Brandeis University Physics 39a/169b

Nuclear Magnetic Resonance

Please read this entire document before doing anything else with this experiment.

Introduction:

In this experiment, we learn the fundamentals of pulsed Nuclear Magnetic Resonance, or NMR, in liquid samples. In its simplest form, NMR involves placing a sample in a very uniform magnetic field, which induces precession of the spin angular momenta of the nuclei under study, in our case, protons, at the resonant frequency, typically a radio frequency (RF) in the MHz range. Applying a pulse of radiation to the sample at the resonant frequency excites nuclei, and after that one can study the results of that excitation, which are remarkably varied, depending on the nature of the sample, the nature of the magnetic field used, and possibly further RF pulses. In our experiments, we have a rather inhomogeneous magnetic field produced by a permanent magnet, and we can vary the duration and timing of a series of RF pulses at the resonant frequency. We study two characteristic times which describe the fate of the excitation of the nuclei. T1 is the "spin lattice relaxation time" which describes the time scale for excitation of the nuclei to leak out of the nuclear system into other dynamical degrees of freedom in the sample, like molecular motion (heat). T2, the "spin-spin relaxation time," is a more subtle time associated with "dephasing" of the excited nuclei, due to their magnetic interactions with one another. There are other significant time scales in the experiment, having to do with the inhomogeneity of the magnetic field and diffusion of the molecules in the liquid, which affect the measurements of T1 and T2, and lead to indirect measurements of the self diffusion constant of the molecules in the sample. The phenomenon of "spin echo" is used to overcome the limitations due to the inhomogeneous magnetic field, and allows us to measure T2 and in addition, spin-spin interactions in liquids with complex molecules.

I. Things to learn in this experiment:

Dynamics of nuclear magnetization:

For this experiment, the most useful model for understanding the phenomena is a semi-classical model of the net magnetization of the nuclei under study. This magnetization is induced by the static magnetic field, and due to the finite temperature, is a very small fraction of the total magnetic moment that would result from the maximum attainable alignment of the proton magnetic moments in the sample. It is the precession of this net magnetization after excitation by an applied RF pulse that produces the RF radiation we study in this experiment, as our clue to the spin dynamics. It is surely the weakest signal we study in this lab. The equations of motion of the net magnetization in response to the RF pulses, the "Bloch equations" involve the two relaxation times referred to above. The paper by Carr and Purcell is the most useful for understanding the magnetization dynamics, especially the dramatic spin echo technique. Other important papers are by Bloembergen, Pound and Purcell (known in the field as "BPP"), on NMR relaxation theory, and Meiboom and Gill on a modified pulse sequence that improves on the spin echo method formulated by Carr and Purcell. In our study of alcohols, we find that the measurement of T2 is complicated by the interactions of the spins on protons in different chemical environments in the alcohol molecules, the spin-spin interaction that is basic to the use of NMR in the study of molecular structure.

Experimental design: The experiment is based on electronic modules for generating and controlling the RF pulses, and detecting the nuclear magnetic resonant radiation. In its simplest form data recording is done with a digital oscilloscope, from which readings can be taken directly. Data can be transferred from the scope to the computer, and finally, a computer interface can replace the pulse control module of the commercial rig, and data can be recorded directly on the computer, by far the preferred method of experimentation. This experiment is a good example of this kind of experimental design. You should try to understand how each part of the experiment works, and the important parameters of its design.

Data Handling and Analysis:

Some data from the digital scope can be recorded manually, or complete data sets can be transferred to the computer. When using the computer interface, data are recorded in files within the computer. Extracting parameters from the data is best accomplished by curve fitting, using EXCEL for simple fits, and Mathematica for more complex functional forms.

II. Preparation and Initial Problem Set:

Experimental set-up:

The electronics modules are pretty fool-proof. The two wires attached to the sample holder in the magnet should not be disconnected from their locations on the electronics box. All other BNC cables can be connected in a logical way from module to module and to the scope. The manufacturer claims that misconnecting them can't hurt anything, but try to be logical anyway!

Reading:

The manufacturer's manual leads you through a basic introduction to the experiment, including connecting things, tuning the receiver, and tuning the RF source to resonance. It then gets you started on measurements in mineral oil. In addition to following the manual, please read the Carr and Purcell paper, to begin to understand the spin echo phenomenon. Pay especial attention to the rotating frame of reference model, and how it accounts for precession of spins around the RF magnetic field, in 90° and 180° pulses.

Some Initial Problems: Think about the size of the signal we are studying in this experiment, and other important parameters.

1) How many protons are in the sample of mineral oil, approximately? Assume the sample is a cylinder 4mm in diameter and 6 mm long.

2) Calculate the nuclear magnetic moment of the sample if all the nuclear spins were aligned parallel to the magnetic field.

3) For our resonant frequency of about 15.5 MHz, what is the static magnetic field of our permanent magnet?

4) A little statistical mechanics: For a single proton magnetic moment μ in a magnetic field of strength H at temperature T, use the Boltzman factor of $exp(\pm \mu H/k_B T)$ where k_B is Boltzman's constant, for the two states, μ parallel or anti-parallel to the magnetic field, to calculate what fraction of the maximum possible nuclear magnetic moment is achieved at room temperature in the field of our magnet.

5) As that magnetic moment rotates at the resonant frequency, assume that half of its total magnetic flux passes through a coil of 10 turns of wire, inducing oscillations of that amount of flux through the coil at the resonant frequency. What EMF does this induce in the coil, and what current does it produce in a resistive load of 50Ω? This is approximately the signal we are studying.

6) Estimates: a) From the resonant frequency, what is the magnetic field? b) From the width in time of the free induction decay after a 90° pulse, what is the range of magnetic field in the sample, to account for the dephasing of the spins? Estimating the sample size, what is the approximate field gradient? c) From the width of the 90° pulse, what is the strength of the RF magnetic field, to account for that amount of precession? d) To prevent field inhomogeneity dephasing of the free induction decay for water, for a time comparable to T1, the spin-lattice relaxati0on time of about 2 seconds, what is the maximum allowable difference of the magnetic field over the sample volume? e) From your answers to c), thinking in terms of the rotating frame of reference in which the static magnetic field disappears at resonance, how close to resonance do you have to be for the RF magnetic field to be 100 times larger than the remnant effective static field in the rotating frame of reference due to being slightly off resonance? f) From your answers to b), c), and e) is the range of fields in the sample a problem for satisfying the limit suggested in e)? The last two estimates help decide whether the experiment has been designed correctly, so that 90° and 180° pulses are accurately meaningful for all the spins in the sample, since large remnant effective fields mean that the spins are not precessing about a pure transverse field.

III. Experiments to Perform:

Once you have the system working well and are confident of how to keep it tuned to resonance, and how to set the 90 and 180 degree pulse lengths accurately, you should perform the following studies:

- Using the digital scope, study T1 and T2 in mineral oil, using both method A and method B for T2, as described in the Carr-Purcell paper. Also compare results for the Carr-Purcell and Meiboom-Gill pulse sequences. Learn how to transfer data from the scope to the computer, and fit data to exponential curves to derive the relaxation times. Then learn how to use the computer interface to gather and analyze the same data.

- Measure T1 and T2 for water. Use method A and the known diffusion constant of water to determine the magnetic field gradient in the sample. Use method B with and without the Meiboom-Gill modification for T2.

- Study alcohols: methanol, ethanol, propanol, determining T1, T2, and diffusion constants. You should be able to see the effects of spin-spin coupling in the alcohols, as oscillations in the spin-echo signal height as a function of delay time. Analyze the signal as a product of a decaying exponential and an oscillating function.