Note of Pulsed EPR Primer

09/25/2021

PhYsiX

Pulse EPR

- Strike the bell, digitize the resultant sound,
  do FT to obtain frequency spectrum

- NMR gain sensitivity by moving to a pulse FT technique,
  because they have many narrow lines over a wide frequency range

- EPR spectra are broad and not as numerous, but by measuring in time
  domain and using multi-dimensional techniques, could extract more info

Advantages

- ESEEM (Electron Spin Echo Envelope Modulation)

  Measure interaction of electron spin with nearby nuclei

- Measure relaxation times more directly than CW techniques

  offer dynamical & distance information

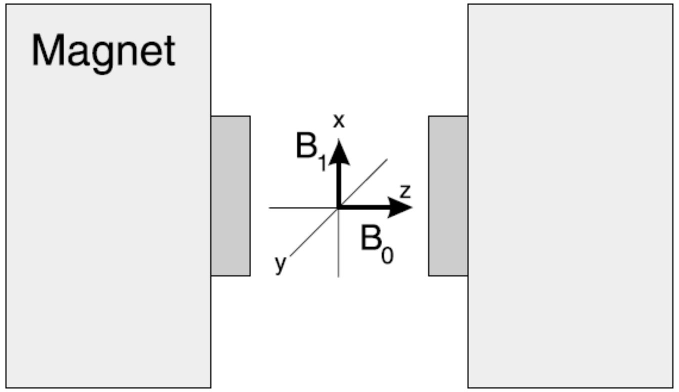
- DEER (Double Electron Electron Resonance), ELDOR (ELectron

  DOuble Resonance): measure particularly long distance in large molecules

Magnetization in the lab frame

- Electron magnetic moment precess in Larmor frequency

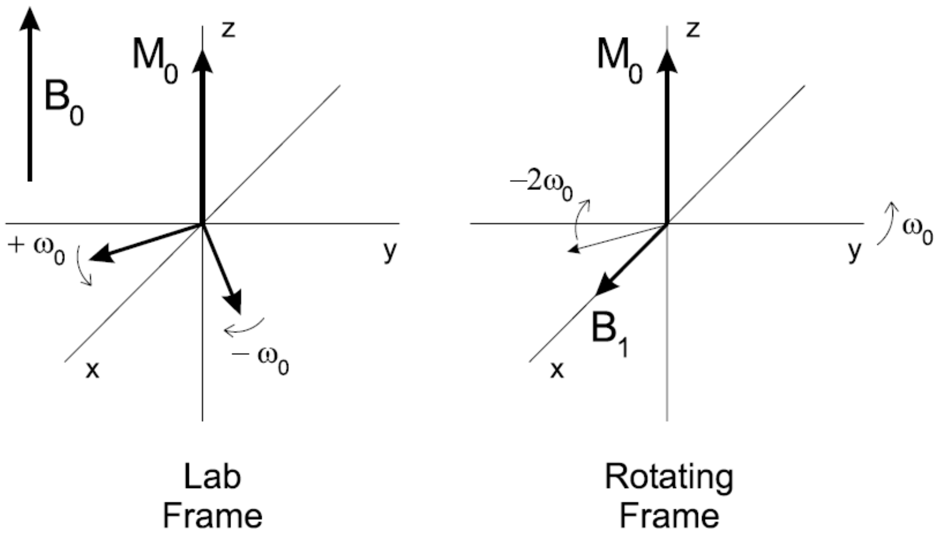
- Surplus of (magnetic orientation) parallel electron spins at thermal equilibrium (Boltzman distribution), net magnetization in z axis



