NMR SPECTROSCOPY

SEM-4, CC-8
PART-1, PPT-13

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Nuclear Magnet Resonance (NMR) Spectroscopy (PART-1, PPT-13)

Introduction

NMR spectroscopy is a form of absorption spectroscopy, similar to UV or IR spectroscopy. It is concerned with the magnetic properties of certain atomic nuclei, and deals with nuclei which behave as tiny magnets. Under appropriate conditions in a magnetic field, a sample can absorb electromagnetic radiation in the radiofrequency (*rf*) region governed by the characteristics of the sample.

Absorption is a function of certain nuclei in the molecule. A plot of the frequencies of the absorption peaks versus peak intensities constitutes an NMR spectrum. Many nuclei may be studied by NMR techniques, but hydrogen and carbon are commonly available.

NMR spectroscopy gives information about the number of magnetically distinct atoms, and the nature of the immediate environment of the type being studied. The chemical environment of specific nuclei is deduced from information obtained about the nuclei.

Two properties of nuclear particles are to be considered in understanding NMR spectroscopy. These are:

1. the net spin associated with the protons and neutrons (both have a spin quantum number of ½)
2. the distribution of positive charge

Theoretical principles: Magnetic Properties of Nuclei

All nuclei carry a charge, but in some nuclei this charge "spins" on the nuclear axis and this circulation of nuclear charge generates a magnetic dipole along the axis (Figure 1). The intrinsic magnitude of the generated dipole is expressed in terms of nuclear magnetic moment, μ. The angular momentum of the spinning charge can be described in terms of the spin numbers I; these numbers have values of 0, 1/2, 1, 3/2, and so on ($I = 0$ denotes no spin).

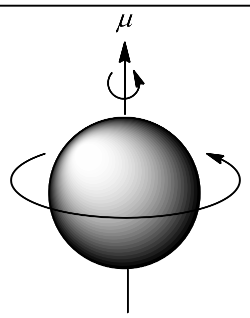


Figure 1
Spinning Charge in Proton
generates Magnetic Dipole

Nuclear Spin or Spin Number

The net resultant of the angular momenta of all the nuclear particles present in an atomic nucleus is called the nuclear spin (I). The spin number, I, is related to the atomic mass and the atomic number of that nucleus. The rules for determining the net spin of a nucleus are as follows:

1. If the number of neutron/s and the number of proton/s are both even, then the nucleus has no overall spin ($I = 0$), e.g., ^{12}C, ^{16}O, etc.
2. If the number of neutron/s plus the number of proton/s is odd, then the nucleus has a half-integer spin ($I = 1/2, 3/2, 5/2$), e.g., ^{1}H, ^{13}C, ^{17}O, ^{35}Cl, etc.
3. If the number of neutron/s and the number of protons are both odd, then the nucleus has an integer spin ($I = 1, 3$), e.g., ^{2}H, ^{14}N, etc.

Nuclear Spin

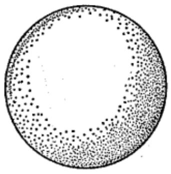
Type of Nuclei	**Atomic Mass**	**Atomic Number**	**Spin Number (I)**	**Examples**	**Nature**
I	odd	odd /even	1/2	$^{1}H_{1}$, $^{13}C_{6}$, $^{15}N_{7}$, $^{19}F_{9}$	NMR Active
			3/2	$^{11}B_{5}$, $^{35}Cl_{17}$, $^{37}Cl_{17}$	
			5/2	$^{17}O_{8}$	
II	even	odd	1	$^{2}H_{1}$, $^{14}N_{7}$	
			3	$^{10}B_{5}$	
III	even	even	0	$^{12}C_{6}$, $^{16}O_{8}$	NMR Inactive

Nuclei of the types I and II would behave as tiny magnets and would come in the purview of NMR spectroscopy, but nuclei of type III will not behave as magnets.

