



NUCLEAR MAGNETIC RESONANCE RESONANCE (NMR) SPECTROSCOPY

Semester V

NUCLEAR PARAMAGNETISM

Protons and neutrons present in the nuclei of atoms spin about their own axes. The nuclei with odd mass number have spins, designated by I and is always an odd integral multiple of $\frac{1}{2}$. Nuclei with even mass number that have odd number of protons also have spins, and the spin quantum number in these cases is an integer, 1,2,3....Thus, ^1H , ^{11}B , ^{19}F , etc., have magnetic moments having spins of $\frac{1}{2}$, whereas ^{12}C , ^{16}O have no magnetic moment.

Many nuclei possess spin angular momentum due to the spinning of the nucleus about its axis. The spin angular momentum of nucleus is a vector combination of the spin angular momentum of the protons and neutrons. The spin characteristics of the nucleus are denoted by I and is called the nuclear spin quantum number. The magnitude of the spin angular momentum $|I|$ is related to the spin angular momentum quantum number I as

$$|I| = \sqrt{I(I+1)} \frac{h}{2\pi} \dots\dots\dots(1)$$

If the nuclear has a spin angular momentum $I \neq 0$, then this corresponds to a spinning positive charge and this will generate a magnetic moment (μ). The magnetic moment, μ of any nucleus is proportional to the spin angular momentum, I and is expresses as

$$\mu_m = \frac{g_N e}{2m_p} I \dots\dots\dots(2)$$

Where g_N is the nuclear g -factor which is characteristic of the particular nucleus, e is the charge on a proton and m_p is the mass of the proton. The quantity $g_N e / 2m_p$ is called the gyromagnetic ratio, γ . Hence we can write the above equation (2) as

$$\mu_m = \gamma I \dots\dots\dots(3)$$

$$= \gamma \sqrt{I(I+1)} \frac{h}{2\pi} \dots\dots\dots(4)$$

When the charge of the particle is positive, the magnetic moment vector (μ_m) and the angular moment vector (I) point in the same direction. But when the particle is negatively charged (electron), these two vectors point in the opposite directions. Equation (2) can also be rewritten as

$$|\mu_m| = \frac{g_N e}{2m_p} \sqrt{I(I+1)} \frac{h}{2\pi}$$



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$$= g_N \mu_N \sqrt{I(I+1)} \frac{h}{2\pi} \dots\dots\dots(5)$$

Where $\mu_N = eh/4\pi m_p$ and is called nuclear magneton and has a value $5.051 \times 10^{-27} \text{JT}^{-1}$.

A nucleus with spin quantum number I can take (2I+1) orientations in the external magnetic field. If I=1/2, then it can take two (2I+1=2X1/2+1=2) orientations only in an external field. We shall consider spin 1/2 nuclei, which are nuclei with I=1/2. These spin 1/2 nuclei can align parallel or anti parallel to the external field. No other orientation is permitted.

The component of the magnetic moment of the nucleus in the nucleus in the direction of the applied magnetic field, μ_z is given by

$$\mu_z = \frac{|g_N| e}{2m_p} I_z \dots\dots\dots(6)$$

Where I_z is the component of spin angular momentum in the direction of the applied magnetic field. Also I_z can be expressed as

$$I_z = m_I \frac{h}{2\pi}$$

Where m_I is the quantum number for Z-component and can take values $-I, \dots, +I$.

The different values of m_I give different values of I_z and μ_z .

Thus, for I=1/2, $m_I = -1/2$ and $+1/2$ and

$$I_z = -\frac{1}{2} \frac{h}{2\pi} \quad \text{and} \quad I_z = +\frac{1}{2} \frac{h}{2\pi}$$

Substituting the values of I_z in equation (6), we have

$$\mu_z = -\frac{|g_N| e}{2m_p} \times \frac{1}{2} \frac{h}{2\pi} = -\frac{1}{2} |g_N| \mu_N \quad (\because \mu_N = eh/4\pi m_p)$$

and

$$\mu_z = \frac{|g_N| e}{2m_p} \times \frac{1}{2} \frac{h}{2\pi} = \frac{1}{2} |g_N| \mu_N$$

The energy of the magnetic dipole in a magnetic field of strength B_z is given as

$$E = -\mu_z B_z$$

$$= \frac{1}{2} |g_N| \mu_N B_z \quad \text{and} \quad -\frac{1}{2} |g_N| \mu_N B_z$$

