NMR Spectroscopy Basics: Spin Physics

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NMR Meets Biology
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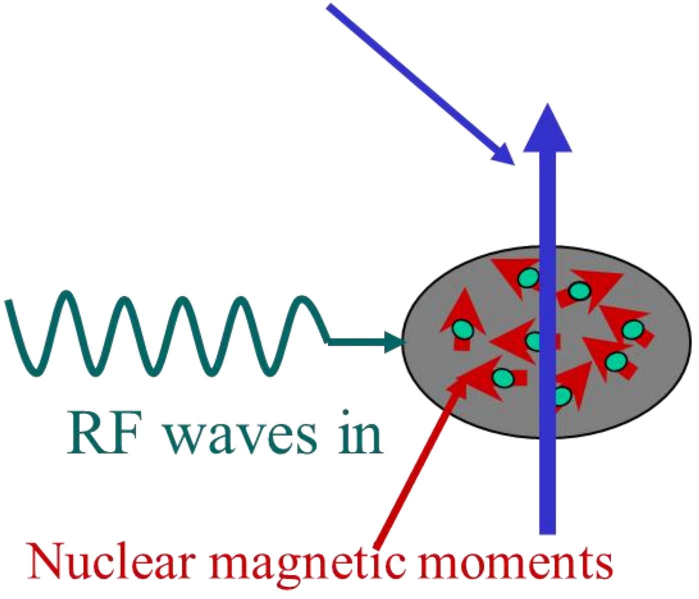
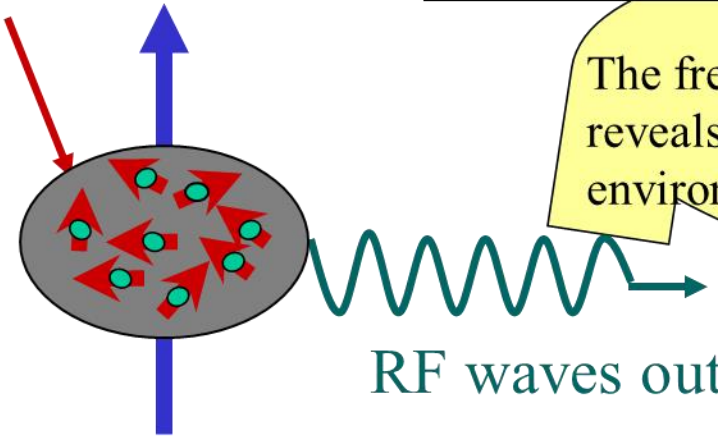


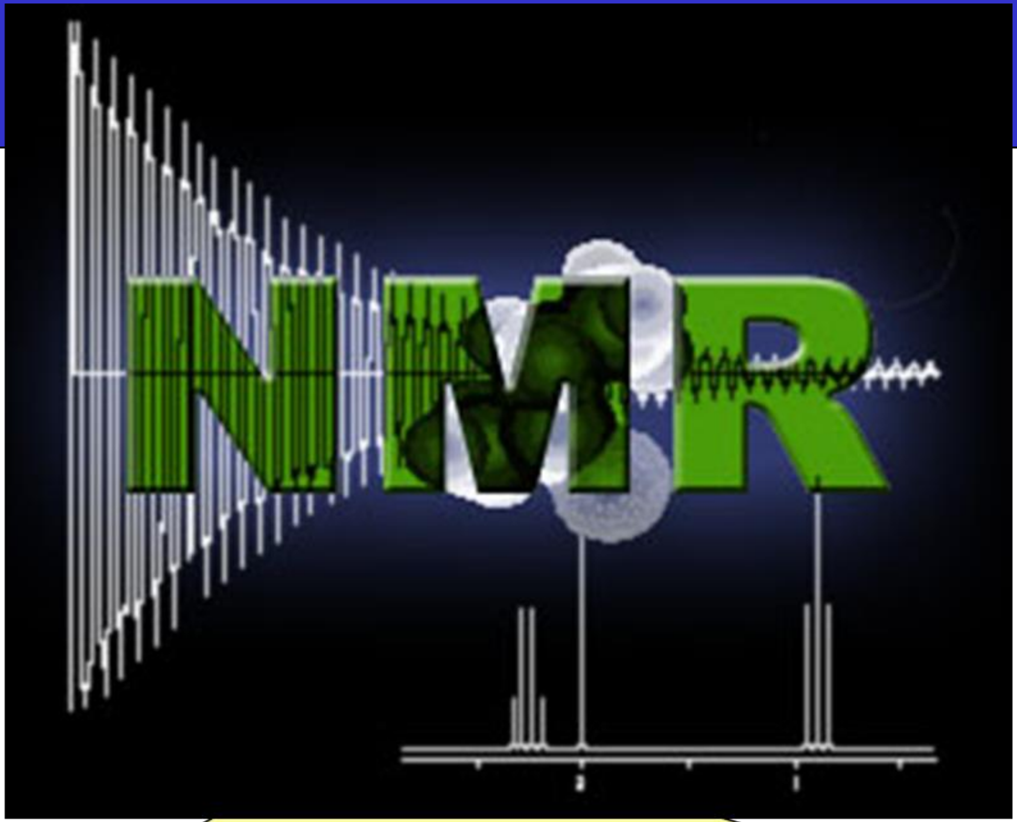
B_0, External magnetic field

RF waves in

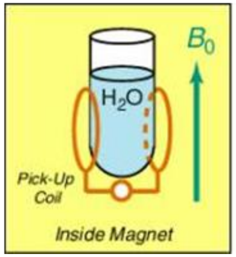
Nuclear magnetic moments in the sample



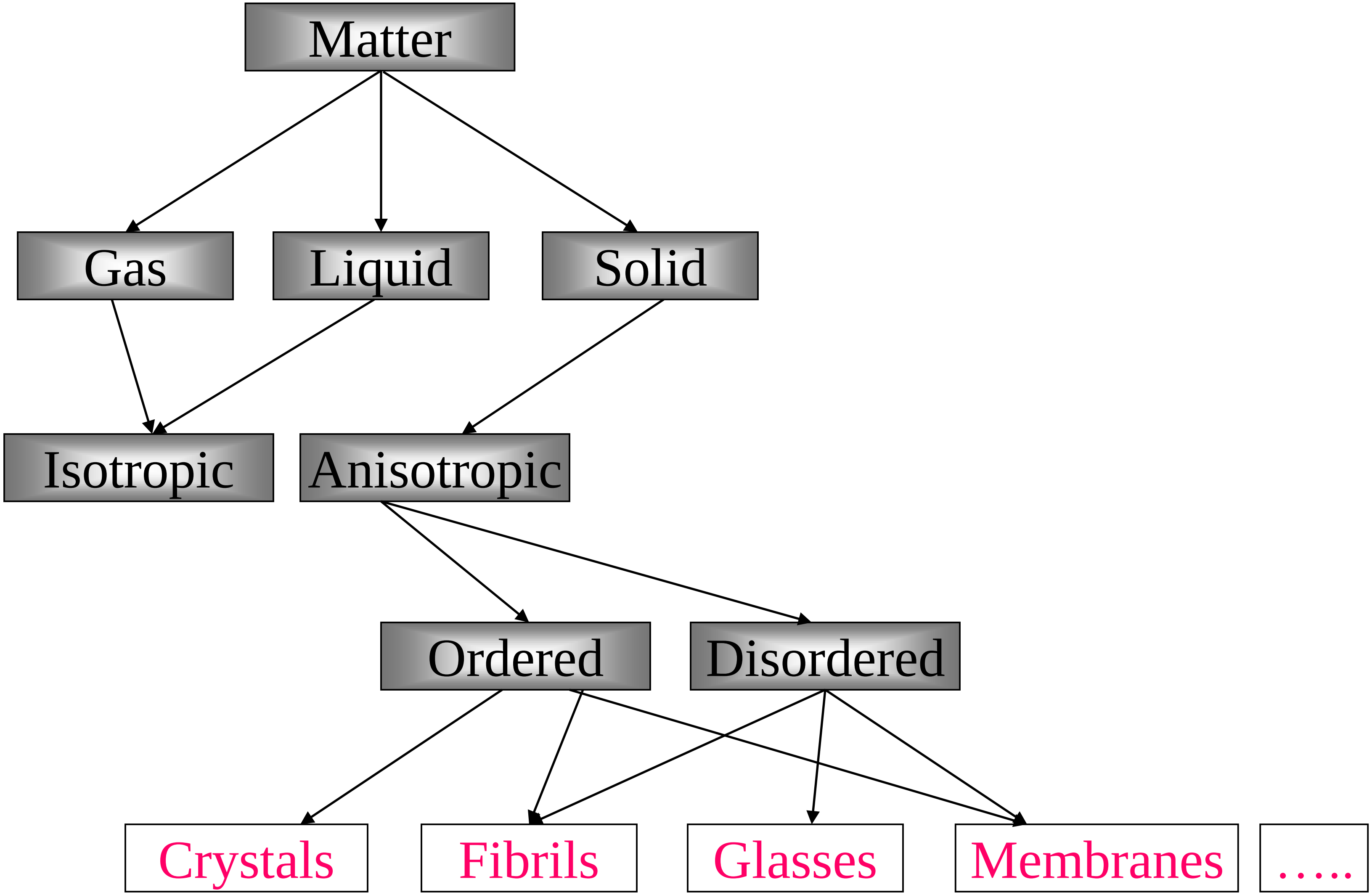
RF waves out



The frequency of emitted RF waves reveals information about the magnetic environment of atomic nuclei



Matter: NMR Classification



Matter

Gas

Liquid

Solid

Isotropic

Anisotropic

Ordered

Disordered

Crystals

Fibrils

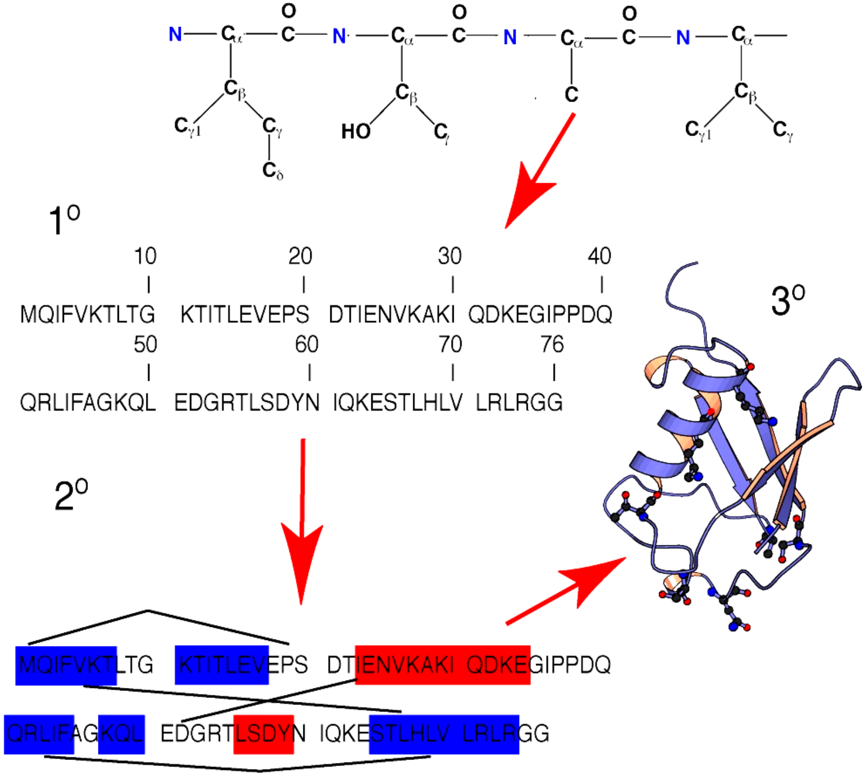
Glasses

Membranes

…..

Solution-State NMR: General Protocol

1. Isotopically label protein (^{15}N, ^{13}C)
2. Assign the chemical shifts
3. Collect restraints
4. Calculate structure
5. Refine (repeat)



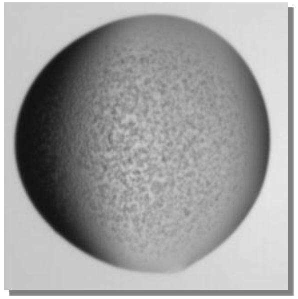
This has been done over 15,000 times in solution!

(http://www.pdb.org/pdb/statistics/holdings.do)

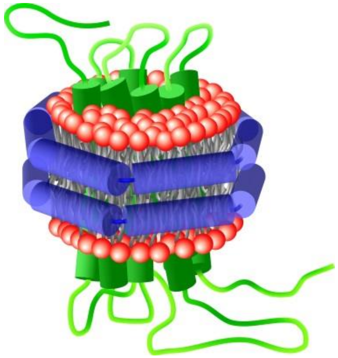
Kumar, A.; Ernst, R.R.; Wüthrich, K. Biochem. Biophys. Res. Comm. 1980, 95, 1–6.
Williamson, M.P.; Havel, T.F.; Wüthrich, K., J. Mol. Biol. 1985, 182, 295–315.

Solid-State NMR in Structural Biology

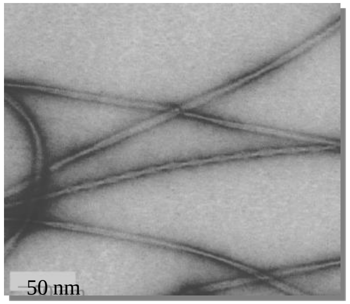
Many proteins cannot be studied by the traditional structural methods (X-ray crystallography or solution NMR)



Nano/microcrystalline globular proteins

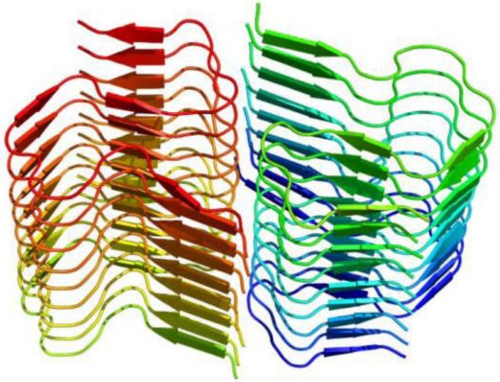


Membrane proteins



Fibrils

Aβ_{42} Fibrils



Bob Griffin and coworkers, 2016

Solution- and Solid-State NMR

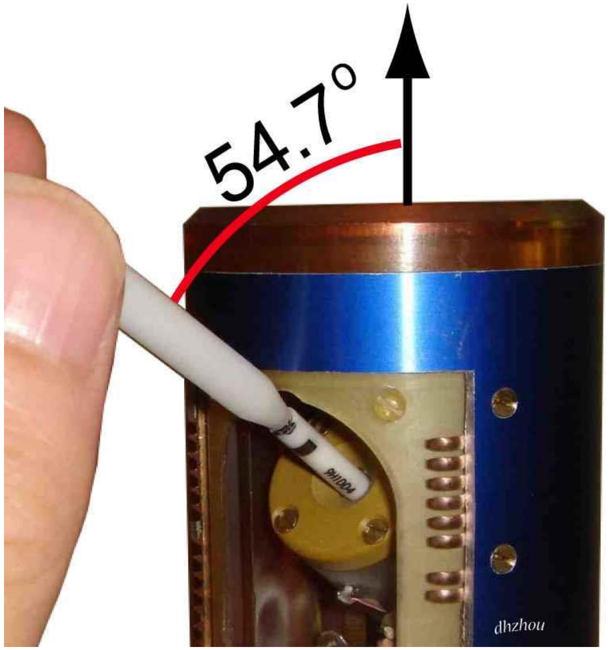
Solution NMR:

- size limitation
- very narrow resonances

Solid-state NMR:

- no size limit on samples
- broader resonances

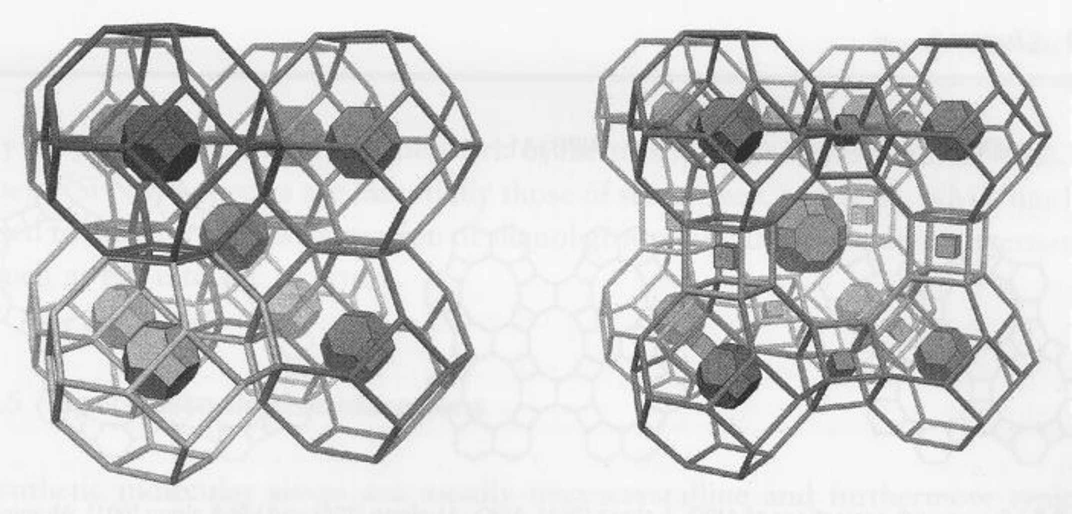
Solution NMR sample tube



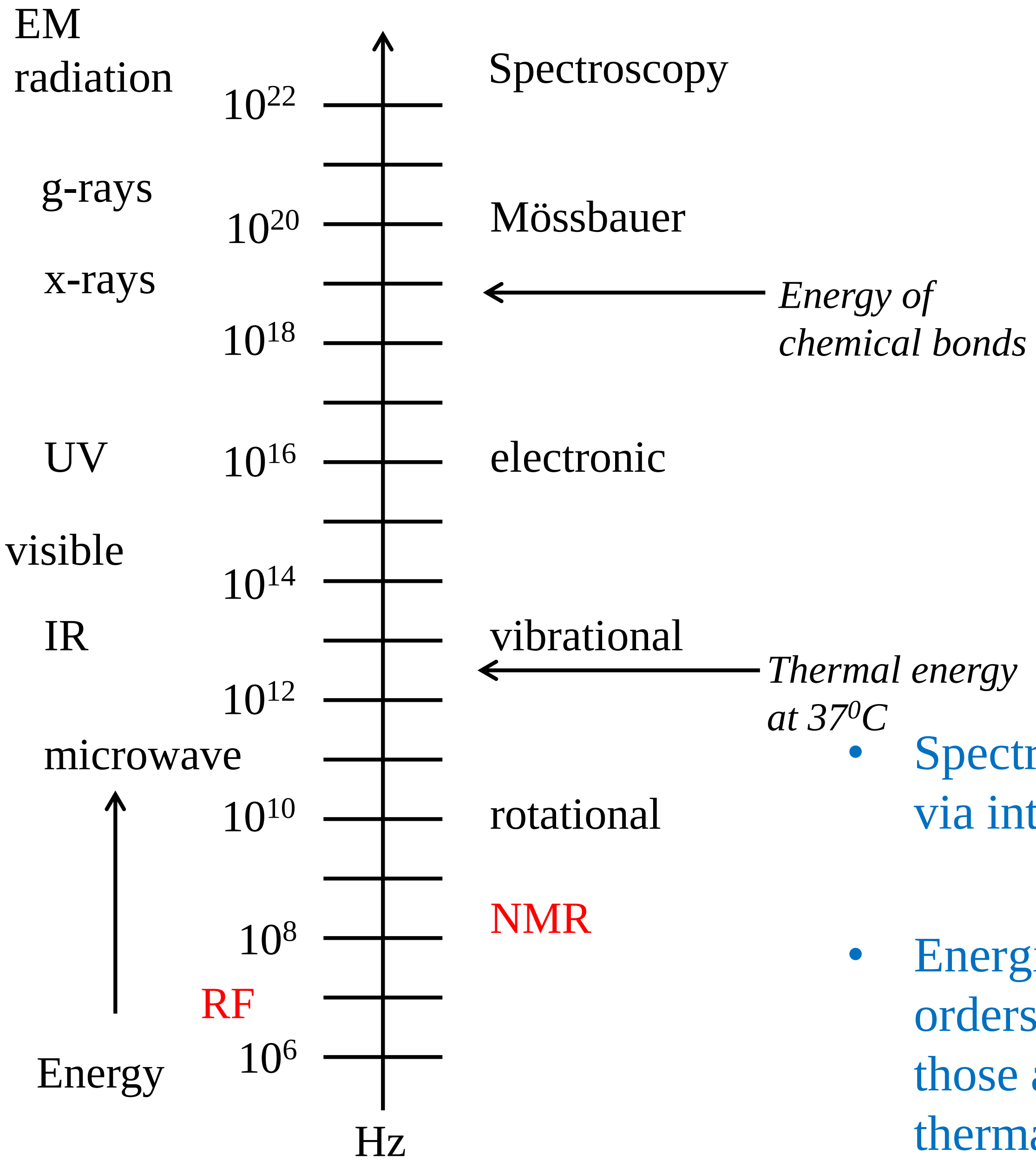
Solid-state NMR probe

Targets for SSNMR: Biology

- Lipid bilayers
- Membranes reconstituted with different additives such as cholesterol, drugs or peptides
- Structure analysis of membrane-active peptides, ion channels, and receptors
- Amyloid fibrils
- Globular proteins, IDP's
- ………………



NMR: Some Features



EM radiation

Spectroscopy

10^{22}

g-rays

10^{20}

Mössbauer

x-rays

Energy of chemical bonds

10^{18}

UV

10^{16}

electronic

visible

10^{14}

IR

vibrational

Thermal energy at 37^0C

10^{12}

microwave

10^{10}

rotational

NMR

10^8

RF

10^6

Energy

Hz

- Spectroscopy: Study of materials via interactions with EM fields

- Energies associated with NMR are orders of magnitude smaller than those associated with typical thermal processes

Reality

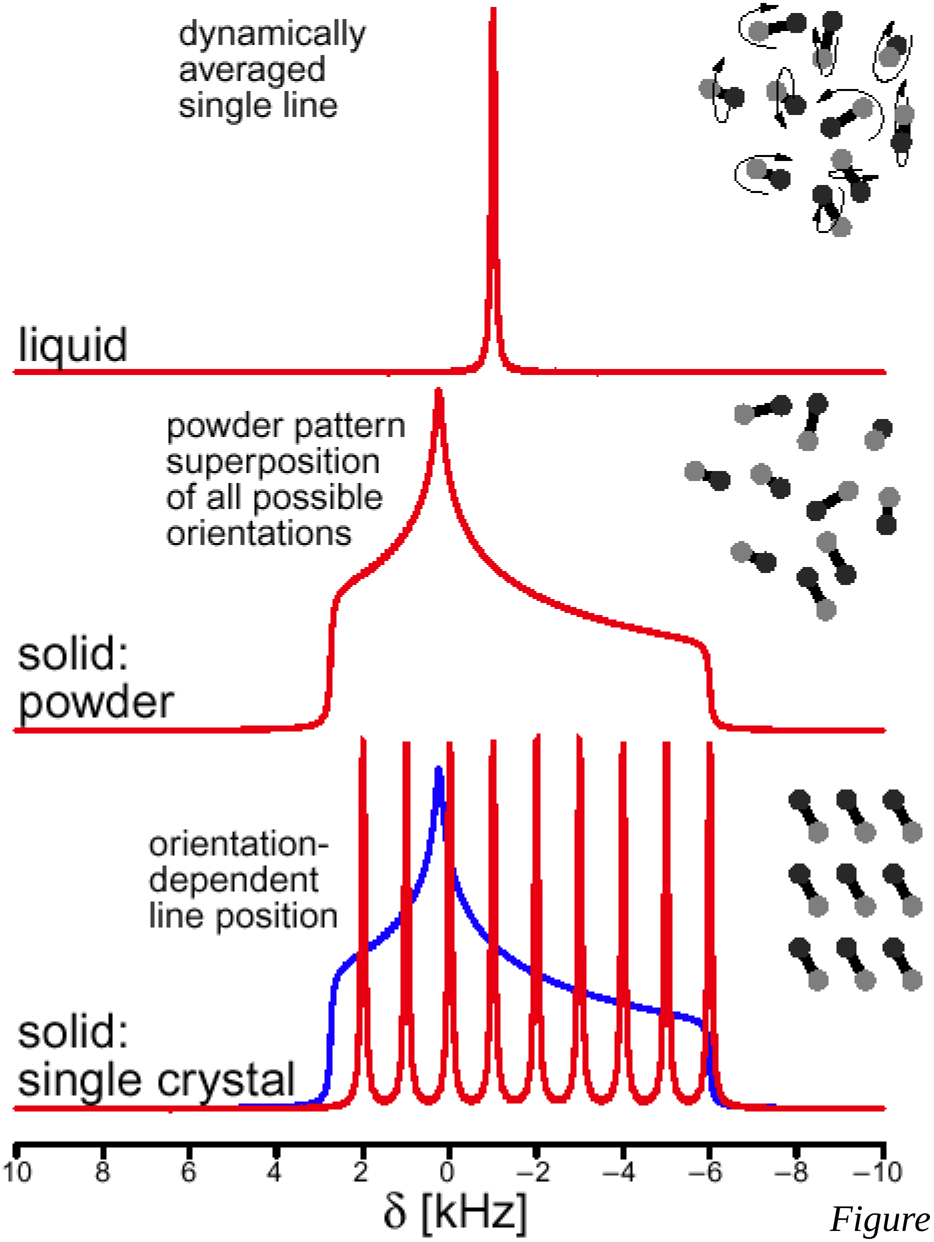
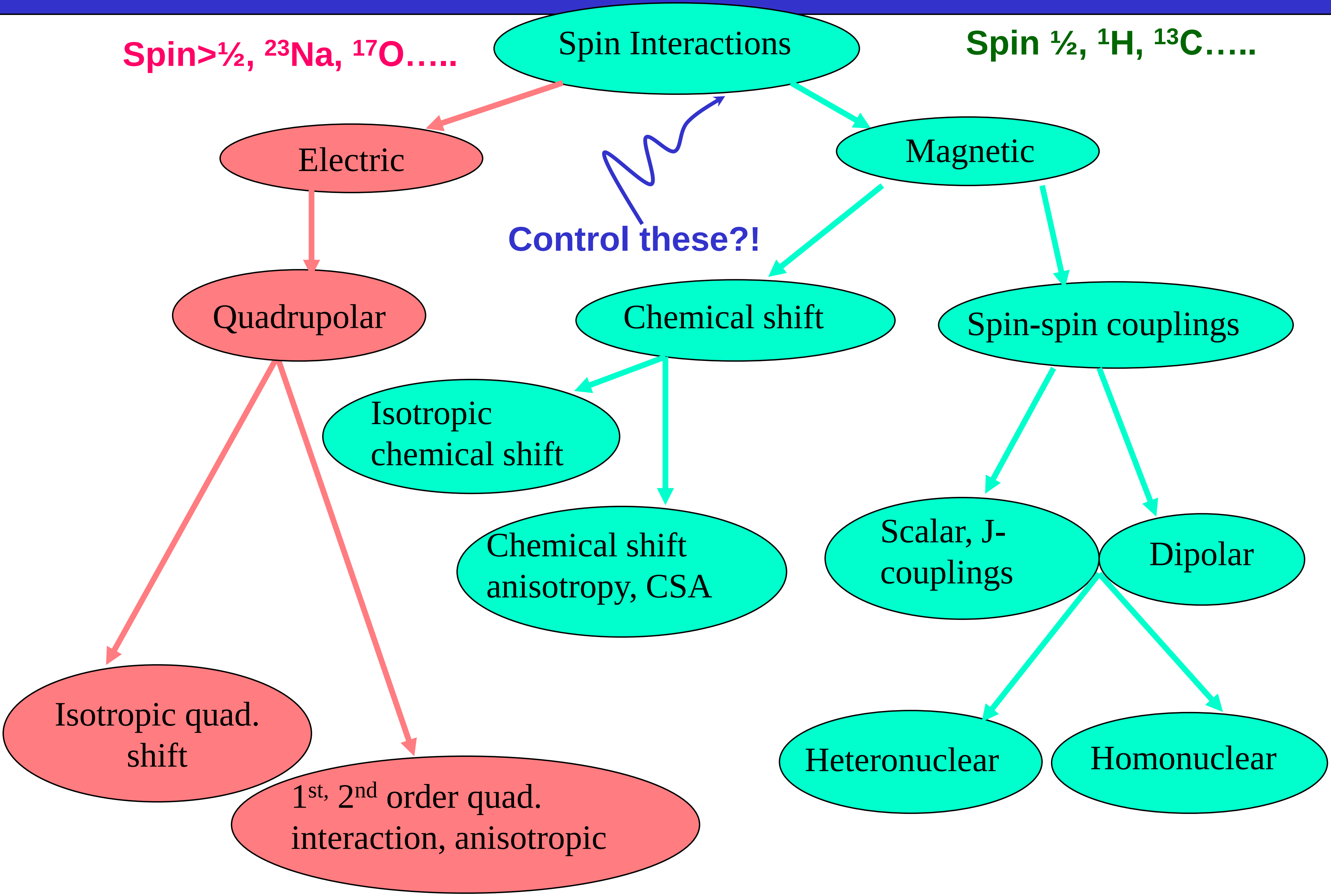


Figure courtesy: Matthias Ernst

Nuclear Spin Interactions



Spin>½, ^{23}Na, ^{17}O…..

Spin Interactions

Spin ½, ^{1}H, ^{13}C…..

Electric

Control these?!

Magnetic

Quadrupolar

Chemical shift

Spin-spin couplings

Isotropic chemical shift

Chemical shift anisotropy, CSA

Scalar, J-couplings

Dipolar

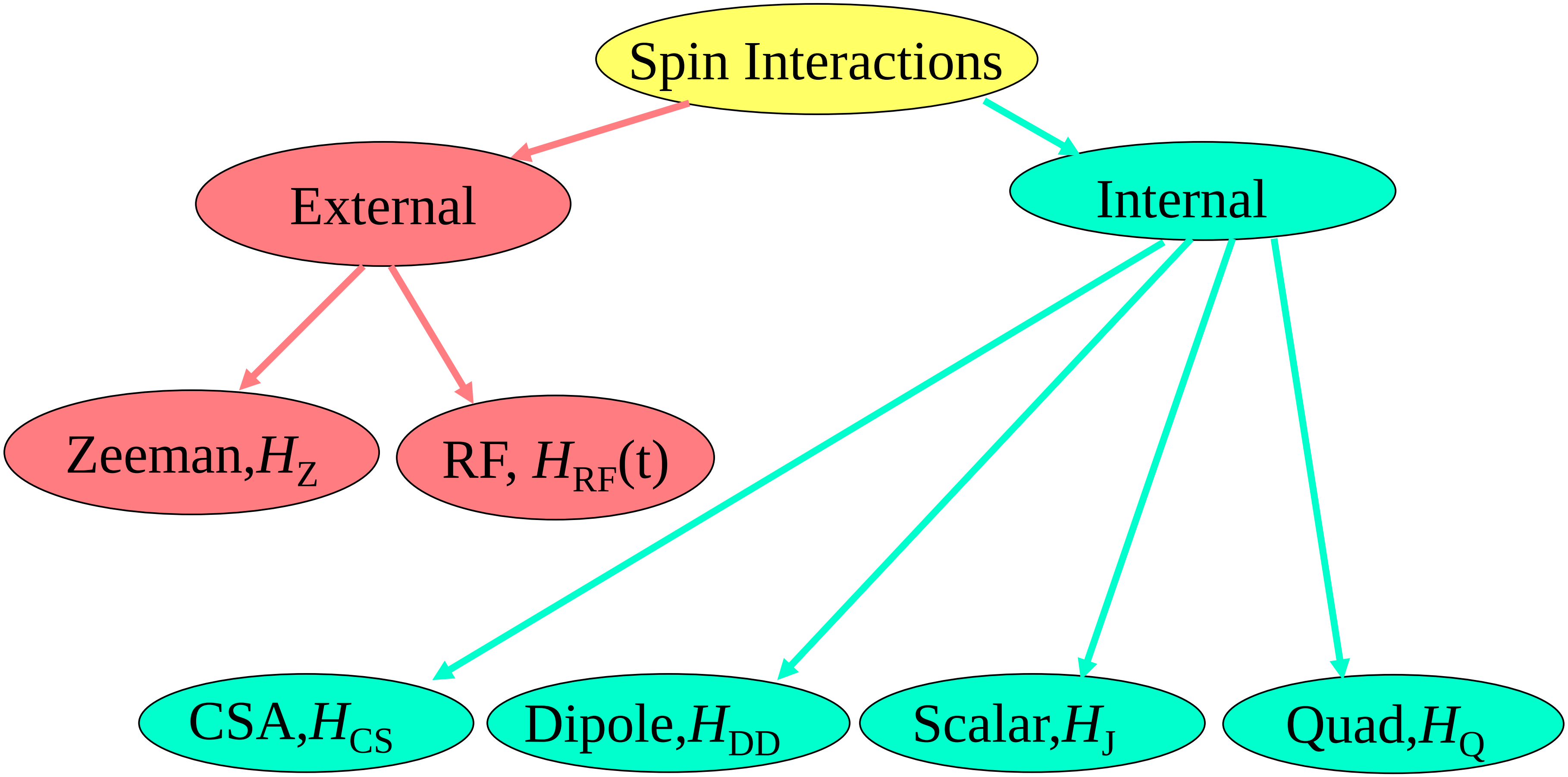
Isotropic quad. shift

1st, 2nd order quad. interaction, anisotropic

Heteronuclear

Homonuclear

Nuclear Spin Interactions



Spin Interactions

External

Internal

Zeeman, H_Z

RF, $H_{RF}(t)$

CSA, H_{CS}

Dipole, H_{DD}

Scalar, H_J

Quad, H_Q

Only the isotropic parts manifest in solution-state.

Spin: Some History

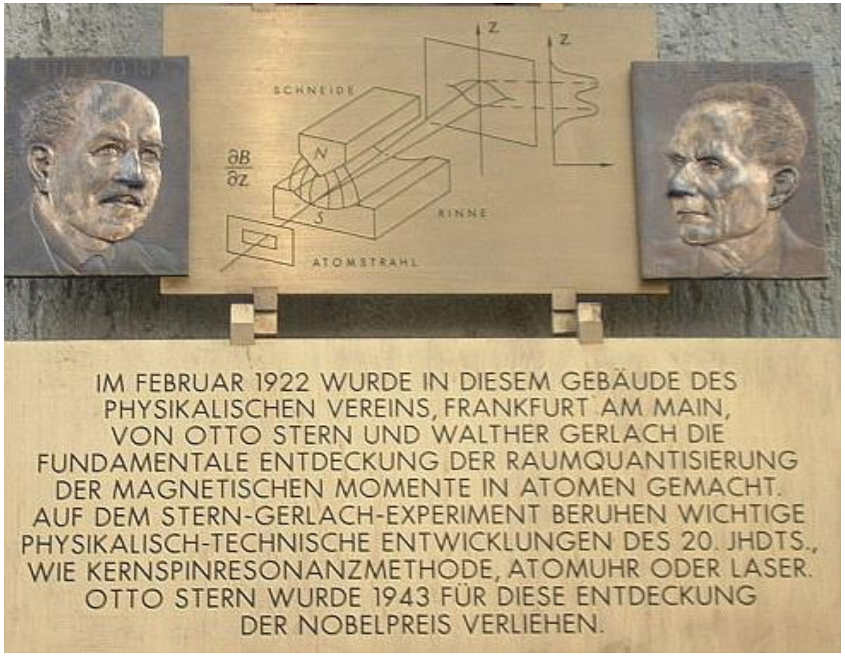
- **Uhlenbeck and Goudsmit**: particles have "spin", corresponding to rotation of a particle spinning around its own axis
- Spin of the electron is ½: two states +½="spin-up" and –½="spin-down"
- This is not fully consistent from what people knew before. However, this is appropriate because spin is a quantum notion (we do not know why!)
- Stern-Gerlach experiment

✓ The beam of atoms is deflected by inhomogeneous field

✓ Reason: intrinsic magnetic moment (spin) of particles

✓ The distribution of the μ-vector is not continuous!

✓ Spin is quantised!!!



IM FEBRUAR 1922 WURDE IN DIESEM GEBÄUDE DES
PHYSIKALISCHEN VEREINS, FRANKFURT AM MAIN,
VON OTTO STERN UND WALTHER GERLACH DIE
FUNDAMENTALE ENTDECKUNG DER RAUMQUANTISIERUNG
DER MAGNETISCHEN MOMENTE IN ATOMEN GEMACHT.
AUF DEM STERN-GERLACH-EXPERIMENT BERUHEN WICHTIGE
PHYSIKALISCH-TECHNISCHE ENTWICKLUNGEN DES 20. JHDTS.,
WIE KERNSPINRESONANZMETHODE, ATOMUHR ODER LASER.
OTTO STERN WURDE 1943 FÜR DIESE ENTDECKUNG
DER NOBELPREIS VERLIEHEN.

Spin: From Basic Symmetries to Quantum Optimal Control, Ilya Kuprov, Springer, 2023

Spin

- Spin of a particle is its intrinsic angular momentum (as if the particle rotates). Honestly, nobody (that is, I) knows where spin comes from.
- Spin is a very fundamental concept, which also affects the symmetry of the w.f. of a system of identical particles. Example: Pauli principle.
- Spin is a quantum notion.

- Spin operators are introduced in the same way as those for the angular momentum:
  - Eigen-states are $\left|S,S_z\right\rangle$; $S^2=S(S+1)$, S_z varies from $-S$ to S.
  - Commutation rules are

$$[\hat{S}_y,\hat{S}_z]=i\hat{S}_x,\ [\hat{S}_z,\hat{S}_x]=i\hat{S}_y,\ [\hat{S}_x,\hat{S}_y]=i\hat{S}_z$$

- An important difference from angular momentum: spin can be half-integer
- Spin operators are $(2S+1)*(2S+1)$ matrices
- For $S=1/2$ such matrices are related to the Pauli matrices

Spin-½

Basis

$$|\alpha\rangle = |\uparrow\rangle$$

$$|\beta\rangle = |\downarrow\rangle$$

- Spin operator can be written as

$$\hat{\vec{S}} = \frac{1}{2}\hat{\vec{\sigma}}, \quad \hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

- Useful relations of the Pauli matrices:

$$\hat{\sigma}_x^2 = \hat{\sigma}_y^2 = \hat{\sigma}_z^2 = \hat{e}, \quad \hat{\sigma}_y\hat{\sigma}_z = i\hat{\sigma}_x, \quad \hat{\sigma}_z\hat{\sigma}_x = i\hat{\sigma}_y, \quad \hat{\sigma}_x\hat{\sigma}_y = i\hat{\sigma}_z$$

$$\hat{\sigma}_i\hat{\sigma}_k + \hat{\sigma}_k\hat{\sigma}_i = 2\delta_{ik}, \quad \left[\hat{\sigma}_i, \hat{\sigma}_j\right] = 2i\varepsilon_{ijk}\hat{\sigma}_k, \quad \mathrm{Tr}\{\hat{\sigma}_i\} = 0$$

- Every 2*2 Hermitian matrix is a linear combination of the unity matrix and the Pauli matrices

Spin-1/2 Angular Momentum Operators

- Spin-1/2 nuclei have two Zeeman eigenstates:

$$|\alpha\rangle = |\frac{1}{2}, \frac{+1}{2}\rangle \qquad |\alpha\rangle = |\uparrow\rangle$$

$$|\beta\rangle = |\frac{1}{2}, \frac{-1}{2}\rangle \qquad |\beta\rangle = |\downarrow\rangle$$

- Angular momentum spin operators in the Zeeman eigenbasis:

$$I_x = \tfrac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad I_y = \tfrac{1}{2i}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \qquad I_z = \tfrac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

- Action of spin operators on the Zeeman eigenstates:

$$I_z|\alpha\rangle = \frac{1}{2}|\alpha\rangle \qquad I^+|\alpha\rangle = 0 \qquad I^-|\alpha\rangle = |\beta\rangle$$

$$I_z|\beta\rangle = \frac{-1}{2}|\beta\rangle \qquad I^+|\beta\rangle = |\alpha\rangle \qquad I^-|\beta\rangle = 0$$

Spin-1/2 Rotation Operators

- Rotation operators:

$$R_x(\beta) = \exp(-i\beta I_x)$$

$$R_y(\beta) = \exp(-i\beta I_y)$$

$$R_z(\beta) = \exp(-i\beta I_z)$$

- Evaluation of rotation:

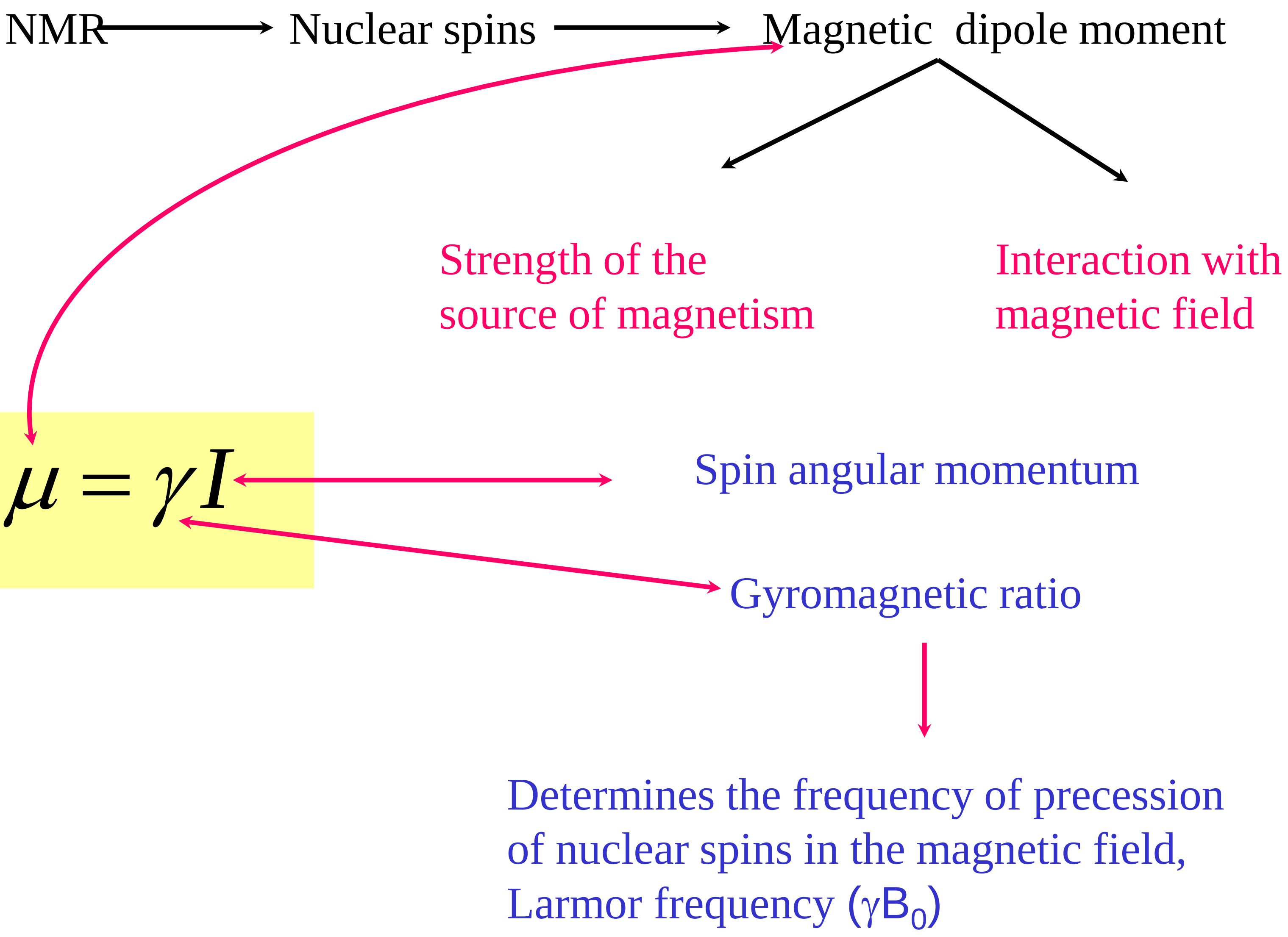
$$R_x(\beta) I_y R_x(-\beta) = I_y \cos\beta + [I_x, I_y] \sin\beta$$

- Spin-1/2 rotation operators:

$$R_x(\beta) = \begin{pmatrix} \cos\frac{1}{2}\beta & -i\sin\frac{1}{2}\beta \\ -i\sin\frac{1}{2}\beta & -\cos\frac{1}{2}\beta \end{pmatrix} \qquad R_y(\beta) = \begin{pmatrix} \cos\frac{1}{2}\beta & -\sin\frac{1}{2}\beta \\ \sin\frac{1}{2}\beta & \cos\frac{1}{2}\beta \end{pmatrix}$$

$$R_z(\beta) = \begin{pmatrix} \exp\{-i\frac{1}{2}\beta\} & 0 \\ 0 & \exp\{i\frac{1}{2}\beta\} \end{pmatrix}$$

Spins in NMR



NMR → Nuclear spins → Magnetic dipole moment

Strength of the source of magnetism

Interaction with magnetic field

$$\mu = \gamma I$$

Spin angular momentum

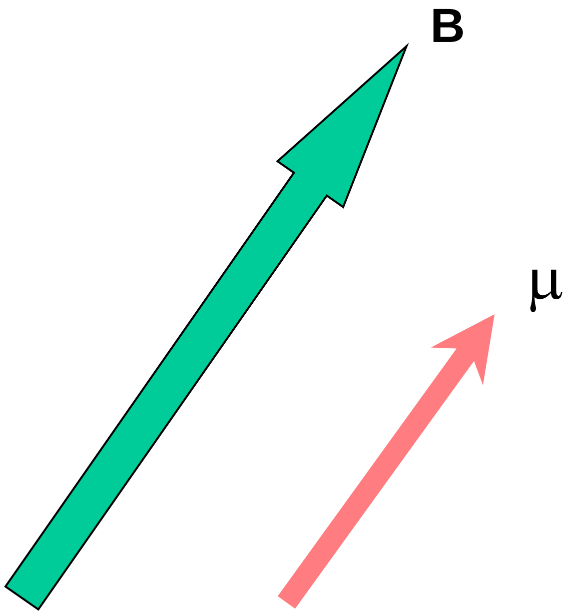
Gyromagnetic ratio

Determines the frequency of precession of nuclear spins in the magnetic field, Larmor frequency (γB_0)

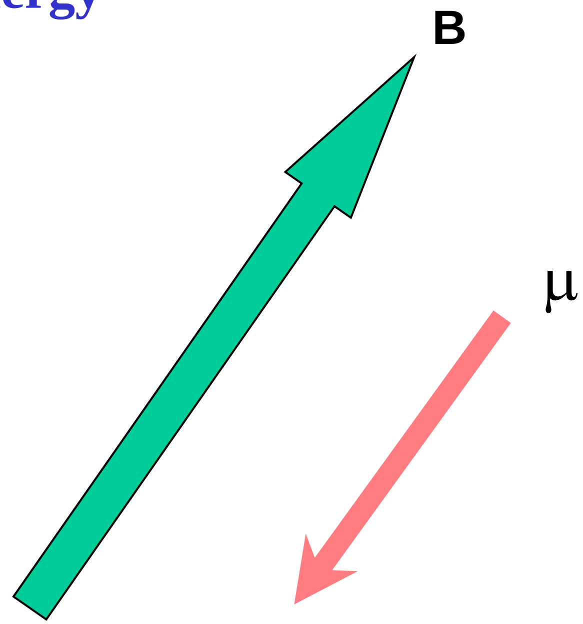
Spins in NMR

Energy of a magnetic dipole moment in a magnetic field B: $E = -\mu . B$

Magnetic energy



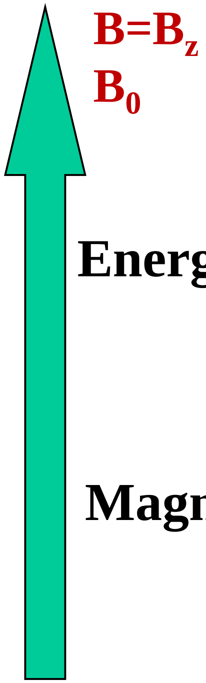
Low energy



High energy

Spins and Moments in NMR

Energy of a magnetic dipole moment in a magnetic field B: $$E = -\mu . B$$



Energy of a magnetic dipole moment in a magnetic field B_0: $$E = -\mu_z B_0$$

Magnetic moment to spin:

$$\begin{aligned} \mu &= \gamma I \\ \mu_z &= \gamma I_z \\ &= \gamma m \hbar \end{aligned}$$

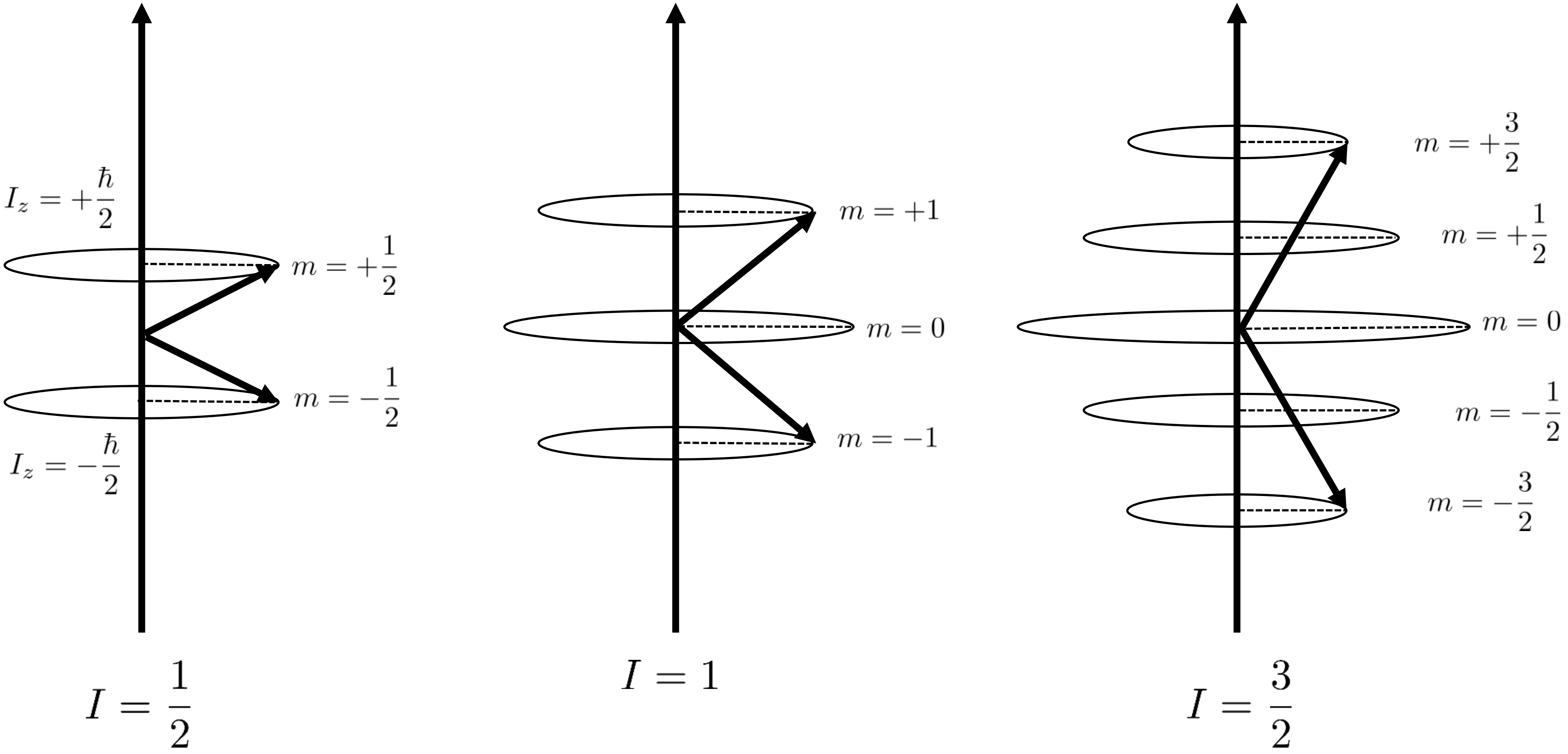
Energy of a magnetic dipole moment in a magnetic field B_0: $$E = -m\hbar\gamma B_0$$

Nuclear precession frequency, Larmor frequency, in B_0: $$\omega_0 = -\gamma B_0$$

Nuclear Spin Quantum Number

Magnitude of the spin quantum number: $L = \hbar I(I+1)$

Projected values on to the z-axis: $m = -I, -I+1, -I+2, \cdots I$

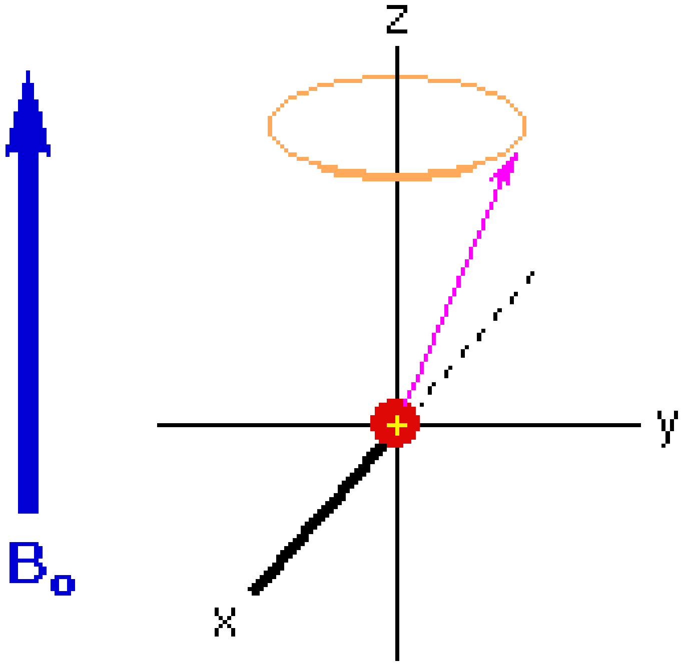


Nuclear Spins & Magnetic Field

Positive γ: Clockwise rotation
Negative γ: Counter-clockwise rotation
(see MHLevitt: Spin Dynamics)

$$\omega_0 = -\gamma B_0$$

A spinning gyroscope in a gravity field

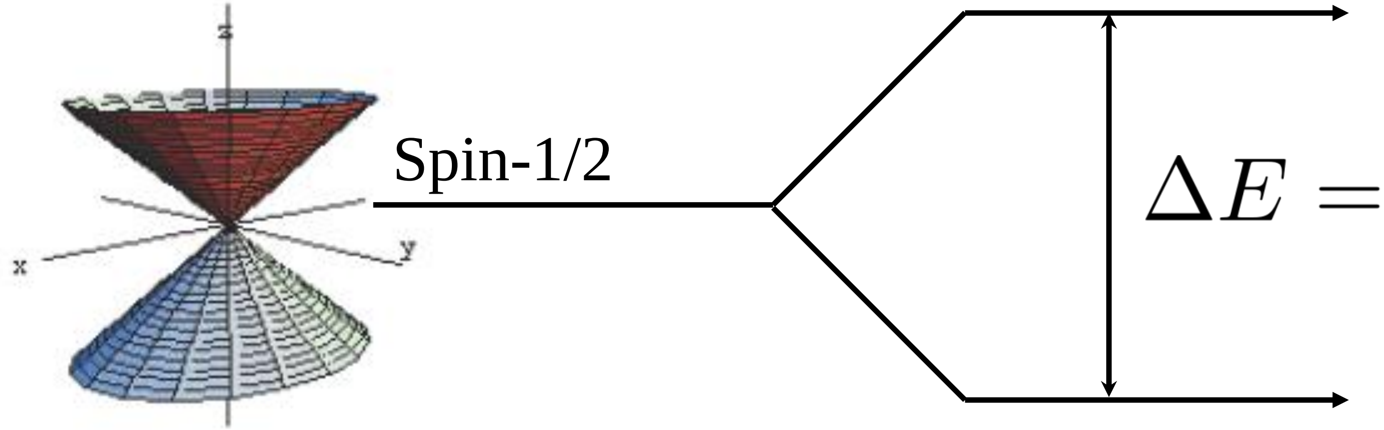


A spinning charge
in a magnetic field

Zeeman Interaction, External Magnetic Field

$$E = -m\hbar\gamma B_0$$

$$\omega_0 = -\gamma B_0$$



Spin-1/2

Zeeman field

|β>

|-1/2>, ½ γB_0

$$\Delta E = \gamma B_0$$

|+1/2>, -½ γB_0

|α>

$\omega_0 = -\gamma B_0$ is called the Larmor frequency

Equation of Motion for the Magnetic Moment

Precessional frequency of a spin: $\omega_0 = -\gamma B_0$

Energy of a magnetic dipole moment in a magnetic field: $E = -\mu . B$

Torque associated with this energy: $C = \mu \times B$

Torque , being the rate of change of angular momentum: $C = \frac{dI}{dt} = \mu \times B$

Equation of motion for the magnetic moment: $\frac{d\mu}{dt} = \gamma\mu \times B$

In the NMR context:

$$\begin{aligned} \frac{d\mu_x}{dt} &= \gamma\mu_y B_0 \\ \frac{d\mu_y}{dt} &= -\gamma\mu_x B_0 \\ \frac{d\mu_z}{dt} &= 0 \end{aligned}$$

Solution:

$$\begin{aligned} \mu_x(t) &= \mu_x(0) cos\gamma B_0 t + \mu_y(0) sin\gamma B_0 t \\ \mu_y(t) &= -\mu_x(0) sin\gamma B_0 t + \mu_y(0) cos\gamma B_0 t \\ \mu_z(t) &= \mu_z(0) \end{aligned}$$

The transverse components oscillate such that: $\mu_x^2(t) + \mu_y^2(t) = \mu_x^2(0) + \mu_y^2(0)$

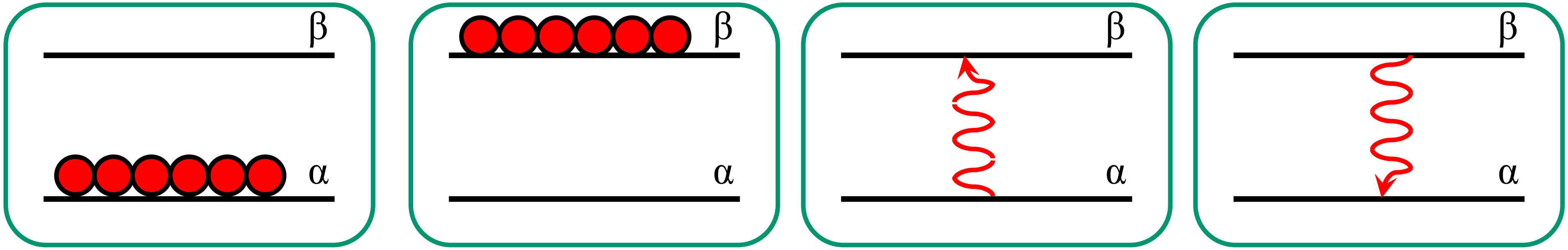
This also suggests a precessional motion of the moment with respect to the field?

