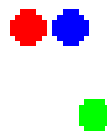


Spectroscopy in Inorganic Chemistry

Nuclear Magnetic Resonance Spectroscopy

● spin



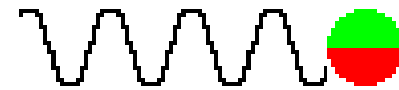
deuterium



helium

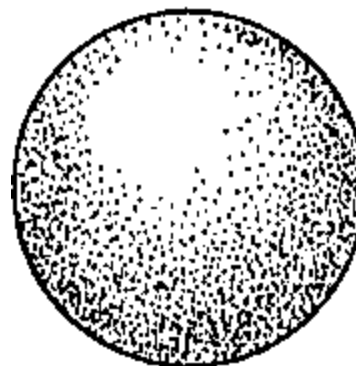
- B : magnetic field of strength
- ν : photon frequency
- γ : gyromagnetic ratio of the particle.

$$\nu = \gamma B$$



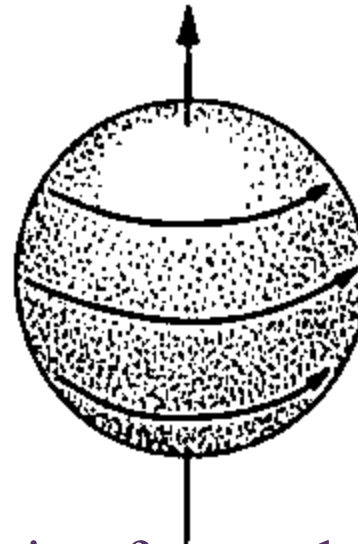
- For hydrogen, $\gamma = 42.58 \text{ MHz / T}$.

- nuclear angular momentum spin quantum number I , the "spin" of the nucleus.
- $I = 0$ no spin, the nucleus has no magnetic moment and no NMR properties



μ : nuclear magnetos, magnetic dipole (spinning charge).

- Nuclei with $I = 1/2$ have especially advantageous NMR properties, and the vast majority of all NMR experiments are done with such isotopes.



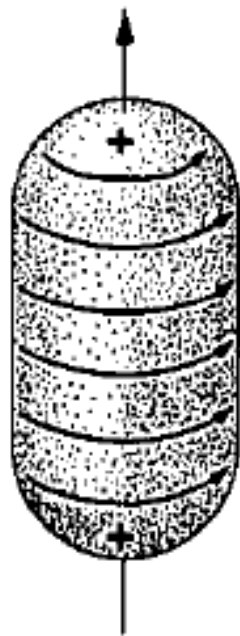
eQ : electric quadrupole moment

e : electrostatic charge

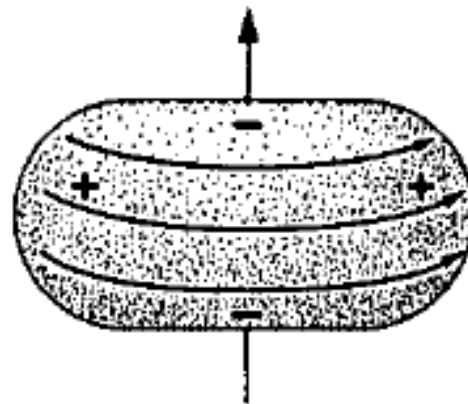
Q : deviation of the nuclear charge distribution from spherical symmetry

- $I > 0$ the nucleus has spin ($I = 1/2, 1, 3/2, 2, \text{etc}$) and a magnetic dipole μ , and thus may be suitable for NMR observation.

- $l \geq 1$.



$l \geq 1, \mu \neq 0, eQ > 0$



$l \geq 1, \mu \neq 0, eQ < 0$

- $I > 1$ the nucleus has spin ($I = 1/2, 1, 3/2, 2, \text{etc}$) and a magnetic dipole μ , and thus may be suitable for NMR observation.

xN_y	even N_{even}	$I = 0$	${}^{12}\text{C}_6$, ${}^{16}\text{O}_8$, ${}^{32}\text{S}_{16}$
$x = \text{mass number}$	odd N_{either}	$I = 1/2$	${}^1\text{H}_1$, ${}^{13}\text{C}_6$, ${}^{15}\text{N}_7$, ${}^{19}\text{F}_9$, ${}^{31}\text{P}_{15}$
$y = \text{atomic number}$		$I = 3/2, 5/2, \text{etc}$	${}^7\text{Li}_3 (3/2)$, ${}^{11}\text{B}_5 (3/2)$
	even N_{odd}	$I = 1, 2, 3, \text{etc}$	${}^6\text{Li}_3 (1)$, ${}^{14}\text{N}_7 (1)$, ${}^2\text{H}_1 (1)$,

$$\text{Number of spin states} = 2I + 1$$

Atom	Isotope	Spin	Larmor frequency (MHZ at 9.306 T)	Abundance (%)	Absolute sensitivity	Quadrupole (barn)
Hydrogen	1H	1/2	-400.00	99.98	1.00E+000	0
Deuterium	2D	1	-61.40	0.02	1.45E-006	0.00273
Lithium	6Li	1	-58.86	7.42	6.31E-004	-0.0008
Lithium	7Li	3/2	-155.45	92.58	2.70E-001	-0.045
Boron	10B	3	-42.98	19.58	3.90E-003	0.074
Boron	11B	3/2	-128.34	80.42	1.30E-001	0.0355
Carbon	13C	1/2	-100.58	1.11	1.76E-004	0
Nitrogen	14N	1	-28.90	99.63	1.01E-003	0.016
Nitrogen	15N	1/2	40.53	0.37	3.85E-006	0
Oxygen	17O	5/2	54.23	0.04	1.08E-005	-0.026
Fluorine	19F	1/2	-376.31	100.00	8.30E-001	0
Sodium	23Na	3/2	-105.80	100.00	9.25E-002	0.12
Magnesium	25Mg	5/2	24.48	10.13	2.71E-004	0.22
Aluminum	27Al	5/2	-104.23	100.00	2.10E-001	0.149
Silicon	29Si	1/2	79.46	4.70	3.69E-004	0
Phosphorus	31P	1/2	-161.92	100.00	6.63E-002	0
Sulfur	33S	3/2	-30.68	0.76	1.72E-005	-0.055
Chlorine	35Cl	3/2	-39.19	75.53	3.55E-003	-0.08
Chlorine	37Cl	3/2	-32.62	24.47	6.63E-004	-0.0632
Potassium	39K	3/2	-18.67	93.10	4.73E-004	0.055
Potassium	41K	3/2	-10.24	6.88	5.78E-006	0.067
Calcium	43Ca	7/2	26.91	0.15	9.28E-006	-0.05

- Nuclei with $I > 0$ have angular momentum P (spinning mass) whose direction is the spin axis. The angular momentum is quantized, and can only have one value:

$$P = \sqrt{I(I+1)} \cdot \frac{h}{2\pi}$$

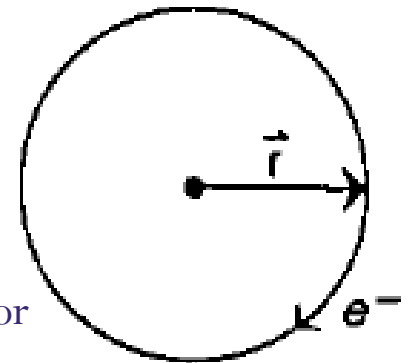
Angular change

angular momentum vector

$$\vec{p}(\varphi) = \vec{r} \times m\vec{v}$$

mass

Linear momentum vector



Position vector of particle e

The nucleus is a more complicated three-dimensional problem

- P: angular momentum
- J: total angular momentum
- I: dimensionless angular momentum

$$\hat{\mathbf{J}} = \hbar \hat{\mathbf{I}} \quad \text{or} \quad \hat{\mathbf{I}} = \hat{\mathbf{J}}/\hbar$$

- P: angular momentum \leftrightarrow μ : nuclear magnetos
- J: total angular momentum \leftrightarrow μ_N : total nuclear magnetos

