Chapter 2

Nuclear Magnetic Resonance, NMR

2.1 Introduction to NMR

Copies of the *TeachSpin* NMR Manual[**?**] will be by the apparatus. Please look over these before the first of the lab sessions.

We will be doing NMR with protons. A proton has a spin I=1/2, and a nuclear magnetic moment μ_p=2.79277 μ_N. The nuclear magneton μ_N= 5.05038 $\times 1-^{-24}$ ergs/gauss. In a magnetic field the energy of the two spin orientation states are:

$$\mathcal{H} = -\boldsymbol{\mu} \cdot \boldsymbol{H} \tag{2.1}$$

If the spin of the proton is aligned along the **y** axis and the magnetic field is along the **z** axis, then the torque $\boldsymbol{\mu} \times H$ induces precession around the magnetic field as shown in Fig. 2.1.

The rate of rotation is: $\omega_L = \mu H/\hbar$. Now suppose one views this precession in a coordinate system which is rotating about the magnetic field with rate ω_R in the same direction as the spin does. Evidently the spin will now appear to rotate with rate: $\omega_s = \omega_L - \omega_R$. This has the effect of reducing the applied field in the rotation coordinate system. If the $\omega_R = \omega_L$ then there appears to be no applied field and the spin appears to be static. This discussion appears to be classical, but in fact yields the same results as the quantum mechanical one[**?**].

Now suppose one applies an rf field with $\omega_{rf} = \omega_L = \omega_R$. If one decomposes the rf field into rotating components, one of these components will be rotating with the rotating coordinate system and thus will appear to be static. (The other component has very little effect and will be ignored in this discussion.) In the rotating system, the nuclear spin will now precess about the co-rotating component of the rf magnetic field.

If the rf stays on for a time so that the spin just ends up in the x-y plane, this is called a $\pi/2$ pulse and is often the first step in a pulsed nmr experiment.

In order to produce a spin-echo one first pulses the spins into the x-y plane, whereupon the spins dephase due to local field variations. After a delay, a 180 degree pulse is applied. This causes the spins that precessed fastest to be rotated so as to lag, and those that

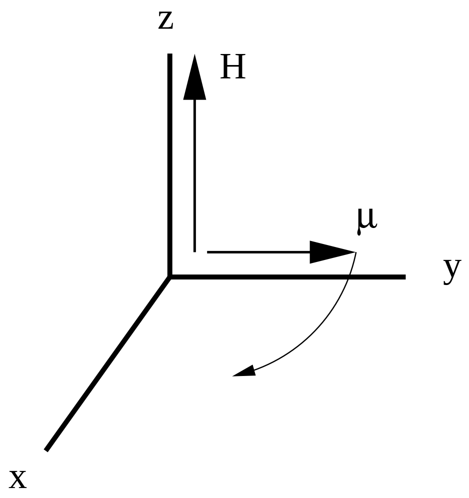

Figure 2.1: Rotation of a nuclear spin in a magnetic field.

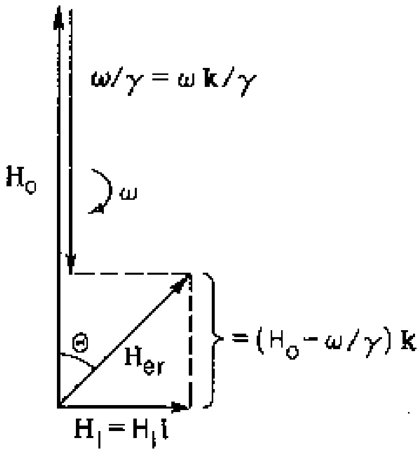

Figure 2.2: The effective field in a rotating coordinate system.

