Chapter 1

1 The NMR Spectrometer

1.1 Components of an NMR Spectrometer

1.1.1 The Magnet

In most current NMR spectrometers the magnetic field is generated by a superconducting magnet (Fig. 1.1). The first stage in reaching the very low temperature needed is an outer stainless steel or aluminum dewar which contains liquid nitrogen. Typically, this has to be refilled every ten days. In practice, it is advisable to do this refilling on a fixed day every week. An inner dewar contains the superconducting coil (4) immersed in liquid helium, which has to be refilled, depending on the construction, every two to eight months. The *helium* refill should be carried out only by experienced people. A room-temperature bore is fitted with the shim coils (7), providing a room-temperature homogeneity adjustment, and a spinner assembly (5), which contains the turbine system for spinning the NMR sample tube. The probe-head (8) is usually introduced into the magnet from the bottom and is connected to at least three radiofrequency (r.f.) cables providing the ^{2}H lock, ^{1}H frequency, and one X-nucleus frequency. Additional devices to control temperature (heater, thermoelement, air, sometimes water to insulate the probe-head from the magnet) are needed. New developments include the digital transmission of the probe-head parameters to the console via a data line.

1 Ports for liquid N_2

2 Ports for liquid He

3 Superinsulation and
   high vacuum

4 Main magnet coils + liquid helium

5 Sample lift and spinner
   assembly

6 NMR tube

7 Shim assembly

8 Probe-head
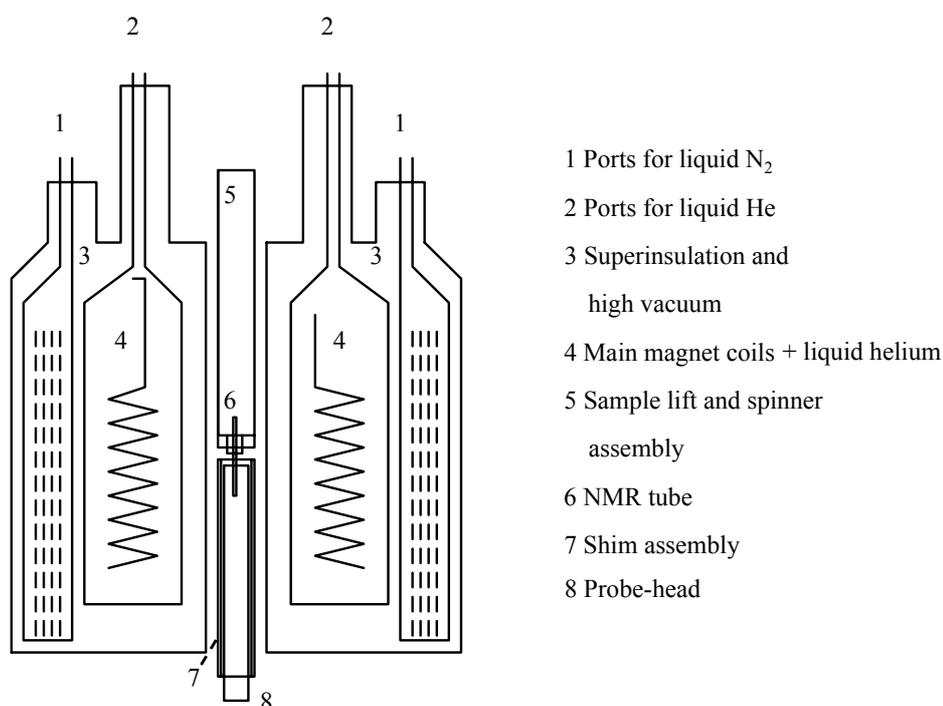
Fig. 1.1 Principles of a superconducting magnet

1.1.2 The Spectrometer Cabinet

The spectrometer cabinet provides at least three radiofrequency channels, i. e. the observe, the lock and another channel, e.g. for decoupling. Usually these frequencies are derived from digital frequency synthesizers which are phase-locked to a central quartz oscillator. These frequencies are controlled, amplified, pulsed, and transmitted to the probe-head. The various NMR signals are preamplified, then mixed with the local oscillator frequency to yield the intermediate frequency (i.f.). The i.f. signal is further amplified, then in a second mixing stage the NMR audio signal is obtained after quadrature phase detection. The two signal components are digitized in the analog-to-digital converter (ADC) and fed into the computer memory or, in the case of the lock signal, used for field/frequency regulation. Figures 1.2 and 1.3 show the principles of the system.
