. < noise, then QP is considered stable; go to (6).

5b. If std. dev. > noise, then repeat steps (3) and (4).

6. Save current QP and compare with previous value.

7a. If QP increases, go to (2).

7b. If QP decreases following first increment, then return to starting shim value, reverse sign of current_step, increment reverse_counter; go to (8).

7c. If QP decreases, assume last three data points fall on a Gaussian bell curve; estimate shim_value(max) for maximum QP; set current_step = shim_value(max) - shim_value(last); increment reverse_counter; go to (8).

8. Current iteration done; for reverse_counter < *iter*, loop to (2).

9. Terminate adjustment of current shim after *iter* iterations; proceed to next statement in script.

Level. Typically DELAY = 2 or 3 should be sufficient, but a longer delay may be necessary for solvents such as methanol-d_6 or acetone-d_6. LOCKDWELL, the number of samples taken

Table 2. **Summary of *tunefile* command language.** [a]

Command	Arguments or Parameters	Description & Comments
ROTATION	ON WAIT OFF WAIT	turn sample rotation on or off; the option WAIT causes the routine to wait for the spinning status OK from the BSMS; ROTATION ON should only be used for on-axis shims.
RSH	*shim_filename*	read in a set of initial shim settings stored in the file *shim_filename*
TIMEOUT	*nnnn*	*nnnn* is an integer in seconds defining the maximum time allowed for complete execution of the current tunefile; shimming will be terminated at this time; the currently best known shim values will be set.
USE_LOCKLEVEL		**Default:** use the **Lock DC Level** (default) as quality parameter (QP).
DELAY	*n*	n is the basic delay time in seconds between the setting of new shim values and the beginning of the evaluation of Lock Level; typically $n = 1 - 4$.
LOCKDWELL	*n*	n is an integer in the range 3 - 32 (default = 5) which defines the minimum number of times the Lock Level will be evaluated to compute a mean and std. dev.; if the Lock Level std. dev. exceeds the noise (indicating instability), additional readings will be taken until the Lock Level is stable. The time required for sampling the Lock Level is ca. $n*0.2$ s.
MAXLOCK	*n.nn*	decimal number in the range 0.4 - 0.8 which defines the maximum Lock Level (default = 0.5); when level exceeds this value during shimming the BSMS AutoGain function will be activated, e.g., to put the lock DC signal near the middle of the Lock Display vertical range (Lock Level = 0.35). The optimization criterion is reinitialized. Note: the full vertical range of the Lock Display window depends on spectrometer hardware but typically corresponds to Lock Level of ca. 0.6; the current Lock Level can be readout with the keyboard command *bsms_getlock*.
USE_FIDAREA		use the **FID area** (*gs* mode) as the QP for shim adjustment. The delay between shim setting and FID acquisition is defined by the relaxation delay in the acq. parameters.
PULPROG	*progr_name*	option for *gs* mode which specifies the use of the pulse program with filename *progr_name* rather than the sequence defined in the current acquisition parameters (*eda*).
LOCK	ON OFF	use one of these commands to activate or deactivate monitoring of the lock status during shimming; ON: if lock is lost during shim manipulations, it will be reestablished before shimming continues; OFF: allows shimming without a lock signal.
shim_name	*initstep iter*	**TUNING execution:** *shim_name* is the name of one shim (e.g. Z2, X, X2Y2, XYZ, etc.) which will now be adjusted to maximize the quality parameter, using an initial stepsize or increment defined by the integer *initstep* and continuing for *iter* number of iterations with successive reduction in stepsize (see description of algorithm). The tunefile must contain one such statement for each shim to be optimized; these statements can be enclosed in a TIMES ... END loop. The proper shim names are those given in the shim settings list which can be viewed with the keyboard command *vish*.
SET	*shim_name initstep endstep*	**SIMPLEX setup:** *shim_name* is the name of a shim; *initstep* is an integer defining the initial stepsize or radius for shim increments; *endstep* is the reduced stepsize or radius required for termination of the Simplex algorithm (see description). SET commands must appear before the SIMPLEX command for the corresponding shims.
SIMPLEX	*shim_1 shim_2 ... shim_n*	**SIMPLEX execution:** the shims listed by names separated by spaces are adjusted simultaneously as a group via the Simplex algorithm.
AUTOSHIM ON	*shim_1 xx shim_2 yy ...*	can be used at the end of a tunefile to activate the BSMS AutoShim routine to maintain long-term field homogeneity using the shim named *shim_1* with constant increment *xx*, *shim_2* with increment *yy*, etc.
TIMES *n* . . . . . . END		a loop construction for repetition of shim commands; the enclosed statements will be repeated n times; several loops can be nested; any of the valid statements in this table may be used loops.

