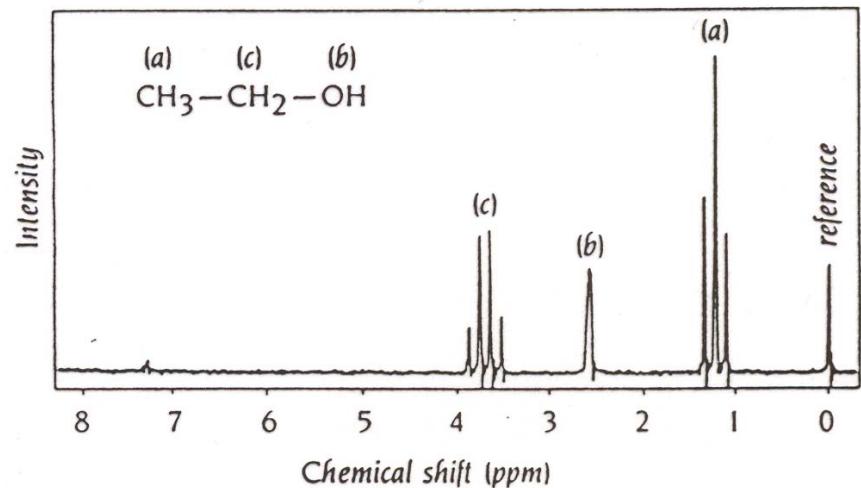


NMR Spectroscopy:

1

NMR: Sophomore Organic Chemistry

- Sophomore organic NMR:
 - 1D, ^1H spectra
 - small organic molecules
 - one signal for each type of ^1H
 - signals split into doublets, triplet, quartets, etc., due to presence of ^1H 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/ 2π = $h/2\pi$ $h \approx 6.6 \times 10^{-34}$ 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_1H , $^{13}_6\text{C}$, $^{15}_7\text{N}$, $^{31}_{15}\text{P}$, $^{19}_9\text{F}$
 - 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 ^{a)} [<i>eQ</i>] [10^{-28} m ²]	Natural abundance) [%]	Relative sensitivity ^{b)}	Gyromagnetic ratio $\gamma^a)$ [10^7 rad T ⁻¹ s ⁻¹]	NMR frequency [MHz] ^{b)} ($B_0 = 2.3488$ T)
¹ H	1/2	–	99.985	1.00	26.7519	100.0
² H	1	2.87×10^{-3}	0.015	9.65×10^3	4.1066	15.351
³ H ^{c)}	1/2	–	–	1.21	28.5350	106.664
⁶ Li	1	-6.4×10^{-4}	7.42	8.5×10^{-3}	3.9371	14.716
¹⁰ B	3	8.5×10^{-2}	19.58	1.99×10^{-2}	2.8747	10.746
¹¹ B	3/2	4.1×10^{-2}	80.42	0.17	8.5847	32.084
¹² C	0	–	98.9	–	–	–
¹³ C	1/2	–	1.108	1.59×10^{-2}	6.7283	25.144
¹⁴ N	1	1.67×10^{-2}	99.63	1.01×10^{-3}	1.9338	7.224
¹⁵ N	1/2	–	0.37	1.04×10^{-3}	-2.7126	10.133
¹⁶ O	0	–	99.96	–	–	–
¹⁷ O	5/2	-2.6×10^{-2}	0.037	2.91×10^{-2}	-3.6280	13.557
¹⁹ F	1/2	–	100	0.83	25.1815	94.077
²³ Na	3/2	0.1	100	9.25×10^{-2}	7.0704	26.451
²⁵ Mg	5/2	0.22	10.13	2.67×10^{-3}	-1.6389	6.1195
²⁹ Si	1/2	–	4.70	7.84×10^{-3}	-5.3190	19.865
³¹ P	1/2	–	100	6.63×10^{-2}	10.8394	40.481
³⁹ K	3/2	5.5×10^{-2}	93.1	5.08×10^{-4}	1.2499	4.667
⁴³ Ca	7/2	-5.0×10^{-2}	0.145	6.40×10^{-3}	-1.8028	6.728
⁵⁷ Fe	1/2	–	2.19	3.37×10^{-5}	0.8687	3.231
⁵⁹ Co	7/2	0.42	100	0.28	6.3015	23.614
¹¹⁹ Sn	1/2	–	8.58	5.18×10^{-2}	-10.0318	37.272
¹³³ Cs	7/2	-3.0×10^{-3}	100	4.74×10^{-2}	3.5339	13.117
¹⁹⁵ Pt	1/2	–	33.8	9.94×10^{-3}	5.8383	21.499

Magnetic Moment

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

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

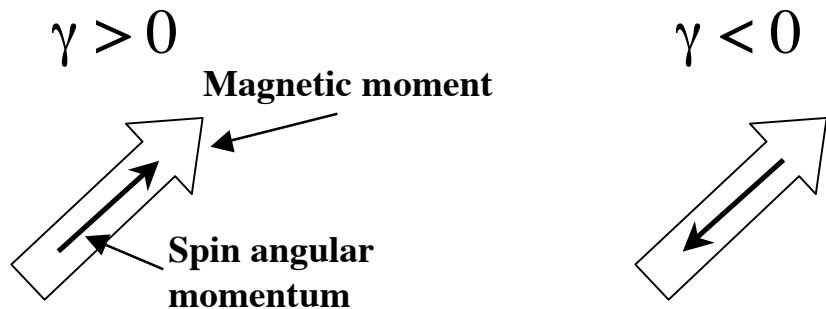
- The μ for the electron is well understood (predicted value from Dirac's integration of relativity and quantum mechanics, and in agreement to 11 significant figures with measured value). For nuclei μ no so well understood.
- we can combine the above equation and that for the angular momentum to obtain 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 γ is the proportionality constant between \mathbf{P} and μ , and is called the **gyromagnetic ratio** (or magnetogyric ratio)
- γ is a constant for a given nucleus