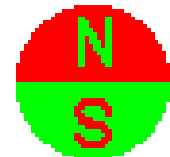
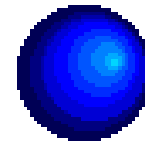
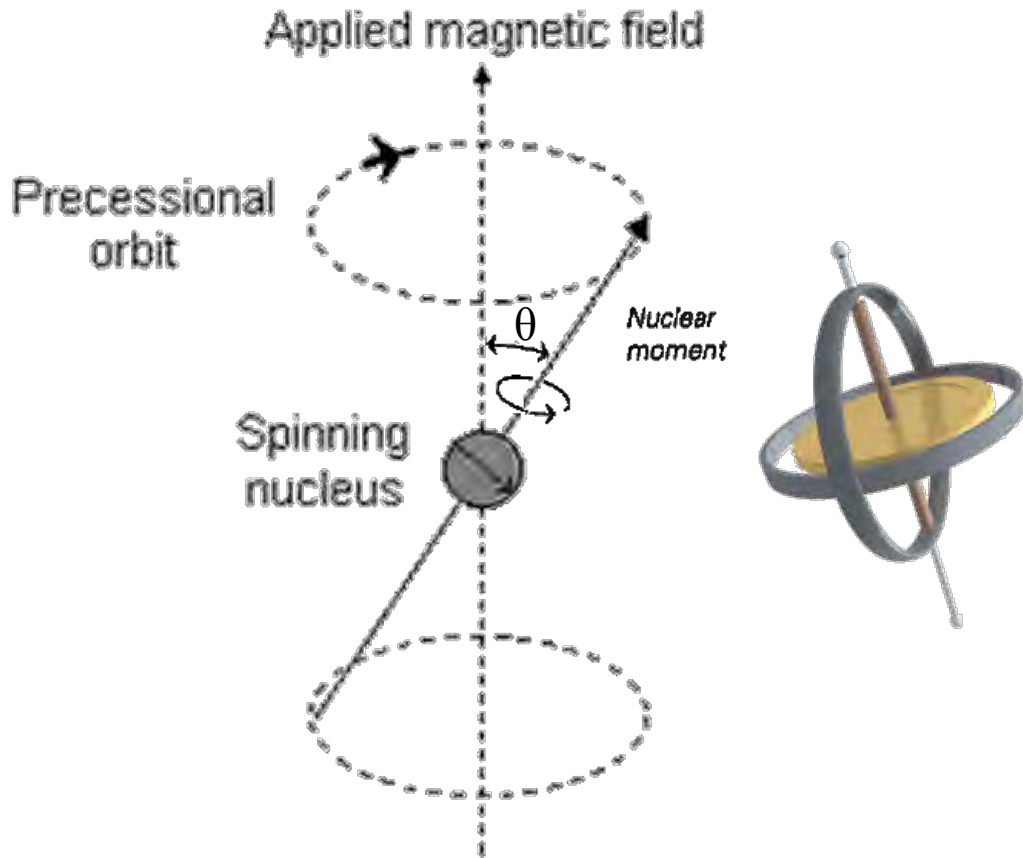
$$\hat{\boldsymbol{\mu}}_N = \gamma \hat{\mathbf{J}} = \gamma \hbar \hat{\mathbf{I}}$$

- Nuclei with $I > 0$ also have a magnetic dipole μ (spinning charge). For the NMR experiment it is the ratio of μ to P that matters (much in the way that m/e is what matters in mass spectrometry). We define γ , the gyromagnetic ratio:

gyromagnetic ratio

$$\gamma = \frac{\mu}{P} \quad \mu = \gamma \mathbf{P}$$

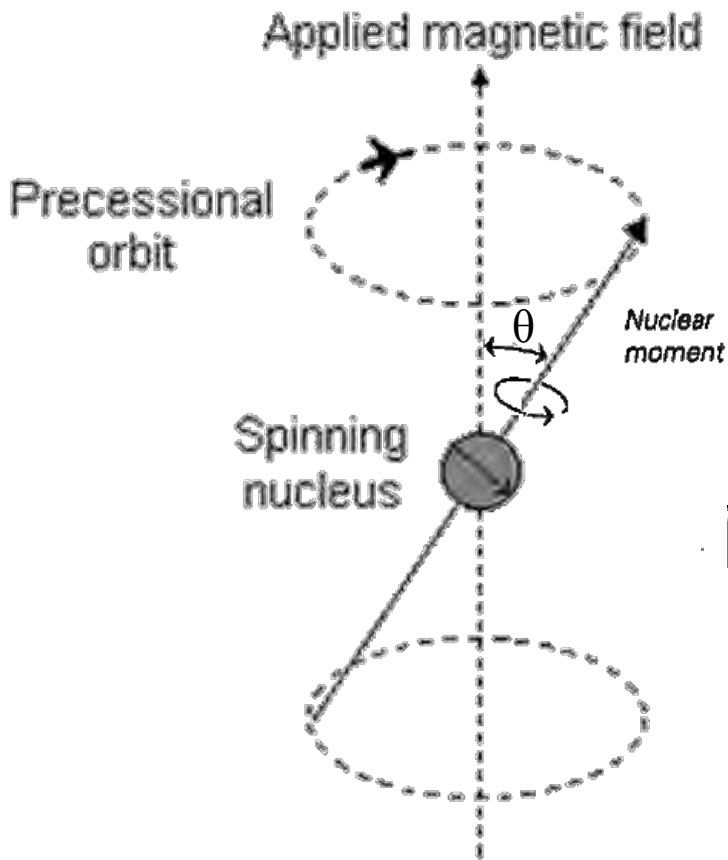
Behavior of bar magnet in the magnetic field



$$\omega_0 \text{ (rad/s)} = \gamma H_0$$

or

$$\nu_0 \text{ (MHz)} = \left(\frac{\gamma}{2\pi} \right) H_0$$

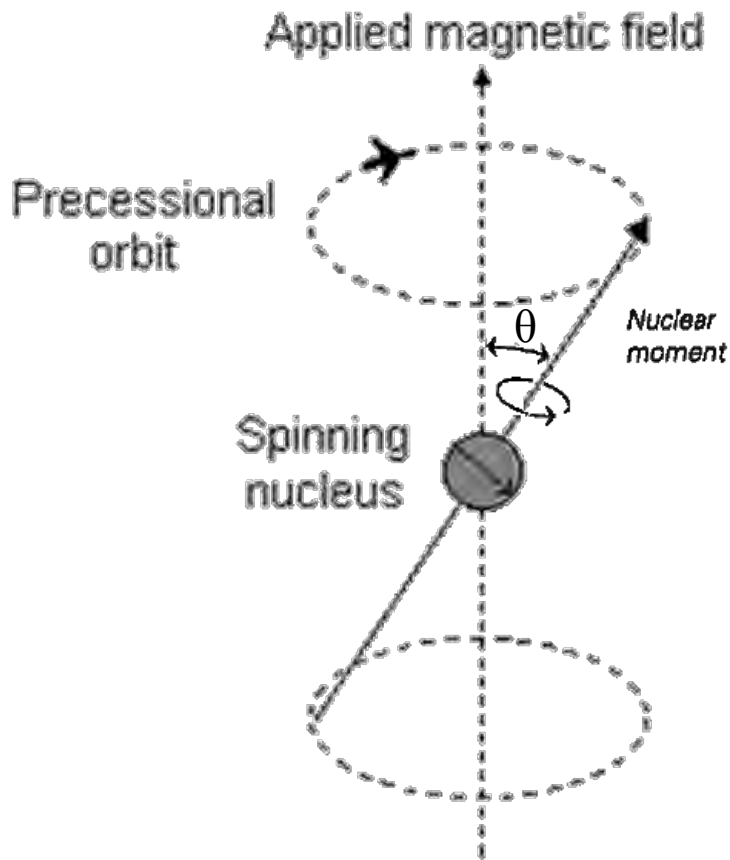


$$\vec{\tau} = \vec{\mu} \times \vec{H}_0 \quad 1$$

$$\vec{\tau} = \frac{d}{dt} (\hbar \vec{I}) \quad 2$$

$$\vec{\mu} = \gamma \hbar \vec{I} \quad \rightarrow \quad \frac{d\vec{\mu}}{dt} = \frac{\gamma d(\hbar \vec{I})}{dt} = \gamma \vec{\tau}$$