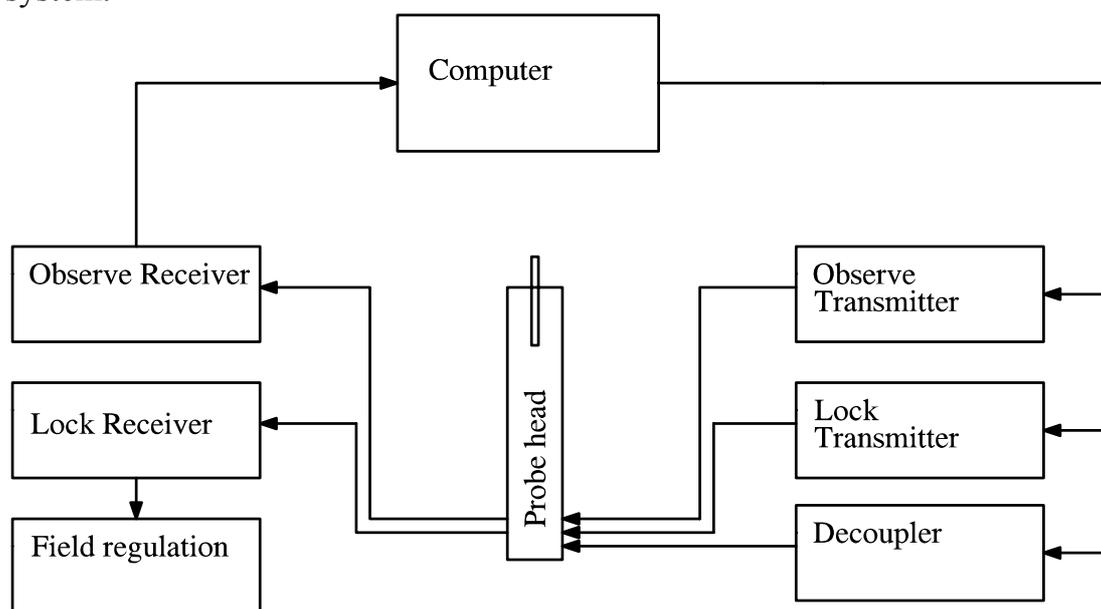
Fig. 1.2 Principles of an NMR spectrometer
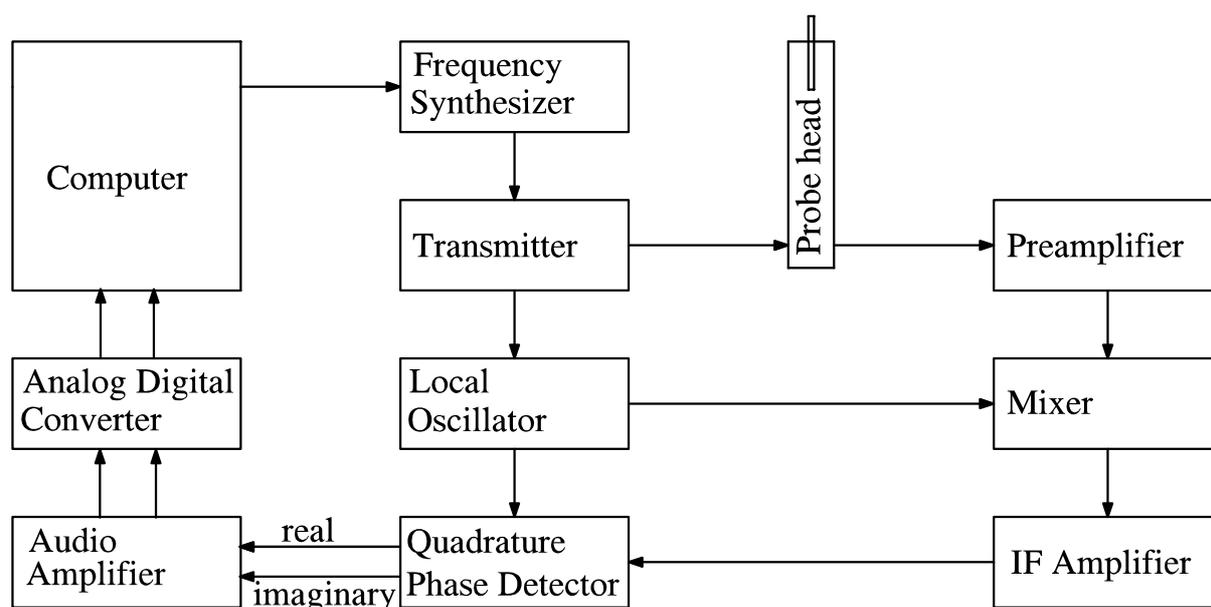
Fig. 1.3 Components of the observe channel

1.1.3 The Computer

Modern NMR instruments are controlled by a PC or a workstation, commonly based on the Windows-NT, LINUX or UNIX operating system. In addition, one finds a process controller integrated into the spectrometer cabinet. The computing system has, in principle, two different tasks. First, the process controller must have on-line control of many spectrometer functions such as lock, generation and timing of r.f. pulses, digitization and accumulation of the NMR signal (FID, free induction decay). Less time demanding are the other, mainly graphic, tasks in the processing of the NMR spectra. However, the massive amount of data in modern two- or multidimensional NMR spectroscopy techniques requires high storage capacities both on disk and in RAM, and a very high speed of computing.

1.1.4 Maintenance

Although most parts of modern NMR spectrometers are more or less maintenance-free, it is the experience of the authors that careful and regular checking of several components can save considerable money and time. Most important is the regular checking of the cryogens, which should be replenished on a strict schedule. Of course all magnet openings equipped with O-rings have to be carefully monitored. This is especially important for very low temperature work which can lead to icing of the O-rings. Regular checking of several hidden fans within the spectrometer console is advisable.

1.2 Tuning a Probe-Head

With a high field superconducting NMR spectrometer it is essential for obtaining a good signal-to-noise ratio, and for some advanced experiments to get any meaningful results at all, that the probe-head should be correctly tuned to the observe frequency with the particular sample of interest. There can be a huge difference depending on whether a compound is dissolved in water or in an organic solvent.

