Experiment G-7b

Pulsed Nuclear Magnetic Reonance
(computer-controlled)

1.   Set up equipment to obtain (using program "Intercom") a $\pi/2$ pulse and observe the free induction decay of a proton sample. Measure the static field H_O and calculate the gyromagnetic ratio of the proton. Estimate the rf field, H_1, and understand the variation of the FID wave form with H_O. What is the effect of the pulse repitition frequency on the signal amplitude?
N.B. DO NOT EXCEED 0.1% DUTY CYCLE ON THE TRANSMITTER.

2. Measure $T_2{}^*$, T_2 and T_1 for as many of the provided samples as possible. Understand the phenomenology of the physical mechanisms which underly these relaxation rates.

3. Observe and understand the origin of the two different resonances in the sample containing inequivalent fluorine nuclei.

(4) Measure the Knight shift in metallic lithium.

References:

1.   C.P. Slichter, *Principles of Magnetic Resonance*, 2nd Ed. p.1, 2, 4.1-7, 8.2,   Springer-Verlag, Berlin (1978)
2.   R.R. Ernst and W. A. Anderson, Review of Scientific Instruments, Vol. 37, p.93 (1966).
3.   T.C. Farrar and E. D. Becker, *Pulse and Fourier Transform NMR* , Academic Press, New York (1971).
4.   D. Shaw, *Fourier Transform NMR Spectroscopy*, Elsevier, Amsterdam (1976).
5.   A. Abragm, *Principles of Nuclear Magnetism,* Clarendon, Oxford (1961).
6.   J.W. Akitt, *NMR and Chemistry: An Introduction to the Fourier Transform-Multinuclear Era*, Chapman and Hall, london (1983).
7.   E. Fukushima and S. Roeder, *Experimental Pulse NMR: A Nuts and Bolts Approach*, Addison-Wesley, Reading (1981).

Pulsed Nuclear Magnetic Resonance
Experiment G-7b

Contents

---

[1]A * indicates references reprinted in the back of these notes.

---

[2]Taken from W.D.Knight, *Solid State Physics*, vol 2, p93(1956).

1 Instructions

DO NOT change any settings on the equipment before getting instructions on it. A description of the apparatus follows the references page.

1. Read the sections on "Getting Started" and "A Brief Description of the Apparatus". Find the proton nuclear magnetic resonance. How can you measure the rf frequency? With a Hall probe measure the magnetic field $\vec{H}_0$ and calculate the nuclear magnetic moment of the proton in nuclear magnetrons. Optimize the $\frac{\pi}{2}$ pulse (Channel 1 on the transmitter), and measure its width with the scope. From this information, calculate the rf field H_1. (You should calculate the nuclear magnetic moments of fluorine and lithium when you measure these later.)

2. Measure T_2^* using the program FID off-resonance for the paramagnetic Cu^{++} solutions: $10^{21}, 10^{20}, 10^{19}$ ions/cc. Estimate the magnetic field inhomogeneity ΔH over the sample volume, and, assuming $T_1 \approx T_2$ and that the relaxation rate is proportional to the ion concentration, estimate T_2 for the 10^{20} ions/cc sample.

3. Measure T_2 for glycerin, for deionized water, and for all of the Cu^{++} ion solutions from 10^{17} to 10^{21}. How do you correct the T_2 values for diffusion? (See the discussion in Abragam's book, pg 57ff.)

4. Do the same, but measure T_1 instead. What is the physical reason for the difference between T_1 and T_2? Are they always different?

5. (Chemical shift) Observe and understand the origin of the difference between the fluorine resonances in the freon sample.

6. Measure the Knight shift in metallic lithium and compare your answer to the published shift. What causes this shift?

2 References[1]

Introductory:

*1. G.E. Pake, *Solid State Physics*, vol. 2, pp 1-92, 1956. (The Physical Sciences Library has this volume, with the call number QC173.S68. See the back of these notes for a reprint.)

2. E. Fukushima and S.B.W. Roeder, *Experimental Pulse NMR, A Nuts and Bolts Approach*, Addison-Wesley Publishing Co., 1981. (The P410/510 Library has this book.)

QC 762.F9G

Other Articles:

3 R.R. Ernst and W. A. Anderson, *Rev. Sci. Instrum.*, vol 37, 93 (1966).

*4. "Relaxation Effects in Nuclear Magnetic Resonance Absorption", N. Bloembergen, E.M. Purcell, R.V.Pound, *Physical Review*, vol 73, p679(1948). A general discussion of relaxation, including the effect of viscosity on T_2, and the relation between T_1 and T_2 in some interesting cases.

*5. "Spin Echoes", E.L. Hahn, *Physical Review*, vol 80, p580(1950). This is the original article detailing the method of spin echoes. This method is used throughout G7.

*6. "Effect of Diffusion on Free Precession in Nuclear Magnetic Resonance Experiments", H.Y.Carr, E.M.Purcell, *Physical Review*, vol 94, p630(1954). Explains how diffusion affects the T_2 measurement. The famous Carr-Purcell pulse sequence is used in the T1 program in G7.

*7. "Nuclear Induction", F. Bloch, *Physical Review*, vol 70, p460(1946). Bloch (Stanford) and Purcell (Harvard) simultaneously and independently discovered NMR in 1946, and were awarded the Nobel Prize in 1952. This paper introduces the famous Bloch equations which are used everywhere NMR is studied.

Books On NMR:

8. A. Abragam, *Principles of Nuclear Magnetism*, Oxford Univ. Press, reprinted 1989. QC762.A15

9. C.P. Slichter, *Principles of Magnetic Resonance*, Third Edition, Springer-Verlag, 1989. See sections 1,2,4.1-7,8.2.

---

[1]A * indicates references reprinted in the back of these notes. GC762.S63

Advanced Topics:

10. J.W. Akitt, *NMR and Chemistry: An Introduction to the Fourier Transform-Multinuclear Era*, Chapman and Hall, London, 1983/

11. C.P. Poole and H.A.Farach, *Relaxation in Magnetic Resonance*, Academic Press, 1971 (QC762 P82 R3)

12. J. Sandström, *Dynamic NMR Spectroscopy*, Academic Press 1982. (In the P410/510 Library)

TRANSMITTER

quench
output

shift out (to mixer)   (in back)

channel 1   channel 2

to scope channel 1

RECEIVER AND MIXER

RF
in

narrow band   reference
in

to scope channel 2

ADC

180

Reset   power on

90

analog in

attenuator
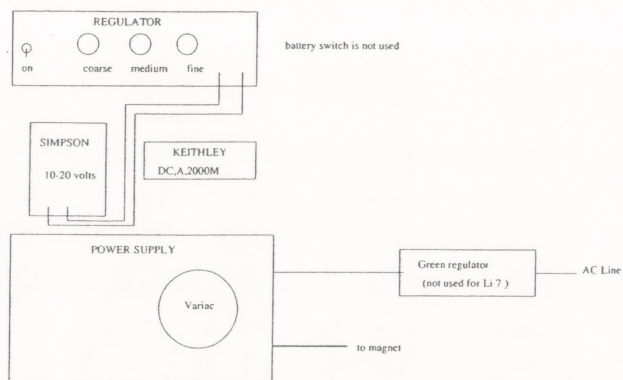
PREAMP

Q in

to receiver   hi Z

to
preamp

from transmitter   coil

to coil
in magnet

FRONT PANEL WIRING

REGULATOR

on   coarse medium fine

battery switch is not used

SIMPSON

10-20 volts

KEITHLEY

DC,A,2000M

POWER SUPPLY

Variac

Green regulator
(not used for Li 7)

AC Line

to magnet

POWER SUPPLY/REGULATOR SETUP

3 A Brief Description of the Apparatus

Note: It is helpful to have a general idea of what "Pulsed NMR" is before reading much further in the documentation. The book by E. Fukushima and S.B.W. Roeder (Reference 2) is a very good place to start.