Density Matrix of a Spin-½ Particle

- D.m. of a spin ½ particle:

$$\rho = \begin{pmatrix} \rho_{\alpha\alpha} & \rho_{\alpha\beta} \\ \rho_{\beta\alpha} & \rho_{\beta\beta} \end{pmatrix}$$

$$\rho = \overline{|\psi\rangle\langle\psi|} \implies \rho^2 = \rho$$



$\rho_{\alpha\alpha}$ $\rho_{\beta\beta}$ $\rho_{-} = \rho_{\alpha\beta}$ $\rho_{+} = \rho_{\beta\alpha}$

- Physical meaning of the elements:

  Diagonal elements are populations

  Off-diagonal elements are coherences ρ_{mn}

  The trace of the d.m. is equal to 1
- The d.m. is a Hermitian matrix: $(N^2 – 1)$ independent parameters
- The equilibrium density matrix becomes:

$$\rho^{eq} = \begin{pmatrix} \frac{1}{2} + \frac{1}{4}B & 0 \\ 0 & \frac{1}{2} - \frac{1}{4}B \end{pmatrix}$$

$$B = \frac{\hbar\omega_o}{k_B T}$$

Two or More Spins ½

- The d.m. for two spins can be expressed in terms of product operators

$$\left\{\hat{E},\hat{S}_x,\hat{S}_y,\hat{S}_z\right\}\otimes\left\{\hat{E},\hat{I}_x,\hat{I}_y,\hat{I}_z\right\}=\left\{\begin{matrix}\hat{E};\hat{S}_x,\hat{S}_y,\hat{S}_z;\hat{I}_x,\hat{I}_y,\hat{I}_z;\hat{S}_x\hat{I}_x,\hat{S}_y\hat{I}_x,\hat{S}_z\hat{I}_x,\\ \hat{S}_x\hat{I}_y,\hat{S}_y\hat{I}_y,\hat{S}_z\hat{I}_y,\hat{S}_x\hat{I}_z,\hat{S}_y\hat{I}_z,\hat{S}_z\hat{I}_z\end{matrix}\right\}$$

- Each product operator is now a 4*4 matrix; likewise, the Hamiltonian is a 4*4 matrix and it is expressed via the product operators

- What is the direct product (Kronecker product)?

$$\hat{A}\otimes\hat{B}=\begin{pmatrix}a_{11} & a_{12}\\ a_{21} & a_{22}\end{pmatrix}\otimes\begin{pmatrix}b_{11} & b_{12}\\ b_{21} & b_{22}\end{pmatrix}=\begin{pmatrix}a_{11}\hat{B} & a_{12}\hat{B}\\ a_{21}\hat{B} & a_{22}\hat{B}\end{pmatrix}=\begin{pmatrix}a_{11}b_{11} & a_{11}b_{12} & a_{12}b_{11} & a_{12}b_{12}\\ a_{11}b_{21} & a_{11}b_{22} & a_{12}b_{21} & a_{12}b_{22}\\ a_{21}b_{11} & a_{21}b_{12} & a_{22}b_{11} & a_{22}b_{12}\\ a_{21}b_{21} & a_{21}b_{22} & a_{22}b_{21} & a_{22}b_{22}\end{pmatrix}$$

- Example with 2 spins:

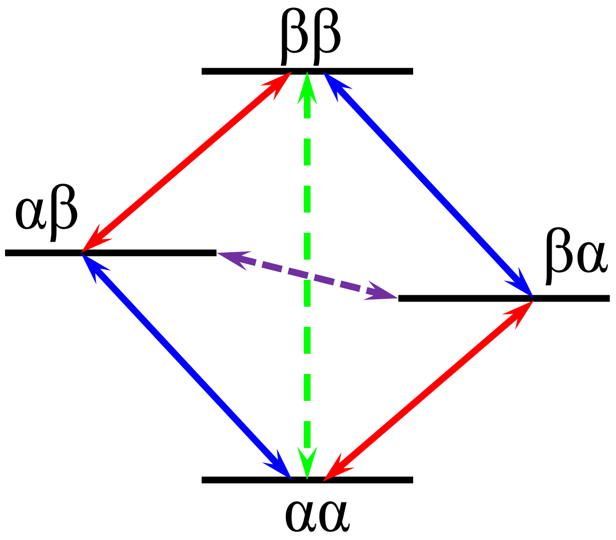
$$\hat{S}_x=\hat{S}_x\otimes\hat{E}=\begin{pmatrix}0 & 1/2\\ 1/2 & 0\end{pmatrix}\otimes\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}=\frac{1}{2}\begin{pmatrix}0 & 0 & 1 & 0\\ 0 & 0 & 0 & 1\\ 1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\end{pmatrix}$$

- Other operators can be constructed in the same way. More spins: use direct products of spin operators

Two Spins-½

- Relation between populations/coherences and d.m. elements

Energy level diagram



Density matrix

	αα	**αβ**	**βα**	**ββ**
αα	$p_{\alpha\alpha}$	**SQC**	**SQC**	**DQC**
αβ	**SQC**	$p_{\alpha\beta}$	**ZQC**	**SQC**
βα	**SQC**	**ZQC**	$p_{\beta\alpha}$	**SQC**
ββ	**DQC**	**SQC**	**SQC**	$p_{\beta\beta}$

- SQCs are given by S_x, S_y, S_xI_z, S_yI_z, I_x, I_y, S_zI_x, S_zI_y
- DQCs and ZQCs are given by combinations of S_xI_x, S_yI_y, S_xI_y, S_yI_x
- We can directly measure only transverse magnetization S_x, S_y, I_x, I_y
- Other operators cannot be observed directly, but they affect the signal
- Coherence order for ρ_{mn}: $p_{mn} = M(|m\rangle) - M(|n\rangle)$

Evolution of the Density Matrix

- The S.e. in the bra and ket representations is

$$\frac{\partial}{\partial t}\left|\Psi\right\rangle = -\frac{i}{\hbar}\hat{H}\left|\Psi\right\rangle, \qquad \frac{\partial}{\partial t}\left\langle\Psi\right| = \frac{i}{\hbar}\left\langle\Psi\right|\hat{H}$$

- The equation for the d.m. is as follows:

$$\frac{\partial}{\partial t}\hat{\rho} = \frac{\partial}{\partial t}\left\{\left|\Psi\right\rangle\left\langle\Psi\right|\right\} = \left\{\frac{\partial}{\partial t}\left|\Psi\right\rangle\right\}\left\langle\Psi\right| + \left|\Psi\right\rangle\left\{\frac{\partial}{\partial t}\left\langle\Psi\right|\right\} = -\frac{i}{\hbar}\left[\hat{H},\hat{\rho}\right]$$

Liouville-von Neumann equation:

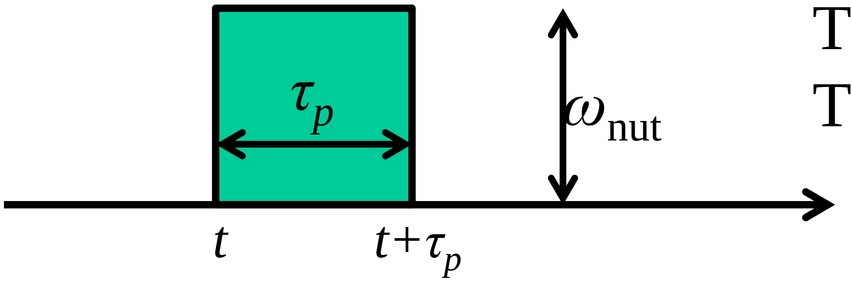
$$\rho(t) = \exp(-\tfrac{i}{\hbar}Ht)\rho_0\exp(\tfrac{i}{\hbar}Ht)$$

$$\rho(t) = U(t)\rho(0)U^{-1}t$$

- U is the propagator, time dependent, and unitary
- The solution is simple for a time-independent Hamiltonian:
- For a time-dependent Hamiltonian we solve the equation numerically in small time steps or use some tricks

RF-Pulses

- What happens to the d.m. (magnetization) when we apply a pulse?



The phase is ϕ_p
The flip angle is $\theta=\omega_{\mathrm{nut}}\tau_p$

- The wave function and density matrix after the pulse

$$|\psi_{after}\rangle = \hat{R}_{\phi_p}(\theta)\,|\psi_{before}\rangle\,; \quad |\psi_{after}\rangle = |\psi_{before}\rangle\,\hat{R}_{\phi_p}(-\theta)$$

$$\hat{\rho}_{after} = \hat{R}_{\phi_p}(\theta)\hat{\rho}_{before}\hat{R}_{\phi_p}(-\theta)$$

- The action of a strong pulse is equivalent to a rotation (we assume that only the B_1-term is relevant)

$$\hat{R}_{\phi_p}(\theta) = exp[-i\omega_{nut}\tau_p(cos\phi_p\hat{S}_x + sin\phi_p\hat{S}_y)]$$

$$= exp[-i\theta(cos\phi_p\hat{S}_x + sin\phi_p\hat{S}_y))]$$

- A π/2-pulse generates a coherence, a π-pulse inverts the populations

$$\hat{R}_{\phi_p}(\pi/2)\hat{S}_z\hat{R}_{\phi_p}(-\pi/2) = -\hat{S}_y, \qquad \hat{R}_{\phi_p}(\pi)\hat{S}_z\hat{R}_{\phi_p}(-\pi) = -\hat{S}_z$$

Sandwich Relationships

- Is there a simple way to calculate the effect of pulses?
- Three cyclically commuting operators:

$$\left[\hat{A},\hat{B}\right]=i\hat{C},\quad \left[\hat{C},\hat{A}\right]=i\hat{B},\quad \left[\hat{B},\hat{C}\right]=i\hat{A}$$

- Example:

$$[\hat{S}_y,\hat{S}_z]=i\hat{S}_x,\ [\hat{S}_z,\hat{S}_x]=i\hat{S}_y,\ [\hat{S}_x,\hat{S}_y]=i\hat{S}_z$$

- The following relation is then true:

$$\exp\left[-i\theta\hat{A}\right]\hat{B}\exp\left[i\theta\hat{A}\right]=\cos\theta\,\hat{B}+\sin\theta\,\hat{C}$$

- A, B, C are like the axis of our 3D-space; we “rotate” *B* “around” A by the angle θ. Cyclic permutations provide two more relations

$$\exp\left[-i\theta\hat{B}\right]\hat{C}\exp\left[i\theta\hat{B}\right]=\cos\theta\,\hat{C}+\sin\theta\,\hat{A}$$

$$\exp\left[-i\theta\hat{C}\right]\hat{A}\exp\left[i\theta\hat{C}\right]=\cos\theta\,\hat{A}+\sin\theta\,\hat{B}$$

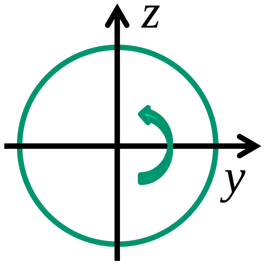
- Of course, these rules apply to the spin operators
- RF-pulses give *x* and *y*-rotations. Free precession gives a *z*-rotation by a time-dependent angle ωt

See M. H. Levitt, “Spin Dynamics”, cyclic commutation

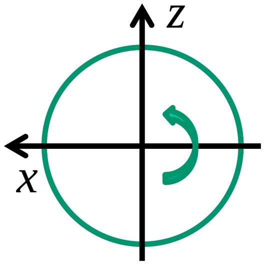
Phase of the Pulse

- Different phases

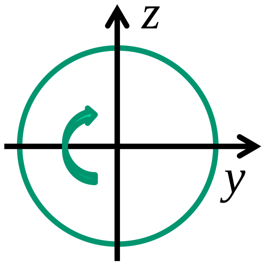
x-pulse, ϕ_p=0



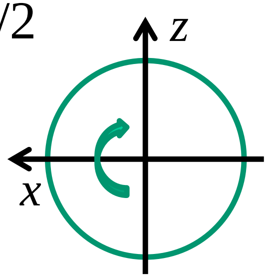
y-pulse, ϕ_p=π/2



–*x*-pulse, ϕ_p=π



–*y*-pulse, ϕ_p=2π/2

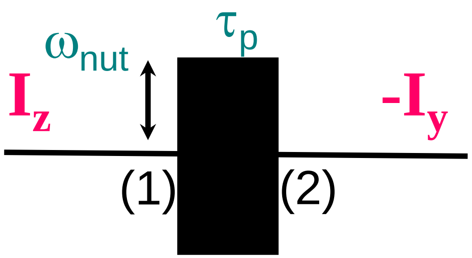


- Pulse of a general phase is a combination of three rotations

$$\hat{R}_{\phi_p}(\theta) = exp[-i\theta(cos\phi_p\hat{S}_x + sin\phi_p\hat{S}_y)] = \hat{R}_z(\phi_p)\hat{R}_x(\theta)\hat{R}_z(-\phi_p)$$

- Rotation about *z* turns the {*x*,*y*} axes; then a pulse is turning the spins around the new *x*; finally, we return to the original frame
- Free precession is just a *z*-rotation

Representation of *x*-Pulse



Assume $\phi_p=0$

Pulse characteristics:

Frequency, ω_{ref}
Phase, ϕ_p
Amplitude, ω_{nut}
Flip angle of the pulse: $\theta = \omega_{nut}\tau_p$

- Pulse and density matrix:

$$\rho^{eq} = \begin{pmatrix} \frac{1}{2}+\frac{1}{4}B & 0 \\ 0 & \frac{1}{2}-\frac{1}{4}B \end{pmatrix}$$

$$\Big\downarrow \quad R_x\left(\frac{\pi}{2}\right)$$

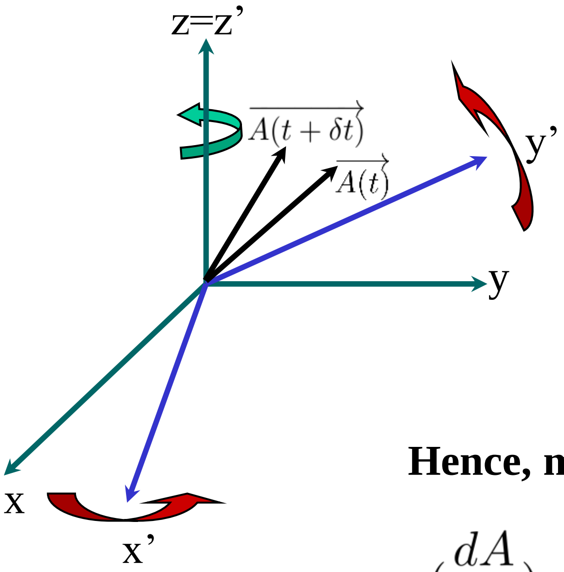
$$\rho = \begin{pmatrix} \frac{1}{2} & -\frac{B}{4} \\ \frac{B}{4} & \frac{1}{2} \end{pmatrix}$$

- Pulse equalises the populations of the two states
- Pulse converts the population difference into coherences

Rotating Frame Transformation

Equation of motion for the magnetic moment:

$$\frac{d\mu}{dt} = \mu \times (\gamma B_0)$$



Rotating coordinate system:

$$A(t) = i' A_{x'} + j' A_{y'} + k' A_{z'}$$

With i', j', and k', rotating with an angular velocity ω:

$$\frac{di'}{dt} = \omega \times i'$$

Hence, motion as viewed from the lab frame:

$$(\frac{dA}{dt})_{lab} = i' \frac{dA_{x'}}{dt} + j' \frac{dA_{y'}}{dt} + k' \frac{dA_{z'}}{dt} + A_{x'} \frac{di'}{dt} + A_{y'} \frac{dj'}{dt} + A_{z'} \frac{dk'}{dt}$$

$$= \underbrace{i' \frac{dA_{x'}}{dt} + j' \frac{dA_{y'}}{dt} + k' \frac{dA_{z'}}{dt}}_{(\frac{\partial A}{\partial t})_{rot}} + \underbrace{\omega \times (i' A_{x'} + j' A_{y'} + k' A_{k'})}_{\omega \times A}$$

Time rate of change of A wrt to i', j', k' $(\frac{\partial A}{\partial t})_{rot}$

All the above imply:

$$(\frac{dA}{dt})_{lab} = (\frac{\partial A}{\partial t})_{rot} + \omega \times A$$

Rotating Frame Transformation

Motion between lab and rotating frames: $(\frac{dA}{dt})_{lab} = (\frac{\partial A}{\partial t})_{rot} + \omega \times A$

Translating all these to magnetic moments: $(\frac{d\mu}{dt})_{lab} = (\frac{\partial \mu}{\partial t})_{rot} + \omega \times \mu$

This implies: $(\frac{\partial \mu}{\partial t})_{rot} = \mu \times (\gamma B_0 + \omega)$

This is the motion of μ in the rotating system, which is the same as in the lab frame, with B_0 replaced by an effective field: $B_{eff} = B_0 + \frac{\omega}{\gamma}$

Rotating Frame Transformation: Consequences

Motion between lab and rotating frames:

$$(\frac{dA}{dt})_{lab} = (\frac{\partial A}{\partial t})_{rot} + \omega \times A$$

Translating all these to magnetic moments:

$$(\frac{d\mu}{dt})_{lab} = (\frac{\partial \mu}{\partial t})_{rot} + \omega \times \mu$$

This implies:

$$(\frac{\partial \mu}{\partial t})_{rot} = \mu \times (\gamma B_0 + \omega)$$

This is the motion of m in the rotating system, which is the same as in the lab frame, with B_0 replaced by an effective field: $B_{eff} = B_0 + \frac{\omega}{\gamma}$

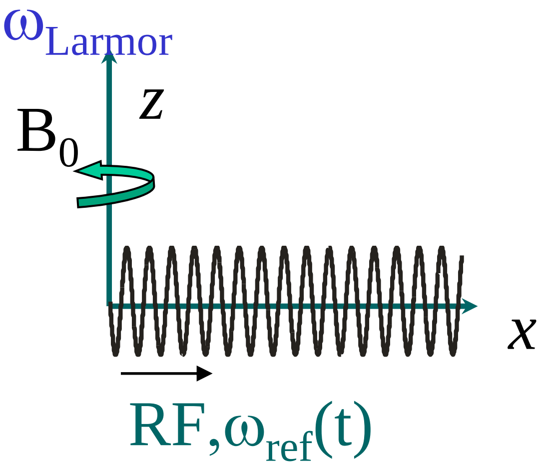
If $\omega=\omega_0=-\gamma B_0$:

$$(\frac{\partial \mu}{\partial t})_{rot} = 0$$

No motion relative to the rotating frame.
The magnetic moment precesses with an angular velocity ω_0 relative to the lab frame about the z-axis:

- Equation of the magnetic moment in the rotating frame is simplified, the moment is static.
- The motion of the moment in the lab frame is a precession about B_0.

Radiofrequency Pulses

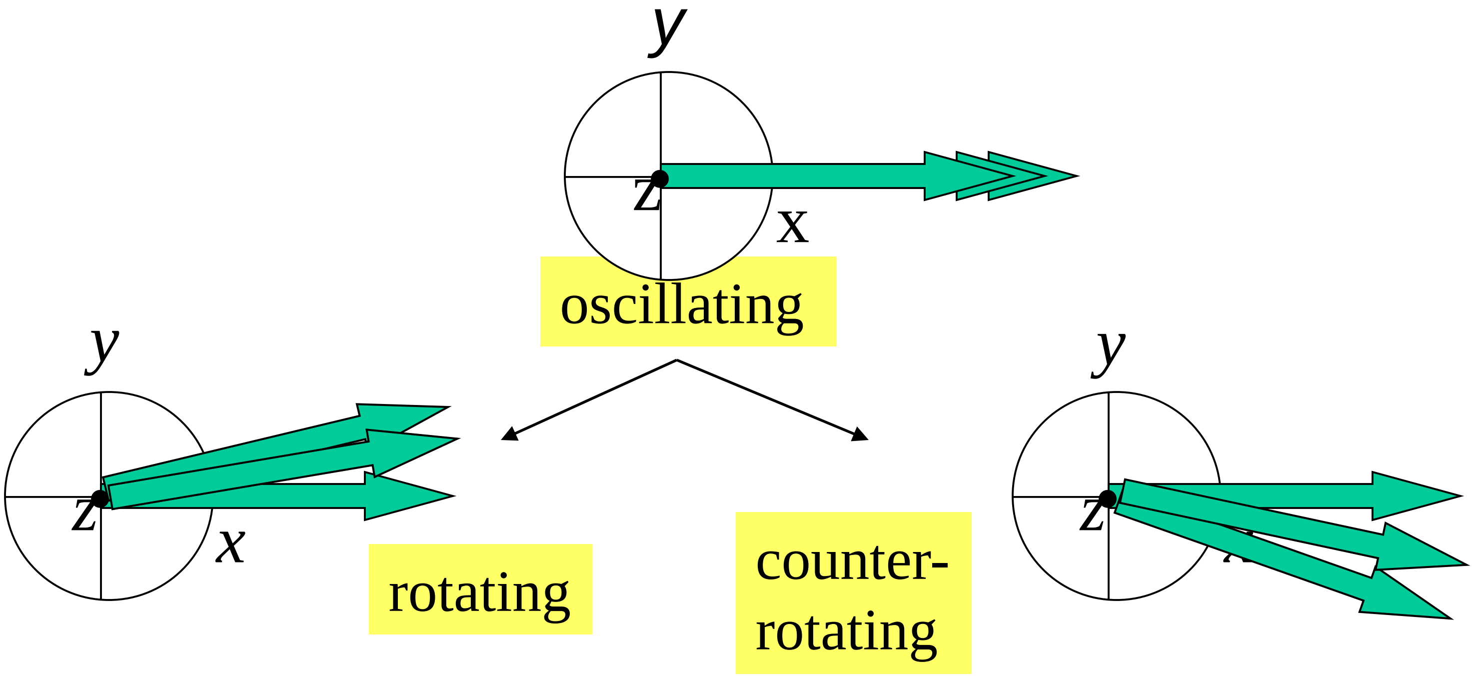


$$B_{RF}(t) = B_{RF}\cos(\omega_{ref}t + \phi_p)e_x$$

$$B_{RF}(t) = B_{RF}^{res}(t) + B_{RF}^{non-res}(t)$$

$$B_{RF}^{res}(t) = \frac{1}{2}B_{RF}\{\cos(\omega_{ref}t + \phi_p)e_x + \sin(\omega_{ref}t + \phi_p)e_y\}$$

$$B_{RF}^{non-res}(t) = \frac{1}{2}B_{RF}\{\cos(\omega_{ref}t + \phi_p)e_x - \sin(\omega_{ref}t + \phi_p)e_y\}$$

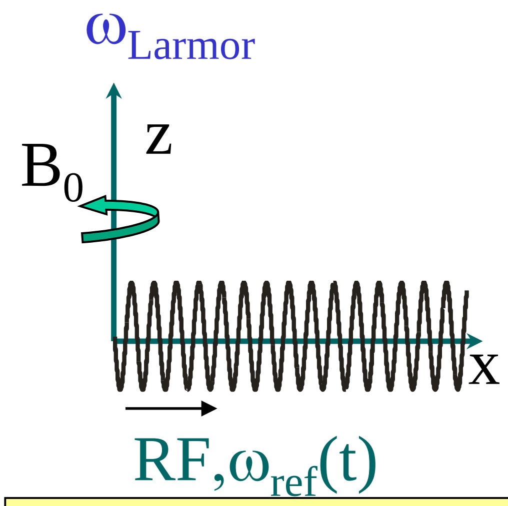


oscillating

rotating

counter-rotating

Radiofrequency Hamiltonian



$$B_{RF}^{res}(t)=\frac{1}{2}B_{RF}\{\cos(\omega_{ref}t+\phi_p)e_x+\sin(\omega_{ref}t+\phi_p)e_y\}$$

Transverse part of the RF Hamiltonian:

$$\boxed{H_{RF}(t)=-\frac{1}{2}\gamma B_{RF}\{\cos(\omega_{ref}t+\phi_p)I_x+\sin(\omega_{ref}t+\phi_p)I_y\}}$$

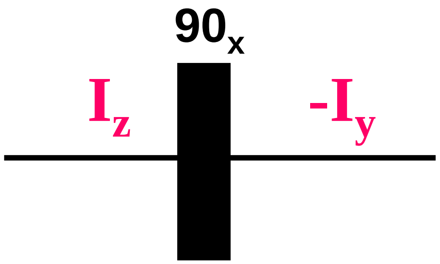
$$\omega_{nut}=\frac{1}{2}\gamma B_{RF}$$ **100 kHz corresponds to 10 μs of 360 pulse**

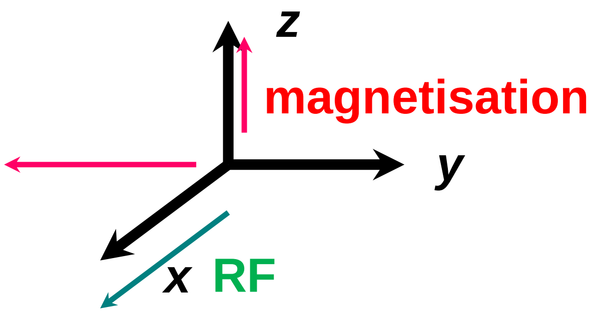
$$\tau_{90}=\frac{1}{4\omega_{nut}}$$

$$H_{RF}=-\frac{1}{2}\gamma B_{RF}R_z(\Phi_p)I_xR_z(-\Phi_p)$$

$\Phi_p(t)=\omega_{ref}t+\phi_{ref}$

Radiofrequency Hamiltonian: Pulses





RF along the x-axis, equilibrium magnetisation along the *z*-axis:

$$e^{-i\frac{\pi}{2}I_x} I_z e^{i\frac{\pi}{2}I_x} = I_z cos(\frac{\pi}{2}) + [I_x, I_z] sin(\frac{\pi}{2})$$

$$= -I_y$$

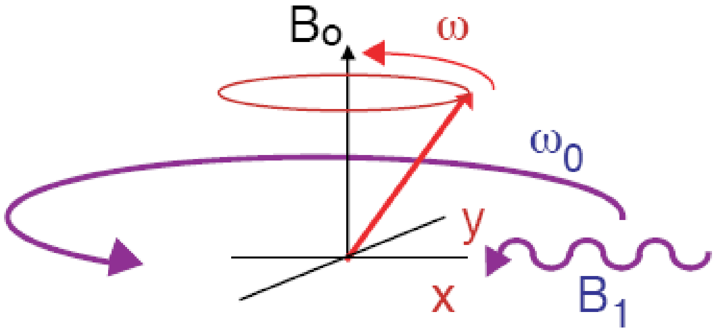
$$\omega_{nut} = \frac{1}{2}\gamma B_{RF}$$

$$\tau_{90} = \frac{1}{4\omega_{nut}}$$

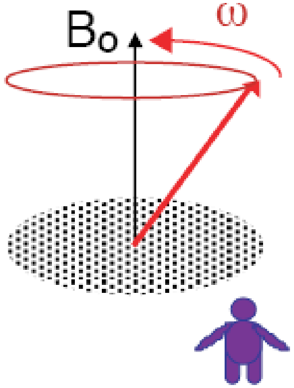
RF field strength (peak RF field in the coil), typically 1-200 kHz, also called nutation frequency

This field strength corresponds to the nutation of the spins by 2π radian

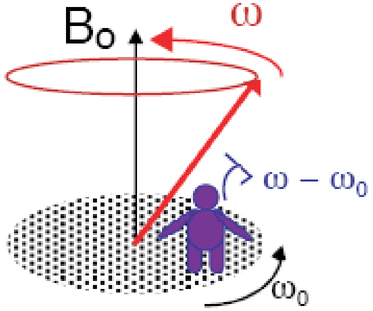
Rotating Frame Transformation



Static B_0 field and rotating B_1 field



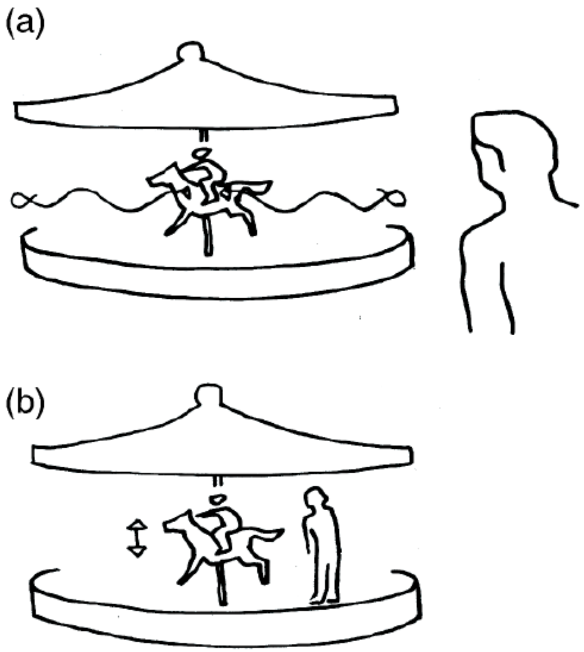
Laboratory frame frequencies



Rotating frame frequencies

Rotating Frame Transformation

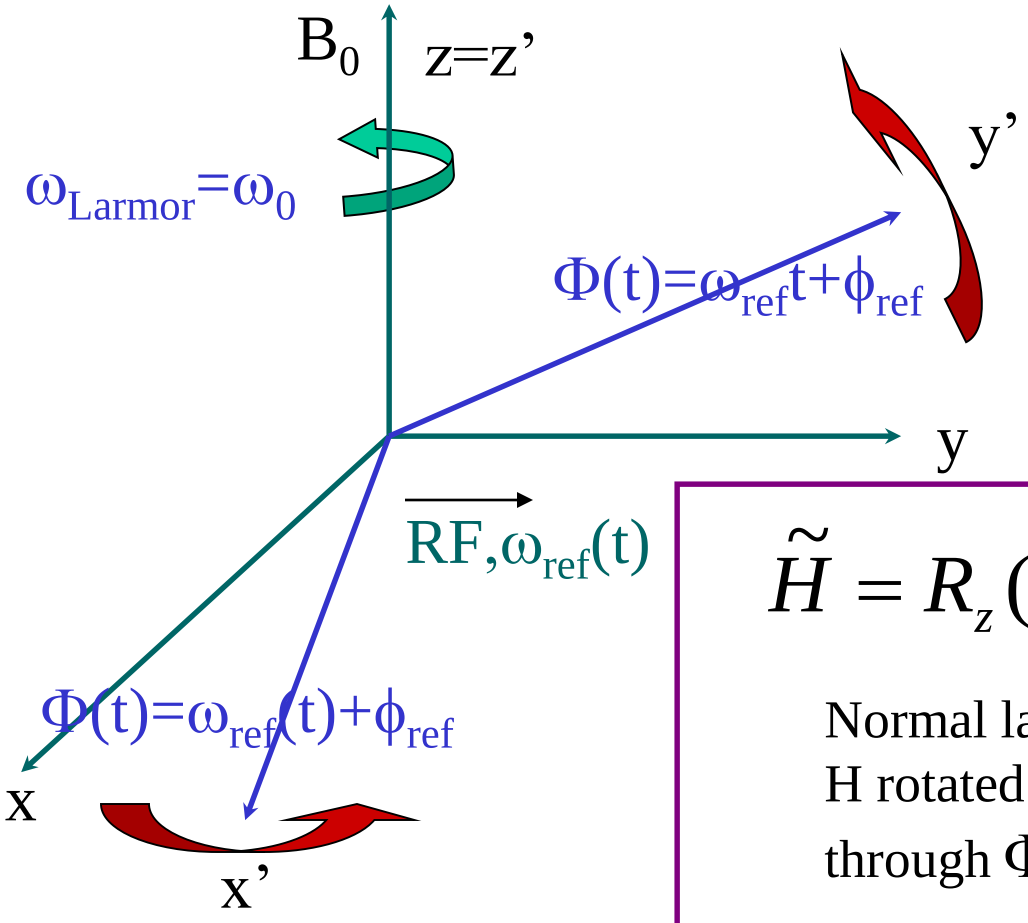
A good analogy would be a child on a merry-go-round in which the horse that the child is riding going up and down. For an observer standing outside (a) there are two motions to see – the spinning of the merry-go-round and the up and down motion. But if the observer hops on to the merry-go-round (b) then ***the spinning motion is subtracted*** *and only the up and down motion is observed – simplifying the details of the motion.*



Rotating Frame Transformation

$$H(t) \xrightarrow[\text{Change reference frame}]{\text{Clever manipulation}} H \quad \textit{(no time dependence!!)}$$

$$|\psi>= R_z(-\Phi)|\psi'>$$



B_0

z=z'

$\omega_{Larmor}=\omega_0$

y'

$\Phi(t)=\omega_{ref}t+\phi_{ref}$

y

$\overrightarrow{\text{RF},\omega_{ref}(t)}$

$\Phi(t)=\omega_{ref}(t)+\phi_{ref}$

x

x'

$$\tilde{H} = R_z(-\Phi)HR_z(\Phi)-\omega_{ref}I_z$$

Normal lab frame H rotated around z through Φ

Gives additional corrections to the spin dynamics

Rotating Frame Transformation: Consequences

Zeeman Hamiltonain

$$H_z = \omega_0 I_z \xrightarrow{rot.\,frame} \tilde{H}_z = \omega_0 R_z(-\Phi) I_z R_z(\Phi) - \omega_{ref} I_z$$

$$= \boxed{(\omega_0 - \omega_{ref})} I_z = \boxed{\Omega_0} I_z$$

off-resonance, off-set frequency

RF Hamiltonian

$$H_{RF} \xrightarrow{rot.\,frame} \tilde{H}_{RF} = -\frac{1}{2}\gamma B_{RF} R_z(-\Phi + \Phi_p) I_x R_z(\Phi - \Phi_p)$$

$$\tilde{H}_{RF} = -\frac{1}{2}\gamma B_{RF} R_z(-\phi_{ref} + \phi_p) I_x R_z(\phi_{ref} - \phi_p)$$

$$\Phi = \omega_{ref} t + \phi_{ref}$$

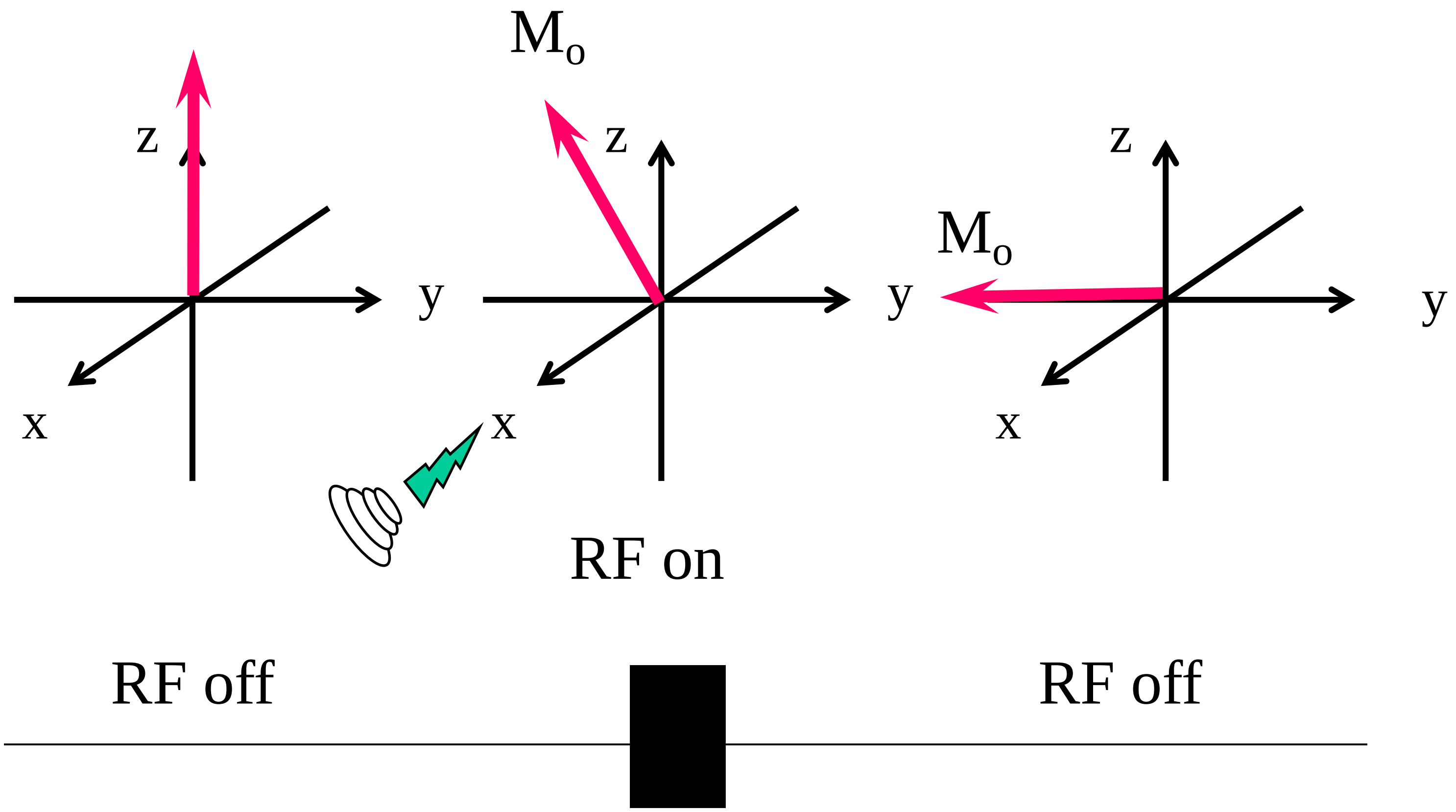
$$\Phi_p = \omega_{ref} t + \phi_p$$

No more time dependence!

Choosing $\phi_{ref}=\pi$ $(\gamma>0)$, and $\phi_{ref}=0$ $(\gamma<0)$

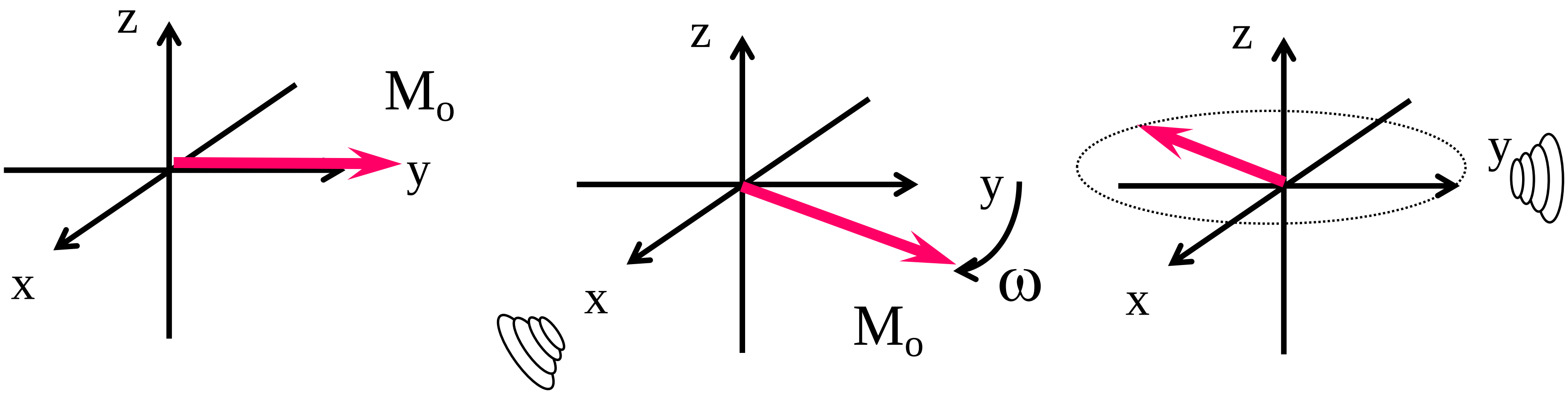
$$\boxed{\tilde{H}_{RF} = \omega_{nut}(I_x \cos\phi_p + I_y \sin\phi_p)}$$

Typical Experiment in NMR: RF Pulse

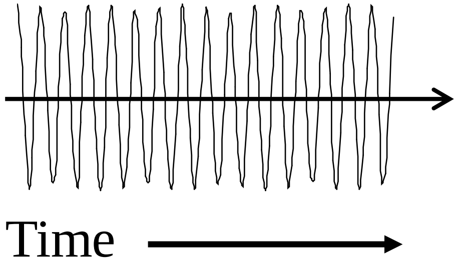


Effect of a 90^o x pulse

After the Pulse: Nuclear Spin Evolution



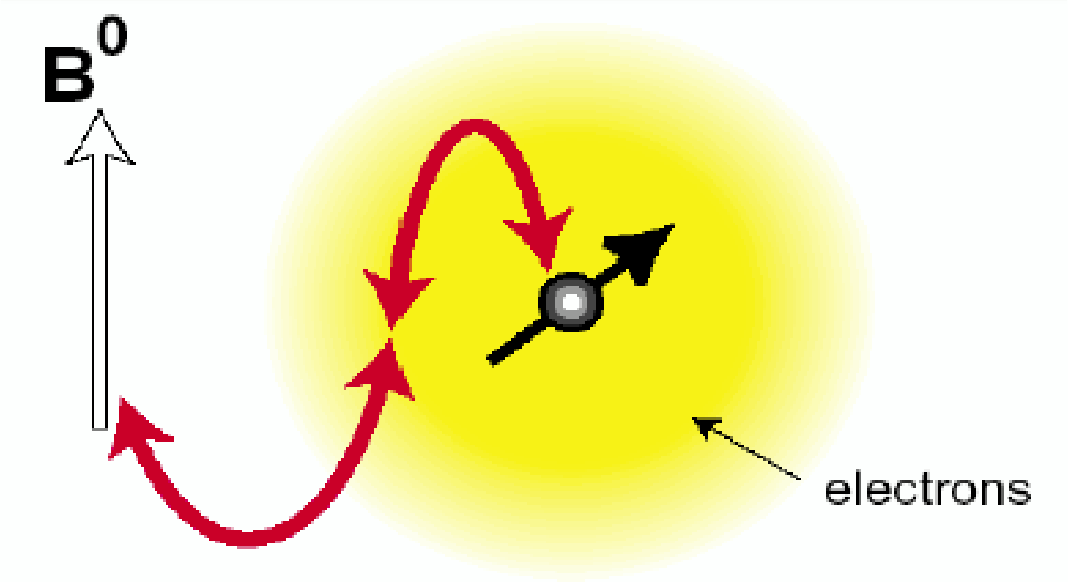
RF receivers pick up the signals



The spins precess in the *xy* plane and relax to the equilibrium value, free induction decay

Some Hamiltonians and Their Representations

Chemical-Shift Anisotropy Hamiltonian



CSA interaction: Indirect magnetic interaction between the external field and the nuclear spins through the electron cloud at each nuclear spin site

Information about the local environment of the nuclear spins

Chemical-Shift Anisotropy Hamiltonian

$$\boldsymbol{B}^j_{local} = \boldsymbol{B}_0 + \boldsymbol{B}^j_{induced}$$

$$\boldsymbol{B}^j_{induced} = \boldsymbol{\delta}^j . \boldsymbol{B}_0$$

$\boldsymbol{\delta}^j$ is the CSA tensor at the nuclear spin site *j*

$$\delta^j = \begin{pmatrix} \delta^j_{xx} & \delta^j_{xy} & \delta^j_{xz} \\ \delta^j_{yx} & \delta^j_{yy} & \delta^j_{yz} \\ \delta^j_{zx} & \delta^j_{zy} & \delta^j_{zz} \end{pmatrix}$$

The chemical-shift tensor

Induced field is not always parallel to the Zeeman field

Only terms relevant, since the static field is along the *z* direction

Chemical-Shift Anisotropy Hamiltonian

$$B^j_{induced} = \delta^j . B_0$$

The CS Hamiltonian is orientation dependent

$$H^j_{CS} = -\mu_j . B^j_{induced}$$

$$= -\gamma_j \delta^j_{xz}(\Theta) B_0 I_{jx} - \gamma_j \delta^j_{yz}(\Theta) B_0 I_{jy} - \gamma_j \delta^j_{zz}(\Theta) B_0 I_{jz}$$

Orientation of the molecule with respect to B_0 and
the position of the nuclear spin within the molecule

Secular approximation:

$$H^j_{CS} = -\gamma_j \delta^j_{zz}(\Theta) B_0 I_{jz}$$

Chemical-Shift Anisotropy Hamiltonian

$$H_{CS}^{j} = -\gamma_j \delta_{zz}^{j}(\Theta) B_0 I_{jz}$$

In liquids, perform an orientational average:

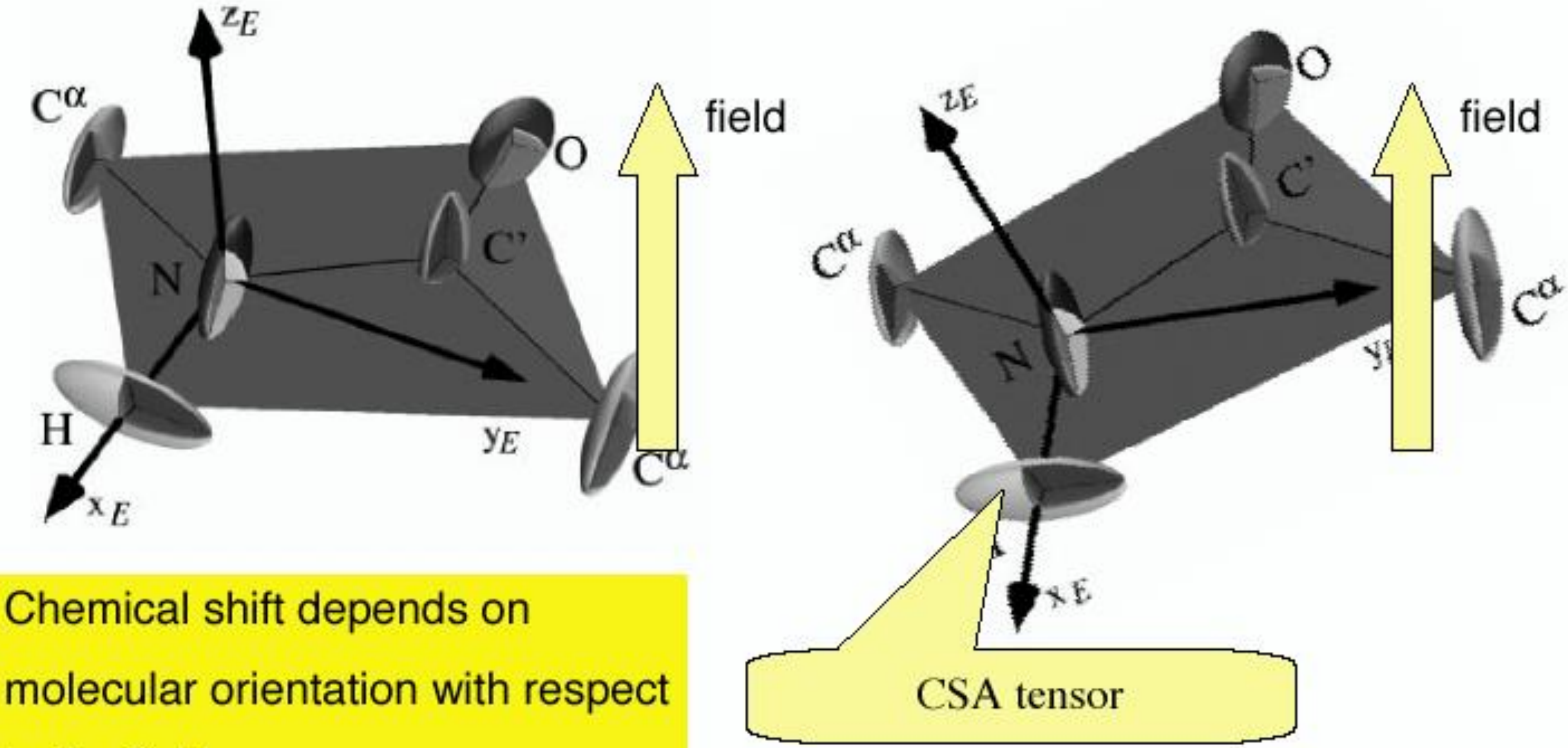
$$H_0^j = H_{static}^j + H_{iso-CS}^j = \omega_0^j I_{jz}$$

The chemically-shifted Larmor frequency $\omega_0^j = -\gamma_j B_0 \, (1 + \delta_{iso-CS}^j)$

In liquids crystals, the resonance position depends upon the orientation (or phase transition which can shift the peak):

$$\overline{\delta_{zz}^{j}(\Theta)} \neq \delta_j^{iso}$$

Chemical-Shift Anisotropy Tensor



Chemical shift depends on molecular orientation with respect to the field

Chemical-Shift Anisotropy Tensor

Irreducible components of a tensor

$$\delta = \delta_{iso}\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix} + \begin{pmatrix}0 & \alpha_{xy} & \alpha_{xz}\\ \alpha_{yx} & 0 & \alpha_{yz}\\ \alpha_{zx} & \alpha_{zy} & 0\end{pmatrix} + \begin{pmatrix}\beta_{xx} & \beta_{xy} & \beta_{xz}\\ \beta_{yx} & \beta_{yy} & \beta_{yz}\\ \beta_{zx} & \beta_{zy} & \beta_{zz}\end{pmatrix}$$

rank 0

rank 1
antisymmetric

rank 2
symmetric

$$\delta_{iso} = \tfrac{1}{3} Tr\delta$$

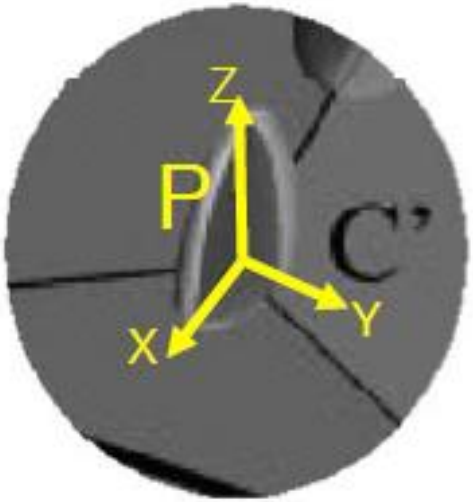
$$\alpha_{\mu\nu} = \tfrac{1}{2}(\delta_{\mu\nu} - \delta_{\nu\mu})$$

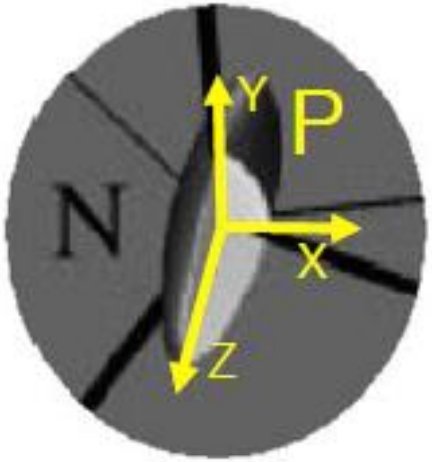
$$\beta_{\mu\nu} = \tfrac{1}{2}(\delta_{\mu\nu} + \delta_{\nu\mu} - 2\delta_{iso}\delta^{\mu}_{\nu})$$

$$\alpha_{ij} = -\alpha_{ji}$$
$$\beta_{ij} = \beta_{ji}$$

Principal Axes

There are three special directions in which the induced field is parallel to the applied field. These are called the principal axes of the tensor (CSA here), denoted as X, Y, and Z. The principal axes are in general different for various chemical sites.





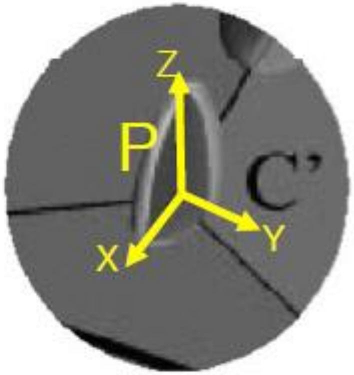
Principal Values

When the applied field is along a principal axis, the induced field is proportional and parallel to the applied field, multiplied by a number, which is called the principal value of the tensor, here, the CSA tensor.

$$\boldsymbol{B}^{j}_{induced}(\text{along X}) = \delta^{j}_{XX}\boldsymbol{B}_{applied} \quad (\text{along X})$$

$$\boldsymbol{B}^{j}_{induced}(\text{along Y}) = \delta^{j}_{YY}\boldsymbol{B}_{applied} \quad (\text{along Y})$$

$$\boldsymbol{B}^{j}_{induced}(\text{along Z}) = \delta^{j}_{ZZ}\boldsymbol{B}_{applied} \quad (\text{along Z})$$



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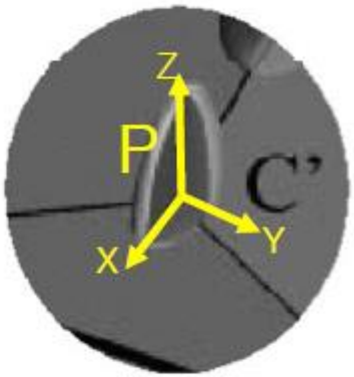
Principal values of the chemical shift tensor for site j

Assignment of the Principal Axes

We use the following convention to assign the principal axes:



- The Z-axis is the one for which the principal value is the furthest from the isotropic shift
- The Y-axis is the one for which the principal value is the closest to the isotropic shift
- The X-axis is the other one

Ordering of the principal values:

$$|\delta^{j}_{ZZ} - \delta^{j}_{iso}| \geq |\delta^{j}_{XX} - \delta^{j}_{iso}| \geq |\delta^{j}_{YY} - \delta^{j}_{iso}|$$

Herzfeld and Berger, J. Chem. Phys. 73, 6021, 1980

Chemical-Shift Anisotropy Tensor

$$\delta = \delta_{iso}\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix} + \begin{pmatrix}0 & \alpha_{xy} & \alpha_{xz}\\ \alpha_{yx} & 0 & \alpha_{yz}\\ \alpha_{zx} & \alpha_{zy} & 0\end{pmatrix} + \begin{pmatrix}\beta_{xx} & \beta_{xy} & \beta_{xz}\\ \beta_{yx} & \beta_{yy} & \beta_{yz}\\ \beta_{zx} & \beta_{zy} & \beta_{zz}\end{pmatrix}$$

$$\delta^j_{iso} = \frac{1}{3}(\delta_{XX} + \delta_{YY} + \delta_{ZZ})$$ Isotropic chemical shift

$$\delta^j_{aniso} = \delta^j_{ZZ} - \delta^j_{iso}$$

CSA value

$$\eta^j = \frac{\delta^j_{YY} - \delta^j_{XX}}{\delta^j_{aniso}}$$

CSA asymmetry (shape)

$$\Delta\delta^j = \delta^j_{ZZ} - \delta^j_{XX}$$

CSA span

$$\delta^j_{PAS} = \delta^j_{iso}\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix} + \delta^j_{ZZ}\begin{pmatrix}-\frac{1}{2}(1+\eta^j) & 0 & 0\\ 0 & -\frac{1}{2}(1+\eta^j) & 0\\ 0 & 0 & 1\end{pmatrix}$$

Anet, O'Leary, Conc. Magn. Reson. 3, 193, 1991

Chemical-Shift Anisotropy Tensor

$$H_{CSA} = -\gamma\hbar I.\delta.B_0$$

$$\delta^j_{iso}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \delta^j_{ZZ}\begin{pmatrix} -\frac{1}{2}(1+\eta^j) & 0 & 0 \\ 0 & -\frac{1}{2}(1+\eta^j) & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Only term in solution-state, trace of the CSA tensor and invariant quantity

The orientation-dependent anisotropic term leading to spectral broadening

$$\delta^j_{iso} = \frac{1}{3}(\delta_{XX} + \delta_{YY} + \delta_{ZZ})$$ Isotropic chemical shift

$$\delta^j_{aniso} = \delta^j_{ZZ} - \delta^j_{iso}$$

CSA value

$$\eta^j = \frac{\delta^j_{YY} - \delta^j_{XX}}{\delta^j_{aniso}}$$

CSA asymmetry (shape)

$$\Delta\delta^j = \delta^j_{ZZ} - \delta^j_{XX}$$

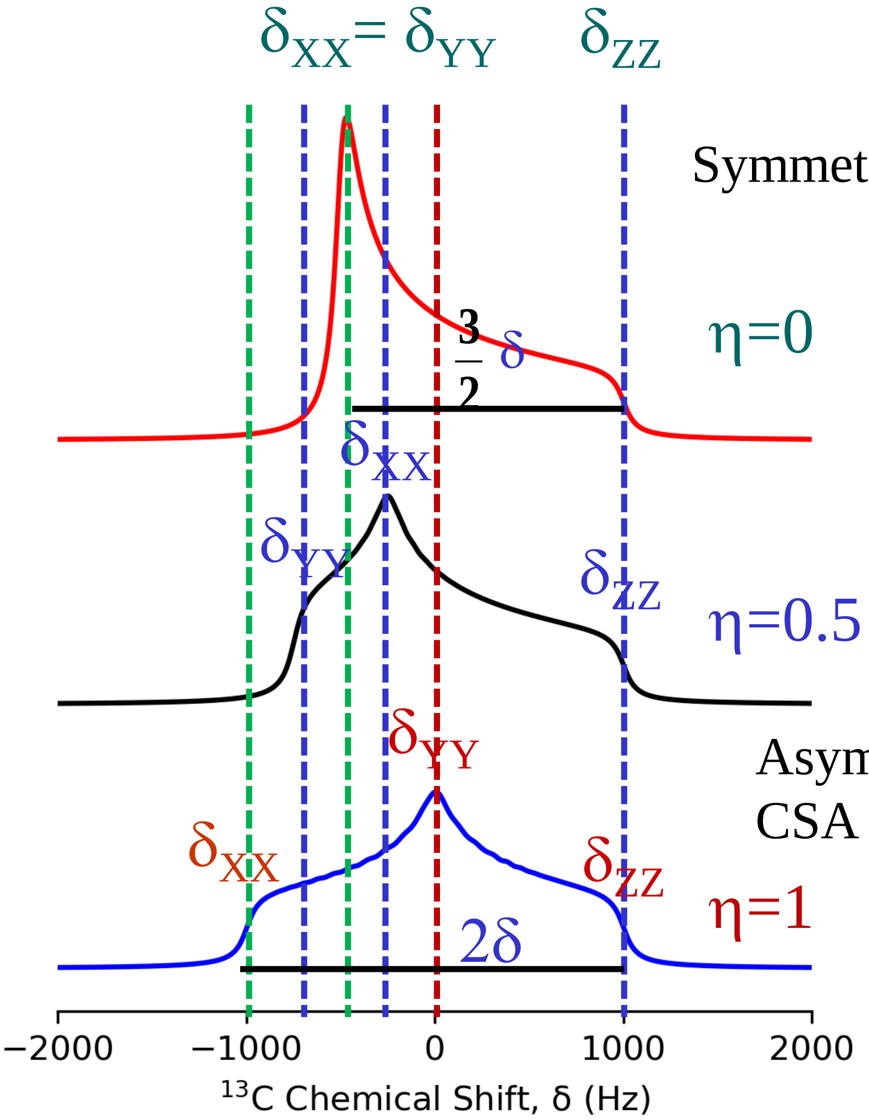
CSA span

Anet, O'Leary, Conc. Magn. Reson. 3, 193, 1991

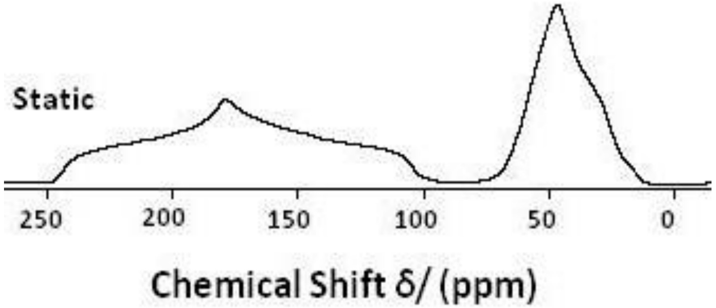
CSA Powder Line Shapes

δ=1 kHz

Symmetric CSA tensor



Asymmetric CSA tensor



Static ^{13}C spectrum of glycine

Chemical-Shift Anisotropy Hamiltonian

CSA Hamiltonian upon secular averaging:

$$H_{CS}^{j} = -\gamma_{j}\delta_{zz}^{j}(\Theta)B_{0}I_{jz}$$

Total Hamiltonian for a site *j*:

$$H_{0}^{j} = H_{static}^{j} + H_{CS}^{j} = \omega_{0}^{j}I_{jz}$$

The chemically-shifted Larmor frequency:

$$\omega_{0}^{j} = -\gamma^{j}B_{0}\,(1+\delta_{zz}^{j}(\Theta))$$

In isotropic liquids
the chemically-shifted Larmor frequency:

$$\omega_{0}^{j} = -\gamma^{j}B_{0}\,(1+\delta_{iso}^{j})$$

In liquids crystals, the resonance position depends upon the orientation (or phase transition which can shift the peak):

$$\overline{\delta_{zz}^{j}(\Theta)} \neq \delta_{j}^{iso}$$

Tensors and PAS

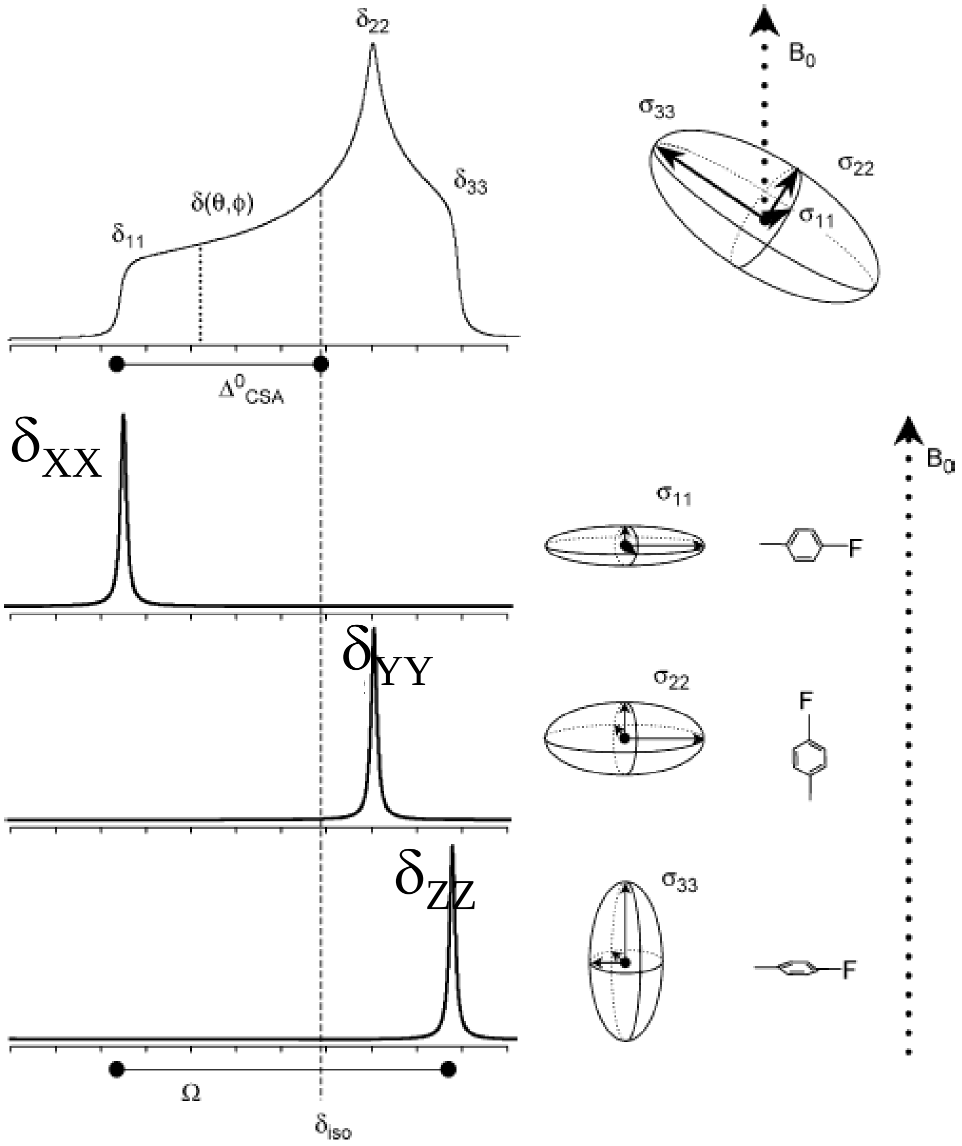
All these tensors, CSA (later DD tensor), are best treated in their principal axis system, PAS, where the tensor is *Diagonal.*

The interaction tensor of each nuclear spin is treated in its PAS.

