Magnetic Resonance

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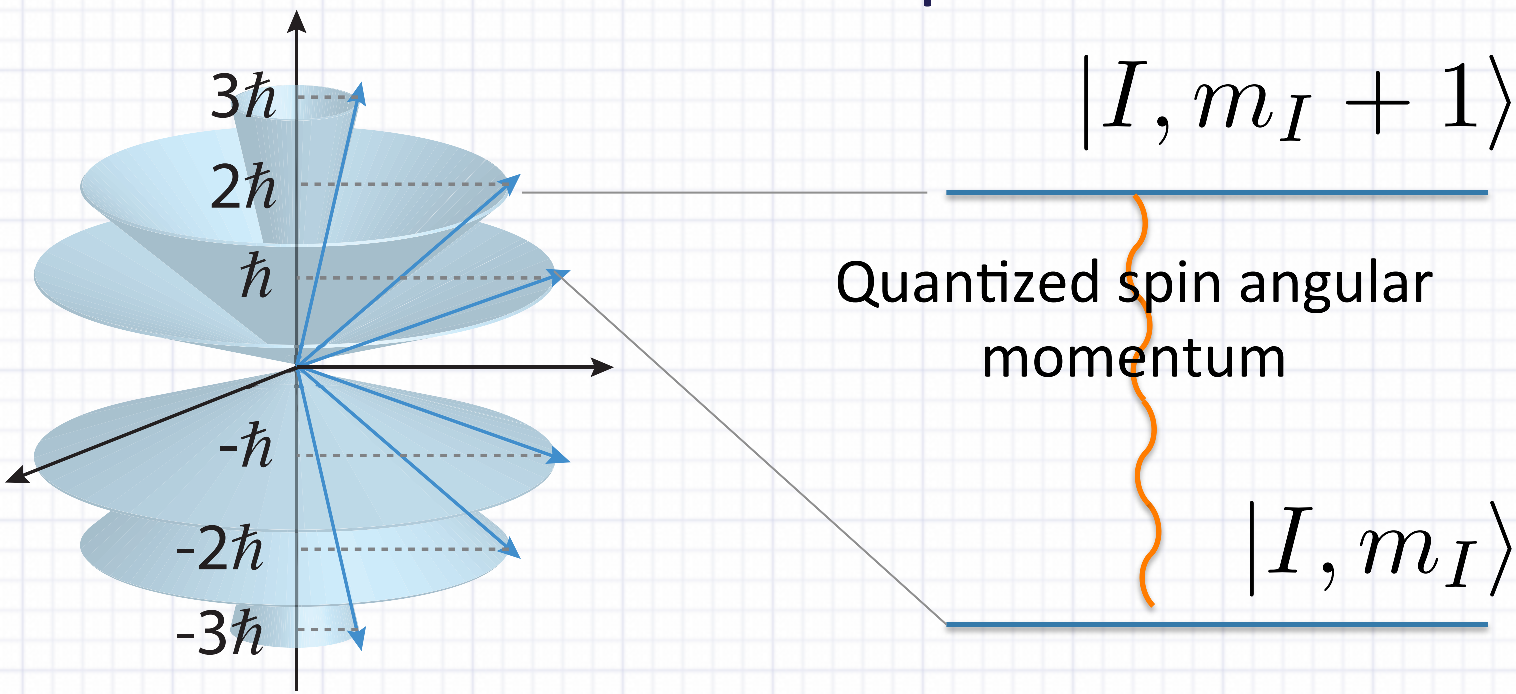
Learning goals

- Principles of magnetic resonance
  - Resonance, spin Hamiltonian
  - Experimental apparatus, detection methods
  - Decoherence and relaxation
- Simple experiments:
  - CW, Rabi, FID, Echo, CPMG, WHH…
- Control and Hamiltonian shaping
  - Dynamical decoupling, Average Hamiltonian Theory

Magnetic resonance

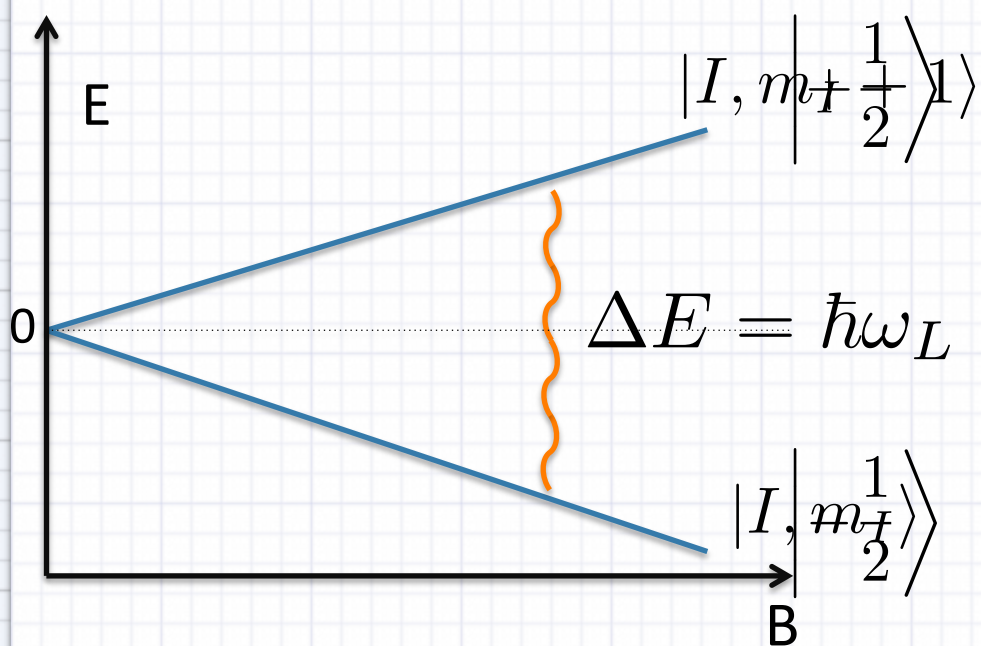
- Magnetic resonance is the exchange of energy between the electromagnetic field and nuclear or electronic spins



Zeeman interaction

- Interaction of spin with a magnetic field

$$\mathcal{H} = \hbar\gamma\vec{B}\cdot\vec{I} = \hbar\vec{\omega}_L\cdot\vec{I}$$