Magnetic Moment

- μ and P usually have the same sign, so γ is positive
 - there are exceptions (^{15}N , ^{29}Si , ^{119}Sn , the electron)



- μ 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 μ 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 :

$$P_z = m\hbar$$

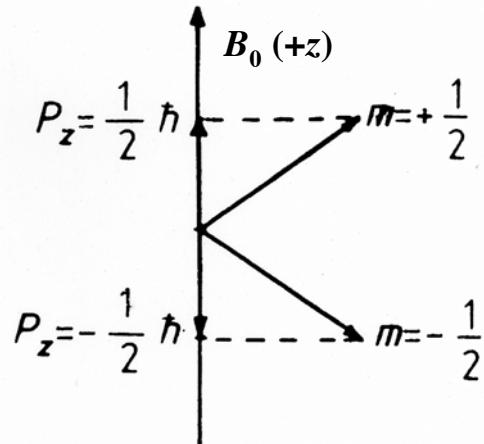
- m is the **magnetic quantum number** (or directional quantum number)

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

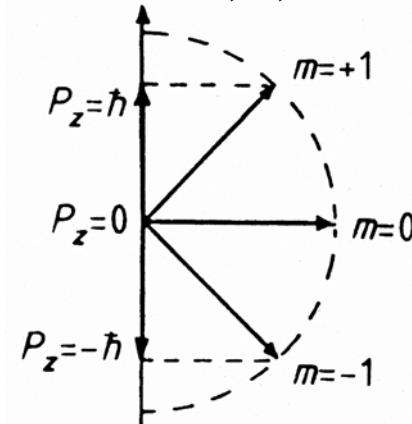
- therefore, there are $(2I+1)$ values for m , and $(2I+1)$ possible orientations for the angular momentum

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

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



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

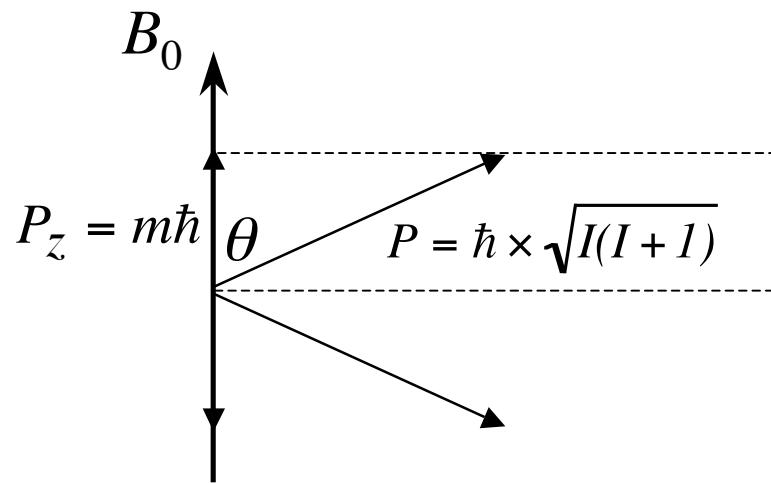


- thus, we know the components of the magnetic moment along z

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

Directional Quantization of Angular Momentum

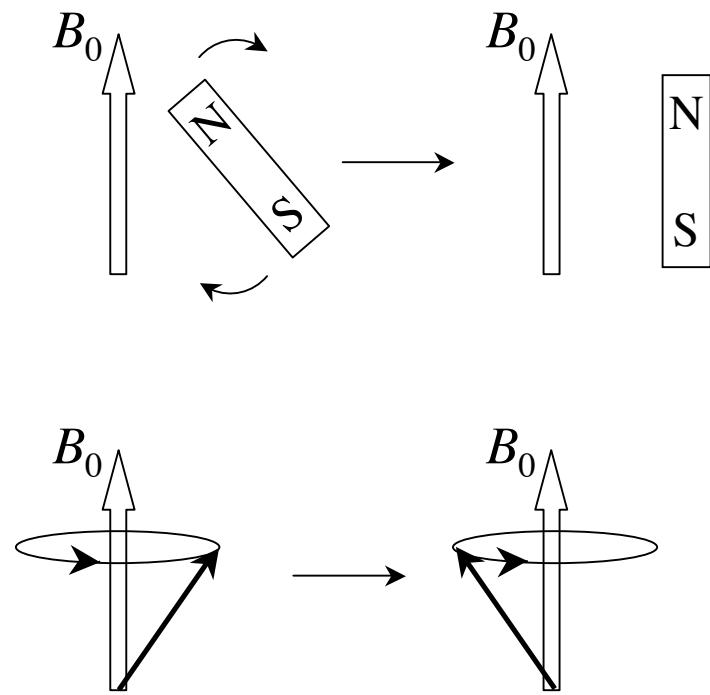
- directional quantization dictates orientation



