# CHAPTER II

# THEORY

## 2.1 Magnetic Properties of Nuclei.[1,6,7,8]

### 2.1 a. Nuclear Magnetic Moments.[1,6,7,8]

With regard to their magnetic properties, nuclei are best classified in terms of their angular momenta and spins. According to general principles of quantum mechanics, the maximum measurable component of the angular momentum of any system (in particular, a nucleus) must be an integral or half-integral multiple of the modified Planck constant $\hbar$ ($= h/2\pi$). If we write the maximum component as I, I is then the spin quantum number. It is found that the nucleus will have 2I+1 distinct states in which the component of angular momentum along any selected direction will have values I, (I-1), (I-2),.... (-I+1), -I. In the absence of external fields, these states will all have the same energy.

We may define a maximum observable component of the magnetic moment $\mu$ in terms of which the complete set of observable values are $m\mu/I$, where m, the magnetic quantum number, may have the values

$$m = I, I-1, I-2, \ldots\ldots, -I+2, -I+1, -I \quad . \qquad (2.1)$$

It is frequently convenient to specify magnetic properties in terms of the ratio $\gamma$ defined by

$$\vec{\mu} = \gamma \hbar \vec{I} \quad , \qquad (2.2)$$

where $\vec{I}$ is the total nuclear angular momentum in units of $\hbar$,

$\gamma$ is the magnetogyric ratio, it has dimensions of radians per gauss second.

Another way in which nuclear moments are sometimes measured is in units of the nuclear magneton $\mu_o$, which is given by(7)

$$\mu_o = \frac{e \hbar}{2 M_p C} = 5.0493 \times 10^{-24} \text{ erg/gauss} \quad (2.3)$$

where $M_p$ is the proton mass,

e is the proton charge, and c is the velocity of light. The magnitude of the nuclear magneton is $5.0493 \times 10^{-24}$ erg./gauss. The observed magnetic moment for a nucleus of spin I can be expressed in terms of nuclear magneton by

$$\vec{\mu} = g \left( \frac{e \hbar}{2 M_p C} \right) \vec{I} \quad (2.4)$$

where $g$, called variously the nuclear $g$ factor, the gyromagnetic ratio, the nuclear spectroscopic splitting factor, is a dimensionless number of the order of unity which, can be determined by experiment or by calculation using quantum electrodynamics. However, $\gamma$ is the more useful quantity for discussing magnetic resonance in many respects. The magnitude of the angular-momentum vector for a system with spin I is

$$\hbar \sqrt{I (I+1)} \quad (2.5)$$

and similar modifications will have to be made for other vectors.

From the table of known nuclear spins there are certain regular features which may be expressed in terms of the atomic

number Z and the mass number A. They may be summarized as follows:[1]

(1) if the mass number A is odd, the nuclear spin I is half integral,

(2) if the mass number A and the charge number Z are both even, the spin is zero,

(3) if the mass number A is even but the charge number Z is odd, the spin is integral. Nuclei with spin I = 0 have no magnetic resonance. It is important to note that some very commonly occurring nuclei such as $C^{12}$ and $O^{16}$ are in this class.

2.1 b. Nuclear Electric Quadrupole Moments.[1,8]

Another nuclear property which is of some importance in connection with NMR experiments is the electric quadrupole moment, which is also related to the spin. Nuclei of spin $I \geq 1$ usually possess electric quadrupole moments. Interactions between the electric quadrupole moment and the electric field gradient at the nucleus in solids, however can be observed in the same manner as nuclear magnetic resonance, but can not be observed in liquids because of the random motion of the molecules.

2.2 Nuclear Energy Levels in a Magnetic Field:[1,5,6,7]

If a nucleus with a magnetic moment $\vec{\mu}$ is introduced into a uniform magnetic field $\vec{H}_o$ after thermal equilibrium has obtained, the potential energy of orientation of a nuclear moment is

$$E = -\vec{\mu} \cdot \vec{H}_o \qquad (2.6)$$

or, from Eq. (2.2) and the properties of $\vec{I}$ ,

$$E = -\gamma \hbar H_o m \quad , \qquad (2.7)$$

where $m = -I, -I+1, \ldots\ldots I-1, I.$

The $2I+1$ distinct values of the energy levels are equally spaced, the separation between them being $\gamma \hbar H_o$. This splitting of energy levels in a magnetic field may be referred to as a nuclear Zeeman splitting, because it is analogous to the magnetic splitting of electronic levels (Zeeman effect). It is illustrated for a system with I = 1 (and consequently with three states) in Fig. 2-1.