Magnetic Properties of Nuclei

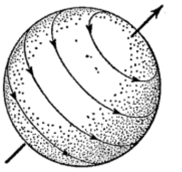
Nuclei whose atomic number and mass number are both even have non-zero spin ($I = 0$). The spins of all particles in the nucleus are paired, and these are non-spinning spherical bodies with the nuclear charge distributed evenly over their surfaces (Figure 2).

This type of nuclei does not have a magnetic moment, i.e., $\mu = 0$. This is because there is no circulation of the nuclear charge. They can give no nuclear resonance signal. They are NMR inactive. Many nuclei, particularly, $^{12}C_{6}$, $^{16}O_{8}$, etc., are of this type.



Spherical
Non-spinning Nucleus
$\mu = 0$
$eQ = 0$

Figure 2



Spherical
Spinning Nucleus
$\mu \neq 0$; $eQ = 0$

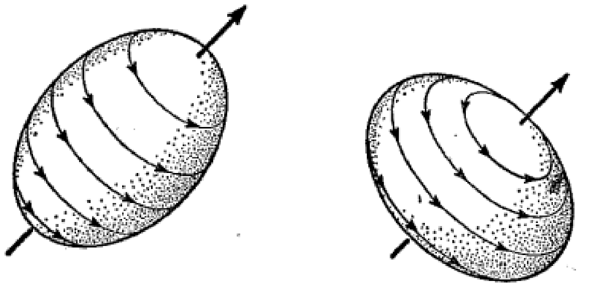
Figure 3

'e' is the unit of electrostatic charge and Q is a measure of the deviation of the charge distribution from spherical symmetry.

The nuclei with spin (*I*) of 1/2 are spherical bodies possessing uniform charge distributions but spinning like tops. They are NMR active nuclei. Several nuclei, e.g., ${}^{1}H_{1}$, ${}^{13}C_{6}$, ${}^{19}F_{9}$, ${}^{31}P_{15}$, etc., are of this type (Figure 3). A spinning nucleus has circulating charge and that generates a magnetic field so that a nuclear magnetic moment results ($\mu \neq 0$). Nuclei such as ${}^{1}H$, ${}^{13}C$, etc., are particularly favourable for resonance experiments.

The spherical charge distribution ascribed to nuclei with spin of 1/2 means that a probing charge approaching them experiences the same electrostatic field, and, therefore, with the spherical spinning nuclei, the electric quadrupole moment (*eQ*) is zero. Nuclei with a spin number of 1 or higher have a non-spherical charge distribution. Such nuclei possess electrical quadrupole moment (*eQ*) in addition to nuclear magnetic moment, μ.

These nuclei ($\mu \neq 0$, $eQ \neq 0$) assume ellipsoids spinning about the principal axis. They are NMR active, and nuclei, e.g., ${}^{2}H_{1}$, ${}^{14}N_{7}$, ${}^{35}Cl_{17}$, etc., belong to this type (Figure 4). This asymmetry affects the relaxation time, and consequently, the coupling with neighbouring nuclei.



Ellipsoidal (Prolate)
Spinning Nucleus
$\mu \neq 0$
$eQ > 0$

Ellipsoidal (Oblate)
Spinning Nucleus
$\mu \neq 0$
$eQ \angle 0$

Figure 4

A charged, elongated (prolate) ellipsoid (*eQ> 0)* will present an anisotropic electrostatic field to an approaching unit charge. Important examples are ${}^{2}H$ and ${}^{14}N$, etc. Nuclei which behave like charged, flattened (oblate) ellipsoids also present an anisotropic electric field to a probing charge ($eQ < 0$). Nuclei of this type include ^{17}O, ^{33}S, ^{35}Cl, etc.

