

Experiment 358: Nuclear Magnetic Resonance

Aim

To become acquainted with the phenomenon of nuclear magnetic resonance and carry out a few quantitative measurements that characterize two common samples.

Theory

No doubt you know of the medical application of NMR – a person is inserted into a large machine with a strong magnetic field, which produces a colorful 3D scan of the body. The doctor promptly looks at the picture and is able to pick out tumors and other internal tissue abnormalities. The different colors on the picture might, for example, be a density map. How does the machine find out the density at each point? The theory below takes us a fair distance towards the answer. Some background knowledge is inevitably assumed. Needless to say, if you come up against ideas, terminology or mathematics you have not seen before, you are expected to read up independently until the matter is clear in your mind.

Nuclear spin

Nuclei have a quantum-mechanical spin (an intrinsic angular momentum), \underline{I} , which is quantized so that $|\underline{I}| = \hbar\sqrt{I(I+1)}$, I being an integer or a half-integer. The associated magnetic moment is $\underline{\mu} = \gamma\underline{I}$ [γ is called the gyromagnetic ratio], and the energy of a spin in a magnetic field is $E = -\underline{\mu} \cdot \underline{B}$. If $\underline{B} = B\hat{z}$, the z -component of $\underline{\mu}$ is $\mu_z = \gamma\hbar m$ where m can range from $-I$ to I in steps of one. In such a magnetic field, the energy gap between any two adjacent levels is $\Delta E = \gamma\hbar B$. From now on we specialize to a hydrogen nucleus which will be used in the experiment. A proton has $I = 1/2$ and thus only two allowed m -values: $\pm 1/2$, spin-up and spin-down, with energies $\pm |\mu_z|B$.

Magnetization

Consider a large ensemble of hydrogen nuclei in thermal equilibrium with their environment. The Boltzmann distribution tells us how many, on average, of the nuclei are to be found in each of the energy states:

$$N_j \propto \exp \left\{ -\frac{E_j}{k_B T} \right\}, \quad (1)$$

where N_j are the number densities. If we label the spin-up and -down states by u and d , respectively, and let $N = N_u + N_d$ (N is a constant), then

$$N_{u/d} = A \exp \left\{ \pm \frac{|\mu_z|B}{k_B T} \right\}, \quad (2)$$

where A is

$$A = \frac{N}{\exp \left\{ +\frac{|\mu_z|B}{k_B T} \right\} + \exp \left\{ -\frac{|\mu_z|B}{k_B T} \right\}}. \quad (3)$$

Clearly $N_u > N_d$, so we can calculate the excess number of spins up:

$$\Delta N = N_u - N_d = N \frac{\exp \left\{ +\frac{|\mu_z|B}{k_B T} \right\} - \exp \left\{ -\frac{|\mu_z|B}{k_B T} \right\}}{\exp \left\{ +\frac{|\mu_z|B}{k_B T} \right\} + \exp \left\{ -\frac{|\mu_z|B}{k_B T} \right\}} = N \tanh \left\{ \frac{|\mu_z|B}{k_B T} \right\}. \quad (4)$$

These are responsible for any *net* magnetization in the sample, $M_z = |\mu_z| \Delta N V$, where V is the sample volume. If $\frac{|\mu_z|B}{k_B T} \ll 1$, as it will be in our experiment, we may use $\tanh(x) \approx x$ and get

$$M_z = \frac{VNB\gamma^2\hbar^2}{4k_B T}. \quad (5)$$

Larmor precession

Consider an angular momentum vector \underline{L} with a magnetic moment $\underline{\mu} = \gamma \underline{L}$ in a magnetic field \underline{B} . Then there is a torque $\underline{\tau} = \underline{\mu} \times \underline{B}$ acting on \underline{L} according to $\underline{\tau} = \frac{d\underline{L}}{dt}$. Equating the two expressions gives

$$\frac{d\underline{\mu}}{dt} = \gamma \underline{\mu} \times \underline{B}. \quad (6)$$

We take the cross-product (recall that $\underline{B} = \hat{z}B$), obtain ODEs for μ_x and μ_y and solve these. The resultant motion is

$$\mu_x(t) = \mu_x(0) \cos(\omega_0 t), \quad \mu_y(t) = \mu_y(0) \sin(\omega_0 t), \quad \mu_z(t) = \mu_z(0), \quad (7)$$

which describes precession of the magnetic moment vector about the z -axis with the **Larmor frequency** $\omega_0 = \gamma B$. Note that the energy of the system remains constant as the angle between \underline{B} and $\underline{\mu}$ is fixed.

Now consider adding another magnetic field to the picture. Let \underline{B}_1 be a weak magnetic field which is confined to the x - y plane and rotates about the z -axis at a constant angular frequency ω_1 . If we transform the situation to the rotating frame in which \underline{B}_1 is stationary, the Larmor precession of $\underline{\mu}$ about \underline{B} now occurs at $\Delta\omega = \omega_0 - \omega_1$, but in addition, $\underline{\mu}$ now *also* precesses about the stationary \underline{B}_1 . When $\Delta\omega$ is large, the azimuthal angle θ of $\underline{\mu}$ will vary rapidly, as will the energy $\underline{\mu} \cdot \underline{B}$, thus causing their interaction to average out over time. But when $\Delta\omega = 0$, the precession about \underline{B} stops (in our rotating frame) and only precession about \underline{B}_1 at the Larmor frequency $\omega_1 = \gamma B_1$ ensues. This precession certainly *does* change θ and thus E .

Quantum-mechanically, the last paragraph sums up to the fact that we can excite a transition between the \underline{B} -split states of the nuclei by applying an excitation (in the form of \underline{B}_1) at the gap-frequency $\hbar\omega_1 = \Delta E$.

Next, suppose initially the azimuthal angle of $\underline{\mu}$ is θ . If we switch on the rotating field \underline{B}_1 for a time τ ($\Delta\theta$) such that $\omega_1\tau$ ($\Delta\theta$) = $\Delta\theta$, this pulse changes the azimuthal angle $\theta \rightarrow \theta + \Delta\theta$. Precession about \underline{B} at ω_0 resumes when the pulse is turned off, but the system has been excited.

In reality, instead of a single spin we have an ensemble. Before the pulse the spins are uniformly distributed inside of a cone with its axis along the z -axis, and its surface at angle θ from the axis [inside this cone, each spin is undergoing Larmor precession at ω_0 independently]. After the pulse, the *entire cone* is tilted away from the z -axis by $\Delta\theta$, and resumes its precession about \underline{B} . Thus the net magnetization behaves the same way as a single spin.

Particularly useful choices of $\Delta\theta$ are $\pi/2$, after which the magnetization rotates about the z -axis in the x - y plane at ω_0 , and π , after which the magnetization is still along the z -axis but points in the opposite direction to \underline{B} (this effectively reverses the sense of precession).

Relaxation processes

So far we have assumed that the spins in our ensemble do not interact with each other, but they do. They also interact with their environment, as a sample is never isolated. Both these types of interactions scramble the alignment of the spins and reduce the net magnetization – these are *decay* processes with characteristic time-constants. It is precisely these time-constants that carry all the sample information in an NMR experiment.