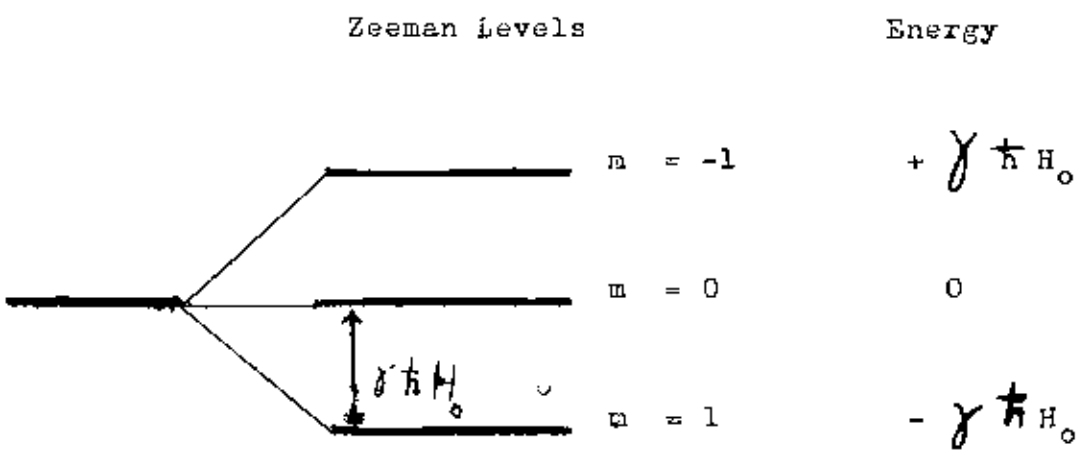


Fig. 2.1 Zeeman Splitting of Nuclear Energy Levels in a Magnetic Field.

The basis of NMR experiments is to introduce transitions between these Zeeman levels by the absorption or emission of energy quanta. For a transition between neighboring levels, the frequency $\nu$ of the electromagnetic radiation require can be found from the basis of the Bohr frequency condition

$$h\nu = \Delta E \quad . \qquad (2.8)$$

The energy difference between any two such levels in a constant external magnetic field $\overrightarrow{H_o}$ is

$$\Delta E = E(m'') - E(m') = \gamma \hbar H_o (m' - m''). \qquad (2.9)$$

Only transitions in which $m$ changes by +1 or -1 are permitted by a so-called Selection rule, and therefore transitions are permitted between adjacent states of an energy level scheme such as that of Fig. 2-1, which applies to a nucleus with $I = 1$. Eqs. (2.8) and (2.9) with appropriate selection rules determines the frequency of the radiation emitted or absorbed by the nuclear magnetic dipole:

$$h\nu = \gamma \hbar H_o$$

$$\therefore \quad \nu = \frac{\gamma H_o}{2\pi} \quad . \qquad (2.10)$$

We see, therefore, that for a given magnetic field $H_o$ transitions will be observed only for a characteristic frequency for each species of the nucleus, this being proportional to both $H_o$ and the magnetogyric ratio $\gamma$, provided that all the environmental effects are ignored.

## 2.3 Distribution of Nuclear Spins in a Magnetic Field. (1,6,7,9)

If $N$ nuclei per unit volume with energy $E(m)$ are placed in a uniform magnetic field $H_o$, they will eventually occupy the $(2I + 1)$ energy levels. According to the Boltzmann probability distribution, the number of nuclear moment populations $N(m)$ is given by,

$$N(m) = \frac{N}{2I+1} \exp\left(\frac{m\gamma\hbar H_o}{kT}\right) . \quad (2.11)$$

At ordinary fields and temperatures, the exponent can be approximated to

$$\frac{m\gamma\hbar H_o}{kT} = m\frac{\mu H_o}{IkT} = m.\delta \ll 1; \quad (2.12)$$

therefore, Eq.(2.11) may be written as

$$N(m) = \frac{N}{2I+1}(1 + m\delta) . \quad (2.13)$$

$m = -3/2$ _____ $N_m = \frac{N}{4}(1-3/2\,\delta)$

$m = -1/2$ _____ $N_m = \frac{N}{4}(1-1/2\,\delta)$

$m = 1/2$ _____ $N_m = \frac{N}{4}(1 + 1/2\,\delta)$

$m = 3/2$ _____ $N_m = \frac{N}{4}(1 + 3/2\,\delta)$

Fig. 2.2 Population Distribution among the Levels $E_m$, for I=3/2 .