Although the construction of the resonant circuits of different probe-heads may vary considerably, one has in general two capacitors to adjust, one which tunes the circuit to the desired resonance frequency (tuning) and one which performs the necessary impedance matching of the network (matching). However, these are mutually interactive and therefore they have to be adjusted in turn.

Professionals tune the probe-head with a wobble generator, which, in addition, provides symmetry information about the frequency dependence of the tuning. In currently built NMR spectrometers wobbling functions are programmed in the software, thus making tuning and matching a very easy process which can be followed on the computer screen. This replaces the older routine with a reflection meter or using an oscilloscope. One simply has to obtain the lowest point on resonance of the wobbling curve. Such a curve is shown in Figure 1.4. Very recent probe-heads can be tuned automatically without operator interference.

```
                                            u / stb
 400     nucleus          = 1H              wobble
         sweep width      = 4.000 MHz
         tuning frequency = 200.133 MHz     1 / 1
         actual frequency = 200.122 MHz

 300

 200

 100


      198.5    199.0    199.5    200.0    200.5    201.0    201.5    ; MHz
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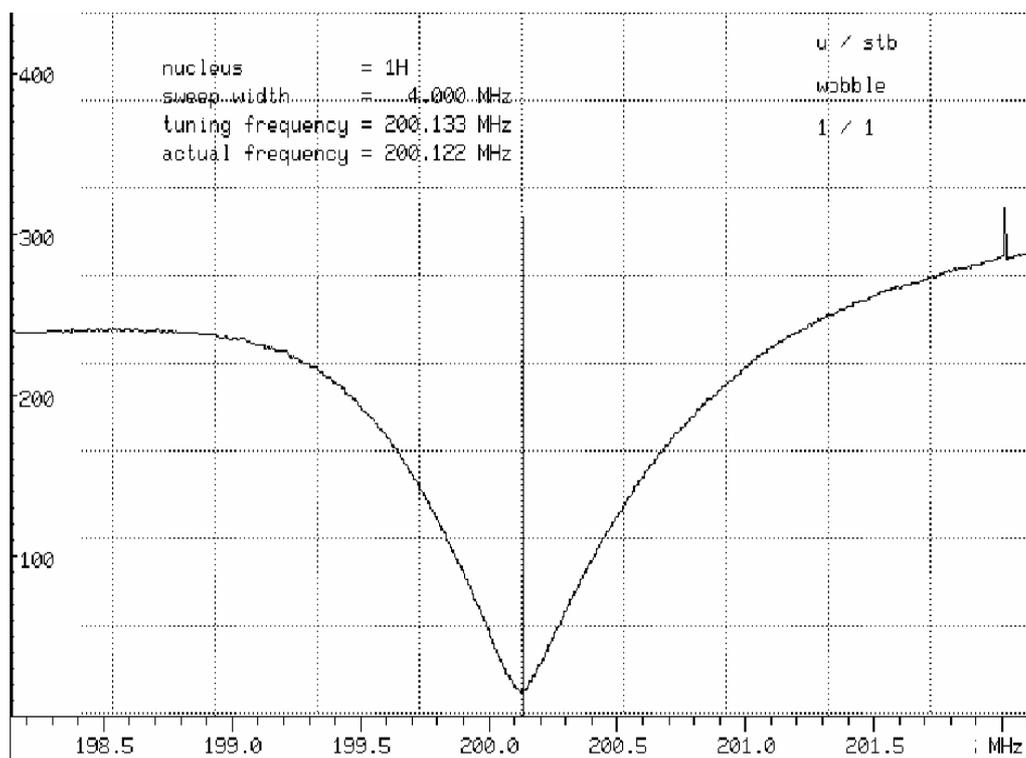
Fig. 1.4 Wobbling curve during probe-head tuning

1.3 The Lock Channel

As neither magnetic fields nor frequencies derived from synthesizers are stable enough for a long period of time, high resolution NMR measurements require a special field/frequency stabilization to allow accumulation of signals, which may be separated by less than one Hz. The basic idea of this stabilization device, called the "lock", is to hold the resonance condition by a separate NMR experiment, which runs parallel to the one in the observe channel. As long as the lock signal is held in resonance the field/frequency relationship is defined also for the observe channel. Figure 1.5 shows the principles of the lock channel.

Usually the ^{2}H resonance of the deuterated solvent is used to provide the NMR lock signal. Thus, an extra ^{2}H lock transmitter is needed, which transmits its frequency in pulsed form to the probe-head, in which the ^{1}H coil is often doubly tuned to both the ^{1}H and ^{2}H frequencies. The deuterium signal is preamplified and processed in the same way as the normal NMR signals in the observe channel. However, the final audio signal is used in dispersion mode to derive a negative or positive control voltage, which regulates the field position. Recent developments employ a so-called digital lock, where the lock i.f. is fed directly into the ADC. The lock signal is displayed on the computer screen and provides a means of shimming the magnet (Section 1.4). This is possible, because a narrower lock signal results in a higher d.c. voltage after rectification. Thus, by adjusting the various shim currents one aims for an optimum lock signal.
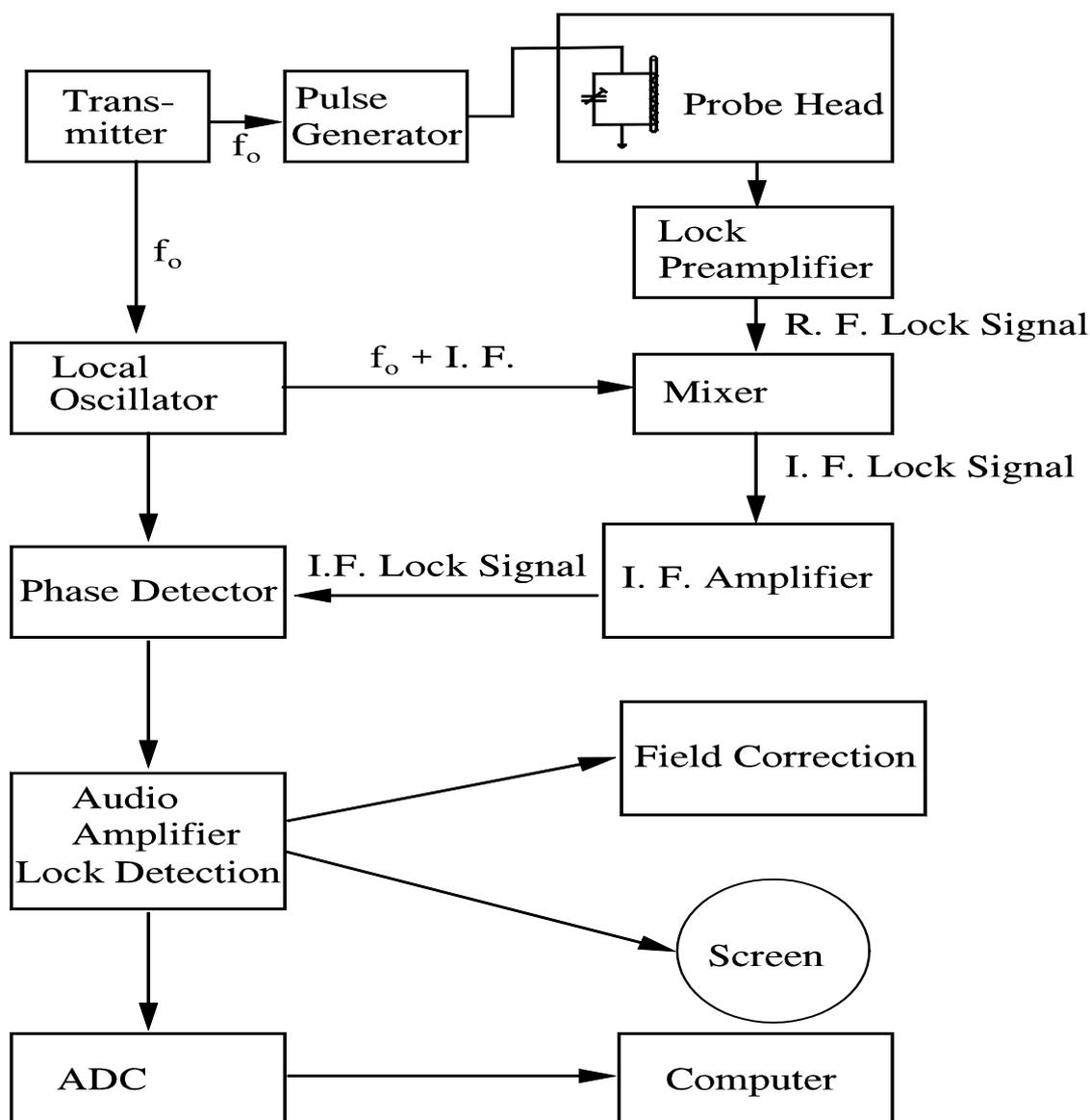
Figure 1.5 Schematic arrangement of the lock channel

