4 Fourier transformation and data processing

In the previous chapter we have seen how the precessing magnetization can be detected to give a signal which oscillates at the Larmor frequency – the free induction signal. We also commented that this signal will eventually decay away due to the action of relaxation; the signal is therefore often called the *free induction decay* or FID. The question is how do we turn this signal, which depends on *time*, into the a spectrum, in which the horizontal axis is *frequency*.

This conversion is made using a mathematical process known as *Fourier transformation*. This process takes the *time domain* function (the FID) and converts it into a *frequency domain* function (the spectrum); this is shown in Fig. 4.1. In this chapter we will start out by exploring some features of the spectrum, such as phase and lineshapes, which are closely associated with the Fourier transform and then go on to explore some useful manipulations of NMR data such as sensitivity and resolution enhancement.

4.1 The FID

In section 3.6 we saw that the x and y components of the free induction signal could be computed by thinking about the evolution of the magnetization during the acquisition time. In that discussion we assumed that the magnetization started out along the $-y$ axis as this is where it would be rotated to by a 90° pulse. For the purposes of this chapter we are going to assume that the magnetization starts out along x; we will see later that this choice of starting position is essentially arbitrary.
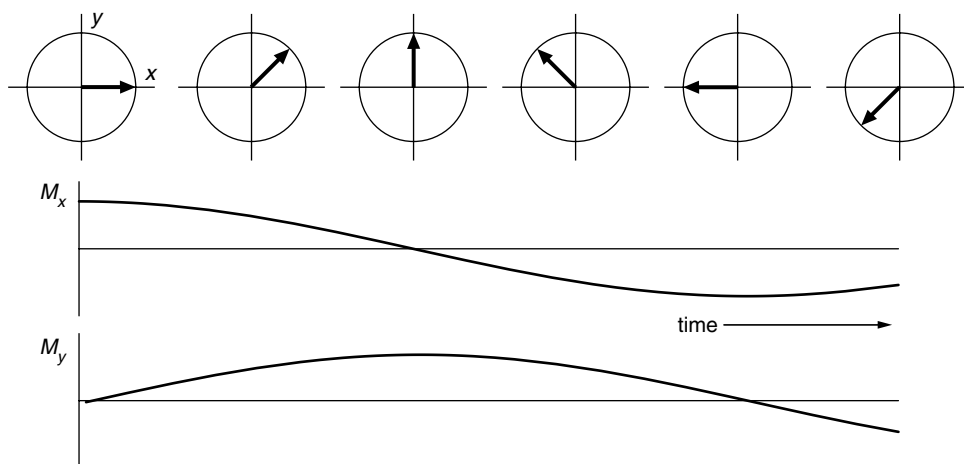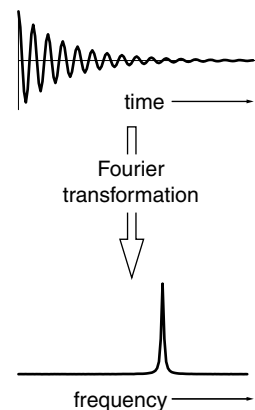

Fig. 4.1 Fourier transformation is the mathematical process which takes us from a function of time (the time domain) – such as a FID – to a function of frequency – the spectrum.
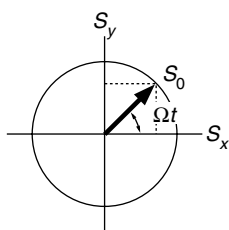

Fig. 4.2 Evolution of the magnetization over time; the offset is assumed to be positive and the magnetization starts out along the *x* axis.

Fig. 4.3 The x and y components of the signal can be thought of as arising from the rotation of a vector S_0 at frequency Ω.

If the magnetization does indeed start along x then Fig. 3.16 needs to be redrawn, as is shown in Fig. 4.2. From this we can easily see that the x and y components of the magnetization are:

$$M_x = M_0 \cos \Omega t$$
$$M_y = M_0 \sin \Omega t.$$

The signal that we detect is proportional to these magnetizations. The constant of proportion depends on all sorts of instrumental factors which need not concern us here; we will simply write the detected x and y signals, $S_x(t)$ and $S_y(t)$ as

$$S_x(t) = S_0 \cos \Omega t \quad \text{and} \quad S_y(t) = S_0 \sin \Omega t$$

where S_0 gives is the overall size of the signal and we have reminded ourselves that the signal is a function of time by writing it as $S_x(t)$ etc.

It is convenient to think of this signal as arising from a vector of length S_0 rotating at frequency Ω; the x and y components of the vector give S_x and S_y, as is illustrated in Fig. 4.3.

As a consequence of the way the Fourier transform works, it is also convenient to regard $S_x(t)$ and $S_y(t)$ as the real and imaginary parts of a complex signal $S(t)$:

$$\begin{aligned} S(t) &= S_x(t) + i\, S_y(t) \\ &= S_0 \cos \Omega t + i\, S_0 \sin \Omega t \\ &= S_0 \exp(i \Omega t). \end{aligned}$$

Fig. 4.4 Illustration of a typical FID, showing the real and imaginary parts of the signal; both decay over time.

We need not concern ourselves too much with the mathematical details here, but just note that the time-domain signal is complex, with the real and imaginary parts corresponding to the x and y components of the signal.

We mentioned at the start of this section that the transverse magnetization decays over time, and this is most simply represented by an exponential decay with a time constant T_2. The signal then becomes

$$S(t) = S_0 \exp(i \Omega t) \exp\left(\frac{-t}{T_2} \right). \tag{4.1}$$

A typical example is illustrated in Fig. 4.4. Another way of writing this is to define a (first order) rate constant $R_2 = 1/T_2$ and so $S(t)$ becomes

$$S(t) = S_0 \exp(i \Omega t) \exp(-R_2 t). \tag{4.2}$$

The shorter the time T_2 (or the larger the rate constant R_2) the more rapidly the signal decays.