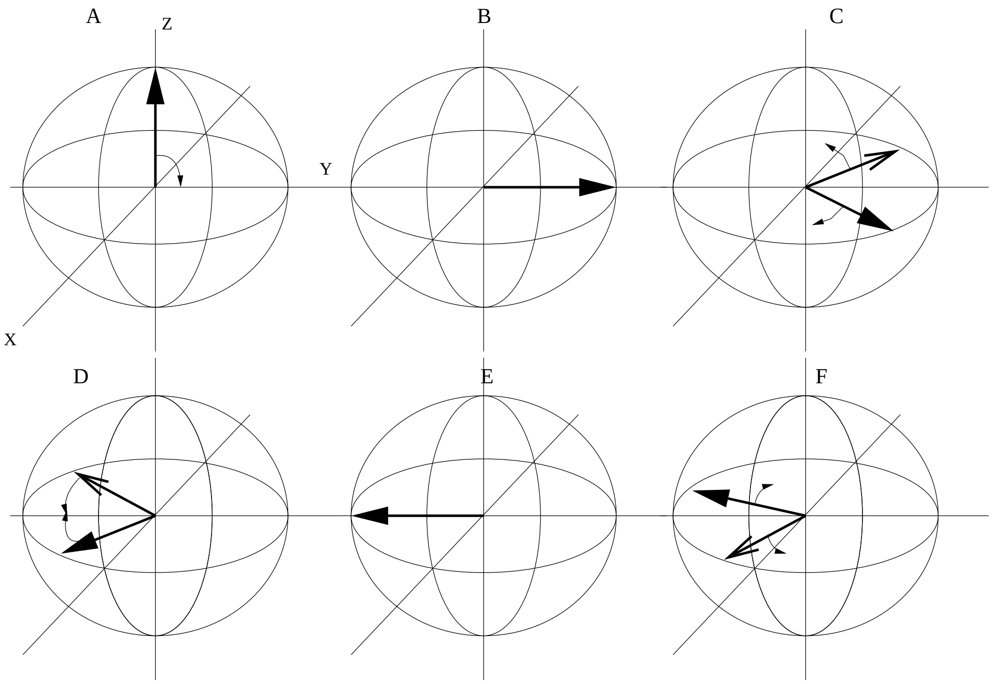

Figure 2.3: The formation of a spin echo using the Carr-Purcell pulse sequence in the rotating frame. In A, spins are aligned and produce a net magnetization in the plus Z direction, parallel to the external field. An rf pulse of magnetic field precesses the spins by $\pi/2$ about the X axis to be along the Y axis as shown in B. Variations in local fields cause the dephasing as shown in C. A second rf pulse, twice as long causes the spins to precess about the X axis by π, leading to D. Now, the same local field variations cause the spins to re-phase as in E, producing and echo. In F one sees the spins again dephasing. Taken from Carr and Purcell[**?**] .

precessed slowest to lead. Following this pulse the various spins will re-phase in just the time that the 180 degree pulse was delayed from the 90 degree pulse. This may be seen in Fig. 2.3.

2.2 T_1 and T_2

This has been taken from Wikpedia.

Different physical processes are responsible for the relaxation of the components of the nuclear spin magnetization vector M parallel perpendicular to the external magnetic field, B_0 (which is conventionally oriented along the z axis). These two principal relaxation processes are termed T_1 and T_2 relaxation respectively.

2.2.1 T_1, the Spin-lattice relaxation time

The longitudinal relaxation time T_1 is the decay constant for the z-component of the nuclear spin magnetization, M_z. For instance, if the z magnetization is zero (e.g. if M has being tilted into the xy plane by a 90° pulse), then it will return to its equilibrium value, $M_{z,\mathrm{eq}}$ as follows:

$$M_z(t) = M_{z,\mathrm{eq}}\left(1 - e^{-t/T_1}\right) \tag{2.2}$$

i.e. the magnetization will recover to 63% of its equilibrium value after one time constant T_1.

T_1 relaxation involves redistributing the populations of the nuclear spin states in order to reach the thermal equilibrium distribution. By definition this is not energy conserving. Moreover, spontaneous emission is negligibly slow at NMR frequencies. Hence truly isolated nuclear spins would show negligible rates of T_1 relaxation. However, a variety of relaxation mechanisms allow nuclear spins to exchange energy with their surroundings, the lattice, allowing the spin populations to equilibrate. The fact that T_1 relaxation involves an interaction with the surroundings is the origin of the alternative description, spin-lattice relaxation.