A schematic diagram for the case I = 3/2 is shown in Fig. 2.2.

As will be stated in the next section, the electromagnetic radiation field $2E_1 \sin(2\pi\nu t)$ can induce transitions of $\Delta m = \pm 1$ only, and does so with equal probabilities for absorption and stimulated emission. Another way to indicate

this fact is tnat, the populations at equilibrium are given by

$$\frac{N(m)}{N(m')} = \exp\left(\frac{\gamma \hbar H_o \Delta m}{kT}\right), \qquad (2.14)$$

$$= 1 \pm \frac{\gamma \hbar H_o}{kT},$$

since, at room temperature, $\gamma \hbar H_o \ll kT$.

It shows that at equilibrium $N(m + \Delta m) \simeq N(m)$.

From this, the Curie susceptibility or the static nuclear susceptibility or volume magnetic susceptibility $\chi_o$ can be determined by

$$\chi_o = \frac{N}{3kT} \gamma^2 \hbar^2 I(I+1). \qquad (2.15)$$

At room temperature, $\chi_o$ is approximately $10^{-10}$ or $10^{-11}$.

It is interesting to note that $\chi_o$ has been measured directly for the protons in solid hydrogen.

## 2.4 Magnetic Resonance Absorption.[1,6,7,8]

### 2.4 a. Classical Treatment.[1,7]

The nature of resonance absorption can be obtained, however, by the consideration of the classical motion of a magnetic dipole in a magnetic field.

Since the magnetic moment $\vec{\mu}$ and angular momentum $\vec{p}$ of a nucleus are related by

$$\vec{\mu} = \gamma \vec{p} \qquad (2.16)$$

where $\gamma$ is the magnetogyric ratio, the classical equation of

motion can be written vectorially as

$$\frac{d\vec{\mu}}{dt} = \gamma ( \vec{\mu} \times \vec{H} ) \qquad (2.17)$$

where $\vec{H}$ is the applied magnetic field. Now if we rotate the vector $\vec{\mu}$ with an angular velocity $\vec{w}$ whose magnitude and direction are given by the vector $\vec{w}$, the expression for the rate of change of $\vec{\mu}$ is

$$\frac{d\vec{\mu}}{dt} = \vec{w} \times \vec{\mu} \; . \qquad (2.18)$$

Comparing these two equations, we see that the effect of the magnetic field $\vec{H}$ is exactly equivalent to a rotation with angular velocity

$$\vec{w} = -\gamma \vec{H} \; . \qquad (2.19)$$

Thus if $\vec{H}$ is a constant field $\vec{H}_o$, the magnetic dipole will precess about the direction of $\vec{H}_o$ with angular velocity $-\gamma \vec{H}_o$ (Fig. 2.3).

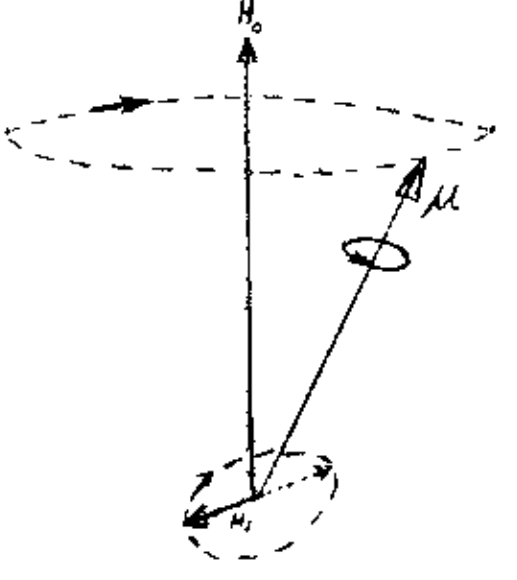


Fig. 2.3 Precession of Magnetic Moment $\mu$ in a Magnetic Field $H_o$.

The angular velocity of this nuclear precession is usually referred to as the Larmor angular frequency.