4.2 Fourier transformation

Fourier transformation of a signal such as that given in Eq. 4.1 gives the frequency domain signal which we know as the spectrum. Like the time domain signal the frequency domain signal has a real and an imaginary part. The real
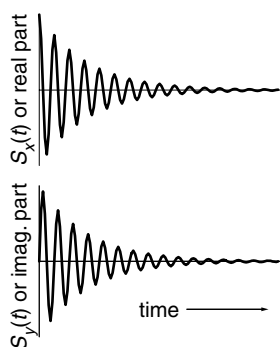
part of the spectrum shows what we call an *absorption mode* line, in fact in the case of the exponentially decaying signal of Eq. 4.1 the line has a shape known as a *Lorentzian*, or to be precise the *absorption mode Lorentzian*. The imaginary part of the spectrum gives a lineshape known as the *dispersion mode Lorentzian*. Both lineshapes are illustrated in Fig. 4.5.
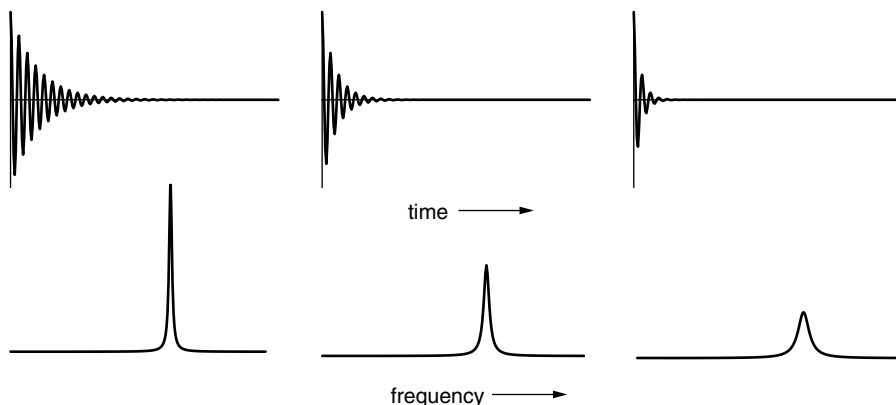

Fig. 4.6 Illustration of the fact that the more rapidly the FID decays the broader the line in the corresponding spectrum. A series of FIDs are shown at the top of the figure and below are the corresponding spectra, all plotted on the same vertical scale. The integral of the peaks remains constant, so as they get broader the peak height decreases.

This absorption lineshape has a width at half of its maximum height of $1/(\pi T_2)$ Hz or (R/π) Hz. This means that the faster the decay of the FID the broader the line becomes. However, the area under the line – that is the integral – remains constant so as it gets broader so the peak height reduces; these points are illustrated in Fig. 4.6.

If the size of the time domain signal increases, for example by increasing S_0 the height of the peak increases in direct proportion. These observations lead to the very important consequence that by integrating the lines in the spectrum we can determine the relative number of protons (typically) which contribute to each.

The dispersion line shape is not one that we would choose to use. Not only is it broader than the absorption mode, but it also has positive and negative parts. In a complex spectrum these might cancel one another out, leading to a great deal of confusion. If you are familiar with ESR spectra you might recognize the dispersion mode lineshape as looking like the *derivative* lineshape which is traditionally used to plot ESR spectra. Although these two lineshapes do look roughly the same, they are not in fact related to one another.

Positive and negative frequencies

As we discussed in section 3.5, the evolution we observe is at frequency Ω i.e. the apparent Larmor frequency in the rotating frame. This offset can be positive or negative and, as we will see later, it turns out to be possible to determine the sign of the frequency. So, in our spectrum we have positive and negative frequencies, and it is usual to plot these with zero in the middle.
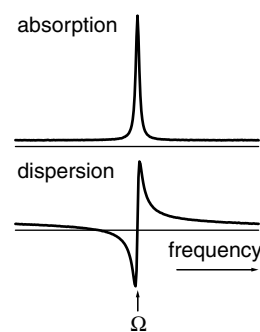

Fig. 4.5 Illustration of the absorption and dispersion mode Lorentzian lineshapes. Whereas the absorption lineshape is always positive, the dispersion lineshape has positive and negative parts; it also extends further.

Several lines

What happens if we have more than one line in the spectrum? In this case, as we saw in section 3.5, the FID will be the sum of contributions from each line. For example, if there are three lines $S(t)$ will be:

$$S(t) = S_{0,1} \exp(i\Omega_1 t) \exp\left(\frac{-t}{T_2^{(1)}}\right)$$
$$+ S_{0,2} \exp(i\Omega_2 t) \exp\left(\frac{-t}{T_2^{(2)}}\right) + S_{0,3} \exp(i\Omega_3 t) \exp\left(\frac{-t}{T_2^{(3)}}\right).$$

where we have allowed each line to have a separate intensity, $S_{0,i}$, frequency, Ω_i, and relaxation time constant, $T_2^{(i)}$.

The Fourier transform is a *linear* process which means that if the time domain is a sum of functions the frequency domain will be a sum of Fourier transforms of those functions. So, as Fourier transformation of each of the terms in $S(t)$ gives a line of appropriate width and frequency, the Fourier transformation of $S(t)$ will be the sum of these lines – which is the complete spectrum, just as we require it.

4.3 Phase

So far we have assumed that at time zero (i.e. at the start of the FID) $S_x(t)$ is a maximum and $S_y(t)$ is zero. However, in general this need not be the case – it might just as well be the other way round or anywhere in between. We describe this general situation be saying that the signal is *phase shifted* or that it has a *phase error*. The situation is portrayed in Fig. 4.7.

In Fig. 4.7 (a) we see the situation we had before, with the signal starting out along x and precessing towards y. The real part of the FID (corresponding to S_x) is a damped cosine wave and the imaginary part (corresponding to S_y) is a damped sine wave. Fourier transformation gives a spectrum in which the real part contains the absorption mode lineshape and the imaginary part the dispersion mode.

In (b) we see the effect of a phase shift, ϕ, of 45°. S_y now starts out at a finite value, rather than at zero. As a result neither the real nor the imaginary part of the spectrum has the absorption mode lineshape; both are a mixture of absorption and dispersion.

In (c) the phase shift is 90°. Now it is S_y which takes the form of a damped cosine wave, whereas S_x is a sine wave. The Fourier transform gives a spectrum in which the absorption mode signal now appears in the imaginary part. Finally in (d) the phase shift is 180° and this gives a negative absorption mode signal in the real part of the spectrum.