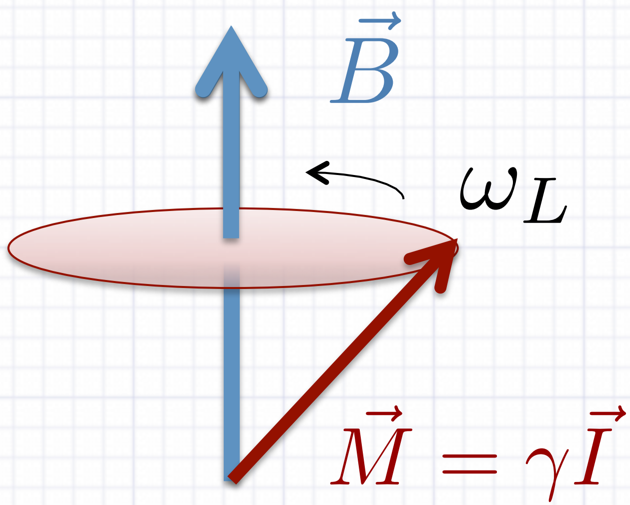


Selection rules:

$$\Delta m_I = \pm 1$$

Classical picture

- Magnetic dipole interacting with a magnetic field: precession at Larmor frequency



$$\frac{d\vec{M}}{dt} = -\gamma \vec{B} \times \vec{M}(t)$$

$$= -\vec{\omega}_L \times \vec{M}(t)$$

Interactions

- Local environment induces changes in the resonant frequency: spectroscopy
  - Chemical shift
    - Local electron currents counteract the applied field:

$$B_{\mathrm{eff}} = B(1-\sigma) \qquad \text{10-100ppm}$$

  - Hyperfine
    - Electron-nuclear spin interaction

$$\vec{S} \cdot \hat{A} \cdot \vec{I} \qquad \text{(kHz-MHz)}$$

  - J-coupling
    - Electron-mediated nuclear-nuclear coupling

$$J \vec{I}_1 \cdot \vec{I}_2 \qquad \text{(Hz)}$$

Interactions

- Local environment induces changes in the resonant frequency: spectroscopy
  - Dipolar coupling
    - Dipole-dipole coupling (nuclear/electron)

$$\frac{\hbar\gamma_i\gamma_j}{|r_{ij}|^3}\left[\vec{I}_i\cdot\vec{I}_j-\frac{3(\vec{I}_i\cdot\vec{r}_{ij})(\vec{I}_i\cdot\vec{r}_{ij})}{|r_{ij}|^2}\right]\qquad\text{(kHz)}$$

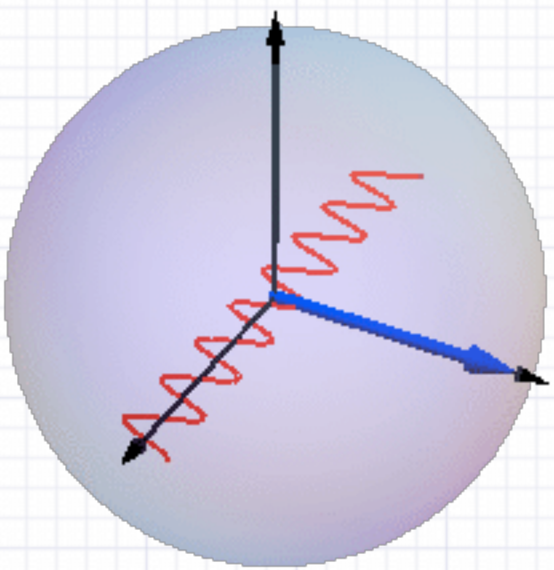
    - Secular component

$$\frac{\hbar\gamma_i\gamma_j}{|r_{ij}|^3}(3\cos\theta_{ij}^2-1)\left[2I_{i,z}I_{j,z}-(I_{i,x}I_{j,x}+I_{i,y}I_{j,y})\right]$$

  - Quadrupolar
    - For spins I>1/2, $\vec{I}\cdot\hat{Q}\cdot\vec{I}$ (0-30 MHz)

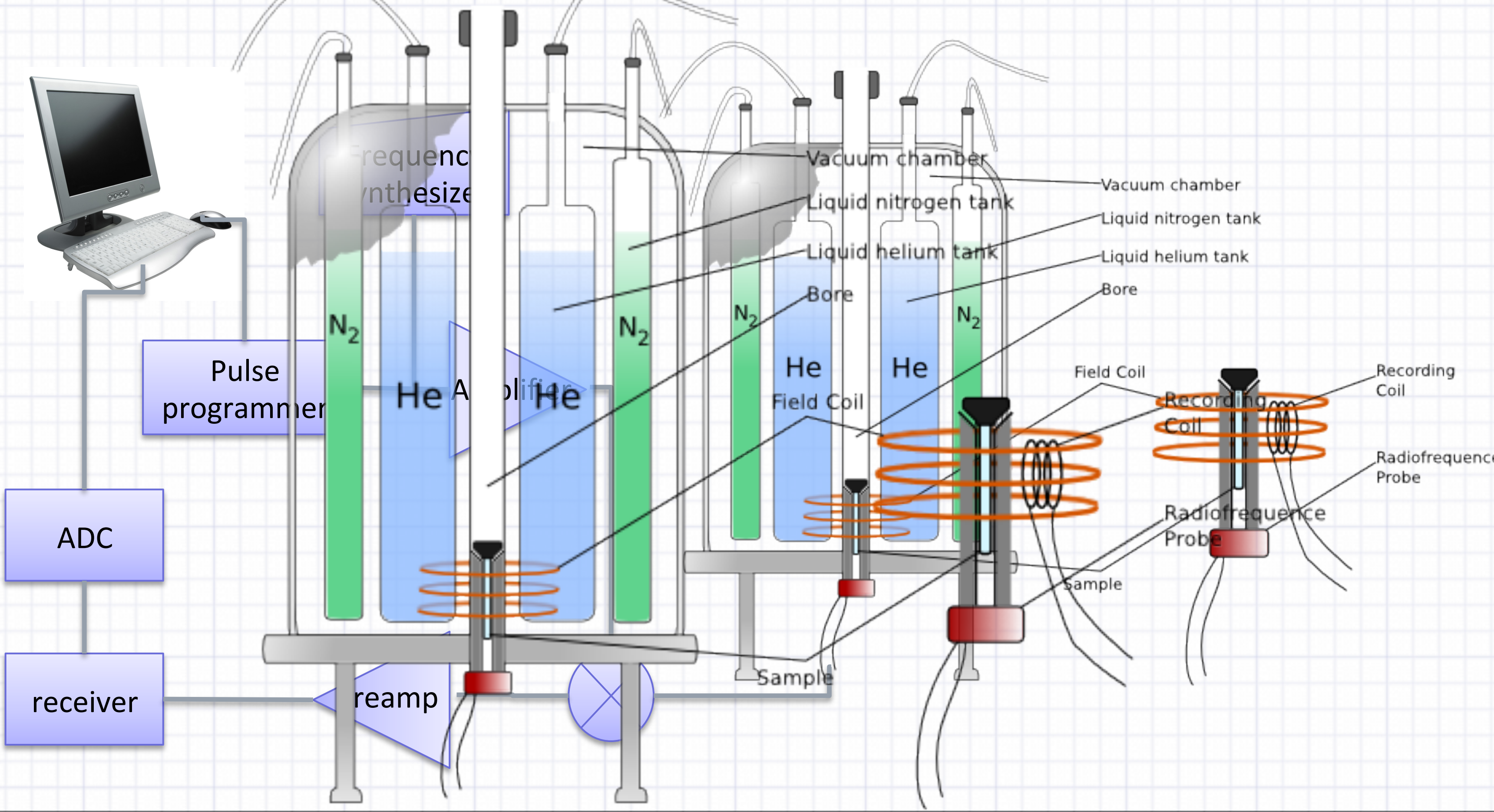
Nuclear Magnetic resonance

- Large magnetic field:
  - Small polarization, large spin ensemble (10^7-10^9)
  - 2 – 23.5 Tesla = 100MHz-1GHz
- Signal observed by induction



