

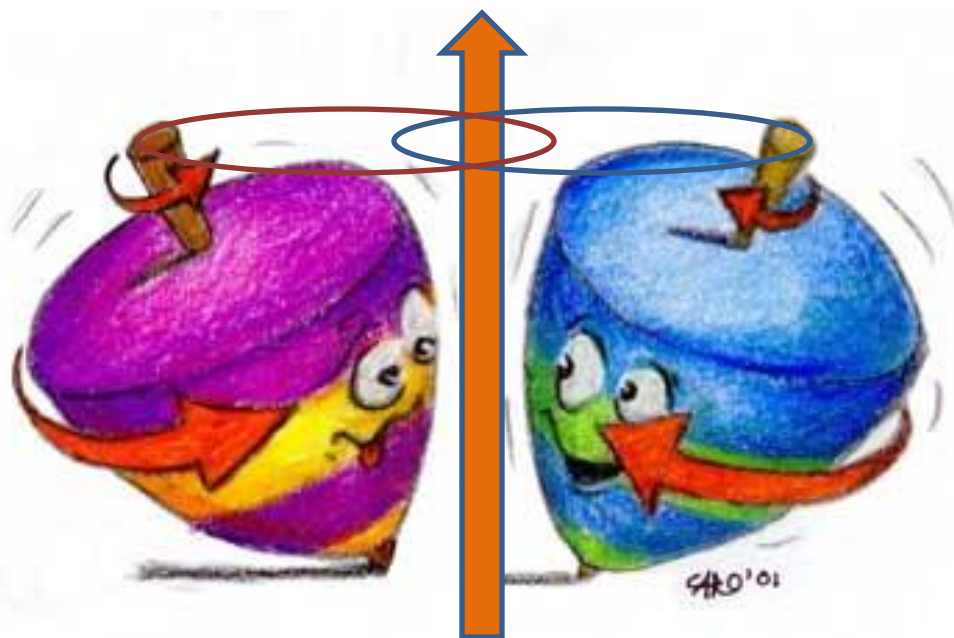
Coherence & Relaxation in Magnetic resonance

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www.rug.nl/zernike/research/groups/phynd/research/spinpolarizedtranspo

$^{15}\text{NIJNTJE}$ EN $^{13}\text{CATRIJNTJE}$



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1. Basic Concepts of Nuclear Spins in a Magnetic Field

1-a. Angular and magnetic moments, magnetization in the magnetic field

The nuclei are characterized by

their spin value, with angular momentum:

$$\bar{I}\hbar; \quad I = 1/2, 1, 3/2, \dots$$

!*

A nucleus with an odd mass number M has an half-integer spin and a nucleus of an even M has an integer spin. Nuclei with an even number of protons and neutrons have nuclear spin I=0.

$$h = 6.6260755 \times 10^{-34} \text{ J.s}$$

Each nuclear spin has a magnetic moment proportional to its angular momentum.

$$\bar{\mu} = \gamma \bar{I}\hbar; \quad \bar{\mu} = g \frac{e}{2m_p} \bar{I}$$

Proton: g = 5.585

Neutron: g = -3.826

$$\mu_N = 5.05084 \text{ J/T}$$

γ = magnetogyric ratio

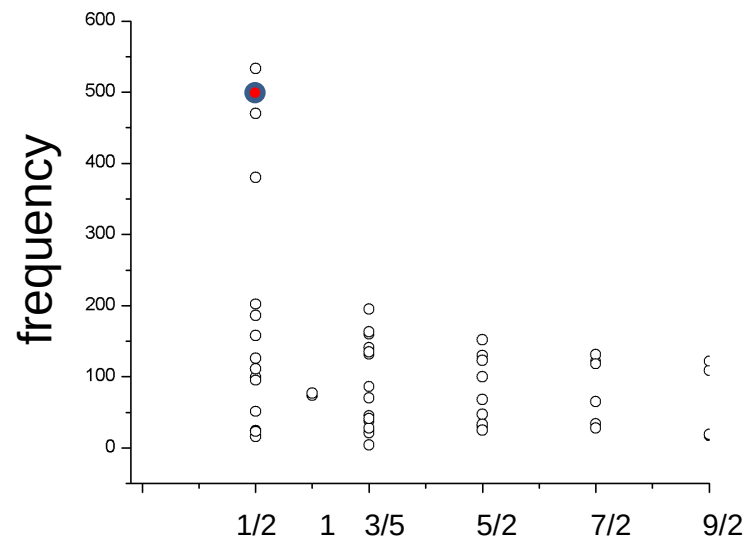
$$\begin{aligned} E &= -\bar{\mu} \cdot \bar{B} \\ h\nu &= -\bar{\mu} \cdot \bar{B} \\ \gamma &= -\nu / B \end{aligned}$$

Nucleus	$\gamma / 2\pi$ (MHz/T)
^1H	42.576
^2H	6.53566
^3He	-32.434
^7Li	16.546
^{13}C	10.705

Nucleus	$\gamma / 2\pi$ (MHz/T)
^{14}N	3.0766
^{15}N	-4.3156
^{17}O	-5.7716
^{23}Na	11.262
^{31}P	17.235
^{129}Xe	-11.777

Tesla	-	MHz
5×10^{-5}		2.1×10^{-3}
2.3		100
7.0		300
9.1		400
11.7		500
18.8		800
21.1		900

Element/Name	Isotope Symbol	Nuclear Spin	Sensitivity vs. ^1H
Hydrogen	^1H	1/2	1.000000
Deuterium	^2H or D	1	1.44 e-6
Tritium	^3H	1/2	-
Helium-3	^3He	-1/2	-
Lithium-6	^6Li	1	0.000628
Lithium-7	^7Li	3/2	0.270175
Beryllium-9	^9Be	-3/2	0.013825
Boron-10	^{10}B	3	0.00386
Boron-11	^{11}B	3/2	0.132281
Carbon-13	^{13}C	1/2	0.000175
Nitrogen-14	^{14}N	1	0.000998
Nitrogen-15	^{15}N	-1/2	3.84E-06
Oxygen-17	^{17}O	-5/2	1.07E-05
Fluorine-19	^{19}F	1/2	0.829825
Neon-21	^{21}Ne	-3/2	6.3E-06
Sodium-23	^{23}Na	3/2	0.092105
Magnesium-25	^{25}Mg	-5/2	0.00027
Aluminum-27	^{27}Al	5/2	0.205263
Silicon-29	^{29}Si	-1/2	0.000367



Phosphorus-31	^{31}P	1/2	0.06614
Sulfur-33	^{33}S	3/2	1.71E-05
Chlorine-33	^{33}Cl	3/2	0.003544
Chlorine-37	^{37}Cl	3/2	0.000661
Potassium-39	^{39}K	3/2	0.000472
Potassium-41	^{41}K	3/2	5.75E-06
Calcium-43	^{43}K	-7/2	9.25E-06
Scandium-45	^{45}Sc	7/2	0.3
Titanium-47	^{47}Ti	-5/2	0.00015
Titanium-49	^{49}Ti	-7/2	0.00021
Vanadium-50	^{50}V	6	0.00013
Vanadium-51	^{51}V	7/2	0.37895
Chromium-53	^{53}Cr	-3/2	8.6E-05
Manganese-55	^{55}Mn	5/2	0.174386
Iron-57	^{57}Fe	1/2	7.37E-07
Cobolt-59	^{59}Co	7/2	0.275439
Nickel-61	^{61}Ni	-3/2	4.21E-05
Copper-63	^{63}Cu	3/2	0.064035
Copper-65	^{65}Cu	3/2	0.035263
Zinc-67	^{67}Zn	5/2	0.000117

1-b. The rotation of the magnetization

The torque on the magnetic moment induced by a magnetic field B

$$\vec{\tau} = \vec{\mu} \times \vec{B}$$

Minimizing energy + angular momentum conservation

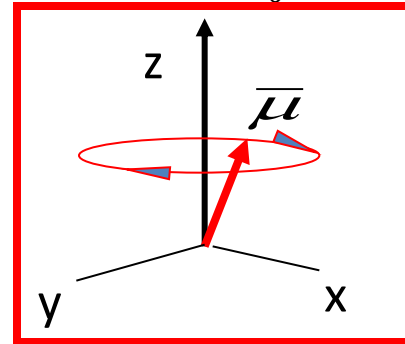
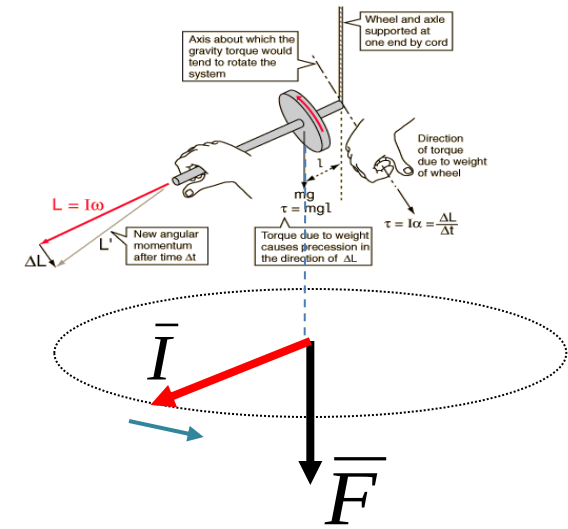
$$\frac{d\vec{\mu}}{dt} = \vec{\mu} \times \gamma \vec{B} = -\vec{\omega}_L \times \vec{\mu}$$

$$\frac{d}{dt} \begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix} = \begin{pmatrix} 0 & \omega_z & -\omega_y \\ -\omega_z & 0 & \omega_x \\ \omega_y & -\omega_x & 0 \end{pmatrix} \begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix}$$

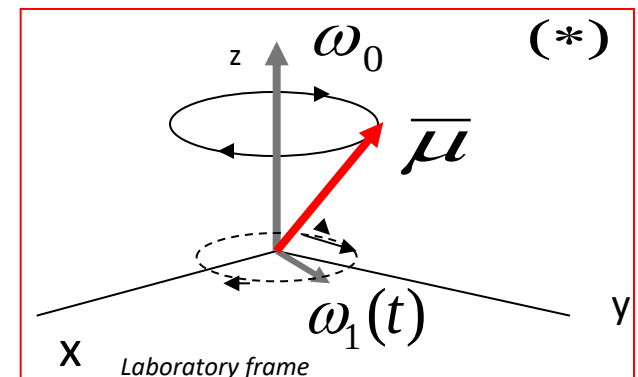
$$\vec{\omega} \equiv \gamma \vec{B}$$

Magnetogyric ratio

$$E = -\vec{\mu} \cdot \vec{B}$$



$$\vec{\omega}(t) = \omega_0 \vec{z} + 2\omega_1 \cos \omega t \vec{x}$$



1-c. The classical rotating frame

$$\frac{d}{dt} \bar{\mu}(t) = \bar{\omega}(t) \times \bar{\mu}(t) \quad - \quad \bar{\omega}(t) = \omega_0 \bar{z} + 2\omega_1 (\cos \omega t + \varphi) \bar{x}$$

RWA

$$R(t) = \begin{pmatrix} \cos \omega t & -\sin \omega t & 0 \\ \sin \omega t & \cos \omega t & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \boxed{\bar{\mu}_{RoF}(t) = R(t) \bar{\mu}(t)} \quad - \quad R(t) \bar{\omega}(t) = \begin{pmatrix} \omega_1 \cos \varphi + \omega_1 \cos(\omega t + \varphi) \\ \omega_1 \sin \varphi - \omega_1 \sin(\omega t + \varphi) \\ \omega_0 \end{pmatrix} \approx \begin{pmatrix} \omega_1 \cos \varphi \\ \omega_1 \sin \varphi \\ \omega_0 \end{pmatrix}$$

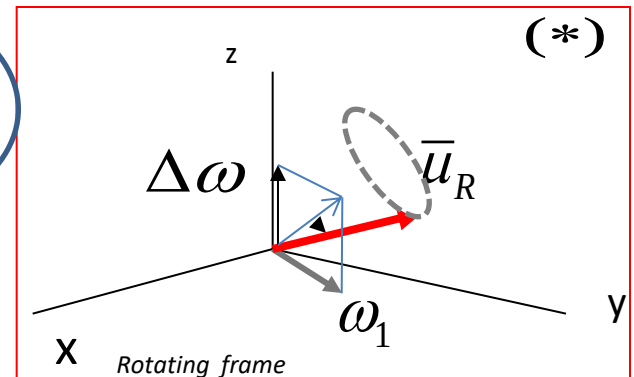
$$\frac{d}{dt} \{R(t) \bar{\mu}(t)\} = \left\{ \frac{d}{dt} R(t) \right\} \cdot \bar{\mu}(t) + R(t) \cdot \frac{d}{dt} \bar{\mu}(t) = \left[\left\{ \frac{d}{dt} R(t) \right\} R^{-1}(t) \right] R(t) \bar{\mu}(t) + R(t) [\bar{\omega}(t) \times \bar{\mu}(t)]$$

$$\frac{d}{dt} R(t) \cdot R^{-1}(t) = \begin{pmatrix} -\omega \sin \omega t & \omega \cos \omega t & 0 \\ -\omega \cos \omega t & -\omega \sin \omega t & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \cos \omega t & -\sin \omega t \\ \sin \omega t & \cos \omega t \\ 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & \omega \\ -\omega & 0 \\ 0 & 0 \end{pmatrix} \rightarrow \begin{pmatrix} 0 & \omega \\ -\omega & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} \mu_{xR}(t) \\ \mu_{yR}(t) \\ \mu_{zR}(t) \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ -\omega \end{pmatrix} \times \begin{pmatrix} \mu_R(t) \\ \mu_R(t) \\ \mu_R(t) \end{pmatrix}$$

$$R(t) \bar{\omega}(t) \times \bar{\mu}_{RoF}(t) = \begin{pmatrix} \omega_1 \cos \varphi \\ \omega_1 \sin \varphi \\ \omega_0 \end{pmatrix} \times \begin{pmatrix} \mu_{RoF}(t) \\ \mu_{RoF}(t) \\ \mu_{RoF}(t) \end{pmatrix}$$

$$\boxed{\frac{d}{dt} \mu_{RoF}(t) = \bar{\omega}_{RoF} \times \mu_{RoF}(t)}$$

$$\bar{\omega}_{RoF} = \begin{pmatrix} \omega_1 \cos \varphi \\ \omega_1 \sin \varphi \\ \omega_0 - \omega \end{pmatrix}$$



Thus the magnetic field in the rotating frame becomes with:

$$\bar{\omega}_{RoF} = \Delta\omega \bar{z} + \omega_1 \cos \varphi \bar{x} + \omega_1 \sin \varphi \bar{y}$$

In NMR we measure:
$$\begin{bmatrix} \mu_{xRoF}(t) \\ \mu_{yRoF}(t) \end{bmatrix}$$

“Signal detection in the laboratory frame, along the direction of the coil:”:

$$\mu_x(t) = \mu_{xRoF}(t) \cos \omega t - \mu_{yRoF}(t) \sin \omega t$$

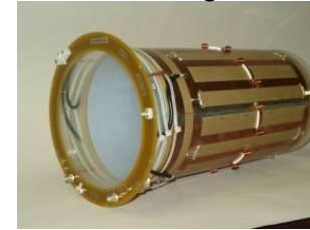
A sample with an overall $\bar{M}(t)$

the S/N voltage at the coil is:

$$S / N = \frac{\pi}{f} \left\{ \frac{1}{2} \eta(\nu) \Delta \nu Q \frac{V_s}{kT} \right\}^{1/2} M_0$$

f = noise of apparatus
 η = filling factor
 ν = frequency
 $\Delta \nu$ = band width
 Q = quality factor
 V_s = sample volume

Bird cage

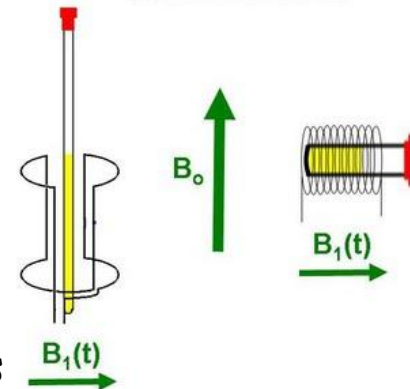


Doty Scientific

National High Magnetic Field Laboratory



The RF Fields for Helmholtz and Solenoid Coils



u-of-o-nmr-facility.blogspot.com/2008/03/prob...

1-d. Concepts in Quantum Mechanics and the Rotating Frame

d-i The wavefunctions

$$\{|\varphi_n\rangle\}_{n=1,N} \quad ; \quad \langle \varphi_n | \varphi_m \rangle = \delta_{nm}$$

$$\langle \varphi_n | A | \varphi_m \rangle = A_{nm}$$

$$|\psi\rangle = \sum_{n=1,N} c_n |\varphi_n\rangle$$

When the representation of an operator is diagonal, then the basis set is the eigenbasis set and the matrix elements the eigenvalues.

When the representation of an operator is not diagonal then after diagonalization we obtain the eigenfunctions and eigenvalues

define a basis set spanning Hilbert space that is orthonormal.

This enables a matrix representation $\overline{\overline{A}}$ of any operator and a vector representation $\overline{C}$ of any wave function.

$$\langle \varphi_n | A | \varphi_m \rangle = A_{nm}$$

$$\overline{\overline{A}} = \begin{pmatrix} a_{11} & & a_{1n} \\ & \ddots & \\ a_{n1} & & a_{nn} \end{pmatrix}$$

$$\langle \alpha_n | D^{-1} A D | \alpha_m \rangle = A_{nn} \delta_{nm}$$

$$\sum_{k,l} \langle \alpha_n | D^{-1} | \varphi_k \rangle \langle \varphi_k | A | \varphi_l \rangle \langle \varphi_l | D | \alpha_m \rangle \quad ; \quad |\varphi_n\rangle = \sum_k |\alpha_k\rangle \langle \alpha_k | D^{-1} | \varphi_n \rangle$$

the eigenvalues of the Hamiltonian are the energies of the system

d-ii The Schrodinger Equation

$$\frac{d}{dt} |\psi\rangle(t) = -\frac{i}{\hbar} H(t) |\psi\rangle(t)$$

a time dependent Hamiltonian doesn't have eigenvalues/energies

The solution of the Schrodinger equation defines an evolution operator

$$|\psi\rangle(t) = U(t,0) |\psi\rangle(0)$$

Vector-matrix representation

$$\frac{d}{dt} \bar{c}(t) = -\frac{i}{\hbar} \bar{H}(t) \bar{c}(t)$$



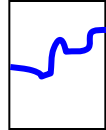
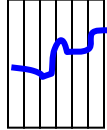
$$\bar{c}(t) = \bar{U}(t) c(0)$$

If the Hamiltonian is time independent then

$$U(t,0) = e^{-i(H/\hbar)t} \equiv 1 - \frac{i}{\hbar} Ht - \frac{1}{2\hbar^2} H^2 t^2 + \dots$$

If the Hamiltonian is time dependent then, with the Dyson operator $\mathcal{T}$:

$$U(t,0) = \mathcal{T} e^{-i \int_0^t (H/\hbar) dt} = \lim_{\substack{\Delta t \rightarrow 0 \\ N \rightarrow \infty}} \prod_{n=1, N} e^{-i(H_n/\hbar)\Delta t}$$

$H(t)$:  $\longrightarrow$  $H_n = H((n-1/2)\Delta t)$

d-iii. The angular momentum operators, definitions

$$\{I_p\} \quad p = x, y, z$$

$$e^{-i\alpha I_x} I_y e^{i\alpha I_x} = I_y \cos \alpha + I_z \sin \alpha$$

$$[I_x, I_y] = i\hbar I_z$$

an cyclic permutation

in the eigenfunction representation:

$$I_z |I, m\rangle = m |I, m\rangle \quad m = -I, \dots, I-1, I$$

$$I_x |I, m\rangle = \frac{1}{2} \sqrt{I(I+1) - m(m+1)} |I, m+1\rangle + \frac{1}{2} \sqrt{I(I+1) - m(m-1)} |I, m-1\rangle$$

$$I_y |I, m\rangle = -\frac{i}{2} \sqrt{I(I+1) - m(m+1)} |I, m+1\rangle + \frac{i}{2} \sqrt{I(I+1) - m(m-1)} |I, m-1\rangle$$

$$I_{\pm} = I_x \pm iI_y$$

$$I_+ |I, m\rangle = \sqrt{I(I+1) - m(m+1)} |I, m+1\rangle$$

$$I_- |I, m\rangle = \sqrt{I(I+1) - m(m-1)} |I, m-1\rangle$$

$$I = 1/2:$$

In the basis set of I_z :

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

Pauli matrices span the whole **2x2** Hilbert space

$$I = 1:$$

In the basis set of I_z :

$$I_z = \begin{pmatrix} 1 & & \\ & 0 & \\ & & -1 \end{pmatrix}; I_x = \frac{1}{2} \begin{pmatrix} 0 & \sqrt{2} & \\ \sqrt{2} & 0 & \sqrt{2} \\ & \sqrt{2} & 0 \end{pmatrix}; I_y = \frac{1}{2} \begin{pmatrix} 0 & -i\sqrt{2} & \\ i\sqrt{2} & 0 & -i\sqrt{2} \\ & i\sqrt{2} & 0 \end{pmatrix}$$

The linear angular momentum operators do not span the whole **3x3** Hilbert space

The missing operators are:

$$I_x I_z + I_z I_x = \frac{1}{2} \begin{pmatrix} 0 & \sqrt{2} & \\ \sqrt{2} & 0 & \sqrt{2} \\ & -\sqrt{2} & 0 \end{pmatrix} \quad I_y I_z + I_z I_y = \frac{1}{2} \begin{pmatrix} 0 & -i\sqrt{2} & \\ i\sqrt{2} & 0 & -i\sqrt{2} \\ & i\sqrt{2} & 0 \end{pmatrix}$$

$$I_z^2 - \frac{1}{2}(I_x^2 + I_y^2) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad I_x^2 - I_y^2 = \frac{1}{2} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

1-e A nucleus in a magnetic field

The spin Hamiltonian

$$H_{LAB} = -\vec{B}_0 \cdot \vec{\mu} = -\vec{\omega}_0 \cdot \vec{I}$$

with the magnetic field in the z-direction of the laboratory frame

and an RF irradiation:

$$H_{LAB} = -\omega_0 I_z + 2\omega_1 \cos(\omega t + \varphi) I_x$$

and the rotating frame:

$$H_{RoF} = -\Delta\omega I_z + \omega_1 \cos \varphi I_x + \omega_1 \sin \varphi I_y$$

For spin=1/2 :

$$\begin{array}{l} |\beta\rangle \text{---} \\ |\alpha\rangle \text{---} \end{array} \left\{ \begin{array}{l} I_z |\alpha\rangle = 1/2 |\alpha\rangle \\ I_z |\beta\rangle = -1/2 |\beta\rangle \end{array} \right.$$

Pauli matrices

$$I_x = \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix}; \quad I_y = \begin{pmatrix} 0 & -i/2 \\ i/2 & 0 \end{pmatrix}; \quad I_z = \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix}$$

cyclic permutations:

$$[I_x, I_y] = iI_z; \quad [I_y, I_z] = iI_x; \quad [I_z, I_x] = iI_y$$

$$e^{i\phi I_z} = \begin{pmatrix} e^{(i/2)\phi} & 0 \\ 0 & e^{(-i/2)\phi} \end{pmatrix}$$

$$e^{i\phi I_x} = \begin{pmatrix} \cos \phi/2 & i \sin \phi/2 \\ i \sin \phi/2 & \cos \phi/2 \end{pmatrix}; \quad e^{i\phi I_y} = \begin{pmatrix} \cos \phi/2 & \sin \phi/2 \\ -\sin \phi/2 & \cos \phi/2 \end{pmatrix}$$

$$e^{-i\phi I_z} \{I_x\} e^{i\phi I_z} = I_x \cos \phi + I_y \sin \phi$$

Remember that $U(t,0) = e^{-i(H/\hbar)t} = D e^{-i(\Lambda/\hbar)t} D^{-1}$

when the Hamiltonian is time independent and

$$HD = D\Lambda \quad H = D\Lambda D^{-1}$$

$$H = \begin{pmatrix} H_{11} & H_{1j} \\ H_{ji} & H_{NN} \end{pmatrix} \text{ is Hermitian} \quad H_{ij} = H_{ji}^*$$

$$U(t) = \begin{pmatrix} U_{11} & U_{1j} \\ U_{ji} & U_{NN} \end{pmatrix} \text{ is unitary} \quad U(t) \cdot U^{-1}(t) = 1$$

$$U_{ij} = (U_{ji}^{-1})^*$$

$$H_{LAB} = -\omega_0 I_z : \begin{pmatrix} e^{i\omega_0/2t} & 0 \\ 0 & e^{-i\omega_0/2t} \end{pmatrix} \begin{pmatrix} c_\alpha(0) \\ c_\beta(0) \end{pmatrix} = \begin{pmatrix} c_\alpha(0)e^{i\omega_0/2t} \\ c_\beta(0)e^{-i\omega_0/2t} \end{pmatrix}$$

$|\beta\rangle$ —————
 $|\alpha\rangle$ —————

$$H_{RoF} = \omega_1 I_x : \begin{pmatrix} \cos \omega_1/2t & i \sin \omega_1/2t \\ i \sin \omega_1/2t & \cos \omega_1/2t \end{pmatrix} \begin{pmatrix} c_\alpha(0) \\ c_\beta(0) \end{pmatrix} = \begin{pmatrix} c_\alpha(0) \cos \omega_1/2t + i c_\beta(0) \sin \omega_1/2t \\ i c_\alpha(0) \sin \omega_1/2t + c_\beta(0) \cos \omega_1/2t \end{pmatrix}$$



$ \gamma\rangle$ —————	$c_\gamma(0) = a$	a
$ \beta\rangle$ —————	$c_\beta(0) = b$	$-b$
$ \alpha\rangle$ —————	$c_\alpha(0) = c$	$-c$

SPINOR effect

I-f The spin-density operator

$$|\psi\rangle(t) = \sum_{n=1,N} c_n(t) |\varphi_n\rangle$$

An arbitrary function can be expanded in a basis set

This defines a set of coefficients $\{c_n(t)\}$ with $\frac{d}{dt} \bar{c}(t) = -\frac{1}{\hbar} \bar{H}(t) \bar{c}(t)$

Let us define an operator with matrix elements

$$\rho_{nm}(t) \equiv \{c_n(t) c_m^*(t)\}$$

$$\rho(t) = \begin{pmatrix} \rho_{11} & \rho_{ij} \\ \rho_{ji} & \rho_{NN} \end{pmatrix}$$

$$H = \begin{pmatrix} H_{11} & H_{ij} \\ H_{ji} & H_{NN} \end{pmatrix}$$

Hermitian

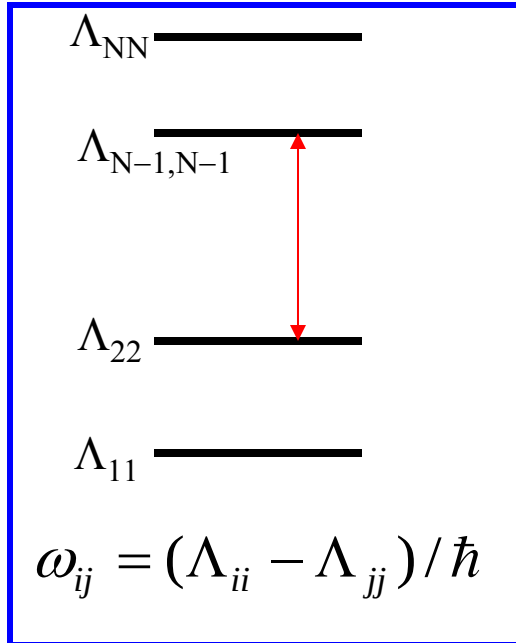
$$\begin{aligned} \frac{d}{dt} \{c_n(t) c_m^*(t)\} &= -\frac{i}{\hbar} \sum_k H_{nk}(t) c_k(t) c_m^*(t) + \frac{i}{\hbar} \sum_k c_n(t) H_{mk}^*(t) c_k^*(t) \\ &= -\frac{i}{\hbar} \sum_k H_{nk}(t) c_k(t) c_m^*(t) + \frac{i}{\hbar} \sum_k c_n(t) c_k^*(t) H_{km}(t) \end{aligned}$$

$$\frac{d}{dt} \rho(t) = -\frac{i}{\hbar} [H(t), \rho(t)]$$

Ensemble Average and thermodynamics

Consider an ensemble average of the matrix elements of the spin-density

In the representation of the eigenbasis of the Hamiltonian the solution for the density matrix elements



$$c_n(t) = e^{-i/\hbar \Lambda_{nn} t} c_n(0)$$

$$c_m^*(t) = e^{+i/\hbar \Lambda_{mm} t} c_m^*(0)$$

then

$$\rho_{nm}(t) = e^{-i/\hbar (\Lambda_{nn} - \Lambda_{mm}) t} \rho_{nm}(0) \times e^{i\varphi_{\text{random}}}$$

with the random phase approximation

$$\bar{\rho}_{nm}(eq) \equiv \overline{c_n(eq) c_m^*(eq)}$$

$$\bar{\rho}_{nm}(eq) = 0$$

coherences

$$\bar{\rho}_{nn}(eq) \neq 0$$

the populations

Thus the equilibrium density operator can be defined by the populations satisfying the Boltzman statistics

$$\bar{\rho}(0) = \frac{1}{Z} e^{-\Lambda / kT}$$

$$\hbar\omega_0 = (1.05 \cdot 10^{-34} \text{ Js}) \cdot (3 \cdot 10^8 \text{ s}^{-1}) = 3.15 \cdot 10^{-26} \text{ J}$$

$$kT = (1.38 \cdot 10^{-23} \text{ JK}^{-1}) \cdot (300 \text{ K}) = 4.14 \cdot 10^{-21} \text{ J}$$

$$\frac{\hbar\omega_0}{kT} = 7.6 \cdot 10^{-6} \quad e^{\frac{\hbar\omega_0}{kT}} \cong 1 - \frac{\hbar\omega_0}{kT} = 0.9999924$$

$$\bar{\rho}_{eq} = \frac{1}{Z} e^{-H / kT} = \frac{1}{Z} \left\{ 1 - \frac{1}{kT} H + \dots \right\}$$

In NMR we solve the Liouville -von Neuman equation to calculate the signals

The signal is proportional to an "observable"

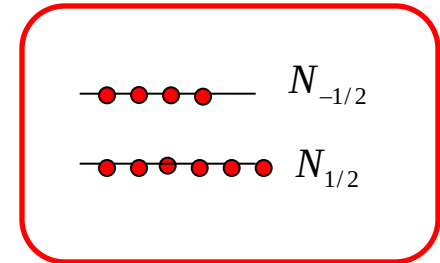
$$\begin{aligned} \langle O \rangle(t) &= \overline{\langle \psi(t) | O | \psi(t) \rangle} = \overline{\sum_{n,m} c_n^*(t) \langle \varphi_n | O | \varphi_m \rangle c_m(t)} \\ &= \sum_{n,m} \bar{\rho}_{mn}(t) O_{nm}(t) = \text{Tr} \{ \bar{\rho}(t) O \} \end{aligned}$$

$$\langle I^- \rangle = \text{Tr} \left(\begin{pmatrix} \rho_{11}(t) & \rho_{12}(t) \\ \rho_{21}(t) & \rho_{22}(t) \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \right) = \rho_{12}$$

$$\begin{aligned} \rho(t) &= \frac{1}{2} [\rho_{11}(t) + \rho_{22}(t)] \mathbb{I} + [\rho_{11}(t) - \rho_{22}(t)] I_z + 2(\text{Re } \rho_{12} I_x - \text{Im } \rho_{12} I_y) \\ &= [\rho_{11}(t) + \rho_{22}(t)] \mathbb{I} + [\rho_{11}(t) - \rho_{22}(t)] I_z + \rho_{12} I^+ + \rho_{12}^* I^- \end{aligned}$$

This requires a definition of the *populations* of the eigenstates.

