

# General principles of magnetic resonance:

## Take-home lessons from previous lecture

1. Electrons and nucleons all have “spin”, and have the same spin quantum number of  $\pm\frac{1}{2}$  ( $\uparrow\downarrow$ ) for the difference in angular momentum between spin states. The rotational velocity change on adding a spin is therefore dependent on mass.
2. The magnetic properties of the particle depend on the movement of charge induced by spinning a charged particle. The electron spins faster than any nucleus by the mass ratio, - it therefore has a bigger magnetic moment ( $\sim 1,864$  x that of a proton).
3. The magnetic dipoles of spin systems can be aligned in a magnetic field. This separates the spins into two populations, - those aligned parallel to the field, and those aligned antiparallel. Absorption of a photon of the resonance energy will flip a spin through  $180^\circ$ . Transitions on absorption of a photon can occur in either direction, either through absorption ( $\uparrow$  to  $\downarrow$ , one photon absorbed) or by stimulated emission ( $\downarrow$  to  $\uparrow$ , one photon absorbed, two emitted).
4. Changes in energy associated with a spin flip are  $\ll kT$ . As a consequence, the populations of the two states are very nearly equal. The net absorption is therefore due to the small fraction of spins that represent the population excess of the low energy level ( $\uparrow$ ),  $\sim 1$  in 10,000 for NMR.

5. The energy for a magnetic transition depends on the separation of the two spin states, which is proportional to the applied magnetic field. When the energy of incoming photons matches the energy difference of separation of the spin population (which will occur at a particular field strength), the the two are said to be in **resonance**, and absorption occurs.

6. The resonance energies for nuclear spin transitions, as detected in NMR, are in the radio frequency (RF-) range, - 10 MHz to 500 MHz (or greater) depending in the gyromagnetic ratio ( $\gamma$ ) of the nucleus, and magnetic field strength ( $B_0$ ):

$$\Delta E = h\nu = \frac{\gamma B_0 h}{2\pi}$$

7. The resonance energies for electron spin transitions, as detected in EPR, are in the microwave range, -  $\sim 10$  GHz for a semiquinone at X-band. The resonance energy depends on the g-value, and the magnetic field strength ( $B_0$ ):

$$\Delta E = h\nu = g\beta B_0$$

8. In continuous wave mode (CW-EPR for example), the instrument measures the absorption of photons as a function of the photon energy, to generate a spectrum. This is, in principle, the same operation as a spectrophotometer.

9. In both NMR and EPR, the lifetimes of the flipped spin states are relatively long, so the transitions can be easily saturated.

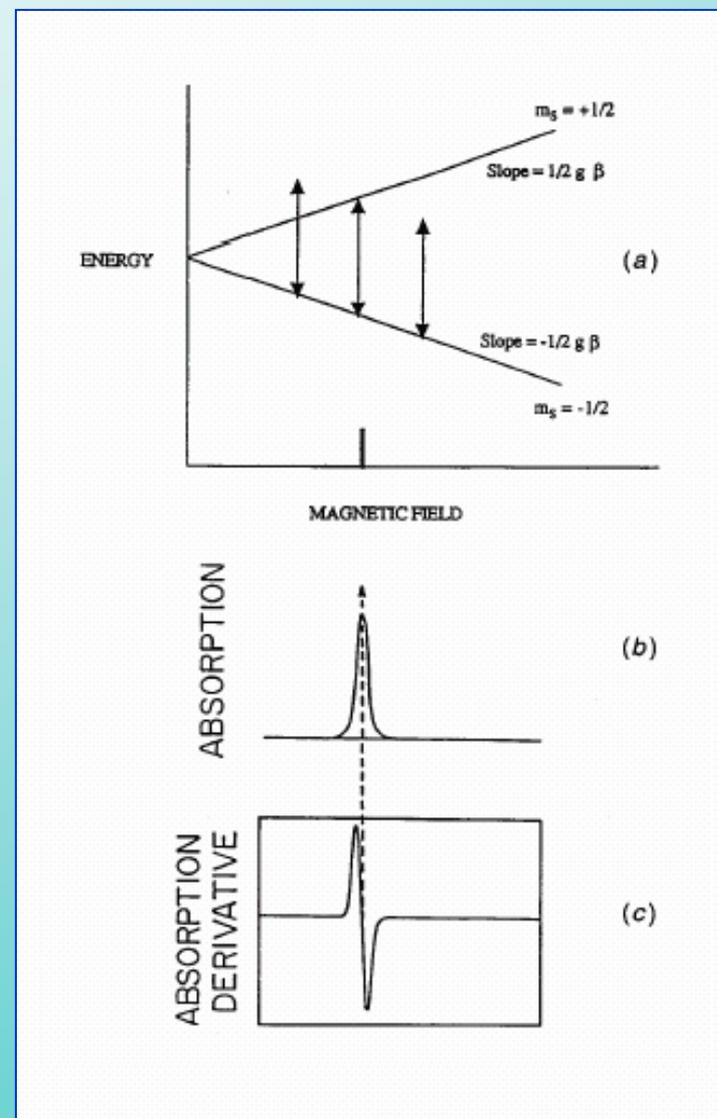
## Two different approaches to magnetic spectroscopy, CW and pulsed methods

### Continuous Wave (CW)

The CW approach is that used in most EPR spectrometers. It was the method used in earlier NMR spectrometers, but has now been supplanted by Fourier Transform NMR (FT-NMR), which is a pulsed method that we will discuss later. The new generation of EPR spectrometers are also pulse-based instruments.

In CW-EPR, the absorbance spectrum of the sample is measured over a range of energies appropriate for the magnetic field strength of the magnet used. However, for technical reasons, the spectrum is obtained by using a constant microwave frequency, and varying the magnetic field strength.

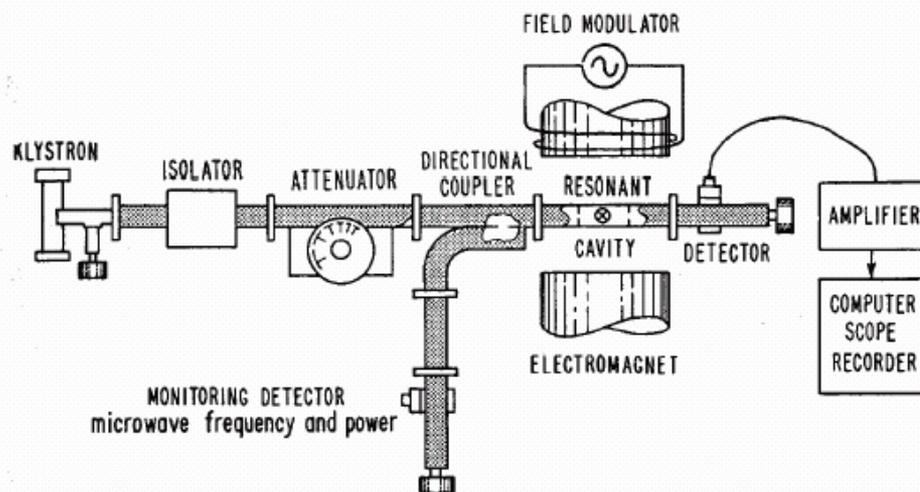
The spectrum is usually presented as the first derivative of the absorption spectrum.



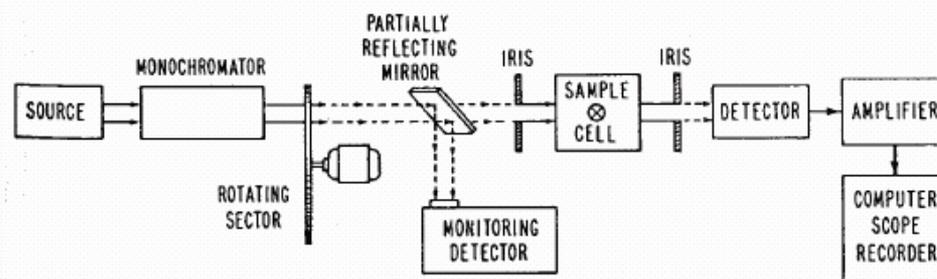
## Comparison of an EPR spectrometer, and a UV-VIS spectrophotometer

In this comparison, several points are noteworthy.

1. In a spectrophotometer, the spectrum is generated by varying the wavelength. As we just discussed, in a CW-EPR spectrometer, we use a fixed wavelength (frequency), but vary the magnetic field. This is achieved by the field scan and modulation coils associated with the magnet.



