

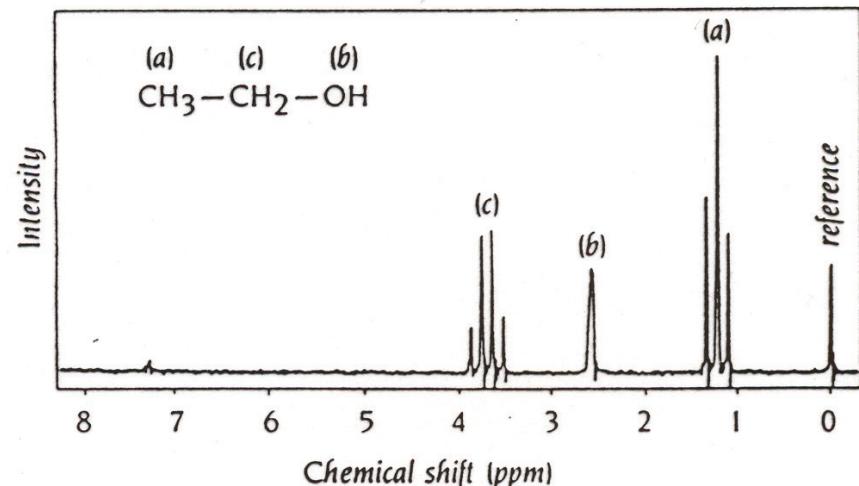
# NMR Spectroscopy:

## 1

# NMR: Sophomore Organic Chemistry

- Sophomore organic NMR:

- 1D,  $^1\text{H}$  spectra
- small organic molecules
- one signal for each type of  $^1\text{H}$
- signals split into doublets, triplet, quartets, etc., due to presence of  $^1\text{H}$  nuclei on neighboring carbon atoms ("coupling")
- frequencies ("chemical shifts") of signals determined by electron density



- This course:

- what gives rise to the signals; microscopic and macroscopic
- what determines signal frequencies, intensities and multiplicities (chemical shifts/couplings/relaxation)
- how are spectra acquired and processed (pulsed Fourier transform methods)
- how can we manipulate nuclear magnetism to get other types of information (complex pulse sequences)
- 2D methods / chemical shift correlation (COSY, TOCSY)
- the nuclear Overhauser effect (NOE, NOESY)
- etc.

# NMR Active Nuclei

- Most elements are comprised of one or more isotopes that are NMR active

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
<u>H</u>															<u>H</u>	<u>He</u>	
<u>Li</u>	<u>Be</u>													<u>B</u>	<u>C</u>	<u>N</u>	<u>O</u>
<u>Na</u>	<u>Mg</u>													<u>Al</u>	<u>Si</u>	<u>P</u>	<u>S</u>
<u>K</u>	<u>Ca</u>	<u>Sc</u>	<u>Ti</u>	<u>V</u>	<u>Cr</u>	<u>Mn</u>	<u>Fe</u>	<u>Co</u>	<u>Ni</u>	<u>Cu</u>	<u>Zn</u>	<u>Ga</u>	<u>Ge</u>	<u>As</u>	<u>Se</u>	<u>Br</u>	<u>Kr</u>
<u>Rb</u>	<u>Sr</u>	<u>Y</u>	<u>Zr</u>	<u>Nb</u>	<u>Mo</u>	<u>Tc</u>	<u>Ru</u>	<u>Rh</u>	<u>Pd</u>	<u>Ag</u>	<u>Cd</u>	<u>In</u>	<u>Sn</u>	<u>Sb</u>	<u>Te</u>	<u>I</u>	<u>Xe</u>
<u>Cs</u>	<u>Ba</u>	*	<u>Hf</u>	<u>Ta</u>	<u>W</u>	<u>Re</u>	<u>Os</u>	<u>Ir</u>	<u>Pt</u>	<u>Au</u>	<u>Hg</u>	<u>Tl</u>	<u>Pb</u>	<u>Bi</u>	<u>Po</u>	<u>At</u>	<u>Rn</u>
Fr	Ra	**	Rf	Ha	Sg	Ns	Hs	Mt									
* <u>La</u> <u>Ce</u> <u>Pr</u> <u>Nd</u> <u>Pm</u> <u>Sm</u> <u>Eu</u> <u>Gd</u> <u>Tb</u> <u>Dy</u> <u>Ho</u> <u>Er</u> <u>Tm</u> <u>Yb</u> <u>Lu</u>																	
** <u>Ac</u> <u>Th</u> <u>Pa</u> <u>U</u> <u>Np</u> <u>Pu</u> <u>Am</u> <u>Cm</u> <u>Bk</u> <u>Cf</u> <u>Es</u> <u>Fm</u> <u>Md</u> <u>No</u> <u>Lr</u>																	

<http://bouman.chem.georgetown.edu/NMRpt/NMRpertbl.html>

# Spin and Spin Angular Momentum

- Classical Angular Momentum

- any rotating macroscopic object possesses angular momentum

- Quantum Angular Momentum

- any rotating system (molecule) possesses angular momentum

- the set of stable rotational states leads to quantized angular momentum

$$L = \hbar \times \sqrt{J(J+1)} \quad \hbar = \text{Planck's constant } (\sim 6.6 \times 10^{-34} \text{ Js})/2\pi$$

- $J$  is integral (0,1,2...)

- angular momentum depends on the molecular rotational state

- angular momentum depends on rate of rotation

- Spin Angular Momentum

- spin is a quantum mechanical concept/phenomenon...there is no good classical analogy

- spin is also a form of angular momentum

- it is *not*, however, produced by rotation of the particle, but is an intrinsic property of the particle

- nuclear magnetism is a manifestation of nuclear spin angular momentum

# Angular Momentum and Nuclear Magnetism

- NMR is a manifestation of nuclear spin angular momentum ( $\mathbf{P}$ )
  - spin angular momentum is **quantized**
  - spin (spin angular momentum) is an intrinsic property of a particle

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

$I$  = angular momentum quantum number = nuclear spin

$\hbar$  = Planck's constant/ $2\pi$  =  $h/2\pi$        $h \approx 6.6 \times 10^{-34} \text{ Js}$

- $I$  can be 0, integral or half-integral
  - $I$  is zero for elements of even mass number (A) and even atomic number (Z)
  - $I$  is integral (nonzero) when A is even and Z is odd
  - $I$  is half-integral when A is odd
- NMR behavior
  - $I = 0$ , **NMR inactive**; examples  $^{12}_6\text{C}$  and  $^{16}_8\text{O}$ , unfortunately
    - these nuclei have no magnetic moment (see below) and are not NMR active
  - $I > 1/2$ , **quadrupolar nuclei**: examples  $^{14}_7\text{N}$ 
    - these nuclei possess an electric quadrupole moment due to non-spherical nuclear charge distribution (short magnetic state life times, broad line widths, complex spectra)
  - $I = 1/2$ , “**spin 1/2**” nuclei: examples  $^1_1\text{H}$ ,  $^{13}_6\text{C}$ ,  $^{15}_7\text{N}$ ,  $^{31}_{15}\text{P}$ ,  $^{19}_9\text{F}$ 
    - these are the mainstay nuclei for organic chemistry and biochemistry