At thermal equilibrium these populations follow the Boltzmann distribution:



$$\frac{N_{-1/2}}{N_{1/2}} = \frac{e^{-E_{-1/2}/kT}}{e^{-E_{1/2}/kT}} = e^{-\hbar\omega_0/kT} \quad \langle I_z \rangle_{ensemble} = \frac{1}{2} \hbar (N_{1/2} - N_{-1/2})$$

The magnitude of $\frac{\hbar\omega_0}{kT}$ at 50-300K is very small.

$$\hbar\omega_0 = (1.05 \cdot 10^{-34} \text{ Js}) \cdot (3 \cdot 10^8 \text{ s}^{-1}) = 3.15 \cdot 10^{-26} \text{ J}$$

$$kT = (1.38 \cdot 10^{-23} \text{ JK}^{-1}) \cdot (300 \text{ K}) = 4.14 \cdot 10^{-21} \text{ J}$$

$$\frac{\hbar\omega_0}{kT} = 7.6 \cdot 10^{-6} \quad e^{\frac{\hbar\omega_0}{kT}} \cong 1 - \frac{\hbar\omega_0}{kT} = 0.9999924$$

and the populations become

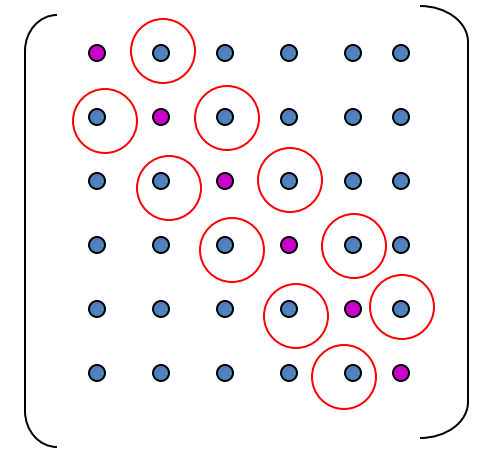
$$N_{1/2} = \frac{1}{2} N \left(1 + \frac{\hbar\omega_0}{2kT}\right) \quad N_{-1/2} = \frac{1}{2} N \left(1 - \frac{\hbar\omega_0}{2kT}\right)$$

The thermal-equilibrium ensemble magnetization becomes

$$\langle M_z \rangle_{ensemble} = \frac{1}{2} \gamma \hbar (N_{1/2} - N_{-1/2}) = \frac{N}{2} \gamma \hbar \cdot \frac{\hbar\omega_0}{2kT} = \frac{N \gamma^2 \hbar^2 B_0}{4kT}$$

1-g NMR is a journey along the matrix elements of the reduced spin density matrix

$$\sigma(t) = \left[\rho(t) - \frac{\mathbf{I}}{ZkT} \right] =$$



$$\frac{d}{dt} \sigma(t) = -\frac{i}{\hbar} [H(t), \sigma(t)]$$

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

$$U(t) = T e^{-i \int_0^t H(t') dt'}$$

$$\langle O \rangle(t) = \text{Tr}(\sigma(t) O(t))$$

Example of pulse on $I=1/2$

$$\begin{pmatrix} \cos \omega_1 / 2t & i \sin \omega_1 / 2t \\ i \sin \omega_1 / 2t & \cos \omega_1 / 2t \end{pmatrix} \begin{pmatrix} 1 & \\ & -1 \end{pmatrix} \begin{pmatrix} \cos \omega_1 / 2t & -i \sin \omega_1 / 2t \\ -i \sin \omega_1 / 2t & \cos \omega_1 / 2t \end{pmatrix} \\ = \begin{pmatrix} \cos \omega_1 t & -i \sin \omega_1 t \\ i \sin \omega_1 t & \cos \omega_1 t \end{pmatrix} = 2(I_z \cos \omega_1 t + I_y \sin \omega_1 t)$$



$$\{E_i = \Lambda_{ii}\}$$

NMR signals

$$\langle I_{x,y} \rangle_R(t) = \text{Tr}(\sigma_R(t) I_{x,y})$$

Coherences that are off diagonal element are detected

Populations that are the diagonal element are not detected

The reduced (high temperature) spin density operator

$$\frac{d}{dt} \sigma(t) = -\frac{i}{\hbar} [H_0, \sigma(t)]$$

$$\sigma_{eq} = \frac{1}{Z} \frac{1}{\hbar k T} H_0$$

$$\sigma(t) = e^{-iH_0 t} \sigma(0) e^{iH_0 t}$$

$$\langle O \rangle = \text{Tr}(\sigma(t) O)$$

The Larmor precession for spin $I=1/2$

$$H = -\omega_0 I_z$$

$$\sigma_{eq} = \frac{1}{Z} \frac{\omega_0}{\hbar k T} I_z$$

$$\sigma(t) = e^{-i\omega_0 I_z t} \sigma(0) e^{i\omega_0 I_z t}$$

$$\sigma(0) = s_x(0) I_x + s_y(0) I_y + s_z(0) I_z$$

$$\langle I_x \rangle = s_x(0) \cos \omega_0 t + s_y(0) \sin \omega_0 t$$

$$\langle I_y \rangle = -s_x(0) \sin \omega_0 t + s_y(0) \cos \omega_0 t$$

$$\langle I_z \rangle = s_z(0)$$

NMR signals in the Rotating frame

$$\frac{d}{dt} \sigma_{\text{RoF}}(t) = -\frac{i}{\hbar} \left[-(\omega_0 - \omega) I_z + H_{1,\text{RoF}}, \sigma_{\text{RoF}}(t) \right]$$

$$\langle O \rangle_R = \text{Tr}(\sigma_R(t) O)$$

$$\text{Signal}(t) \equiv \langle I_{x,\text{RoF}} \rangle + i \langle I_{y,\text{RoF}} \rangle$$

$$\sigma(0) = s_x(0) I_x + s_y(0) I_y + s_z(0) I_z$$

$$H_1 = \omega_1 I_y$$

$$\langle I_x \rangle_R = s_x(0) \cos \omega_1 t - s_z(0) \sin \omega_1 t$$

$$\langle I_y \rangle_R = s_y(0)$$

$$\langle I_z \rangle_R = s_z(0) \cos \omega_1 t + s_x(0) \sin \omega_1 t$$



“quadrature detection”

The magnetization in a magnetic field for spin $I=1/2$ only

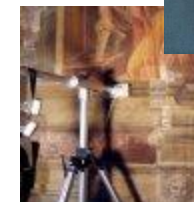
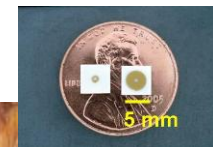
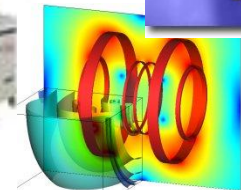
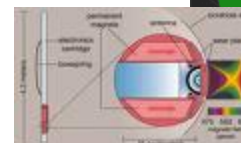
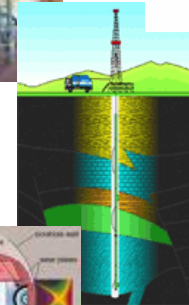
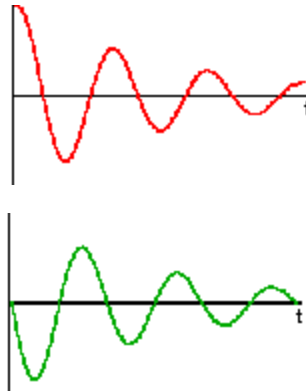
$$\bar{\omega}_R = (\omega_0 - \omega)\bar{z} + \omega_1\bar{x} \cos \varphi + \omega_1\bar{y} \sin \varphi$$

The Feynman, Vernon, Hellwarth
the vector representation of a
two level system

$$\bar{\mu}_R(t) = \left\{ \langle \mathcal{I}_x \rangle_R(t), \langle \mathcal{I}_y \rangle_R(t), \langle \mathcal{I}_z \rangle_R(t) \right\}$$

the NMR Signals

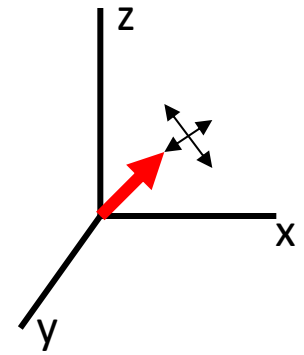
by Faraday's and Lenz's rules
the induction in the coil is
measured by current detection



2. Basic Concept of Pulsed NMR

2-a. T_1 and T_2 relaxation, a simple description

Suppose the spins experience
a fluctuating field in all directions



Lab frame

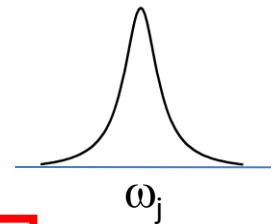
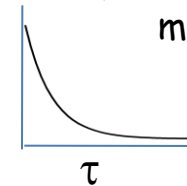
rotating frame

$$\begin{pmatrix} h_x g_x(t) \\ h_y g_y(t) \\ h_z g_z(t) \end{pmatrix} \rightarrow \begin{pmatrix} h_{xR}(t) = h_x g_x(t) \cos \omega t + h_y g_y(t) \sin \omega t \\ h_{yR}(t) = h_y g_y(t) \cos \omega t - h_x g_x(t) \sin \omega t \\ h_{zR}(t) = h_z g_z(t) \end{pmatrix}$$

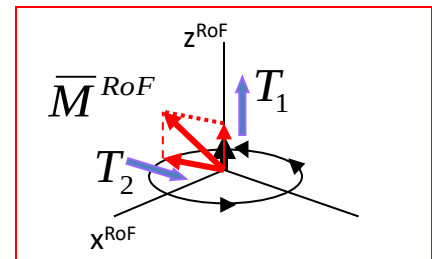
Only slow fluctuations
in the rotating frame
influence the magnetic
moments of the spins

Correlation function: $G_p(\tau) = h_p^2 \overline{[g_p(t)g_p(t+\tau)]}$

Spectral density: $j_p(\omega_j) = h_p^2 \int_{-\infty}^{\infty} G(\tau)G(0)e^{i\omega_j t} d\tau$



$$\left. \begin{pmatrix} \mu_x(t) \\ \mu_y(t) \\ \mu_z(t) \end{pmatrix} \right\} \begin{matrix} 1/T_2 \propto j(0), j(\omega) \\ 1/T_1 \propto j(\omega) \end{matrix}$$



2-b. The Bloch equation of spin-half nuclei

Remember: the reduced spin-density operator for $I=1/2$ can be written as:

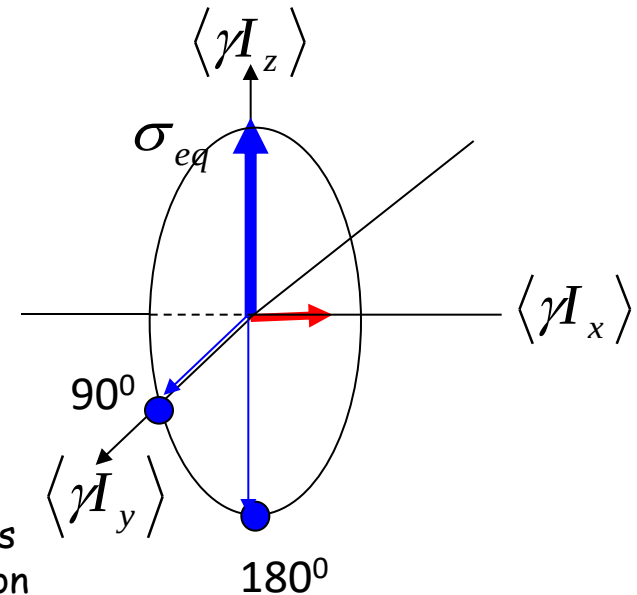
$$\sigma_{RoF}(t) = s_x(t)I_x + s_y(t)I_y + s_z(t)I_z$$

$$S_x(t) = \gamma \langle I_x \rangle_{RoF}(t) = 1/2 \gamma s_x(t) ; S_y(t) = \gamma \langle I_y \rangle_{RoF}(t) = 1/2 \gamma s_y(t)$$

$$\sigma_{RoF}(t) = \frac{1}{2} \begin{pmatrix} s_z(t) & s_x(t) - is_y(t) \\ s_x(t) + is_y(t) & -s_z(t) \end{pmatrix} \quad S(t) = \gamma \{S_x(t) + iS_y(t)\} = \gamma \text{Tr}\{\sigma(t)I^-\}$$

$$H_{RoF} = -\Delta\omega I_z - \omega_1(I_x \cos \varphi + I_y \sin \varphi)$$

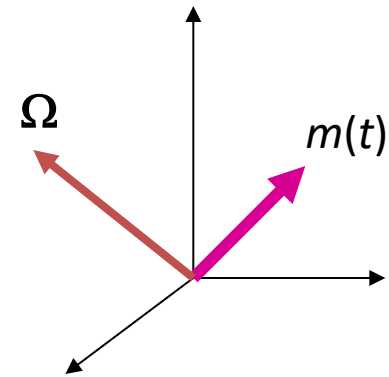
$$\varphi = 0, \Delta\omega = 0 \quad \sigma_{RoF}(t) = A e^{-i\omega_1 I_x t} I_z e^{i\omega_1 I_x t}$$



Thus we can apply
 90° or 180° pulses
 in the x-direction
 and in the y-direction
 Off resonance can become very disturbing

The Bloch vector:

$$\bar{m}(t) = \begin{pmatrix} m_x(t) \\ m_y(t) \\ m_z(t) \end{pmatrix} = \gamma \begin{pmatrix} \langle I_x \rangle(t) \\ \langle I_y \rangle(t) \\ \langle I_z \rangle(t) \end{pmatrix}$$



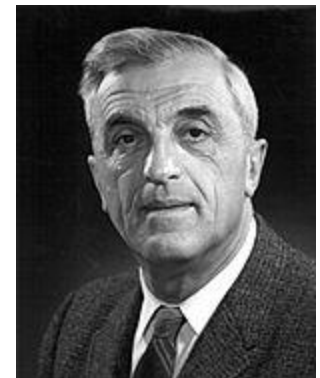
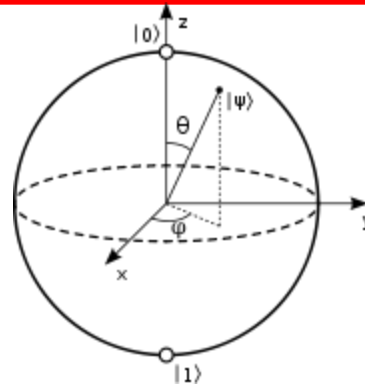
Bloch vector rotation

$$\frac{d}{dt} \bar{m}(t) = \bar{m}(t) \times \bar{\Omega}$$

$$\bar{\Omega} = \begin{pmatrix} \omega_1 \cos \varphi \\ \omega_1 \sin \varphi \\ \Delta\omega \end{pmatrix}$$

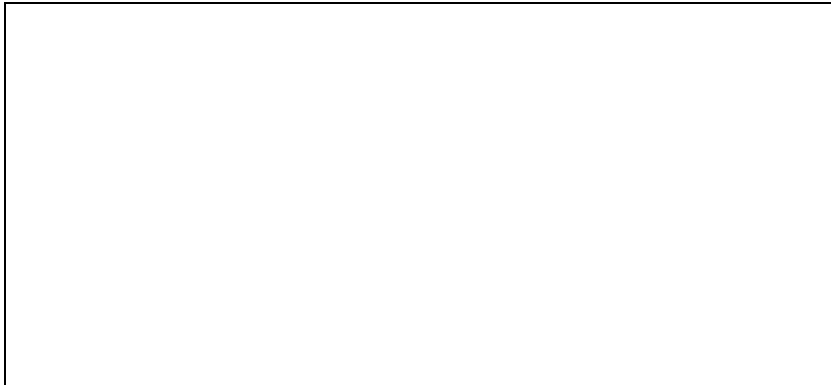
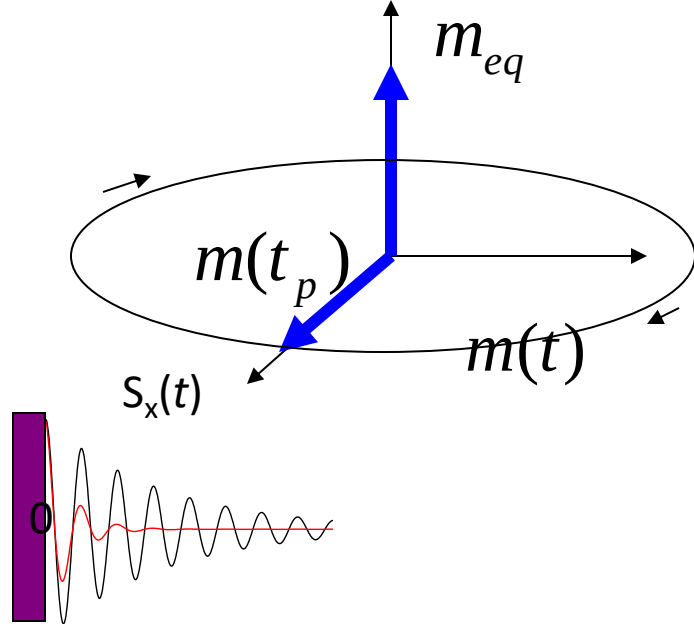
The Bloch equation:

$$\frac{d}{dt} \begin{pmatrix} m_x(t) \\ m_y(t) \\ m_z(t) \end{pmatrix} = \begin{pmatrix} 0 & \Delta\omega & -\omega_1 \cos \varphi \\ -\Delta\omega & 0 & \omega_1 \sin \varphi \\ \omega_1 \cos \varphi & -\omega_1 \sin \varphi & 0 \end{pmatrix} \begin{pmatrix} m_x(t) \\ m_y(t) \\ m_z(t) \end{pmatrix} - \begin{pmatrix} 1/T_2 & & \\ & 1/T_2 & \\ & & 1/T_1 \end{pmatrix} \begin{pmatrix} m_x(t) \\ m_y(t) \\ m_z(t) - m_{eq} \end{pmatrix}$$



Modern NMR

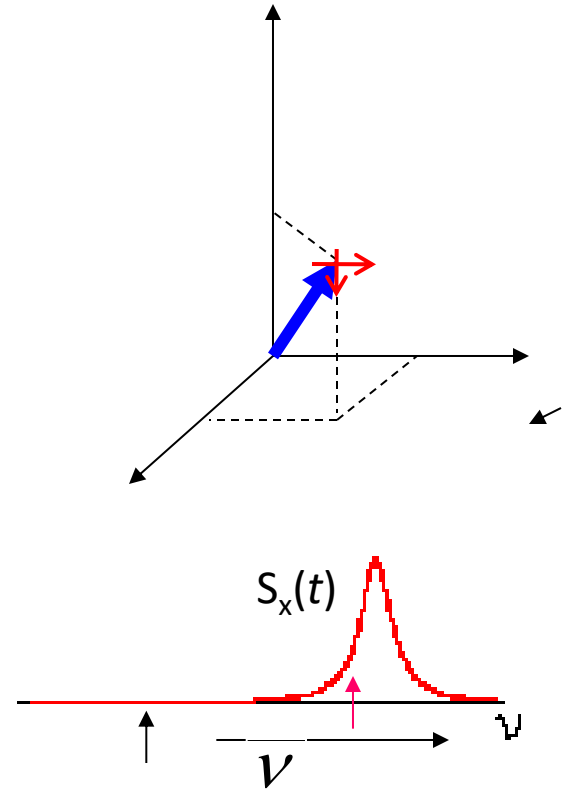
After short RF pulses
Free induction Decay signals are detected



In MR we measure both transverse magnetization components simultaneously

"Earlier" NMR

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



$$\tilde{M}_x = \frac{\Delta\omega \cdot (\gamma B_1) \cdot T_2^2}{1 + (\Delta\omega T_2)^2 + (\gamma B_1)^2 \cdot T_1 \cdot T_2} \cdot M_0$$

$$\tilde{M}_y = \frac{(\gamma B_1) \cdot T_2}{1 + (\Delta\omega T_2)^2 + (\gamma B_1)^2 \cdot T_1 \cdot T_2} \cdot M_0$$

$$\tilde{M}_z = \frac{1 + (\Delta\omega T_2)^2}{1 + (\Delta\omega T_2)^2 + (\gamma B_1)^2 \cdot T_1 \cdot T_2} \cdot M_0$$

Saturation term

absorption

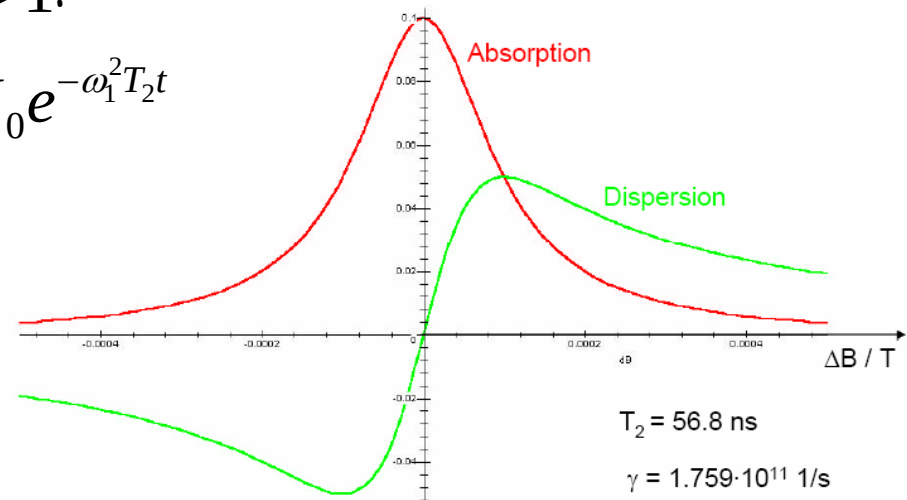
$$\tilde{M}_y \cong \frac{(\gamma B_1) \cdot T_2}{1 + (\Delta\omega T_2)^2} \cdot M_0$$

dispersion

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

During irradiation
at the saturation condition $\omega_1^2 T_1 T_2 \gg 1$:

$$M_z(t) \cong M_0 e^{-\omega_1^2 T_2 t}$$



Calculated with: bloch_nosat.mws

 $T_2 = 56.8 \text{ ns}$ $\gamma = 1.759 \cdot 10^{11} \text{ 1/s}$ $B_1 = 1 \cdot 10^{-5} \text{ T}$

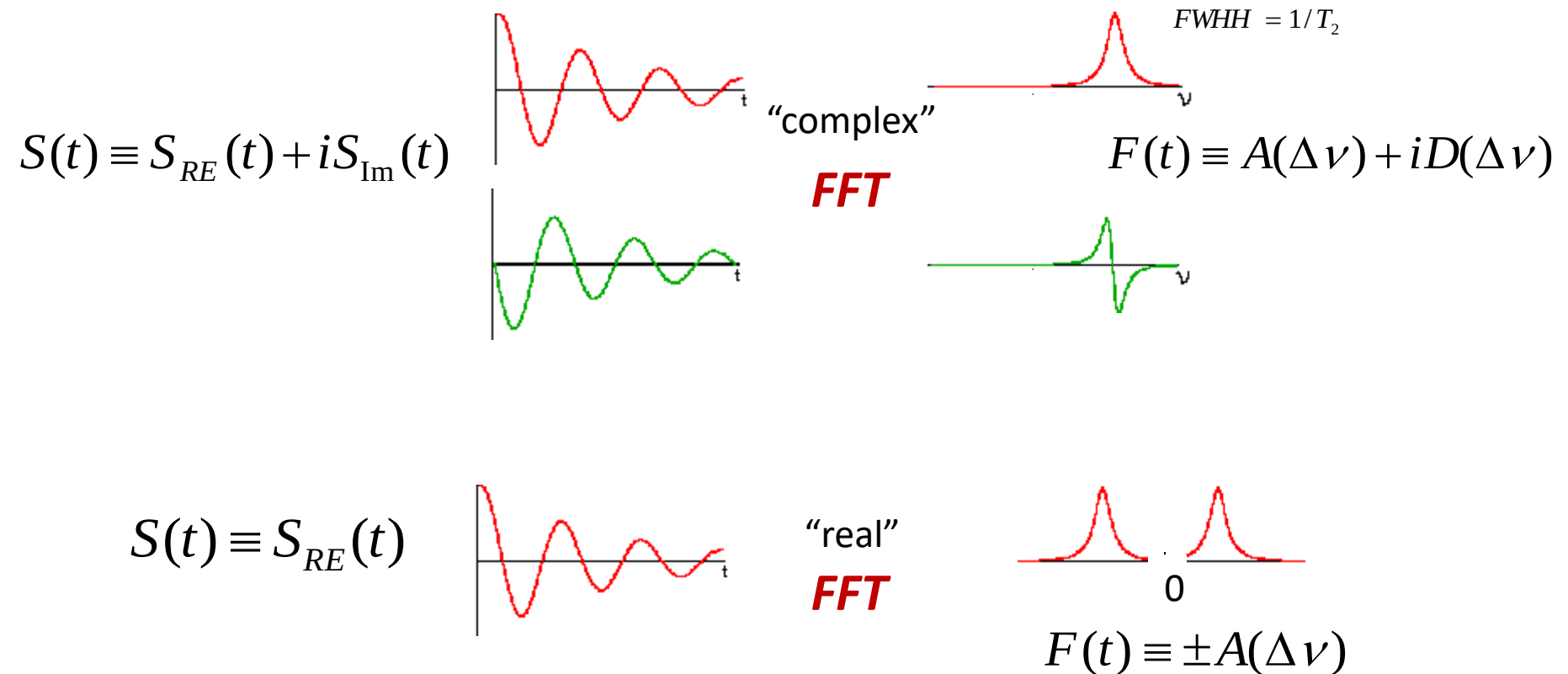
3-c. Pulsed NMR and FFT

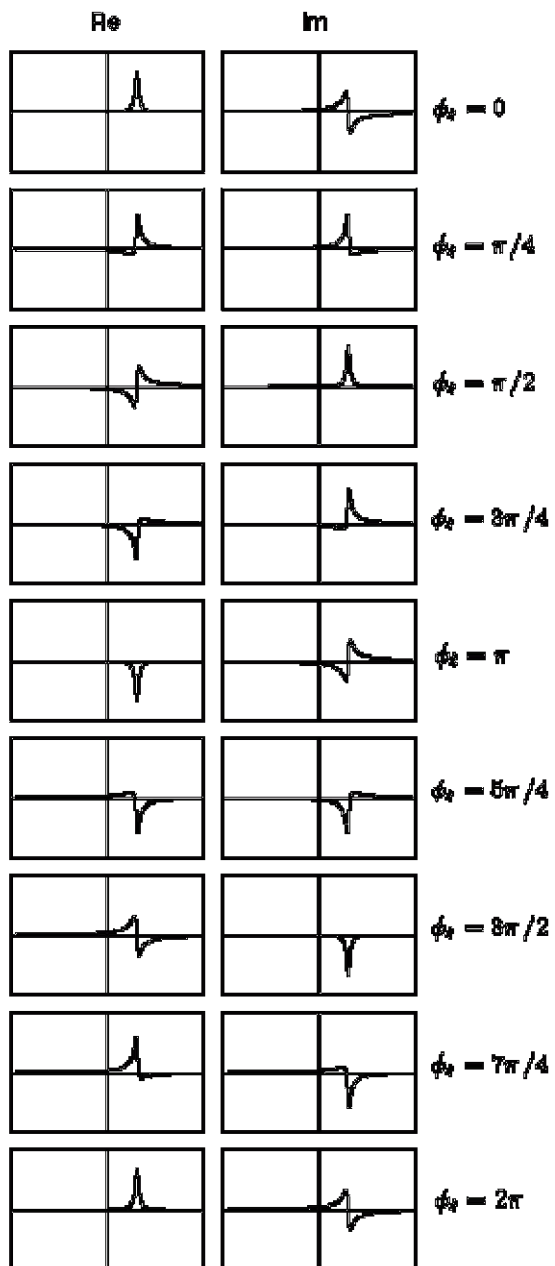
after a 90° pulse:

$$S_x = \langle \mathcal{H}_x \rangle(t) = M_0 \cos \Delta\omega t \times e^{-t/T_2}$$

$$S_y = \langle \mathcal{H}_y \rangle(t) = M_0 \sin \Delta\omega t \times e^{-t/T_2}$$

Fast Fourier Transform



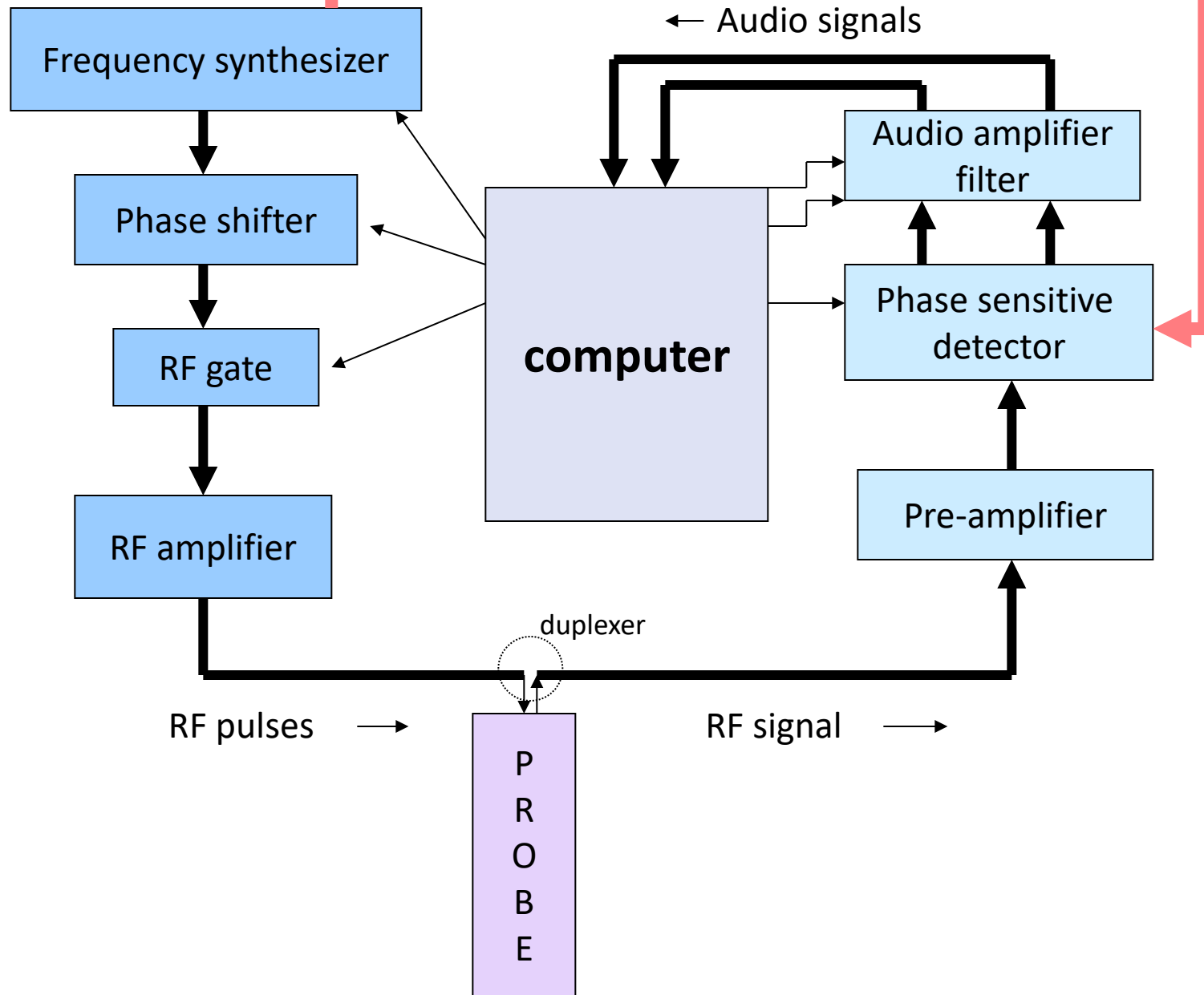


Phase shifting

$$S_x(t) = s_x(t) \cos \psi + s_y(t) \sin \psi$$

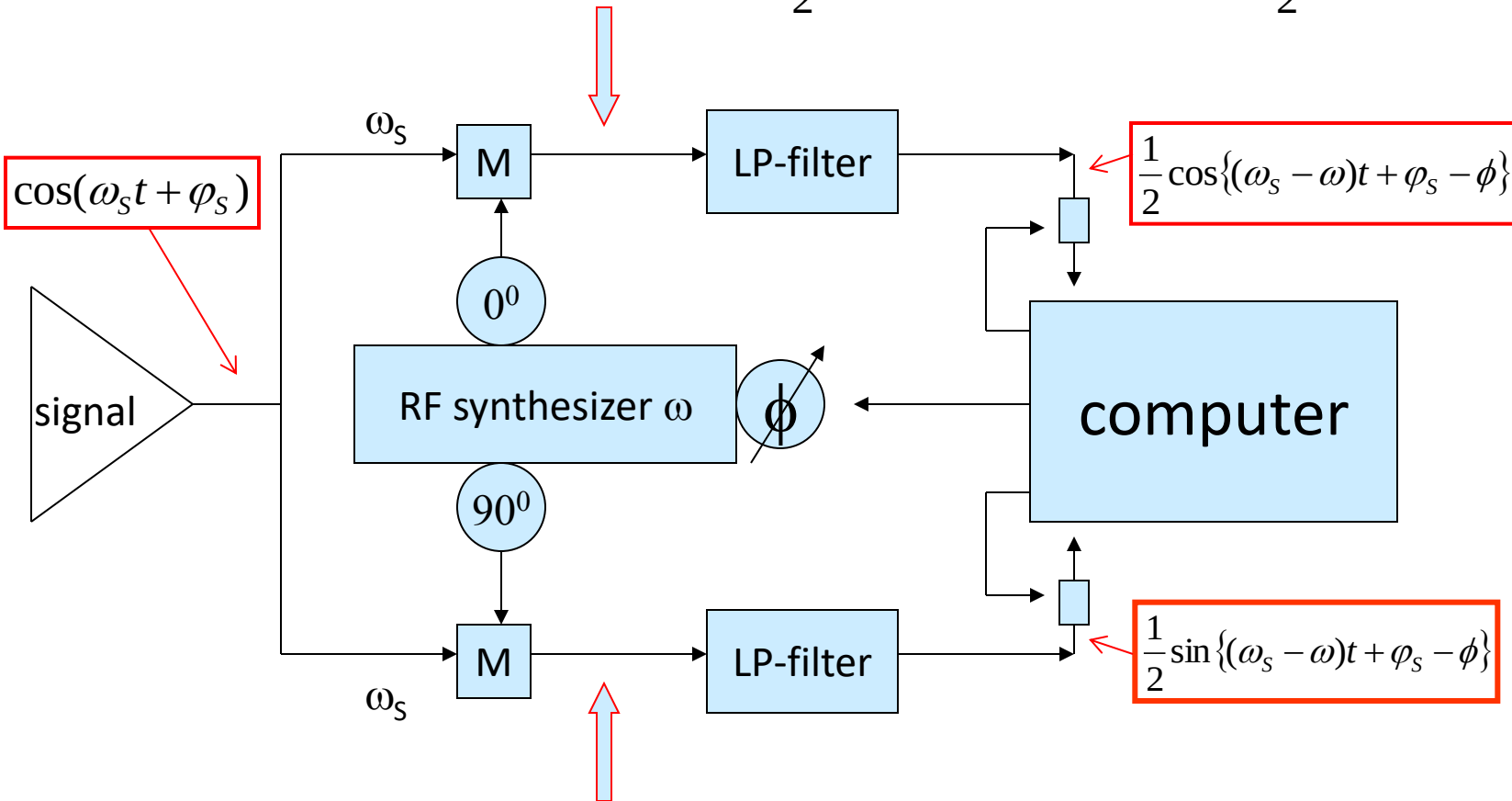
$$S_y(t) = -s_x(t) \sin \psi + s_y(t) \cos \psi$$

