CHEM F111 : General Chemistry

Semester II: AY 2017-18

Lecture 17 (19-02-2018)

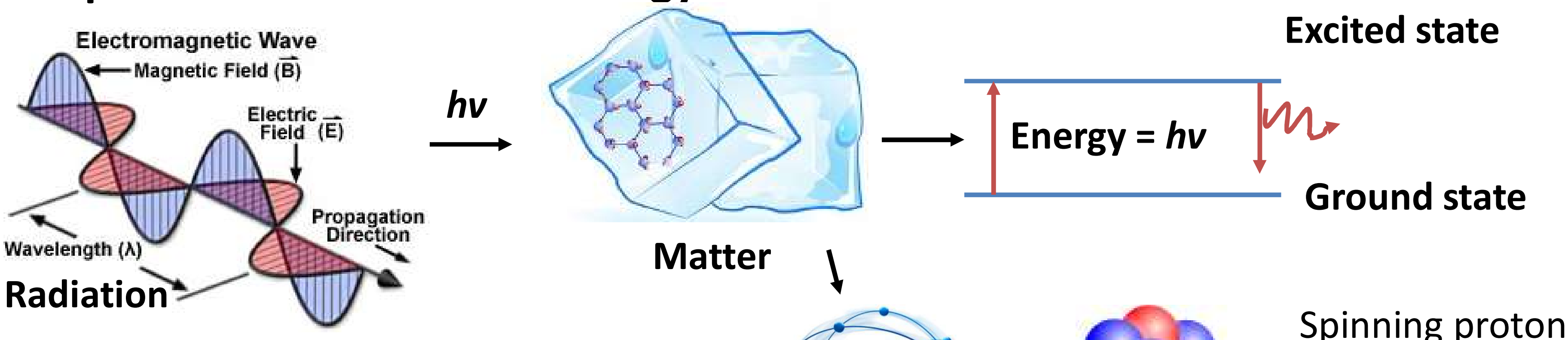
Nuclear Magnetic Resonance (NMR) Spectroscopy

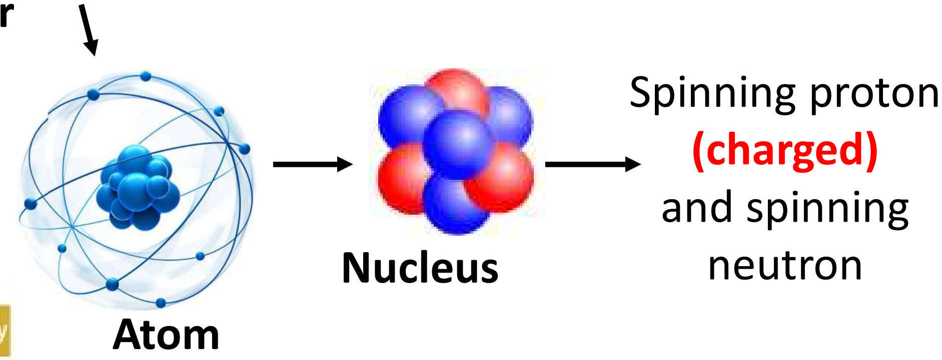
Topics to be covered in NMR (^{1}H and ^{13}C)