What we see is that in general the appearance of the spectrum depends on the position of the signal at time zero, that is on the phase of the signal at time zero. Mathematically, inclusion of this phase shift means that the (complex) signal becomes:

$$S(t) = S_0 \exp(i\phi) \exp(i\Omega t) \exp\left(\frac{-t}{T_2}\right). \tag{4.3}$$
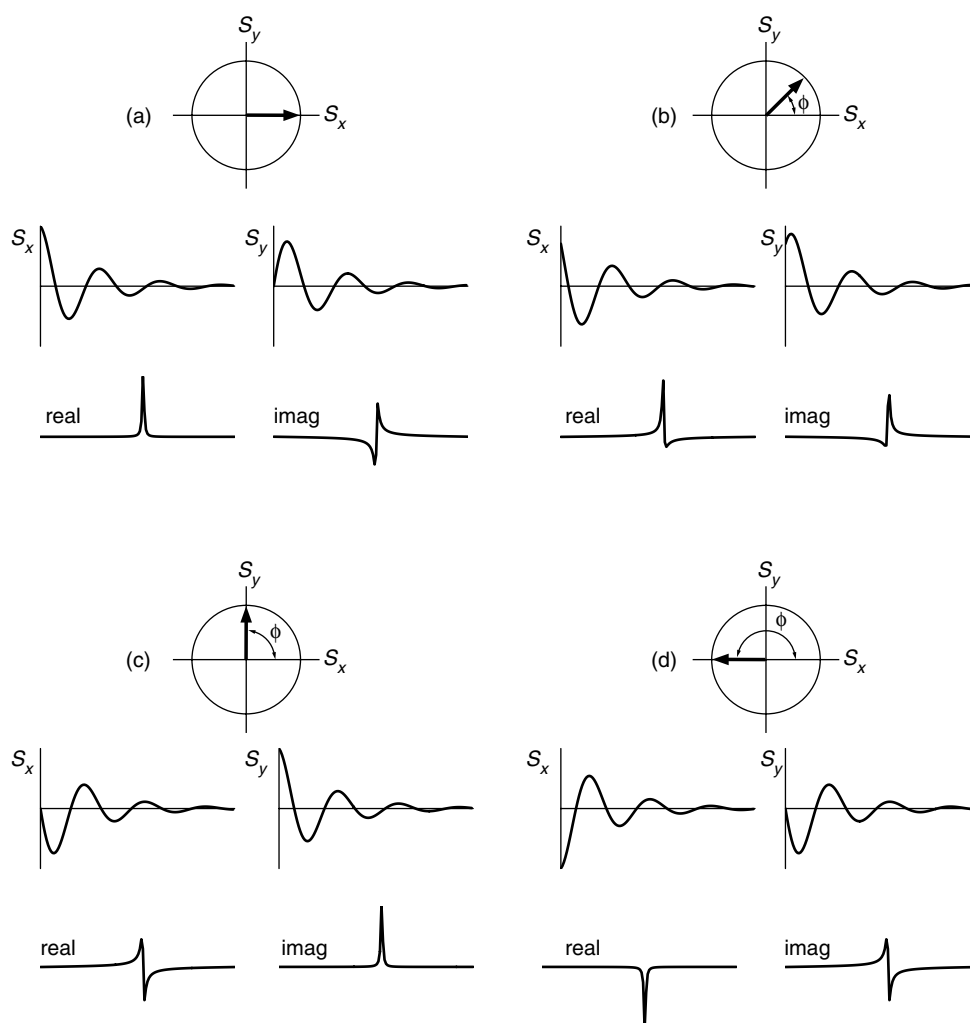
Fig. 4.7 Illustration of the effect of a phase shift of the time domain signal on the spectrum. In (a) the signal starts out along *x* and so the spectrum is the absorption mode in the real part and the dispersion mode in the imaginary part. In (b) there is a phase shift, ϕ, of 45°; the real and imaginary parts of the spectrum are now mixtures of absorption and dispersion. In (c) the phase shift is 90°; now the absorption mode appears in the imaginary part of the spectrum. Finally in (d) the phase shift is 180° giving a negative absorption line in the real part of the spectrum. The vector diagrams illustrate the position of the signal at time zero.

Phase correction

It turns out that for instrumental reasons the axis along which the signal appears cannot be predicted, so in any practical situation there is an unknown phase shift. In general, this leads to a situation in which the real part of the spectrum (which is normally the part we display) does not show a pure absorption lineshape. This is undesirable as for the best resolution we require an absorption mode lineshape.

Luckily, restoring the spectrum to the absorption mode is easy. Suppose with take the FID, represented by Eq. 4.3, and multiply it by $\exp(i\phi_{\text{corr}})$:

$$\exp(i\phi_{\text{corr}})S(t) = \exp(i\phi_{\text{corr}}) \times \left[S_0 \exp(i\phi)\exp(i\Omega t)\exp\left(\frac{-t}{T_2}\right) \right].$$

This is easy to do as by now the FID is stored in computer memory, so the

multiplication is just a mathematical operation on some numbers. Exponentials have the property that $\exp(A)\exp(B) = \exp(A + B)$ so we can re-write the time domain signal as

$$\exp(i\phi_{\text{corr}})S(t) = \exp(i(\phi_{\text{corr}} + \phi))\left[S_0 \exp(i\Omega t)\exp\left(\frac{-t}{T_2}\right)\right].$$

Now suppose that we set $\phi_{\text{corr}} = -\phi$; as $\exp(0) = 1$ the time domain signal becomes:

$$\exp(i\phi_{\text{corr}})S(t) = S_0 \exp(i\Omega t)\exp\left(\frac{-t}{T_2}\right).$$

The signal now has no phase shift and so will give us a spectrum in which the real part shows the absorption mode lineshape – which is exactly what we want. All we need to do is find the correct ϕ_{corr}.

It turns out that the phase correction can just as easily be applied to the spectrum as it can to the FID. So, if the spectrum is represented by $S(\omega)$ (a function of frequency, ω) the phase correction is applied by computing

$$\exp(i\phi_{\text{corr}})S(\omega).$$

Such a correction is called a *frequency independent* or *zero order* phase correction as it is the same for all peaks in the spectrum, regardless of their offset.

In practice what happens is that we Fourier transform the FID and display the real part of the spectrum. We then adjust the phase correction (i.e. the value of ϕ_{corr}) until the spectrum appears to be in the absorption mode – usually this adjustment is made by turning a knob or by a "click and drag" operation with the mouse. The whole process is called *phasing the spectrum* and is something we have to do each time we record a spectrum.

In addition to the phase shifts introduced by the spectrometer we can of course deliberately introduce a shift of phase by, for example, altering the phase of a pulse. In a sense it does not matter what the phase of the signal is – we can always obtain an absorption spectrum by phase correcting the spectrum later on.

Frequency dependent phase errors

We saw in section 3.11 that if the offset becomes comparable with the RF field strength a 90° pulse about x results in the generation of magnetization along both the x and y axes. This is in contrast to the case of a hard pulse, where the magnetization appears only along $-y$. We can now describe this mixture of x and y magnetization as resulting in a *phase shift* or *phase error* of the spectrum.

