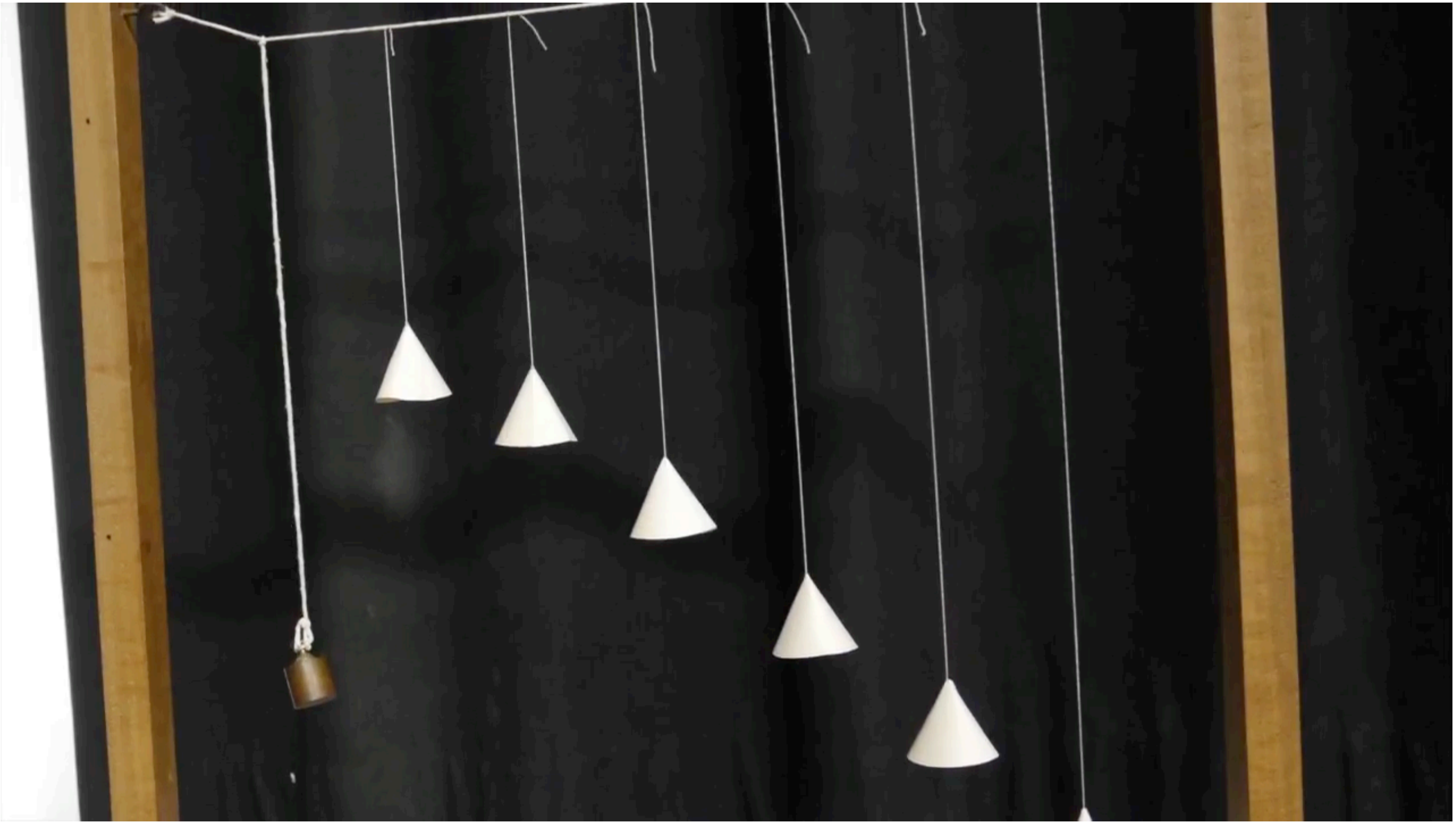
Today's class:

NMR Spectroscopy

This lecture follows the materials from the following books

- *Physical Chemistry for Life Sciences, by PW Atkins and JD Paula, Oxford, 2006*
- *Physical Biochemistry by David Sheehan, 2nd Ed, Wiley, 2009*