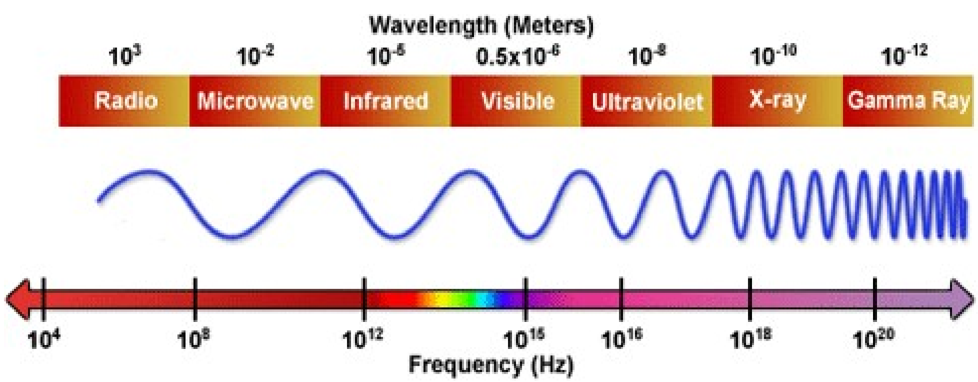
- ❑ Nucleus behavior under magnetic field (Zeeman effect)
- ❑ Nuclear Resonance: Interaction of nucleus with EMR in magnetic field
- ❑ Effect of population difference and Gyromagnetic Ratio (γ) on peak intensity
- ❑ Effect of electronic environment around nucleus on resonating frequency
- ❑ Effect of shielding and deshielding on chemical shift (δ)
- ❑ Nucleus spin-spin coupling (peak splitting)
- ❑ Analysis of ^{1}H-NMR spectrum of organic compounds
- ❑ ^{13}C-NMR and spectral analysis

Nuclear Magnetic Resonance (NMR) Spectroscopy

Electromagnetic radiation is absorbed when the energy of photon corresponds to difference in energy between two states.







Electronic	UV-Vis	Rotational	Microwave
Vibrational	Infrared	Nuclear Spin	Radiofrequency

Absorption spectroscopy: In the energy transfer process, electromagnetic radiation interacts with either the oscillating electric dipole (electronic, vibrational, rotational spectra) or **the oscillating magnetic dipole (Magnetic Resonance).**

Nuclear Magnetic Resonance (NMR) Spectroscopy

Nuclear Magnetic Resonance (NMR)**: NMR is concerned with change in the direction of nucleus spin orientation as the result of the absorption of radiofrequency radiation (~4-900 MHz).**

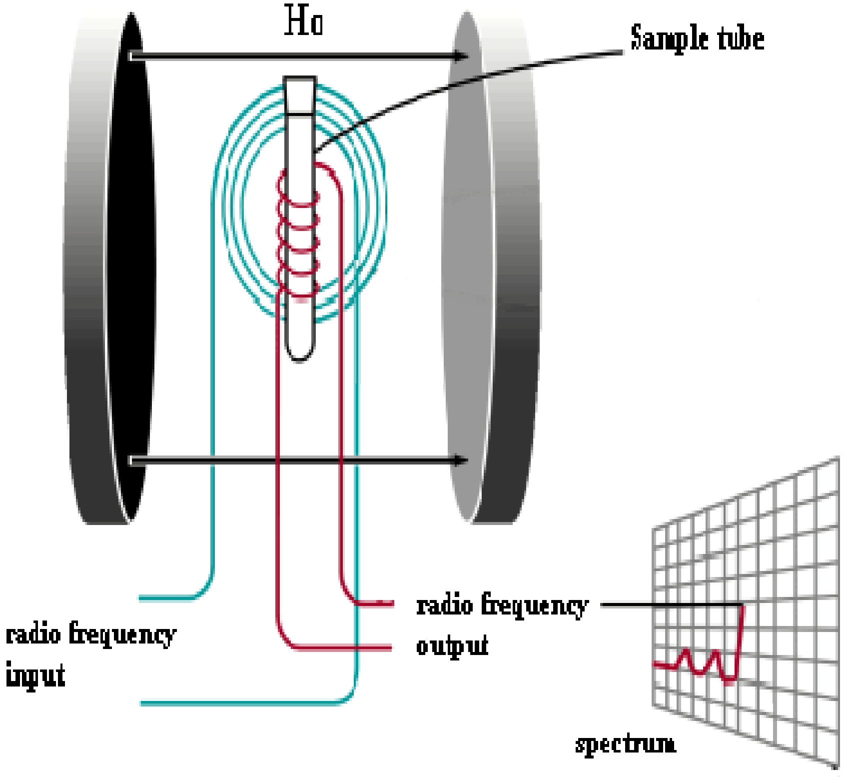
- **nuclei (instead of outer electrons) are involved in absorption process**
- **sample needs to be placed in magnetic field to cause different energy states**

