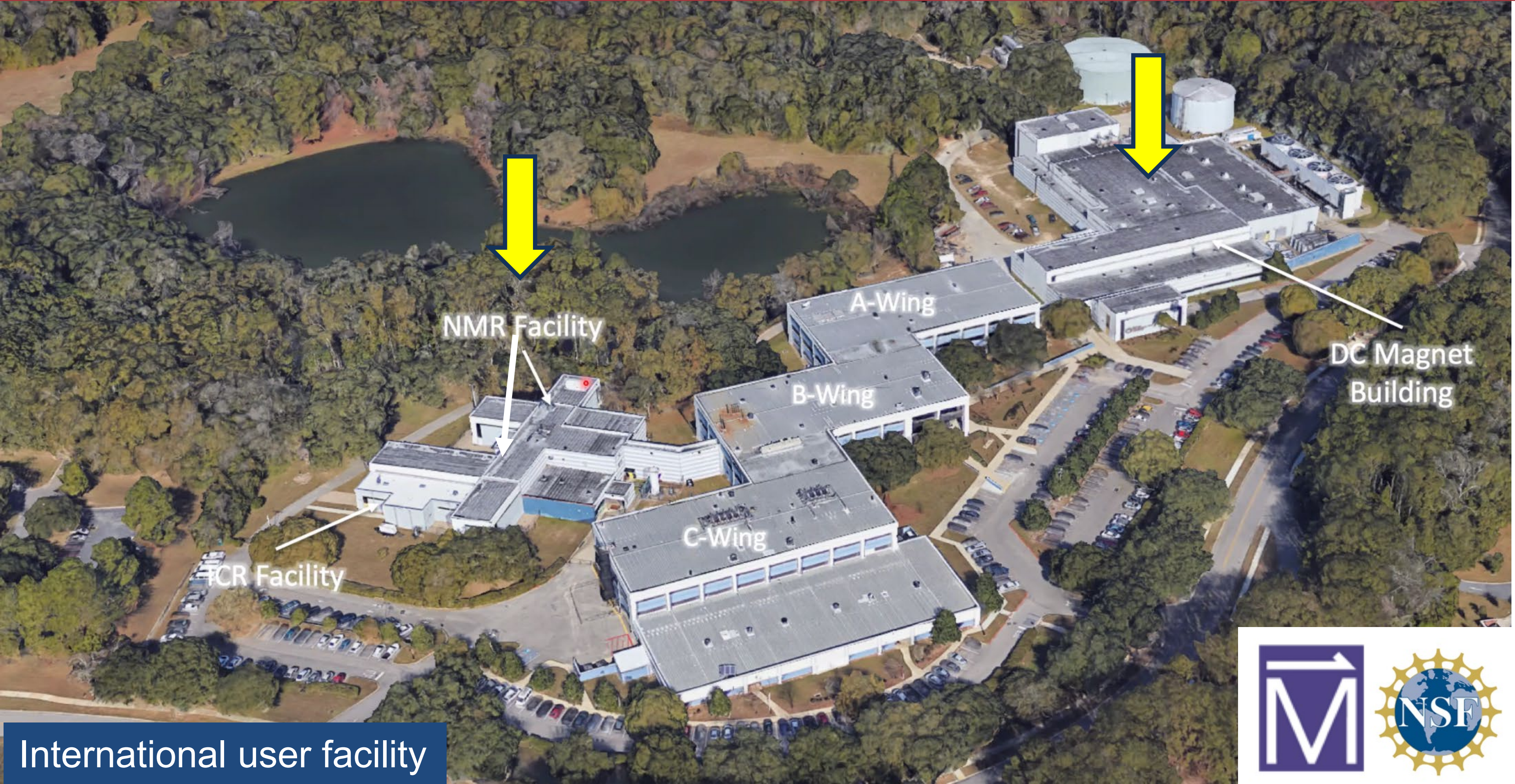
Welcome to the MagLab

PANACEA/NIH Maglab workshop

Broad introduction to magnetic resonance

Frédéric Mentink-Vigier

Maglab Headquarters Tallahassee, FL



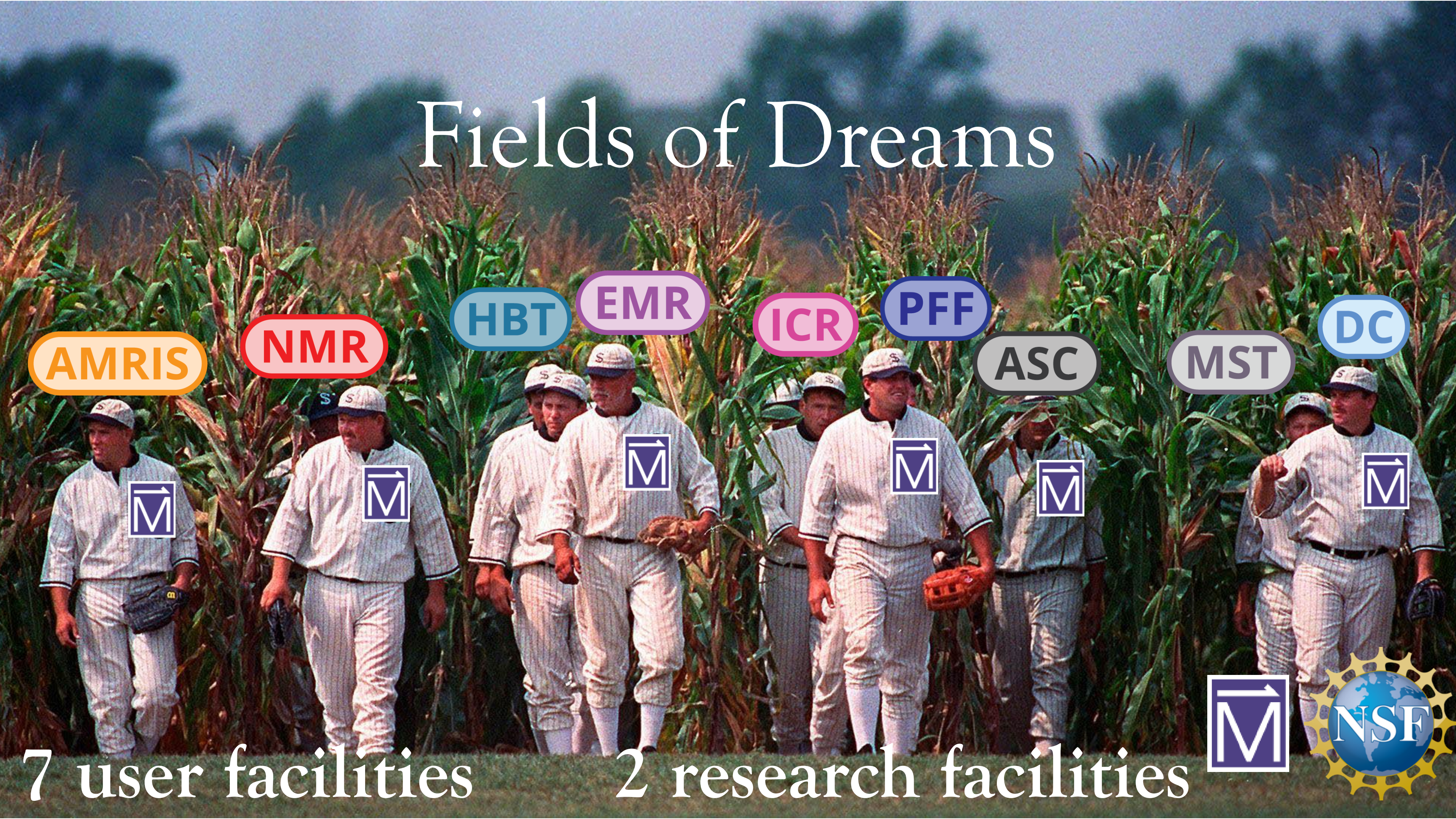
International user facility

The National High Magnetic Field Laboratory

- Founded in 1990 Member institutions:
  - Florida State University
  - University of Florida
  - Los Alamos National Laboratory

- World record magnets
  - 36 T resistive & hybrid (NMR)
  - 45 T hybrid
  - Pulsed fields: 60 T, 77.8 T, 90+ T
  - Research in chemistry, biochemistry, biology, physics, materials science, & engineering

Fields of Dreams



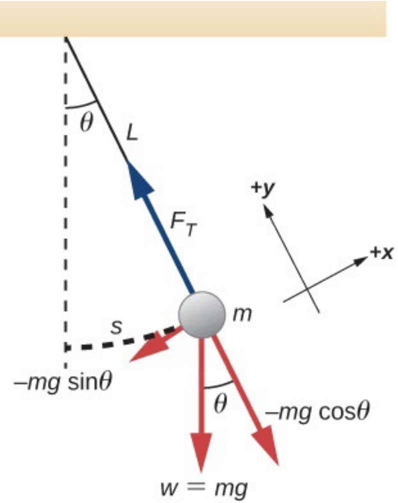
7 user facilities 2 research facilities

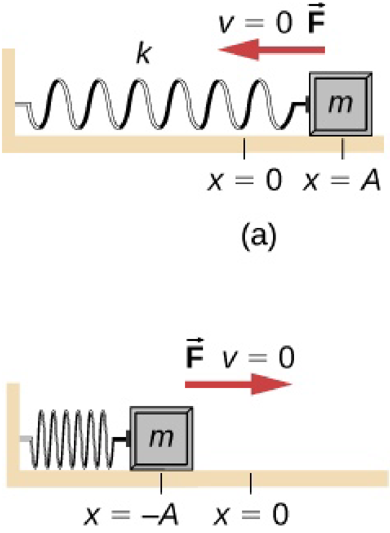
Basic of magnetic resonance

- Definition of resonance:

In physics, resonance is a phenomenon that occurs when a vibrating system or object is driven by another force or system at a frequency that matches its natural frequency, leading to a significant increase in the amplitude of vibrations.

- Basic example:





$$\theta(t) = \theta_0 \cos(\omega t + \phi)$$
$$\omega = \sqrt(g/l)$$

$$x(t) = x_0 \cos(\omega t + \phi)$$
$$\omega = \sqrt(k/m)$$

Basic of magnetic resonance

- Frictionless compass in a magnetic field
  - Compass has a moment of inertia *I* (equivalent of a mass)
  - Compass has magnetic moment μ
  - Magnetic moment interact with magnetic field B_0

  - Compass has potential energy, E_p
  - Compass has kinetic energy, E_c
  - Conservation of mechanical energy, E_m

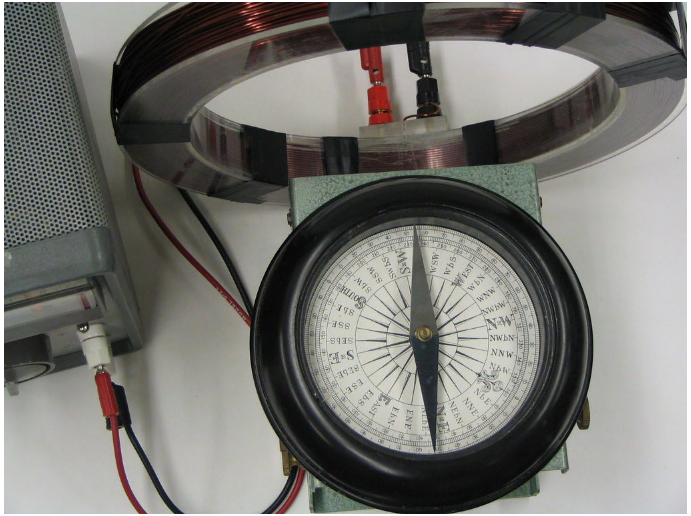
$$E_P = -\vec{\mu}.\overrightarrow{B_0} = -\mu B_0\cos(\theta) \approx -\mu B_0(1-\frac{1}{2}\theta^2)$$

$$E_c = \frac{1}{2}I\dot{\theta}^2$$

$$E_m = E_c + E_p = \frac{1}{2}I\dot{\theta}^2 + \frac{1}{2}\mu B_0\theta^2 = \text{cste}$$

$$\ddot{\theta} + \frac{\mu B_0}{I}\theta = 0$$

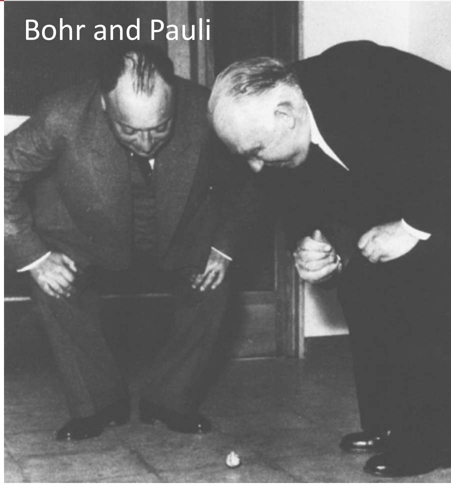
→ $\theta(t) = \theta_0\cos(\omega t + \phi)$ with $\omega = \sqrt{\frac{\mu B_0}{I}}$



