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NUCLEAR MAGNETIC RESONANCE

References for Nuclear Magnetic Resonance

1. Slichter, Principles of Magnetic Resonance, Harper and Row, 1963. chapter 1 gives a general introduction to NMR theory.
2. Operating Manual, Hall Effect. Gaussmeter

1. INTRODUCTION

Nuclear Magnetic Resonance (NMR) experiments were originally used for accurate measurements of nuclear magnetic moments in condensed matter. Subsequently, NMR techniques have had widespread application in solid state physics and studies of chemical structure and dynamics, as well as becoming a standard method for the accurate measurement of magnetic fields and, more recently, producing a powerful instrument for medical diagnoses. Four points are studied.

1. Magnetic field measurements. Observations of “saturation” and of the small “hysteresis” of an iron core magnet.
2. Observations of nuclear magnetic resonance of protons (magnetic moment of an isolated proton corresponds to a nmr frequency 42.5759 MHz in a 10 KG field) in a magnetic field by detection of resonant radio frequency absorption by protons in water or mineral oil. The effect on the spin-lattice relaxation time, T_1, of very small concentrations of paramagnetic ions is also observed.
3. The absolute value of the proton’s magnetic moment is measured, the precision being limited by the accuracy of the magnetic field measurement.
4. A very precise measurement of the ratio of the magnetic moment of the deuteron (nmr frequency 6.53566 Hz in a 10 KG field) to that of the proton, by measuring the NMR frequencies of H_2O and D_2O in the same magnetic field. Magnetic moments of other nuclei can also be measured.

2 APPARATUS

2.1 Electromagnet

An iron H-frame magnet, with carefully machined pole pieces, produces a very uniform field, B_0, of up to 1 Tesla at the center of the cylindrical gap, which is 4 inches in diameter and 1 inch wide. The water cooled coils of the magnet are powered by a variable D.C. supply which furnishes up to 24 ampères of current, regulated to be constant to 1 part in 10^5.

2.2 Hall Effect Gaussmeter

A Hall Effect Gaussmeter with accuracy of .25% is provided. In this gaussmeter, a small current (I_x ~100 ma) is passed along the x-axis of a thin crystal of high-purity indium arsenide (a semiconductor). When the crystal is placed in a magnetic field, B_z along its z–axis, the Hall effect produces a small voltage V_y across the y–axis, with $V_y \propto B_z I_x$. The constant of proportionality can be checked by placing the element in the gap of a calibrated permanent magnet. The accuracy of the measurement in this case is limited by the accuracy of the calibrated magnet, as well as the temperature coefficient of indium arsenide (0.1%/°C) and the uncertainty in the current and voltage readings.

2.3 Marginal Oscillator to Detect NMR

A sensitive method for detecting the small absorption of radio-frequency energy in NMR is to place a sample inside the coil in the resonant circuit of a marginal oscillator. The absorption of energy by the sample lowers the "Q–factor" of the oscillator tank circuit changing the oscillation amplitude. For a fixed value of the magnetic field, B_0, one could in principle tune the oscillator frequency until it reaches its resonant value, by observing a decrease in oscillation amplitude.

Because of the oscillator noise this is not possible. The D.C. magnetic field is modulated by adding a small 60 Hertz field which sweeps back and forth through the resonant value 120 times per second. The detected oscillator output is observed on an oscilloscope whose horizontal deflection is driven by the field modulating voltage. The coherently superimposed signal becomes larger than the noise.

There are four controls on the oscillator:

1. An on–off switch.
2. A 3-position switch to select the range of feedback.
3. A variable resistor to make fine adjustments on the feedback–i.e., to adjust for a "marginal" level of oscillation.
4. A variable capacitor to tune the frequency of the oscillator. Different probe coils must be used for different oscillator frequency ranges. Each sample-holding r.f. coil

is mounted in a brass tube, which is attached to the oscillator by a coaxial (UHF) connector and can be inserted into the electromagnet gap. The "detected" level of the oscillator amplitude brought out to a coaxial (BNC) connector and connected with a cable to the vertical amplifier of the oscilloscope.

