Lec 2 5th stage

Advanced Pharmaceutical Chemistry
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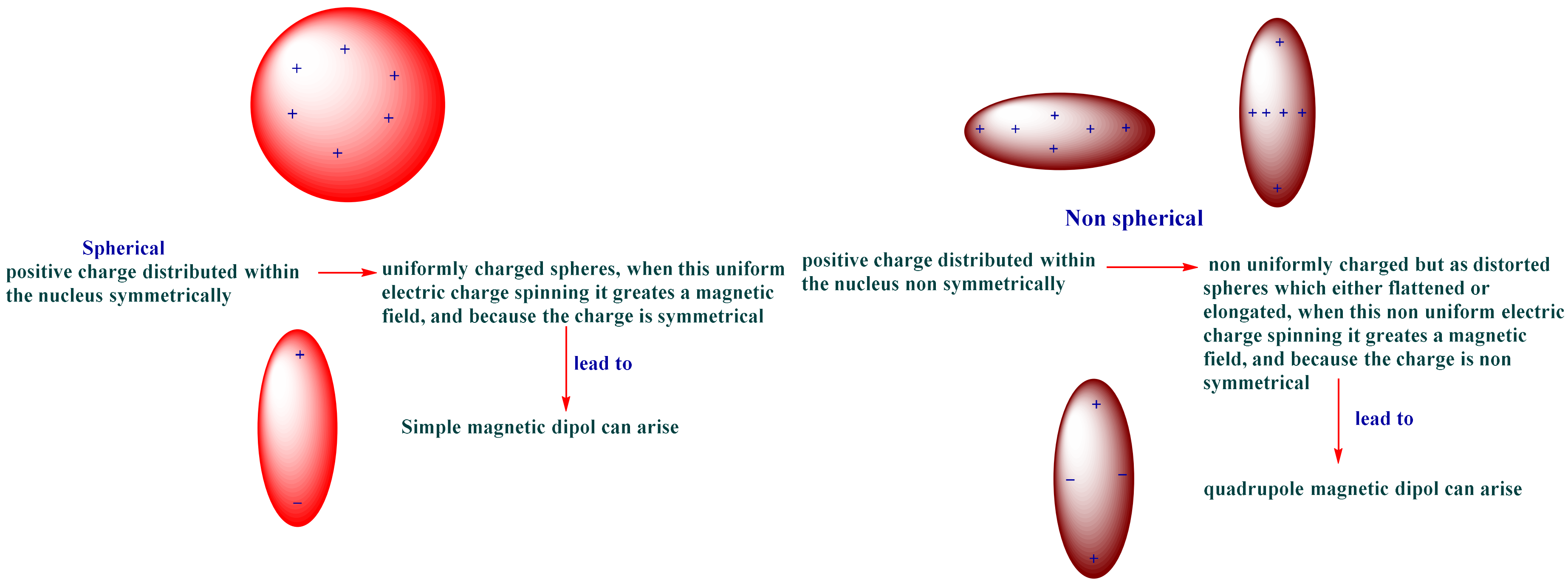
All nuclei with I=1/2 have a spherical (symmetrical) distribution of spinning charge, so the electric and magnetic fields surrounding such nuclei are spherical, homogeneous, and isotropic in all directions. By contrast, nuclei with I> ½ have a non spherical distribution of spinning charge, resulting in nonsymmetrical electric and magnetic fields. This imparts an electric quadrupole (Q) to the nucleus, a property that can complicate their NMR behavior; As a result, the most commonly studied nuclei are those with a nuclear spin of ½ (such as ^{1}H, ^{13}C, ^{15}N, ^{31}P, ^{19}F).



Nuclei with spin quantum number =1/2 or 0.5

I= $\sqrt{\sqrt[2]{3/4}} = 0.87\ units(\hbar)$

So the magnitude of angular momentum is 0.87, but there are only two allowed orientations for I with respect to the z-axis, and, these allowed orientations must have components along the Z-axis of 0.5 (1/2) in the lower energy case and -0.5 (-1/2) in the higher energy case.

Homework:- complete the following table.