Different Types of Nuclei

Type	Spin No. (I)	Distribution of Charge	Example	Nature
I	0	Spherical	$^{12}C_6$, $^{16}O_8$	NMR Inactive
II	1/2	Spherical	$^{1}H_1$, $^{13}C_6$	NMR Active
III	1 or higher	Ellipsoidal (Prolate)	$^{2}H_1$, $^{14}N_7$	NMR Active
IV	1 or higher	Ellipsoidal (Oblate)	$^{17}O_8$, $^{35}Cl_{17}$	NMR Active

Effect of Spinning Nuclei in a Magnetic Field and Splitting of Energy levels

When a magnetic nucleus is placed in a uniform external magnetic field, it will behave as magnet and tend to orient itself in relation to the magnetic field, B_0. The spinning nucleus, thus, behaves as a tiny magnet of magnetic moment, μ. The magnetic moment vectors of the spinning nuclei have only certain specified average values along the axis of the principal magnetic field.

The permitted values of the vector moment can be described by a set of magnetic quantum numbers *m*, which are derivable from the nuclear spin. The individual spin states fit into the sequence:

$$+I, (I - 1), - - -, (-I + 1), -I$$

For each nucleus with spin, the number of allowed spin states it may adopt is quantized, and is determined by its spin quantum number *I*. For each nucleus, *I* is a physical constant and there are '$2I + 1$' allowed spin states. Therefore, the magnetic nucleus may assume any one of ($2I + 1$) orientations with respect to the direction of the applied magnetic field. The spin number (*I*), thus, determines the number of orientations a nucleus may assume in a uniform external magnetic field.

Energy Levels for a Nucleus with Spin Quantum Number ½

A nucleus with spin 1/2 will thus have two possible orientations and the magnetic quantum numbers are +1/2, and -1/2. In the absence of an external magnetic field, all the spin states of a given nucleus are of equal energy i.e., the energy levels are degenerate.

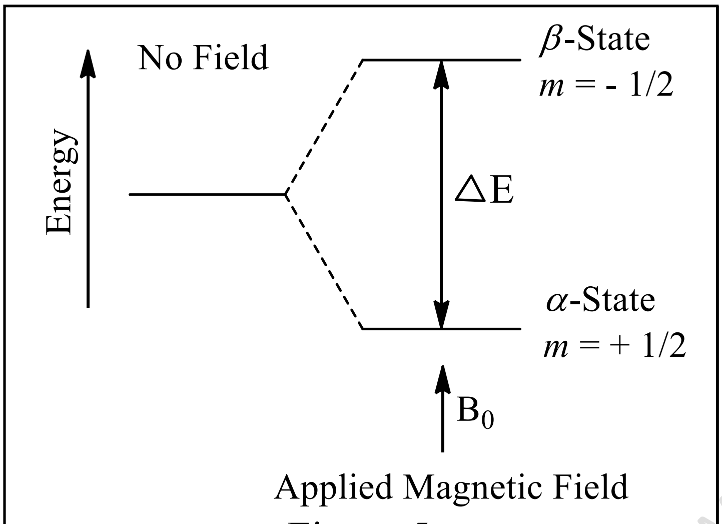


Figure 5

If a magnetic field is applied, then the energy levels split. Each level is given a *magnetic quantum number, m*. In the lower energy level (α-state), the nuclear magnet is aligned with the field, and in the higher energy level (β-state), the nuclear magnet opposed the field (Figure 5).