For special cases, e.g. for ^{2}H NMR spectroscopy, an ^{19}F lock is used instead of the ^{2}H resonance. The lock substance can be just the solvent, as described above, or may be provided within a capillary for chemical reasons. Special applications, such as probe-heads used as detectors for LC-NMR, use an external lock derived from an extra capillary within the probe-head.

On current NMR instruments, which are equipped with automatic sample changers, the lock capture and lock-in procedure is done by the instrument itself. However, any beginner in the NMR field should first learn how to do it manually. This is the basic start of any NMR experiment and a meaningful shimming procedure is only possible after having properly locked in.

There are several parameters which control the lock display on the computer screen. First, one needs a device to sweep the magnetic field (mostly forward and backward) over the lock resonance position, usually a triangle modulation. Its amplitude and sweep rate can be adjusted. Secondly, the position of the magnetic field must be adjusted to find the lock signal and to fix it at its lock-in position. The r.f. power of the lock transmitter, the gain of the lock receiver, and the phase and d.c. offset of the lock

signal have to be correctly chosen. As for any NMR application, the lock transmitter power should not saturate the signal, and thus the lock transmitter must be sufficiently attenuated. The noise level of the receiver, however, should not be excessive. The lock-in procedure (i. e. pressing the "lock" button) automatically switches off the field sweep and holds the lock signal at its resonance position. After the lock-in procedure the operator should fine-adjust the magnetic field homogeneity by maximizing the lock signal level. Further attenuation adjustment of the transmitter power may be needed to ensure that the lock signal is not saturated.

By locking on a particular solvent signal the software adjusts all dependent offsets automatically using a look-up table, where the chemical shifts of the lock solvents are entered. If, for some reason, one wants to measure NMR spectra without the lock, one must turn off the field modulation manually; however, one has to be aware of the magnet field drift.

1.4 The Art of Shimming

The process of optimizing the magnetic field homogeneity for recording high resolution spectra is called "shimming" a magnet. Usually this is done by observing an NMR signal which has a natural line-width less than 0.1 Hz. This line-width corresponds to a homogeneity of the magnetic field better than 1 ppb for a 500 MHz spectrometer. Adjusting the homogeneity can be performed in different ways, by observing on the computer screen (i) a swept NMR signal (without lock), (ii) the lock level (with locking), or (iii) the FID or the area of the FID on the observe channel. The homogeneity is checked by the procedures described in Experiments 3.3, 3.4, and 3.6.