Spin quantum number and derived quantities

Spin quantum number I	Examples	Angular momentum, I $\sqrt{I(I+1)}$ in units of $h/2\pi$	Number of spin state (allowed orientation) $2I+1$	Magnetic quantum number-the z-axis components of I (allowed values of spin) m_I
0	^{4}He, ^{12}C, ^{16}O			
1/2	^{1}H, ^{13}C, ^{15}N ^{19}F, ^{29}Si , ^{31}P			
1	^{2}H, ^{14}N			
3/2	^{11}Be, ^{23}Na ^{35}Cl, ^{37}Cl			
2	^{8}Li*, ^{20}F*			
5/2	^{17}O,^{27}Al			

A combination of their spin angular momentum and positive charge causes nuclei to have a magnetic moment (compare the effect of an electric current in a circular wire). This magnetic moment is directly proportional to the angular momentum:

Gyromagnetic ratio
Magnetogyric ratio

$$\mu = \gamma \mathbf{I} \quad \text{.....................} 4$$

$$\gamma = \frac{\mu z}{\mathbf{I}z}$$

is the ratio between the magnetic dipole and the angular momentum

Gyromagnetic ratio Magnetogyric ratio:- is the strength of the nuclear magnet

For proton (^{1}H) γ = 2.675* 10^{8} rad T^{-1} s^{-1}→ relative abundance = 99.98%
For ^{13}C= 6.726*10^{7} rad T^{-1} s^{-1}→ relative abundance = 1.1%

Since I is quantized, accordingly also μ is quantized and we can express μ in terms of the spin quantum number, I or μz in terms of the magnetic quantum number, m_I:

$$\mu = \gamma \hbar \sqrt{I(I+1)} \ldots\ldots\ldots\ldots\ldots\ldots.. 5$$

And

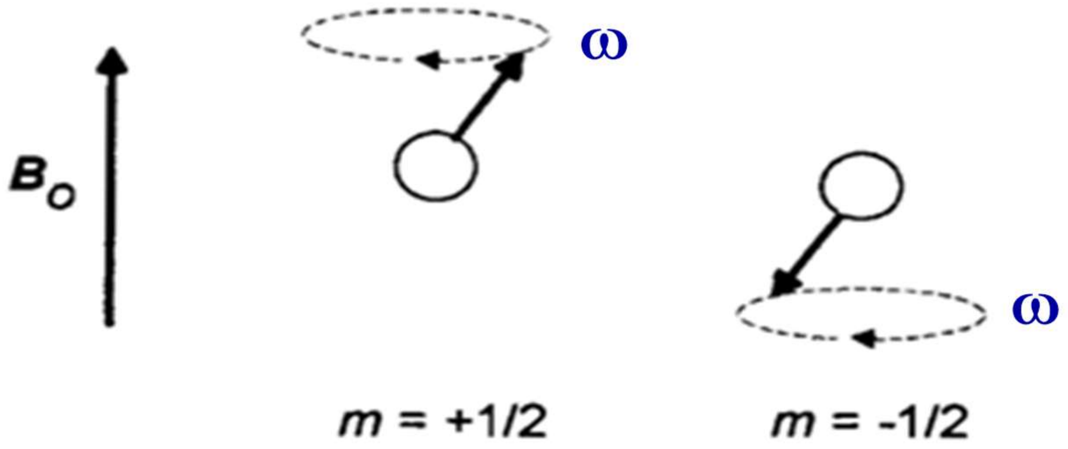
In a magnetic field, B_0, (direction in z-axis)

m_I = magnetic quantum number.

$$\mu z = \gamma \hbar m I \ldots\ldots\ldots 6$$

Precession and Larmor frequency

Many atoms (e.g., ^{1}H, ^{13}C, ^{15}N, ^{31}P) behave as if the positively charged nucleus was spinning on an axis. The spinning charge, like an electric current, creates a tiny magnetic field. When placed in a strong external magnetic field, the magnetic nucleus tries to align with it like a compass needle in the earth's magnetic field. Because the nucleus is spinning and has angular momentum, the torque exerted by the external field results in a circular motion called precession