Oscillation with gyromagnetic ratio $\gamma = \sqrt{\frac{\mu}{I}}$

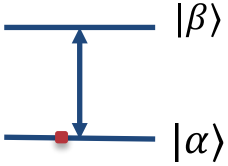
Note: spins are not like compasses
If you are curious
https://www.youtube.com/watch?v=_2hXRP6qZtM

From classical to quantum mechanical



Bohr and Pauli

- Spins == magnetic moment
  - Magnetic moment with finite projection along the magnetic field
  - $E_p \rightarrow \widehat{H}_z = \gamma\hbar\hat{S}_z B_z$
  - Change of formalism: $E_m \rightarrow \widehat{H}_0 = \widehat{H}_z$
  - Now using the Schrödinger equation as equation of motion $i\hbar\frac{\partial|\psi\rangle}{\partial t} = \widehat{H}_z|\psi\rangle$ (Or Liouville Von-Neumann)
  - From $E_p \rightarrow \widehat{H}_z$ we can determine the energy accessible and eigenstates

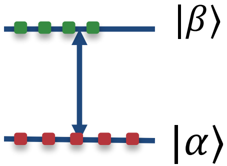


$$\widehat{H}_z = \gamma\hbar\hat{S}_z B_z$$

$$\Delta E = \gamma\hbar B_z$$

Single spin, $|\psi\rangle$ is perfect for description

$$i\hbar\frac{\partial|\psi\rangle}{\partial t} = \widehat{H}_z|\psi\rangle$$



$$\Delta E = \gamma\hbar B_z$$

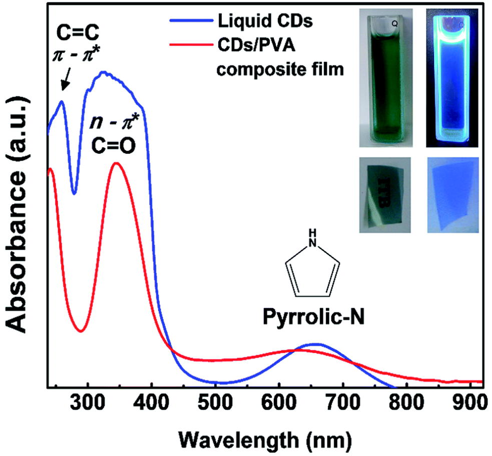
Collection of spins $\hat{\rho} = \overline{|\psi\rangle\langle\psi|}$ is perfect for description

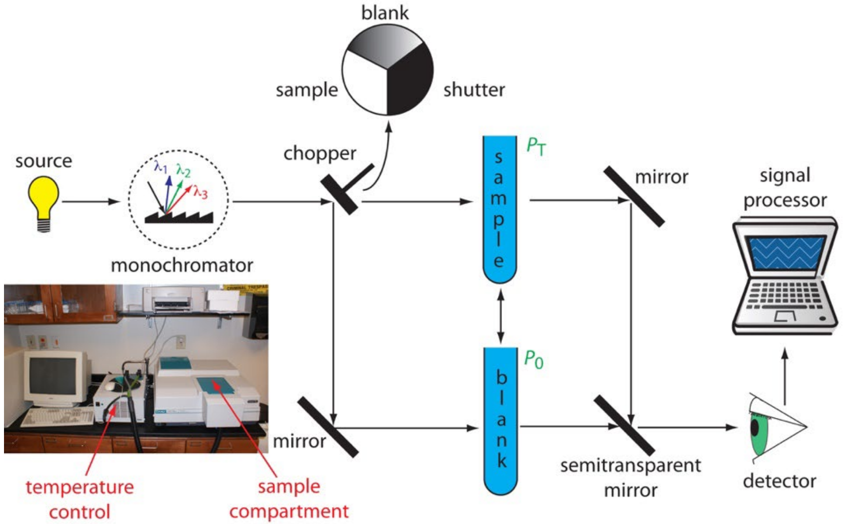
$$i\hbar\frac{\partial\hat{\rho}}{\partial t} = [\widehat{H}_z, \hat{\rho}]$$

Note: for all fundamental particles, spin is $\hbar/2$, only γ changes

Spectroscopy

- Most familiar with: UV-visible



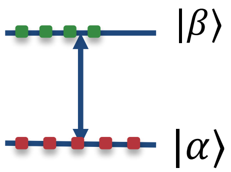


- Beer-Lambert law:
- $I_{\text{transmitted}} = I_0 e^{-klc}$, l is sample length, c, concentration of absorbing sample
- k is absorption coefficient and this relates the imaginary component of dielectric constant $\epsilon = \epsilon' + i\epsilon''$
- Important relation between transmission and reflection
- $\frac{I_{\text{transmitted}}}{I_0} = T$ and $R + T + \text{Abs} = 1$ (conservation of energy)

A change in absorption implies a change in transmission and in reflection

Relation between polarization and absorption

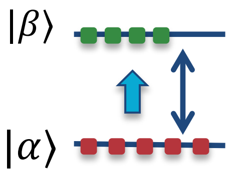
- Absorption and polarization



$$\Delta E = \gamma\hbar B_z$$

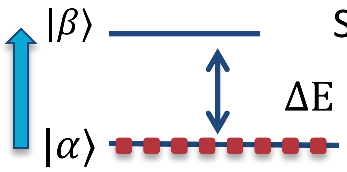
At thermal equilibrium, $k_B T \sim 6.25$ THz at RT

$$\hat{\rho} = e^{-\frac{\hat{H}_z}{k_B T}}, \qquad \text{and} \qquad P = \frac{N_{|\alpha\rangle} - N_{|\beta\rangle}}{N_{|\alpha\rangle} + N_{|\beta\rangle}} = \frac{e^{\frac{\Delta E}{2k_B T}} - e^{-\frac{\Delta E}{2k_B T}}}{e^{\frac{\Delta E}{2k_B T}} + e^{-\frac{\Delta E}{2k_B T}}}$$



Weak Polarization → NMR

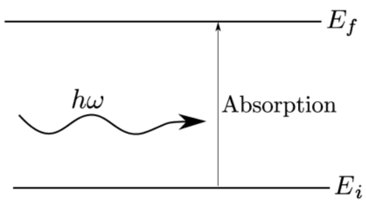
$\Delta\text{E} \ll \text{kT}$

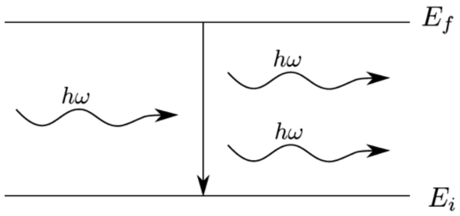


Strong Polarization → optics

$\Delta\text{E} \approx \text{kT}$

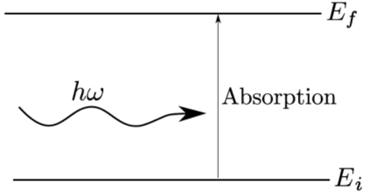
- Under irradiation (i.e. presence of a density of photons $\rho(\nu)$)
  - $\frac{dN_\alpha}{dt} = -C\frac{dN_\alpha}{dt}\rho(\nu) + B\frac{dN_\beta}{dt}\rho(\nu) + A\frac{dN_\beta}{dt}$ (C = absorption, B stimulated emission, A spontaneous emission)
  - $\frac{dN_\beta}{dt} = +C\frac{dN_\alpha}{dt}\rho(\nu) - B\frac{dN_\beta}{dt}\rho(\nu) - A\frac{dN_\beta}{dt}$



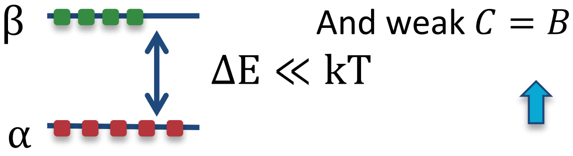


Relation between polarization and absorption (CW spectroscopy)

- Under irradiation (i.e. presence of a density of photons $\rho(\nu)$)
  - $\frac{dN_\alpha}{dt} = -C\frac{dN_\alpha}{dt}\rho(\nu) + B\frac{dN_\beta}{dt}\rho(\nu) + A\frac{dN_\beta}{dt}$ (C = absorption, B stimulated emission, A spontaneous emission (NMR/EPR, A is negligible))
  - $\frac{dN_\beta}{dt} = +C\frac{dN_\alpha}{dt}\rho(\nu) - B\frac{dN_\beta}{dt}\rho(\nu) - A\frac{dN_\beta}{dt}$



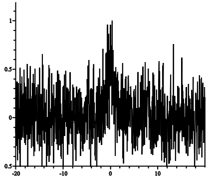
  - $C = B \propto \frac{2\pi}{\hbar}\left|\langle\alpha|\hat{V}|\beta\rangle\right|^2$ where $\hat{V}$ is the irradiation (e.g. additional time dependent electromagnetic field)
  - If $N_\alpha \sim N_\beta$ then $\frac{I_{\text{transmitted}}}{I_0} = T \sim 1 - \delta$, $\delta \ll 1$ and $R + T + \text{Abs} = 1$ (conservation of energy), sample near transparent
  - the change of signal before and after is small



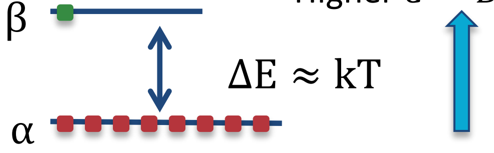
Weak Polarization
And weak $C = B$

$\Delta E \ll kT$

Majority of NMR experiments
→ low NMR signal but high resolution

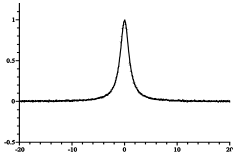


Strong Polarization
Higher $C = B$



$\Delta E \approx kT$

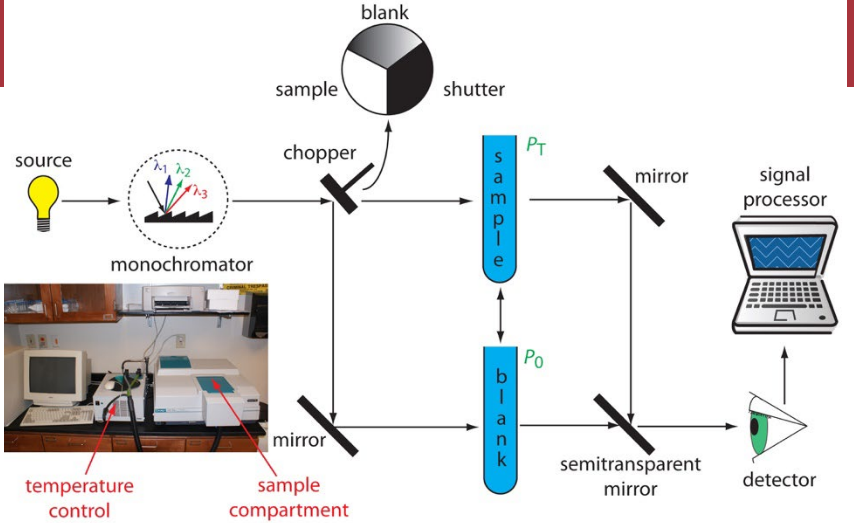
Routine condition in high field EPR at low temperature, lower resolution