The energy separation of the two states of spin -1/2 nuclei (Fig1) is

$$\begin{aligned} \Delta E &= E_\beta - E_\alpha \\ &= \frac{1}{2} |g_N| \mu_N B_z - \left(-\frac{1}{2} |g_N| \mu_N B_z \right) \\ &= |g_N| \mu_N B_z \\ \nu &= \frac{\Delta E}{h} = \frac{|g_N| \mu_N B_z}{h} \end{aligned} \quad \dots\dots\dots(7)$$

The β state lies above the α state and corresponds to $m_I = -1/2$ and $m_I = +1/2$ as shown in the Fig1.

The splitting of the nuclear energy into $(2I+1)$ levels for a nucleus spin I is known as the nuclear Zeeman effect and is the primary phenomenon in NMR spectroscopy

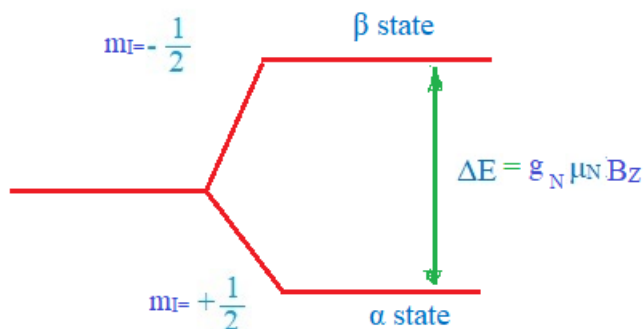


Figure1: Splitting of energy level of a proton in presence of magnetic field

If an electromagnetic radiation of frequency ν as given by equation (7) is allowed to interact with the nuclei, then the nuclei from lower energy level may absorb energy and go to higher energy level.

The difference in energy between nuclear spin states in magnetic fields that can be produced in the laboratory is very small at room temperature and therefore, the populations in the various states are nearly equal. According to Boltzmann distribution

$$\frac{N_\beta}{N_\alpha} = e^{-\Delta E/kT} \approx 1 - \frac{\Delta E}{kT} + \dots$$

or

$$\frac{N_\alpha}{N_\beta} = 1 + \frac{\Delta E}{kT} = 1 + \frac{g_N \mu_N B_Z}{kT} \dots \dots \dots (8)$$

Thus, the excess population in the low-energy state is extremely small. Only the spins in the low energy state can absorb radiation.

In magnetic field, because of the interaction between the magnetic moment of the charged particle and the applied field, the charged particle experiences a torque λ which makes the angular momentum precess around the direction of the applied field (Fig.2). This precessional frequency is called Laemore frequency and directly proportional to the applied field ,i.e.,

$$\omega = \gamma B_Z \dots \dots \dots (9)$$

where γ is the gyromagnetic ratio and B_Z is the strength of the applied magnetic field felt by the proton.

From equation (3) we replace γ by μ_m/I to get

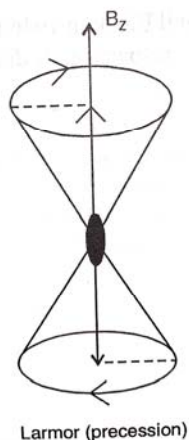


Figure 2: Larmore (precession) frequency

$$\omega = \frac{\mu_m}{I} B_Z = 2\pi\nu$$

So
$$\nu = \frac{\mu_m B_Z}{2\pi I}$$

Substituting the value of μ_m and I we obtain



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$$\nu = \frac{g_N \mu_N \sqrt{I(I+1)} \cdot B_Z}{2\pi \sqrt{I(I+1)} \frac{h}{2\pi}} \dots\dots\dots (10)$$

$$\nu = \frac{g_N \mu_N B_Z}{h} \dots\dots\dots (11)$$

Equation (11) is identical with equation (7) implying that the Larmore frequency is equal to the angular frequency separation between the two nuclear magnetic energy levels.

When the radiofrequency is applied at right angle to the magnetic field it produces a rotating magnetic field. It is necessary that the frequency of rotation of rotating magnetic field be exactly the same as Larmore frequency. Only when such a condition is met ,i.e, the two frequencies are in resonance, the nuclei will absorb energy. This is the reason why this phenomenon is called nuclear magnetic resonance and the condition for resonance is

$$h\nu = g_N \mu_N B_Z \dots\dots\dots (12)$$

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