If we set up another coordinate system, rotating with the Larmor angular frequency $-\gamma \vec{H}_o$, then if there were no other magnetic field acting, the magnetic moment $\vec{\mu}$ would remain stationary in the new frame. In the rotating frame, the static magnetic field is effectively reduced to zero. Now suppose another smaller magnetic field $\vec{H}_1$ is introduced, a field that is of constant magnitude and perpendicular to the original field $\vec{H}_o$ but is rotating about that direction (Fig. 2.3). If the field $\vec{H}_1$ is rotating at the Larmor frequency itself, then, in the rotating system, it will behave like a constant field and the torque, being always in the same direction, will cause large oscillations in the angle between $\vec{\mu}$ and the steady field $\vec{H}_o$. If the rate of rotation of $H_1$ passes through the Larmor frequency, the oscillations will be greatest at the Larmor frequency itself and will show up as a resonance phenomenon.

2.4 b. Quantum-mechanical Treatment.[1,6,7,8]

We suppose that a nucleus of total spin I is placed in a uniform magnetic field $\vec{H}_o$ in the Z-direction, so that the stationary state wave functions may be labeled by m, the component of I in the Z-direction. If, in addition, we have an oscillating magnetic field $\vec{H}_1$ in the x-direction with amplitude $2H_1$ and frequency $\nu$. Note that the oscillating magnetic field consists of two superimposed fields which rotate in opposite directions. Consider the field[7]

$$\left.\begin{aligned} H_x &= 2H_1 \cos 2\pi\nu t \\ H_y &= 0 \\ H_z &= 0 \end{aligned}\right\} . \qquad (2.20)$$

This is evidently expressible as the sum of the two fields,(7)

$$\left\{\begin{aligned} H_x \text{ right} &= H_1 \cos 2\pi\nu t \\ H_y \text{ right} &= H_1 \sin 2\pi\nu t \\ H_z \text{ right} &= 0 \end{aligned}\right\} \text{ and } \left\{\begin{aligned} H_x \text{ left} &= H_1 \cos 2\pi\nu t \\ H_y \text{ left} &= -H_1 \sin 2\pi\nu t \\ H_z \text{ left} &= 0 \end{aligned}\right\} , \qquad (2.21)$$

which rotate about the Z-axis with frequency $\nu$, but in opposite directions in the x-y plane each of amplitude $H_1$.

Now, let $\psi$ be the wave function of a nuclear spin.(6) Then, the Hamiltonian operator becomes

$$i\hbar\dot{\psi} = \mathcal{H}\psi , \qquad (2.22)$$



where

$$\mathcal{H} = \mathcal{H}^\circ + \mathcal{H}' , \qquad (2.23)$$

and

$$\left.\begin{aligned} \mathcal{H}^\circ &= -\gamma\hbar H_o I_z \\ \mathcal{H}' &= \gamma\hbar I_x \cdot 2H_1 \cos 2\pi\nu t \end{aligned}\right\} . \qquad (2.24)$$

We choose the zero-order function to be $\psi_o = u_m$, where

$$\mathcal{H}^\circ u_m = E_m u_m \; ; \; E_m = -\gamma\hbar H_o m. \qquad (2.25)$$

Then, following customary procedure, we place

$$\psi = \sum_{m'} a_{m'}(t) u_{m'} e^{-iE_{m'}t/\hbar} \qquad (2.26)$$

and find for the first order coefficients $a^{(1)}_{m'}$

$$a^{(1)}_{m'} = \frac{1}{i\hbar} \sum_{m''} \langle m' | \mathcal{H}' | m'' \rangle \, a^{(o)}_{m''} \, e^{i\omega_{m'm''}(t)} \quad (2.27)$$

where $\omega_{m'm''} = \dfrac{(E_{m'} - E_{m''})}{\hbar}$.

If we suppose that $a^{(o)}_{m} = 1$ and

$a^{(o)}_{m''} = 0$, $\left(m'' \neq m'\right)$

the result of the integration of Eq. (2.27) is, for values of t in the proper range,

$$\left| a^{(1)}_{m'}(t) \right|^2 = t\gamma^2 H_1^2 \left| \langle m' | I_x | m \rangle \right|^2 \delta(\nu_{m'm} - \nu). \quad (2.28)$$

Here $\delta(\nu_{m'm} - \nu)$ has the usual integrable singularity at $\nu_{m'm} = \nu$: $\int \delta(\nu_{m'm} - \nu)\, d\nu = 1$, if $\nu$ ranges over $\nu_{m'm}$, otherwise $\int \delta(\nu_{m'm} - \nu)\, d\nu = 0$.