The PAS *Z*-axis of the CSA tensor corresponds to the long axis of the elliposid representing the CSA tensor.

The PAS *Z*-axis of the DD tensor between the nuclear spins *i* and *j* is along the vector joining the nuclear spins *i* and *j* (here *X* and *Y* are arbitrary).

Chemical-Shift Anisotropy: Response



A. S. Ulrich, Progress in Nuclear Magnetic Resonance Spectroscopy 6 46 (2005) 1–21

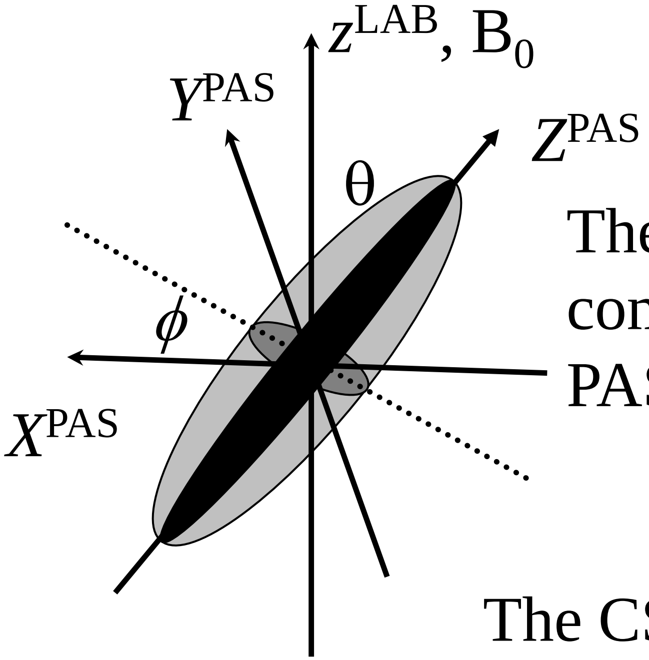
CSA Shielding Convention

- We will use the deshielding convention for the chemical shift, d (as opposed to another convention, shielding convention, σ):

$$\sigma^{j}_{aniso} = -\delta^{j}_{aniso}$$

Chemical-Shift Anisotropy Tensor

$$H_{CSA} = -\gamma\hbar\delta_{zz}^{lab} B_0 I_z$$ In the lab frame



The orientation dependence of the CSA tensor comes on account of a transformation from PAS to LAB frame, through θ and ϕ

The CS frequency then becomes

$$\boxed{\omega_{CSA}(\theta,\phi) = -\omega_0\delta_{iso} - \frac{1}{2}\omega_0\delta(3\cos^2\theta - 1 + \eta\sin^2\theta\cos 2\phi)}$$

$\eta=0$, axially symmetric tensor, $\delta_{xx}=\delta_{yy}$

Chemical-Shift Anisotropy Tensor

In the lab frame, Hamiltonian

$$\boldsymbol{H_{CSA} = -\gamma\hbar\delta_{zz}^{lab} B_0 I_z}$$

In the lab frame, energy from CS

$$\boldsymbol{E_{CSA} = -\gamma\hbar\delta_{zz}^{lab} B_0 < I, m \mid I_z \mid I, m >}$$

Spectral frequency for ½ to –½

$$\boldsymbol{\omega_{CSA} = -\gamma\delta_{zz}^{lab} B_0 = -\omega_0\delta_{zz}^{lab}}$$

Remember

$$\boldsymbol{\delta_{zz}^{lab} = \begin{pmatrix} 0 & 0 & 1 \end{pmatrix} \delta^{lab} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}}$$

Tensor from a frame *f* to lab

$$\boldsymbol{\delta_{zz}^{lab} = P^f \delta^f P^{f^T}}$$

$$\omega_{CSA}(\theta,\phi) = -\omega_0\delta_{iso} - \frac{1}{2}\omega_0\delta(3\cos^2\theta - 1 + \eta\sin^2\theta\cos 2\phi)$$

Chemical-Shift Frequency: From PAS to Lab

CS contribution to the spectral frequency:

$$\omega_{CSA} = -\omega_0 P^f \delta^f P^f$$

Euler angles transformation:

$$P^{PAS} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\phi)$$

Chemical-shift frequency:

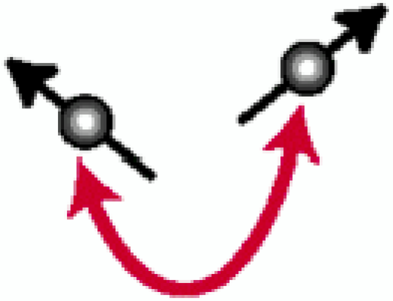
$$\omega_{CSA}(\theta,\phi) = -\omega_0(\delta_{XX}\sin^2\theta\cos^2\phi + \delta_{YY}\sin^2\theta\sin^2\phi + \delta_{ZZ}\cos^2\phi)$$

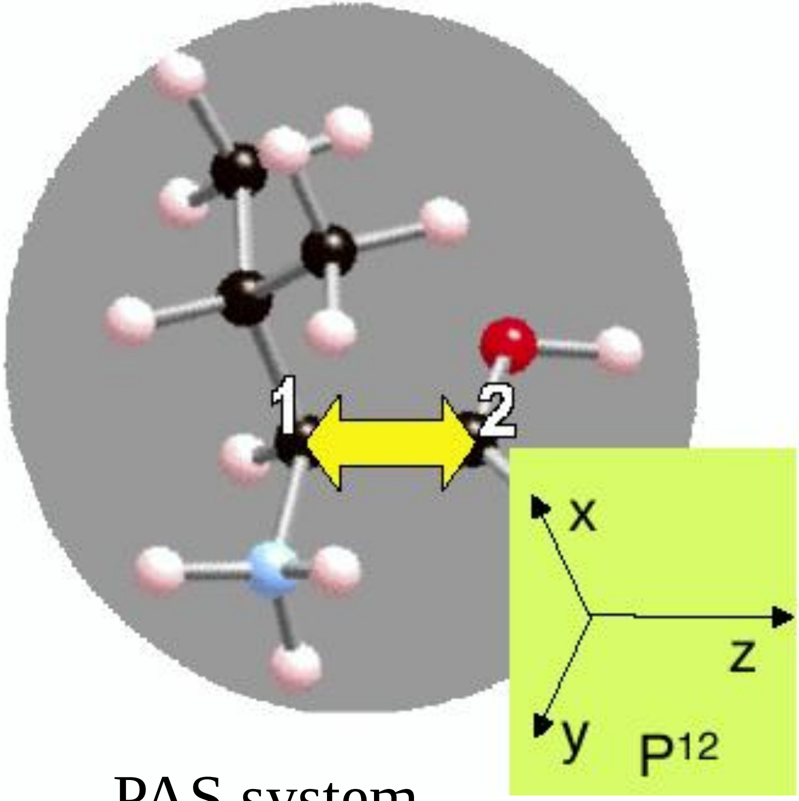
Using definitions:

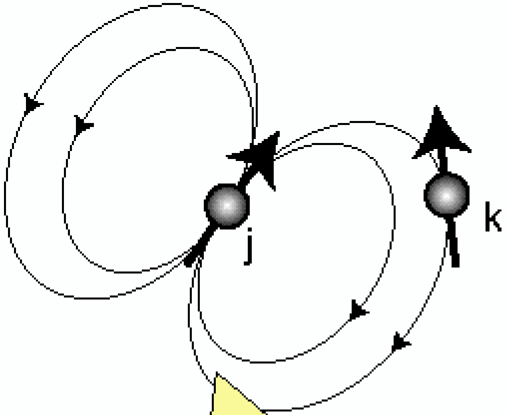
$$\omega_{CSA}(\theta,\varphi) = \underset{\displaystyle\downarrow}{-\omega_0\delta_{iso}} - \frac{1}{2}\omega_0\delta(3\cos^2\theta - 1 + \eta\sin^2\theta\cos 2\varphi)$$

$-\omega_0\delta_{iso} = \omega_{iso}$ Isotropic chemical-shift frequency

Dipole-Dipole Interaction







The magnetic field generated by one spin influences its neighbour

PAS system
of a DD tensor

DD coupling is the direct magnetic interaction between two nuclear spins, orientation dependent, both distance and angles

Dipole-Dipole Hamiltonian

Classical interaction energy between two dipoles $\vec{\mu}_j$ and $\vec{\mu}_k$, separated by $\vec{r}_{jk}$:

$$E_{DD}^{ij} = \frac{\mu_0}{4\pi}\left\{\frac{\vec{\mu}_i \cdot \vec{\mu}_j}{r_{ij}^3} - 3\frac{(\vec{\mu} \cdot \vec{r}_{ij})(\vec{\mu}_j \cdot \vec{r}_{ij})}{r_{ij}^5}\right\}$$

Substituting for $\mu = \gamma\hbar I$, we get the expression for the dipole-dipole Hamiltonian between I_j and I_k:

$$\mathcal{H}_{jk}^{DD} = -\left(\frac{\mu_0}{4\pi}\right)\gamma_j\gamma_k\hbar^2\left(\frac{I_j \cdot I_k}{r_{jk}^3} - 3\frac{(I_j.r)(I_k.r)}{r_{jk}^5}\right)$$

Defining DD coupling constant: $b_{jk} = -\frac{\mu_0}{4\pi}\frac{\gamma_j\gamma_k\hbar}{r_{jk}^3}$

DD coupling in Hz: $\dfrac{b_{jk}}{2\pi}$

Hamiltonian becomes: $\mathcal{H}_{jk}^{DD} = b_{jk}\left(I_j \cdot I_k - \frac{3}{r_{jk}^2}(I_j.r)(I_k.r)\right)$

- Two protons at 3A separation, DD coupling = -4.5 kHz
- Two ^{13}C at 1.5A separation, DD coupling = -2.2 kHz
- Two ^{13}C at 5A separation, DD coupling = -61 Hz
- Two ^{13}C at 8 A separation, DD coupling = -15 Hz :

Dipole-Dipole Hamiltonian

DD Hamiltonian:

$$\mathcal{H}_{jk}^{DD} = b_{jk}\Big(I_j \cdot I_k - \frac{3}{r_{jk}^2}(I_j.r)(I_k.r)\Big)$$

Defining $\vec{e}_{jk}$ as a unit vector pointing in the direction of $\vec{r}_{jk}$, $\vec{e}_{jk} = \frac{\vec{r}_{jk}}{r_{jk}}$:

$$\mathcal{H}_{jk}^{DD} = b_{jk}\Big(I_j \cdot I_k - 3(I_j.e_{jk})(I_k.e_{jk})\Big)$$

Defining $\hat{1}$ as identity operator and letting $\hat{e}$ be the dyadic product of $\vec{e}_{jk}$ with itself ($\langle u|\hat{e}|v\rangle = e_u e_v$):

$$\mathcal{H}_{jk}^{DD} = b_{jk}\Big(I_j \cdot \hat{1} \cdot I_k - 3I_j \cdot e_{jk} \cdot I_k\Big)$$

In dyadic notation:

$$\mathcal{H}_{jk}^{DD} = b_{jk}\Big(I_j \cdot D_{jk} \cdot I_k\Big)$$

With the elements of the 3×3 matrix $\hat{D}$: $\langle \mu|D_{jk}|\nu\rangle = \delta_{\mu\nu} - 3e_{j\mu}e_{k\nu}$

$$= \delta_{\mu\nu} - 3e_{\mu\nu}$$

Dipole-Dipole Hamiltonian

In dyadic notation: $\mathcal{H}_{jk}^{DD} = b_{jk}\left(I_j \cdot D_{jk} \cdot I_k\right)$

With the elements of the 3×3 matrix $\hat{D}$: $\langle\mu|D_{jk}|\nu\rangle = \delta_{\mu\nu} - 3e_{j\mu}e_{k\nu}$

$$= \delta_{\mu\nu} - 3e_{\mu\nu}$$

$$\mu,\ \nu \equiv x,\ y$$

In general D_{jk}:

$$\boldsymbol{D_{jk}} = \begin{pmatrix} 1-3e_{xx} & -3e_{xy} & -3e_{xz} \\ -3e_{yx} & 1-3e_{yy} & -3e_{yz} \\ -3e_{zx} & -3e_{zy} & 1-3e_{zz} \end{pmatrix}$$

Dipole-Dipole Hamiltonian

$$D_{jk} = \begin{pmatrix} 1-3e_{xx} & -3e_{xy} & -3e_{xz} \\ -3e_{yx} & 1-3e_{yy} & -3e_{yz} \\ -3e_{zx} & -3e_{zy} & 1-3e_{zz} \end{pmatrix} \longrightarrow D_{jk}^{PAS} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix}$$

Trace = 0, no isotropic part, only the rank 2 anisotropic part present

Since, only the Z-axis needs to be defined for DD tensor in the PAS, *X* and Y are arbitrary

Dipolar Alphabet

$$\mathcal{H}_{DD}^{jk} = b_{jk}(A + B + C + D + E + F)$$

$$A = I_{jz}I_{jz}(3\cos^2\theta_{jk} - 1)$$

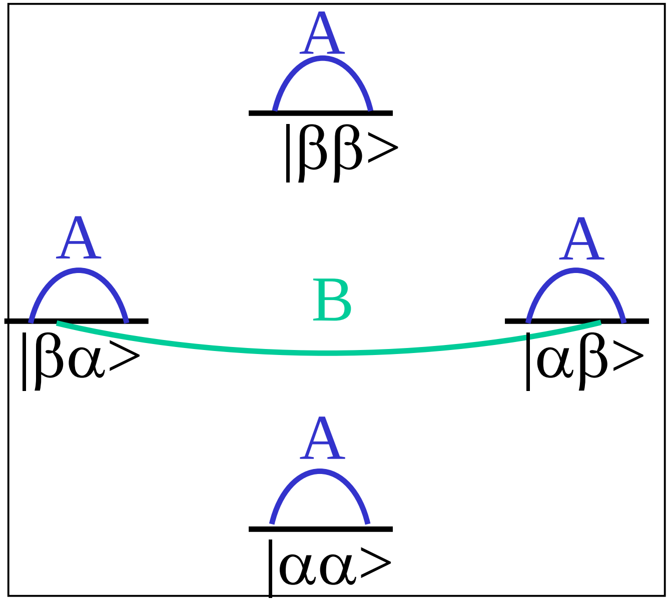
$$B = -\frac{1}{4}(I_{j+}I_{k-} + I_{j-}I_{k+})(3\cos^2\theta_{jk} - 1)$$

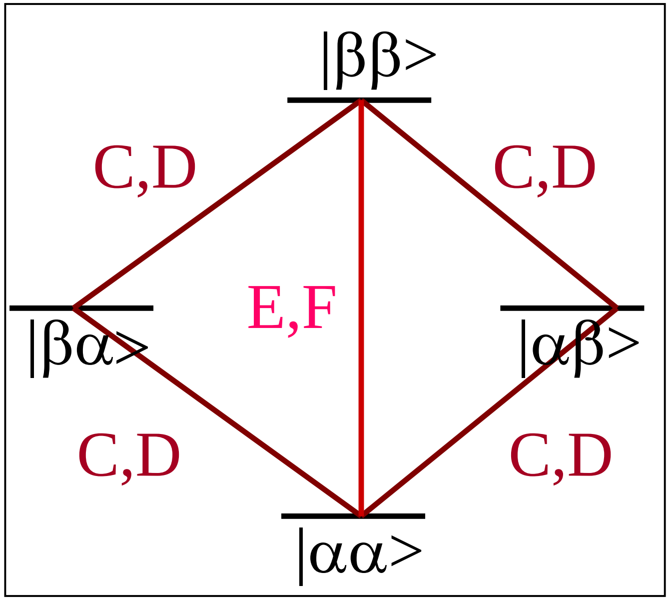
$$C = \frac{3}{2}(I_{jz}I_{k+} + I_{j+}I_{kz})\sin\theta_{jk}\cos\theta_{jk}e^{-i\phi}$$

$$D = \frac{3}{2}(I_{jz}I_{k-} + I_{j-}I_{kz})\sin\theta_{jk}\cos\theta_{jk}e^{i\phi}$$

$$E = \frac{3}{4}(I_{j+}I_{k+})\sin^2\theta_{jk}e^{-2i\phi}$$

$$F = \frac{3}{4}(I_{j-}I_{k-})\sin^2\theta_{jk}e^{2i\phi}$$



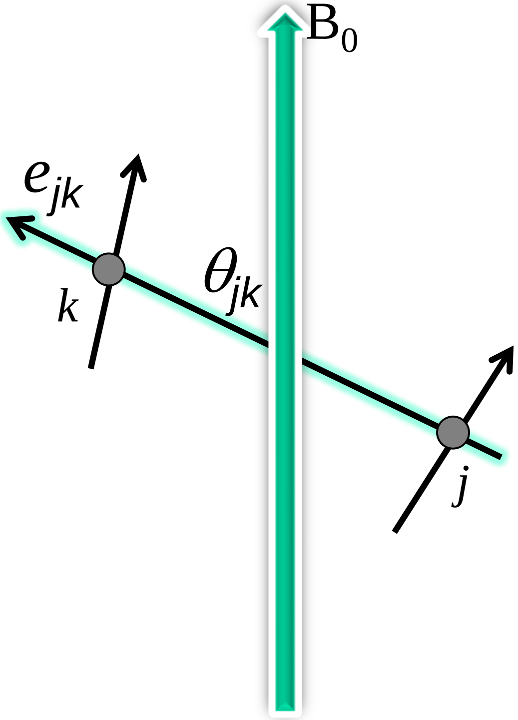


Heteronuclear Dipole-Dipole Hamiltonian

High-field, secular approximation:

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{DD}^{jk}$$

$$= -(\omega_{0I_j} I_{jz} + \omega_{0I_k} I_{kz}) + b_{jk} A$$



$$d_{jk} = b_{jk}\tfrac{1}{2}(3\cos^2\theta_{jk} - 1)$$

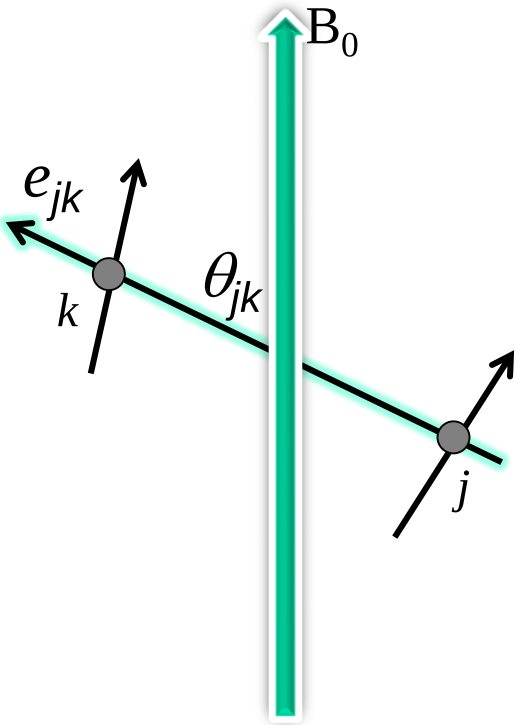
$$A = d_{jk} 2 I_{jz} I_{kz}$$

$$\mathcal{H}_{jk}^{DD}(\theta_{jk}) = d_{jk} 2 I_{jz} I_{kz}$$

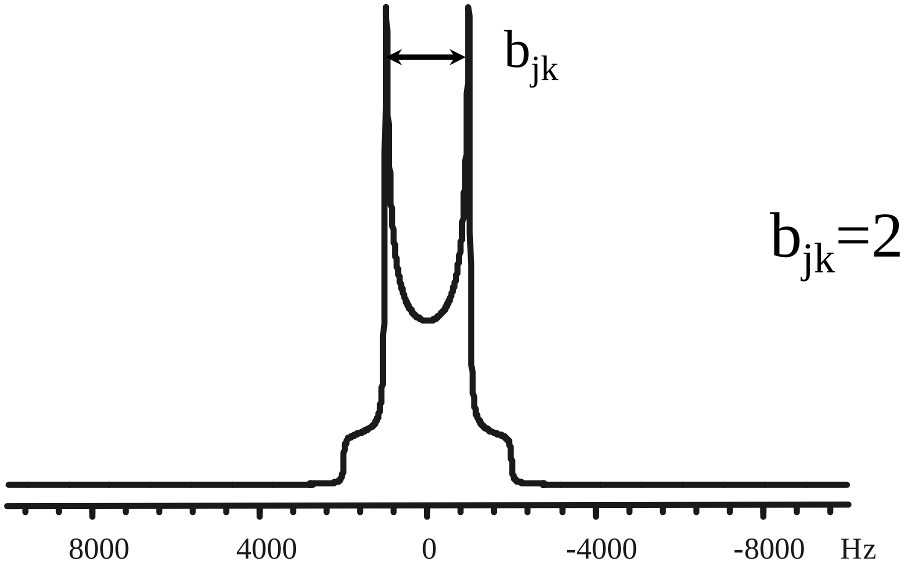
The I_k spectrum coupled to I_j then will have two transitions, one having $(1 - 3\cos^2\theta)$ dependence, and the other $-(1 - 3\cos^2\theta)$ dependence, hence, mirror images.

Heteronuclear Dipole-Dipole Powder Line Shapes: Pake Doublet

The I_k spectrum coupled to I_j then will have two transitions, one having $(1 - 3\cos^2\theta)$ dependence, and the other $-(1 - 3\cos^2\theta)$ dependence, hence, mirror images.



$$\mathcal{H}_{jk}^{DD}(\theta_{jk}) = d_{jk} 2 I_{jz} I_{kz}$$



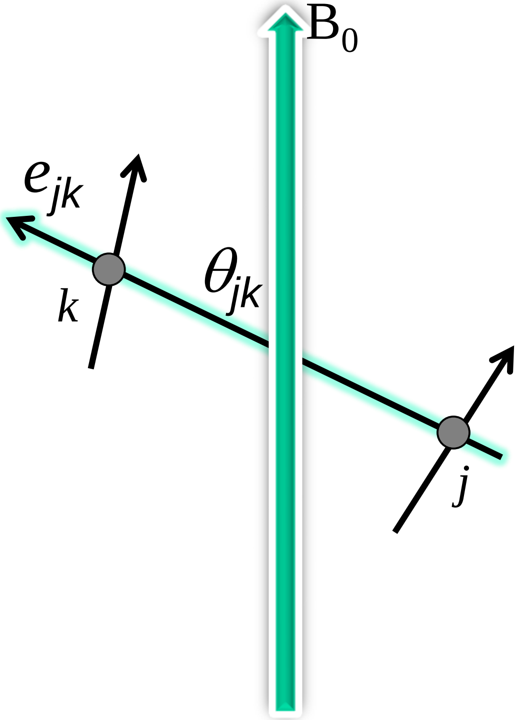
b_{jk}=2000 Hz

Homonuclear Dipole-Dipole Hamiltonian

High-field, secular approximation:

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{DD}^{jk}$$

$$= -(\omega_{0I_j} I_{jz} + \omega_{0I_k} I_{kz}) + b_{jk}(A + B)$$



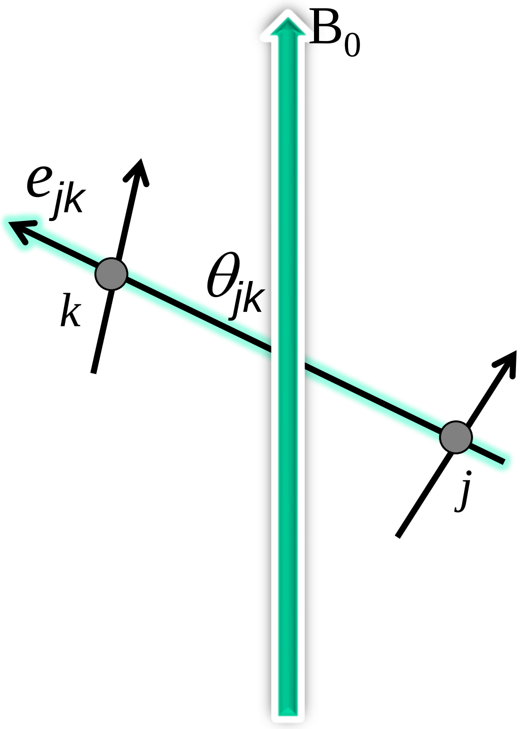
$$d_{jk} = b_{jk}\tfrac{1}{2}(3\cos^2\theta_{jk} - 1)$$

$$\mathcal{H}_{jk}^{DD}(\theta_{jk}) = d_{jk}(3I_{jz}I_{kz} - I_j \cdot I_k)$$

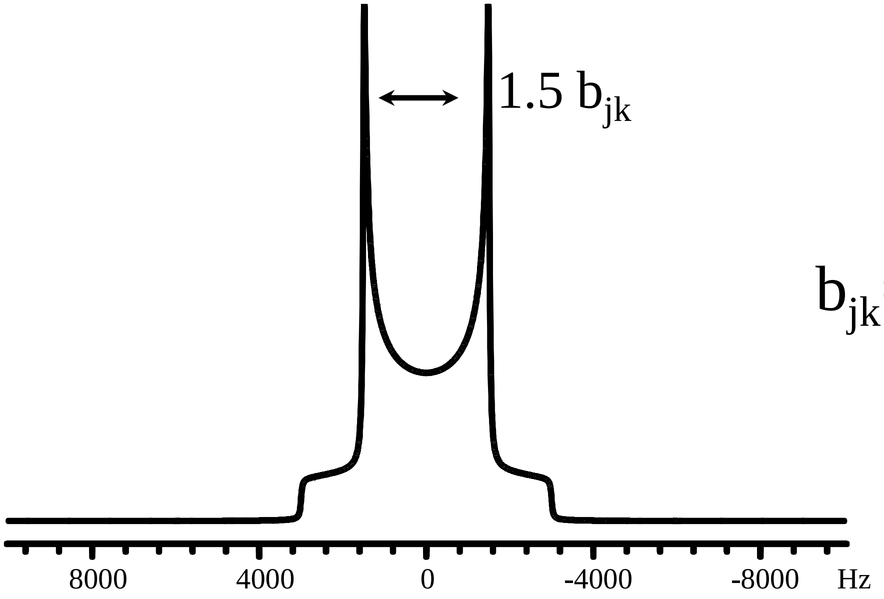
The I_k spectrum coupled to I_j then will have two transitions, one having $(1 - 3\cos^2\theta)$ dependence, and the other $-(1 - 3\cos^2\theta)$ dependence, hence, mirror images.

Homonuclear Dipole-Dipole Powder Line Shapes: Pake Doublet

The I_k spectrum coupled to I_j then will have two transitions, one having $(1 - 3\cos^2\theta)$ dependence, and the other $-(1 - 3\cos^2\theta)$ dependence, hence, mirror images.

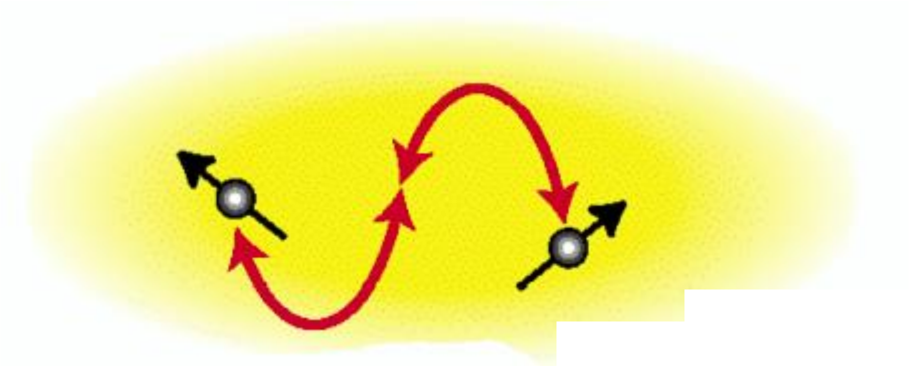


$$\mathcal{H}_{jk}^{DD}(\theta_{jk}) = d_{jk}(3I_{jz}I_{kz} - \mathbf{I}_j \cdot \mathbf{I}_k)$$



b_{jk}=2000 Hz

Scalar Coupling Hamiltonian



$$H_{jk}^{J} = 2\pi J_{jk} I_j . I_k$$

Scalar coupling is a magnetic interaction between the nuclear spins mediated via an electron cloud, through-bond Interaction.

Too weak in solid-state NMR, still observable with the advent of high-resolution schemes.

J-Coupling Hamiltonian: Homonuclear

$$H^{J}_{jk} = 2\pi J_{jk} I_j . I_k$$

$$\Big\downarrow \text{ High field}$$

First-order secular term:

$$H_J = 2\pi J_{jk} I_j . I_k$$

J-Coupling Hamiltonian: Heteronuclear

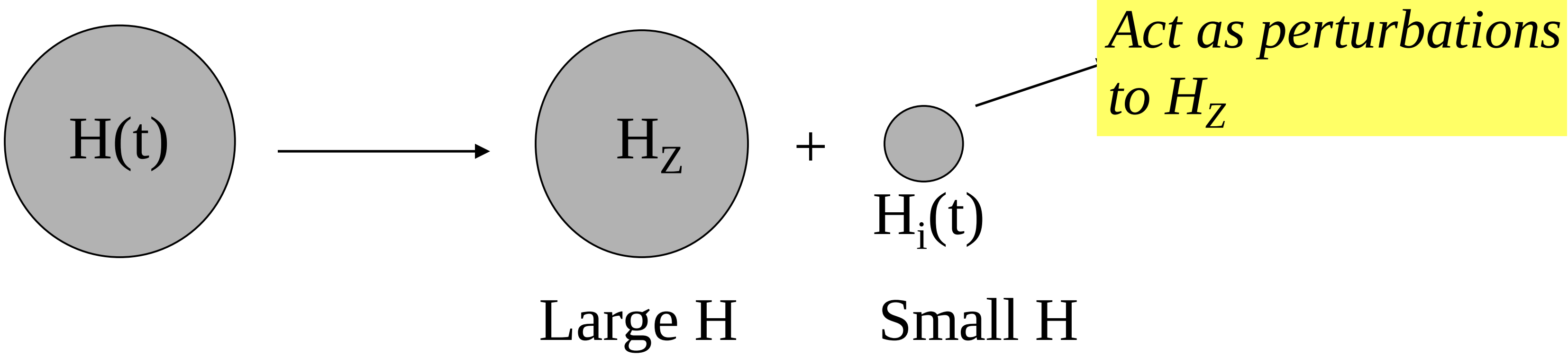
$$H_{jk}^{J} = 2\pi J_{jk} I_{j} . I_{k}$$

$$\Big\downarrow \text{ High field}$$

First-order secular term:

$$H_{jk}^{J} = 2\pi J_{jk} I_{jz} I_{kz}$$

Secular Approximation



- Only those parts of $H_i(t)$ that have the same eigenfunction as H_Z (having matrix elements in the eigen basis of H_Z) will contribute to energy level shifts in the first-order

- This means, to first-order energy correction, we need consider only those parts of $H_i(t)$ such that $[H_Z,H_i]=0$; Secular Approximation

- In solution-state, this is often disguised as weak-coupling (AX), but not valid in strong-coupling cases (AB)

Secular approximation simplifies our internal Hamiltonians

Secular Approximation

Strictly speaking, secular approximation is more than commutativity. If A is the large Hamiltonian and B is the small Hamiltonian, a matrix element of B may be dropped if its magnitude is small compared to the corresponding difference in the eigenvalues of A

Consider $A = \omega_0 I_z ; B = \omega_x I_x + \omega_z I_z$

Eigenvalues= $\frac{1}{2}\omega_0, -\frac{1}{2}\omega_0$

B representation in the basis of A

$$B = \frac{1}{2}\begin{pmatrix} \omega_z & \omega_x \\ \omega_x & -\omega_z \end{pmatrix}$$

$$\downarrow$$

Secular approximation:

$$B = \frac{1}{2}\begin{pmatrix} \omega_z & 0 \\ 0 & -\omega_z \end{pmatrix}$$

Provided, the following condition holds good (besides commutativity)

$$\omega_x << \omega_0$$

Scalar Coupling Hamiltonian

The J-coupling tensor on account of the rapid molecular tumbling has only the isotropic part

The secular part of the J-coupling Hamiltonian depends on whether the two coupled spins are homonuclear or heteronuclear

Homonuclear case:

$$H_{jk}^{J} = 2\pi J_{jk} I_j . I_k$$

$$= 2\pi J_{jk} (I_{jx} I_{kx} + I_{jy} I_{ky} + I_{jz} I_{kz})$$

Heteronuclear case:

$$H_{jk}^{J} = 2\pi J_{jk} I_{jz} I_{kz}$$

Unlike chemical shifts, J-coupling is independent of the applied magnetic field

Scalar Coupling Hamiltonian: Secular Approximation

$$A = \omega_{01} I_{1z} + \omega_{02} I_{2z}; B = 2\pi J_{12} I_1 . I_2$$

Basis sets of A=|+1/2,+1/2>, =|+1/2,-1/2>, =|-1/2,+1/2>, =|-1/2,1/2>

$$A = \frac{1}{2}\begin{pmatrix} \omega_{01}+\omega_{02} & 0 & 0 & 0 \\ 0 & \omega_{01}-\omega_{02} & 0 & 0 \\ 0 & 0 & -\omega_{01}+\omega_{02} & 0 \\ 0 & 0 & 0 & -\omega_{01}-\omega_{02} \end{pmatrix}$$

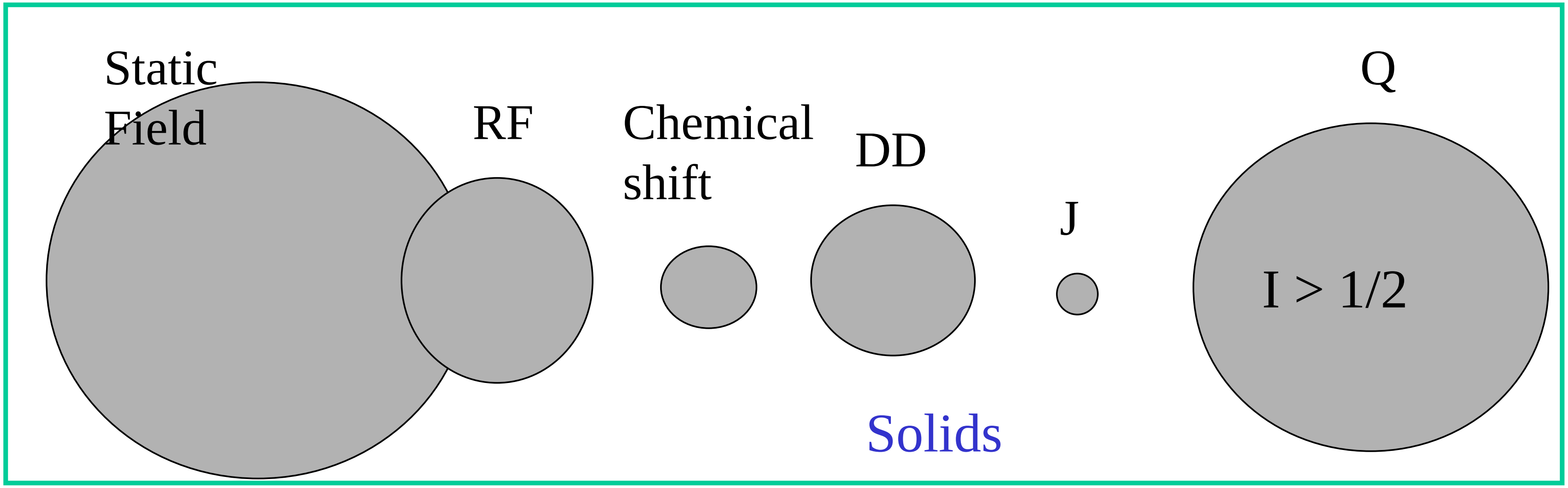
$$B = \begin{pmatrix} \frac{1}{2}\pi J_{12} & 0 & 0 & 0 \\ 0 & -\frac{1}{2}\pi J_{12} & \pi J_{12} & 0 \\ 0 & \pi J_{12} & -\frac{1}{2}\pi J_{12} & 0 \\ 0 & 0 & 0 & \frac{1}{2}\pi J_{12} \end{pmatrix}$$

Secular approximation is valid (and then B will be diagonal) when

$$|\omega_{01} - \omega_{02}| << |\pi J_{12}|$$

This condition is satisfied for heteronuclear case (γ_1 and γ_2 different, of when the chemical-shift difference is sufficiently large for homonuclear case (weak coupling)

Relative Magnitude of Interactions: After Motional Averaging



Static Field

RF

Chemical shift

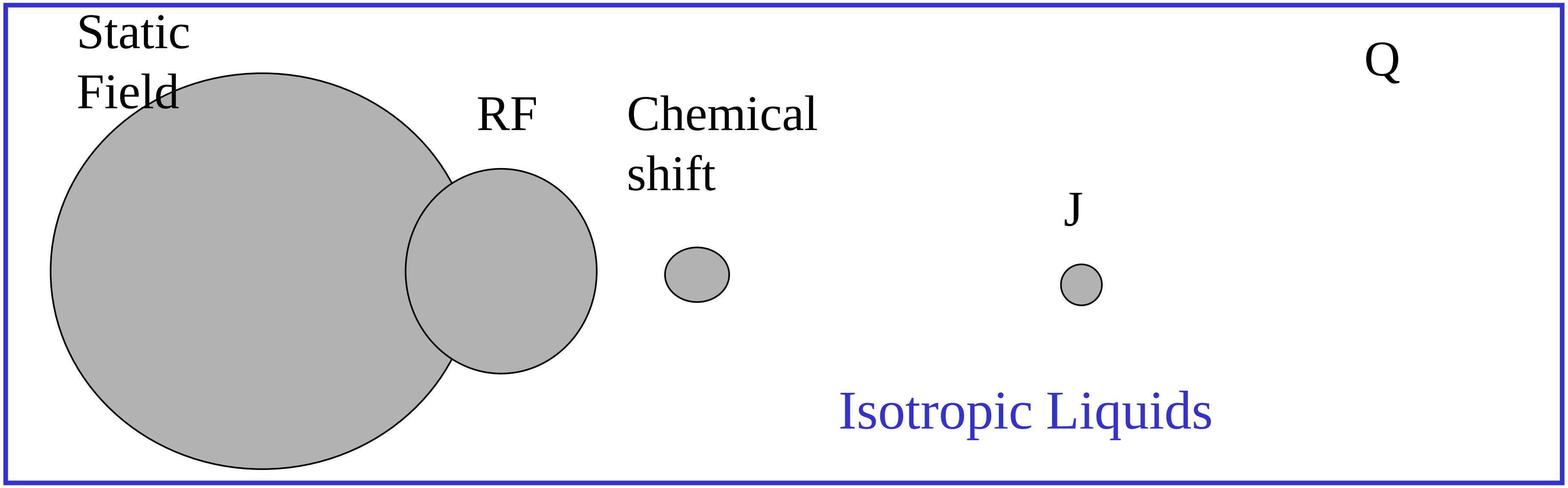
DD

J

Q

I > 1/2

Solids



Static Field

RF

Chemical shift

J

Q

Isotropic Liquids

M. H. Levitt, Spin Dynamics

Product Operator Formalism

- POF-complete and QM description of NMR experiments (solution state)

A version of DM theory

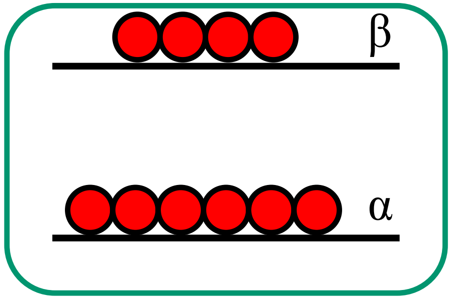
- POF have a well-defined physical meaning

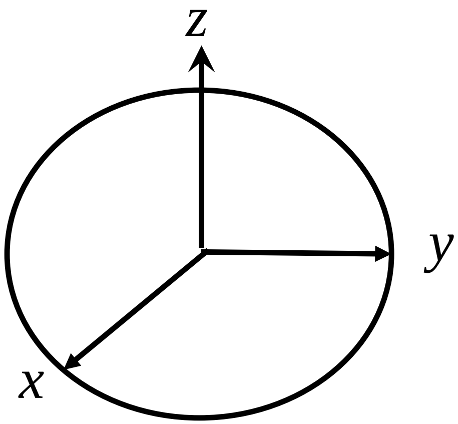
Pulses and delays are geometrical Rotations

- Illustrative to look at vector model

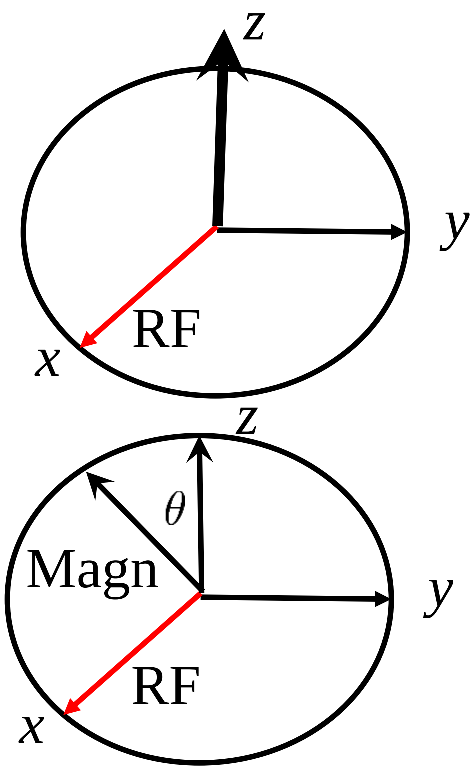
Useful in describing the behavior of an ensemble of non-interacting spins, ½

- At thermal equilibrium: Unequal populations of the two levels leads to a net magnetization along the field (z) direction. This may be treated as a vector. The vector model fully relies on its behavior. (Lower level more populated at thermal equilibrium.)





Product Operator Formalism



- RF pulses are rotations about *x* or *y*-axes.

- Angle of rotation is $\theta = \omega_{nut} t$, where ω_{nut} is the RF field strength and t is the duration for which the pulse is applied. The rotation is in the *yz*-plane.

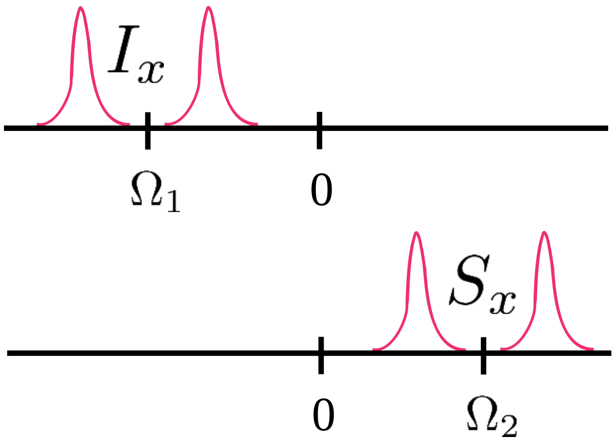
- Free precession is a rotation about the *z*-axis at frequency Ω, which is the offset (difference between the Larmor and transmitter frequencies. Here, the rotation angle is $\theta = \Omega t$.

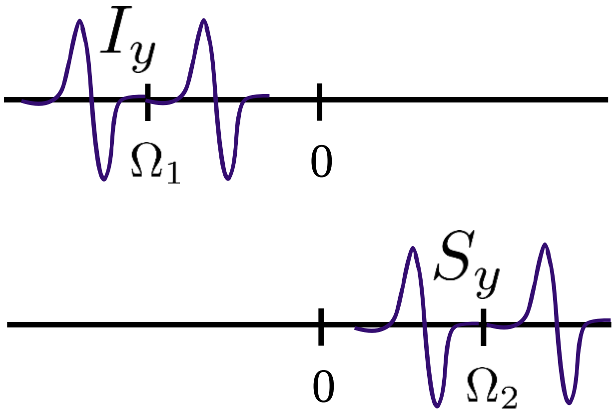
Product Operators

- Product operators for a non-interacting two-spin system.

Operator	Significance
I_x	*x*-component of *I*-spin magnetisation
I_y	*y*-component of *I*-spin magnetisation
I_z	*z*-component of *I*-spin magnetisation
S_x	*x*-component of S-spin magnetisation
S_y	*y*-component of *S*-spin magnetisation
S_z	*z*-component of *S*-spin magnetisation
$2I_xS_z$	Antiphase *I*-spin magnetisation
$2I_yS_z$	Antiphase *I*-spin magnetisation
$2I_zS_x$	Antiphase *S*-spin magnetisation
$2I_zS_y$	Antiphase *S*-spin magnetisation
$2I_zS_z$	Longitudinal two-spin order
$2I_xS_x$	Two-spin coherence
$2I_yS_y$	Two-spin coherence
$2I_xS_y$	Two-spin coherence
$2I_yS_x$	Two-spin coherence

Product Operators: The Looks





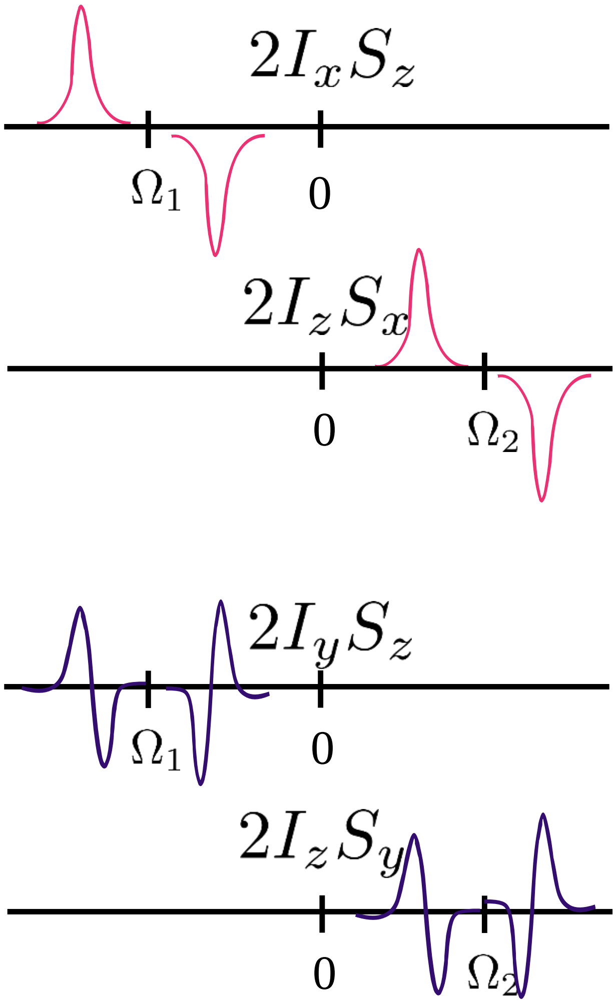
- In-phase magnetisation of spins *I* and *S*

- Absorption mode for magnetisation aligned along *x*

- Dispersion mode for magnetisation aligned along *y*

Operator
I_x
I_y
I_z
S_x
S_y
S_z
$2I_xS_z$
$2I_yS_z$
$2I_zS_x$
$2I_zS_y$
$2I_zS_z$
$2I_xS_x$
$2I_yS_y$
$2I_xS_y$
$2I_yS_x$

Product Operators: The Looks



- Anti-phase magnetization

- The operator $2I_xS_z$ is the *I*-spin magnetization that is anti-phase with respect to the coupling to spin-*S*

Operator
I_x
I_y
I_z
S_x
S_y
S_z
$2I_xS_z$
$2I_yS_z$
$2I_zS_x$
$2I_zS_y$
$2I_zS_z$
$2I_xS_x$
$2I_yS_y$
$2I_xS_y$
$2I_yS_x$

Product Operators: The Looks

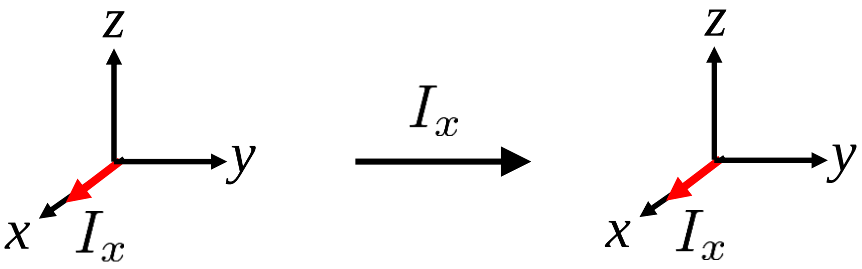
- Multiple-quantum coherence terms

Operator
I_x
I_y
I_z
S_x
S_y
S_z
$2I_xS_z$
$2I_yS_z$
$2I_zS_x$
$2I_zS_y$
$2I_zS_z$
$2I_xS_x$
$2I_yS_y$
$2I_xS_y$
$2I_yS_x$

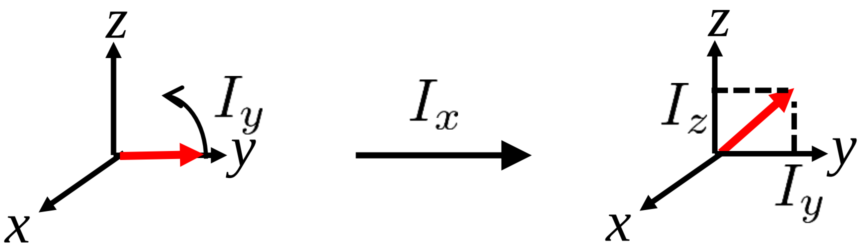
Product Operators: Example 1- RF Pulses

- Pulse of flip angle θ along the *x*-axis

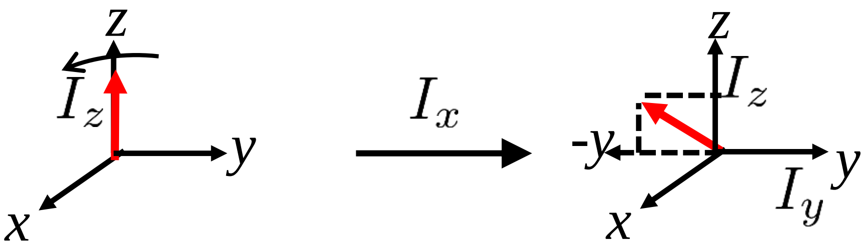
$$I_x \xrightarrow{I_x} I_x$$



$$I_y \xrightarrow{I_x} I_y cos\theta + I_z sin\theta$$



$$I_z \xrightarrow{I_x} I_z cos\theta - I_y sin\theta$$



Product Operators: Example 2- Chemical-Shift Evolution

- The relevant single-spin Hamiltonian

$$\mathcal{H}_{free} = \Omega_I I_z + \Omega_S S_z$$

Ω's being the offset

- Evolution under this Hamiltonian for I_x

$$I_x \xrightarrow{\mathcal{H}_{free}t} I_x cos\Omega_I t + I_y sin\Omega_I t$$

- Evolution under this Hamiltonian for I_y

$$I_y \xrightarrow{\mathcal{H}_{free}t} I_y cos\Omega_I t - I_x sin\Omega_I t$$

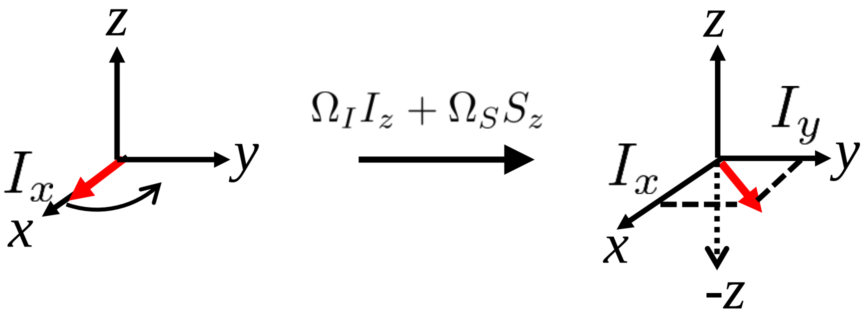
- Evolution under this Hamiltonian for I_z

$$I_z \xrightarrow{\mathcal{H}_{free}t} I_z$$

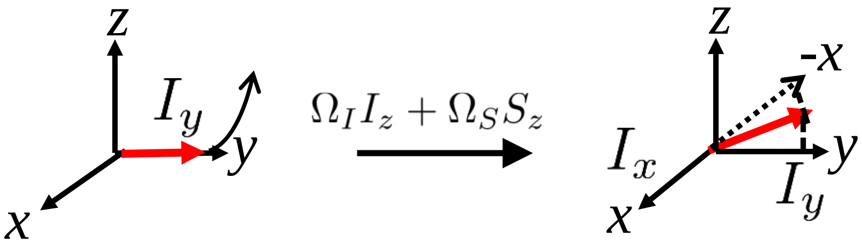
Product Operators: Example 2- Chemical-Shift Evolution

$$\mathcal{H}_{free} = \Omega_I I_z + \Omega_S S_z$$

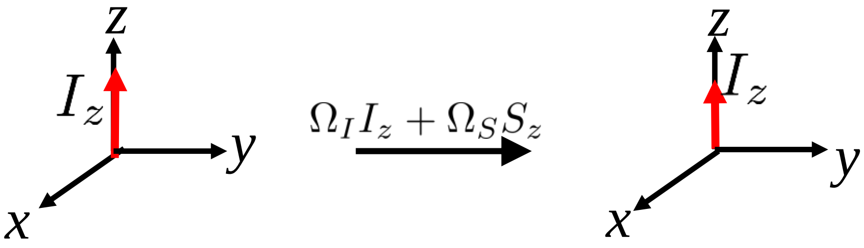
$$I_x \xrightarrow{\mathcal{H}_{free}t} I_x cos\Omega_I t + I_y sin\Omega_I t$$



$$I_y \xrightarrow{\mathcal{H}_{free}t} I_y cos\Omega_I t - I_x sin\Omega_I t$$



$$I_z \xrightarrow{\mathcal{H}_{free}t} I_z$$



Product Operators: Example 2- Chemical-Shift Evolution

- The relevant single-spin Hamiltonian

$$\mathcal{H}_{free} = \Omega_I I_z + \Omega_S S_z$$

Ω's being the offset

- Evolution under this Hamiltonian for I_x

$$I_x \xrightarrow{\Omega_I t I_z + \Omega_S t S_z} I_x cos\Omega_I t + I_y sin\Omega_I t$$

- Evolution of the $2I_xS_z$ term under a 90^0 pulse about the y-axis
  - The relevant Hamiltonian is

$$\mathcal{H} = \omega_{nut} I_y + \omega_{nut} S_y$$

$$2I_xS_z \xrightarrow{\frac{\pi}{2} I_y} -2I_zS_z \xrightarrow{\frac{\pi}{2} S_y} -2I_zS_x$$

$$\text{Remember}: \omega_{I,S} t = \frac{\pi}{2} \text{for a 90 pulse}$$

- This means that the anti-phase magnetisation of spin I has been transferred into anti-phase magnetisation of spin S. This is called coherence transfer and plays a great role in both one- and multi-dimensional NMR

Product Operators: Example 3- Scalar Coupling

$$\mathcal{H}_J = 2\pi J_{IS} I_z S_z; \; J_{IS} \text{ is the coupling in Hz.}$$

- Evolution under coupling causes interconversion of in-phase and anti-phase magnetisation

$$I_x \xrightarrow{\mathcal{H}_J = 2\pi J_{IS} I_z S_z} I_x cos\pi J_{IS}t + 2I_y S_z sin\pi J_{IS}t$$

- In-phase magnetisation along *x* becomes
 anti-phase along *y*

$$2I_x S_z \xrightarrow{\mathcal{H}_J = 2\pi J_{IS} I_z S_z} 2I_x S_z cos\pi J_{IS}t + 2I_y sin\pi J_{IS}t$$

- Anti-phase magnetisation along *x*
 becomes in-phase along *y*

$$-2I_z S_z \xrightarrow{\mathcal{H}_J = 2\pi J_{IS} I_z S_z} -2I_x S_y cos\pi J_{IS}t + 2S_y sin\pi J_{IS}t$$

- The above, but for spin S

- Complete interconversion of in-phase and anti-phase magnetization requires a delay of

$$\pi J_{IS}t = \frac{\pi}{2} \qquad \text{i.e. a delay of} \frac{1}{2J_{IS}}$$

$$I_x \xrightarrow{2\pi J_{IS} t I_z S_z \qquad t=\frac{1}{2J_{IS}}} 2I_y S_z$$

Product Operators: Some References

- O.W. Sorensen, G. W. Eich, M. H. Levitt, G. Bodenhausen, R. R. Ernst, Prog. NMR Sectrosc. 16, 163, 1983

