Spin Resonance Spectroscopy

Atomic Spectra → spin of electron → fine structure of spectral lines.

Nuclear spin → hyperfine structure of spectral lines

electron, proton, neutron each possess an intrinsic spin $\frac{1}{2}$.

Some nuclei as a result of coupling display net nuclear magnetic moment, called nuclear spin (I)

Now, we discuss the sort of spectra the spins can give rise rather than their influence on other types of spectra.

Absorption and emission of radiation takes place when energy difference of set of energy levels of the atom or molecule and frequency of radiation match as per Einstein frequency condition.

The matching of frequency is basis of Resonance.

Resonance → condition of strong effective coupling of frequencies.

Spins → Three fundamental particles electron, proton and neutron, each particle has a spin half.

For a nucleus, the net mass is the sum of masses of neutrons and protons minus mass defect

Net charge → Equal to total charge of all protons

Net Spin → vector sum of spins of neutrons and protons

(i) Nuclei with even p and even n have zero spin, e.g. $_2He^4$, $_6C^{12}$, $_8O^{16}$ etc (charge, mass even)

(ii) Nuclei with both p and n odd, integral spin (charge odd, mass even)

$_1H^2$, $_7N^{14}$

(iii) Nuclei with odd mass have half integral spin

$_1H^1$, $_7N^{15}$

Nuclear Magnetic Moment

Nuclear angular momentum is given by

$$= I^* \hbar$$

$$= \sqrt{I(I+1)}\ \hbar \simeq I\hbar$$

and nuclear magnetic moment is given by

$$\mu_I = \frac{e}{2M_p} g_I I^* \hbar$$

$$\simeq \frac{e}{2M_p} g_I I \hbar$$

$g_I \rightarrow$ nuclear g factor

$$g_I = \frac{G M_p p}{M}$$

$p \rightarrow$ number of protons

$M \rightarrow$ nuclear mass

$G \rightarrow$ numerical factor

$M_p \rightarrow$ mass of proton

The nuclear magneton is

$$\mu_N = \frac{eh}{4\pi M_p} = 5.050 \times 10^{-27}\ JT^{-1}$$

nuclear g factor $\rightarrow$ positive $\rightarrow$ varies from half to six

Interaction between Nuclear Spin & Mag. field

The interaction energy is given by

$$E = -\mu_I \cdot B \quad \text{---(1)}$$

$$E = -\frac{e}{2M_p} g_I I \hbar B \quad \text{---(2)}$$

Nuclear magnetic moment interacts with applied magnetic field

Where M_I is nuclear spin magnetic moment quantum number. Due to quantization of I, M_I assumes the values $-I$ to $+I$ with a difference of one.

The energy separation is then

$$\Delta E = \frac{g_I e \hbar B}{2M_p} = g_I \mu_N B \text{ Joule} \quad \text{---(3)}$$

In terms of frequency

$$\frac{\Delta E}{h} = \frac{g_I \mu_N B}{h} \text{ Hz} \quad \text{---(4)}$$

For hydrogen nucleus, we have

$$g_I = 5.585, \quad \frac{eh}{4\pi M_p} = 5.05 \times 10^{-27} \text{ J T}^{-1}$$

Taking a typical value $B = 2.3487$ T

for nucleus

$$\frac{\Delta E}{h} = \frac{5.585 \times 5.05 \times 10^{-27} \times 2.3487}{6.63 \times 10^{-34}}$$

$$= 100 \times 10^{6} \text{ Hz} \quad \text{---(5)}$$

for electron

$$\frac{\Delta E}{h} = \frac{2 \times 9.273 \times 10^{-27} \times 2.3487}{6.63 \times 10^{-34}} = \quad \text{---(6)}$$

$= 6.56599 \times 10^{10}$ Hz

$= 65699 \times 10^{6}$ Hz

This suggest that the electron spin spectra falls at considerably larger frequency.

at $B = 0.34$ T

$\frac{\Delta E}{h} = \underline{9500 \times 10^{6}}$ Hz (value of $B = 0.34$ T taken for practical convenience)

<u>The Larmor Precession</u> : When a magnetic field is applied to nucleus, the field tends to ~~drag~~ align the magnetic moments along its direction. It is opposed by the rotational inertia of the nucleus and the result is precession of nuclear magnetic moment vector along B direction. The action is analogous to mechanical gyroscope.

<u>Mechanical gyroscopes</u> :- When a couple is applied, it does not tilt the axis of gyroscope but induces precession in its motion.

The precessional frequency is given by

$$\omega = \frac{\text{magnetic moment}}{\text{angular momentum}} \times B \text{ rad s}^{-1}$$

$$\nu = \frac{\mu_I B}{2\pi I} \text{ Hz}$$

$$= \frac{g_I \mu_N B}{h}$$

$$= \left(\frac{g_I \mu_N}{h} B\right) \text{Hz} \quad \text{for } \underline{\text{hydrogen}}$$

Study of Resonance Spectra

This precessional frequency is same as the frequency between two energy states. It is the basis of resonance phenomenon.

→ Particle spins can interact with the radiation if precessional frequency is the same as that of radiation. If frequency is different, no exchange of energy (or change of spin states) takes place. This phenomenon is one of resonance. For nuclei it is known as nuclear magnetic resonance (NMR) and for electron it is called electron spin resonance (ESR) or electron paramagnetic resonance (EPR)

Experimentally two alternatives:— (i) fixed magnetic field is applied to a set of nuclei having same Larmor frequency (say 100 MHz) and a radiation beam is swept over a range including 100 MHz. Resonance absorption will take place at 100 MHz only.

(ii) frequency is kept fixed at 100 MHz and magnetic field is varied over a range until absorption occurs.

The probability of transition is proportional to the population of the state. Upper and lower states are equally populated, upward and downward transitions are equally probable.

However lower states slightly more populated than upper state.