Spin-lattice relaxation

In the absence of a magnetic field, the magnetic energy levels of an H-nucleus are not split and thus are equally populated. When we turn on \underline{B} , the Boltzmann distribution (2) takes some time to build up. The redistribution of nuclei occurs as a result of (re-)thermalization with the lattice (the environment) via multiple exchanges of small energy quanta (phonons). If p_u and p_d are probabilities that a single nucleus

will be excited or de-excited (respectively), the rate equations for the number densities are

$$\frac{dN_u}{dt} = N_d p_u - N_u p_d, \quad (8)$$

$$\frac{dN_d}{dt} = -\frac{dN_u}{dt}, \quad \text{as } N = N_u + N_d. \quad (9)$$

In steady state, $N_d p_u = N_u p_d$, and using (2),

$$\frac{p_u}{p_d} = \frac{N_u}{N_d} = \exp \left\{ -\frac{2|\mu_z|B}{k_B T} \right\} \approx -\frac{2|\mu_z|B}{k_B T}. \quad (10)$$

Further, define $p = (p_u + p_d)/2$ and obtain

$$\frac{p_{u/d}}{p} = 1 \mp \frac{|\mu_z|B}{k_B T}. \quad (11)$$

Next, since $\Delta N = N_u - N_d$, $\frac{d\Delta N}{dt} = 2\frac{dN_u}{dt}$, and substituting (11) into (8) gives

$$\frac{d\Delta N}{dt} = -2p \left(N_d \frac{p_u}{p} - N_u \frac{p_d}{p} \right) = -2p \left(\Delta N - N \frac{|\mu_z|B}{k_B T} \right). \quad (12)$$

Clearly, in steady state $\Delta N = N \frac{|\mu_z|B}{k_B T} \equiv \Delta N_{ss}$. Defining the shifted quantity $\Delta N' = \Delta N - \Delta N_{ss}$ and $T_1 = 1/(2p)$, the solution to (12) is trivially

$$\Delta N'(t) = \Delta N'(0) \exp \left(-\frac{t}{T_1} \right). \quad (13)$$

Recall that $M_z = |\mu_z| V \Delta N$, and define $M_0 = |\mu_z| V \Delta N_{ss}$, to arrive at the corresponding solution for the magnetization:

$$M_z(t) = M_z(0) \exp \left(-\frac{t}{T_1} \right) + M_0 \left[1 - \exp \left(-\frac{t}{T_1} \right) \right]. \quad (14)$$

Thus, T_1 is the time-constant due to interaction of the nuclear spins with their chemical environment. As such, it depends on the nucleus itself and on the temperature and physical state of the sample. It can range from 0.1 ms to several days.

Spin-spin relaxation

Each nuclear spin in a sample induces a weak, local magnetic field which changes the effective field “seen” by its neighbors. These neighbors, therefore, precess at a frequency slightly shifted from ω_0 . This reduces the phase coherence between the spins – *dephases* them – and results in a reduction of $|\underline{M}|$ (which is a vector sum of the individual magnetic moments). This perturbing magnetic field is very small in liquids and gases as the molecules constantly and rapidly change orientation.

Consider an initial situation whereby all N magnetic moments are aligned along one vector in the x - y plane. Let the field at the n^{th} site be $B_n = B + b_n$ where b_n is the local perturbation due to other spins. The corresponding Larmor frequency is $\omega_n = \omega_0 + \gamma b_n$. We shall assume that the b_n 's are evenly distributed about zero. If we go to a frame rotating at ω_0 such that the net magnetization is stationary, as time goes on, the individual magnetic moments will fan out further and further from their sum with angular frequencies γb_n . Mathematically,

$$|\underline{M}| = \left| \sum_{n=1}^N \underline{\mu}_n(t) \right| = |\underline{\mu}| \sum_{n=1}^N \cos(\gamma b_n t). \quad (15)$$

Using the power-series expansion of $\cos(x)$ to lowest order in x , for small t (15) becomes

$$|\underline{M}(t)| = |\underline{\mu}| \sum_{n=1}^N \left(1 - \frac{\gamma^2 b_n^2 t^2}{2} \right) = |\underline{\mu}| \left(N - \frac{\gamma^2 t^2 N}{2} \sum_{n=1}^N \frac{b_n^2}{N} \right) = |\underline{\mu}| N \left(1 - \frac{\gamma^2 t^2}{2} \langle b_n^2 \rangle \right). \quad (16)$$

We will heuristically take $\langle b_n^2 \rangle$ and replace it with $\langle b_n^2 \rangle / t$ because we know that the magnetic field from aligned spins is stronger than that of randomly oriented moments, and this randomization of spins is clearly happening over time. This leads to

$$|\underline{M}(t)| = |\underline{\mu}| N \left(1 - \frac{\gamma^2 \langle b_n^2 \rangle}{2} t \right), \quad (17)$$

which has the same form as the lowest order power-series expansion of the exponential function. Defining $T_2 = 1 / (\gamma^2 \langle b_n^2 \rangle)$, we generalize (17) to large times as well, and write

$$|\underline{M}(t)| = |\underline{\mu}| N \exp \left\{ -\frac{t}{T_2} \right\}. \quad (18)$$

Of course the last few steps have not been as rigorous as one would hope, but, after all, the end result is correct.

Experiment

We will perform NMR experiments using the Earth's magnetic field as \underline{B} . Of course \underline{B}_E is very weak (decreasing SNR), but it is also relatively homogeneous, so we can use large samples (increasing SNR). Overall, meaningful data is still obtainable. The equipment is stationed in the *Quantum Lab* side-room of the main advanced lab, and should not be moved. We have a PC to control the equipment, a DC power supply (black box), a probe (solenoid) installed in a tall stand, and the main controller box that interfaces between all the other pieces (large white box). The probe is made up of four different types of coils slotted into each other:

- The outer coil is the *polarizing* one. In the section on magnetization, we saw that a net magnetization will arise if a magnetic field splits the energy levels, and logically, the stronger the field, the bigger the energy splitting and the level-occupancy differences, thus resulting in a stronger net \underline{M} . \underline{B}_E is extremely weak, so the initial \underline{M} is small. If we slowly (a.k.a. *adiabatically*) turn on another field, much stronger than \underline{B}_E , \underline{M} will adiabatically follow. Slowly introducing another field gradually changes the energy levels, inducing a bigger splitting and net \underline{M} . By the time the polarizing field is fully on, \underline{M} is very large but points in the direction of \underline{B}_p , not \underline{B}_E . We then adiabatically turn off \underline{B}_p so that \underline{M} remains large in magnitude but returns to its previous alignment with \underline{B}_E . Of course, if we wait long enough, the occupancies will return to their original Boltzmann distribution through processes described in the spin-lattice relaxation section, and \underline{M} will become small again. But if we perform our experiment before M decays, this polarizing trick increases SNR significantly. Note that \underline{B}_p lies along the solenoid axis when on.
- The next coils in (from the outside) are the “shim” coils. These are three coils, capable of changing the magnetic field in all three directions. They are required to cancel out, as much as possible, the inhomogeneities of the Earth's field across the sample, thus reducing noise and strengthening the signal.
- Then we have the gradient coil. This enables us to create a linearly-changing (with position) magnetic field along the solenoid axis, which would make the Larmor frequency vary across the sample. We will not need to use this feature.
- Finally, the inner-most coil is the B_1 -coil which is used to excite the sample and then detect the produced signal. For example, $\pi/2$ (and π) pulses are induced through this coil (as described in the section on Larmor precession). This coil is *also* used to then detect M_y as it rotates about the z -axis at ω_0 . The principle of detection is based on Faraday's law of induction – what we actually detect is an induced voltage. It works like this: assume that the coil is positioned so that the x -axis coincides with the solenoid axis, and \hat{z} lies along \underline{B}_E . After a $\pi/2$ -pulse, \underline{M} rotates in the x - y plane. A changing flux in the y - z plane will induce a voltage in the coil according to $\mathcal{E} = -\frac{d\phi}{dt}$. As we can see, the y -axis is the only relevant degree of freedom. Thus, $\phi \propto \mu_y(t) = \mu_y(0) \sin(\omega_0 t)$ and $\mathcal{E} \propto \omega_0 \mu_y(0) \cos(\omega_0 t)$. In reality, we know that the magnetization decays with time, so the signal we will detect will be damped

SHM. Note that the Fourier transform of an exponentially-decaying sinusoid is a Lorentzian, centered at the frequency of oscillation and with FWHM inversely-proportional to the decay time-constant.