1. The transmitter, sample coil, preamp and receiver. Briefly, the transmitter generates short ($\approx 25\mu s$) pulses of 10 MHz rf. ($\frac{\pi}{2}$ pulse, channel 1) or $\approx 50\mu s$ long, (π pulse, channel 2). The $\frac{\pi}{2}$ pulse turns the nuclear spins by 90° so that they are precessing around the magnetic field direction at the Larmor frequency. This frequency is set by the magnetic field, so can be slightly different from the fixed frequency of the RF. When the spins are all aligned they generate a time-varying magnetization which is picked up in the coil and into the preamp. This occurs after the $\frac{\pi}{2}$ pulse. The preamp is quenched so that it does not respond to the $\frac{\pi}{2}$ pulse, but does respond to the subsequent (decaying) magnetization RF pulse. In the receiver, a mixer mixes the transmitter RF and the signal pulse. The mixed signal passes through a low-pass filter, giving a low frequency signal which oscillates at the difference frequency between the spin signal and the transmitter RF. The envelope of this signal, which is what you observe on the

6

scope, decays exponentially in time. If two NMR signals are present, each with slightly different frequencies, beats are also observed. A diagram on the following pages shows the interconnections between these circuits.

2. The sequence starts when the computer sends a signal to channel 1 on the transmitter from the output labeled "90" on the ADC panel. This generates a $\frac{\pi}{2}$ pulse, quenches the preamp for the receiver to avoid blasting the receiver, and triggers the scope. The sequence of $\frac{\pi}{2}$ and π pulses (90 and 180 output from the ADC) into the transmitter channel 2 are controlled by the computer. The lengths of these two pulses must be set by you, using the "spin echo" setting on the transmitter. Ask your instructor for more details about this procedure.

3. The signal after these pulses are gone is received by the now un- quenched receiver. It is mixed with a 10 MHz reference signal from the transmitter, and the resulting low frequency signal is amplified with an amplifier time constant usually (but not always) set to 30 μsec. The signal into the receiver passes through an external attenuator, which can vary, but is normally set to 10 dB. The receiver output from "narrow band" goes to the scope channel 2.

4. It is important that the settings on the preamp be left unchanged. Of course the preamp power supply must be on!

5. The power supply to the magnet must be regulated to within a few parts per million. This cannot ordinarily be achieved with commercially available power supplies, so there is a regulator designed for this experiment by Prof. Hartill. This regulator is rather delicate, and can be burned out if the instructions are not followed. Fixing it may cause a serious delay in getting the experiment back online. The best way to bring up the current is to set the range and coarse controls to the right values, with the fine control in the middle of its range. Then raise the variac, keeping an eye on both the Simpson meter and the Keithley. The proton resonance corresponds to a reading in the vicinity of 274-275 ma. The Simpson meter should never exceed 20 volts. If the coarse and medium controls are not correctly set, you will get 20 volts, but not have the right current to see the resonance. Raise or lower the regulator controls and adjust the variac again to get about 15 volts. This gives the best regulation.

6. For the Li^7 resonance, much more current is needed. You will have to remove the "green regulator" and plug the power supply directly into the wall. The coarse control will have to be set near to the top of its range.

4 Getting Started – Observing the Proton Resonance

This section will show you how to how to turn on the NMR pulse spectrometer, how to establish the resonance and generate perfect $\frac{\pi}{2}$ and π pulses. This first section will guide you through the setting up the hardware and observing the proton resonance without using the computer interface. The second part of the section will then introduce you to the computer interface.

4.1 Turning on the Apparatus

The apparatus must be initialized in a definite order to avoid damage to the electronics. One very important thing to remember: **THE DUTY CYCLE OF THE TRANSMITTER MUST NOT EXCEED 0.1%.** In practical terms, the repetition rate of the transmitter should not exceed 5 Hz. When the computer is controlling the pulse rate, it automatically checks to see the 0.1% requirement is satisfied. When you start with the pulse generator, you can burn out the transistors in the transmitter with a rep rate that is too high. **DO NOT EXCEED 5 HZ AT ANY TIME!**.

For the initial turn-on, follow the procedure below. After you have set up the transmitter pulses the first time you turn on, the next times, you can go directly to computer control, skipping item 0. below.

The "Pulse Programmer and Data Acquisition System", the module just below the receiver, will be referred to below as "PPDAS" or just "ADC" (Analog to Digital Converter) for short.

Note: If, after turning everything on, you see large noise pulses on channel 2 instead of a resonance signal, push the "RESET" button located on the PPDAS panel. This resets the clock from a weird state it sometimes gets into.

0. Set the DATAPULSE pulse generator to 5 Hz (10 Hz,variable knob to mid-scale). Remove the cable from the "90" output on module #2 on the PPDAS and connect it to the pulse generator + output, which is set to 5 volts. The width is not critical, but should be about 5 μs. This cable should now be connected from the pulse generator output to the TRIGGER IN on the transmitter. The pulse generator now controls the pulse sequences instead of the computer.

   The sequence 1-10 below should be followed when turning on the apparatus from a cold start, even when the computer is connected instead of the pulse generator.

1. Turn on the Heathkit Tri-Power Supply. The voltage reading should be in the 15-18 volt range. Do not attempt to change this. Call your instructor if it is out of range.

2. Turn on the Sorenson NOBATRON power supply.

3. Turn on the Heathkit Regulated Power Supply, which is located on the magnet. The voltage setting should be halfway between MIN and MAX, and the current setting should be MAX. Again, make no changes, but call your instructor if this looks incorrect.

4. Make sure that the magnet variac (the big black knob on the magnet power supply) is turned to zero (i.e. fully counterclockwise). Turn on the magnet supply. If the light beside the switch fails to go on, check that the green regulator near the wall behind the magnet is on and plugged in. The magnet supply should be plugged into this regulator.

5. Turn on the PPDAS (panel with ADC). The light beside the switch should glow.

6. Turn on the digital multimeter. It should be on the 2000 mA DC range. Check that the Simpson meter is on the 50 volt DC range.   20m

7. Insert the 10^{19} Cu^{++} ions/cc sample in the magnet sample holder.

8. Turn on the magnet regulator on the rack above the Lambda (which is not used). Set the range control to 3.94, the coarse control to 9.02 and the fine control to 8.23. (These are only nominal settings.) Turn the variac slowly up until the digital meter reads 274.3 mA and the Simpson meter (13) volts. (The regulation range is 10-20 volts. You risk burning out the regulator if you exceed this voltage.) Let the magnet warm up for about an hour to avoid drift problems. (After about an hour, the fine control had to be reset to 8.20.) The BATT switch on the regulator is not used.

