Nuclear Magnetic Resonance

PHYS 310

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I. CLASSICAL MAGNETIC MOMENTS

Consider a simple classical model of particle with charge q and mass m traveling in a circular path with radius R at a speed v. The orbital angular momentum is

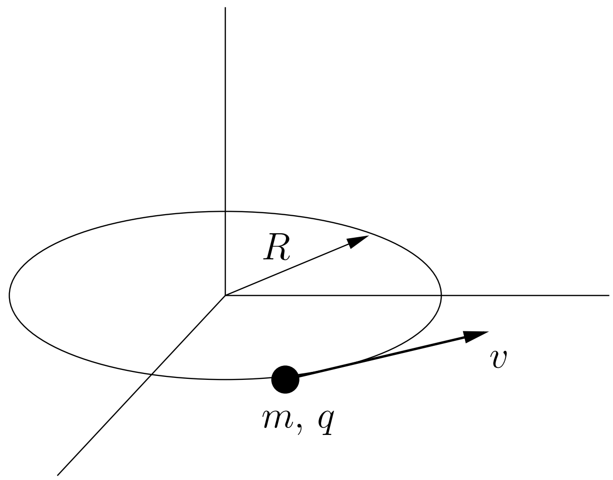

FIG. 1: Classical point particle traveling in a circle.

$$
\begin{aligned}
L &= |\mathbf{r} \times \mathbf{p}| \\
&= mvR. \qquad (1)
\end{aligned}
$$

The magnetic dipole moment of a current loop is

$$\mu = IA, \qquad (2)$$

where I is the current, and A is the area of the loop. (See, *e.g.*, Griffiths, *Introduction to Electrodynamics*, Sect. 5.4.3.) In our simple model the current can be given in terms of the period of the particle's orbit T, giving

$$
\begin{aligned}
\mu &= \frac{q}{T}\pi R^2 \\
&= \frac{qv}{2\pi R}\pi R^2 \\
&= \frac{qvR}{2}, \qquad (3)
\end{aligned}
$$

and this can be rewritten in terms of the angular momentum of the particle as

$$\mu = \frac{q}{2m}L. \qquad (4)$$

This just states that the magnetic moment is proportional to the angular momentum.

(Notational note: There is a confusing array of symbols used to represent angular momentum: **L** usually designates an orbital angular momentum; **S** usually designates an intrinsic electronic spin; **J** usually designates total electronic angular momentum (orbital plus spin); **I** often designates nuclear angular momentum; and **F** often designates the total angular momentum of an atom (total electronic plus nuclear). In the simple model above the angular momentum is orbital, so we used **L**. In discussing real nuclei below we will use the symbol **I**.)

Real systems are more complex than this simple model. For example, the particle may travel in an elliptical path (with constant angular momentum; for extended bodies (like a spherical shell, or a solid sphere) the contribution of each mass element dm must be considered, and the total moment is the integral over the mass distribution. . We also shouldn't expect the relationship expressed in Eq. (4) to hold exactly for microscopic particles which must be described using quantum mechanics, especially when treating inherently non-classical entities such as the intrinsic spin of particles. But the proportionality between magnetic moment and angular momentum does hold in general, and the quantity $q/2m$ can be taken as a rough order-of-magnitude estimate of the size of atomic moments. It is standard to include a "g-factor" to account for the discrepancy between this naive classical model and real moments. For example, the proton magnetic moment is written as

$$\boldsymbol{\mu}_p = g_p \frac{e}{2m} \mathbf{I}, \tag{5}$$

where **I** is the proton angular momentum, $e = +1.6 \times 10^{-19}\,\mathrm{C}$, $m = 1.67 \times 10^{-27}\,\mathrm{kg}$, and g_p is the proton g-factor, which happens to have the approximate value 5.59. Another way to parametrize this is to lump the constants together and write

$$\boldsymbol{\mu}_p = \gamma \mathbf{I}, \tag{6}$$

where the constant γ is called the gyromagnetic ratio (sometimes referred to as the magnetogyric ratio). For protons $\gamma/2\pi = 4.26\,\mathrm{kHz/Gauss} = 42.6\,\mathrm{MHz/T}$.