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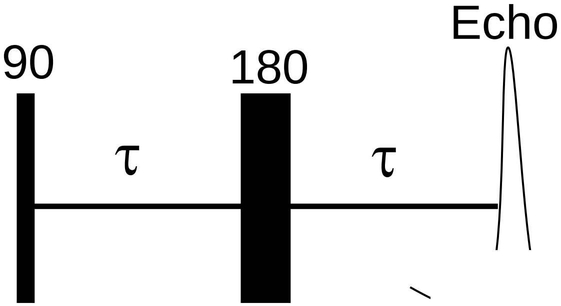
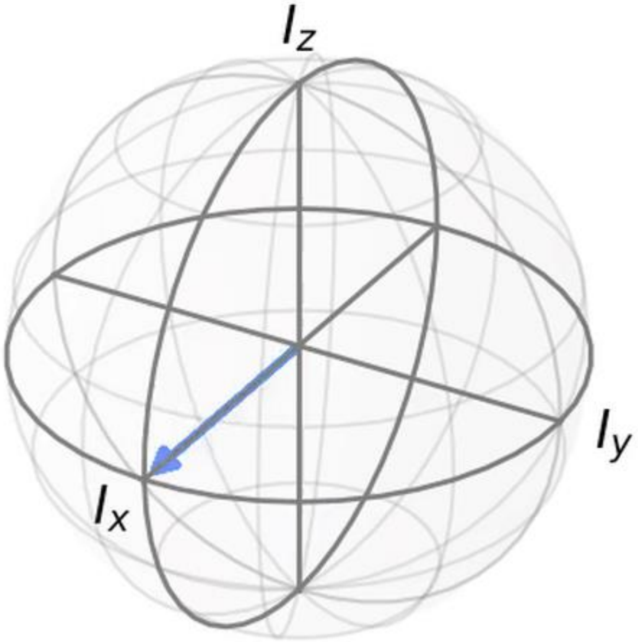
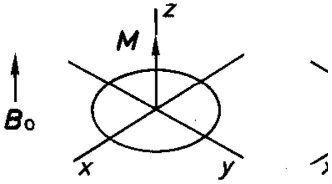
Experiments under Static Conditions

Spin Echoes: Spin-1/2



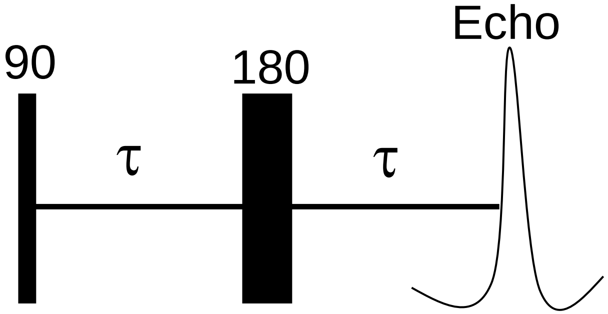
Spin-echo experiment
Refocuses chemical-shift interaction
and heteronuclear dipole-dipole interaction





RF pulses

Spin Echoes: Spin-1/2

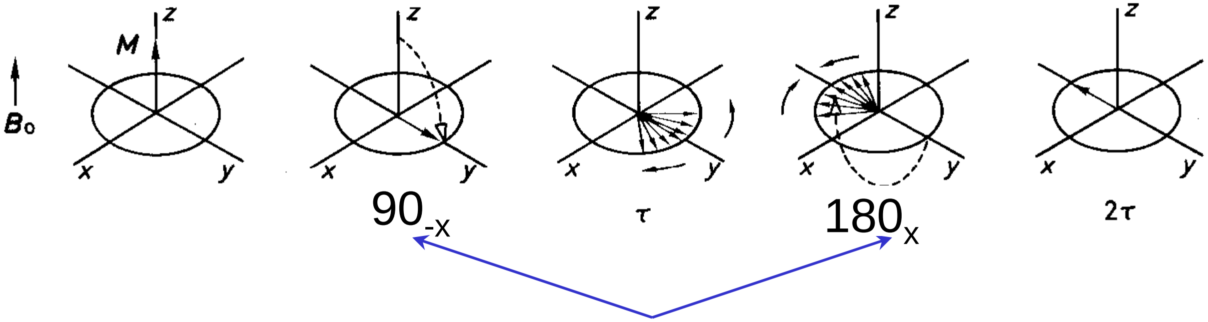


Spin-echo experiment
Refocuses chemical-shift interaction
and heteronuclear dipole-dipole interaction

$$\mathcal{H}_{CS} \propto I_z$$

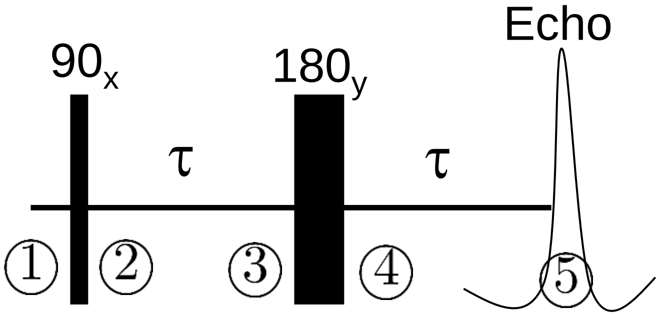
$$\mathcal{H}_{DD}^{hetero} \propto I_z S_z$$

Spin Echo (Hahn Echo) Sequence:



RF pulses

Spin Echoes: Spin-1/2-Density Matrix Analysis



Spin-echo experiment
Refocuses chemical-shift interaction
and heteronuclear dipole-dipole interaction

$$\mathcal{H} = \omega_0 I_z$$

$$\rho_{\textcircled{1}} = \rho^{eq} = \tfrac{1}{2}1 + \tfrac{1}{2}BI_z$$

$$\rho_{\textcircled{2}} = -\tfrac{1}{2}BI_y$$

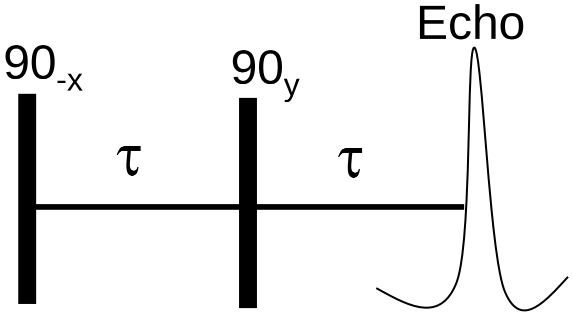
$$\rho_{\textcircled{3}} = \tfrac{1}{2}B[-I_y \cos\omega_0\tau + I_x \sin\omega_0\tau] \exp(-\lambda\tau)$$

$$\rho_{\textcircled{4}} = \tfrac{1}{2}B[-I_y \cos\omega_0\tau - I_x \sin\omega_0\tau] \exp(-\lambda\tau)$$

$$\begin{aligned}\rho_{\textcircled{5}} &= \frac{1}{2}B[-I_y \cos^2\omega_0\tau + I_x \cos\omega_0\tau \sin\omega_0\tau - I_x \cos\omega_0\tau \sin\omega_0\tau \\ &\quad - I_y[\sin^2\omega_0\tau] \exp(-\lambda\tau) \\ &= -\frac{1}{2}BI_y \exp(-\lambda\tau)\end{aligned}$$

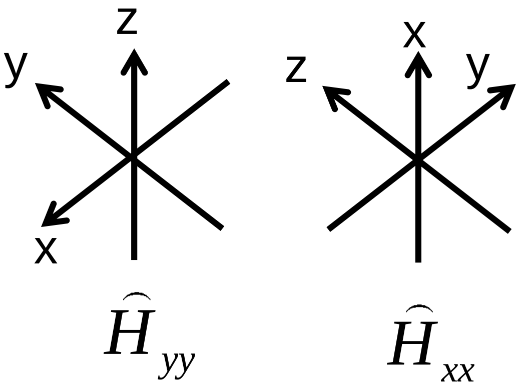
$\rho_{\textcircled{5}}$ is independent of the resonance offset, ω_0
$\Longrightarrow$ the signal at ⑤ is independent of B_0
$\Longrightarrow$ echo/refocussing

Spin Echoes: Spin-1/2 but Homonuclear



Echo experiment to refocus homonuclear dipole-dipole coupling

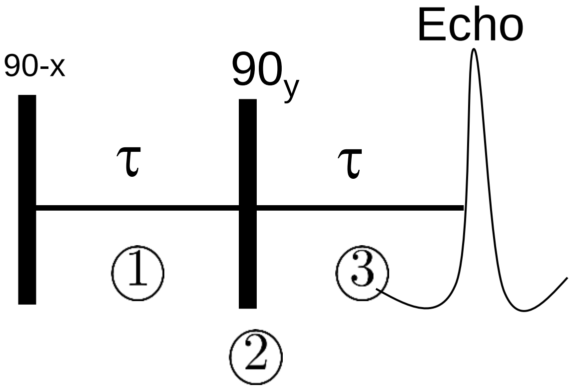
$$H = H_{zz} \sim [3I_{1z}I_{2z} - I_1 \cdot I_2]$$



$$H(2\tau) = H_{zz} + H_{xx} \sim -[3I_{1y}I_{2y} - I_1 \cdot I_2] = -H_{yy}$$

Refocussing of interactions

Homonuclear Spin Echo: Analysis



Echo experiment to refocus
homonuclear dipole-dipole coupling

$$\mathcal{H}_{DD}^{homo} \propto 3I_{1z}I_{2z} - I_1 \cdot I_2$$

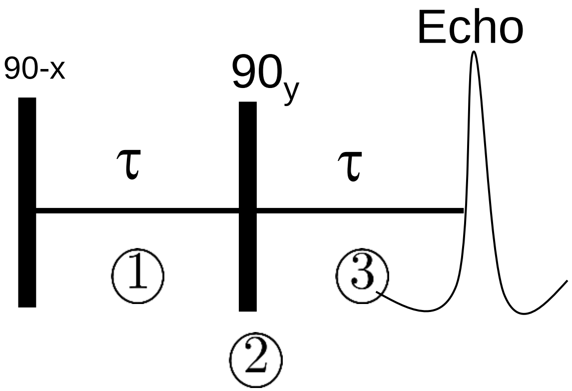
$$\rho(2\tau) = U_{\textcircled{3}}(2\tau,\tau)U_{\textcircled{2}}(\tau,\tau)U_{\textcircled{1}}((\tau,0)\rho(0)[U_{\textcircled{1}}(\tau,0)]^{-1}[U_{\textcircled{2}}(\tau,\tau)]^{-1}[U_{\textcircled{3}}]^{-1}((2\tau,\tau)$$

$$\rho(0) = I_{1y} + I_{2y}$$

$$U_{\textcircled{1}}(\tau,0) = e^{\frac{-i\mathcal{H}_{DD}^{homo}\tau}{\hbar}}, U_{\textcircled{2}}(\tau,\tau) = e^{\frac{-i\mathcal{H}_{DD}^{homo}\tau}{\hbar}}, U_{\textcircled{3}}(2\tau,\tau) = e^{\frac{-i\mathcal{H}_{DD}^{homo}\tau}{\hbar}}$$

$$\mathcal{H}_{DD}^{homo} = A(3I_{1z}I_{2z} - I_1 \cdot I_2)$$

Homonuclear Spin Echo: Analysis



Echo experiment to refocus
homonuclear dipole-dipole coupling

$$\mathcal{H}_{DD}^{homo} \propto 3I_{1z}I_{2z} - I_1 \cdot I_2$$

$$U_{\textcircled{1}}(\tau,0) = e^{\frac{-i\mathcal{H}_{DD}^{homo}\tau}{\hbar}}$$

$$U_{\textcircled{2}}(\tau,\tau)U_{\textcircled{1}}(\tau,0) = e^{-i\frac{\pi}{2}I_y}e^{\frac{-i\mathcal{H}_{DD}^{homo}\tau}{\hbar}} = e^{-i\frac{\pi}{2}I_y}e^{\frac{-i\mathcal{H}_{DD}^{homo}\tau}{\hbar}}e^{i\frac{\pi}{2}I_y}e^{-i\frac{\pi}{2}I_y}$$

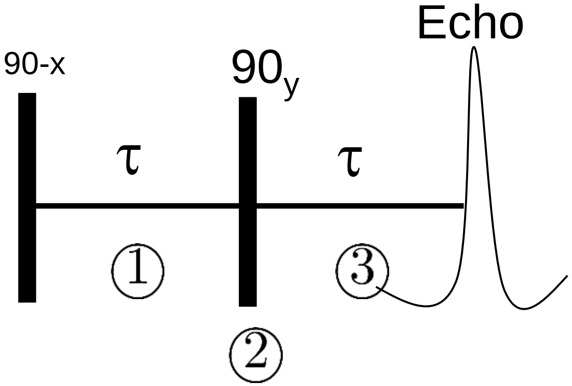
$$= e^{-iA(3I_{1x}I_{2x}-I_1\cdot I_2)\tau}e^{-i\frac{\pi}{2}I_y}$$

$$U_{\textcircled{3}}(2\tau,\tau)U_{\textcircled{2}}(\tau,\tau)U_{\textcircled{1}}(\tau,0) = e^{-iA(3I_{1z}I_{2z}-I_1\cdot I_2)\tau}$$

$$e^{-iA(3I_{1x}I_{2x}-I_1\cdot I_2)\tau}e^{-i\frac{\pi}{2}I_y}$$

$$= e^{-iA(I_1\cdot I_2-3I_{1y}I_{2y})\tau}e^{-i\frac{\pi}{2}I_y}$$

Homonuclear Spin Echo: Analysis



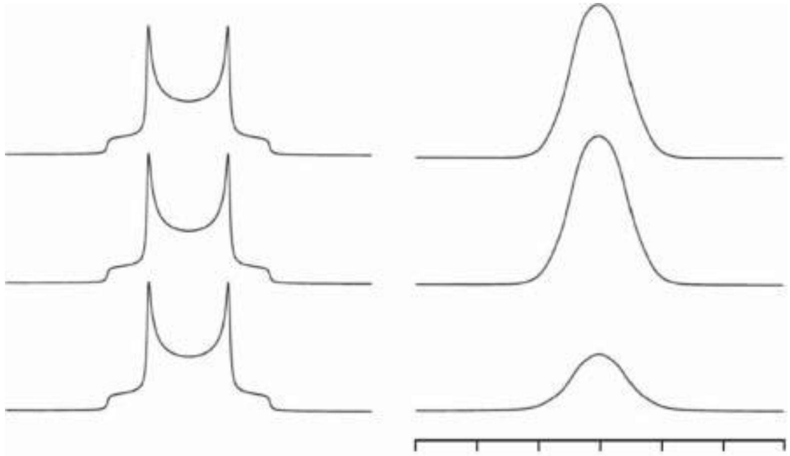
Echo experiment to refocus homonuclear dipole-dipole coupling

$$\mathcal{H}_{DD}^{homo} =\propto 3I_{1z}I_{2z} - I_1 \cdot I_2$$

$$\rho(2\tau) = U_{\textcircled{3}}(2\tau,\tau)U_{\textcircled{2}}(\tau,\tau)U_{\textcircled{1}}((\tau,0)\rho(0)[U_{\textcircled{1}}(\tau,0)]^{-1}[U_{\textcircled{2}}(\tau,\tau)]^{-1}[U_{\textcircled{3}}]^{-1}((2\tau,\tau)$$

$$U_{\textcircled{3}}(2\tau,\tau)U_{\textcircled{2}}(\tau,\tau)U_{\textcircled{1}}(\tau,0) = e^{-iA(I_1\cdot I_2-3I_{1y}I_{2y})\tau}e^{-i\frac{\pi}{2}I_y}$$

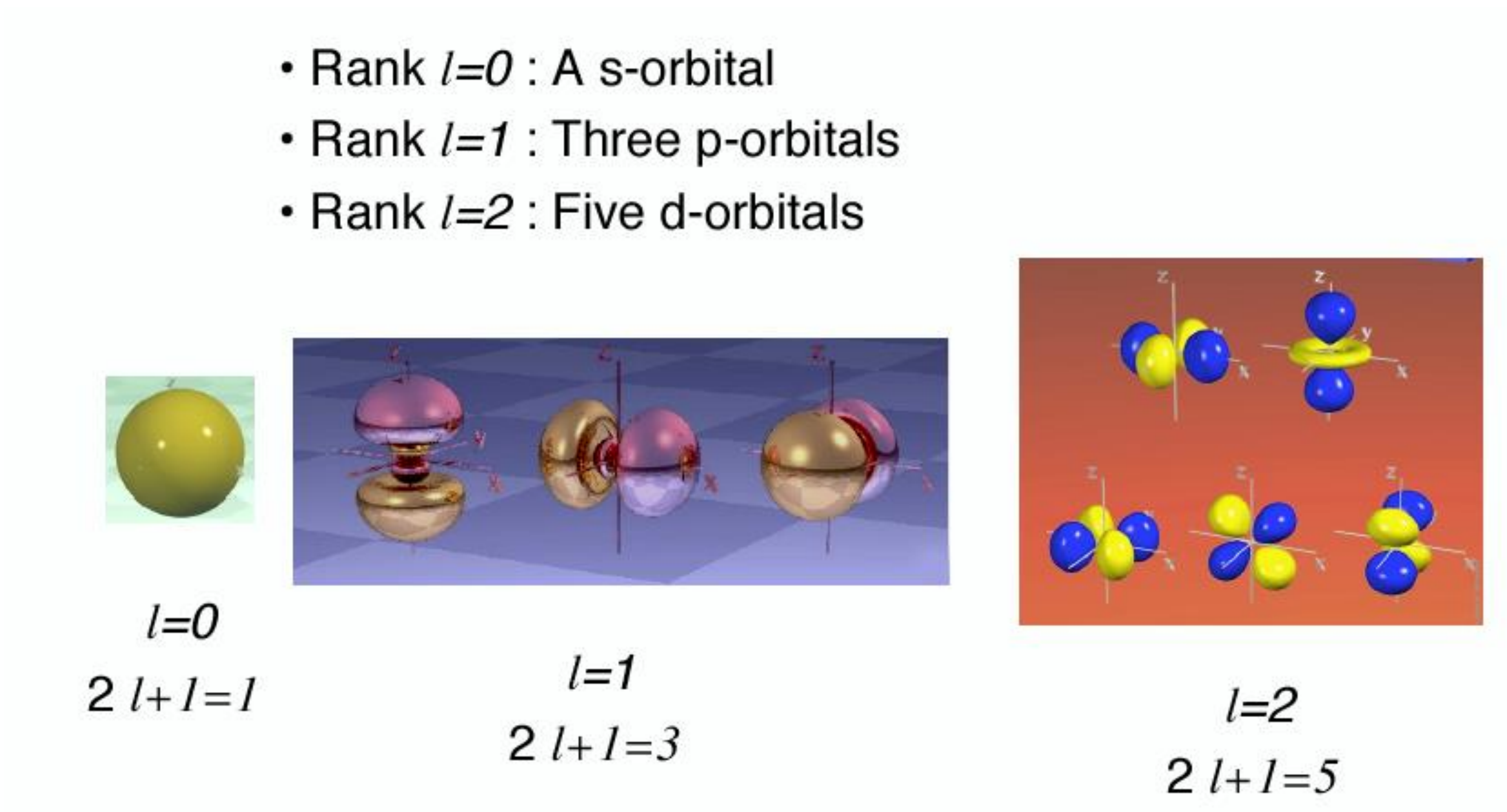
$$\rho(2\tau) = I_{1y} + I_{2y} = \rho(0)$$



That is the echo!

Mueller and Geppi, Solid State NMR, Principles, Methods and Applications

Spherical Tensors: Examples



- Rank $l=0$: A s-orbital
- Rank $l=1$: Three p-orbitals
- Rank $l=2$: Five d-orbitals

$l=0$

$2l+1=1$

$l=1$

$2l+1=3$

$l=2$

$2l+1=5$

Spherical Tensors

A spherical tensor of rank l is a set of 2 l +1 objects such that when any of them is rotated in three dimensions, the result is a superposition of the same set of objects

Rotation of spherical tensors

$$\boldsymbol{R(\Omega) T_{lm} R(\Omega)^{\dagger} = \sum_{m'=-l}^{l} T_{lm'} D^{l}_{mm'}(\Omega)}$$

Complex numbers

Rotation operator

Spherical tensor element of rank l

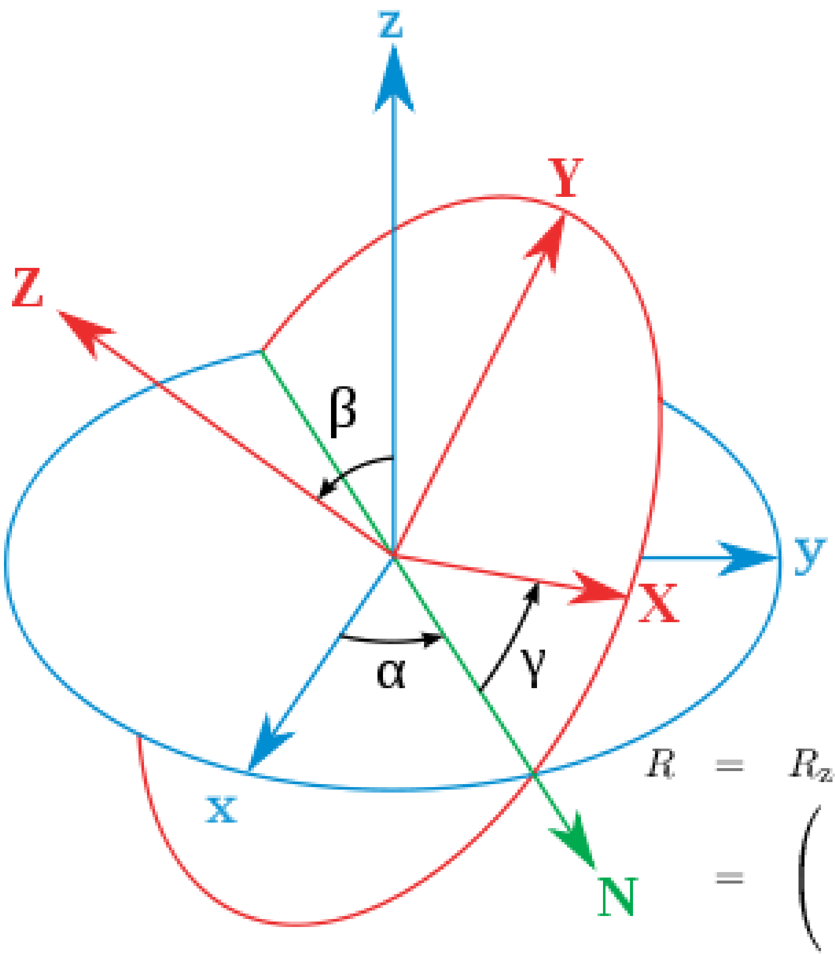
Rotational Signatures of the Internal Spin Interactions

Interaction	Space Rank l	Spin Rank λ
Iso-CS	0	1
CSA	2	1
J	0	0
Hetero-DD	2	1
Homo-DD	2	2

Rotation of molecules

Rotation of spins

Euler Angles



$$\begin{aligned}
R &= R_{z''}(\gamma)\cdot R_{y'}(\beta)\cdot R_z(\alpha)\\
&= \begin{pmatrix} c\gamma & s\gamma & 0\\ -s\gamma & c\gamma & 0\\ 0 & 0 & 1\end{pmatrix}\cdot\begin{pmatrix} c\beta & 0 & -s\beta\\ 0 & 1 & 0\\ s\beta & 0 & c\beta\end{pmatrix}\cdot\begin{pmatrix} c\alpha & s\alpha & 0\\ -s\alpha & c\alpha & 0\\ 0 & 0 & 1\end{pmatrix}\\
&= \begin{pmatrix} c\gamma c\beta c\alpha - s\gamma s\alpha & c\gamma c\beta s\alpha + s\gamma c\alpha & -c\gamma s\beta\\ -s\gamma c\beta c\alpha - c\gamma s\alpha & -s\gamma c\beta s\alpha + c\gamma c\alpha & s\gamma s\beta\\ s\beta c\alpha & s\beta s\alpha & c\beta\end{pmatrix}
\end{aligned}$$

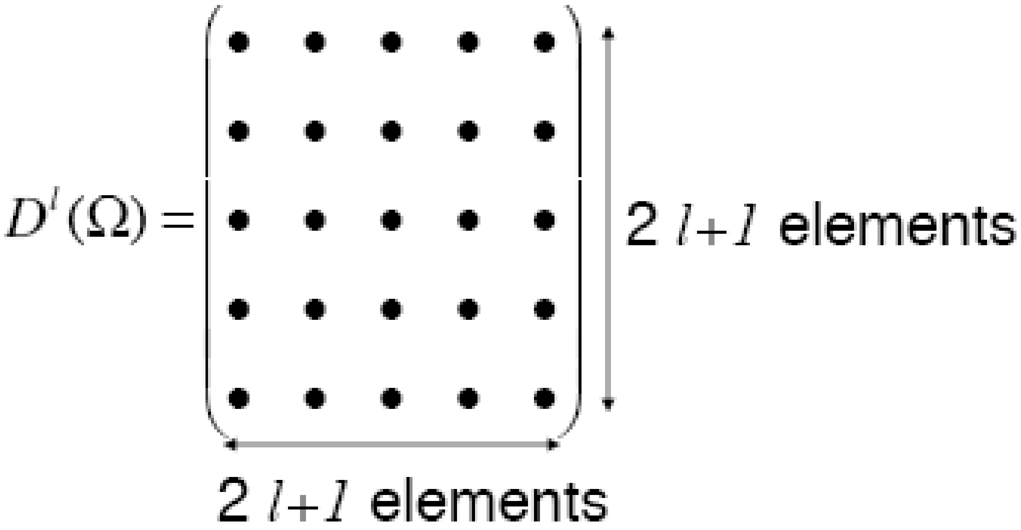
Rotation of Spherical Tensors

$$R(\Omega)T_{lm}R(\Omega)^{\dagger} = \sum_{m'=-l}^{l} T_{lm'}D^{l}_{mm'}(\Omega)$$

Rotation operator
for Euler angles Ω

Elements of Wigner matirx
for Euler angles Ω

Wigner Matrices



$$D^l_{m'm}(\Omega) = \exp(-im'\alpha)\, d^l_{m'm}(\beta) \exp(-im\gamma)$$

Wigner matrix element

Reduced Wigner matrix element

Reduced Wigner Matrix Elements (Rank 0 and 1)

$$d^0(\beta) = 1$$

$$d^1_{00}(\beta)$$

$$d^1_{mm'}(\beta) = \begin{array}{cc} \begin{pmatrix} \frac{1}{2}(1+\cos\beta) & -\sin\beta/\sqrt{2} & \frac{1}{2}(1-\cos\beta) \\ \sin\beta/\sqrt{2} & \cos\beta & -\sin\beta/\sqrt{2} \\ \frac{1}{2}(1-\cos\beta) & \sin\beta/\sqrt{2} & \frac{1}{2}(1+\cos\beta) \end{pmatrix} & \begin{array}{l} m=-1 \\ m=0 \\ m=1 \end{array} \\ \begin{array}{ccc} m'=-1 & \qquad m'=0 & \qquad m'=1 \end{array} & \end{array}$$

Reduced Wigner Matrix Elements (Rank 2)

$$d^2_{00}(\beta)$$

$$d^2_{mm'}(\beta)=$$

$$\begin{array}{cccccc}
 & & & & & m=-2 \\
\frac{1}{4}(1+cos\beta)^2 & -\frac{1}{2}sin\beta(1+cos\beta) & \sqrt{\frac{3}{8}}sin^2\beta & -\frac{1}{2}sin\beta(1-cos\beta) & \frac{1}{4}(1-cos\beta)^2 & \\
\frac{1}{2}sin\beta(1+cos\beta) & \frac{1}{2}(2cos^2\beta+cos\beta-1) & -\sqrt{\frac{3}{8}}sin2\beta & \frac{1}{2}(2cos^2\beta-cos\beta-1) & -\frac{1}{2}sin\beta(1-cos\beta) & \\
\sqrt{\frac{3}{8}}sin^2\beta & \sqrt{\frac{3}{8}}sin2\beta & \frac{1}{2}(3cos^2\beta-1) & -\sqrt{\frac{3}{8}}sin2\beta & \sqrt{\frac{3}{8}}sin^2\beta & \\
\frac{1}{2}sin\beta(1-cos\beta) & -\frac{1}{2}(2cos^2\beta-cos\beta-1) & \sqrt{\frac{3}{8}}sin2\beta & \frac{1}{2}(2cos^2\beta+cos\beta-1 & -\frac{1}{2}sin\beta(1+cos\beta) & \\
\frac{1}{4}(1-cos\beta)^2 & \frac{1}{2}sin\beta(1-cos\beta) & \sqrt{\frac{3}{8}}sin^2\beta & \frac{1}{2}sin\beta(1+cos\beta) & \frac{1}{4}(1+cos\beta)^2 & \\
 & & & & & m=2 \\
m'=-2 & m'=-1 & m'=0 & m'=1 & m'=2 &
\end{array}$$

Summary of NMR Interactions

Interaction	**Liquids**	**Solids**	**Field (B_0) dependence**	**Notes**
Zeeman (chemical shift)	Line position	Line position and structure	Linear	For liquids this is just the position of each peak, but for solids each peak can have a range of chemical shifts depending on the orientation of its electronic environment with the magnetic field. This is known as the chemical shift anisotropy and can have a larger range for nuclei in more asymmetric electronic environments.
Radiofrequency pulses	Amplitude	Amplitude	None	Same for liquids and solids
J coupling	Line structure	Not normally observed (?!)	None*	Basically the same for solids and liquids but not normally observed in solids due to much wider lines
Dipolar coupling	Relaxation	Line structure	None*	Averages to zero in liquids due to isotropic motions (but does still result in relaxation effects). In solids can completely dominate the spectra especially for large γ nuclei like protons
Quadrupolar interaction (spin > ½)	Relaxation	Line structure	None*	Averages to zero in liquids due to isotropic motions, but in solids can completely dominate the spectra especially for nuclei with large quadrupole moments (^{14}N, ^{2}H) in asymmetric electronic environments.

***To first order**

Magic-Angle Spinning, MAS

Reality

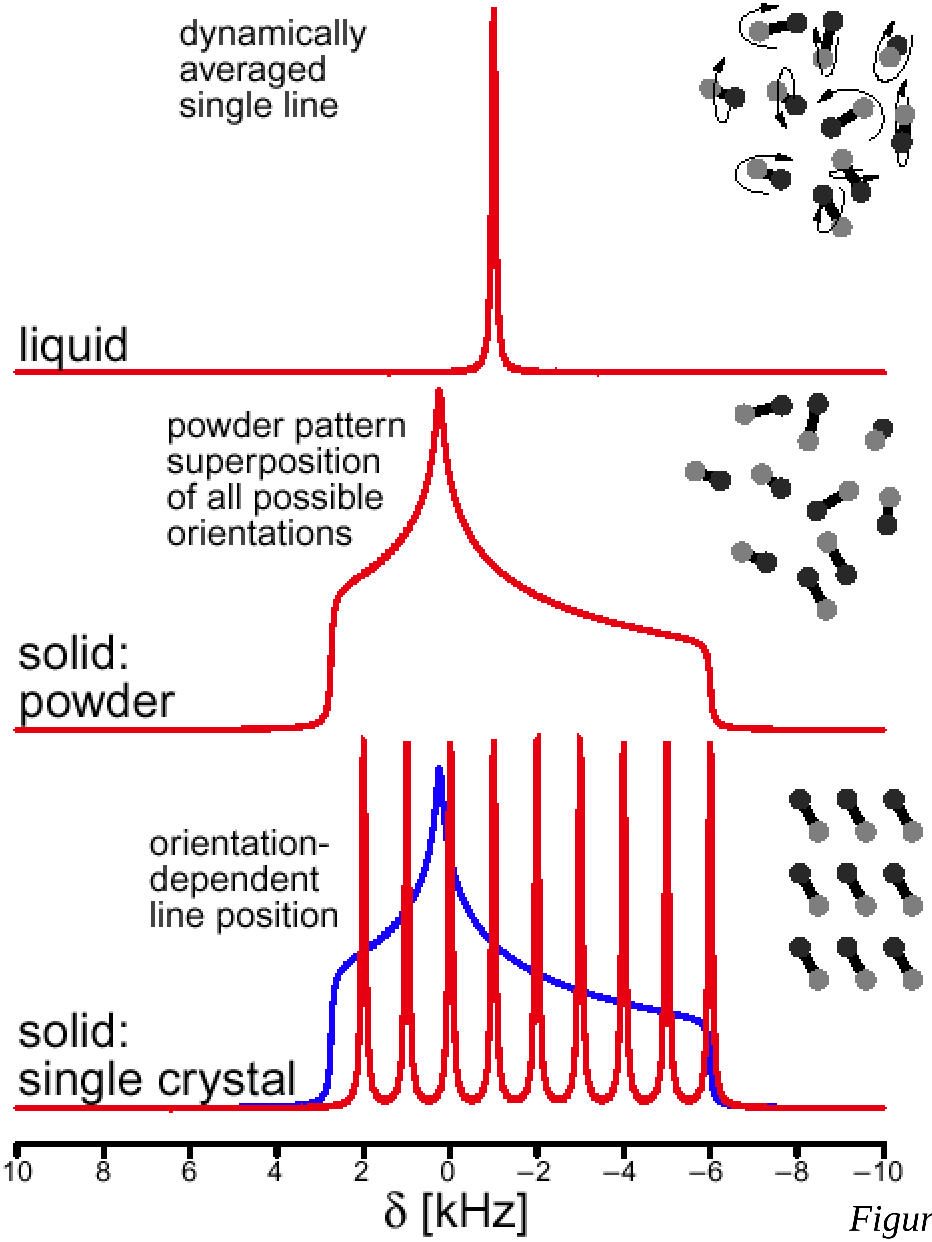
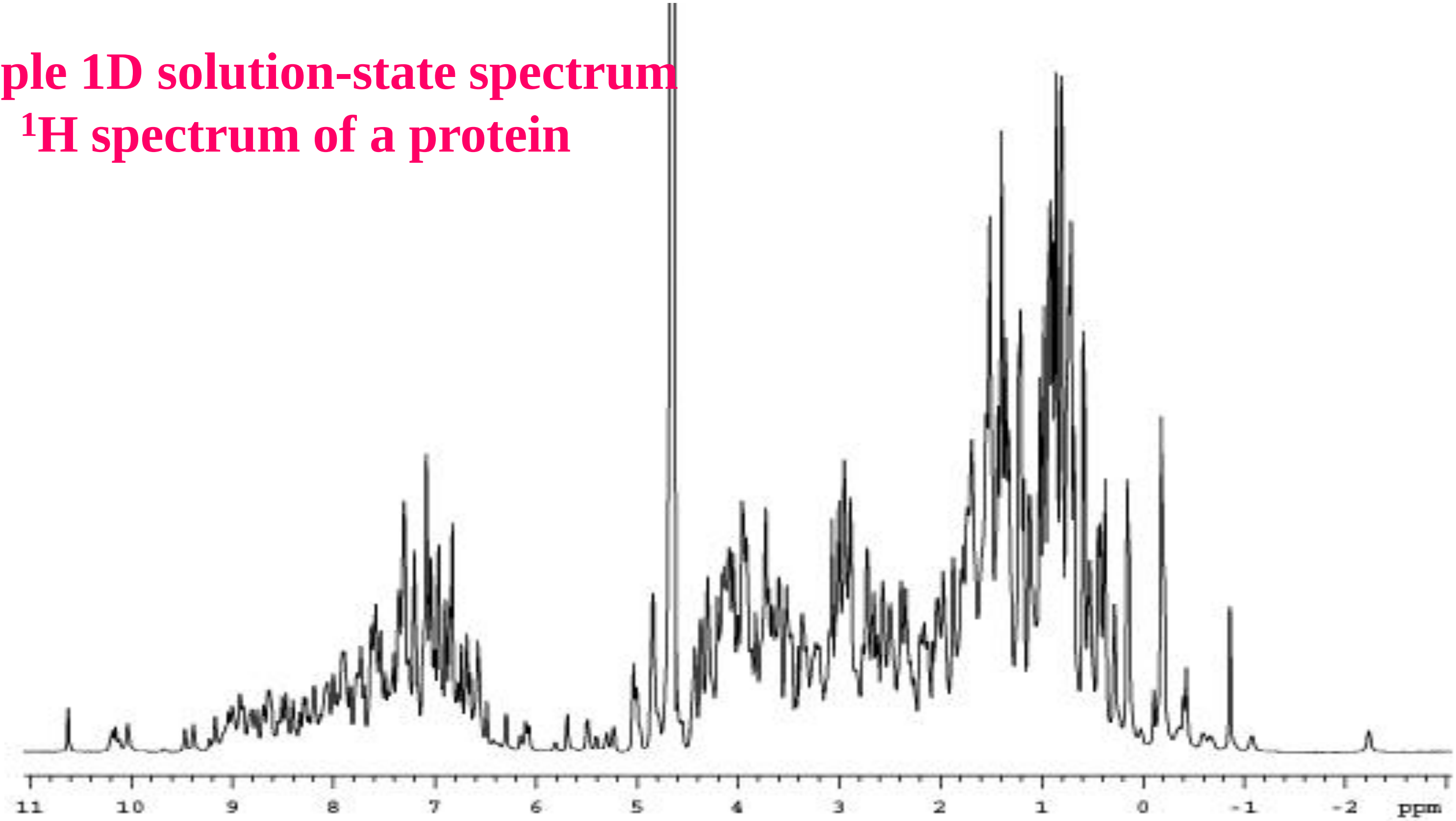


Figure courtesy: Matthias Ernst

Reality

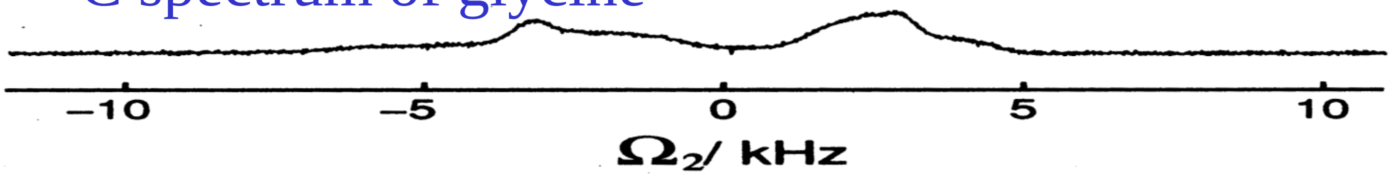
Simple 1D solution-state spectrum

^{1}H spectrum of a protein



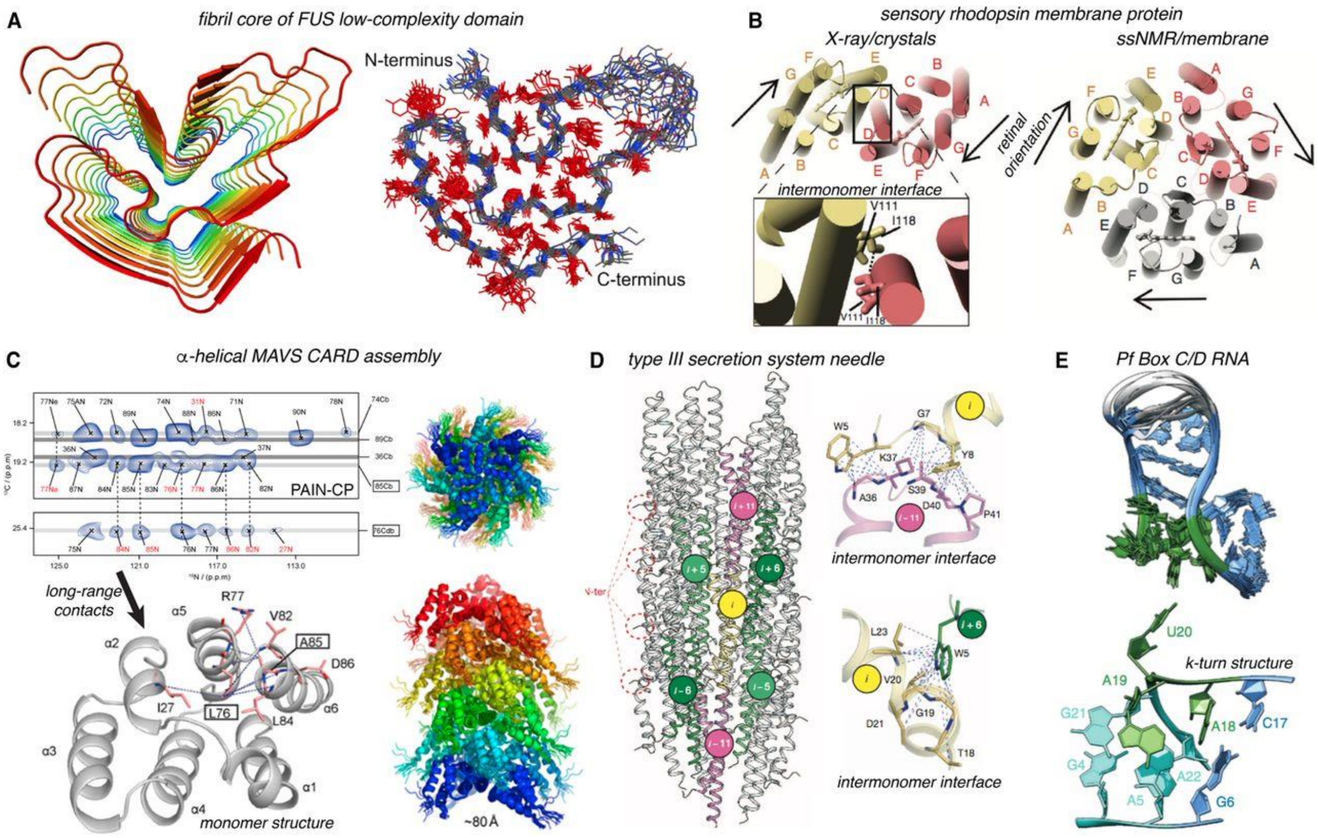
Simple 1D solid-state spectrum

^{13}C spectrum of glycine



Solid-State NMR at Frontiers

- Higher fields
- Higher MAS
- Better coils
- Proton detection
    - Sensitivity
    - Sample volume

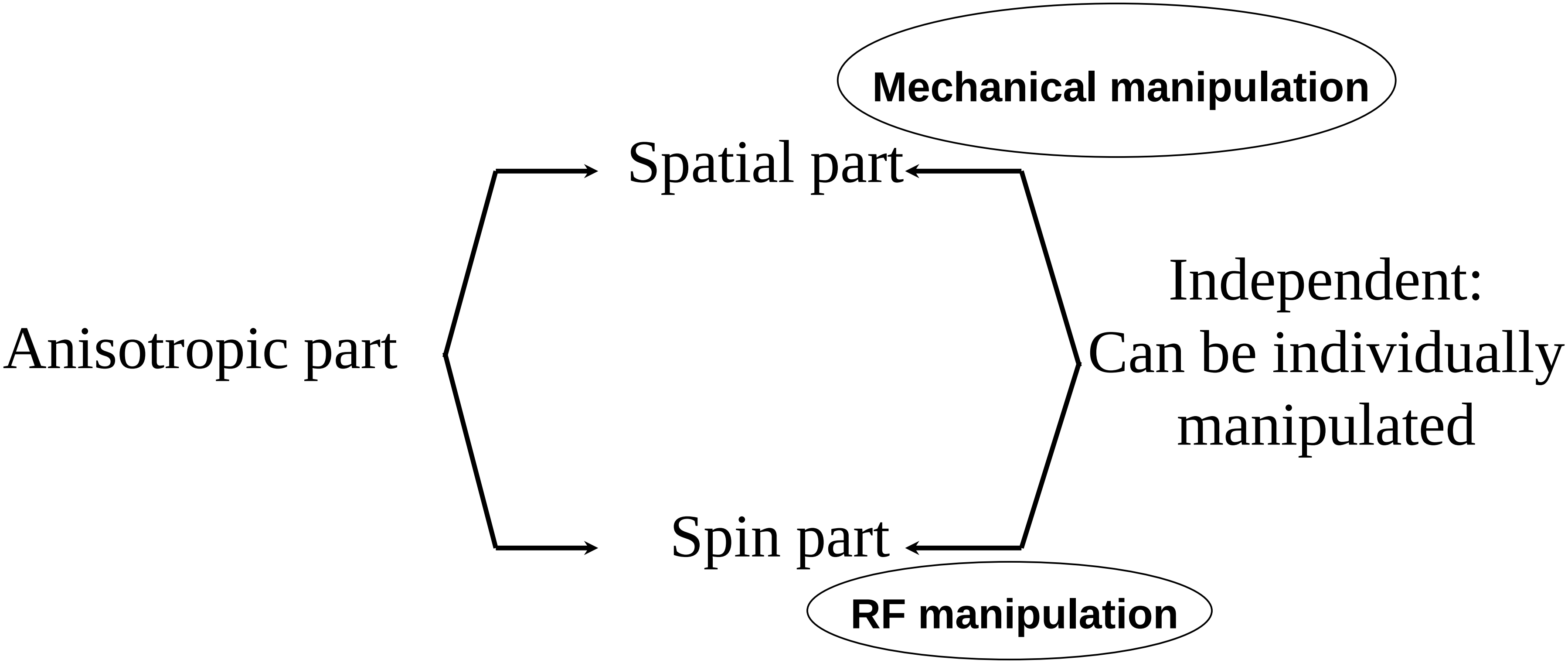


Patrick van del Wel, Emerging topics in life sciences, 2, 57, 2018
Reif, Ashbrook, Emsley, Hong, Nat. Rev. Methods Primers, 2021:1:2.doi: 10.1038/s43586-020-00002-1
Ahlawat, Mote, Lakomek, Agarwal, Chem. Rev. 122, 9643-9737, 2022

Remedies

- **Mimick the inherent averaging processes in solution-state to obtain high-resolution, isotropic information**
- **Goal #1:(Resolution and Sensitivity): Remove anisotropic parts and retain only isotropic parts: Decoupling**
- **Goal #2: Get back the anisotropic parts for elucidation of geometry parameters: Recoupling**

Remedies



Mechanical manipulation

Spatial part

Anisotropic part

Independent:
Can be individually
manipulated

Spin part

RF manipulation

Hamiltonians and their Manipulation

$$H_{TOTAL} = \left[H_{SPACE} \otimes H_{SPIN} \right]^{anisotropic} + H^{isotropic}$$

Spatial Part: Manipulation

- Rotating the crystallites in a given powder
- Sample spinning: Mechanical manipulation
- Easier to visualise
- Difficult to implement

Spin Part: Manipulation

- Rotating the spins in a given powder
- Spins rotation: Manipulation by RF pulses
- Easier to implement
- Difficult to visualise

Interaction	Space Rank, l	Spin Rank, λ
Iso-CS	0	1
CSA	2	1
J	0	0
Hetero-DD	2	1
Homo-DD	2	2

Hamiltonians and their Manipulation

$$\mathrm{H}_{TOTAL} = \left[\mathrm{H}_{SPACE} \otimes \mathrm{H}_{SPIN}\right]^{anisotropic} + \mathrm{H}^{isotropic}$$

$$H = \sum_{m=-l}^{l} [A_{lm}]^L [T_{l-m}]^L$$

Space part

Spin part

Interaction	Space Rank, l	Spin Rank, λ
Iso-CS	0	1
CSA	2	1
J	0	0
Hetero-DD	2	1
Homo-DD	2	2

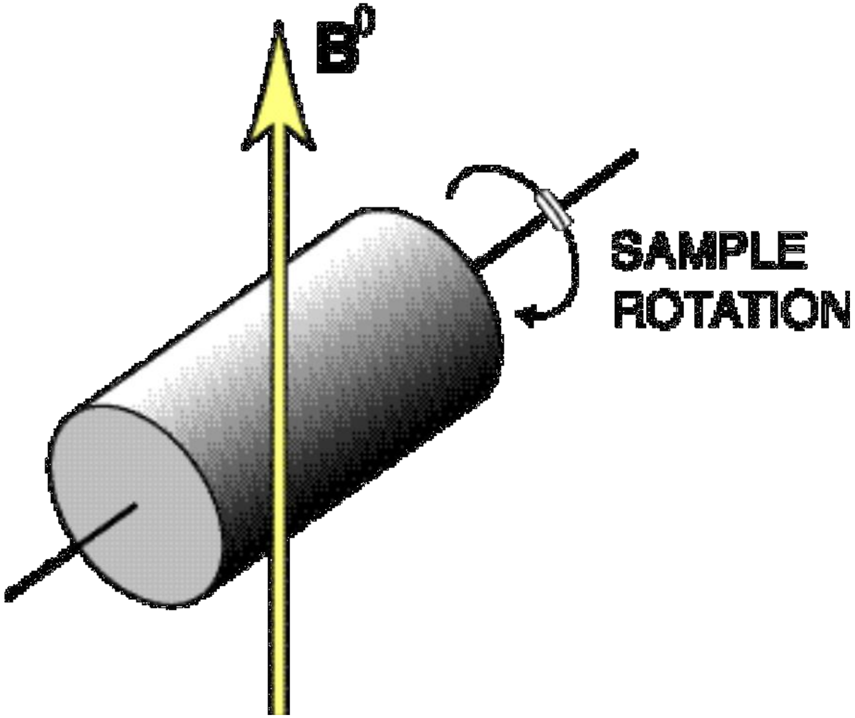
$$H = \sum_{m=-2}^{2} [A_{2m}]^L [T_{2-m}]^L$$

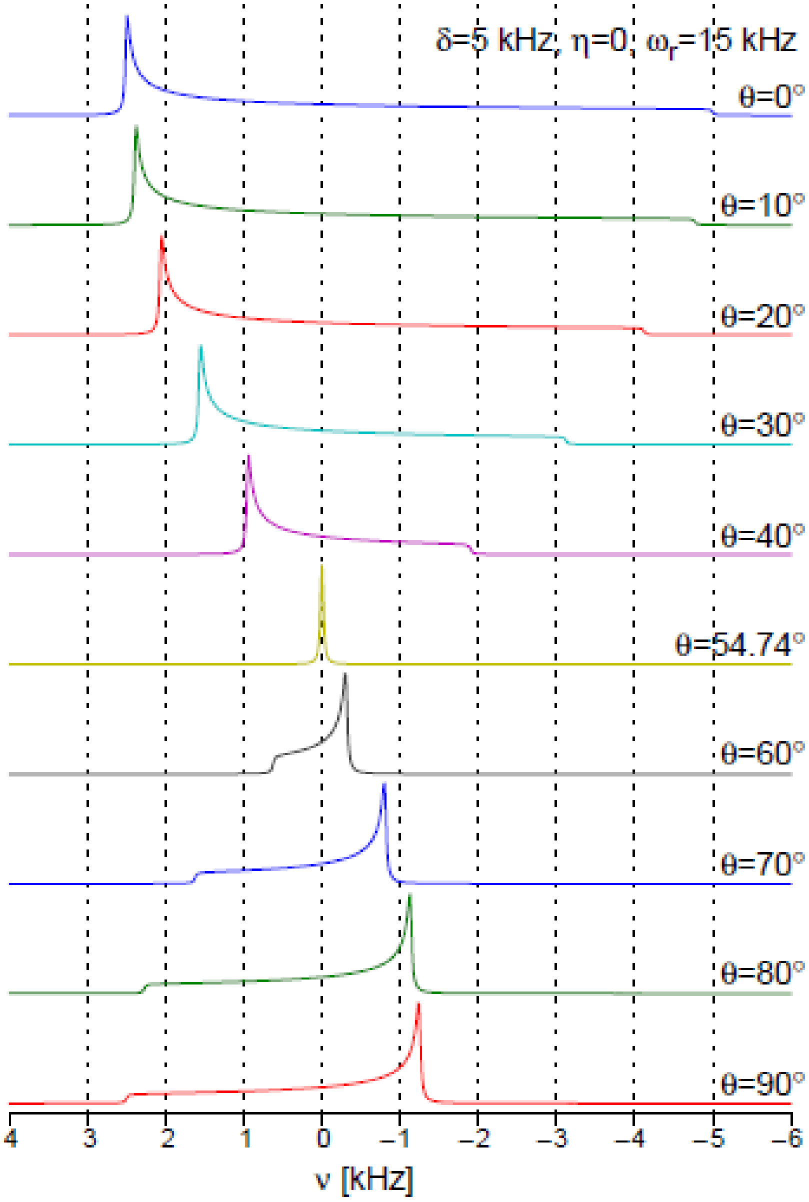
NMR case

$$H = [A_{20}]^L [T_{20}]^L$$

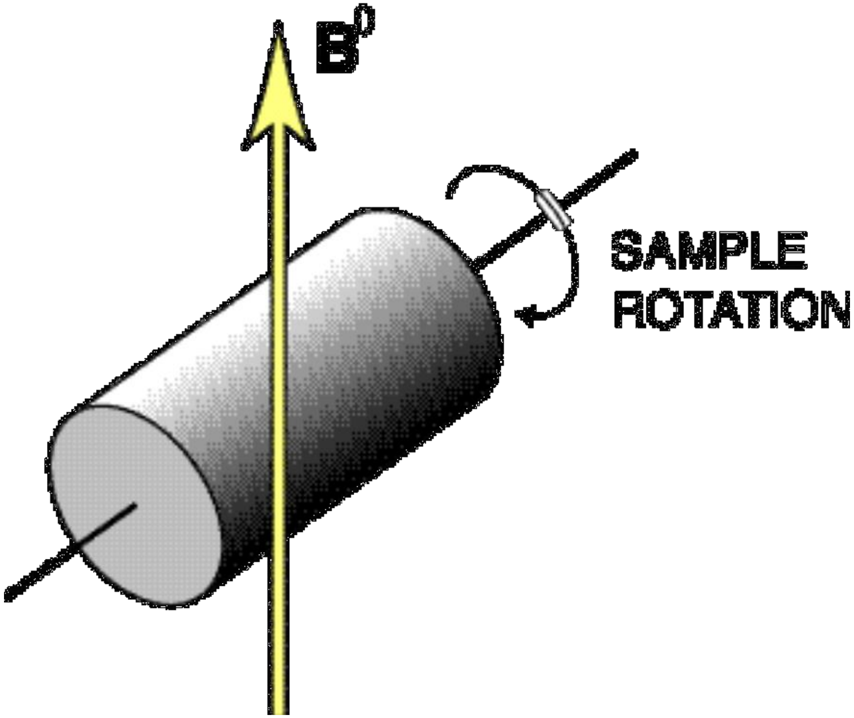
High field, secular approximation

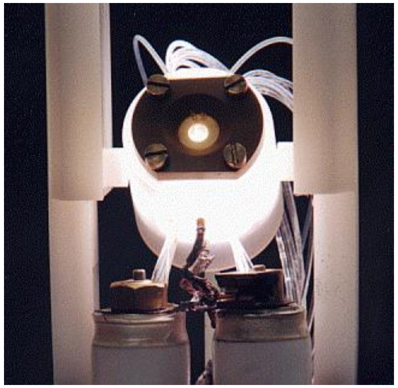
Powder at Various Rotor Angles: Spinning





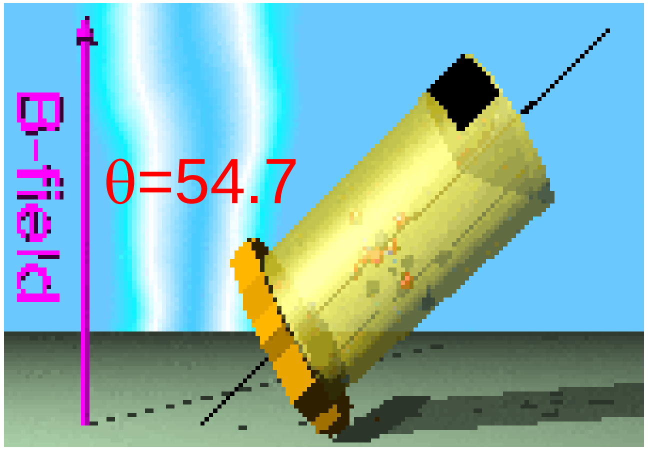
Magic-Angle Spinning (MAS)

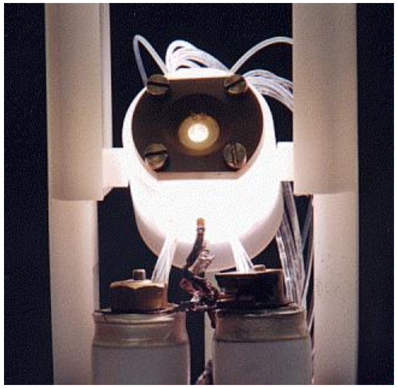




Average out the chemical shift anisotropy, to achieve good sensitivity and resolution

Magic-Angle Spinning (MAS)

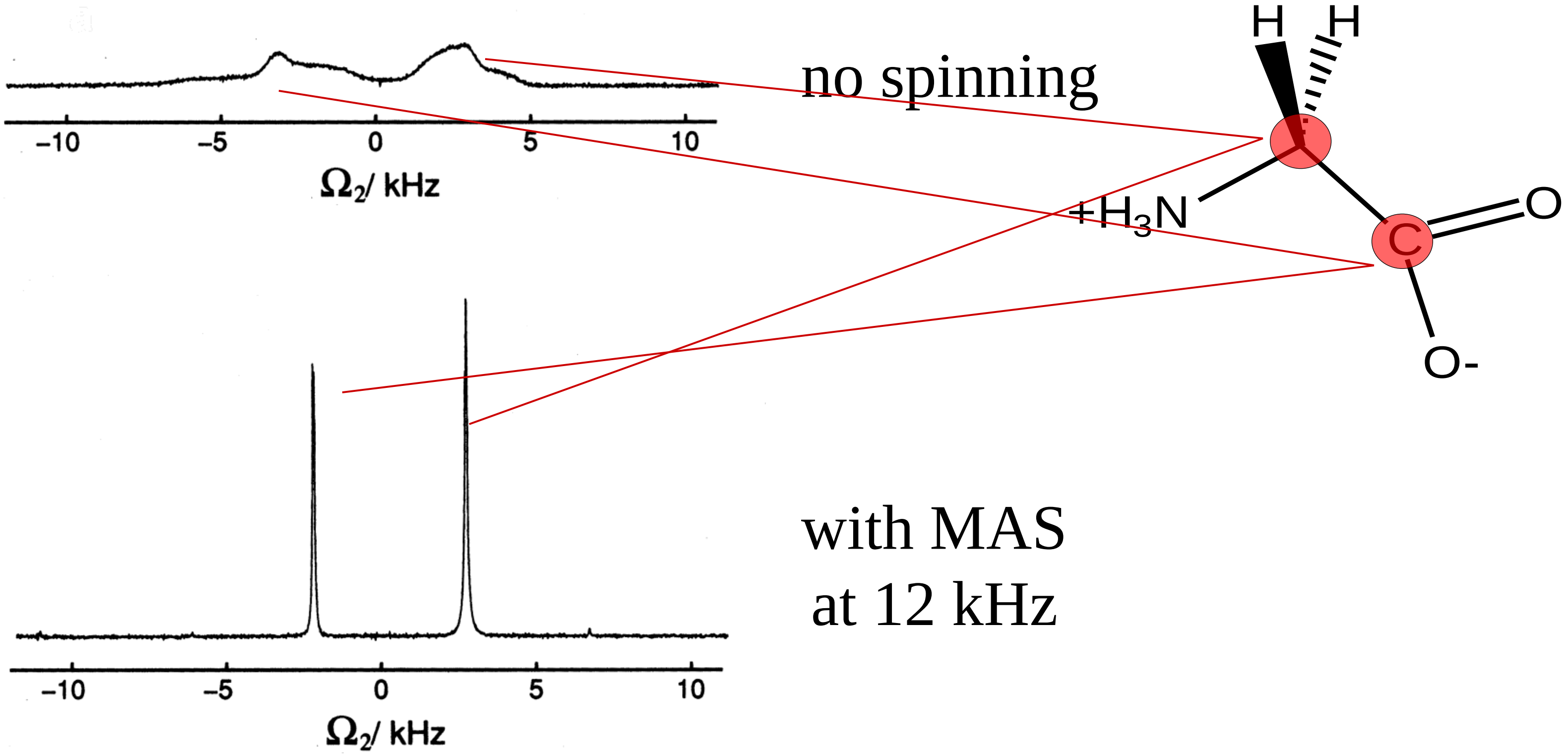




Averages out the chemical shift anisotropy, to achieve good sensitivity and resolution