NMR system

- Superconducting magnet + spectrometer



EPR/ESR

- Electron paramagnetic resonance
- Electron spin resonance
- Higher frequency and higher polarization
  - Microwave instead of radiofrequency

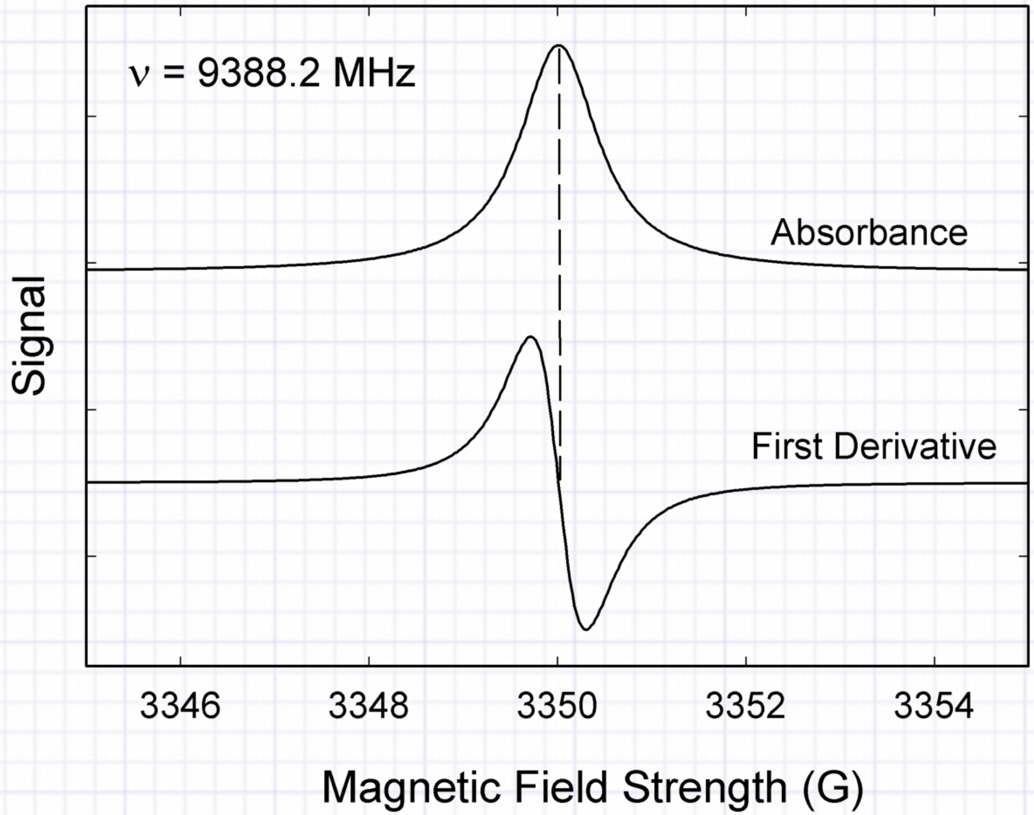
Waveband	L	S	C	X	P	K	Q	U	V	E	W	F
ω [GHz]	1	3	4	10	15	24	35	50	65	75	95	111
B [T]	0.03	0.11	0.14	0.33	0.54	0.86	1.25	1.8	2.3	2.7	3.5	3.9

Detection

- Induction coil: e.g. liquid-state NMR
- Optical (ODMR): e.g. Nitrogen-Vacancy center
- Electrical (EDMR): e.g. quantum dots
- Magnetic resonance force microscopy (MRFR)
- Faraday rotation, Squids magnetometers

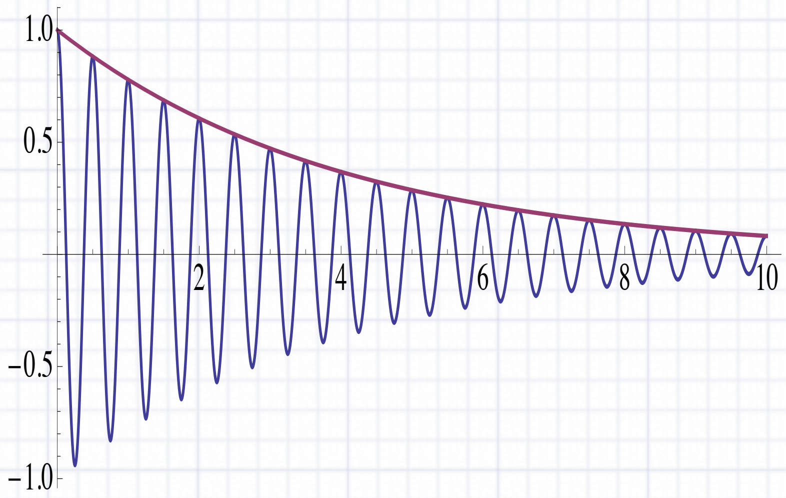
CW vs. FT: Continuous wave

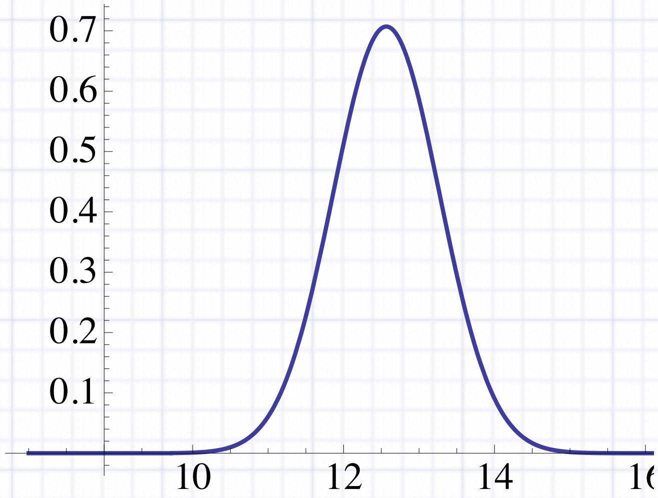
- Scan the magnetic field or the excitation frequency