Barton's Pendulum



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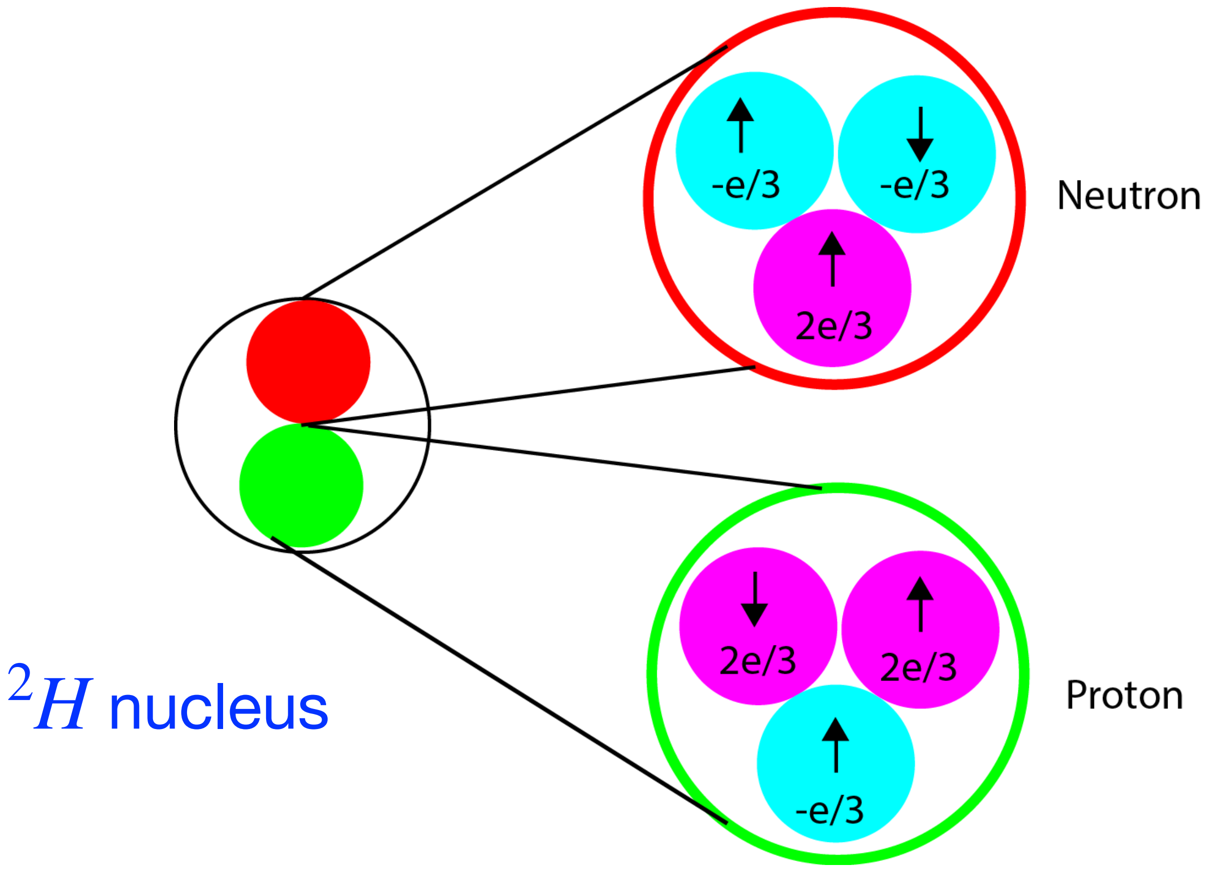
Nuclear spins