The B_1 coil has an inductance and a resistance, and if we connect a capacitor in parallel with this coil we get an LCR circuit, with the induced \mathcal{E} acting as the voltage source. For best results, we will want to make the detection LCR circuit resonant with ω_0 by tuning C (the resonant frequency is $1/\sqrt{LC}$), as it clearly increases SNR.

Set-up

Turn on the PC and open the **Prospa** program from the desktop. When you will be ready to do experiments, the equipment is turned on by flicking the power switch on the main, white controller box. Do not leave this switch on for prolonged time-intervals unnecessarily, and never turn off the power while an experiment is actually running. If you are lucky, the equipment has not been moved since it has been optimized in mid-December 2011, in which case everything is already set-up. However, this is extremely unlikely, and you must go through the procedure below anyway, even if it is just to make sure that everything is as it should be.

Hardware

Notice the high aluminum stand in the middle of the room with the probe sitting upside down in the cradle at the top. On the waist-high shelf of the stand you ought to find a ruler pushed up against two of the legs and a compass sitting on top of the ruler. The idea is as follows: firstly, serious magnetic field inhomogeneities will make it very difficult to see a signal, and since field-lines cluster around iron objects, we need to get the probe away from all the iron in the room – hence the aluminum stand, far away from other equipment, walls, floor and ceiling. In fact, a field inhomogeneity ΔB causes the effective spin-spin relaxation time constant T_2^* to become much shorter (that is, the signal decays faster) according to

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \gamma \Delta B. \quad (19)$$

Also, we want to have the coil axis perpendicular to the Earth's field. Have a look at the compass: the short black bar is magnetic, and aligns itself along field-lines. The longer and much finer aluminum bar (orthogonal to it) is for reading the compass. The ruler on the shelf is purely for ease of alignment as now you can look from the top and tell if the aluminum bar in the compass runs along the ruler which is parallel to the solenoid axis. Align the probe axis to be orthogonal to the Earth's field if it is not already so.

You should find another ruler and a protractor by the PC. Take a piece of paper, and draw a square, roughly 8 by 8 cm. Add a horizontal line that goes through the middle of the square. Using the protractor, find the line that lies -62.5° below the “positive” end of your horizontal line, and draw it fully across the square. Cut out the square with the two lines on it (if it is currently on a larger sheet of paper). Now, on one end of the probe you will see a small red arrow. We need to align this arrow with the Earth's magnetic field, which at our location runs at an inclination of -62.5° to the horizontal plane. Hold up your paper square to the arrow-end of the probe, with the horizontal line as horizontal as possible and the center of the square as close to the coil axis as you can. If the arrow does not point along your -62.5° -line (preferably from the 117.5° mark), rotate the probe in its cradle until it does.

Software

We have two samples for the experiment: a water bottle with a Magritek label, and an oil bottle. Make sure neither of the samples is in the probe.

Turn on the equipment, select **EFNMR** from the main menu, and then click on **MonitorNoise**. A pop-up window such as that displayed in Fig. 1 (a) will come up. Set all the parameters to those in the figure (don't worry about what they mean yet!), then click **Run**. The probe will continuously take data, and display it in two forms: on the left we have the time-series and on the right, the Fourier transform mod-squared, called the power spectrum. A sample run is shown in Fig. 1 (b). Read the RMS noise value – if it is between 6-8

μV , you have a nice, low noise level. Anything below 10 should be fine, but the smaller the better. If you are satisfied with the noise level (record it in your lab-book!), click on the **stop** button to end the experiment (you can end *all* experiments in this way if for some reason you wish to halt the data taking midway). If not, you can move the probe around, together with the stand, while the program is running to find a better location. Remember that you must align the probe with B_E as above at each new position you want to try. Close the **MonitorNoise** dialog box.

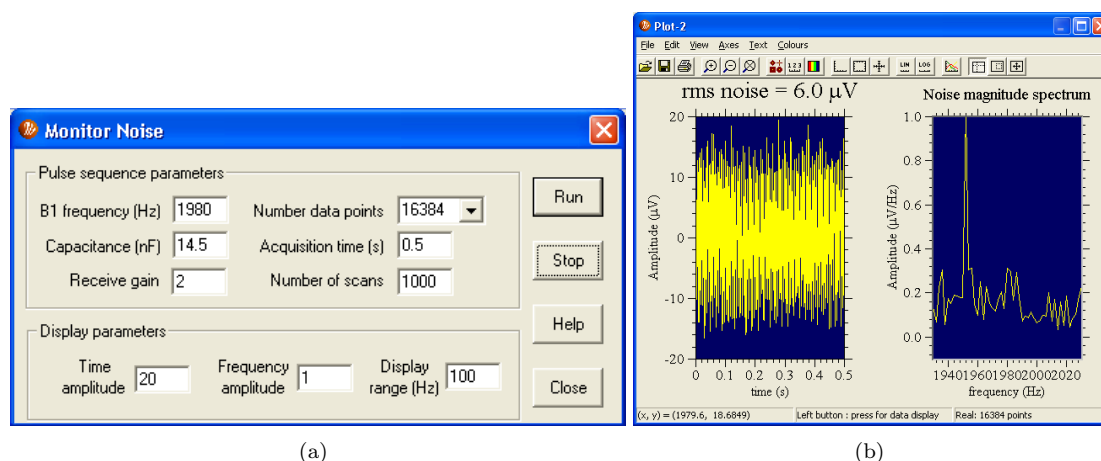


Figure 1: The **MonitorNoise** dialog box and typical plots produced.

Next, select **EFNMR** from the main menu, and then click on **AnalyseCoil**. A pop-up window such as that in Fig. 2 (a) should appear; the bar on the right indicates completion, so at first it will not be blue. You are asked for a working directory. Create a folder (somewhere where you can find it later!!) with your name – all your data will go here. You are also asked for an experiment name – **Prospa** will automatically create a sub-folder in your main directory for each experiment you run. It is fine to leave all the names as the defaults suggested by **Prospa**. Click **Alanyse** and let it run until the program tells you it's done. As the output, you should have three graphs as in Fig. 2 (b). Moreover, you will notice some text has appeared in the command window ('**CLI**' panel in **Prospa**), as shown in Fig. 2 (c). Write down the returned parameters for B_1 coil capacitance, inductance and resonant frequency.

Note: While working through this section, there may be graphs you would like to save for inclusion in the final report (which ones, if any, is up to you). Do so by selecting the graph panel (click on the blue strip at the top of the window), maximizing it, and then hold down the keys **Ctrl+C** simultaneously to copy the figure. Then open Paint, paste the image (**Ctrl+v**), and save either in your local folder on the PC or on your memory stick (note that this PC is not connected to the network).

