Chapter II

PRINCIPLES OF MEASUREMENTS

2.1 Motion of Free Spin under a Static Field

When a spin with magnetic moment ($\bar{\mu}$) is placed in an external magnetic field, $\bar{H}$, the magnetic moment experiences a torque, $\bar{\Gamma}$, tending to align it in the direction of the field. The effect of the torque changes the angular momentum, $\bar{J}$.,

$$\frac{d\bar{J}}{dt} = \bar{\Gamma} = \gamma \bar{\mu} \times \bar{H} .$$

Since $\bar{\mu} = \gamma \bar{J}$, where γ is the gyromagnetic ratio, one obtains the equation of motion for the magnetic moment :

$$\frac{d\bar{\mu}}{dt} = \gamma (\bar{\mu} \times \bar{H}) \qquad (2.1)$$

The nuclear magnetization $\bar{M}$ is defined by $N\langle\mu\rangle$, where $\langle\mu\rangle$ is the average magnetic moment and N is the number of nuclei in a unit volume. If only a single isotope is important we consider only a single value of γ , so that

$$\frac{d\bar{M}}{dt} = \gamma (\bar{M} \times \bar{H}) . \qquad (2.2)$$

When $\bar{H} = H_o\hat{k}$, in thermal equilibrium at temperature T the magnetization will be along z-direction, i.e.,

$$M_x = 0 \; ; \; M_y = 0 \; ; \; M_z = M_o = \chi_o H_o = CH_o/T , \qquad (2.3)$$

where the Curie constant $C = N\mu^2/3k_B$, k_B is the Boltzmann constant. The magnetization of a system of spins with $I = \frac{1}{2}$ is related to the population difference $N_- - N_+$ of the lower and upper levels in Fig 2.1 :

$$M_z = (N_- - N_+)\,\mu ,$$

where the N's refer to a unit volume. The population ratio in thermal equilibrium is just given by the Boltzmann factor

$$N_-^o/N_+^o = \exp(-2\mu H_o/k_BT) \qquad (2.4)$$

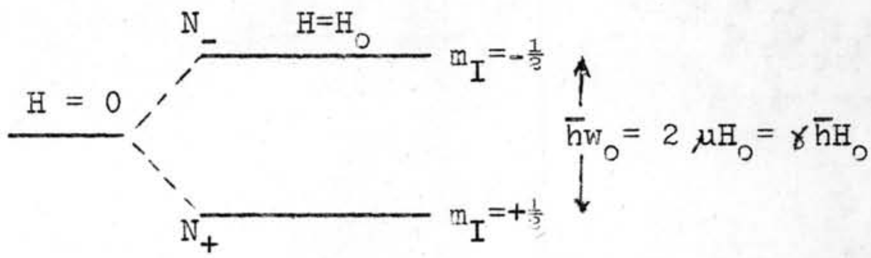

Fig.2.1 Zeeman levels of spin ½

$$\frac{W_+}{W_-} = \exp(-2\mu H_o/k_BT) , \qquad (2.5)$$

The population difference, n, is simply $(N_+ - N_-)$ and its rate of change is given by

$$\frac{dn}{dt} = 2N_-W_- - 2N_+W_+$$
$$= 2W_+\left[N_-(1+\gamma\hbar H_o/k_BT) - N_+\right] . \qquad (2.6)$$

Then to the first order approximation,

$$(\gamma\hbar H_o/k_BT)N_- \cong (N_o/2)(\gamma\hbar H_o/k_BT) \equiv n_o , \qquad (2.7)$$

where n_o is the population difference when thermal equilibrium between the lattice and spin system exist. We get

$$\frac{dn}{dt} = 2W_+(n_o - n) , \qquad (2.8)$$

with the solution of

$$n_o - n = (n_o - n_i)\exp(-2W_+t) ,$$

where n_i is the initial value for n. The time constant$(2W_+^{-1})$ is defined as the spin-lattice relaxation time, T_1, which is also called the thermal or longitudinal relaxation time.

Alternatively, the spin-lattice relaxation time can be written in terms of the magnetization by multiplying

Eq.(2.3) by $\bar{\mu}$, one obtains :

$$\bar{\mu}\frac{dn}{dt} = 2W_+\mu\left[N_-(1+\gamma\hbar H_o/k_BT)-N_+\right]. \quad (2.9)$$

Since $\quad -\mu(N_+-N_-) = -\mu n = -M_z \quad ,$

and $\quad \mu N_-(\gamma\hbar H_o/k_BT) = M_o$

Then we obtain the fundamental equation,

$$\frac{dM_z}{dt} = 2W(M_o-M_z) = (M_o-M_z)/T_1 \ , \quad (2.10)$$

where $T_1 \equiv (2W)^{-1}$, W is the transition probability, and T_1 is the characteristic time that magnetization returns to equilibrium.