[a] Command lines are those lines in the script that are not marked with a leading # symbol; syntax: one command per line with arguments and parameters separated by one or more blanks.

for the Lock Level, should be at least 5 to obtain a good average value to be able to distinguish small changes in Lock Level. The stability check (algorithm step 4) will also compensate for a DELAY that is too short.

When the FID is used for shimming (*gs* mode), the acquisition parameters should be optimized in terms of sufficient relaxation delay and low flip angle to avoid fluctuations in successive FIDs, sufficient receiver gain to utilize ADC dynamic range, sufficient time-domain size to acquire a visible FID with little trailing noise. If shimming for good lineshape (minimal hump) is the goal, then it is often useful in a first round to truncate the FID by reducing TD to give more weight to the beginning of the FID in the calculation of the area. For FID shimming the Tuning parameters DELAY, LOCK, MAXLOCK, and LOCKDWELL have no effect.

If large improvements are made during shimming, the Lock Level may exceed the vertical scale of the display. This is not a problem for the shim routine since the Lock Level can still be measured. However, if it is desired that the signal remain visible for the operator, the AutoGain function can be made available via the MAXLOCK command with a value of typically 0.5 - 0.6. When Lock Level approaches MAXLOCK, shimming will be interrupted to reduce Lock Gain to give a new Lock Level of ca. 0.3.

The key to efficient use of the Tuning algorithm is the *initial* increment size for each shim (*initstep*), which must be sufficiently large to cause a clearly detectable change in the quality parameter (Lock Level). If the step size is too small, then (i) changes may get lost in the noise of the lock signal, (ii) the algorithm may have difficulty in determining the correct direction of incrementation, and (iii) the time required to arrive at and detect a maximum Lock Level will increase. If the initial step size is too large, then lock may be lost or iterations will be wasted with large unproductive jumps in shim settings. The value of *initstep* will also affect the proper choice of *iter*, the number of times the stepsize will be reduced (step 7c).

Note that the sensitivity of the Lock Level to shim increments depends on the following:

❐ the shim sensitivity (spectrometer-dependent ratio of actual shim current to digital shim setting),

❐ the shim gradient order (higher orders usually require larger increments),

❐ the deuterium solvent linewidth (larger linewidth means larger increment; e.g. DMSO > D_2O > $CDCl_3$ > CD_3OD).

Each time the Tuning method passes through a maximum (*i.e.* *QP* decreases), the increment for the next step is reversed in sign and reduced in magnitude (backtracking). The use of a fairly large *initstep* helps to avoid becoming trapped at a local optimum. The allowed number of reversals is defined by *iter* and must be

sufficiently large that a close approach to maximum is possible but not so large that time is wasted with very small increments and oscillations. There is no point in trying to find a precise maximum for a single shim when several shims must be iterated, perhaps in several cycles. In practice, *iter* = 4 - 8 seems reasonable with *initstep* defined as described above. *Note:* the procedure converges quite rapidly since the new increment is not simply set to half the previous one, for example, but is set to a value calculated to reach the center of Gaussian bell curve for *QP*, defined by the previous data points.

The Tuning procedure requires one command line for each shim to be adjusted (ca. 30 s per shim with *iter* = 5). One strategy would be to shim from low to high order and back to low order, whereby it is possible to reduce *initstep* for the return cycle.

```
Z   30  4
Z2  40  5
Z3  100 5
Z2  20  4
Z   15  4
```

Another technique would be to shim from high to low order in several cycles using a constant set of *initstep* values.

```
TIMES 3
    XY   1500 6
    X2Y2 1500 6
    XZ2  500  6
    YZ2  500  6
    XZ   300  5
    YZ   300  5
    X    30   4
    Y    30   4
END
```

Shimming on the FID

Both the Tuning and Simplex algorithms can be applied in the *gs* data acquisition mode using the *area* under the FID envelope as the quality parameter. In principle, the ^{1}H FID is 7 times more "sensitive" to B_0 adjustments than the deuterium lock signal at the lower Larmor frequency. Thus, the FID area may vary with small shim changes even when the lock level appears constant.