9. Turn on the TEKTRONIX oscilloscope. CH1 should be connected to TRIGGER IN on the transmitter. CH2 is connected to NARROW BAND on the receiver to observe the resonance signal. The scope settings initially (adjust them later to suit yourself) should be:

   - TRIGGER: edge,rising,CH1,normal,dc. The level is 1.2 volts.
   - CH1: dc,BW limit=off,coarse,1x. CH1 1.00 v.
   - CH2: dc,BW limit=off,coarse,1x. CH2 1.00 v.
   - HORIZONTAL: window,level, holdoff 2 msec
   - ACQUIRE: sample

10. The transmitter settings should be:

   - PHASE SHIFT: 11 o'clock
   - PULSE DELAY: 2.55
   - INTERNAL ECHO: off
   - CH. 1: 0.80
   - CH. 2: 5.50
   - ATTENUATOR: 10 dB

11. The receiver settings should be:

   - BOXCAR OFFSET: 5 o'clock

- DC OFFSET: 11 o'clock
- C_L= 5 o'clock, R_L = 1 o'clock, R_D = 2 o'clock, BX GAIN = 12 o'clock
- COUPLING: AC
- BANDPASS: 30 μs
- ATTENUATOR on top of unit: all out.

12. Tune the fine control until you see a resonance which looks like a decaying exponential, without "wiggles". If you are far off the resonance, you will see rapid oscillations. Very far off the resonance, you will see nothing. If that happens, recheck that everything is connected as it should be. If you still don't see the resonance, call your instructor.

What you should see is the "free induction decay" (FID) pulse after the 90° ($\frac{\pi}{2}$). This is the pulse which turns the spins at right angles to the DC magnetic field. You can maximize the amplitude of this pulse by varying the setting of channel 1. Also, check the tuning of the resonant circuit, again maximizing the signal amplitude. (This is the short black stub on the left box of the two boxes mounted on the magnet.)

Next, turn on the INTERNAL ECHO and adjust the pulse delay so that there is a few milliseconds delay between the first pulse (channel 1) and the second pulse (channel 2). Tune the width of the channel 2 pulse to maximize the spin echo, which is a bump appearing at 2τ, with τ equal to the separation between pulse 1 and pulse 2. Channel 2 is the 180° pulse (π). Maximizing the spin echo corresponds to achieving π rotation of the spins. Turn off the INTERNAL ECHO before proceeding.

The rest of the experiment assumes that you have set up both pulses correctly.

4.2 Initializing the Interface

After you have succeeded in seeing the proton resonance try doing it with the computer interface. The DATAPULSE pulse generator will no longer be needed as the "90" and "180" jacks on the ADC will now supply the appropriate trigger pulses. The NMR software is started by typing nmr at the DOS prompt. Make sure that all of the hardware is powered up before doing this. After a short pause you will see this screen:

```
It is necessary to configure the zero point of of the ADC.  Doing this
properly allows for maximum useful range of the ADC and ensures that
ground on the analog input is defined as 0 in the software.  This process
should be repeated whenever a DC drift is noticed in the data.  This
will occur if the DC offset on the analog input changes.

1.  While viewing the analog input to the ADC on the DC coupled
    oscilloscope, adjust the DC offset on the receiver until
    no offset is seen on the scope.

2.  Now adjust the offset on the ADC until only the LED next to
    the number 128 is on.

When finished press <ENTER>.
```

The ADC that is used for the experiment can register values between 0 and 255 (8-bit). Since we are going to be dealing with both negative and positive voltages it is important that ground be defined near the middle of this range. With everything powered up and while looking at the analog input signal on an oscilloscope (*make sure it is DC coupled*), adjust the DC offset knob on the receiver until no DC offset is visible on the oscilloscope. After this is done we want to set the value on the ADC that we want assigned to this voltage, which should be zero volts if the first step was done correctly. With the analog input plugged into the ADC, adjust the offset *on the ADC* until the code displayed on the LEDs is equal to 127 or 128. The LEDs represent each bit of an 8 bit number, so 127 would be equal to LEDs 64, 32, 16, 8, 4, 2, and 1 all turned on. Likewise, 128 is coded by just turning on LED 128. After you have setup the ADC properly press the ENTER key. This will store the zero point in the software. Occasionally a DC offset develop over time on the analog input, if this occurs, it will be necessary to reinitialize the ADC. This can be done from the main menu.

4.3   The Main Menu

Once you have finished with the hardware initialization you will be taken to the main menu:

```
This software controls the NMR pulse transmitter and data acquisition systems.

Please choose an option from the menu below:

(1)   Pulse Transmitter - useful for hardware testing and setup
(2)   Digitize FID - acquire and manipulate free induction decay data
(3)   Measure T1 - use a sequence of pi and pi/2 pulse pairs to measure T1
(4)   Measure T2 - use the Carr-Purcell technique to measure T2
(5)   Reinitialize ADC
(6)   Exit
```

From this menu you will be able to access all of the procedures needed to do your study of NMR. For now we will just be concerned with menu option 1. The others will be discussed in detail later.

4.4   Pulsing the Sample

Before doing any measurements, you should first check to be sure that you can actually see the proton resonance on the oscilloscope. To do this set the scope to trigger on the output of the 90 ($\frac{\pi}{2}$ pulse) terminal from the pulse programmer. This is the same signal that should also be going to the transmitter, you will have to use a T connector to do this. With the other scope channel view the analog input to the ADC (again a T connector will be necessary). Load a sample into the magnet, for example 10^{19} Cu^{++}/cc, and select option 1 from the main menu. You will see:

```
NMR->PULSE

(1)   Start pi/2 pulsing
(2)   Start pi pulsing
(3)   Stop pulsing
(4)   Adjust pulsing rate
        Current period is       253.     ms
        Current frequency is    3.96     Hz

(5)   Return to main menu
```

Selecting option 1 will begin sending $\frac{\pi}{2}$ pulses to the sample at a rate of 3.96 Hz. Once the $\frac{\pi}{2}$ pulsing has started, you can begin to adjust the hardware parameters (magnetic field and possibly scope options) to see the proton resonance clearly.

At any time you can stop the pulsing or switch to sending π pulses by selecting the appropriate menu option. Note that if you switch to π pulses it will be necessary to adjust the cabling so the scope triggers on the signal coming from the 180 output on the pulse programmer instead of the 90 output.