2-d. The NMR Spectrometer



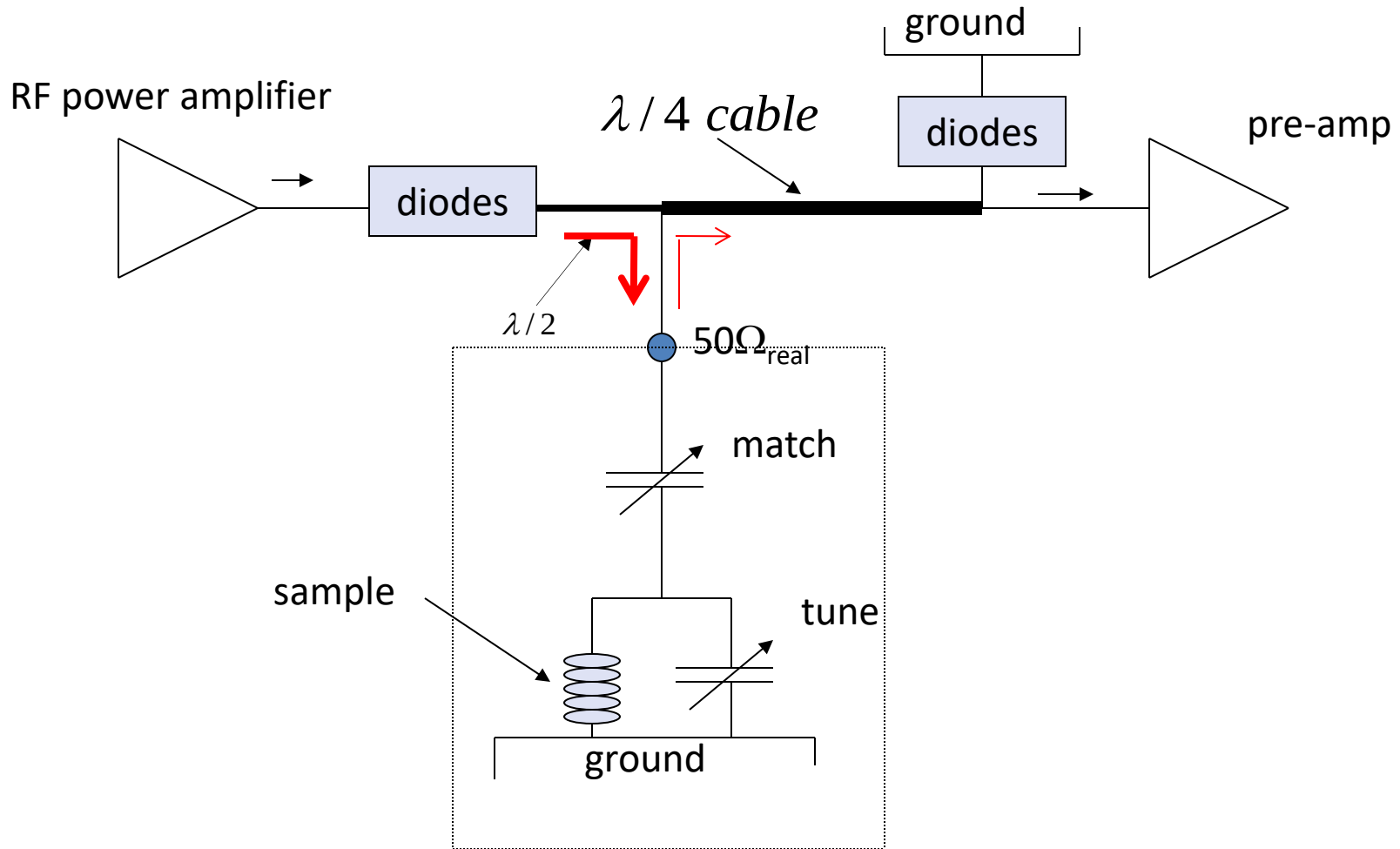
Phase sensitive signal detection

$$\cos(\omega_s t + \varphi_s) \cos(\omega t + \phi) = \frac{1}{2} \cos\{(\omega_s + \omega)t + \varphi_s + \phi\} + \frac{1}{2} \cos\{(\omega_s - \omega)t + \varphi_s - \phi\}$$

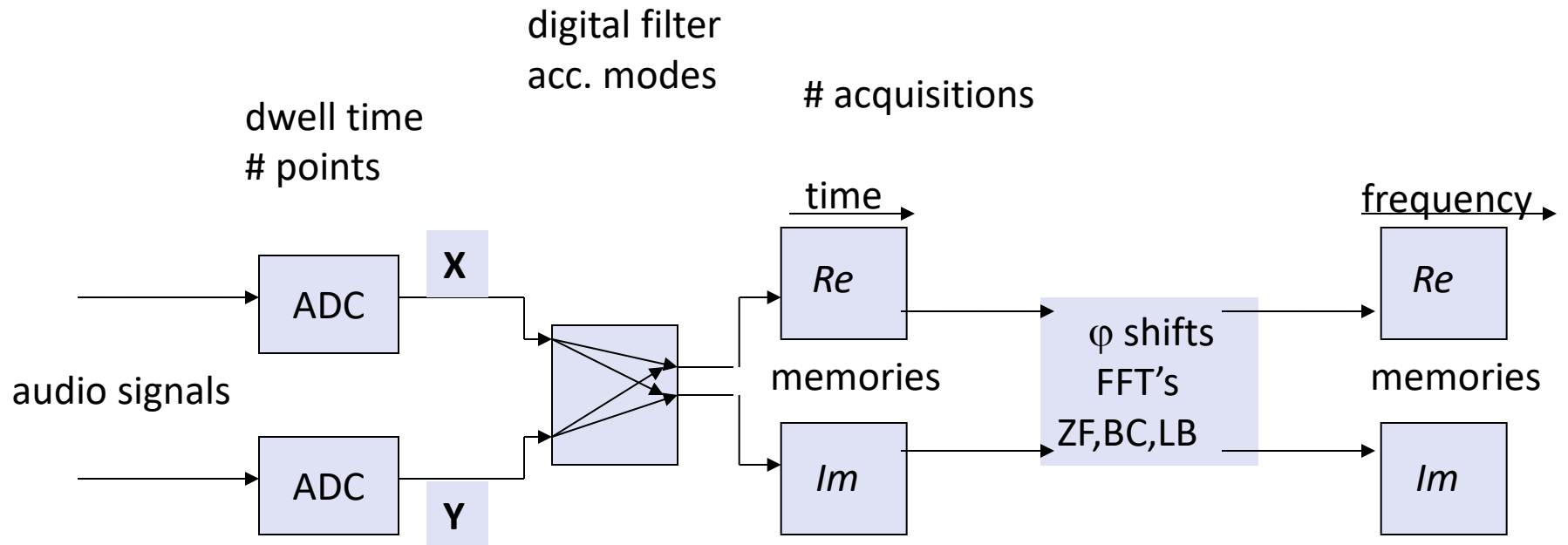


$$\cos(\omega_s t + \varphi_s) \cos(\omega t + \pi/2 + \phi) = \frac{1}{2} \cos\{(\omega_s + \omega)t + \varphi_s + \pi/2 + \phi\} + \frac{1}{2} \cos\{(\omega_s - \omega)t + \varphi_s - \pi/2 - \phi\}$$

Duplexer and Probe



data acquisition



$$\begin{Bmatrix} +X \\ +Y \end{Bmatrix} \quad \begin{Bmatrix} -Y \\ +X \end{Bmatrix} \quad \begin{Bmatrix} -X \\ -Y \end{Bmatrix} \quad \begin{Bmatrix} +Y \\ -X \end{Bmatrix} \rightarrow \begin{Bmatrix} \text{Re} \\ \text{Im} \end{Bmatrix}$$

4 accumulation modes

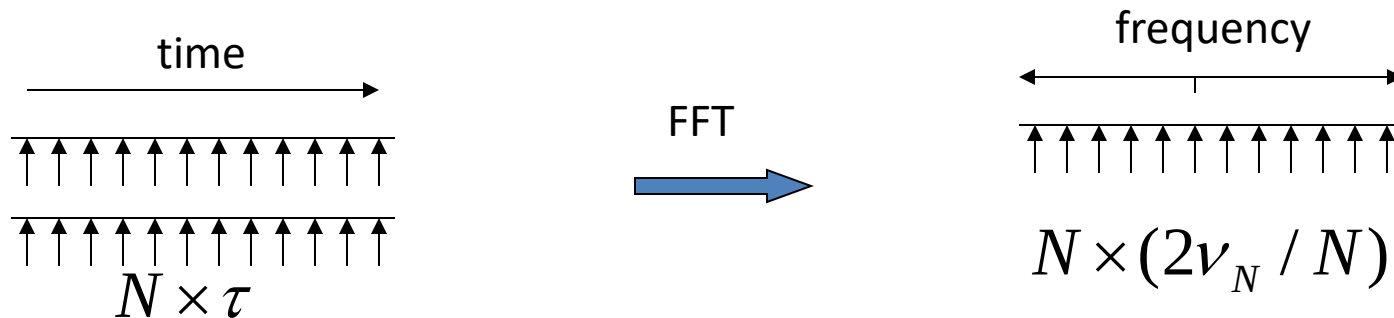
2-e. Data acquisition and FFT

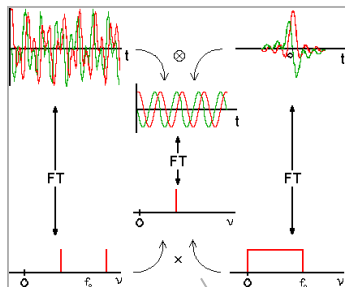
Sampling with dwell time τ results in Nyquist frequency $\nu_N = (2\tau)^{-1}$

The spectral bandwidth after FFT is then $-\nu_N \leq \Delta\nu \leq \nu_N$

Folding or aliasing occurs when $|\Delta\nu| > \nu_N$: a line at $\Delta\nu_{\text{spectru}} = \Delta\nu_{\text{real}} - 2m\nu_N$ appears in the spectrum

If the number of acquired points is N then the spectral resolution is $1/2N\nu_N$

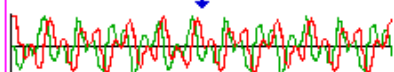




SAMPLE

NMR

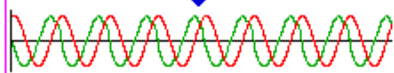
OVER SAMPLING



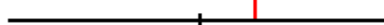
-FT→



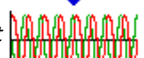
DIGITAL FILTERING



-FT→



DECIMATION

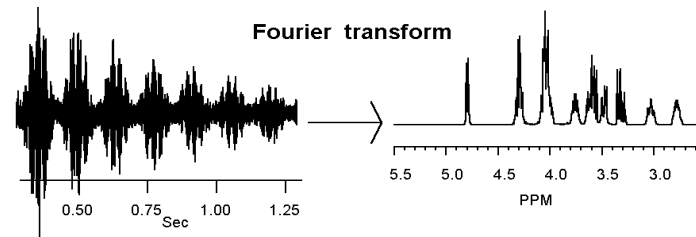
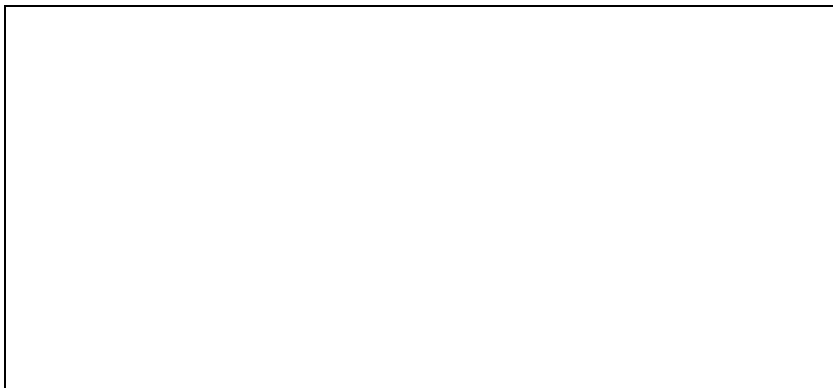


-FT→

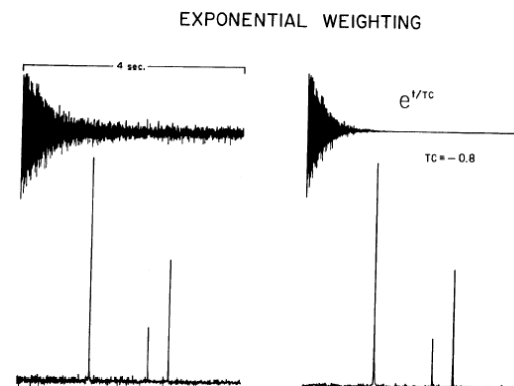
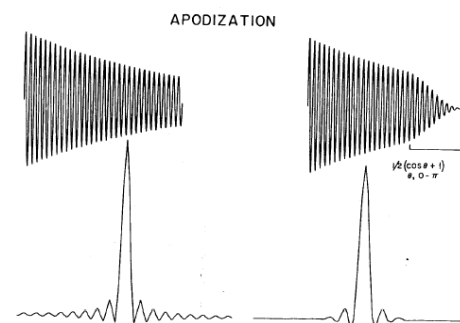


each n-th point is kept

See: <http://www.cis.rit.edu/htbooks/nmr/>



Zero-filling: spectral resolution enhancement, but limitations.

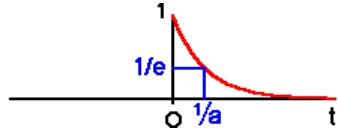


1. exponent $e^{-t/\tau}$

2. Gaussian $e^{-t^2/\tau}$

3. Square shape $f(t) = \begin{cases} 0 & 0 < t < \tau \\ 1 & t > \tau \end{cases}$

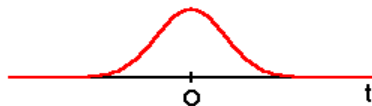
Lorentzian:



FFT

$$\frac{\tau + i\tau^2\Delta\omega}{(1 + \Delta\omega^2\tau^2)}$$

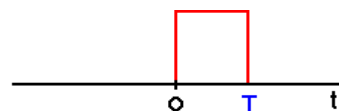
Gaussian:



FFT

$$e^{-\Delta\omega^2\tau}$$

Sinc function



FFT

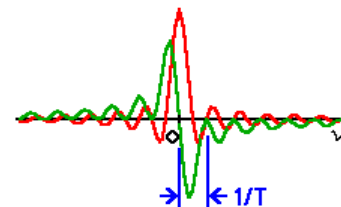
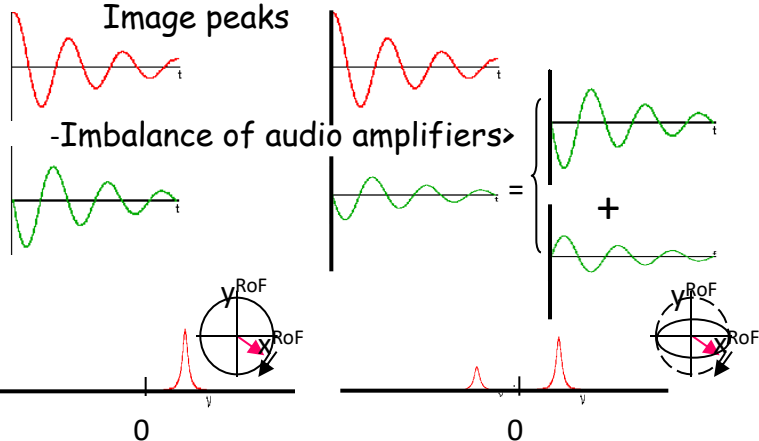


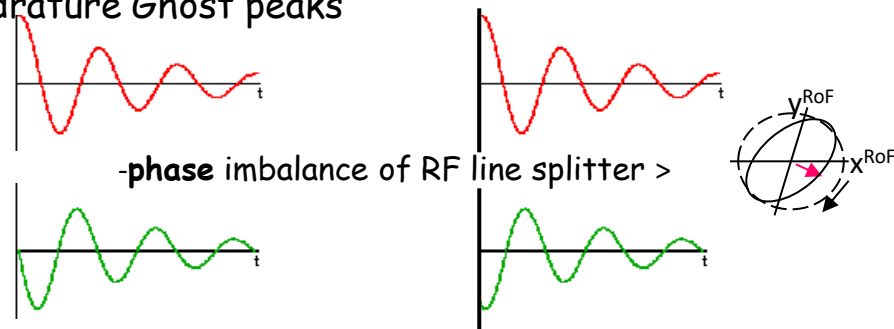
Image peaks

-Imbalance of audio amplifiers>

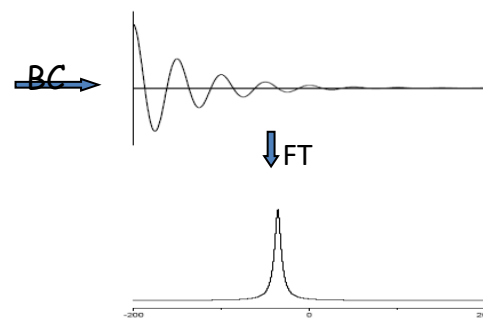
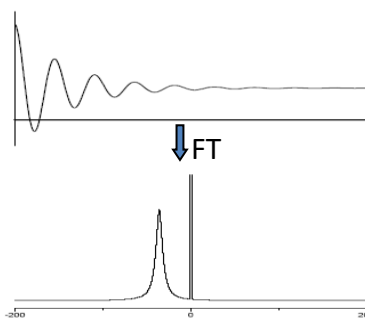


Quadrature Ghost peaks

-phase imbalance of RF line splitter >

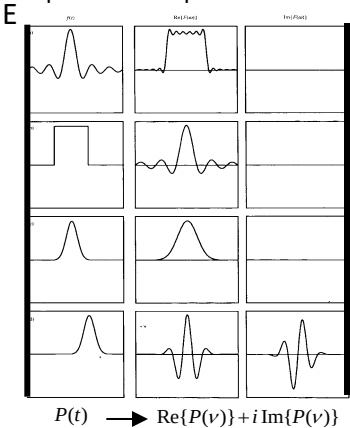


Baseline correction



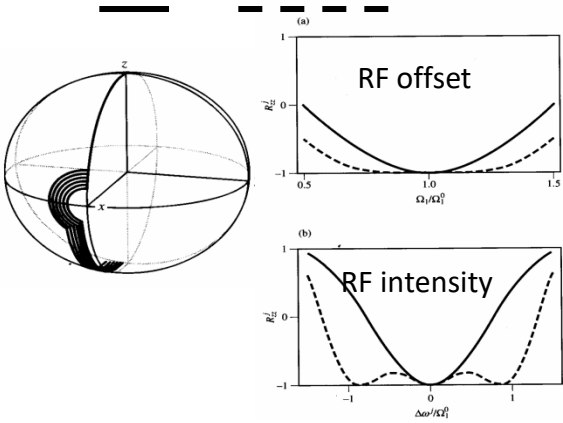
2-f. Off-resonance and RF-inhomogeneity effects on pulses

Excitation profiles do **not** follow the FT of the pulse, except when the pulses are weak (0^0 - 45^0).



Composite pulses
An example

$$180^0 \text{ vs. } 90_y^0 180_x^0 90_y^0$$



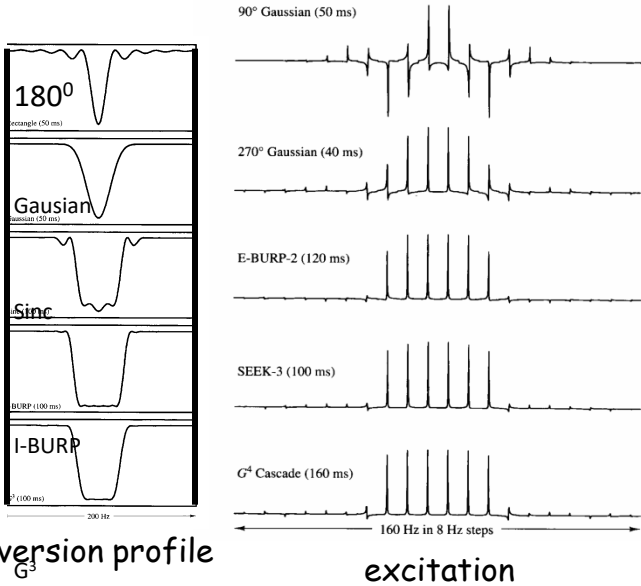
Other inversion and excitation pulses:

Examples:

$$P(t) = \omega_1 \sum_{n=1,N} A_n e^{-B_n(t-t_n^{max})^2}$$

BURP-n

$$P(t) = \omega_1 \sum_{n=0,N} A_n \cos(n\omega t) + B_n \sin(n\omega t)$$



For other composite pulses and selective pulses : see Encyclopedia NMR

Composite pulses: such as “inversion pulses”, “echo pulses”, “decoupling pulses”

More general echo-pulse sequences such as

$$Y - \{X - \bar{X}\}_n$$

$$Y - \{X - X - \bar{X} - \bar{X}\}_n$$

$$Y - \{X - Y - X - Y\}_n$$

$$Y - \{X - Y - X - Y - Y - X - Y - X\}_n$$

For example “ideal 360°” pulse for decoupling:

$$MLEV - 4 - - - MLEV - 16 \quad : RR\bar{R}\bar{R}, \quad RR\bar{R}\bar{R}\bar{R}\bar{R}\bar{R}\bar{R}$$

$$Shaka's \quad : 180_{180} 270_0 90_{180} 180_0 270_{180} 90_0$$

$$WALZ - 4 - - - WALZ - 64 \quad : 90_0 180_{180} 270_0 90_{180} 180_0 270_{180}$$

Other examples:

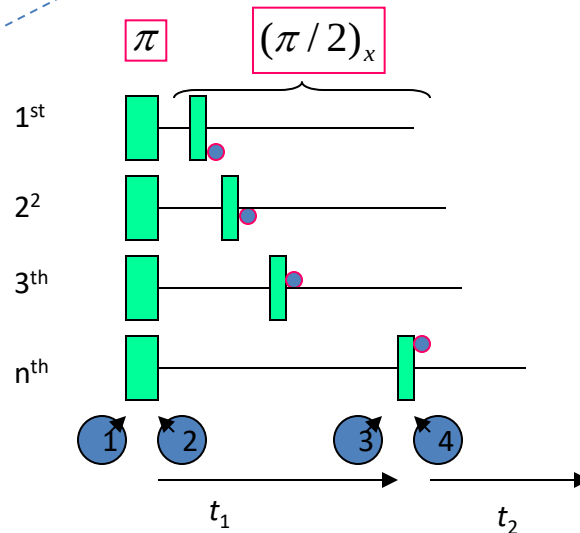
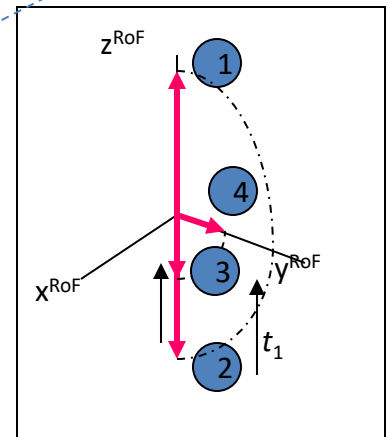
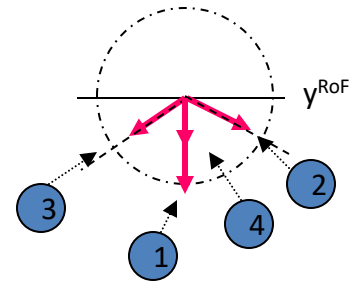
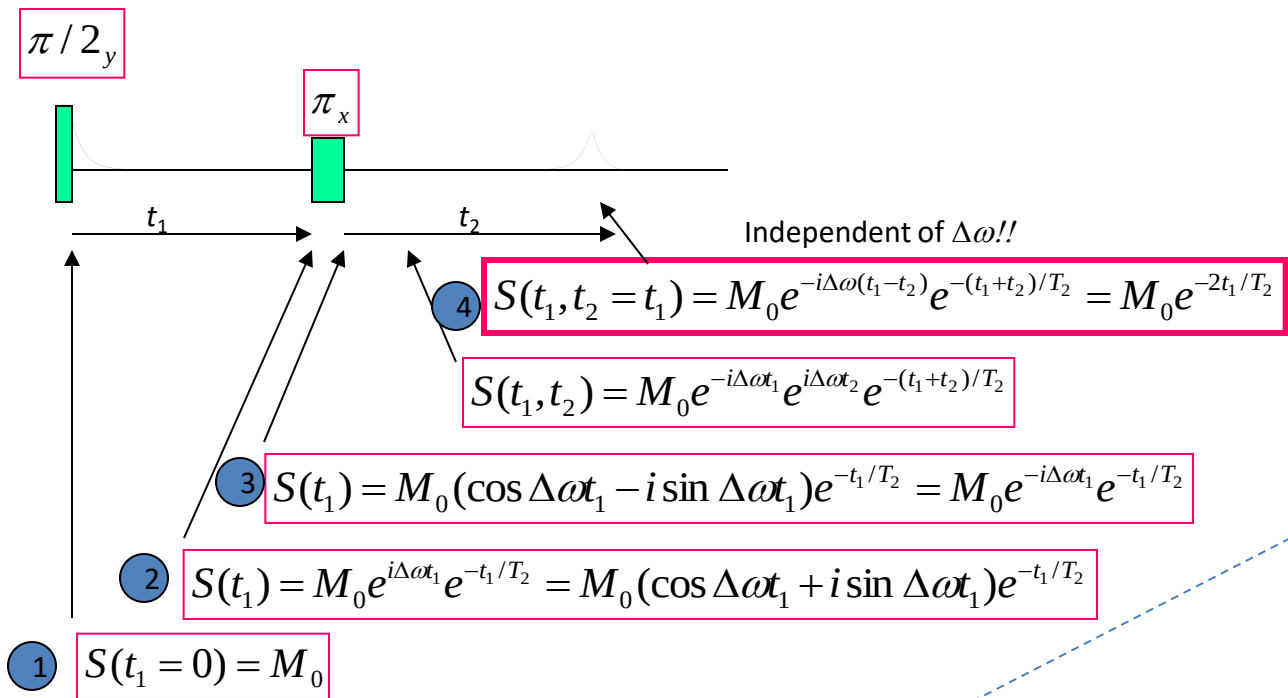
GARP - 1

DIPSI - 2

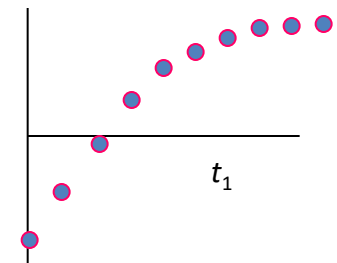
DIPSI - 3

See: nmr.ioc.ac.ru/val/shapes/c-w/c-w.htm

2-g. T_2 and T_1 : Hahn Echoes and Inversion recovery



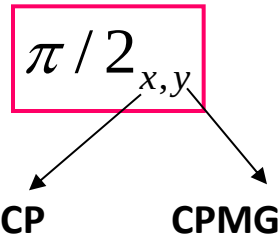
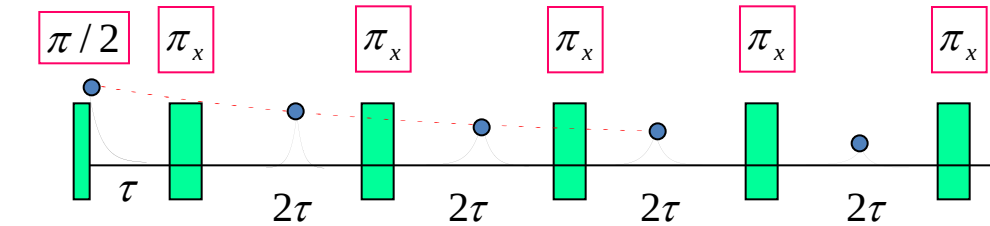
$$S(t_1) = M_0 (1 - 2 e^{-t_1/T_1})$$



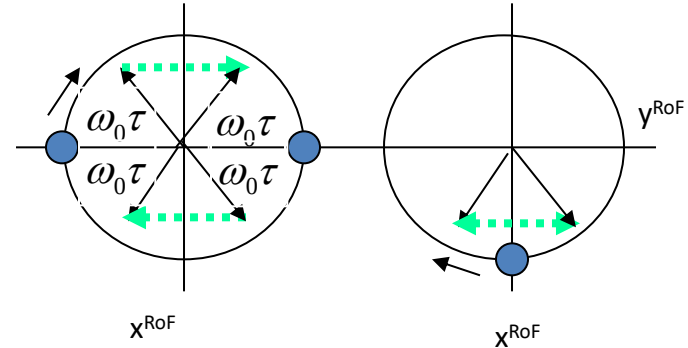
The Carr-Purcell-Meiboom-Gill pulse sequence



Edward Purcell
(1912-1997)



Sequences differ in the phase of the 1st-pulse



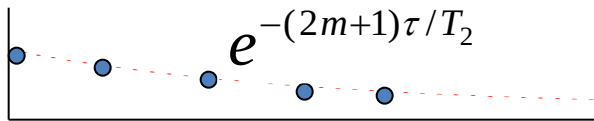
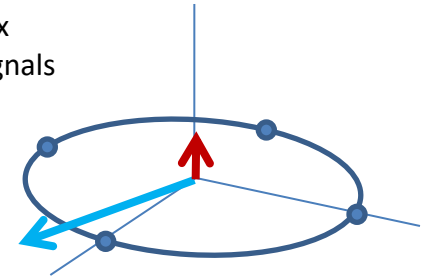
CP

Alternating y and -y
echo signals

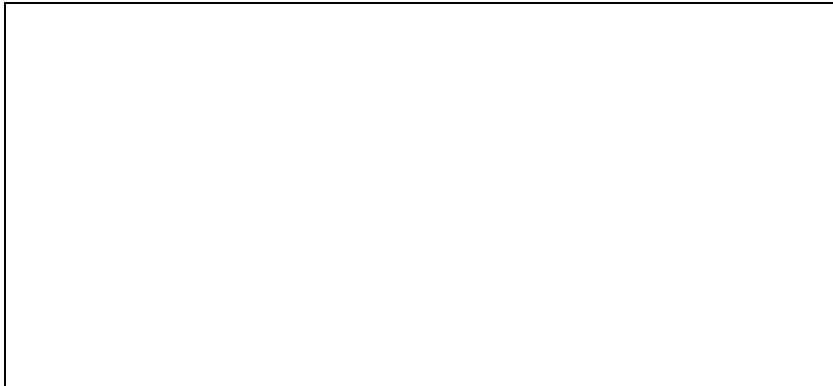
CPMG

Only x
Echo signals

● =echo positions



Explain the real essence of CPMG!