$$\frac{d\vec{\mu}}{dt} = \dot{\vec{\mu}} = -\gamma \vec{H}_0 \times \vec{\mu}$$



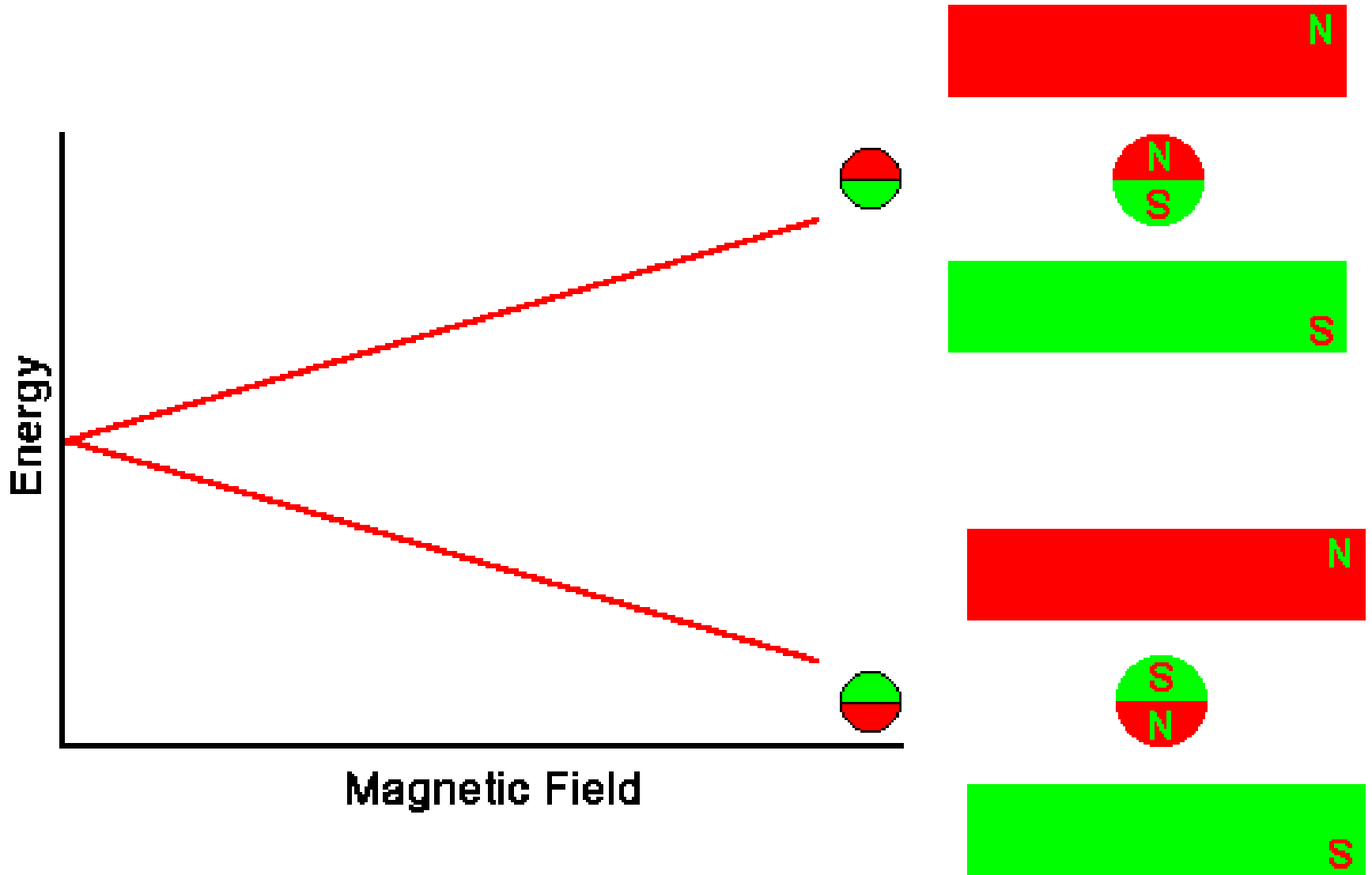
$$\omega_0 \text{ (rad/s)} = \gamma H_0$$

or in MHz

$$\nu_0 \text{ (MHz)} = \left(\frac{\gamma}{2\pi} \right) H_0$$

$$E = -\vec{\mu} \cdot \vec{H}_0 = -|\mu||H_0| \cos \theta$$

The NMR transition

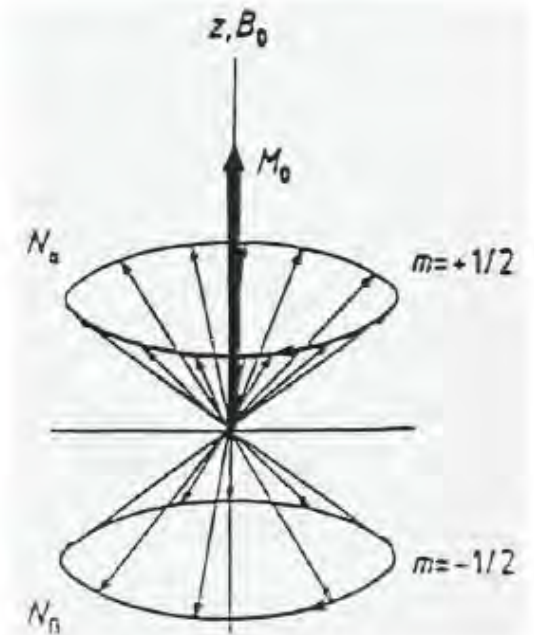
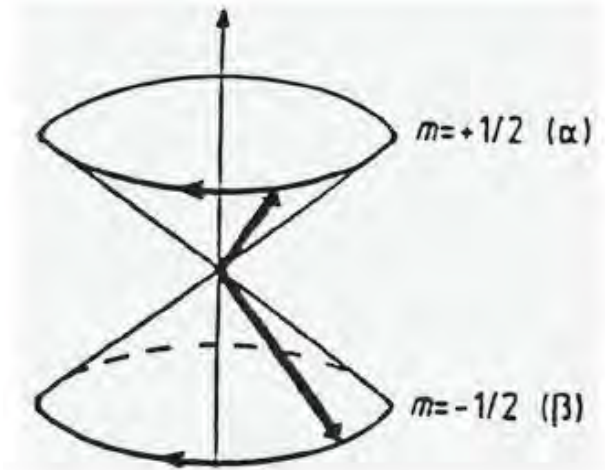
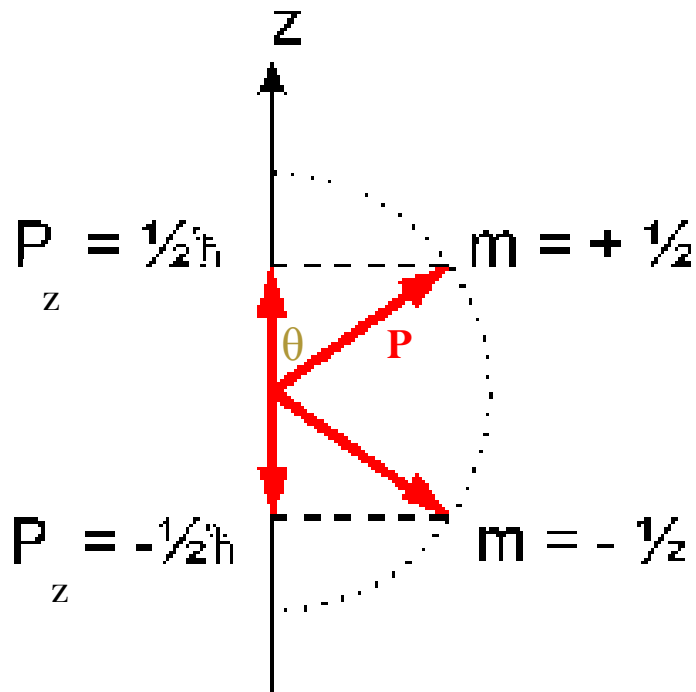


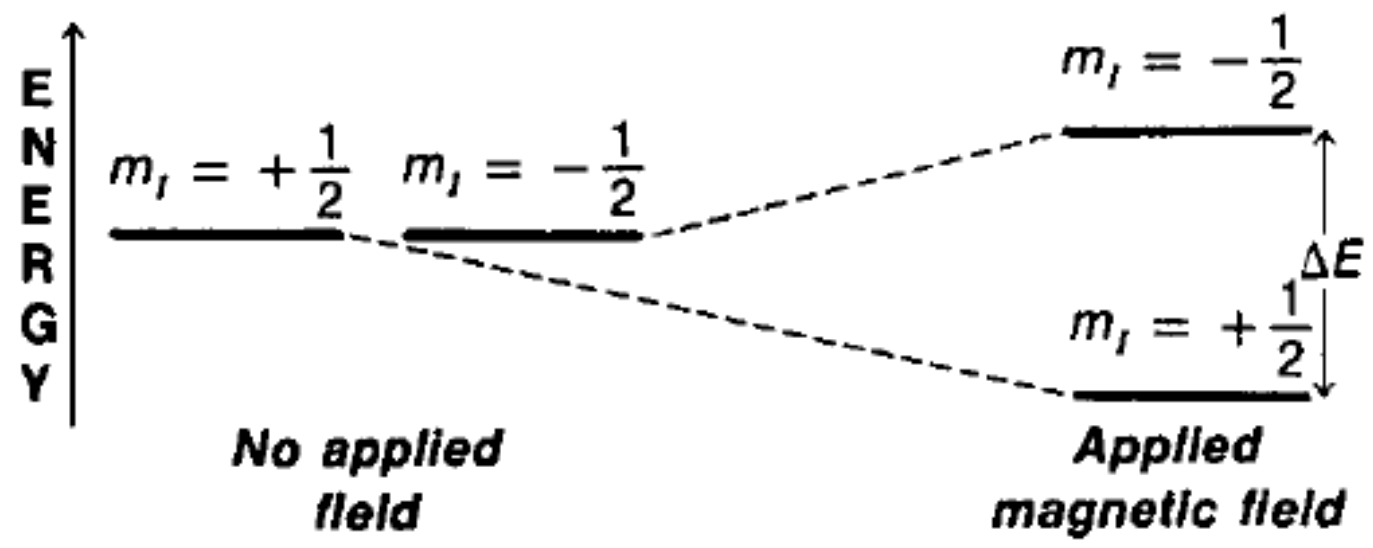
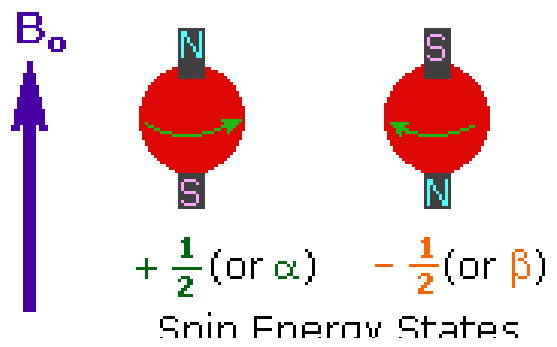
NMR