# Nuclei and their Properties

- some nuclear properties important for NMR spectroscopy

Nuclide	Spin <i>I</i>	Electric quadrupole moment <sup>a)</sup> [ <i>eQ</i> ] [ $10^{-28}$ m <sup>2</sup> ]	Natural abundance) [%]	Relative sensitivity <sup>b)</sup>	Gyromagnetic ratio $\gamma^a)$ [ $10^7$ rad T <sup>-1</sup> s <sup>-1</sup> ]	NMR frequency [MHz] <sup>b)</sup> ( $B_0 = 2.3488$ T)
<sup>1</sup> H	1/2	–	99.985	1.00	26.7519	100.0
<sup>2</sup> H	1	$2.87 \times 10^{-3}$	0.015	$9.65 \times 10^3$	4.1066	15.351
<sup>3</sup> H <sup>c)</sup>	1/2	–	–	1.21	28.5350	106.664
<sup>6</sup> Li	1	$-6.4 \times 10^{-4}$	7.42	$8.5 \times 10^{-3}$	3.9371	14.716
<sup>10</sup> B	3	$8.5 \times 10^{-2}$	19.58	$1.99 \times 10^{-2}$	2.8747	10.746
<sup>11</sup> B	3/2	$4.1 \times 10^{-2}$	80.42	0.17	8.5847	32.084
<sup>12</sup> C	0	–	98.9	–	–	–
<sup>13</sup> C	1/2	–	1.108	$1.59 \times 10^{-2}$	6.7283	25.144
<sup>14</sup> N	1	$1.67 \times 10^{-2}$	99.63	$1.01 \times 10^{-3}$	1.9338	7.224
<sup>15</sup> N	1/2	–	0.37	$1.04 \times 10^{-3}$	-2.7126	10.133
<sup>16</sup> O	0	–	99.96	–	–	–
<sup>17</sup> O	5/2	$-2.6 \times 10^{-2}$	0.037	$2.91 \times 10^{-2}$	-3.6280	13.557
<sup>19</sup> F	1/2	–	100	0.83	25.1815	94.077
<sup>23</sup> Na	3/2	0.1	100	$9.25 \times 10^{-2}$	7.0704	26.451
<sup>25</sup> Mg	5/2	0.22	10.13	$2.67 \times 10^{-3}$	-1.6389	6.1195
<sup>29</sup> Si	1/2	–	4.70	$7.84 \times 10^{-3}$	-5.3190	19.865
<sup>31</sup> P	1/2	–	100	$6.63 \times 10^{-2}$	10.8394	40.481
<sup>39</sup> K	3/2	$5.5 \times 10^{-2}$	93.1	$5.08 \times 10^{-4}$	1.2499	4.667
<sup>43</sup> Ca	7/2	$-5.0 \times 10^{-2}$	0.145	$6.40 \times 10^{-3}$	-1.8028	6.728
<sup>57</sup> Fe	1/2	–	2.19	$3.37 \times 10^{-5}$	0.8687	3.231
<sup>59</sup> Co	7/2	0.42	100	0.28	6.3015	23.614
<sup>119</sup> Sn	1/2	–	8.58	$5.18 \times 10^{-2}$	-10.0318	37.272
<sup>133</sup> Cs	7/2	$-3.0 \times 10^{-3}$	100	$4.74 \times 10^{-2}$	3.5339	13.117
<sup>195</sup> Pt	1/2	–	33.8	$9.94 \times 10^{-3}$	5.8383	21.499

# Magnetic Moment

- The angular momentum  $\mathbf{P}$  has associated with it a magnetic (dipole) moment ( $\boldsymbol{\mu}$ )

$$\boldsymbol{\mu} = \gamma \mathbf{P}$$

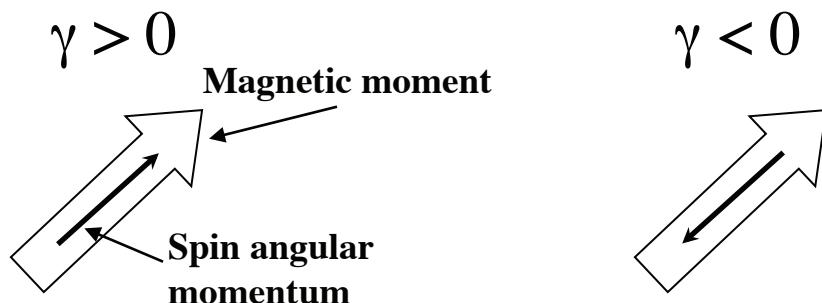
- The  $\boldsymbol{\mu}$  for the electron is well understood (predicted value from Dirac's integration of relativity and quantum mechanics, and in agreement to 11 significant figures with measured value). For nuclei  $\boldsymbol{\mu}$  no so well understood.
- we can combine the above equation and that for the angular momentum to obtain the following:

$$\boldsymbol{\mu} = \hbar \gamma \times \sqrt{I(I+1)}$$

- nuclei with non-zero spin angular momentum have an associated magnetic moment
- if  $I = 0$ , no magnetic moment: these nuclei are not NMR active
- the constant  $\gamma$  is the proportionality constant between  $\mathbf{P}$  and  $\boldsymbol{\mu}$ , and is called the **gyromagnetic ratio** (or magnetogyric ratio)
- $\gamma$  is a constant for a given nucleus

# Magnetic Moment

- $\mu$  and  $P$  usually have the same sign, so  $\gamma$  is positive  
-there are exceptions ( $^{15}\text{N}$ ,  $^{29}\text{Si}$ ,  $^{119}\text{Sn}$ , the electron)



- $\mu$  and  $P$  in diamagnetic materials, electron spin pairing cancels (to a good approximation) the electron magnetism
  - paramagnetic and ferromagnetic material magnetism is due to the unpaired electron spins

# Directional Quantization of Angular Momentum

- The angular momentum for a nucleus with angular momentum  $P$  and magnetic moment  $\mu$  in a static magnetic field that we will designate  $B_0$  will be oriented directionally
  - the  $z$  component (projection),  $P_z$ , will be an integral or half-integral of  $\hbar$ :

$$P_z = m\hbar$$

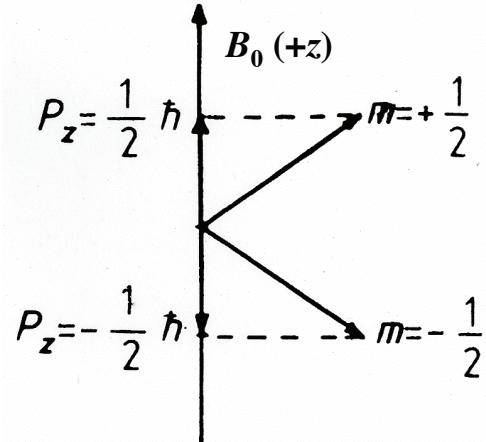
- $m$  is the **magnetic quantum number** (or directional quantum number)

$$m = I, I-1, \dots, -I$$

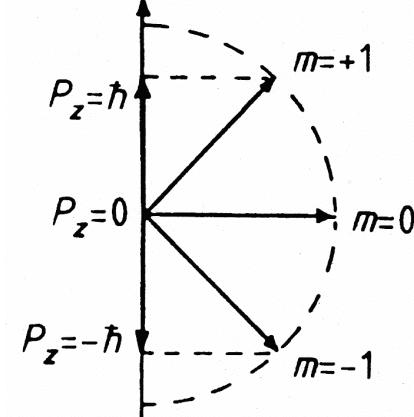
- therefore, there are  $(2I+1)$  values for  $m$ , and  $(2I+1)$  possible orientations for the angular momentum

$I=1/2: m=+1/2 \text{ and } -1/2$

NOTE: by convention, the static magnetic field,  $B_0$ , is pointed along the  $+z$  axis



$I=1: m=+1, 0, \text{ and } -1$

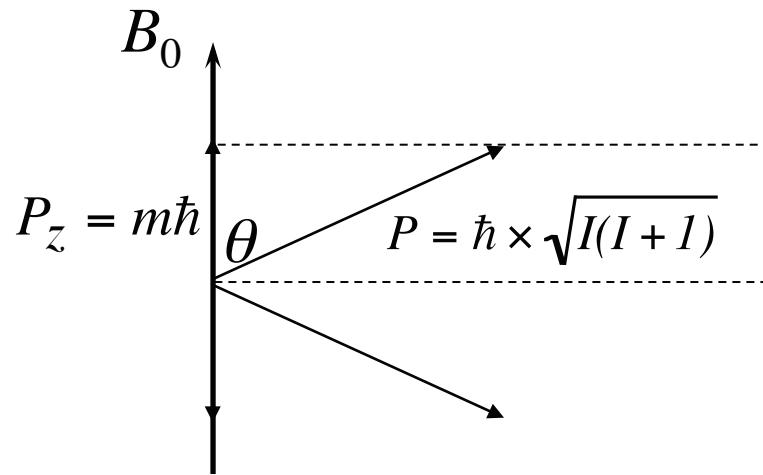


- thus, we know the components of the magnetic moment along  $z$

$$\mu_z = \gamma P_z = m \gamma \hbar$$

# Directional Quantization of Angular Momentum

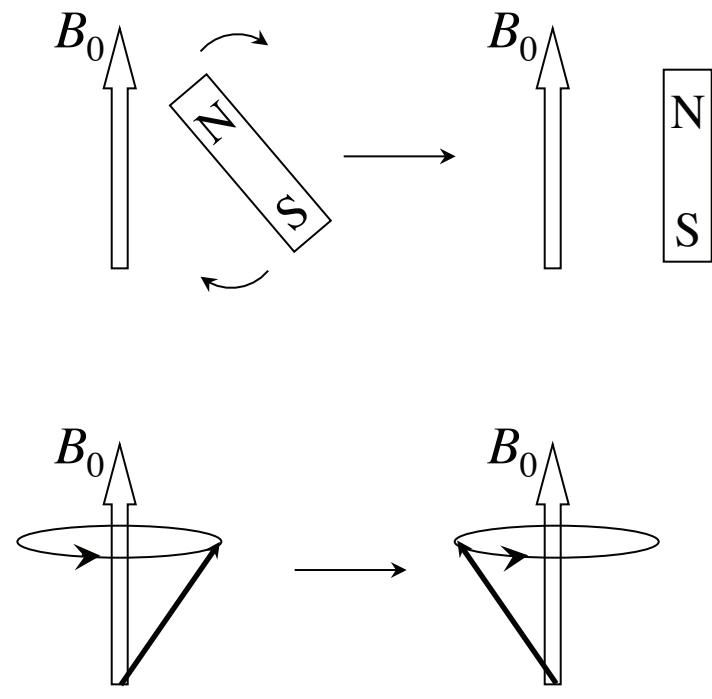
- directional quantization dictates orientation