Now comes the moment of truth: you must “find” the signal. For the time-being, do not worry about what exactly the apparatus is doing and just follow the instructions – details will be given later. Basically, we will excite the system with a $\pi/2$ -pulse and watch for the decaying signal. Insert the water sample into the probe, making sure that the bottle is centered in the coil. In the time-domain, the signal should appear as an exponentially-decaying sine function that decays down to a steady level of noise, and in the frequency domain we would like to see a nice Lorentzian peak. Go to the **EFNMR** submenu, and select the **PulseAndCollect** experiment. Set the initial parameters to those displayed in Fig. 3 (a). This is just a starting point and you may need to change things later. Now click on the **Shims** button in the **PulseAndCollect** dialog box. A window such as that in Fig. 3 (b) should appear. These are the initial artificial magnetic field offsets that are meant to cancel out the local field inhomogeneities. Again, set the numbers to the values in the figure. Now click **Run**. If the plots on your screen look like the ones in Fig. 3 (c), you have found the signal! If they do not:

- If you cannot see a nice clean peak in the spectrum but you see (even a little bit of) a decaying signal in the time-series (you can zoom in to a part of a plot by selecting a region first, then clicking on the zoom-in button), this means you're simply not looking in the right part of the spectrum – this

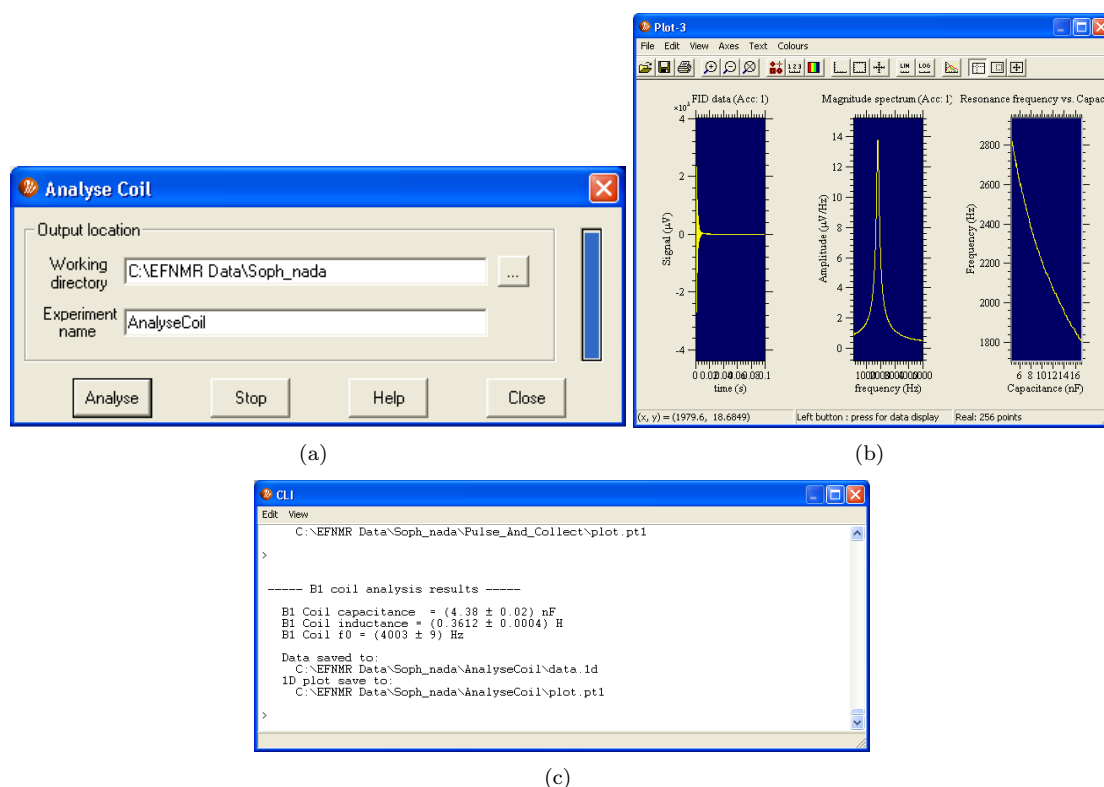


Figure 2: The **AnalyseCoil** dialog box, typical output plots and returned parameters.

is easily fixed. Start from 1900 Hz for the **B1 frequency** parameter, go up in steps of 25 Hz up to 2050 Hz. At each **B1** value, perform a run with the water sample and without it until you find a peak that disappears when the water sample is taken out. Change the **B1 frequency** parameter to the frequency of your peak. Note that a real signal peak will have a *width*, whereas noise peaks will be very narrow. Also, if unsure whether a peak is real or not, increase **Number of scans** to three, and wait for the three runs to be taken and averaged. If the signal is real, the peak will get more and more prominent with each added data set, and if it is noise it will average out.

- If you cannot see a meaningful signal in the time domain either, this means your noise levels are higher than you think or the apparatus is very poorly aligned (assuming the sample is actually *in*). Recheck these points. You may want to reduce the **Acquisition time** parameter to 0.1 s so that the signal is obvious when present. If this doesn't help, set the shims parameters to zero and try again. If all this fails, call a demonstrator to help you because it really ought to work.

Assuming you have found a signal and can see some decaying oscillations and the true peak in the spectrum, it is time to optimize this signal. Note that this will only work if the highest peak in the selected part of the spectrum (**B1 frequency** \pm **Display range**/2) is the real thing. Go to the **EFNMR** submenu, and select the **AutoShim** experiment. Set the initial parameters to those displayed in Fig. 4 (a) [except for those that you have already determined yourself, such as **B1 frequency**]. Notice that the **Search range** is selected as a small number assuming we are already pretty close to optimum, but if your data looks like it will need a lot of correcting, you may wish to specify a larger value, say 10 mV. Also, a long **Acquisition time** is chosen here, based on the same assumption. If your signal is very short you may want to start off with a smaller value (*e.g.* 1 s) and then repeat **AutoShim** with a larger time and smaller search range. Run the script. When **Propsa** tells you it is done and asks you whether you want to save the new shims parameters, if the final plots [Fig. 4 (b)] look good, choose yes. Write down the shims parameters returned in the command window [Fig. 4 (c)]. If deemed necessary, repeat **AutoShim** for a finer optimization, as described above. Change the **B1 frequency** parameter to the frequency of your peak. Points on graphs can be read off using the third button from the right on the toolbar of the plot window: click and drag the mouse pointer towards the peak, and read the coordinates at the bottom left corner of the window.