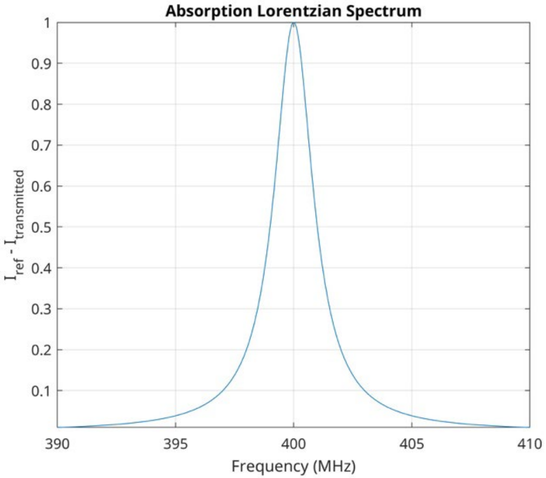


Continuous wave NMR/EPR

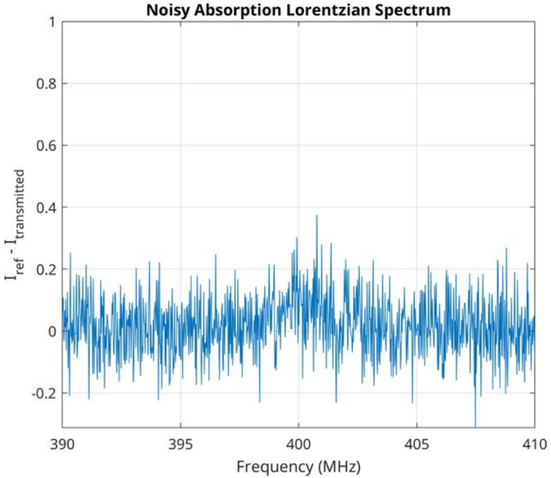
- Thought experiment, we want to measure the Larmor frequency for a given magnetic field find photon frequency such that
  $h\nu = \Delta E = \gamma\hbar B_z$

- Like UV visible:
  - Change wavelength/frequency ν (continuous wave spectroscopy)
  - Measure $I_{\text{ref}} - I_{\text{transmitted}}$





expectation



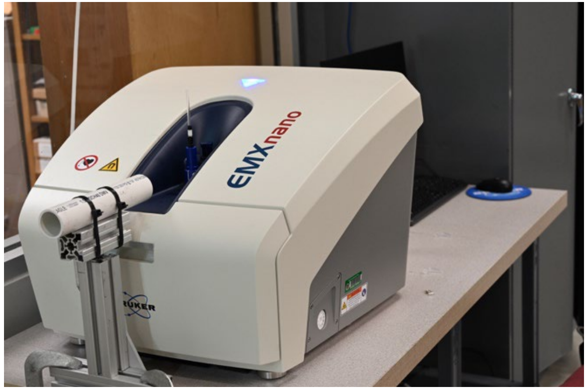
reality

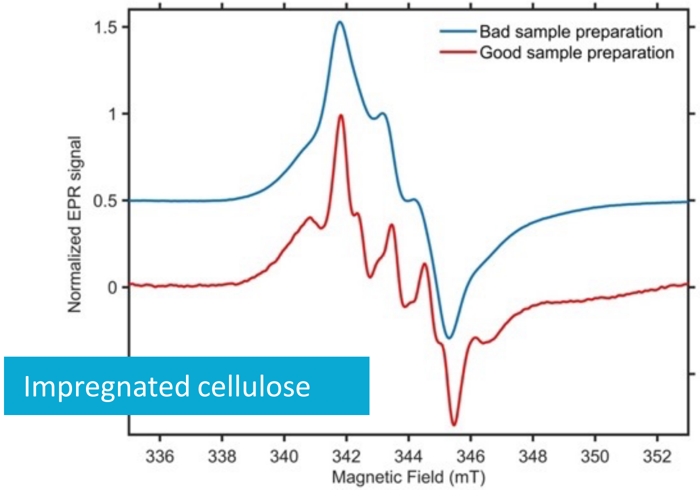
Low polarization, low concentration instrumental noise
→ Too low contrast
$(I_{ref} - I_{transmitted} \sim 0)$

Yet CW EPR exist…

An introduction to EPR

- Simplest EPR experiments: room temperature CW
  - Commercial benchtop EPR
    - Radical concentration check
    - Determine optimal formulation: improve sample preparation for matrix free applications
    - Track of the degradation:
      - check sample aging
      - radical degradation often observed in cellular milieu, in-cell, fungi, native biofilms…





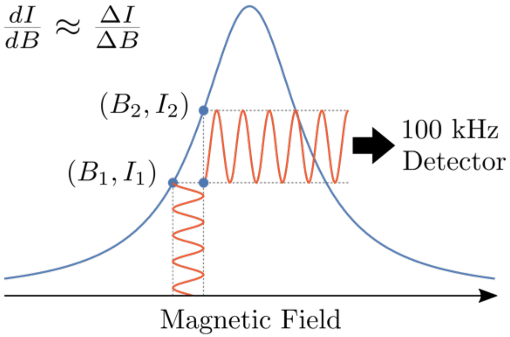
Impregnated cellulose

Why this shape?

Continuous wave EPR

- Tricks
  - #1 Look at reflection, not transmission (R+T+Abs=1)
  - #2 Have a resonator for fixed photon frequency
  - #3 sweep field, not frequency (to have a resonator)

- One more trick: look at the derivative
  - Sweep magnetic field (B_0) and add a modulation field $\mathrm{B}_m \cos(f_m t)$
  - Noise from experiment decays like $1/f_m$



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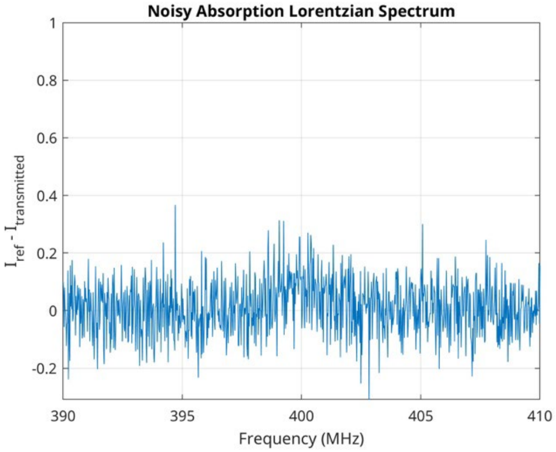
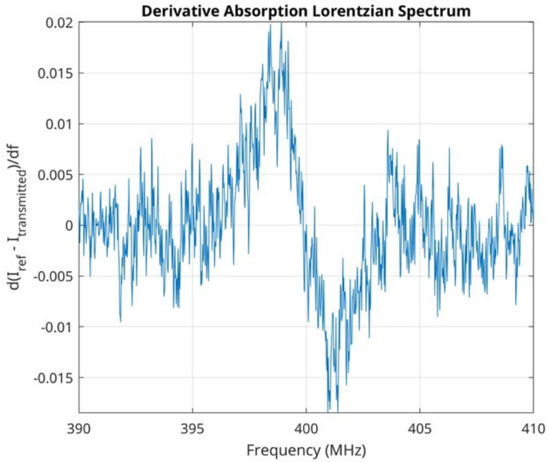
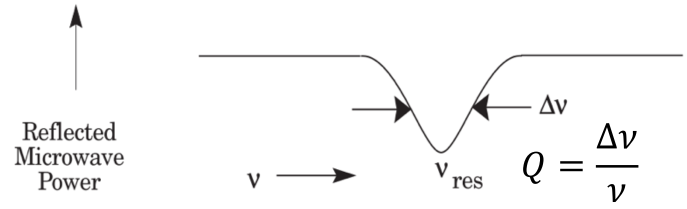




Most common form of EPR

Resonant circuit

- Why a resonant circuit?
  - $R + T + Abs_{\text{cavity}} + Abs_{\text{sample}} = 1$
  - Maximizes locally the number of photons/input power (low Watts needed)
  - For NMR and EPR:
    - Separate Electric field from Magnetic field
    - Low E-field = low sample warming
  - Serves as frequency filter (lower noise)

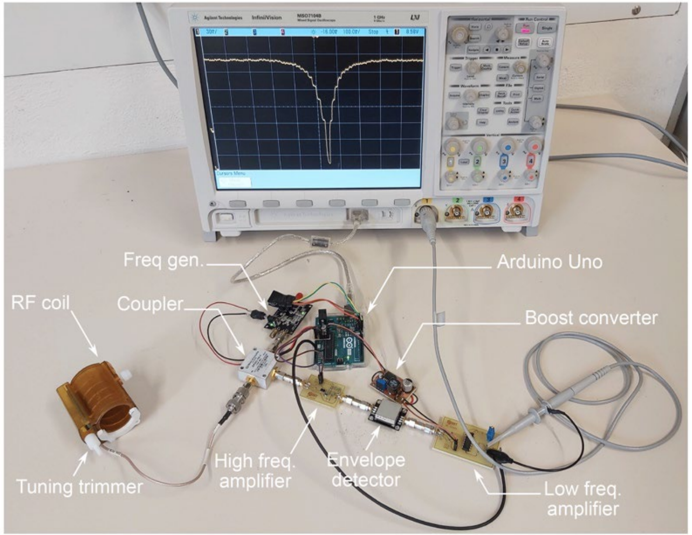


$$Q = \frac{\Delta\nu}{\nu}$$

Figure 5-2 Reflected microwave power from a resonant cavity.

- Circuit must be matched
  - This is to ensure that R ~ 0 when no resonance

Condition	R	T	Abs_{cavity}	Abs_{sample}	R + T + A
At Resonance	> 0	0	< 1	>0	1
Off Resonance	≈ 0	0	≈ 1	0	1

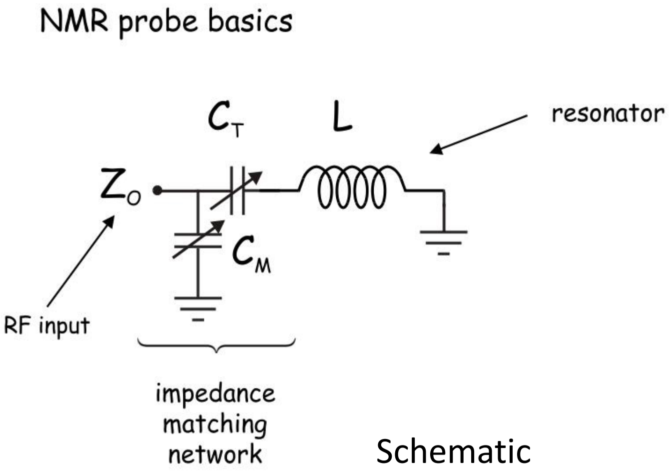


tuning curve “wobb”

Resonant circuit

- Example: RLC circuit in NMR
  - RF power delivered by coax cables (impedance 50 Ω)
  - Circuit matched to have impedance of 50 Ω at given frequency (matching cable impedance)
  - Maximum B1 field homogeneity (inside coil)
  - Minimum E1 field inside coil

- Example: Cavity in EPR
  - mw power delivered via waveguide
  - mw form standing waves in the cavity
  - Maximum B1 field homogeneity (at the center of the cavity)
  - Minimum E1 field at the center of the cavity



Schematic
Found online

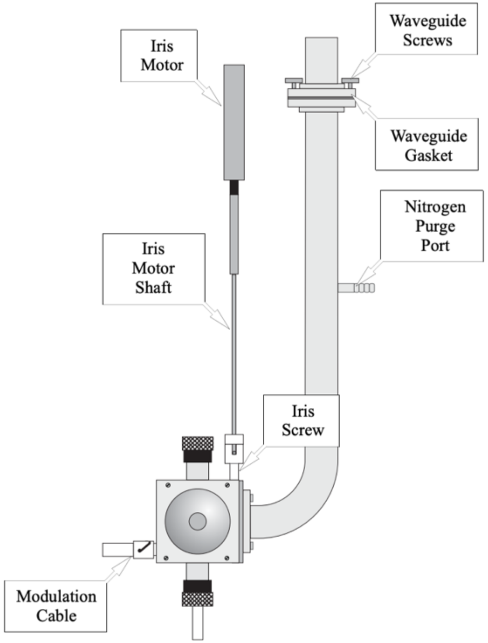


Figure 5-20 Connections on the ER 4122SHQ cavity.

Fourier transform NMR/EPR

- Sweeping field == slow → how obtain all information at once?
  - Fourier transform NMR/EPR
  - **Multiplexing** = Simultaneously detects signals from all spins at once.