Magnetization in rotating frame

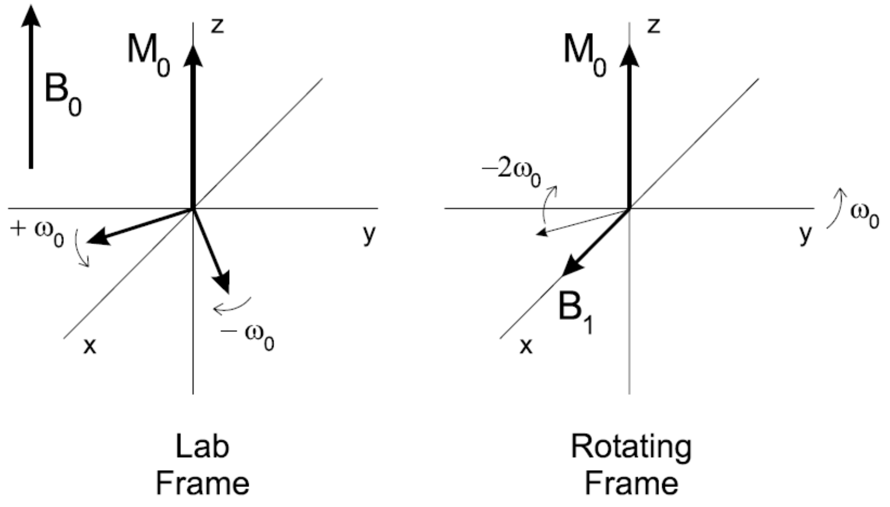
- Linearly polarized microwaves could be sum of two magnetic fields rotating in opposite directions

- Only stationary B_1 and M_0 in rotating frame



Magnetization in rotating frame

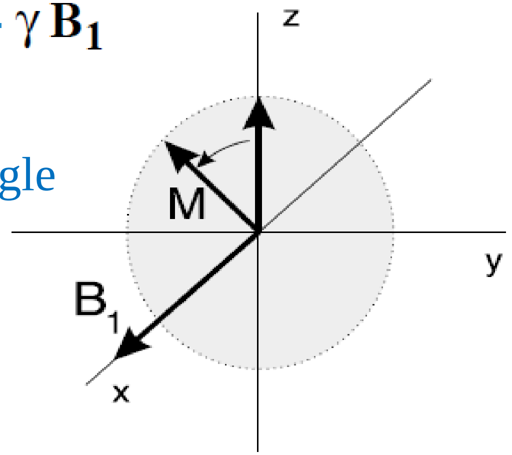
- Linearly polarized microwaves could be sum of two magnetic fields rotating in opposite directions
- Only stationary B_1 and M_0 in rotating frame
- Tip angle depend on both magnitude of B1 and length of pulse
- B1 parallel to +x: +x pulse



Rabi frequency?

$$\omega_1 = -\gamma B_1$$

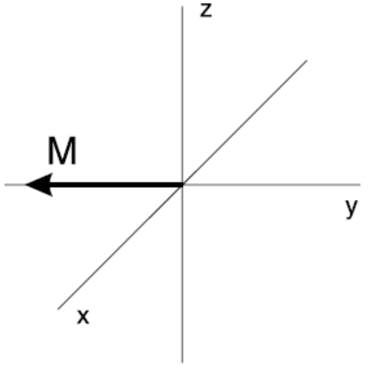
tip angle



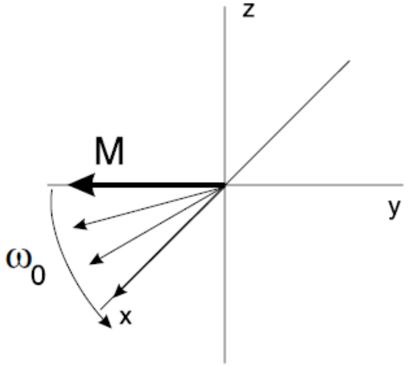
FID (why called induction decay?)

a decaying RF current in the inductor

- M along –y rotate in x-y plane in lab frame
- Generate current and voltage in resonator as a generator
- A $\pi/2$ pulse maximizes magnetization in x-y plane and therefore maximize the signal