Who is Who?



[Wolfgang Pauli](#) 1900 - 1958
[Nobel Prize 1945 \(Physics\)](#)

[Isidor Isaac Rabi](#) 1898 - 1988
[Nobel Prize 1944 \(Physics\)](#)

[Felix Bloch](#) 1905 - 1983
[Nobel Prize 1955 \(Physics\)](#)

[Edward Purcell](#) 1912 - 1997
[Nobel Prize 1955 \(Physics\)](#)

[Richard Ernst](#) 1933- [Nobel Prize 1991 \(Chemistry\)](#)

[John B. Fenn](#) 1917-
[Nobel Prize 2002 \(Chemistry\)](#)

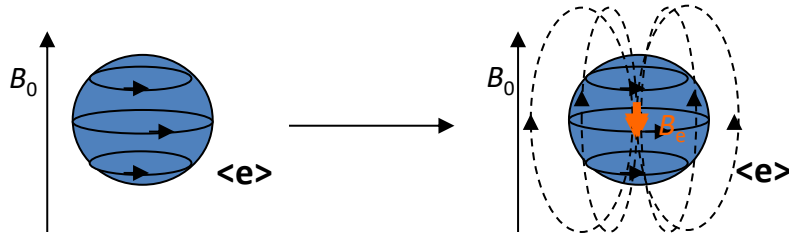
[Koichi Tanaka](#) 1959-
[Nobel Prize 2002 \(Chemistry\)](#)

[Kurt Wüthrich](#) 1938-
[Nobel Prize 2002 \(Chemistry\)](#)

3. NMR Interactions and basic pulse sequences

3-a Chemical shift

The external magnetic field generates an overall current in the s-orbital of the electrons proportional to this field and we get diamagnetic shift).

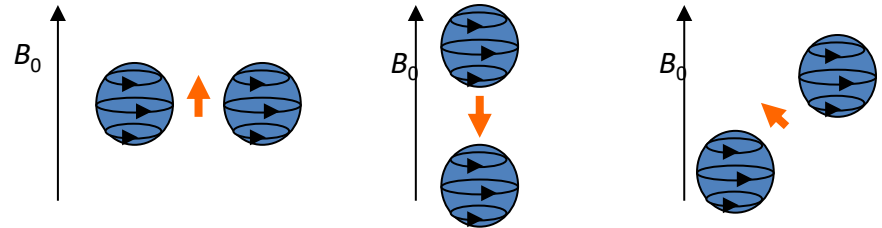


The chemical shift can be represented as a tensor in matrix form. Choosing a coordinate system with B_0 pointing in its z-direction:

$$\bar{B}_e = \begin{pmatrix} B_x^e \\ B_y^e \\ B_z^e \end{pmatrix} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix} \quad |\bar{B}_e| \ll B_0$$

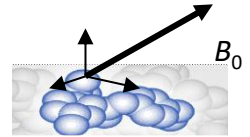
$$B_0 + \sigma_{zz} B_0 + \dots$$

Electrons in p-orbitals behave of course differently and create an orientational dependent field(paramagnetic shift)



Or: The chemical shift can be represented as a tensor in matrix form. Choosing the "Principle Axis System" coordinate system on the molecule, with the direction of the field defined by polar angles (φ, θ):

$$\bar{B}_e = \begin{pmatrix} B_x^e \\ B_y^e \\ B_z^e \end{pmatrix} = \begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix} \begin{pmatrix} B_0 \cos \varphi \sin \theta \\ B_0 \sin \varphi \sin \theta \\ B_0 \cos \theta \end{pmatrix}$$



Only the component in the direction of the main field is relevant:

$$\begin{pmatrix} \sigma_{xx} B_0 \cos \varphi \sin \theta \\ \sigma_{yy} B_0 \sin \varphi \sin \theta \\ \sigma_{zz} B_0 \cos \theta \end{pmatrix} \cdot \begin{pmatrix} \cos \varphi \sin \theta \\ \sin \varphi \sin \theta \\ \cos \theta \end{pmatrix} = B_0 (\sigma_{xx} \cos^2 \varphi \sin^2 \theta + \sigma_{yy} \sin^2 \varphi \sin^2 \theta + \sigma_{zz} \cos^2 \theta)$$

Chemical Shift Anisotropy

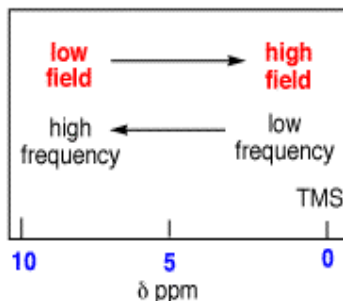
isotropic shift

asymmetry parameter

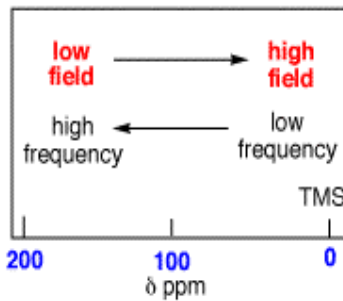
$$\Delta\sigma_{PP} = \sigma_{PP} - \sigma_{iso} \quad \sigma_{iso} = \frac{\sigma_{xx} + \sigma_{yy} + \sigma_{zz}}{3} \quad \eta = \frac{\Delta\sigma_{xx} - \Delta\sigma_{yy}}{\Delta\sigma_{zz}}$$

$$B_e = B_0 \sigma_{iso} + B_0 \Delta\sigma_{zz} \left\{ \frac{(3\cos^2 \theta - 1)}{2} + \eta \frac{1}{2} \sin^2 \theta \cos 2\varphi \right\}$$

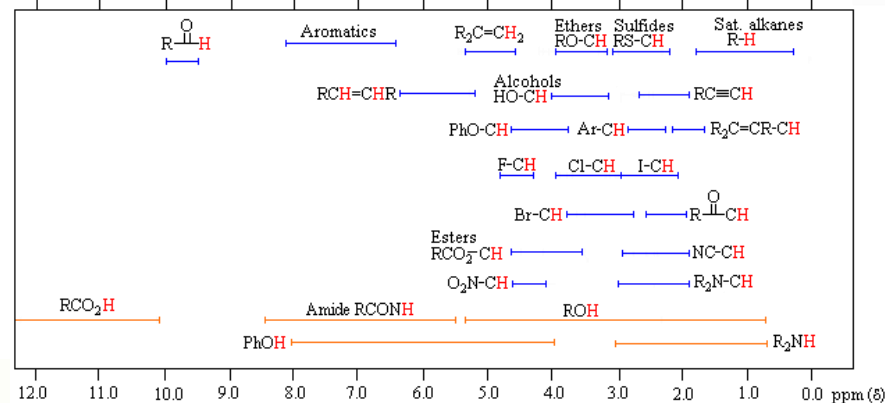
¹H NMR Chart Paper



¹³C NMR Chart Paper



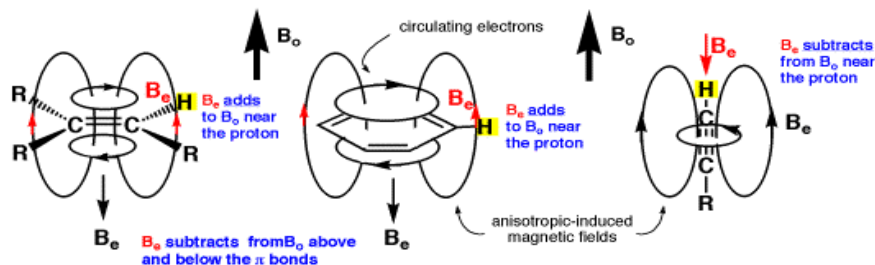
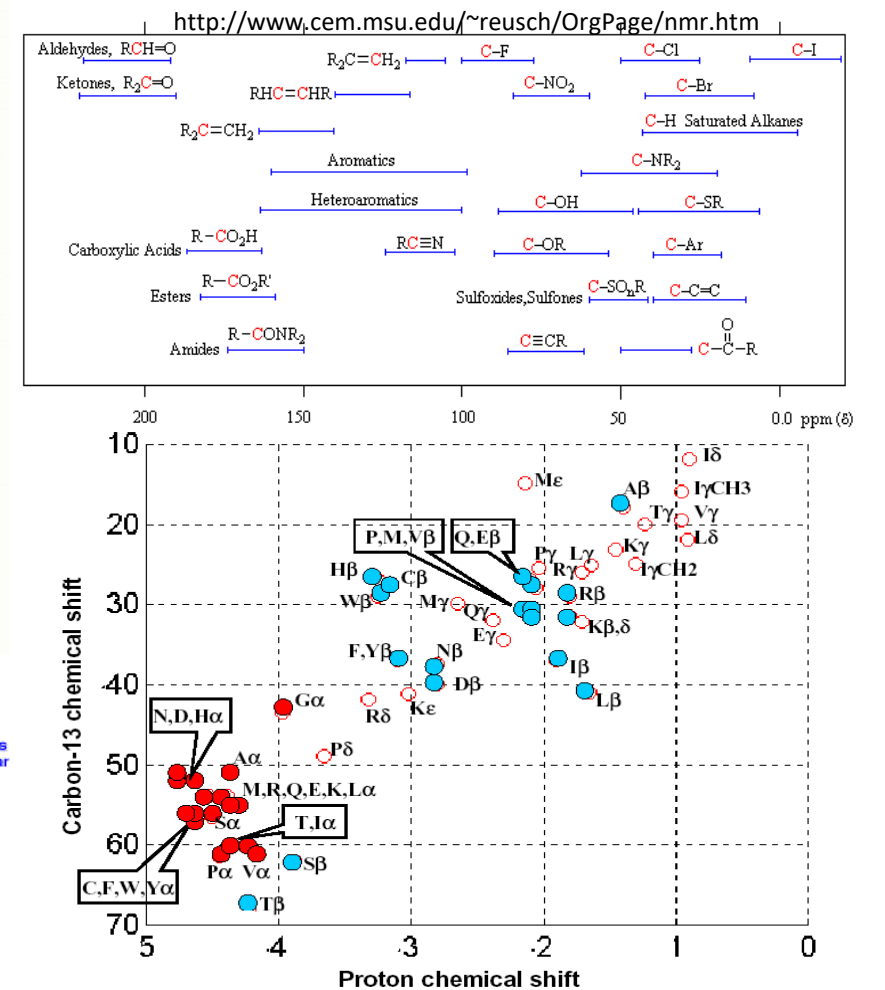
$$\delta(\text{ppm}) = \frac{V_{\text{spin}} - V_{\text{TMS}}}{V_{\text{TMS}}}$$



¹⁵N Chemical Shifts in Organic Compounds* Bruker Almanac



* Relative to external liquid ammonia at 25°C. Data taken from: G. C. Levy and R. L. Lichter: "Nitrogen-15 Nuclear Magnetic Resonance"



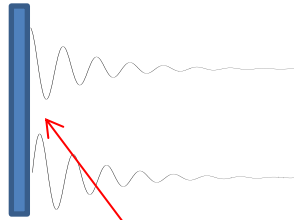
$$\sigma(eq) = A(I_{zi} + I_{zj})$$

$$H_{RoF} = \delta_i I_{zi} + \delta_j I_{zj}$$

$$\delta \equiv \text{sec}^{-1}$$

i

j



$$\sigma(0) = A(I_{xi} + I_{xj})$$

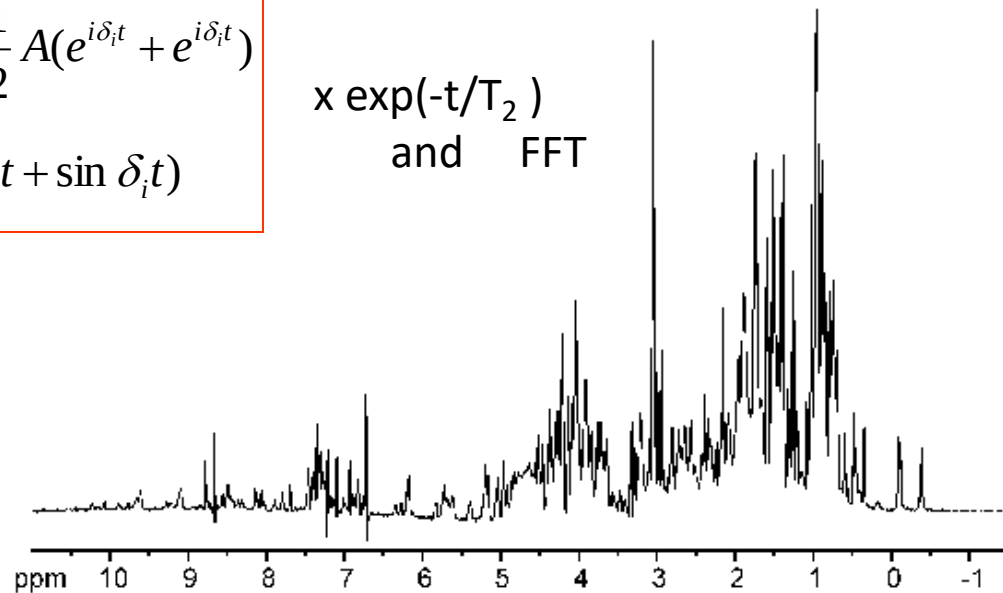
$$\begin{aligned} \sigma(t) &= A(I_{xi} \cos \delta_i t + I_{yi} \sin \delta_i t + I_{xj} \cos \delta_j t + I_{yj} \sin \delta_j t) \\ &= \frac{1}{2} A(I_i^+ e^{i\delta_i t} + I_i^- e^{-i\delta_i t} + I_j^+ e^{i\delta_j t} + I_j^- e^{-i\delta_j t}) \end{aligned}$$

$$\text{Tr}(\sigma(t) I_x) = S_x(t) = \frac{1}{2} A(\cos \delta_i t + \cos \delta_j t)$$

$$\text{Tr}(\rho(t) I^-) = S(t) = \frac{1}{2} A(e^{i\delta_i t} + e^{i\delta_j t})$$

$$\text{Tr}(\sigma(t) I_x) = S_y(t) = \frac{1}{2} A(\sin \delta_i t + \sin \delta_j t)$$

x exp(-t/T₂)
and FFT



$$\sigma_i(eq) = \frac{A}{2} \begin{pmatrix} 1 & \\ & -1 \end{pmatrix} \begin{pmatrix} |\alpha_i\rangle \\ |\beta_i\rangle \end{pmatrix}$$

$$\sigma_j(eq) = \frac{A}{2} \begin{pmatrix} 1 & \\ & -1 \end{pmatrix} \begin{pmatrix} |\alpha_j\rangle \\ |\beta_j\rangle \end{pmatrix}$$

The same in Matrix form

$$I_{zi} = \frac{1}{2} \begin{pmatrix} 1 & & & \\ & -1 & & \\ & & 1 & \\ & & & -1 \end{pmatrix} \begin{pmatrix} |\alpha_i\alpha_i\rangle \\ |\alpha_i\beta_j\rangle \\ |\beta_i\alpha_j\rangle \\ |\beta_i\beta_j\rangle \end{pmatrix}; I_{zj} = \frac{1}{2} \begin{pmatrix} 1 & & & \\ & 1 & & \\ & & -1 & \\ & & & -1 \end{pmatrix} \begin{pmatrix} |\alpha_i\alpha_i\rangle \\ |\alpha_i\beta_j\rangle \\ |\beta_i\alpha_j\rangle \\ |\beta_i\beta_j\rangle \end{pmatrix}$$

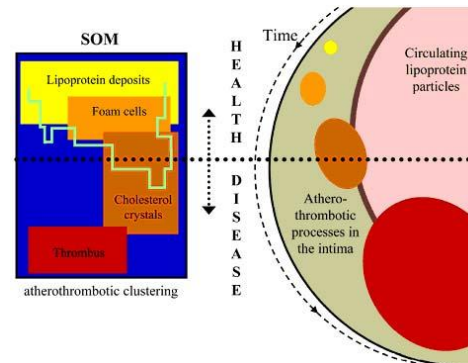
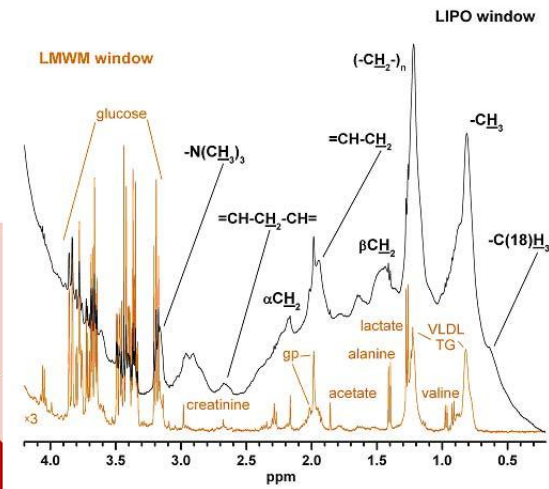
—————	4 = $\beta\beta$
=====	3 = $\alpha\beta$
=====	2 = $\beta\alpha$
—————	1 = $\alpha\alpha$

$$I_{xi} = \frac{1}{2} \begin{pmatrix} & 1 & & \\ 1 & & & \\ & & 1 & \\ & & & \end{pmatrix}; I_{xj} = \frac{1}{2} \begin{pmatrix} & 1 & & \\ & & 1 & \\ 1 & & & \\ & 1 & & \end{pmatrix}; I_{xi} + I_{xj} = \frac{1}{2} \begin{pmatrix} & 1 & 1 & \\ & & & 1 \\ 1 & & & \\ & 1 & 1 & \end{pmatrix}$$

$$I_{yi} = \frac{1}{2} \begin{pmatrix} & -i & & \\ i & & & \\ & & -i & \\ & & & i \end{pmatrix}; I_{xj} = \frac{1}{2} \begin{pmatrix} & -i & & \\ & & -i & \\ i & & & \\ & i & & \end{pmatrix}; I_{yi} + I_{yj} = \frac{1}{2} \begin{pmatrix} & -i & -i & \\ i & & & -i \\ & & -i & \\ & i & i & \end{pmatrix}$$

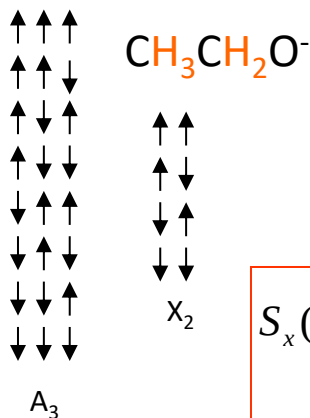
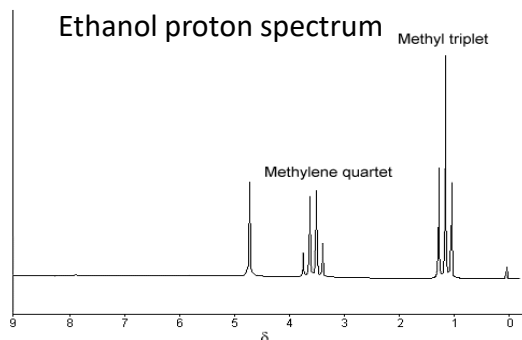
$$e^{-i\delta_i I_{zi}} I_{xi} e^{i\delta_i I_{zi}} = I_{xi} \cos \delta_i t + I_{yi} \sin \delta_i t$$

Characteristic ^1H NMR spectra for a T1DM patient



3-b The Spin-Spin interaction

The interaction of two spins mediated by their overlapping wavefunctions is the *Spin-Spin Interaction* or *j-coupling*.



To describe the interaction we will restrict ourselves here to the "secular" interaction only.

This excludes the interaction between two neighboring equivalent spins.

$$S_x(t) = \frac{1}{2} A(\cos \delta_i t + \cos \delta_i t) \cos jt$$

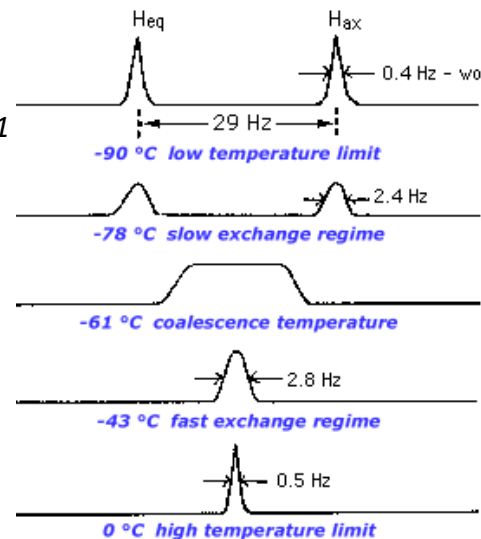
$$S(t) = \frac{1}{2} A(e^{i(\delta_i+j)t} + e^{i(\delta_i-j)t} + e^{i\delta_j+j)t} + e^{i(\delta_j-j)t})$$

$$S_y(t) = \frac{1}{2} A(\sin \delta_i t + \sin \delta_i t) \cos jt$$

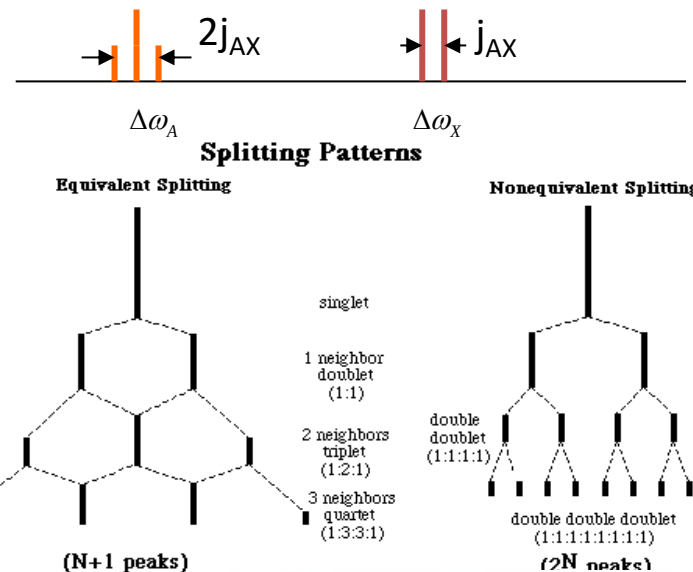
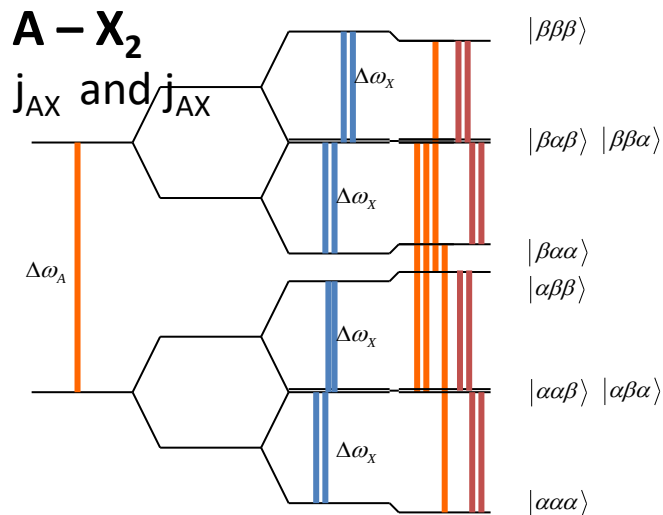
$$H_{\text{RoF}} = \delta_i I_{zi} + \delta_j I_{zj} + 2j I_{zi} I_{zj}$$

$$j \equiv \text{sec}^{-1}$$

cyclohexane- d_{11}



The extension to more coupled spins is straightforward:

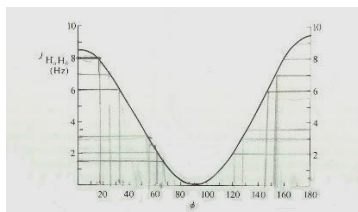
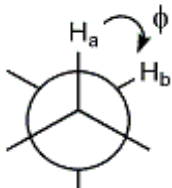


Karplus equation:

Dihedral Angle: ϕ

$0 < \phi < 90^\circ : {}^3J_{ab} = j_0 \cos 2\phi - 0.28$

$90 < \phi < 180^\circ : {}^3J_{ab} = j_{180} \cos 2\phi - 0.28$



Some characteristic values for J-couplings: One-Bond Coupling Constants	
Type	¹ J(Hz)
¹ H – ¹ H	280
¹³ C – ¹ H	110 – 260
³¹ P – ¹ H	20 – 700
¹³ C – ¹⁹ F	– 280 to – 350
¹³ C – ¹³ C	170
³¹ P – ³¹ P	100 – 500
³¹ P – ¹⁹ F	1000

Some representative one-bond coupling constants					
Homonuclear Examples			Heteronuclear Examples		
Structure	² J(Hz)	Structure	² J(Hz)	Structure	² J(Hz) ^a
H-C-H	- 12.4	H-C(CH ₃) ₃ -H	- 13	¹³ C-C- ¹ H	5
H-Si-H	+ 2.8	H-C(CH ₃) ₄ -H	- 10.5	¹⁹ F-C- ¹ H	45
H-Sn-H	+ 15.3	H-C(CH ₃) ₃ -H	- 9	¹⁹ F-C- ³¹ P	160
H-C(F)-H	- 9.6	H-C(CH ₃) ₂ -H	- 4.3	¹ H-C- ³¹ P	7 – 14
H-C(Cl)-H	- 10.8	CH ₂ =CH ₂	+ 2.5		

^a Absolute values.

$$\sigma_i(eq) = \frac{A}{2} \begin{pmatrix} 1 & \\ & -1 \end{pmatrix} \begin{pmatrix} |\alpha_i\rangle \\ |\beta_i\rangle \end{pmatrix}$$

$$\sigma_j(eq) = \frac{A}{2} \begin{pmatrix} 1 & \\ & -1 \end{pmatrix} \begin{pmatrix} |\alpha_j\rangle \\ |\beta_j\rangle \end{pmatrix}$$

$$2I_{zi}I_{zj} = \frac{1}{2} \begin{pmatrix} 1 & & & \\ & -1 & & \\ & & -1 & \\ & & & 1 \end{pmatrix}$$

—————	$4 = \beta\beta$
=====	$3 = \alpha\beta$
=====	$2 = \beta\alpha$
—————	$1 = \alpha\alpha$

$$I_{zi} = \frac{1}{2} \begin{pmatrix} 1 & & & \\ & -1 & & \\ & & 1 & \\ & & & -1 \end{pmatrix} \begin{pmatrix} |\alpha_i\alpha_i\rangle \\ |\alpha_i\beta_j\rangle \\ |\beta_i\alpha_j\rangle \\ |\beta_i\beta_j\rangle \end{pmatrix}; I_{zj} = \frac{1}{2} \begin{pmatrix} 1 & & & \\ & 1 & & \\ & & -1 & \\ & & & -1 \end{pmatrix} \begin{pmatrix} |\alpha_i\alpha_i\rangle \\ |\alpha_i\beta_j\rangle \\ |\beta_i\alpha_j\rangle \\ |\beta_i\beta_j\rangle \end{pmatrix}$$

$$I_{xi} = \frac{1}{2} \begin{pmatrix} & 1 & & \\ 1 & & & \\ & & & 1 \\ & & 1 & \end{pmatrix}; I_{xj} = \frac{1}{2} \begin{pmatrix} & 1 & & \\ & & 1 & \\ & & & \\ 1 & & & \end{pmatrix}; I_{xi} + I_{xj} = \frac{1}{2} \begin{pmatrix} 1 & 1 & & \\ & & 1 & \\ & & & 1 \\ 1 & 1 & & \end{pmatrix}$$

$$I_{yi} = \frac{1}{2} \begin{pmatrix} & -i & & \\ i & & & \\ & & & -i \\ & & i & \end{pmatrix}; I_{xj} = \frac{1}{2} \begin{pmatrix} & -i & & \\ & & -i & \\ & & & \\ i & & & \end{pmatrix}; I_{yi} + I_{yj} = \frac{1}{2} \begin{pmatrix} -i & -i & & \\ & & -i & \\ & & & -i \\ i & & & \end{pmatrix}$$

$$2I_{xi}I_{zj} = \frac{1}{2} \begin{pmatrix} & 1 & & \\ 1 & & & \\ & & & -1 \\ & & -1 & \end{pmatrix}; 2I_{zi}I_{xj} = \frac{1}{2} \begin{pmatrix} & 1 & & \\ & & & -1 \\ & & 1 & \\ 1 & & & -1 \end{pmatrix}$$

$$2I_{xi}I_{zj} = \frac{1}{2} \begin{pmatrix} & -i & & \\ i & & & \\ & & & i \\ & & -i & \end{pmatrix}; 2I_{zi}I_{xj} = \frac{1}{2} \begin{pmatrix} & -i & & \\ & & & i \\ & & i & \\ & & & -i \end{pmatrix}$$

$$e^{-i\delta_i I_{zi} t} I_{xi} e^{i\delta_i I_{zi} t} = I_{xi} \cos \delta_i t + I_{yi} \sin \delta_i t$$

$$e^{-i2j I_{zi} I_{zj} t} I_{xi} e^{i2j I_{zi} I_{zj} t} = I_{xi} \cos jt + 2I_{yi} I_{zj} \sin jt$$