If the sample tube contains D_2O, for example, then the ^{1}H NMR spectrum of residual HDO consists of a collection of Lorentzian lineshapes with the same natural linewidths $\Delta n_o = 1/\pi T_2$ but with a distribution of resonance frequencies reflecting the spatial variation of B_0 (inhomogeneity) across the sample ($\Delta w = \gamma \Delta B_0$). The distribution ΔB_0 can have arbitrary form, leading to non-Lorentzian lineshapes with a broad signal base (hump), asymmetries, shoulders, even line splittings. The FID area approaches a maximum value when all inhomogeneities are eliminated and all Lorentzians are exactly superimposed with the longest possible decay time T_2.

Tips for setting the initstep *parameter required for computerized shimming.*

1. Choose a sample, solvent, and volume typical for your applications. Turn on sample rotation if it will be used in your experiments or for shimming.

2. Adjust the Lock Display window to extend full screen vertically and turn on the background Grid.

3. With Lock Off, adjust the Lock DC baseline to be near the bottom of the display.

4. If necessary, read in a known set of shim settings that give reasonably good homogeneity.

5. With Lock On, establish deuterium lock, adjust Lock Power to be at least 6 dB below saturation levels; adjust LockGain to place the Lock Level near the top of the display, e.g., on the first grid line from the top; adjust Lock Phase for maximum Lock Level.

6. Manually adjust low-order shims as needed to maximize the Lock Level and readjust Gain as needed.

7. Store the current shim settings with *wsh shimtemp*, for example. View and print out this list with *vish shimtemp*.

8. Determine the current digital Lock Level, e.g., first grid line from the top, with the command *bsms_getlock*.

9. With the BSMS panel, manually change the Z shim setting until the Lock Level decreases by about 10% as monitored by *bsms_getlock*, i.e., about half the distance to the next lower display grid line. Write down the required Z *increment* (the difference between the previous and current settings) on your shim list. Return Z to its previous setting by pressing the Z button again.

10. Repeat procedure (9) for Z2 - Z5 (but not Z6 or higher) and write down the increments on your list.

You now have a list of shim increments which can serve as a guide for defining the parameter *initstep* in appropriate tunefiles for the **Tuning** and simplex algorithms. For a first trial we recommend using ca. 50% of the measured increment as the *initstep* value for the more sensitive low-order shims and up to 100% of the increment for higher-order shims. Further adjustments of *initstep* may be necessary after watching the behavior of the Tuning procedure.

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However, there is an additional effect that becomes apparent for concentrated samples delivering a very strong signal, e.g., > 5% H_2O, and leads to artificial linebroadening (shortening of the FID decay time). This effect is called *radiation damping* and occurs when the rf coil is tuned to resonance and is tightly coupled with the sample. Radiation damping is proportional to coil filling factor η, coil Q, sample magnetization M_o (concentration), and Larmor frequency v_o, but it is *independent* of flip angle. For a 5-mm H_2O sample (110 M proton concentration) at v_o > 500 Hz, the linewidth due to damping will be ca. 60 Hz.

Thus, at the current high magnetic fields that we enjoy, it will not be possible to accurately shim samples with ^{1}H concentrations of more than 0.1 - 0.5 M under normal conditions with an optimally tuned probehead. The danger of radiation damping for a given sample can be judged by simply looking at the receiver gain setting (RG) being used relative to the value required for a pure H_2O sample. For RG_{sample} / RG_{H2O} > 100 damping effects will be < 1% of the effect observed with H_2O. Solvent suppression techniques are not much help for shimming since the small fluctuations in residual solvent signal from transient to transient lead to an unstable FID area parameter, making it difficult to judge the effects of shim adjustments, except by visual inspection of the tail of the FID containing the solute signals. Radiation damping can be minimized by simply detuning the probehead to far off-resonance (using just the tuning capacitor).