Rotating Frame



Lab Frame

Off-Resonance effects

Rotating frame: frequency of microwave field B_1

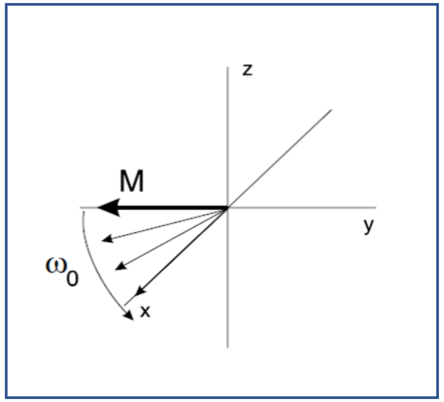
Larmor frequency: defined by γ and B_0

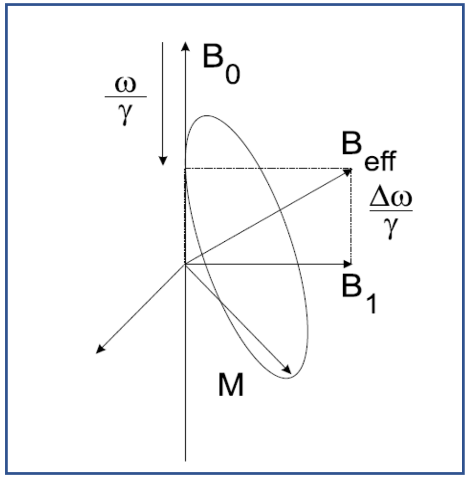
- EPR spectra contain many different frequencies so not all parts can be exactly on resonance simultaneously

- Individual frequency components -> Magnetization components rotating in x-y plane

- Non-zero B_0: tip magnetization differently

- Cannot tip magnetization into x-y plane as effectively, magnetization does not move in an arc, but in a cone





Broad EPR signals

- Not able to tip all the M into x-y plane to create FID
- Maximize w_1 or minimize $\pi/2$ pulse length
- A $\pi/2$ pulse maximizes magnetization in x-y plane and therefore maximize the signal

How to get this spectrum?

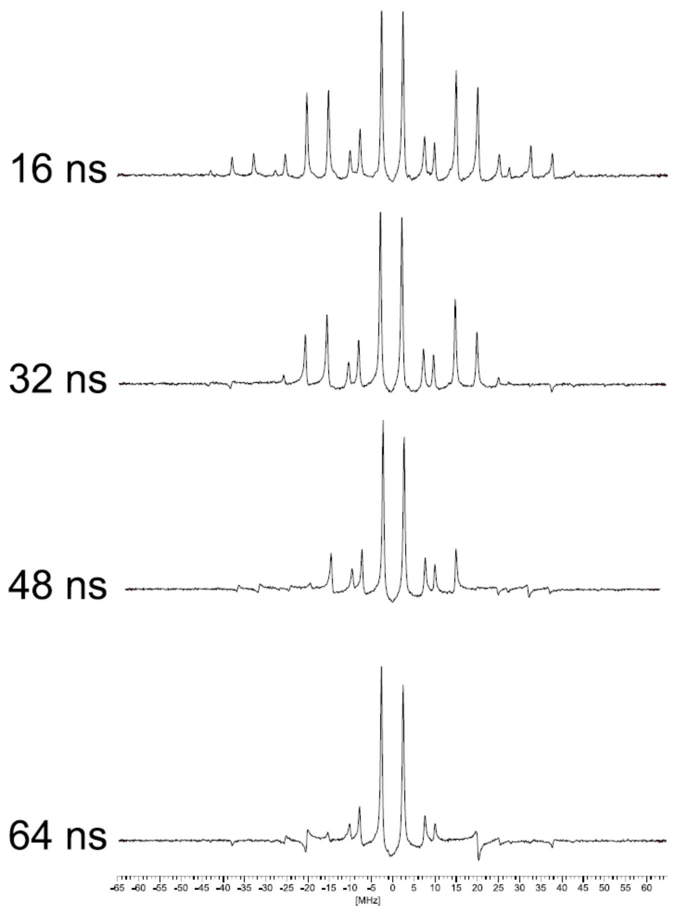


Figure 13 The effect of pulse length on an FT-EPR spectrum of the perinaphthenyl radical.