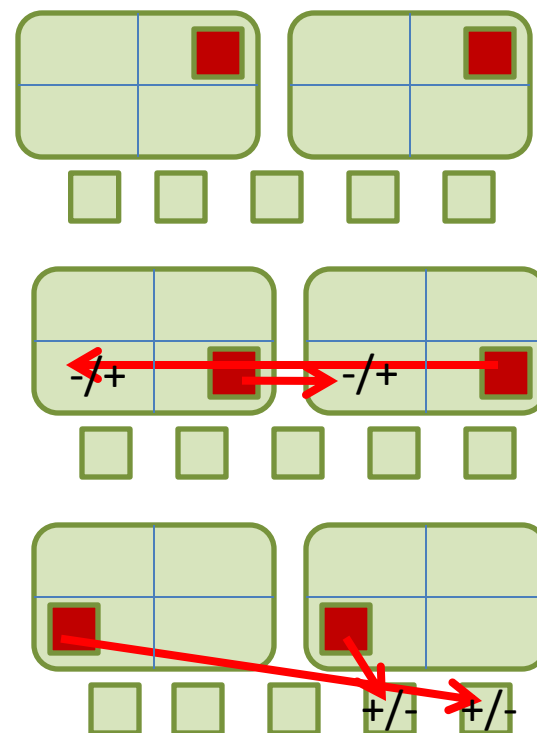
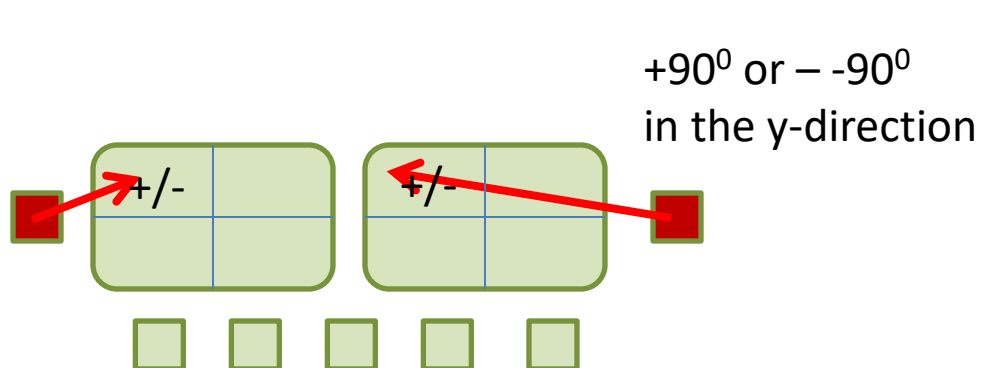
$$e^{-i\delta_i I_{zi} t} I_{yi} e^{-i\delta_i I_{zi} t} = I_{yi} \cos \delta_i t - I_{xi} \sin \delta_i t$$

$$e^{ij2 I_{zi} I_{zj} t} I_{yi} e^{ij2 I_{zi} I_{zj} t} = I_{yi} \cos jt - 2I_{xi} I_{zj} \sin jt$$

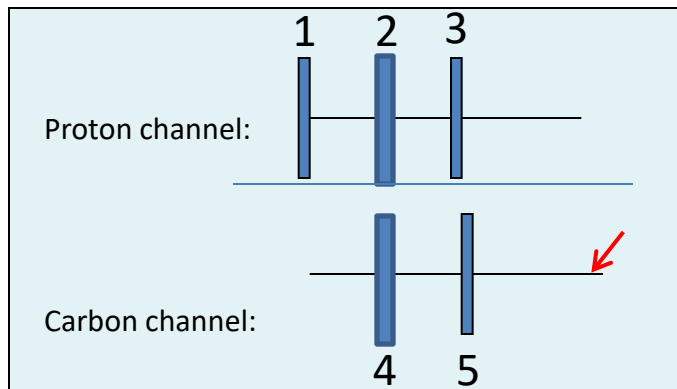
3.c AX spin system

$$\begin{array}{|c|} \hline I_z^A \\ \hline \end{array}
 \begin{array}{c}
 I_x^A \Leftrightarrow I_y^A \\
 \Updownarrow \qquad \qquad \Updownarrow \\
 2I_y^A I_z^X \Leftrightarrow 2I_x^A I_z^X
 \end{array}
 \begin{array}{c}
 I_x^X \Leftrightarrow I_y^X \\
 \Updownarrow \qquad \qquad \Updownarrow \\
 2I_z^A I_y^X \Leftrightarrow 2I_z^A I_x^X
 \end{array}
 \begin{array}{|c|} \hline I_z^X \\ \hline \end{array}$$

$$I_z^A I_z^X \quad I_x^A I_x^X \quad I_y^A I_y^X \quad I_x^A I_y^X \quad I_y^A I_x^X$$



INEPT

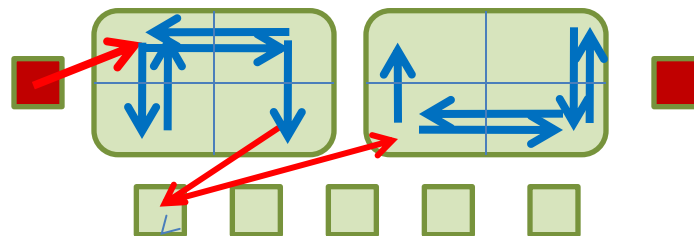
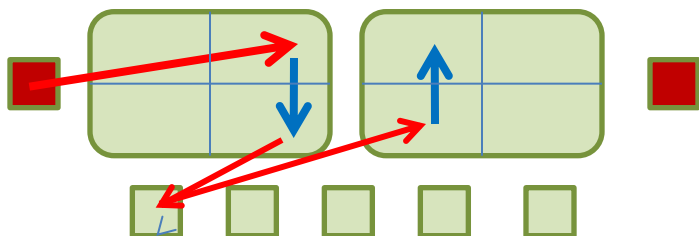


INEPT ($\delta = 0$, without (2,4))

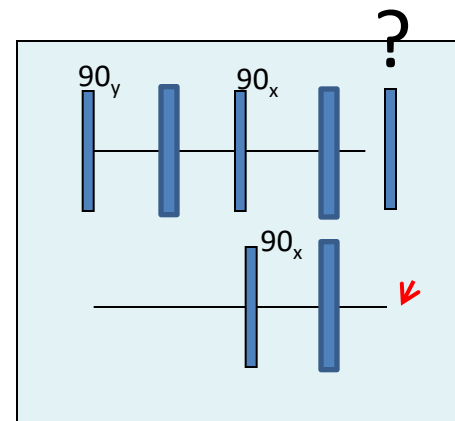
$$I_z^A \rightarrow I_y^X$$

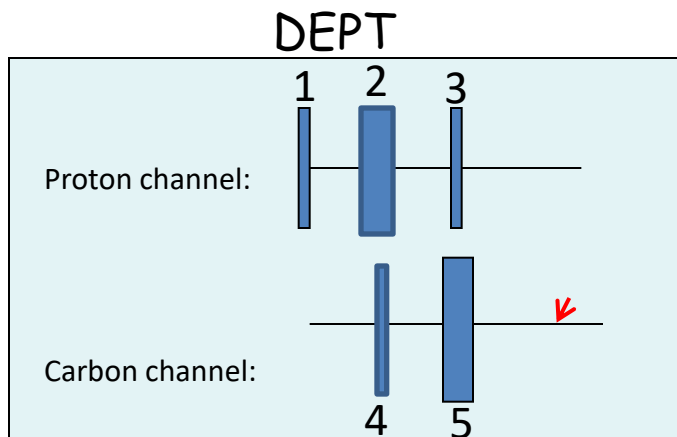
1: $x-x-x-x-x-x-x-x-\bar{x}-\bar{x}-\bar{x}-\bar{x}-\bar{x}-\bar{x}-\bar{x}-\bar{x}$
 2: $x-\bar{x}-x-\bar{x}-x-\bar{x}-x-\bar{x}-x-\bar{x}-x-\bar{x}-x-\bar{x}$
 3: $y-y-\bar{y}-\bar{y}-y-y-\bar{y}-\bar{y}-y-y-\bar{y}-\bar{y}-y-y-\bar{y}-\bar{y}$
 4: $x-\bar{x}-x-\bar{x}-x-\bar{x}-x-\bar{x}-x-\bar{x}-x-\bar{x}-x-\bar{x}$
 5: $x-x-x-x-y-y-y-y-\bar{x}-\bar{x}-\bar{x}-\bar{x}-\bar{y}-\bar{y}-\bar{y}-\bar{y}$
 D: $x-x-\bar{x}-\bar{x}-y-y-\bar{y}-\bar{y}-x-x-\bar{x}-\bar{x}-y-y-\bar{y}-\bar{y}$

INEPT ($\delta \neq 0$)



$$I_z^A \xrightarrow{1_{xA}} -I_y^A \xrightarrow{jt=\frac{\pi}{2}} I_x^A I_z^X \xrightarrow{3_{yA}} -I_z^A I_z^X \xrightarrow{5_{xX}} -I_y^A I_z^X \xrightarrow{jt=\frac{\pi}{2}} I_x^X$$

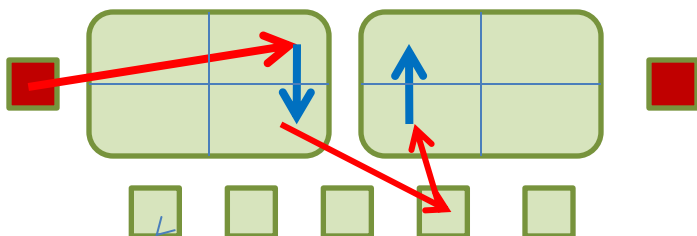




$$I_x^A \rightarrow I_x^X$$

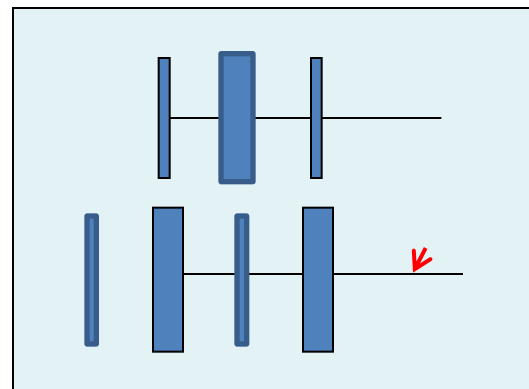
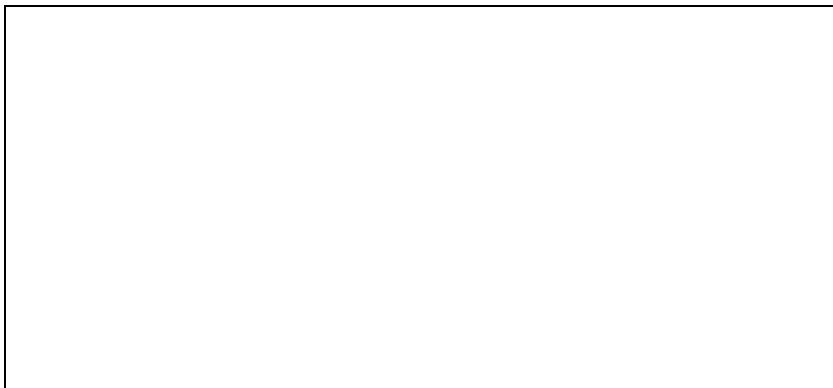
1: $x-x-x-x-x-x-x-x-x-x-x-x-x-x-x-x$
 2: $x-\bar{x}-y-\bar{y}-x-\bar{x}-y-\bar{y}-x-\bar{x}-y-\bar{y}-x-\bar{x}-y-\bar{y}$
 3: $y-y-y-y-\bar{y}-\bar{y}-\bar{y}-\bar{y}-y-y-y-y-\bar{y}-\bar{y}-\bar{y}-\bar{y}$
 4: $x-x-x-x-x-x-x-x-x-y-y-y-y-y-y-y-y-y$
 5: $x-\bar{x}-x-\bar{x}-x-\bar{x}-x-\bar{x}-y-\bar{y}-y-\bar{y}-y-\bar{y}-y-\bar{y}$
 D: $y-y-\bar{y}-\bar{y}-\bar{y}-\bar{y}-y-y-\bar{x}-\bar{x}-x-x-x-x-\bar{x}-\bar{x}$

INEPT ($\delta_{i,j} = 0$)



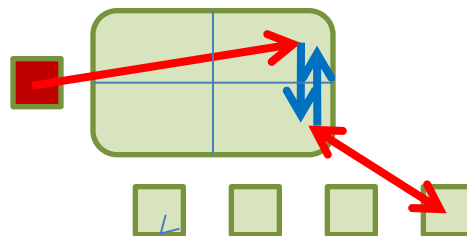
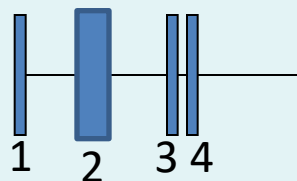
DEPT removes distortions occurring in INEPT due to varying j -couplings

$$I_z^A \xrightarrow{90_{xA}} -I_y^A \xrightarrow{j} 2I_x^A I_z^B \xrightarrow{90_{xX}} -2I_x^A I_y^B \xrightarrow{j} -2I_x^A I_y^B \xrightarrow{90_{yA}} 2I_z^A I_y^X \xrightarrow{j} I_x^X$$



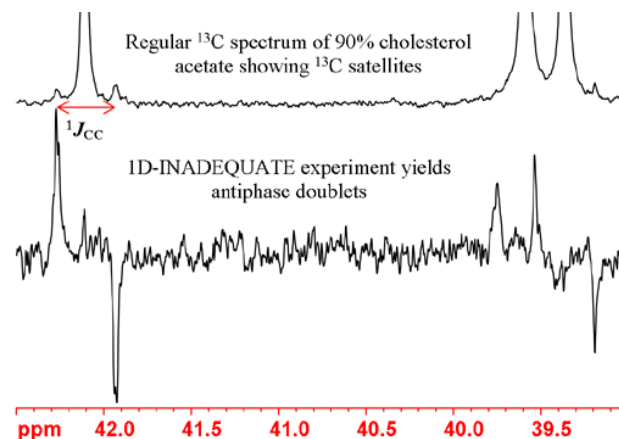
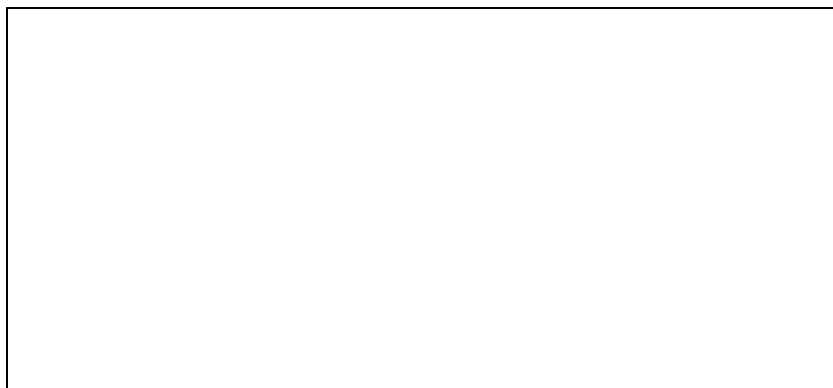
INADEQUATE

Carbon channel:

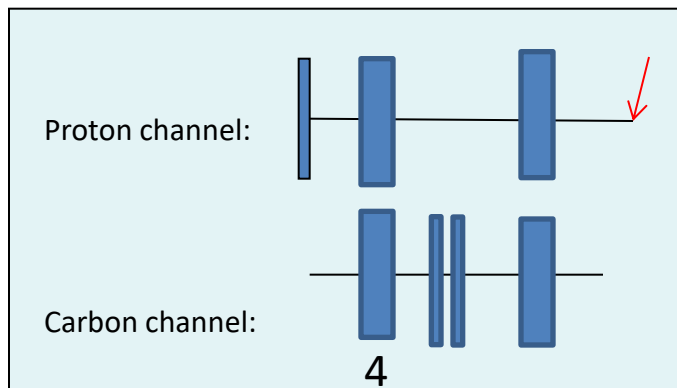


1: $x - x - x - x$
 2: $x - x - x - x$
 3: $x - x - x - x$
 4: $x - \bar{x} - y - \bar{x}$
 D: $x - y - \bar{x} - \bar{y}$

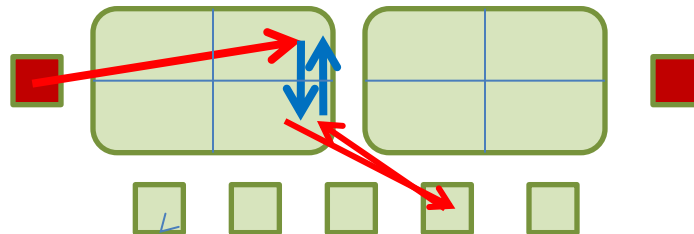
$$\begin{array}{llll}
 I_z^A \xrightarrow{90_x} -I_y^A \xrightarrow{j} 2I_x^A I_z^A \xrightarrow{90_x} -2I_x^A I_y^A \xrightarrow{90_x} -2I_x^A I_z^A \xrightarrow{j} -I_y^A & D: y & + & \\
 I_z^A \xrightarrow{90_x} -I_y^A \xrightarrow{j} 2I_x^A I_z^A \xrightarrow{90_x} -2I_x^A I_y^A \xrightarrow{90_y} 2I_z^A I_y^A \xrightarrow{j} -I_x^A & D: \bar{x} & + & \\
 I_z^A \xrightarrow{90_x} -I_y^A \xrightarrow{j} -I_y^A \xrightarrow{90_x} -I_z^A \xrightarrow{90_x} I_y^A & D: y & - & \\
 I_z^A \xrightarrow{90_x} -I_y^A \xrightarrow{j} -I_y^A \xrightarrow{90_x} -I_z^A \xrightarrow{90_y} -I_x^A & D: \bar{x} & + & 0
 \end{array}$$



Double Quantum Filter



$$(\delta_i = 0)$$



$$\begin{array}{l}
 I_z^A \xrightarrow{90_{xA}} -I_y^A \xrightarrow{j} 2I_x^A I_z^B \xrightarrow{90_{xx}} -2I_x^A I_y^B \xrightarrow{90_{xx}} -2I_x^A I_z^X \xrightarrow{j} -I_y^A \quad D: \bar{y} \quad + \\
 I_z^A \xrightarrow{90_{xA}} -I_y^A \xrightarrow{j} 2I_x^A I_z^B \xrightarrow{90_{xx}} 2I_x^A I_y^B \xrightarrow{90_{xx}} 2I_x^A I_z^X \xrightarrow{j} I_y^A \quad D: y \quad + \\
 I_z^A \xrightarrow{90_{xA}} -I_y^A \xrightarrow{j} -I_y^A \xrightarrow{90_{xx}} -I_y^A \xrightarrow{90_{xx}} -I_y^A \xrightarrow{j} -I_y^A \quad D: \bar{y} \quad - \\
 I_z^A \xrightarrow{90_{xA}} -I_y^A \xrightarrow{j} -I_y^A \xrightarrow{90_{xx}} -I_z^A \xrightarrow{90_{xx}} -I_y^A \xrightarrow{j} -I_y^A \quad D: y \quad +
 \end{array}
 \left. \begin{array}{l} + \\ + \\ - \\ + \end{array} \right\} 0$$

3-d Heteronuclear Spin Decoupling

Some decoupling schemes for suppression of off-resonance effects and B_1 inhomogeneities:

Try to apply ideal 360° pulses, moving the I_z operator through a pathway that averages to zero:

Examples are:

360°

Waugh's

Shaka's

Levitt's

$360^\circ)_0 \ 360^\circ)_{180}$

$270^\circ)_0 \ 270^\circ)_{180}$

$180^\circ)_{180} \ 180^\circ)_0 \ 180^\circ)_{180} \ 180^\circ)_0$

Levitt's: use R as composite 180° and construct

MLEV-4 $RR\bar{R}\bar{R}$

MLEV-8 $RR\bar{R}\bar{R}\bar{R}\bar{R}\bar{R}\bar{R}\bar{R}$ with

$R = 90_0 240_{90} 90_0$

$R = 90_0 180_0 90_0$

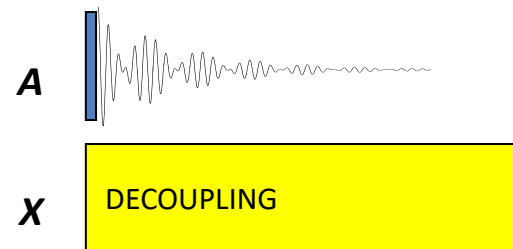
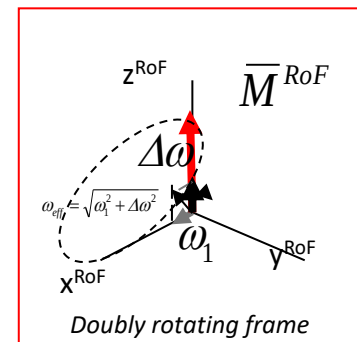
"GARP-1 ; DIPSI-2; -3"

WALTZ $90_0 180_{180} 270_0 90_{180} 180_x 270_{180} = 1\bar{2}3 \ 123 \ 12\bar{3} \ 1\bar{2}3$

$$R \rightarrow P_{90} R P_{90}^{-1} \rightarrow P_{180} P_{90} R P_{90}^{-1} P_{180}^{-1}$$

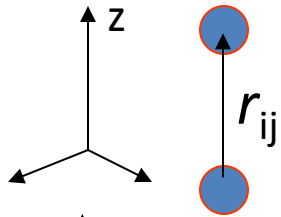
$$\rightarrow P_{90} R_z P_{90}^{-1} P_{180} P_{90} R P_{90}^{-1} P_{180}^{-1}$$

$$\rightarrow R = 270_0 270_{180} \xrightarrow{\text{Shakds}} 180_{180} 270_0 90_{180} 180_0 270_{180} 90_0$$

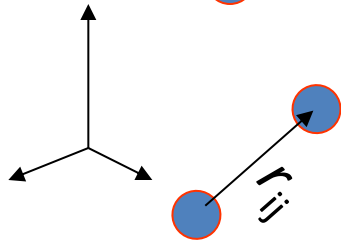


3-e The dipole-dipole interaction

This very important interaction is average to zero in liquids, but is the source of many relaxation mechanisms.



$$H_D^{PAS} = \frac{\mu_0 \gamma_i \gamma_j}{4\pi (r_{ij})^3} (3(\bar{I}_i \cdot \bar{e}_{ij})(\bar{I}_j \cdot \bar{e}_{ij}) - \bar{I}_i \cdot \bar{I}_j) = \frac{\mu_0 \gamma_i \gamma_j}{4\pi (r_{ij})^3} (3I_{zi} I_{zj} - \bar{I}_i \cdot \bar{I}_j)$$

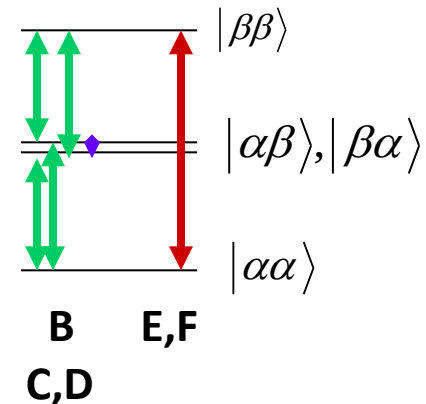


$$H_D = A + B + C + D + E + F$$

$$\overline{(3\cos^2 \beta - 1)} = 0$$

$$H_{LAB} = \omega_{0i} I_{zi} + \omega_{0j} I_{zj} + \frac{\mu_0 \gamma_i \gamma_j}{4\pi r_{ij}^3} \cdot \frac{1}{2} (3\cos^2 \beta - 1) (3I_{zi} I_{zj} - \bar{I}_i \cdot \bar{I}_j)$$

$$H_D = \begin{pmatrix} A_0 & C_{-1} & C_{-1} & E \\ D_{+1} & -A_0 & B & C_{-1} \\ D_{+1} & B & -A_0 & C_{-1} \\ F_{+2} & D_{+1} & D_{+1} & A_0 \end{pmatrix}$$



$$(A+B: A_0^2 T_0^2 = D_0^2(\alpha, \beta, \gamma) [A_0^{PAS}] T_0^2)$$

$$C = D_{01}^2(\alpha, \beta, \gamma) [A_0^{PAS}] T_{-1}^2$$

$$D = D_{0-1}^2(\alpha, \beta, \gamma) [A_0^{PAS}] T_1^2$$

$$E = D_{02}^2(\alpha, \beta, \gamma) [A_0^{PAS}] T_{-2}^2$$

$$F = D_{0-2}^2(\alpha, \beta, \gamma) [A_0^{PAS}] T_2^2$$

$$T_0^2 = \frac{1}{2}(3I_{zi}I_{zj} - \bar{I}_i \cdot \bar{I}_j)$$

$$T_{\pm 1}^2 = \frac{\mp 1}{2}(I_{zi}[I_{xj} \pm iI_{yj}] + [I_{xi} \pm iI_{yi}]I_{zj})$$

$$T_{\pm 2}^2 = \frac{1}{2}(I_{xi} \pm I_{yi})(I_{xj} \pm I_{yj})$$

$$D_{mm'}^\ell = e^{-im\alpha} d_m^\ell(\beta) e^{-im'\gamma}$$

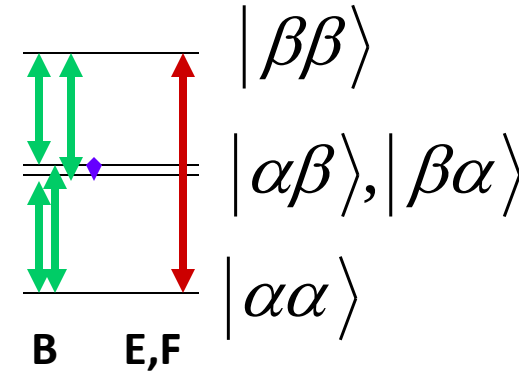
$$d_{m,n}^{(2)}(\beta)$$

$\begin{smallmatrix} n \\ m \end{smallmatrix}$	2	1	0	-1	-2
2	$\cos^4(\beta/2)$	$-\frac{1}{2}(1+\cos\beta)\sin\beta$	$\sqrt{3/8}\sin^2\beta$	$\frac{1}{2}(\cos\beta-1)\sin\beta$	$\sin^4(\beta/2)$
1	$\frac{1}{2}\sin\beta(\cos\beta+1)$	$\cos^2\beta-\frac{1}{2}(1-\cos\beta)$	$-\sqrt{3/2}\sin\beta\cos\beta$	$\frac{1}{2}(1+\cos\beta)-\cos^2\beta$	$\frac{1}{2}\sin\beta(\cos\beta-1)$
0	$\sqrt{3/8}\sin^2\beta$	$\sqrt{3/8}\sin(2\beta)$	$\frac{1}{2}(3\cos^2\beta-1)$	$-\sqrt{3/8}\sin(2\beta)$	$\sqrt{3/8}\sin^2\beta$
-1	$-\frac{1}{2}(\cos\beta-1)\sin\beta$	$\frac{1}{2}(1+\cos\beta)-\cos^2\beta$	$\sqrt{3/2}\sin\beta\cos\beta$	$\cos^2\beta-\frac{1}{2}(1-\cos\beta)$	$-\frac{1}{2}(1+\cos\beta)\sin\beta$
-2	$\sin^4(\beta/2)$	$-\frac{1}{2}(\cos\beta-1)\sin\beta$	$\sqrt{3/8}\sin^2\beta$	$\frac{1}{2}(1+\cos\beta)\sin\beta$	$\cos^4(\beta/2)$

3-g Some simple principles of Nuclear Relaxation

See earlier, for the difference between T_1 and T_2

Suppose the source of relaxation is the nuclear dipole-dipole interaction



$$H_D = \begin{pmatrix} A_0 & C_{-1} & C_{-1} & E \\ D_{+1} & -A_0 & B & C_{-1} \\ D_{+1} & B & -A_0 & C_{-1} \\ F_{+2} & D_{+1} & D_{+1} & A_0 \end{pmatrix}$$

$$C,D \quad (A_m \equiv (A+B)_0, C_{-1}, D_{+1}, E_{-2}, F_{+2})(t) = A_0^{PAS} D_{m,0}(\Omega(t))$$

Assume:

$$G_m(\tau) = \overline{A_m(t+\tau)A_m(t)} \approx (A_0^{PAS})^2 e^{-\tau/\tau_c}$$

$$\frac{1}{T_2} = (A_0^{PAS})^2 [J(0) + J(\omega_0) + J(2\omega_0)]$$

$$\frac{1}{T_1} = (A_0^{PAS})^2 [J(\omega_0) + J(2\omega_0)]$$

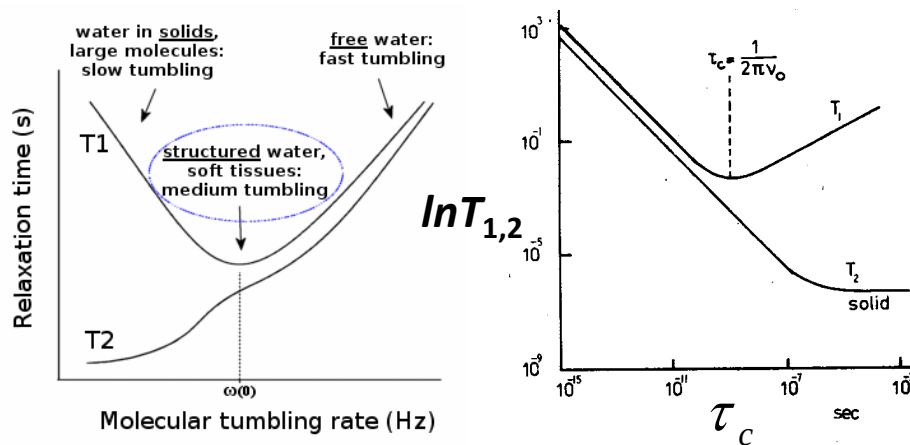
$$J(\omega) = (A_0^{PAS})^2 \int_0^\infty e^{-\tau/\tau_c} e^{-i\omega\tau} d\tau$$

$$\frac{1}{T_2} = \frac{C}{2} \left\{ 3\tau_c + \frac{5\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{2\tau_c}{1 + (2\omega_0)^2 \tau_c} \right\}$$

$$\frac{1}{T_1} = \frac{C}{2} \left\{ \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + (2\omega_0)^2 \tau_c} \right\}$$

$$C = \frac{3\mu_0^2}{160\pi^2} \frac{\gamma^4}{r^6}$$

For H_2O $\tau_c \sim 10^{-12}$ and $\omega_0 \sim 100\text{MHz}$ $T_1 = T_2 \sim 3\text{ s}$

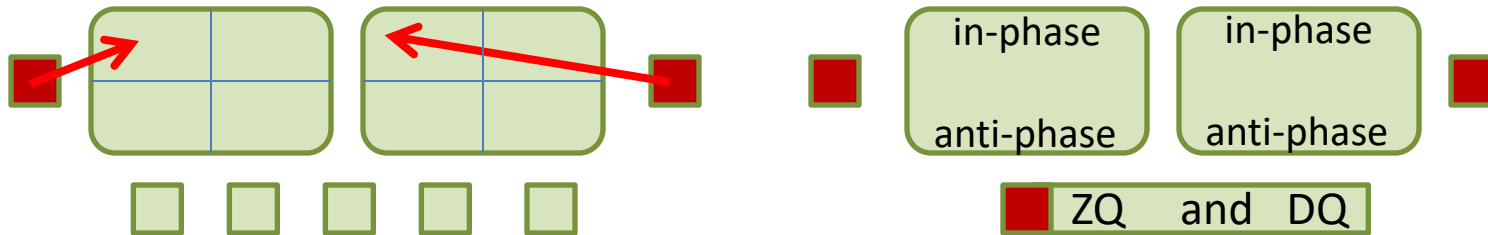


Proton T_1 values of tissues and proteins!