4.4.1 Changing the Clock Settings

To change the rate at which the sample is pulsed, select option 4 from the menu. You will be given the clock configuration screen:

```
By adjusting the clock rate one is able to pulse the transmitter and
acquire data on a wide variety of time scales.


Please choose a clock setting from the table below:
```

| Setting	Time per Channel (milliseconds)	Time per Memory Cycle (milliseconds)	Memory Cycle Rate (Hz)
1	0.386E-02	15.8	63.3
2	0.772E-02	31.6	31.6
3	0.154E-01	63.2	15.8
4	0.309E-01	126.	7.91
5	0.617E-01	253.	3.96
6	0.123	506.	1.98
7	0.247	0.101E+04	0.989
8	0.494	0.202E+04	0.494
9	0.988	0.405E+04	0.247
10	1.98	0.809E+04	0.124
11	3.95	0.162E+05	0.618E-01
12	7.90	0.324E+05	0.309E-01

One pulse is sent to the transmitter every memory cycle, therefore the rightmost column indicates the various pulse frequencies available. Simply enter the number of the setting you wish to select. You will be returned to the pulse menu and the transmitter will begin pulsing at the new frequency. The clock configuration screen is common to all parts of the NMR software. Its setting is maintained even when switching among the various measurement routines.

5 A Brief Hardware Digression

Before discussing how to use the software to measure things like T_2^*, T_1, and T_2, we should make a very brief digression into how the system sends a pulse train to the transmitter and acquires data from the ADC. It is hoped that a short discussion here will enhance your understanding of the software.

The software works by writing commands into a block of memory. This block of memory has 4096 containers, or "channels". Into each channel various commands can be written, like "send π pulse" or "sample analog input." The pulse programmer and ADC hardware then read out this memory at a certain rate (defined by the clock setting). For example in

the case of simply pulsing the sample once every memory cycle, the memory might look like this:

$\pi/2$	NULL	NULL	NULL	NULL	$\cdots\cdots\cdots$	NULL
1	2	3	4	5		4096
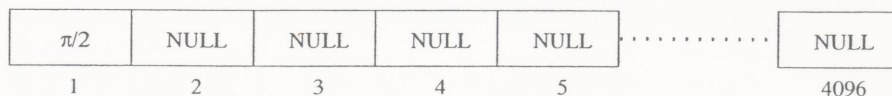
Therefore, when channel 1 is read (once every memory cycle), a $\frac{\pi}{2}$ pulse is sent to the transmitter. Nothing is done when channels 2 through 4096 are read. This better explains the significance of the columns in the clock configuration screen. The time per memory cycle is the time it takes to read all 4096 channels of the memory. The time per channel is the time delay between reading two adjacent channels in the memory. In many of the measurements you will set up the pulse train in terms of channels. The "real time" equivalents are based on the current clock setting and will also be displayed. This setup has the advantage that the same pulse train can be used on a wide variety of samples by simply adjusting the clock setting. With all of this said, there are two restrictions to keep in mind with this setup. Obviously, the total length of any pulse train cannot exceed 4096 channels. Also, only a maximum of 512 of the 4096 channels can be used to acquire data from the ADC. Now lets continue our discussion of the software.

6 Digitizing the Free Induction Decay of a Sample

The relaxation time T_2^* includes three effects: 1) magnet inhomogeneity, 2) spin-spin relaxation (T2), and 3) spin-lattice relaxation (T^1). An approximation formula for T_2^* is:

$$\frac{1}{T_2^*} = \gamma \Delta H_0 + \frac{1}{T_2} + \frac{1}{2T_1}$$

The spin echo experiment was invented to isolate the effects of spin-spin relaxation and determine T_2, the intrinsic effect, without the purely extrinsic effect of magnet inhomogeneity, which in principle could be removed by building a better magnet with a more uniform field.

Selecting option 2 from the main menu will allow you to digitize the FID of a sample. You will be brought to the FID menu:

```
NMR->FID

( 1)  Configure digitization parameters
( 2)  Acquire data with current parameters
( 3)  Calculate T2* from data
( 4)  Do Fourier transform of data
( 5)  Store data on disk
( 6)  Load data from disk
( 7)  List data on screen
( 8)  Plot data on screen
( 9)  Plot data on printer
(10)  Return to main menu
```

14

6.1   Configuring Parameters and Acquiring Data

Selecting option 1 will allow you to configure the parameters for FID digitization. The parameters are displayed in this screen:

```
NMR->FID->CONFIGURE


Current FID digitization configuration:

    PULSE SETUP                                 Channels     Real Time (ms)
    -------------------------------------------------------------------------
1   Recovery time after pi/2 pulse                 3            0.1852
       Digitization begins at this time -->                    0.2469
2   Time between ADC samples                       1            0.6173E-01
       Digitization ends at this time -->                      63.40


    RUN INFORMATION
    -------------------------------------------------------------------------
3   Number of runs (data will be averaged)                      10
4   Time (in seconds) between runs                             3.000


5   Clock setting:
       Time per channel (milliseconds)                        0.6173E-01
```

Enter number of parameter to change (0 to return to FID menu):

   You can change any one of the parameters by entering the number of the parameter you wish to change. A discussion of the various parameters follows:

1. `Recovery time after pi/2 pulse` - This parameter sets the number of channels to wait after the $\frac{\pi}{2}$ pulse before digitizing the FID. Occasionally the first few channels after the pulse will be quite noisy so you might want to leave these out the sample.

2. `Time between ADC samples` - Since we are limited to only 512 ADC samples in any memory cycle, you might want to skip a few channels in between samples. This will allow you to sample over a longer period of time. The time after the $\frac{\pi}{2}$ pulse at which last sample of data will be taken is also displayed.

3. `Number of runs` - This controls how many times to repeat the measurement. Data for each time point will be averaged over all of the runs.

4. `Time (in seconds) between runs` - This sets the time to wait in between runs. Some samples have long relaxation times, so you might want to let the sample fully relax before beginning the next run.

5. `Clock setting` - This will take you to the clock configuration screen. From there you can change the clock rate. When you do so, the "real time" values in the FID configuration screen will be updated.

After you have configured the FID parameters, enter 0 to return to the main menu. From there you can enter option 2 to acquire the data.

6.2 Analyzing Data

By selecting option 3 from the FID menu you can fit the acquired data to determine the time constant of the FID. You will be asked whether the your data was taken on resonance or off resonance. If your digitized data has any sign of oscillation at all, the off resonance option is most likely the best choice. You will be give the fitted value for T_2^*, and a goodness of fit parameter "R", where R=1 for a perfect fit.

It is recommended that you use all of the "online" fitting tools as just a check to see that your data makes sense. Because of the design of the fitter, very accurate fits are not easy to get. Data can be easily imported to your favorite *modern* analysis software for more complete analysis. This also allows you to easily generate figures for your writeup.

6.3 Storing and Loading Data From Disk

It is possible to store raw FID data or its Fourier transform to a file on disk. Data will be stored to the directory from which you executed the `nmr` command. *It is highly recommended that you create your own directory on the local disk and start the software from there. Your data will then be stored in this directory.* To store data to disk select option 5 from the menu. You will be asked whether to store the FID data or its Fourier transform. Depending on the option you select, the data will be stored in a file called `FIDnn.DAT` or `FFTnn.DAT` where `nn` is a two-digit number that you will be prompted for. When storing some forms of data a log file will also be created. This file will have the `.LOG` extension. This file contains information about the configuration of the software when the data was taken.

The same data can also be loaded back into the software for analysis and viewing by selecting option 6 from the main menu. Again you will be prompted for the data type and the file number.