- 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

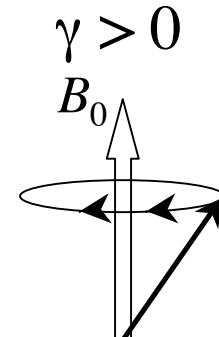
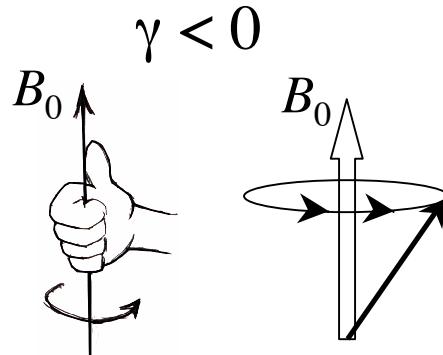
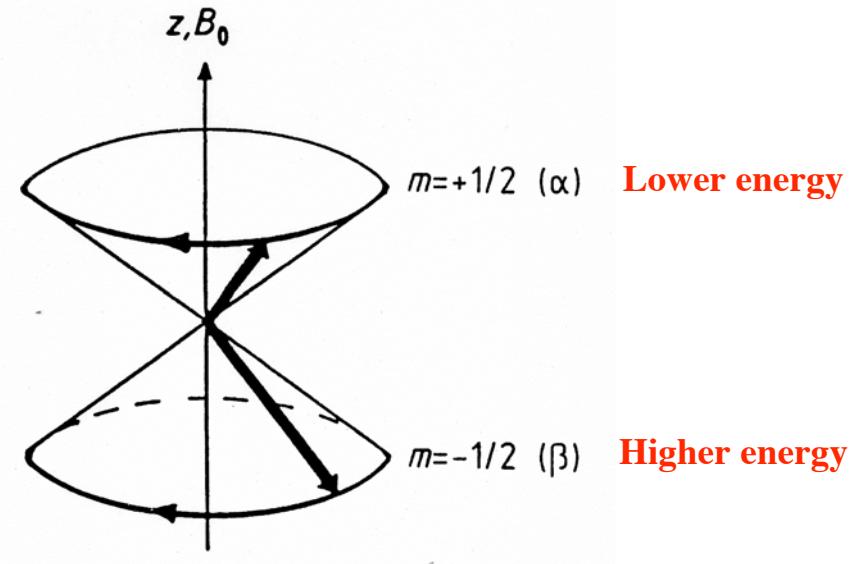
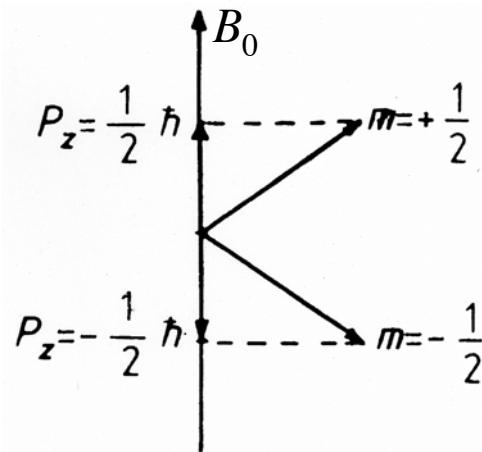


- Put a bar magnet in a magnetic field and it rotates to minimize the energy
- Put a nuclear spin in a magnetic field, and the torque on the magnetic moment (angular momentum) imposed by the field causes the nuclear dipoles/magnetic moments to move around the field (B_0) on a cone with a constant angle 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 γ
- 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°

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



Precession

- The rate of precession is dependent on γ and B_0 , and is termed the **Larmor frequency** (ν_L) for the particular nucleus:

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

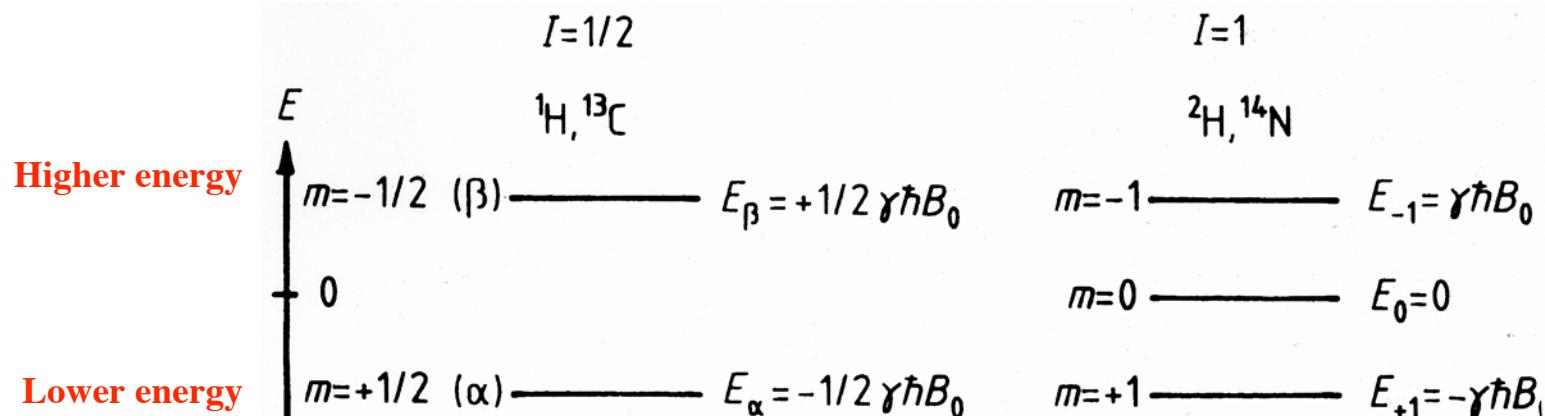
- For positive γ , the Larmor frequency is negative
- Frequency directly proportional to field strength (B_0)
-magnetic field strengths are often designated in terms of the Larmor frequency of a particular nucleus (^1H) at that field strength

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 $I = 1/2$ (^1H , ^{13}C), $m = +1/2$ and $m = -1/2$:
 - for $m = +1/2$, μ_z is parallel to the static external field (B_0) direction, and is lower energy
 - for $m = -1/2$, μ_z is antiparallel to B_0 , and is higher energy
- in quantum mechanics, for $I = 1/2$, $m = +1/2$ is the **α spin state** (α spin), and $m = -1/2$ is the **β spin state**