4. Two Dimensional NMR Spectroscopy

A

X



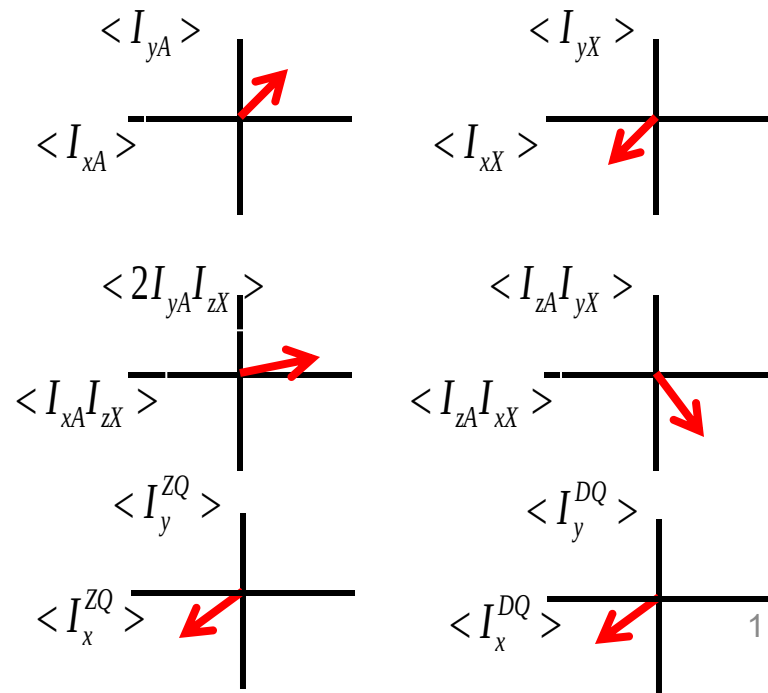
$$S_A(t) = \text{Tr}(\sigma(t)I_A^-)$$

$$S_X(t) = \text{Tr}(\sigma(t)I_X^-)$$

$$I_x^{ZQ} = \frac{1}{2}(I_A^+I_X^- + I_A^-I_X^+) \quad I_z^{ZQ} = \frac{i}{2}(-I_A^+I_X^- + I_A^-I_X^+)$$

$$I_x^{ZQ} = \frac{1}{2}(I_A^+I_X^+ + I_A^-I_X^-) \quad I_z^{ZQ} = \frac{i}{2}(-I_A^+I_X^+ + I_A^-I_X^-)$$

15 operators



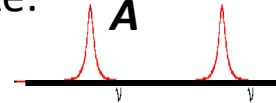
After single 90° pulse on $I_{z,A}$

$$\bar{s}_A(t) = s_A(0) \cos jt e^{i\delta_A t} = \frac{1}{2} s_A(0) \{ e^{i(\delta_A + j)t} + e^{i(\delta_A - j)t} \}$$

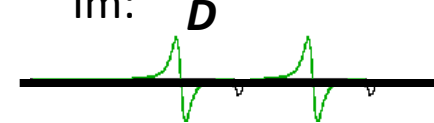
↓ **FFT**

$$S_A(\omega) = 0.5[A(\delta_A + j) + iD(\delta_A + j)] + 0.5[A(\delta_A - j) + iD(\delta_A - j)]$$

Re:



Im:



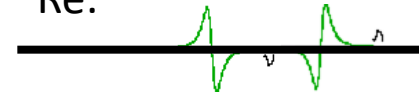
Signal after $I_{x,A} I_{z,X}$

$$S_A(t) = s_A(0) \sin jt e^{i(\delta_A + \pi/2)t} = \frac{-i}{2} s_A(0) \{ e^{i(\delta_A + j + \pi/2)t} - e^{i(\delta_A - j + \pi/2)t} \}$$

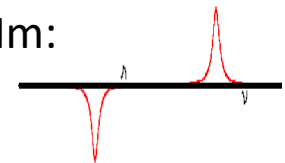
↓ **FFT**

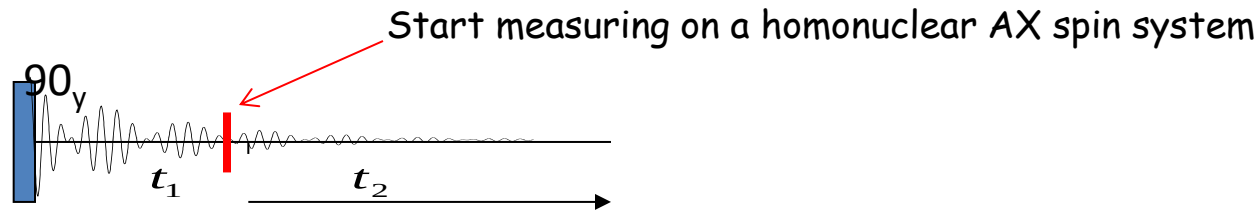
$$\bar{s}_A(\omega) = 0.5[D(\Delta\omega_A + j/2) - iA(\Delta\omega_A + j/2)] - 0.5[D(\Delta\omega_A - j/2) - iA(\Delta\omega_A - j/2)]$$

Re:



Im:





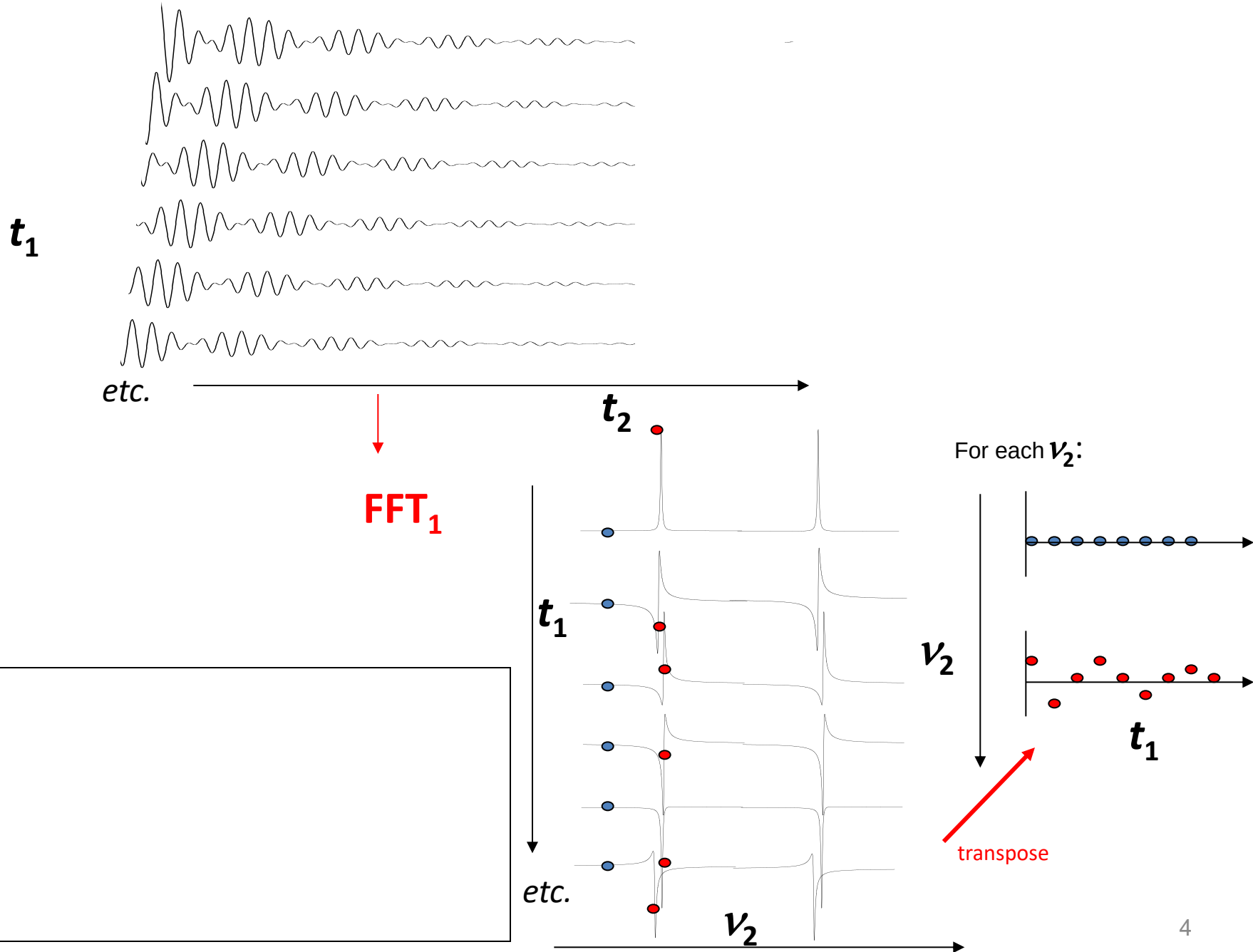
$$S_A(t_1, t_2) = \frac{1}{2} \left\{ s_0^A (e^{i(\Delta\omega_A + j)t_1} e^{i(\Delta\omega_A + j)t_2} + e^{i(\Delta\omega_A - \pi j)t_1} e^{i(\Delta\omega_A - \pi j)t_2}) \right\}$$

Double FFT.

$$S_A(\omega_1, \omega_2) = 0.5S \left\{ \begin{aligned} &[A_1(\delta_A + j) + iD_1(\delta_A + j)][A_2(\delta_A + j) + iD_2(\delta_A + j)] \\ &+ [A_1(\delta_A - j) + iD_1(\delta_A - j)][A_2(\delta_A - j) + iD_2(\delta_A - j)] \end{aligned} \right\}$$

$$\text{Re } S_A(\omega_1, \omega_2) = 0.5S \left\{ \begin{aligned} &[A_1(\delta_A + j)A_1(\delta_A + j) - D_1(\delta_A + j)D_2(\delta_A + j)] \\ &[A_1(\delta_A - j)A_1(\delta_A - j) - D_1(\delta_A - j)D_2(\delta_A - j)] \end{aligned} \right\}$$

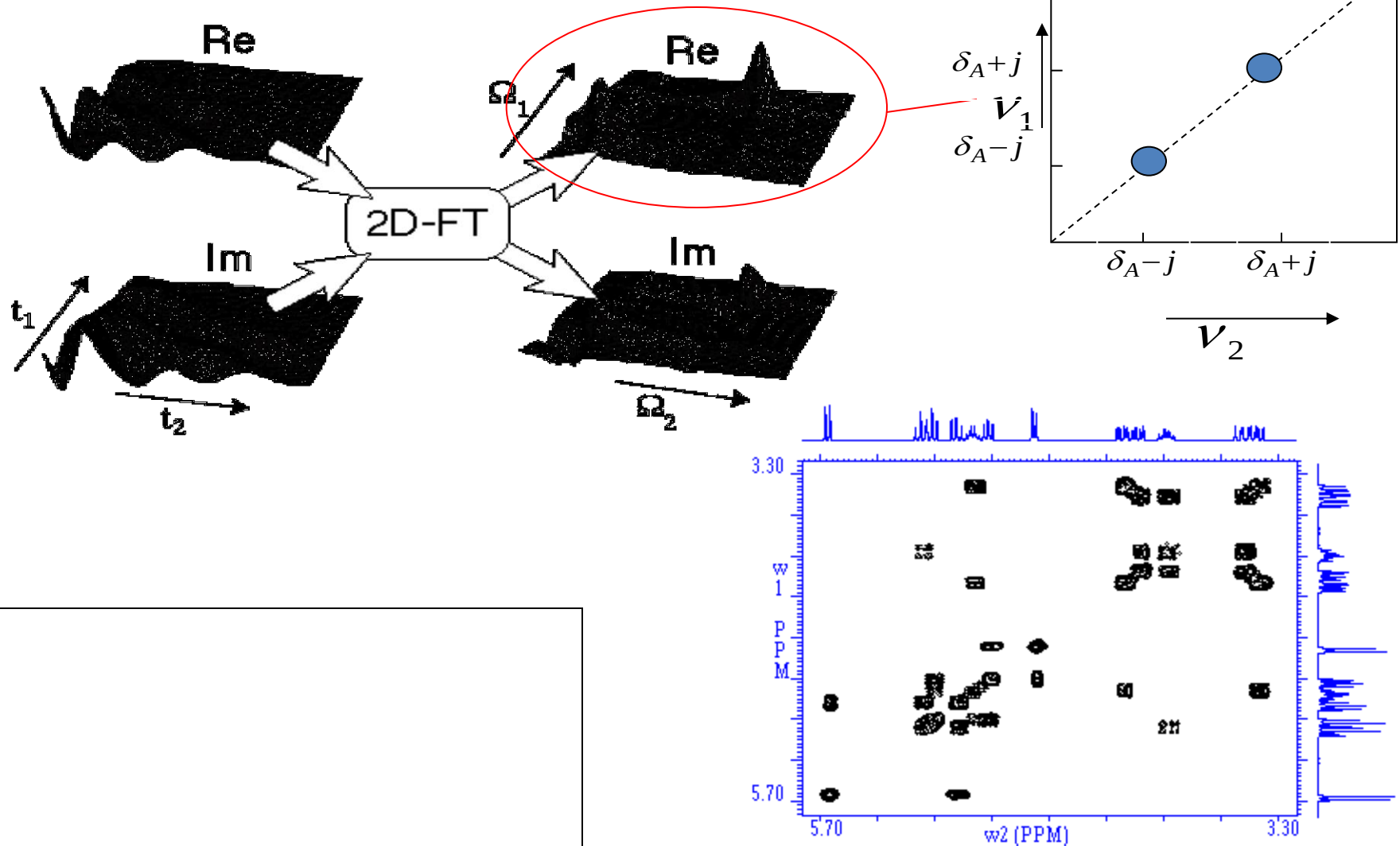
A supportive-slide to understand!

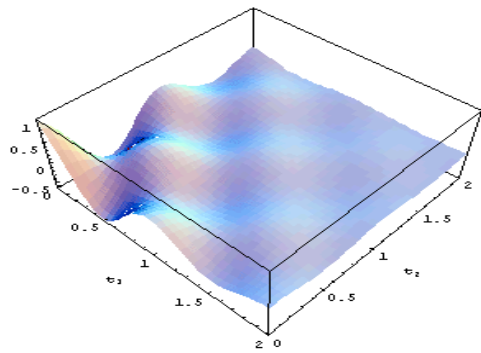


Two-dimensional twisted-line spectrum

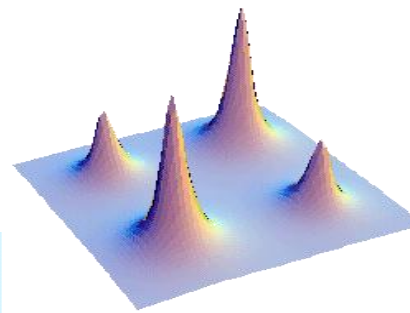
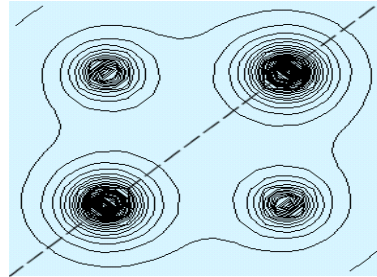
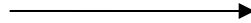
$$\text{Re}(s_A(\omega_1, \omega_2)) =$$

$$0.5[A_1(\Delta\omega + \pi j) \times A_2(\Delta\omega + \pi j) - D_1(\Delta\omega + \pi j) \times D_2(\Delta\omega + \pi j)] \\ + 0.5[A_1(\Delta\omega - \pi j) \times A_2(\Delta\omega - \pi j) - D_1(\Delta\omega - \pi j) \times D_2(\Delta\omega - \pi j)]$$





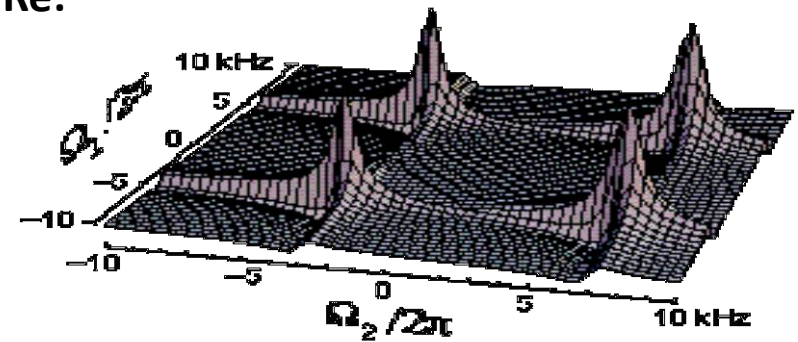
FFT₁+realFFT₂



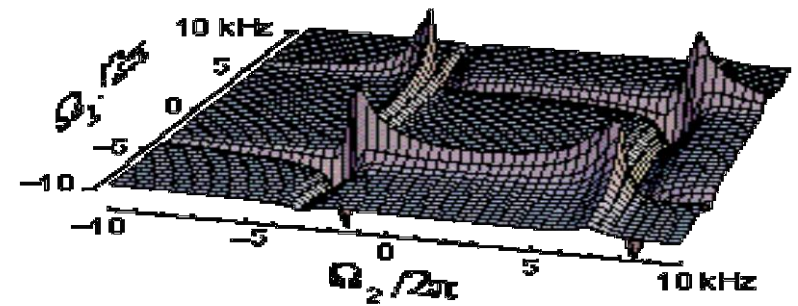
For the $\nu_l > 0$ of the spectrum

shape of twisted peaks:

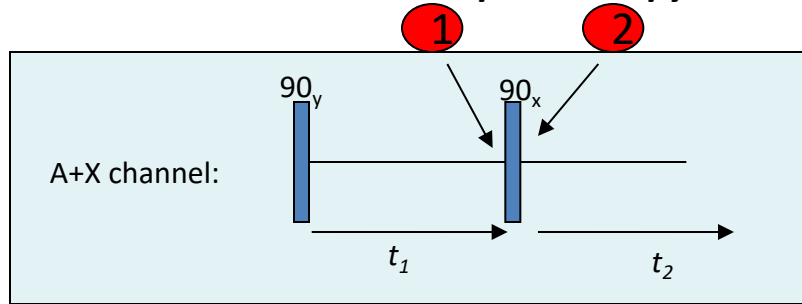
Re:



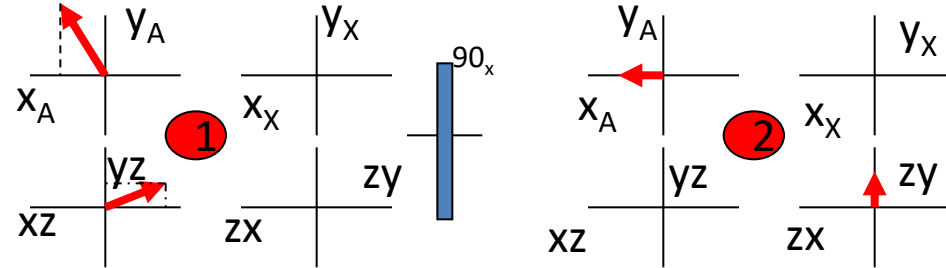
Im:



Two-Dimensional COSY Spectroscopy



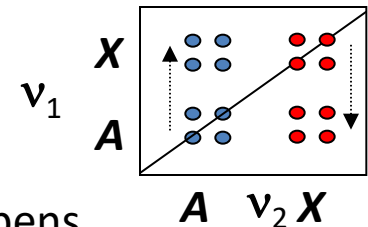
Starting from spin A



$$\begin{aligned} \langle I_{x,A} \rangle(t_1) &= s_0^A \cos jt_1 e^{i\delta_A t_1} \\ \langle I_{y,A} I_{z,X} \rangle(t_1) &= s_0^A \sin jt_1 e^{i(\delta_A t_1 + \pi/2)} \end{aligned}$$

$$\begin{aligned} S_A(t_1, t_2) &= \langle I_{x,A}(t_1) \rangle \cos jt_2 e^{i\delta_A t_2} + 0 \\ S_X(t_1, t_2) &= 0 - \langle I_{z,A} I_{y,X} \rangle(t_1) \sin jt_2 e^{i\delta_A t_2 + \pi/2} \end{aligned}$$

FFT₂+FFT₁:

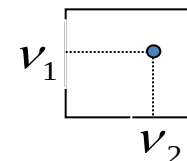


The same happens
when we start
with the X-spin

Thus each peak originates from
a time domain term

$$" a(\omega_1, \omega_2) e^{i\omega_1 t} e^{i\omega_2 t} "$$

Thus after two Fourier transformations we get two two-dimensional spectra (real&imaginary) that tell us about chemical shift correlation via j-coupling
 Each peak in the 2D spectrum is a result of a double FFT and is a twisted line.



$$\bar{s}(t_1, t_2) = \dots + a(v_1, v_2) e^{i\omega_1 t_1} e^{i\omega_2 t_2} e^{-t_1/T_2} e^{-t_2/T_2} + \dots$$

FFT₂ + FFT₁ :

$$\begin{aligned} S(\omega_1, \omega_2) &= (A(\omega_1) + iD(\omega_1))(A(\omega_2) + iD(\omega_2)) \\ &= (A(\omega_1)A(\omega_2) - D(\omega_1)D(\omega_2)) + i(A(\omega_1)D(\omega_2) + D(\omega_1)A(\omega_2)) \end{aligned}$$

Twisted line

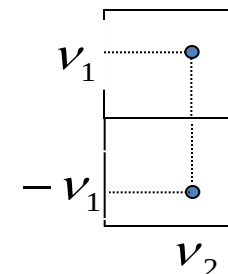
However **if**:

$$s(t_1, t_2) = \dots \cos \omega_1 t_1 e^{i\omega_2 t_2} \dots$$

FFT₂ + realFFT₁ :

$$\begin{aligned} s(\omega_1, \omega_2) &= (A(\omega_1) + A(-\omega_1))(A(\omega_2) + iD(\omega_2)) \\ &= (A_1(\omega_1)A_2(\omega_2) + A_1(-\omega_1)A_2(\omega_2)) + i(A_1(\omega_1)A_2(\omega_2) + A_1(-\omega_1)D_2(\omega_2)) \end{aligned}$$

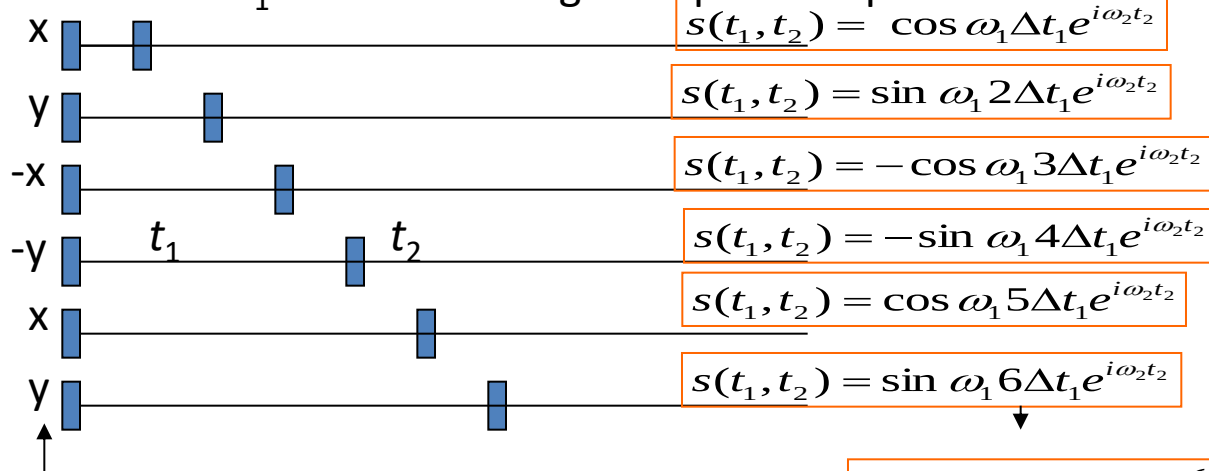
two 2D absorbtion lines



To overcome the twisted lines it is common to perform experiments that are of type II and do something about the ambiguity of $+v_1$ or $-v_1$.

TPPI = time proportional phase increment

For each t_1 value we change the pulse sequence such that



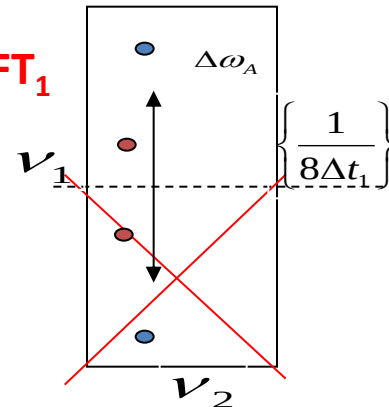
The phases of the pulse

We can write this as:

$$s(t_1, t_2) = \cos \left\{ \omega_1 + \frac{\pi}{2\Delta t_1} \right\} n\Delta t_1 e^{i\omega_2 t_2}$$

$$t_1 = n\Delta t_1$$

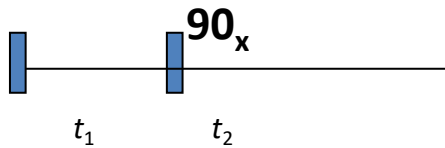
$v_2 + \text{realFT}_1$



The lines are shifted away from 0 by an amount such that all $+v$ and $-v$ lines show up at positive v_1 .

SATES =

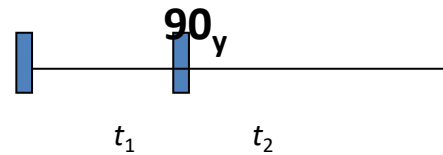
For each t_1 we do two experiments and combine the data as follows:



$$s(t_1, t_2) = \cos \omega_1 \Delta t_1 e^{i\omega_2 t_2}$$

FFT₂

$$s(t_1, \omega_2) = \cos \omega_1 t_1 (A_2(\omega_2) + iD_2(\omega_2))$$



$$s(t_1, t_2) = i \sin \omega_1 \Delta t_1 e^{i\omega_2 t_2}$$

FFT₂

$$s(t_1, \omega_2) = i \sin \omega_1 t_1 (A_2(\omega_2) + iD_2(\omega_2))$$

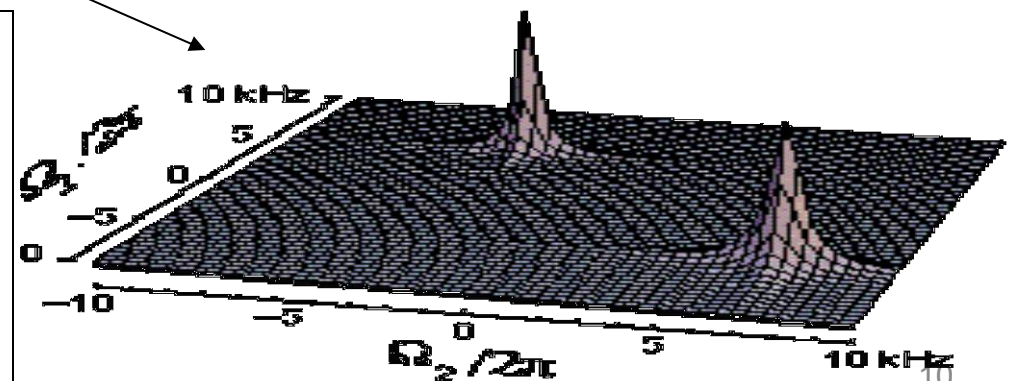
Generate a new 2D signal from
the two "real" signals of the two spectra

$$s'(t_1, \omega_2) = \cos \omega_1 t_1 A_2(\omega_2) + i \sin \omega_1 t_1 A_2(\omega_2)$$

FFT₁

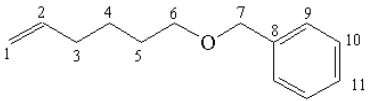
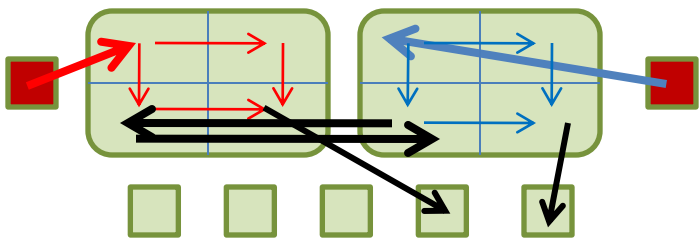
$$s'(\omega_1, \omega_2) = \underline{A_1(\omega_1) A_2(\omega_2) + i D_1(\omega_1) A_2(\omega_2)}$$

"States" spectrum

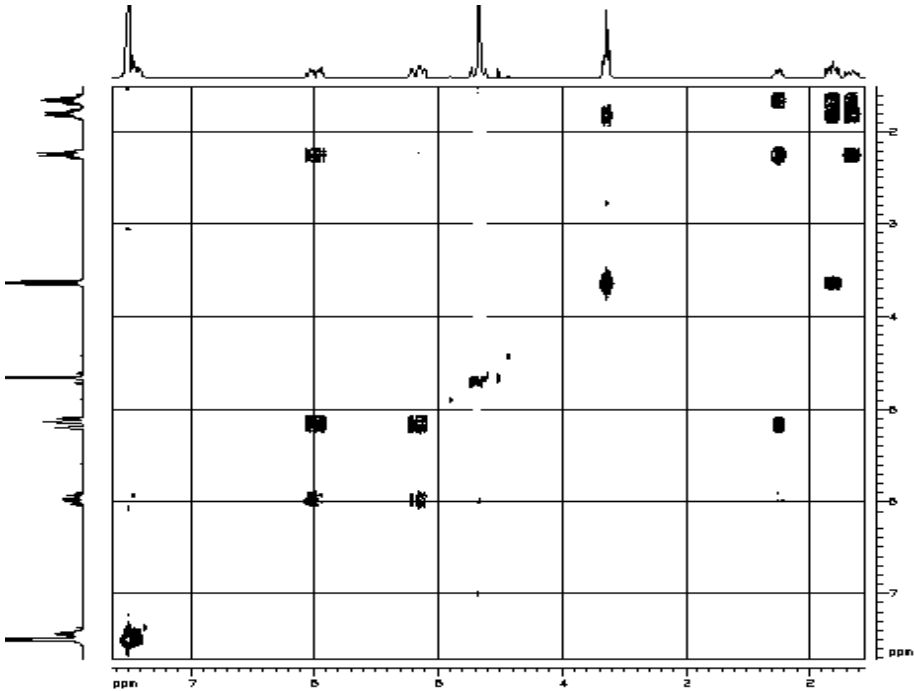


Additional 2D experiments:

Through **phase cycling** and gradients the proper magnetization pathway is chosen, and the undesired pathways are suppressed.