CW vs. FT: - Fourier Transform

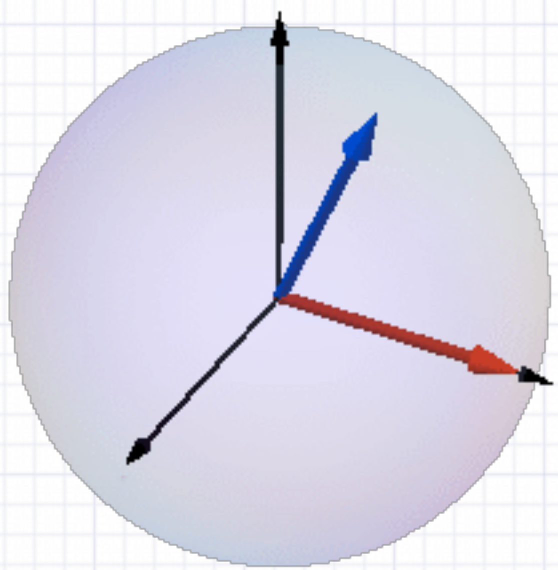
- Rotate the spin to the transverse plane and observe its evolution
  - Spectrum obtained by Fourier Transform





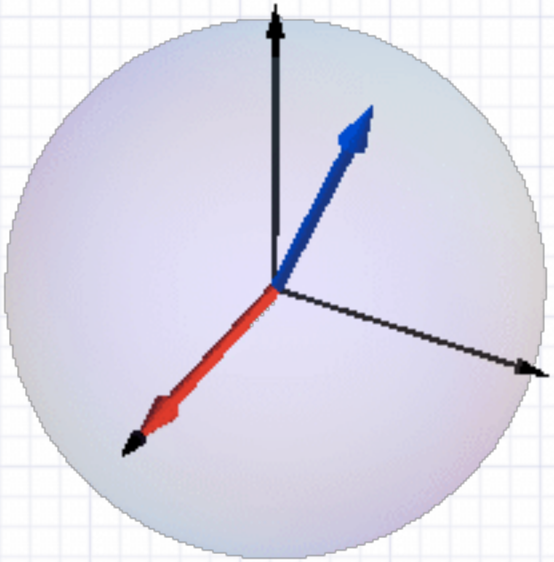
Pulse control

- rf field "rotating" at the Larmor frequency
  - In a frame rotating at the Larmor frequency, it becomes a static field



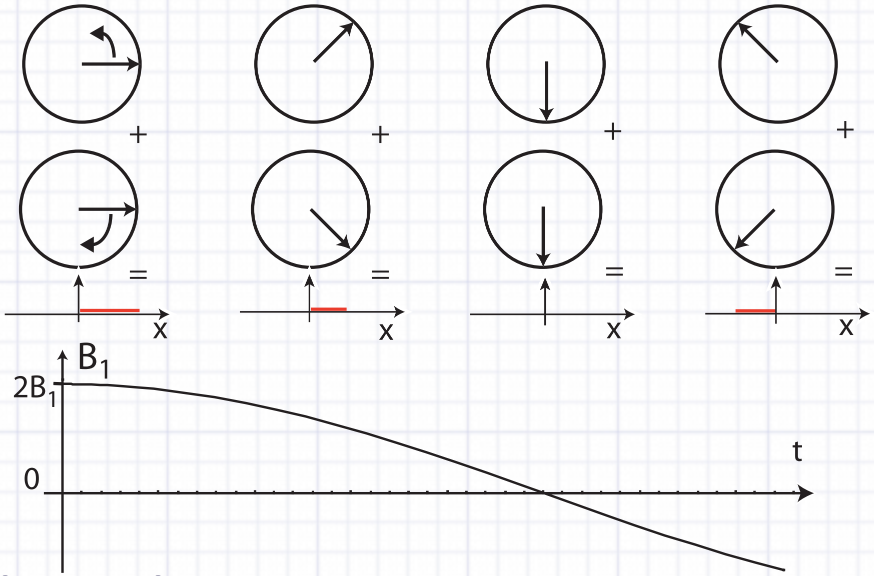
Pulse control

- rf field “rotating” at the Larmor frequency
  - It induces a rotation of the spin



Rotating-Wave Approximation

- rf and μw fields are oscillating, not rotating

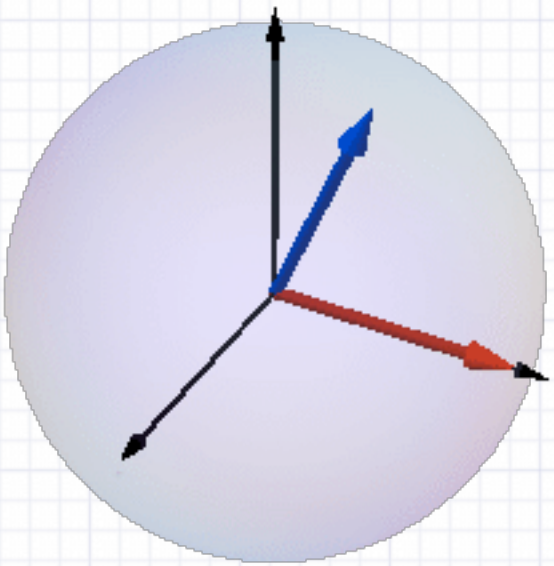


  - we neglect the counter-rotating component
  - Far off-resonance, it is averaged in time if

$$\omega_{\mathrm{res}} \gg \Omega_{\mathrm{Rabi}}$$

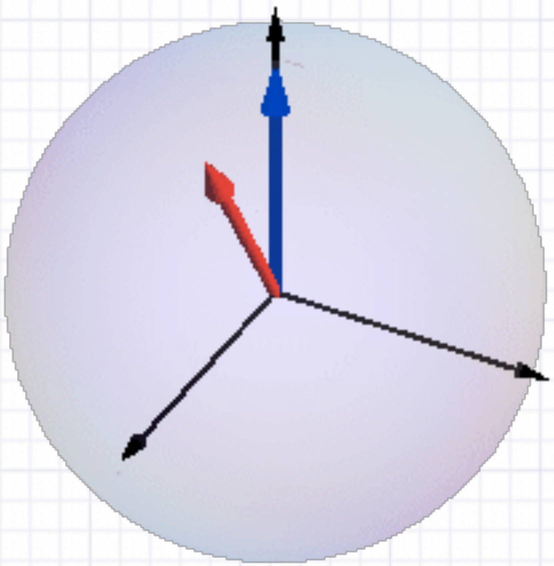
Pulse control

- If the rf field does not rotate at the Larmor frequency
  - Not on resonance



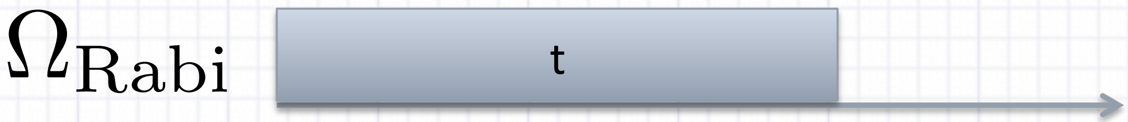
Pulse control

- In the rotating frame there is a residual component along the z-axis
  - The rf is not as effective in rotating the spin