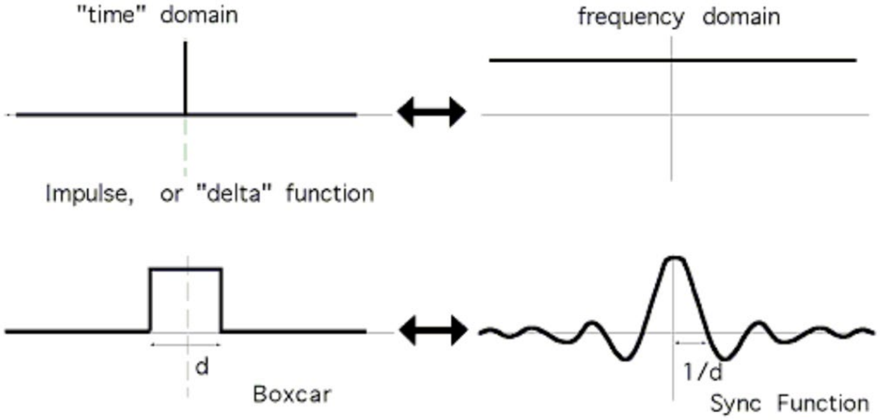
Concept	Role in NMR/MRI/EPR
Linear Response	Describes how spins respond to RF pulses.
Impulse Response	The FID (time-domain signal).
Transfer Function	The spectrum (FT of the FID).

- Relies on Linear Response theory
  - general theory applicable to many field
  - Apply a perturbation, look for the answer
  - Condition: must be a small perturbation
    (otherwise, non-linear answer, e.g. radiation damping)

- How does it work?
  - Dirac distribution, δ (infinite sharp pick at given time)
  - Fourier transform Dirac = white noise: all frequencies covered
  - Short pulse $B_1(t) = B_1\delta(t)$ → all spins excited (all freq. present)
  - FID given by $S(t) = \int_{-\infty}^{+\infty} B_1\delta(t)h(t+\tau)d\tau$ (response)
  - $\mathrm{FT}\big(S(t)\big) = \mathrm{FT}\big(\delta(t)\big) \times \mathrm{FT}\big(h(t)\big) = S(\omega)$ ← the spectrum

$$\int_{-\infty}^{\infty} \delta(x)dx = 1.$$

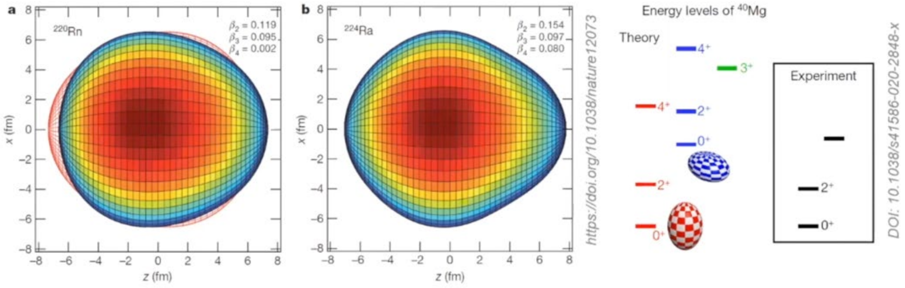
- Practice: δ not possible, we use shaped pulses
  - E.g. rectangular pulses

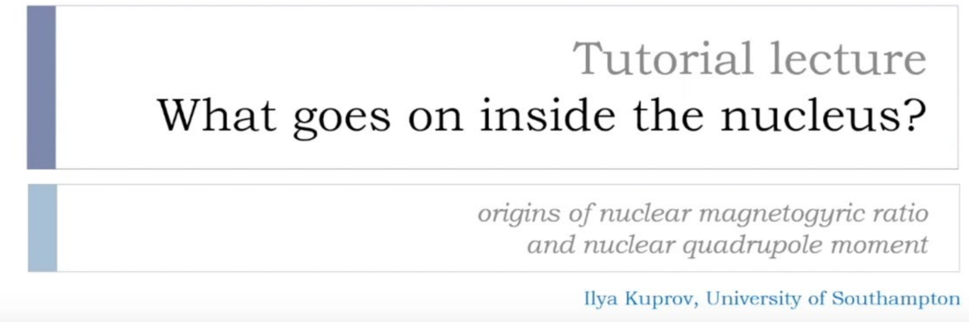


EPR and NMR real case

- Nuclei are made of nucleons:
  - Protons and neutrons, each have spin 1/2
  - Arrangement follows quantum mechanical rules
    - Nuclei have fundamental and excited states
    - Fundamental levels could have total spin $\neq 0$

https://www.youtube.com/watch?v=lPc1jxo8-Uw





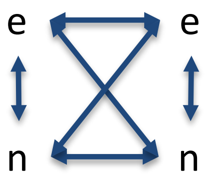
Tutorial lecture

What goes on inside the nucleus?

origins of nuclear magnetogyric ratio and nuclear quadrupole moment

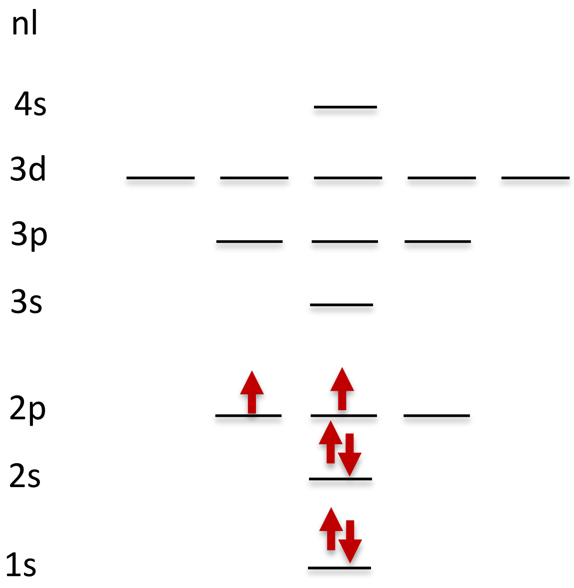
Ilya Kuprov, University of Southampton

- Nuclear spins and electrons spins in chemical systems
  - Electrons in orbitals with other electrons
  - Electrons interacting with nuclei
  - Nuclei interacting with electric gradients
  - Nuclei interacting with nuclei