In the very first days of NMR spectroscopy shimming was performed mechanically (in the original meaning shims are small pieces of metal), but in modern spectrometers an electronic device called the shim system is used for the shimming process. This device is essentially a set of coils controlling very specific magnetic field contours. Because the homogeneity must be maintained over the total volume of NMR observation (probe coil), the shim system is installed in the room-temperature bore of the magnet and surrounds the probe-head and especially the sample region. The currents for the shim coils can create various gradients of any desired strength and shape and can be controlled separately by potentiometers from the spectrometer console. Table 1.1 shows the common room-temperature shims together with their specific functions and their interaction order. There is a second set of shims called cryoshims, which are adjusted during the installation of the magnet.

1.4.1 The Shim Gradients

The different shims are also called shim gradients. One has to adjust the shim currents so that they cancel any gradients in the NMR sample as accurately as possible. There are two types of gradients: spinning ($Z0$–$Z5$) and non-spinning shims where z is the coordinate direction of the field B_o. Spinning the sample averages the field inhomogeneities along two axes but not along the axis about which the sample is spun.

Table 1.1 Common room temperature shims with function and interaction order

Common Shim Name	Function	Gradient order	Inter-action order
Z0	1	0	0
Z1	z	1	0
Z2	$2z^2 - (x^2 + y^2)$	2	1
Z3	$z[2z^2 - 3(x^2 + y^2)]$	3	2
Z4	$8z^2[z^2 - 3(x^2 + y^2)] + 3(x^2 + y^2)^2$	4	2
Z5	$48z^3[z^2 - 5(x^2 + y^2)] + 90z(x^2 + y^2)^2$	5	2
X	x	1	0
Y	y	1	0
ZX	zx	2	2
ZY	zy	2	2
XY	xy	2	1
$X^2 - Y^2$	$x^2 - y^2$	2	1
Z^2X	$x[4z^2 - (x^2 + y^2)]$	3	2
Z^2Y	$y[4z^2 - (x^2 + y^2)]$	3	2
ZXY	zxy	3	2
$Z(X^2 - Y^2)$	$z(x^2 - y^2)$	3	2
X^3	$x(x^2 - 3y^2)$	3	1
Y^3	$y(3x^2 - y^2)$	3	1

Therefore the shim procedure can be divided into two steps: shimming with and shimming without spinning the sample. Usually the sample spinning produces an amplitude modulation of the NMR signal, which gives rise to spinning sidebands on both sides of the signal. The spinning sidebands occur at integer multiples of the spinning frequency and become smaller as the homogeneity increases or the spinning rate is increased. Shimming is not a simple maximization process, because the shims have different gradient order and different interaction order (see Table 1.1). For the shim process you should use sample tubes with a filling height prescribed by the manufacture to avoid vortices. The following classification follows the gradient order. The total number of available shim gradients increases with the magnetic field strength of the magnet:

Zero order: The Z0 shim is the only zero order shim. This is the field position in most instruments.

First order: The Z1, X and Y shims are first order shims. These gradients produce a linear variation of magnetic field strength and have shapes like the p atomic orbitals. They are optimized by a simple maximization process; this corresponds to an interaction order of 0.

Second order: There are five second order shim gradients (see Table 1.1; on older instruments Z2 is called curvature), which have shapes like d atomic orbitals, e.g. Z2