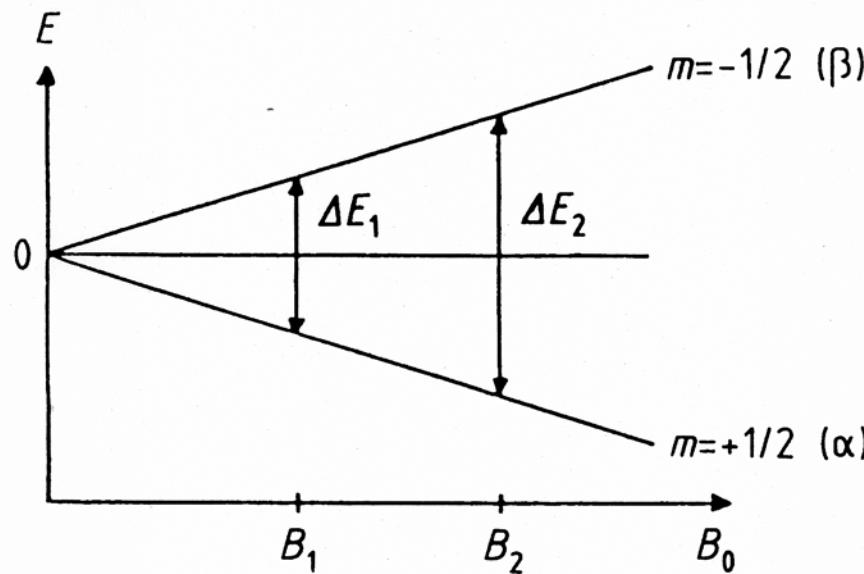


Nuclear Energy Levels in a Static Magnetic Field

- 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 γ and on B_0



Energy Level Populations

- At thermal equilibrium the energy difference between α and β 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^{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 γ and on B_0

Energy Level Populations

- For spin 1/2 nuclei, at thermal equilibrium the energy difference between α and β 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_α = number of nuclei in the α state
 N_β = number of nuclei in the β state
 k_B = Boltzman constant
 T = temperature (Kelvin)

Example: Calculate the ration of α to β spins at 300 °K for ^1H nuclei at a B_0 field strengths of 5.875 Tesla (250 MHz) and 18.8 Tesla (800 MHz).

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

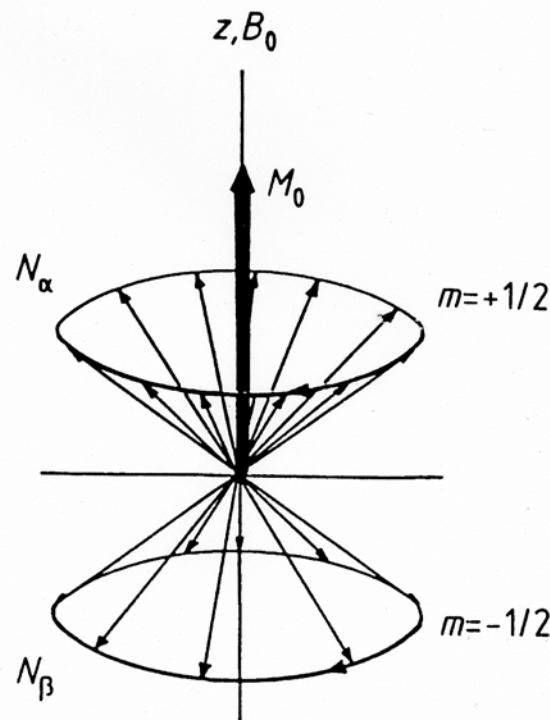
$$\frac{N_\beta}{N_\alpha} = 1 - \frac{26.7519 \times 10^7 \times 1.0546 \times 10^{-27} \times 5.875}{1.3805 \times 10^{-16} \times 300} = 0.99996$$

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

- Because ΔE is small, the populations of the α and β 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 α and β states prevents these states from being equally populated
 - slightly more spins are in the lower energy α state than in the β 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 α spins is larger than the number of β 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:

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

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

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

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

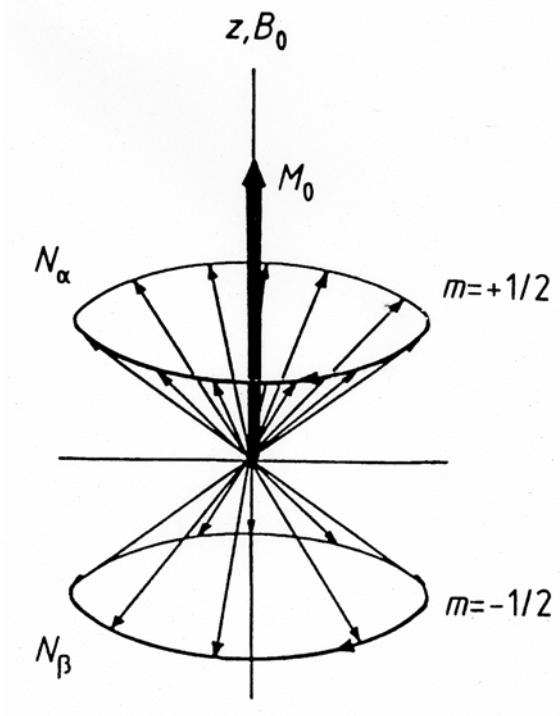
$$\sum_{m=-I}^I m^2 = \frac{I(I+1)(2I+1)}{3}$$

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 γ^2 and I
 - $-1/T$
 - and, not to forget, N (the number of nuclei, or the concentration of the sample, if you like!)