The transition probability $P_{mm'}$ between two states m and $m'$ corresponding to absorption or emission of radiation is

$$P_{mm'} = \gamma^2 H_1^2 \left| \langle m' | I_x | m \rangle \right|^2 \delta(\nu_{mm'} - \nu) \quad (2.29)$$

where $\delta$ is the Dirac $\delta$ - function,

$\langle m' | I_x | m \rangle$ is the quantum-mechanical matrix element of

$I_x$ between states m and m' ,

and $\nu_{mm'}$ is the frequency corresponding to the energy gap between these states, i.e.,

$$h\,\nu_{mm'} = |m-m'|\,\gamma\hbar\,H_0 , \qquad (2.30)$$

where $|m-m'| = \Delta m$. The transition can occur by the selection rule $\Delta m = \pm 1$.

From Eq. (2.29) , it predicts absorption only if the frequency $\nu$ exactly coincides with the natural frequency $\nu_{mm'}$. In practice, the lines are broadened by various factors. By introducing a line-shape function $g(\nu)$ which is proportional to the absorption at frequency $\nu$ , such that[1]

$$\int_0^\infty g(\nu)\,d\nu = 1 , \qquad (2.31)$$

then a semi-empirical transition probability will be

$$P_{mm'} = \gamma^2 H_1^2 \cdot |\langle m' | I_x | m \rangle|^2 g(\nu). \qquad (2.32)$$

2.4 c. Line Broadening.[1,10]

As previously mention, absorption occurs not at one single sharp frequency, but over a range of frequencies giving a broadened line. This broadening is due to a variety of causes some of which we shall consider in this section.

Natural Width Due to Spontaneous Emission.[1,10] The natural width of any transition is determined by the finite lifetime of the upper state, and is found to be quite negligible compared with widths due to other causes.

Width Due to Spin-Lattice Relaxation.[1,10] The order of

magnitude of the broadening can be estimated from the uncertaint principle

$$\Delta E \; \Delta t \simeq \frac{1}{2} \hbar. \qquad (2.33)$$

Since $\Delta E = h \Delta \nu$ , then the uncertainty in the frequency of absorption is $1/(2 \pi \Delta t)$. Thus the line width measured on a frequency scale, owing to spin-lattice relaxation, will be of the order of $1/T_1$ , where $T_1$ is the spin lattice relaxation time.

Additional Magnetic Dipole Broadening.[1] Under certain circumstances, the interaction of magnetic dipoles can lead to a greater broadening than that given by the spin-lattice relaxation. This happens for nuclei staying in the same relative positions for a long time, as in solids or highly viscous liquids. It is convenient to define another characteristic time $T_2$ , smaller than $T_1$. To do this, the maximum value of the line-shape function $g(\nu)$ is introduced as,

$$T_2 = 1/2 \cdot \left[ g(\nu) \right]_{max} . \qquad (2.34)$$

Because the interaction between nuclear magnetic moments is the largest cause of broadening in many solids, $T_2$ is sometimes referred to as the spin-spin relaxation time.

Electric Quadrupole Effect.[1,10] A further cause of broadening can exist for nuclei with spin $I > 1/2$ , in which, electric quadrupole moments will interact with electric field gradients.

Magnetic Field In-homogeneity Broadening.[10] A further cause of broadening is the variation of the static magnetic

field $H_o$ over the dimension of the sample.

2.5 Spin - Lattice Relaxation Time. $(T_1)$ [1,7]

In addition to the equilibrium of nuclear spins in a magnetic field, we have to consider the rate at which this distribution is approached. As we shall see, this is a very important factor in determining the nature of N M R absorption. Suppose, for example, we have an assembly of nuclear spins (with I = 1/2) which is initially not in a magnetic field, so that the populations of the two nuclear spin states are equal. If a steady magnetic field $H_o$ is then applied to the system, we may inquire how long it takes for the populations to reach their new equilibrium values. If $n_-$ and $n_+$ are the number of nuclei per unit volume in the upper and lower Zeeman states, respectively, we attempt to determine the value of difference (or excess number per unit volume)

$$n = n_+ - n_- \qquad (2.35)$$

as a function of time.

Let $W_{(- \rightarrow +)}$ and $W_{(+ \rightarrow -)}$ be the total probabilities per unit time of a single transition of a given nucleus to make upward or downward transitions by interaction with other molecular degrees of freedom. These two probabilities will be slightly different, for in equilibrium the total number of upward transitions per unit time must be equal to the corresponding number of downward transitions.