Relaxation times

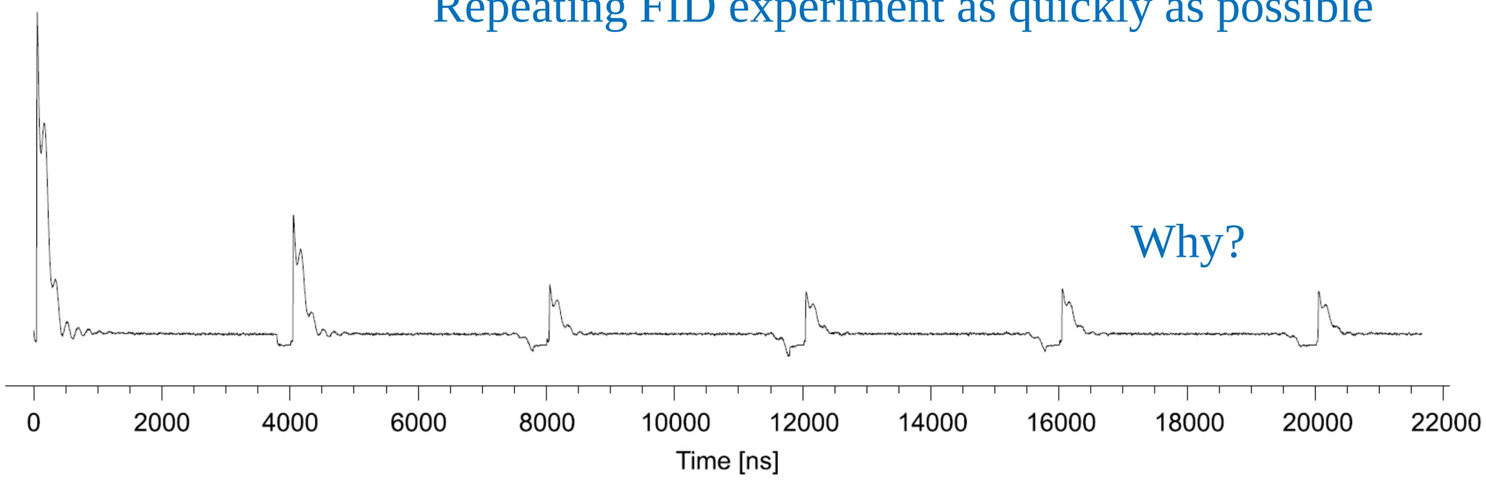
- Electron spins interact with surroundings, Mxy will decay away and return to z
- Information about frequency spectrum is somehow encoded in transverse magnetization in the rotating frame

Spin Lattice Relaxation time $\mathbf{T_1}$

- When we apply $\pi/2$ pulse to sample, we no longer have thermal equilibrium
- Rotates M to xy plane -> M along z goes to 0, i.e. population difference goes to 0
- Eventually return to thermal equilibrium -> spin-lattice relaxation
- π pulse, an inverse pulse
- Rate constant is T_1

Repeating FID experiment as quickly as possible

Why?



