CHAPTER II

THE THEORY OF NUCLEAR MAGNETIC RESONANCE

2.1 Magnetic and Angular Momentum Properties of the Nucleus (5).

We can compute the magnetic moment of a nucleus of spinning spherical shell from the equation,

$$\mu = g\left(\frac{e}{2MC}\right)p, \qquad (2.1)$$

where
μ = magnetic moment,
g = nuclear g - factor,
e = electronic charge,
M = mass of proton,
C = velocity of light,
p = angular momentum.

The angular momentum vector p is given by $p = \hbar I$, where $\hbar = \frac{h}{2\pi}$, I = nuclear spin and h = Plank's constant. The magnetic moment is proportional to the angular momentum, and we can write,

$$\mu = \gamma(\hbar I), \qquad (2.2)$$

where $\gamma = \frac{e}{2MC}$ = gyromagnetic ratio.

If we substitute $p = \hbar I$ in eq. (2.1), we obtain

$$\mu = g\left(\frac{e}{2MC}\right)\hbar I, \qquad (2.3)$$

or

$$\mu = g I \mu_0, \qquad (2.4)$$

where $\mu_0 = \frac{e\hbar}{2MC} = 5.050 \times 10^{-24}$ erg/gauss,
= Nuclear Magneton .

2.2 The Larmor Precession; Energy in the Magnetic Field (2).

If a magnet of dipole moment μ is placed in magnetic field H, a torque is exerted on the magnetic dipole,

$$L = \mu \times H. \quad (2.5)$$

Newton's law of rotational motion states that the rate of change of angular momentum of a system is equal to the torque applied to it, or

$$dp/dt = L. \quad (2.6)$$

Since the torque on a nucleus with magnetic moment μ is given by the equation (2.5), it follows that

$$dp/dt = \mu \times H \quad (2.7)$$

Since $\mu = g\,(e / 2MC)\,p$, we have

$$dp/dt = -g\,(e/2MC)\,H \times p \quad (2.8)$$

which is the equation of motion for a vector p of constant magnitude precessing with angular velocity

$$W_o = -g\,(e/2MC)\,H. \quad (2.9)$$

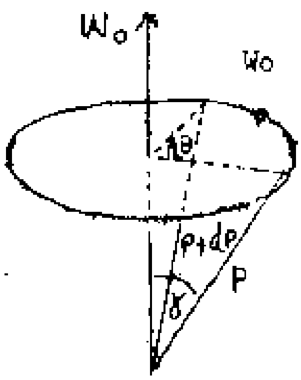

Fig. 1 VECTOR DIAGRAM OF A PRECESSING ANGULAR MOMENTUM VECTOR OF CONSTANT MAGNITUDE IN A MAGNETIC-FIELD.

From the Fig. 1, we have

$$dp = W_o \times p\,dt. \quad (2.10)$$

We conclude that if a nucleus of magnetic moment $\mu = g\,(e/2MC)\,p$ is placed in a magnetic field, the magnetic moment vector (or the angular momentum vector) precesses with the angular frequency (eq. (2.10)) regardless of the angle between μ and H. This is called the Larmor Precession Frequency.

Since quantum mechanical arguments show that the value of p.p is $I\,(I+1)\,\hbar^2$, the length of the angular momentum vector is

$$|p| = \left[I\,(I+1) \right]^{\frac{1}{2}} \hbar \quad \text{. - - - - - - - - - -(2.11)}$$

The nuclear magnetic moment of a nucleus with spin I is a vector of length.

$$|\mu| = g\,(e/2MC) \left[I\,(I+1) \right]^{\frac{1}{2}} \hbar \quad \text{. - - - - - - - - (2.12)}$$

It has a component

$$\mu_H = g\,(e\hbar/2MC)\,m, \quad \text{- - - - - - - - - - - - - - - (2.13)}$$

where $m = I,\ I-1,\ I-2,$ - - - - - - - -, $-I$, along the direction of an externally applied magnetic field H, and a component of length

$$\mu_{\perp} = g\,(e\hbar/2MC) \left\{ I\,(I+1) - m^2 \right\} \quad \text{- - - -(2.14)}$$

which is perpendicular to the external field and precesses with an angular frequency of magnitude

$$w_0 = g\,(e/2MC)\,H \quad \text{. - - - - - - - - - - - - - (2.15)}$$

As may be derived from eq. (2.5), the potential energy U of a magnetic moment μ in a magnetic field H is, apart from an additive constant,

$$U = -\mu . H = -\mu_H H \quad ------(2.16)$$

The energy of our nuclear dipole in a state characterized by m is

$$U(m) = -g (e\hbar/2MC) mH, \quad --------(2.17)$$

and a nucleus of spin I has intergral 2I + 1 energy levels (one for each value of m) accessible to it in consequence of its interaction with a magnetic field H. These are called the Zeeman levels, since they are similer to those responsible for the Zeeman splittings in atomic spectra. It should be noted explicitly that the foregoing equations are valid whether g is negative or positive