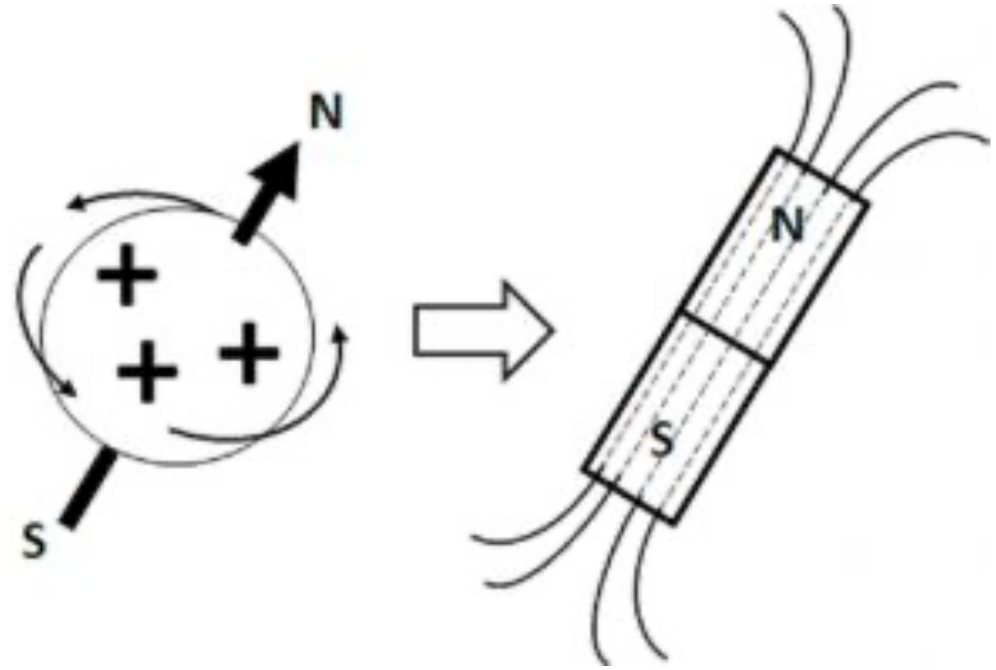


- Protons and neutrons are made of quarks which have spin and charge like electrons.
- This impart spin to protons and neutrons
- They are half-spin particles
- Depending on the composition of the nucleus it may or may not have net spin

E.g. ^{1}H nucleus = 1 proton : spin = 1/2

^{2}H nucleus = 1 proton + 1 neutron : spin = 1 or 0

Nuclear magnetic moment



Non-zero nuclear "spin" provides a "quantum magnetic moment" to the atomic nucleus.

$$\mu = \gamma I$$

$\mu =$ magnetic moment of the nucleus

$\gamma =$ magnetogyric or gyromagnetic ratio unique to a nucleus

$I =$ spin angular momentum of the nucleus

The spin angular momentum of the nucleus is quantized

The spin angular momentum of the nucleus can be written as

$$I = m_l \hbar$$

Where m_l = spin quantum number

In NMR spectroscopy, I is often expressed as just characteristic nuclear spin which results from pairing of the spins of protons and neutrons present in the nucleus.

I values for different nuclear compositions

Number of protons	Number of neutrons	I
Even	Even	0
Odd	Odd	Integer (1, 2, 3, . . .)
Even	Odd	Half-integer ($\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, . . .)
Odd	Even	Half-integer ($\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, . . .)