Nuclear levels

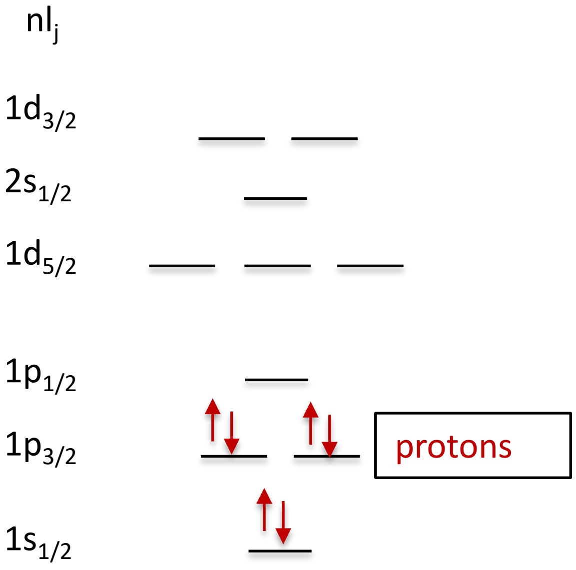
Carbon orbitals



Electrons
Atomic orbitals

Carbon - 12

^{12}C → $I = 0$

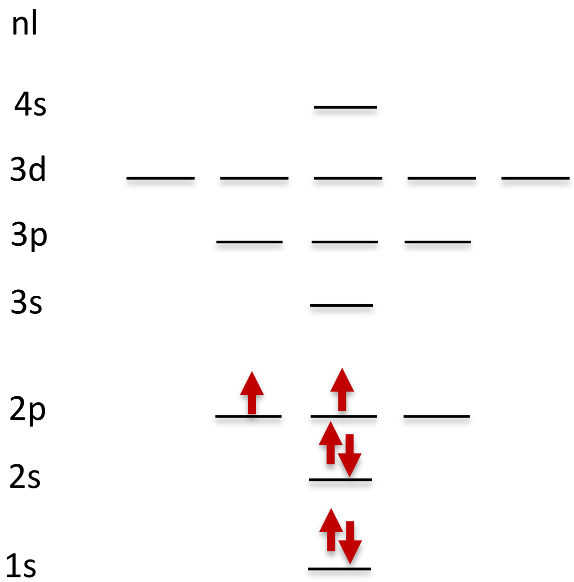


$I = 0$ when spin paired

Nucleons
Energy states

Nuclear levels

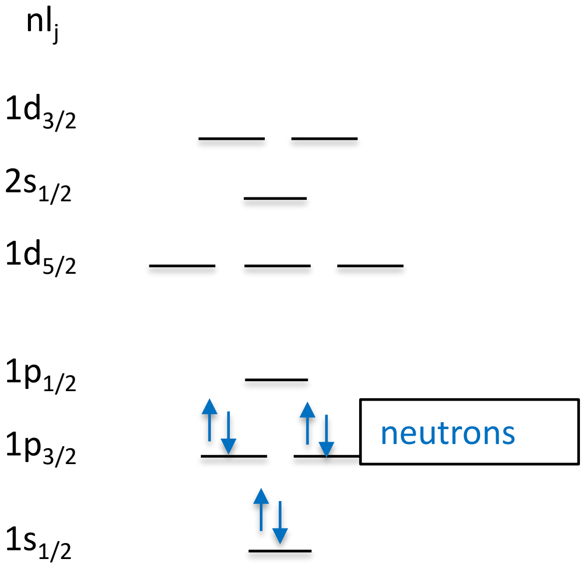
Carbon orbitals



Electrons
Atomic orbitals

Carbon - 12

^{12}C → I = 0

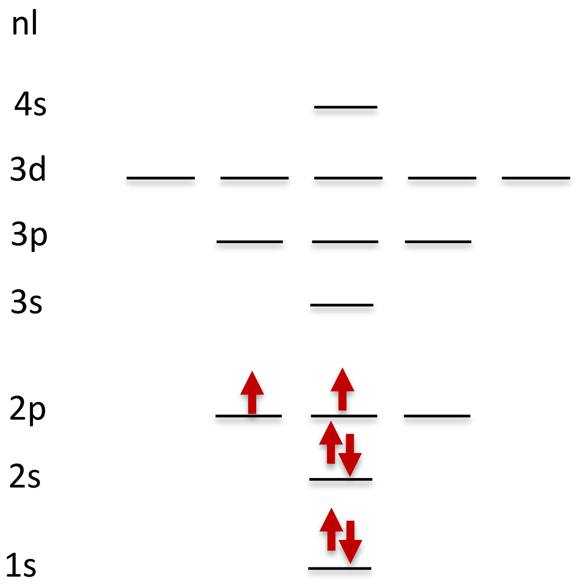


I = 0 when spin paired

Nucleons
Energy states

Nuclear levels

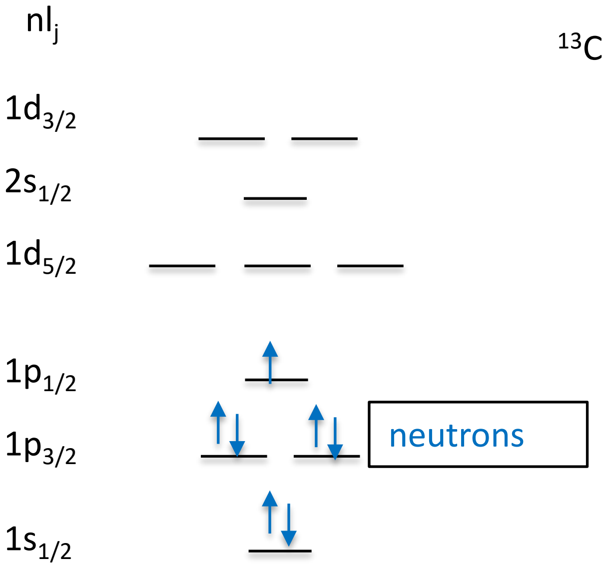
Carbon orbitals



Electrons
Atomic orbitals

Carbon - 13

^{13}C → 1 more neutron I = ½



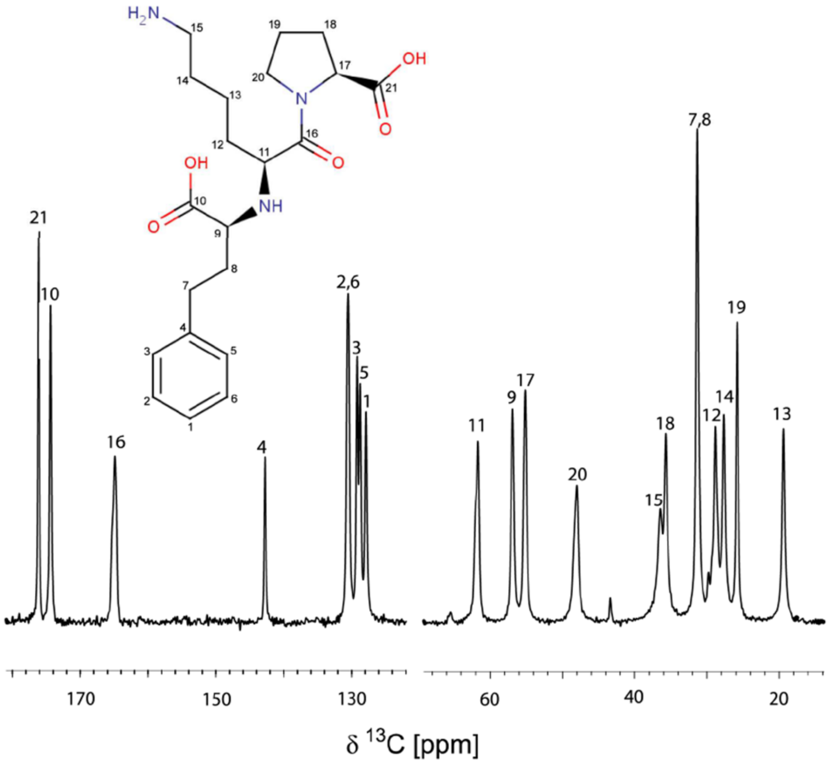
Nucleons
Energy states

Nuclear interactions in molecules

Interaction	who	Origin/Description	Relevance to Magnetic Resonance	Typical Scale/Effect	Hamiltonian
Zeeman Interaction	n	Interaction between nuclear magnetic moments and an external magnetic field $\vec{\mu}.\vec{B}_0$.	Fundamental for NMR/MRI: Splits energy levels, enabling resonance at the Larmor frequency.	**Isotropic** MHz frequency range	$\hat{H}_z = \gamma\hbar\hat{S}_z B_z$
Dipole-Dipole Coupling	n-n	Direct magnetic interaction between nuclear spins. Originates from classical magnetism.	Causes line broadening and splitting; used in structural studies (e.g., NOESY, solid-state NMR, via CP). **Liquid state (OE)** **Solid-state (DQ exp)**	**Anisotropic** ~kHz (depends on distance/r^3)	$\hat{H}_{1,2} = \vec{\hat{S}}_1 D_{1,2} \vec{\hat{S}}_2$
Chemical Shift	n-e	Shielding of nuclei by electron clouds, altering local magnetic field. Originates from molecular orbitals.	Provides chemical environment information (e.g., distinguishing CH_3 from OH). **Liquid state/solid state**	**Anisotropic** ppm (parts per million)	$\hat{H}_{csa} = \vec{\hat{S}}_1 \sigma_1 \vec{B_0}$
J-Coupling (Scalar Coupling)	n-e-e-n	Indirect interaction mediated by bonding electrons. Originates from spin-spin coupling via electrons.	Splits NMR peaks into multiplets; reveals molecular connectivity (e.g., ^{1}H-^{1}H or ^{1}H-^{13}C coupling). **Liquid state - INADEQUATE**	**Isotropic** Hz to hundreds of Hz	$\hat{H}_{1,2} = J\hat{S}_1\hat{S}_2$
Quadrupolar Interaction	n- electric field gradient	Interaction between nuclear electric quadrupole moment and electric field gradients. Originates from non-spherical charge distribution.	Broadens lines for nuclei with spin > 1/2 (e.g., ^{14}N, ^{35}Cl); complicates spectra. **Solid state/NQR**	**Anisotropic** MHz (for large quadrupoles)	$\hat{H}_{Q,1} = \vec{\hat{S}}_1 Q \vec{\hat{S}}_1$
Knight Shift	n-e	Shift in NMR frequency due to conduction electrons in metals. Originates from Fermi contact interaction.	Observed in metallic systems; probes electronic structure. **Solid state**	**Isotropic** ppm to %	$\hat{H}_{ks} = \sigma_1 \hat{S}_z B_0$

NMR: An atom-by-atom picture of molecules

- ^{13}C solid-state NMR spectrum of *lisinopril* and the proposed spectral assignments

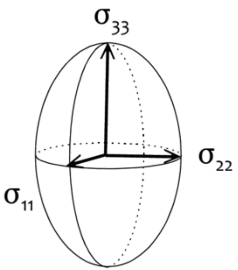


NMR: Very low energy spectroscopy

✅ Exquisite sensitivity
❌ Very weak signals
🧲 NMR benefits from high fields!

Chemical shift anisotropy

- CSA

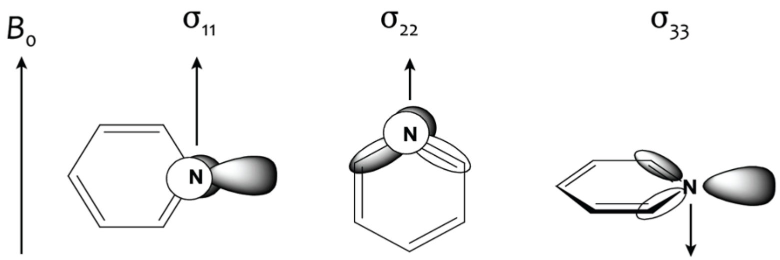


$$\sigma = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}$$

CS tensor in the molecular frame

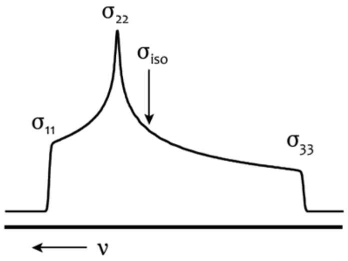
$$\sigma^{PAS} = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}$$

CS tensor in its own **principal axis system (PAS)**



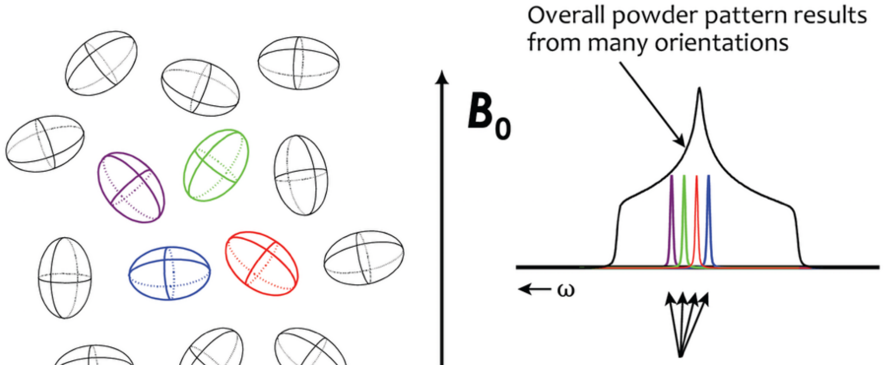
σ_{33}: Direction of highest shielding

σ_{11}: Direction of lowest shielding



These orientations, and the many possible others, give rise to the solid-state NMR **powder pattern**

- Case of a powder

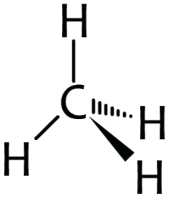


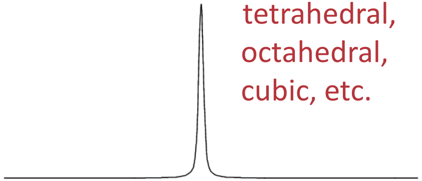
Overall powder pattern results from many orientations

Individual crystallites have the tensors oriented in one position w.r.t. B_o, and give rise to a discrete frequency

CSA and local symmetries

- Aside from the fact that the CS tensor is the origin of isotropic chemical shifts that are observed in solution, there is also a rich connection between electronic structure, symmetry and CSA.

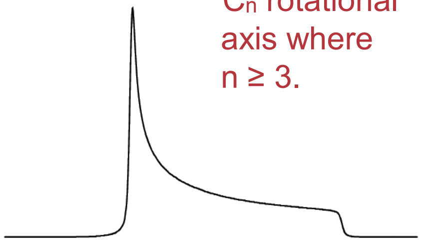




tetrahedral, octahedral, cubic, etc.

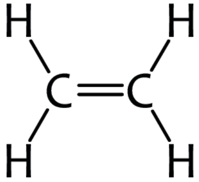
Spherical symmetry: shielding is similar in all directions, very small CSA.

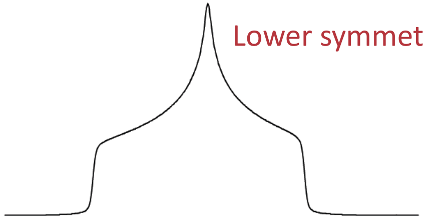
$H-C\equiv C-H$



C_n rotational axis where n ≥ 3.

Axial symmetry: molecule is // to $\mathbf{B}_0$ maximum shielding; when molecule is ⊥ to $\mathbf{B}_0$ maximum deshielding



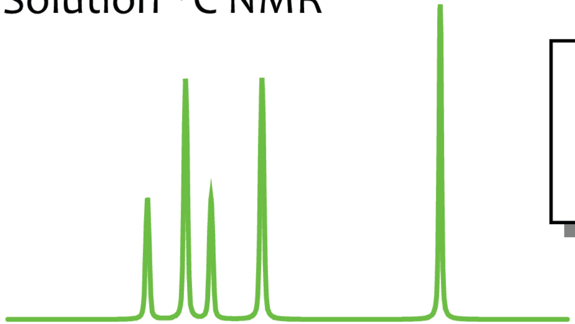


Lower symmetries

Non-axial symmetry: Shielding is different in three directions

Solution vs. Solid-State NMR

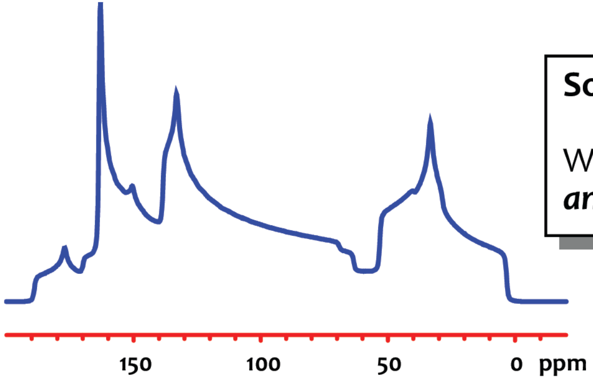
Solution ^{13}C NMR



Liquids:

We observe the average, or ***isotropic*** values of NMR interactions

Solid State ^{13}C NMR

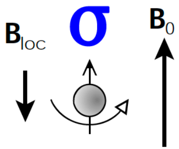


Solids:

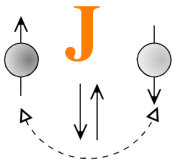
We observe orientation dependence, or ***anisotropic*** features of NMR interactions

Solution vs. Solid-State NMR

Important interactions in solution & the solid-state:

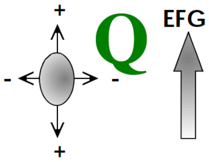


Chemical Shielding
- electronic environment
- nature of chemical bonding
- bond angles and lengths
- coordination numbers
- site differentiation

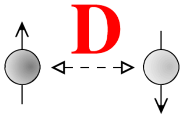


J-Coupling
- Through-bond connectivities
- Bond character
- Dynamics

Also important in the solid-state:



Quadrupolar Interaction
- Local atomic environments
- Nearest neighbours
- Cylindrical and/or axial symmetry
- Site differentiation

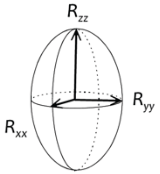


Dipolar Coupling
- Through-space connectivities
- Bond lengths
- Dynamics

Recover resolution

- Solid state → Anisotropies
  - Leeds to overlapping signals
  - Lack of site-specific information