Figure 3.25 illustrates very clearly how the x component increases as the offset increases, resulting in a phase error which also increases with offset. Therefore lines at different offsets in the spectrum will have different phase errors, the error increasing as the offset increases. This is illustrated schematically in the upper spectrum shown in Fig. 4.8.

If there were only one line in the spectrum it would be possible to ensure that the line appeared in the absorption mode simply by adjusting the phase
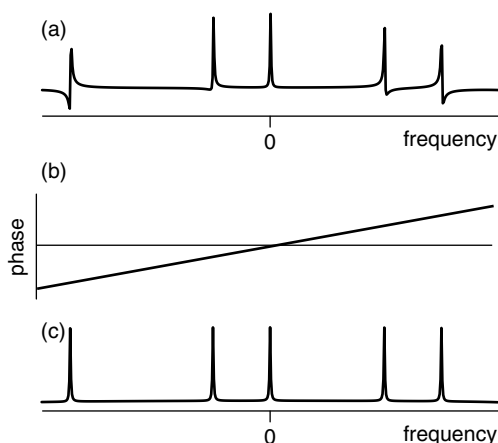
Fig. 4.8 Illustration of the appearance of a frequency dependent phase error in the spectrum. In (a) the line which is on resonance (at zero frequency) is in pure absorption, but as the offset increases the phase error increases. Such an frequency dependent phase error would result from the use of a pulse whose RF field strength was not much larger than the range of offsets. The spectrum can be returned to the absorption mode, (c), by applying a phase correction which varies with the offset in a linear manner, as shown in (b). Of course, to obtain a correctly phased spectrum we have to choose the correct slope of the graph of phase against offset.

in the way described above. However, if there is more than one line present in the spectrum the phase correction for each will be *different*, and so it will be impossible to phase all of the lines at once.

Luckily, it is often the case that the phase correction needed is directly proportional to the offset – called a *linear* or *first order* phase correction. Such a variation in phase with offset is shown in Fig. 4.8 (b). All we have to do is to vary the rate of change of phase with frequency (the slope of the line) until the spectrum appears to be phased; as with the zero-order phase correction the computer software usually makes it easy for us to do this by turning a knob or pushing the mouse. In practice, to phase the spectrum correctly usually requires some iteration of the zero- and first-order phase corrections.

The usual convention is to express the frequency dependent phase correction as the value that the phase takes at the extreme edges of the spectrum. So, for example, such a correction by $100°$ means that the phase correction is zero in the middle (at zero offset) and rises linearly to $+100°$ at on edge and falls linearly to $-100°$ at the opposite edge.

For a pulse the phase error due to these off-resonance effects for a peak with offset Ω is of the order of (Ωt_p), where t_p is the length of the pulse. For a carbon-13 spectrum recorded at a Larmor frequency of 125 MHz, the maximum offset is about 100 ppm which translates to 12500 Hz. Let us suppose that the $90°$ pulse width is 15 μs, then the phase error is

$$2\pi \times 12500 \times 15 \times 10^{-6} \approx 1.2 \text{ radians}$$

which is about $68°$; note that in the calculation we had to convert the offset from Hz to rad s^{-1} by multiplying by 2π. So, we expect the frequency dependent phase error to vary from zero in the middle of the spectrum (where the offset is zero) to $68°$ at the edges; this is a significant effect.

For reasons which we cannot go into here it turns out that the linear phase

correction is sometimes only a first approximation to the actual correction needed. Provided that the lines in the spectrum are sharp a linear correction works very well, but for broad lines it is not so good. Attempting to use a first-order phase correction on such spectra often results in distortions of the baseline.

4.4 Sensitivity enhancement

Inevitably when we record a FID we also record noise at the same time. Some of the noise is contributed by the amplifiers and other electronics in the spectrometer, but the major contributor is the thermal noise from the coil used to detect the signal. Reducing the noise contributed by these two sources is largely a technical matter which will not concern use here. NMR is not a sensitive technique, so we need to take any steps we can to improve the signal-to-noise ratio in the spectrum. We will see that there are some manipulations we can perform on the FID which will give us some improvement in the signal-to-noise ratio (SNR).

By its very nature, the FID decays over time but in contrast the noise just goes on and on. Therefore, if we carry on recording data for long after the FID has decayed we will just measure noise and no signal. The resulting spectrum will therefore have a poor signal-to-noise ratio.
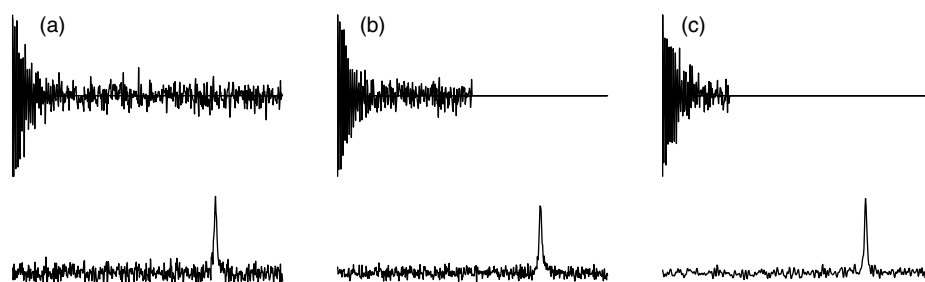

Fig. 4.9 Illustration of the effect of the time spent acquiring the FID on the signal-to-noise ratio (SNR) in the spectrum. In (a) the FID has decayed to next to nothing within the first quarter of the time, but the noise carries on unabated for the whole time. Shown in(b) is the effect of halving the time spent acquiring the data; the SNR improves significantly. In (c) we see that taking the first quarter of the data gives a further improvement in the SNR.

This point is illustrated in Fig. 4.9 where we see that by recording the FID for long after it has decayed all we end up doing is recording more noise and no signal. Just shortening the time spent recording the signal (called the *acquisition time*) will improve the SNR since more or less all the signal is contained in the early part of the FID. Of course, we must not shorten the acquisition time too much or we will start to miss the FID, which would result in a reduction in SNR.

Sensitivity enhancement

Looking at the FID we can see that at the start the signal is strongest. As time progresses, the signal decays and so gets weaker but the noise remains at the same level. The idea arises, therefore, that the early parts of the FID are

"more important" as it is here where the signal is the strongest.