II. MOTION OF MOMENTS IN MAGNETIC FIELDS

The motion of a magnetic moment $\boldsymbol{\mu}$ in a field $\mathbf{B}$ is derived from the equation of motion relating the time derivative of angular momentum to the net applied torque,

$$\frac{d\mathbf{I}}{dt} = \boldsymbol{\tau}. \tag{7}$$

The torque is given by $\boldsymbol{\mu}\times\mathbf{B}$, and using this along with Eq. (6) gives

$$\frac{d\boldsymbol{\mu}}{dt} = \gamma\boldsymbol{\mu}\times\mathbf{B}. \tag{8}$$

A. Moments in a constant field

Assume that the magnetic field is uniform and constant in time. It is conventional to let the field point along the z axis so that

$$\mathbf{B} = B_0\hat{\mathbf{k}}. \tag{9}$$

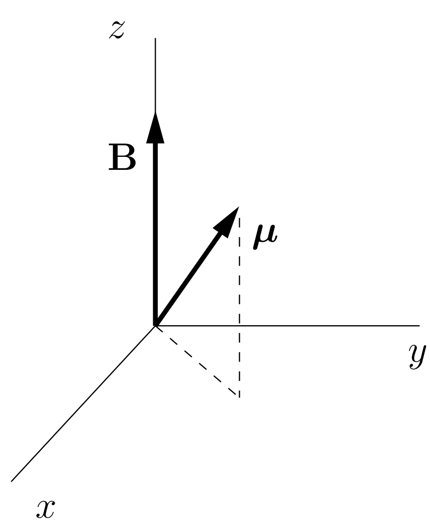

FIG. 2: Magnetic moment in a magnetic field oriented parallel to the z axis.

Problem 1 Determine the direction of the instantaneous torque on the illustrated dipole, and describe the resulting motion of the dipole.

Problem 2 Use Eq. (8) and the static field of Eq. (9) to show that components of $\boldsymbol{\mu}$ obey the equations

$$\frac{d\mu_x}{dt} = \gamma B_0 \mu_y, \tag{10a}$$

$$\frac{d\mu_y}{dt} = -\gamma B_0 \mu_x, \tag{10b}$$

$$\frac{d\mu_z}{dt} = 0. \tag{10c}$$

Problem 3 Solve Eqs. (10a)–(10c) to show that

$$\mu_x(t) = A\cos(\gamma B_0 t + \phi), \tag{11a}$$

$$\mu_y(t) = -A\sin(\gamma B_0 t + \phi), \tag{11b}$$

$$\mu_z(t) = \mu_z(0). \tag{11c}$$

Show that this solution is consistent with the qualitative result you obtained in Problem 1.

The results of the preceding problem give the important result: the torque on magnetic moments in a constant field lead to precession, and the precession frequency of a moment in a field is given by

$$\omega_{\mathrm{p}} = \gamma B_0. \tag{12}$$

This is analogous to the motion of tops with angular momentum in a gravitational field: frictionless spinning tops do not fall over, they precess.

B. Moments in combined static and rotating fields

Imagine that you are in a frame that it is rotating about the z axis at exactly the precession frequency ω_{p}. In this frame the moment is stationary; from the point of view of an observer in the rotating frame there is no acceleration of the moment. The observer in this frame doesn't "see" the constant magnetic field applied parallel to the z axis.

Now imagine that we apply a field of magnitude B_1 in the x-y plane which rotates along with the rotating frame at ω_{p}. In the rotating frame this field is a stationary field in the x direction, as illustrated in Fig. 3. To an observer in the rotating frame the total effective field is this stationary field along the x axis, and the moment precesses about this field at a rate γB_1, as is illustrated in the figure. (For a more quantitative derivation of the equations of motion in the non-inertial rotating frame, see the Appendix.)