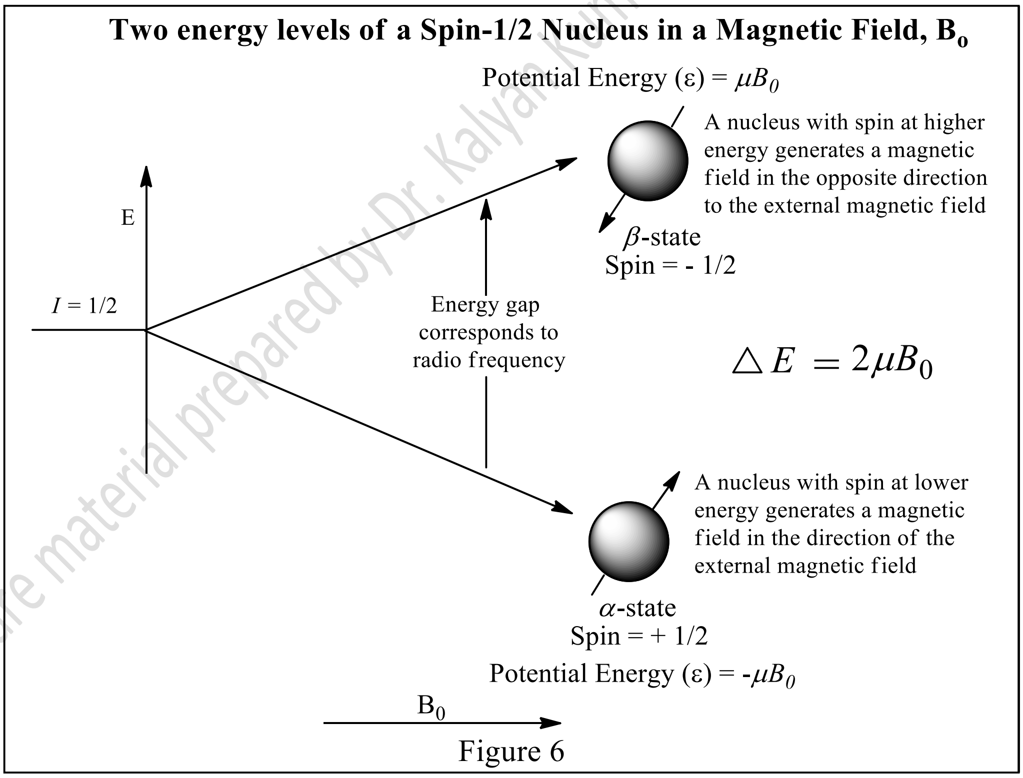


Figure 6

Factors Affecting ΔE in the Magnetic Field

The energy absorption by a spinning nucleus is a quantized process, and the energy absorbed must equal the energy difference between the two states involved.

$$E_{\text{absorbed}} = (E_{-1/2\text{ state}} - E_{+1/2\text{ state}}) = h\nu$$

This energy difference is a function of the strength of the applied magnetic field, B_0. The stronger is the applied magnetic field, the greater is the energy difference between the possible spin states.

$$\text{Therefore, } \Delta E = f\,(B_0)$$

The magnitude of the energy level separation also depends on the particular nucleus involved. Each spinning nucleus has a different ratio of magnetic moment to angular momentum since each has different charge and mass.

This ratio, called the magnetogyric ratio or gyromagnetic ratio, γ, is a constant for each nucleus, and determines the energy dependence on the magnetic field; therefore,

$$\Delta E = f\,(\gamma B_0)$$

Since the angular momentum of the nucleus is quantized in units of $h/2\pi$, the final equation takes the form:

$$\Delta E = \frac{h\gamma B_0}{2\pi} \text{ ----------------- Equation 1}$$

Equation 1 simply states that ΔE is proportional to B_0. γ is constant for a particular nucleus. It is the proportionality constant between the magnetic moment μ and the spin number I.

$$\gamma = \frac{2\pi\mu}{hI} \text{ ----------------- Equation 2}$$

Absorption of Energy

Once two energy levels for the protons (I=1/2) have been established, it is possible to introduce energy in the form of radiofrequency radiation (ν_1) to effect a transition between these energy levels in a stationary magnetic field of given strength B_0. The fundamental NMR equation correlating the applied radiofrequency (ν_1) with the applied magnetic field strength (B_0) is

$$\nu_1 = \frac{\gamma B_0}{2\pi} \text{ ----------------- Equation 3}$$

The introduced radiofrequency (ν_1) is given in megahertz (MHz). A frequency of 60 MHz is needed at a magnetic field (B_0) of 1.41 Tesla for the proton (or any other desired combination in the same ratio) ($\gamma = 2.6753\text{x}10^8$ rad. s^{-1}. T^{-1} for the proton).