This effect can be exploited by deliberately multiplying the FID by a function which starts at 1 and then steadily tails away to zero. The idea is that this function will cut off the later parts of the FID where the signal is weakest, but leave the early parts unaffected.
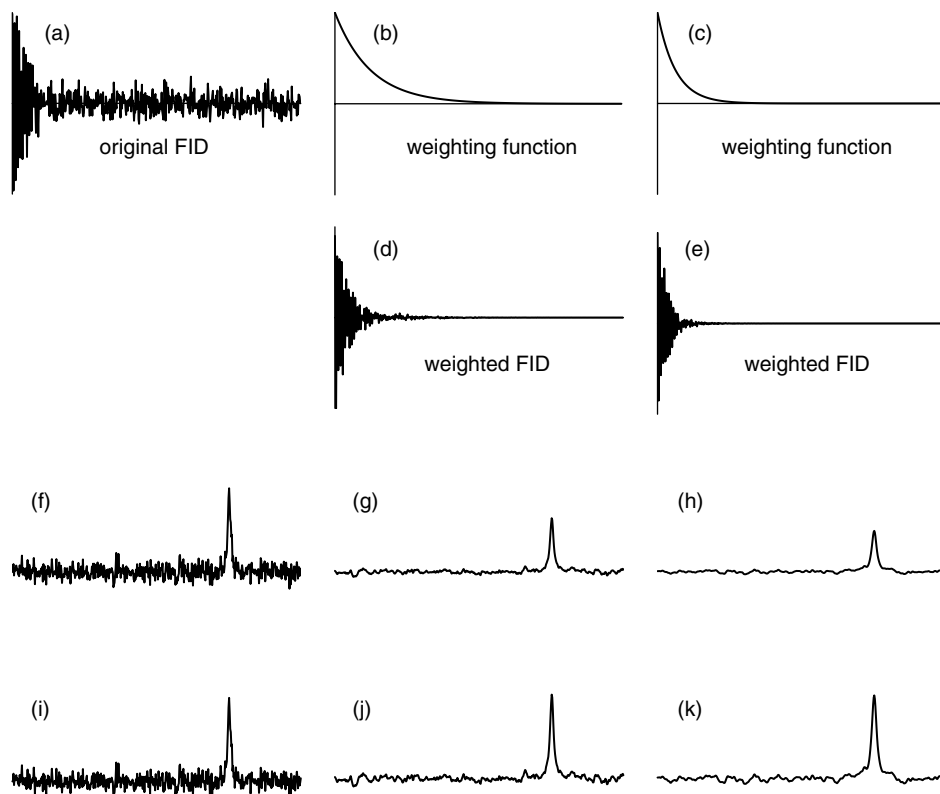

Fig. 4.10 Illustration of how multiplying a FID by a decaying function (a weighting function) can improve the SNR. The original FID is shown in (a) and the corresponding spectrum is (f). Multiplying the FID by a weighting function (b) gives (c); Fourier transformation of (c) gives the spectrum (g). Note the improvement in SNR of (g) compared to (f). Multiplying (a) by the more rapidly decaying weighting function (d) gives (e); the corresponding spectrum is (h). The improvement in SNR is less marked. Spectra (f) – (h) are all plotted on the same vertical scale so that the decrease in peak height can be seen. The same spectra are plotted in (i) – (k) but this time normalized so that the peak height is the same; this shows most clearly the improvement in the SNR.

A typical choice for this function – called a *weighting function* – is an exponential:

$$W(t) = \exp(-R_{\mathrm{LB}}t) \tag{4.4}$$

where R_{LB} is a rate constant which we are free to choose. Figure 4.10 illustrates the effect on the SNR of different choices of this decay constant.

Spectrum (g) shows a large improvement in the SNR when compared to spectrum (f) simply because the long tail of noise is suppressed. Using a more rapidly decaying weighting function, (d), gives a further small improvement in the SNR (h). It should not be forgotten that the weighting function also acts on the signal, causing it to decay more quickly. As was explained in section 4.2 a more rapidly decaying signal leads to a broader line. So, the use

of the weighting function will not only attenuate the noise it will also broaden the lines; this is clear from Fig. 4.10.

Broadening the lines also reduces the peak height (remember that the integral remains constant) – something that is again evident from Fig. 4.10. Clearly, this reduction in peak height will reduce the SNR. Hence there is a trade-off we have to make: the more rapidly decaying the weighting function the more the noise in the tail of the FID is attenuated thus reducing the noise level in the spectrum. However, at the same time a more rapidly decaying function will cause greater line broadening, and this will reduce the SNR. It turns out that there is an optimum weighting function, called the *matched filter*.

Matched filter

Suppose that the FID can be represented by the exponentially decaying function introduced in Eq. 4.2:

$$S(t) = S_0 \exp(i\Omega t) \exp(-R_2 t).$$

The line in the corresponding spectrum is of width (R_2/π) Hz. Let us apply a weighting function of the kind described by Eq. 4.4 i.e. a decaying exponential:

$$W(t) \times S(t) = \exp(-R_{\mathrm{LB}} t) \left[S_0 \exp(i\Omega t) \exp(-R_2 t) \right].$$

The decay due to the weighting function on its own would give a linewidth of (R_{LB}/π) Hz. Combining the two terms describing the exponential decays gives

$$W(t) \times S(t) = S_0 \exp(i\Omega t) \exp\left(-(R_{\mathrm{LB}} + R_2)t\right).$$

From this we see that the weighted FID will give a linewidth of

$$(R_{\mathrm{LB}} + R_2)/\pi.$$

In words, the linewidth in the spectrum is the sum of the linewidths in the original spectrum and the additional linebroadening imposed by the weighting function.

It is usual to specify the weighting function in terms of the extra line broadening it will cause. So, a "linebroadening of 1 Hz" is a function which will increase the linewidth in the spectrum by 1 Hz. For example if 5 Hz of linebroadening is required then $(R_{\mathrm{LB}}/\pi) = 5$ giving $R_{\mathrm{LB}} = 15.7 \ \mathrm{s}^{-1}$.

It can be shown that the best SNR is obtained by applying a weighting function which matches the linewidth in the original spectrum – such a weighting function is called a *matched filter*. So, for example, if the linewidth is 2 Hz in the original spectrum, applying an additional line broadening of 2 Hz will give the optimum SNR.

We can see easily from this argument that if there is a range of linewidths in the spectrum we cannot find a value of the linebroadening which is the optimum for all the peaks. Also, the extra line broadening caused by the matched filter may not be acceptable on the grounds of the decrease in resolution it causes. Under these circumstances we may choose to use sufficient line broadening to cut off the excess noise in the tail of the FID, but still less than the matched filter.