corresponds to the dz^2 orbital. These gradients cause quadratic variations in field strength. For three of them the interaction order is 1, for the other two the interaction order is 2. First order interaction means that the shims are adjusted by a successive iterative process. After the adjustment of the complete set of shims, you have to readjust the first shim of the set and you will find a different optimum. Successive iterations will lead to smaller and smaller changes on readjustment until no further change is observed. A typical example is *Z1* and *Z2*. After optimization of *Z1* followed by *Z2*, you will find a new optimum for *Z1* when readjusted. With an interaction order of 2 you have to change a given shim first and then adjust others before any improvement of the homogeneity can be observed. This means: change the shim a measured amount and optimize the other shims of the set. If this leads to a better response proceed to change the shim in the same direction another measured amount and repeat the process until the response (lock level or FID area) starts to decline. If the initial response is worse try the other direction.

Third order: The complete set of third order shims has seven different gradients corresponding to the shape of the seven f atomic orbitals. A complete set of these gradients is found on 600 and 800 MHz spectrometers. These gradients produce cubic variations of field strength. Usually there is only one 4th order and one 5th order shim gradient on high field instruments.

1.4.2 The Shimming Procedure

In the following shimming procedure, which is described very precisely by Conover [1], it is assumed that the sample is in the center of the shim-set. If this is not the case the center of the shim-set has to be located first. This is done by moving the sample with respect to the receiver coil. Usually the field centering has been performed by the manufacturer's engineer in the course of the installation of the magnet.

First Round

If the magnetic field is in a state of unknown homogeneity or is known to have poor homogeneity, use the swept NMR signal, usually the deuterium lock signal, for the first steps in the shimming process. Otherwise proceed with the second round.

1.   Spin the sample (20 to 30 Hz) and adjust the phase of the lock signal for absorption. The signal-to-noise ratio should be sufficient to allow signal height and the ring-down pattern (wiggles) to be observed. The ring-down pattern can be used for the final adjustment. Adjust *Z1* and *Z2* interactively to produce the tallest swept signal (first order process).
2.   Stop the spinner and adjust *X* and *Y* for the tallest swept signal response (first-order process).
3.   Adjust *X* and *ZX* for the tallest swept signal (second-order process).
4.   Adjust *Y* and *ZY* for the tallest swept signal (second-order process).
5.   Adjust *XY* and *X2 − Y2* for the tallest swept signal (first-order process)

6.   If any large shim changes were observed in the above process then repeat the process from 1. The NMR spectrometer should now be capable of operating with a field-frequency lock.
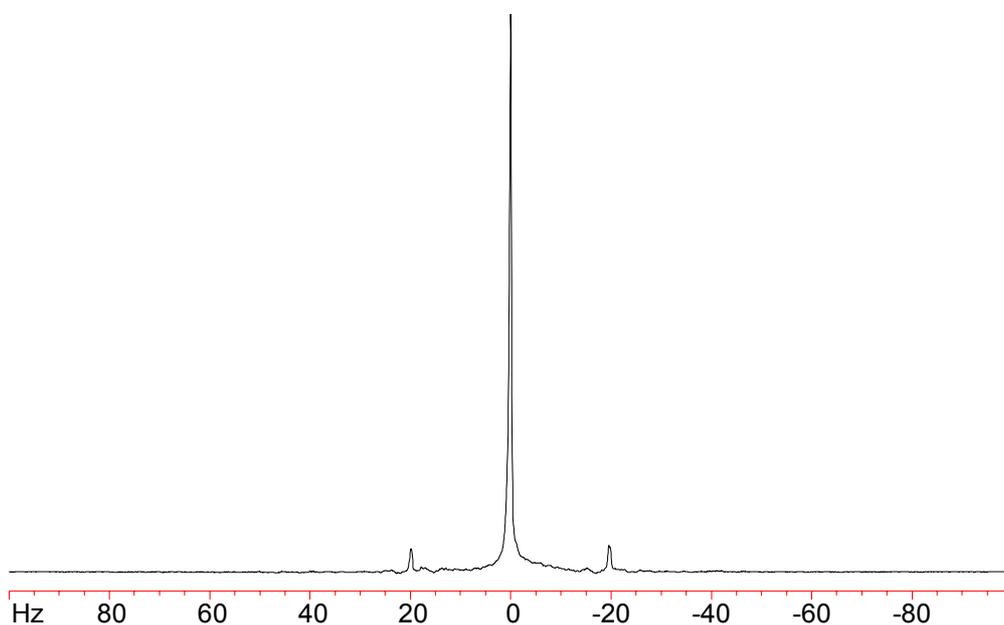
Fig. 1.6 Spinning sidebands obtained after incorrectly setting the X gradient

Second Round (Spinning Shims)