Magnetic properties for nuclei important in biology

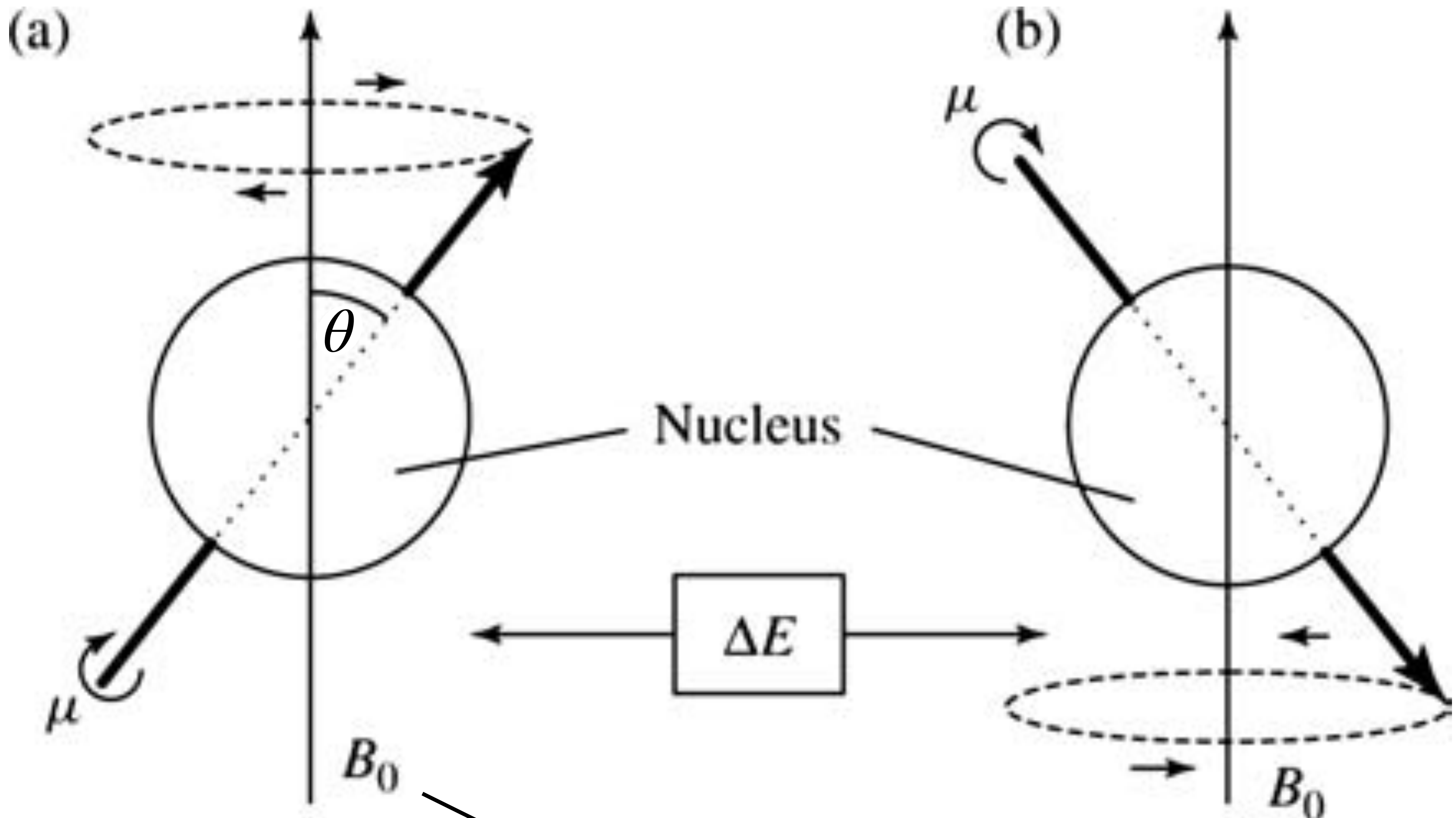
Nucleus	Natural abundance/percent	Spin, I	$\gamma_N/(10^7\ T^{-1}\ s^{-1})$
^{1}H	99.98	½	26.752
^{2}H (D)	0.0156	1	4.1067
^{12}C	98.99	0	—
^{13}C	1.11	½	6.7272
^{14}N	99.64	1	1.9328
^{16}O	99.96	0	—
^{17}O	0.037	5/2	−3.627
^{19}F	100	½	25.177
^{31}P	100	½	10.840
^{35}Cl	75.4	3/2	2.624
^{37}Cl	24.6	3/2	2.184