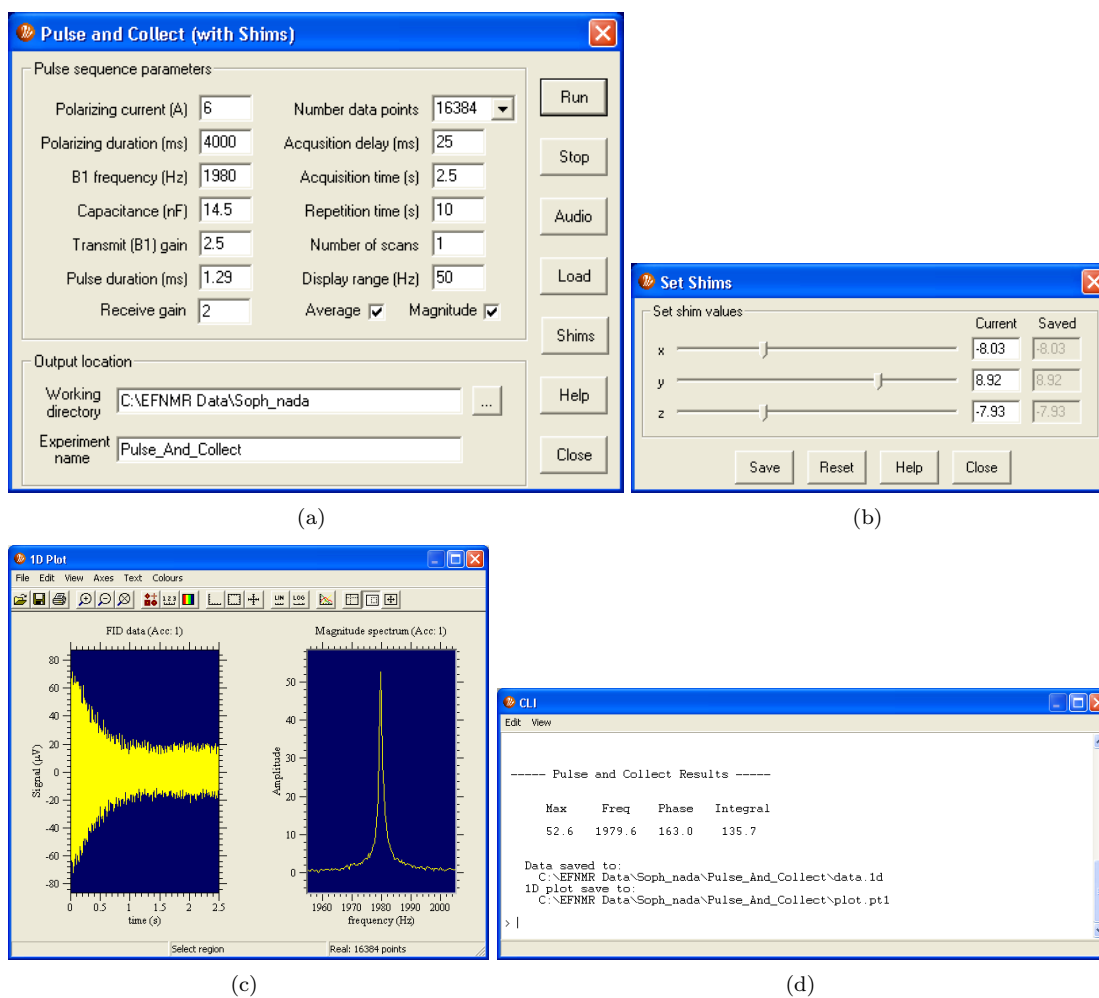
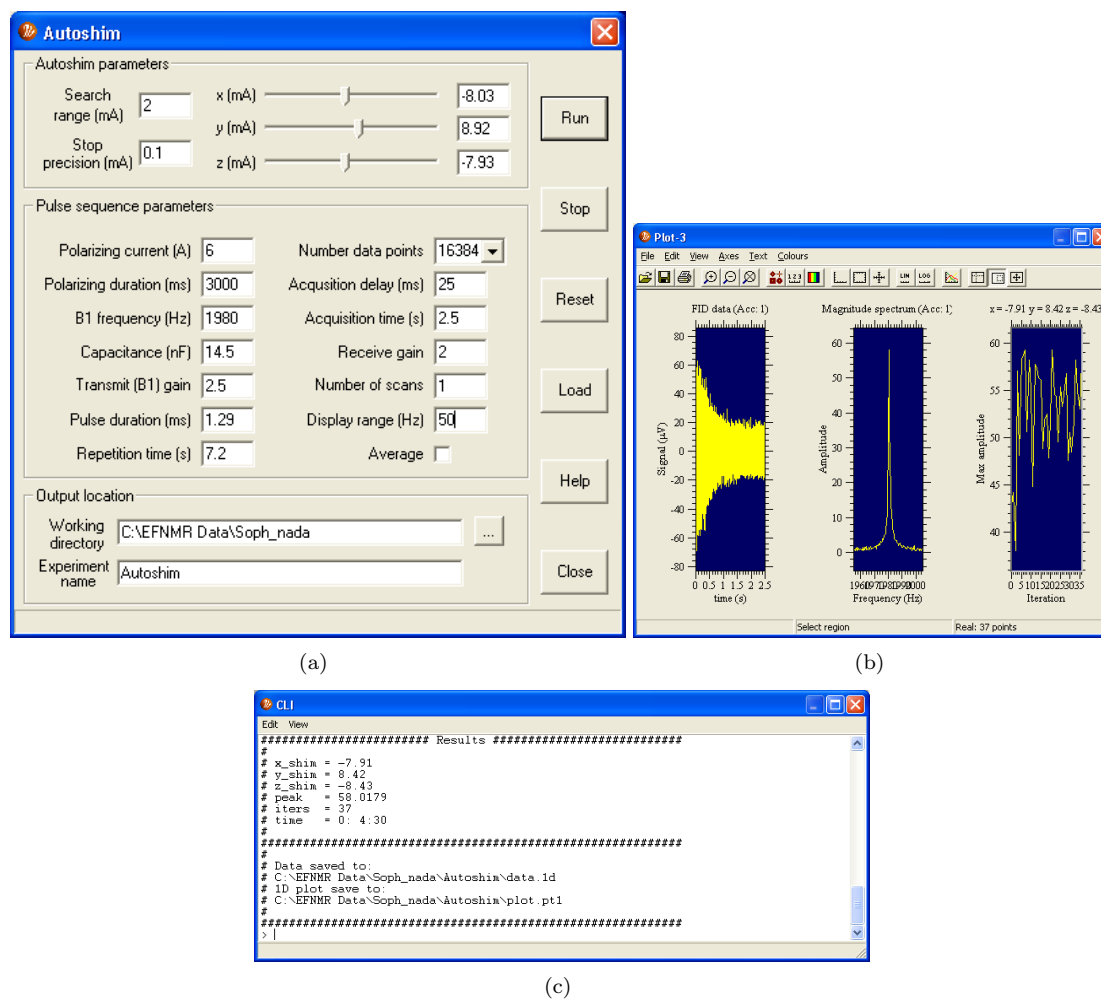


Figure 3: The **PulseAndCollect** dialog box, shims parameters, typical output plots and returned parameters.

Figure 4: The **AutoShim** dialog box, typical output plots and returned parameters.

Once you are satisfied that the signal is cleanly observed in your setup, we proceed to tune the capacitance of the detection LCR circuit to match the resonant frequency to the Larmor frequency. Open the **PulseAndCollect** experiment again. *Temporarily* (only for this procedure) change the **Acquisition delay** from 25 to 2 ms, the **Polarization duration** from 4000 to 1000 ms, and **Display range** 50 to 500 Hz. Run the experiment. You should get a plot such as that in Fig. 5. The spike is your NMR signal, and the broad sinc function is the response of the coil to the short B_1 -pulse. We would like the spike to be superimposed on top of the sinc function. If the spike is at a higher frequency, reduce the **Capacitance** parameter a bit and vice versa. Repeat the exercise until the two peaks are superimposed. Record the optimal capacitance and leave this parameter at this value from now on. Return all other parameters to their old values and run another **PulseAndCollect** scan – you may notice that the resonance peak has shifted a little. Enter the new frequency into the **B1** field to replace the old value.