- for  $m = 1/2$ ,  $\cos\theta = \frac{m\hbar}{\hbar\sqrt{I(I+1)}} = \frac{1/2}{\sqrt{3/4}}$        $\theta = 54.7^\circ$

# Precession

- In the absence of a magnetic field, the distribution of magnetic moments of an ensemble of nuclei is *isotropic* (all possible orientations represented)
- In a static magnetic field, nuclear magnetic (dipole) moments *precess* about the applied field
  - nuclear spins behave this way because of their angular momenta
  - the applied field,  $B_0$ , is almost always assumed to be applied in the  $+z$  direction

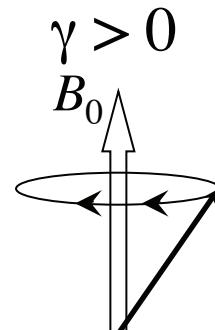
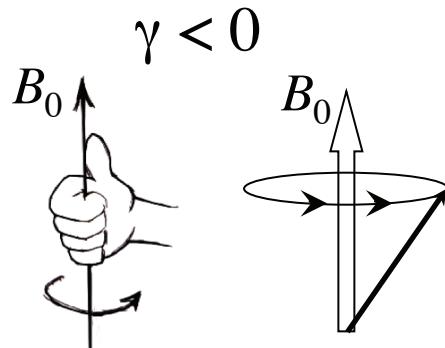
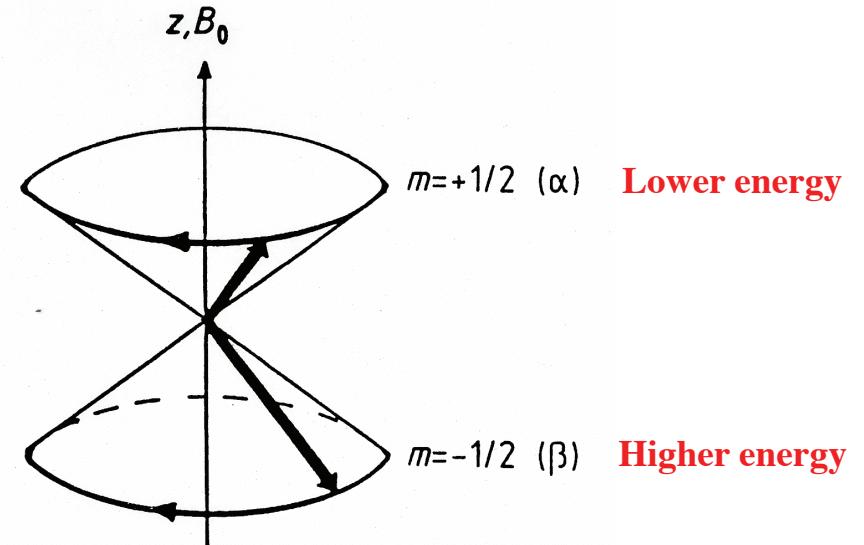
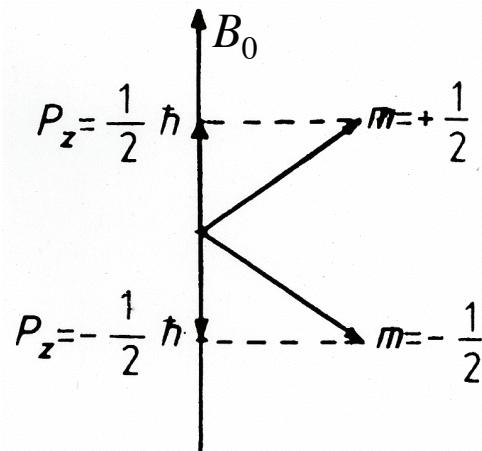


- Put a bar magnet in a magnetic field and it rotates to minimize the energy
- Put a nuclear spin in a magnetic field, and the torque on the magnetic moment (angular momentum) imposed by the field causes the nuclear dipoles/magnetic moments to move around the field ( $B_0$ ) on a cone with a constant angle between the moment and the field (*precession* or *Larmor precession*)
- The dipoles/moments are said to *precess* about  $B_0$

# Precession

- The direction (clockwise or counterclockwise) of precession is dependent on the sign of  $\gamma$
- The angle of precession is also fixed as a result of the directional quantization  
-for  ${}^1\text{H}$ , with  $I = 1/2$ , this angle is  $54.7^\circ$

$I=1/2: m=+1/2$  and  $-1/2$



# Precession

- The rate of precession is dependent on  $\gamma$  and  $B_0$ , and is termed the **Larmor frequency** ( $\nu_L$ ) for the particular nucleus:

$$\omega_0 = -\gamma B_0 \text{ (radians/sec)} \quad \nu_L = \omega_0 / (2\pi) = -\frac{\gamma B_0}{2\pi} \text{ (Hertz or cycles/sec)}$$

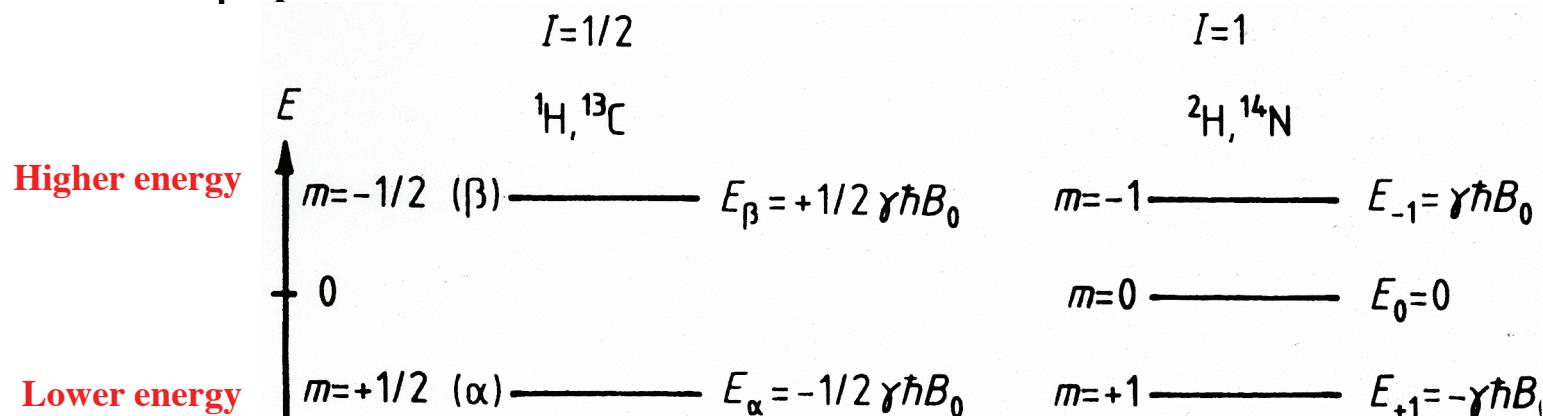
- For positive  $\gamma$ , the Larmor frequency is negative
- Frequency directly proportional to field strength ( $B_0$ )
  - magnetic field strengths are often designated in terms of the Larmor frequency of a particular nucleus ( $^1\text{H}$ ) at that field strength

# Nuclear Energy Levels in a Static Magnetic Field

- In the absence of a static, external magnetic field, the  $2I+1$  states, the **spin states**, of a nucleus, are energetically equivalent or **degenerate**
- In the presence of the magnetic field, the energies of the spin states are no longer degenerate - this is called the **Zeeman effect**  
-in the presence of a static, external magnetic field,  $B_0$ , the energies of the spin states are:

$$E = -\mu_z B_0 = -m\gamma\hbar B_0 \quad (\text{remember, } \mu_z = m\gamma\hbar)$$