6.4 Viewing the Data

Options 7, 8, and 9 provide methods of viewing the data. You can list the raw numeric data on the screen or use the graphics mode to plot the data on the screen or printer.

7 Measuring T_2

The figure below shows the measurement of a sample containing Cu^{++} ions in the experiment G7a using a spin-echo technique. The plot shows that the spin-echo is not a perfect exponential vs. the time, but contains a t^3 term due to diffusion.

$$A(t) = ae^{-\frac{t}{T_2} - bt^3}$$

G7a: log echo amplitude vs time
T2 = 50.06 milliseconds
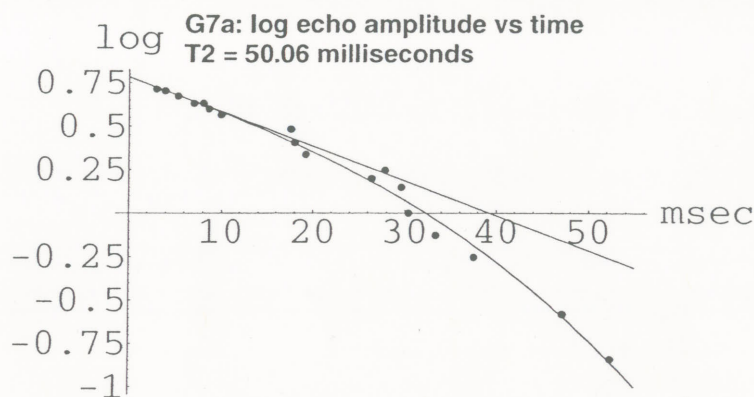
The G7b experiment uses a clever trick invented by Carr and Purcell to eliminate the effect of diffusion. After a $\frac{\pi}{2}$ pulse, a sequence of π pulses is given. The envelope of the echo decays can be shown to follow a purely exponential time dependence, from which T_2 can be calculated directly, without the additional t^3 term. Notice the scatter of the points in the figure above. This is due to a slight drift in the magnetic field while the measurement was being taken. This instrumental effect is eliminated in the G7b experiment.

Selecting option 3 from the main menu will take you to the T_2 measurement routine. The T_1 menu looks very similar to the menu for the FID routine; therefore, we will only point out the differences here.

7.1 Configuring Parameters and Acquiring Data

Selecting option 1 from the T_2 menu will allow you to configure the pulse sequence. The configuration screen appears below:

```
NMR->T2->CONFIGURE


Current Carr-Purcell configuration:


    PULSE SETUP                                    Channels      Real Time (ms)
    ----------------------------------------------------------------------------

1   Time from initial pi/2 to first pi pulse          80            4.938
2   Number of acquisition channels for echo           40            2.469


3   Number of pi pulses                                              4


       Final echo center at -->                      640           39.51


    RUN INFORMATION
    ----------------------------------------------------------------------------

4   Number of runs (data will be averaged)                          10
5   Time (in seconds) between runs                                  3.000


6   Clock settings:
       Time per channel (milliseconds)                           0.6173E-01


Enter number of parameter to change (0 to return to T2 menu):
```

The Carr-Purcell sequence involves sending a $\frac{\pi}{2}$ pulse to the sample, and then at subsequent regular intervals sending a series π of pulses to the sample. Each π pulse produces an echo. T_2 is the time constant with which the echo amplitudes decay. The configurable parameters for the Carr-Purcell sequence are:

1. `Time from initial pi/2 to first pi pulse` - This sets the time from the $\frac{\pi}{2}$ pulse to the first π pulse. Subsequent π pulses will occur at intervals spaced by twice this time after the first π pulse. For example with the setup shown above there would be a π pulse at channel 80, then 3 more π pulses at channels, 240, 400, and 560.

2. `Number of acquisition channels for echo` - This sets the number of channels used to digitize the echo. The echoes occur halfway between π pulses. The echo digitization channels will be centered about this point. Because of this, the number of echo acquisition channels cannot exceed the π to π pulse separation (given by $2 \times$ parameter 1).

3. `Number of pi pulses` - This specifies the number of π pulses to use. In addition, the time of the final echo is displayed. This value should be roughly twice the expected value of T_2 for the sample.

18

The other parameters can be configured as previously mentioned. Pay special attention the delay between runs. For some samples it might be possible that T_2 is much shorter than T_1. Always make sure the delay time well exceeds *all* relaxation times for the sample.

7.2   Analyzing Data

An online T_2 fitter is available from the T2 menu to determine T_2 from the data. The software will attempt to pick out the echo peaks and fit decay of the peaks to determine T_2. The fitter will ask if you how many echoes to eliminate from the beginning and end of the echo train. You should not fit echoes near the end of the train that do not have clear peaks. You will also be prompted to enter the value to which the echoes decay. If the zero point of the ADC is properly initialized this value should be zero. You can estimate the decay asymptote by plotting the data on the screen. After the fit is performed, the peaks and their times will be printed to the screen along with T_2 and the goodness of fit value R. The peak data can be recorded in order to aid in doing an offline fit. If the data is saved to disk, the entire echo train is saved (not just the peaks) so any offline analysis will have to extract the peaks first.

7.3   Diffusion Effects

Now that you have learned how to make a precise measurement of T_2, we can return to the question of why the G7a measurement, in the figure above, disagreed with the measurement reported here. What happened to the effect of diffusion, which gave the t^3 term in the amplitude decay in the G7a experiment? Of course there is still diffusion, and it still diminishes the signal, but when one uses the Carr-Purcell sequence, as we have done here, one gets a pure exponential decay. The catch is that it *still* includes a diffusion term. The exponent in this experiment is a combination of the true spin-spin relaxation and a diffusion term which depends here on $\tau^2 t$ instead of t^3. τ is the time between the $\frac{\pi}{2}$ pulse and the π pulse. Call $\frac{1}{T_2}$ as measured using the program T2 $\frac{1}{T_{2,apparent}}$. Then $\frac{1}{T_{2,apparent}} = \frac{1}{T_2} + \frac{1}{T_{2\prime}}$. $\frac{1}{T_{2\prime}}$ contains the effect of self-diffusion. It is proportional to τ^2, so if you measure $T_{2,apparent}$ for different values of τ, and make a plot of $\frac{1}{T_{2,apparent}}$ vs. τ^2, you should get a straight line, which extrapolates, at $\tau = 0$ to $\frac{1}{T_2}$, which is what you are trying to measure here. This correction will be important for long spin-spin relaxation times, probably for the $10^{17}, 10^{18}, 10^{19}$ Cu^{++} ions/cc samples and not very important for short relaxation times, where the diffusion has little time to take place. It will be an important correction for pure water, but probably is not important for glycerine, due to the high viscosity, for example. You will have to check it out.

A derivation of the exponential behavior for the self-diffusion term for the Carr-Purcell sequence can be found in the book by Abragam, pages 60-61 (see references).

7.4   Systematic Errors For T_2

The decay of the echo amplitudes depends not only on $T_{2,apparent}$, but also on the accuracy of setting the widths of the $\frac{\pi}{2}$ and π pulses. This should be done using the pulse generator and the ECHO ON switch. Explore how sensitive the result is on the widths of these pulses.