T = Tesla, unit of magnetic field

1 T = magnetic field which exert 1 N force on a 1 C charge moving at a speed 1 m/s

$$1\ T = \frac{N\,.\,s}{C\,.\,m} = \frac{kg}{A\,.\,s^{-2}}$$

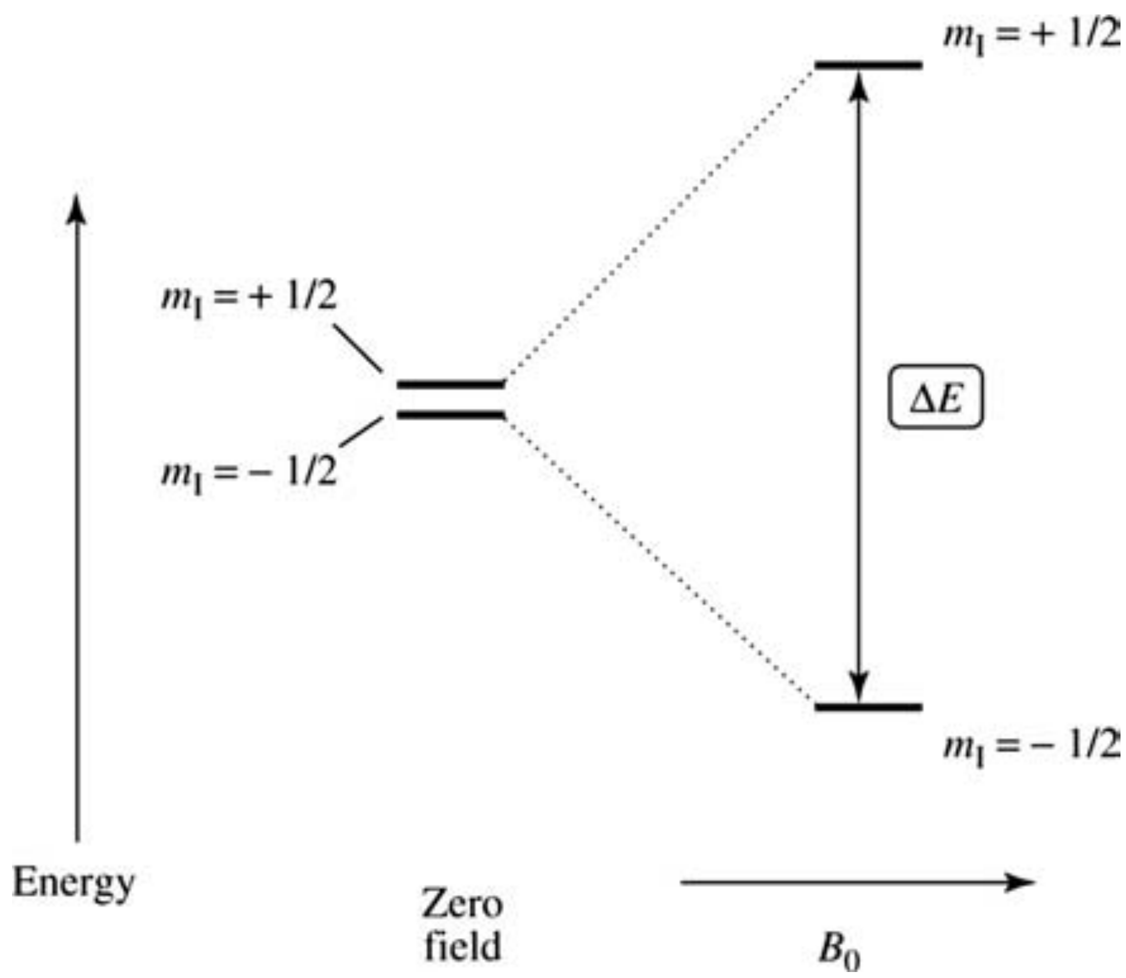
Nuclear spins in external magnetic field



external magnetic field

- In external magnetic field, nucleus with finite spin can adopt a ‘parallel’ or an ‘anti-parallel’ orientation to the field
- Nucleus undergo precessional motion around the field - Larmor Precession
- The frequency of this precession in called Larmor frequency

Spin states for nuclear spin in external magnetic field



No spin ($I = 0$) no such splitting in external magnetic field

Nuclear energy levels split in two spin states of high and low energies due to coupling with the external magnetic field