- **Nuclear:** Related to the nucleus of an atom
- **Magnetic:** Nuclei possessing magnetic dipole
- **Resonance:** Phenomena of energy absorption by an oscillating medium, when there is a correspondence between frequency of oscillating medium and incoming EMR frequency (signal).
- **NMR** was first experimentally observed by Bloch and Purcell in 1946 (received Nobel Prize in 1952) and quickly became commercially available and widely used. NMR is routinely and widely used as the preferred technique to rapidly elucidate the chemical structure of most organic compounds.

NMR: The technique

- **Homogeneous magnetic field: High fields (superconducting magnets used)**

- **A radiofrequency source and Analyzer**



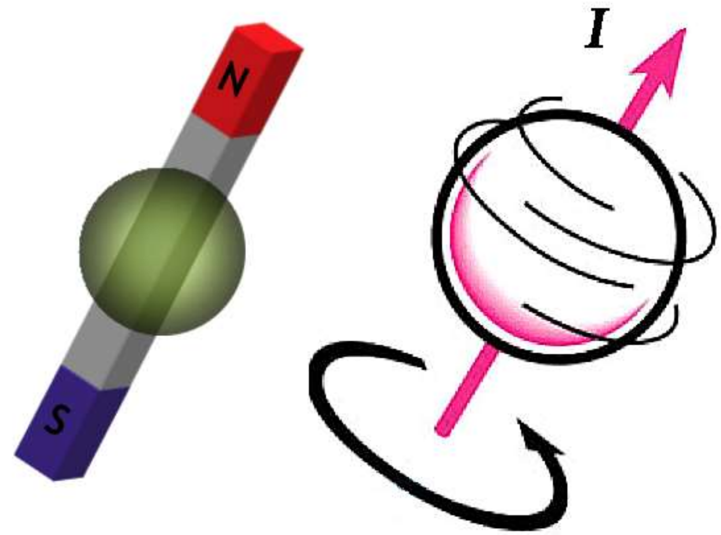
Nobel Prizes have been awarded to scientists for their work in NMR and MRI:

1. 1943 Physics: Otto Stern (USA)
2. 1952 Physics: Felix Bloch and Edward Purcell (USA)
3. 1944 Physics: Isidor Rabi (USA)
4. 1991 Chemistry: Richard Ernst (Switzerland)
5. 2002 Chemistry: Kurt Wüthrich (Switzerland)
6. 2003 Physiology/Medicine: Paul Lauterbur (USA) and Peter Mansfield (UK)

NMR is an important spectroscopic technique for Physics, Chemistry and Medicine.