Spin the sample at 20 to 30 Hz, make sure that there is no vortex, especially if using a probe-head for 10 mm sample tubes. A vortex will lead to a false shim optimum, especially for $Z2$. If the lock signal is used for shimming, avoid saturation by using as low a lock power as possible. If the FID or FID area is used for shimming, use a pulse repetition time which is long enough for full relaxation; otherwise the NMR signal is saturated. The lock phase should be carefully adjusted and re-examined each time a large change is made to a shim with an even interaction order [$Z3$, $Z4$, $Z5$, ZX, ZY, Z^2X, Z^2Y, ZXY, $Z(X^2 - Y^2)$].

1.   Optimize $Z1$ and $Z2$ (first order process).
2.   Optimize $Z3$ (second order process). Note the setting of $Z3$ and the response. Change $Z3$ to degrade the response by 20–30%. Repeat the process in step 1. If the new setting for $Z3$ has yielded a better response then continue in the same direction. If the new response is less then try the other direction for $Z3$.
3.   Optimize $Z4$ (second order process). Note the position of $Z4$ and the response. Change $Z4$ to degrade the response by 30–40%. Repeat the process in step 1. Adjust $Z3$ to provide the optimum response. If the $Z3$ shim change is considerable, then repeat step 1 again and readjust $Z3$ for maximum response. If, after optimizing $Z3$, $Z2$, and $Z1$, the new response is better than the previous one, continue in the same direction. If the response is worse then try the other direction.

4.   The $Z5$ shim normally needs to be adjusted only with wide-bore magnets and large-diameter sample tubes. Change $Z5$ enough to degrade the response by 30–50%. Repeat step 1 and reoptimize $Z3$. Adjust $Z4$ for maximum response. If either $Z3$ or $Z4$ changed by a considerable amount, repeat step 1 and reoptimize $Z3$ and $Z4$. If the new response obtained after this procedure is better than before, continue in the same direction. If the response is worse, try the other direction with $Z5$.

| Hz | 40 | 30 | 20 | 10 | 0 | -10 | -20 | -30 | -40 |
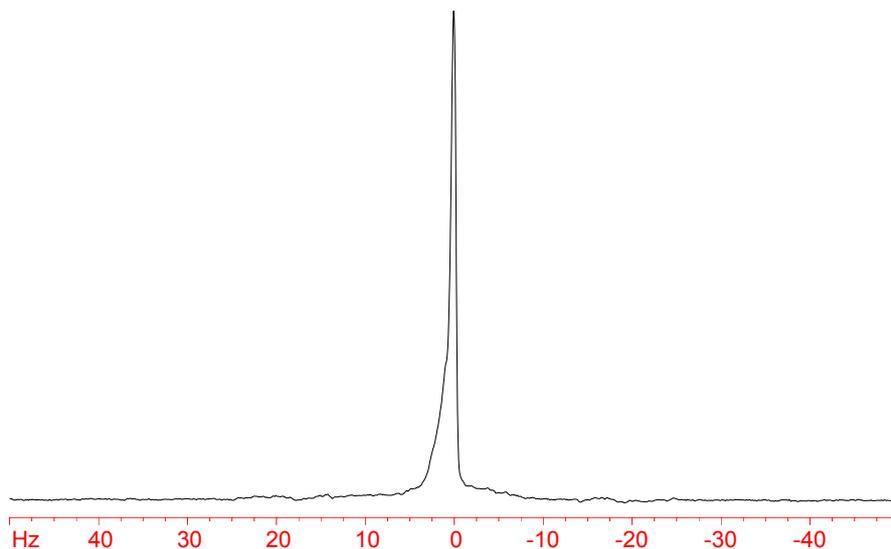
Fig. 1.7 Typical result obtained after incorrectly setting the Z4 gradient

Third Round (Non-Spinning Shims)

This shim-set has to be adjusted while the sample is not spinning. Changing the shim gradients with Z-components causes changes in the spinning shim set. The spinning shim sequence should be repeated after completion of the non-spinning shim procedure, especially if one of the non-spinning shims changes significantly.

1.   Turn the spinner off. Adjust X and Y for maximum response (first-order process).
2.   Note the position of ZX and the response. Change ZX to degrade the response by 10% and adjust X for a maximum response. If the new response is better, continue in the same direction with ZX. If the response is less, try the opposite direction with ZX.
3.   Repeat step 2 but using the Y and ZY shims.
4.   Adjust XY and $X^2 - Y^2$ interactively (first-order process) for maximum response. If either XY or $X^2 - Y^2$ changed significantly then repeat steps 2 and 3.
5.   Adjust Z^2X (second-order process). Note the position of Z^2X and the response. Change Z^2X enough to degrade the response by 30%. Maximize the response with ZX. Optimize the response with X. If the new response is larger than the initial response continue with Z^2X in the same direction. If the response is less then try the other direction.
6.   Repeat step 5 but using Z^2Y, ZY and Y.