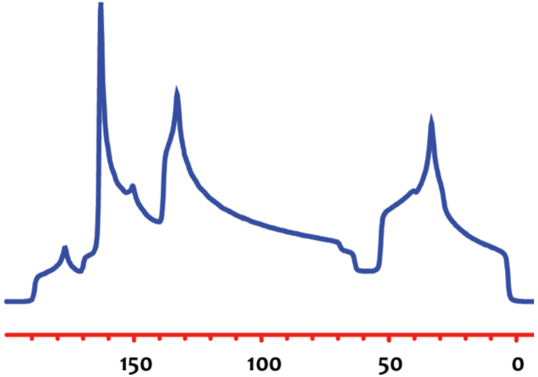
- Tensors = iso + aniso
  - Example, Axial tensor
  - Expected spectrum

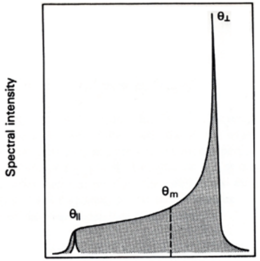


$R_{xx} = R_{yy}$

$$R_{zz}^{LAB} = R_{iso} + R_{\parallel}\underbrace{\left(\frac{3\cos^2\theta - 1}{2}\right)}_{\text{Anisotropic part}}$$

Solid State ^{13}C NMR





← Powder pattern

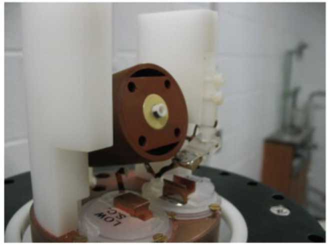
$$\langle I_+(t)\rangle = \int \exp[-i\omega_{int}(\theta)t]\,\underbrace{p(\theta)d\theta}_{\text{Probability of finding a crystallite with orientation }\theta}$$

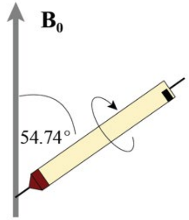
$\theta_\parallel = 0°$,	B_0 along unique axis,	$\omega = R_{iso} + R_\parallel$
$\theta_\perp = 90°$,	B_0 along unique axis,	$\omega = R_{iso} - R_\parallel/2$
$\theta_m = 54.74°$,	B_0 along unique axis,	$\omega = R_{iso}$ [$\theta = \cos^{-1}(\sqrt{3}/3)$]

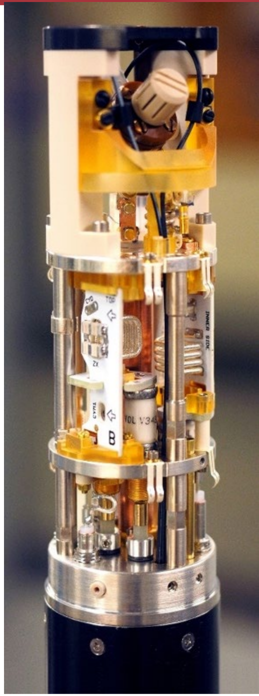
Higher resolution → Magic Angle Spinning

Magic Angle Spinning

- Put sample in rotor
- Spin sample fast at magic angle w.r.t magnetic field → MAS
  - E. R. Andrew, A. Bradbury, and R. G. Eades (1958–1959) demonstrated the technique and its theoretical basis.
  - I. J. Lowe (1959) published further experimental results.
  - name "magic angle spinning" was introduced by C. J. Gorter in 1960



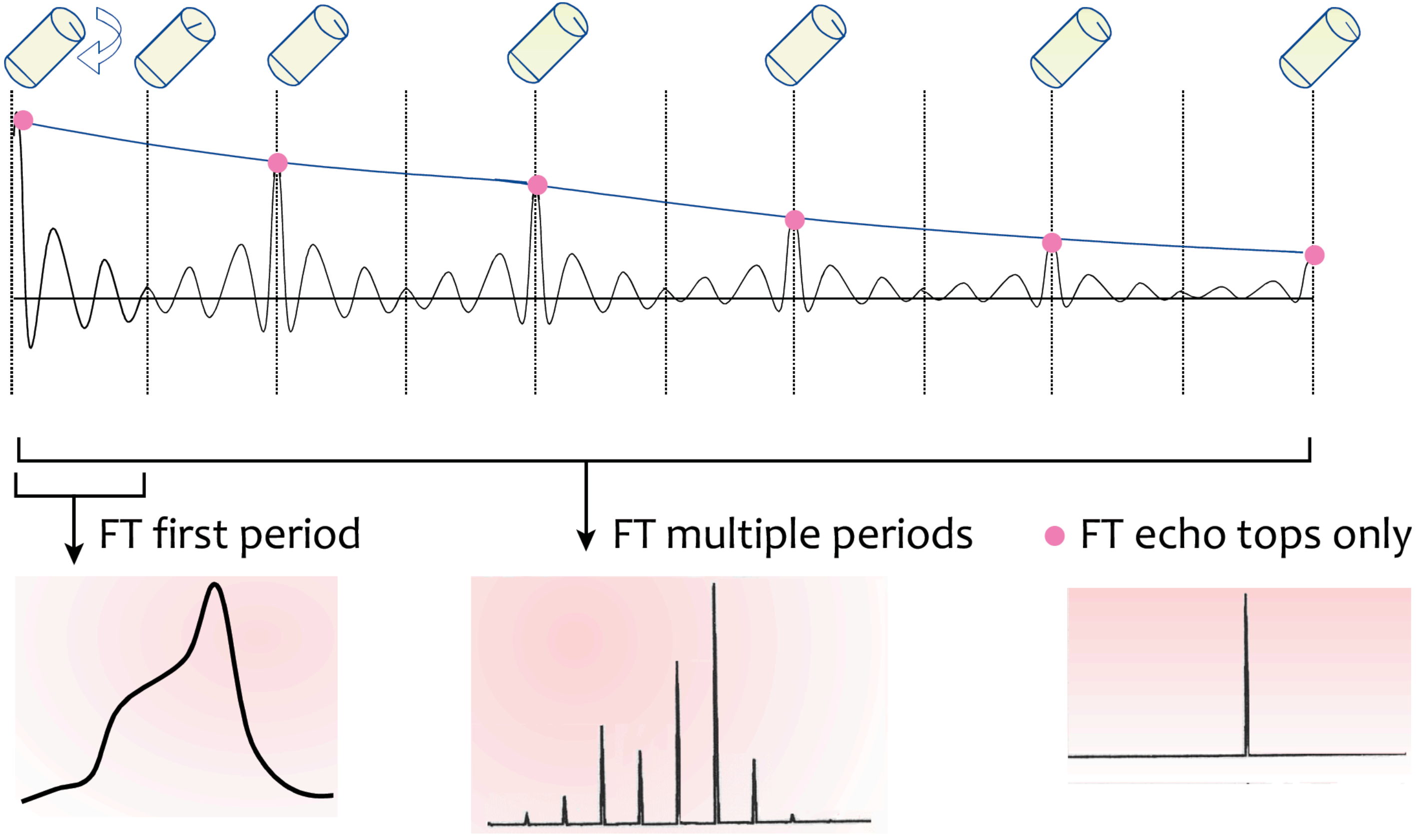




- For Axial CSA, and Crystal with orientation $\Omega = (\beta, \alpha)$
  - $H_{\text{CSA}}(t) = \gamma B_O \sigma(\Omega, t) I_z$
  - Effective Larmor frequency for spinning frequency ω_r
  - $\omega(\Omega, t) = \omega_{\text{iso}} + \frac{1}{2}\delta_{\text{aniso}}[\sqrt{2}\sin(2\beta)\cos(\alpha - \omega_r t) + \sin^2\beta\cos(-2\omega_r t + 2\alpha)]$ (with some angle convention)

FIR under MAS

- Should be familiar to those setting the magic angle



FT first period

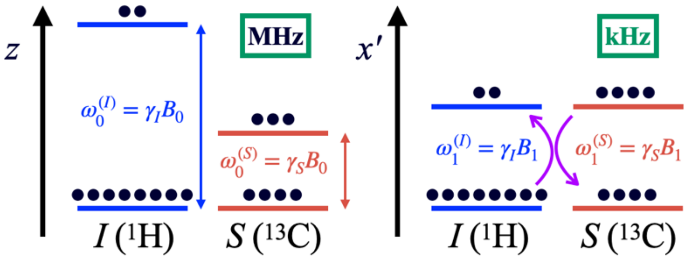
FT multiple periods

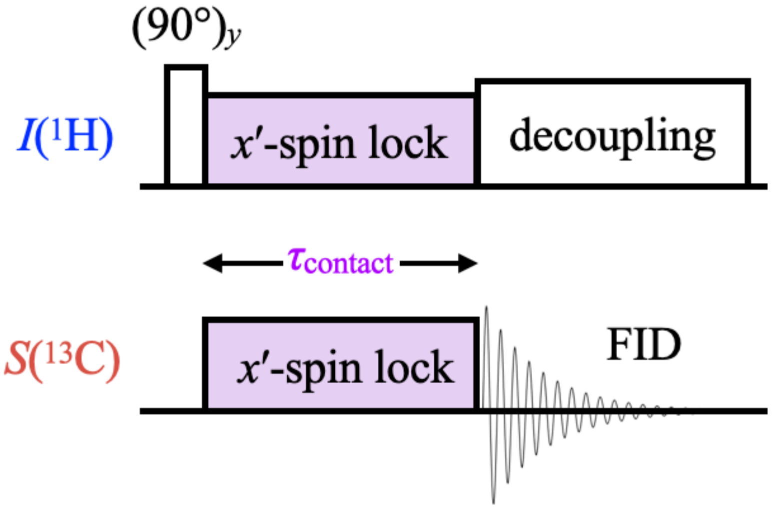
● FT echo tops only

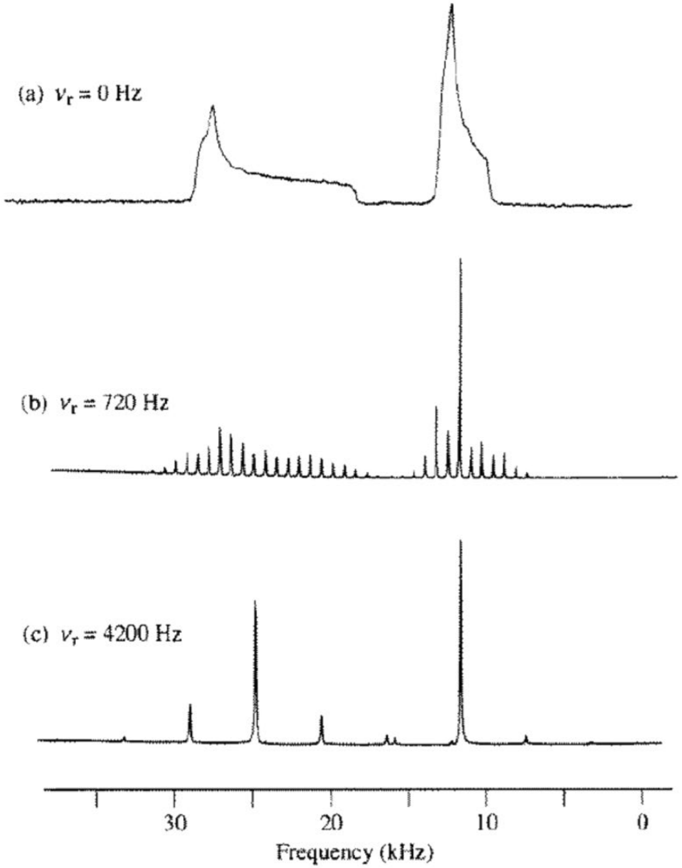
Question: why not just always do the FT of the top of the echos?