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Set RG to a value typical for normal samples in deuterated solvents (e.g. RG = 500 - 1000 on AVANCE spectrometers; 40 - 100 on AM/AC systems. Then with a normal pulse-acquire acquisition in gs mode and a pulse width of ca. $2\ \mu s$, adjust the probehead's tuning element in one direction until the FID amplitude is no longer offscale and does not exceed the digitizer's voltage range. Shimming can now be performed as usual, but don't forget to retune the probehead back to resonance for the desired measurement.

Final Remarks

Here we have discussed some general shimming strategies and tips which are applicable in general to all spectrometers and probeheads, even to *in vivo* NMR and imaging. Many of the aspects of the methods described here can also be employed during manual shimming and help to produce more systematic results. Above all, the operator should always keep in mind that shimming is not to be thought of as a random process; for a given sample form and position, the results are highly reproducible.

The Tuning method described above is well-suited for daily routine with a series of samples with one diameter and similar volumes. The basic shim settings will be known, and it will probably be sufficient to adjust off-axis and 3D shims to 2nd- or 3rd-order just once a day for older magnets (to account for the effects of liquid nitrogen level) or even less often for newer systems. Sample-to-sample variations will be seen primarily in the Zn shims and perhaps small corrections to 1st-order X,Y combinations. With constant sample volumes, it may be sufficient to adjust just Z, $Z2$, perhaps $Z3$, along with X,Y and perhaps XZ,YZ. If sample spinning is being used for the measurements, then simply fine adjustment of Zn should give the desired results.

The more sophisticated computerized shimming methods (Simplex, GradShim) to be described in the next SpinReport reveal their full power when basic shimming "in the dark" is performed in search of the direction and amplitude of high-order shims.

Here a few additional tips.

1. Always mount the NMR probehead in the same angular orientation within the shim system; all shim corrections due to probehead materials will be highly reproducible.

2. Standardize the brand of sample tube, sample volumes and vertical position relative to the rf coil.

3. Make sure samples are *well-mixed* and at temperature *equilibrium* (always use active temperature control and not "ambient" temperature); concentration or temperature gradients look and behave like B_0 gradients and can be temporarily shimmed away.

4. When switching between spinning and nonspinning modes, always readjust at least Z and possibly $Z2$ shims in each state to compensate for the change in sample vortex.

5. When a sample is symmetrically shortened along the Z axis (affects $Z2,Z4,Z6$) or placed asymmetrically above or below a central position (affects $Z,Z3,Z5$), the required directions of change for the Z gradients will always be systematic and the required amount of change in shim values will reflect the magnitude in the change in geometry.

6. Changes in sample length will have only small effects on off-axis shims but may require some minor corrections to the 3D shims containing Z components.

7. The importance and sensitivity of off-axis and 3D shims increase with sample diameter.

8. The use of different sample diameters in a given probehead will require significant changes in Zn gradients even if sample height is kept constant since susceptibility effects depend on sample volume.

9. Shim settings c_i for very long samples placed at maximum depth should be considered as a reference point for which "sample" effects are at a minimum. The *changes* Δc_i required for short samples will be systematic; correct changes in a high-order shims generally result in a minimum in the Δc_i required for lower-order shims.

10. The correspondence between shims and samples will remain consistent for a given magnet and shim system combination since it depends primarily on the direction of current flow (polarity) in the magnet and shims. With AVANCE spectrometers shim polarities and the angular orientation of the shim system relative to the magnet and its cryoshims have now been standardized.

11. The FID shape in the *gs* display window corresponds to some degree to the lineshape in the FT spectrum (after 90° rotation); a broad hump can be detected as a rapid initial decay in the FID. However, it is useful to look carefully at the spectrum since the shape and asymmetry of the hump indicate which shims are at fault. Even-order Zn shims shift the hump to higher or lower frequencies; odd-order shims affect the width of the hump in a symmetrical manner.

12. In general, it is best to initially concentrate on lineshape (the initial part of the FID, the shape of peaks at the base); good resolution (linewidth at half-height) usually comes all by itself once the high-order shims are correct; a large hump means a considerable loss in peak height and S/N and difficulty in integration.

13. Keep a history of shim settings; it is easy to "drift" away from correct values for high-order shims over time, especially when many different users employ manual shimming.