Precessional Motion of the Nuclear Magnet

When the spinning nucleus is placed in a uniform external magnetic field (B_0), its rotational axis (or axis of rotation) draws out a circle perpendicular to the B_0, i.e., the nucleus *precesses* around the external magnetic field. This characteristic motion of the nucleus is called *precession* (Figure 7). The frequency of precession is termed as *precessional frequency* or *Larmor frequency* (ν_L).

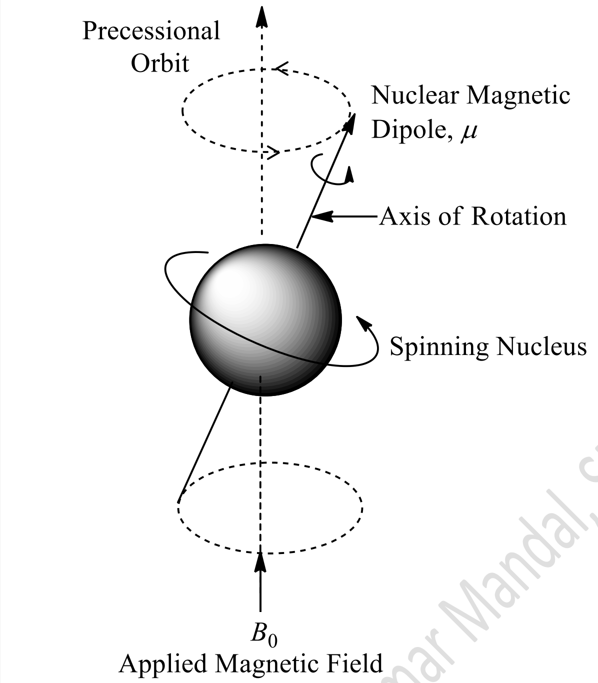


Figure 7: Precession of a Nuclear Moment in an Applied Field of Strength, B_0

The Absorption of Radiation by a Nucleus in a Magnetic Field

Phenomenon of Resonance: Protons absorb energy because they begin to precess in an applied magnetic field. The frequency of precession is directly proportional to the strength of the applied magnetic field. The stronger is the applied field, the higher is the rate of precession. When an applied radiofrequency (ν_1) is exactly equal to the precessional frequency of the spinning nucleus (Larmor frequency ν_L in MHz), the state of nuclear magnetic resonance is attained.

Only under this condition, the spinning nucleus absorbs energy, flips from α- to β-state and gives rise to signal.This condition is called resonance. The basic NMR relationship can be written as:

$$\nu_L = \nu_1 = \frac{\gamma B_0}{2\pi}$$

Population Densities of Nuclear Spin States

For a proton if the applied magnetic field has a strength of 1.41 Tesla, resonance occurs at 60 MHz, and the difference in energy between the two spin states of the proton is approximately 2.39x10^{-5} kJ/mole.

$$\triangle E = 2\mu B_0$$ ----------------- Equation 4

μ = 2.79268 *n.m.*; 1 *n.m.* = 5.05 x 10^{-27} J.T^{-1}; B_0 = 1.4 T; N = 6.023 x 10^{23}

Thermal energy resulting from room temperature is sufficient to populate both of these energy levels since the energy separation between the two levels (*α*- and *β*-states) is very small. Therefore, only a small proportion of "target" nuclei (excess population) is in the lower energy state and can absorb radiation.

The slight excess of population (*N*) in the lower energy state ($N_\alpha > N_\beta$) is determined by the Boltzmann distribution. Under ordinary condition in a magnetic field the nuclei assume a Boltzmann distribution with a small but finite excess of 0.001% nuclei always present in the lower energy state.

When the nucleus is in a strong external magnetic field, the initial population of the energy levels is different. Therefore, if the operating frequency of the NMR instrument is increased, the energy difference between the two states increases, which causes an increase in this excess population in the lower energy state.

Variation of ^{1}H Excess Nuclei (in approximately 2 million nuclei) with Operating Frequency

Frequency (MHz)	40	60	100	300	600
Excess Nuclei	6	9	16	48	96