Precession of the magnetic moment in each of the two possible spin states of an *I* =1/2 nucleus in external magnetic field

The magnetic moment vector of a nucleus in a magnetic field is preccesses with characteristic angular frequency called the larmor frequency (ω) in radians per second as follow:-

External magnetic field in Tesla

larmor frequency in radians per second → $\omega = (\mu / I)\, B_0, \quad \omega = \gamma B_0$ 7

If we choose to express this in frequency units (s^{-1}, Hz) then since

$$\nu = \frac{\omega}{2\pi} \quad \text{......................8}$$

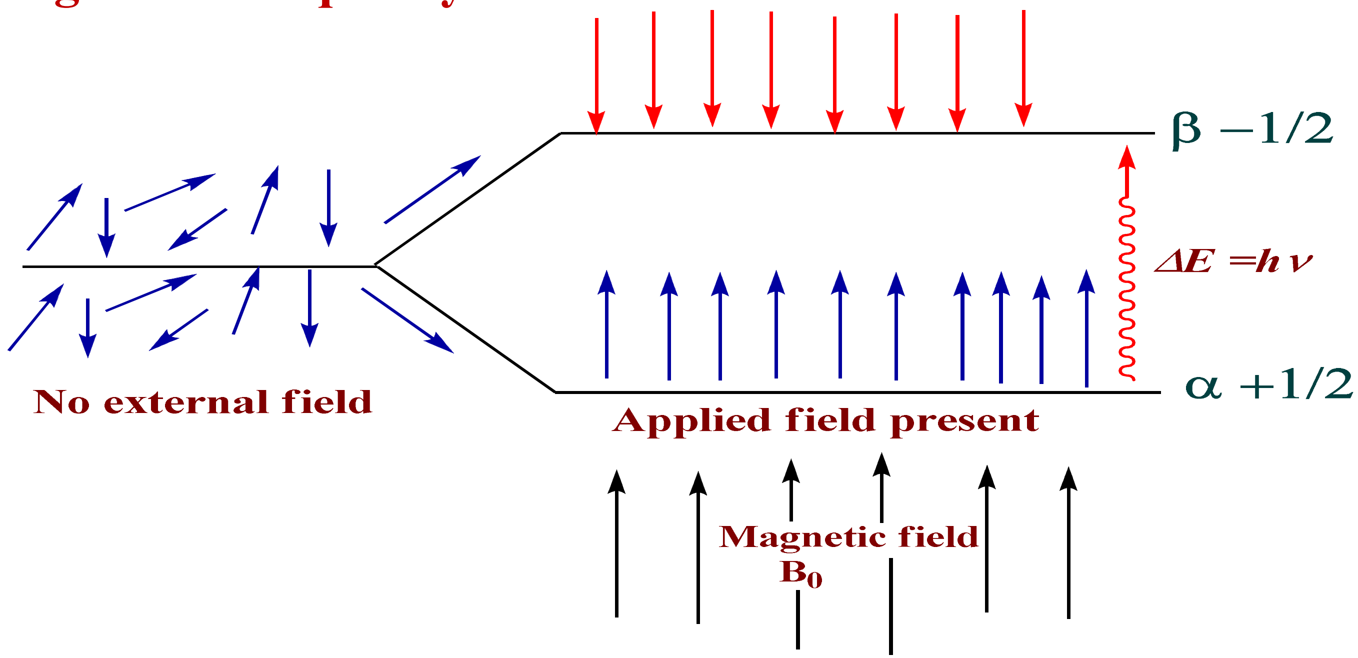
$$\nu = \frac{\mu}{2\pi I}$$

Precessional frequency in units(s^{-1}, Hz) → $\nu = \frac{\gamma B_0}{2\pi}$ 9

Precessional frequency (v):- is the number of revolutions per second made by the magnetic moment vector of the nucleus around the external magnetic field B_0. Or may be defined as equal to the frequency of electromagnetic radiation in megacycle per second necessary to induce a transition from one spin state to other.