If at t = o an unmagnetized specimen is placed in a magnetic field $H_o\hat{k}$, the magnetization will increase from the initial value $M_z = 0$ to a final value $M_z = M_o$. By integrating Eq.(2.10), we obtain :

$$M_z(t) = M_o(1-e^{-t/T_1}) \ .$$

Taking account of Eq.(2.10), the z-component of equation of motion (2.2) becomes,

$$dM_z/dt = \gamma(\bar{M}\times\bar{H})_z + (M_o-M_z)/T_1 \ , \quad (2.11a)$$

where $(M_o-M_z)/T_1$ is an extra term in the equation of motion, arising from interactions not included in the magnetic field H. That is, besides precessing about the magnetic field, $\bar{M}$ will relax to the equilibrium value $\bar{M}_o$.

If in a static field $H_o\hat{k}$ the transverse magnetization component M_x is not zero, then M_x will decay to zero, and similarly for M_y. The decay occurs because in thermal equilibrium the transverse components are zero. We can modify the equations to provide for transverse relaxation:

$$dM_x/dt = \gamma(\overline{M} \times \overline{H})_x - \overline{M}_x/T_2 \; ; \qquad (2.11b)$$

$$dM_y/dt = \gamma(\overline{M} \times \overline{H})_y - \overline{M}_y/T_2 \; ; \qquad (2.11c)$$

where T_2 is called the transverse relaxation time or the spin-spin relaxation time. The set of equations(2.11) are called the Bloch equations.

In the experiments an rf magnetic field is usually applied along the x-or y-axis. Our main interest is in the behavior of the magnetization in the combined rf and static fields. The Bloch equations are plausible, but not exact; they do not describe all spin phenomena, particularly in solid.

In addition, the spin-spin or transverse relaxation time, T_2, is defined as the characteristic time required for the precessing spins to lose phase.[15] Since local field variations give a range of absorption frequencies, a line width of the order of $H_{loc.}$ is obtained. Usually the line shape function $g(\omega)$ is defined such that $T_2 = \frac{1}{2}\, g(\omega)_{max}$.

2.2 Motion of Free Spin under an Alternating Magnetic Field.

The effect of an alternating magnetic field $H_x(t) = H_{xo} \cos(\omega t)$ is most readily analyzed by breaking it into two rotating components, each of amplitude H_1, one rotating clockwise and the other counterclockwise. We denote the rotating field by H_R and H_L :

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[15] For detail see, e.g. D.P. Ames, Mc Donell Company, "Nuclear Magnetic Resonance" Handbook of Physics(2nd.ed.; New York : Mc Graw-Hill Book Co. 1967).

$$\bar{H}_R = H_1\left[\hat{i}\cos\omega t + \hat{j}\sin\omega t\right] ,$$
$$\bar{H}_L = H_1\left[\hat{i}\cos\omega t - \hat{j}\sin\omega t\right] . \qquad (2.7)$$

Since one component will rotate in the same sense as the precession of the moment, and the other in the opposite sense. One can show that near resonance the counter-rotating component may be neglected.[16] Then Eq.(2.7) may be written as :

$$\bar{H}_1(t) = H_1\left[\hat{i}\cos\omega_z t + \hat{j}\sin\omega_z t\right] , \qquad (2.8)$$

where ω_z is the component of ω along z-axis and may be positive or negative.

Considering the equation of motion of a spin including the effects both of $\bar{H}_1(t)$ and of the static field $\bar{H}_o = H_o\hat{k}$, we may obtain :

$$d\bar{\mu}/dt = \gamma\bar{\mu} \times \left[\bar{H}_o + \bar{H}_1(t)\right] \qquad (2.9)$$

The time dependence of $\bar{H}_1$ can be eliminated by using a rotating coordinate (x', y', z') that rotates about the z-direction at frequency ω_z. In such a rotating frame of reference, H_1 will be static and so does H_o. Let us take H_1 along x'-axis and with a coordinate transformation, Eq.(2.9) becomes :

$$\delta\bar{\mu}/\delta t = \bar{\mu} \times \left[\hat{k}'(\omega_z + \gamma H_o) + \hat{i}'\gamma H_1\right] , \qquad (2.10)$$

where $\delta\bar{\mu}/\delta t$ representing the time rate of change of $\bar{\mu}$ with

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[16] For detial see, e.g. C.P. Slichter, Principles of Magnetic Resonance (New York; Evanston and London: Harper and Row, 1963) p.18.