Note that the rates of T_1 relaxation are generally strongly dependent on the NMR frequency and so may vary considerably with magnetic field strength, B.

2.2.2 T_2, the Spin-spin relaxation time

The transverse relaxation time T_2 is the decay constant for the component of M perpendicular to B_0, designated M_{xy}, M_T, or $M_\perp$. For instance, initial xy magnetization at time zero will decay to zero (i.e. equilibrium) as follows:

$$M_{xy}(t) = M_{xy}(0)e^{-t/T_2} \tag{2.3}$$

i.e. the transverse magnetization vector drops to 37% of its original magnitude after one time constant T_2.

T_2 relaxation is a complex phenomenon, but at its most fundamental level, it corresponds to a decoherence of the transverse nuclear spin magnetization. Random fluctuations of the local magnetic field lead to random variations in the instantaneous NMR precession frequency of different spins. As a result, the initial phase coherence of the nuclear spins is lost, until eventually the phases are disordered and there is no net xy magnetization. Because T_2 relaxation involves only the phases of other nuclear spins it is often called ”spin-spin” relaxation.

T_2 values are generally much less dependent on field strength, B, than T_1 values.

2.2.3 T_2* and magnetic field inhomogeneity

In an idealized system, all nuclei in a given chemical environment in a magnetic field spin with the same frequency. However, in real systems, there are minor differences in chemical environment which can lead to a distribution of resonance frequencies around the ideal. Over time, this distribution can lead to a dispersion of the tight distribution of magnetic spin vectors, and loss of signal (Free Induction Decay). In fact, for most magnetic resonance experiments, this "relaxation" dominates. This results in intra-voxel dephasing, a phenomenon related to the motion of spins in fluids, velocity differentials as well as directional effects; for example, in tissues, can be related to capillary diffusion.

However, decoherence because of magnetic field inhomogeneity is not a true "relaxation" process; it is not random, but dependent on the location of the molecule in the magnet. For molecules that aren't moving, the deviation from ideal relaxation is consistent over time, and the signal can be recovered by performing a spin echo experiment.

The corresponding transverse relaxation time constant is thus T_2*, which is usually much smaller than T_2. The relation between them is:

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_{inhom}} = \frac{1}{T_2} + \gamma \Delta B_0 \tag{2.4}$$

where γ represents gyromagnetic ratio, and ΔB_0y the difference in strength of the locally varying field.

Unlike T_2, T_2* is influenced by magnetic field gradient irregularities. The T_2* relaxation time is always shorter than the T_2 relaxation time and is typically milliseconds for water samples in imaging magnets.

2.2.4 The reason that T_1 is slower than T_2

As a general rule, the following always holds true: $T_1 > T_2 > T_2$*.

If T_2 were to be slower than T_1, then the magnetizations perpendicular to the initial direction would have not dephased by the time the sample had returned to equilibrium. This is physically impossible, as once the sample has returned to equilibrium, there is no magnetization perpendicular to the original direction. Hence, T_1 must be greater than or equal to T_2.

2.3 Experiments

2.3.1 Getting Started

Observe the spin echo for the mineral oil sample. Tune the apparatus for the largest and cleanest measurement. The lab instructor will help at this stage. It is suggested that you make all the different types of measurements first with the mineral oil sample before proceeding to the other samples.

2.3.2 Samples

- Mineral Oil, the sample you will start with.

- Water and Glycerine, various concentration of glycerine
- Paramagnetic Salts, various concentrations of $CuSO_4$ and/or $Fe(NO_3)_3$

2.3.3 T_1 Measurements

See page 32 of the TeachSpin Manual. Measure T_1 by the techniques described after page 32.

2.3.4 T_2 Measurements

Measure T_2 using the 2 pulse technique, the multiple pulse technique, and the Meiboom-Gill technique. Be sure to compare your results. These techniques are described on pages 34 and 35 of the TeachSpin Manual.

2.3.5 Analysis

Determine how the two constants depend on the characteristics of the samples.