4.5 Resolution enhancement

We noted in section 4.2 that the more rapidly the time domain signal decays the broader the lines become. A weighting function designed to improve the SNR inevitably leads to a broadening of the lines as such a function hastens the decay of the signal. In this section we will consider the opposite case, where the weighting function is designed to *narrow* the lines in the spectrum and so increase the resolution.

The basic idea is simple. All we need to do is to multiply the FID by a weighting function which *increases* with time, for example a rising exponential:

$$W(t) = \exp(+R_{RE}t) \quad R_{RE} > 0.$$

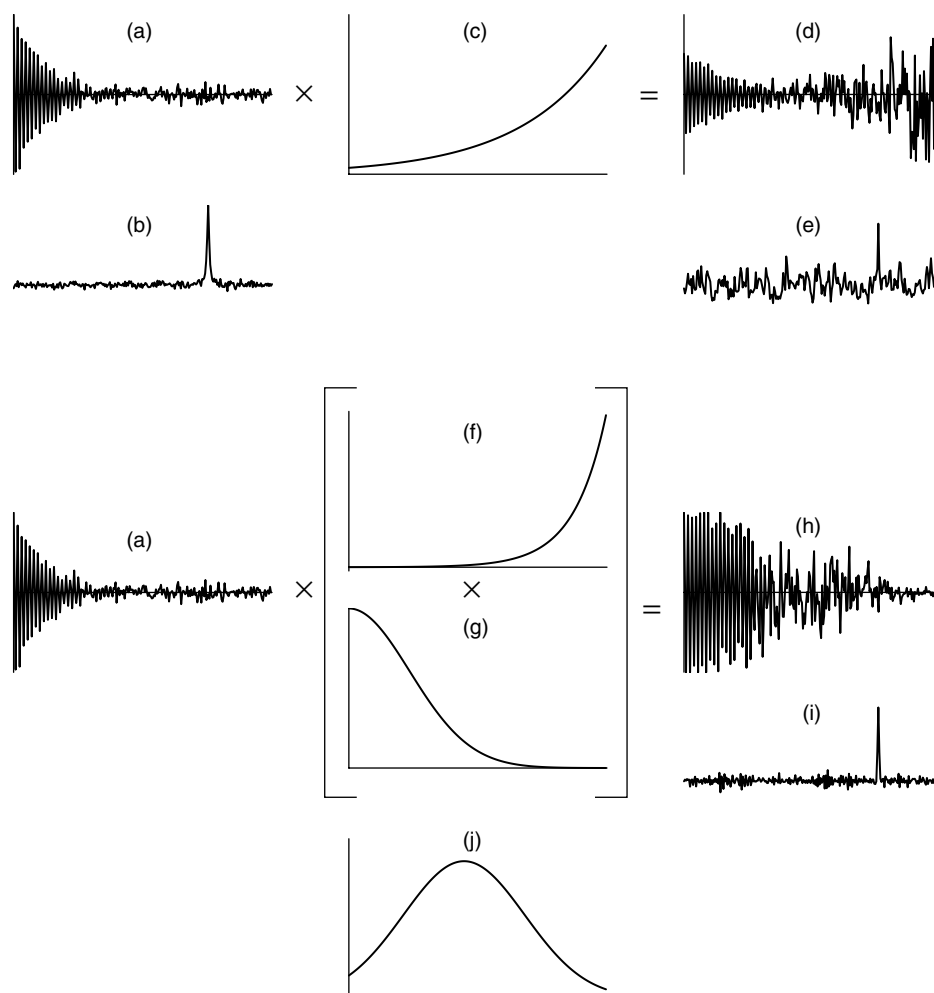This function starts at 1 when $t = 0$ and then rises indefinitely.

Fig. 4.11 Illustration of the use of weighting functions to enhance the resolution in the spectrum. Note that the scales of the plots have been altered to make the relevant features clear. See text for details.

The problem with multiplying the FID with such a function is that the noise in the tail of the FID is amplified, thus making the SNR in the spectrum very poor indeed. To get round this it is, after applying the positive exponential we multiply by a second decaying function to "clip" the noise at the

tail of the FID. Usually, the second function is chosen to be one that decays relatively slowly over most of the FID and then quite rapidly at the end – a common choice is the Gaussian function:

$$W(t) = \exp(-\alpha t^2),$$

where α is a parameter which sets the decay rate. The larger α, the faster the decay rate.

The whole process is illustrated in Fig. 4.11. The original FID, (a), contains a significant amount of noise and has been recorded well beyond the point where the signal decays into the noise. Fourier transformation of (a) gives the spectrum (b). If (a) is multiplied by the rising exponential function plotted in (c), the result is the FID (d); note how the decay of the signal has been slowed, but the noise in the tail of the FID has been greatly magnified. Fourier transformation of (d) gives the spectrum (e); the resolution has clearly been improved, but at the expense of a large reduction in the SNR.

Referring now to the bottom part of Fig. 4.11 we can see the effect of introducing a Gaussian weighting function as well. The original FID (a) is multiplied by the rising exponential (f) and the decaying Gaussian (g); this gives the time-domain signal (h). Note that once again the signal decay has been slowed, but the noise in the tail of the FID is not as large as it is in (d). Fourier transformation of (h) gives the spectrum (i); the resolution has clearly been improved when compared to (b), but without too great a loss of SNR.

Finally, plot (j) shows the product of the two weighting functions (f) and (g). We can see clearly from this plot how the two functions combine together to first increase the time-domain function and then to attenuate it at longer times. Careful choice of the parameters R_{RE} and α are needed to obtain the optimum result. Usually, a process of trial and error is adopted.

If we can set R_{RE} to cancel exactly the original decay of the FID then the result of this process is to generate a time-domain function which only has a Gaussian decay. The resulting peak in the spectrum will have a Gaussian lineshape, which is often considered to be superior to the Lorentzian as it is narrower at the base; the two lineshapes are compared in Fig. 4.12. This transformation to a Gaussian lineshape is often called the *Lorentz-to-Gauss* transformation.