Rabi Rotations

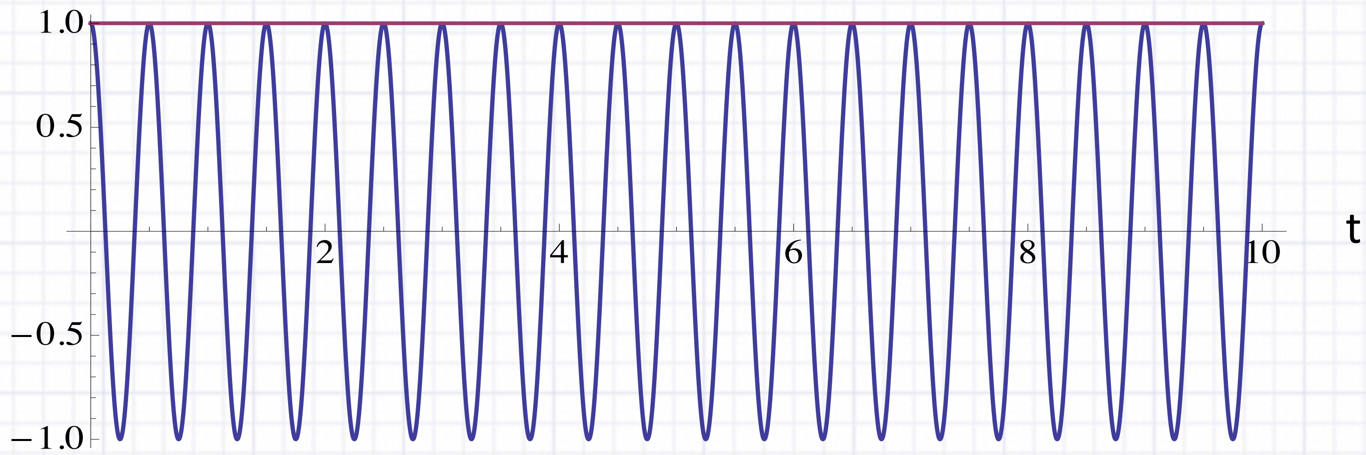
- Oscillations driven by rf field:



  - Calibrate pulse length
  - Achieve longer coherence because of partial decoupling from environment

Ramsey (Free Induction Decay)

- Oscillations driven by internal Hamiltonian:



  - Measure transverse polarization
  - Oscillation at the Larmor frequency

Bloch Equations

- Classical picture of a dipole in a magnetic field

$$\frac{d\vec{M}}{dt} = \gamma \vec{M}(t) \times \vec{B}$$

- Add decay:
  - Transverse decay $$-\frac{1}{T_2}(M_x \hat{x} + M_y \hat{y})$$
  - Longitudinal decay $$-\frac{1}{T_1}(\vec{M} - M_0) \cdot \hat{z}$$

Relaxation

- Longitudinal relaxation
  - Energy exchange, change in $\langle I_z \rangle$
  - Relaxation toward thermal equilibrium
  - Time-scale: T_1
- Transverse relaxation
  - Decay of transverse components, $\langle I_{x,y} \rangle$
  - Loss of coherence, dephasing
  - Time-scale: $T_2 < T_1$
    - Interaction with spin bath
    - Often non-Markovian (super-exponential decay)

Thermal state

- At room temperature, the equilibrium state is highly mixed

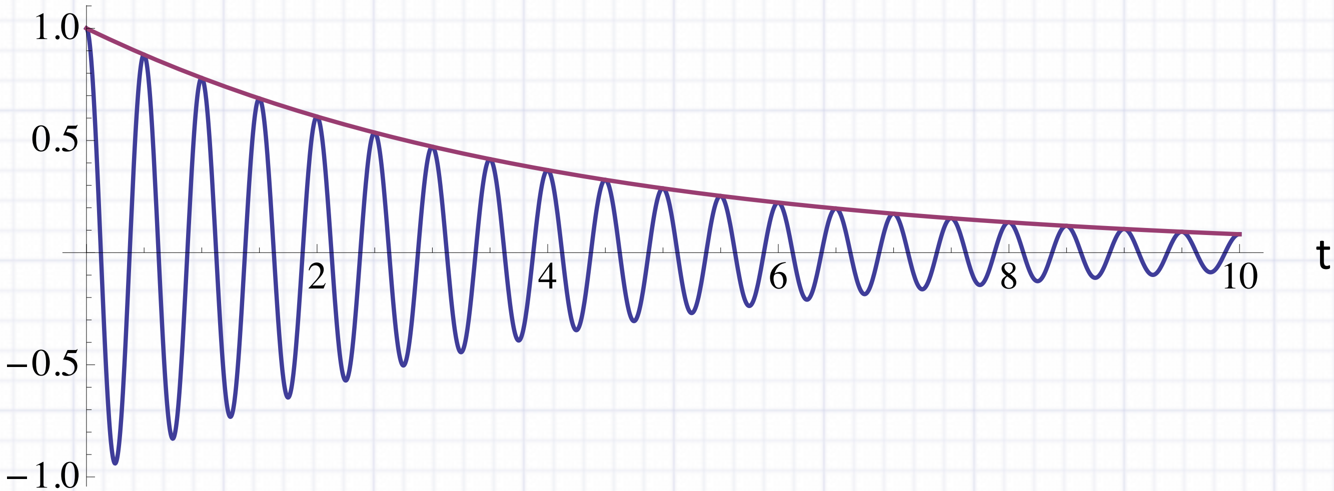
$$\rho = e^{-\beta\mathcal{H}}/Z \approx \frac{\mathbb{1}}{\text{dim}} - \epsilon \sum_k I_{z,k}$$

- Only the deviation from identity gives rise to the dynamics and the signal

$$\rho \sim \sum_k I_{z,k}$$

Ramsey (Free Induction Decay)