- Thus, the  $(2I+1)$  states give rise to  $(2I+1)$  energy levels, or **nuclear Zeeman levels**
  - for  $I = 1/2$  ( $^1\text{H}$ ,  $^{13}\text{C}$ ),  $m = +1/2$  and  $m = -1/2$ :
  - for  $m = +1/2$ ,  $\mu_z$  is parallel to the static external field ( $B_0$ ) direction, and is lower energy
  - for  $m = -1/2$ ,  $\mu_z$  is antiparallel to  $B_0$ , and is higher energy
- in quantum mechanics, for  $I = 1/2$ ,  $m = +1/2$  is the  **$\alpha$  spin state** ( $\alpha$  spin), and  $m = -1/2$  is the  **$\beta$  spin state**

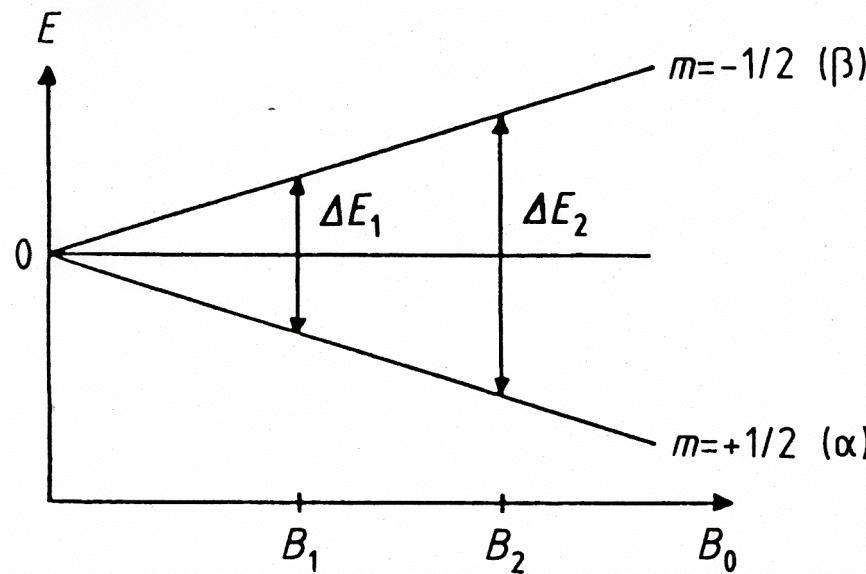


# Nuclear Energy Levels in a Static Magnetic Field

- The  $2I+1$  energy levels are equally spaced, and the energy difference between any two adjacent energy levels is given by the following:

$$\Delta E = \gamma \hbar B_0$$

- The energy difference is linearly dependent on  $\gamma$  and on  $B_0$



# Energy Level Populations

- At thermal equilibrium the energy difference between  $\alpha$  and  $\beta$  states prevents these states from being equally populated
- The relative population of a particular state is given by the Boltzman distribution:

$$\frac{N_m}{N} = \frac{\exp\left(\frac{-E_m}{k_B T}\right)}{\sum_{m=-I}^I \exp\left(\frac{-E_m}{k_B T}\right)} = \frac{\exp\left(\frac{m\hbar\gamma B_0}{k_B T}\right)}{\sum_{m=-I}^I \exp\left(\frac{m\hbar\gamma B_0}{k_B T}\right)}$$

*In our case,  $E_m = -m\gamma\hbar B_0$*

$N_m$  = number of nuclei in the  $m^{\text{th}}$  state

$N$  = total number of spins (nuclei)

$k_B$  = Boltzman constant

$T$  = temperature (Kelvin)

- Near 273 °K,  $m\gamma\hbar B_0/k_B T \ll 1$ , and the exponential functions can be expanded to first order using a Taylor series:

$$\frac{N_m}{N} \approx \frac{\left(1 + \frac{m\hbar\gamma B_0}{k_B T}\right)}{\sum_{m=-I}^I \left(1 + \frac{m\hbar\gamma B_0}{k_B T}\right)} \approx \frac{\left(1 + \frac{m\hbar\gamma B_0}{k_B T}\right)}{(2I+1)}$$

- The relative population of a given state is dependent on  $\gamma$  and on  $B_0$

# Energy Level Populations

- For spin 1/2 nuclei, at thermal equilibrium the energy difference between  $\alpha$  and  $\beta$  states prevents these states from being equally populated
- The ratio of the populations of the spin states follows from Boltzman statistics:

$$\frac{N_\beta}{N_\alpha} = \exp\left(\frac{-\Delta E_m}{k_B T}\right) \approx 1 - \left(\frac{\Delta E}{k_B T}\right) \approx 1 - \left(\frac{\gamma \hbar B_0}{k_B T}\right)$$

$N_\alpha$  = number of nuclei in the  $\alpha$  state  
 $N_\beta$  = number of nuclei in the  $\beta$  state  
 $k_B$  = Boltzman constant  
T = temperature (Kelvin)

**Example:** Calculate the ration of  $\alpha$  to  $\beta$  spins at 300 °K for  $^1\text{H}$  nuclei at a  $B_0$  field strengths of 5.875 Tesla (250 MHz) and 18.8 Tesla (800 MHz).

$$\gamma(^1\text{H}) = 26.7529 \times 10^7 \text{ Hz/T}, k_B = 1.3805 \times 10^{-16} \text{ erg/}^\circ\text{K}, \hbar = 1.0546 \times 10^{-27} \text{ erg S}$$

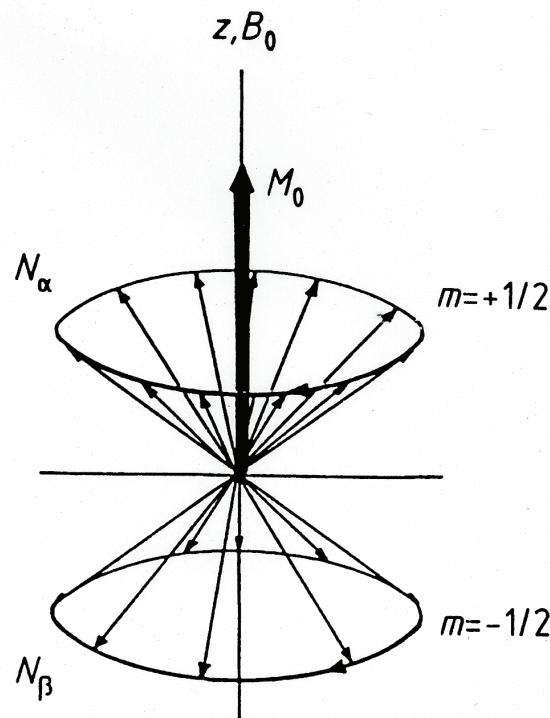
$$\frac{N_\beta}{N_\alpha} = 1 - \frac{26.7519 \times 10^7 \times 1.0546 \times 10^{-27} \times 5.875}{1.3805 \times 10^{-16} \times 300} = 0.99996$$

$$\frac{N_\beta}{N_\alpha} = 1 - \frac{26.7519 \times 10^7 \times 1.0546 \times 10^{-27} \times 18.8}{1.3805 \times 10^{-16} \times 300} = 0.99987$$

- Because  $\Delta E$  is small, the populations of the  $\alpha$  and  $\beta$  states are nearly equal
- The difference in the numbers is in parts per million (ppm)
- *NMR is insensitive !!!*

# Macroscopic Magnetization

- For spin 1/2 nuclei, at thermal equilibrium the energy difference between  $\alpha$  and  $\beta$  states prevents these states from being equally populated
  - slightly more spins are in the lower energy  $\alpha$  state than in the  $\beta$  state
  - addition of the  $z$  components of all of the nuclear magnetic (dipole) moments gives a **bulk, or net, magnetization vector**,  $M_0$ , pointed along  $+z$  (parallel with  $B_0$ , since the number of  $\alpha$  spins is larger than the number of  $\beta$  spins)



- At thermal equilibrium, all of the spins/dipoles have components in the  $x$ - $y$  plane (the *transverse* plane), but the dipoles are randomly distributed around the  $z$  axis, so no *net* magnetization exists in the transverse plane (in either the  $x$  or  $y$  direction)

**Lower energy**

$$\frac{N_\beta}{N_\alpha} = \exp\left(\frac{-\Delta E_m}{k_B T}\right) \approx 1 - \left(\frac{\Delta E}{k_B T}\right) \approx 1 - \left(\frac{\gamma \hbar B_0}{k_B T}\right)$$

**Higher energy**

# Macroscopic Magnetization

- What is the magnitude of  $M_0$ ? On what does it depend?