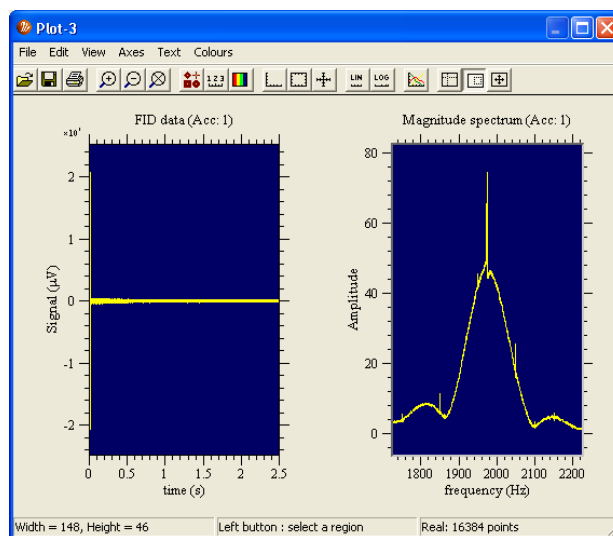
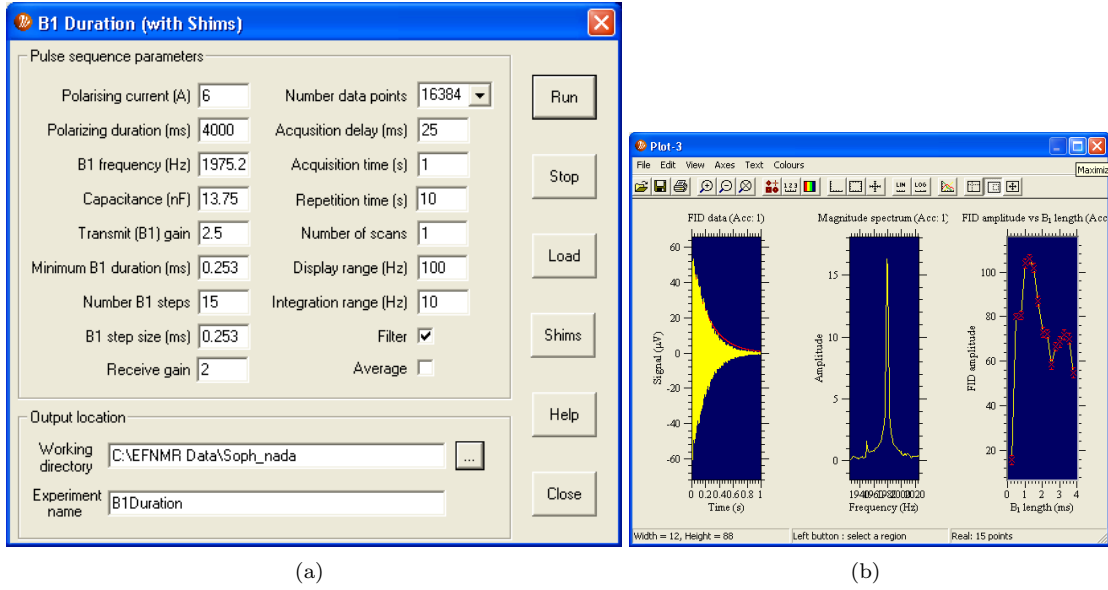


Figure 5: The ring-down output plots. Optimal capacitance was 13.75 nF here.

We must now determine how long the B_1 field must be on to truly induce a θ tilt of 90° . We will go through a number of pulse times and see the effect they have on the signal amplitude: it should be maximal after a 90° pulse and minimal after a 180° one (make sure you understand *why!*). Once again from the **EFNMR** menu, select the **B1Duration** experiment – see Fig. 6 (a). Calculate half the Larmor period for your peak in ms and enter this value for both **Minimum B1 Duration** and **B1 step size**. You may take all other parameters to be the same as in the example figure (except for those you have already determined experimentally yourself!). Note the parameter **Integration range**. The amplitude of the signal is proportional to the area under the signal peak; this is chosen so that the entire peak fits in to this range (in our example, the range is 10 Hz, so we integrate ± 5 Hz from the specified **B1 frequency**). Run the experiment and maximize the plot window when done; we are interested in two particular points on the RHS graph. The time of the first maximum is the $\pi/2$ -pulse duration and the first minimum after that is the π -pulse duration. Write down both values. What is the relation between them? Is this to be expected? Open the **SpinEcho** experiment from the **EFNMR** menu and enter the two numbers into the **90 pulse duration** and **180 pulse duration** fields for later use.

Experimental procedures

You have now finished calibrating the machine and are ready to make some actual measurements. These measurements will make use of two fundamental procedures, so it will be easier to understand those first.

Figure 6: The **B1Duration** dialog box and typical output plots.

Pulse-and-collect

The basic pulse-and-collect experiment is shown in Fig. 7. We start by adiabatically increasing the magnetization via a polarizing pulse duration τ_p , then we wait for time t , apply a $\pi/2$ B_1 pulse, wait an acquisition delay time interval and start taking data. The signal detected is

$$S(t) = \gamma B_E B_1 V \frac{V N B_p \gamma^2 \hbar^2}{4 k_B T} \left[1 - \exp\left(-\frac{\tau_p}{T_1}\right) \right] \exp\left(-\frac{t}{T_2^*}\right) \cos(\gamma B_E t) \sin(\Delta\theta). \quad (20)$$

We have already “measured” the $\cos(\gamma B_E t)$ – it is responsible for the peak in the spectrum at the Larmor frequency and the fast oscillations in the time domain. Likewise, we have already investigated the effect of the $\sin(\Delta\theta)$ term in the **B1Duration** experiment when we changed $\Delta\theta$ and saw the amplitude vary as a rectified sine. Together, these two terms are completely expected on the basis of the results in the Larmor precession section. The term $\frac{V N B_p \gamma^2 \hbar^2}{4 k_B T} \left[1 - \exp\left(-\frac{\tau_p}{T_1}\right) \right]$ is explained in the sections on magnetization and spin-lattice relaxation (what assumption do we make regarding the net magnetization prior to the polarization pulse?), while $V \exp\left(-\frac{t}{T_2^*}\right)$ is caused by spin-spin relaxation in a non-homogeneous field (actually, in the theory section we have N , not V , in the expression, but these are proportional to each other). The factor of γB_E comes from the detection process (see fourth bullet point under the Experiment section heading). The scaling by B_1 has not been covered, but is hardly surprising.

Spin-echo

The basic spin-echo experiment is shown in Fig. 8. The whole purpose of the exercise is to isolate the effects of T_2 from those of the field inhomogeneities, as at the moment they seem to be rolled up into one number, T_2^* . The sequence begins with a polarizing pulse (not shown for clarity), followed by a $\pi/2$ -pulse, much like the pulse-and-collect experiment. Once the magnetization is in the x - y plane, the individual spins begin to be dephased by spin-spin interactions and field inhomogeneities. This may be imagined as the magnetic moments fanning-out about their average (they all still rotate at the Larmor frequency, but each now has a different phase). However, a time τ_E afterwards, we apply a π -pulse. As we know, the effect of this is to reverse the precession direction of each spin. Since the field inhomogeneities remained constant over this time, their effect is reversed a further τ_E after the π -pulse when all the spins are once again realigned. The effect due to other spins is irreversible due to the random motion of the spins in the time-interval concerned. So, $2\tau_E$ after the $\pi/2$ -pulse we have a signal amplitude that has only been decayed by spin-spin interactions during this time interval.