respect to the coordinate system $\hat{i}$, $\hat{j}$, $\hat{k}$. By setting $\omega_z = -\omega$, the angular frequency of the rotating frame is equal to the Larmor frequency by in reverse direction, Eq. (2.10) can be written as :

$$\frac{\delta \mu}{\delta t} = \bar{\mu} \times \gamma \left[(H_o - \frac{\omega}{\gamma}) \hat{k}' + H_1 \hat{i}' \right] = \bar{\mu} \times \gamma \bar{H}_{eff}, \quad (2.11)$$

where $\bar{H}_{eff} = (H_o - \frac{\omega}{\gamma}) \hat{k}' + H_1 \hat{i}'$

Note that the magnetic moment in the rotating frame experienced effectively a static magnetic field $\bar{H}_{eff}$. The moment therefore precesses in a come of fixed angle about the direction of H_{eff} at angular frequency γH_{eff}. The situation is illustrated in Fig. 2.2 for a magnetic moment which, at t = 0, was oriented along the z-direction.

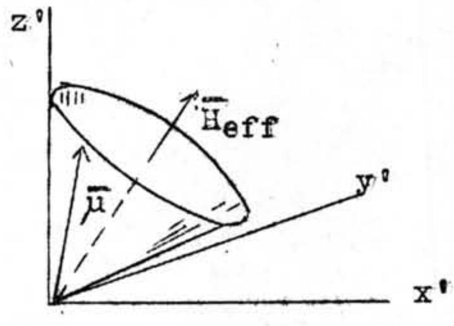

Fig. 2.2. Motion of magnetic moment in rf field.

If H_o is above resonance ($H_o > \omega/\gamma$), the effective field has a positive z-component, but when H_o lies below the resonance ($H < \omega/\gamma$), the effective field has a negative z-component.

When the resonance condition is fulfilled exactly ($\omega = \gamma H_o$), the effective field is then simply $H_1 \hat{i}'$. A magnetic moment that is parallel to static field initially will then precess in the

y'-z' plane. If we were to turn on H_1 for a short time (that is, apply a rf pulse train of duration t_ω), the magnetic moment would precess through an angle $\theta = \gamma H_1 t_\omega$. If t_ω were chosen such that $\theta = \pi$, the pulse would simply invert the moment. Such a pulse is referred to a "180 degree pulse". If $\theta = \pi/2$ (90 degree pulse), the magnetic moment is turned from the z' direction to the y'-direction. Following the turn-off of H_1, the moment would then remain at rest in the rotating frame and hence precess in the laboratory frame, pointing normal to the static field.

2.3 The Proton Spin-Echo.[17, 12]

We put a sample of material we wish to study in a coil, the axis of which is oriented perpendicular to $\bar{H}_o$. In thermal equilibrium there will be an excess of moments pointing along H_o. Applying a rf alternating voltage to the coil, an alternating magnetic field, H_1, is performed with a direction perpendicular to $\bar{H}_o$. By properly adjusting H_1 and t_ω, a 180^o pulse may be obtained. That is the magnetic moment inverted to a direction, opposed to $\bar{H}_o$. In this situation, there is no induction tail, Like-wise, a 90^o pulse may be obtained. The total net magnetic moment processes in the equatorial plane as shown in Fig. 2.3.C and induces a maximum rf signal, we called an induction tail. For liquid and gaseous samples this signal decays, in a time long compared to t_ω. That is corresponding to its relaxation time.

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[17]E.L. Hahn, "Spin Echoes," Physical Review, 80(1950)580.

In fact, it is known that the static field is not exactly homogeneous. Let ΔH_z be the magnetic field inhomogeneity over the sample volume. The incremental moments will precess at a slightly different frequencies. Viewed from the rotating frame of reference , the incremental moment vectors appear to fan out as illustrated in Fig. 2.3D.

In order to obtain an echo, a 180° pulse is applied at a time τ after the 90°. τ is chosen larger than the artificial decay time of the induction tail but smaller than the natural lifetime of the nuclear signal. Neglecting relaxation, the incremental vectors rotate 180° about the x'-axis as shown in Fig. 2.3E. When the rf field is removed at the end of the 180°pulse, all incremental vectors are again in the equatorial plane. Since it is assumed that each nucleus remains in the same H_z, each will continue to precess in the same sense and with exactly the same angular frequency as it did before the 180° pulse is applied. Because of this memory and because of their new relative positions after the 180° pulse, the incremental moment vectors will all recluster (see Fig. 2.3F) together in exactly τ units of time after the 180° pulse. This is at time 2τ from the first 90° pulse, there will be a maximum total magnetic moment vector (see Fig. 2.3G) and hence maximum induced signal or a "Spin echo" (see Fig. 2.4). Following $t = 2\tau$ the incremental vectors again fan out and the echo decays in the same manner that it is formed.