Resonance

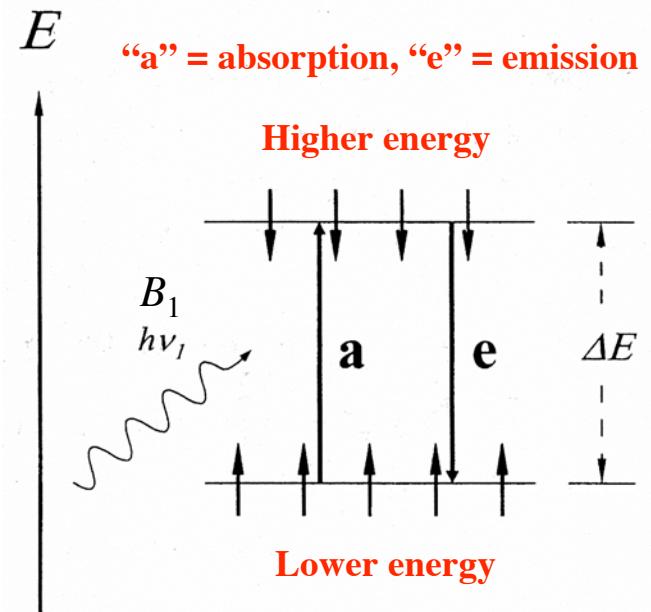
- The relationship between the Larmor frequency and ΔE is as follows:

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

- Transitions between energy levels (between α and β spin states for spin 1/2 nuclei) are quantized, and can only be promoted by an energy ΔE
- In NMR the transitions are promoted by an applied electromagnetic field, B_1 , with a frequency, ν_1 (radiofrequency) matching the Larmor frequency of the nucleus

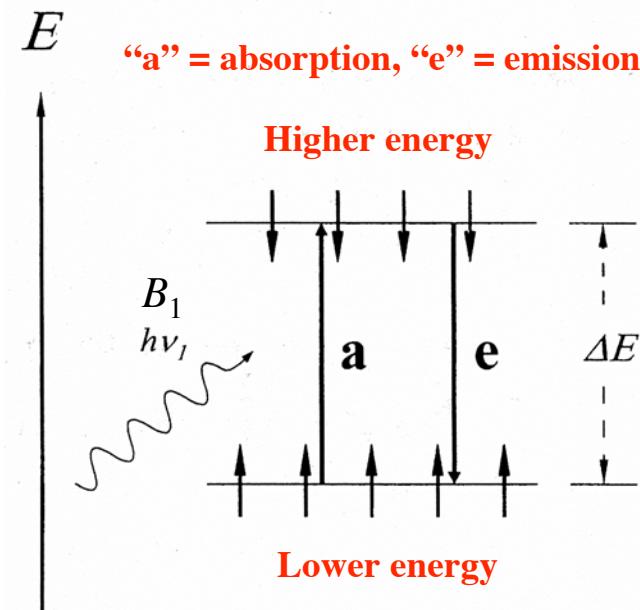
$$\nu_1 = \nu_L = \left| \frac{\gamma}{2\pi} \right| B_0, \Delta E = h\nu_1$$

- 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 α to β spin states
- for a system of nuclei at thermal equilibrium, a B_1 field applied for a *long* time leads to equilibration of α and β 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 ^1H precession in the magnetic field
 - thus, in a “400 MHz” magnet, a ^1H 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]	
	^1H	^{13}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:

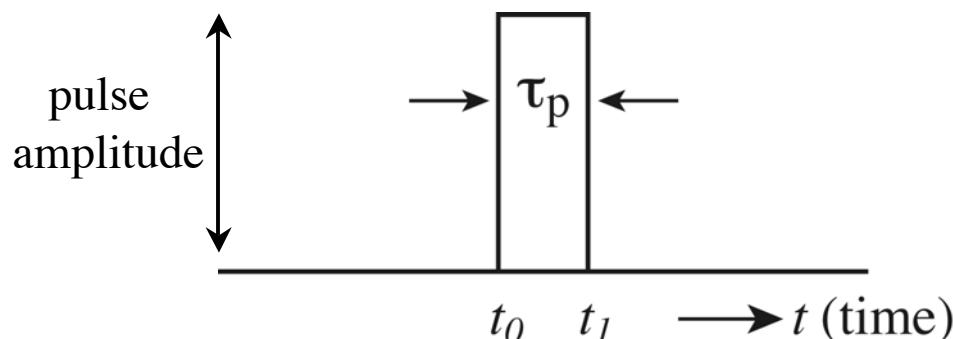
- assume need to discriminate between signals ≤ 1 Hz apart (need “1 Hz resolution”)
- because $E = h\nu$ and $\nu = 1$ Hz, $E = h$
- the Heisenberg uncertainty principle states $\Delta E \Delta t \sim h$, and because $E = h$, $\Delta t = 1$ s
- thus, it will take 1 second to “scan” each interval of 1 Hz

- if we are performing a ^1H 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