Examples of MAS

- Typical solid state NMR experiment







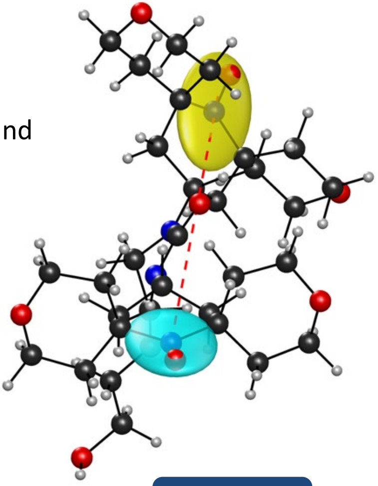
Electron interactions in molecules

Interaction	who	Origin/Description	Relevance to Electron Spins	Typical Scale/Effect	Hamiltonian
Electron Zeeman Interaction	e	Interaction between electron magnetic moments and an external magnetic field	Fundamental for EPR: Splits energy levels, enabling resonance at microwave frequencies (e.g., X-band ~9 GHz).	GHz frequency range	$\hat{H}_z = \gamma\hbar\hat{S}_z B_z$
Spin-Orbit Coupling	e-e	Coupling between electron spin and orbital angular momentum. Originates from relativistic effects.	Influences relaxation, g-factor anisotropy, and fine structure.	GHz frequency range	$\hat{H}_\mathrm{g} = \lambda\overrightarrow{\hat{S}}\,.\overrightarrow{\hat{L}}$
Hyperfine Interaction	e-n	Interaction between electron spins and nearby nuclear spins. Originates from Fermi contact and dipolar coupling.	Splits EPR lines; provides info on electron-nuclear distances and molecular structure (e.g., in radicals/metal complexes).	MHz to GHz	$\hat{H}_{1,2} = \overrightarrow{\hat{S}_1} A_{1,2} \overrightarrow{\hat{\mathrm{I}}_2}$
Fine Structure (Zero-Field Splitting)	e-e	Splitting of electron spin levels due to spin-spin coupling in systems with S>1/2. Originates from spin-orbit coupling and electron-electron dipolar interaction.	Reveals electronic structure and geometry (e.g., transition metal ions, high-spin states).	MHz-THz	$\hat{H}_{D,1} = \overrightarrow{\hat{S}_1} D \overrightarrow{\hat{S}_1}$
Exchange Interaction	e-e	Coupling between unpaired electron spins on different centers. Originates from overlap of orbitals.	Critical for magnetic ordering (ferro/antiferromagnetism) and spin labeling (e.g., in organic radicals).	Variable (strong to weak)	$\hat{H}_{1,2} = J\hat{S}_1\hat{S}_2$
Dipole-Dipole Interaction	e-e	Direct magnetic interaction between electron spins. Originates from classical magnetism.	Causes line broadening; used in distance measurements (e.g., PELDOR/DEER for biomolecules).	~10–100 MHz (depends on distance)	$\hat{H}_{d,1} = \overrightarrow{\hat{S}_1} d \overrightarrow{\hat{S}_2}$

An introduction to EPR

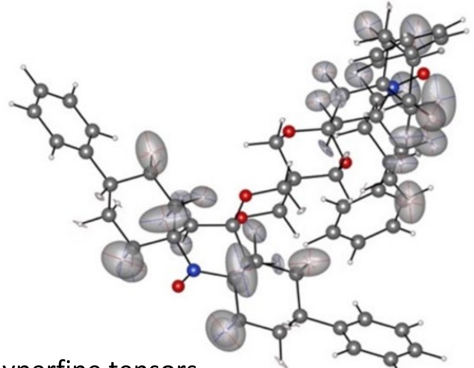
Magnetic interactions: N. Wili, JMRO, 2023, 16–17, 100108.

- *g*-tensor ↔ chemical shift (isotropic-anisotropic)
  - Anisotropy arise from orbital angular momentum
  - Nitroxides [2.01-2.002] (~ 1 GHz at 9.4 T)
  - BDPA [2.0027-2.0025] (~80 MHz at 9.4 T)
  - $\widehat{H}_{\mathrm{Zeeman}} = \beta \vec{B}_0 \hat{g} \hat{\vec{S}} = \beta g \hat{S}_z B_0$
- Dipolar and exchange interaction (homonuclear dipolar/J coupling)
  - **spin-spin coupling** through space + some orbital angular momentum ($D_{a,b}$~10s MHz range)
  - interaction through nascent bonds ($|J_{a,b}|$~ 0- 100 MHz)
  - $\widehat{H}_{\mathrm{D/J}} = D_{a,b}(2S_{z,a}S_{z,b} - \frac{1}{2}(S_{+,a}S_{-,b} + S_{-,a}S_{+,b})) - 2J_{a,b}\,(S_{z,a}S_{z,b} + \frac{1}{2}(S_{+,a}S_{-,b} + S_{-,a}S_{+,b}))$
- Hyperfine coupling (hetero-nuclear dipolar coupling)
  - spin-spin coupling through space + some orbital angular momentum (~ 1-10s MHz range)
  - $\widehat{H}_{\mathrm{e,n}} = A_{Iso}(S_{z,a}I_z + \frac{1}{2}(S_{+,a}I_- + S_{-,a}I_+)) + A_{\mathrm{aniso}}(2S_{z,a}I_z - \frac{1}{2}(S_{+,a}I_- + S_{-,a}I_+)) + B_{\mathrm{aniso}}S_{z,a}I_+ + B^*_{\mathrm{aniso}}S_{z,a}I_-$



g-tensors and $D_{a,b}$ / $J_{a,b}$

AMUPol[1]



Hyperfine tensors

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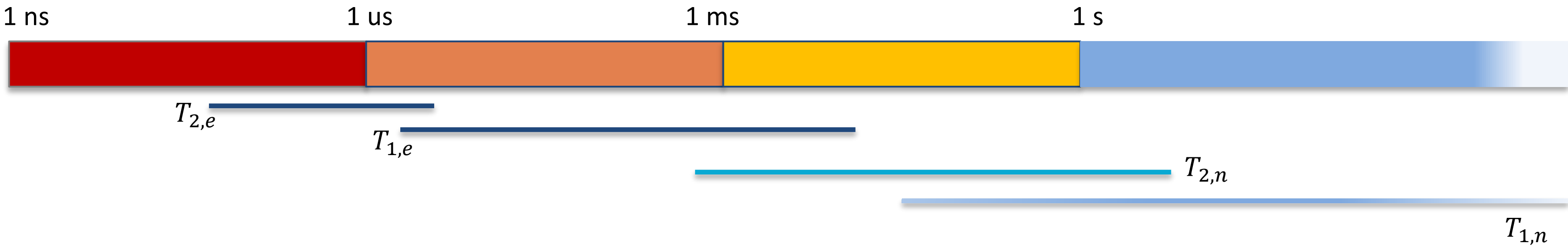
[1] 10.1002/anie.201304657

EPR/NMR

- EPR is NMR are equivalent but
  - Interaction electron spin/ ~ 658 times greater than for proton: Larmor frequency **MHz → GHz**
  - Electron spins sits in orbitals → sensitive to bonds and angular momentum
  - Electron spins in a molecule/metal always contains orbital angular momentum “contamination”

- Stronger interactions
  - Couplings ~ 658 to 658^2 stronger **Hz-kHz → 100 kHz – MHz**
  - Sensitive to orbital overlap (exchange interaction = bond forming)

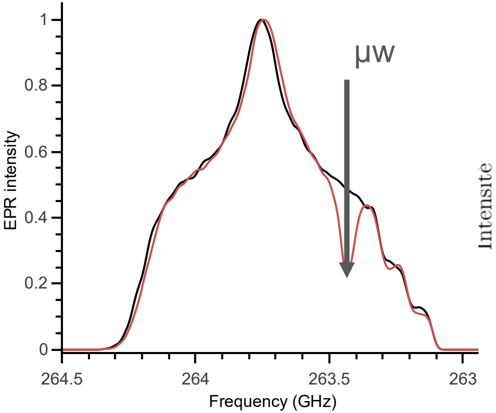
- Faster relaxation
  - T_1 ~ us to ms vs ms-s to h for nuclei
  - T_2 ~ us vs ms to s for nuclei

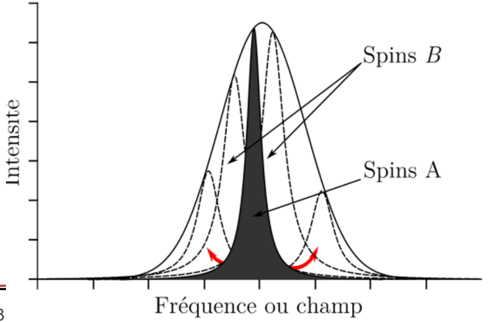


Main limitation of EPR: Lines are broad, FT EPR is near impossible

An introduction to EPR

- Pulsed EPR: **less common**
  - Closer to wide-line NMR: selective pulses
  - Pulses ~ 10 - 1000 ns ⟷ 1 – 100 MHz nutation frequencies
  - Requires high power (W to kW)
    - 9-10 GHz is common
    - up to 395 GHz with very selective pulses





- Selective pulses = limitations
  - Intrinsic T_2 hard to determine
  - echo decay T_2, includes effects of “instantaneous” and “spectral” diffusion

$$\left(\frac{1}{T_{2,e}}\right)_{\mathrm{ID}} \propto \boxed{C}\langle \sin^2 \boxed{\left(\frac{\theta}{2}\right)}\rangle \boxed{f(B_0)}$$

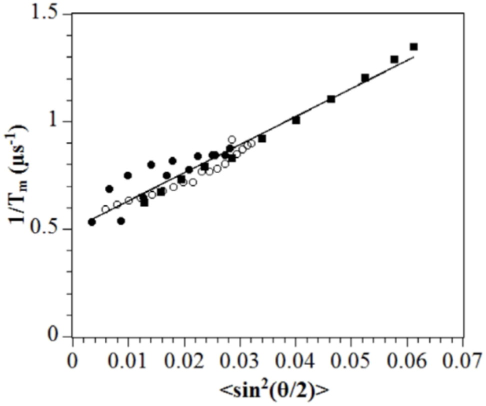
EPR intensity

Radical concentration

Pulse angle

10.1016/0022-2364(80)90231-0
10.1016/0022-2364(81)90216-X

A. Raitsimring, 2013

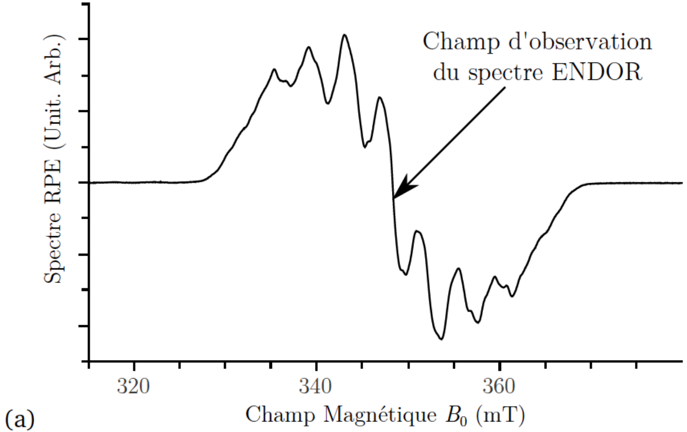


10.1088/0953-8984/25/31/316002

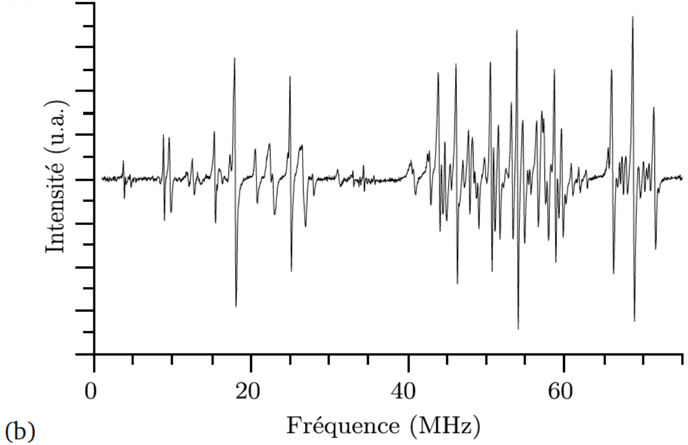
Some examples

- Effect of Hyperfine couplings
  - Examples in gallium oxide single crystal

EPR spectrum
Ti^{3+} in $\beta - \mathrm{Ga_2O_3}$



NMR spectrum
(collected with ENDOR)



1. F. Mentink-Vigier, L. Binet and D. Gourier, Strong isotopic effect in the electron-mediated nuclear-nuclear interaction in solids, Physical Review B, 2011, 83, 214409.
2. F. Mentink-Vigier, L. Binet, G. Vignoles, D. Gourier and H. Vezin, Giant titanium electron wave function in gallium oxide: A potential electron-nuclear spin system for quantum information processing, Physical Review B, 2010, 82, 184414.
3. F. Mentink-Vigier, L. Binet, D. Gourier and H. Vezin, Origin of the decoherence of the extended electron spin state in Ti-doped β-Ga 2 O 3, Journal of Physics: Condensed Matter, 2013, 25, 316002.