Theory behind NMR spectroscopy

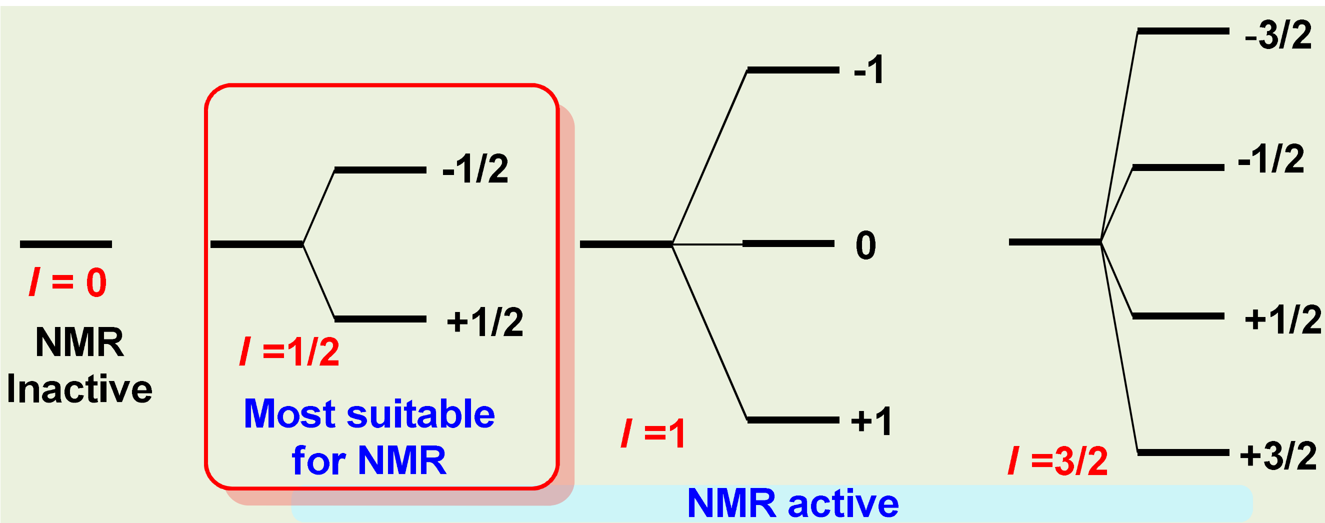
- **Nuclear Spin, *I*:** Just like electrons, a charged nucleus is also spinning (intrinsic property) around its own axis possess spin angular momentum (P) and generate a magnetic field with a nuclear magnetic dipole moment ($\mu = \gamma P$). (behaves like a tiny magnet)

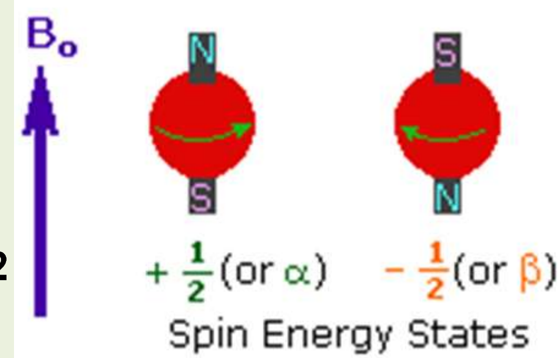


- The magnitude of angular momentum could be represented in terms of nuclear spin quantum number, I.
- I can take $2I+1$ different orientations relative to an arbitrary axis, which can be defined by a quantum number m_I, where m_I can take the values $= I, I-1, \ldots\ldots\ldots -I$. m_I quantizes the orientation of the nuclear magnetic moment vector.

Nuclear Spin, *I*: Not all nucleus are suitable for NMR

Atomic Mass	Atomic Number	
	Even	Odd
Even	*I* = 0 (**NMR In-active**) (^{12}C, ^{16}O)	Integral value (I = 1, 2, 3) e.g. ^{2}H= 1; ^{14}N=1)
Odd	Half Integer (I=1/2, 3/2, 5/2) e.g. **^{13}C= 1/2**, ^{17}O= 5/2	Half Integer (I =1/2, 3/2) e.g. **^{1}H =1/2**, ^{15}N = 1/2





The nuclear spin states α and β are degenerate in the absence of external magnetic field.

I = ½ are most suitable nuclei for NMR

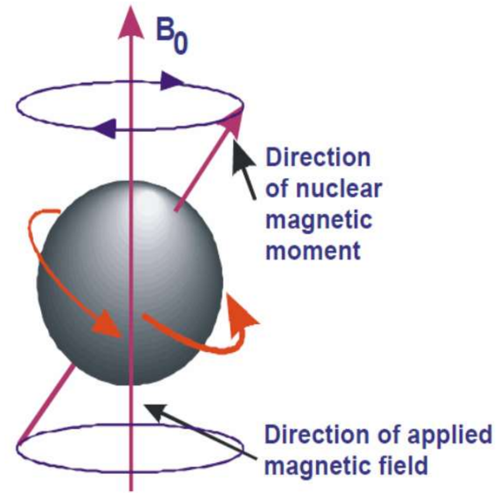
Proton (^{1}H) and carbon (^{13}C) are the most important nuclear spins to organic chemists.