2.4 Frequency Meter.

The high frequency signal is also brought out through a coaxial connector. After amplification (in a separate amplifier circuit), the signal is fed into a digital frequency meter for accurate measurement of the resonant frequency.

2.5 Field Modulating Circuit.

The modulating field is provided by two small coils, perpendicular to the r.f. coil and attached to the r.f. probe. The probe must be inserted in the gap of the electromagnet so that the 60 Hz modulating field adds a small oscillating component parallel to the main field. The modulation coils on the probe are connected by a separate cable through a variable resistor to the 6 V output of a transformer, driven at 60 Hz by the A.C. line. A variable RC network is used to shift the phase of a separate 60-Hertz output, which is connected to the horizontal plates of the oscilloscope.

2.6 Sample Holders

Liquid samples are held in small glass test tubes which fit vertically inside the r.f. coil. Samples for proton resonance include mineral oil, which has a convenient spin-lattice relaxation time (T_1), and distilled water with various trace concentrations of paramagnetic ions to provide a range of values of T_1. A sample of enriched D_2O and solutions containing other nuclei (with non-zero spin) are also available.

3. MEASUREMENTS.

3.1 Field measurements.

Use the Hall Effect Gaussmeter to measure the approximate strength of the field as a function of coil current over the entire range of excitation, noting in particular the departure from linearity at high field.

Start making measurements at zero magnet current and increase it in fixed steps until it can increase no further. Then take measurements starting at the maximum current and reducing it in fixed steps. **When making these measurements it is important to**

keep the sign of the change fixed over the range of measurements.

Experimental Details.

a) The power supply is interlocked so that it will turn on only if there is a sufficient flow of water through the magnet coils.

b) The current meter on the magnet power supply gives a crude indication of the output current; the digital voltmeter across a calibrated external shunt gives a more accurate reading of the current. The helipot dials settings on the supply give a very accurate method of reproducing a current setting.

c) The power supply is permanently connected to the magnet, since a break in the current–carrying connection would cause a strong and dangerous arc and possibly damage the magnet coils. Explain why.

d) The operating manual for the Hall Effect Gaussmeter describes how to calibrate the meter, either according to the factory calibration stamped on the probe, or, by inserting the probe into the gap of a small calibrated permanent magnet. Note that the probe must always be rotated about its axis to maximize the output reading and thus insure that the magnet field is along the crystal's z–axis.

3.2 Observation of nuclear magnetic resonances.

Use the marginal oscillator to observe the nuclear magnetic resonance of protons in a sample of mineral oil (or of water with enough $CuSO_4$ dissolved to shorten T_1). By observing the NMR signal and its resonant frequency, note the: i) uniformity of the main magnetic field, B_0, as you move the sample in the gap, and ii) the relative magnitude of the modulating field as you vary the resistance in the modulating coil circuit. Note qualitatively the effect on the absorption signal of adding paramagnetic ions to water.

Experimental Details.

a) For a given sample, the signal-to-noise ratio is proportional to the square of the resonant frequency, so it is prudent to make measurements near the maximum field available.

b) The oscillator uses different probes for different frequency ranges, which are marked on the probes.

c) Operation of the marginal oscillator is very sensitive to the level of feedback, which is determined in a trial fashion by adjusting the continuously variable resistor marked "Oscillator Current Control." At one extreme, there will be no oscillation, with no indication on the frequency meter or the oscilloscope trace. At the other extreme the oscillation will be too strong and thus insensitive to the change of coil Q at resonance.

d) In order to find the NMR signal on the scope most easily, it is advisable first to tune with the maximum amplitude of field modulation. The horizontal plates of the scope are directly fed by a separate 60-Hz sine wave, with the magnitude unaffected by the change of modulation amplitude and the phase adjustable with respect to the modulation phase. The phase of the scope sweep should be adjusted so that the resonance signal for the increasing modulation field falls on top of the signal for decreasing field (and reversed horizontal deflection of the scope). See figure 2b. For precise measurement of the NMR frequency, the amplitude of the modulation should be reduced once the signal has been found. The effect of the modulating field is then minimized when the oscillator frequency is adjusted to bring the superimposed NMR signals to the center of the scope trace. See Fig. 2c.