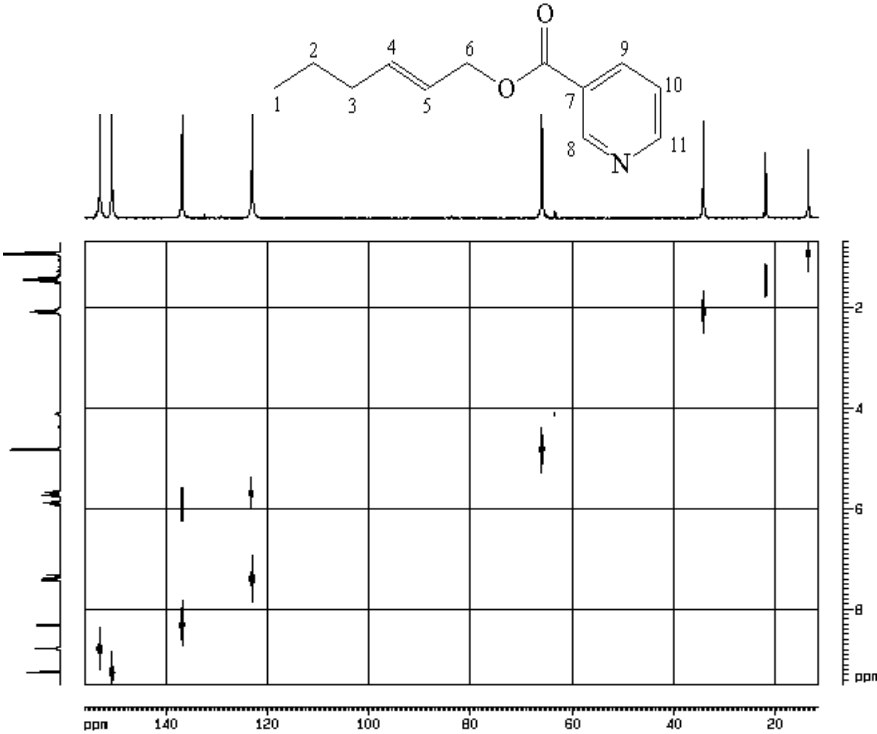
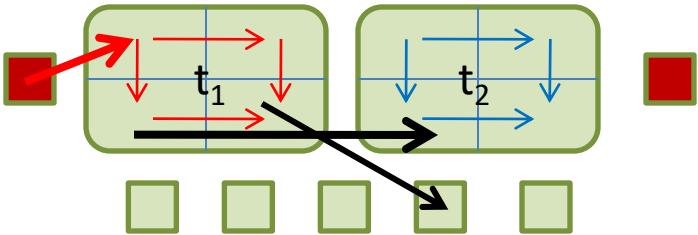
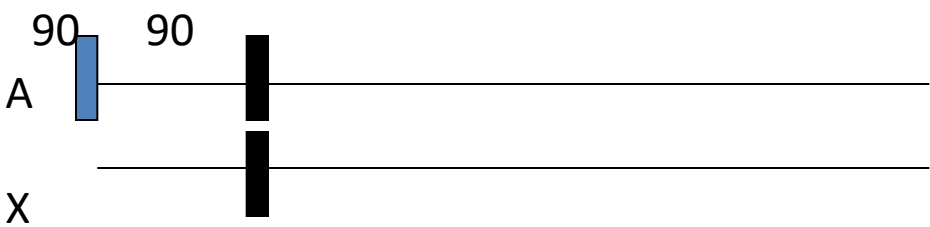


See 200 and More NMR Experiments
Stefan Berger & Siegmund Braun
Wiley-VCH (2004)
"200-Berger-Braun"

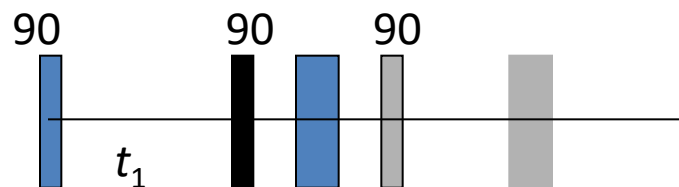
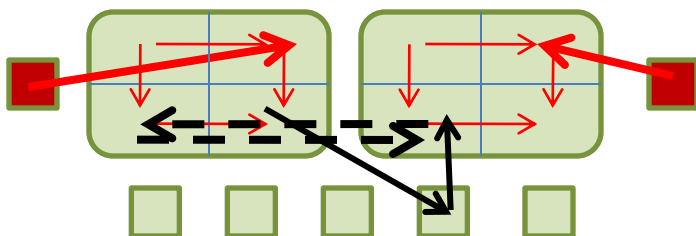


Additional 2D experiments:

HETCOR-COSY

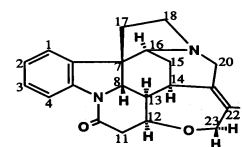


Double Quantum Filtered COSY

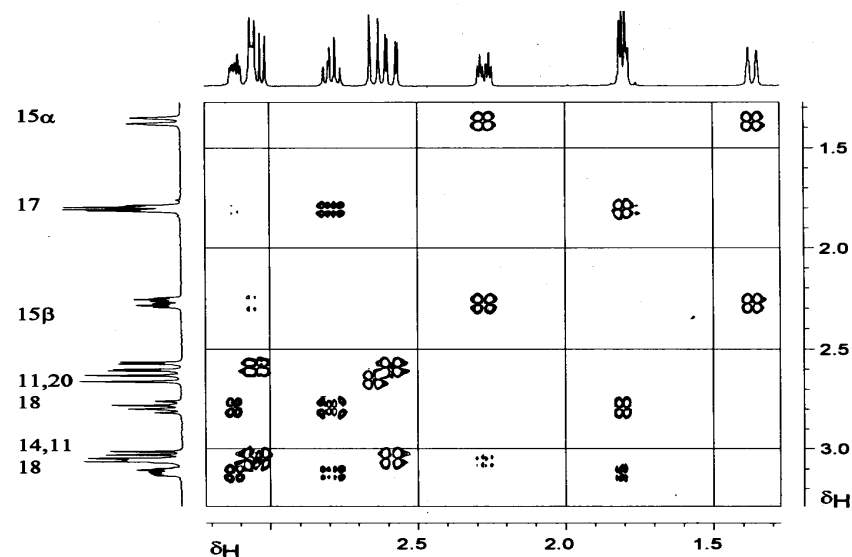


$$I_{z,A1} \rightarrow I_{y,A1} \rightarrow I_{x,A1} I_{z,A2} \xrightarrow{x} I_{x,A1} I_{y,A2} \xrightarrow{y} I_{z,A1} I_{y,A2} \rightarrow I_{xA2}$$

gs-DQF-COSY

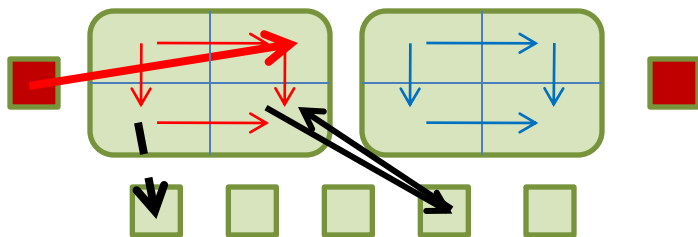
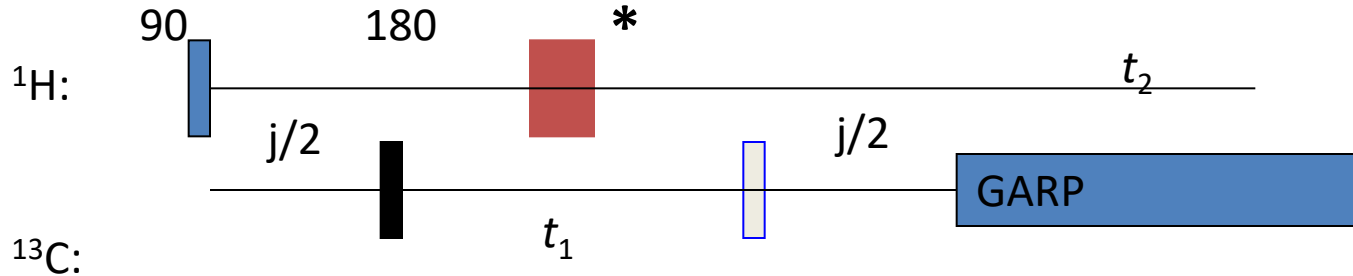


15 α

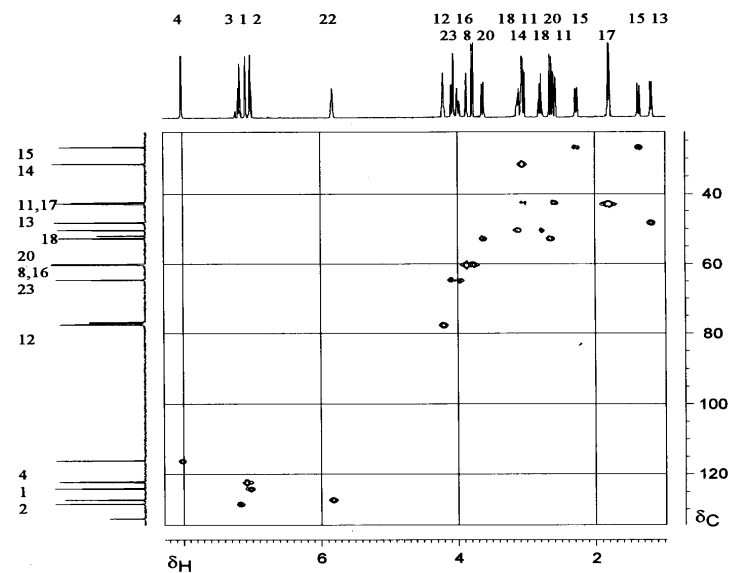
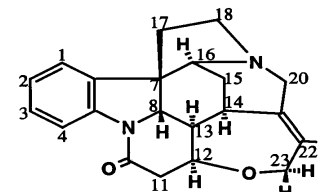


200 Berger-Baun

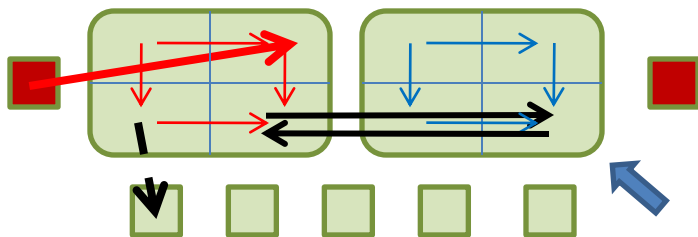
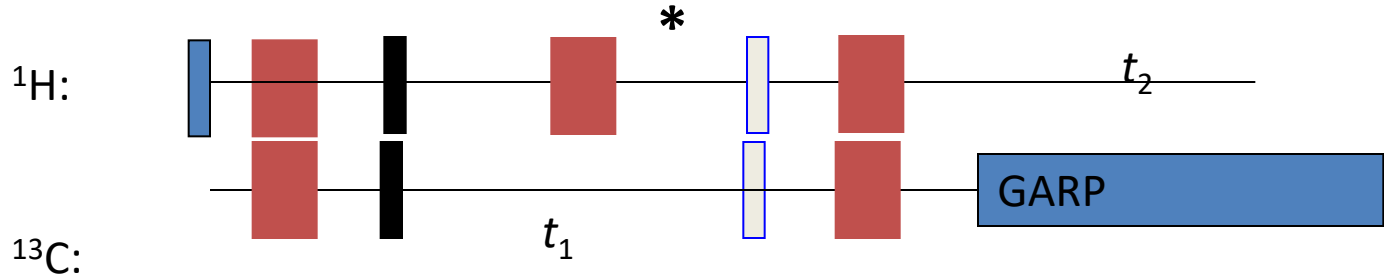
HMQC



*The 180° refocuses both $\Delta\omega_A$ and j but not $\Delta\omega_X$

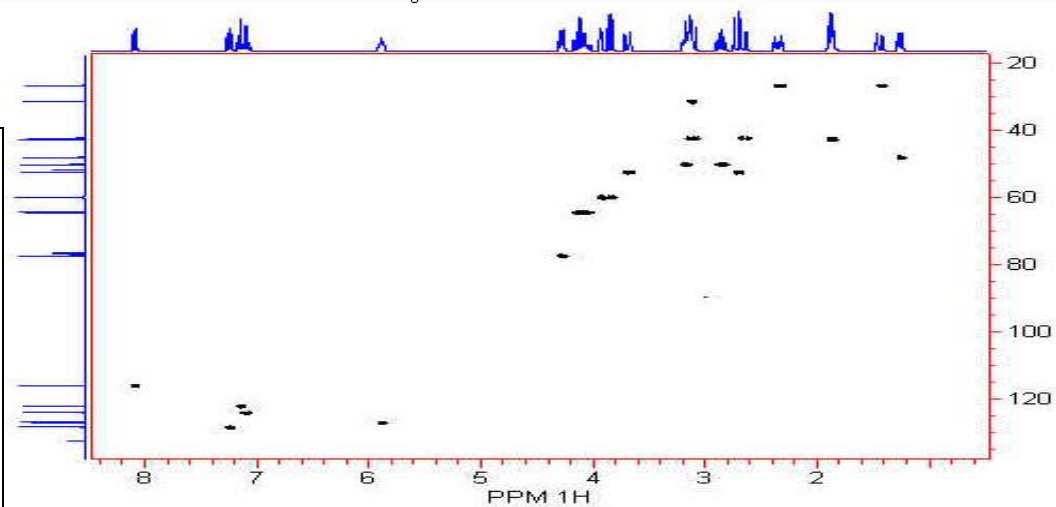
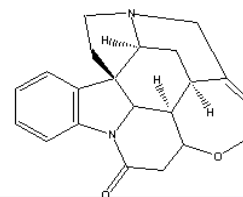


HSQC



*The 180° refocuses again both

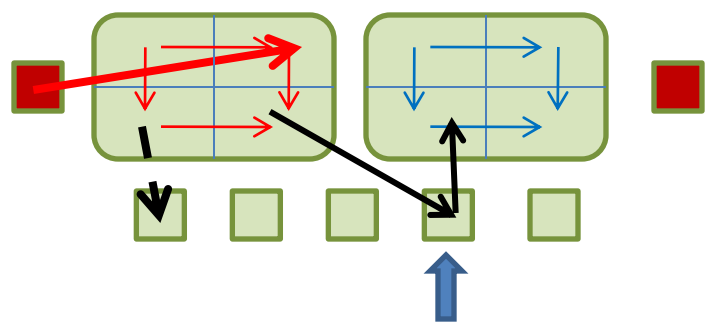
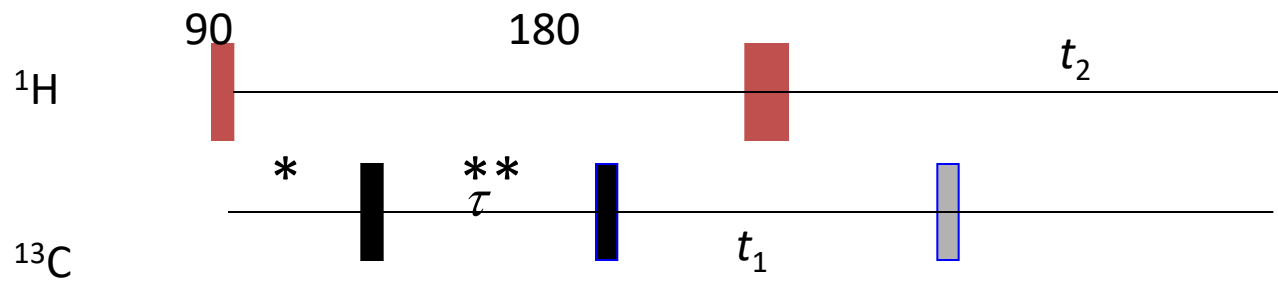
$$\Delta\omega_A \text{ and } \mathbf{j}$$



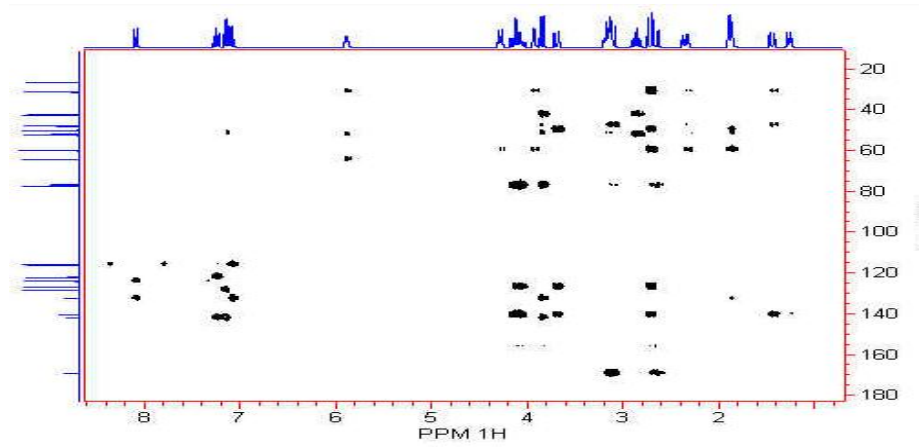
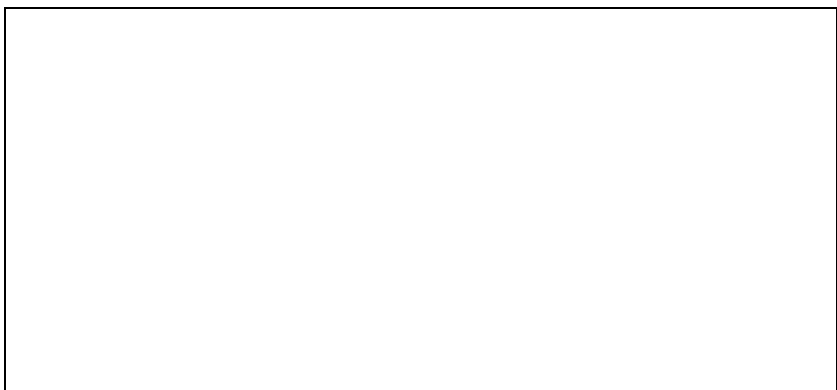
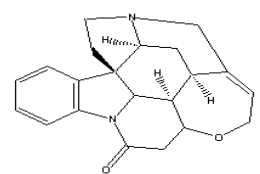
HMBC

(small couplings)

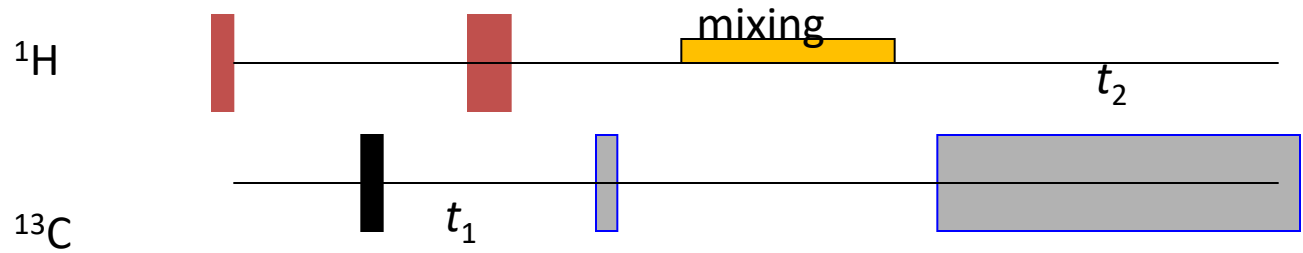
=HMQC with distance (j) differentiation



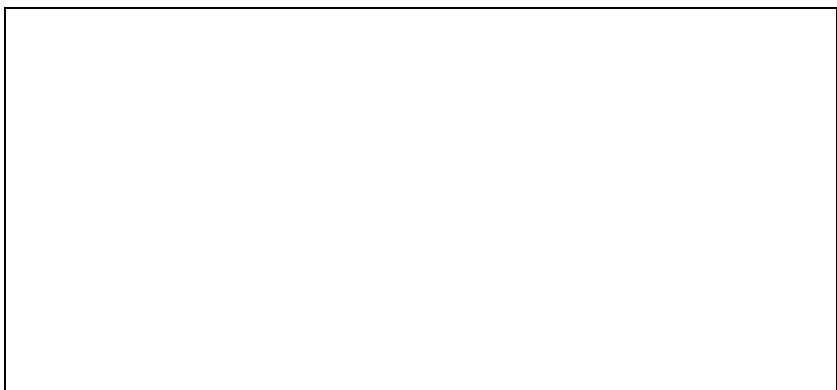
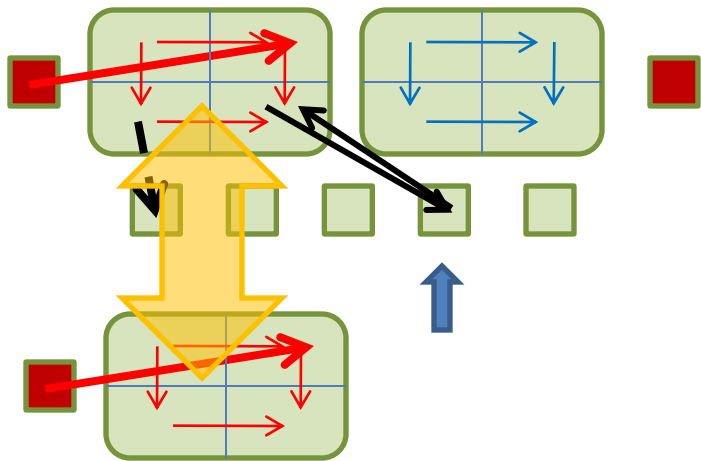
*short distance interaction are suppressed
** long distance interactions are creating correlations



HMQC+TOCSY



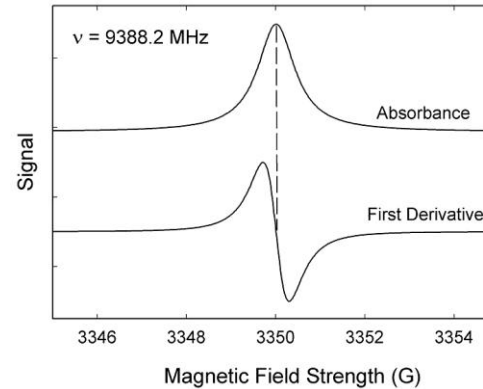
for example MLEV-8 mixing



TROSY

Still missing

5. CW EPR and pulsed EPR



S-band 2-4 GHz
X-band 7-12.5 GHz
Q-band 30-50 GHz
W-band 75-111 GHz

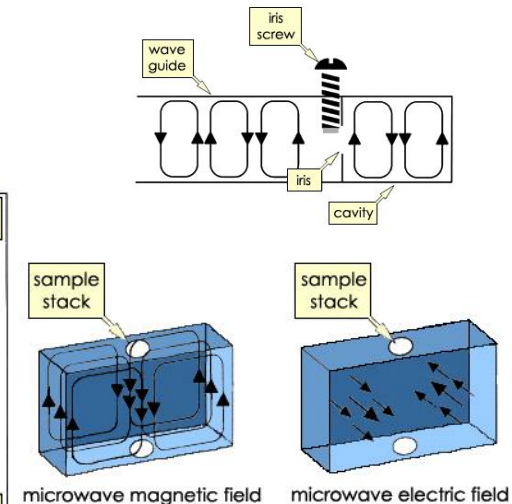
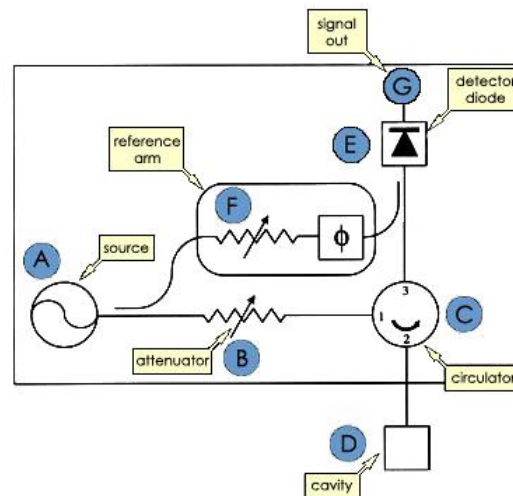
$$\frac{\omega_{0S}}{\omega_{0H}} = 656$$

Short introduction:

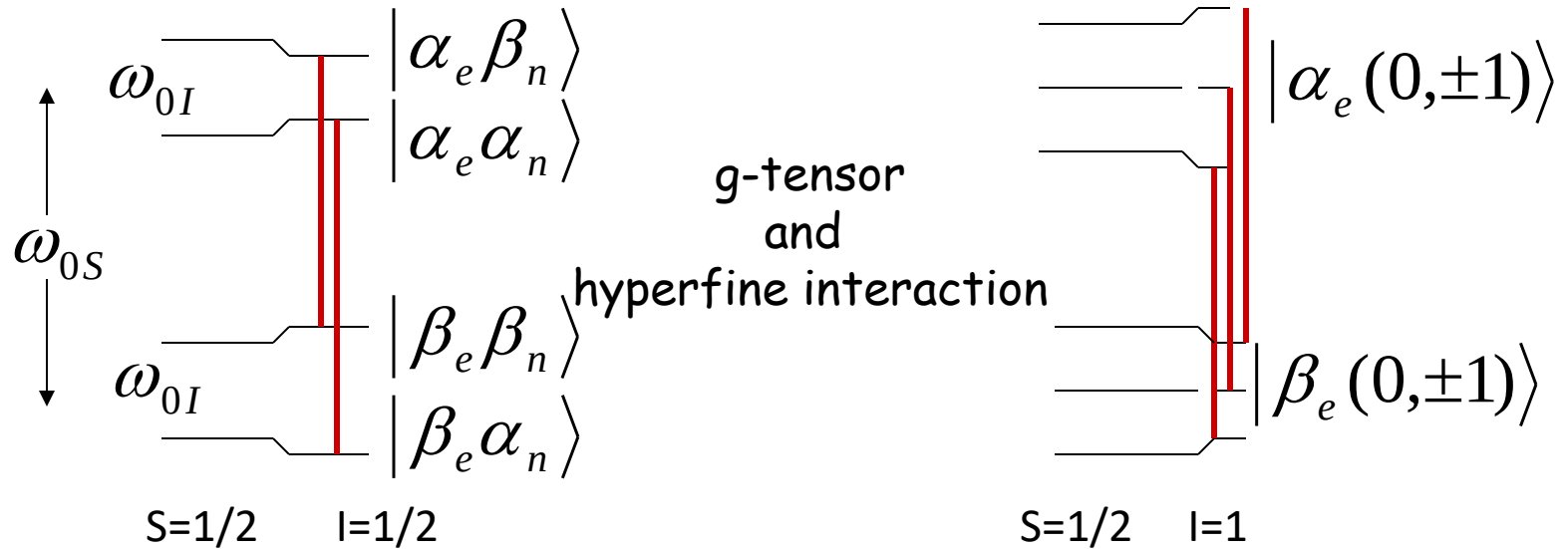
electronic ground states
g-tensor
hyperfine interaction
zero-field splitting

3.35 Tesla: 93.88GHz(free electron) vs 143MHz(proton)

www.bruker-biospin.com

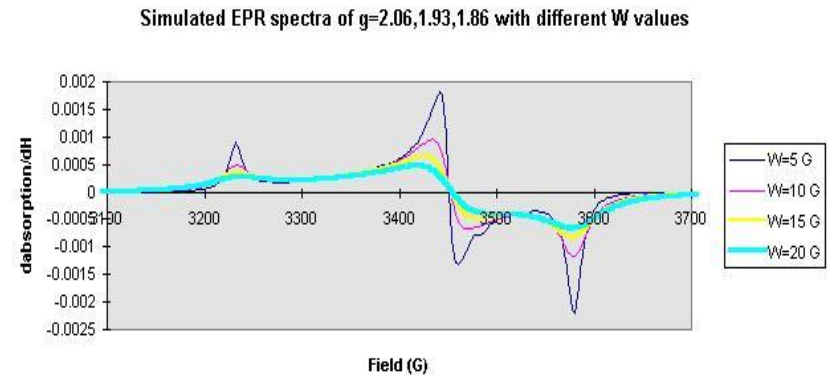
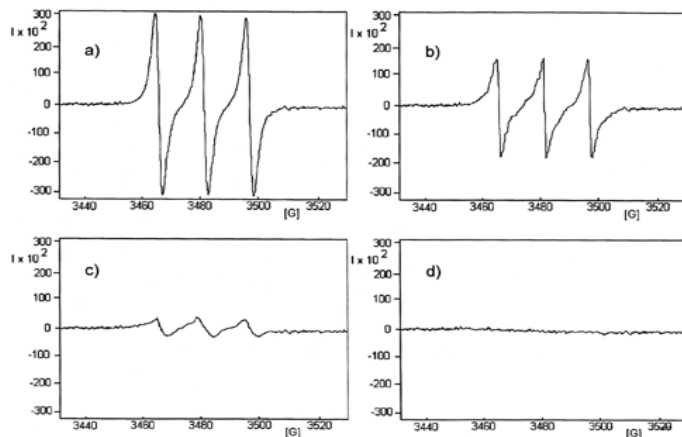


2-a Some basics of Electron Paramagnetic Resonance



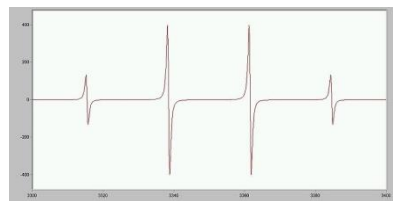
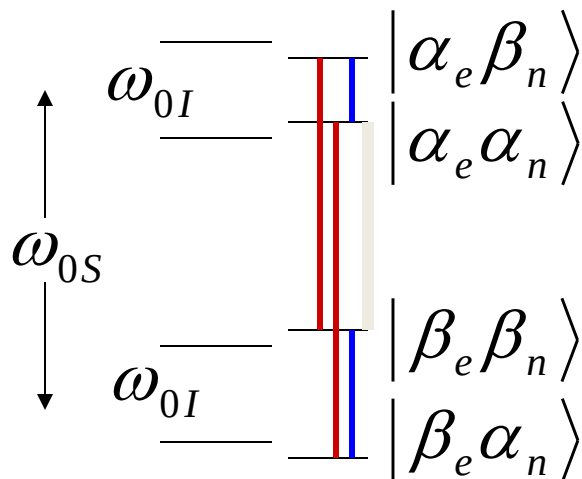
$$H = (\omega_{0e} + (g_{iso} + g(\Omega))\mu_B)S_z - \omega_{0I}I_z + A_{iso}I_z.S_z + A_0(\Omega)S_zI_z + A_{\pm 1}(\Omega)S_zI^{\pm}$$

Pseudo secular



CW EPR in solutions and solids

2-b Pulsed EPR experiments

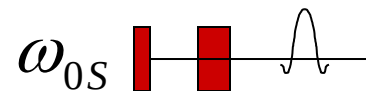


Simulated EPR spectrum of the CH_3 radical

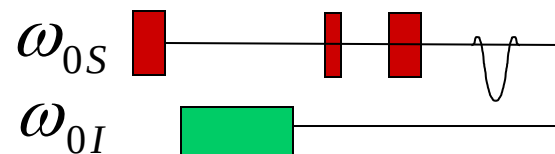


Simulated EPR spectrum of the $\text{H}_2\text{C}(\text{OCH}_3)$ radical

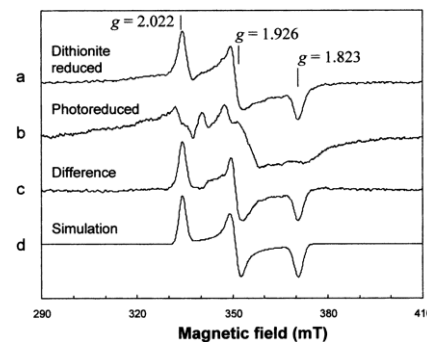
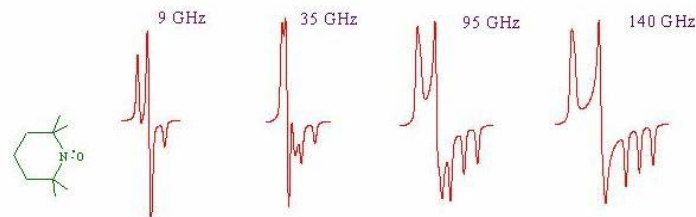
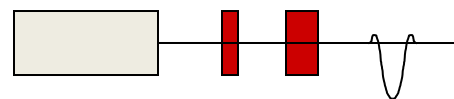
EPR echo detection



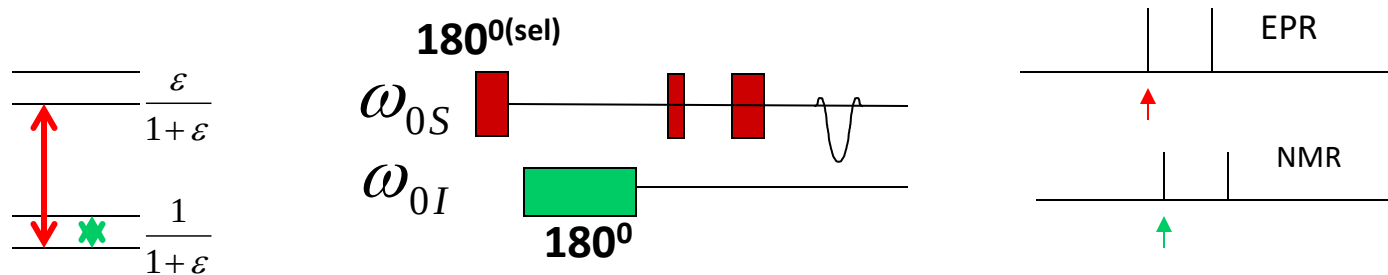
ENDOR spectroscopy



ELDOR spectroscopy



ENDOR



$$\sigma = \begin{pmatrix} 1-\varepsilon & & & \\ & 1-\varepsilon & & \\ & & \varepsilon & \\ & & & \varepsilon \end{pmatrix} \rightarrow \begin{pmatrix} \varepsilon & & & \\ & 1-\varepsilon & & \\ & & 1-\varepsilon & \\ & & & \varepsilon \end{pmatrix} \rightarrow \begin{pmatrix} 1-\varepsilon & & & \\ & \varepsilon & & \\ & & 1-\varepsilon & \\ & & & \varepsilon \end{pmatrix}$$

If on-resonance
 $\omega_{0I} \pm A$

Signals: $1-2\varepsilon$ $2\varepsilon-1$ 0

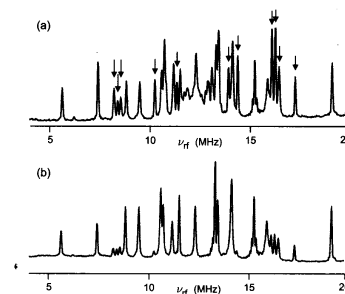
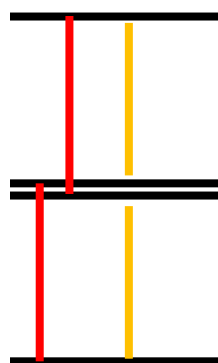


Figure 12.2.8 Hyperfine contrast selectivity. Davies-ENDOR spectra of $[(2,2\text{-bipyridylamine})\text{Cu}]^{2+}$ diluted into a single crystal of the corresponding Ni(II) complex, for two sets of m.w. pulse lengths, temperature 10 K: (a) Lengths of the m.w. pulses $t_{\text{m.w.}}^{(1)} = 400$ ns, $t_{\text{m.w.}}^{(2)} = 200$ ns, and $t_{\text{m.w.}}^{(3)} = 400$ ns; both proton and nitrogen transitions are observed, arrows indicate proton transitions; and (b) Lengths of the m.w. pulses $t_{\text{m.w.}}^{(1)} = 20$ ns, $t_{\text{m.w.}}^{(2)} = 100$ ns, and $t_{\text{m.w.}}^{(3)} = 200$ ns; most of the proton transitions are suppressed. (Adapted from Ref. [4].)