7. Adjust *ZXY* (second-order process). Note the position of *ZXY* and the response. Change *ZXY* enough to degrade the response by 20%. Maximize the response with *XY*. If the new response is larger than the initial one, continue with *ZXY* in the same direction. If the response is less, try the other direction.
8. Repeat step 7 but using $Z(X^2 - Y^2)$ and $X^2 - Y^2$.
9. Adjust X^3 and *X* interactively for maximum response (first-order process).
10. Adjust Y^3 and *Y* interactively for maximum response (first-order process).
11. If the non-spinning shim settings have significantly changed, then repeat the second round. If there are significant changes in the spinning shims, repeat the non-spinning shim procedure also.

Final Round

After all spinning and non-spinning shim gradients have been optimized the NMR instrument should be delivering less than 0.5 Hz line-width with a good line-shape (see Exp. 3.5) and minimal spinning sidebands. After all these efforts, the shim settings should be saved electronically.

1.4.3 Gradient Shimming

Recent developments use a probe-head with *x-, y-* and *z*-axis pulsed field gradients. With such a device it is possible to record an image of the homogeneity. With this the computer calculates the required changes for good homogeneity and finds the optimum after a few iterations [3, 4]. This procedure can also be performed with a *z*-only gradient probe-head providing that the shims containing *x* and *y* elements have been adjusted by hand. A more recent method uses a *z*-gradient probe-head to adjust the *z*-shims, but the normal room temperature shim gradients to perform a 3D gradient shimming.

   In practice one starts by generating a field map which indicates how the probe-head in use reacts towards the settings of the shims. This is done with a sample giving a strong signal, usually water. Figure 1.8 shows a typical field map for a *z*-gradient probe-head. On the *x*-axis of the plot the length of the r.f. coil is measured and the *y*-axis gives in relative units the signal response towards changes of the shim settings. The field map has, in principle, to be created only once for each probe head.
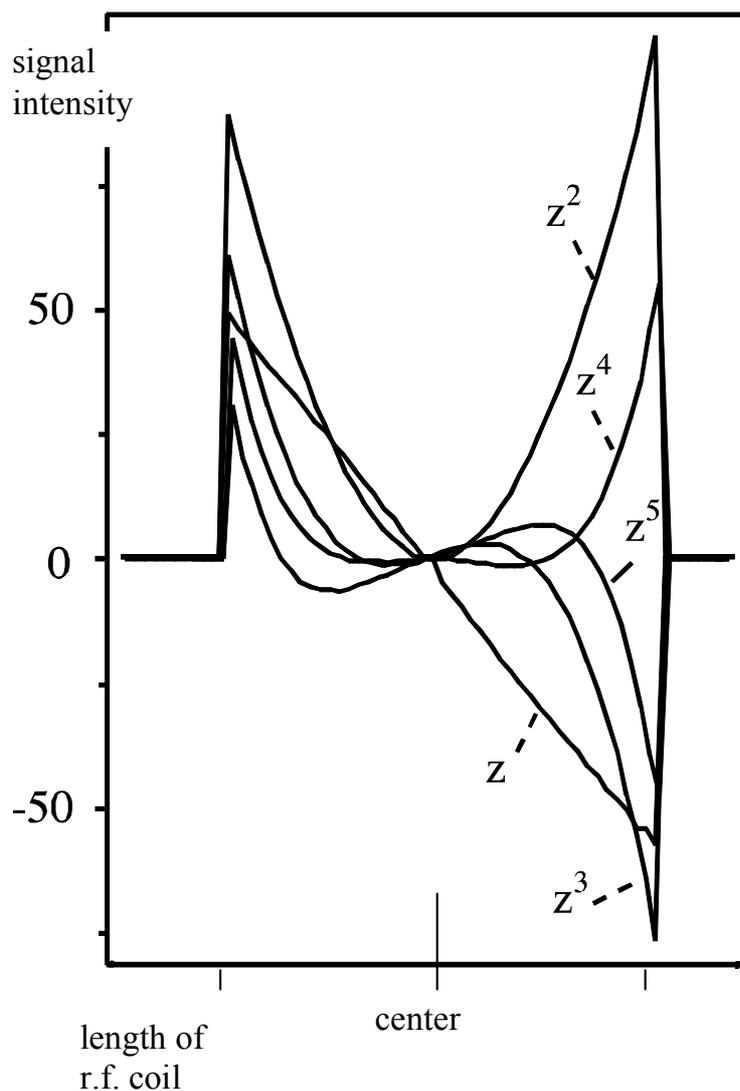
Figure 1.8 Field map obtained with a *z* gradient probe-head

Using the values of the field map the actual shims are adjusted in several iteration steps; again the sample should contain just one strong signal. Since the *x*- and *y*- shim groups do not change too much in practice, the *z*-gradient shimming method is a time-saving approach to obtain very good *z*-shims, especially for biological samples dissolved in water. A typical result depicting the *z*-homogeneity achieved across the sample is shown in Figure 1.9. Note the change in vertical scale compared to Figure 1.8.

Current developments include the gradient shimming on the deuterium lock signal, so that one can use gradient shimming directly on the actual sample. Other developments use selective pulses to generate the shim information from one chosen signal.
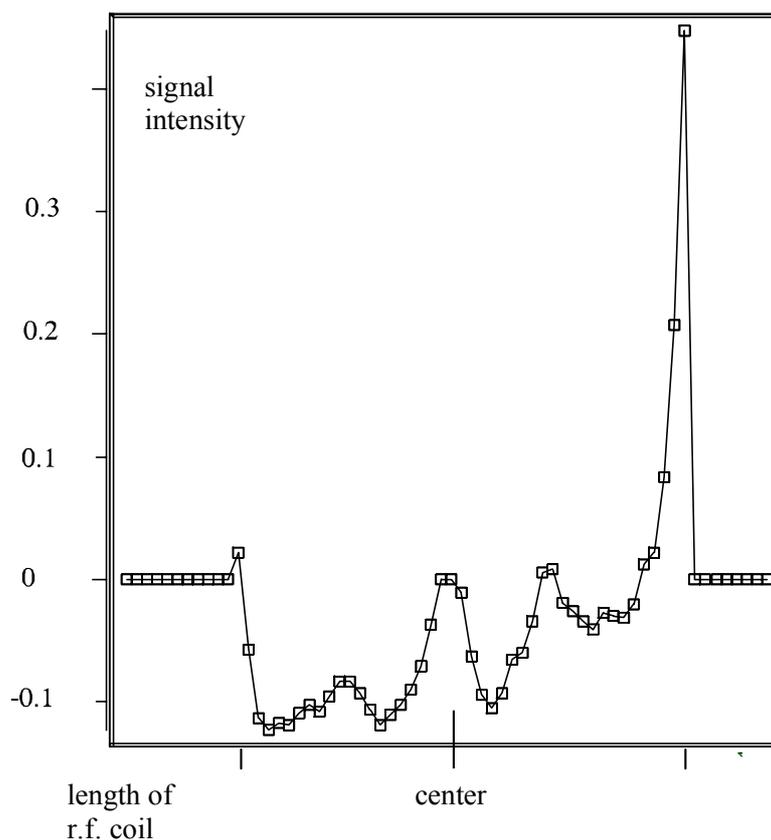
Figure 1.9 *z*-Homogeneity obtained with a *z*-gradient probe-head after gradient shimming

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[4] J. Hu, T. Javaid, F. Arias-Mendoza, Z. Liu, R. McNamara, T. R. Brown, *J. Magn. Reson. Ser. B* **1995**, *108*, 213−219.