-summing the  $z$  components of all of the nuclear magnetic (dipole) moments gives  $M_0$ :

$$M_0 = \gamma\hbar \sum_{m=-I}^I m N_m \quad (\text{remember, } \mu_z = m\gamma\hbar)$$

-we also recall the following:

$$N_m = N \exp\left(\frac{-E_m}{k_B T}\right) / \left( \sum_{m=-I}^I \exp\left(\frac{-E_m}{k_B T}\right) \right) \approx \left(1 + \frac{m\hbar\gamma B_0}{k_B T}\right) / \sum_{m=-I}^I \left(1 + \frac{m\hbar\gamma B_0}{k_B T}\right)$$

-a little arithmetic and we find the following:

$$M_0 \approx N\gamma\hbar \sum_{m=-I}^I m \exp(m\gamma\hbar B_0 / k_B T) / \sum_{m=-I}^I \exp(m\gamma\hbar B_0 / k_B T)$$

$$M_0 \approx N\gamma\hbar \sum_{m=-I}^I m \left(1 + \frac{m\hbar\gamma B_0}{k_B T}\right) / \sum_{m=-I}^I \left(1 + \frac{m\hbar\gamma B_0}{k_B T}\right)$$

$$M_0 \approx \frac{N\gamma^2\hbar^2B_0}{k_B T(2I+1)} \sum_{m=-I}^I m^2 \approx \frac{N\gamma^2\hbar^2B_0 I(I+1)}{3k_B T}$$

$$\sum_{m=-I}^I \left(1 + \frac{m\hbar\gamma B_0}{k_B T}\right) = (2I+1)$$

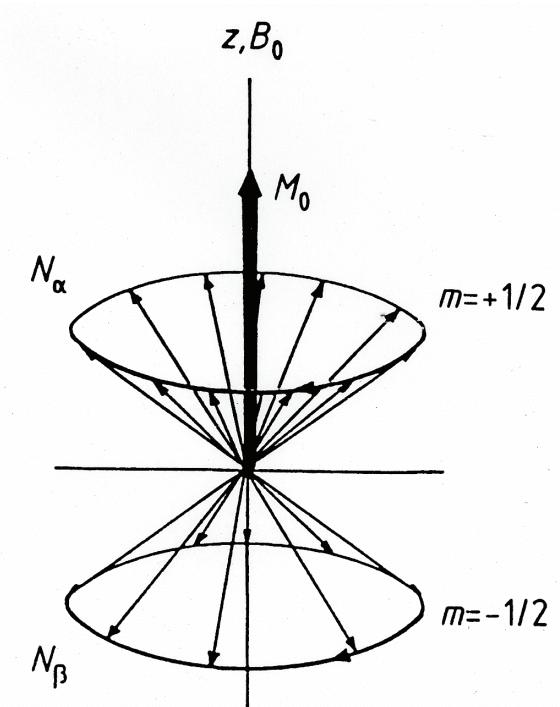
$$\sum_{m=-I}^I m^2 = \frac{I(I+1)(2I+1)}{3}$$

# Macroscopic Magnetization

$M_0 \equiv$  bulk magnetic moment  
 $\equiv$  macroscopic magnetization

$$M_0 = \frac{N\gamma^2 \hbar^2 B_0 I(I+1)}{3k_B T}$$

- The magnitude of  $M_0$  depends on:
  - the magnitude of the static magnetic field,  $B_0$
  - the identity of the nucleus; its  $\gamma^2$  and  $I$
  - $-1/T$
  - and, not to forget,  $N$  (the number of nuclei, or the concentration of the sample, if you like!)



# Resonance

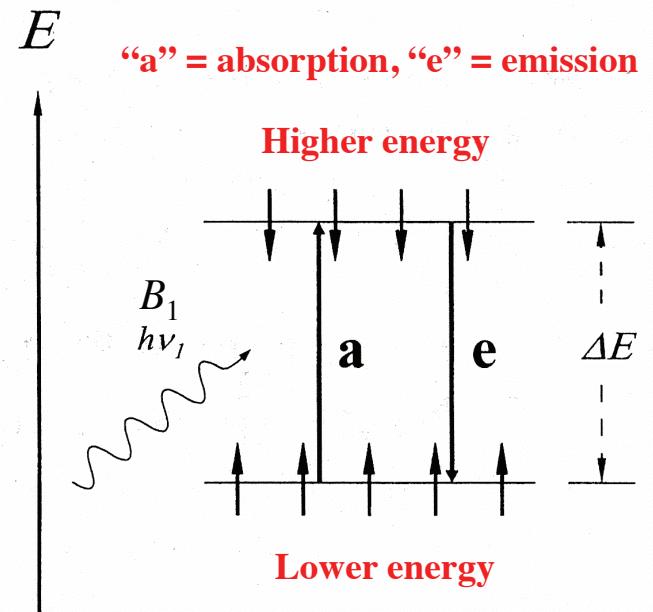
- The relationship between the Larmor frequency and  $\Delta E$  is as follows:

$$\Delta E = \gamma \hbar B_0 \text{ and } \nu_L = \left| \frac{\gamma}{2\pi} \right| B_0, \text{ therefore } \Delta E = h\nu_L$$

- Transitions between energy levels (between  $\alpha$  and  $\beta$  spin states for spin 1/2 nuclei) are quantized, and can only be promoted by an energy  $\Delta E$
- In NMR the transitions are promoted by an applied electromagnetic field,  $B_1$ , with a frequency,  $\nu_1$  (radiofrequency) matching the Larmor frequency of the nucleus

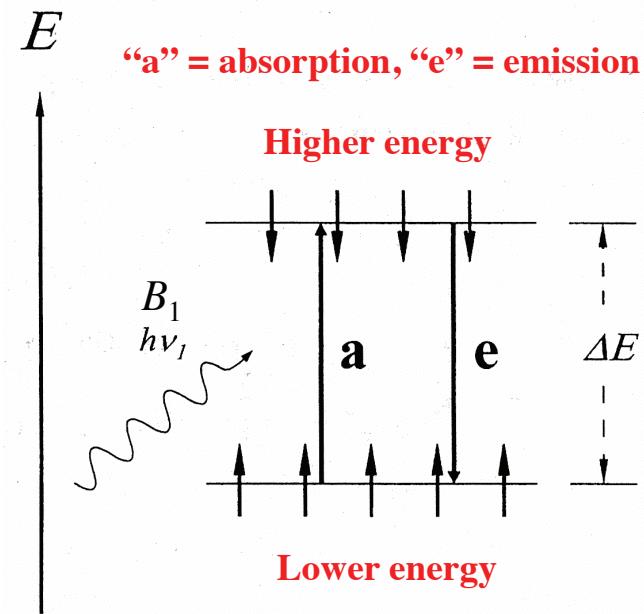
$$\nu_1 = \nu_L = \left| \frac{\gamma}{2\pi} \right| B_0, \Delta E = h\nu_1$$

- This is known as **resonance** ( $\nu_1 = \nu_L$ ), when the frequency (radiofrequency) of our externally applied electromagnetic field matches the Larmor frequency of the nucleus of interest
  - external field called  $B_1$
- absorption** (transitions from lower to higher energy,  $\alpha \rightarrow \beta$ ) and **emission** (transitions from higher to lower energy,  $\beta \rightarrow \alpha$ ) occur with equal probability



# Resonance

- for a system of nuclei at thermal equilibrium, a  $B_1$  field applied for a *short* time promotes a *net* conversion of  $\alpha$  to  $\beta$  spin states
- for a system of nuclei at thermal equilibrium, a  $B_1$  field applied for a *long* time leads to equilibration of  $\alpha$  and  $\beta$  spin states
  - this is known as *saturation*



# Resonance Frequencies

- Magnetic field strengths are measured in Tesla
- Often, magnetic field strengths are measured in “MHz”, referring to the Larmor frequency of  $^1\text{H}$  precession in the magnetic field
  - thus, in a “400 MHz” magnet, a  $^1\text{H}$  nucleus will precess at approximately 400 MHz
  - so, the Larmor precession frequency is a “natural” measure of magnetic field strength

$B_0$ [T]	Resonance frequencies [MHz]	
	$^1\text{H}$	$^{13}\text{C}$
1.41	60	15.1
1.88	80	20.1
2.11	90	22.63
2.35	100	25.15
4.70	200	50.3
5.87	250	62.9
7.05	300	75.4
9.40	400	100.6
11.74	500	125.7
14.09	600	150.9
17.62	750	188.2
18.79	800	201.2