Resolution and Sensitivity Enhancement by MAS

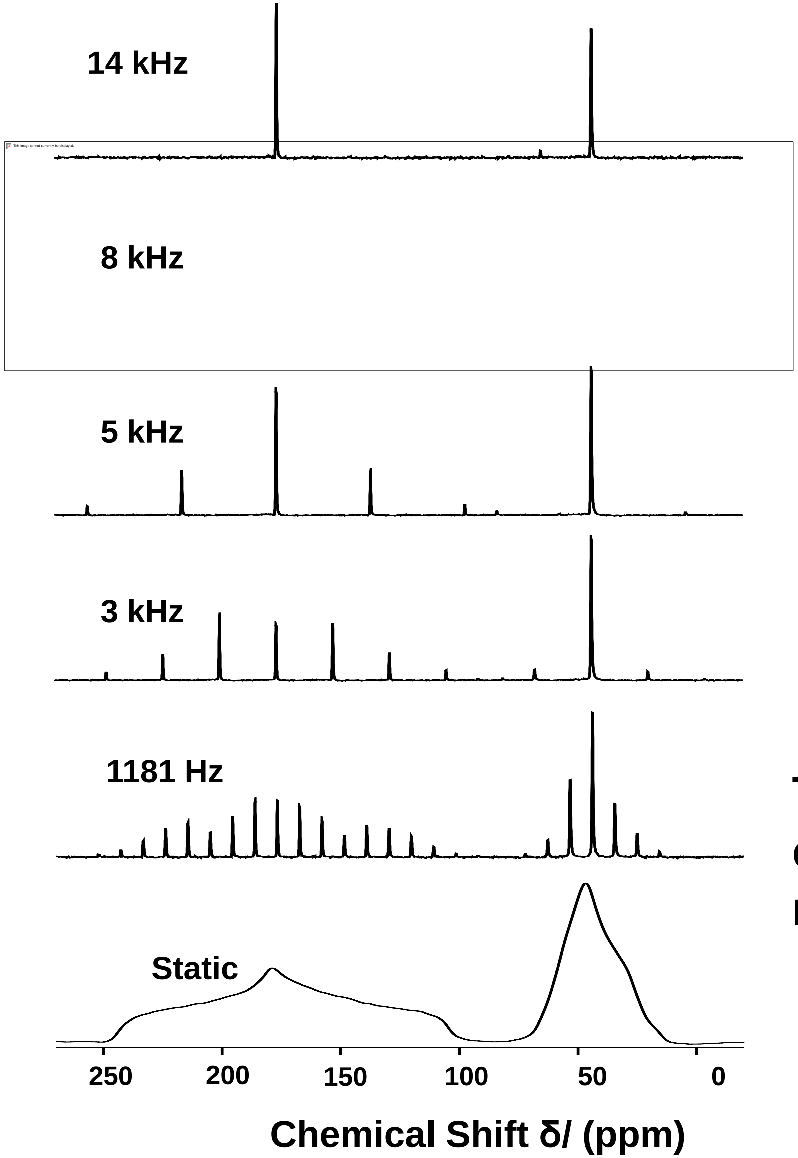
^{13}C spectra of [$^{13}C_2$]-glycine



no spinning

with MAS
at 12 kHz

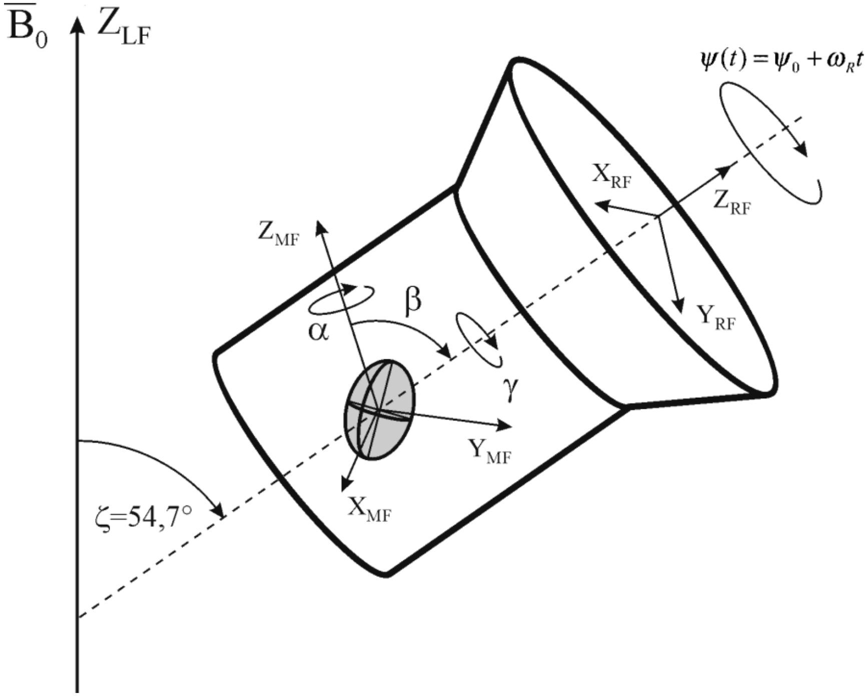
Magic-Angle-Spinning Spectra: Resolution Enhancement

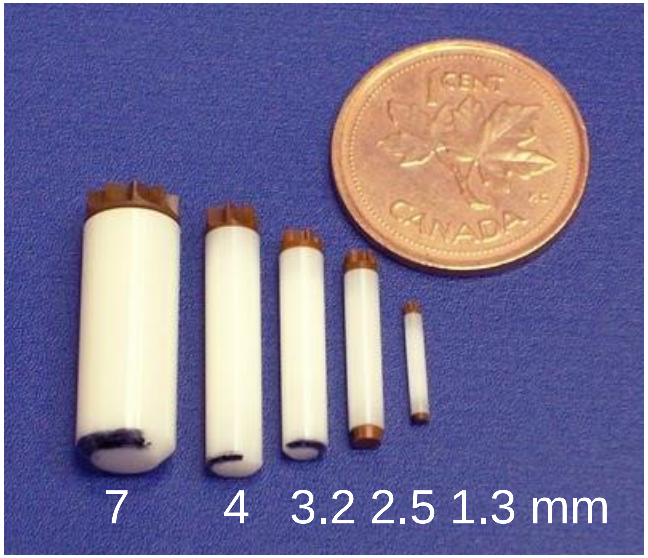


Glycine

The powder pattern breaks up into a centreband and sidebands spaced at integer multiples of the rotor frequency

MAS Rotor Types

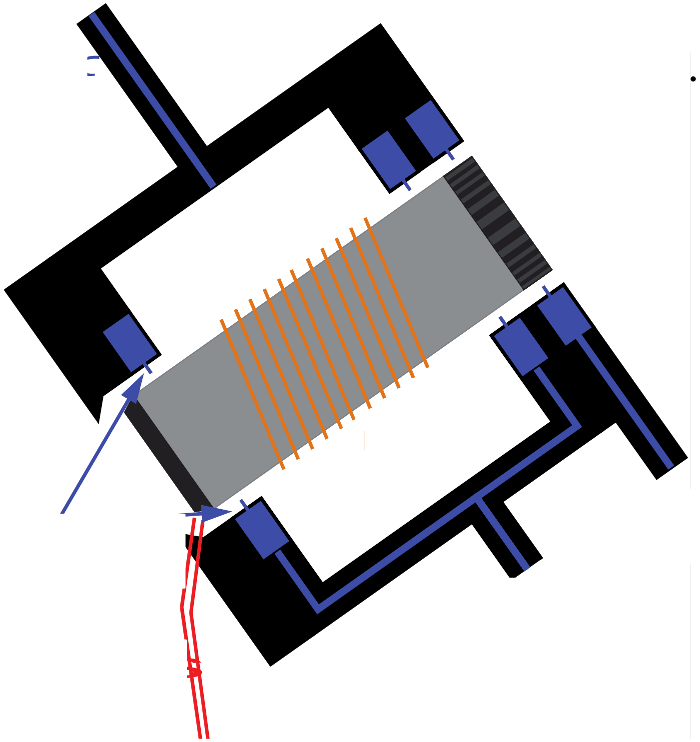




7 4 3.2 2.5 1.3 mm

Angular Frequency to Linear Velocity

Magic Angle Spinning (MAS)



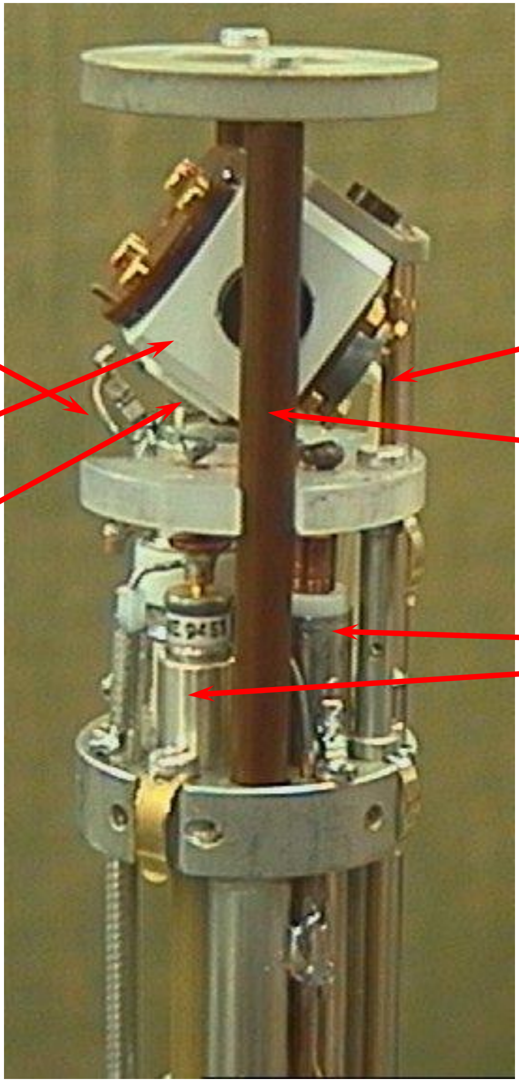
A 0.8 mm rotor spinning at 100 kHz …

… has a speed of 250m/s when rolling along the ground…

……. needs only 44 hours to roll around the earth….

Angular frequency ~ 120-130 kHz

Standard Bore MAS Probe



proton trap

BN stator

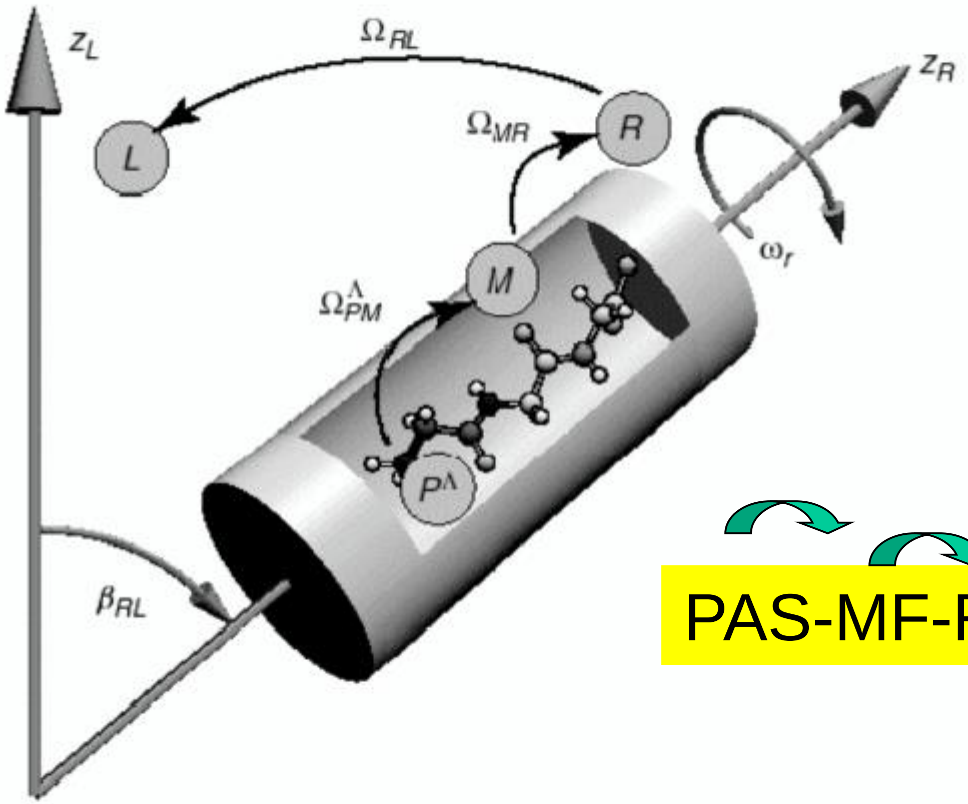
RF coil

stator flip mechanism

bearing gas inlet

RF electronics

Reference Frames in Solid-State NMR



PAS-MF-RF-LF

Transformation via the relevant Euler angles necessary for visualisation and simulations

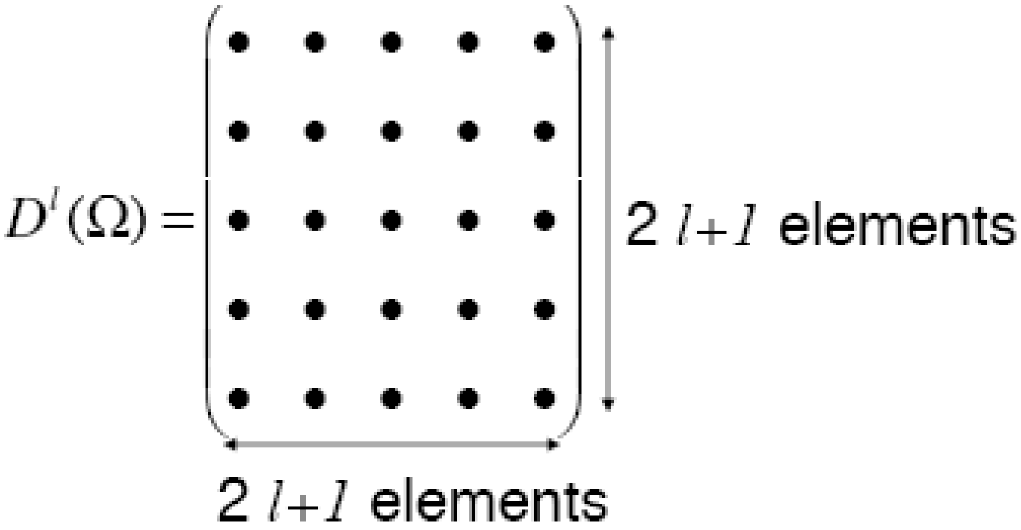
Rotation of Spherical Tensors

$$R(\Omega)T_{lm}R(\Omega)^{\dagger} = \sum_{m'=-l}^{l} T_{lm'}D^{l}_{mm'}(\Omega)$$

Rotation operator for Euler angles Ω

Elements of Wigner matirx for Euler angles Ω

Wigner Matrices



$$D^l_{m'm}(\Omega) = \exp(-im'\alpha)\, d^l_{m'm}(\beta)\, \exp(-im\gamma)$$

Wigner matrix element

Reduced Wigner matrix element

Reduced Wigner Matrix Elements (Rank 0 and 1)

$$d^0(\beta) = 1$$

$$d^1_{00}(\beta)$$

$$d^1_{mm'}(\beta) = \begin{array}{cc} \left(\begin{array}{ccc} \frac{1}{2}(1+\cos\beta) & -\sin\beta/\sqrt{2} & \frac{1}{2}(1-\cos\beta) \\ \sin\beta/\sqrt{2} & \cos\beta & -\sin\beta/\sqrt{2} \\ \frac{1}{2}(1-\cos\beta) & \sin\beta/\sqrt{2} & \frac{1}{2}(1+\cos\beta) \end{array}\right) & \begin{array}{l} m=-1 \\ m=0 \\ m=1 \end{array} \\ \begin{array}{ccc} m'=-1 & \quad m'=0 \quad & m'=1 \end{array} & \end{array}$$

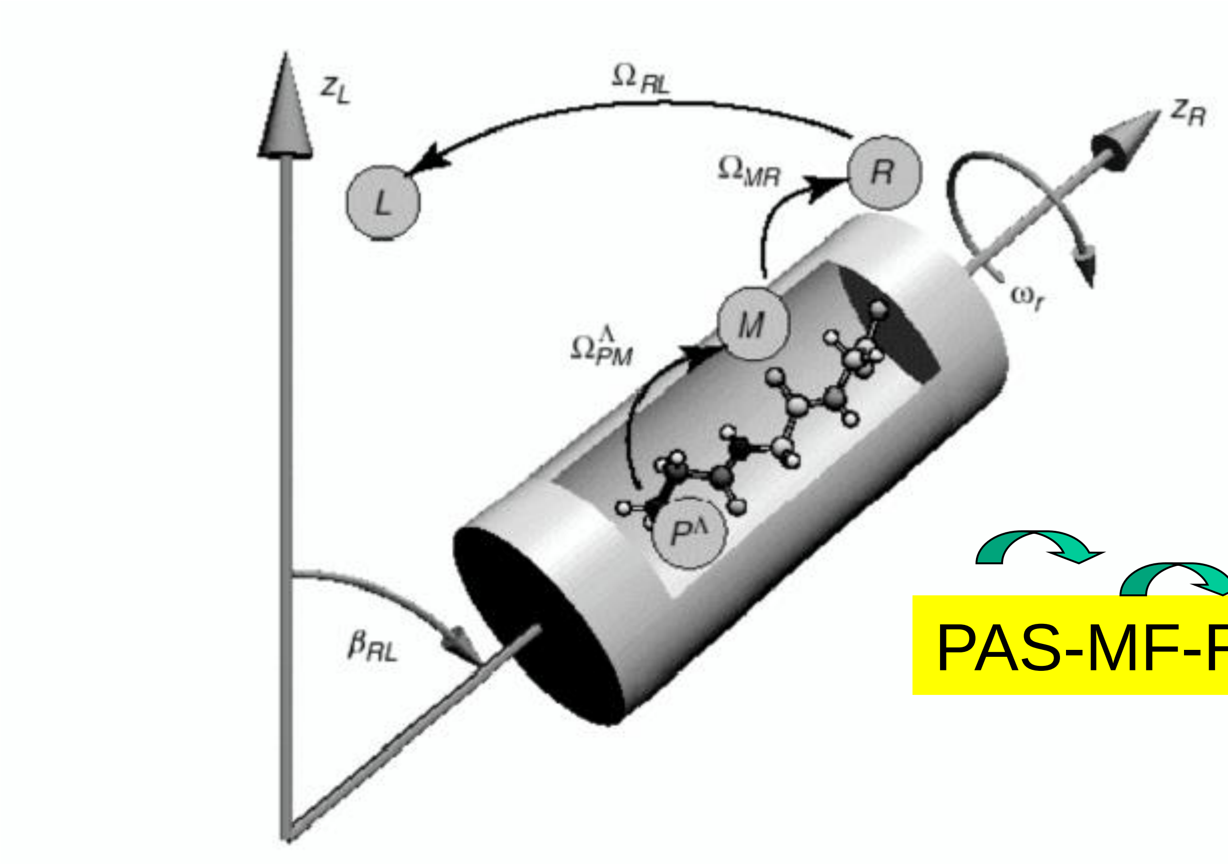
Reduced Wigner Matrix Elements (Rank 2)

$$d^{2}_{00}(\beta)$$

$$d^{2}_{mm'}(\beta)=$$

$$\begin{array}{cccccc}
\frac{1}{4}(1+cos\beta)^2 & -\frac{1}{2}sin\beta(1+cos\beta) & \sqrt{\frac{3}{8}}sin^2\beta & -\frac{1}{2}sin\beta(1-cos\beta) & \frac{1}{4}(1-cos\beta)^2 & m=-2 \\
\frac{1}{2}sin\beta(1+cos\beta) & \frac{1}{2}(2cos^2\beta+cos\beta-1) & -\sqrt{\frac{3}{8}}sin2\beta & \frac{1}{2}(2cos^2\beta-cos\beta-1) & -\frac{1}{2}sin\beta(1-cos\beta) & \\
\sqrt{\frac{3}{8}}sin^2\beta & \sqrt{\frac{3}{8}}sin2\beta & \frac{1}{2}(3cos^2\beta-1) & -\sqrt{\frac{3}{8}}sin2\beta & \sqrt{\frac{3}{8}}sin^2\beta & \\
\frac{1}{2}sin\beta(1-cos\beta) & -\frac{1}{2}(2cos^2\beta-cos\beta-1) & \sqrt{\frac{3}{8}}sin2\beta & \frac{1}{2}(2cos^2\beta+cos\beta-1 & -\frac{1}{2}sin\beta(1+cos\beta) & \\
\frac{1}{4}(1-cos\beta)^2 & \frac{1}{2}sin\beta(1-cos\beta) & \sqrt{\frac{3}{8}}sin^2\beta & \frac{1}{2}sin\beta(1+cos\beta) & \frac{1}{4}(1+cos\beta)^2 & m=2 \\
m'=-2 & m'=-1 & m'=0 & m'=1 & m'=2 &
\end{array}$$

Reference Frames in Solid-State NMR



PAS-MF-RF-LF

Transformation via the relevant Euler angles necessary for visualsation and simulations

Wigner Matrix Chains

$$D^l(\Omega_{AC}) = D^l(\Omega_{AB})D^l(\Omega_{BC})$$

$$D^l_{m'm}(\Omega_{AC}) = \sum_{m''=-l}^{l} D^l_{m'm''}(\Omega_{AB})D^l_{m''m}(\Omega_{BC})$$

$$D^l(\Omega_{AD}) = D^l(\Omega_{AB})D^l(\Omega_{BC})D^l(\Omega_{CD})$$

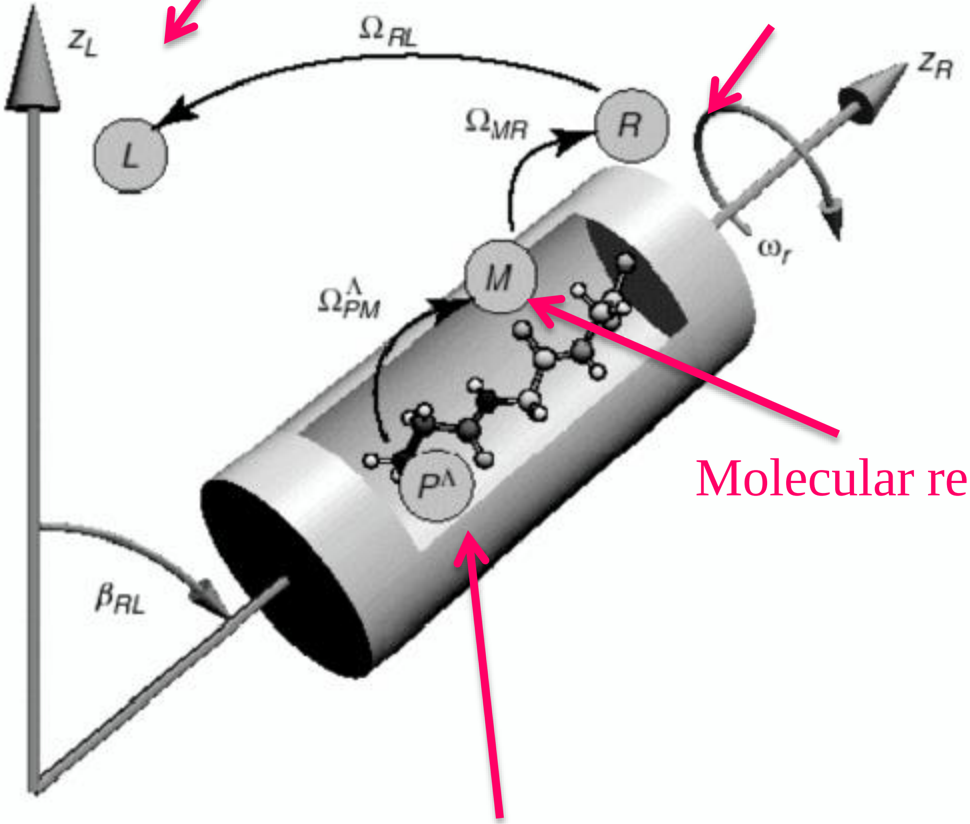
$$D^l_{m'm}(\Omega_{AD}) = \sum_{m''=-l}^{l} \sum_{m'''=-l}^{l} D^l_{m'm''}(\Omega_{AB})D^l_{m''m'''}(\Omega_{BC})D^l_{m'''m}(\Omega_{CD})$$

Frame Transformations of Spherical Tensors

$$\begin{pmatrix} [T_{2,-2}]^A \\ [T_{2,-1}]^A \\ [T_{2,0}]^A \\ [T_{2,1}]^A \\ [T_{2,2}]^A \end{pmatrix} = \begin{pmatrix} \ddots & \vdots & \iddots \\ \cdots & D^2(\Omega_{AB}) & \cdots \\ \iddots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} [T_{2,-2}]^B \\ [T_{2,-1}]^B \\ [T_{2,0}]^B \\ [T_{2,1}]^B \\ [T_{2,2}]^B \end{pmatrix}$$

$$\begin{pmatrix} [T_{2,-2}]^A \\ [T_{2,-1}]^A \\ [T_{2,0}]^A \\ [T_{2,1}]^A \\ [T_{2,2}]^A \end{pmatrix} = \begin{pmatrix} \ddots & \vdots & \iddots \\ \cdots & D^2(\Omega_{AB}) & \cdots \\ \iddots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} \ddots & \vdots & \iddots \\ \cdots & D^2(\Omega_{BC}) & \cdots \\ \iddots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} [T_{2,-2}]^C \\ [T_{2,-1}]^C \\ [T_{2,0}]^C \\ [T_{2,1}]^C \\ [T_{2,2}]^C \end{pmatrix}$$

Chain of Reference Frames in Solid-State NMR



Laboratory reference frame

Rotor reference frame

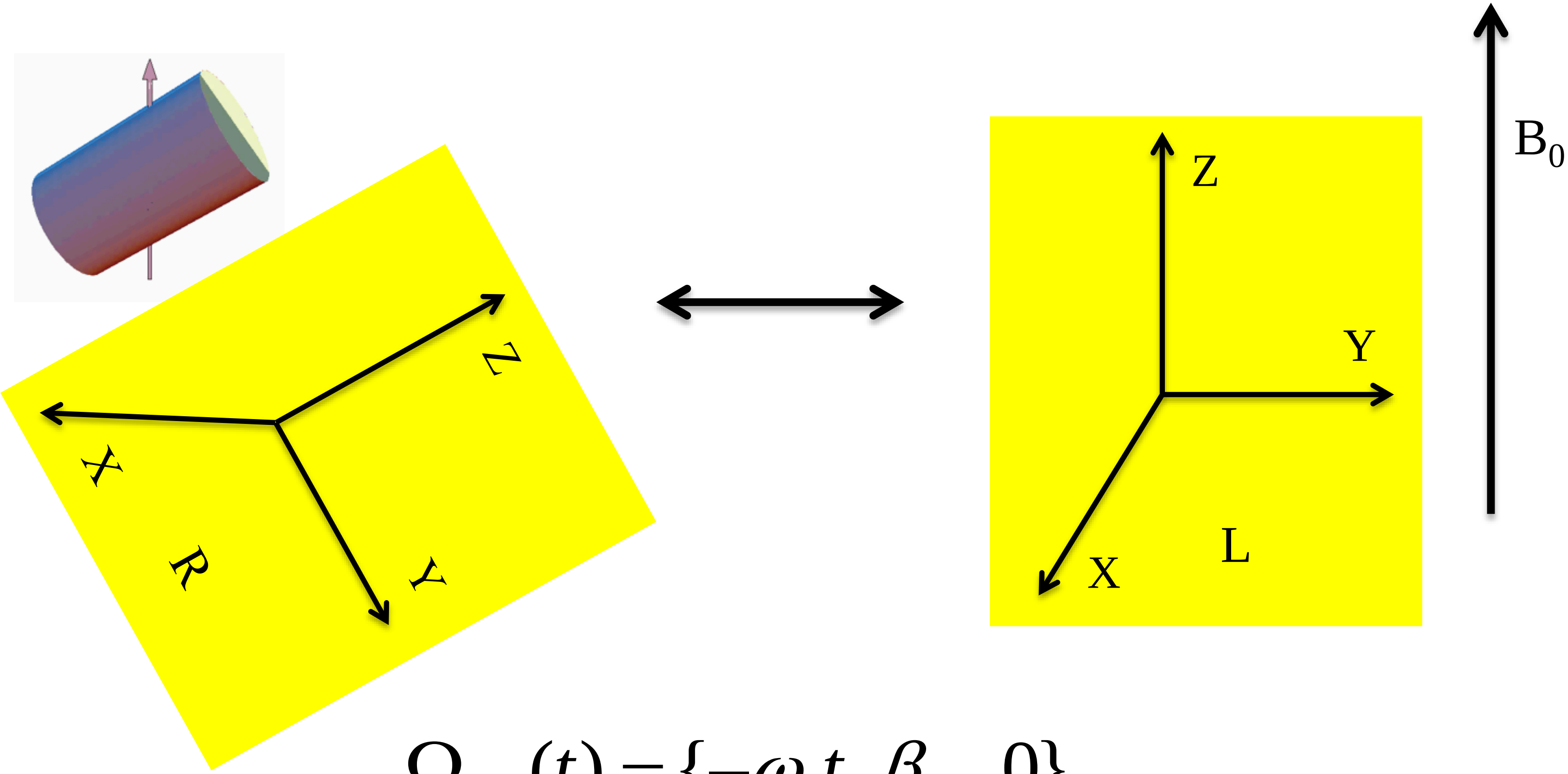
Molecular reference frame

Principal axis frame of a spin interaction

Rotor to Lab Frame Transformation

Rotor reference frame

Lab reference frame

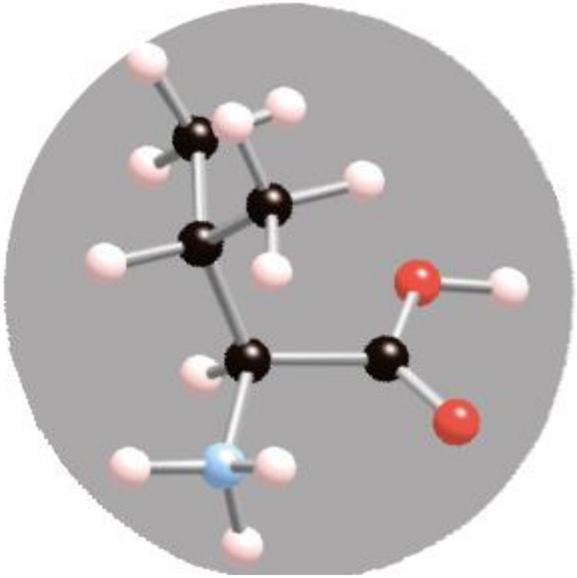


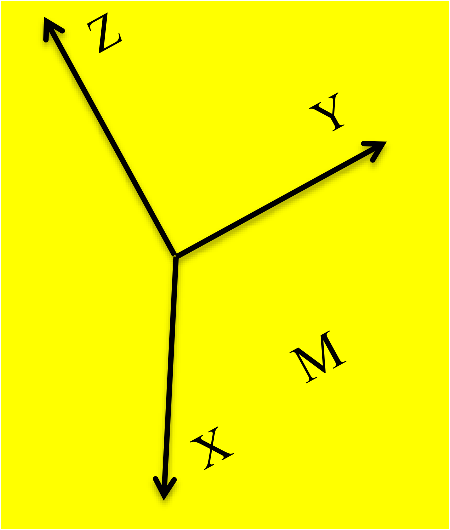
$$\Omega_{RL}(t) = \{-\omega_r t, \beta_{RL}, 0\}$$

Spinning frequency

Rotor (magic) angle

Molecular Frame





Ω_{MR}

Molecular frame is more arbitrary, although in certain cases, calculations are simpler with a good choice

Different Euler angles for different molecules

Chain of Transformations in Solid-State NMR

$$D^l(\Omega^\Lambda_{PL}) = D^l(\Omega^\Lambda_{PM})D^l(\Omega^\Lambda_{MR})D^l(\Omega^\Lambda_{RL}(t))$$

Orientation of an interaction, Λ, with respect to the molecular frame. Depends only on the interaction, not on time or crystallite

Orientation of the rotor wrt
To the static field, time dependent

Orientation of molecular frame wrt to rotor frame, depends only on crystallite, not on interaction or time

Irreducible Tensor Representation of the Hamiltonians

$$H = \sum_{m=-l}^{l} [A_{lm}]^{L} [T_{l-m}]^{L}$$

Space part

Spin part

$$H = \sum_{m=-2}^{2} [A_{2m}]^{L} [T_{2-m}]^{L}$$

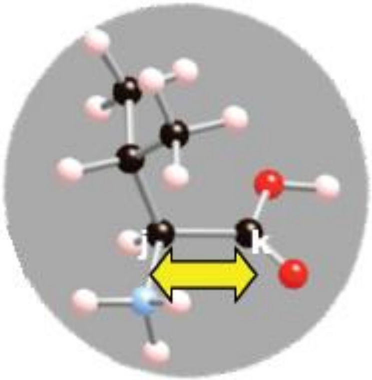
NMR case

$$H = [A_{20}]^{L} [T_{20}]^{L}$$

High field,
secular approximation

DD Coupling Hamiltonian

$$H_{DD}^{jk} = [A_{20}^{jk}]^{L}[T_{20}^{jk}]^{L}$$



$$T_2^{jk} = \begin{pmatrix} T_{2-2}^{jk} \\ T_{2-1}^{jk} \\ T_{20}^{jk} \\ T_{21}^{jk} \\ T_{22}^{jk} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} I_j^- I_k^- \\ \frac{1}{2}\left(I_j^- I_{kz} + I_{jz} I_k^-\right) \\ 6^{-1/2}\left\{2 I_{jz} I_{kz} - \frac{1}{2}\left(I_j^+ I_k^- - I_j^- I_k^+\right)\right\} \\ -\frac{1}{2}\left(I_j^+ I_{kz} + I_{jz} I_k^+\right) \\ \frac{1}{2} I_j^+ I_k^+ \end{pmatrix}$$

Spin tensor

$$[A_2^{jk}]^{P} = \begin{pmatrix} 0 \\ 0 \\ 6^{1/2} b_{jk} \\ 0 \\ 0 \end{pmatrix} \qquad b_{jk} = -\left(\frac{\mu_0}{4\pi}\right)\frac{\hbar \gamma_j \gamma_k}{r_{jk}^3}$$

Space tensor in the PAS

DD Coupling Hamiltonian

$$H_{DD}^{jk} = [A_{20}^{jk}]^L [T_{20}^{jk}]^L$$

$$= \sum_{m=-2}^{2} [A_{20}^{jk}]^P D_{m0}^{2}(\Omega_{PL}^{jk})[T_{20}^{jk}]^L$$

$$= [A_{20}^{jk}]^P D_{00}^{2}(\Omega_{PL}^{jk})[T_{20}^{jk}]^L$$

$$= [A_{20}^{jk}]^P d_{00}^{2}(\beta_{PL}^{jk})[T_{20}^{jk}]^L$$

Zero at the magic angle

$$= b_{jk}\frac{1}{2}(3\cos^2\theta_{PL}^{jk} - 1)\{2I_{jx}I_{ky} - \frac{1}{2}(I_j^+ I_k^- - I_j^- I_k^+)\}$$

Isotropic Chemical-Shift Hamiltonian

$$H_{iso}^{j} = \omega_{iso}^{j} I_{jz}$$

Spin rank 1

$$\omega_{iso}^{j} = \delta_{iso}^{j} \omega_{0}^{j}$$

Space rank 0

$$\omega_{0}^{j} = -\gamma^{j} B_{0}$$

CSA Hamiltonian

Spin rank 1

$$H^{j}_{CSA} = [A^{j}_{20}]^{L}[T^{j}_{20}]^{L} B_0 = [A^{j}_{20}]^{L} I_{jz} B_0$$

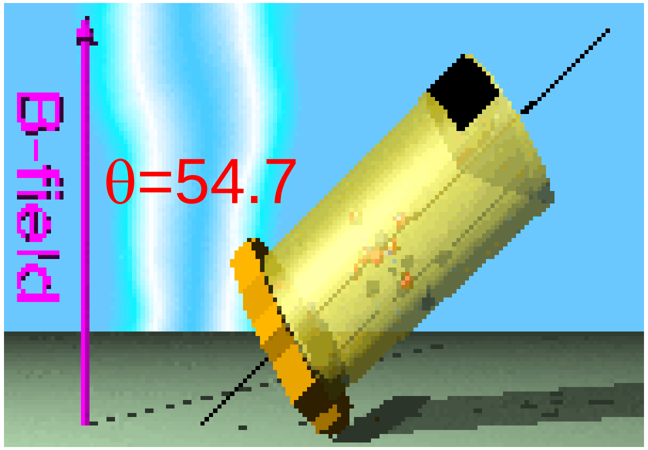
Space rank 2

Space tensor in the PAS

$$[A^{j}_{2}]^{P} = \omega^{j}_{aniso} \begin{pmatrix} -6^{-1/2}\eta^{j} \\ 0 \\ 1 \\ 0 \\ -6^{-1/2}\eta^{j} \end{pmatrix}$$

$$\omega^{j}_{aniso} = \delta^{j}_{aniso}\,\omega^{j}_{0}$$

Average Hamiltonian Theory and MAS



$$\alpha_{RL} = -\omega_r t$$

$$\beta_{RL} = 54.7$$

$$\gamma_{RL} = \text{arbitrary}$$

Isolated spin-1/2 experiencing CSA:

$$H^{j}(t) = \omega^{j}_{iso} I_{jz} + H^{j}_{CSA}(\Omega_{MR}, t)$$

CSA Hamiltonian under MAS

$$H_{CSA}^{j} = [A_{20}^{j}]^{L} I_{jz} B_0$$

$$= \sum_{m=-2}^{2} [A_{2m}^{j}]^{R} D_{m0}^{2}(\Omega_{RL}) I_{jz} B_0$$

$$= \sum_{m'=-2}^{2} \sum_{m=-2}^{2} [A_{2m'}^{j}]^{M} D_{m'm}^{2}(\Omega_{MR}) D_{m0}^{2}(\Omega_{RL}) I_{jz} B_0$$

$$= \sum_{m'=-2}^{2} \sum_{m=-2}^{2} [A_{2m'}^{j}]^{M} D_{m'm}^{2}(\Omega_{MR}) e^{im\omega_r t} d_{m0}^{2}(\beta_{RL}) I_{jz} B_0$$

Concept of Average Hamiltonian

If the Hamiltonian is such that:

- It is periodic, H(t),=H(t+NT)
- It varies sufficiently fast with respect to time

Then the spin system behaves as if it is subjected to a time average of H(t) over the period T (then the Hamiltonian also becomes time independent):

$$H(t) \Rightarrow \overline{H}^{(1)} = \frac{1}{T}\int H(t)dt$$

Average Hamiltonian

Average CSA Hamiltonian Under MAS

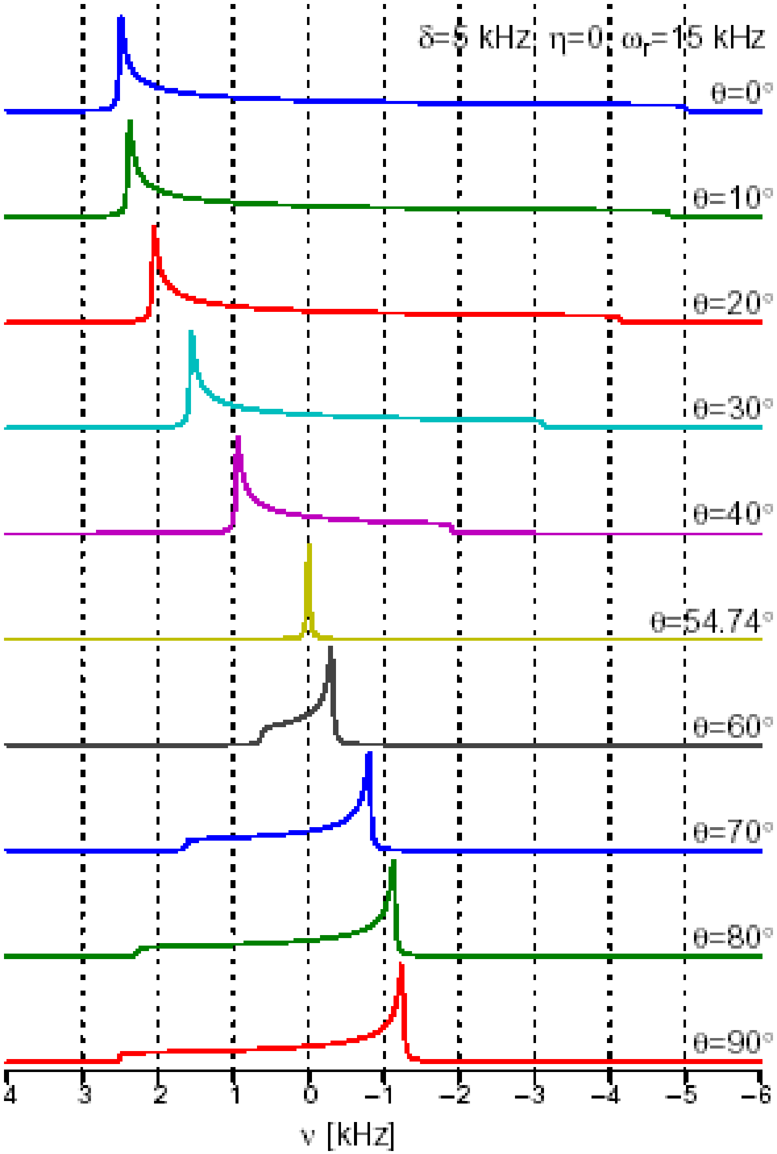
$$H^{j}_{CSA}(\Omega_{MR}) = \sum_{m'=-2}^{2}\ \sum_{m=-2}^{2} [A^{j}_{2m'}]^{M} D^{2}_{m'm}(\Omega_{MR})\overline{e^{im\omega_r t}}\, d^{2}_{m0}(\beta_{RL}) I_{jz} B_0$$

$$= \sum_{m'=-2}^{2} [A^{j}_{2m'}]^{M} D^{2}_{m'0}(\Omega_{MR}) d^{2}_{00}(\beta_{RL}) I_{jz} B_0$$

Zero for β_{RL}=54.7

Exact MAS, hence, averages CSA to zero, provided the rotation is sufficiently fast.

CSA Powder Pattern and Rotation Angle



For angles other than 54.7, scaled versions of static powder pattern appear, with scale factor ranging from 1 to –0.5

Isotropic spectrum results at the magic angle, 54.7

DD Hamiltonian Under MAS

$$H_{DD}^{jk}(\Omega_{MR},t) = [A_{20}^{jk}]^L [T_{20}^{jk}]^L$$

$$= \sum_{m=-2}^{2} [A_{2m}^{jk}]^R D_{m0}^{2}(\Omega_{RL}) [T_{20}^{jk}]^L$$

$$= \sum_{m'=-2}^{2} \sum_{m=-2}^{2} [A_{2m'}^{jk}]^M D_{m'm}^{2}(\Omega_{MR}) D_{m0}^{2}(\Omega_{RL}) [T_{20}^{jk}]^L$$

$$= \sum_{m'=-2}^{2} \sum_{m=-2}^{2} [A_{2m'}^{jk}]^M D_{m'm}^{2}(\Omega_{MR}) e^{im\omega_r t} d_{m0}^{2}(\beta_{RL}) [T_{20}^{jk}]^L$$

Average DD Hamiltonian Under MAS

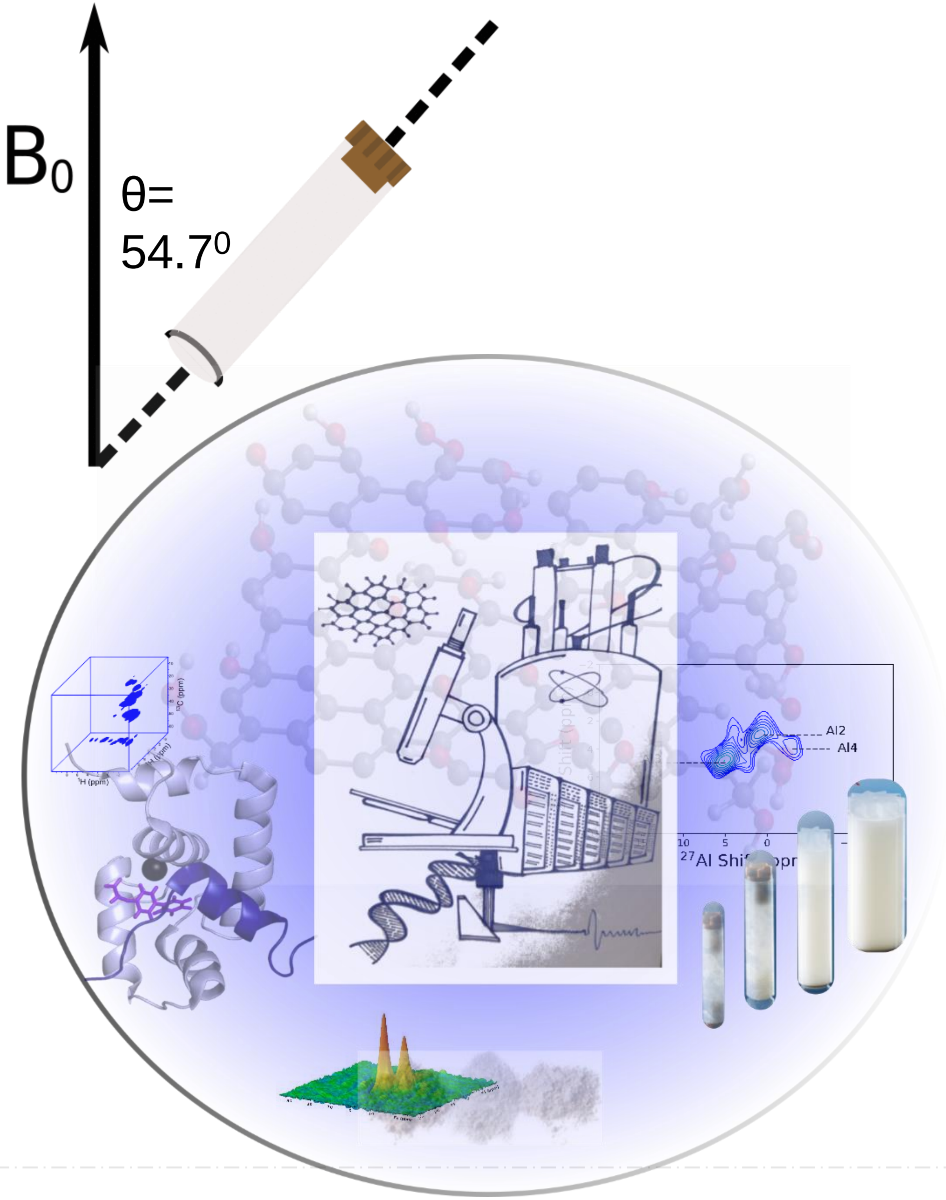
$$H_{DD}^{jk}(\Omega_{MR},t) = \sum_{m'=-2}^{2}\sum_{m=-2}^{2}[A_{2m'}^{jk}]^{M} D_{m'm}^{2}(\Omega_{MR})\overline{e^{im\omega_r t}}\, d_{m0}^{2}(\beta_{RL})[T_{2m'}^{jk}]^{L}$$

$$= \sum_{m'=-2}^{2}[A_{2m'}^{jk}]^{M} D_{m'0}^{2}(\Omega_{MR})\, d_{00}^{2}(\beta_{RL})[T_{20}^{jk}]^{L}$$

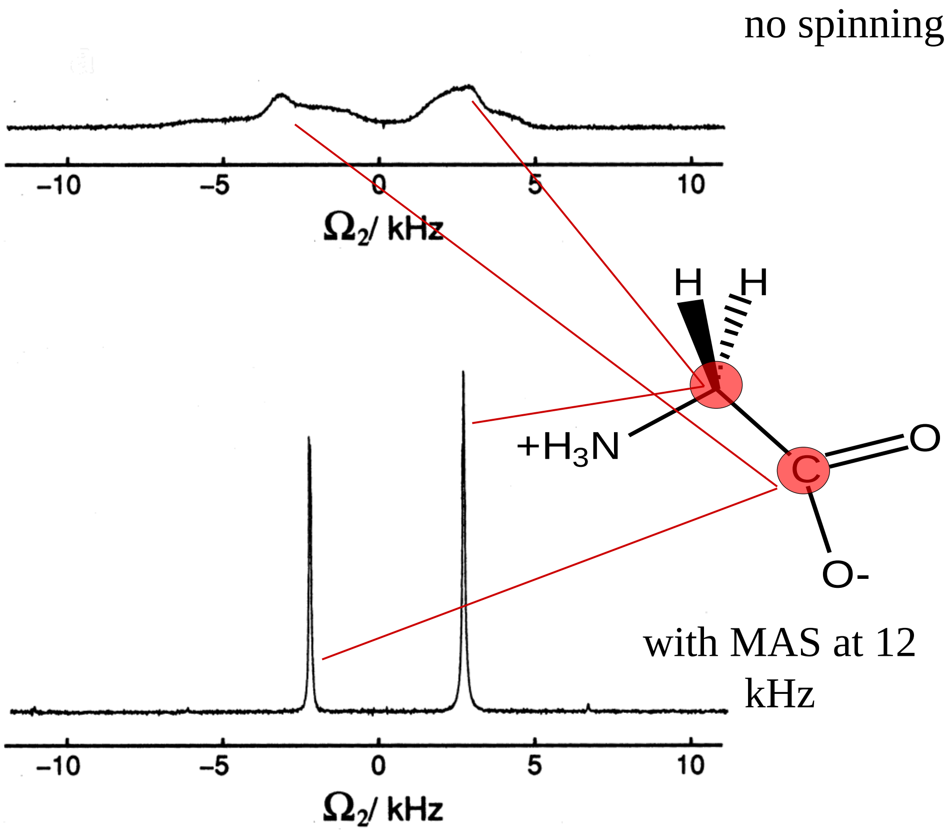
Zero for β_{RL}=54.7

Exact MAS, hence, averages DD to zero, provided the rotation is sufficiently fast.

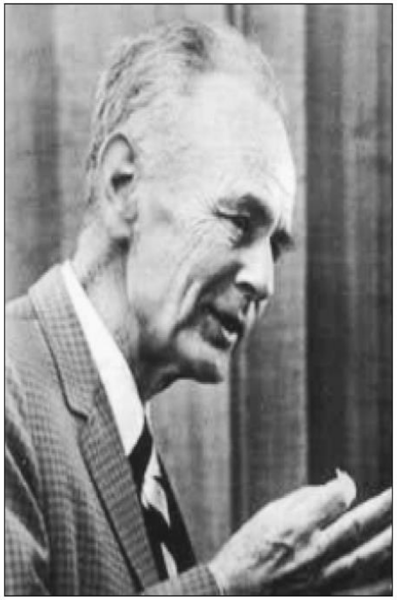
Magic-Angle-Spinning Solid-State NMR



^{13}C spectra of [$^{13}C_2$]-glycine



Tracking Spins in NMR



Floquet

Wilhelm Magnus

F. Fer

Floquet theory

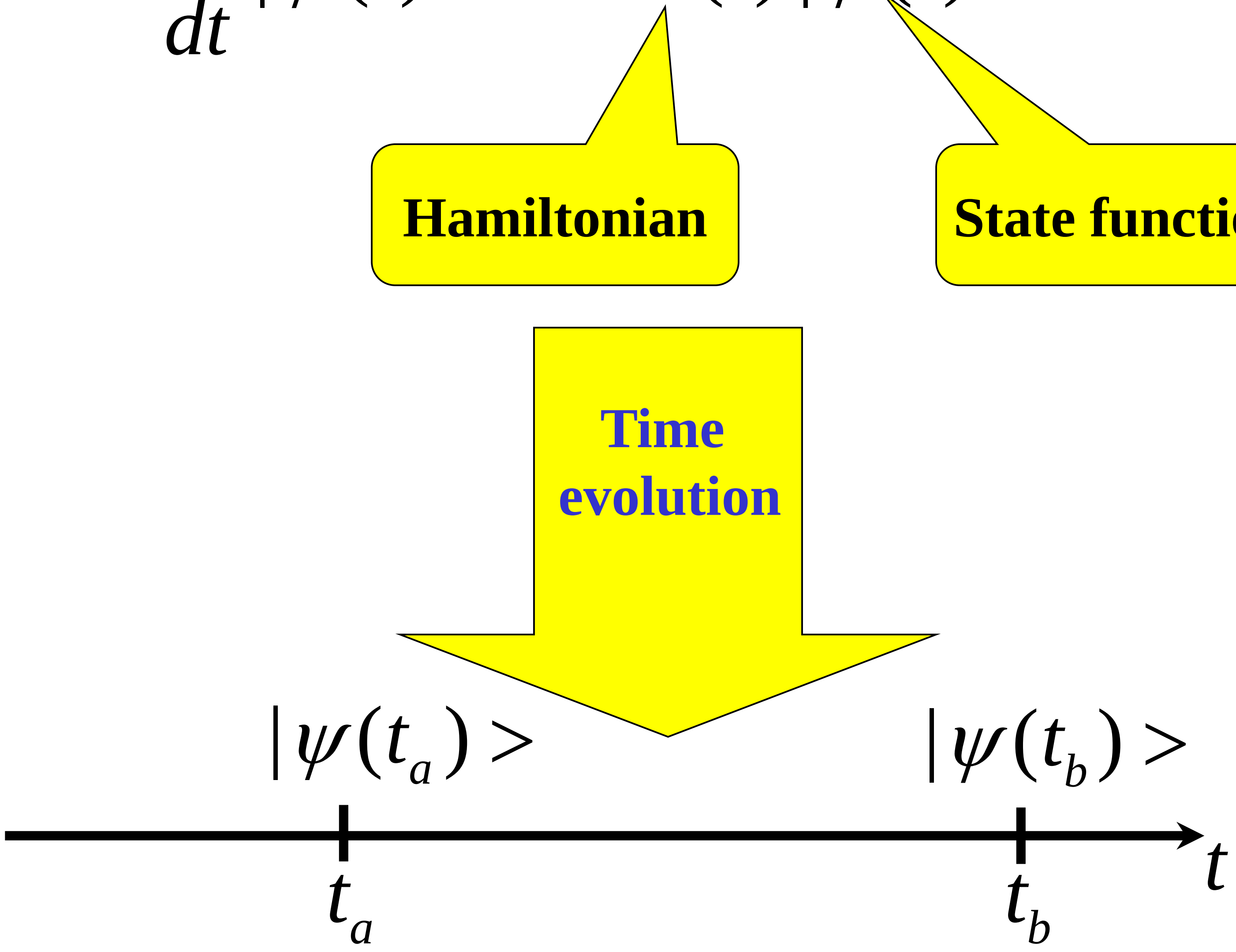
Magnus expansion
Average Hamiltonian theory

Fer expansion

Many more: Wilcox, Salzman, Pechukas, Burum

Time Development of the Spin System

$$\frac{d}{dt}|\psi(t)>=-iH(t)|\psi(t)>$$



Hamiltonian

State function

Time evolution

$|\psi(t_a)>$

$|\psi(t_b)>$

Phase Cycling
and
Pulsed Field Gradients

Separating Wheat from Chaff

NMR

- Inherently a low-sensitive method
- Plenty of unwanted signal to make matters worse
- Desired signals are very less
- How to select out the desired signals effectively

Phase Cycling or Pulse Field Gradients

Fourier Transform

The Fourier Transform (FT) converts the time domain signal to the frequency domain. There are several types of FT, and we will examine the discrete FT (DFT), because it works on discrete points like NMR data

DFT

$$f_n = \frac{1}{\sqrt{N}} \sum_{k=0}^{N-1} d_k e^{-2\pi ikn/N}$$

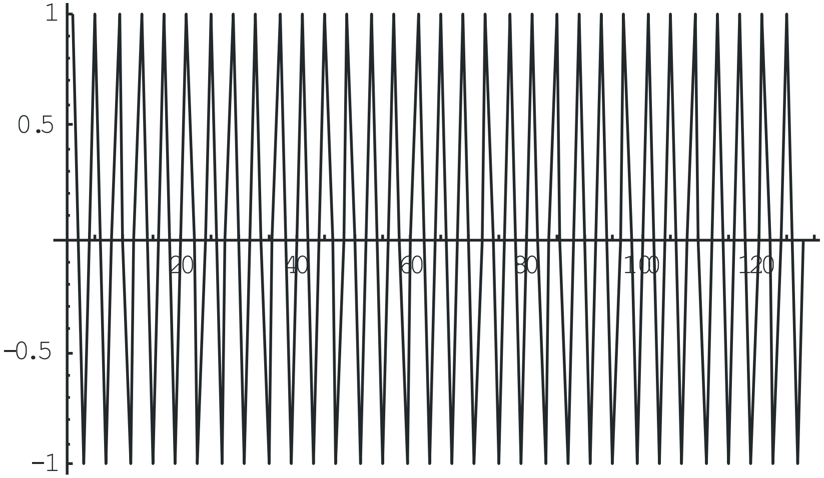
f_n is the nth point in the "frequency vector"

N is the number of time data points, d_k

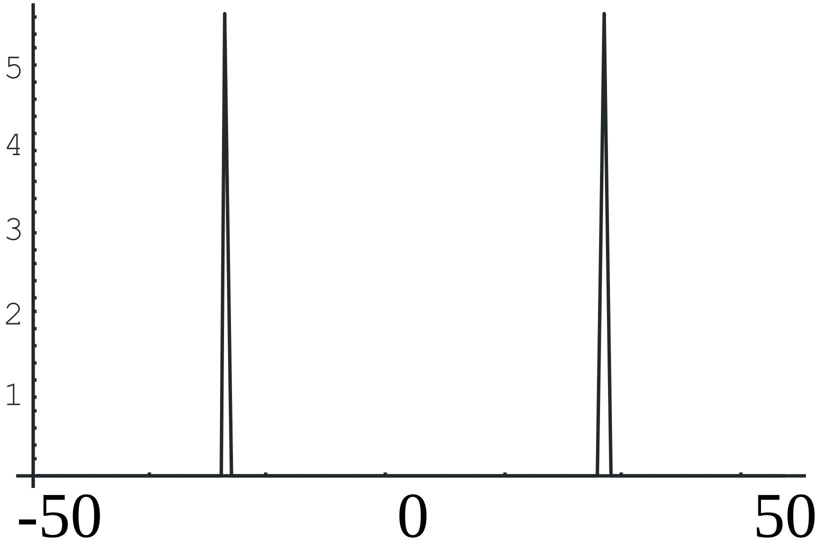
i is $\sqrt{-1}$

k and n are integers that refer to the points in d_k and f_n

FT: Appearance



Here is a 25 Hz time-domain signal from Cos[2*Pi*25*t] sampled for 128 points from t=0 to t=1.27 sec with 0.01 sec spacing between points



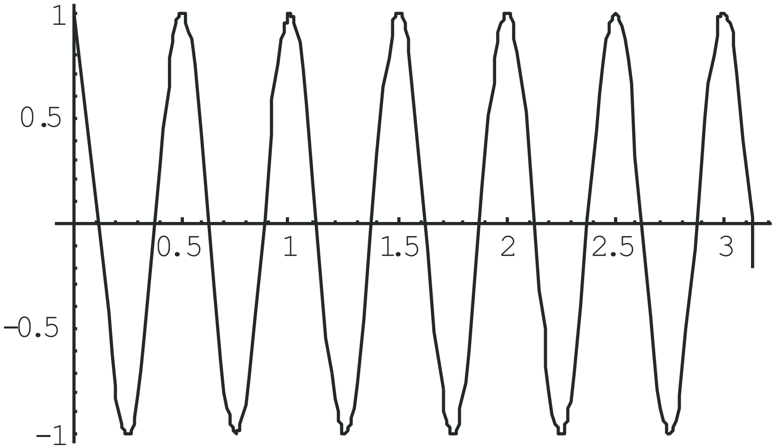
Here is the real part of the DFT of the signal above. Several things are worth noting:

1) There are 2 peaks, each 25 Hz from either edge.