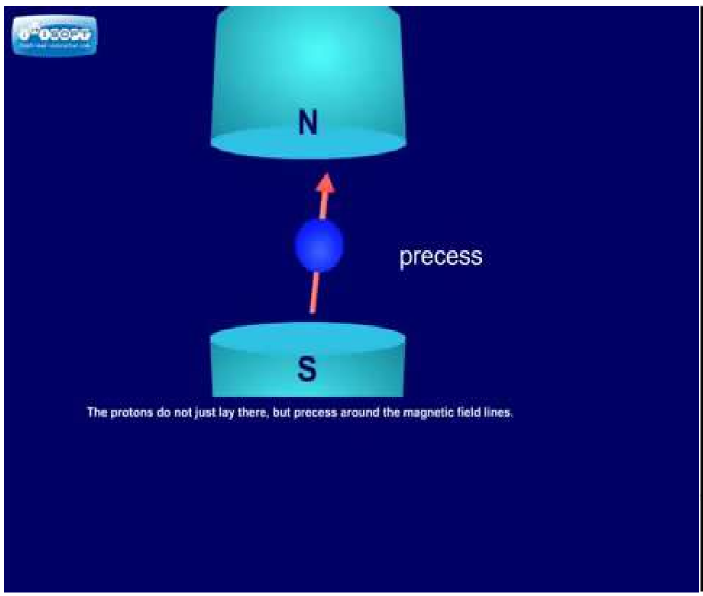
Nuclei in magnetic field: Nucleus precession

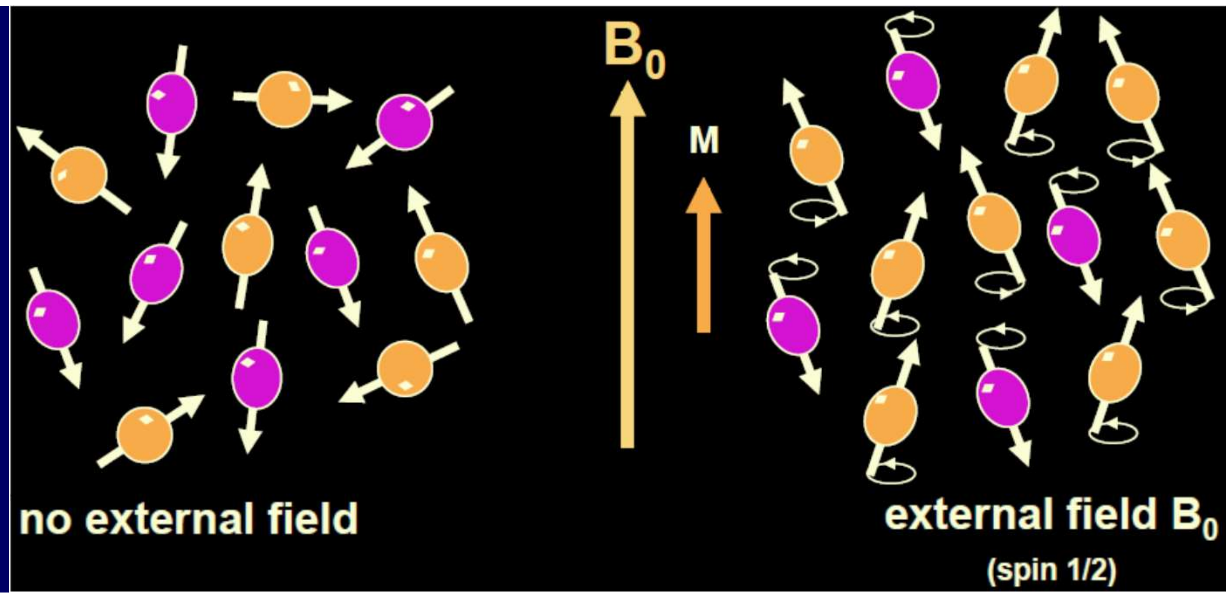
• A nucleus with non zero spin ($I \neq 0$) behaves like a tiny magnet and start precessing under magnetic field.