$$E = \mu B_0 = m_l \gamma \hbar B_0$$

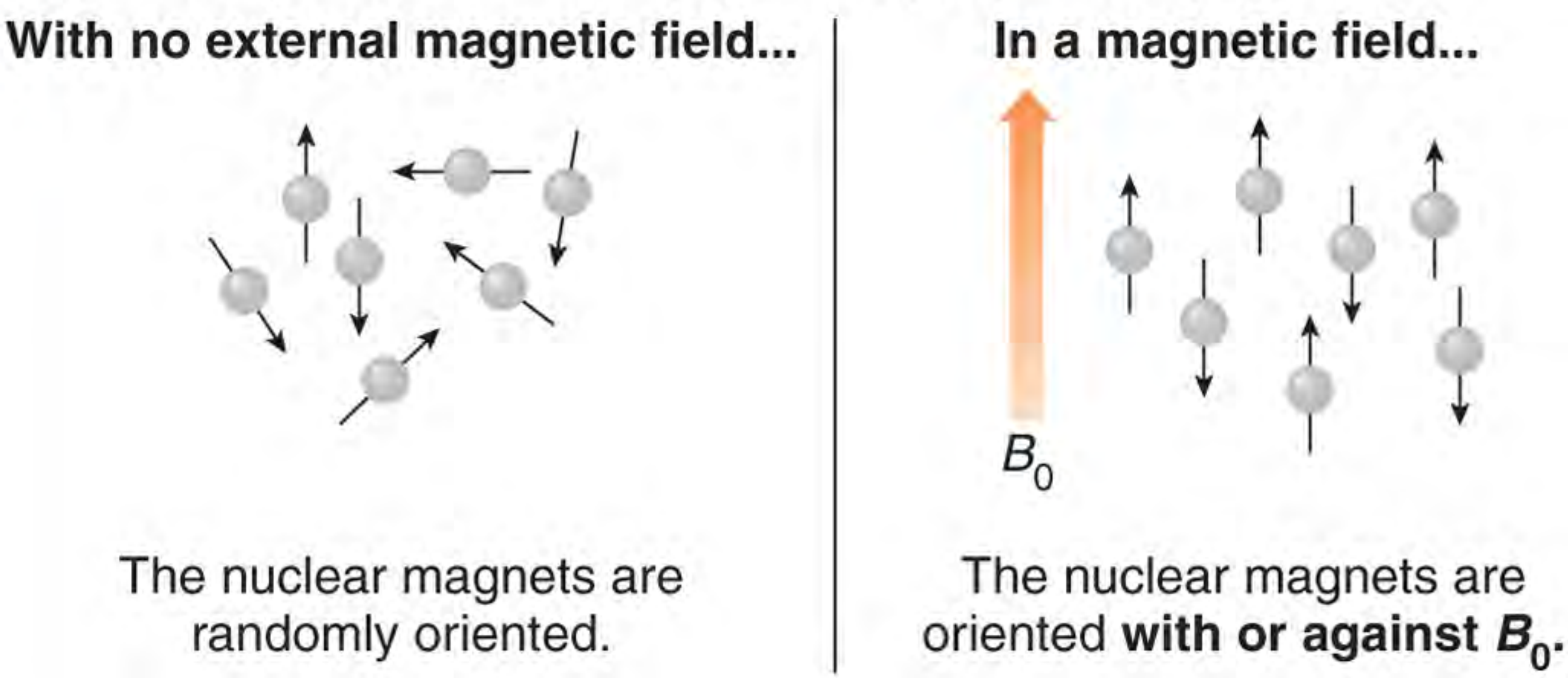
Low energy state: α $\quad m_l = -1/2 \implies E_\alpha = = -\frac{1}{2}\gamma\hbar B_0$

High energy state: β $\quad m_l = 1/2 \implies E_\beta = \frac{1}{2}\gamma\hbar B_0$