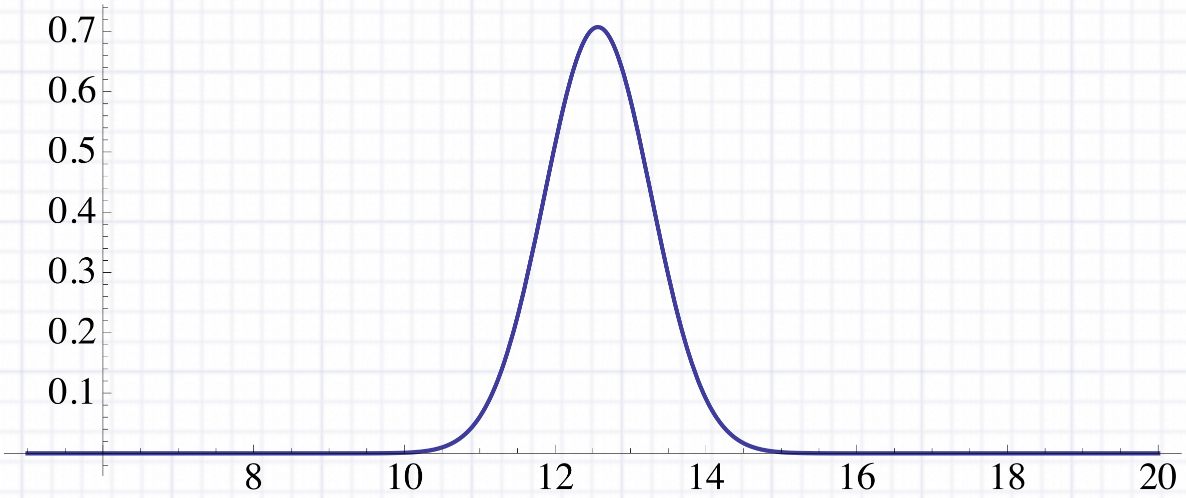
- Oscillations driven by internal Hamiltonian:



  - T_2- decay of signal

FID Spectrum

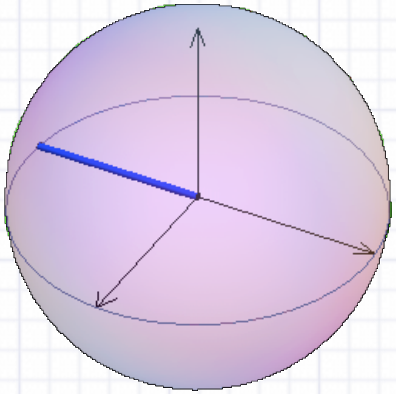
- Fourier Transform of FID gives the spectrum

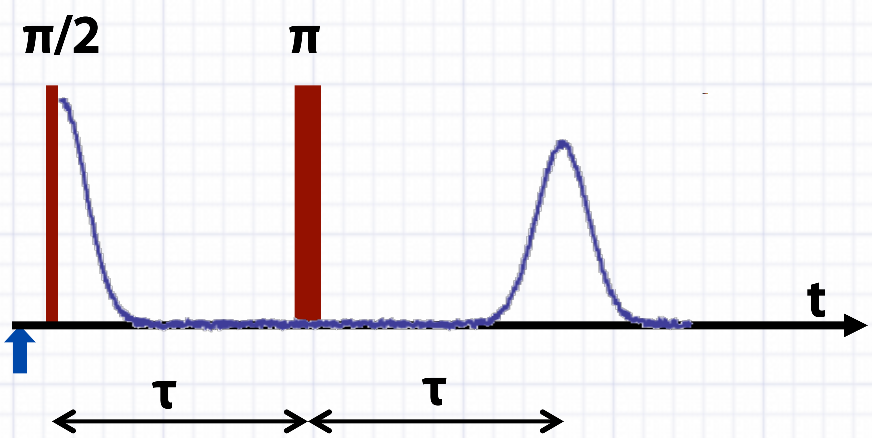


- FWHM = $1/\pi T_2$

Spin Echo

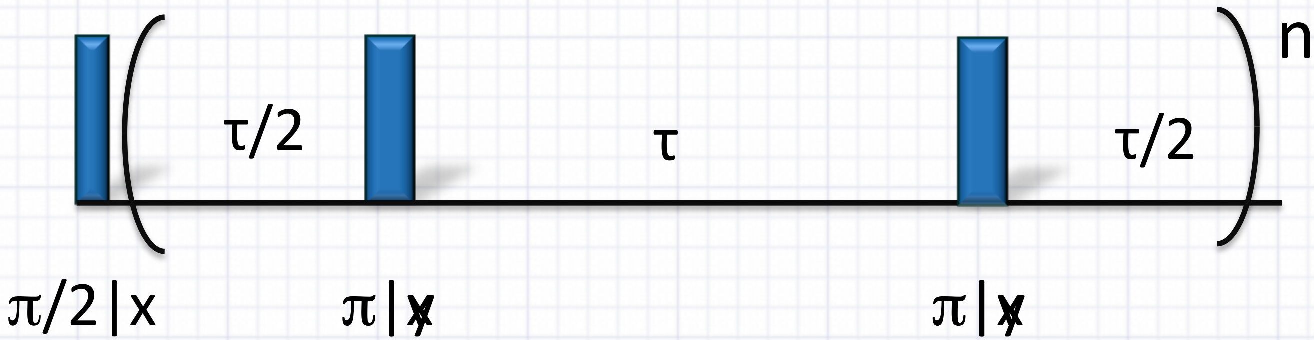
- Simple sequence "inverts" the arrow of time
  - Spins precess at different frequencies: dephasing
  - π pulse inverts the speed: spins are refocused





CPMG – Dynamical decoupling

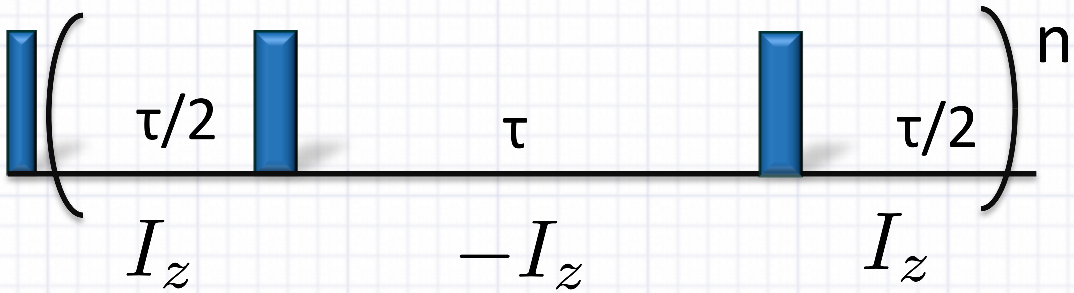
- Spin echo works for quasi-static fields
  - If noise varies in time, refocusing is not perfect
  - To look at longer times: keep applying π-pulses!