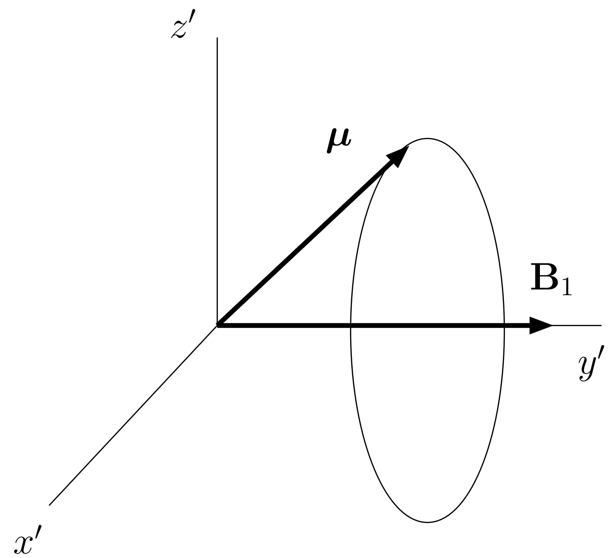

FIG. 3: Motion of a dipole in a combined static and rotating field *as viewed in a frame rotating at the precession frequency* $\omega_{\rm p}$. The static field is oriented parallel to the z axis and the rotating field is oriented parallel to the x axis of the rotating frame. The rotation rate of the field and the magnetic field both match the precession frequency of the moment about the static field.

In the lab frame the motion of the moment does not appear quite so simple. The motion is a combination of the precession in the rotating frame with the motion of the rotating frame. The precession about the rotating field is usually much slower than $\omega_{\rm p}$, the precession frequency of the rotating field itself. In this case the moment rapidly precesses about the z axis while the angle that the moment makes with respect to the z axis gradually changes. The tip of the moment $\boldsymbol{\mu}$ traces out a spiral path on the surface of a sphere, as is illustrated in Fig. 4.

The net effect of the static and rotating fields is to tip the spins *if* the frequency of the rotating field matches $\omega_{\rm p}$, the precession frequency of a single spin in the static field. If the rotation frequency doesn't exactly match $\omega_{\rm p}$, the spins are not tipped as effectively. This flipping of the spins when the applied rf frequency matches the precession frequency is what is known as nuclear magnetic resonance.

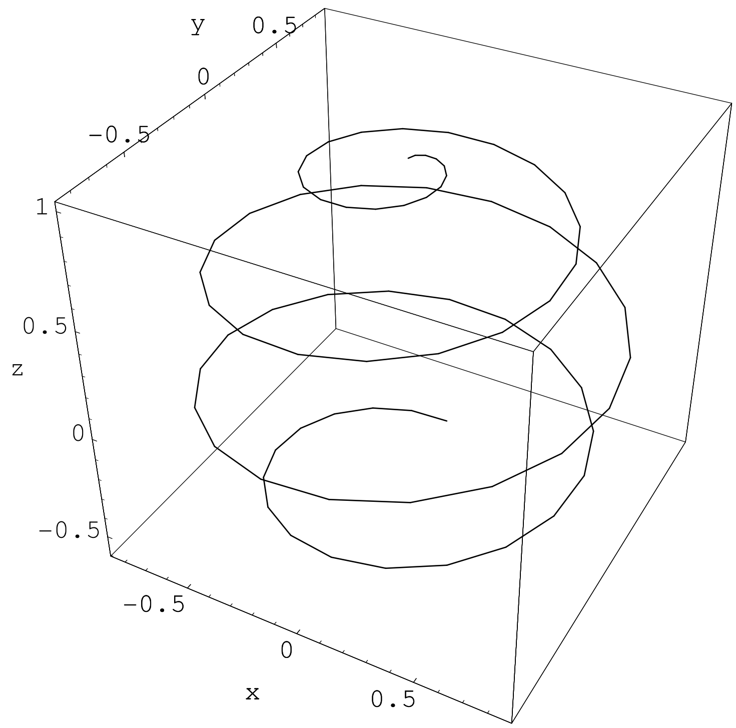

FIG. 4: Motion of a dipole in a combined static and rotating field *as viewed in the lab frame.* The line represents the path followed by the tip of the vector $\boldsymbol{\mu}$.