- magnets from 300 - 900 MHz (900 MHz being the largest commercially available magnet for high-field solution NMR) are available to researchers

# Continuous Wave (CW) NMR

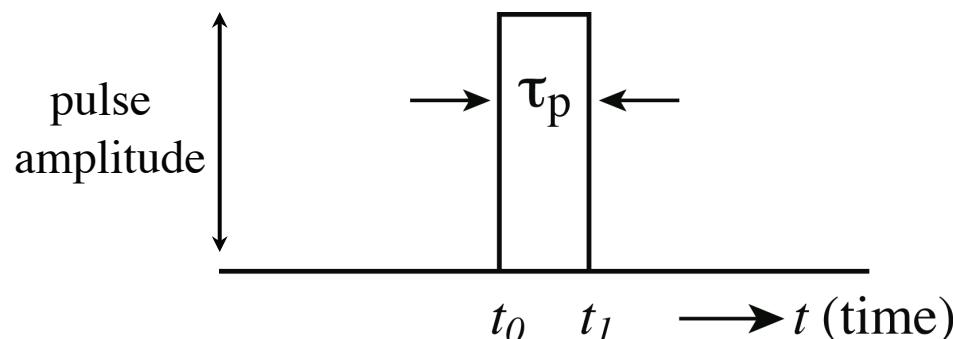
- NMR can be performed like other spectroscopies (UV/vis, IR) by simply slowly varying the frequency of monochromatic incident radiation and monitoring for absorption
- problems: very low signal-to-noise per unit of acquisition time

## Example:

- assume need to discriminate between signals  $\leq 1$  Hz apart (need “1 Hz resolution”)
  - because  $E = h\nu$  and  $\nu = 1$  Hz,  $E = h$
  - the Heisenberg uncertainty principle states  $\Delta E \Delta t \sim h$ , and because  $E = h$ ,  $\Delta t = 1$  s
  - thus, it will take 1 second to “scan” each interval of 1 Hz
  - if we are performing a  $^1\text{H}$  experiment, and want a (typical) spectral width of 10 ppm or 4000 Hz, it will take 4000 seconds to do a single scan (about 67 minutes)
  - if we need to improve the signal-to-noise, we can collect multiple scans and add them together: to increase the signal-to-noise by 2 fold, we must collect 4 scans (4.5 hours), and if we need to increase it by 4 fold, we must collect 16 scans (18 hours ! )
  - a 16 scan experiment using modern pulsed Fourier transform methods will take perhaps 30 seconds to 1 minute
- CW methods have been essentially entirely supplanted by pulsed Fourier transform methods

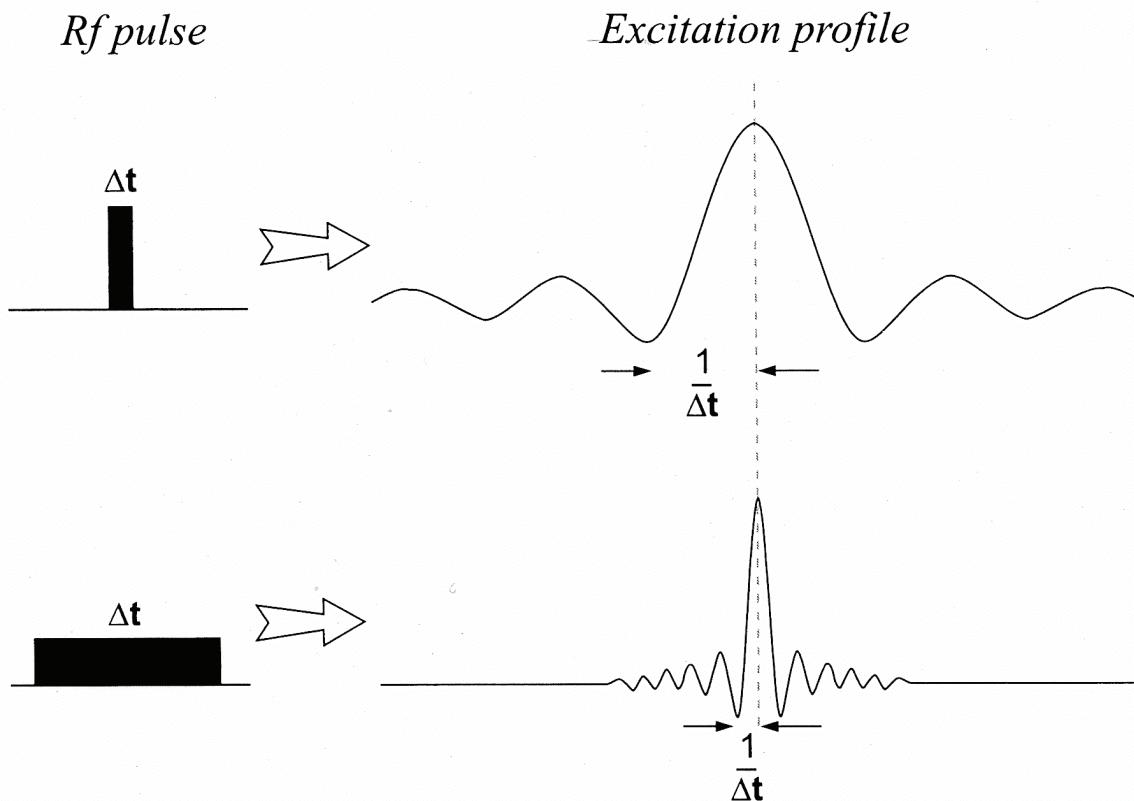
# Pulse NMR

- Older NMR spectroscopy methods utilized a radiofrequency “sweep” to “find” Larmor frequencies of nuclei in molecules (called CW or continuous wave techniques)
- Modern methods, for the most part without exception, rely on **pulsed Fourier transform** techniques to obtain the frequencies
- In pulsed Fourier transform NMR, for a given nucleus ( $^1\text{H}$  for example), all frequencies are excited simultaneously by a short, high power radiofrequency pulse ( $B_1$  field)
  - the pulse is applied at a particular frequency,  $\nu_1$ , but a short pulse excites a large, continuous band of frequencies (the **bandwidth**) centered around  $\nu_1$
  - the useful or effective bandwidth is proportional to  $1/\tau_p$  ( $\tau_p$  is the **pulse length**, also called the **pulse width or pulse duration**)
  - $\tau_p$  is usually very short, i.e.  $\mu\text{s}$  (microseconds)
- The **pulse amplitude** is a measure of the power with which the pulse is applied, and determines the strength of the  $B_1$  field



# Pulse Width

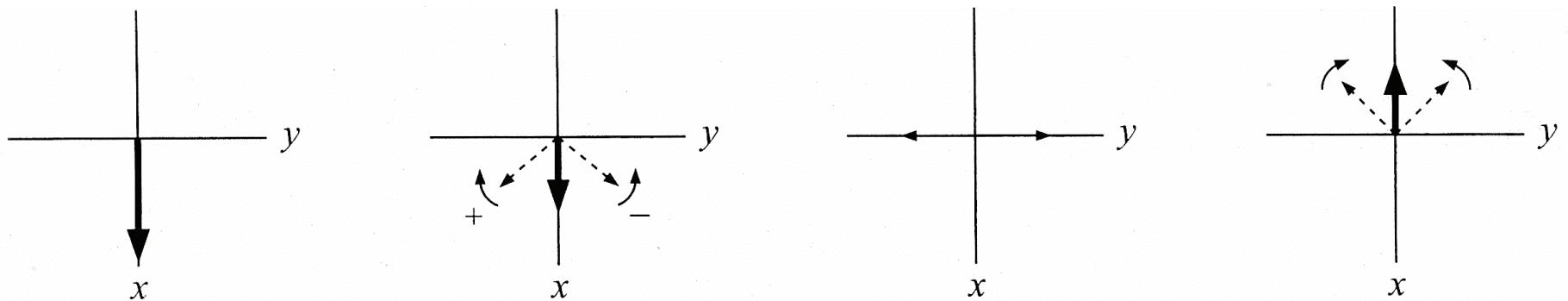
- Example: pulse width / bandwidth / excitation profile
  - using a 400 MHz magnet, in order to excite a typical  $^1\text{H}$  frequency range (4000 Hz), would need a pulse length  $< 1/(2000 \text{ Hz}) = 500 \mu\text{s}$
  - typically, pulse  $< 10 \mu\text{s}$  (100,000 Hz) are used (more uniform excitation, smaller “off resonance” effects, etc.)