Transverse Relaxation time $\mathbf{T_2}^*$

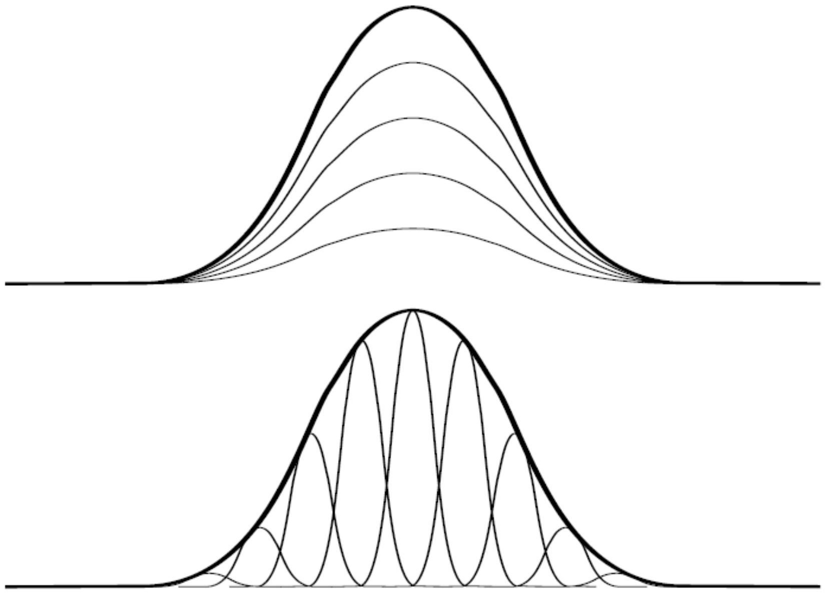
How to understand "broadening" ?

- Different magnetic fields: may arise from unresolved hyperfine structure

- Might result in a Gaussian lineshape

a) Homogeneous broadening. The lineshape is determined by the relaxation times and therefore lorentzian lineshapes are a common result. (See Equation [13] and Figure 21.) The EPR spectrum is the sum of a large number of lines each having the same Larmor frequency and linewidth.

b) Inhomogeneous broadening. The lineshape is determined by unresolved couplings because the EPR spectrum is the sum of a large number of narrower individual homogeneously broadened lines that are each shifted in frequency with respect to each other. Gaussian lineshapes are a common result.



spin packets

Transverse Relaxation time T_2^*

- Shape of this transverse magnetization decay is in general not exponential but instead reflects the shape of the EPR spectrum

- Characterization time T_2^*

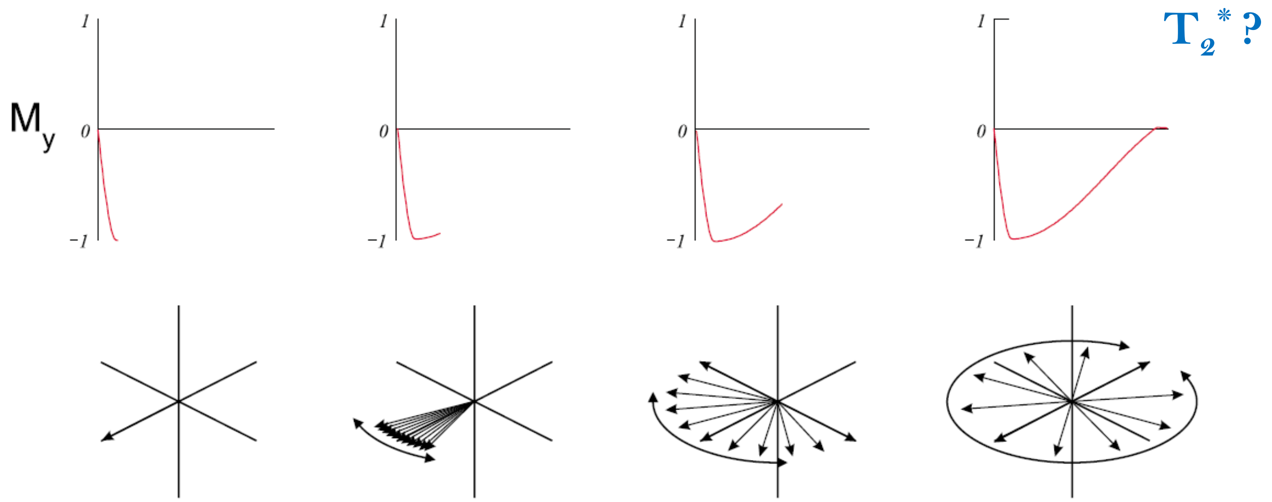


Figure 18 Fanning out of the transverse magnetization and the decrease of the transverse magnetization.