How do we create a rotating magnetic field? We don't. We create an oscillating field in one direction, say parallel to the x axis, and take advantage of a mathematical trick. An oscillating field parallel to the x axis (and perpendicular to the direction of the static field) can be written

$$\mathbf{B}_\perp(t) = 2B_1 \cos\omega t\,\hat{\mathbf{i}}. \tag{13}$$

(You will see why there we write this with a "extra" factor 2 in a moment.) Adding and subtracting the quantity $B_1 \sin\omega t\,\hat{\mathbf{j}}$ to this field doesn't change anything, but it does allow us to rewrite the oscillating field as

$$\mathbf{B}_\perp(t) = B_1\left(\cos\omega t\,\hat{\mathbf{i}} + \sin\omega t\,\hat{\mathbf{j}}\right) + B_1\left(\cos\omega t\,\hat{\mathbf{i}} - \sin\omega t\,\hat{\mathbf{j}}\right) \tag{14}$$

The field given by this equation is exactly the same as that given by Eq. (13, but now it is written as the sum of two rotating fields, rotating in opposite directions. The addition of counter-rotating fields is illustrated in Fig. 5.

The "part" of the field rotating in the same sense as the precessing moment acts to tip the spins from their existing orientation relative to the z axis; the counter-rotating "part" has a negligible effect. (In the rotating frame the counter-rotating field appears to rotate at $2\omega_{\mathrm{p}}$, and doesn't stay "in step" with the moment, and the effects of this counter-rotating term are negligible under the conditions of typical NMR experiments.)

Problem 4 Convince yourself that the two terms on the right side of Eq. (14) are in each circularly rotating fields. Determine which one corresponds to clockwise rotation as viewed from the positive z direction, and which corresponds to counter-clockwise rotations.

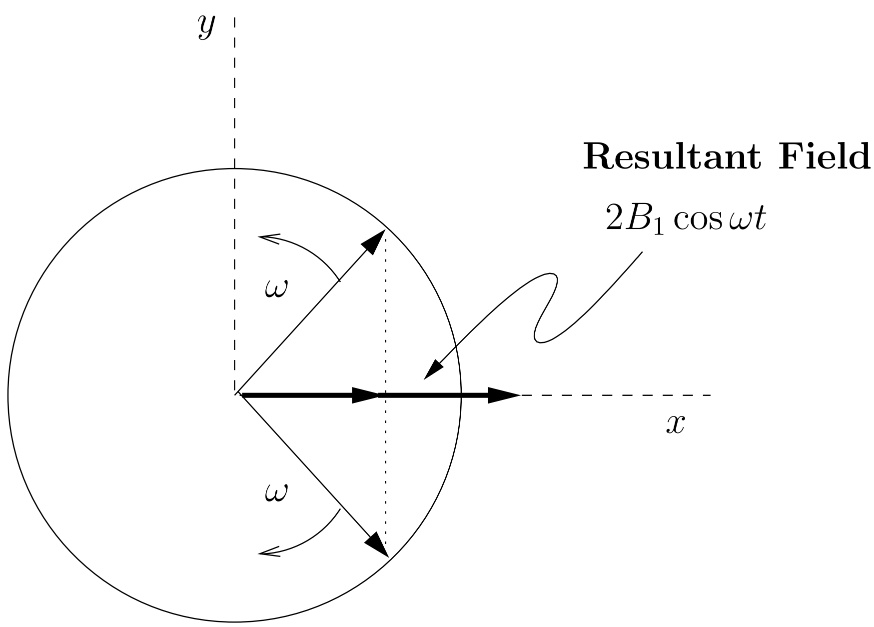

FIG. 5: Two counter-rotating fields combine to form an oscillating field in a single direction.

III. MEASUREMENT OF PRECESSING MOMENTS

In order to detect precessing spins take advantage of Faraday's Law. If the moments are precessing together with the same phase there is a resulting precession of the net magnetization vector $\mathbf{M}$. (If the moments are all in random phases of precession, the x and y components average to zero.) The precessing magnetization results in a changing flux through the pick-up coils illustrated in Fig. 6, which generates a detectable emf oscillating at the precession frequency. The magnitude of the emf depends on the magnitude of $\mathbf{M}$ and