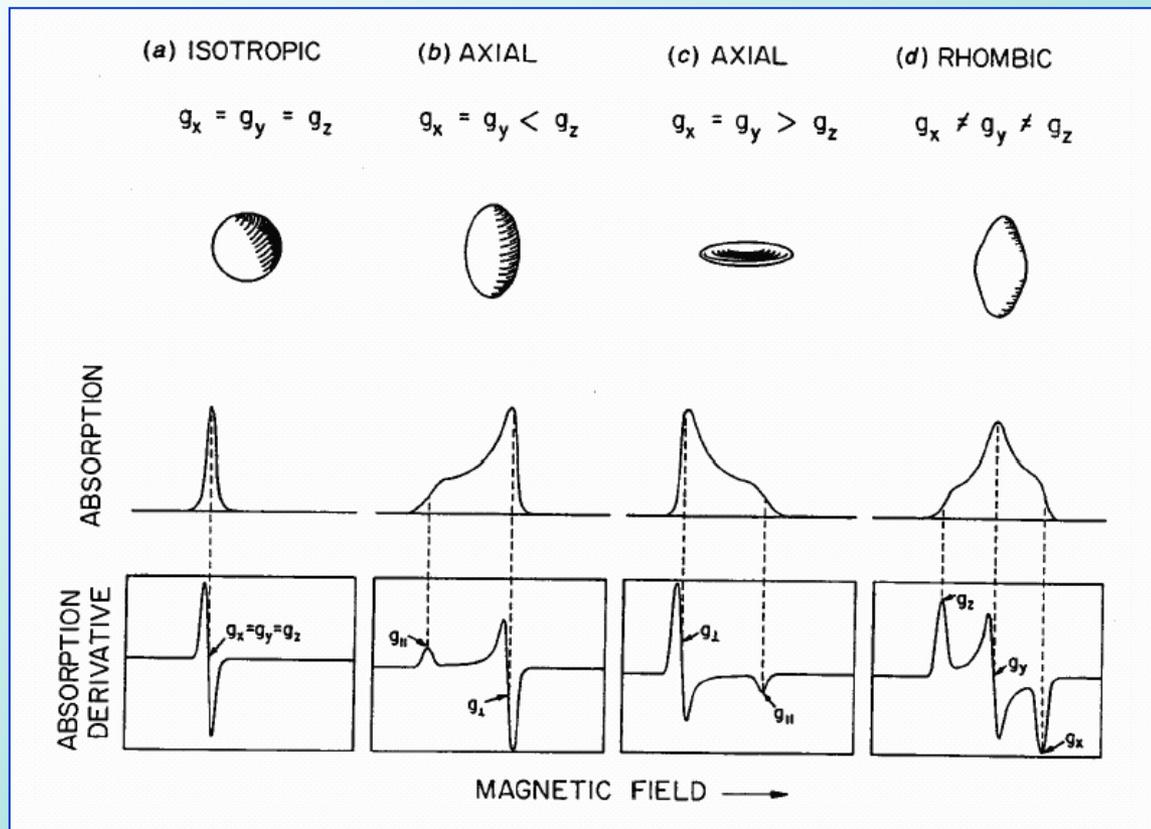
(a)



(b)

2. In the spectrophotometer shown, the light-beam is chopped by a rotating sector. This gives it a period function, and allows use of phase and frequency sensitive detection electronics, which improve the signal to noise ratio.

3. In the CW-EPR spectrometer, the signal is modulated at 100 kHz by modulation of the magnetic field. This allows use of frequency and phase sensitive amplification to improve the S/N ratio. The intensity and *modulation* frequency are monitored to provide a reference channel. The output signal is an amplified difference.



Because of the use of a modulated signal and frequency selective amplification, the detection electronics only respond to a **change** in absorbance in the sample. As a consequence, the spectrum is output as the first derivative of the absorbance spectrum.

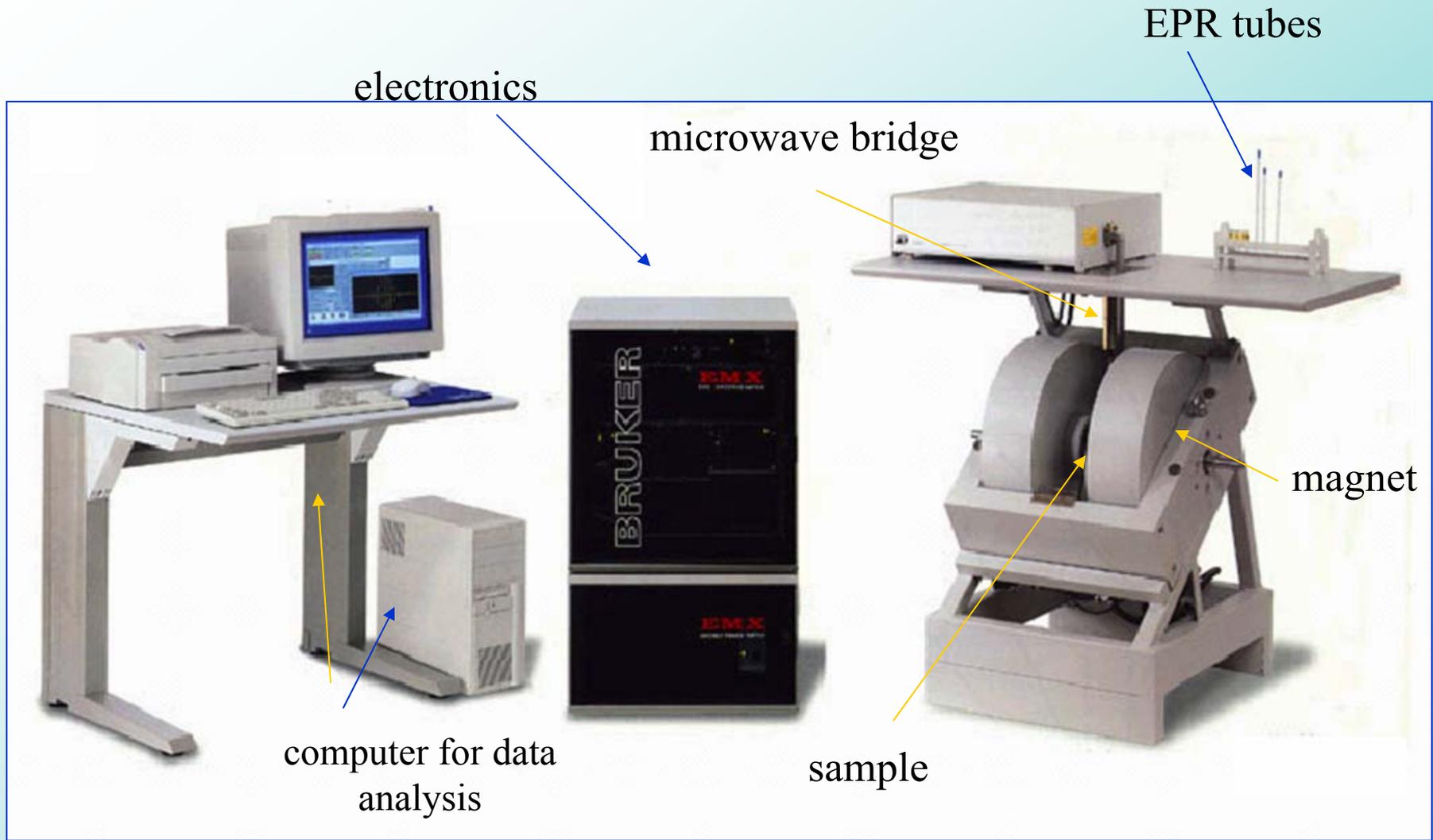
## Choice of EPR range

Use of a fixed microwave frequency and a varying field in CW-EPR is determined by the difficulty of generating microwaves of sufficient intensity. The choice was originally dependent on the development of radar technology. Radar uses microwaves, with different frequencies for different purposes, and also needs a lot of power. Although alternative technologies are now available, the design of EPR spectrometers was based on the availability of klystron microwave sources from the radar applications, with the frequencies below.

The g-factor is a constant but the field for resonance changes with microwave frequency.

Microwave Band	Microwave Frequency (GHz)	$B_0$ (for $g=2$ ) Gauss
L	1.1	392
S	3.0	1070
X	9.5	3389
K	24.0	8560
Q	35.0	12485
W	94.0	33600

EPR spectroscopists talk about W-band, Q-band, S-band, etc., EPR spectrometers. Most work reported has been done at X-band, with microwave frequencies of  $\sim 9.5$  GHz, and magnetic field strength  $\sim 3400$  Gauss, or 0.34 Tesla.



electronics

microwave bridge

EPR tubes

magnet

computer for data analysis

sample

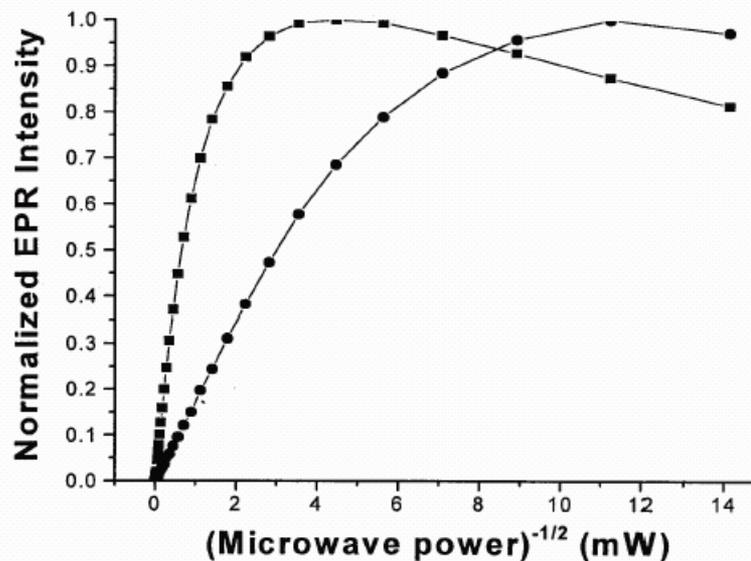
## Saturation in an EPR experiment

An important difference between spectrophotometry and EPR or NMR spectroscopy is in the relaxation properties of the sample. In absorption of light in the near-UV and visible range, the changes in energy levels are large, and the life-times of the excited states are short. At the intensities normally employed, the ground-state energy levels are never significantly depleted.