Spin-spin relaxation time $\mathbf{T_2}$

- In a homogeneously broadened spectrum, all the spins experience the same magnetic field
- Spins interact with each other -> mutual and random spin flip-flops
- Molecular motion can also contribute
- These fluctuations contribute to a faster fanning out of M
- Result in Lorentzian lineshapes, in general exponential

Fourier transform facts

- 实的函数可能有复的Fourier变换
- 偶函数有实的FT，奇函数有纯虚的FT
- 时域的指数型decay在频域为Lorentz线型
- 时域的Gaussian decay在频域为Gaussian
- 时域decay很快的信号在频域很宽。慢……窄

Fourier transform facts

- Linear phase distortion (and correction)
- 时域的时间偏移 -> 频域的相移 （Re -- Im）

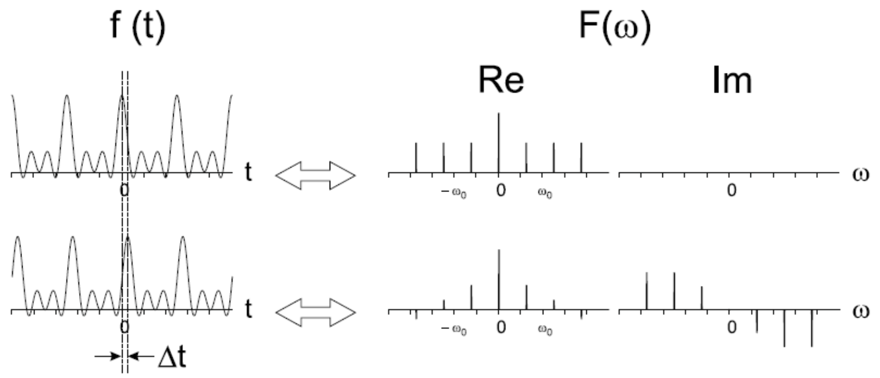


Figure 23 The time shift properties of the Fourier transform.

If we are not exactly on resonance with the center of a symmetric signal, we will get an oscillation between the real and imaginary components.

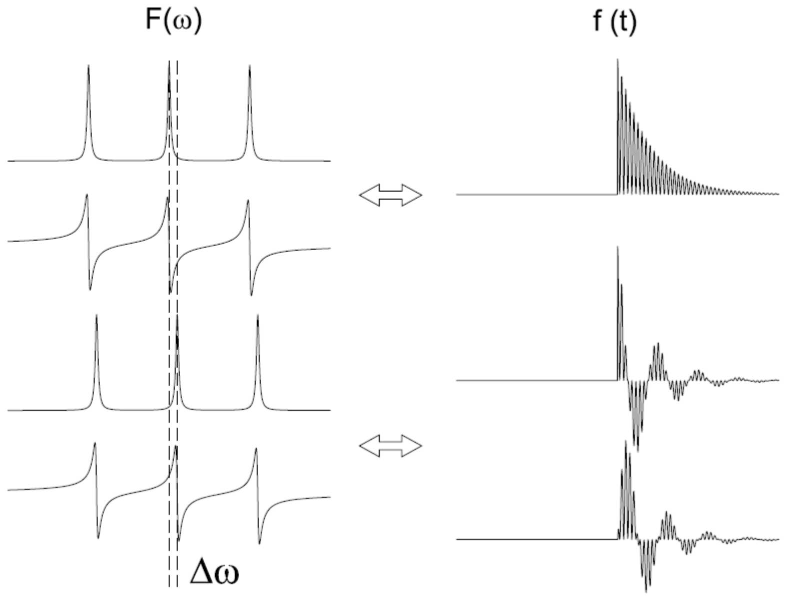


Figure 31 The effect of a frequency shift.