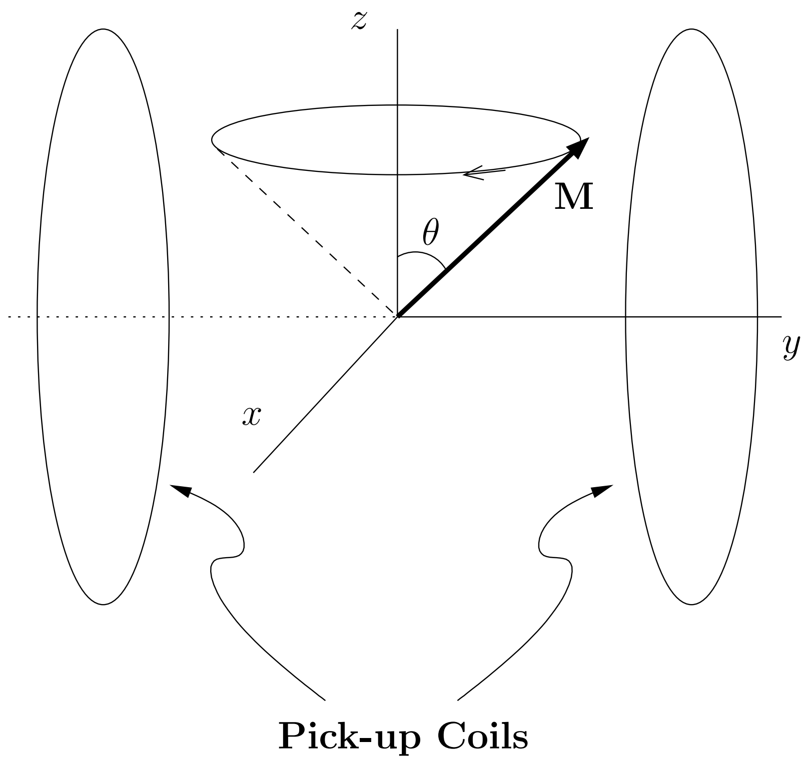

FIG. 6: A precessing magnetization **M** results in an emf in pickup coils around the sample.

the angle θ; the largest signals will be generated when $\theta = 90°$.

The signal from pick-up coils will be something like

$$S(t) = S_0 e^{-t/T} \cos\left(\omega_{\mathrm{p}} t + \phi\right), \tag{15}$$

where the time T characterizes the time it takes for any detectable coherent precession of M to die away. (We will discuss decay processes a little more in the next section.) The amplified signal from the pick-up coils is available at the Receiver output labeled `RF Out`. While it's nice to see this signal, we don't really care about the high-frequency oscillations; the interesting physics is contained in the decaying amplitude of this signal. To get an output that is proportional to the amplitude of the oscillation the raw signal is rectified and run through a low pass filter, as is schematically illustrated in Fig. 7. The result of this is available at the Receiver `Detector Out`.

As discussed above, the most effective flipping of the spins occurs when the applied rf frequency ω_{rf} exactly matches the precession frequency ω_{p}. The mixer output helps determine whether this condition is met. A mixer is a circuit that multiplies two oscillating signals together, producing an output with frequency components at the sum and difference

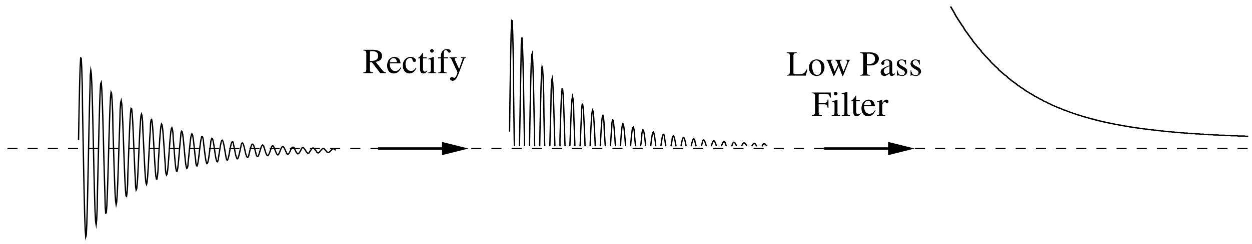

FIG. 7: The detected rf signal is rectified and passed through a low-pass filter to give an output that this proportional to the slowly varying amplitude of the oscillation.