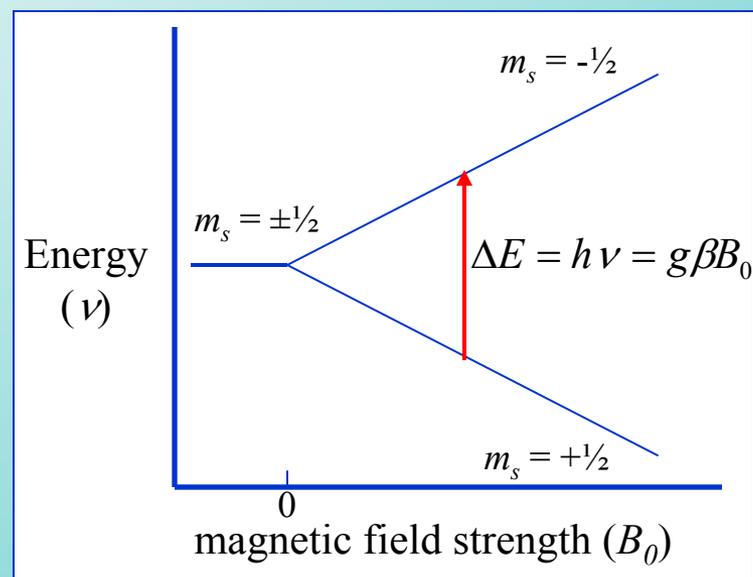
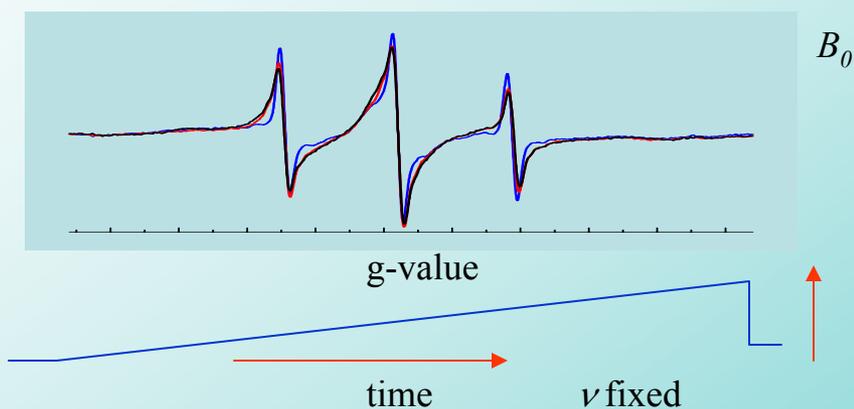
By contrast, in EPR and NMR measurements, the energy levels are much smaller, and the lifetimes of the flipped spin states are much longer. The excited spins relax back to the  $m_s + 1/2$  level by coupling to local magnetic fields in the immediate environment. As a result the spin states have lifetimes that are long, and much affected by the environment, and can thus provide local structural information.

At the microwave or RF intensities commonly available, spin systems can be easily saturated, because the rate of excitation to  $m_s - 1/2$  exceeds the rate of decay.

Saturation characteristics help to differentiate two different species in a sample.



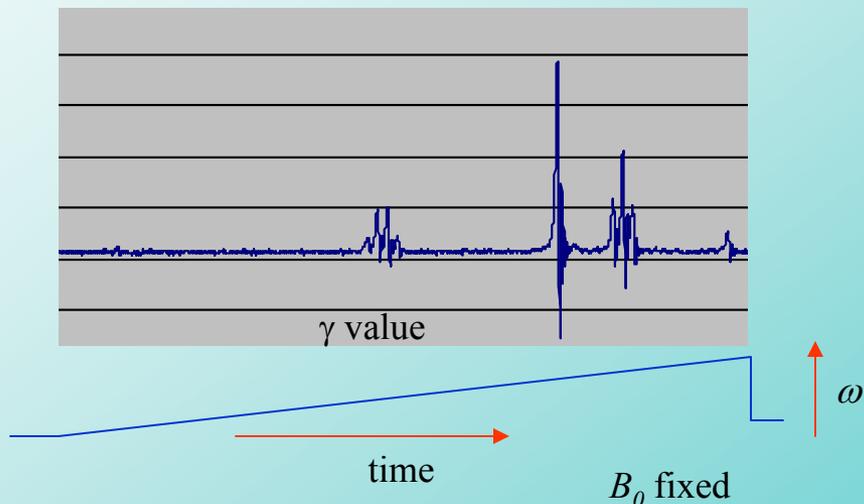
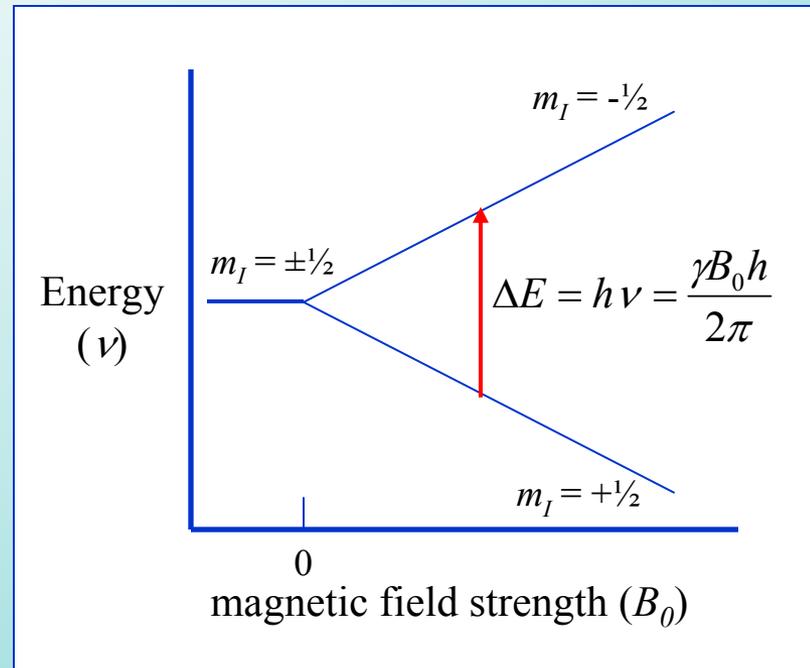
In **CW-EPR**, because of the fixed frequency generated by available microwave sources, the apparatus is set up so that a spectrum is obtained by varying the magnetic field,  $B_0$ , at constant energy or frequency ( $E = h\nu$ ). The g-value of the system is a good choice as the characteristic property of a paramagnetic species because the value is independent of the magnetic field strength, and therefore of instrument.



Many of the Figs, and the general treatment in the following section, are taken from a nice set of lectures on the web by [Guillermo Moyna](http://208.7.154.206/gmoyna/NMR_lectures/NMR_lectures.html)

[http://208.7.154.206/gmoyna/NMR\\_lectures/NMR\\_lectures.html](http://208.7.154.206/gmoyna/NMR_lectures/NMR_lectures.html)