93/01/20

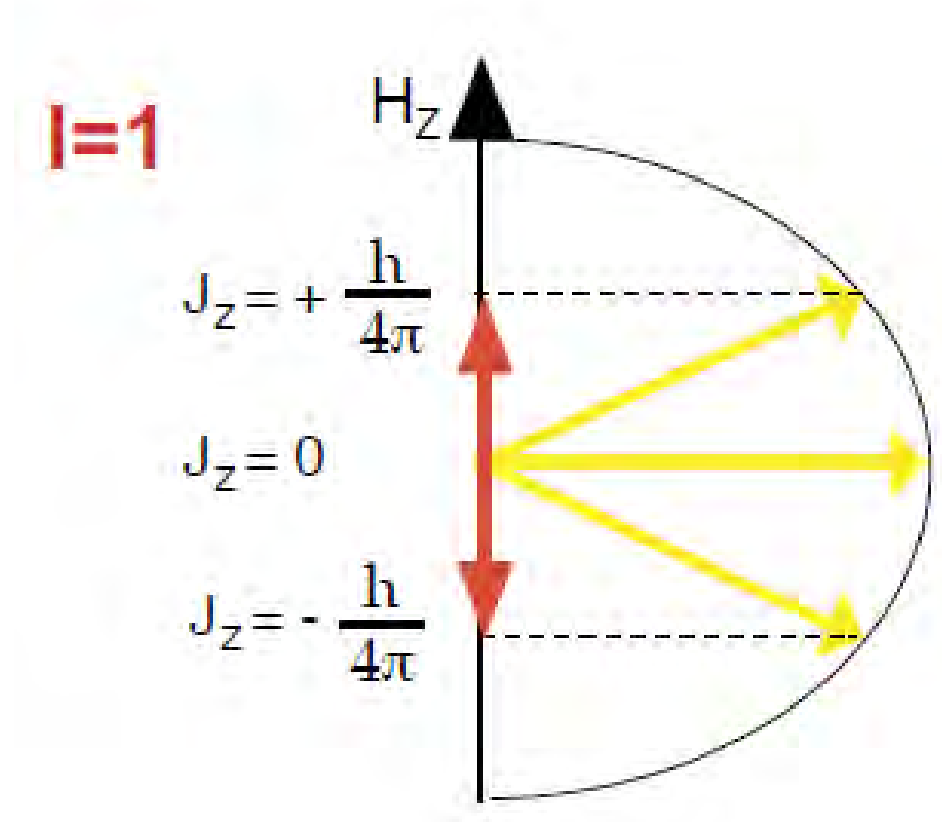
angular momentum

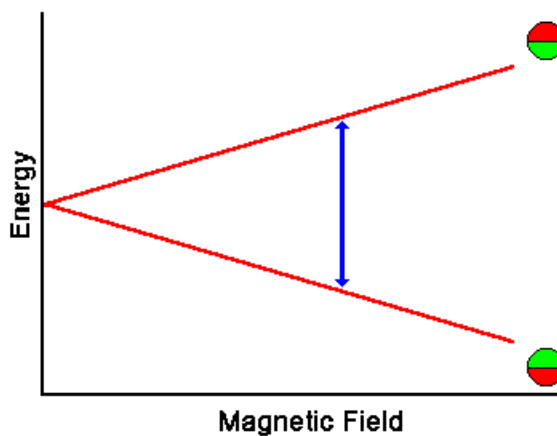
$$P = [I(I+1)]^{1/2} h/2\pi$$





- $I=1$

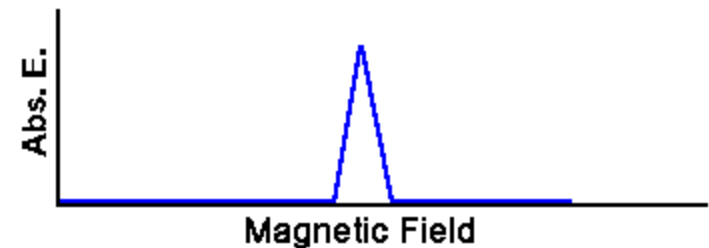
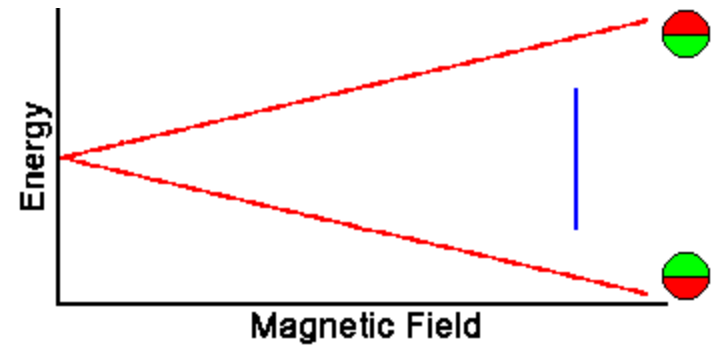




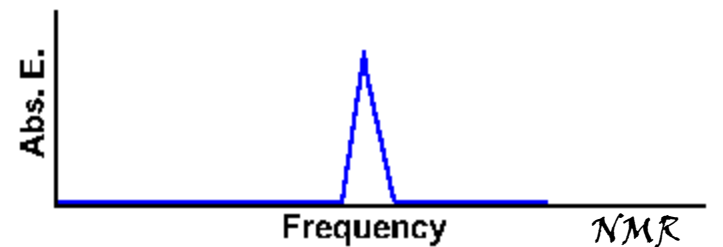
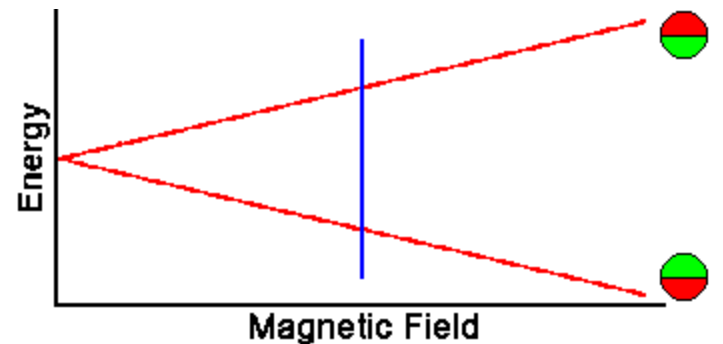
$$E = h \gamma B$$

- continuous wave (CW) NMR

A) constant frequency

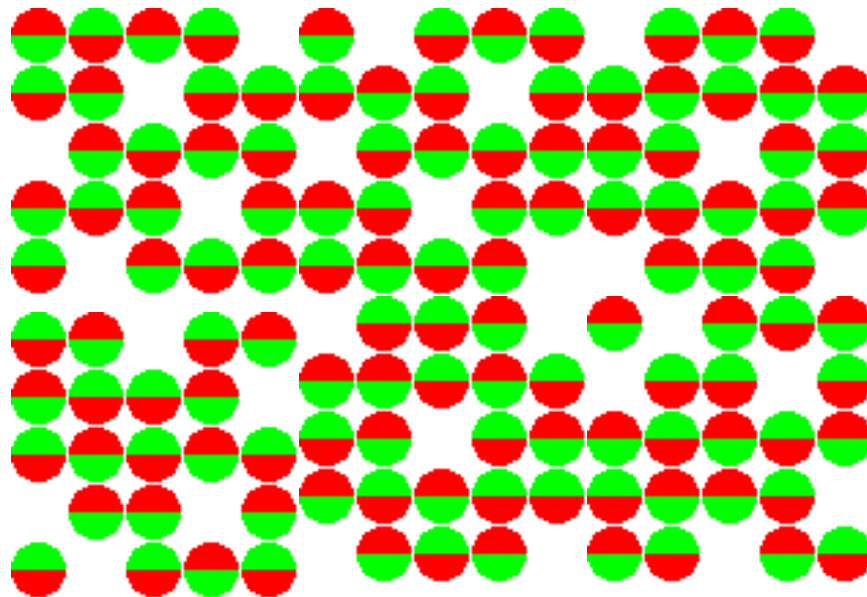


B) constant magnetic field



NMR

93/01/20



At room temperature, the number of spins in the lower energy level, N^+ , slightly outnumbers the number in the upper level, N^- . Boltzmann statistics tells us that

$$N^-/N^+ = e^{-E/kT}$$

temperature \downarrow $N^- / N^+ \downarrow$

- There is a slight excess (1,000,048 vs 1,000,000 for protons in a 300 MHz instrument) in the lower energy state