Figure 2 a, b, c.

e) In order to determine the accuracy of the precise measurements in procedure 4, use the proton resonance signal to

1. determine the approximate variation in magnetic field (i.e., frequency) as you move the probe in the magnet gap
2. determine the approximate variation of the position of the signal on the scope trace as the frequency is slightly changed, for several settings of modulation amplitude.

f) for a given setting of the oscillator, the amount of energy absorbed will increase for shorter spin-lattice relaxation times (T_1). By adding small amounts of a paramagnetic salt, such as a copper sulfate, T_1 for water can be substantially reduced compared to the time between successive passages through resonance with 60 Hz modulation. Investigate this effect by using solutions of different concentration, e.g. from 0.1 to 10 mg. of $CuSO_4$ to 1 g. of water.

3.3 The proton magnetic moment

Measure the magnetic moment of the proton *i.e.* the gyromagnetic ratio ω/B_0 by precise measurements of ω and B_0. The precision will be limited by the absolute measurement of B_0.

Experimental Details.

After measuring the NMR frequency, replace the marginal oscillator and its probe by the Hall probe, without changing the value of B_0. Take care to measure the field at the position that the sample occupied.

3.4 The ratio of the H_2O and D_2O moments.

Make a precise measurement of a fundamental quantity, the ratio of the magnetic moment of the deuteron to that of the proton, by comparing the NMR frequency in heavy water, D_2O, with that in H_2O. Since you can make both measurements without changing the current in the magnet, the accuracy of the ratio is limited primarily by your ability i) to position the samples in the same uniform region of the magnetic field, and ii) to find the centers of the NMR signals and thus determine their frequencies at resonance. You can estimate the uncertainty related to each of these limitations from the (similarly numbered) measurements in section 3.2.

Measurements can also be made of ^7Li and ^{19}F in suitable solutions.

Experimental Details.

In view of the spin, S = 1, and g-value = 0.86, of the deuterium nucleus, the NMR frequency is much less than that of the proton. This means that the signal-to-noise ratio is much worse; it is difficult to find the NMR signal. You will have to use a lower frequency probe on the marginal oscillator, and you will have to use the following procedure just to detect the weak deuterium resonance:

a) As mentioned, the deuteron resonance is weak and may be difficult to find so that you will want to work at the highest magnetic field possible. One reason for mapping out the field with the gaussmeter is to determine the maximum magnetic field the magnet produces.

b) Work within a few percent of this maximum field. Since the nmr frequency of deuterium corresponds to 6.53566 MHz per 10 KG you can calculate the frequency at which your oscillator should work. You will probably have to select a new probe to be able to work at that frequency. The problem now is to adjust the oscillator feedback settings at that frequency in order to maximize the signal to noise ratio. But this adjustment requires that you have a nmr signal in view.

c) This is accomplished by substituting the heavy water sample with a mineral oil sample while keeping the oscillator frequency unchanged. The proton signal from mineral oil is very big and it will be easily detected when you lower the magnetic field to bring the protons into resonance.

d) With this signal in view, you can optimize the oscillator feedback settings to maximize the proton signal.

e) When this is done replace the mineral oil sample with the heavy water sample keeping the magnetic field unchanged. Since the heavy water sample usually contains a few percent ordinary water molecules you should immediately see the now weak proton signal from the heavy water sample. This signal will be comparable to the deuteron signal you will see shortly.

f) Once again it is a good idea to adjust the feedback settings to optimize the signal to noise ratio.

g) After this is done you can increase the magnetic field and the deuterium signal should appear when the field is increased sufficiently.

h) At this point replace the heavy water sample with mineral oil (changing the probe also if necessary) and adjust the oscillator frequency to bring the proton resonance into view. In replacing the probe be careful that the sample position is not changed.

i) The Li and F resonances, at higher frequencies than that of deuterium, will be easier to detect–assuming that the spin-lattice relaxation times are sufficiently short in the liquid samples used.