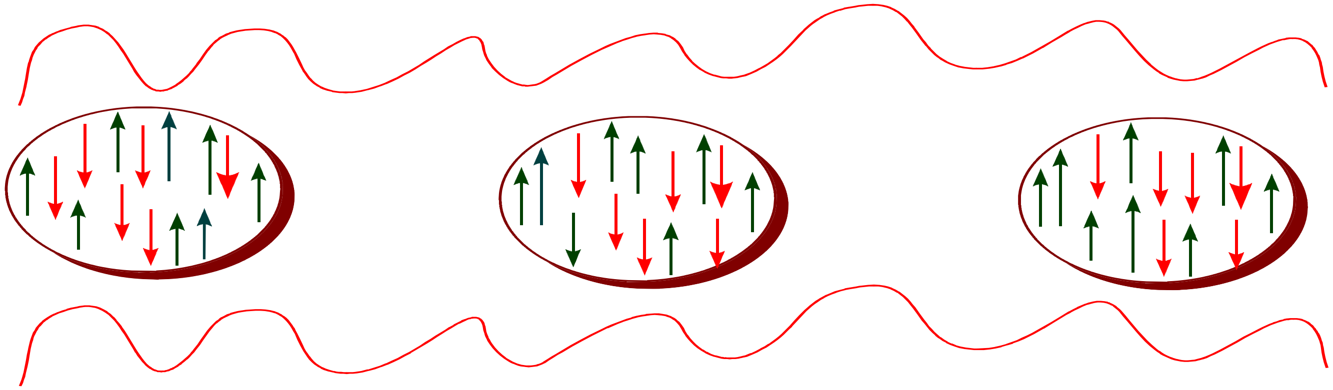
Homework:- (a) at 5.87 T, what is the precession frequency υ (MHz) of a ^1H nucleus? A ^{13}C nucleus?. (b) In what region of the electromagnetic spectrum does radiation of these frequencies occur? Answer (a) for ^1H= 250 MHz, for ^{13}C = 62.9 MHz.

Field strength and frequency



In the absence of B_0 the magnetic nuclei all have the same energy. when B_0 is applied, the aligned and opposed orientations correspond to different energies, the energy difference, ΔE , having the dimension hν

Some of the lower energy nuclei absorb radiation and move up to the higher energy state: that is, they undergo a transition from being aligned with the field to become opposed to the field. At the same time, some of the higher energy nuclei are stimulated to emit energy, and they therefore change their opposed orientation and become aligned with the field. These transition will only arise when the magnetic energy gap between the nuclear energy levels is matched exactly with the incoming radiofrequency, that is, when they are in resonance, and $\Delta E = h\nu$.