2.3 Nuclear Magnetic Resonance (1, 2, 5).

If we place a bare nucleus, such as a proton, in a magnetic field of strength Ho. We have seen that nuclei posseses two very important properties associated with angular momentum. These properties are the spin number I and the magnetic moment μ. When such nucleus is placed in a static uniform magnetic field Ho, it may take up one of (2 I + 1) orientations and (2 I + 1) energy levels. Transitions among these levels are possible. The energy difference between any two such levels in the constant external magnetic field Ho is

$$U(m'') - U(m') = g\mu_0 H_0 (m' - m'') \quad ------(2.18)$$

Bohr's explaination involved the postulates that a system characterized by two discrete energy states saparated by energy ΔU may make a transition from one state to the other accompanied by either emission or absorption of a quantum of electromagnetic radiation of energy

$$h\nu = \hbar w' = \Delta U \quad \text{-----------} \quad (2.19)$$

The transitions are permitted by the selection rule, for example $\Delta m = \pm 1$, and the transitions are permitted between adjacent states of energy level scheme such as that of Fig. 2 which

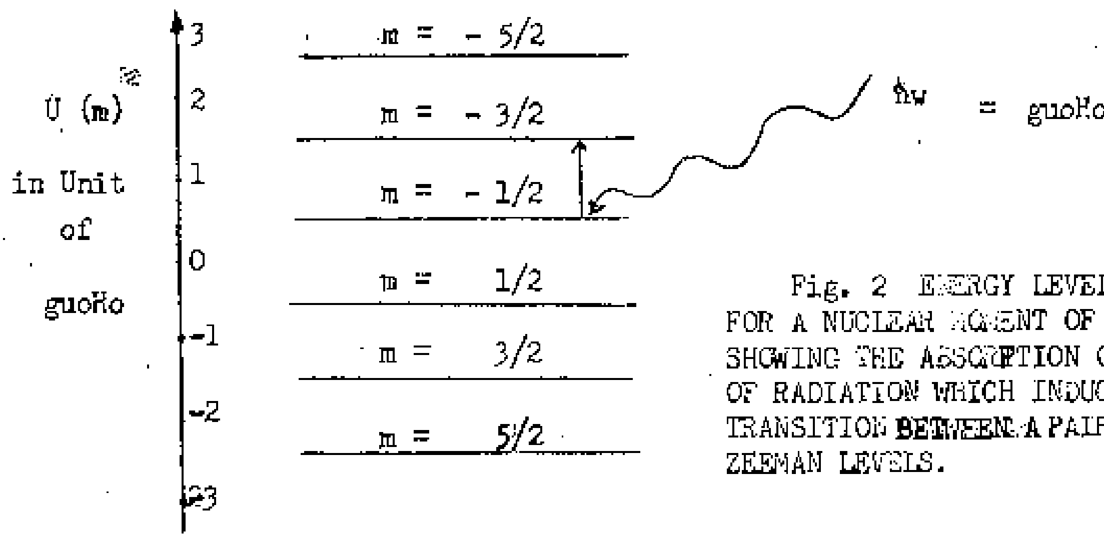

Fig. 2 ENERGY LEVEL DIAGRAM FOR A NUCLEAR MOMENT OF SPIN 5/2 SHOWING THE ABSORPTION OF A QUANTUM OF RADIATION WHICH INDUCES A TRANSITION BETWEEN A PAIR OF ADJACENT ZEEMAN LEVELS.

applies to a nucleus with $I = 5/2$. The selection rule applied to eqs. (2.18) and (2.19) determines the frequency of the radiation emitted or absorbed by the nuclear magnetic dipole,

$$\hbar W_o = h\nu_o = g\mu_o H_o \quad \text{------} \quad (2.20)$$

which is precisely the Larmor frequency of eq. (2.9). Protons in a field 10,000 gauss precess at a frequency $\nu_o = 42.6 \times 10^6$ cps, which is in the radio - frequency range.