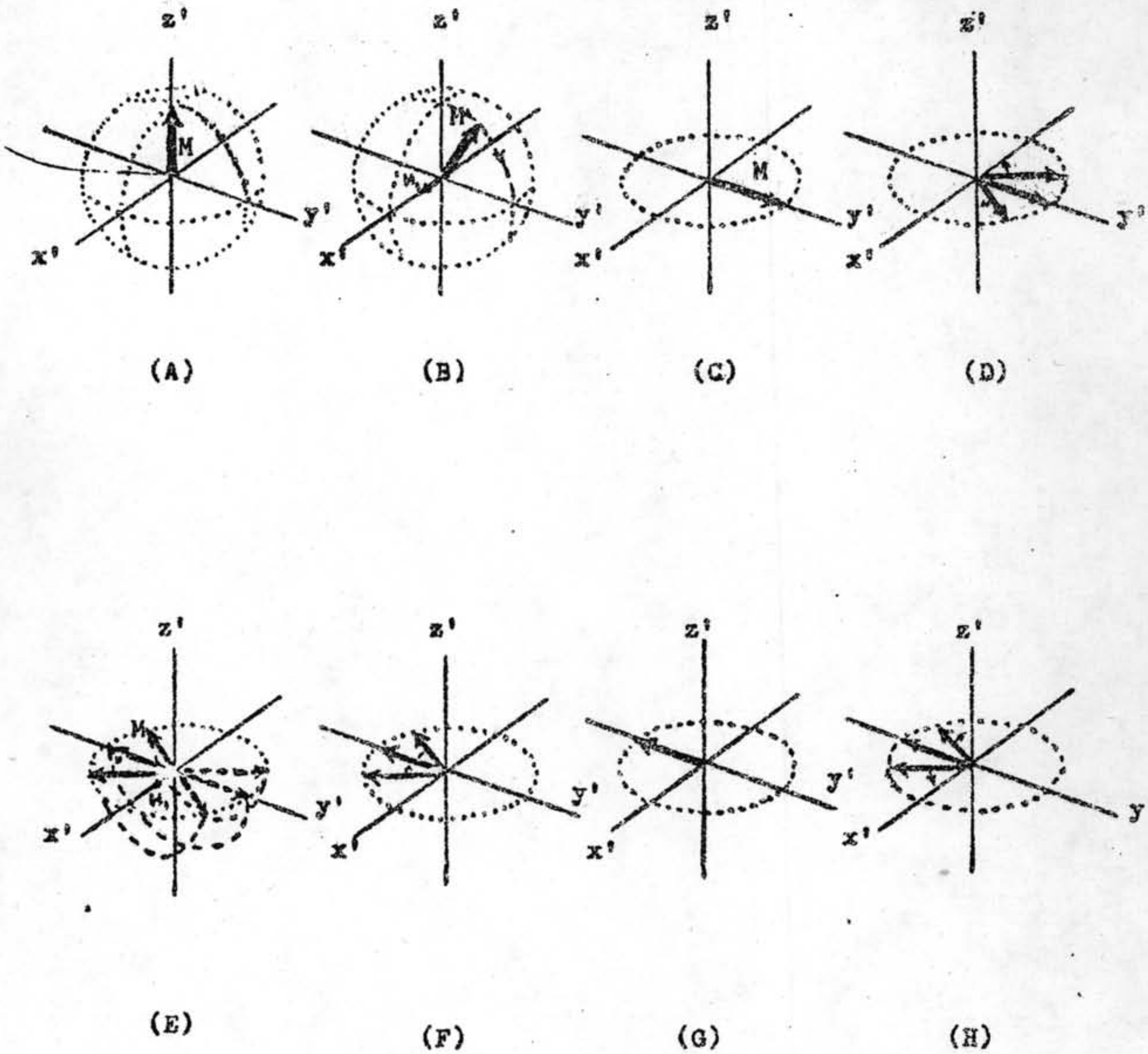

Fig.2.3 Motion of magnetic moment perturbed by a 90°- 180° pulse in a rotating frame and a spin-echo formation.