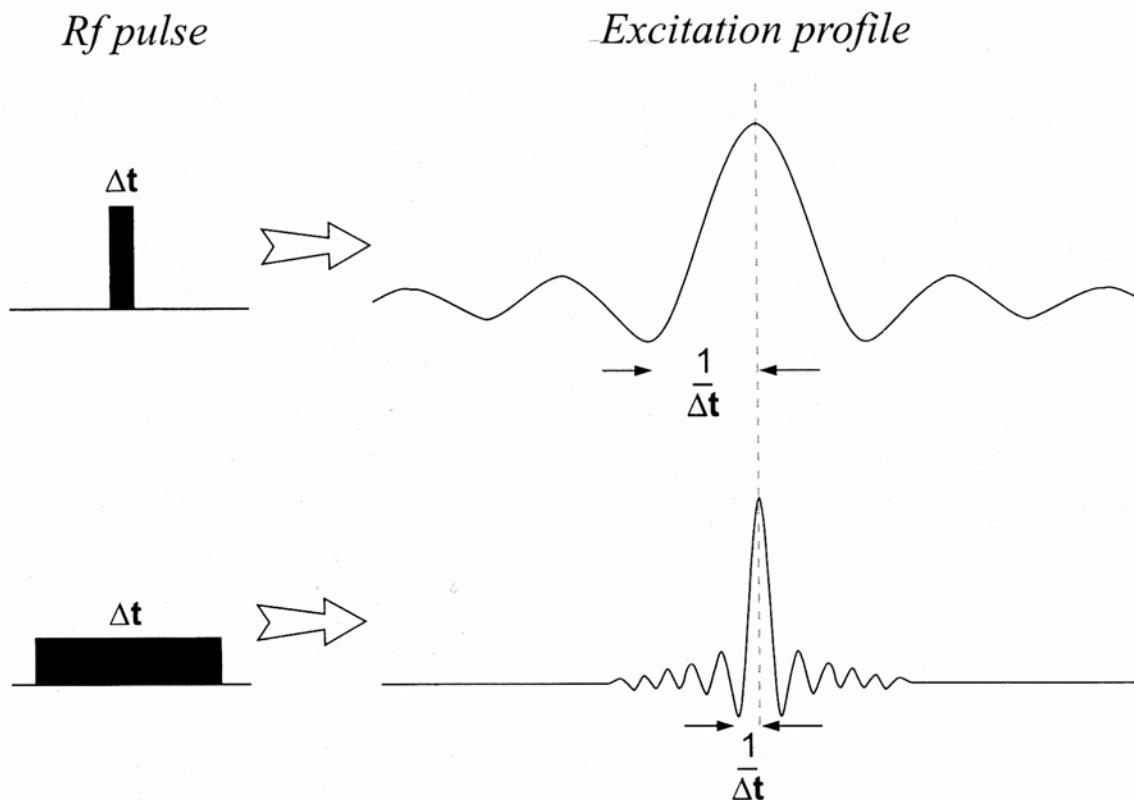
Pulse NMR

- 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 (^1H 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, ν_1 , but a short pulse excites a large, continuous band of frequencies (the **bandwidth**) centered around ν_1
 - the useful or effective bandwidth is proportional to $1/\tau_p$ (τ_p is the **pulse length**, also called the **pulse width or pulse duration**)
 - τ_p is usually very short, i.e. μs (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

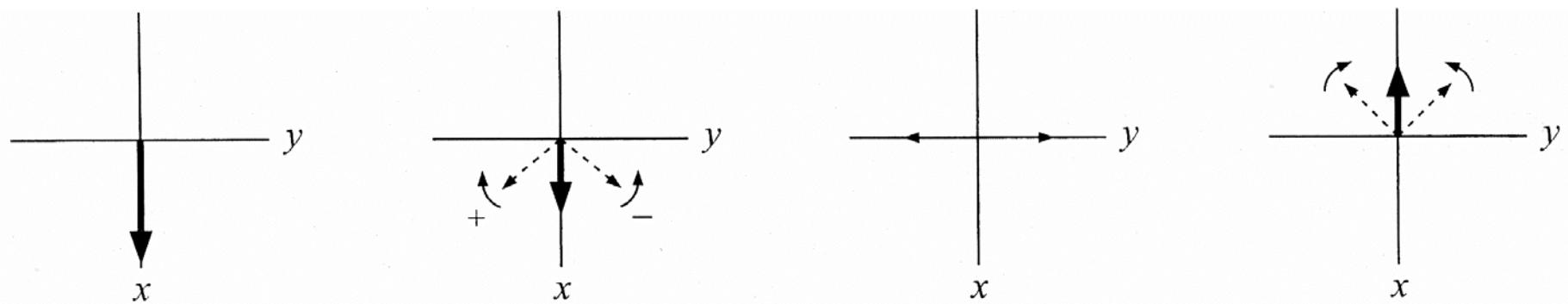
- Example: pulse width / bandwidth / excitation profile
 - using a 400 MHz magnet, in order to excite a typical ^1H frequency range (4000 Hz), would need a pulse length $< 1/(2000 \text{ Hz}) = 500 \mu\text{s}$
 - typically, pulse $< 10 \mu\text{s}$ (100,000 Hz) are used (more uniform excitation, smaller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



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

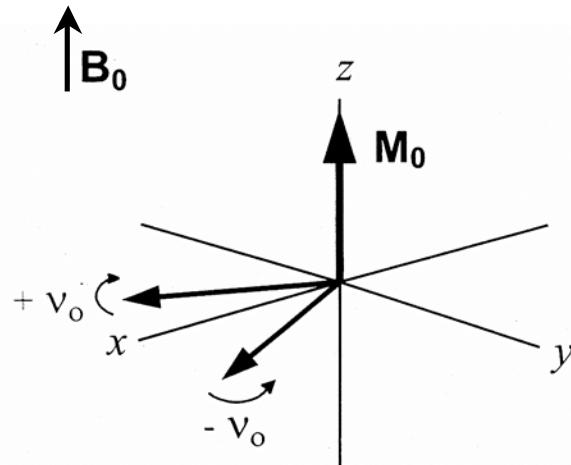
B_1 Field and Rotating Frame of Reference

- 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

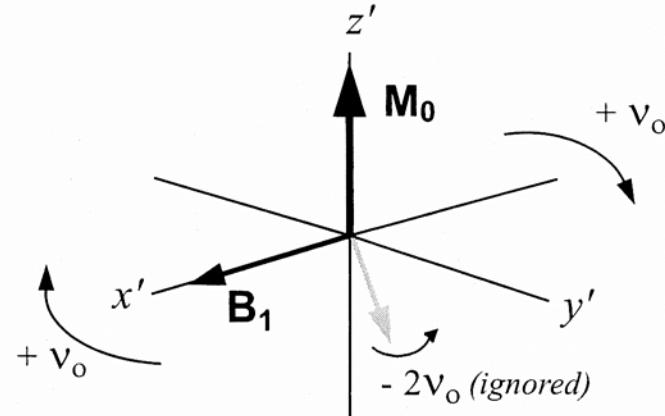


B_1 Field and Rotating Frame of Reference

- 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 frame
- 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