of the two input frequencies. If we take the product of the signal from the precessing spins and the applied rf we have $A(t)\cos\omega_{\rm rf}t\cos\omega_{\rm p}t$ where $A(t)$ contains the slowly decaying envelope of the signal. Using trigonometric identities we have

$$A(t)\cos\omega_{\rm rf}t\cos\omega_{\rm p}t = \frac{1}{2}A(t)\left[\cos\left(\omega_{\rm p}+\omega_{\rm rf}\right)t + \cos\left(\omega_{\rm p}-\omega_{\rm rf}\right)t\right]. \tag{16}$$

Since $\omega_{\rm p} \simeq \omega_{\rm rf}$, the difference $\omega_{\rm p} - \omega_{\rm rf}$ is very small compared to the sum $\omega_{\rm p} + \omega_{\rm rf}$. This makes it easy to filter the high frequency term, leaving

$$V_{\rm mixer} \propto A(t)\cos\left(\omega_{\rm p}-\omega_{\rm rf}\right)t. \tag{17}$$

When $\omega_{\rm p} = \omega_{\rm rf}$ this has the same form as the detector output; when $\omega_{\rm p} \neq \omega_{\rm rf}$ the mixer output shows low-frequency "beats" at the difference frequency. The oscillator frequency should be adjusted to eliminate the beats, and the mixer output and the detector output should have the same shape when the resonance condition $\omega_{\rm p} = \omega_{\rm rf}$ is met.

IV. RELAXATION

Up to this point we have considered the motion of isolated dipole moments. In real samples there are very many moments and we actually measure the average magnetization **M**, which is the dipole moment per unit volume. In addition, the spins in a real sample are not isolated: they interact with their environment. In the liquid samples you will investigate the molecules undergo random collisions, during which any given proton "sees" rapidly varying magnetic fields from the neighboring molecules.

The net effect of the interaction with the environment on the measured magnetization can be lumped into two categories: transverse relaxation and longitudinal relaxation. Transverse relaxation refers to the loss of detected signal because of the tendency of precessing spins to get out of phase with each other. The spins may start out in perfect alignment, say along the x-axis, but they may precess at slightly different rates due to inhomogeneities in the field, or due to collisions that interrupt the uniform precession, so eventually the spins may point in random directions in the x-y plane, in which case $M = 0$. The characteristic time for this process is often called T_2. (This process is often called spin-lattice relaxation, although this can be misleading because there is no lattice in a liquid sample.) Longitudinal relaxation refers to the relaxation of M_z back as the magnetization returns to its equilibrium orientation along the z axis. The characteristic time for this process is often called T_1. ((This process is often called spin-spin relaxation.) We will not discuss the details of the various relaxation processes in this document, only some techniques for measuring the distinct relaxation times.

A. Measurement of the Longitudinal Relaxation Time, T_1.

The decay of M_z can be measured with a sequence of two rf pulses, with a variable delay between the pulses. The process is illustrated in Fig. 8, in which the axes are all assumed to be fixed in the *rotating frame*. The duration of the first rf pulse is such that the initial magnetization along the z axis is rotated 180° so that it points in the direction of the negative z axis. After a waiting time τ, the magnetization vector will have become shorter. Note: this is entirely due to longitudinal relaxation. Because the magnetization is along the z direction it will not induce any signal in the pickup coils, so the relaxation is not yet observable. To measure the length of the magnetization vector it must first be rotated 90° into the x'-y' plane, and this can be achieved with a second rf pulse of half the duration of the first pulse. By repeating this sequence with varying delays between pulses, the time-dependent decay of $\mathbf{M}$ due to longitudinal relaxation can be observed.

B. Measurement of the Transverse Relaxation Time, T_2.

Transverse decay mechanisms fall into two categories: interesting and uninteresting. The main "uninteresting" decay is due to inhomogeneity of the static magnetic field. The fact