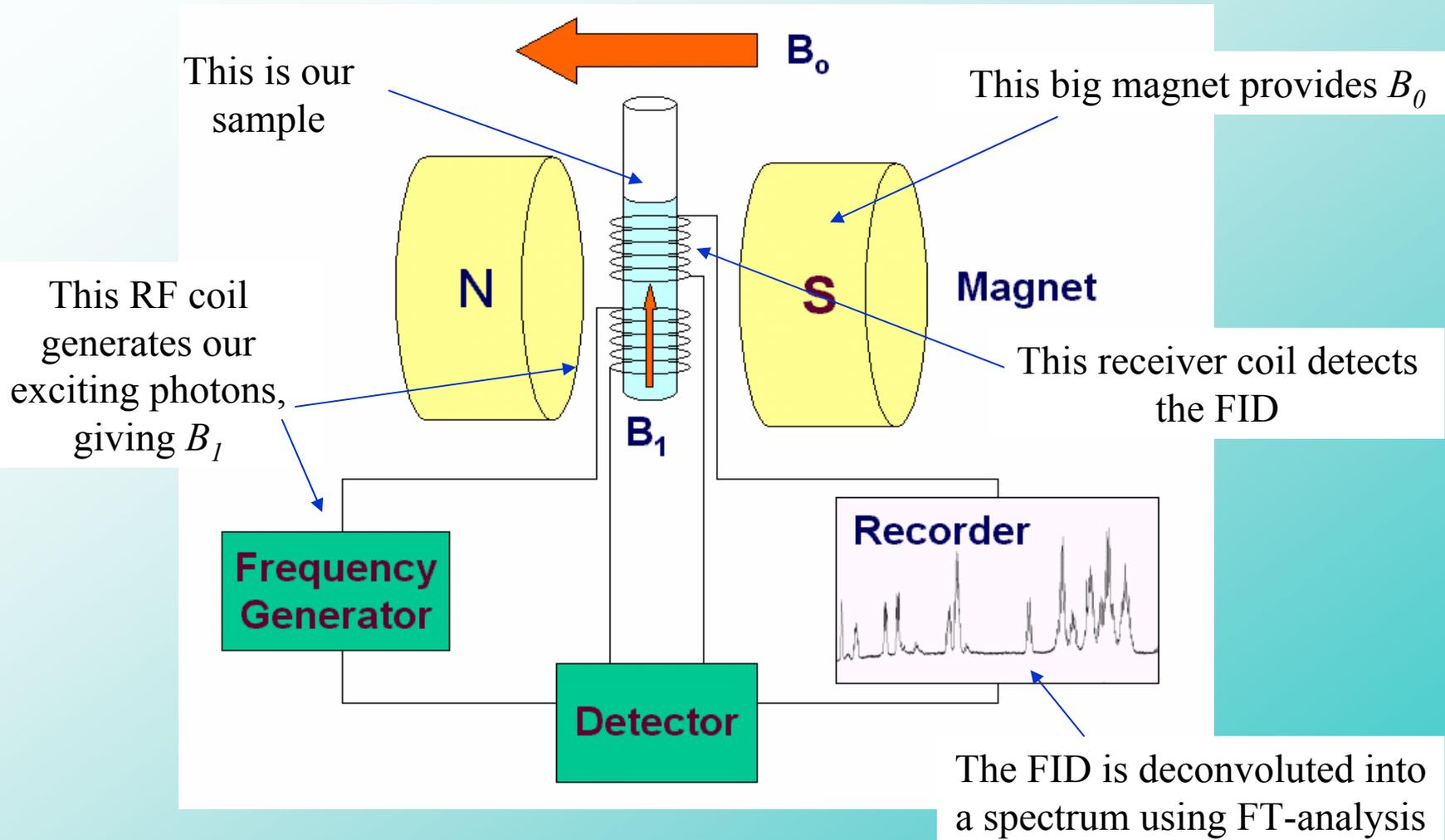
In **CW-NMR**, the approach is a little different than in CW-EPR. Because radio waves are much easier to handle (to “tune”, - that’s how radio stations keep their identity), it is convenient to take an NMR spectrum by varying the radio wave frequency while keeping the magnetic field constant. The gyromagnetic ratio,  $\gamma$ , is independent of field strength, and is therefore a useful property for characterization of particular species, since it’s a property of the nucleus and therefore field (and instrument) independent.



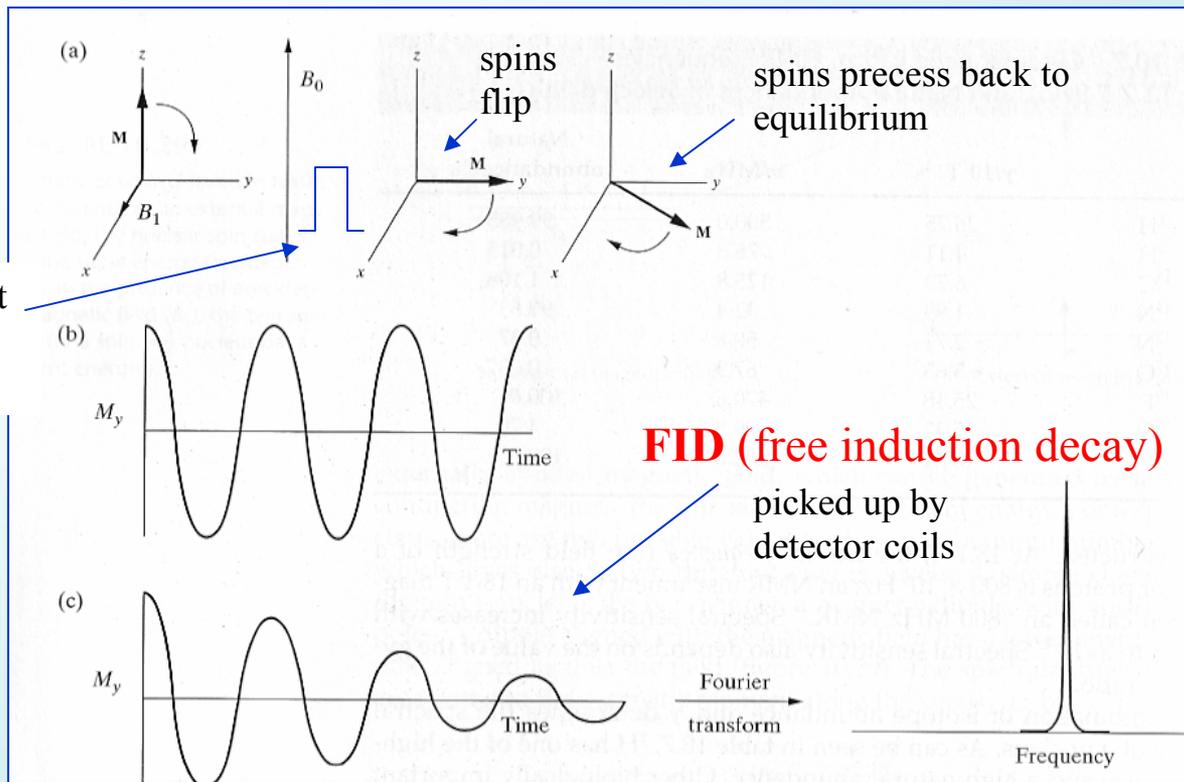
### Simple pulsed FT-NMR.

In **pulsed FT-NMR**, the sample is placed in a fixed magnetic field, which aligns the magnetic dipoles as before. A pulse of radio waves of the resonance frequency and the right duration has the effect of introducing an additional magnetic field that will flip the spins to a new orientation. The spins will then relax back to their equilibrium orientation, emitting photons of the frequency of their transition – Free Induction Decay (FID). A detector coil measures the RF emission as a kinetic trace. The frequencies are extracted by Fourier transform (FT) analysis.

Pulsed NMR is much more sensitive than CW-NMR, because each trace is accumulated in a few ms. As a consequence, averaging procedures can be used to improve signal-to-noise.



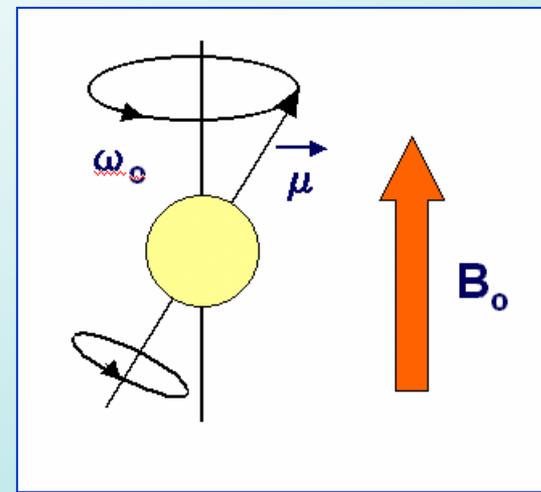
RF pulse at  
resonance  
frequency



If a sample with a single spin population is used, the emitted RF signal will have a simple harmonic content reflecting the single transition excited. The waveform will decay due to **precession** of the spin, leading to a damping of the oscillations. The frequency of the transition can be extracted from the time-domain signal by Fourier transform analysis. In practice, use of a square wave pulse introduces harmonics that effectively cover a wider and more useful frequency range than a single frequency, and can detect transitions of different frequencies.

## Precession

Before we discuss pulsed methods in greater detail, we need to get a more convenient view-point of our population of spins.