Irradiation with radiofrequency energy

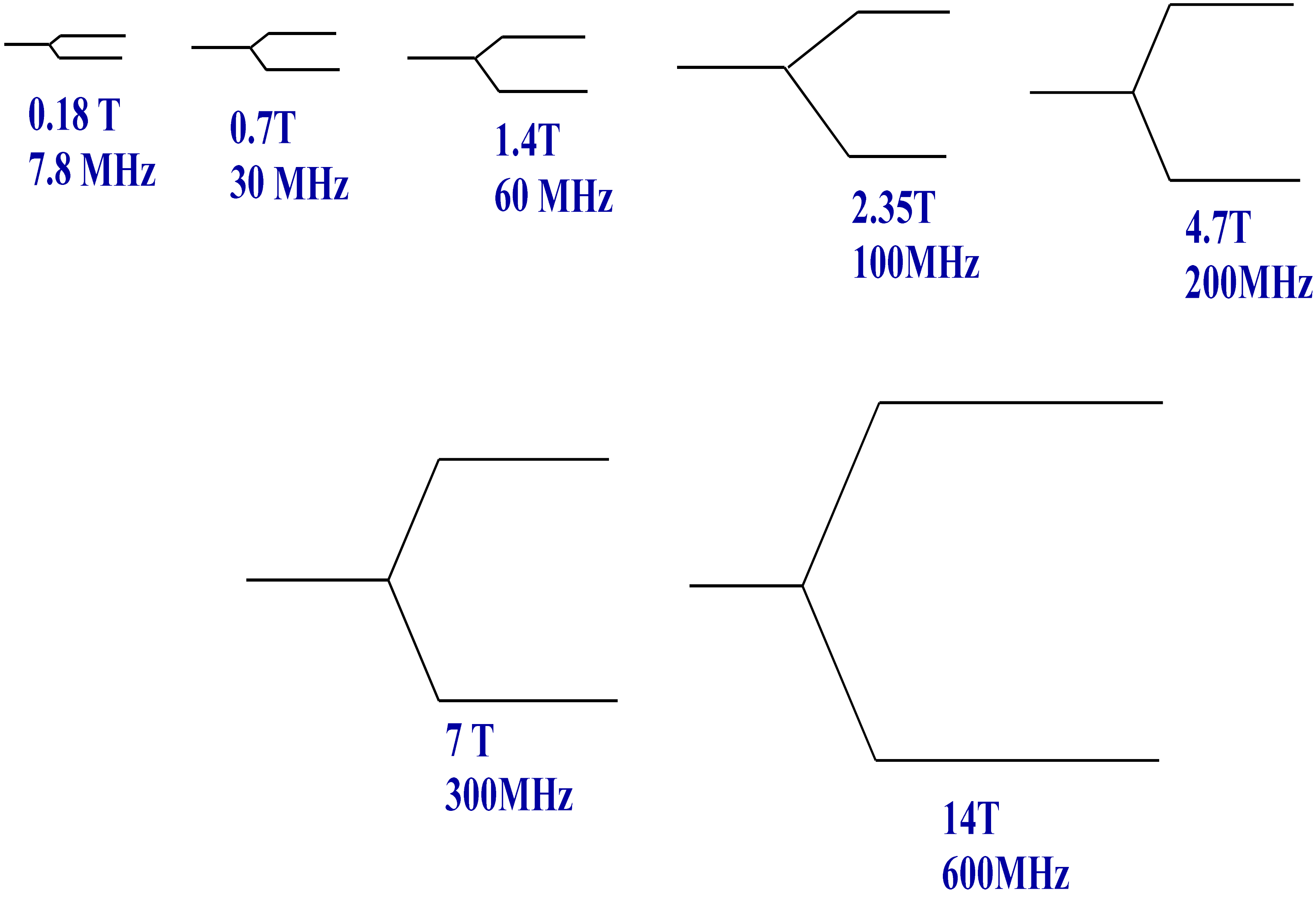
When the nuclei (in the magnetic field) are irradiated with radiofrequency energy of the appropriate frequency, some of them undergo transition from the aligned to the opposed orientations and vice versa

The study of nuclear magnetic resonance (NMR) is concerned with these energy levels, and with the frequency of radiation absorbed during resonance. The magnetic nuclei can occupy various magnetic sublevels, and that

- the frequency necessary to cause nuclear transitions is different for each element or isotope.
- This resonance frequency is found to vary in direct proportion to the applied field (for all magnetic nuclei); thus the larger the magnetic field the higher frequency necessary to achieve resonance. That is

$$\nu \propto B_0$$

For the proton we can represent this as in the following figure.



Example: - **what is the frequency needed to induce transitions between the ^{13}C nuclear energy levels when the field strength is (a) 4.7 T and (b) 1.88T.**

Solution:-

$$\nu = \frac{\gamma B_0}{2\pi} = \frac{6.726 \times 10^7 \times 4.7}{2(3.14)} = \frac{50337898 \text{ Hz}}{10^6} = 50 \text{ MHz}$$

$$\nu = \frac{\gamma B_0}{2\pi} = \frac{6.726 \times 10^7 \times 1.88}{2(3.14)} = \frac{20135159.24 \text{ Hz}}{10^6} = 20 \text{ MHz}$$

1MHz= 10^6 Hz , 1GHz = 10^9 Hz

Homework :- **what field strength is necessary in an instrument designed for studying proton NMR at (a) 60MHz (b) 200MHz, (c) 600 MHz .**