Pulsed Nuclear Magnetic Resonance

An Experiment for UCSB's Advanced Laboratory

Foreword

Pulsed nuclear magnetic resonance is fascinating in its own right, and is also an incredibly important tool for investigating microscopic dynamical properties of condensed matter, determining the structure of molecules, imaging soft tissues and blood flow, and even implementing quantum computation algorithms. The purpose of this laboratory is two-fold: to show you some amazing macroscopic manifestations of quantum physics (and thereby gain an understanding of pulsed NMR), and to teach you to master a rather complex piece of experimental apparatus. The knowledge, experience and understanding you gain in this laboratory exercise will place you in a very good position to use this pulsed NMR apparatus to investigate microscopic dynamical properties of liquids, and to use research grade pulsed NMR apparati in the future to answer a wide variety of questions.

Reading materials available

Attached to this is the documentation for the PS1A spectrometer provided by TeachSpin. In the Senior Lab Library are also four books which may be very helpful.

1. Farrar and Becker, *"Pulse and Fourier Transform NMR."* This book is short, at a level which should be very accessible to Physics Senior at UCSB, and contains concise explanations of many things which may not be explained in the TeachSpin documentation.
2. Bloembergen, *"Encounters in Magnetic Resonances."* This is a collection of classic papers and the Ph. D. thesis of one of the pioneers of NMR, Nicolaas Bloembergen. Bloembergen eventually won a Nobel prize, and, as you will gather from reading his commentary or autobiographical notes, is also quite a character. Browsing in this book is highly recommended.
3. Abragam, *"Principles of Nuclear Magnetism."* "This book is the first (and possibly the last) attempt to give in a single volume a comprehensive account of all the concepts, methods, theories and results of the discipline called Nuclear Magnetism, that is the collective behaviour of nuclear spins in bulk matter, as it was perceived [in 1961]" (from the preface).
4. Slichter, *"Principles of Magnetic Resonance."* The standard textbook for a graduate-level course in NMR.

Instructions

I.   BEFORE you come to lab, read the attached introduction all the way through. After you have read it once, answer the questions below. Many of these are "order-of-magnitude" estimates of various quantities you will be measuring. As a physicist, making quick order-of-magnitude estimates is one of the most important skills you can have. It seems trivial—just plugging numbers into formulas—but it actually takes care

and practice, getting the units right, etc. . . Think about the numbers you get, and make sure they make sense!

    a. You observe a proton magnetic resonance signal at f=15.0 MHz. What is the size of the magnetic field?

    b. For a proton magnetic resonance experiment with signal at 15 MHz, and T=300K, what is the ratio of the population of the excited spin state to the ground spin state?

    c. How many protons are in one mm^3 of water?

    d. What is the magnetization of 1 mm^3 of water under the conditions described in question b? What is the magnetic field induced by this magnetization at a distance of 1mm (approximately)? (You will probably need to check your E&M book!) This is the magnetic field you will be measuring. How big is it compared to the earth's magnetic field?

    e. Why are the magnetic fields of the permanent magnet and the magnetic field induced by the Helmholtz transmitter coils at right angles?

    f. What mechanisms are responsible for the decay of the oscillating magnetization induced after the application of a 90º tipping pulse? Which of these mechanisms can be reversed? How?

    g. If you were designing a pulsed NMR system for higher sensitivity (and cost!) than this one, what might you do differently? Why?

II. Now, turn to the section of the manual entitled "The instrument" (p. 14). It's not a bad idea to read this section before you start turning knobs and doing things. At the least, you need to understand the diagrams on pp. 15 and 24. Please answer these questions before you start playing.

    a. Why is the connector on the rf output different from all of the other connectors?

    b. What does the rf amplitude detector do?

    c. What does the mixer do? How is the information coming out of the mixer different from that coming out of the rf amplitude detector?

III. Now that you understand a bit about magnetic resonance, and about the instrument, you can profitably begin to play with the oscilloscope and the pulsed NMR spectrometer.

Learning to use the oscilloscope is an important and essential part of this lab. This 'scope is probably different from others you have used in lower-division labs--or you may have never really learned to use an oscilloscope, in which case it's high time. This 'scope, the HP54600, is modern (as of Y2K) and like ones in use in many laboratories. Learning to use it is thus a worthwhile investment of your time, independent of this course.

Turn to the section entitled **"Getting Started"** (p. 26), which contains most of what you will do in this lab. The NMR spectrometer is a rather complex piece of electronic equipment. Even after reading about it, the number of switches,

buttons and connectors may still be a bit intimidating. However, it is very logically organized. Like any complicated thing, the way to understand it is to go through it methodically, understanding one piece at a time.

The Getting Started section of the manual takes you through the instrument one section at a time. Go through the following parts of the Getting Started section manual, answering the questions in the manual as well as those below. Your lab notebook should include **printouts** of the following oscilloscope traces (*in italics*), along with an explanation of what each one means.

Getting Started A: Pulse programmer
1. *Single pulses.* Using the cursors on the oscilloscope, measure and record the actual length of the pulses.
2. *A two-pulse sequence.* Again, use the cursors to compare the separation between the pulses to what the instrument says it should be.
3. *Multiple-pulse sequences with different delay times.* What happens when the repetition time is longer than the delay time?

Getting Started B: Receiver
The "dummy signal" at the rf frequency (near 15 MHz) for 2 different tunings of the receiver. To do this, you will need to hook the "cw rf out" to the dummy signal probe, and insert this probe into the sample holder in the magnet. You need to figure out how to get the rf into and out of the receiver module.