The magnetic moment of each nucleus is defined by:

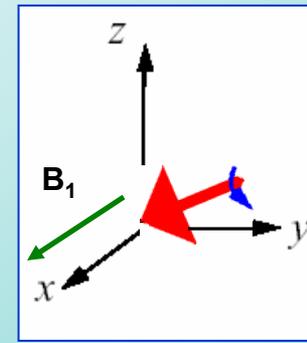
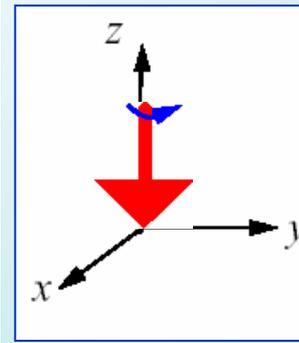
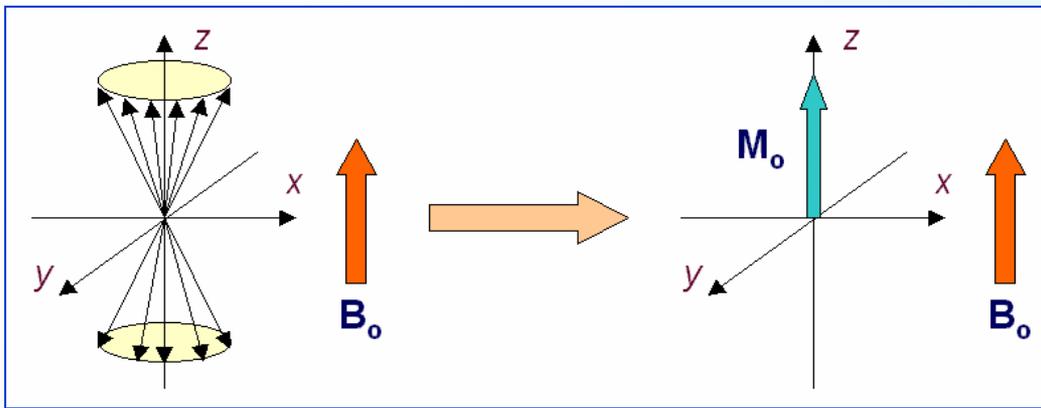
$$\vec{\mu} = \frac{\gamma I \hbar}{2\pi}$$

The nucleus associated with  $\vec{\mu}$  is spinning due to the spin angular momentum,  $I$ . In an external magnetic field, there are therefore two forces acting on it, - one, the external field, that wants to bring it towards  $B_0$ , and another, its angular momentum, that wants to keep it spinning. The net result is that  $\vec{\mu}$  ends up precessing around the axis of  $B_0$ . The frequency of this precession is given by the Larmor frequency:

$$\nu_{precession} = \frac{\omega}{2\pi} = \frac{\gamma B_0}{2\pi}$$

This is the same frequency (energy) as given by the energy of transition between the two spin states, as we can see by substitution:

$$\Delta E = h\nu = \frac{\gamma B_0 \hbar}{2\pi}, \quad \text{or} \quad \nu = \frac{\gamma B_0}{2\pi}$$



Because of the complications due to all the different magnetic moments associated with a bunch of precessing nuclei, the physicists have come up with a neat trick to simplify discussion. The general idea is as follows.

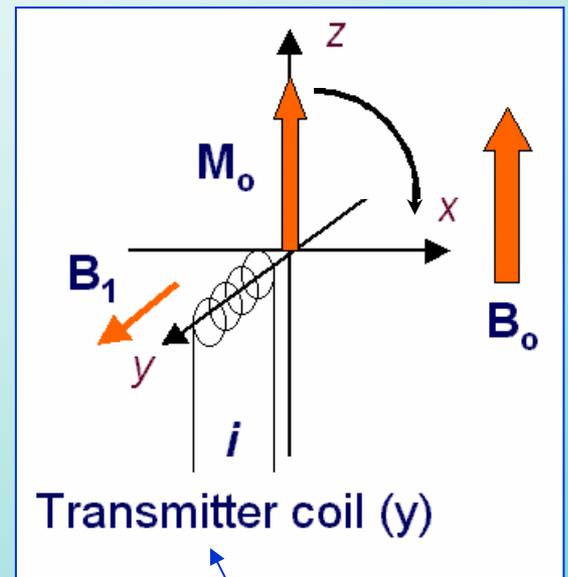
1. We change the frame of reference of our system to one which **rotates at the Larmor frequency**. A nice analogy is to think of the roundabout in a children's playground that the kids cling to while it is whirled around. From the parents perspective, it spins, but from the perspective of a kid in the middle, all the children are static (and the parents whirl around, which adds to the fun).

In this rotating frame of reference, all the nuclei are static.

2. We make a vector sum of the  $\vec{\mu}$  values for the nuclei (the fraction responsible for the net absorption). This results in a vector  $M_0$  which is in the same direction as  $B_0$ , but now represents a **population** of spins in our rotating frame.
3. We can now discuss what happens if we apply a supplementary field,  $B_1$ .

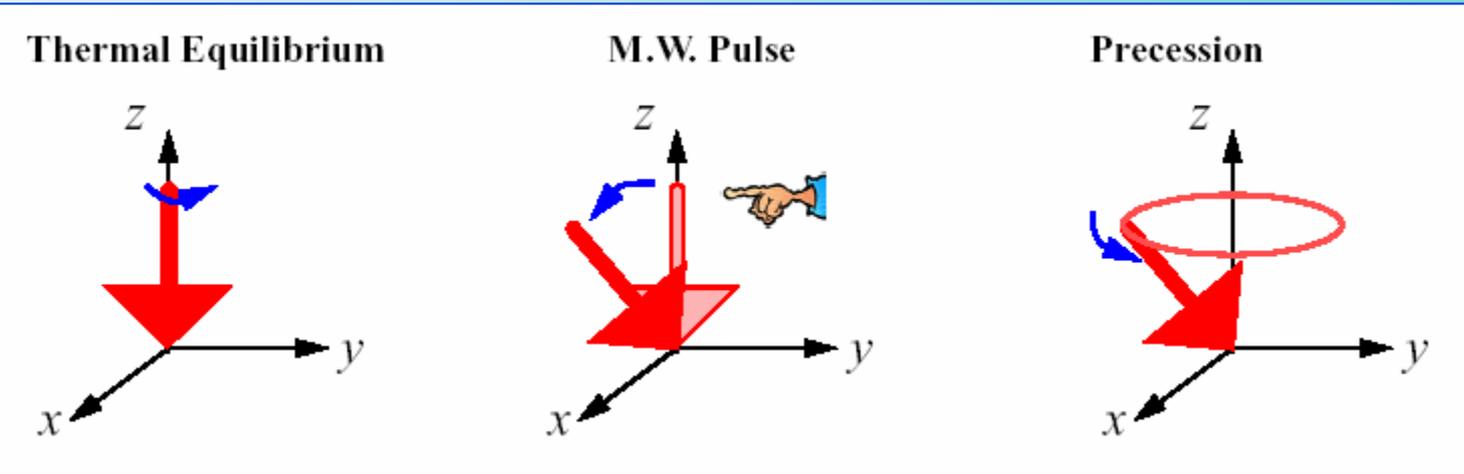
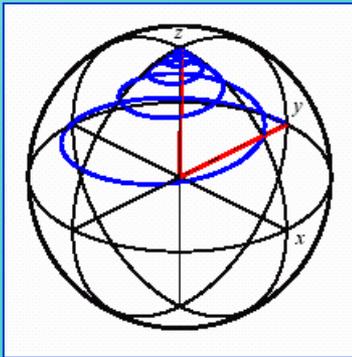
We can apply the equivalent of a supplementary magnetic field ( $B_1$ ) by giving a pulse of RF photons (for NMR), or microwave (MW) photons (for EPR), at the resonance energy, along an appropriate axis of our system. The vector of our spins is now tilted to a new angle with respect to our reference axis (the z-axis), and will then **precess in the x,y plane**, back towards the equilibrium position. The angle to which we deflect the vector depends on the duration of the pulse. Two important pulse lengths are the  $\pi$  and  $\pi/2$  pulses. A  $\pi$  pulse rotates the vector through  $180^\circ$ , while a  $\pi/2$  pulse rotates the vector through  $90^\circ$  around the axis of  $B_1$ .

In most pulse experiments, the first pulse is a  $\pi/2$  pulse.