To summarize, if one subjects a sample containing nuclear magnets to radiation at the Larmor frequency, which is the order of megacycles in ordinary laboratory magnetic fields, a nucleus in a lower Zeeman energy state may absorb a quantum of energy from the radiation field and makes a transition to the next higher energy state. If the frequency of the radiation is not near the Larmor frequency, we expect little for no absorption, and hence the absorption is what physicists call a "nuclear magnetic resonance".

2.4 Quantum Mechanical Transition Probability (2).

Quantum mechanics does not give us complete information as to the energy, angular momentum, and position of each nucleus at any time, but it does provide us with all that we need to know, namely, the probability that a nuclear magnetic moment initially in a state m will at some later time t be found in a state m'. This probability, expressed per unit time, will be denoted by $P\ (m \longrightarrow m')$.

If a nucleus in one of its Zeeman energy states is immersed in a radiation bath with energy in the frequency range $d\nu$ near ν given by $\rho(\nu)\ d\nu$, one expects the probability of transition to be proportional to the number of quanta present with frequency near the Lamor frequency, that is, propostional to $\rho(\nu_0)$. In fact the quantum mechanical result obtained by perturbation theory is

$$P\ (m \longrightarrow m') = (2\pi/3\hbar^2)\ g^2\ u_0^2\ |\ I_{mm'}\ |^2\ \rho(\nu_0) \quad -(2.21)$$

The quantity $|\ I_{mm'}\ |$, which is the so called matrix element of the nuclear spin, is usually of order of magnitude unity, when $|m' - m| > 1$ it vanishes, giving rise to the selection rule mentioned in sec. 2.3. When this transition probability is applied to the problem of nuclear magnetic resonance it is shown by Pound (1) that the signal to noise ratio is given by

$$\frac{V_s}{V_n} = \left(\frac{Y \xi N \gamma I (I+1) h^2}{48 kT} \right) \left(\frac{V_c Q \nu_o^3 T_2}{k T B_2 F T_1} \right)^{\frac{1}{2}}, \quad \text{---(2.12)}$$

where Y = static susceptibility,

ξ = the filling factor,

N = total number of nuclei per cm^3.,

γ = gyromagnetic ratio,

T = temperature of spin and lattice in thermal equilibrium,

V_c = the effective volume in which the energy is stored,

Q = Q -value of the coil,

F = the noise figure of the amplifier,

B_2 = the effective band width of the amplifier,

k = Boltzmann's constant,

T_1 = the spin-lattice relaxation time,

and T_2 = the spin-spin relaxation time,

2.5 The Spin-Lattice Relaxation Time and the Spin-Spin Relaxation Time (1, 2, 5).

There are two factors that affect to the line width and nuclear magnetic resonance signal. The first, is the spin-lattice relaxation time or the thermal relaxation time. It is the time required for all but 1/e of the equilibrium excess number to reach the lower state. This time is denoted by T_1 , which can be shown to be

$$T_1 = \frac{1}{2p}, \quad \text{-----------------(2.23)}$$

where p is the transition probability from eq. (2.21). T_1 is concerned only with the maintenance of the equilibrium distribution of populations of nuclei between spin states. Any process which reduces the transition probability, increases T_1. If T_1 is large, the time required to establish the equilibrium value of n (2,6), that is the excess population of the lower energy spin state, becomes long, leading in extreme cases to difficulty in obtaining on nuclear magnetic resonance signal. The second, is the spin-spin relaxation time. It is the time for spins to precess out of phase of each other. This is also connected with the inverse of the line width. It is denoted by T_2, which can be shown to be

$$T_2 = \frac{1}{2} g (\nu)_{max.} , \qquad (2.24)$$

where $g (\nu)_{max.}$ is the maximum value of the normalized shape function (1,7) of the absorption line

$$\int_0^{\infty} g (\nu) \, d\nu = 1 . \qquad (2.25)$$

T_2 is concerned with the life time of spin states as a result of participation in some relaxation process. If T_2 is small, the spread frequencies of the spin state transitions is increased, causing a broadening of the absorption peak, and concurrently a reduction in the singal strength which in the limit can quench the nuclear magnetic resonance signal.