  - Carr-Purcell sequence
    - With Meiboom-Gill trick to correct pulse errors

Average Hamiltonian Theory

- Goal: modulate internal Hamiltonian to create effective interaction.
  - E.g. : to refocus interaction with environment



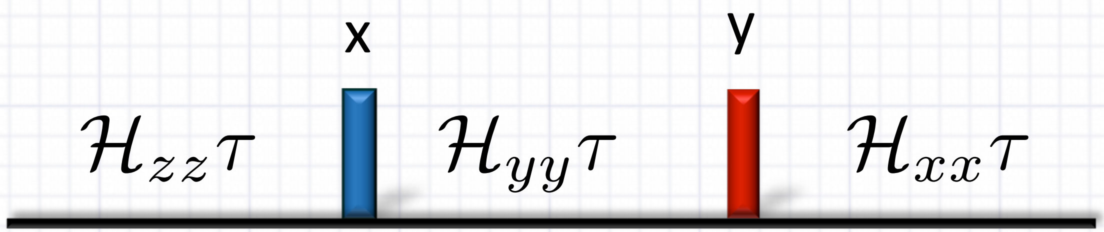
  - Toggling-frame Hamiltonian

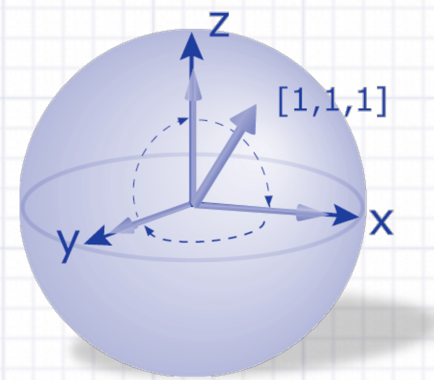
$$\mathcal{H} \sim I_z \rightarrow \mathcal{H}(t) = U_{rf}\mathcal{H}U_{rf}^{\dagger}$$

  - Averaged Hamiltonian $\frac{1}{2}I_z\tau - I_z\tau + \frac{1}{2}I_z\tau = 0$

Average Hamiltonian Theory

- Two-spin Hamiltonian $\mathcal{H}_{zz} \sim 3I_{i,z}I_{j,z} - I_i \cdot I_j$
  - In the toggling frame:





the Hamiltonian becomes on average

$$\bar{\mathcal{H}} = \frac{1}{3}(\mathcal{H}_{xx} + \mathcal{H}_{yy} + \mathcal{H}_{zz}) = 0$$

- Refocusing of internal couplings

Average Hamiltonian Theory

- AHT gives rule for quick calculation of effective average Hamiltonian
  - It helps in designing pulse sequences
- Effective Hamiltonian from Magnus expansion

$$U = e^{-it\bar{\mathcal{H}}} = \exp\{-it[\bar{H}^{(0)} + \bar{H}^{(1)} + \bar{H}^{(2)} + \ldots]\}$$

$$\bar{H}^{(0)} = \frac{1}{t}\int_0^t H(t')dt'$$

$$\bar{H}^{(1)} = -\frac{i}{2t}\int_0^t dt' \int_0^{t'} dt''[H(t'), H(t'')]$$

AHT

- Conditions:
  - $\mathcal{H}_{rf}$ cyclic: $U_{rf}(t_{c,}0)= \pm 1$
  - $\mathcal{H}_{rf}$ periodic: $\mathcal{H}_{rf}(t)=\mathcal{H}_{rf}(nt_c+t)$

  } $U_{rf}(Nt_{c,}0)= 1$

  - $t_c|\mathcal{H}_{int}|\approx t_c\,\omega << 1$ (convergence condition)
  - Stroboscopic observation at $t=nt_c$
- Advantages:
  - Evolution at $t=nt_c$ is determined by the average Hamiltonian over 1 cycle.
  - Toggling-frame Hamiltonian coincide with lab-frame

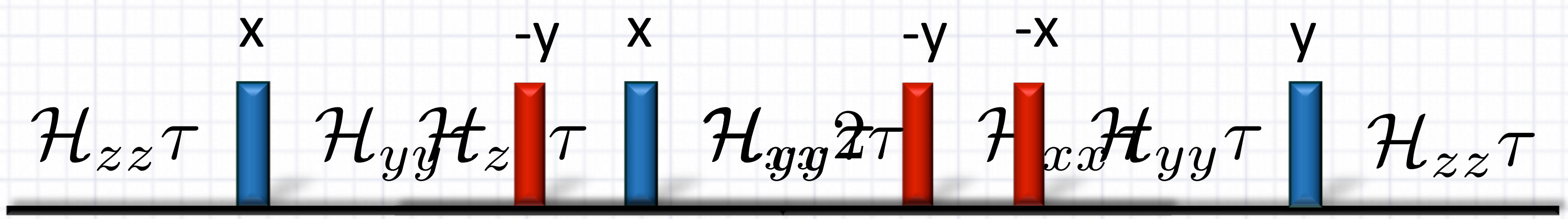
Non ideal rf perturbations

- Pulse-width error: $\mathcal{H}_{\delta} = -(\pm\, \delta_{\pm x}/t_w) I_x$
- B_1 inhomogeneities for ith nucleus: $\mathcal{H}_{\varepsilon i} = -(\pm\, \varepsilon_i/t_w) I_x$
- Phase-misadjustement error: $\mathcal{H}_{p} = -(\pm\, \varphi_{\pm x}) I_y$
- Pulse transients error: $\mathcal{H}_{T} = -\, \omega_T(t) I_y$

- The errors can be included in the internal Hamiltonian to calculate their effects

Symmetric sequences

- Higher orders and pulse errors can be corrected by symmetrized sequences
  - Solid-echo sequence:



  - WAHUHA (Waugh Haeberlen Hahn)

$\mathcal{H}(t) = \mathcal{H}(t_c - t)$: all odd terms are zero

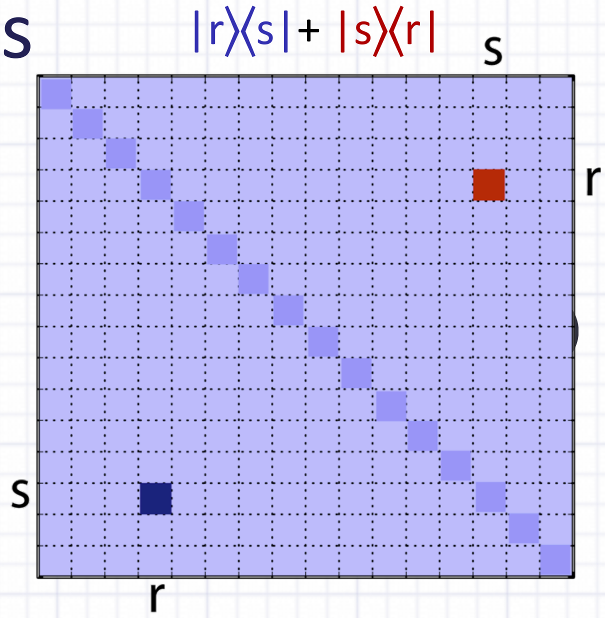
Supercycles

- Build symmetrized sequence from basic units
  - For example, MREV-8 repeats the basic WAHUHA cycle twice with the x pulses reversed in phase. This removes the effects of rf inhomogeneity, since toggling frame terms in I_z are inverted during the second half
- Dynamical decoupling
  - Periodic DD (repeat basic sequence)
  - Concatenated DD (nest basic sequence)
  - Optimal/Quadratic DD (optimized for a given noise spectrum)