Difference between the states

$$\Delta E_{\alpha\beta} = \gamma\hbar B_0$$

Nuclear Magnetic Resonance



$$\Delta E_{\alpha\beta} \approx 0 \quad \text{if } B_0 = 0$$

$$\Delta E_{\alpha\beta} = \gamma\hbar B_0 \quad \text{if } B_0 \neq 0$$

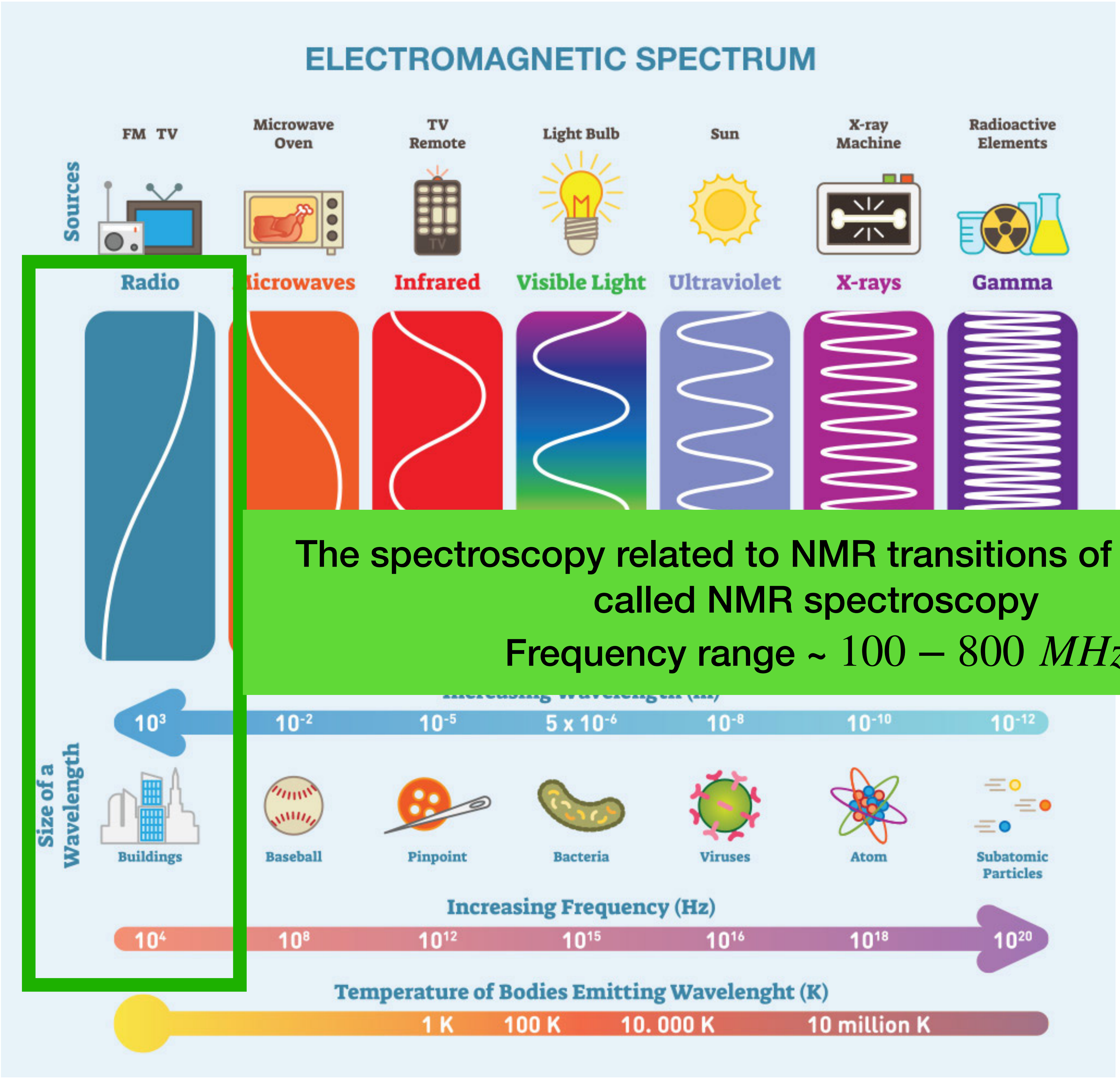
- Immediately after, population in the states are related as: $N_\beta < N_\alpha$
- If the sample is exposed to radiation of frequency ν, the energy separations come into resonance with the radiation when the frequency satisfies the resonance condition:

$$h\nu = \gamma\hbar B_0 \implies \nu = \frac{\gamma B_0}{2\pi}$$

- At resonance there is strong coupling between the nuclear spins and the radiation, and strong absorption occurs as the spins flip from α (low energy) to β (high energy).
- We refer to these transitions as **nuclear magnetic resonance** (NMR) transitions.

Selection rule for NMR: $\Delta m_l = \pm 1$

NMR transitions absorb radiowaves!



The spectroscopy related to NMR transitions of molecules is called NMR spectroscopy

Frequency range ~ $100 - 800\ MHz$

Image courtesy: pasco.com

NMR transition frequencies for important nuclei

Table 3.6. Magnetic properties of some nuclei important in biochemistry

Nucleus	I	Natural abundance (%)	γ rad·s^{-1} T^{-1}	NMR ν at T = 2.3488 (MHz)
^{1}H	1/2	99.98	26.752	100
^{2}H	1/2	0.015	4.107	15.35
^{12}C	0	98.9	—	—
^{13}C	1/2	1.10	6.7283	25.144
^{14}N	1	99.63	1.9338	7.224
^{16}O	0	99.76	—	—
^{32}S	0	95.02	—	—
^{31}P	1/2	100	10.8394	40.481
^{35}Cl	3/2	75.77	2.642	9.798
^{15}N	1/2	0.37	−2.7126	10.133