•Nucleus start precession either same or opposite direction of the external magnetic field (classical way).

•Precession of nucleus magnetic moment under external magnetic field with **Larmor frequency, ($\omega=\gamma B_o$) (in rad s^{-1})**.



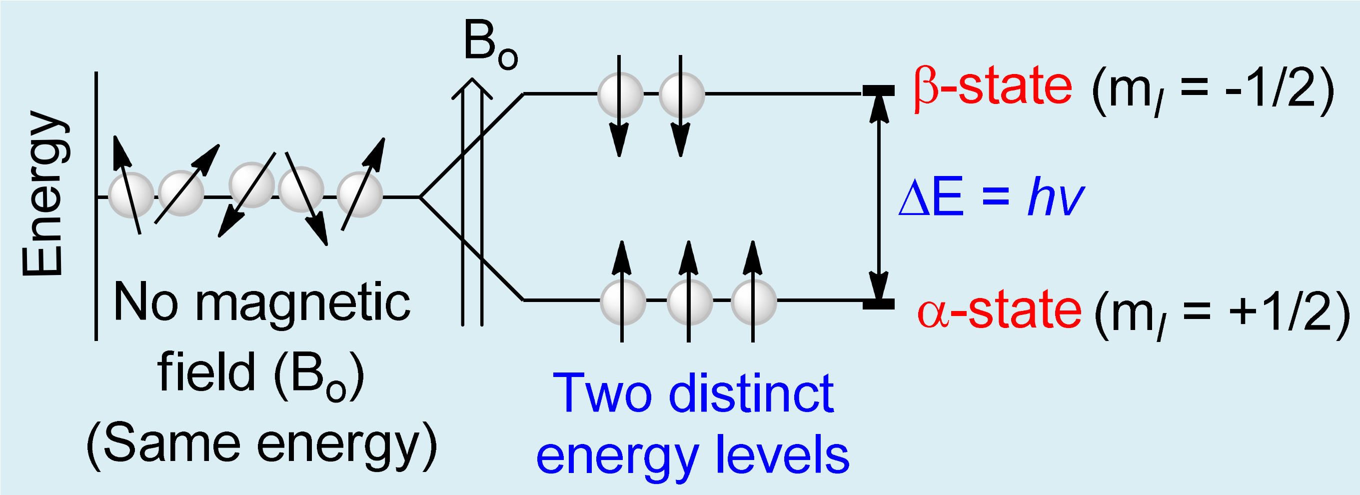




•Nuclei transit from one state to other state by absorbing energy corresponding to the radio frequency region of EMR.

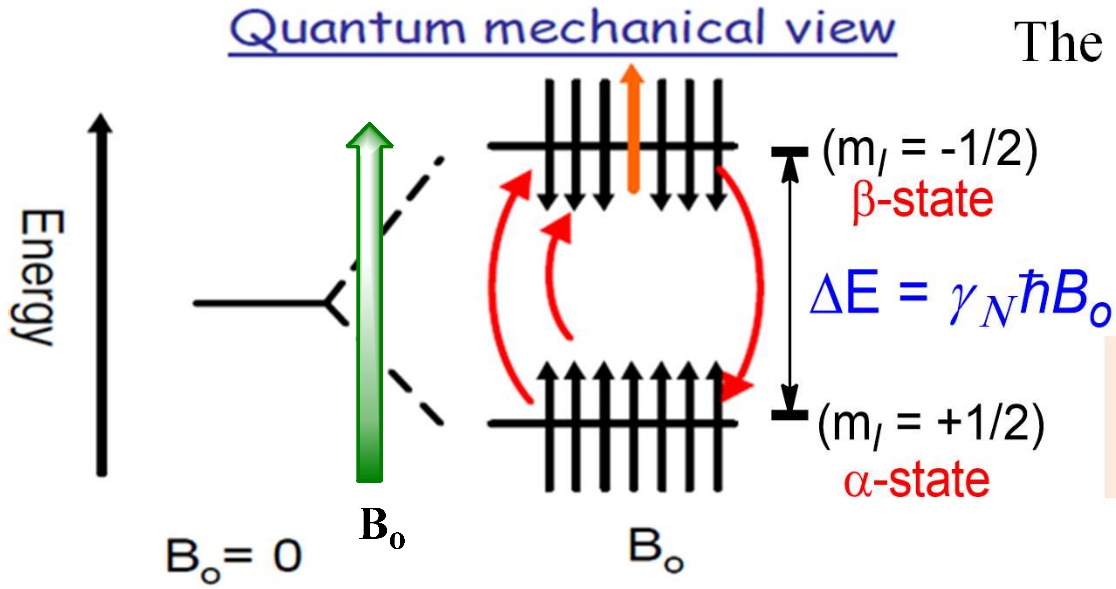
Nuclei in Magnetic field: *Zeeman Effect*