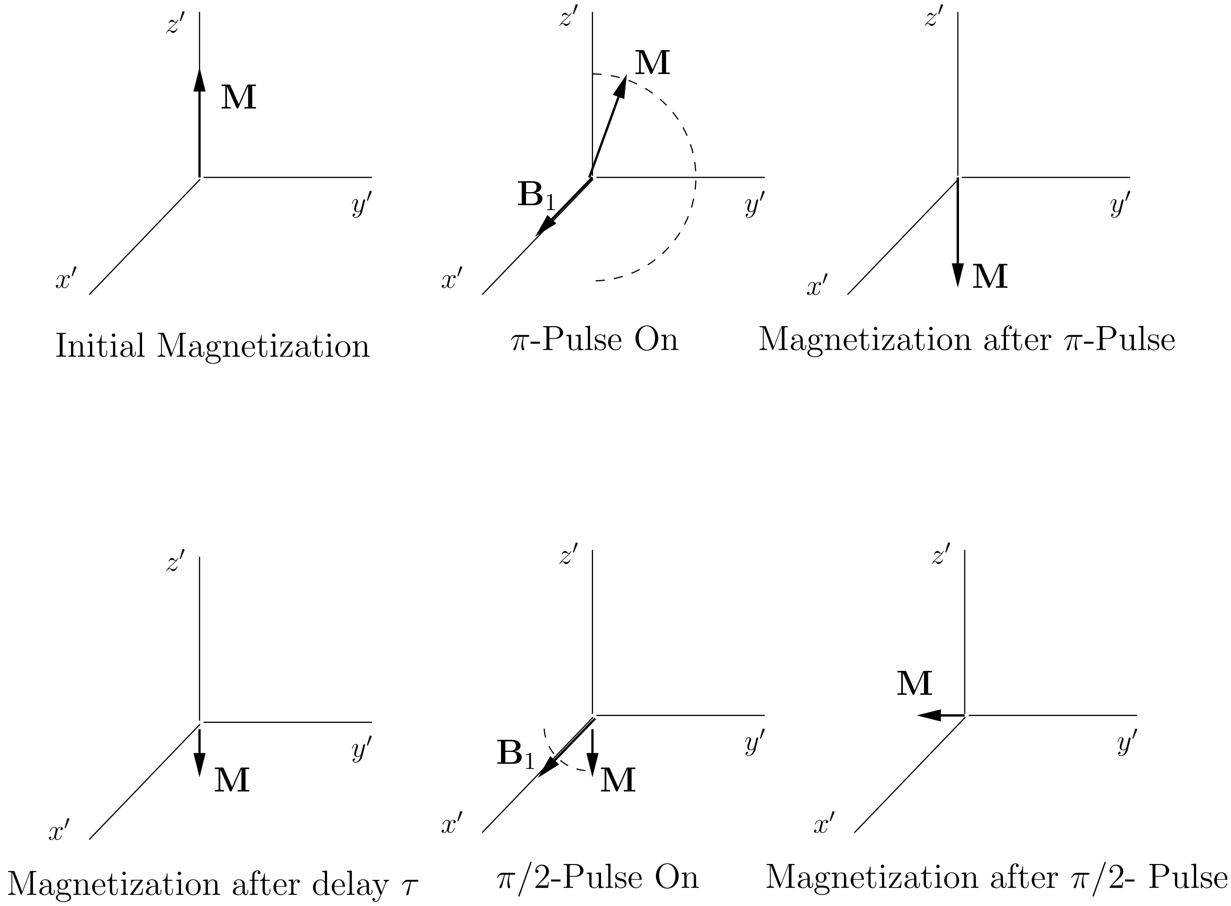

FIG. 8: 180°-90° pulse sequence used to measure the longitudinal relaxation time T_1.

that the field varies slightly over the size of the sample means that different spins feel slightly different magnetic fields, leading to slightly different precession rates, which means that initially in-phase precessing spins will eventually spread out. This doesn't tell us anything about the spins themselves, or their interactions with each other or their environment; thus the classification as "uninteresting." The spin-echo technique described in this section allows us to get information about "interesting" relaxation processes.

The generation of spin echoes is illustrated in Fig. 9. Consider a set of stationary spins with a transverse decay which is entirely due to field inhomogeneities. A first rf pulse rotates the initial magnetization 90° so that it lies along the positive x' axis. If the moments all precessed at exactly the same rate, they would all remain aligned with the x' axis (in the rotating frame), and the magnetization would remain constant. Some spins precess faster than the average, which means they move clockwise when viewed looking down from the positive z' axis in the rotating frame, and some slower, which means they move counterclockwise.