Phase errors will accumulate after several π pulses, leading to distortion of the echo shape. After how many pulses do phase errors become important? Does this lead to an overestimate or an underestimate of $T_{2,apparent}$?

The number of echo acquisition channels must be great enough to determine the maximum value of the echo.

Do the echos depend on the repetition rate of the pulse sequences, i.e. the time to wait between sequences. We have always used 1 second. Is that long enough? When would you need to make this longer?

7.5   Physics Questions About Spin-Spin Relaxation

What do you learn about spin-spin relaxation in the various samples? Plot $\frac{1}{T_2}$ vs. Cu ion concentration on a log-log plot. What does the slope of this plot tell you?

How does T_2 depend on a) being in a liquid relative to being in a solid (check out the different between melted and solid paraffin), b) the viscosity of the liquid (compare glycerine and water, for example)?

8   Measuring T_1

In order to measure T_1, a π pulse is applied to the sample, followed by a $\frac{\pi}{2}$ pulse. There is a sequence in which the time between the π and $\frac{\pi}{2}$ pulses is stepped through equally spaced time intervals. For each interval ("station"), the data is averaged for a number of measurements. The final result is then presented as an amplitude for each station.

When the π pulse is applied, the spins are reversed. The polarization is now antiparallel to the magnetic field, and it begins to relax toward the parallel direction. If we were to call the initial polarization just *before* the π pulse P_0, then the polarization would have the time dependence, after the π pulse:

$$P(t) = P_0 \left(1 - 2e^{-\frac{t}{T_1}}\right)$$

In order to measure the relaxation of the spins from antiparallel back to parallel, we apply a $\frac{\pi}{2}$ pulse at time t. This gives us a magnetization in the $x - y$ plane and a signal we can measure to get $P(t)$ at that time. After that, we have to wait for the spins to line up parallel to the field to begin the sequence again with another π pulse. By fitting the amplitudes for each pulse stations to the equation above we can determine a value for T_1 for the sample. What does this value for T_1 tell you about spin-lattice relaxation in the various samples? Should $T_1 = T_2$ or can they be different. Why?

Selecting option 3 from the main menu will take you to the T_1 measurement routine.

8.1 Configuring Parameters and Acquiring Data

Option 1 of the T_1 menu takes you to the configuration screen:

```
NMR->T1->CONFIGURE
```

```
Current T1 measurement configuration:
```

PULSE SETUP	Channels	Real Time (ms)
1 Base time from pi to pi/2 pulse	80	4.938
2 Number of recovery channels after pi/2 pulse	3	0.1852
3 Number of pi, pi/2 pulse pairs		6
Maximum pi to pi/2 pulse time -->		29.63

RUN INFORMATION	
4 Number of runs (data will be averaged)	10
5 Time (in seconds) between runs	3.000
6 Clock settings:	
Time per channel (milliseconds)	0.6173E-01

```
Enter number of parameter to change (0 to return to T1 menu):
```

Recall that to measure T_1 we send a π pulse to the sample, and then some time later we send a $\frac{\pi}{2}$ pulse. By plotting the amplitude of the FID after the $\frac{\pi}{2}$ as a function of the time between these two pulses, we can view the time dependent relaxation of the sample. Therefore we need to setup a scheme to measure this FID over a variety of π to $\frac{\pi}{2}$ pulse separations. The configurable parameters are:

1. `Base time from pi to pi/2 pulse` - This sets the smallest separation time. All other separations will be a multiple of this time.

2. `Number of recovery channels after pi/2 pulse` - As with FID digitization, this allows the system to wait momentarily after the $\frac{\pi}{2}$ pulse before beginning digitization to avoid recording noise that frequently occurs after a pulse. Such noise would make it impossible to get a decent measurement of the FID amplitude. *Incorrectly setting this parameter is the most likely cause for garbage data. Experiment with different settings to see what works best.*

3. `Number of pi, pi/2 pulse pairs` - This sets the number of different π to $\frac{\pi}{2}$ pulse times to measure. Each is a multiple of the base time (option 1). The maximum π to $\frac{\pi}{2}$ pulse time is also displayed. This time should be roughly twice as long as the estimated T_1 for the sample.

The other options are identical those used in the FID measurement. It is worth mentioning again the importance of selecting a delay time between runs that allows the sample to fully relax. As with the FID software, data can be acquired from the main T_1 menu in the same fashion.

8.2 Analyzing Data

As with the FID an online fitter exists to check your T_1 data. You can fit your data by selecting the appropriate option from the main menu. The fitter will then ask you how man data points ("stations") you would like to remove from the beginning and the end of the fit. For example, if the last data points are useless, you can choose not to fit them. It will then ask you whether or not to use the last data point as the large time asymptote. If the last point is not consistent with the large time asymptote, then you should enter the value by hand. This can best be estimated by plotting the data on the screen. After the fit is performed you will get a value for T_1 and also a value for R which, as mentioned before, is a measure of the goodness of fit.

9 Resonance Splitting Due To Inequivalent Nuclei

The resonant frequency of a given nucleus in a static field $\vec{H}_0$ will depend on the local environment of the nucleus. If there are two different environments for the nucleus, the resonance will be split. This will give a beat structure in the FID and in the spin echos. (Why? Don't forget that we have mixed down from the 10 MHz resonance frequency. The FID and spin echo represent envelopes of this response.) By Fourier transforming the FID or echo, the splitting of resonance can be determined. At the same time, it is usually possible to determine T_2^* by the width of the peak in the frequency spectrum.

Here we measure a Lithium Li^7 resonance in $LiNO_3$ and metallic Li. You can also look at the fluorine (F^{19}) resonance in freon and teflon. The magnet regulator range control is set for ≈ 410 for Fluorine and ≈ 950 for Lithium. In order to run at the much higher current required for Lithium, you must disconnect the regulator and plug the magnet power supply directly into the wall. Use the pulse feature to set up the FID on the scope. Use a low pulsing rate. At resonance, the current readings on the Keithley DVM are ~ 287 ma for F^{19}, ~ 717 mA for Li^7. The previous notes suggested a receiver time constant of 100 ms to start. You should check that the clock setting does not make the repetition rate too fast, thus decreasing the amplitude of the pulses. Change this to increase the amplitude if necessary.

Readjust the $\frac{\pi}{2}$ pulse width potentiometer on the transmitter front panel until you have maximized the amplitude of the FID. Measure the static field H_0 using a Hall probe (Gauss meter), and calculate the gyromagnetic ratio of the nucleus.

Turn on the INTERNAL ECHO switch, and adjust the pulse width of the π pulse to maximize the amplitude of the echo, and minimize the FID after the π pulse. You can compare the widths of the π and $\frac{\pi}{2}$ pulses using the oscilloscope. These adjustments need to be repeated when one is observing very different samples. Be sure to turn off the INTERNAL ECHO switch before taking data. Investigate the F^{19} resonance first.