Thus $$n_+ W_{(+ \rightarrow -)} = n_- W_{(- \rightarrow +)} \qquad (2.36)$$

At equilibrium, we found that

$$\frac{W_{(- \longrightarrow +)}}{W_{(+ \longrightarrow -)}} = \frac{n_+}{n_-} = 1 + \frac{\gamma \hbar H_o}{kT} \quad . \qquad (2.37)$$

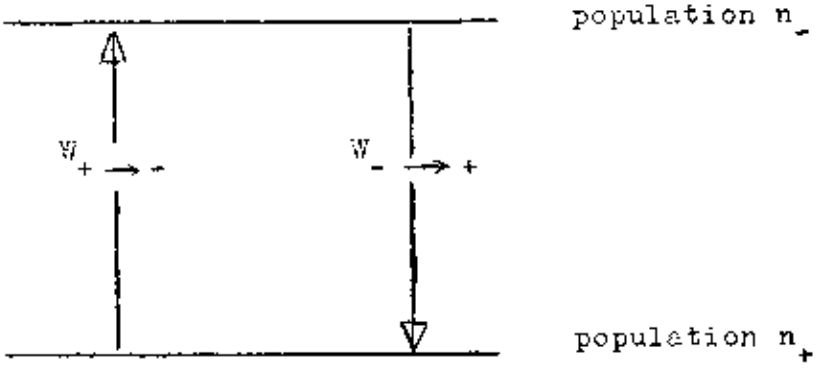


Fig. 2.4 The Populations at the Upper and Lower States.

We must suppose that the total probabilities W are related to the quantum-mechanical probabilities P through the Boltzmann factor of the final state, even when equilibrium has not yet obtained[7]:

$$W_{(p \longrightarrow q)} = P_{(p \longrightarrow q)} \exp \left(-E_q/kT\right) . \qquad (2.38)$$

Since $P_{(+ \longrightarrow -)} = P_{(- \longrightarrow +)} = P$ , for the case $I = 1/2$, we obtain

$$W_{(+ \longrightarrow -)} = P \exp \left( - \frac{\gamma \hbar H_o}{kT} \right) ,$$
$$W_{(- \longrightarrow +)} = P \exp \left( + \frac{\gamma \hbar H_o}{kT} \right) . \qquad (2.39)$$

The excess number n changes by 2 for each transition. This fact and the definition of the probabilities lead to the differential equation

$$\frac{dn}{dt} = 2\, n_- W_{(- \longrightarrow +)} - 2n_+ W_{(+ \longrightarrow -)} . \qquad (2.40)$$

Since $n \ll N$, the differtial equation for the total number of spins,[7] by substituting

$$W_{(+ \longrightarrow -)} = P \left\{ 1 - \frac{1}{2} \cdot \frac{\gamma \hbar H_o}{kT} \right\}$$

$$W_{(- \longrightarrow +)} = P \left\{ 1 + \frac{1}{2} \cdot \frac{\gamma \hbar H_o}{kT} \right\} , \qquad (2.41)$$

obtained from Eq.(2.39), into Eq. (2.40) can be found as

$$\frac{dn}{dt} = 2\, P(n_o - n) , \qquad (2.42)$$

where $n_o = \frac{1}{2} N \frac{\gamma \hbar H_o}{kT}$ is the equilibrium value of n. Integration of Eq. (2.42) yields

$$n = n_o \left\{ 1 - \exp(-2Pt) \right\} . \qquad (2.43)$$

The characteristic time,

$$T_1 = \frac{1}{2P} , \qquad (2.44)$$

is called the spin-lattice relaxation time or the thermal relaxation time. This time is a measure of rate at which the spin system comes into thermal equilibrium. The value of P can be computed from Eq. (2.32).

## 2.6 Spin-spin interaction time, $(T_2)$.[6,7]

In fact, the total magnetic field at any single nucleus consists not only of the applied field $H_o$, but includes also the resultant of the local fields produced by the static components of neighboring magnetic dipoles. Depending upon

the arrangement of its neighbors among the 2I + 1 values of $\mu_H$, a given nucleus sees a slightly larger or slightly smaller field than that externally applied. One can obtain an estimate of the expected width for the shape function $g(\nu_{mm'})$ by considering the local magnetic field produced at a particular nuclear moment by its neighbors. The field of a magnetic moment $\mu$ at a distance $r$ is of the order of $\mu/r^3$.