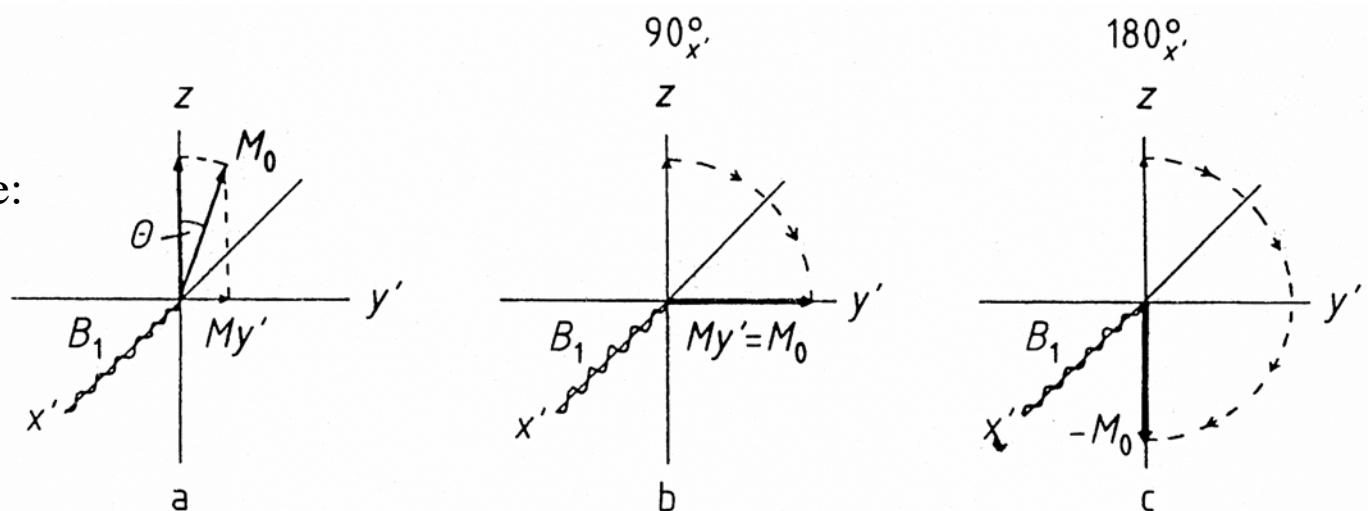
Pulse Angle

- 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** (Θ), is dependent on the strength of the B_1 field (pulse amplitude), the pulse width (τ_p) and γ for the nucleus

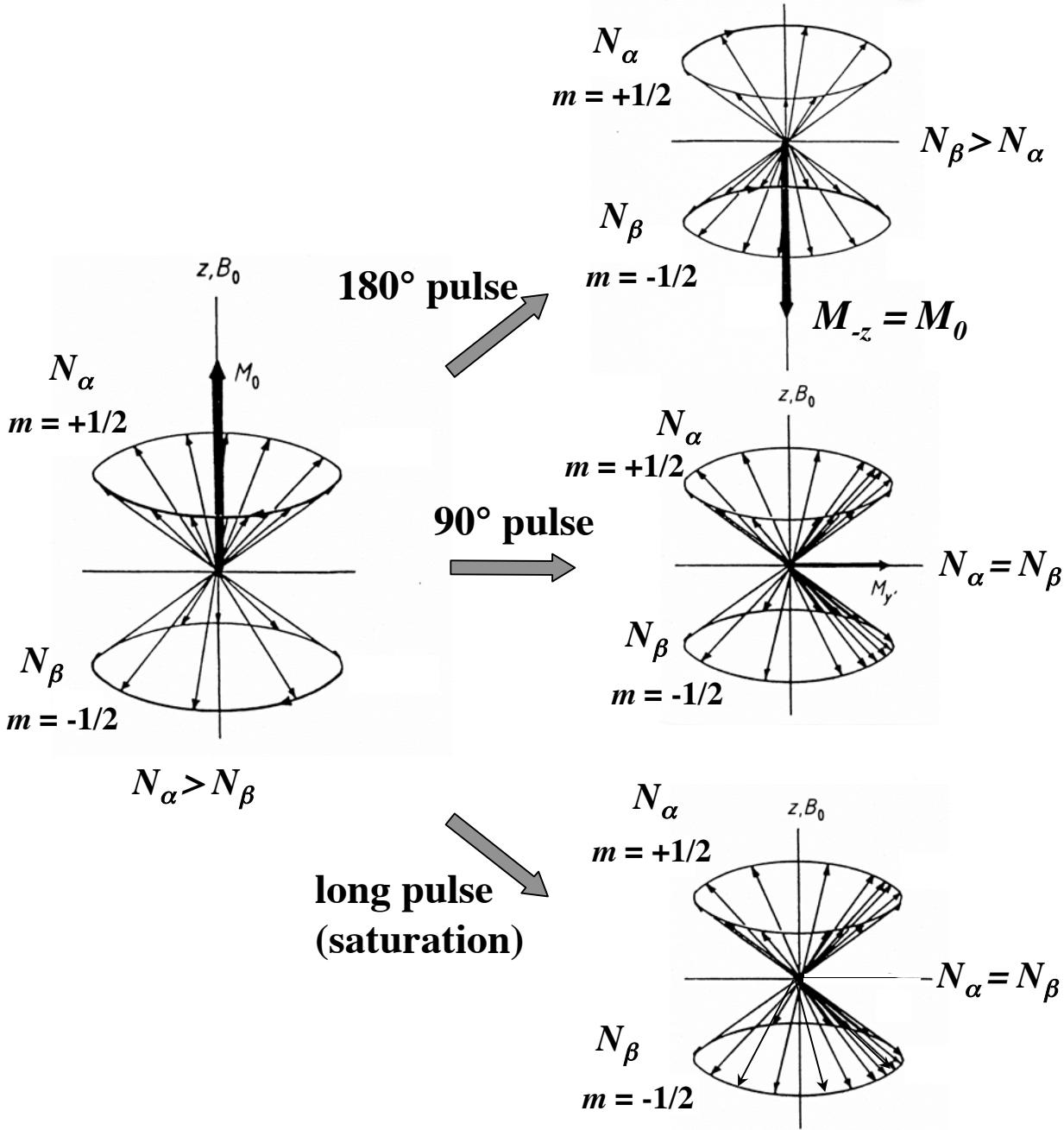
$$\Theta = \gamma B_1 \tau_p$$

- A 90° ($\pi/2$) pulse in the x direction rotates \mathbf{M}_0 90° 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° (π) pulse rotates \mathbf{M}_0 180° (to $-\mathbf{M}_0$)