9.1   Fluorine (F^{19})

There are two samples containing F^{19}: one is a clear liquid in an unmarked tube. This is thought to be Freon-113. There are inequivalent fluorine atoms in different environments with a relatively large chemical shift producing a splitting of the resonance. The other sample is a rod of teflon, which is polymerized CF_2. Here there is no splitting. The relaxation times are completely different for freon and teflon. Begin with the freon sample, which is easiest to observe. Set the RANGE on the regulator to 5.20 and adjust the variac and coarse/fine controls until the Keithley reads 292.4 and the regulator voltage is between 10 and 20 volts. The $\frac{\pi}{2}$ and π pulses will require readjustment, since the length must be slightly longer (about 6%) for fluorine compared to hydrogen. Tune these using the pulse option in the software. Note which clock setting gives you the largest amplitude. T_1 must be comparable to this. Notice the visible beat if you tune slightly off resonance. We estimated the length between minima as $2.4 \pm .2$ ms using the scope.

A few simple remarks about beats may be in order here. Let $\tilde{f} \equiv f_L - f_0, f_L$ is the Larmor frequency of one group of the spins in the magnetic field you have set, $f_0 = 10$MHz. Let Δf be the splitting between the two types of fluorine spins. Then, by a trig identity:

$$\cos 2\pi \tilde{f} t + \cos 2\pi (\tilde{f} + \Delta f)t = 2 \cos 2\pi (\tilde{f} + \frac{\Delta f}{2})\, \cos \pi \Delta f t$$

The beats correspond to zeros of the second term on the right side of the equation above. It is easy to show that, if the zeros occur at t_n,

$$t_{n+1} - t_n = \frac{1}{\Delta f}$$

So we see by our simple scope measurement of the minima between the beats, that $\Delta f \approx 400$ Hz. Notice, in comparison with 10 MHz, this is about 40 parts per million, corresponding to a local magnetic field difference of slightly less than $\frac{1}{10}$ gauss!

Try now to digitize the FID with the software and do a Fourier transform on it. This transform can then be written to disk and the splitting can be extracted from it. Try experimenting with different clock settings as this affects the resolution of the FFT.

The peaks cannot be treated as two isolated peaks, but one must take into account the interference between them, since they overlap. The frequency spectrum is a plot of the absolute magnitude of the Fourier transform of the amplitude vs. time. Since the amplitude is a real number, the upper half of the spectrum, which actually corresponds to negative frequencies, gives the complex conjugate of the lower half. Only frequencies up to half the maximum value in the plot are correctly represented.

The teflon sample shows a fluorine resonance signal, but is very much smaller, and does not have the splitting due to inequivalent F^{19} atoms. It is a polymer of CF_2.

9.2   Lithium (Li^7)

The nuclear magnetic moment of Li^7 is much smaller than for the proton or for fluorine. More field is needed to make the Larmor frequency equal 10 MHz. The increased current

will overheat the magnet unless there is water flow. This in turn requires that the interlock switch be closed, using the "cheat cord". Ask Nick if you need help with this. Do not run the magnet without water!

Set the range at 10.00 and raise the variac to about 65. The Keithley should read 716.1 mA when you are exactly on the resonance. Again vary the coarse control and the variac so that the regulator voltage is between 10 and 20 volts.

The attenuator was set at 5 dB. The signal is very noisy, so a longer receiver time constant is used – try 300 μs. The feedthrough signal lasts about 200 μsec after the width is set, so be aware of this.

You should increase the width of Channel 1 ($\frac{\pi}{2}$ pulse) to maximize the FID. It has to be much wider than for protons or fluorine signals. We found, using the INTERNAL ECHO, that it was possible to reach the proper width using Channel 2.

There are 3 samples to measure: $LiNO_3$ in solution, Li metal (in mineral oil) and a mixture of the two, which was prepared in order to facilitate measurement of the Knight shift. The first figure shows the FID for an average of 64 runs for the $LiNO_3$: Start by using the solution of $LiNO_3$, about 3×10^{21} Li ions/cc.
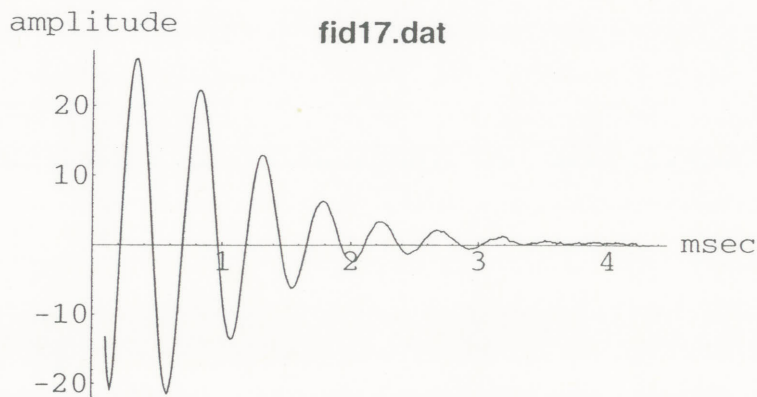
The Li metal, taken on the same time scale, and again averaging for 64 runs is shown next:
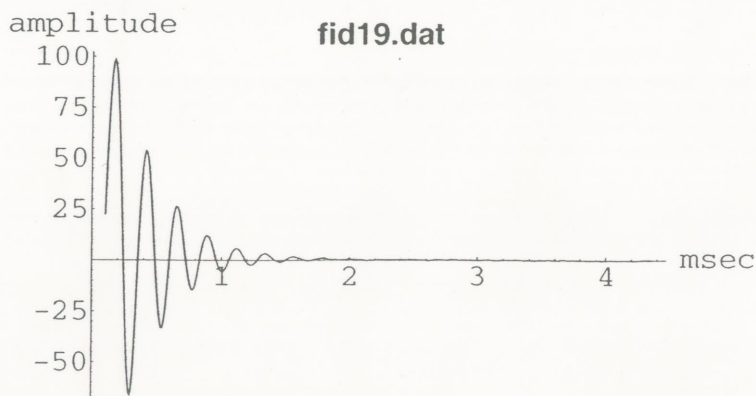
Finally, the mixture was analyzed, again under exactly the same conditions:

amplitude
fid20.dat

FREQUENCY SPECTRUM
fid20.dat
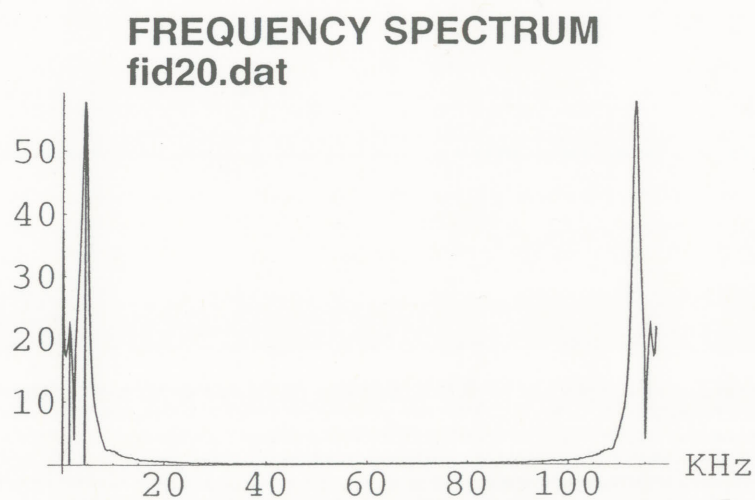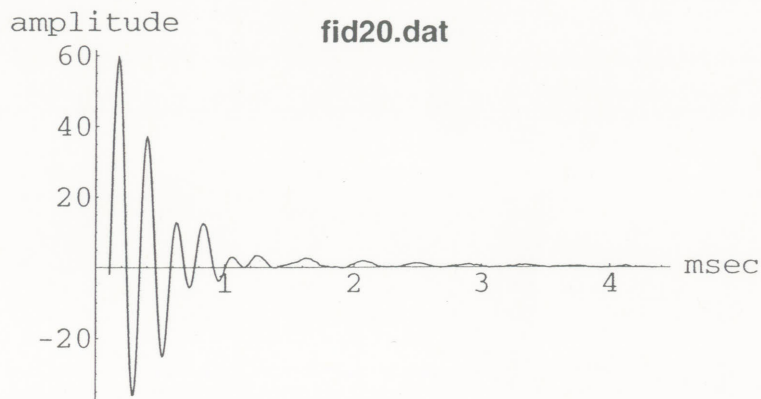
Locating two peaks in the last spectrum, we find one peak at 4.35 KHz, and another at 1.37 KHz. Taking the difference, we obtain a splitting (Knight shift) of 2.98 ± 0.32 KHz. Working with the separate samples, the FID17.DAT file ($LiNO_3$) has a peak at 2.06 KHz, while the FID19.DAT file (Li metal) has a peak at 4.12 KHz. The difference is 2.06 KHz. Which method is more accurate for determining the Knight shift? It isn't obvious. You should discuss this. Take data and obtain your own numbers. Would it help to use higher frequency resolution?

The published value of the Knight shift in lithium is 2.49 KHz = .0249% of 10 MHz.

9.2.1 Knight Shifts For Various Selected Elements [2]

| Element(Metal)	Frequency Shift: $\frac{\Delta f}{f}$ in percent	Compared to Compound
Li^7	.0249	LiCl
Na^{23}	.113	NaCl
Ga^{71}	.449	$GaCl_2$
Rb^{87}	.653	RbOH
Nb^{93}	.85	Nb_2O_5
Hg^{199}	2.5	$Hg(NO_3)_2$

The Knight shift is due to the hyperfine interaction between the atomic electrons and the nuclear spin. In a magnetic field, the electrons in a metal are polarized to a certain extent, and this increases the effective magnetic field at the nucleus. Valuable information about the electronic states can be obtained by measuring this shift, which increases roughly, but not exactly with Z due to the higher density of electrons around heavier nuclei. The article by Knight in the reference contains many more details.

---

[2]Taken from W.D.Knight, *Solid State Physics*, vol 2, p93(1956).

9.3 Methanol (CH$_3$OH)

As a final example, we study the methanol sample. This clearly has inequivalent protons – three have a carbon bond, and one has an oxygen bond.

The relaxation time T_1 appears to be long (measure it!) so when setting up with the pulse software use slow repetition rates. (This applies to the Li metal measurements, too.) The attenuator was set to 5 dB. Averaging over a very large number of runs helped.
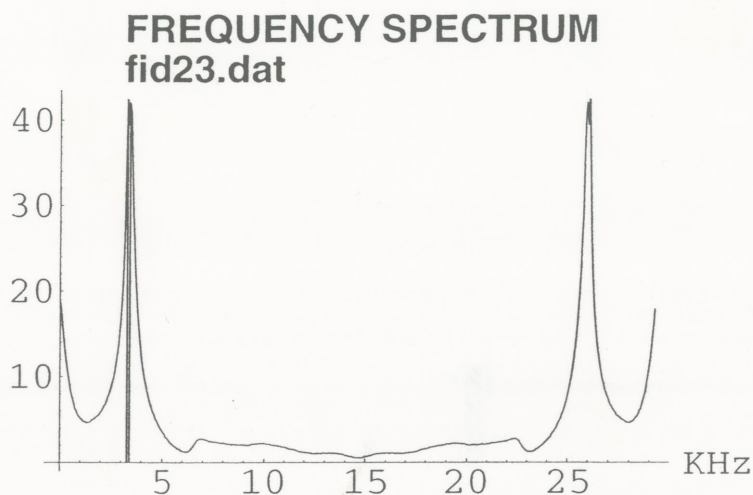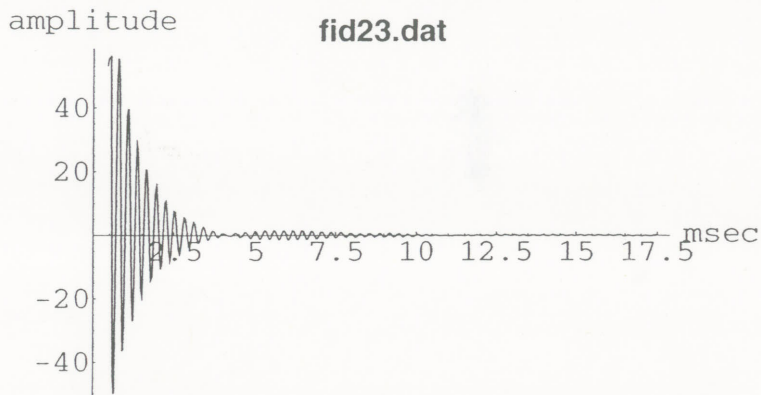
The amplitude vs. time plot does show a beat structure indicative of a splitting in the range of 200 Hz. The FFT plot of the frequency spectrum indicated two peaks separated by 115 ± 81 Hz. This is near the limit of the resolution, and the two peaks are not visibly separated on the plot above, although the separation was derived by analysis of the FFT data off-line. The high frequency side of the resonance peak looks rather odd, indicating (perhaps) some distortion where the pulse amplitude is large. The problem here appears to be that the magnet inhomogeneity, which produces a $T_2^* \approx 1$ msec, causes the envelope to decay rather quickly, making measurement of splittings below 1 KHz rather problematic. The cure would be a more homogeneous magnetic field or a smaller sample, plus very careful centering with the wooden shims provided.

A   Miscellaneous Notes

- The disk drive in the PC is a single density drive. In order to get data in and out of it you can take a standard high density disk and put tape over the hole in the corner which is used to tell the computer about the density of the disk. There will be two holes in the corners of the disk. One will have a "switch" that slides back and forth to block or open the hole. This is how the disk can be made write protected (switch open). You should put tape over the other hole to make the computer think the disk is single density. After inserting the disk you can type `format a:` to format the disk.

- If the digitized data looks excessively noisy or has a bizarre form, try (1) increasing the time delay between runs; (2) changing the base clock reduction factor. If the data exhibits plateaus, you're probably saturating the ADC. Insert some attenuation using the external attenuator. Do not use the switches on the receiver module.

- Occasionally, the pulse programmer will rapidly trigger several times in succession without acquiring data. Try increasing the base clock reduction factor.

- When fast clock rates are used in taking T_2 data, the echo peaks will appear displaced from the center of the digitized data. This is not your fault.

- Look on the wall for further hints, and the complete schematics of the apparatus.