Parameters for the Lorentz-to-Gauss transformation

The combined weighting function for this transformation is

$$W(t) = \exp(R_{\text{RE}}t)\exp(-\alpha t^2).$$

The usual approach is to specify R_{RE} in terms of the linewidth that it would create on its own if it were used to specify a *decaying* exponential. Recall that in such a situation the linewidth, L, is given by R_{RE}/π. Thus $R_{\text{RE}} = \pi L$. The weighting function can therefore be rewritten

$$W(t) = \exp(-\pi L t)\exp(-\alpha t^2).$$

For compatibility with the linebroadening role of a decaying exponential it is usual to define the exponential weighting function as $\exp(-\pi L t)$ so that
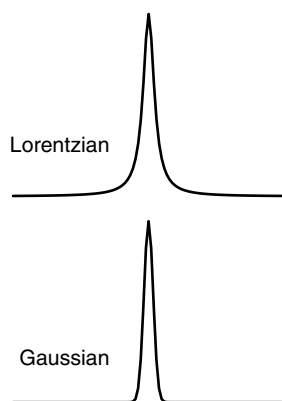

Fig. 4.12 Comparison of the Lorentzian and Gaussian lineshapes; the two peaks have been adjusted so that their peak heights and widths at half height are equal. The Gaussian is a more "compact" lineshape.

a positive value for L leads to line broadening and a negative value leads to resolution enhancement.

From Fig. 4.11 (j) we can see that the effect of the rising exponential and the Gaussian is to give an overall weighting function which has a maximum in it. It is usual to define the Gaussian parameter α from the position of this maximum. A little mathematics shows that this maximum occurs at time t_{max} given by:

$$t_{max} = -\frac{L\pi}{2\alpha}$$

(recall that L is negative) so that

$$\alpha = -\frac{L\pi}{2t_{max}}.$$

We simply select a value of t_{max} and use this to define the value of α. On some spectrometers, t_{max} is expressed as a fraction, f, of the acquisition time, t_{acq}: $t_{max} = f t_{acq}$. In this case

$$\alpha = -\frac{L\pi}{2f t_{acq}}.$$

4.6 Other weighting functions

Many other weighting functions have been used for sensitivity enhancement and resolution enhancement. Perhaps the most popular are the *sine bell* are variants on it, which are illustrated in Fig. 4.13.
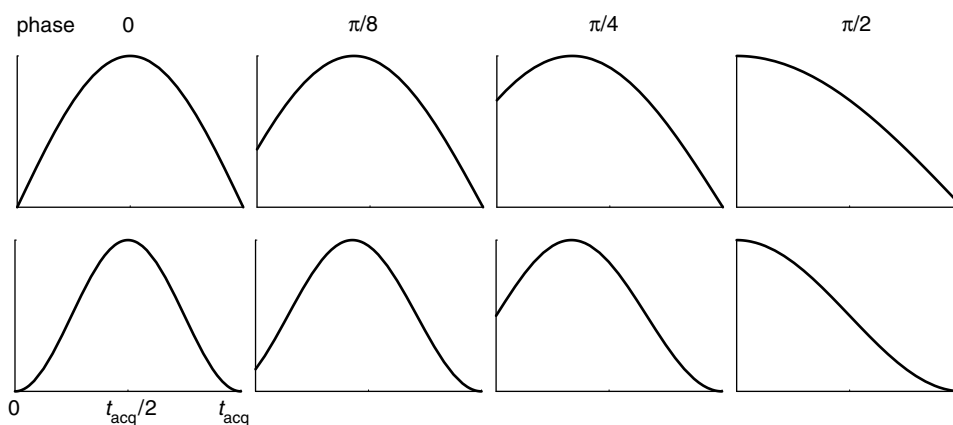

Fig. 4.13 The top row shows sine bell and the bottom row shows sine bell squared weighting functions for different choices of the phase parameter; see text for details.

The basic sine bell is just the first part of a $\sin\theta$ for $\theta = 0$ to $\theta = \pi$; this is illustrated in the top left-hand plot of Fig. 4.13. In this form the function will give resolution enhancement rather like the combination of a rising exponential and a Gaussian function (compare Fig. 4.11 (j)). The weighting function is chosen so that the sine bell fits exactly across the acquisition time; mathematically the required function is:

$$W(t) = \sin\left(\frac{\pi t}{t_{acq}}\right).$$

The sine bell can be modified by shifting it the left, as is shown in Fig. 4.13. The further the shift to the left the smaller the resolution enhancement effect will be, and in the limit that the shift is by $\pi/2$ or $90°$ the function is simply a decaying one and so will broaden the lines. The shift is usually expressed in terms of a phase ϕ (in radians); the resulting weighting function is:

$$W(t) = \sin\left(\frac{(\pi - \phi)t}{t_{\text{acq}}} + \phi\right).$$

Note that this definition of the function ensures that it goes to zero at t_{acq}.

The shape of all of these weighting functions are altered subtly by squaring them to give the *sine bell squared* functions; these are also shown in Fig. 4.13. The weighting function is then

$$W(t) = \sin^2\left(\frac{(\pi - \phi)t}{t_{\text{acq}}} + \phi\right).$$

Much of the popularity of these functions probably rests of the fact that there is only one parameter to adjust, rather than two in the case of the Lorentz-to-Gauss transformation.

4.7 Zero filling

Before being processed the FID must be converted into a digital form so that it can be stored in computer memory. We will have more to say about this in Chapter 5 but for now we will just note that in this process the signal is sampled at regular intervals. The FID is therefore represented by a series of *data points*. When the FID is Fourier transformed the spectrum is also represented by a series of data points. So, although we plot the spectrum as a smooth line, it is in fact a series of closely spaced points.
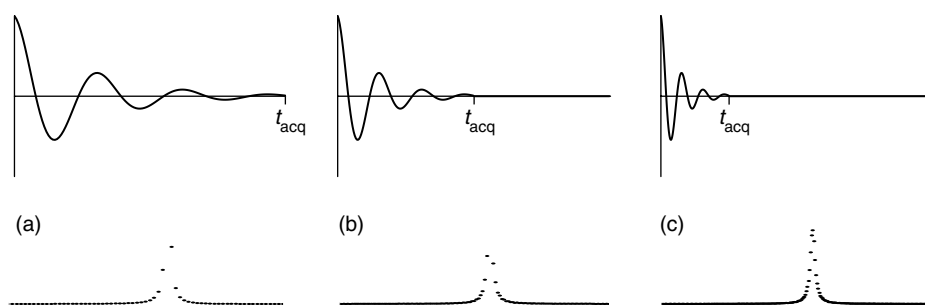

Fig. 4.14 Illustration of the results of zero filling. The FIDs along the top row have been supplemented with increasing numbers of zeroes and so contain more and more data points. Fourier transformation preserves the number of data points so the line in the spectrum is represented by more points as zeroes are added to the end of the FID. Note that the FID remains the same for all three cases; no extra data has been acquired.