In the rotating frame:



Pulse Angle



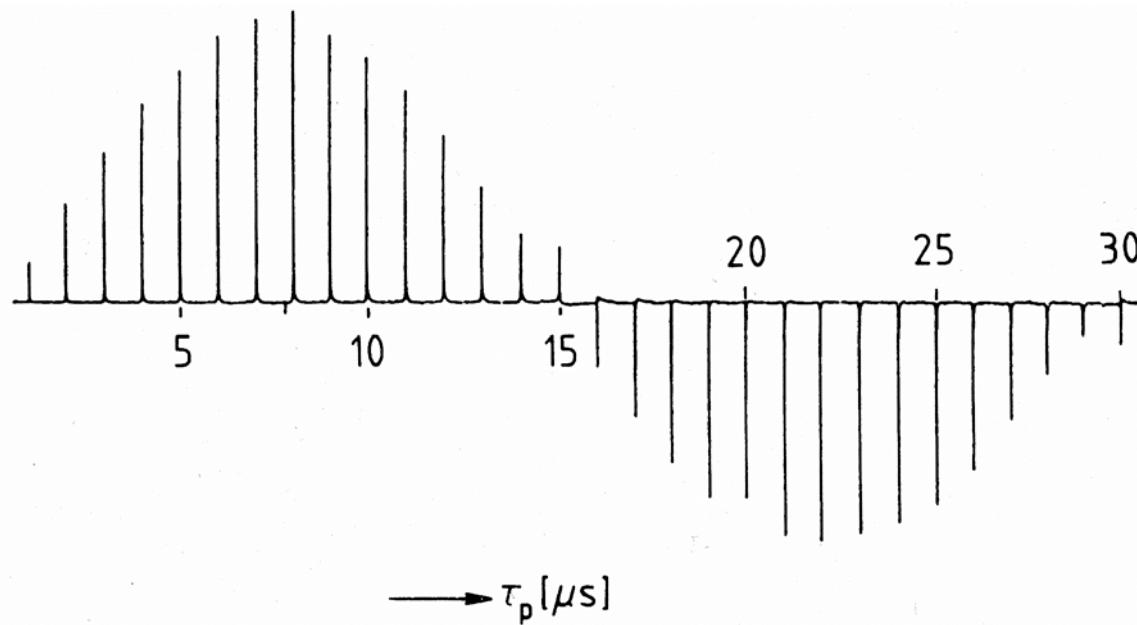
- A 180° (π) pulse exchanges the populations of N_α and N_β

- A 90° ($\pi/2$) pulse equilibrates N_α and N_β and creates “**phase coherence**” among dipoles. This results in net **transverse** magnetization.

- A long pulse equilibrates N_α and N_β
- Uniform, random distribution of dipoles around z

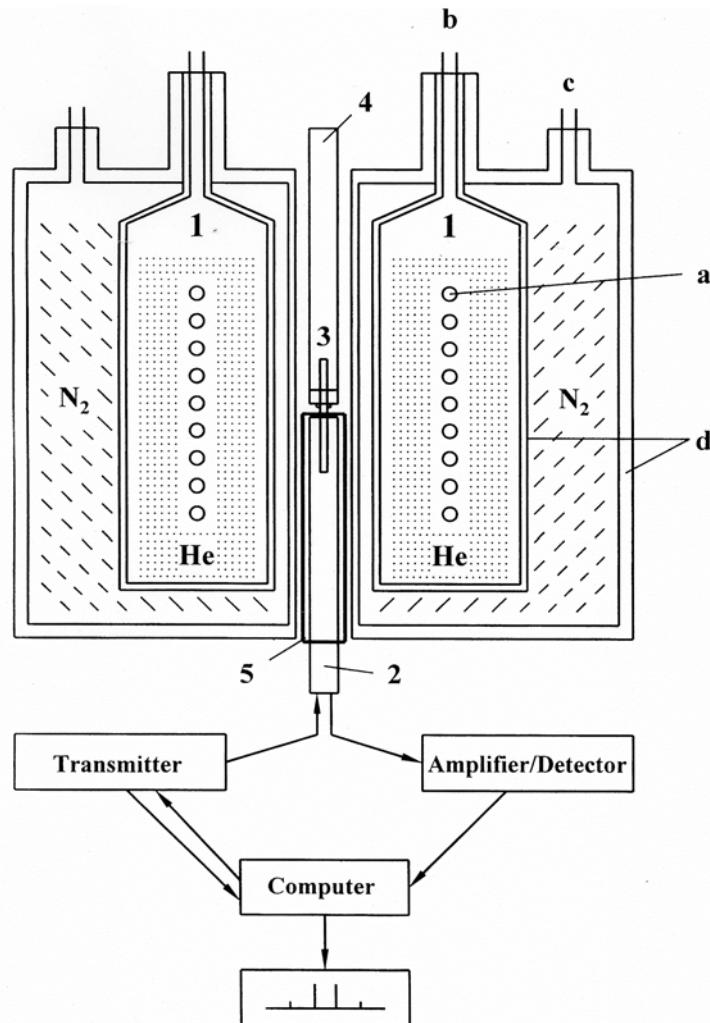
Signal Amplitude and Pulse Angle

- 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 N₂

Superconducting Magnets