- When placed in a magnetic field (B_0) nuclei that possess ***spin*** align themselves according to their energy states. This effect on their alignment is called the ***Zeeman Effect***.
- The nuclear magnetic field can either be aligned with the external magnetic or oppose the external magnetic field.



On applying an external magnetic field (B_o), the two degenerate states (α & β) for I = 1/2 nuclei splits into two non-degenerate energy levels. The spins states are said to be split into two populations, -1/2 (anti-parallel), higher in energy and +1/2 (parallel), lower energy state with energy ($\mathbf{E}_{m_I} = -\mu_N B_o$).

Nuclei in magnetic field: Quantum mechanical view



The energy of each level is given by:

$$E_{m_I} = -\mu_N B_o;$$

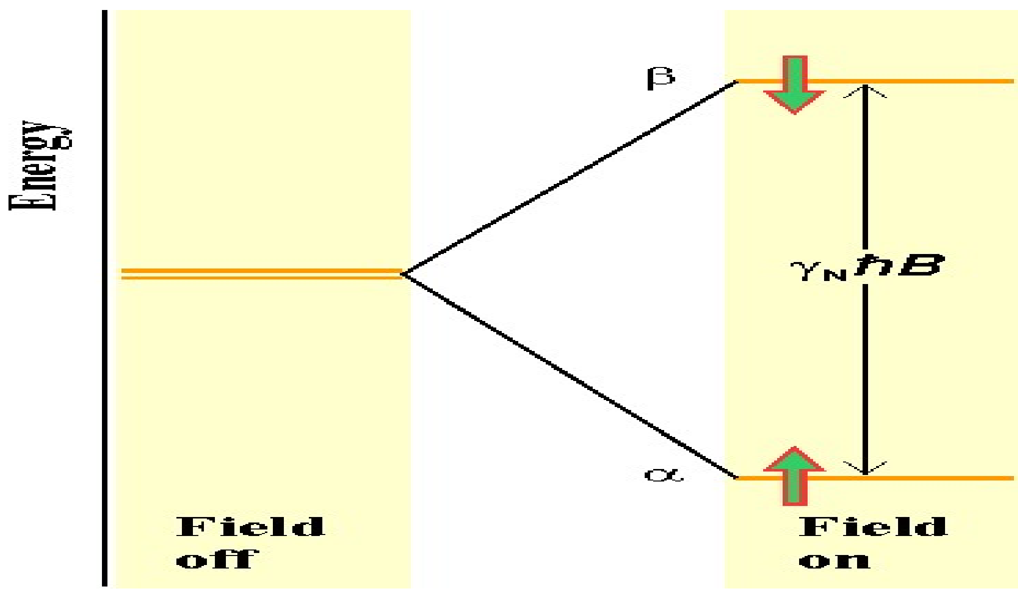
$$E_{m_I} = -\gamma_N \hbar\, m_I B_o;$$