At T = 300 K and B₀ = 5.875 T (250 MHz),

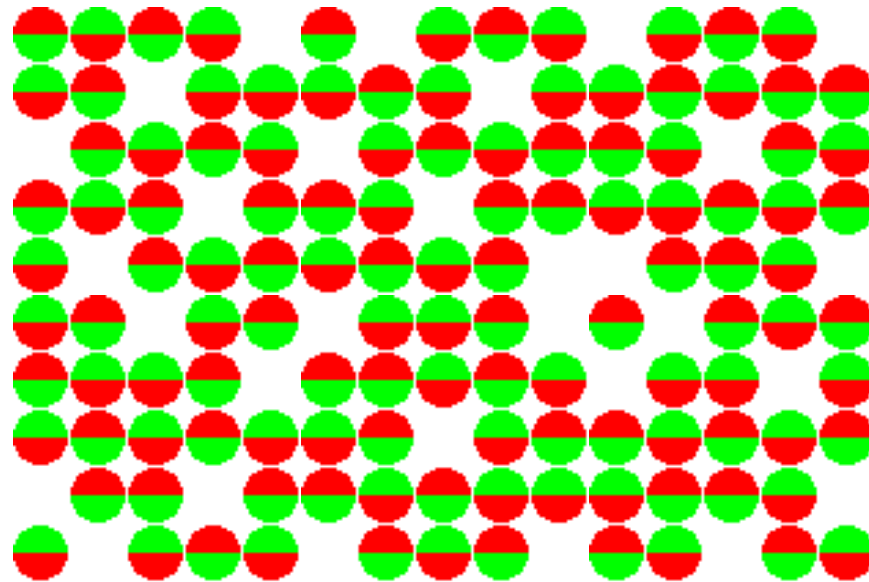
¹H:

$$\frac{N_{\beta}}{N_{\alpha}} = 1 - \frac{26.7519 \times 10^7 \times 1.0546 \times 10^{-27} \times 5.875}{1.3805 \times 10^{-16} \times 300}$$

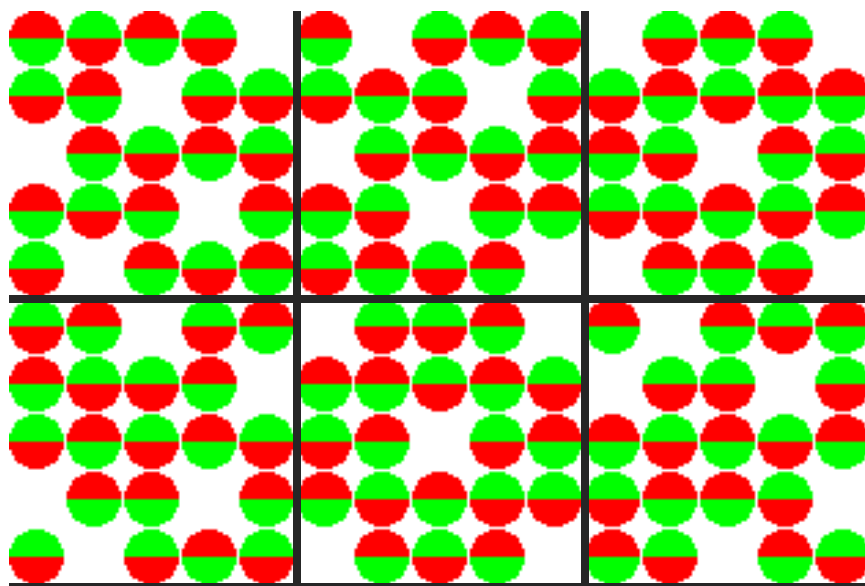
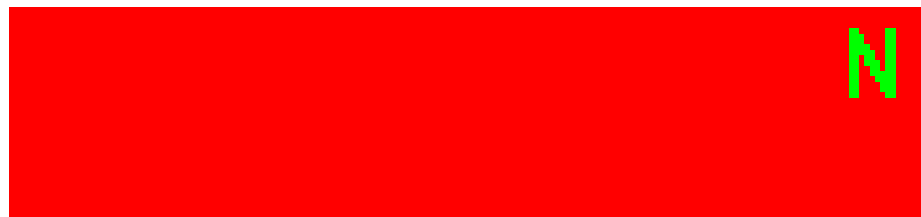
$$N_{\beta} \approx (1 - 0.00004)N_{\alpha} = 0.99996N_{\alpha}$$