Fourier transform facts

- Linear phase distortion (and correction)
- 时域的时间偏移 -> 频域的相移 （Re -- Im）

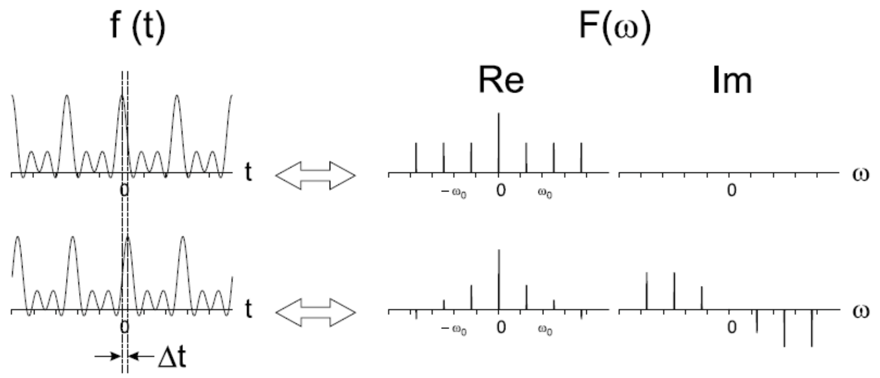


Figure 23 The time shift properties of the Fourier transform.

As the linewidth of the EPR signal increases, the FID decays more quickly.

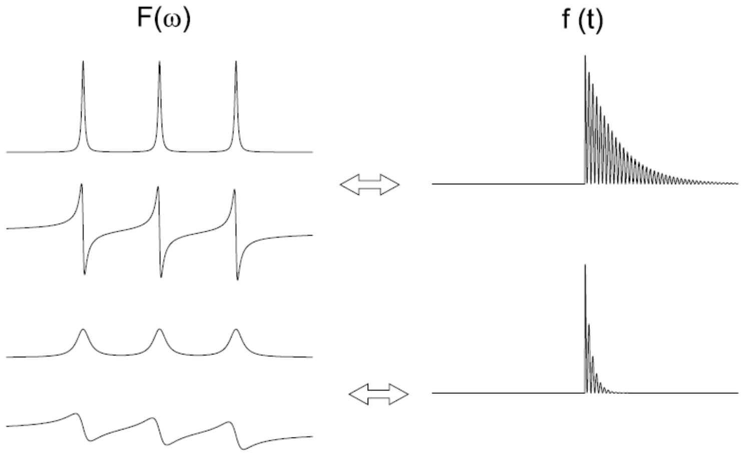


Figure 29 The effect of linewidth.

As the splitting of the EPR signal decreases, the oscillations in the FID become slower.

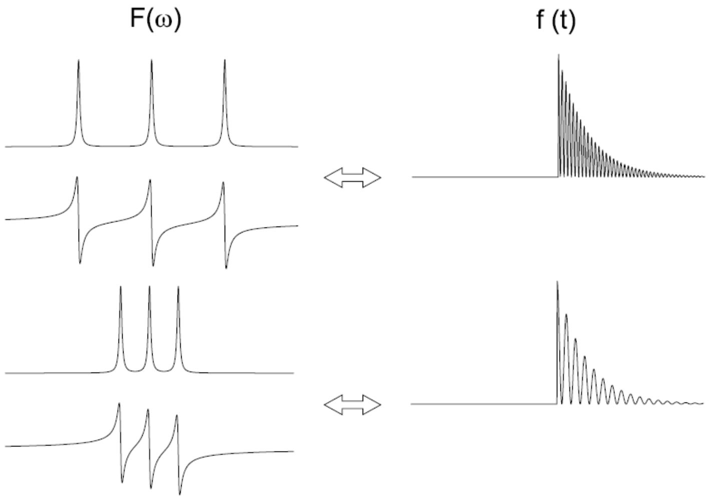


Figure 30 The effect of line splittings.

Multiple pulses = Echoes

How do we know?

produces a signal that decays away (FID). If our EPR spectrum is $\boxed{\text{inhomogeneously broadened}}$, we can recover this disappeared signal with another microwave pulse to produce a Hahn echo.