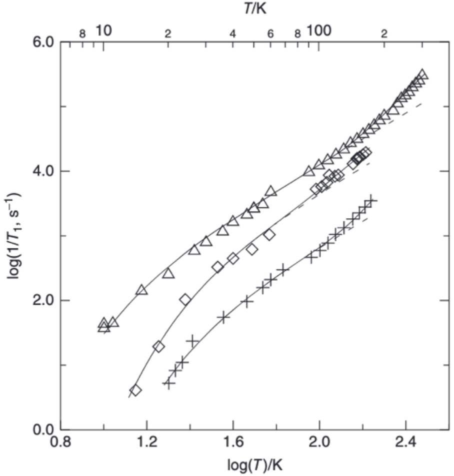
An introduction to EPR

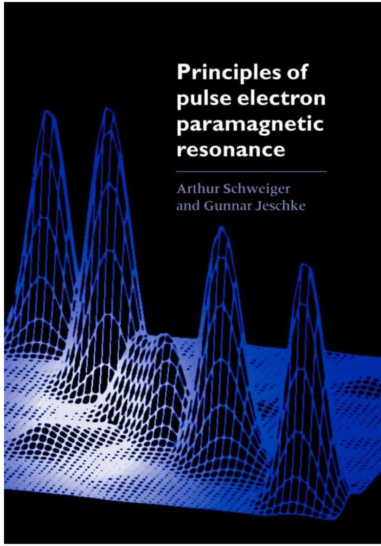
- Selective pulses = limitations
  - Intrinsic T_1 can be contaminated by “spectral” diffusion
    - Inversion - recovery → saturation (pulse train) – recovery

    - If available, use Arbitrary Waveform Generator
      - X-band (10.1016/j.jmr.2012.02.013 and 10.1016/j.jmr.2014.06.016)
      - W-band (10.1016/j.jmr.2023.107447 and 10.1007/s00723-022-01499-3)
    - literature by Eaton and Eaton
      - Relaxation times of organic radicals of various properties as function of solvent/temperature
      - 10.1006/jmra.1995.1169
      - 10.1080/00268970701724966
      - 10.1002/9780470034590.emrstm1507

- **Plethora of pulse sequences**
  - DEER/PELDOR/RIDME/SIFTER/DQC: measure e-e interaction
  - ELDOR-NMR/ENDOR: measure e-n interactions

Measure at lower [radical]
- Avoids spectral diffusion
- Avoids instantaneous diffusion





Principles of pulse electron paramagnetic resonance

Arthur Schweiger and Gunnar Jeschke

https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Electron_Paramagnetic_Resonance_(Jenschke)

10.1093/oso/9780198506348.001.0001

A short introduction to EPR

- EPR frequency in ”bands”
  - L, S, **X**, **Q**, **W**, G
  - 1-2, 2-4, 7-11, 35-50, 60-100, 110-330 GHz

High frequency pulse EPR
→ very challenging
→ Few labs with the capabilities

- Very high field pulses EPR by Goldfarb and Prisner’s group (up to 263 GHz)
- Maglab, Kaminker’s group up to 395 GHz

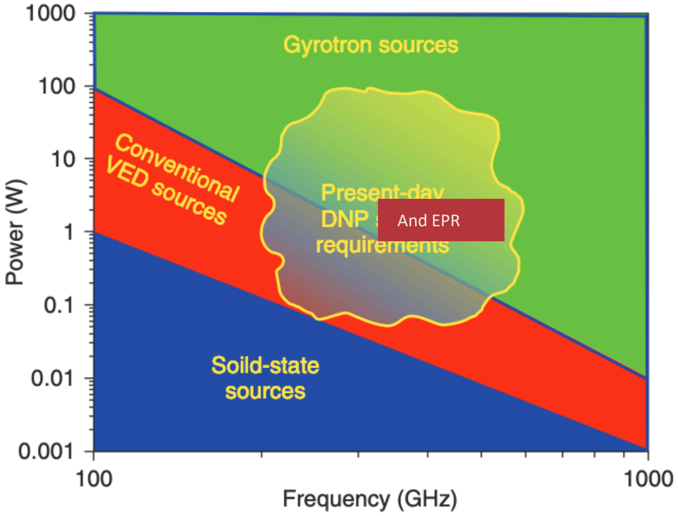


Figure 10. Schematic diagram of output power capabilities versus frequency for solid-state, conventional VED, and gyrotron DNP sources

10.1002/9780470034590.emrstm1582

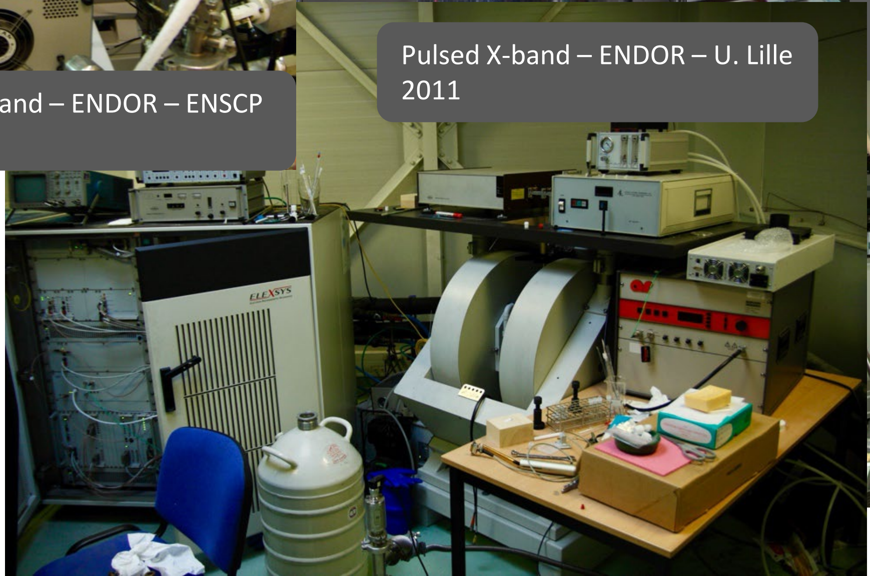
EPR instrument I used

CW X/Q-band – ENDOR – ENSCP
2010

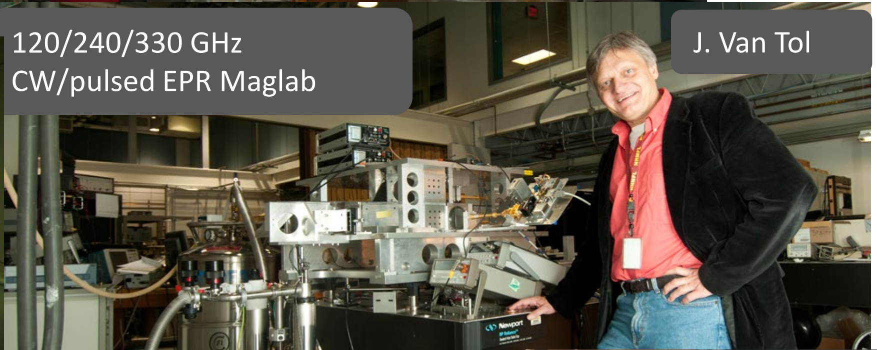
W-Band EPR/DNP/NMR
Weizmann Institute 2012

A. Collauto

W-Band EPR
Weizmann Institute 2013



Pulsed X-band – ENDOR – U. Lille
2011



120/240/330 GHz
CW/pulsed EPR Maglab

J. Van Tol

CW X-band Maglab 2018

Bonus: introduction to Liouville Space

- Coherent process
  - Liouville von-Neumann equation
    - Uses Hilbert space formalism
    - Matrices size 2^N for N spin ½

$$i\hbar\frac{\partial}{\partial t}\hat{\rho} = \left[\hat{H},\hat{\rho}\right] = \hat{H}\hat{\rho} - \hat{\rho}\hat{H}$$

- Great to understand coherent process
  - pulse sequences
  - most solid-state spectra

- Insufficient to understand/simulate DNP process…
- Cannot account for relaxation in a neat way.

- What is Liouville space?
  - A space where the density Matrix is a vector…(?)
  - Essential for including relaxation
  - You probably have already encountered Liouville space…

The Bloch Equation…

Bonus: introduction to Liouville Space

- Bloch equation for spin ½ under magnetic field B_0 and RF irradiation w_1
  - In the rotating Frame $\hat{H} = \Delta\omega\hat{S}_z + \omega_1\hat{S}_x$

$$\hat{\rho} = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix}$$

$\hat{\rho}$ is a complex matrix

→ need to determine 4 independent elements

→ $\hat{\rho}$ can be written as a linear combination of 2x2 matrices $\hat{O}_i$

$$\hat{\rho} = \sum a_i \hat{O}_i$$

- So let's define a space defined by
  - span{E, $\hat{S}_z$, $\hat{S}_y$, $\hat{S}_x$}, then $\hat{\rho} = \rho_E\hat{E} \quad + \rho_{Sz}\hat{S}_z + \rho_{Sy}S_y + \rho_{Sx}\hat{S}_x$
  - Then we can find a 4x4 matrix $\hat{\hat{H}}$ such that now

$$\hat{\rho} = \begin{bmatrix} \rho_E \\ \rho_{Sz} \\ \rho_{Sy} \\ \rho_{Sx} \end{bmatrix} = \hat{\hat{H}}\hat{\rho} = \begin{pmatrix} x & x & & \\ x & x & x & \\ & x & x & x \\ & & x & x \end{pmatrix} \begin{bmatrix} \rho_E \\ \rho_{Sz} \\ \rho_{Sy} \\ \rho_{Sx} \end{bmatrix}$$

$$i\hbar\frac{\partial}{\partial t}\hat{\rho} = [\hat{H}, \hat{\rho}] = \hat{H}\hat{\rho} - \hat{\rho}\hat{H}$$

Bonus: introduction to Liouville Space

- How to find $\widehat{\hat{H}}$ (called super-operator)
  - substitute rho by each element of the span{E, $\hat{S}_z$, $\hat{S}_y$, $\hat{S}_x$}, in the Liouville Von-Neuman equations then

$$i\hbar\frac{\partial}{\partial t}\widehat{\hat{S}}_z=\left[\hat{H},\hat{S}_z\right]=\left[\Delta\omega\hat{S}_z+\omega_1\hat{S}_x,\hat{S}_z\right]=\omega_1\left[\hat{S}_x,\hat{S}_z\right]=-\omega_1 i\hbar S_y$$

  - And we find $\widehat{\hat{H}}$ as

$$i\hbar\frac{\partial}{\partial t}\hat{\rho}=i\hbar\frac{\partial}{\partial t}\begin{bmatrix}\rho_E\\ \rho_{Sz}\\ \rho_{Sy}\\ \rho_{Sx}\end{bmatrix}=\widehat{\hat{H}}\hat{\rho}=\begin{pmatrix}0&0&0&0\\0&0&-\omega_1&0\\0&\omega_1&0&\Delta\omega\\0&0&-\Delta\omega&0\end{pmatrix}\begin{bmatrix}\rho_E\\ \rho_{Sz}\\ \rho_{Sy}\\ \rho_{Sx}\end{bmatrix}$$

  - We add T1, T2 relaxation and Boltzmann Equilibrium ($\hat{\rho}_{\mathrm{eq}}=E+\rho_{Sz}^{0}\widehat{S}_z$ at thermal equilibrium)

Almost there…

$$i\hbar\frac{\partial}{\partial t}\hat{\rho}=i\hbar\frac{\partial}{\partial t}\begin{bmatrix}\rho_E\\ \rho_{Sz}\\ \rho_{Sy}\\ \rho_{Sx}\end{bmatrix}=\widehat{\hat{H}}\hat{\rho}=\begin{pmatrix}0&0&0&0\\ \rho_{Sz}^{0}/T_1&-1/T_1&-\omega_1&0\\0&\omega_1&-1/T_2&\Delta\omega\\0&0&-\Delta\omega&-1/T_2\end{pmatrix}\begin{bmatrix}\rho_E\\ \rho_{Sz}\\ \rho_{Sy}\\ \rho_{Sx}\end{bmatrix}$$

Full Bloch equation with thermal equilibrium*

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