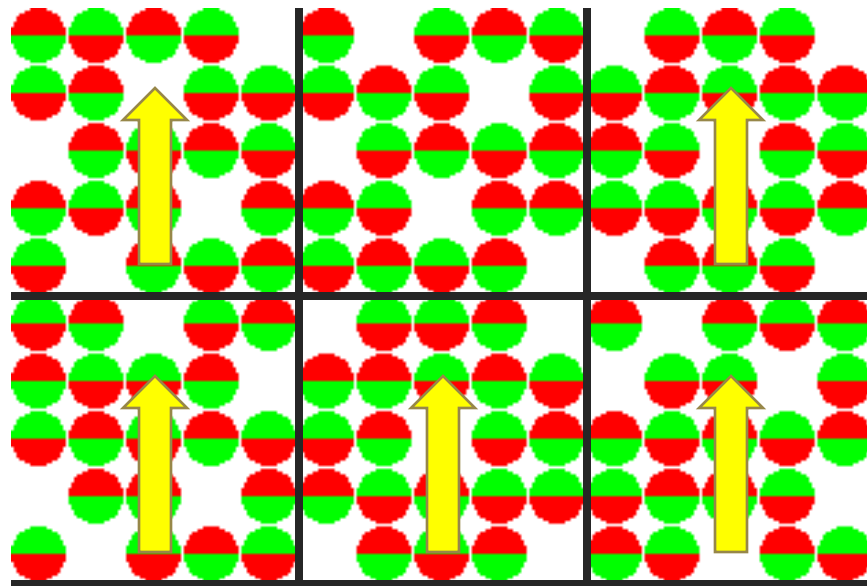
For B₀ = 18.8 T (800MHz),

$$N_{\beta} \approx 0.99987N_{\alpha}$$



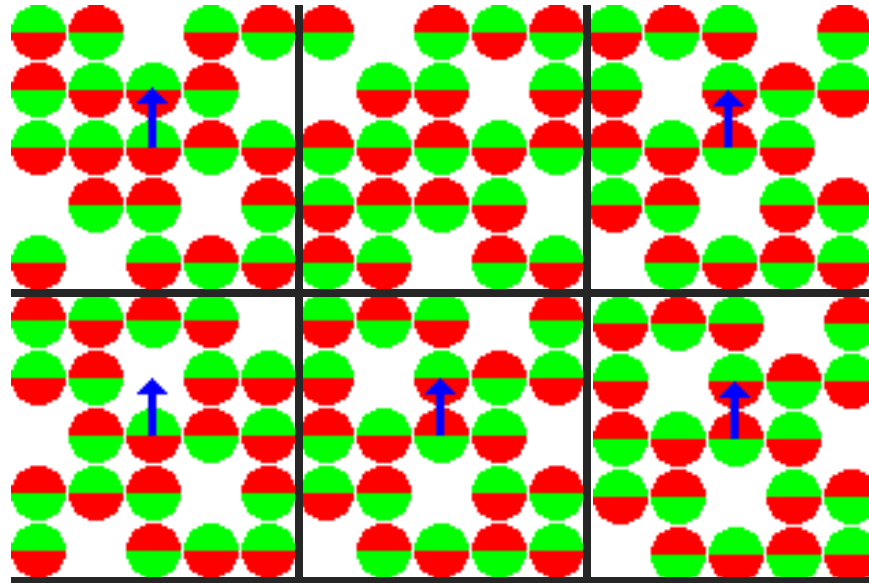
Spin Packets

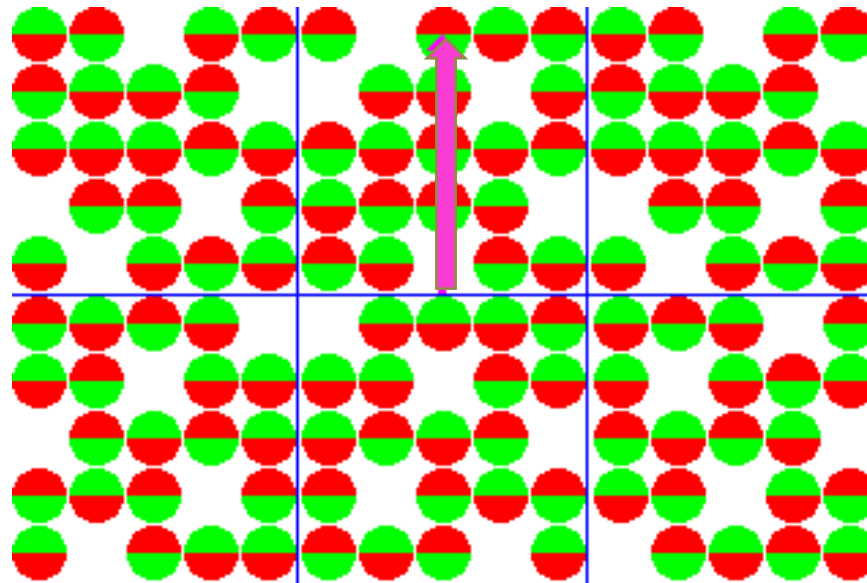


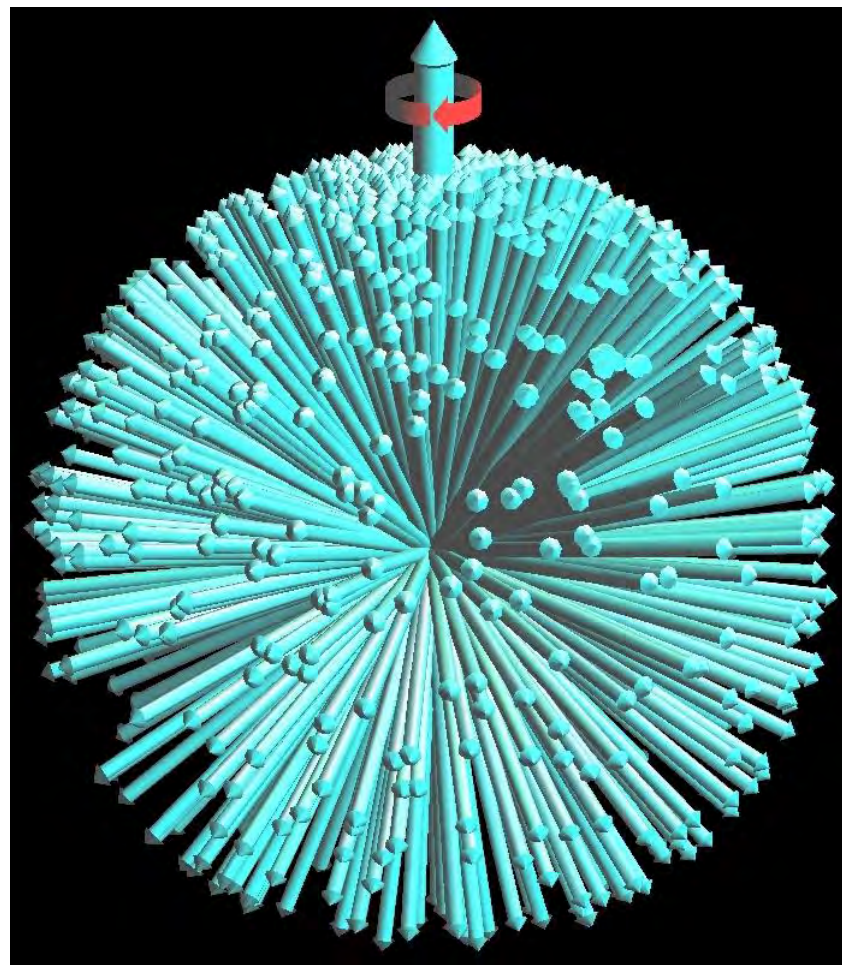
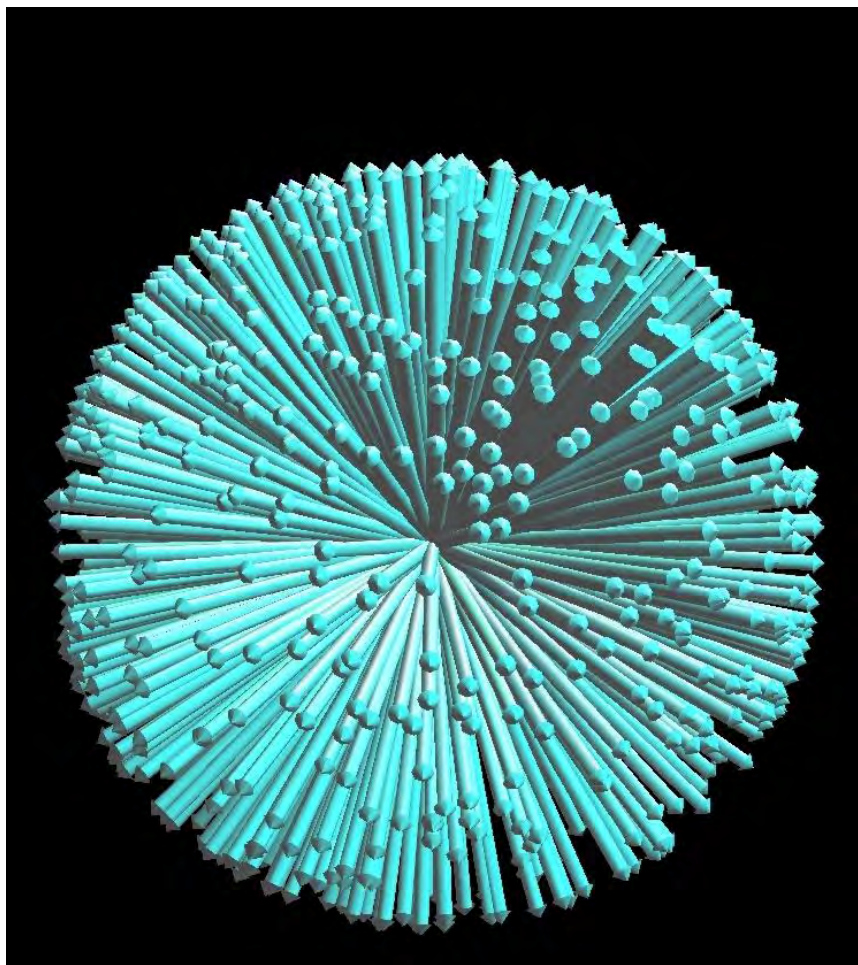


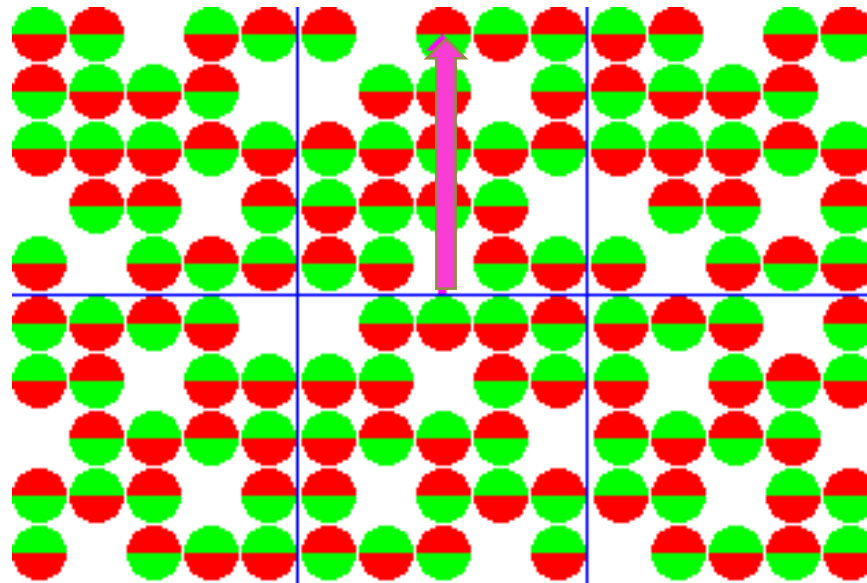


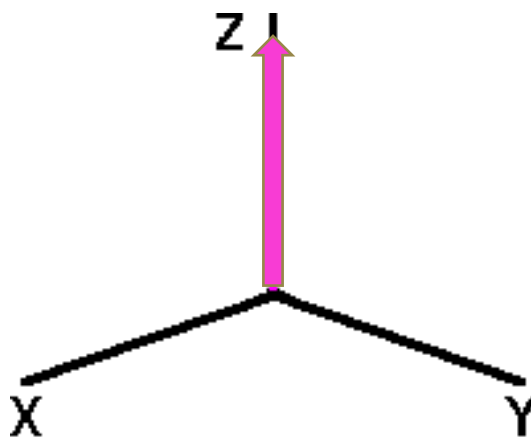
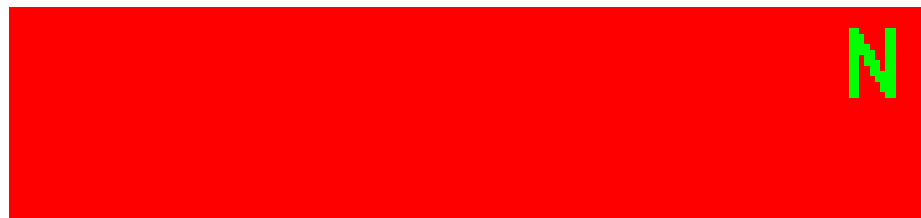
The size of each vector is proportional to $(N^+ - N^-)$.