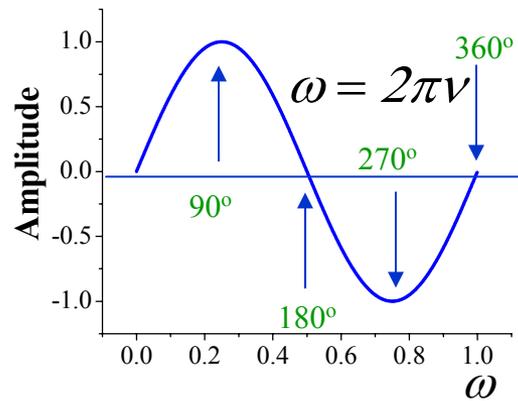
This generates our RF photons

Precession in x, y plane

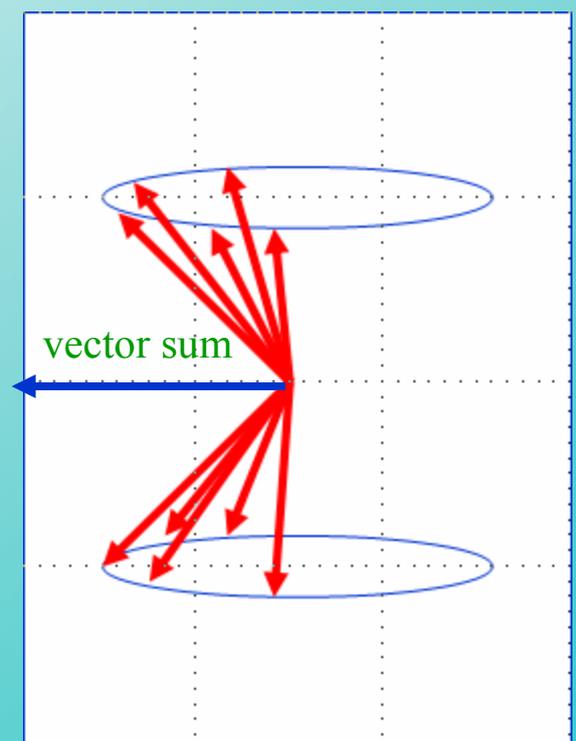
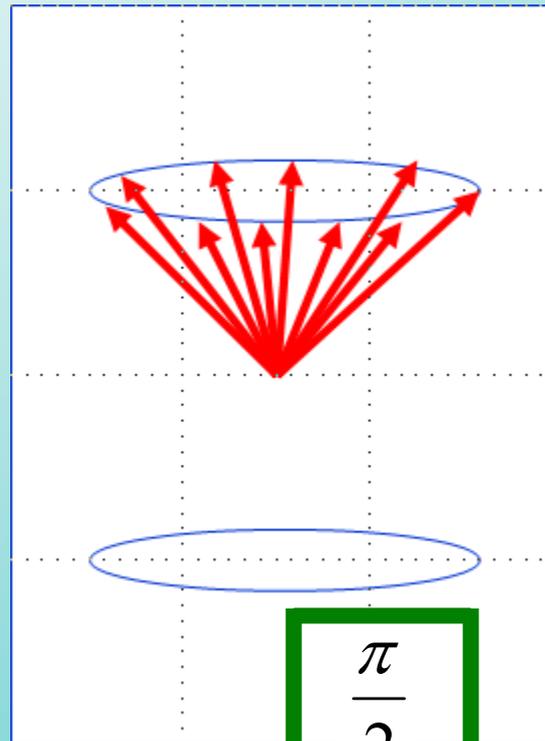
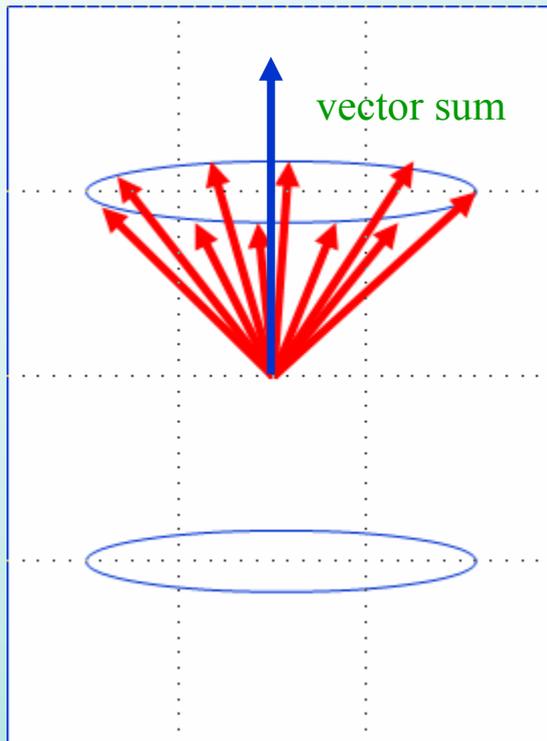


Why do our spins flip through just  $90^\circ$ ? Is QM all wrong, - can we have  $\frac{1}{2}$  quanta?

QM is not wrong.  
Photons have a  
“memory” based on  
the transition that  
generated them. They  
“remember”:



The energy of transition,  
and hence frequency.  
The orientation of the  
transition, - polarity.  
The phase of the transition.  
Photons look for “home”



# Matching of phase, frequency and orientation

wrong phase  
wrong frequency  
wrong polarity



z



wrong phase  
wrong frequency



x

Madonna is looking for Mr. Right

y

right phase

right frequency

wrong polarity

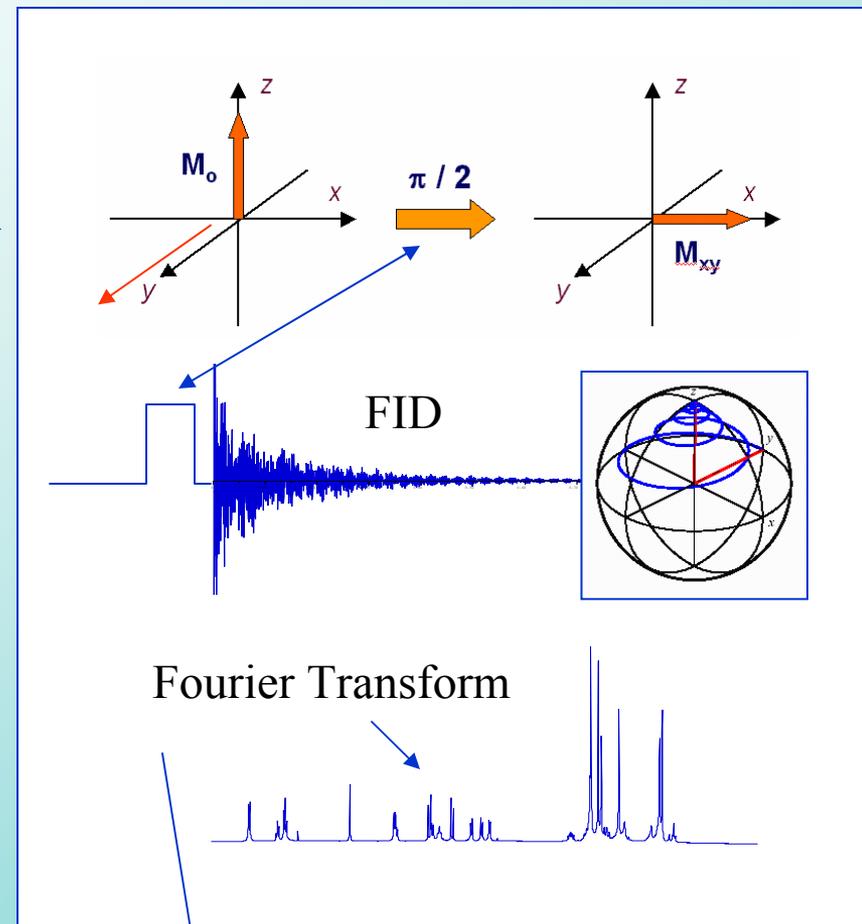


Mr. Right

One pulse NMR, and detection of the Free Induction Decay (FID)

We took a quick look at 1-pulse-NMR in a previous slide. A great deal more information from the 1-pulse approach can be obtained if an RF pulse covering a range of frequencies is applied.

This will then excite all transitions in the frequency range, and they will all decay, and emit at their specific frequencies. This gives a complicated signal in the time domain, but the frequency contributions can be readily deconvoluted by Fourier Transform analysis. Before we can discuss this further, we need to understand relaxation processes.



$$M(\omega) = \int_{-\infty}^{\infty} M(t) e^{i\omega t} dt$$

# Relaxation phenomena

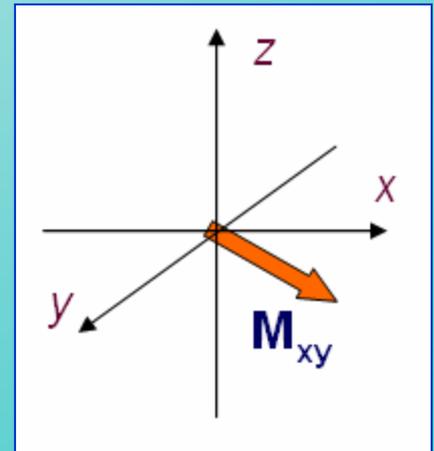
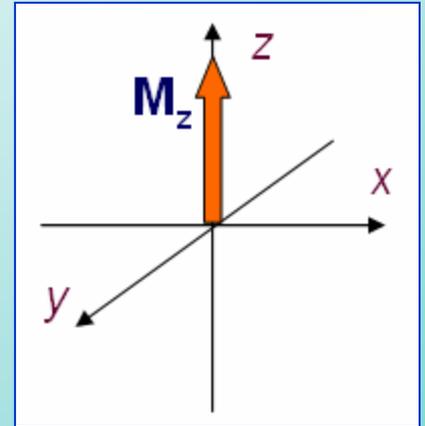
So far we haven't said anything about the phenomena that brings the magnetization back to equilibrium. **Relaxation** is what takes care of this. There are two types of relaxation, and both are time-dependent exponential decay processes with characteristic times:

## Longitudinal or Spin-Lattice relaxation (characterized by time $T_1$ ):

- Depends on interaction with components which have their magnetization aligned along the **z** axis ( $M_z$ ) by the external field.
  - Loss of energy from the system to the surroundings (lattice) as heat, due to random **dipolar coupling to aligned spins**.
  - Dipolar coupling to specific spins. An important class of interactions are those which allow dipolar coupling of reproducible energy, due to an orientation of a **neighboring spin that is fixed structurally** (NOE effect).
  - Interaction with paramagnetic electron spins (ENDOR, ESEEM), etc.