- Excitation profile for rectangular pulse is (unfortunately) sinc shaped ( $\sin x / x$ )

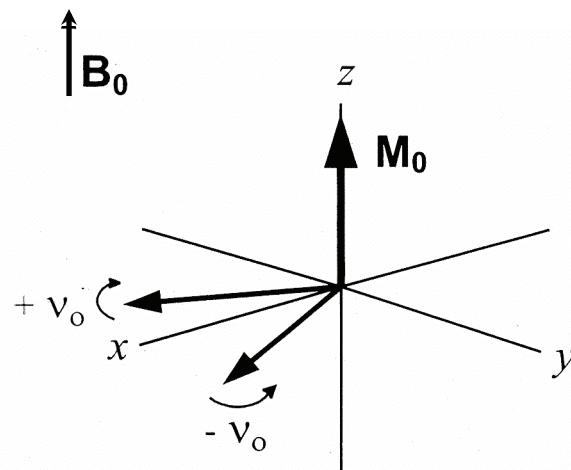
# $B_1$ Field and Rotating Frame of Reference

- The  $B_1$  field is applied (or exists) in the *transverse* ( $x$ - $y$ ) plane (perpendicular to the  $B_0$  field, which exists in the  $z$  or *longitudinal* direction).
  - the  $B_1$  field is *an oscillating magnetic field*
  - the frequency of oscillation is near the resonance frequencies of the nuclei of interest
  - normally, the frequency of oscillation is **chosen** to be the center of the expected Larmor frequency range of the nuclei of interest
- It is the interaction of the  $B_1$  field and the nuclear spin dipoles that is relevant in NMR
- The plane-polarized  $B_1$  field can always be considered as two circularly-polarized component counter-rotating magnetic vectors in the transverse plane
  - the resultant vector corresponds to the applied oscillating  $B_1$  field

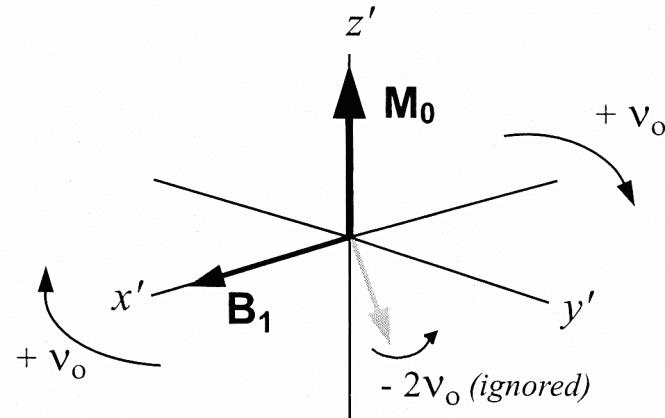


# $B_1$ Field and Rotating Frame of Reference

- We can now simplify by assuming that our frame of reference (the *rotating frame*), is rotating at the frequency of one of these counter-rotating vectors.
  - the instantaneous torque exerted by the other component on our nuclear dipoles averages to zero with time and can be ignored
- Strictly,  $B_1$  is defined as the component rotating at the rotating frame frequency
- Thus, a  $B_1$  field can be applied along any axis ( $x$ ,  $y$ ,  $-x$ ,  $-y$ , any angle in between: any “phase”) in the transverse plane in the rotating plane
- The frequency at which  $B_1$  is applied defines the center of the NMR spectrum, is called the *carrier frequency*, defines the rotating frame frequency and a reference frequency defining relative Larmor frequencies



Laboratory  
frame



Rotating  
frame

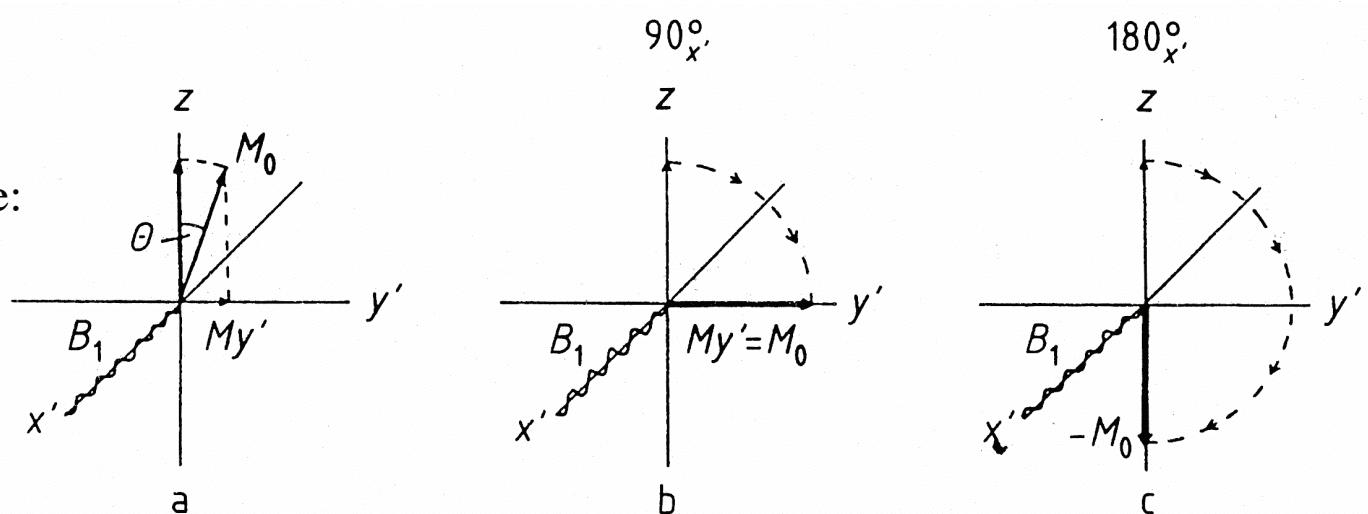
# Pulse Angle

- What happens to our bulk/net magnetization vector,  $\mathbf{M}_0$ , when a  $B_1$  pulse is applied?
  - the pulse/ $B_1$  field is applied in the transverse plane, perpendicular to  $\mathbf{M}_0$
  - $B_1$  and  $\mathbf{M}_0$  exert a torque on one another, thus  $\mathbf{M}_0$  moves
  - the effect of the  $B_1$  field/pulse is to rotate  $\mathbf{M}_0$  towards the transverse plane
  - the angle of rotation, the **pulse angle** ( $\Theta$ ), is dependent on the strength of the  $B_1$  field (pulse amplitude), the pulse width ( $\tau_p$ ) and  $\gamma$  for the nucleus