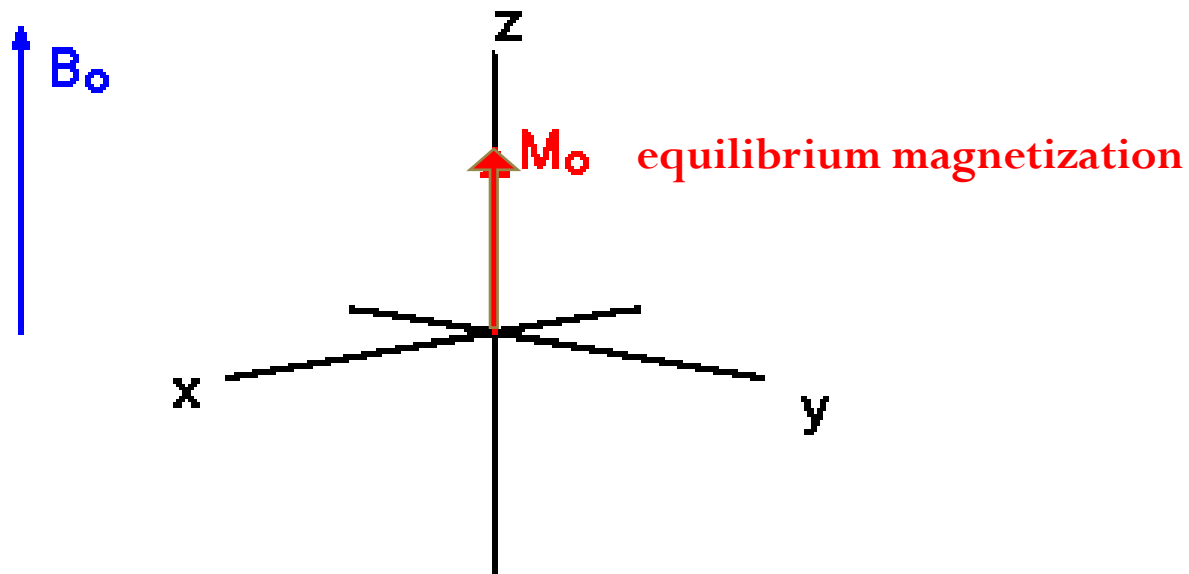




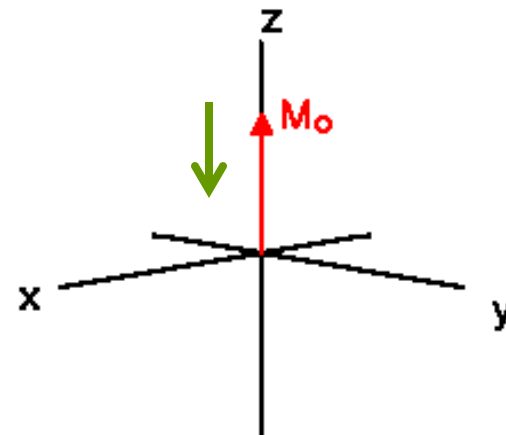
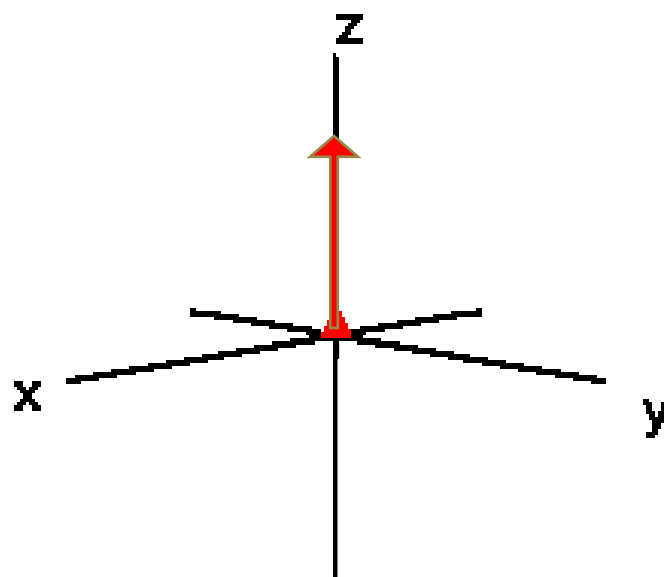






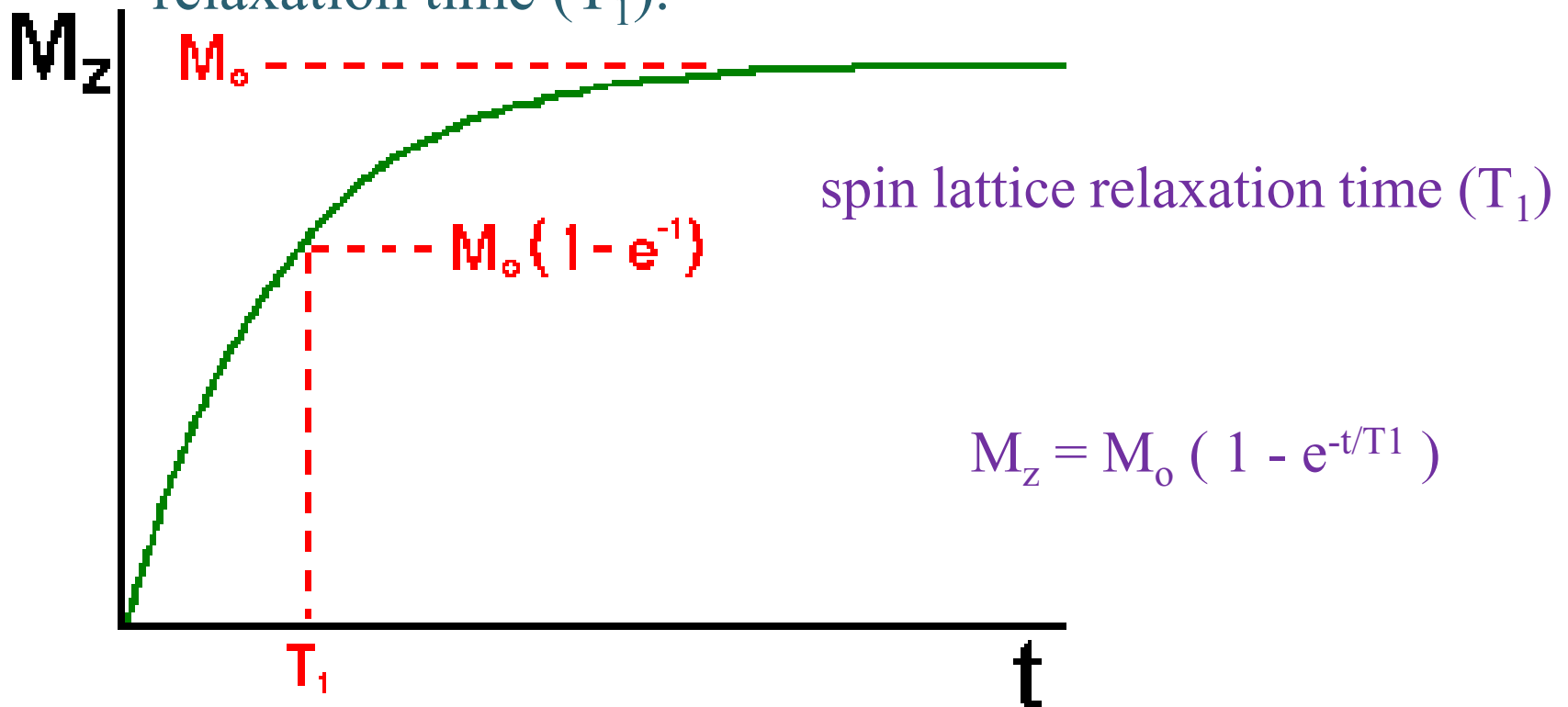


T₁ Processes

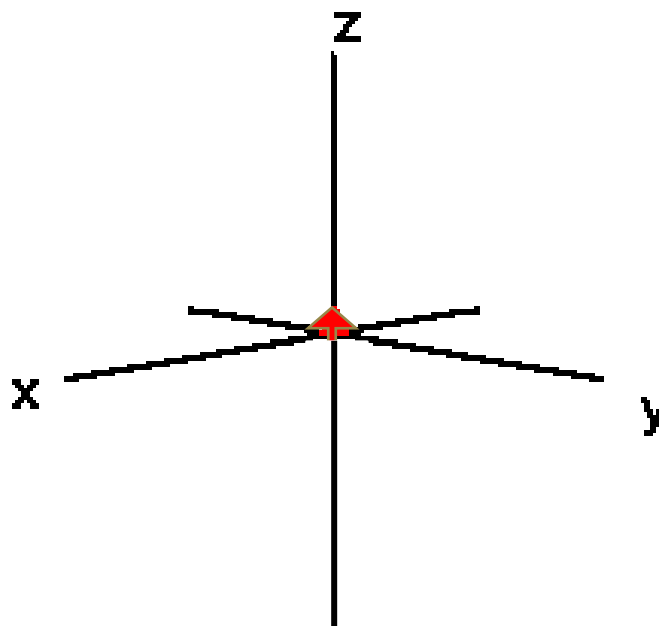
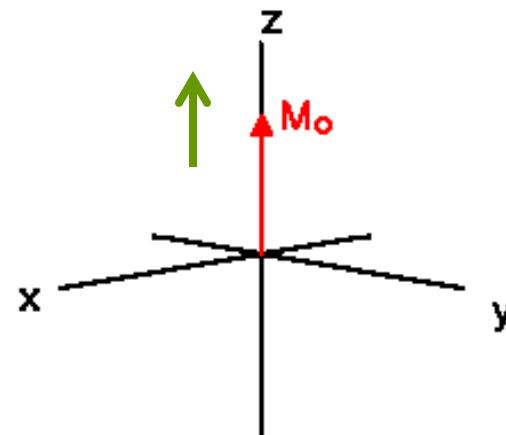