If we consider a point one Angstrom unit away from a nuclear magneton, we find [6,7]

$$H_{loc} \cong \mu_0/(10^{-8}\text{cm})^3 = 5 \text{ gauss.}$$

Thus in solids one expects $g(\nu_{mm'})$ to have a width corresponding to the effect of distributing the magnetic fields at the nuclei over several gauss. Since $g(\nu_{mm'})$ is a normalized function, its peak value is an inverse measure of the width. In fact, a spin-spin interaction time, or relaxation time, $T_2$ is defined by[6]

$$T_2 = \frac{1}{2} \cdot \left[ g(\nu) \right]_{max} . \qquad (2.45)$$

The vibration of local fields over $H_{loc} \simeq 5$ gauss determines a spread in the nuclear Larmor frequencies of $2\pi\Delta\nu \simeq \gamma H_{loc}$. It follows that one expects for protons[6]

$$T_2 \simeq \frac{1}{\gamma H_{loc}} \simeq 10^{-5} \text{ sec.}$$

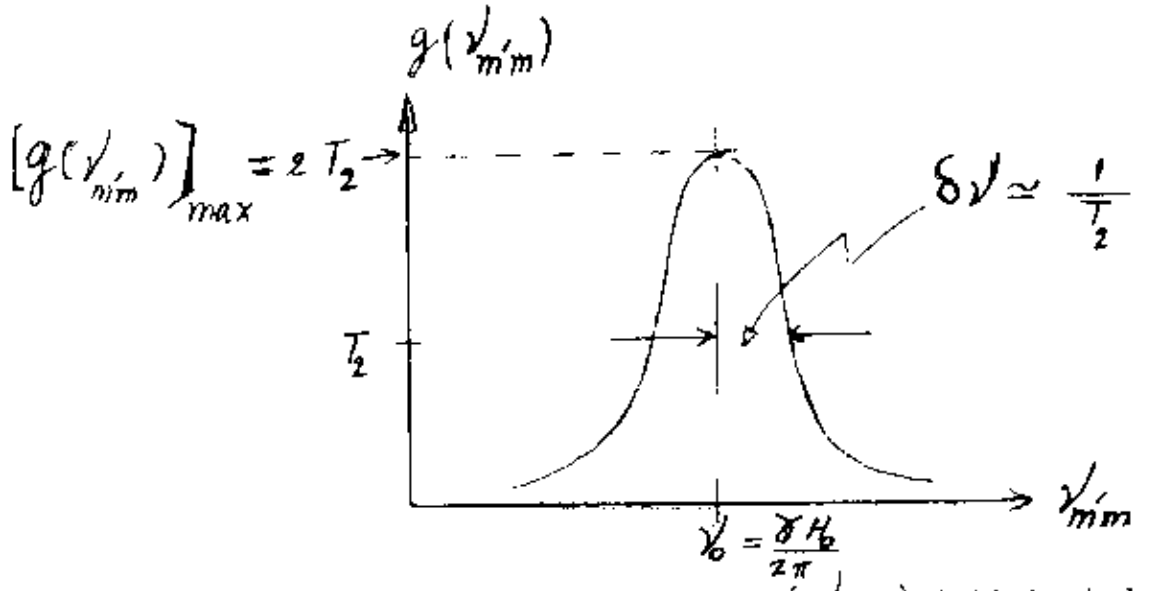


Fig. 2.5 The Shape Function $g(\nu_{m'm})$ Anticipated for Magnetic Resonance in Bulk Matter.[6]

Figure 2.5 represents the shape function $g(\nu_{m',m})$.[6] The expectations are generally borne out for solids, but line widths are usually narrower, and $T_2$ correspondingly larger.

## 2.7 Saturation[1,8,11]

We now define two new spin operators, the promotion operator $I_+$ and the demotion operator $I_-$, which are characterize by

$$\left.\begin{aligned} I_+ &= I_x + iI_y \\ I_- &= I_x - iI_y, \end{aligned}\right\} \qquad (2.46)$$

or $$I_x = \frac{1}{2}(I_+ + I_-). \qquad (2.47)$$

Consider the non-diagonal matrix elements $\langle m|I_x|m-1\rangle$ we get

$$\langle m|I_x|m-1\rangle = \frac{1}{2}\langle m|I_+|m-1\rangle + \frac{1}{2}\langle m|I_-|m-1\rangle .$$

From the properties of promotion and demotion operators,

we know that[11]

$$\left.\begin{aligned} \langle m | I_+ | m-1 \rangle &= \sqrt{(I + m)(I - m + 1)}\,, \\ \langle m | I_- | m-1 \rangle &= 0\,. \end{aligned}\right\} \qquad (2.48)$$

Then

$$\left| \langle m | I_x | m-1 \rangle \right|^2 = \frac{1}{4}(I + m)(I - m + 1)\,. \qquad (2.49)$$