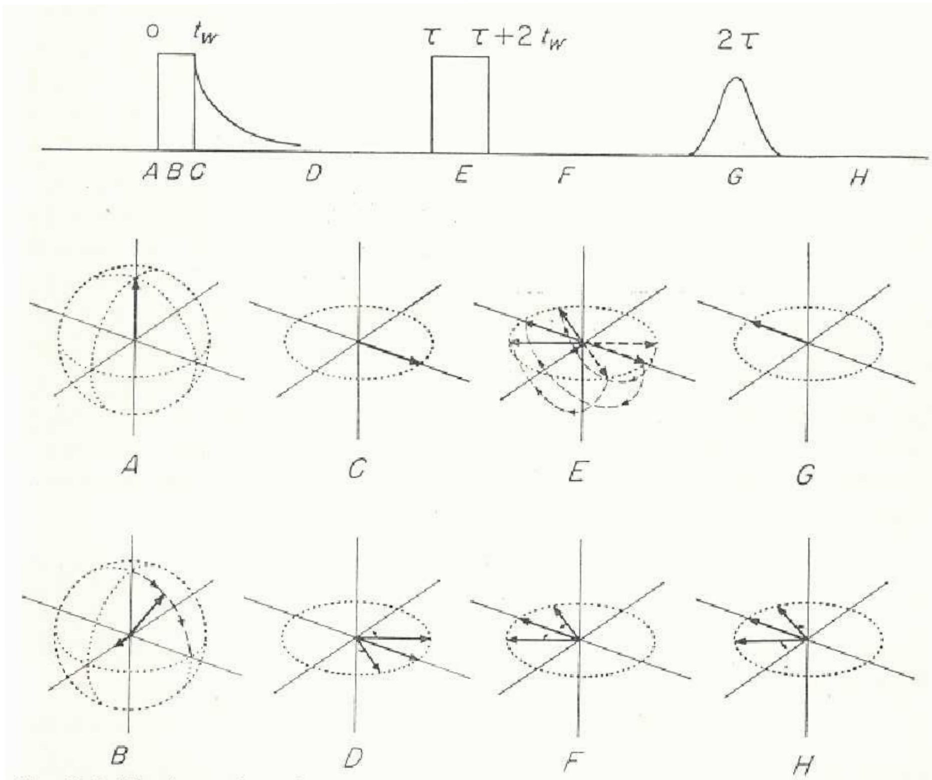

FIG. 3-8. The formation of an echo after successive 90 and 180° pulses. (From Carr and Purcell.[86])

FIG. 9: Illustration of formation of spin echoes. The square pulses in the top line represent the amplitude of the applied rf as a function time, and the decay and echo are the amplitude of the detected rf from the precessing magnetization. The drawings A through H indicate the positions of the precessing spins at times corresponding to the letters on the graph of the rf amplitude. From Carr and Purcell, Phys. Rev. **94**, 630 (1954).

This leads to a "fanning out" of the moments in the rotating frame, and a decrease in the magnitude of the net magnetization. After some time τ an rf pulse is applied that rotates the spins 180° about the x' axis. The "fast" spins in the illustration still move clockwise, and the "slow" spins counterclockwise, but after the 180° flip the spins are all *converging* on the negative x' axis. After an additional time τ the spins are all once again aligned, meaning the M has reformed, which leads to a large "echo" signal. The decay due to field inhomogeneities has been reversed by this 90°-180° pulse sequence. In real experiments there are other mechanisms leading to transverse decay, and the reduction of the magnetization signal as a function of delay time τ is due to these "interesting" processes.

V. EXPERIMENT

1. Read the *TeachSpin PS-1* manual.

2. Measure the field of the PS-1 magnet.

3. Follow the procedures given in the following parts of the *Getting Started* section of the manual:

   (a) All of Section A.

   (b) All of Section B.

   (c) All of Section C.

   (d) Section D (Discuss with your instructor whether to follow Option 1 or 2 on p. 30.)

4. Observe longitudinal relaxation with a 180°-90° pulse sequence. Vary the delay time τ and make record qualitative observations in your notebook.

5. Observe transverse relaxation with a 90°-180° pulse sequence. Vary the delay time τ and make record qualitative observations in your notebook.

6. After discussions with your instructor, perform a set of quantitative measurements with the PS-1 spectrometer.