γ_N = nuclear gyromagnetic (or magnetogyric) ratio

$$E_{m_I} = -g\mu_N B_o m_I$$

$$E_{m_I} = -\gamma_N \hbar B_o m_I = -g_N \mu_N B_o m_I$$

$$\rightarrow \boxed{\gamma_N = \mu_N g_N/\hbar}$$



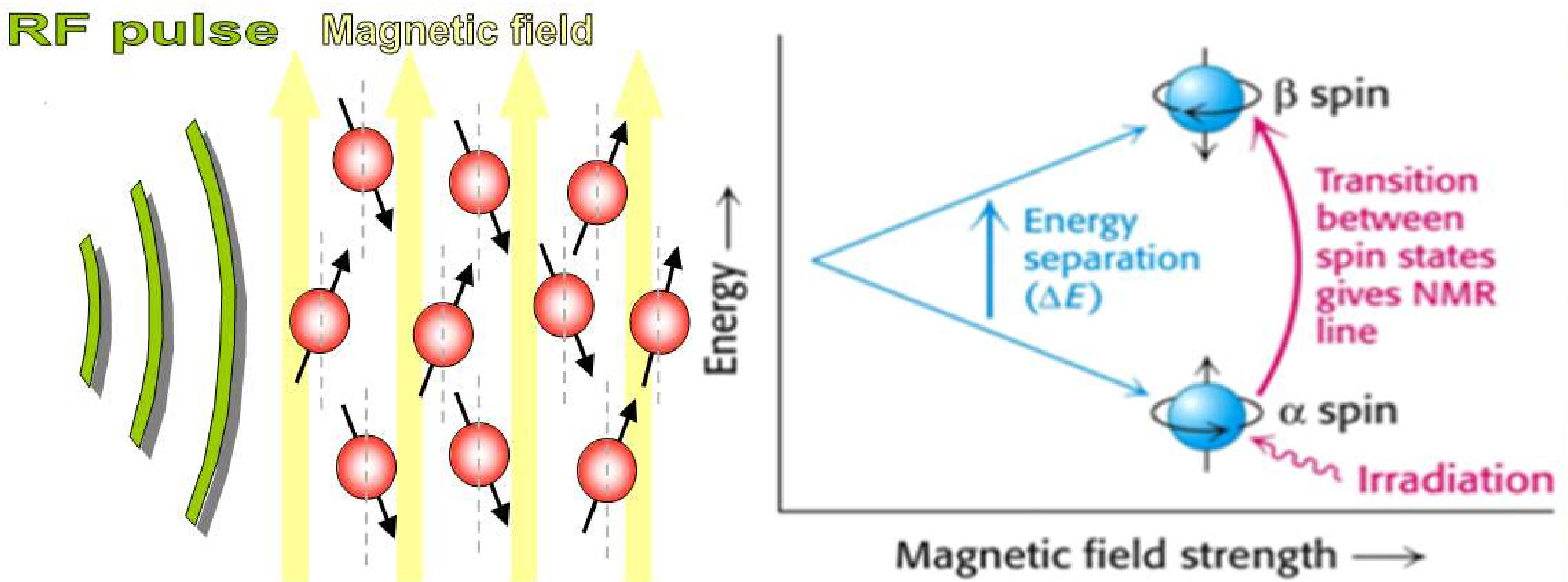
g = Nuclear g-factor: experimentally determined.

μ_N = Nuclear magneton ($\mu_N = e\hbar/2m_p$) $\mu_N = 5.05\times10^{-27}$ J/T

Resonance-A general phenomenon for energy pumping

$E_{m_I} = -\gamma_N \hbar B_o m_I$; $\Delta E = E_\beta - E_\alpha = \gamma_N \hbar B_o$

$h\nu = \gamma_N \hbar B_o$ Thus, $\nu = \gamma_N B_o / 2\pi$ (selection rule: $\Delta m_I = 1$)



- Nuclei transit from α-state to β-state by absorbing energy corresponding to the radio frequency region of EMR. [Resonance]

Do all the nuclei with I= ½ resonate at same radio frequency (ν)?