## Transverse or Spin-Spin relaxation (with time $T_2$ ):

- $T_2$  acts on the components of magnetization lying on the  $\langle xy \rangle$  plane ( $M_{xy}$ ). Usually these are **through-bond couplings** to spins whose orientation is fixed with respect to the test spin by covalent bonding.
  - **Spin-spin interactions** dephase  $M_{xy}$
  - Also by imperfections in the magnet homogeneity (fanning out).
  - Cannot be bigger than  $T_1$ .



In order to understand relaxation from a phenomenological point of view, we have to introduce the *Bloch equations* (left), which describe the evolution of the spin system with time under the effects of magnetic fields along the three axes,  $x$ ,  $y$ , and  $z$ .

$$dM_x(t) / dt = \gamma [ M_y(t) * B_z - M_z(t) * B_y ] - M_x(t) / T_2$$

$$dM_y(t) / dt = \gamma [ M_z(t) * B_x - M_x(t) * B_z ] - M_y(t) / T_2$$

$$dM_z(t) / dt = \gamma [ M_x(t) * B_y - M_y(t) * B_x ] - ( M_z(t) - M_o ) / T_1$$

$$M_x(t) = M_o * \cos( \omega_{\text{eff}} t ) * e^{-t/T_2} \quad (\omega_{\text{eff}} = \omega_o - \omega)$$

$$M_y(t) = M_o * \sin( \omega_{\text{eff}} t ) * e^{-t/T_2}$$

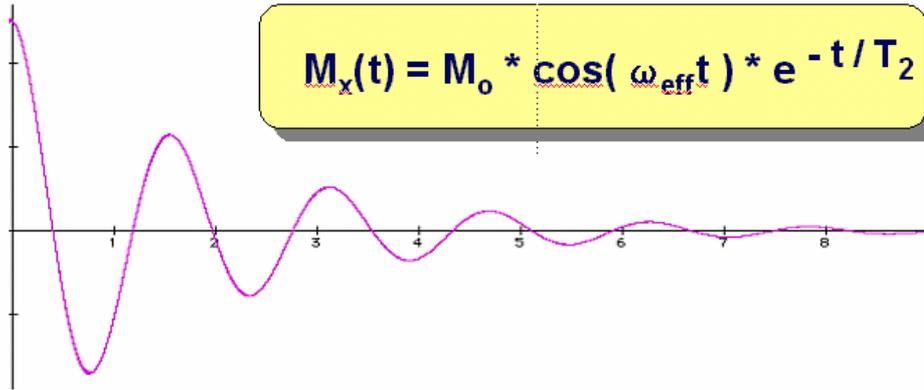
$$M_z(t) = M_o * ( 1 - e^{-t/T_1} )$$

Without worrying too much about all the terms, we can see that these show:

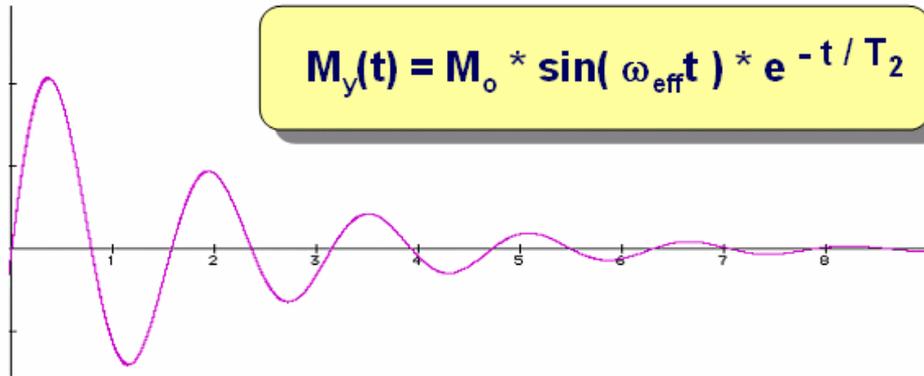
1. The rate of change of magnetization with time along the three axes;
2. That the rates for each axis include contributions from magnetization in other axes.
3. Relaxation in the  $x, y$  plane is determined by  $T_2$ , that along the  $z$ -axis by  $T_1$

The equations on the right are solutions for the idealized case in which all the spins have initially been flipped to the  $x, y$  plane by application of a  $\pi/2$  pulse.

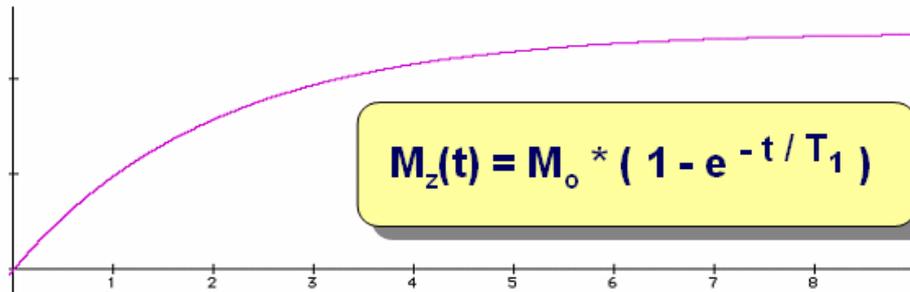
- Graphically, we have the following:



$$M_x(t) = M_0 * \cos(\omega_{eff}t) * e^{-t/T_2}$$



$$M_y(t) = M_0 * \sin(\omega_{eff}t) * e^{-t/T_2}$$



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

Magnetization in the  $x$ -axis has a harmonic component that decays with  $T_2$ . This our FID

Magnetization disappears from the  $y$ -axis out of phase with its appearance in the  $x$ -axis, with  $T_2$ .

The rate of appearance of net magnetization in the  $z$ -axis is given by  $T_1$ .

This is the main contribution if we flip our spin vector through  $180^\circ$  with a  $\pi$  pulse

## Take-home messages from our discussion of relaxation processes

$T_1$  is the characteristic time for spin-lattice relaxation (spins aligned with the field).

$T_2$  is the characteristic time for spin-spin relaxation (spins coupled through bonds).

$T_1$  and  $T_2$  can be measured separately by use of appropriate pulse sequences.

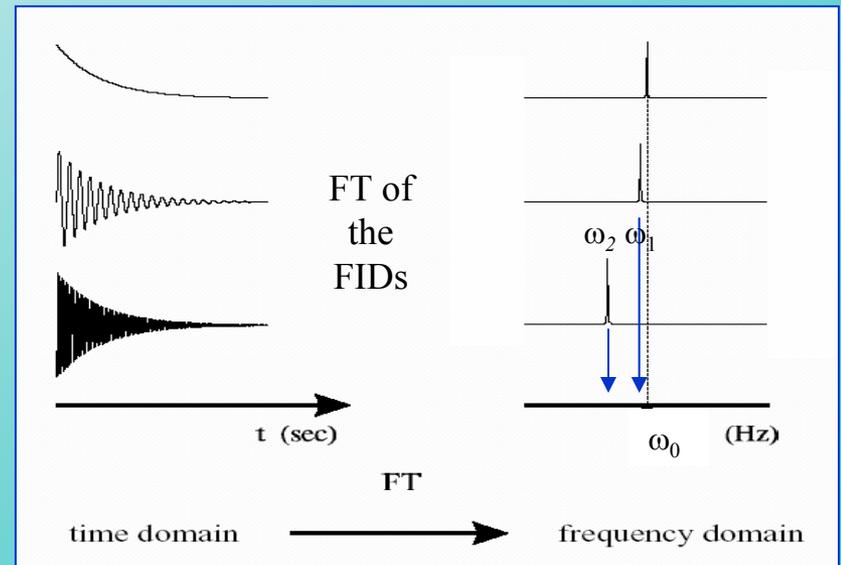
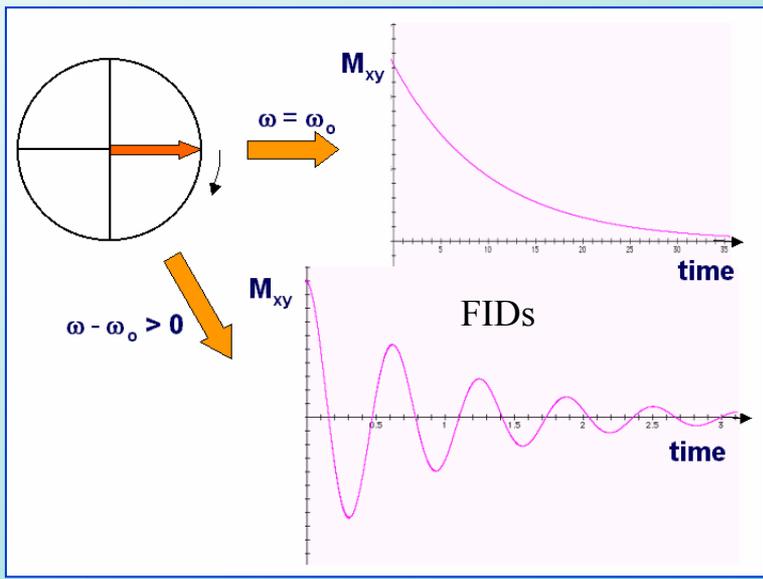
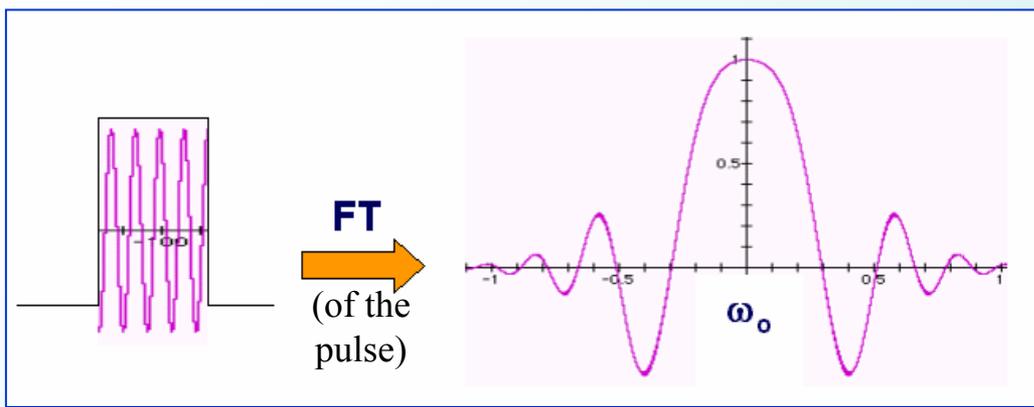
$T_1$  and  $T_2$  arise from different sorts of interactions, both of which provide useful information about the environment of the nuclear (or electron) spins.