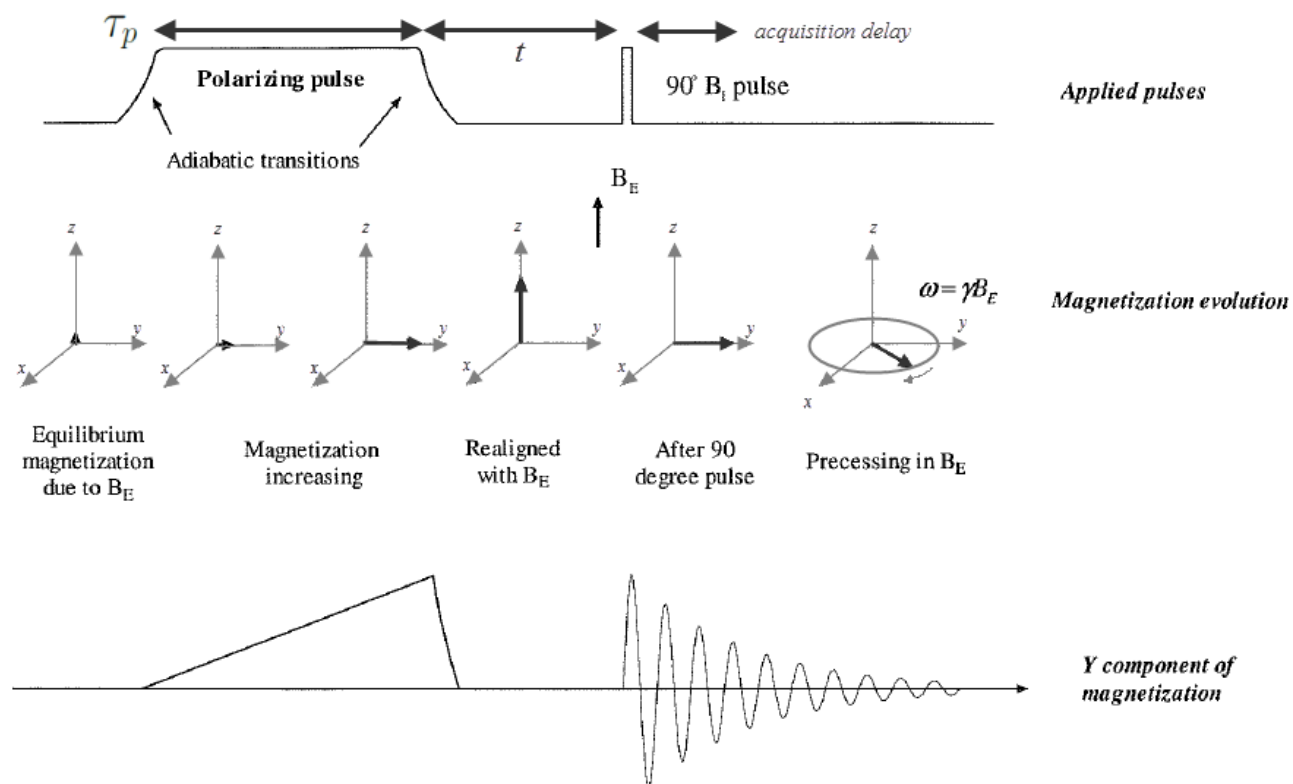


Figure 7: The basic pulse-and-collect experiment.

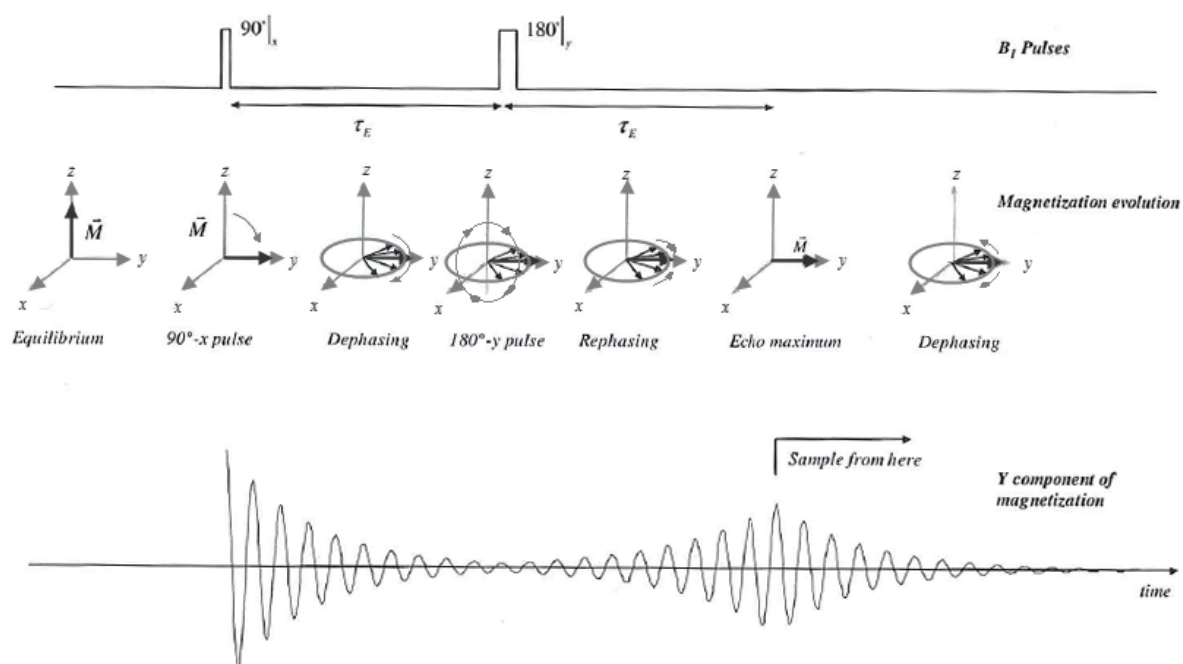


Figure 8: The basic spin-echo experiment.

Measuring T_2

We use the basic spin-echo experiment to isolate and measure the effects of spin-spin relaxation. We run many spin-echoes with different τ_E 's (see Fig. 8) and record the signal amplitude a time $2\tau_E$ after the $\pi/2$ -pulse. These data points are predicted to fall on the curve $S = S_0 \exp\{-2\tau_E/T_2\}$ and by fitting the data, we can easily get T_2 .

Start by running a quick **PulseAndCollect** experiment and update the Larmor frequency if necessary (it may have slightly changed). Select the **T2** experiment from the **EFNMR** menu [Fig. 9 (a)]. Set all parameters (which you have not determined yourself at some point) to the values in the figure. Click on the **Shims** button and offset the z correction by dragging the marker about 5 mA off from the proper value determined earlier by **Autoshim**. *Do not click save!* When the experiment is done, you will click **reset** and close the shims window, but for the purposes of this sequence of spin-echoes, we need the signal to decay fully between the $\pi/2$ - and π -pulses, so we purposefully spoil field homogeneity. Click **Run** and wait for the machine to acquire data. This may take a couple of minutes. The plot will be updated every two scans (as we are averaging two per run) and eventually you will see a fine exponential curve such as that in Fig. 9 (b). If there are a few noticeably scattered points on this graph, you may wish to run it again. If only one point is off, you can write down the data from the command window, excluding the troublesome point, and fit it yourself in Matlab. Save the plots and write down your value for T_2 of water.

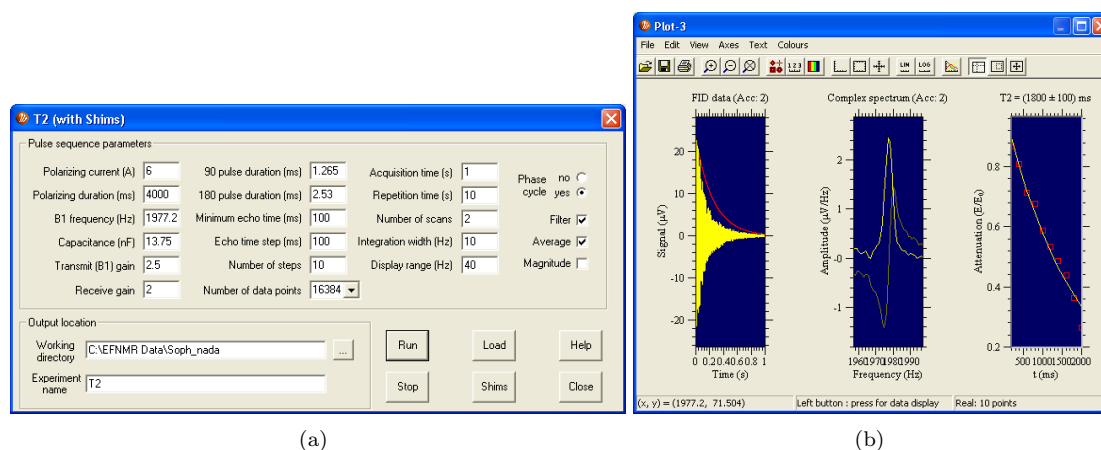


Figure 9: The **T2** dialog box and typical output plots.