Solid State NMR

- Dipolar Hamiltonian
- Control: multiple-pulse sequences to refocus or manipulate the dipolar Hamiltonian
- Multiple Quantum Coherences
  - $|s\rangle\langle r|$, coherence order n=r-s
    - r+s+q=m-spin state.

$$\sigma_{i_1}^{+}\sigma_{i_2}^{+}\cdots\sigma_{i_r}^{+}\sigma_{j_1}^{-}\cdots\sigma_{j_s}^{-}\sigma_{k_1}^{z}\cdots\sigma_{k_q}^{z}$$



Multiple quantum NMR

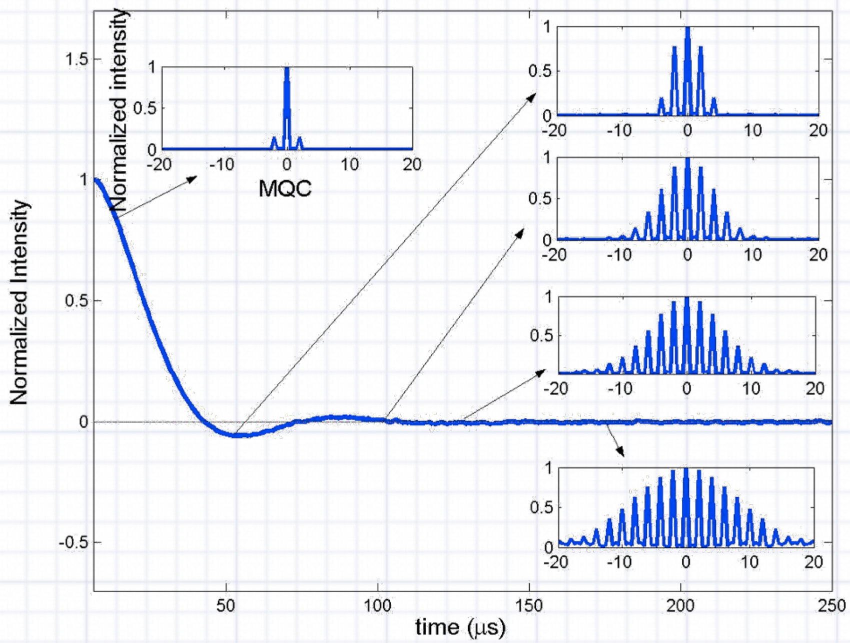
- Multiple Quantum Coherences order *n* :
  - *n=ΔM*, difference in Zeeman quantum number between any two states in a coherent superposition.
  - In terms of single spin Pauli operators :

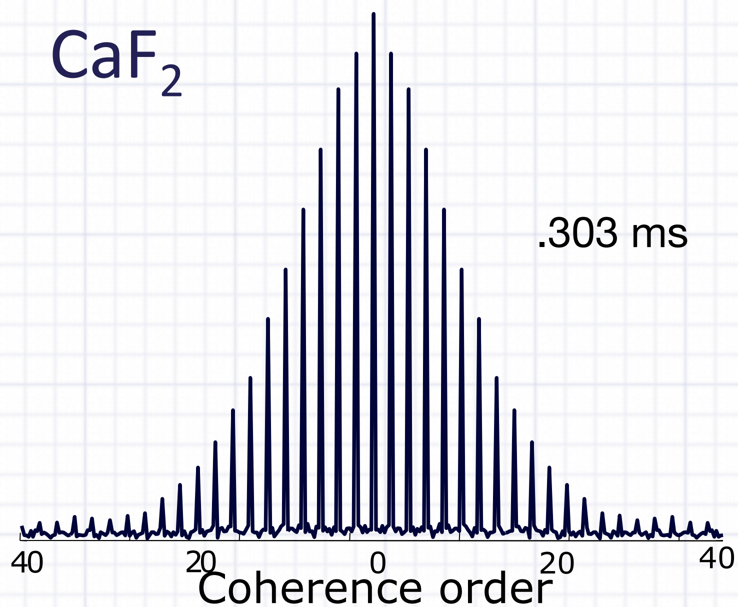
$$\sigma_{i_1}^{+}\sigma_{i_2}^{+}\cdots\sigma_{i_r}^{+}\cdot\sigma_{j_1}^{-}\cdots\sigma_{j_s}^{-}\cdot\sigma_{k_1}^{z}\cdots\sigma_{k_q}^{z} \rightarrow n = r - s$$

- Indirect observation of correlations among spins

MQC experiments

- Directly observed ~50 coherences
  – Much larger number of spins involved.





H. Cho, et al. Phys. Rev. B , ***72***, *054427, (2005)*

Conclusions

- Magnetic resonance has a long history
  - and a lot of acronyms!
- Strengths:
  - Simplicity of (basic) Hamiltonian
  - Complexity of full systems

    (e.g. solid state, relaxation)
  - Control:

    Many schemes to manipulate quantum evolution

    (somebody already did it 50 years ago!)

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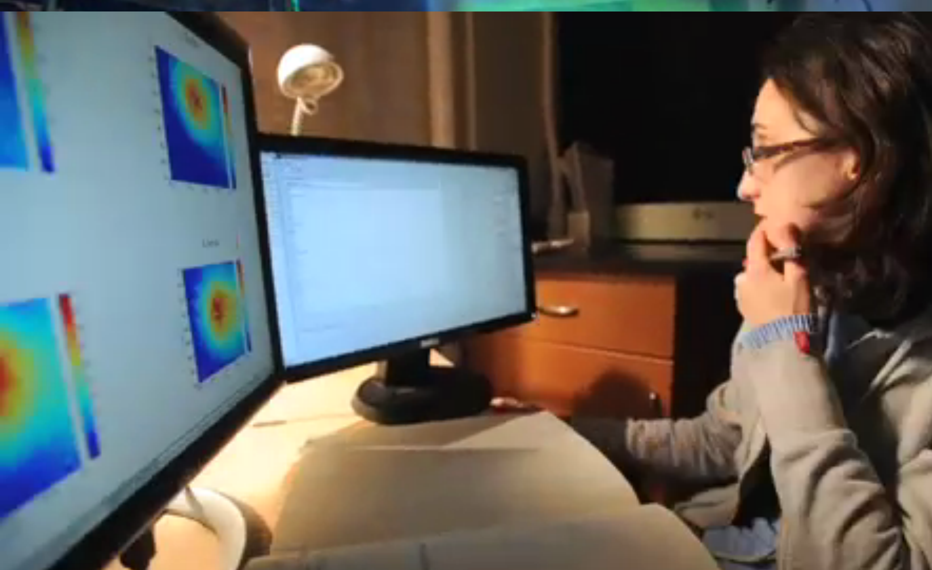

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