### Relaxation of the spin population

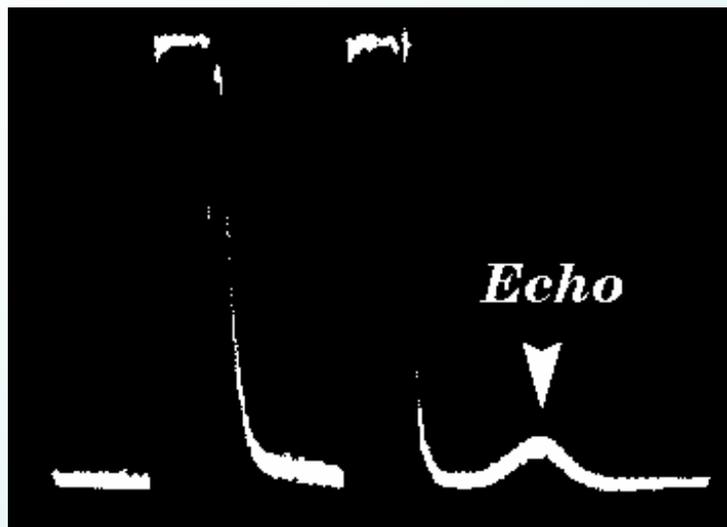
- The two different relaxation time constants,  $T_1$  and  $T_2$ , both contribute to the overall time needed for the spin system to relax back to its equilibrium population mix.
- The combination determines the duration of the FID.
- The times can be much longer than the transition times for the spin flipping.
- Because the relaxation times are long, the spin population can be easily saturated. When saturated, the populations in the  $\uparrow$  and  $\downarrow$  states are equal, and no **net** absorption occurs, so no signal is seen.

# How do we sample transitions with a range of energies?

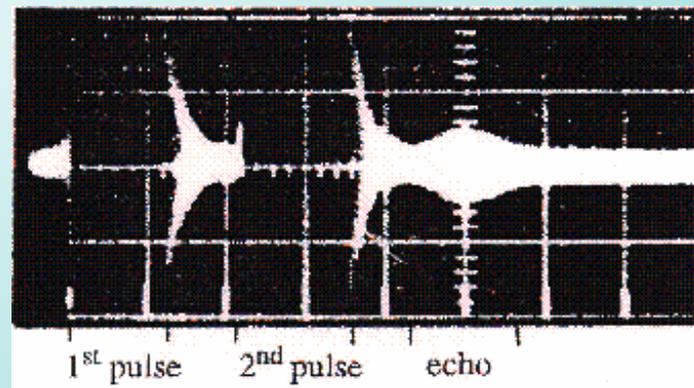
The square wave pulse centered at frequency  $\omega_0$  contains harmonics that effectively cover a range on either side of  $\omega_0$ . The detector coil is tuned to  $\omega_0$ , so the FT of the FID for a transition at the central frequency is a smooth curve. The transitions away from  $\omega_0$  show harmonics, and the frequency shows up as a shift away from  $\omega_0$  after Fourier transformation.



## Spin-echo pulsed magnetic resonance



E. Hahn, "Spin echoes", Phys. Rev. 80, 580 (1950)



R.J. Blume, "Electron spin relaxation times in sodium-ammonia solutions", Phys. Rev. 109, 1867 (1958)

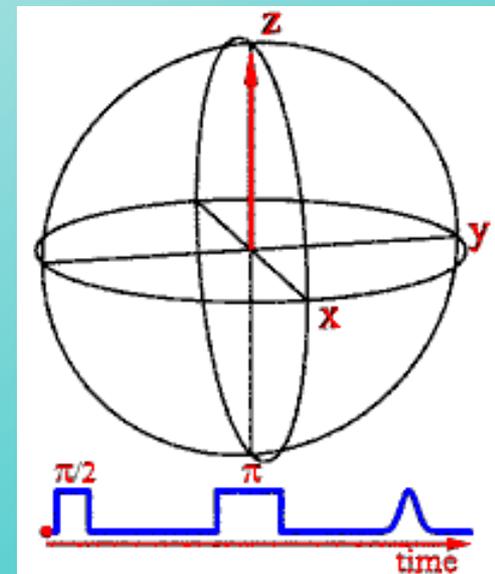
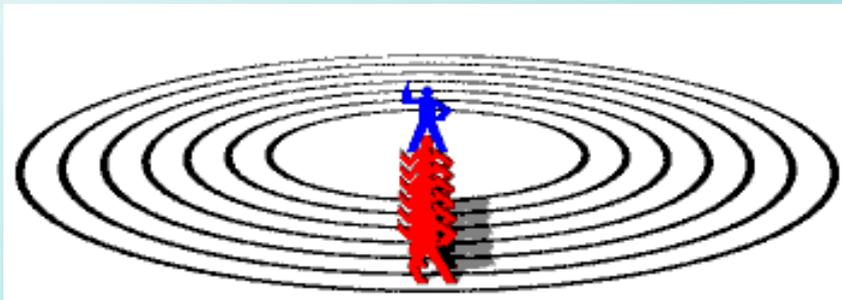
NMR spin echoes were discovered by Hahn in the early 1950s, and EPR echoes almost two decades later by Blume. The time lag reflects the much higher frequencies of EPR spectroscopy, and the need for development of improved electronics to follow the time course of EPR spin echoes.

The general idea of the spin echo approach is to use  $\pi$  and  $\pi/2$  pulses to bunch all the spins together, so that they are synchronized. Suitable choice of pulse, and the time between pulses, makes it possible to explore in detail the evolution of the spin states, and their detailed kinetics.

The synchronization can be visualized in terms of the cartoons below.

On the left, we have a representation of the “racetrack” synchronization model. The first BANG is the pulse that starts the transitions moving. The second BANG is a pulse that sends them back along the same path. Since the rates of transition ( $\equiv$  frequencies) are characteristic for each “player”, each goes back at the rate they started. As a result, they’re in synch when they get back to the start.

The animation on the right shows a “pancake” model. The  $\pi/2$  pulse flips the spin population to the  $x, y$  plane where it starts to precess. The  $\pi$  pulse flips all the spins over (like tossing a pancake). They continue to evolve, but the orientation is changed, so they end up back in synch, and generate the echo.



## What does spin-echo gives us that the 1-pulse FID doesn't?

1. By synchronization of the spins, we increase the sensitivity.
2. By judicious use of pulse length, we can select orientations in our rotationally frozen frame of reference.
3. By varying the time between pulses, and looking at the effect on the echo (the synchronized population), we can explore the time-course of the different components of the relaxation process.
4. This allows us to look at each different spin (which is seen at a different frequency in the spectrum after FT), and the effect of local environment on their  $T_1$  and  $T_2$  relaxations.
5. The  $T_1$  and  $T_2$  components of relaxation contain information about the structural neighborhood of each species in our spectrum.
6. Structural information includes (a) nature of neighboring atoms; (b) bond lengths and their angular components; (c) distances; (d) energies.
7. From this information we can build 3-D structures at atomic resolution.