This is illustrated in Fig. 4.14 (a) which shows the FID and the corresponding spectrum; rather than joining up the points which make up the spectrum we have just plotted the points. We can see that there are only a few data points which define the line in the spectrum.

If we take the original FID and add an equal number of zeroes to it, the corresponding spectrum has double the number of points and so the line is represented by more data points. This is illustrated in Fig. 4.14 (b). Adding a set of zeroes equal to the number of data points is called "one zero filling".

We can carry on with this zero filling process. For example, having added one set of zeroes, we can add another to double the total number of data points ("two zero fillings"). This results in an even larger number of data points defining the line, as is shown in Fig. 4.14 (c).

Zero filling costs nothing in the sense that no extra data is required; it is just a manipulation in the computer. Of course, it does not improve the resolution as the measured signal remains the same, but the lines will be better defined in the spectrum. This is desirable, at least for aesthetic reasons if nothing else!

It turns out that the Fourier transform algorithm used by computer programs is most suited to a number of data points which is a power of 2. So, for example, $2^{14} = 16384$ is a suitable number of data points to transform, but 15000 is not. In practice, therefore, it is usual to zero fill the time domain data so that the total number of points is a power of 2; it is always an option, of course, to zero fill beyond this point.

4.8   Truncation

In conventional NMR it is virtually always possible to record the FID until it has decayed almost to zero (or into the noise). However, in multi-dimensional NMR this may not be the case, simply because of the restrictions on the amount of data which can be recorded, particularly in the "indirect dimension" (see Chapter X for further details). If we stop recording the signal before it has fully decayed the FID is said to be "truncated"; this is illustrated in Fig. 4.15.
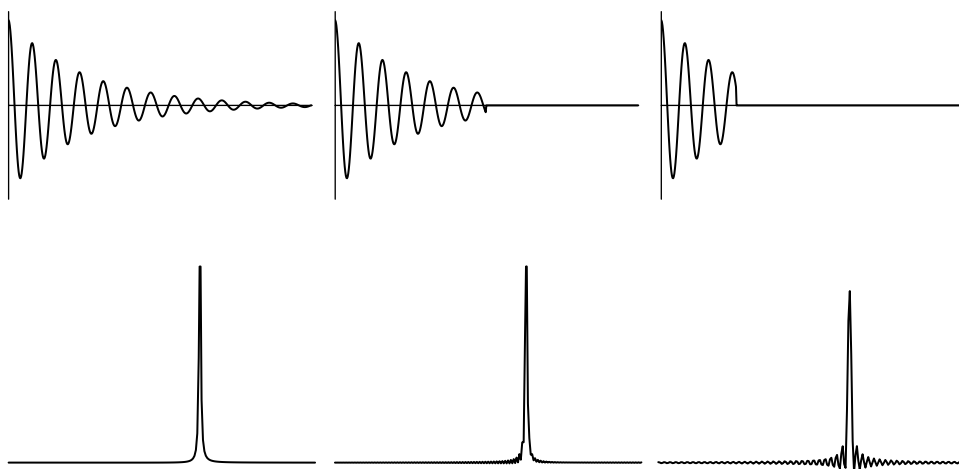

Fig. 4.15 Illustration of how truncation leads to artefacts (called *sinc wiggles*) in the spectrum. The FID on the left has been recorded for sufficient time that it has decayed almost the zero; the corresponding spectrum shows the expected lineshape. However, if data recording is stopped before the signal has fully decayed the corresponding spectra show oscillations around the base of the peak.

As is shown clearly in the figure, a truncated FID leads to oscillations around the base of the peak; these are usually called *sinc wiggles* or *truncation artefacts* – the name arises as the peak shape is related to a sinc function. The more severe the truncation, the larger the sinc wiggles. It is easy to show that the separation of successive maxima in these wiggles is $1/t_{\mathrm{acq}}$ Hz.

Clearly these oscillations are undesirable as they may obscure nearby weaker peaks. Assuming that it is not an option to increase the acquisition time, the way forward is to apply a decaying weighting function to the FID so as to force the signal to go to zero at the end. Unfortunately, this will have the side effects of broadening the lines and reducing the SNR.

Highly truncated time domain signals are a feature of three- and higher-dimensional NMR experiments. Much effort has therefore been put into finding alternatives to the Fourier transform which will generate spectra without these truncation artefacts. The popular methods are *maximum entropy*, *linear prediction* and *FDM*. Each has its merits and drawbacks; they all need to be applied with great care.

4.9 Exercises

E 4–1
In a spectrum with just one line, the dispersion mode lineshape might be acceptable – in fact we can think of reasons why it might even be desirable (what might these be?). However, in a spectrum with many lines the dispersion mode lineshape is very undesirable – why?

E 4–2
Suppose that we record a spectrum with the simple pulse-acquire sequence using a 90° pulse applied along the x axis. The resulting FID is Fourier transformed and the spectrum is phased to give an absorption mode lineshape.

   We then change the phase of the pulse from x to y, acquire an FID in the same way and phase the spectrum using the *same* phase correction as above. What lineshape would you expect to see in the spectrum; give the reasons for your answer.

   How would the spectrum be affected by: (a) applying the pulse about $-x$; (b) changing the pulse flip angle to 270° about x?

E 4–3
The gyromagnetic ratio of phosphorus-31 is 1.08×10^8 rad s^{-1} T^{-1}. This nucleus shows a wide range of shifts, covering some 700 ppm.

   Suppose that the transmitter is placed in the middle of the shift range and that a 90° pulse of width 20 μs is used to excite the spectrum. Estimate the size of the phase correction which will be needed at the edges of the spectrum. (Assume that the spectrometer has a B_0 field strength of 9.4 T).

E 4–4
Why is it undesirable to continue to acquire the FID after the signal has decayed away?

   How can weighting functions be used to improve the SNR of a spectrum? In your answer described how the parameters of a suitable weighting function can be chosen to optimize the SNR. Are there any disadvantages to the use of such weighting functions?

E 4–5
Describe how weighting functions can be used to improve the resolution in a spectrum. What sets the limit on the improvement that can be obtained in practice? Is zero filling likely to improve the situation?

E 4–6
Explain why use of a sine bell weighting function shifted by 45° may enhance the resolution but use of a sine bell shifted by 90° does not.

E 4–7
In a proton NMR spectrum the peak from TMS was found to show "wig-

gles" characteristic of truncation of the FID. However, the other peaks in the spectrum showed no such artefacts. Explain.

How can truncation artefacts be suppressed? Mention any difficulties with your solution to the problem.