2) The spectral width is 100 Hz

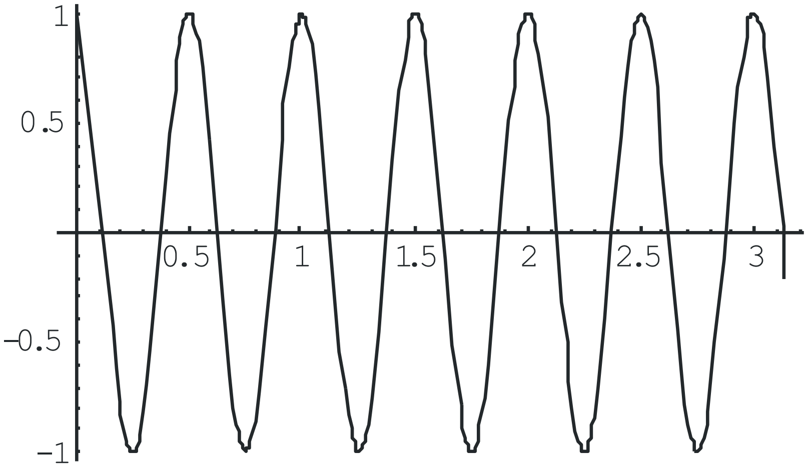
3) The peaks are quite sharp

Why 2 Peaks from One Frequency?



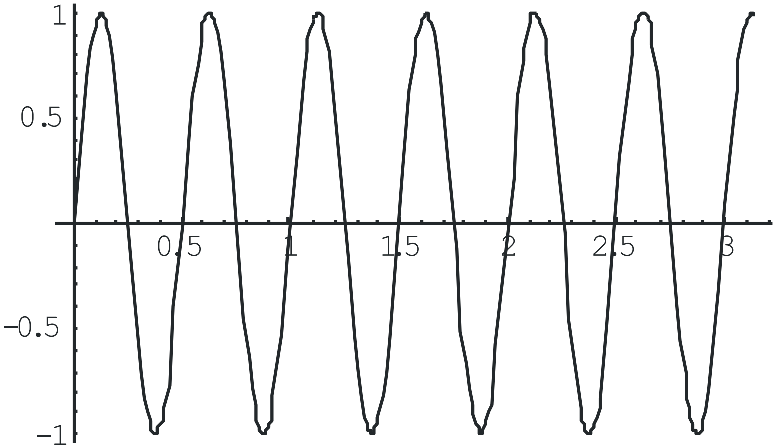
Here is a plot of Cos[2*Pi*2*t]

These are indistinguishable even though they have opposite frequencies. Therefore, the FT results in 2 frequencies, one positive and the other negative



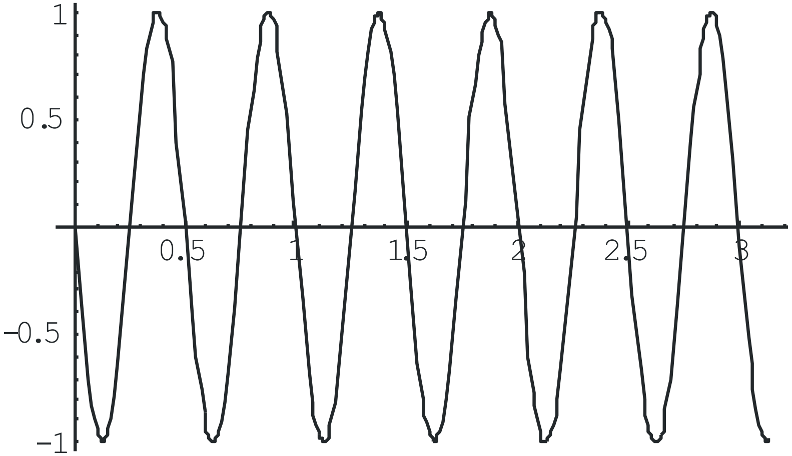
Here is a plot of Cos[2*Pi*(-2)*t]

Why 2 Peaks from One Frequency?



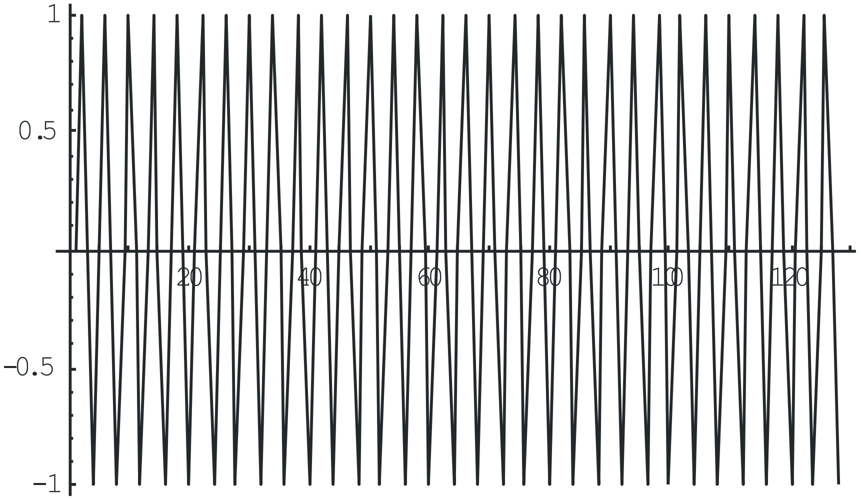
Here is a plot of Sin[2*Pi*2*t]

We *can* distinguish different signs in Sin functions

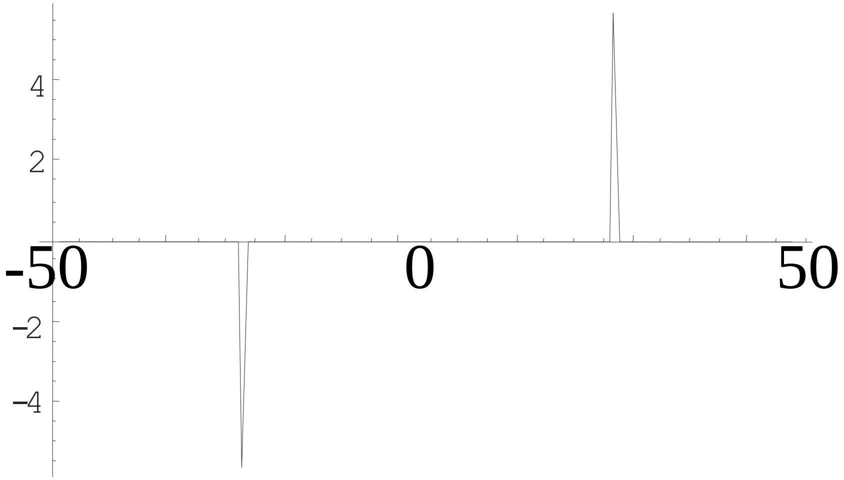


Here is a plot of Sin[2*Pi*(-2)*t]

FT of a Sine Function



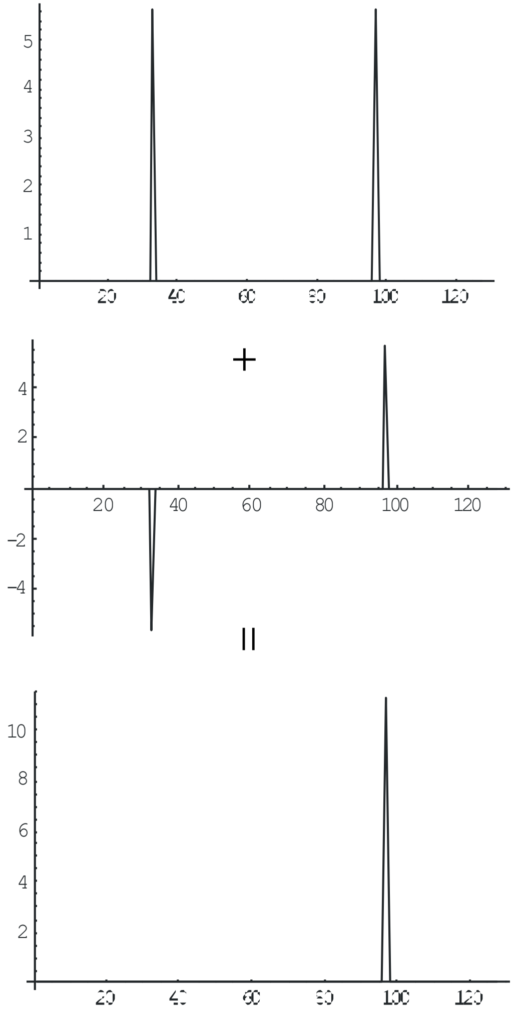
Here is a 25 Hz time-domain signal from Sin[2*Pi*25*t] sampled for 128 points from t=0 to t=1.27 sec with 0.01 sec spacing between points.



Here is the imaginary part of the DFT of the signal above. Several things are worth noting:

1) There are 2 peaks, each 25 Hz from either edge. Now they are opposite each other!
2) The spectral width is 100 Hz
3) The peaks are quite sharp

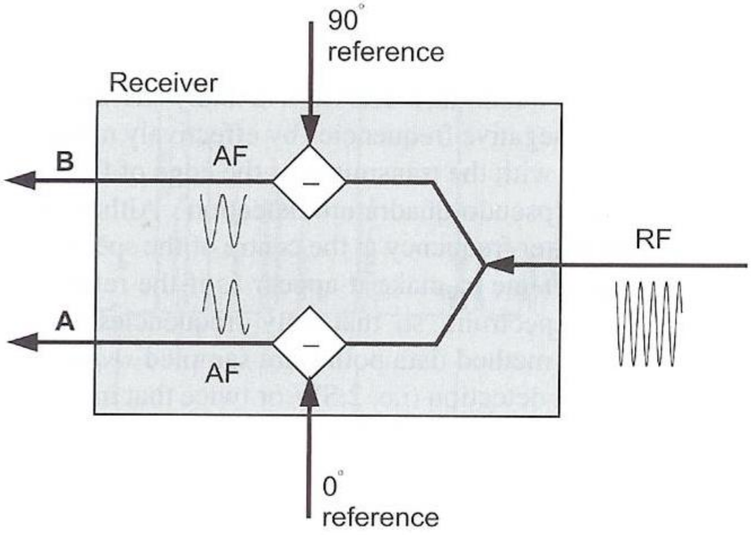
Adding Sine and Cosine FT's



FT of cosine function

FT of sine function

Sum



NMR Receiver

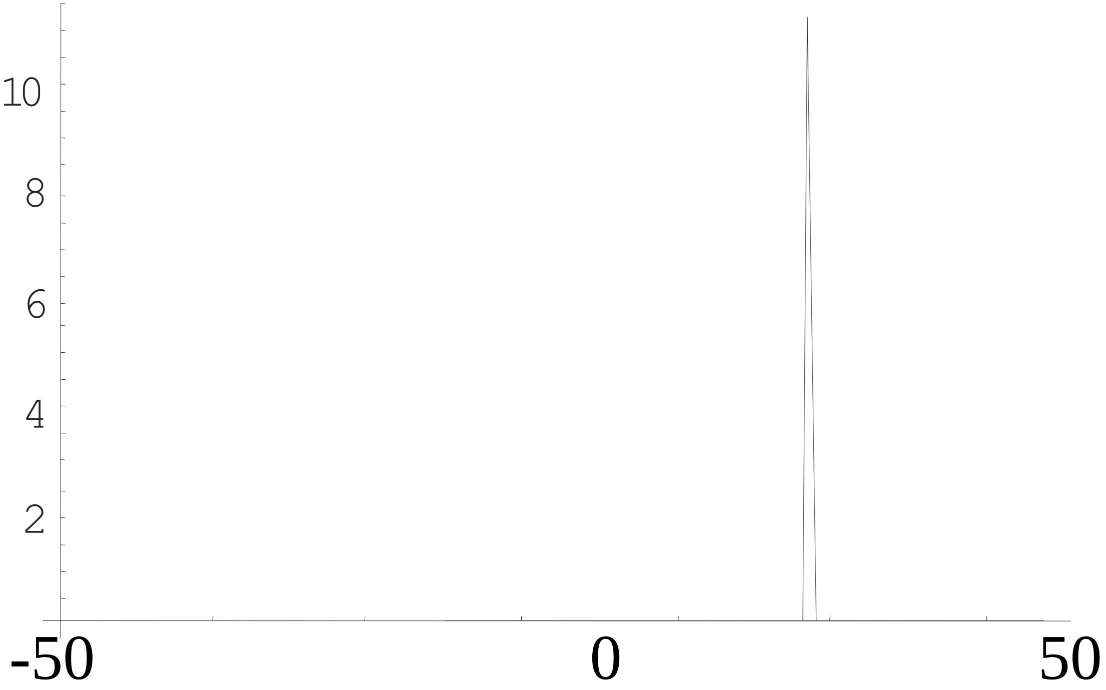
Quadrature Detection

In order to distinguish the sign of frequencies, NMR signals must be collected along both the x (e.g. cosine) and y (e.g. sine) axes. This is called quadrature detection. The signal is treated as a "real" part (cosine) and an "imaginary" part (sine). They are both equally real and important, but this allows easy mathematical manipulation from Euler's relations:

$$\boxed{\underbrace{Cos(t)}_{\text{real}} + \underbrace{iSin(t)}_{\text{imaginary}} = e^{it}} \qquad \boxed{\underbrace{Cos(t)}_{\text{real}} - \underbrace{iSin(t)}_{\text{imaginary}} = e^{-it}}$$

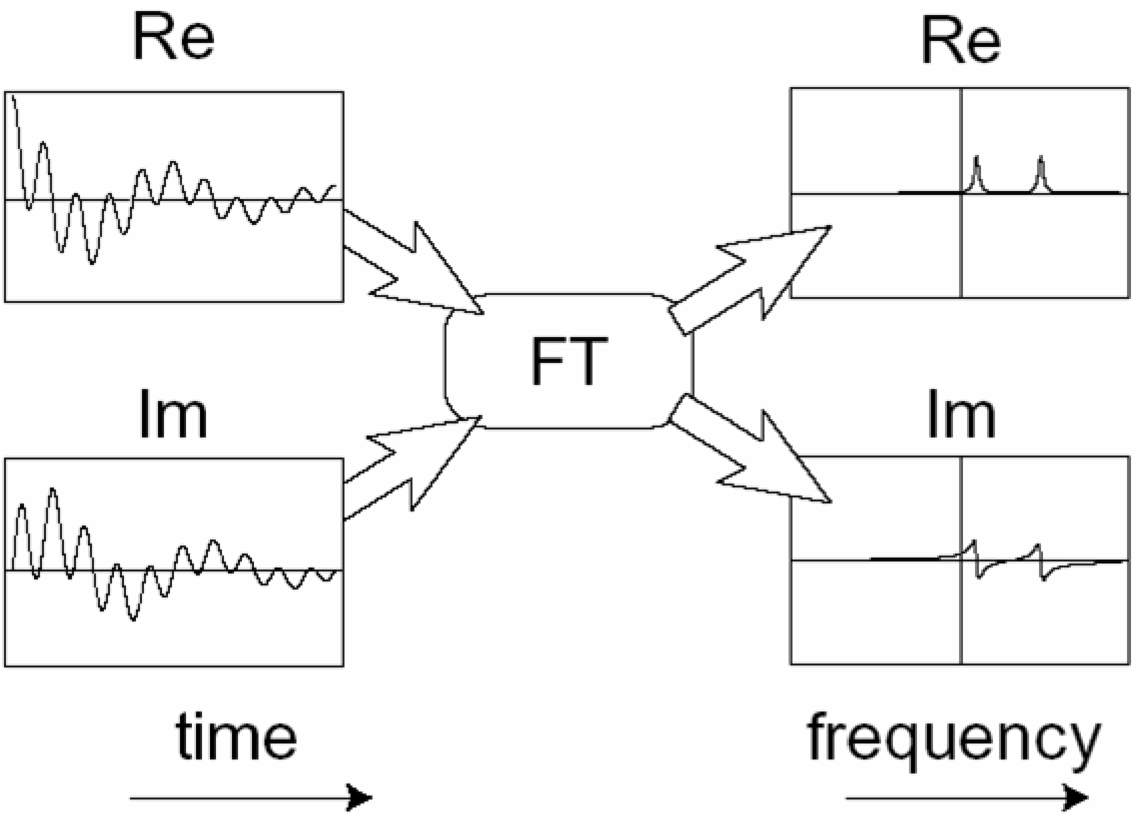
Quadrature Detection

d = Cos[2*Pi*25*t] + I*Sin[2*Pi*25*t]

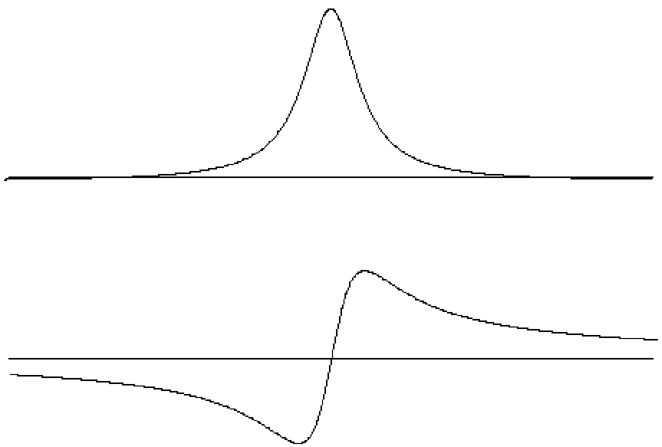


The DFT of the 128 point function defined above with a frequency of 25 Hz

Quadrature Detection: The Full Story



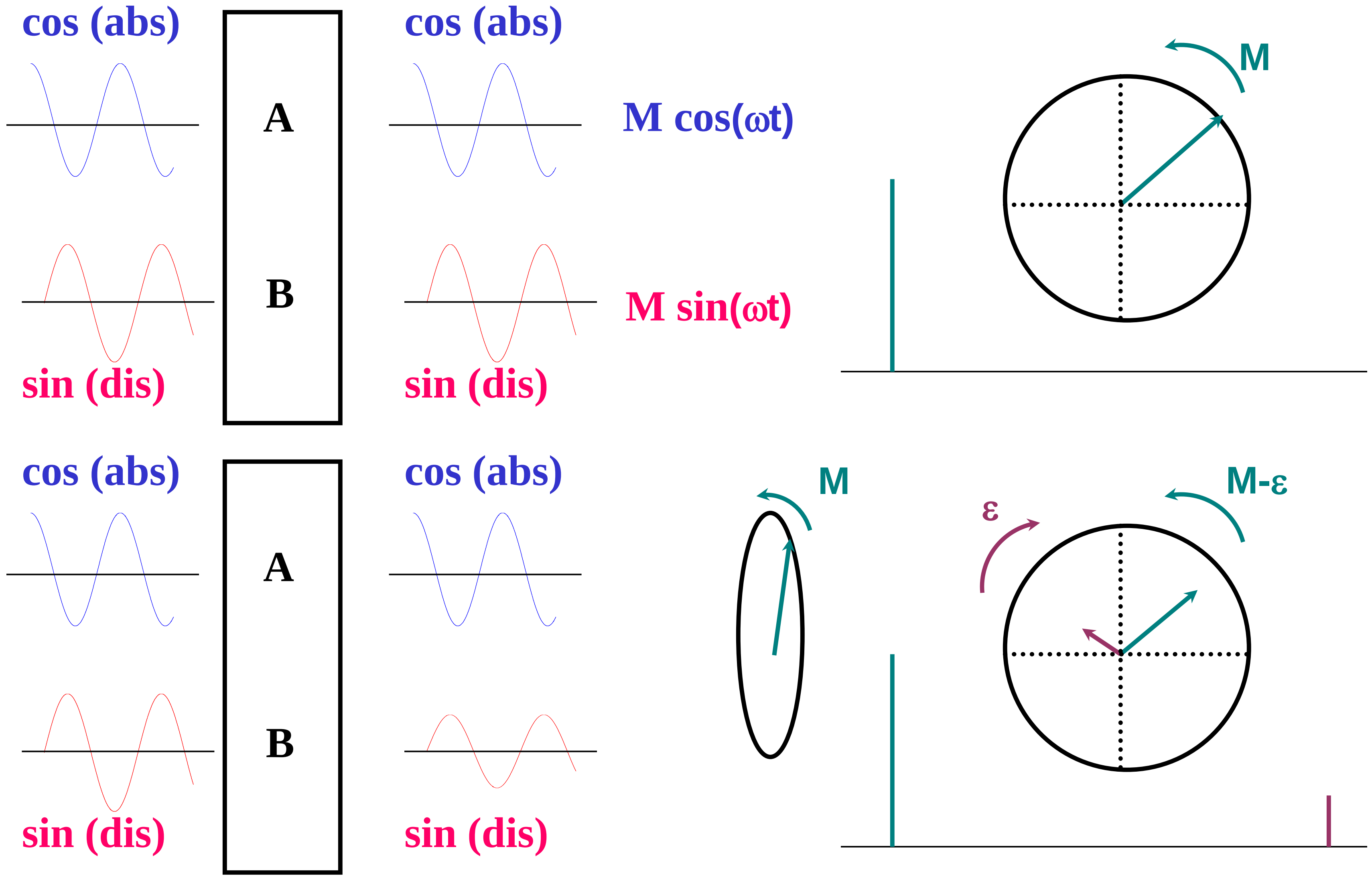
Absorptive



Dispersive

CYCLOPS (Cyclically Ordered Phase Sequence)

Channels A and B need to be orthogonal and they should amplify both absorptive and dispersive components of the signals identically



cos (abs)

A

cos (abs)

M cos(ωt)

M

B

sin (dis)

sin (dis)

M sin(ωt)

cos (abs)

A

cos (abs)

M

ε

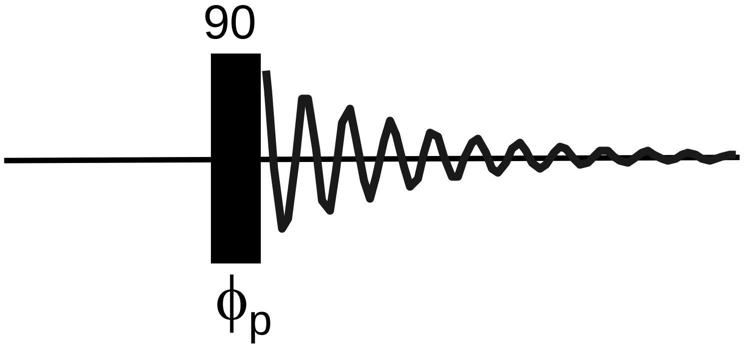
M-ε

B

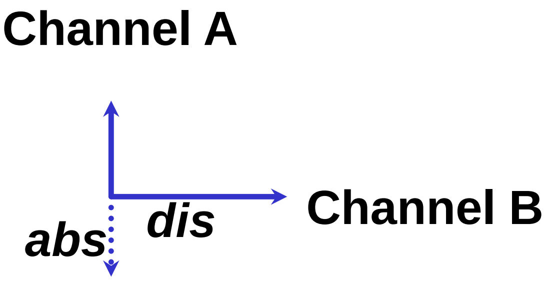
sin (dis)

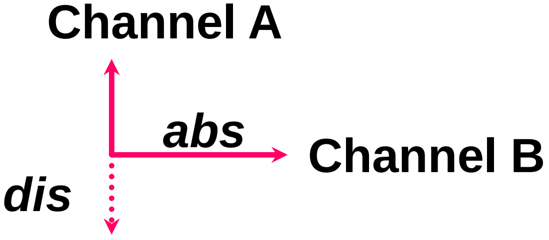
sin (dis)

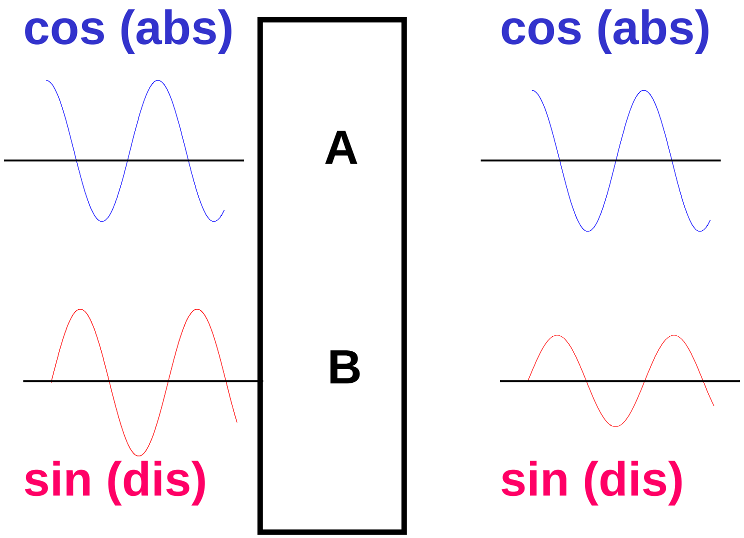
CYCLOPS

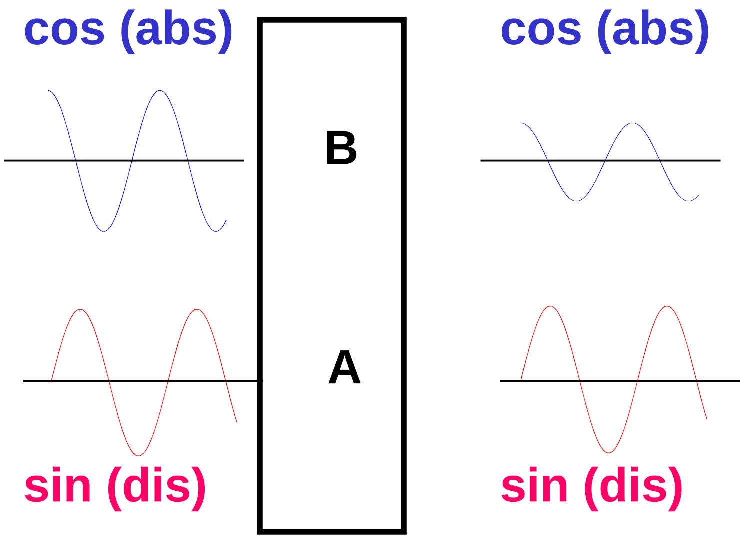


Scan	Pulse	Magn.	A:cos	B:sin
1	+x	-y	-y	+x
2	+y	+x	+x	+y
3	-x	+y	+y	-x
4	-y	-x	-x	-y

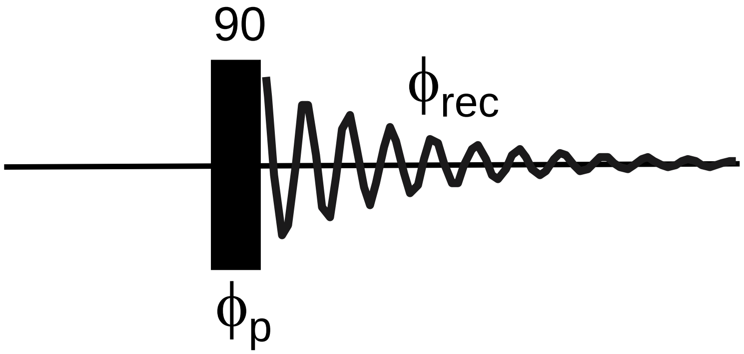






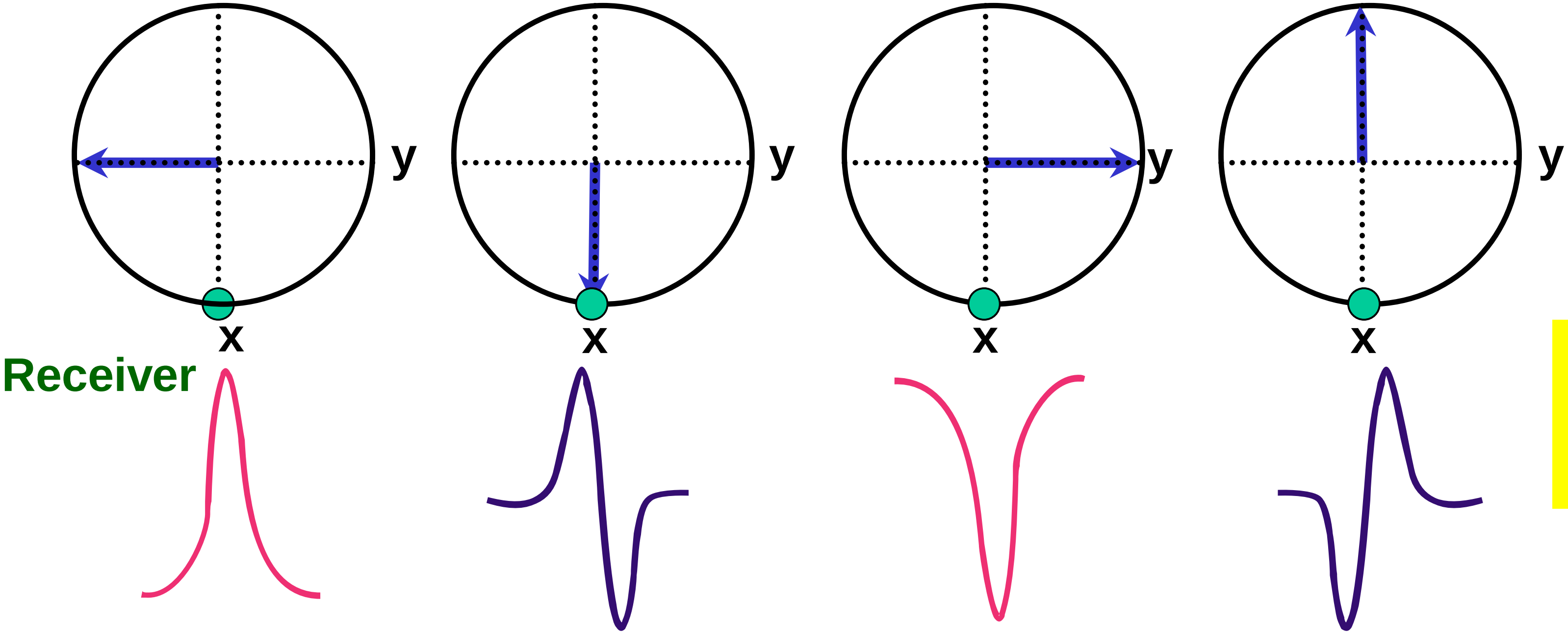


CYCLOPS



Scan	Pulse	Magn.	A:cos	B:sin
1	+x	-y	-y	+x
2	+y	+x	+x	+y
3	-x	+y	+y	-x
4	-y	-x	-x	-y

CYCLOPS compensates for amplitude and phase imbalances of the quadrature channels. How does the signal look like?

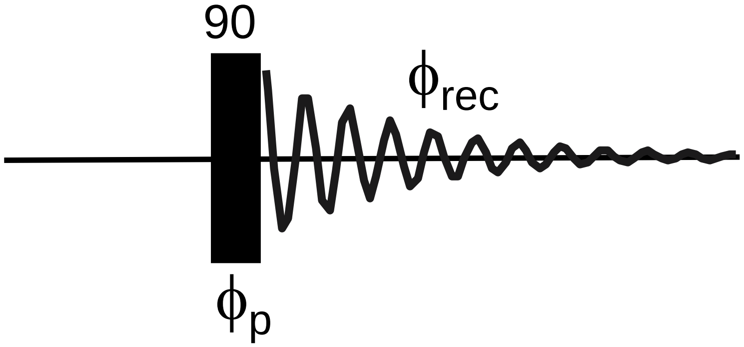


ϕ_{rec}=x

Net signal

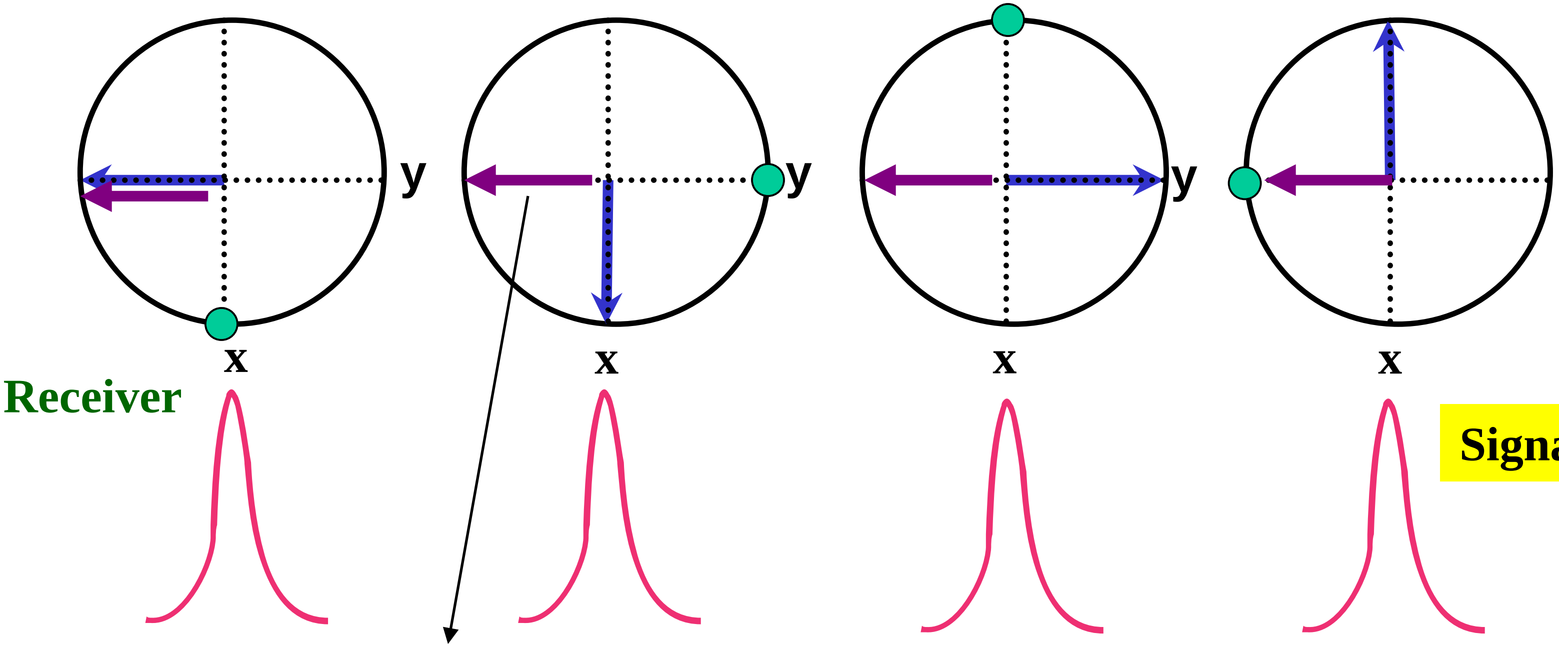
0!

CYCLOPS: Phase Cycling



Scan	Pulse	Magn.	Rec.	A:cos	B:sin
1	+x	-y	+x	-y	+x
2	+y	+x	+y	+x	+y
3	-x	+y	-x	+y	-x
4	-y	-x	-y	-x	-y

CYCLOPS compensates for amplitude and phase imbalances of the quadrature channels. How does the signal look like?



Signal adds up!

Unwanted signals like this (DC offset) will then go to zero

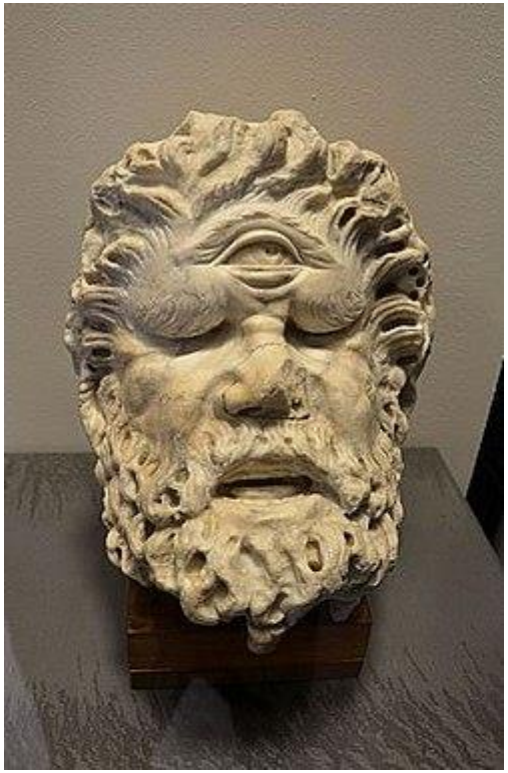
CYCLOPS: Phase Cycling

- **Phase cycling**
  - **The pulse and the receiver are cycled together in phase**
  - **The receiver should follow the phase of the desired signal**
  - **The number of steps in a phase cycle depends on how many undesired signals need to be suppressed and how many desired signals need to be selected**
  - **CYCLOPS is a 4-step phase cycle**
  - **CYCLOPS can correct for the phase and amplitude imbalances of the receiver channels with a 2-step phase cycle, 0,90**
  - **CYCLOPS can remove zero peaks (DC offsets) with another 2-step phase cycle, 0,180**
  - **Hence, overall one needs a 4-step phase cycle, 0, 90, 180, 270, in other words +x, +y, -x, -y (Is this correct?)**
  - **One can do CYCLOPS in 3 steps, with both pulses and receiver cycled as 0, 120, 240**

CYCLOPS/CYCLOPES

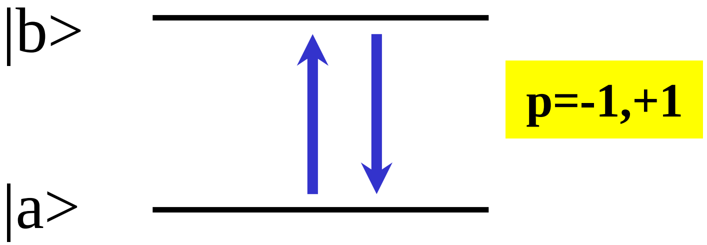
CYCLOPES are giant one-eyed creatures in Greek (and later Roman mythology).

They are three brothers: Brontes, Steropes, Arges (Arges made the thunderbolt for Zeus, God of lightning among others. Indra, Hindu God of lightning had Vajra as an equivalent.)

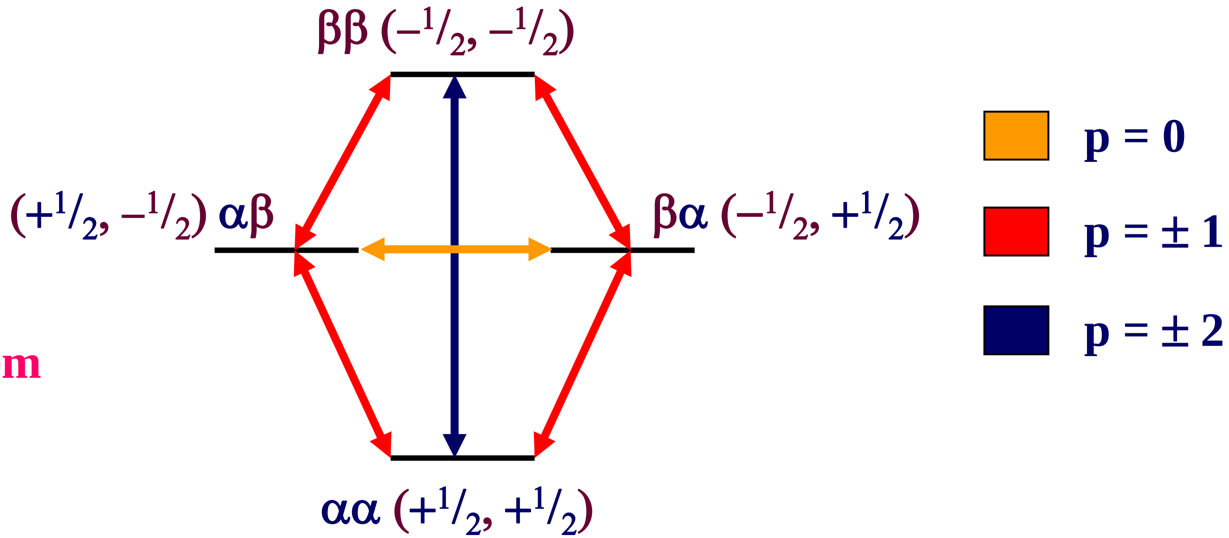


Phase Cycling: Quantitative Derivation

Coherence order of -1 or +1 for single spin-1/2
Single-quantum transitions



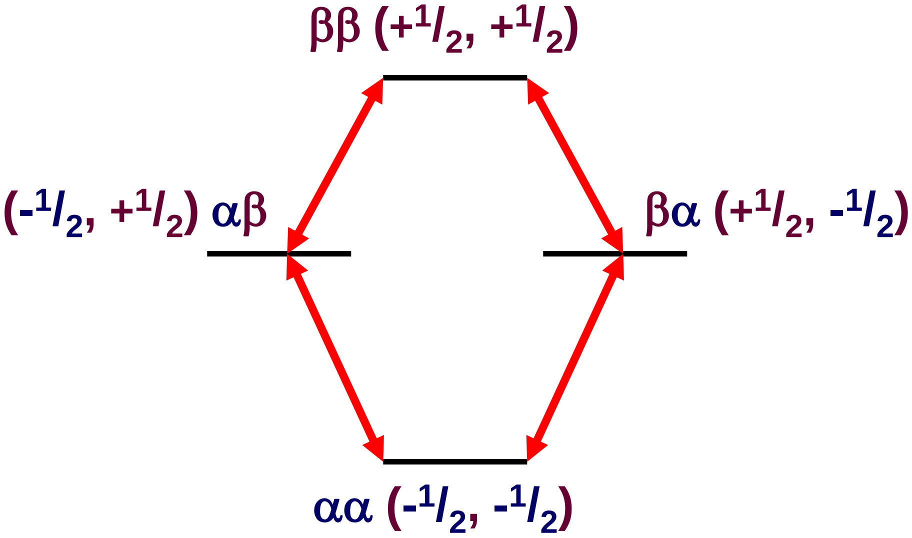
For a two-spin ½ system



Zero-quantum, Double-quantum, and single-quantum transitions

Phase Cycling: Coherence Order

A 90 pulse on equilibrium magnetisation I_z creates transverse (xy) magnetisation, the single-quantum transition elements



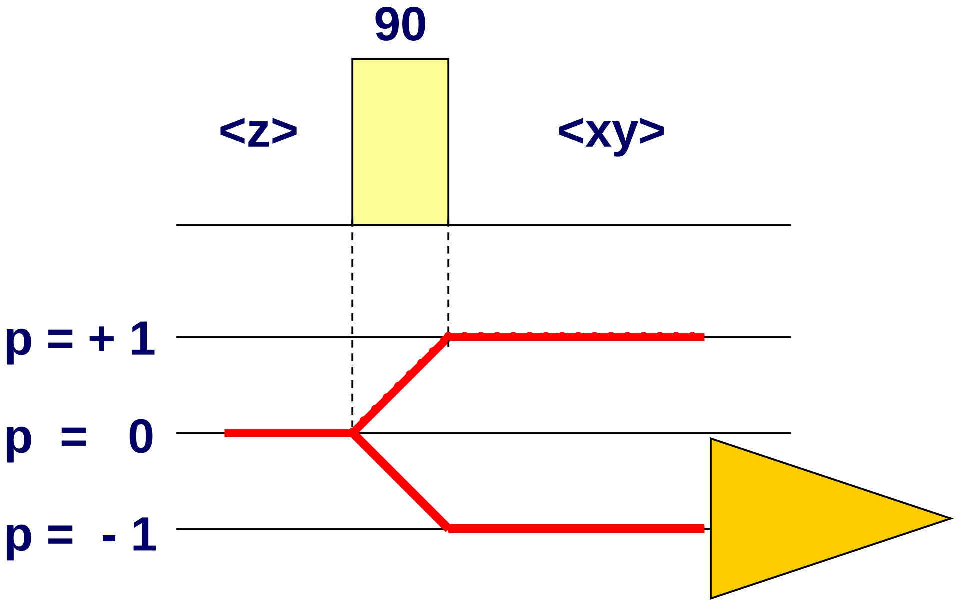
$\beta\beta\ (+{}^{1}/_{2}, +{}^{1}/_{2})$

$(-{}^{1}/_{2}, +{}^{1}/_{2})\ \alpha\beta$

$\beta\alpha\ (+{}^{1}/_{2}, -{}^{1}/_{2})$

$\alpha\alpha\ (-{}^{1}/_{2}, -{}^{1}/_{2})$

🟥 p = ± 1



90

<z>

<xy>

p = + 1

p = 0

p = - 1

We represent the SQC or any coherence by coherence transfer pathway diagrams, musical stave

Change of coherence order, $\Delta p=-1$

Phase Cycling: Coherence Order

A coherence of order σ, represented by the density operator $\sigma^{(p)}$, evolves under a z-rotation of angle ϕ according to

$$\exp(-i\phi F_z)\sigma^{(p)}\exp(i\phi F_z) = \exp(-ip\phi)\sigma^{(p)}$$

↓

Definition of coherence order

Total z-component of the spin angular momentum

The effect of a z-rotation on a term like $I_1^+ I_2^+$

$$\exp(-i\phi I_{1z})\exp(-i\phi I_{2z})\exp(-i\phi I_{1z})\exp(-i\phi I_{2z})$$

$$= \exp(-i\phi I_{1z})\exp(-i\phi)I_{I_{1+}I_{2+}}\exp(i\phi I_{1z})$$

$$= \exp(-i\phi)\exp(-i\phi)I_{I_{1+}I_{2+}}$$

$$= \exp(-2i\phi)I_{I_{1+}I_{2+}}$$

Hence, a coherence (here DQ term) that experiences a phase shift of 2ϕ could be referred to as p=2

Phase Cycling: Coherence Order

Consider *p* to *p'* by a pulse: How the phase of the pulse affects the phase of the coherence?

$$\boxed{U_0\sigma^{(p)}U_0^{-1} = \sigma^{(p')} + H.OTerms} \quad \boxed{U_\phi = \exp(-i\phi F_z)U_0\exp(i\phi F_z)}$$

The effect of the phase-shifted pulse on the initial state:

$$U_\phi\sigma^{(p)}U_\phi^{-1}$$

$$= \exp(-i\phi F_z)U_0\exp(i\phi F_z)\sigma^{(p)}\exp(-i\phi F_z)U_0^{-1}\exp(i\phi F_z)$$

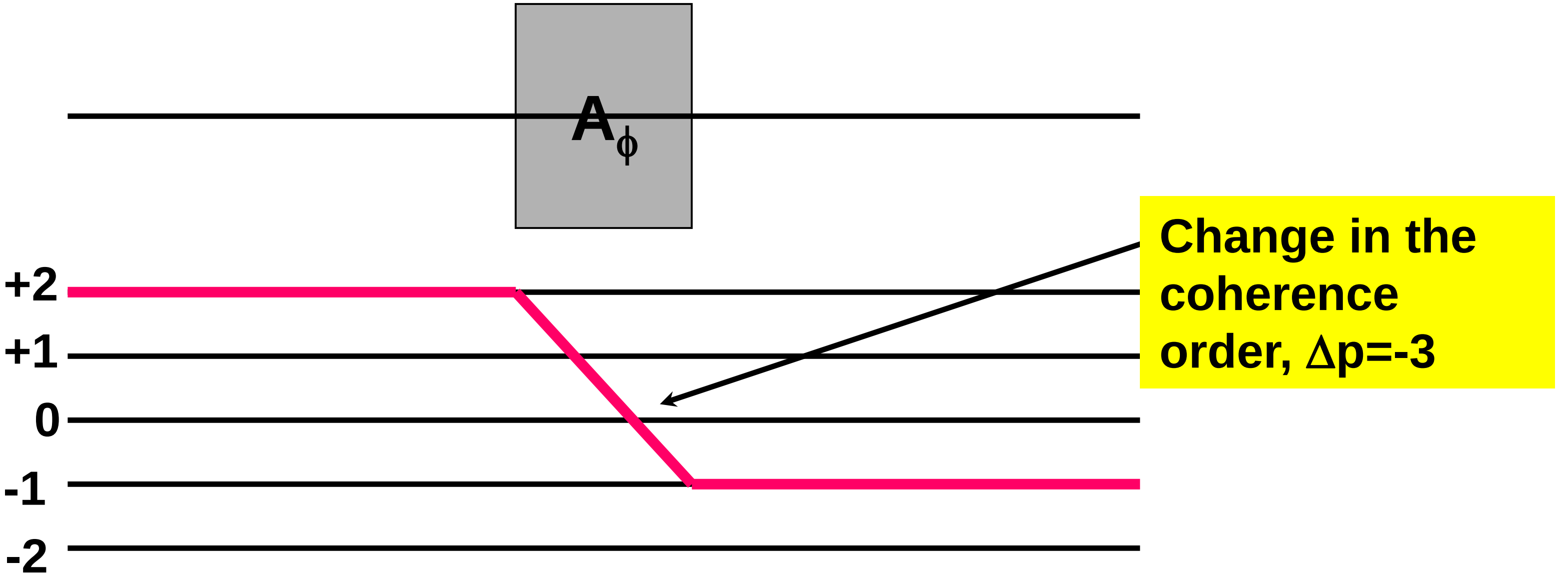
$$= \exp(ip\phi)\exp(-i\phi F_z)U_0\sigma^{(p)}U_0^{-1}\exp(i\phi F_z)$$

$$= \exp(ip\phi)\exp(-i\phi F_z)\sigma^{(p')}\exp(i\phi F_z)$$

$$= \exp(ip\phi)\exp(-ip'\phi)\sigma^{(p')} = \exp(-i\Delta p\phi)\sigma^{(p')}$$

If a pulse shifted in phase by ϕ causes a coherence order change of Δp, the coherence acquires a phase label of (-Δp ϕ)

Phase Cycling: Coherence Order



Change in the coherence order, Δp=-3

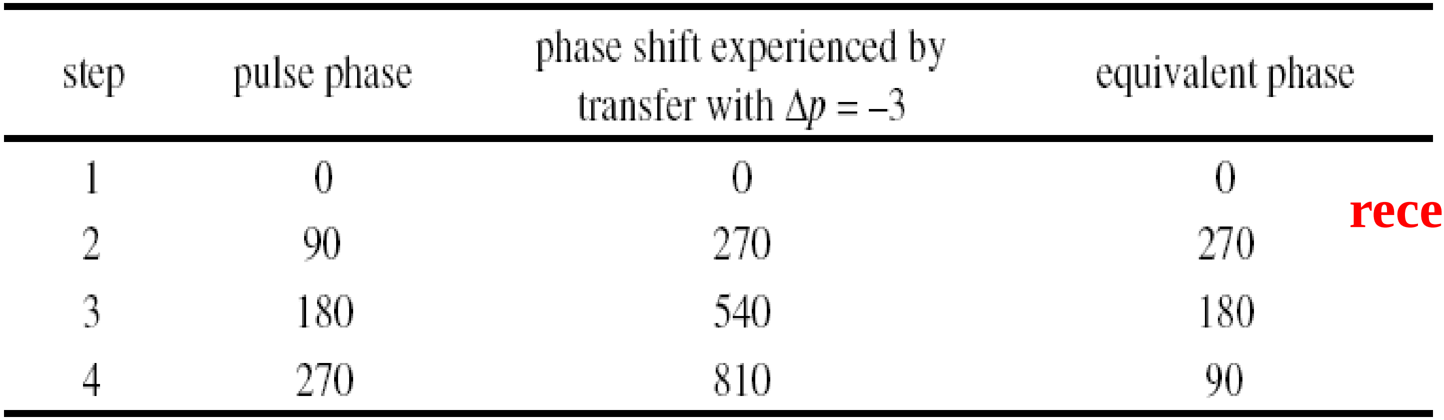
Phase cycling: Transformation/rotation of signals under phase shifts of the RF pusles

Z(ϕ) tells us the amplitude of conversion of +2 coherence to -1 coherence

$$Z(\phi) = Z(0)\exp(i\Delta p\phi)$$

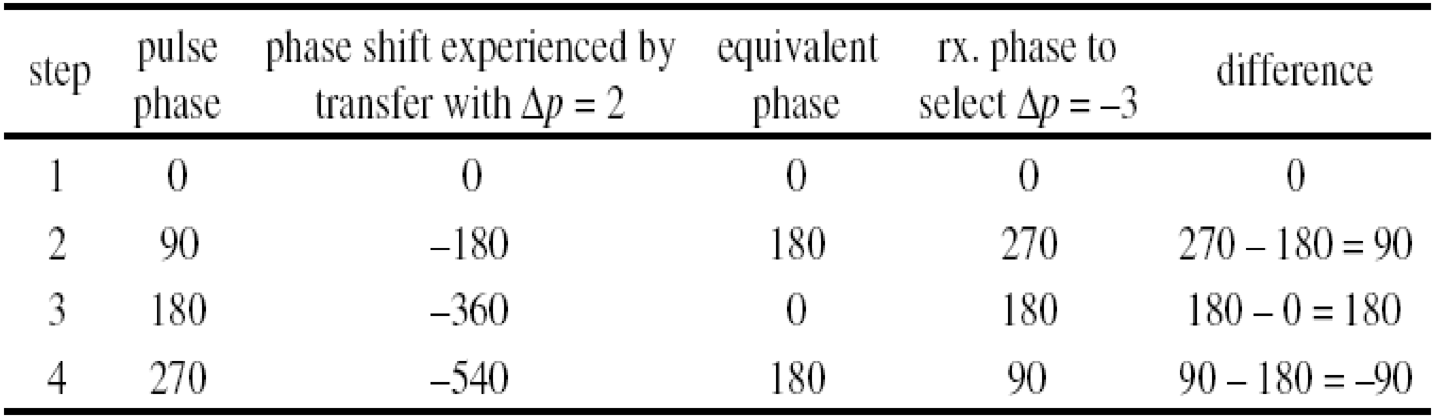
For Δp=-3, when the phase of the pulse changes by ϕ, the phase of the amplitude, Z, changes by 3ϕ. How do we catch that particular signal?

Phase Cycling: Coherence Order



step	pulse phase	phase shift experienced by transfer with $\Delta p = -3$	equivalent phase
1	0	0	0
2	90	270	270
3	180	540	180
4	270	810	90

receiver



step	pulse phase	phase shift experienced by transfer with $\Delta p = 2$	equivalent phase	rx. phase to select $\Delta p = -3$	difference
1	0	0	0	0	0
2	90	–180	180	270	270 – 180 = 90
3	180	–360	0	180	180 – 0 = 180
4	270	–540	180	90	90 – 180 = –90

Hence, Δp=-3 selected, whilst Δp=2 not
In fact, this phase cycle will select all Δp=-3+4n
where n=-1,+1,-2,+2,….