Replace the water sample with the oil bottle. Run a single (unaveraged) **PulseAndCollect**. Notice that the peak has not shifted but the quality of the data is markedly worse than for water. Since the sample volume is practically the same, we must conclude that the damping is stronger. Now average four scans and observe the considerable noise reduction. During the **T2** experiment for water we chose **Minimum echo time** and **Echo time step** so that the range covered along the x -axis (*i.e.* $2\tau_E$) was similar to T_2 of the sample. For oil, T_2 is much shorter. The shortest value you can specify for **Minimum echo time** and **Echo time step** is 25 ms. Set these parameters to 25 ms, set **Number of scans** to 4, and run the **T2** experiment for oil. Remember to deshim temporarily for the duration of the experiment. Record the T_2 value for oil and save the plots. Swap samples back to water.

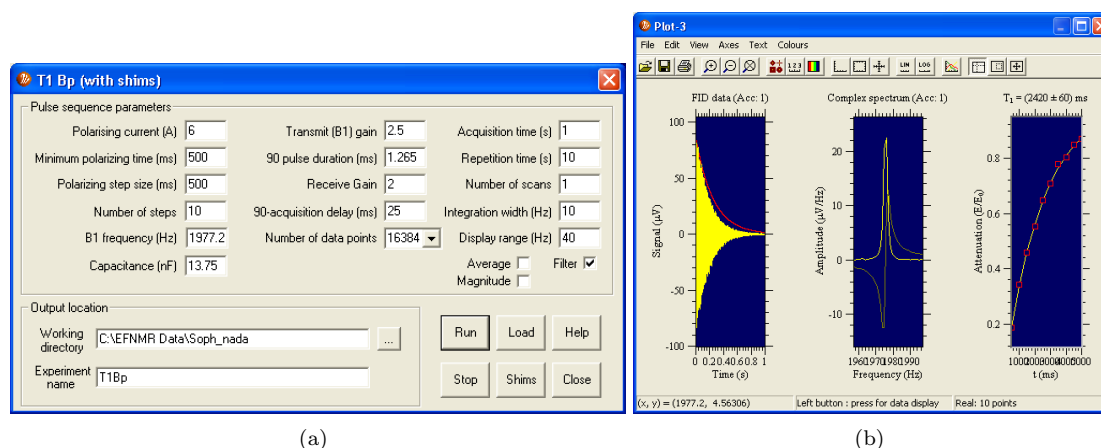
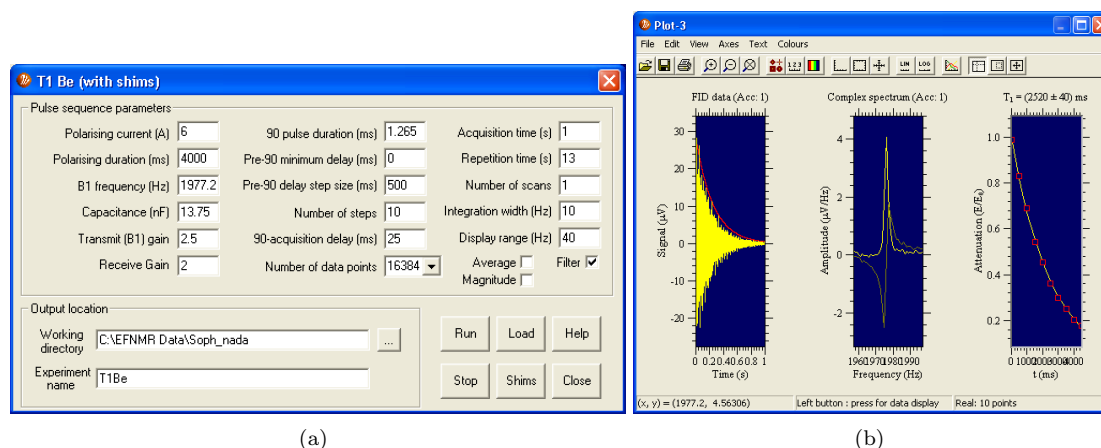
Measuring T_1

Recall that T_1 is the characteristic time scale of the magnetization build-up/decay in a magnetic field and is dependent on the chemical environment. However, T_1 certainly should not depend on the specific magnetic field being used. We will thus measure it twice, once in B_p and once in B_E . This is accomplished as follows:

- In the first case, we run a series of pulse-and-collect experiments with different τ_p 's (see Fig. 7) and record the signal amplitude at each value. The data points thus taken should have the functional form $S = S_0 [1 - \exp(-\tau_p/T_1)]$. This is a growing exponential because the magnetization is building up.

- In the second, we can measure T_1 by running a series of pulse-and-collect experiments with different pulse delay times, labeled t in Fig. 7. These points should follow the curve $S = S_0 \exp(-t/T_1)$, a decaying exponential, as the magnetization decays after the polarizing pulse ends.

Select the **T1Bp** experiment from the **EFNMR** menu and set the parameters according to Fig. 10 (a). Again we aim to cover a range of time values on the order of T_1 . Run the experiment – you should get a clean exponential such as that in Fig. 10 (b). Save the plots and write down your first measurement of T_1 in water. Next, choose the **T1Be** experiment and with Fig. 11 for guidance, run the experiment and document the results. Do your two values for T_1 agree within experimental error?

Figure 10: The **T1Bp** dialog box and typical output plots.Figure 11: The **T1Be** dialog box and typical output plots.

Swap the water sample for oil. Repeat the **T1Bp** experiment, averaging every four scans with **Minimum polarizing time** and **Polarizing step size** both set to 15 ms. Record T_1 and save the plots. Also repeat the **T1Be** experiment, averaging every four scans with **Pre-90 delay step size** set to 15 ms. Record T_1 and save the plots. Do your two measurements agree within experimental error?

Optional

This section will not be marked. If you are curious and have time to spare, you may like to try some of the imaging experiments that are possible with the provided equipment. These are described in chapter 5 of the

Terranova-MRI user manual, available on the bench next to the equipment. You are not expected to try and understand in detail how and what is being done, but are given an opportunity to “play” and produce some MRI scans of your own. Have fun!

Analysis and write-up

Needless to say, you need to write a comprehensive and thorough description of the work you have done in the course of the lab (try to demonstrate that you understand what is going on!). Back up your statements by referring to the theory section and by providing experimental evidence. Also, please answer the following questions:

1. Given that $\gamma = 2.675 \times 10^8 \text{ T}^{-1}\text{s}^{-1}$ for a proton, and that at our location $|B_E| = 54 \text{ }\mu\text{T}$ (Auckland central, at sea level), calculate the expected Larmor frequency ω_0 and $f_0 = \omega_0/(2\pi)$. Is f_0 similar to that obtained in your experiment? If not, how can we account for the discrepancy?
2. In the theory section, the excitation field \underline{B}_1 was a rotating field in the x - y plane. In the practical experiment, \underline{B}_1 was applied along the coil axis (which we decided was going to be aligned with \hat{y}) and oscillated sinusoidally with time. Clearly this does not significantly change the effects predicted with a rotating field because the experiment worked. How may this be explained?
3. Use your data from the **AnalyseCoil** experiment and your knowledge of the experimental f_0 to calculate the coil capacitance that would bring the LCR circuit into resonance with the NMR signal. Is it close to the value found by the “ring-down” method?
4. Why do we want to use a $\pi/2$ excitation pulse in particular in the basic pulse-and-collect sequence? What would happen if we used a different angle? (Think about the detection process).
5. Devise and describe a *simple* experiment using the hardware and software available which would enable you to test whether the spin-echo sequence actually does get rid of the effect of field inhomogeneities a time $2\tau_E$ after the $\pi/2$ pulse. Testing this experimentally (according to your devised procedure) is optional.