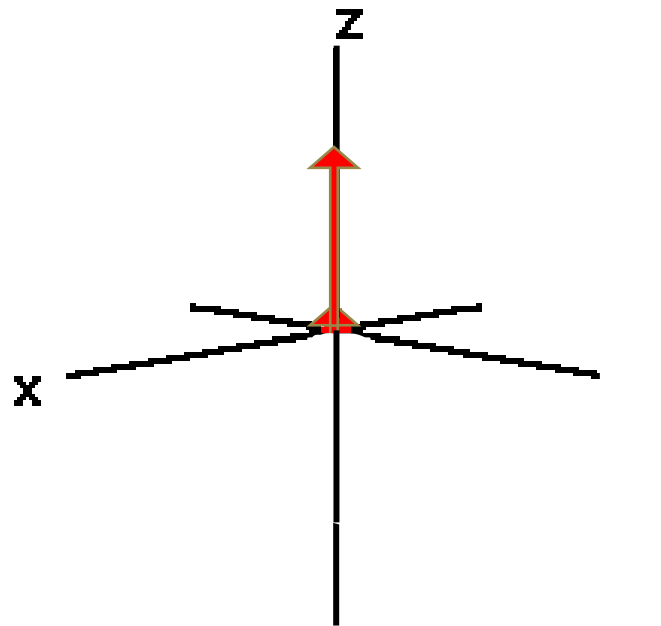
If enough energy (frequency equal to the energy difference between the spin states) is put into the system, it is possible to saturate the spin system and make $M_z=0$

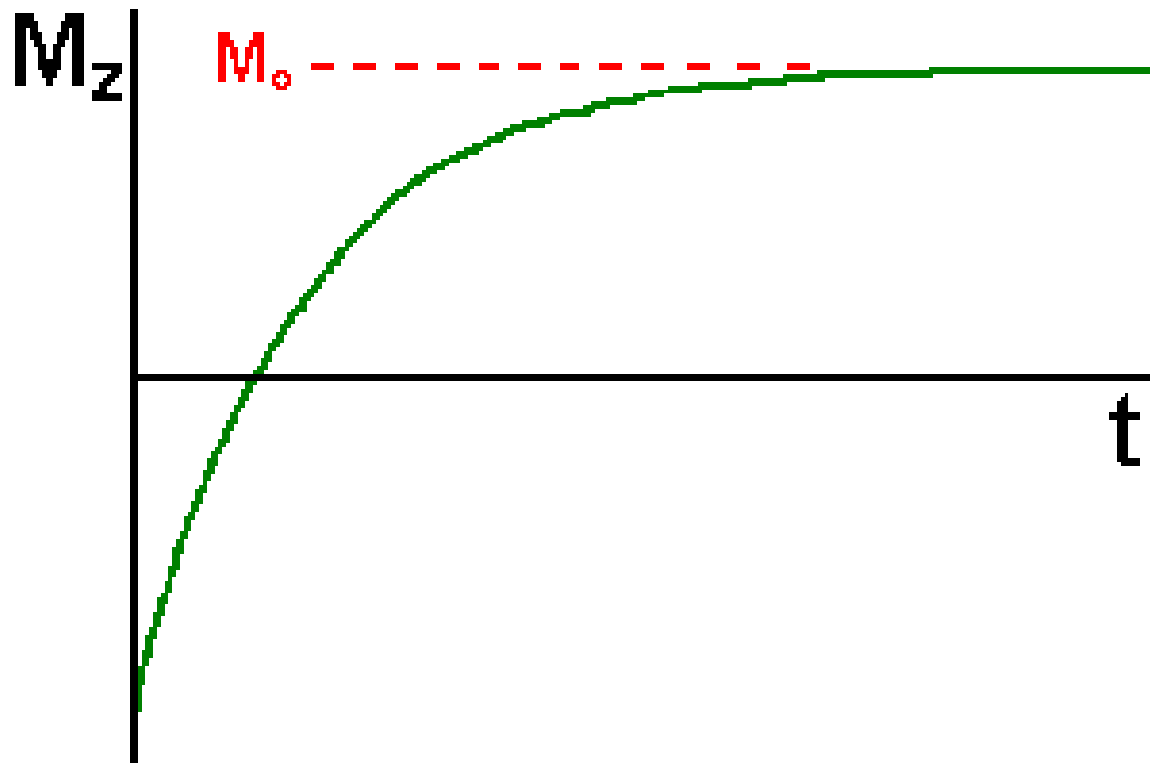
- The time duration for this process called spin lattice relaxation time (T_1).



After excitation



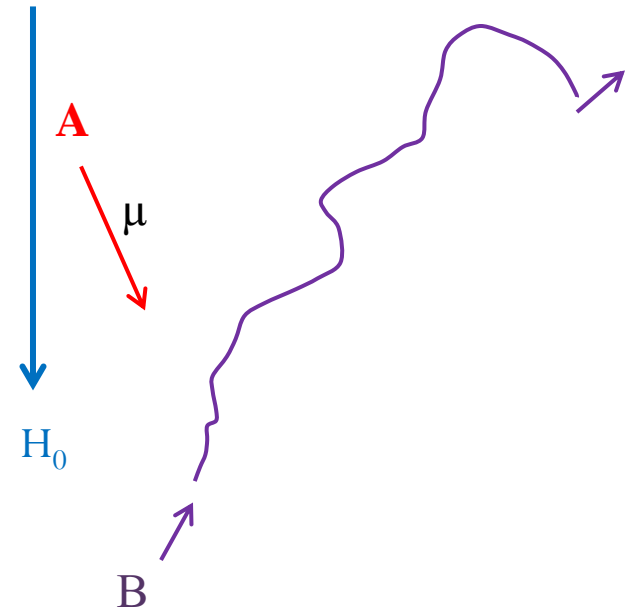




$$M_z = M_0 (1 - 2e^{-t/T_1})$$

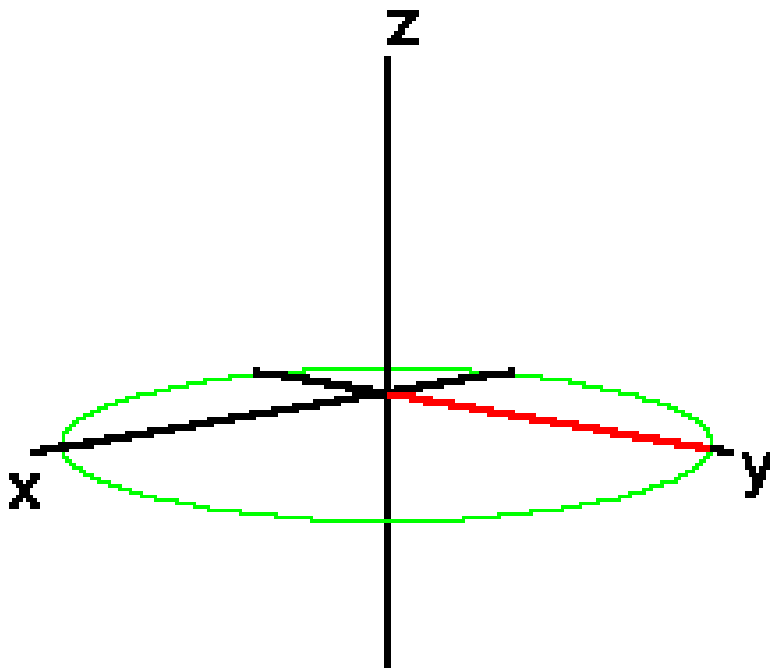
T_1 Mechanism

- T_1 relaxation is sometimes called spin-lattice relaxation.
- In this type of relaxation the energy lost as the nucleus returns to the lower energy state is transferred to the molecule in the form of heat. This means that the total number of nuclei in the excited state decreases

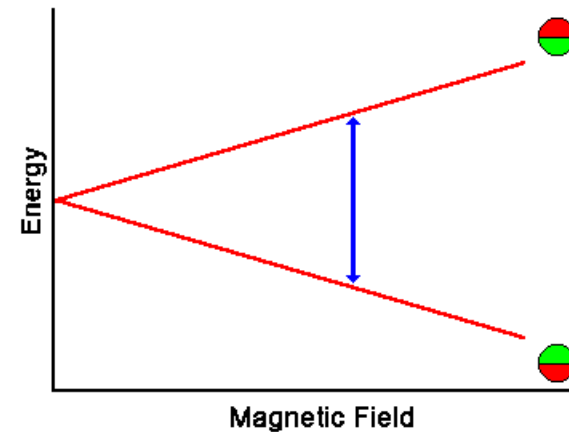


Precession

- If the net magnetization is placed in the XY plane



Larmor frequency



it will rotate about the Z axis at a frequency equal to the frequency of the photon which would cause a transition between the two energy levels of the spin. This frequency is called the Larmor frequency.

T₂ Processes

- In addition to the rotation, the net magnetization starts to dephase because each of the spin packets making it up is experiencing a slightly different magnetic field and rotates at its own Larmor frequency. The longer the elapsed time, the greater the phase difference. Here the net magnetization vector is initially along +Y. For this and all dephasing examples think of this vector as the overlap of several thinner vectors from the individual spin packets