Phase Cycling: Coherence Order

Phase cycling: General rule-

If the pulse phase gets cycled as

$$\phi_k = \frac{2\pi}{N}k, k = 0,1,2,\ldots,N-1$$

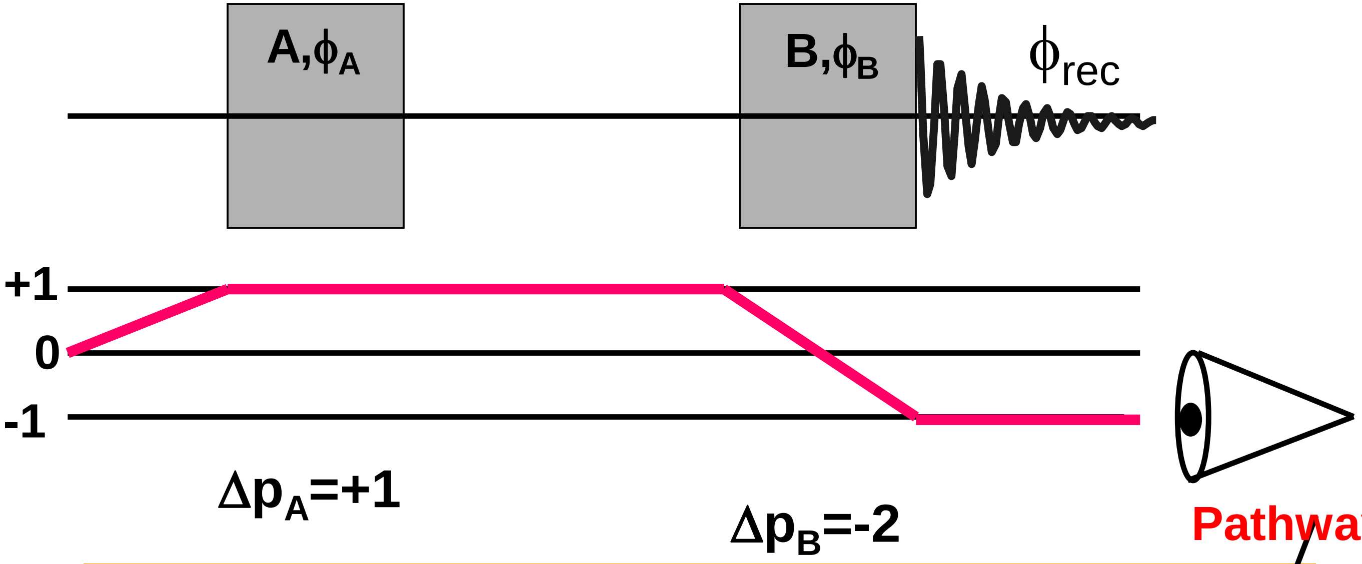
A coherence order change, Δp, gets selected, if the receiver phase

$$\phi_{rec} = -\Delta p.\phi_k$$

For each step and summing up the signal

Also $\Delta p \pm nN$ **get selected**

Phase Cycling: Selection Rule



Pathway phase

$$S(t;\phi_A,\phi_A,\phi_{rec}) = \sum_{path} S_{path}(t;\phi_A,\phi_A,\phi_{rec})$$

$$S_{path}(t;\phi_A,\phi_A,\phi_{rec}) = S_{path}(t;0,0,0)\exp(-i\phi_{path})$$

$$\phi_{path} = \Delta p_A\phi_A + \Delta p_B\phi_B + \phi_{rec}$$

Phase-cycle condition demands ϕ_{path}=0

$$\phi_{rec} = -\sum_i \Delta p_i\phi_i$$

Coherence and Phase Cycle Rules

Only pulses can change coherence order. Pulses on <z> magnetization (p = 0) generate p = ±1, while pulses on <xy> magnetization can create higher coherence order, depending on the number of coupled spins

We can only detect coherence with order ±1, because it correspond to *single-quantum transitions*, or <xy> magnetization

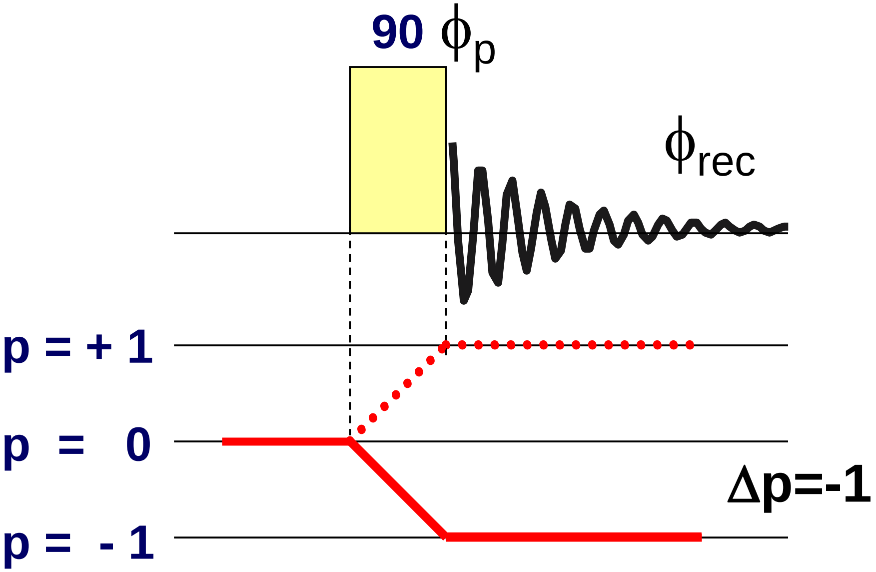
The number of cycles and steps per cycle needed will depend on the order of the coherence we want to select/transfer

In order to select or detect a certain component of the coherence order generated by a pulse of phase ϕ, the phase of the selecting pulse or receiver is given by:

$$\phi_{rec} = -\sum_i \Delta p_i \phi_i$$

where Δp is the coherence change we want to follow generated by the pulse of phase ϕ, and ϕ is its phase

CYCLOPS: Phase Cycling



$$\phi_{rec} = -\sum_i \Delta p_i \phi_i$$

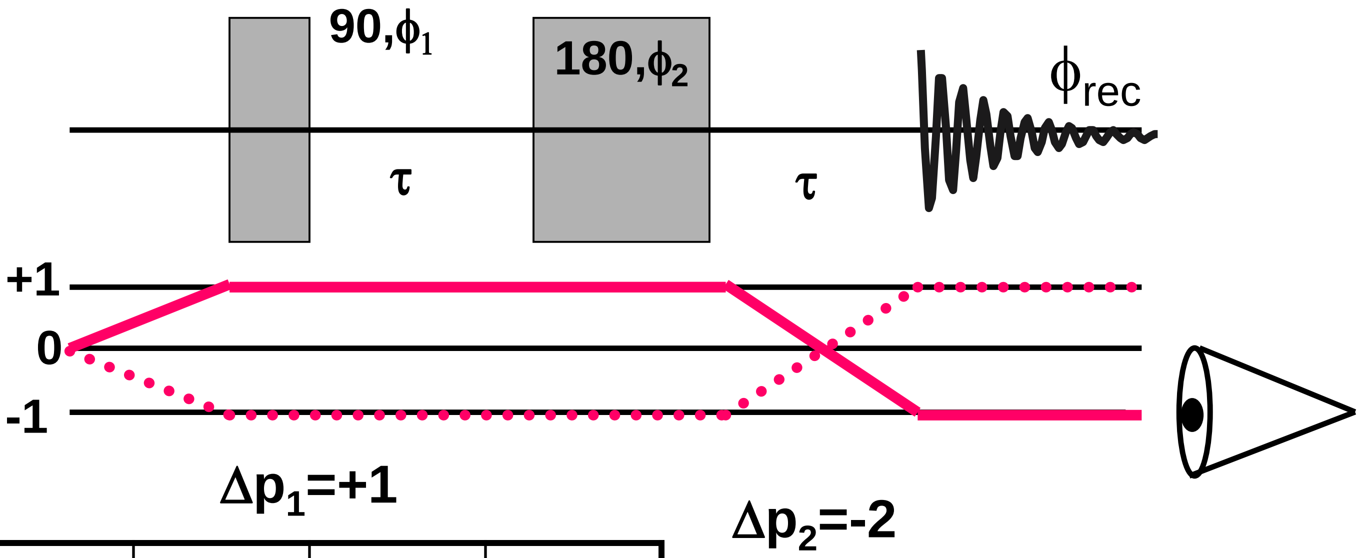
Here, ϕ=0,90,180,270

Hence, ϕ_{rec}=+1.ϕ=0,90,180,270

Scan, Cycle counter,m	ϕ_{pulse}	ϕ_{rec}
1	+x	+x
2	+y	+y
3	-x	-x
4	-y	-y

This phase cycle will remove Δp=+1 pathway, to select which ϕ_{rec}=0,270,180,90

Spin Echo: Phase Cycling



Scan	ϕ_1	ϕ_2	Magn.	Rec
1	+x	+x=0	+y	+x=0
2	+x	+y=90	-y	-x=180
3	+x	-x=180	+y	+x=0
4	+x	-y=270	-y	-x=180

But now on top of this, we have to do CYCLOPS on the first pulse

$$\phi_{rec} = -\Delta p_1 \phi_1 - \Delta p_2 \phi_2 = -\phi_1 + 2\phi_2$$

ϕ_1= 0 0 0 0 90 90 90 90 180 180 180 180 270 270 270
ϕ_2= 0 90 180 270 0 90 180 270 0 90 180 270 0 90 180 270
ϕ_{rec}= 0 180 0 180 270 90 270 90 180 0 180 0 90 270 90 270
16-step phase cycle

Nested Phase Cycle

The spin-echo phase cycle (EXORCYCLE) is a classic example of nested phase cycle

Bodenhausen, Kogler,and Ernst, J. Magn. Reson. 58, 370, 1984

Bain, J. Magn .Reson. 56, 418, 1984

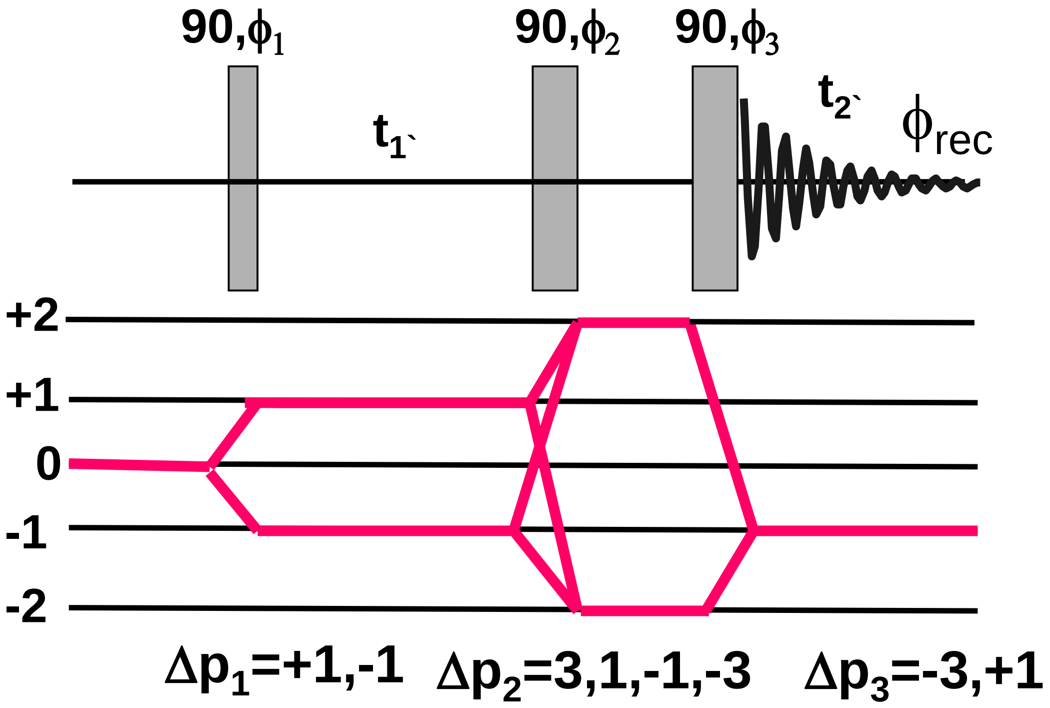
A more economical way of phase cycling called COGWHEEL method was introduced by the Levitt group

M. H. Levitt et al., J. Magn. Reson. 155, 300, 2002

Also see publications by Jerschow's group and Norbert Mueller's group

Also see Multiplex phase cycling, and combinations of cogwheel and multiplex philosophies for multiple data acquisition and fastening the experiments

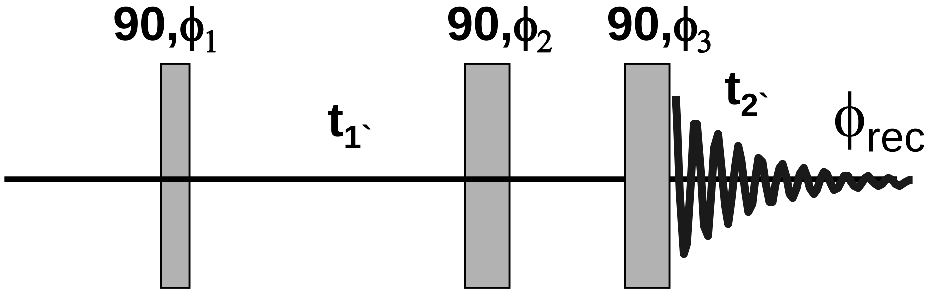
DQF COSY: Phase Cycling

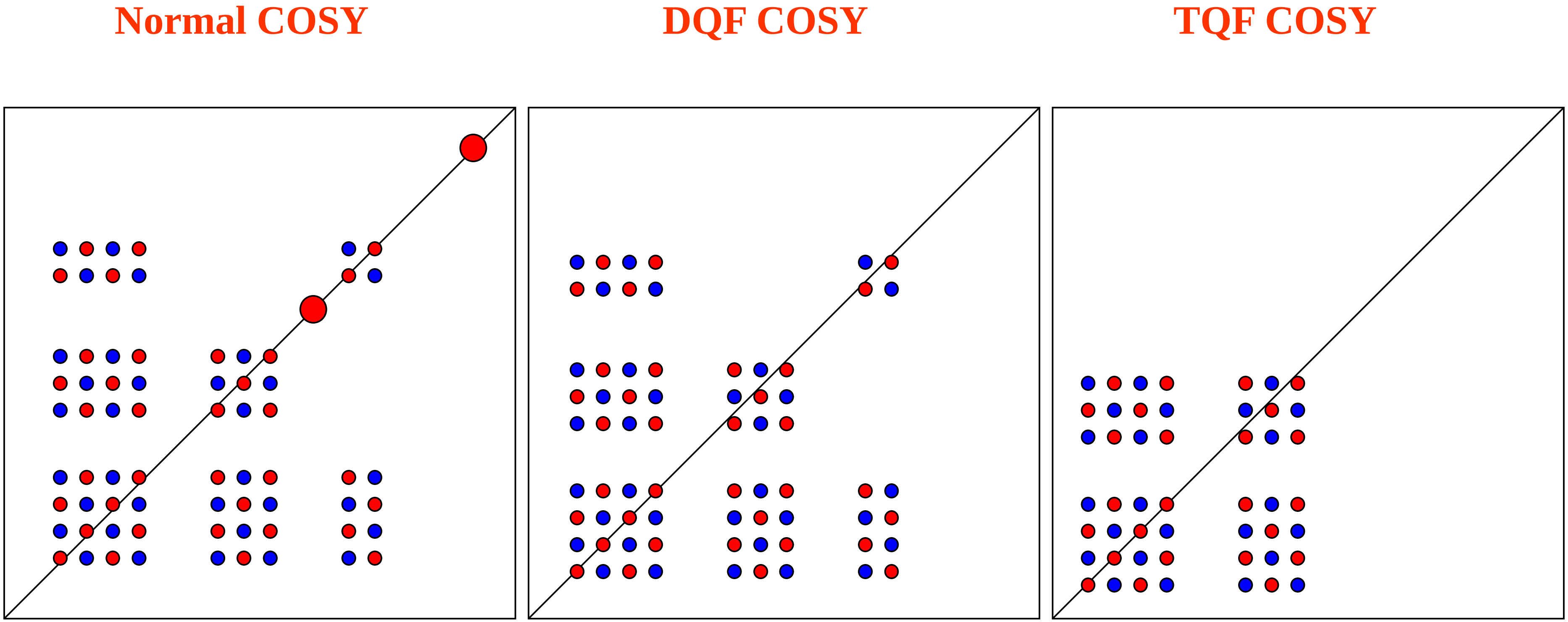


Cycle counter	ϕ_1	ϕ_2	ϕ_3	Rec
1	0	0	0	0
2	180	0	0	180
3	0	0	90	270
4	180	0	90	90
5	0	0	180	180
6	180	0	180	0
7	0	0	270	90
8	180	0	270	270

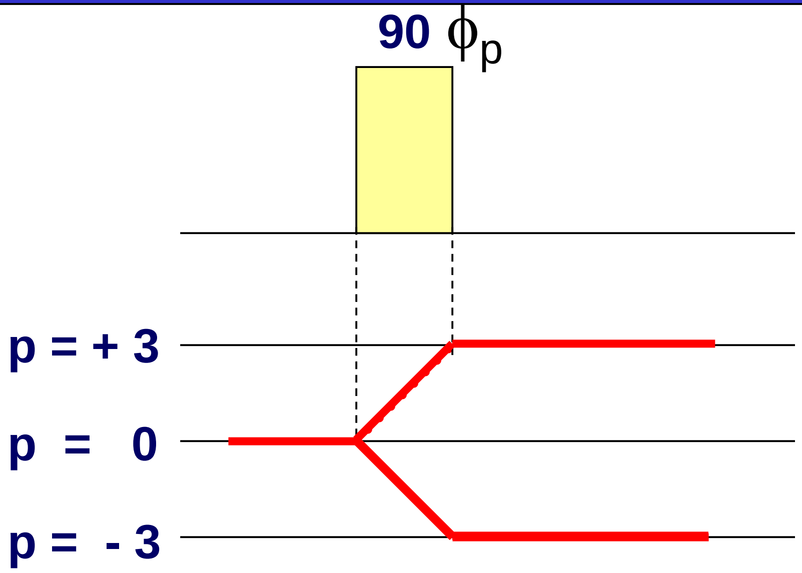
This phase cycle removes all the other undesired pathways, check this!

MQF COSY

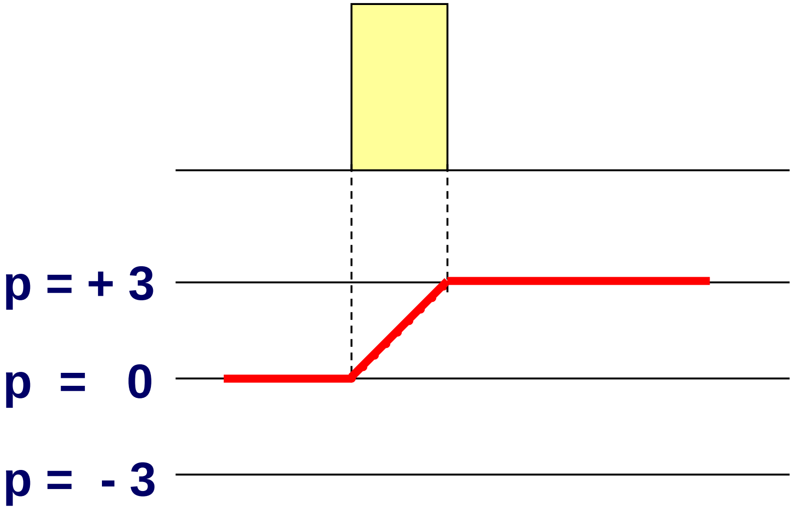

90,ϕ_1
90,ϕ_2
90,ϕ_3
t_1`
t_2`
ϕ_{rec}


Normal COSY
DQF COSY
TQF COSY

Selection of Higher Coherences



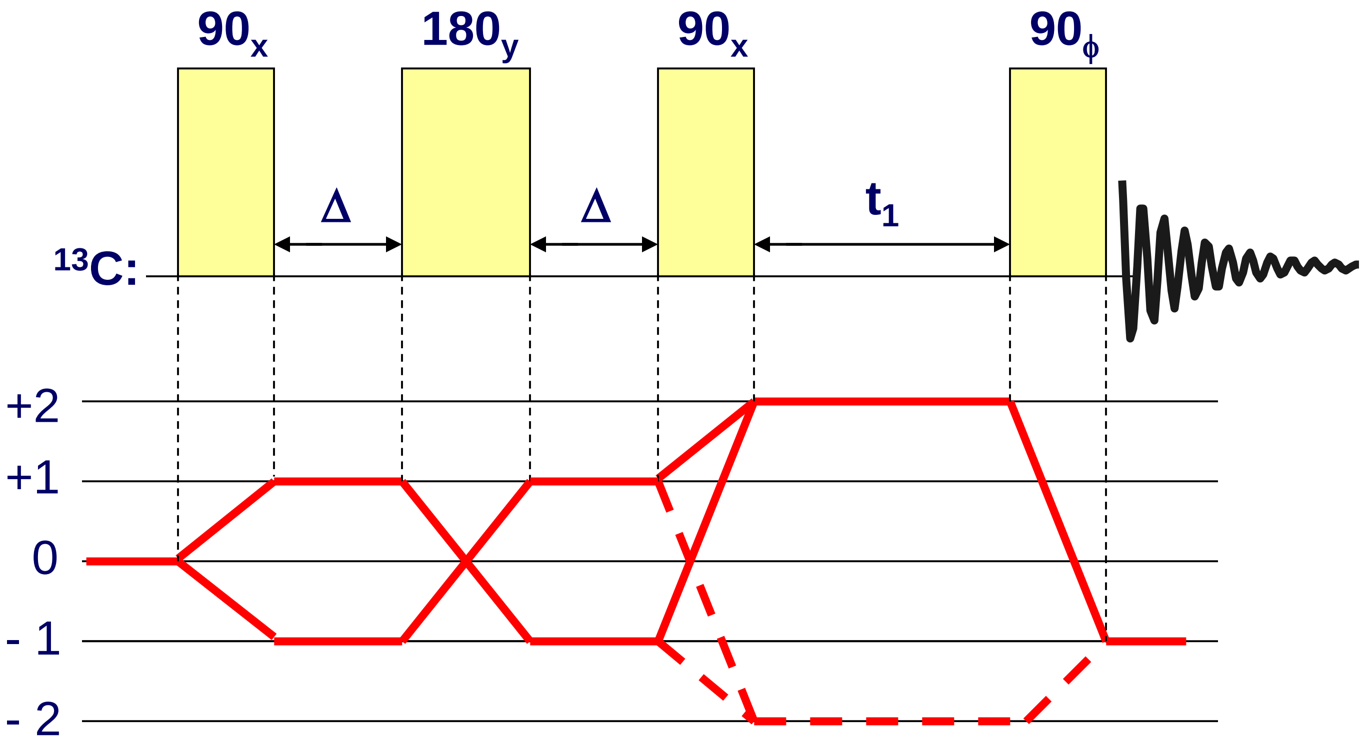
Scan, Cycle counter,m	ϕ_{pulse}
1	0
2	60
3	120
4	180
5	240
6	300



Scan, Cycle counter,m	ϕ_{pulse}	Scan, Cycle counter,m	ϕ_{pulse}
1	0	7	180
2	30	8	210
3	60	9	240
4	90	10	270
5	120	11	300
6	150	12	330

INADEQUATE

Incredible Natural Abundance Double-Quantum Transfer Experiment

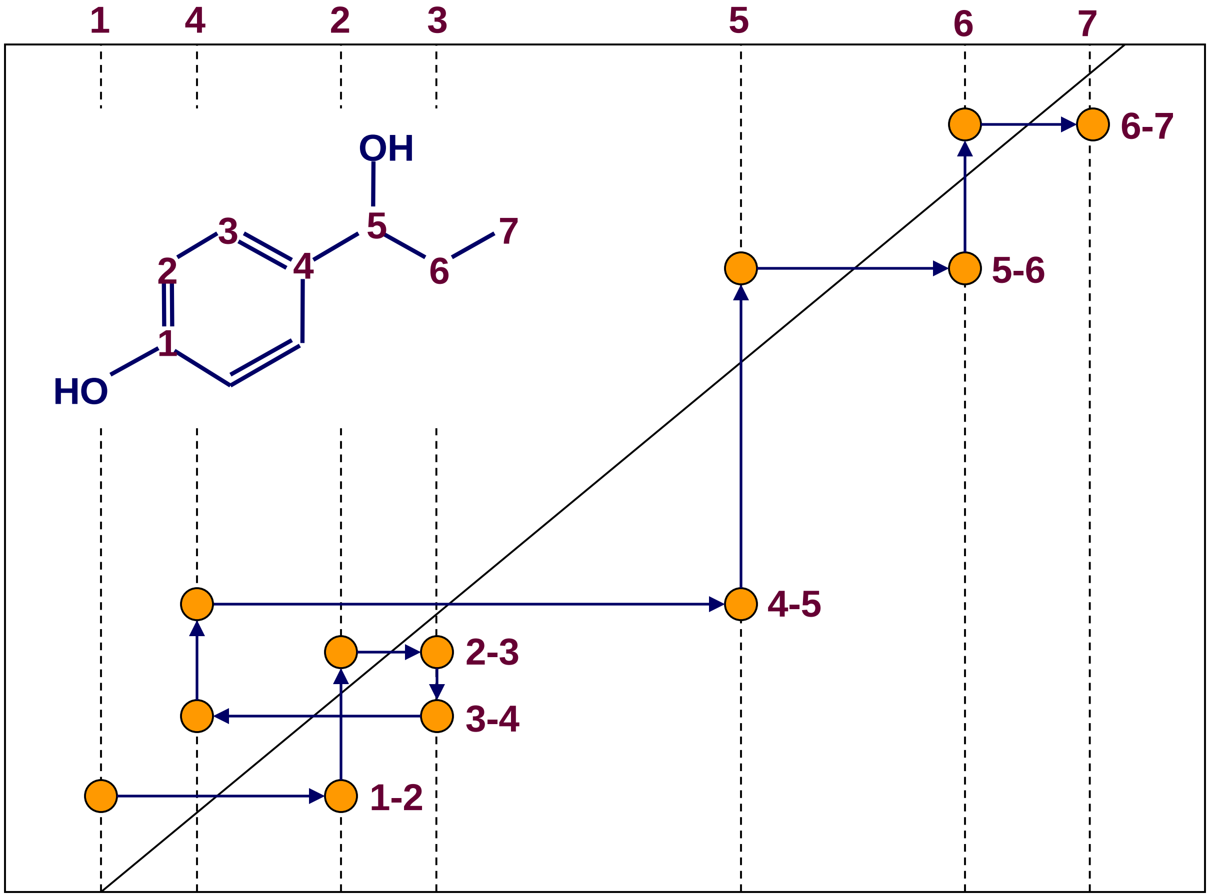


Pulse 1,3:	0 3 2 1 4 7 6 5 2 5 4 3 6 1 0 7 3 6 5 4 7 2 1 0 1 4 3 2 5 0 7 6
	0 3 2 1 4 7 6 5 2 5 4 3 6 1 0 7 3 6 5 4 7 2 1 0 1 4 3 2 5 0 7 6
Pulse 2:	0 3 2 1 4 7 6 5 2 5 4 3 6 1 0 7 3 6 5 4 7 2 1 0 1 4 3 2 5 0 7 6
	4 7 6 5 0 3 2 1 6 1 0 7 2 5 4 3 7 2 1 0 3 6 5 4 5 0 7 6 1 4 3 2
Pulse 3:	0 1 2 3 0 1 2 3 0 1 2 3 0 1 2 3 0 1 2 3 0 1 2 3 0 1 2 3 0 1 2 3
	0 1 2 3 0 1 2 3 0 1 2 3 0 1 2 3 0 1 2 3 0 1 2 3 0 1 2 3 0 1 2 3
Receiver:	0 0 0 0 0 0 0 0 2 2 2 2 2 2 2 2 1 1 1 1 1 1 1 1 3 3 3 3 3 3 3 3
	0 0 0 0 0 0 0 0 2 2 2 2 2 2 2 2 1 1 1 1 1 1 1 1 3 3 3 3 3 3 3 3

INADEQUATE

Assignments

Long-range information



Lineshapes

Typical NMR signal

$$S(t) = B\exp(i\Omega t)\exp(i\Phi)\exp(-\frac{t}{T_2})$$

↓ **Amplitude**

↓ **Overall phase factor=ϕ_{signal}-$\phi_{receiver}$**

FT ↓

$$S(\omega) = B[A(\omega) + iD(\omega)]\exp(i\Phi)$$

$$A(\omega) \downarrow \frac{T_2}{1+(\omega-\Omega)^2 T_2^2} \qquad D(\omega) \downarrow \frac{(\omega-\Omega)T_2^2}{1+(\omega-\Omega)^2 T_2^2}$$

↓ **Absorpion mode Lorentzian centred at $\omega=\Omega$**

↓ **Dispersion mode Lorentzian**

Normally one displays the real part of S(ω)

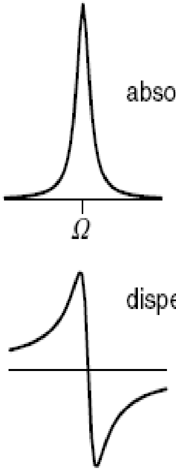
$$\mathrm{Re}(S(\omega)) = B[\cos\Phi A(\omega) - \sin\Phi D(\omega)]$$

Mixture of both absorption and dispersion line shapes

Lineshapes

NMR spectral line shape:

$$\mathrm{Re}(S(\omega)) = B[\cos\Phi A(\omega) - \sin\Phi D(\omega)]$$



How to get pure absorption mode line shapes? Make Φ=0, multiply S(ω) by a phase factor exp(iθ)

$$S(\omega)\exp(i\theta) = B[A(\omega) + iD(\omega)]\exp(i\Phi)\exp(i\theta)$$

$$= B[A(\omega) + iD(\omega)]\exp(i\Phi + \theta)$$

Now choose θ=–Φ, phase factor is removed and the Re(S(ω)) is in pure Absorption mode: **Phase correction**

Coherence Transfer Pathways

Selection of CTP: Guidelines

Frequency discrimination

STATES/TPPI

Line shape features

Absorption-mode line shapes
Real FT

Typical 2D

$$\cos(\Omega_i t_1) I_{ix} \xrightarrow{mixing} \cos(\Omega_j t_1) I_{jx}$$

The 2D signal $\equiv \cos(\Omega_i t_1) \exp(i\Omega_j t_2)$

Amplitude modulated data set in t_1

Coherence Transfer Pathways

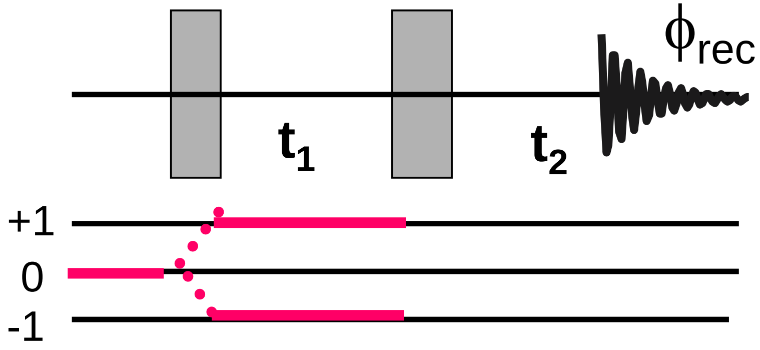
Typical 2D

$$\cos(\Omega_i t_1) I_{ix} \xrightarrow{mixing} \cos(\Omega_j t_1) I_{jx}$$

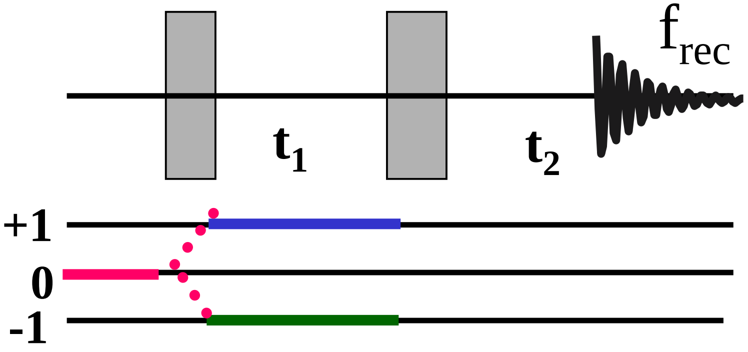
$$\frac{1}{2}\cos(\Omega_i t_1)(I_i^+ + I_i^-) \xrightarrow{mixing} \cos(\Omega_j t_1) I_{jx}$$

Amplitude modulation, hence, results from a selection of both the +1 and -1 coherence pathways

- **Retaining symmetrical pathways**
- **No frequency discrimination**
- **Pure absorption-mode lineshapes**



Coherence Transfer Pathways



Selecting p=1 pathway only during t_1

At the start of t_1, the signal

$$I_x = \frac{1}{2}(I^+ + I^-)$$

During t_1, this evolves into

$$\frac{1}{2}\exp(i\Omega\ t_1)I_-$$

The 2D signal is then given by:

$$S_P(t_1,t_2) = \frac{1}{4}\exp(i\Omega\ t_1)\exp(i\Omega\ t_2)$$

Phase modulated data set in t_1

Selecting p=-1 pathway only during t_1

The 2D signal is then given by:

$$S_N(t_1,t_2) = \frac{1}{4}\exp(-i\Omega\ t_1)\exp(i\Omega\ t_2)$$

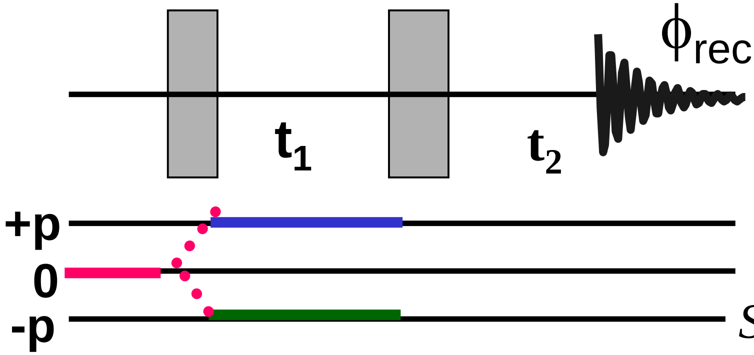
Phase modulation, hence, results from a selection of either the +1 or -1 coherence pathways

- **Frequency discrimination**
- **Phase twisted lineshapes**

Frequency discrimination achieved by selecting one pathway with appropriate phase cycle

This procedure is called anti-echo (P-type) or echo (N-type) selection scheme

Quadrature in t_1 Dimension



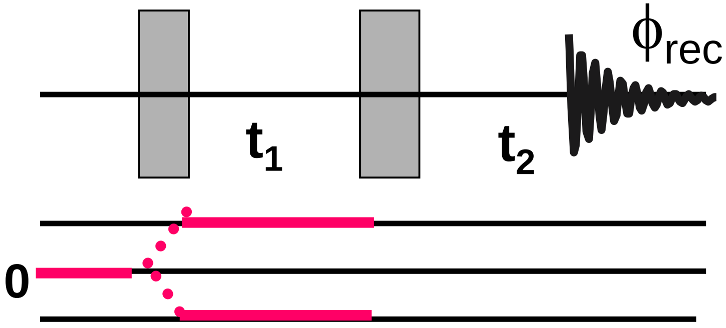
Anti-Echo/Positive signal

$$S(t_1,t_2)_P \approx \exp(i\Omega_1 t_1)\exp(-t_1/T_2)\exp(i\Omega_2 t_2)\exp(-t_2/T_2)$$

$$S(t_1,t_2)_N \approx \exp(-i\Omega_1 t_1)\exp(-t_1/T_2)\exp(i\Omega_2 t_2)\exp(-t_2/T_2)$$

Echo/Negative signal

Phase-modulated signal



Normally, 2D experiments record both P and N pathways, resulting in a signal of the form

$$S(t_1,t_2)_C \approx \cos(i\Omega_1 t_1)\exp(-t_1/T_2)\exp(i\Omega_2 t_2)\exp(-t_2/T_2)$$

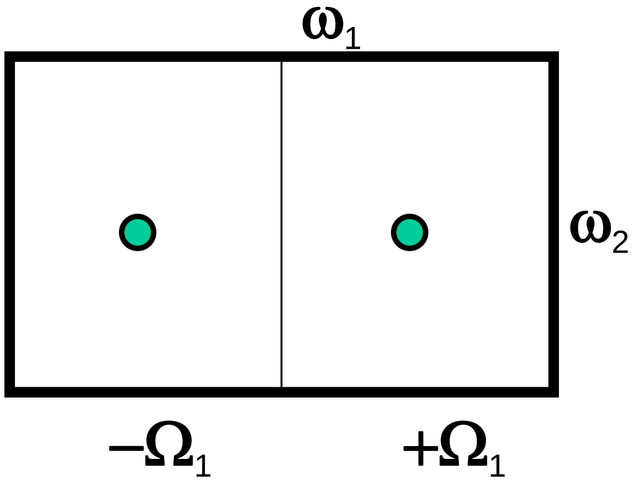
or

$$S(t_1,t_2)_S \approx \sin(i\Omega_1 t_1)\exp(-t_1/T_2)\exp(i\Omega_2 t_2)\exp(-t_2/T_2)$$

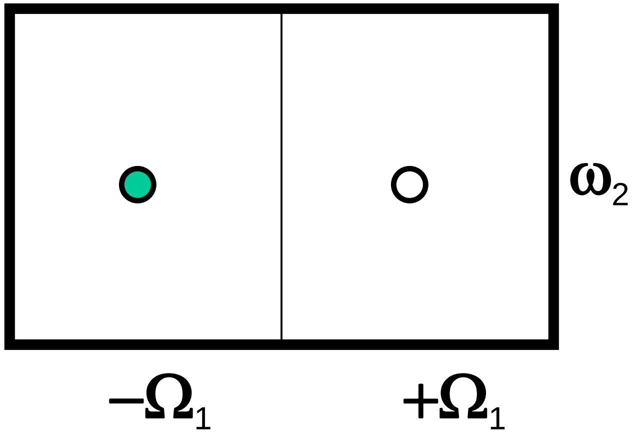
Amplitude-modulated signal

Quadrature in t_1 Dimension

$$S(t_1,t_2) \approx \cos(i\Omega_1 t_1)\exp(-t_1/T_2)\exp(i\Omega_2 t_2)\exp(-t_2/T_2)$$



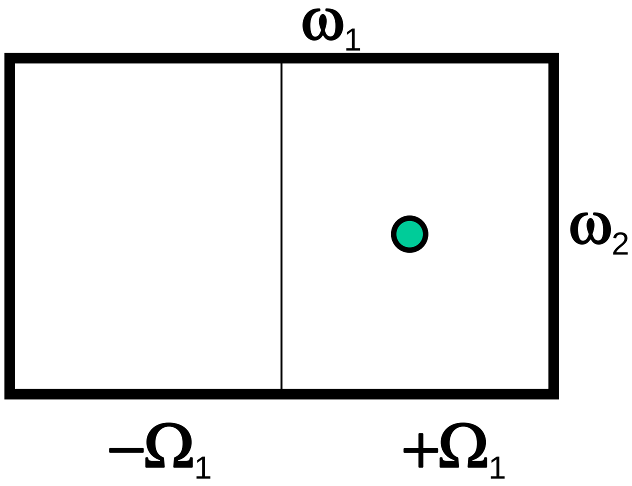
$$S(t_1,t_2) \approx \sin(i\Omega_1 t_1)\exp(-t_1/T_2)\exp(i\Omega_2 t_2)\exp(-t_2/T_2)$$



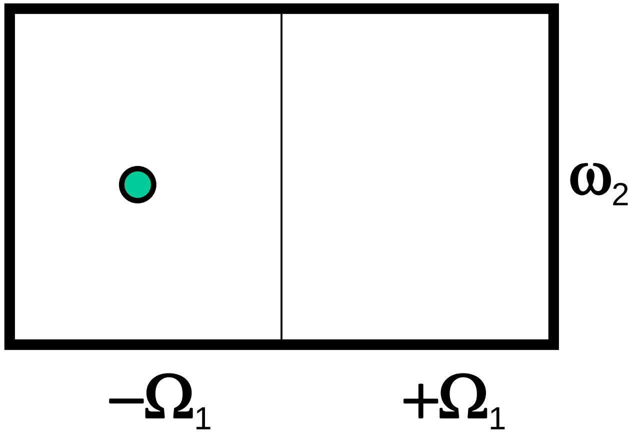
Amplitude modulation: No frequency discrimination

Quadrature in t_1 Dimension

$$S(t_1,t_2) \approx \exp(i\Omega_1 t_1)\exp(-t_1/T_2)\exp(i\Omega_2 t_2)\exp(-t_2/T_2)$$

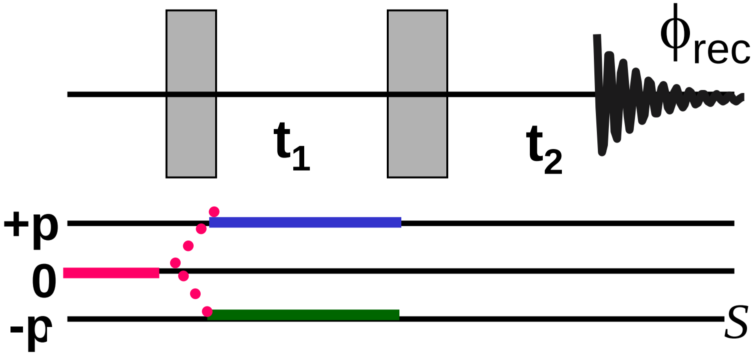


$$S(t_1,t_2) \approx \exp(-i\Omega_1 t_1)\exp(-t_1/T_2)\exp(i\Omega_2 t_2)\exp(-t_2/T_2)$$



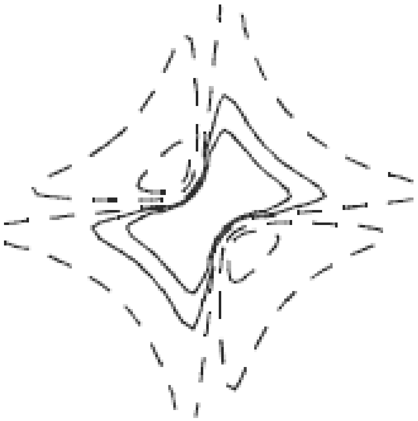
Phase modulation: Frequency discrimination possible

To Collect or Not To Collect Both the Pathways



$$S(t_1,t_2)_P \approx \exp(i\Omega_1 t_1)\exp(-t_1/T_2)\exp(i\Omega_2 t_2)\exp(-t_2/T_2)$$

$$S(t_1,t_2)_N \approx \exp(-i\Omega_1 t_1)\exp(-t_1/T_2)\exp(i\Omega_2 t_2)\exp(-t_2/T_2)$$



Mixture of absorptive and dispersive lineshapes giving rise to twisted peak appearance for the 2D contour peaks

Collection of both the pathways is necessary to get pure-absorptive lineshapes

Why Collect Both Pathways

$$S(t_1,t_2)_P \approx \exp(i\Omega_1 t_1)\exp(-t_1/T_2)\exp(i\Omega_2 t_2)\exp(-t_2/T_2)$$

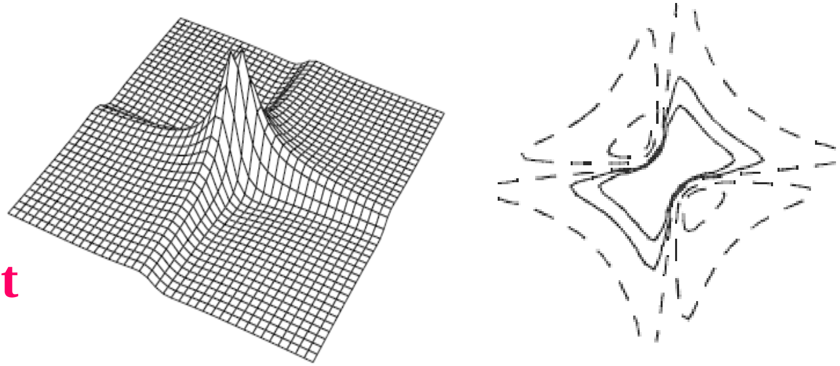
$$S(t_1,F_2)_P = \exp(i\Omega_1 t_1)\exp(-t_1/T_2)[A_2 + iD_2]$$

$$S(F_1,F_2)_P = [A_{1+} + iD_{1+}][A_2 + iD_2]$$

↓

Absorption and dispersion lines at +Ω

$$\mathrm{Re}(S(F_1,F_2)_P) = [A_{1+}A_2 - D_{1+}D_2]$$



Phase-twisted line shapes at (F_1,F_2)= (+Ω,+Ω)

Collection of both the pathways is necessary to get pure-absorptive lineshapes

Why Collect Both Pathways

$$S(t_1,t_2)_C = \frac{1}{2}\cos(\Omega_1 t_1)\exp(-t_1/T_2)\exp(i\Omega_2 t_2)\exp(-t_2/T_2)$$

$$S(t_1,F_2)_C = \frac{1}{2}\cos(\Omega_1 t_1)\exp(-t_1/T_2)[A_2 + iD_2]$$

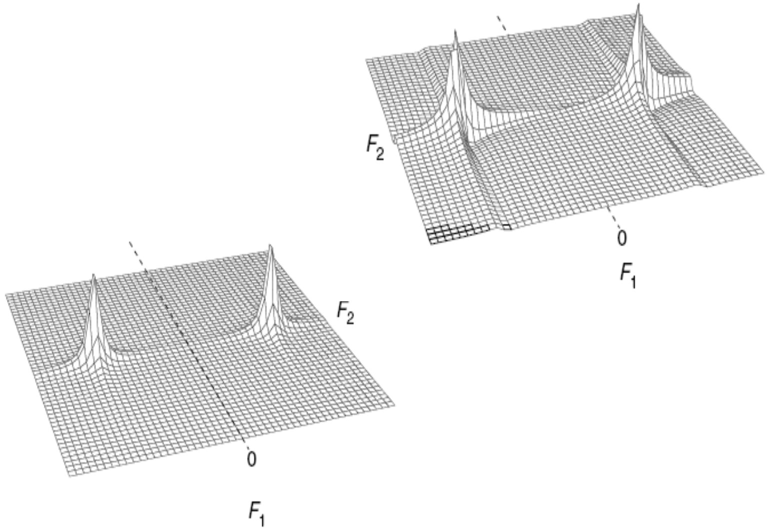
$$= \frac{1}{4}[\exp(i\Omega_1 t_1) + \exp(-i\Omega_1 t_1)]\exp(-t_1/T_2)[A_2 + iD_2]$$

$$\mathrm{Re}[S(F_1,F_2)_C] = \frac{1}{4}[A_{1+}A_2 - iD_{1+}D_2] + \frac{1}{4}[A_{1-}A_2 + iD_{1-}D_2]$$

Terrible! No frequency discrimination, and moreover, two phase-twisted line shapes, one at (F_1,F_2)= (+Ω,+Ω), and the other at (F_1,F_2)= (-Ω.+Ω)

$$\mathrm{Re}[S(t_1,F_2)_C] = \frac{1}{2}\cos(\Omega_1 t_1)\exp(-t_1/T_2)A_2$$

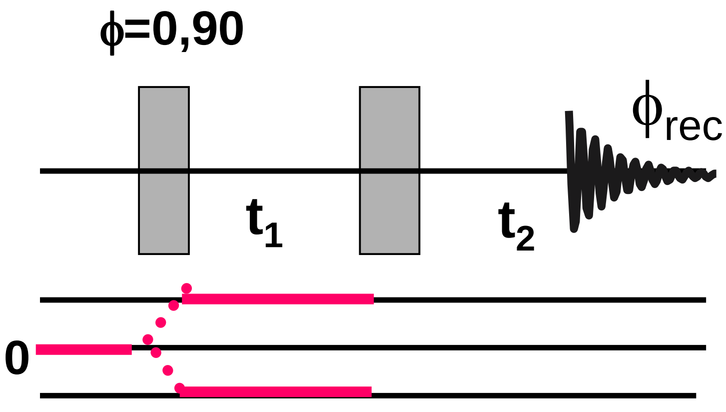
$$\mathrm{Re}[S(F_1,F_2)_C] = \frac{1}{4}(A_{1+}A_2 + A_{1-}A_2)$$



Two double-absorption mode lineshapes without frequency discrimination

Quadrature in t_1 Dimension, STATES Method

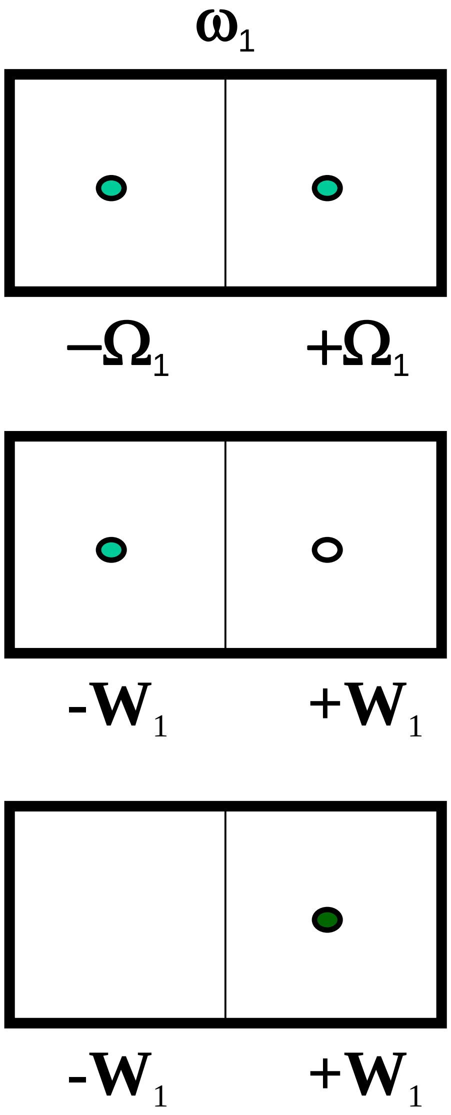
Same t_1, do 2 experiments



ϕ=0, cosine

ϕ=90, sine

Difference,
cos-sin

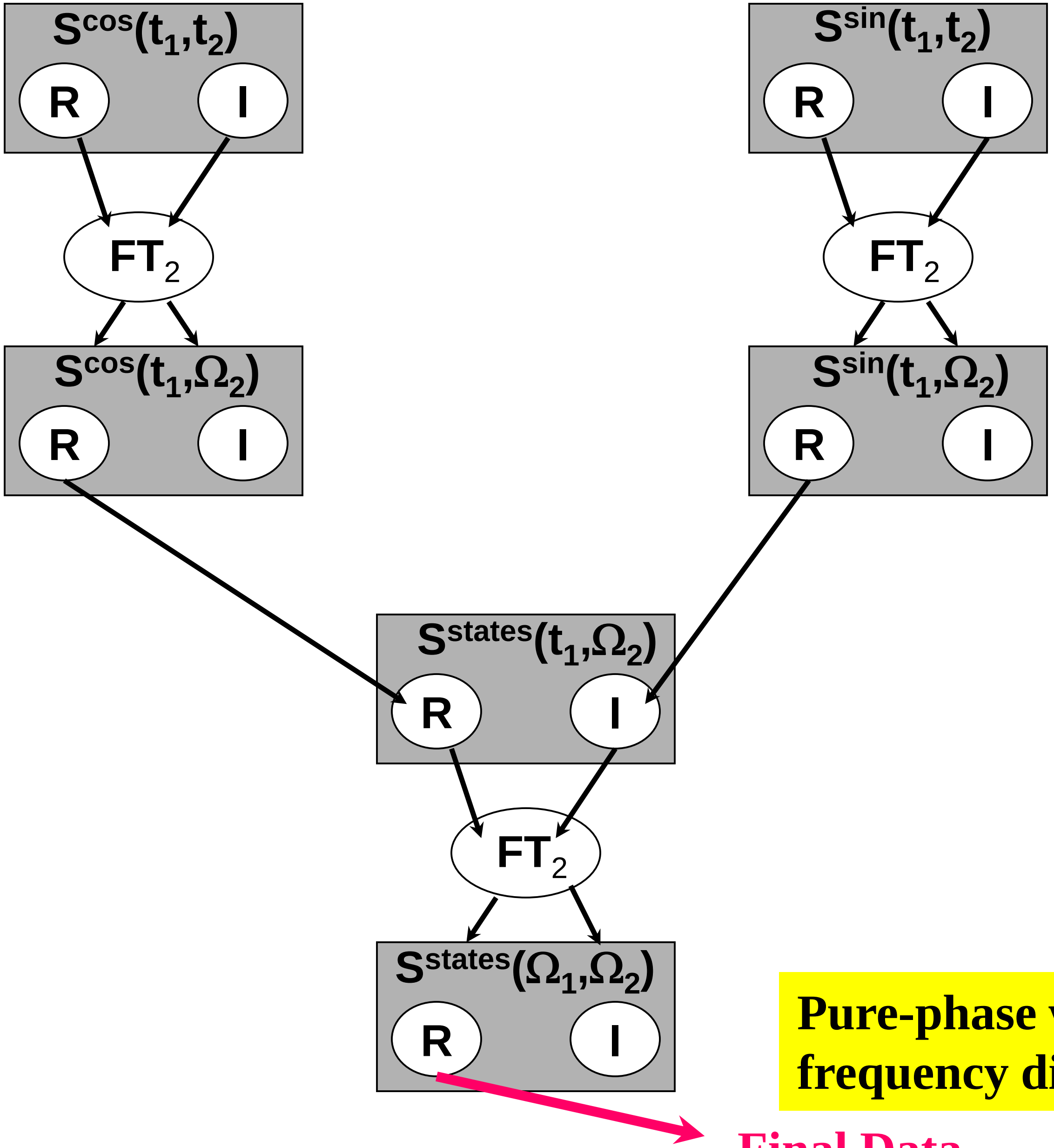


Thus, quadrature is accomplished in t_1 as well

Frequency discrimination, STATES phase cycling method (also, TPPI, Time Proportional Phase Increment)

States, Haberkorn, Ruben, J. Magn. Reson. 48, 286, 1982
Marion, Wuthrich, Biochem. Biophys. Res. Commun. 113, 967, 1983

2D Spectrum: STATES+Pure-Absorptive Line Shape



$S^{cos}(t_1,t_2)$

R I

FT$_2$

$S^{cos}(t_1,\Omega_2)$

R I

$S^{sin}(t_1,t_2)$

R I

FT$_2$

$S^{sin}(t_1,\Omega_2)$

R I

$S^{states}(t_1,\Omega_2)$

R I

FT$_2$

$S^{states}(\Omega_1,\Omega_2)$

R I

Final Data

Pure-phase with frequency discrimination

Pulsed Field Gradients in NMR: Theory and Practice

Keeler et al., Methods in Enzymology, Academic Press, San Deigo, 1994, pp145

PFG’s in NMR

- Coherence transfer pathways
- Pathway selection by phase cycling and PFG
- DQF-COSY

Coherences and Populations

Population is a generalisation of longitudinal magnetisation: The corresponding spin operators are I_z, S_z and their linear combinations

Coherence is a generalisation of transverse magnetisation: I_x, S_x, I_{1+}, I_{1-} are some of the corresponding spin operators

The observable transverse magnetisation is classified as having a coherence order $p = \pm 1$**, single-quantum coherence**

$p = \pm 2$ **Double-quantum coherence**

$p = \pm 3$ **Triple-quantum coherence**

$p = 0$ **Zero-quantum coherence, *z* magnetisation**

Phase Cycling: Separating Wheat from Chaff

- **Suppression of artifacts**

- **Selection of the desired CTP, rejection of the undesired CTP**

- **A pulse can change the coherence level and the phase of the coherence level**

- **If the pulse phase is changed by Δq, those coherences, for which the pulse induces a coherence level shift Δp, change the phase ϕ by Δp*Δq. In other words**

$$\Delta\phi = \Delta p * \Delta\theta$$

Refocusing condition (for selection of desired signals)

$$\sum_i \Delta\phi_i + \phi_{rec} = 0$$

Phase of the reciever

Coherence and Density Matrix

Density matrix characterises the state of a spin system

Populations are the diagonal elements of the density matrix

Coherences are the off-diagonal elements of the density matrix

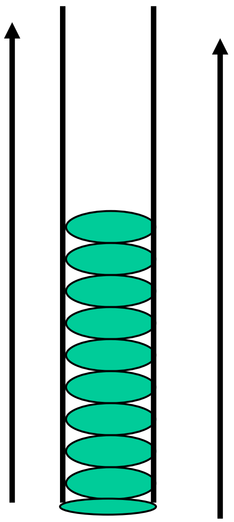
The density matrix may be separated into contributions from different coherence orders, denoted $\sigma^{(p)}$

$$\sigma = \sum_{p=-p_m}^{p=p_m} \sigma^{(p)}$$

p_m, the maximum coherence order, is equal to the number of mutually coupled spins

What are Gradients?

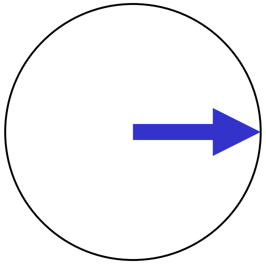
B_0, applied magnetic field



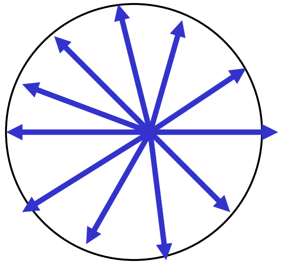
Spatially varying small magnetic field along z direction, pulsed field gradients

Different portions of the sample experience different magnetic fields, and thus have different Larmor frequencies

Before the gradients, the transverse magnetisation vectors are aligned

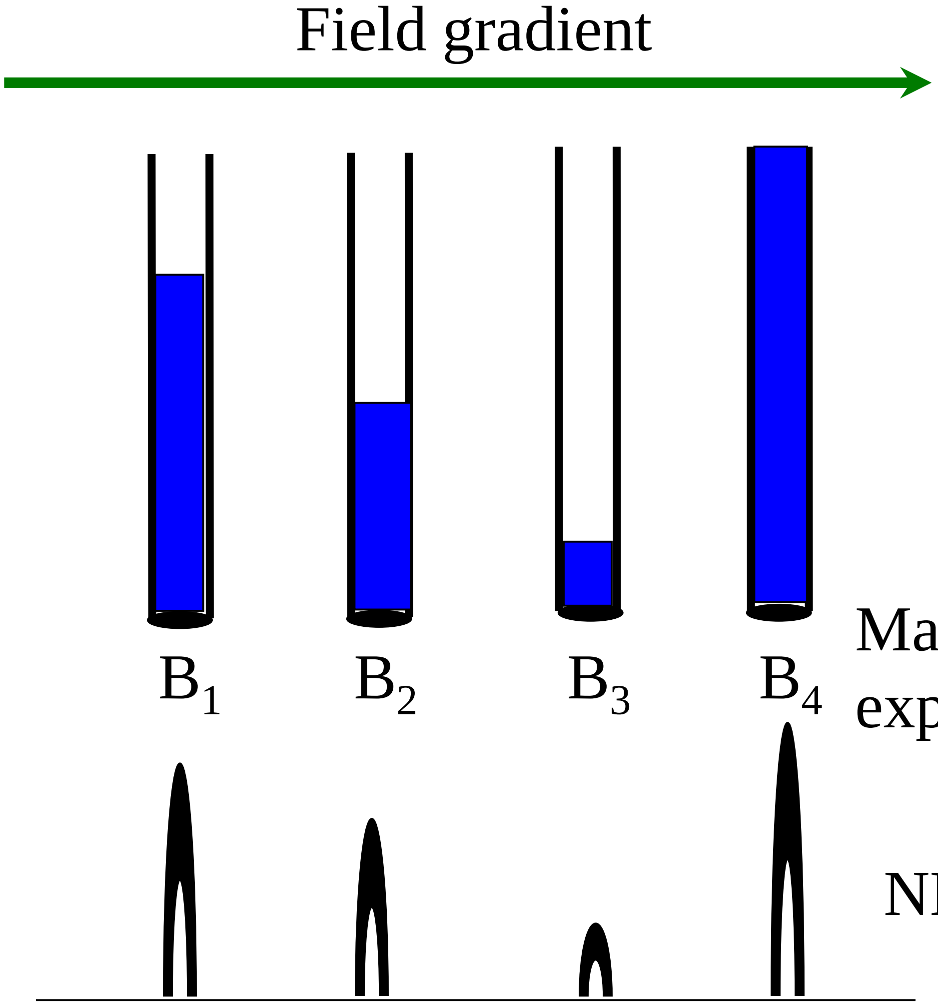


During the gradients, due to different Larmor frequencies, the magnetisation dephases, the net magnetisation becoming zero



Gradients dephase magnetisation, but, one can apply appropriate gradients to restore the lost magnetisation in a desired way

Spatial Encoding with Gradients



Magnetic fields experienced

NMR spectrum

Gradients Vs. Phase Cycling

Phase cycling:

- All signals are present.
- Desired pathway selection via subtraction.
- Imperfection in pulses and phases will interfere with subtraction
- Imperfect subtraction can lead to considerable amount of t_1 noise, particularly for solvent signals which may obscure with cross peaks, affecting resolution
- Experiments need to be repeated as many times the number of phase cycles steps are
- Experiment time is sometimes dictated by the phase cycle steps and not by the signal

Gradient pulses:

Gradients dephase all the signals.

Gradients can then refocus certain signals by applying gradients of different durations and strengths (This is because the dephasing rate varies for each of the coherence, DQC dephase twice as fast as SQC).

Gradients enable the observation of only the required signals

No subtraction process, no repetition of the experiment required

Formal Definition of Coherence Order

Coherences of different orders respond at different rates to *z*-rotations: central property in both phase cycling and gradient schemes.

The effect of a *z*-rotation on a coherence order *p*, $\sigma^{(p)}$, can be written as

$$\sigma^{(p)} \xrightarrow{\phi F_z} \sigma^{(p)} \exp(-ip\phi)$$

Definition of coherence order, *p*

***z*-rotation can be brought about by phase shifted pulses (phase cycling) or by applying spatially varying magnetic fields (pulsed field gradients).**

Gradient Induced Dephasing

- **The Larmor frequency at a particular point**

$$\omega(z) = \gamma(B_0 + Gz)$$

- **After time t the phase**

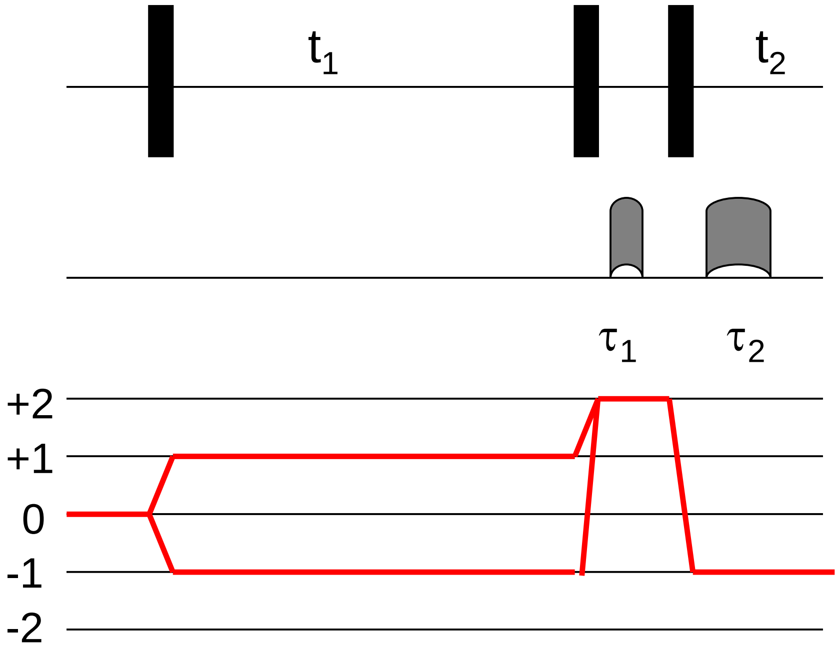
$$\phi(z) = \gamma(B_0 + Gz)t$$

- **More generally**

$$\phi(z) = Gzt\sum_i \gamma_i p_i$$

γGzt **is the spatially dependent phase induced by the gradient pulse**

CTP Selection with Gradients



DQF-COSY

$$\phi_1 = B_{g1} p_1 \tau_1$$

$$\phi_2 = B_{g2} p_2 \tau_2$$

Net phase is $\phi_1+\phi_2$ and this should be zero for a selection of pathways p_1 and p_2. This refocusing condition means that among the components dephased with the first gradient, one particular component is rephased with the second gradient

The refocusing condition $$\frac{B_{g1}\tau_1}{B_{g2}\tau_2} = -\frac{p_2}{p_1}$$

For example, in DQF-COSY, where $p_1=2$ and $p_2=-1$ either $\tau_2=2\tau_1$ or $B_{g2}=2B_{g1}$

CTP Selection with Gradients

The refocusing condition, in general, is

$$\sum_i B_{gi} p_i \tau_i = 0$$

Gradient pulses select only the ratio of coherence orders

Phase cycle by r steps of 360/r selects a particular change in the coherence order $\Delta p = p_2 - p_1$, and further pathways which have $(p_2 - p_1) \pm Nr$ where N= 0, 1, 2, ….