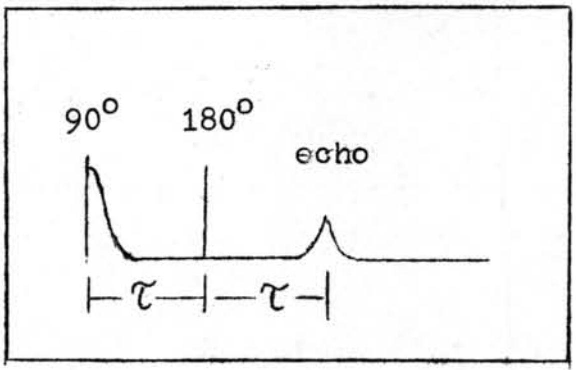

Fig. 2.4 The induced signal 90°, 180° and echo.

In providing of a "Spin-echo" as we have described above, it is known that τ is chosen to be shorter than the "natural" lifetime of the nuclear signal. The natural lifetime of the nuclear signal is the time that it takes the spin to move out of phase solely by spin-spin interaction, neglecting the field inhomogeniety effect. But in fact, the atomic diffusion in the presence of an inhomogeneous magnetic field also affects the echo signal by moving a spin from one magnetic field to another. An analytical expression for the echo amplitude is given by[12]

$$\exp\left[-t/T_2 - \gamma^2 GDt^3/12\right],$$

where t is the time after the 90° pulse is applied, T_2 is the transverse relaxation time, γ is the gyromagnetic ratio, G is the field gradient and D is the diffusion constant.

2.4 Method for Measuring Spin-Spin Relaxation Time (T_2)

In the measurement of T_2 the effect of diffusion D on the echo amplitude can be minimized by applying a series of 180° pulses after the 90° pulse is applied. This series of pulses is known as the Carr- Purcell (C.P) series.[12]

A single 90° pulse is used to obtain an entire echo envelope without requiring the sample to return to thermal equilibrium. This is accomplished by initiating the measurement with the usual 90° pulse at $t = 0$. A 180° pulse is then applied at time $t = \tau$. The usual echo appears at time $t = 2\tau$. Next, to illustrate with a particularly simple case, and additional 180° pulse is applied at time $t = 3\tau$. By reasoning identical to that previously used in connection with the first echo, it can be seen that the incremental vectors will recluster at time $t = 4\tau$. Thus, a second echo is formed. If this process is continued throughout the natural lifetime of the nuclear signal, additional echoes of decreasing amplitude are formed. The envelope of these echoes indicates the decay of the polarization in the equatorial plane. Then T_2 can be measured directly by plotting the logarithm of the maximum echo amplitude at $t_o = 2\tau$ versus arbitrary value of 2τ. The decay time constant of the echo envelope gives the value of T_2, since we have $M_z=M_o\exp(-t/T_2)$.

For a special case, when $T_2 \ll 1/\gamma\Delta H$, the spin-echo can not be formed. T_2 can be measured directly from a conduction decayed nuclear signal after a 90° pulse is applied. Measuring the half width of this nuclear signal which is defined as $T_{\frac{1}{2}}$, then T_2 can be obtained by using a relation of $T_2 = T_{\frac{1}{2}}/\ln 2$.

2.5 Method for Measuring Spin-Lattice Relaxation (T_1)

Using the properties of 180° and 90° pulse, a null method has been introduced by Carr-Purcell[12] for the measurement of the longitudinal of spin-lattice relaxation time. This type of measurement is initiated by a 180° pulse. The total magnetization is inverted from $M_z = M_o$ to $-M_o$. If the system obeys the Bloch equation, $(dM_z/dt) = -(1/T_1)(M_z - M_o)$, the magnetization begins to return to its equilibrium position according to $M_z(t) = M_o\left[1-2\exp(-t/T_1)\right]$. $M_z(t)$ at different values of τ can be determined by measuring the free precessing signal produced by applying a 90° pulse at a time after the 180° pulse has been applied. For very short value of τ the 90° pulse nutates the total magnetization vector of nearly maximum amplitudé from the south pole $(-M_o)$ of the reference sphere to the equatorial plane. A tail with nearly maximum amplitude follows the 90° pulse.

For very large value of τ, compared to the spin-lattice relaxation time, the 90° pulse nutates the reformed total magnetic moment vector of nearly maximum amplitude from the north pole down to the equatorial plane. Again a tail of nearly maximum value follows that 90° pulses. For intermediate value of τ the tails will have smaller amplitudes. For one value in particular, which will be designated τ_{null}, there will be no tail. Since the system relaxes or returns to equilibrium exponentially, with the time constant T_1, it is easily shown that T_1 may be calculated directly from the measured value of τ_{null} by using the relation;

$$\tau_{null} = T_1 \ln 2$$

For an incorrect setting of the 180° pulse, it could lead to an error in determining T_1. Deviation from 180° in either direction would give a shorter τ_{null} and hence would give too small a value for T_1.