Substitute Eq. (2.48) into Eq. (2.32), we get

$$P_{m \longrightarrow m-1} = \frac{1}{4}\gamma^2 H_1^2\, g(\nu)\,(I + m)(I - m + 1). \qquad (2.49)$$

For the case $I = 1/2$, this reduces to

$$P = \frac{1}{4}\gamma^2 H_1^2\, g(\nu). \qquad (2.50)$$

The over-all absorption of energy from the oscillating magnetic field is proportional to the product of P and the difference of populations :[1]

$$P(n_+ - n_-) = Pn\,. \qquad (2.51)$$

The tendency of this net absorption of energy will be to reduce the excess population n and so reduce the probability of further absorption. The magnitude of such an effect will increase with the amplitude of the oscillating field and is referred to as <u>saturation</u>. It is limited, of course, by the tendency of the spin-lattice relaxation process to restore the excess population to its equilibrium value.

In the absence of the oscillating field, the rate of change of n is determined by the spin-lattice relaxation equation (2.42). Now, this must be modified by the addition of a term

- 2Pn to the right-hand side, since each transition induced by the oscillating field reduces n by 2. Thus

$$\frac{dn}{dt} = - \frac{n - n_o}{T_1} - 2 n P . \qquad (2.52)$$

This may be rewritten

$$\frac{dn}{dt} = - \frac{1 + 2 PT_1}{T_1} . \left( n - \frac{n_o}{1 + 2PT_1} \right) . \qquad (2.53)$$

According to Eq. (2.53), by substituting P with Eq. (2.50), n approaches a new steady value

$$\frac{n_o}{1 + \frac{1}{2} \gamma^2 H_1^2 T_1 g(\nu)} \qquad (2.54)$$

at a rate for which the chararacteristic time is

$$\frac{T_1}{1 + \frac{1}{2} \gamma^2 H_1^2 T_1 g(\nu)} . \qquad (2.55)$$

If the value of $H_1$ is large, the value of n given by Eq.(2.54) may be much less than its equilibrium value, and the corresponding net absorption of energy will be reduced. The greatest degree of saturation occurs at the maximum value of $g(\nu)$, where absorption is reduced by a factor

$$( 1 + \gamma^2 H_1^2 T_1 T_2 )^{-1} \qquad (2.56)$$

This is frequently called the <u>saturation factor</u>.

2.8 Phenomena Dependent on Sweep Rate.[1]

If the rate of change of $H_o$ is fast enough, the signal changes its shape and shows a series of characteristic oscillations, or " wiggles, " in the tail after passing resonance. This phenomenon was first observed by Bloembergen, Purcell, and Pound, The effect of the r.f. field $H_1$ near the resonance condition is to turn the magnetic moment away from its equilibrium value parallel to the strong field $H_o$. Under the slow-passage conditions, the magnetic moment will return to the equilibrium value according to the adiabatic solution after $H_o$ has passed the resonance value. If the variation $H_o$ is rapid, the moment will not be able to follow it, and that the magnetic moment will still be left in a nonequilibrium direction after $H_o$ has passed so far beyond the resonance value that the rf, field is no longer able to exert any effective torque. During this period, the magnetic moment and the rf, field $H_1$ will be rotating about the direction of $H_o$ at different rates, so that they will alternately go in and out of phase. The absorption signal, which measures the out of phase component, will therefore show a series of damped oscillations after passage through resonance.

2.9 The Application of Nuclear Magnetic Resonance in Measuring the Magnetic Field.[12,13]

The nuclear magnetic resonance phenomenon is proving of great value in the accurate measurement of magnetic fields. The accuracy is limited only by the measurement of frequency and of course the homogeneity of the magnetic field. Absolute

accuracy of better than $\pm$ 0.2 percent is obtainable, depending only on precise measurement of frequency. Higher accuracy is possible in comparing fields and in measuring field changes.

In making a measurement the tuning capacitor of the R.F. oscillator unit is varied until the resonant peak appears on the C.R.O. screen. The field strength is then determined from the well-known equation for the precessional frequency which in this case reduces to

$$H_c = (234.87 \pm 0.29) \times 10^{-6} \nu, \qquad (2.57)$$

where $H_o$ is the magnetic field strength in gauss; and $\nu$ is the Larmor frequency or resonant frequency in c/s.

From the magnetic field strengths at the various positions between the gap of the electromagnet, we can determine the homogeneity of the magnetic field.