Gradients can only select one pathway, there is hence a loss of signal as compared with phase cycling method of equal length

Conclusion

- **Phase cycling/Field gradients an integral part of any NMR experiment**
- **Nested, Cogwheel, Multiplex phase cycle schemes available in the literature**
- **Cogwheel gaining some prominence, especially in solid state and TROSY kind of experiments in solution-state NMR *(Zuckerstaetter and Mueller, Concepts in Magnetic Resonance, 81, 30, 2007*)**

Relaxation in Nuclear Magnetic Resonance: Phenomenology

Relaxation References

A. Abragam: Principles of Nuclear Spin Magnetism

C. P. Slichter: Principles of Magnetic Resonance

J. Kowalewski andd L. Mäler, Nuclear Spin Relaxation in Liquids: Theory, Experiments, and Applications

A. G. Redfied: Adv. Magn. Reson., 1, 1, 1961

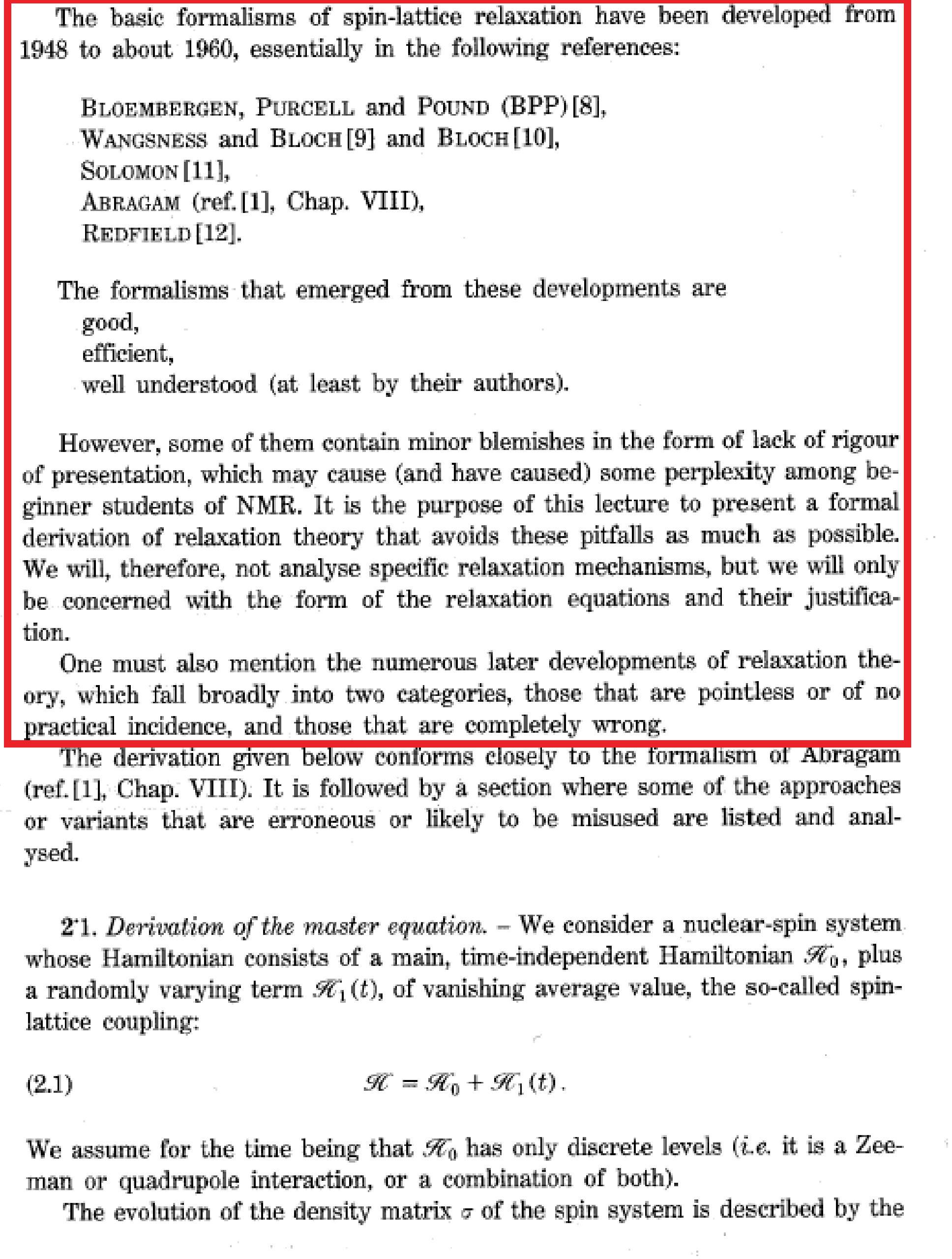
L. Werbelow and D. M. Grant: Adv. Magn. Reson., 9, 189, 1977

N. Murali and V. V. Krishnan, Conc. Magn. Reson., 17, 86, 2003 (A primer in nuclear magnetic relaxation in liquids)

J. Jeener, Superoperators in magnetic resonance, Adv. Magn. Reson. 10,
1-50, 1982

Phenomenological Approcah to NMR Relaxation

- Some basic quantum mechanics
- Operators, observables, eigen functions, ….
- Density operator
- Bloch equation
  - Lab frame/Rotating frame/solutions
- CW/Pulsed NMR
- Basic ideas of longitudinal and transverse relaxation time
- Relaxation mechanisms



The basic formalisms of spin-lattice relaxation have been developed from 1948 to about 1960, essentially in the following references:

Bloembergen, Purcell and Pound (BPP) [8],
Wangsness and Bloch [9] and Bloch [10],
Solomon [11],
Abragam (ref. [1], Chap. VIII),
Redfield [12].

The formalisms that emerged from these developments are
good,
efficient,
well understood (at least by their authors).

However, some of them contain minor blemishes in the form of lack of rigour of presentation, which may cause (and have caused) some perplexity among beginner students of NMR. It is the purpose of this lecture to present a formal derivation of relaxation theory that avoids these pitfalls as much as possible. We will, therefore, not analyse specific relaxation mechanisms, but we will only be concerned with the form of the relaxation equations and their justification.

One must also mention the numerous later developments of relaxation theory, which fall broadly into two categories, those that are pointless or of no practical incidence, and those that are completely wrong.

The derivation given below conforms closely to the formalism of Abragam (ref. [1], Chap. VIII). It is followed by a section where some of the approaches or variants that are erroneous or likely to be misused are listed and analysed.

2·1. *Derivation of the master equation.* – We consider a nuclear-spin system whose Hamiltonian consists of a main, time-independent Hamiltonian $\mathscr{H}_0$, plus a randomly varying term $\mathscr{H}_1(t)$, of vanishing average value, the so-called spin-lattice coupling:

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_1(t)\,. \tag{2.1}$$

We assume for the time being that $\mathscr{H}_0$ has only discrete levels (*i.e.* it is a Zeeman or quadrupole interaction, or a combination of both).

The evolution of the density matrix σ of the spin system is described by the

Figure 1.2: Quote from Maurice Goldman
Copied from: Maurice Goldman "Introduction to Some Basic Aspects of NMR." in Proceedings of the International School of Physics "Enrico Fermi" Course CXXIII, Editor Bruno Maraviglia, pp. 1-68, North Holland, Amsterdam (1993).

Relaxation: Nuclear Spin

- **Relaxation: Process by which magnetisation (phase coherence among spins) returns to its equilibrium value (given by the Boltzmann distribution)**

- **Two time constants in the case of NMR:**

  - **Restoration of longitudinal magnetisation, $\boldsymbol{M_z = \gamma\hbar\overline{< I_z >}}$: Characterised by a time constant, $\boldsymbol{T_1}$**
  - **Decay to zero of transverse magnetisation, $\boldsymbol{M_{x,y} = \gamma\hbar\{\overline{< I_x >} + i\overline{< I_y >}\}}$: Characterised by a time constant, $\boldsymbol{T_2}$**

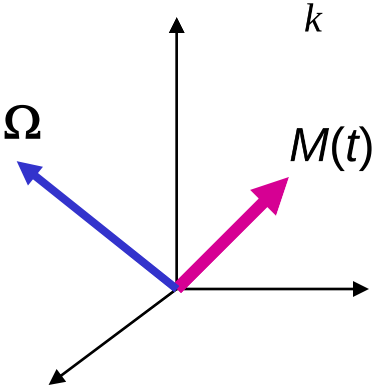
Relaxation: Nuclear Spin

- Relaxation driven by molecular motion
- Relaxation, in NMR, can be quite slow. Useful, as one can measure it!
- Relaxation can be used to probe molecular motions
- Nuclear Overhauser Effect, NOE, due to relaxation. This leads to estimate of distances and molecular structure

The Bloch Equation for Spin-Half Nuclei

The Bloch vector:
$$\overline{M(t)} = \begin{pmatrix} M_x(t) \\ M_y(t) \\ M_z(t) \end{pmatrix} = \gamma \begin{pmatrix} \langle I_x \rangle(t) \\ \langle I_y \rangle(t) \\ \langle I_z \rangle(t) \end{pmatrix}$$

$$M = \sum_k \mu_k$$



Bloch vector rotation:
$$\frac{d}{dt}\overline{M}(t) = \overline{M(t)} \times \overline{\Omega}$$

The Bloch equation:
$$\boxed{\frac{d}{dt}\overline{M}(t) = \overline{M}(t) \times \overline{\Omega} - \Gamma\left(\overline{M}(t) - \overline{M}_{eq}\right)}$$

$$\overline{\Omega} = \begin{pmatrix} \omega_1 \cos\varphi \\ -\omega_1 \sin\varphi \\ \Delta\omega \end{pmatrix} \qquad \Gamma = \begin{pmatrix} 1/T_2 & & \\ & 1/T_2 & \\ & & 1/T_1 \end{pmatrix} \qquad \overline{M}_{eq} = \begin{pmatrix} 0 \\ 0 \\ M_0 \end{pmatrix}$$

The Bloch Equation for Spin-Half Nuclei

If all the magnetic moments are identical and if the magnetic field, B, is uniform:

$$\frac{d}{dt}M(t) = M(t)\times\Omega = \gamma\left[\sum_k \mu_k\right]\times B = \gamma M \times B$$

Once the spin system is perturbed:

$$\frac{d}{dt}M(t) = \gamma M \times B - \frac{M_x - M_x^{eq}}{T_2}\hat{i} - \frac{M_y - M_y^{eq}}{T_2}\hat{j} - \frac{M_z - M_z^{eq}}{T_1}\hat{k}$$

$$\frac{d}{dt}M(t) = \gamma M \times B - \frac{M_x}{T_2}\hat{i} - \frac{M_y}{T_2}\hat{j} - \frac{M_z - M_0}{T_1}\hat{k}$$

The Bloch Equation for Spin-Half Nuclei

$$\frac{d}{dt}M(t) = \gamma M \times B - \frac{M_x}{T_2}\hat{i} - \frac{M_y}{T_2}\hat{j} - \frac{M_z - M_0}{T_1}\hat{k}$$

Bloch equations in the laboratory frame:

$$\frac{d}{dt}\begin{pmatrix} M_x \\ M_y \\ M_z \end{pmatrix} = \begin{pmatrix} \frac{1}{T_2} & \gamma B & 0 \\ -\gamma B & \frac{1}{T_2} & 0 \\ 0 & 0 & \frac{1}{T_1} \end{pmatrix} \begin{pmatrix} M_x \\ M_y \\ M_z - M_0 \end{pmatrix}$$

Bloch equations solutions in the laboratory frame:

$$\boxed{\begin{aligned} M_z(t) &= M_0 + (M_z(0) - M_0)e^{-\frac{t}{T_1}} \\ &= M_0(1 - e^{-\frac{t}{T_1}}) \qquad ; M_z(0) = 0 \end{aligned}}$$

Solutions of the Bloch Equations for Spin-Half Nuclei

The longitudinal magnetisation:

$$M_z(t) = M_0 + (M_z(0) - M_0)e^{-\frac{t}{T_1}}$$

$$= M_0(1 - e^{-\frac{t}{T_1}}) \qquad ; M_z(0) = 0$$

The transverse magnetisation:

$$M_\pm(t) = M_\pm(0)\exp(-\frac{t}{T_2} \mp i\gamma Bt)$$

$$M_x(t) = e^{-\frac{t}{T_2}}[M_x(0)\cos\gamma Bt + M_y(0)\sin\gamma Bt]$$

$$M_y(t) = e^{-\frac{t}{T_2}}[-M_x(0)\sin\gamma Bt + M_y(0)\cos\gamma Bt]$$

The transverse magnetisation with:

$$M_x(0) = M_y(0) = M_0$$

$$M_x(t) = M_0 e^{-\frac{t}{T_2}}\cos\gamma Bt$$

$$M_y(t) = -M_0 e^{-\frac{t}{T_2}}\sin\gamma Bt$$

Relaxation in the Presence of a Time-Varying RF Field

Consider an RF with angular frequency, ω, perpendicular to B_0 and with constant magnitude. ϕ is its phase with respect to the lab frame *x* and *y* axes.

$$B_1(t) = B_1[\cos(\omega t + \phi)\hat{i} + \sin(\omega t + \phi)\hat{j}]$$

Assume ϕ=0 at *t*=0

$$\begin{aligned} B_z &= B_0 \\ B_x &= B_1 \cos \omega t \\ B_y &= -B_1 \sin \omega t \end{aligned}$$

This corresponds to a field perpendicular to B_0 and rotating about the *z*-axis in a clockwise direction.

Bloch Equation with RF Field

$$\frac{d}{dt}M(t) = \gamma M \times B - \frac{M_x - M_x^{eq}}{T_2}\widehat{i} - \frac{M_y - M_y^{eq}}{T_2}\widehat{j} - \frac{M_z - M_z^{eq}}{T_1}\widehat{k}$$

$$\frac{d}{dt}M_x - \gamma B_0 M_y - \gamma B_1 M_z \sin \omega t + \frac{M_x}{T_2} = 0$$

$$\frac{d}{dt}M_y + \gamma B_0 M_x - \gamma B_1 M_z \cos \omega t + \frac{M_y}{T_2} = 0$$

$$\frac{d}{dt}M_z + \gamma B_1 M_x \sin \omega t + \gamma B_1 M_y \cos \omega t \frac{M_z - M_0}{T_1} = 0$$

Bloch Equations with RF Field

Transforming these equations into a rotating frame at an angular frequency, w, about the *z*-axis, and defining:

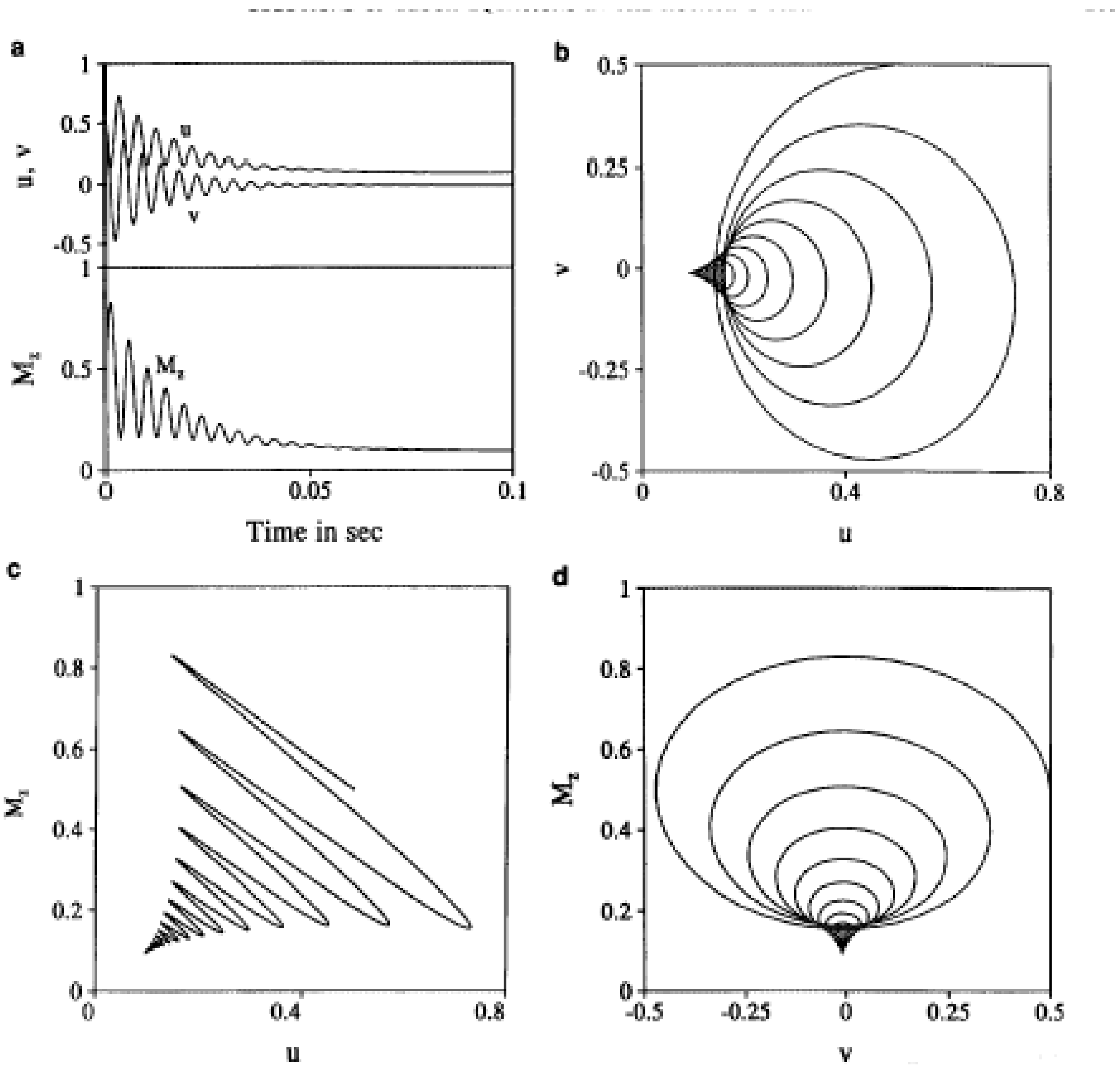
$$\alpha = \frac{1}{T_1}; \beta = \frac{1}{T_2}; \delta = \gamma B_0 - \omega, \omega_1 = \gamma B_1$$

$$\boxed{\begin{aligned} &\frac{du}{dt} + \beta u + \delta v = 0 \\ &\frac{dv}{dt} + \beta u - \delta v + \omega_1 M_z = 0 \\ &\frac{dM_z}{dt} + \alpha M_z - \omega_1 v = \alpha M_0 \end{aligned}}$$

Here, the *x* and *y* components of *M* in the lab frame are related to the *u* and *v* components in the rotating frame as:

$$\boxed{\begin{aligned} M_x &= u \cos \omega t - v \sin \omega t \\ M_y &= -(v \cos \omega t + u \sin \omega t) \end{aligned}}$$

Magnetisation Trajectories



Bloch Equations: Solution Under Steady State and CW NMR

$$u^{\infty} = \tilde{M}_x = \frac{\gamma B_1 \delta T_2^2}{1+(\delta T_2)^2+(\gamma B_1)^2 T_1 T_2} M_0$$

$$v^{\infty} = \tilde{M}_y = \frac{-\gamma B_1 \delta T_2}{1+(\delta T_2)^2+(\gamma B_1)^2 T_1 T_2} M_0$$

$$M_z^{\infty} = \tilde{M}_z = \frac{1+(\delta T_2)^2}{1+(\delta T_2)^2+(\gamma B_1)^2 T_1 T_2} M_0$$

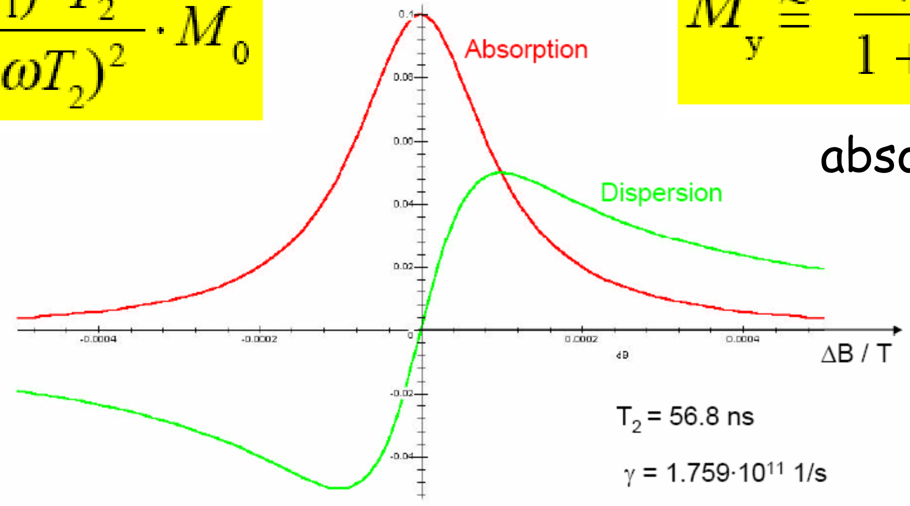
Saturation term

$$\tilde{M}_{\mathrm{x}} \cong \frac{\Delta\omega \cdot (\gamma B_1) \cdot T_2^2}{1 + (\Delta\omega T_2)^2} \cdot M_0$$

dispersion

$$\tilde{M}_{\mathrm{y}} \cong \frac{(\gamma B_1) \cdot T_2}{1 + (\Delta\omega T_2)^2} \cdot M_0$$

absorption



T_2 = 56.8 ns

γ = 1.759·10^{11} 1/s

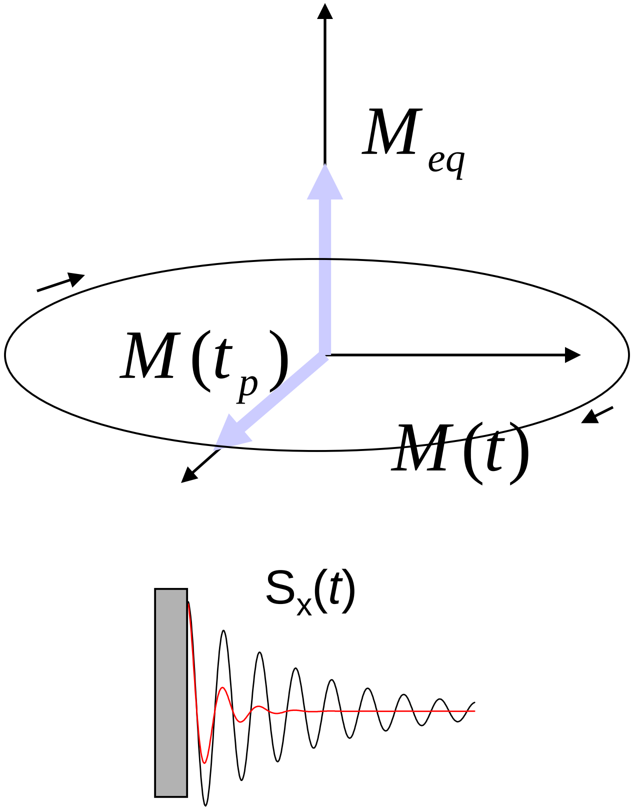
B_1 = 1·10^{-5} T

Calculated with: bloch_nosat.mws

http://www.uni-stuttgart.de/gkmr/lectures/lectures_WS_0203/magnetisation_blochequ.PDF

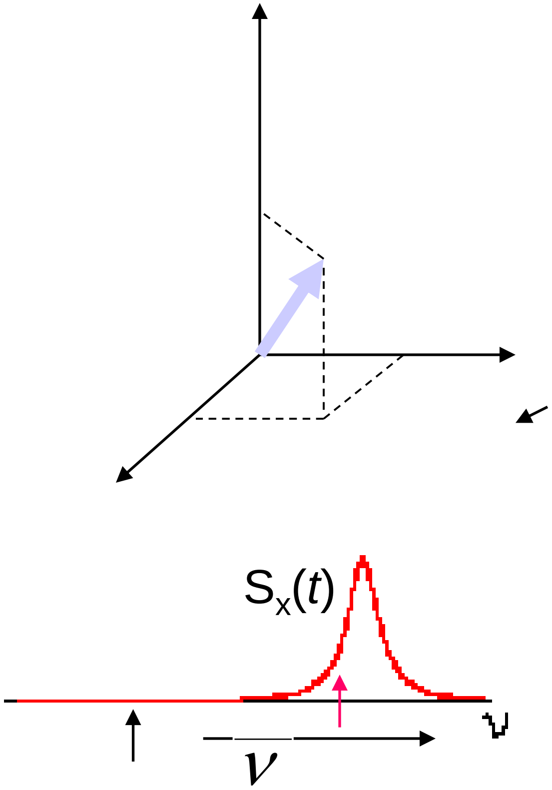
Modern NMR

After short RF pulses
Free induction Decay signals are detected



“Earlier” NMR

Steady state CW signals are measured
during (weak) RF irradiation



In MR we measure both transverse magnetization components simultaneously

Pulsed NMR

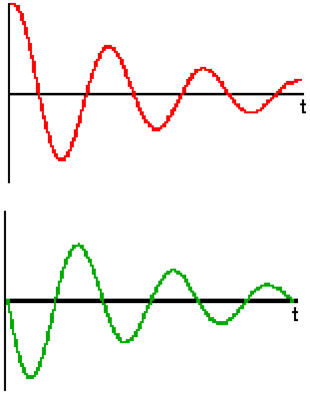
After a 90^0 pulse:

$$s_x = \langle \gamma I_x \rangle (t) = M_0 \cos \Delta\omega t \times e^{-t/T_2}$$

$$s_x = \langle \gamma I_y \rangle (t) = M_0 \sin \Delta\omega t \times e^{-t/T_2}$$

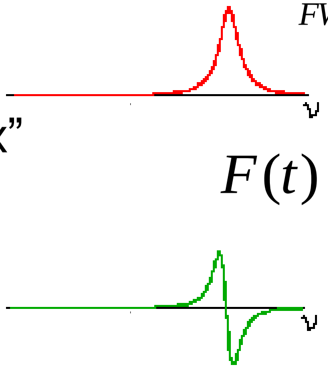
Fast Fourier Transform

$$S(t) \equiv S_{RE}(t) + iS_{\mathrm{Im}}(t)$$



“complex”

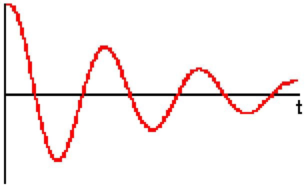
FT



$FWHH = 1/T_2$

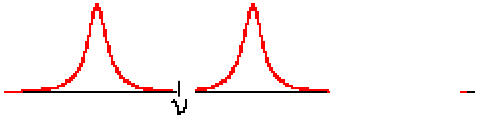
$$F(t) \equiv A(\Delta\nu) + iD(\Delta\nu)$$

$$S(t) \equiv S_{RE}(t)$$



“real”

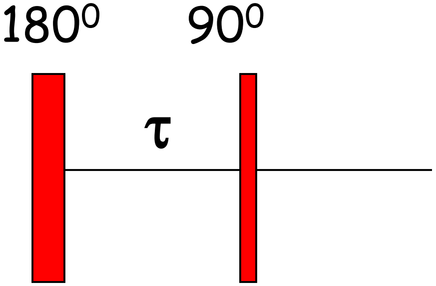
FT



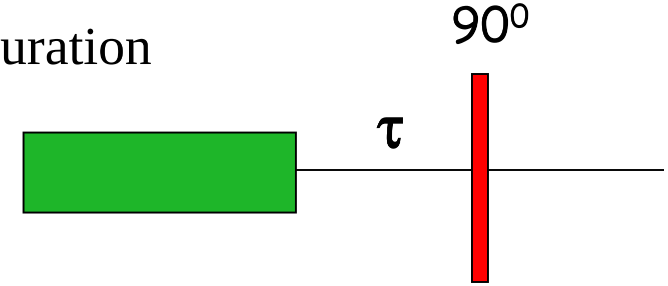
$F(t) \equiv A(\Delta\nu)$

Simple T_1 Experiments

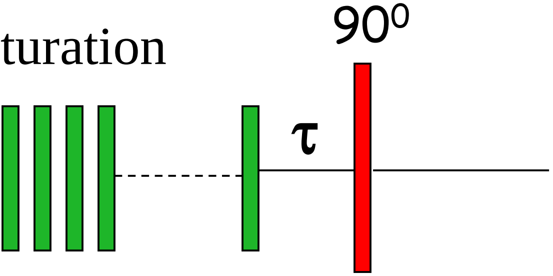
Inversion recovery



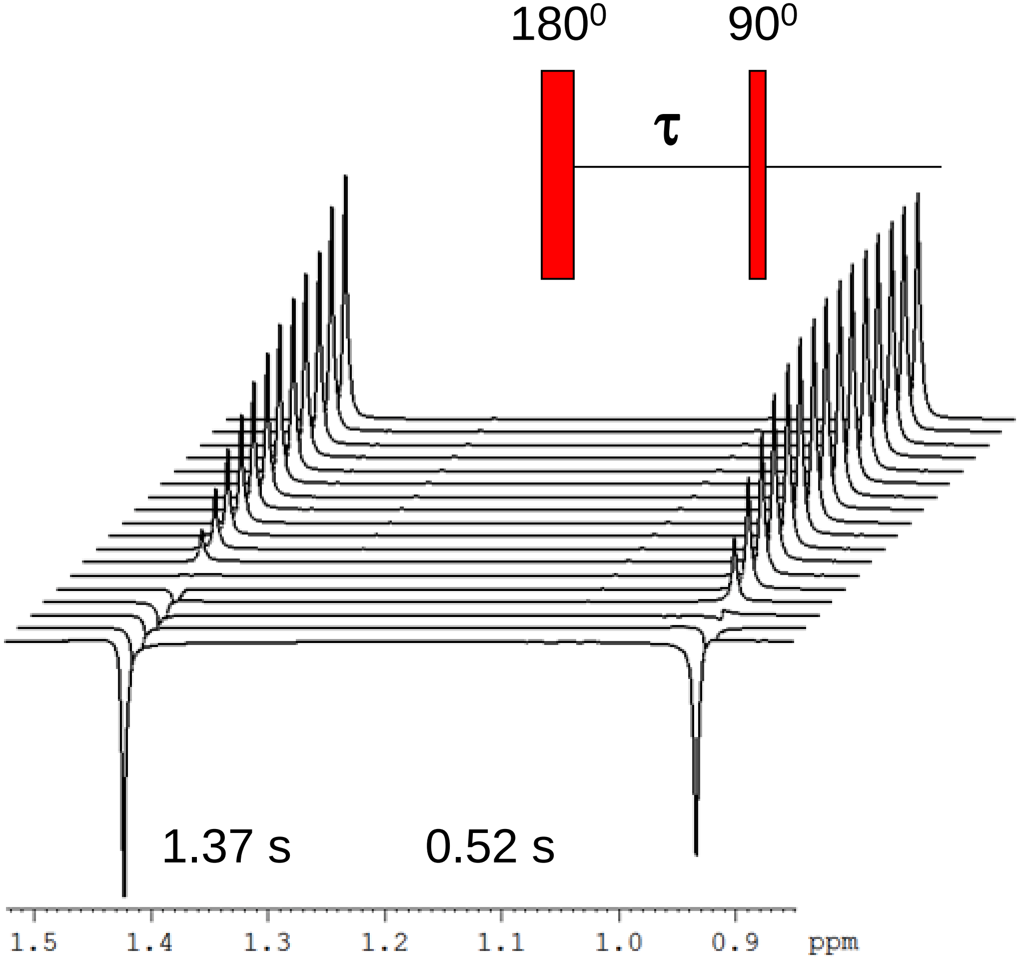
saturation

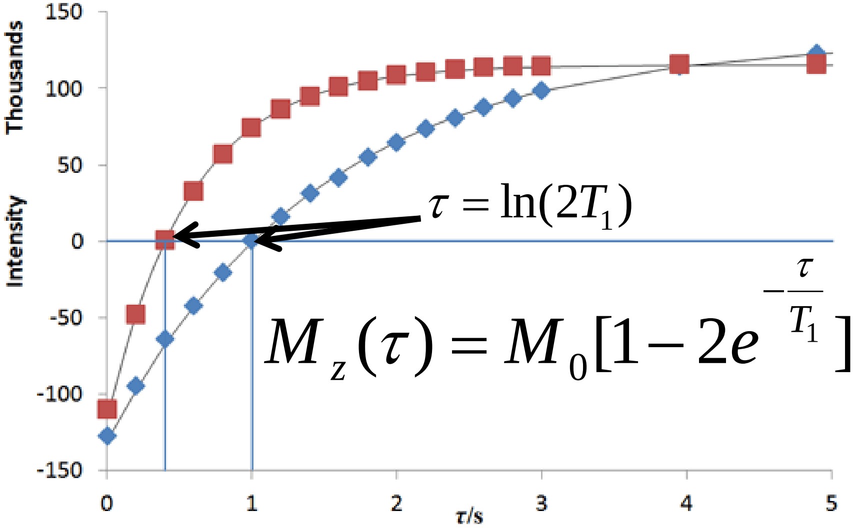


Pulse saturation



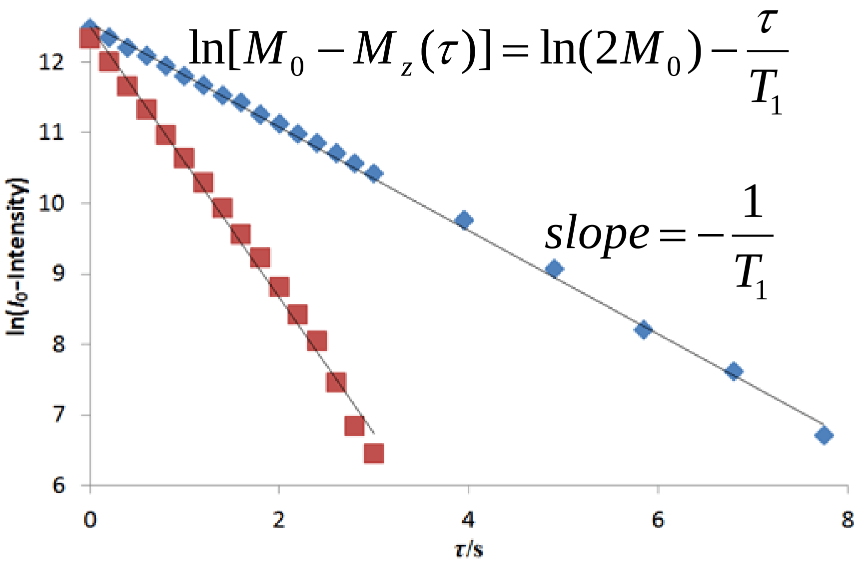
Inversion Recovery





$$\tau = \ln(2T_1)$$

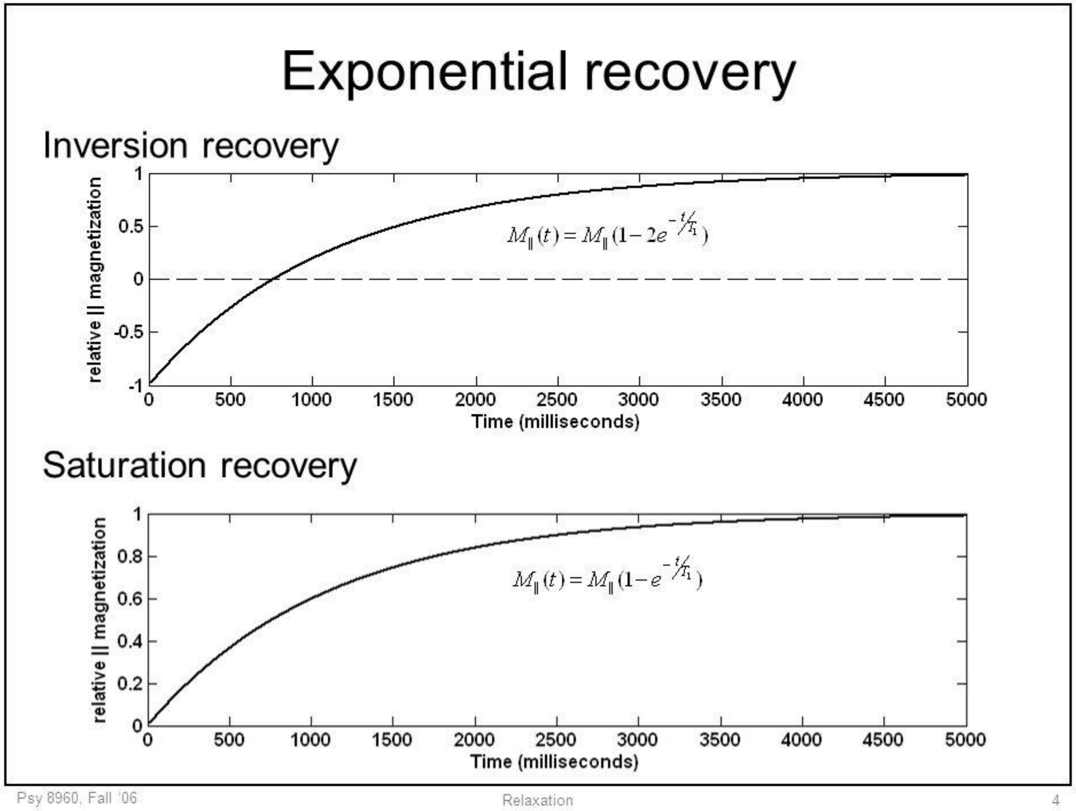
$$M_z(\tau) = M_0[1 - 2e^{-\frac{\tau}{T_1}}]$$



$$\ln[M_0 - M_z(\tau)] = \ln(2M_0) - \frac{\tau}{T_1}$$

$$slope = -\frac{1}{T_1}$$

Saturation Recovery



Exponential recovery

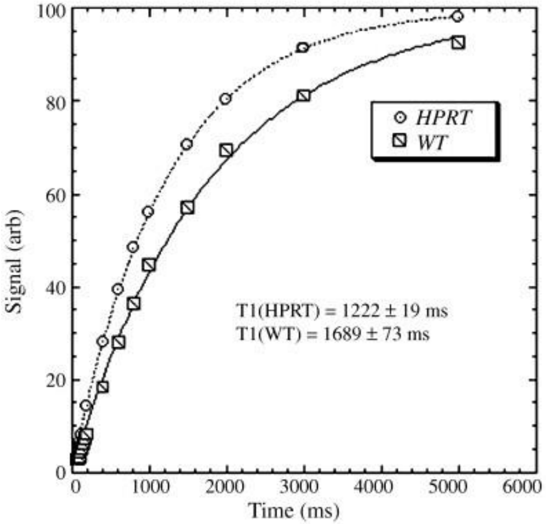
Inversion recovery

$M_\parallel(t) = M_\parallel(1-2e^{-t/T_1})$

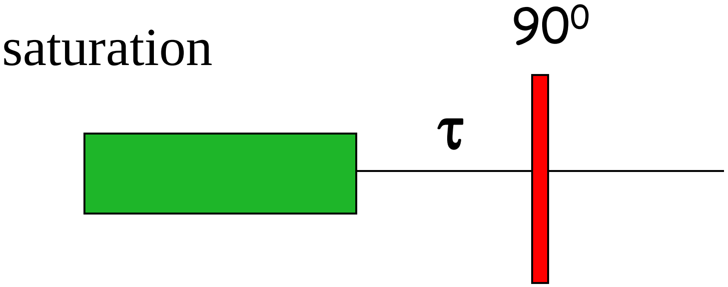
Saturation recovery

$M_\parallel(t) = M_\parallel(1-e^{-t/T_1})$

Psy 8960, Fall '06 Relaxation 4



T1(HPRT) = 1222 ± 19 ms
T1(WT) = 1689 ± 73 ms



saturation

90^0

τ

Saturation Recovery

- SR is less sensitive than IR

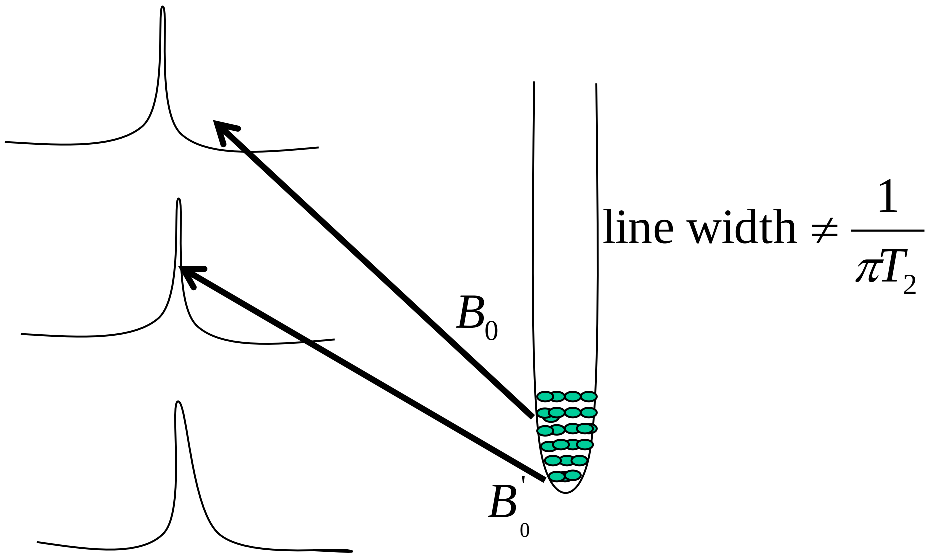
- It is not necessary to wait for a long time (10 T_1) as in the case of IR (magnetisation should get back to equilibrium before repetition) and a priori unknown time between scans

- SR is a quick method to measure T_1 than IR

- Useful in cases where the lineshapes are very broad, like in the case of quadrupolar nuclear spins or if the signal cannot be inverted

T_2 - Measurements

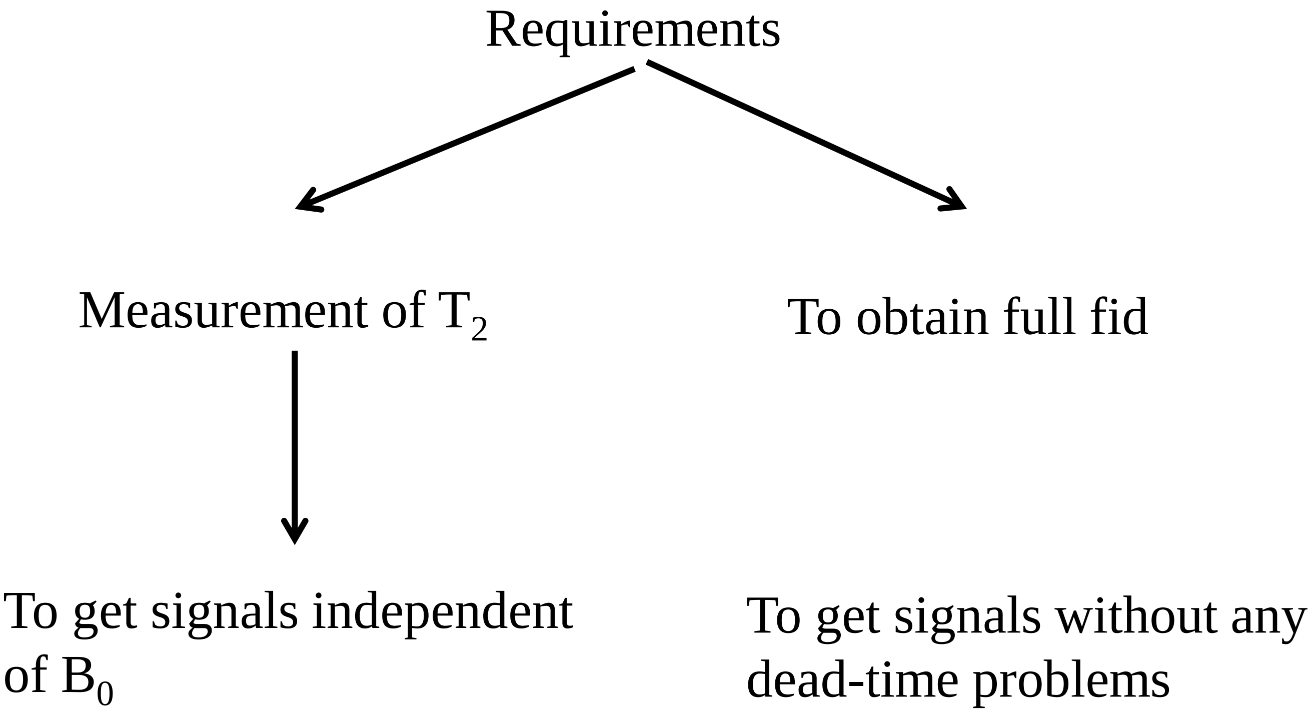
- Homogeneous broadening due to fluctuating microscopic magnetic fields: This is quantified in T_2
- Inhomogeneous broadening: Due to the variation of the macroscopic magnetic field over the volume of the sample due to instrumental imperfections or susceptibility effects
- The observed transverse relaxation time, T_2' is due to both these effects



$$\text{line width} \neq \frac{1}{\pi T_2}$$

- Can the inhomogeneous effects/decay be distinguished from homogeneous decay for an accurate measurement of T_2
- Other effects to be removed are the dead-time delay, how can we get back the signal with initial point in tact so that phase distortions are absent

T_2 - Measurements



Requirements

Measurement of T_2

To obtain full fid

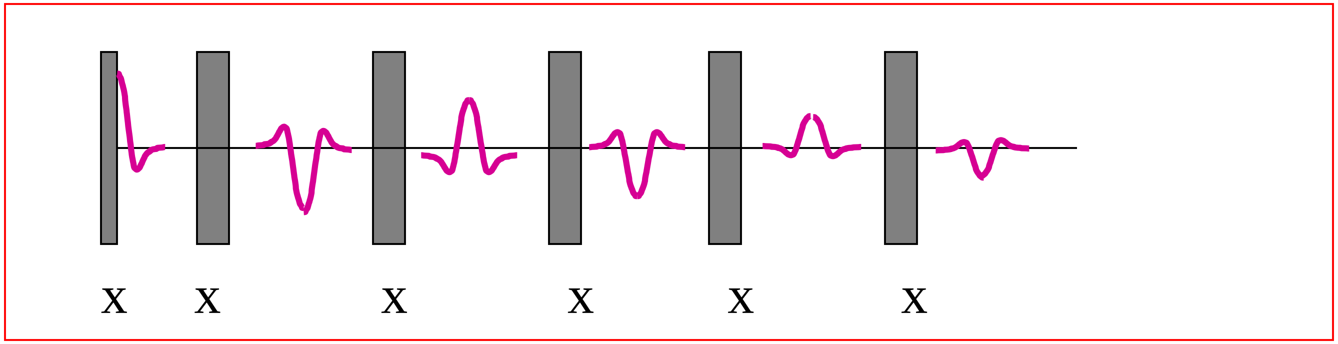
To get signals independent of B_0

To get signals without any dead-time problems

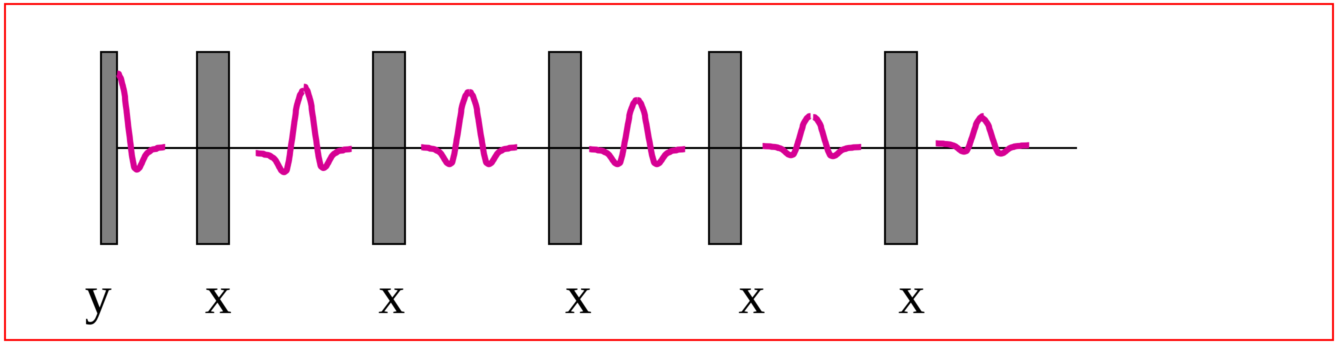
Spin-echo schemes

Measuring Spin-Spin Relaxation Times

Carr - Purcell

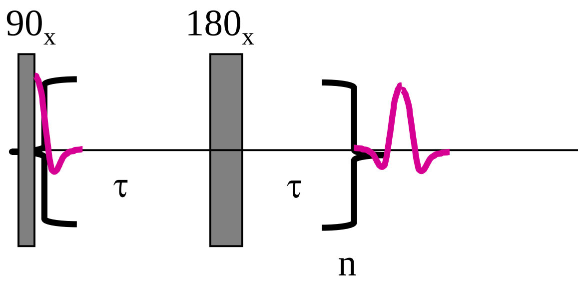


Carr - Purcell – Meiboom - Gill

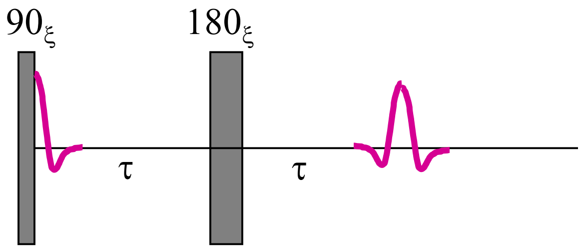


Finite pulse compensation (even echoes will be free of pulse errors)

T_2 - Measurements



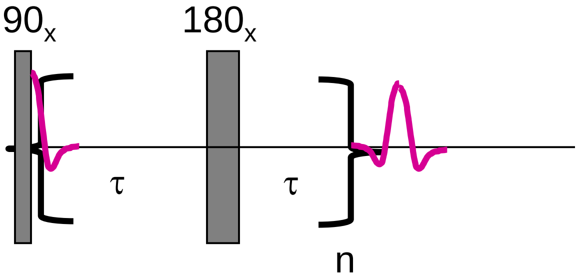
Keep incrementing n



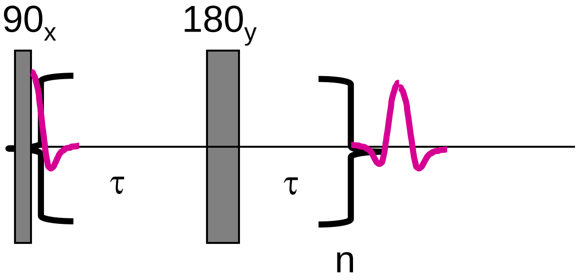
Keep incrementing τ
Like inversion recovery
(logical thing to do?)

In the method two, formation of the echoes depends on the isochromats (spin vectors) experiencing exactly the same field through out the duration of the pulse sequence. If any particular spin diffuses into a neighbourhood region during the sequence, it will experience a slightly different magnetic field from that where it began, and thus will not be fully refocussed. As τ increases, such diffusion losses become more severe and the relaxation data more unreliable. (However, this is a way to measure molecular diffusion in liquid-state NMR.)

T_2 – Measurements: CPMG Scheme

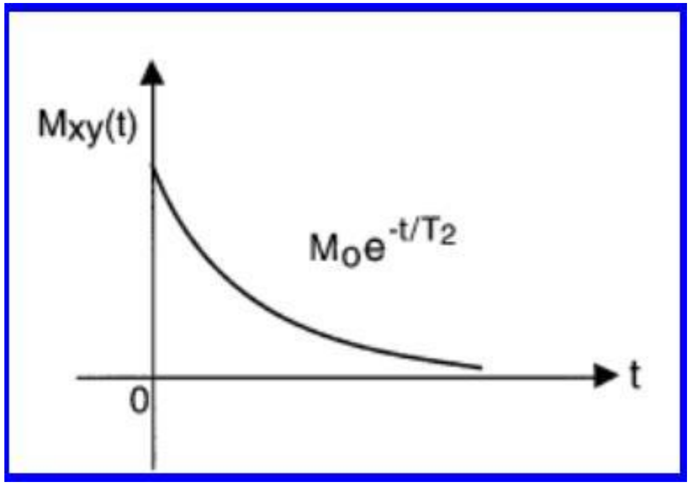


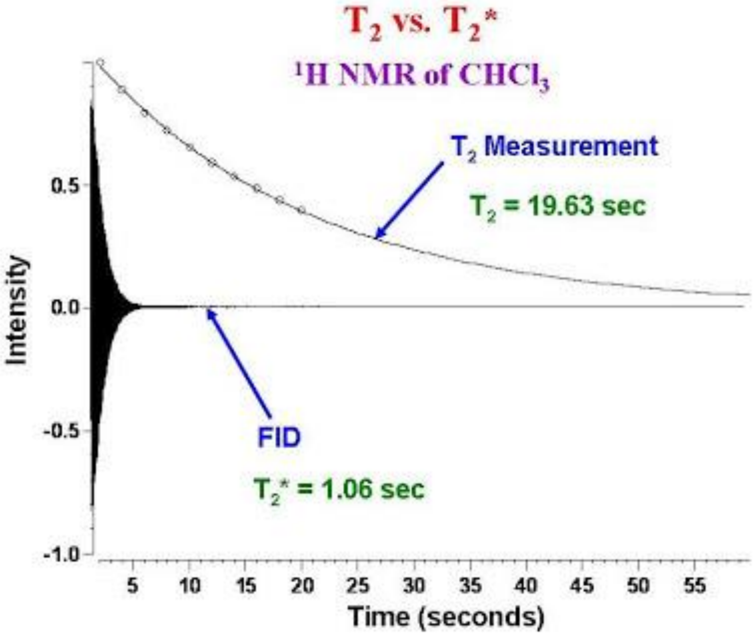
Keep incrementing *n*
CP *scheme*



Keep incrementing *n*
Free of pulse imperfections
CPMG scheme

T_2 and T_2'





Even in a well-shimmed magnet, the actual T_2 of the example here is 19 times than the observed value. The observed value corresponds to 0.33 Hz as FWHH.

Relaxation Time Constants

The longitudinal and transverse relaxation mechanisms are independent of each other.

The restraints on T_1 and T_2 require that the magnetisation vector can never exceed the thermal equilibrium value by pulses or by relaxation processes.

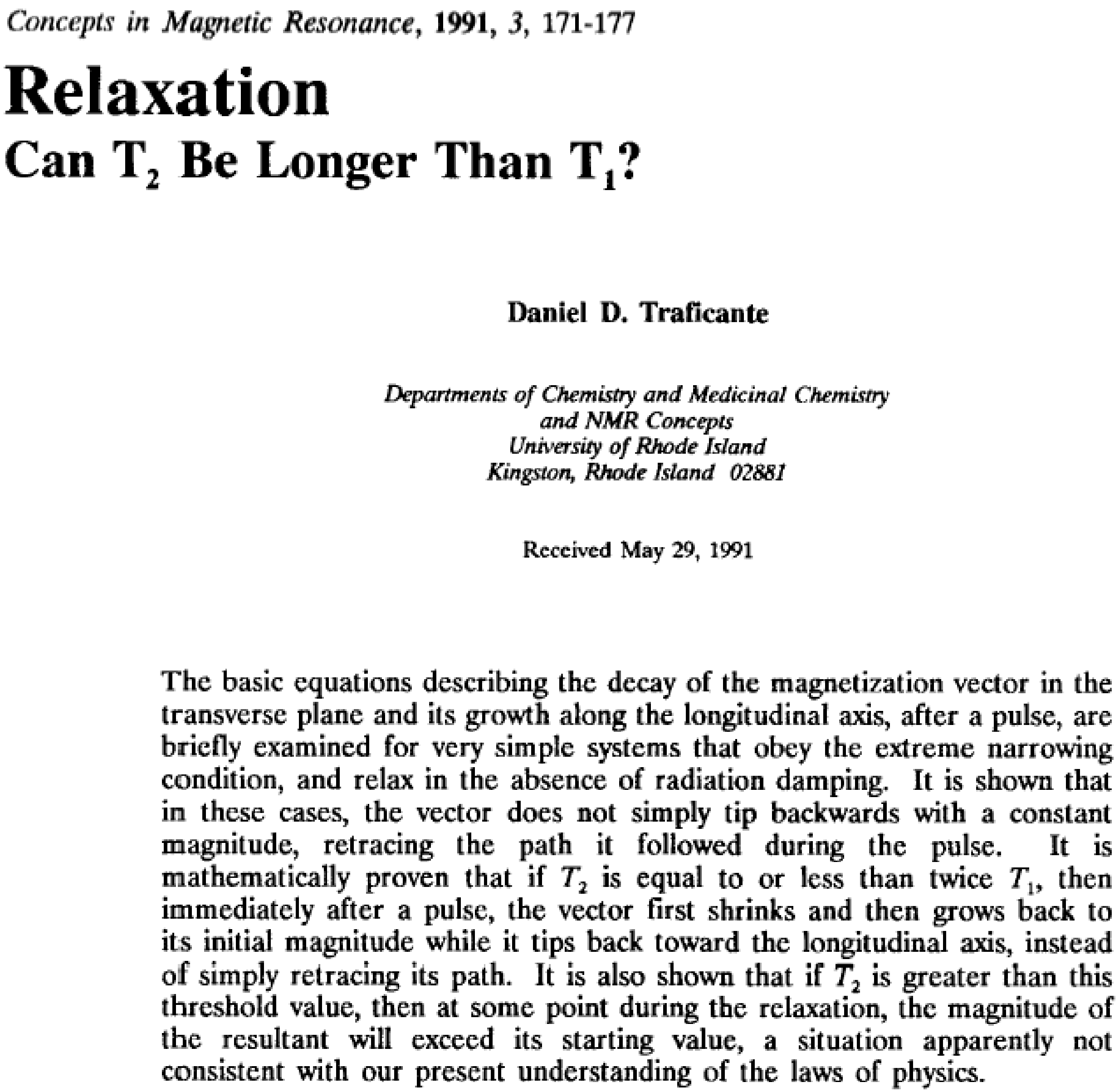
This means that the norm is always limited by $\sqrt{M_x^2 + M_y^2 + M_z^2} \leq M_0$

A common restraint is $T_1 > T_2$

But mathematically it turns out that $T_1 \geq T_2 / 2$

Relaxation in
Nuclear Magnetic Resonance:
Transition Rate Theory

Relaxation Time Constants



Concepts in Magnetic Resonance, **1991**, *3*, 171-177

Relaxation

Can T_2 Be Longer Than T_1?

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Received May 29, 1991

The basic equations describing the decay of the magnetization vector in the transverse plane and its growth along the longitudinal axis, after a pulse, are briefly examined for very simple systems that obey the extreme narrowing condition, and relax in the absence of radiation damping. It is shown that in these cases, the vector does not simply tip backwards with a constant magnitude, retracing the path it followed during the pulse. It is mathematically proven that if T_2 is equal to or less than twice T_1, then immediately after a pulse, the vector first shrinks and then grows back to its initial magnitude while it tips back toward the longitudinal axis, instead of simply retracing its path. It is also shown that if T_2 is greater than this threshold value, then at some point during the relaxation, the magnitude of the resultant will exceed its starting value, a situation apparently not consistent with our present understanding of the laws of physics.

NMR Relaxation: Towards Transition Rate Theory

- **Relaxation mechanisms**
- Correlation times, functions
- **Spectral densities**
- Transition probabilities, W’s
- **Relaxation in a two coupled spin-1/2 system**
- Dipolar relaxation
- **Solomon equations**
- Nuclear Overhauser effect

Relaxation: Some Intuitive Arguments

- A spin in an external magnetic field undergoes Larmor precession
- Relaxation revolves around phase (de)coherence among groups of spins
- Relaxation is brought about by fluctuating magnetic fields around the nuclear spin sites

  – Only magnetic fields can do this as only they can interact with the magnetic moment of a spin ½ nuclei. Nuclei with spins greater than ½, quadrupolar nuclei, can also interact with electric-field gradients. This is a much stronger interaction.

- A nuclear spin can change its magnetic moment associated with any change in the surrounding magnetic fields, either in magnitude and/or direction

- NMR relaxation is mainly brought out by spatial and temporal fluctuations/variation in the surrounding/local magnetic fields at the respective nuclear spin sites

Relaxation Sources

Where do the fluctuations come from?

- Random events:
  - Rotational diffusion
  - Translational diffusion
  - Vibrational/librational motions
  - Conformational sampling/variability

- Non-random events:
  - Magic-angle spinning
  - B_0 quenching