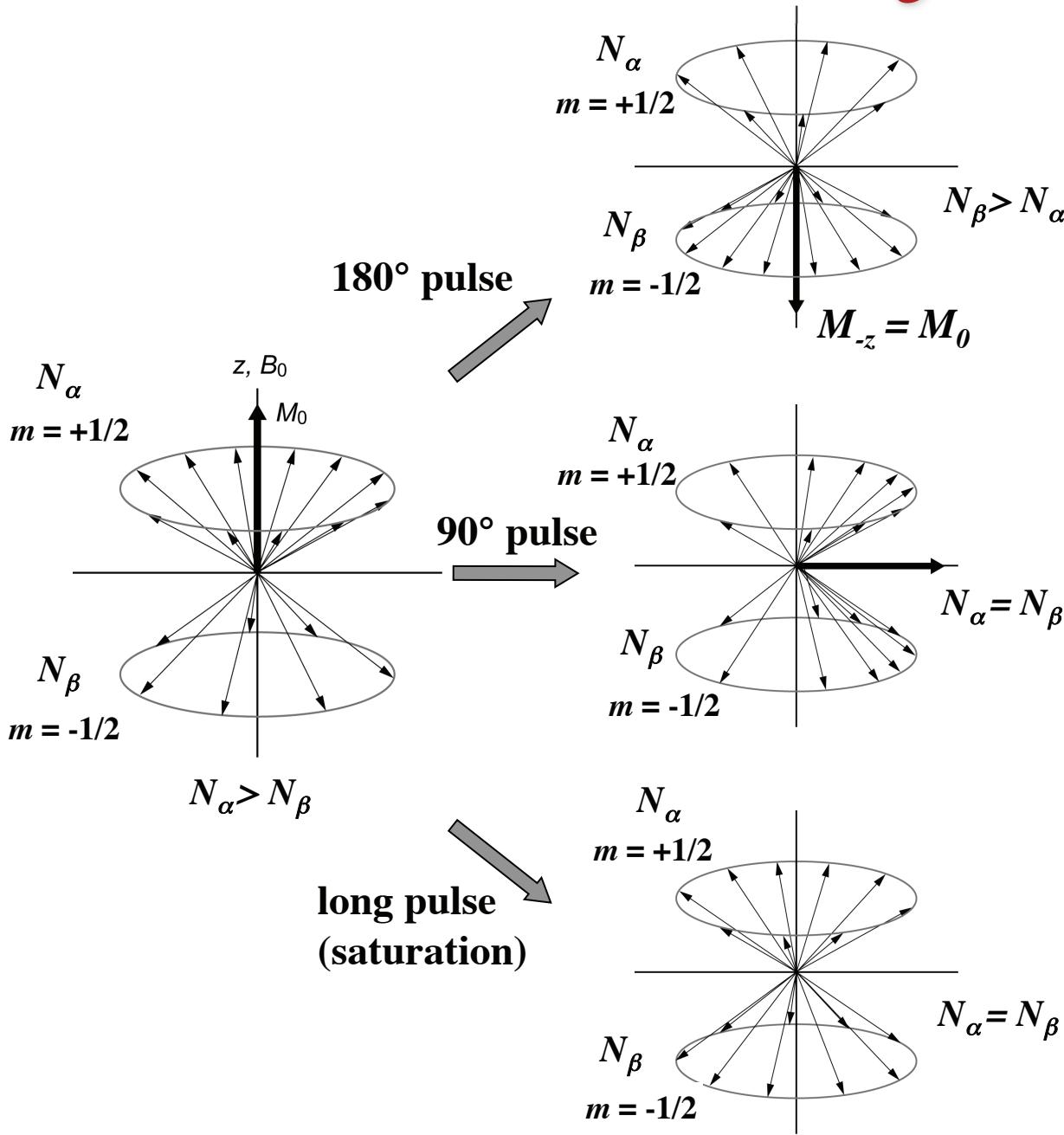
$$\Theta = \gamma B_1 \tau_p$$

- A  $90^\circ$  ( $\pi/2$ ) pulse in the  $x$  direction rotates  $\mathbf{M}_0$   $90^\circ$  so that the magnitude of the net magnetization in the transverse plane, pointed in the  $+y$  direction, is equal to the initial  $z$  magnetization ( $\mathbf{M}_y = \mathbf{M}_0$ )
- A  $180^\circ$  ( $\pi$ ) pulse rotates  $\mathbf{M}_0$   $180^\circ$  (to  $-\mathbf{M}_0$ )

In the rotating frame:



## Pulse Angle



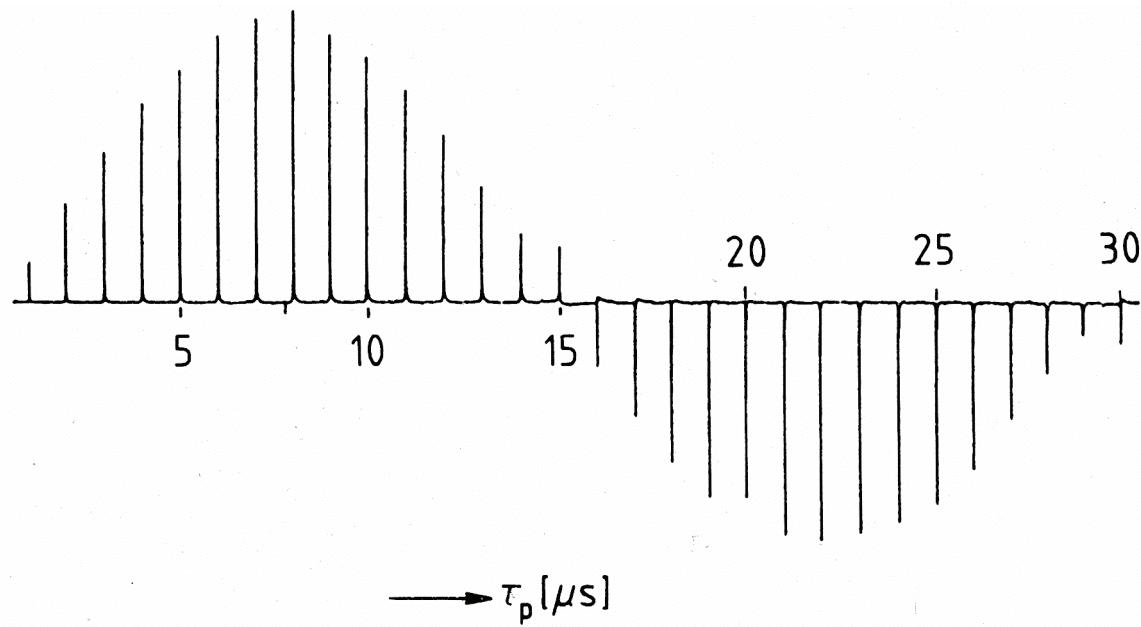
- A  $180^\circ$  ( $\pi$ ) pulse exchanges the populations  $N_\alpha$  and  $N_\beta$

- A  $90^\circ$  ( $\pi/2$ ) pulse equilibrates  $N_\alpha$  and  $N_\beta$  and creates “**phase coherence**” among dipoles. This results in net **transverse** magnetization.

- A long pulse equilibrates  $N_\alpha$  and  $N_\beta$
- Uniform, random distribution of dipoles around  $z$

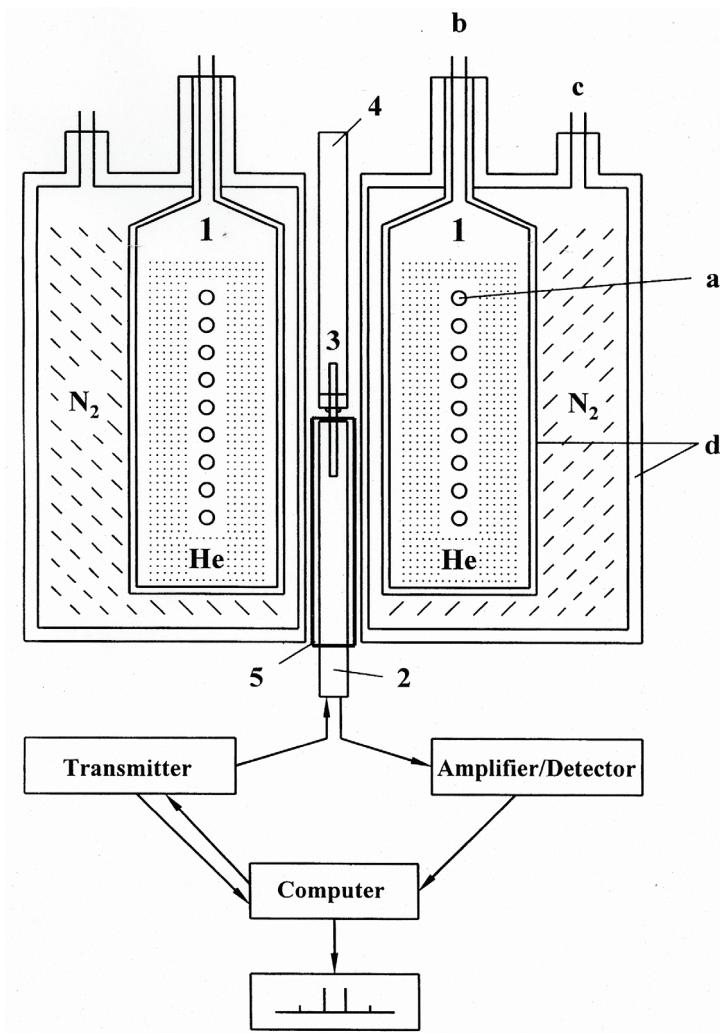
# Signal Amplitude and Pulse Angle

- What happens to our signal when the pulse angle varies?
  - later, we will see how a signal is actually generated, and how we change that signal into a form convenient for us to view and interpret
  - for now, in any case, the amplitude of the signal that we observe will be dependent on the pulse width, and therefore the pulse angle, in a cyclic manner, as shown below



# Superconducting Magnets

- Superconducting magnets are “simple” electromagnets that maintain a magnetic field (an electrical current in the coils of the electromagnet) by keeping the coils of the magnet at or below 4 °K, where the material comprising the coils is superconducting



- No externally applied current is used to “power” the magnet
- The electromagnet coils are bathed by liquid He
- The liquid He is kept cool by liquid N<sub>2</sub>

## Superconducting Magnets