> *Note:* The oscilloscope you are using has a "bandwidth" of 100 MHz (meaning the amplifiers can respond to signals with frequency components as high as roughly 100 MHz) and sweep speeds as fast as 2 ns/div. However, the maximum "sampling rate" of the analog-to-digital converter at the heart of this scope is only 20 MSamples/s (50 ns between samples). How is this possible? (I'll answer this one!)
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> At relatively low sweep speeds, like the ones you used in part A, the display on the CRT was sampled as you would expect, one point after another. The voltages displayed on the CRT are recorded in the time required for one sweep, and the display is showing you a sequence of voltages measured in "real time." You can see the individual sampled points if you turn the "vectors off" in the display menu.
>
> At the higher sweep speeds (such as sweep speeds necessary to measure a 15 MHz signal), the voltages displayed on the CRT are recorded over a period of time which is longer than the time required for one sweep. This can work fine, as long as your signal is repetitive, but does not work for non-repetitive signals. Crudely, it works as follows. Say you want to digitize at a resolution of 1 point/ns (10^9 samples/s), but your digitizer can only sample at 1 point/50 ns (20×10^6 samples/s). Following a first trigger, you could digitize points at 0, 50, 100, 150, . . . ns. Following a second trigger, you could digitize points at 1, 51, 101, 151, . . . ns. Following the third trigger, you could digitize points at 2, 52, 102, 152, . . . ns, and so on. After a time 50 times as long as the time required for one sweep, you would have your waveform, effectively sampled at 10^9 samples/s. The actual sampling algorithm is more complicated than this, but the idea is the same.

Getting Started C: Spectrometer
This section tells you how to hook up the three modules.

Getting Started D: Single Pulse NMR Experiment-Free Precession (Induction) Decay
Now, we're getting to some physics!

1. You may skip this one.
2. *Free-induction decay of mineral oil—rf out.* You can use a trick to look directly at the free-induction decay signal, that is the oscillating magnetization induced by the precessing spins after a 90° pulse. This precession is a transient signal, which occurs near the rf frequency, and hence is too fast for our scope to sample in real time. However, it turns out that, when you sweep speed of the scope to 20 μs/division, the scope samples at a rate of 5 Msamples/s. Set the spectrometer up as suggested in D.2, set the scope to 20 μs/division, and look directly at the "rf out" on the oscilloscope. You should see a damped oscillation. How does the apparent frequency of this oscillation compare with the frequency of the spin precession? Explain what is going on. (Hint: this is an example of "aliasing", wherein a signal contains frequency components faster than 1/2 the sampling rate. You can try to figure this out for yourself, or see Farrar and Becker, "Pulse and Fourier Transform NMR," p. 70.).
   Free-induction decay of mineral oil—detector out and mixer out, both on and off resonance.
   What is the difference between the signals coming out of "detector out", "rf out" and "mixer out?" Why are there "beats" in the mixer signal when the rf frequency is not tuned to the precession frequency of the spins?

Getting Started E: Magnetic field contours.
Free-induction decay signals on and off "sweet spot" in magnet.
You need not plot the magnetic field as a function of position in the x-y plane, as suggested on p. 31, if you do not wish to. However, try moving the sample around vertically and horizontally in the magnet, and look at how the length of the free-induction decay (FID) transient changes. The "sweet spot" of the magnet is the spot at which the FID transient lasts longest. Find the sweet spot. Print out FID signals both on and well off the sweet spot.
What is special about the sweet spot? Why does the FID transient last longest there?

Getting Started F: Rotating Coordinate Systems (Optional)
Getting started F, G and H contain most of the physics of this lab, and also require a good deal more thought than the previous sections.

From a careful study of the amplitude of the single-pulse FID signal as a function of the duration of the rf excitation pulse and the frequency of rf excitation, you can map out the physics of a two-level system in a resonant or nearly resonant oscillating field. See Farrar and Becker, Chapter 1, esp. section 1.6, for a summary and equations which might be used to fit to your data.

Getting Started G: Spin Lattice Relaxation Time T_1
Measure T_1 of mineral oil or glycerin following the three procedures described in pages 32-34. The first procedure really is not very accurate, but gives you an order of magnitude. The second and third methods (1. and 2. on p. 33) are quite

accurate and really clever. You will need to work out an equation which you will then use to extract T_1. Please put your derivation in your lab book. Give us your answer for T_1, including error bars. Explain how you got the error bars. Plot out any oscilloscope traces you would like to to document your procedure.

Getting Started H: Spin-spin relaxation time T_2.
The spin echo is a truly remarkable macroscopic manifestation of quantum mechanics. Take some time to appreciate this.
1. *Two-pulse spin echo*.
Question: compare the shape of the spin echo pulse to the shape of the FID pulse. How is it different? Explain.

2. Multiple pulse-multiple echo sequences
A. *Carr-Purcell Multiple-pulse spin echo*.
B. *Meiboom Gill Multiple-pulse spin echo*
Optional: explain the difference between Carr-Purcell and Meiboom-Gill spin echo sequences. (See, for example, Farrar and Becker, "Pulse and Fourier Transform NMR).
Measure the relaxation time T_2 for mineral oil. Give your answer including error bars. Explain in detail how you did the measurement.

Question: Compare the Free-Induction Decay time, the T_1 and the T_2 you measured in this lab. Are they the same or different? Explain briefly.

4. Pulsed NMR experiments (optional)
Read paper 1.3 in Bloembergen's "Encounters in magnetic resonances." This is a brief, classic paper. The main results are expanded upon in paper 1.4, which is Bloembergen's thesis. Try repeating some of his measurements—for example, exploring the dependence of T_1 and T_2 on the concentration of paramagnetic salts dissolved in water, or on the viscosity of a glycerin/water mixture.
Other experiments are suggested in the attached write-up from TeachSpin.