- FIDs of broad spectra decay away very quickly
- Characterization time T_2^*

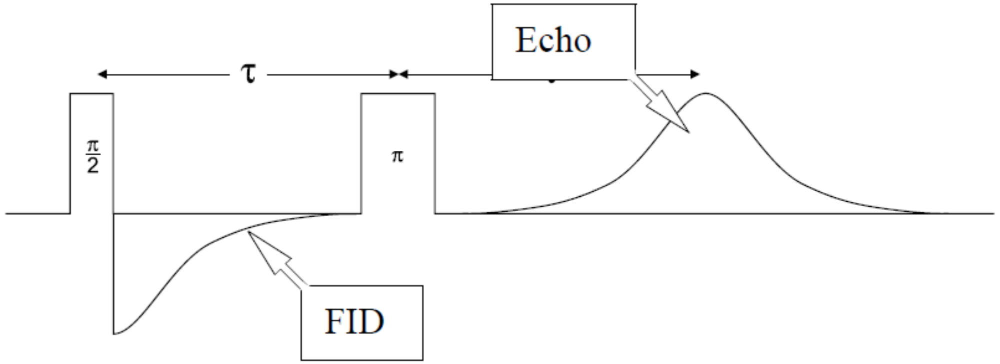


Figure 34 A Hahn echo.

?

chapter that we cannot detect signals during an approximately 80 ns period after the microwave pulse. This period of time is called the deadtime. If the FID is very short, it will disappear before the deadtime ends. If we make τ long enough, we can ensure that the echo appears after the deadtime.

ESR setup

Why arbitrary pulses?

- Spectrometer: generate well-defined pulses of microwave radiation and capture the response from the DUT

- fast frequency-swept amplitude-modulated pulses

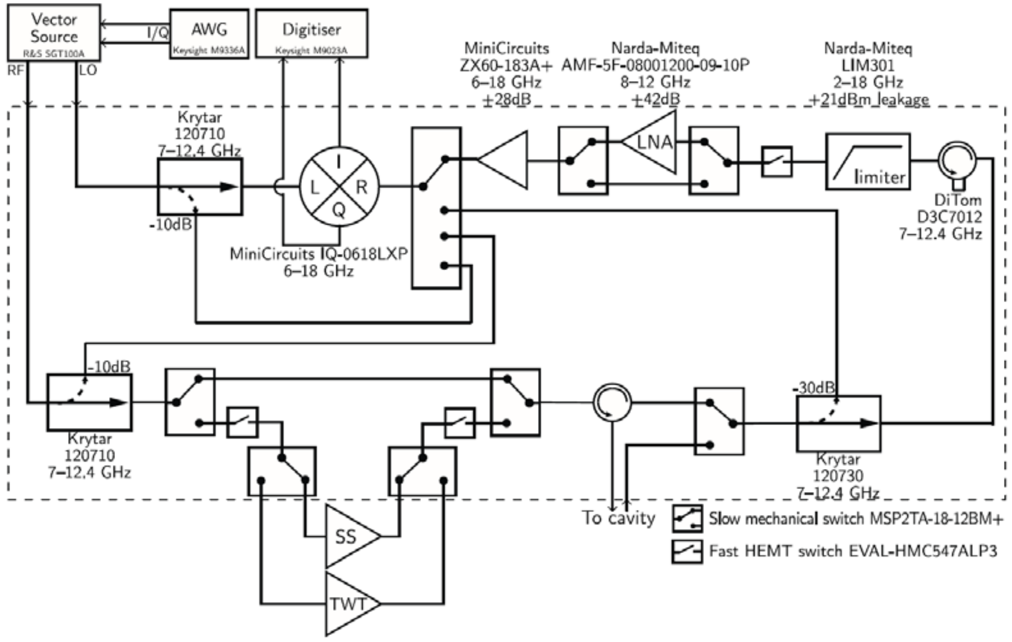


Figure 4.10: Schematic of the X-band 7–12 GHz microwave bridge which the 2–4 GHz bridge was designed to emulate to maintain compatibility with the rest of the spectrometer.

Er in Si

- S

Er–O center, labeled Er-1,[19] which, possibly because of a long T_1, is not ESR active.[20] We have not yet linked any of the ESR centers to the