DEER



Dipole-dipole interaction between unpaired electrons

$$H = \omega_{0S1} S_{z1} + \omega_{0S2} S_{z2} + \omega_{DD} S_{z1} S_{z2}$$

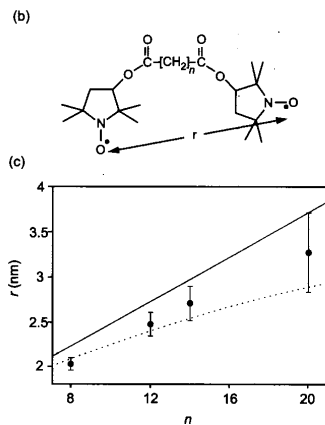
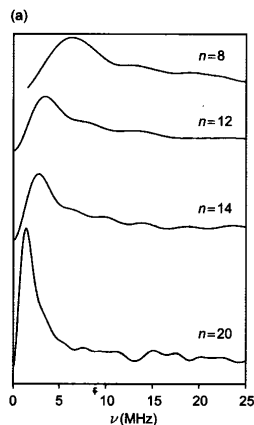
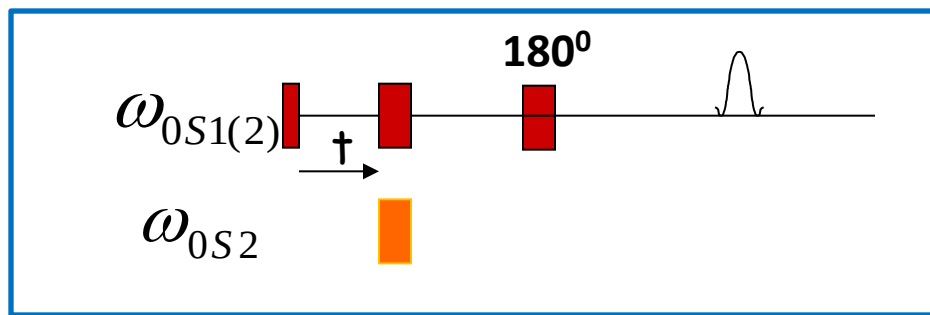


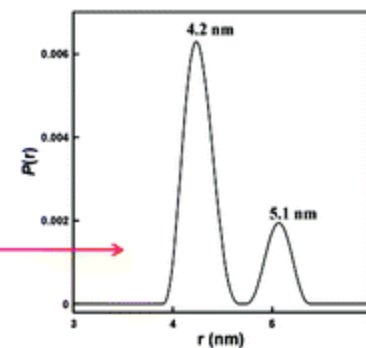
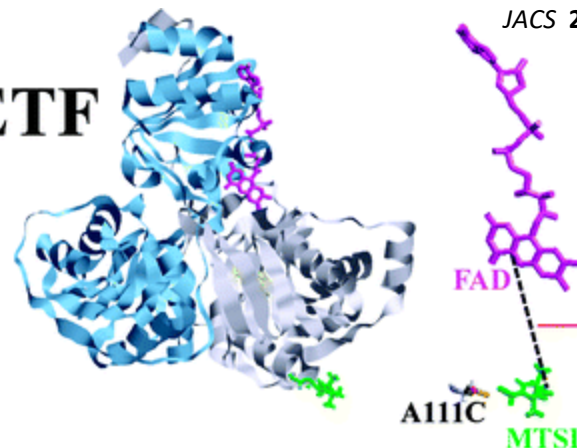
Figure 13.3.4 Determination of conformational statistics of flexible biradical molecules with n



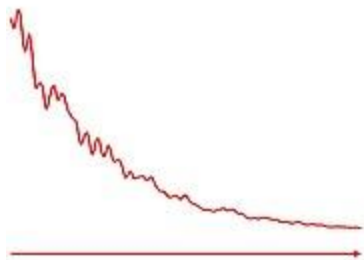
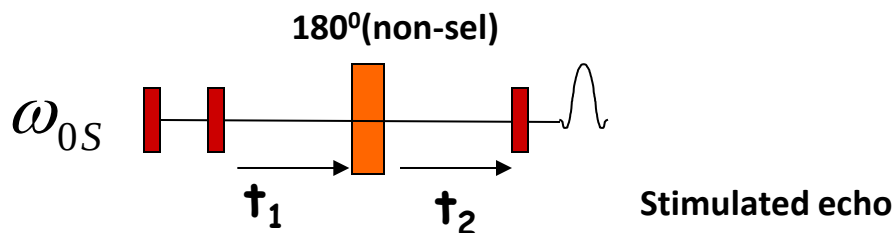
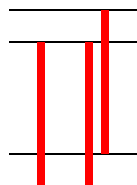
Michael A. Swanson[†], Velavan Kathirvelu[†], Tomas Majtan[‡], Frank E. Frerman[‡], Gareth R. Eaton[†] and Sandra S. Eaton^{*†}

JACS 2009, 131 (44), pp 15978–15979

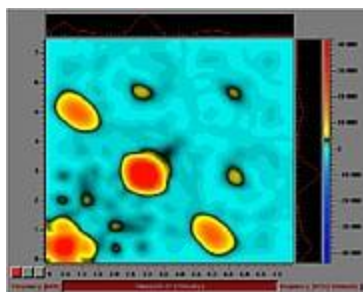
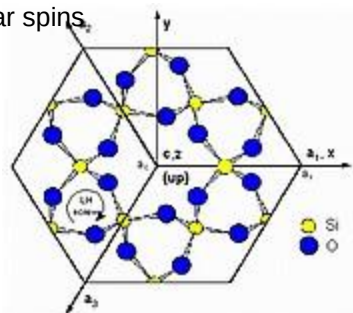
ETF



HYSCORE



2-pulse ESEEM signal of ^1H nuclear spins.



2D-HYSCORE spectrum of natural abundance ^{29}Si in quartz

http://www.bruker-biospin.com/eseem_hyscore.html

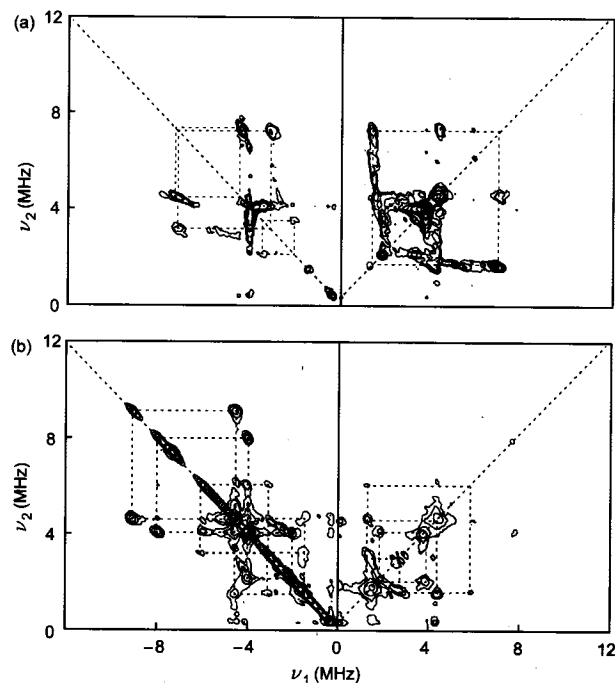
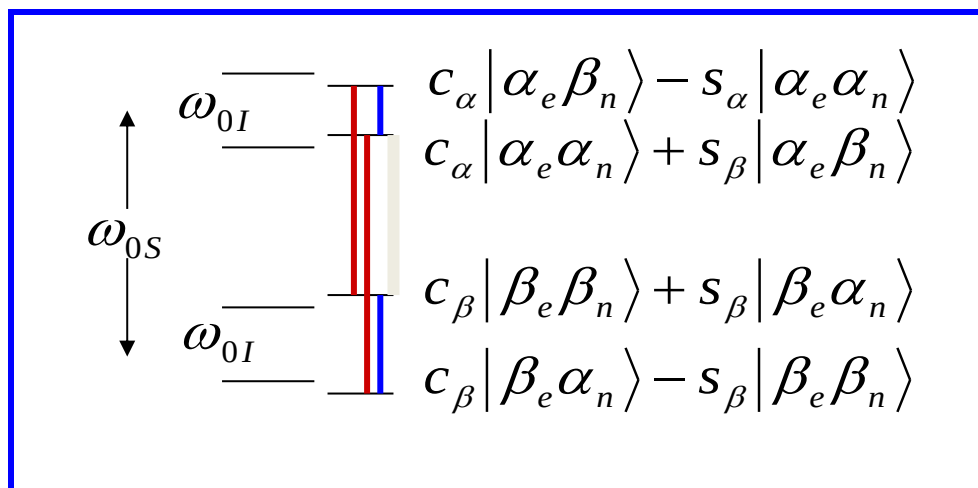
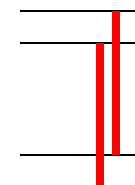
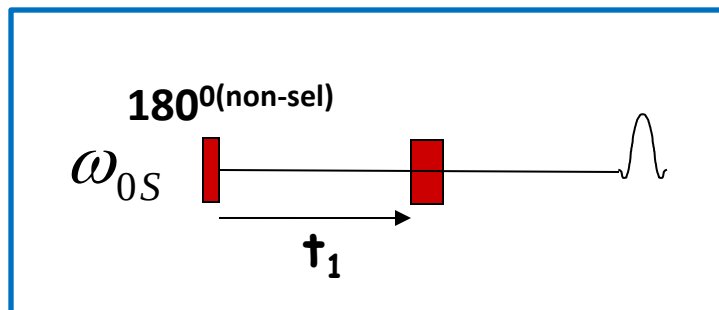


Figure 11.5.6 HYSCORE and DONUT-HYSCORE spectra of the complex of VO^{2+} with the bis-hydroxamate ion binder RL515, $\tau_1 = 240$ ns: (a) HYSCORE spectrum; and (b) DONUT-HYSCORE spectrum, $\tau_2 = 400$ ns. (Adapted from Ref. [41].)

ESEEM



“Forbidden transition”

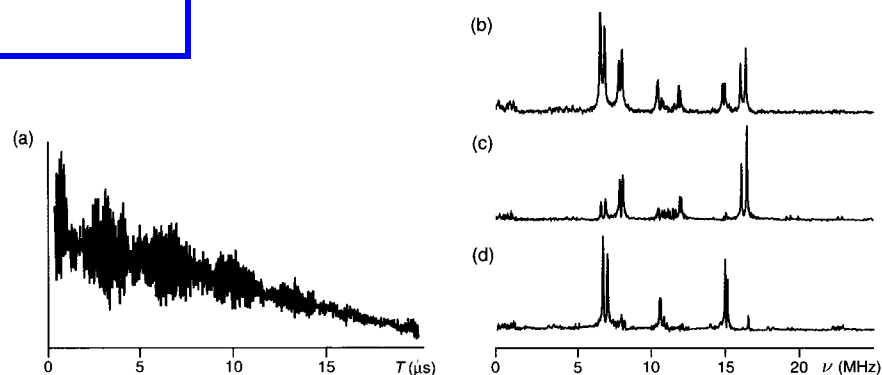
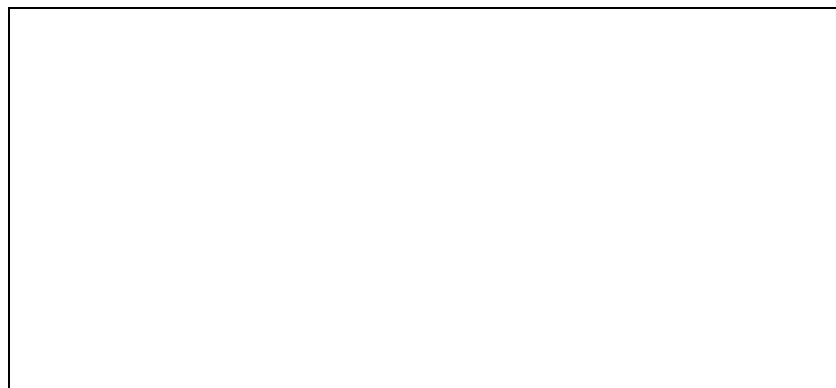
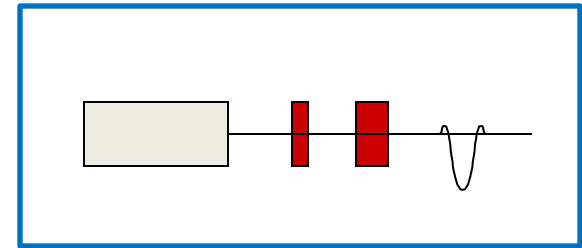
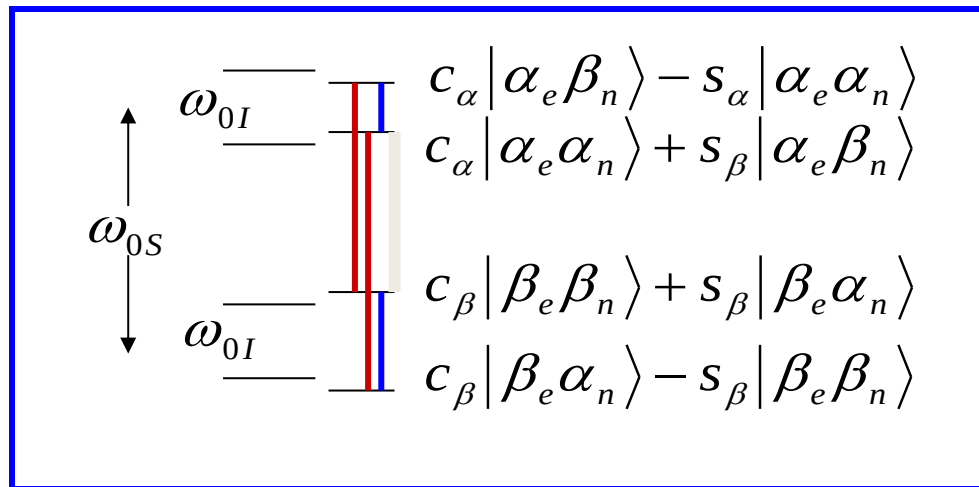


Figure 11.1.9 Comparison between the soft-hard three-pulse modulation technique and the standard three-pulse ESEEM experiment on a Cu(II)-doped triglycine sulfate single crystal, temperature 30 K, width of the detection window of the boxcar IONs: (a) Modulation trace of the soft-hard three-pulse approach with selective pulses of 600 ns and a non-selective pulse of 20 ns, $\tau_1 = 0$; (b) Corresponding absolute-value spectrum; and (c-d) Absolute-value spectra obtained with the three-pulse ESEEM sequence, $1, \pi/2 = 10$ ns, and 7 values of 230 ns (c) and 250 ns (d). (Adapted from Ref. [16].)

ELDOR detected NMR

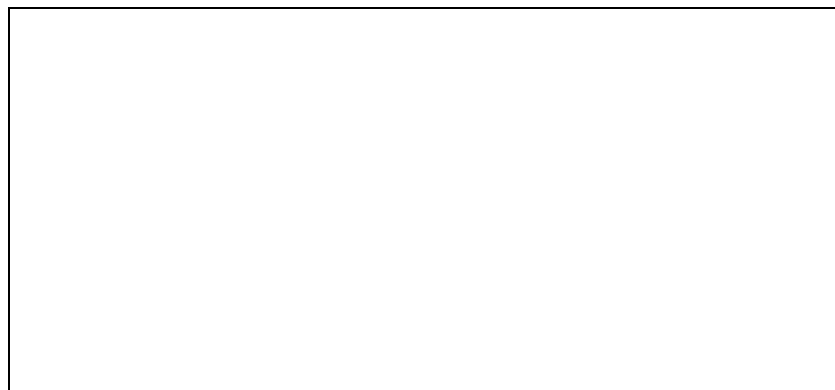


Effective intensity of irradiation at $\omega_{0D} - \omega_{0I}$ is very small

$$\omega_{1eff} = \omega_1 c_\beta s_\alpha \approx \frac{A_\pm}{\omega_{0I}} \omega_1$$

After a long “forbidden” pulse at

$$\omega_{0S} - \omega_{0I}$$



$$\sigma = \begin{pmatrix} 1-\varepsilon & & & \\ & 1-\varepsilon & & \\ & & \varepsilon & \\ & & & \varepsilon \end{pmatrix} \rightarrow \begin{pmatrix} 1-\varepsilon & & & \\ & 1/2 & & \\ & & 1/2 & \\ & & & \varepsilon \end{pmatrix}$$

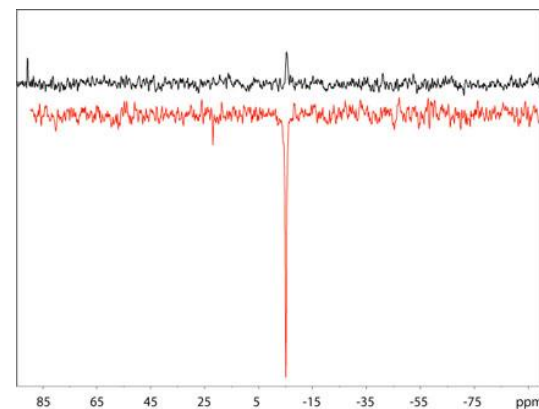
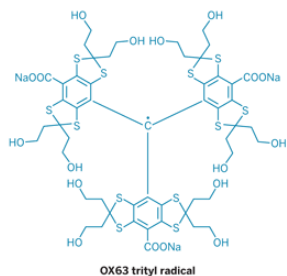
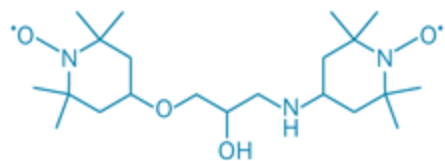
$1-2\varepsilon$
 $1/2-\varepsilon$

Saturation of forbidden transition

MW irradiation + electron relaxation

Solid

Liquid



www.mrl.ucsb.edu/mrl/research/Songi.html



2^0K DNP polarization
 +
 desolution to 300K and 600MHz
 +
 NMR detection

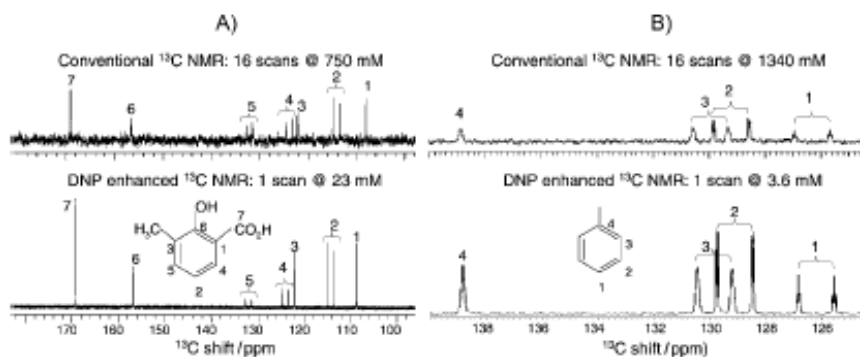
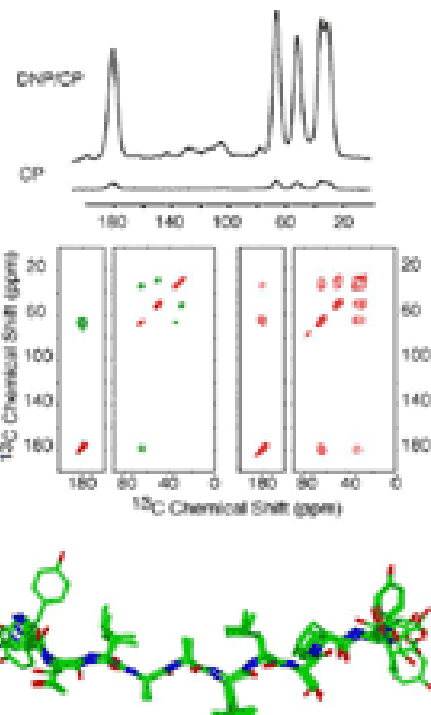


Figure 5. Comparison of conventional and hyperpolarized ^1H -coupled 1D ^{13}C NMR aromatic regions of 3-methylsalicylic acid (A) and toluene (B) dissolved in methanol. Notice the relative ratio between the analyte concentrations, as well as the higher signal shown by the quaternary carbon atoms due to their longer T_1 relaxation time.



6. Solid State NMR

6-a The main interactions: the chemical shift anisotropy

$$H_{CSA}^{RoF} = \omega_0 \sigma_{iso} I_z + \omega_0 \Delta \sigma_{ZZ} \left\{ \frac{(3 \cos^2 \theta - 1)}{2} + \eta \frac{1}{2} \sin^2 \theta \cos 2\varphi \right\} I_z$$

Chemical Shift Anisotropy

isotropic shift

asymmetry parameter

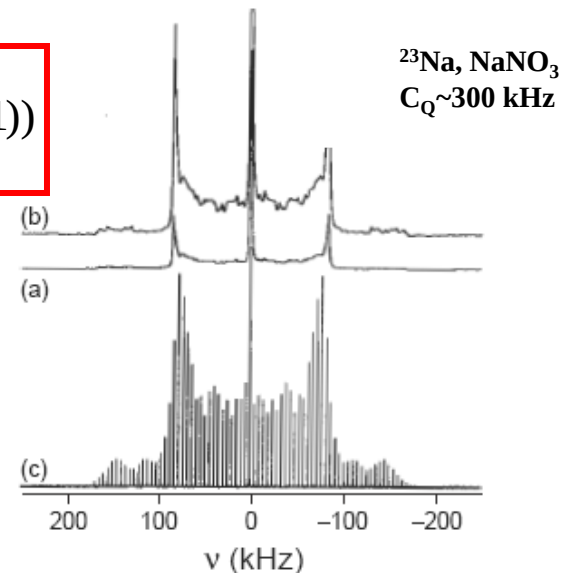
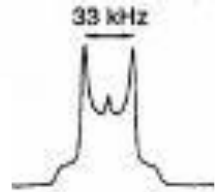
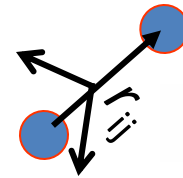
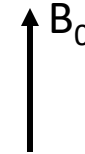
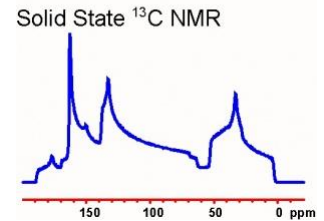
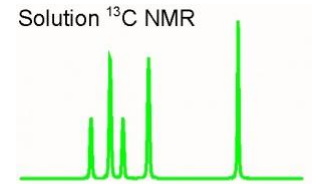
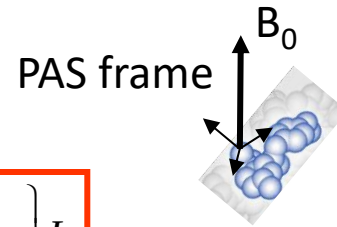
$$\Delta \sigma_{PP} = \sigma_{PP} - \sigma_{iso} \quad \sigma_{iso} = \frac{\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ}}{3} \quad \eta = \frac{\Delta \sigma_{XX} - \Delta \sigma_{YY}}{\Delta \sigma_{ZZ}}$$

and the dipolar interaction

$$H_{LAB}^{RoF} = \frac{\mu_0 \gamma_i \gamma_j}{4\pi r_{ij}^3} \cdot \frac{1}{2} (3 \cos^2 \beta - 1) (3 I_{zi} I_{zj} - \bar{I}_i \cdot \bar{I}_j)$$

and the quadrupolar interaction

$$H_{QUAD}^{RoF} = \frac{e^2 q Q}{I(2I-1)} \left\{ \frac{(3 \cos^2 \theta - 1)}{2} + \eta \frac{1}{2} \sin^2 \theta \cos 2\varphi \right\} (3 I_z^2 - I(I+1))$$



...Jakobsen, JMR, 95, 88, 1991

6-b Magic Angle Spinning

$$3\cos^2 \theta_m - 1 = 0$$

$$H(t) = (\Delta\omega_i + \sigma_{iso,i}) I_{zi}$$

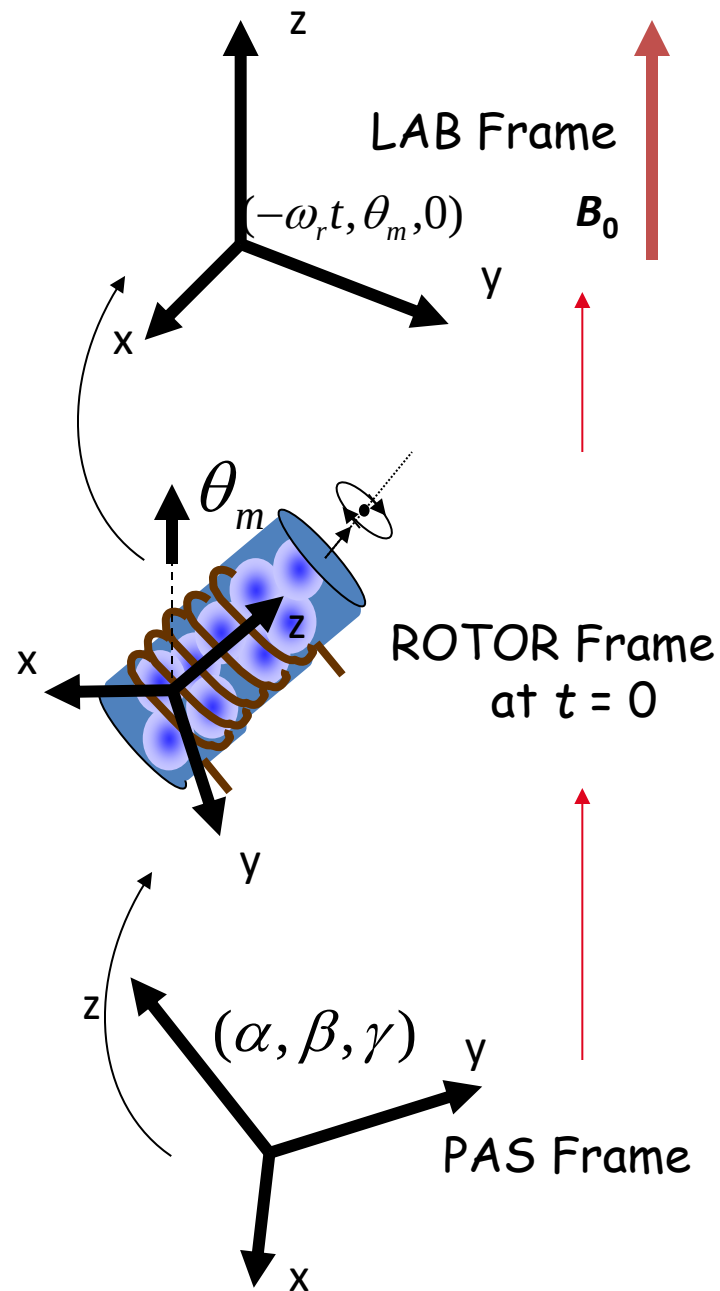
$$+ \sum_{n=-2}^2 \sigma_{0i} \cancel{(g_{0i})} + \sum_{n=\pm 1, \pm 2} g_{ni} e^{in\omega_r t} I_{zi}$$

$$+ \sum_{n=2}^2 \Delta_{ij} \left\{ \cancel{G_{0ij}} + \sum_{n=\pm 1, \pm 2} G_{nij} e^{in\omega_r t} \right\} \frac{1}{2} (2I_{zi} I_{zj} - (I_{xi} I_{yi} + I_{yi} I_{yj}))$$

$$H(t) = (\Delta\omega + \sigma_{iso}) I_{zi}$$

$$+ \sum_{m=-2}^2 \sigma_{0i} \{ |g_1| \cos(\omega_r t + \psi_1 + \gamma) + |g_1| \cos(2\omega_r t + \psi_2 + 2\gamma) \} I_{zi}$$

$$+ \sum_{m=2}^2 \Delta_{ij} \{ |G_1| \cos(\omega_r t + \gamma) + |G_1| \cos 2(\omega_r t + \gamma) \} \frac{1}{2} (2I_{zi} I_{zj} - (I_{xi} I_{yi} + I_{yi} I_{yj}))$$

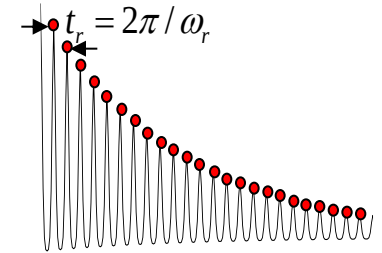


The vector representation of the MAS "CSA-only" NMR case

As long as the Bloch vector represents the nuclear magnetization:

$$\Theta(t) = \Delta\omega t + \frac{\Delta\sigma|g_1|}{\omega_r} (\sin(\omega_r t + \psi_1 + \gamma) - \sin(\psi_1 + \gamma)) + \frac{\Delta\sigma|g_2|}{2\omega_r} (\sin(2\omega_r t + \psi_2 + 2\gamma) - \sin(\psi_2 + 2\gamma))$$

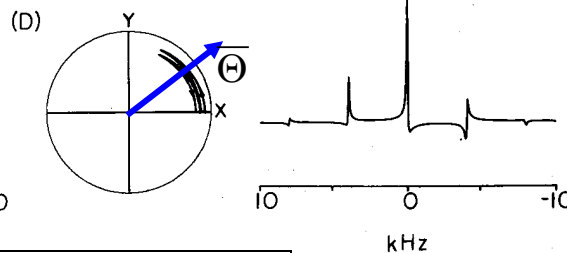
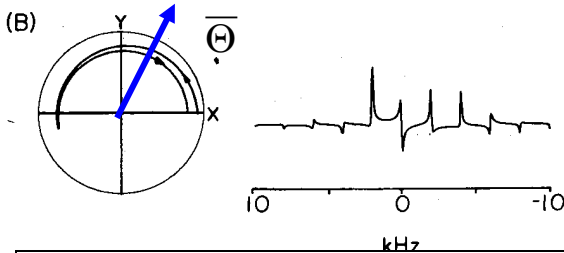
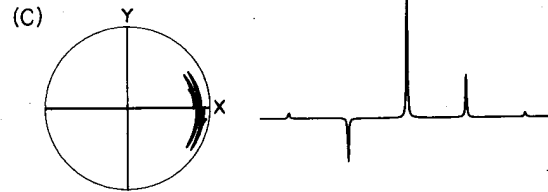
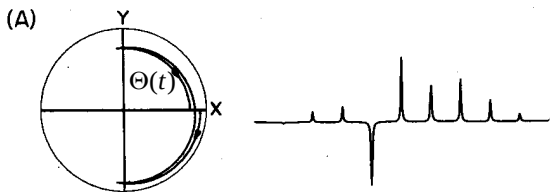
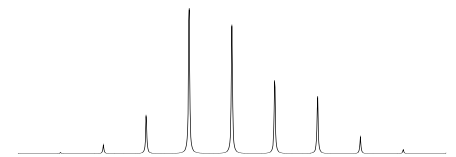
$$\overline{\Theta} = -\frac{\Delta\sigma|g_1|}{\omega_r} \sin(\psi_1 + \gamma) - \frac{\Delta\sigma|g_2|}{2\omega_r} \sin(\psi_2 + 2\gamma)$$



FT

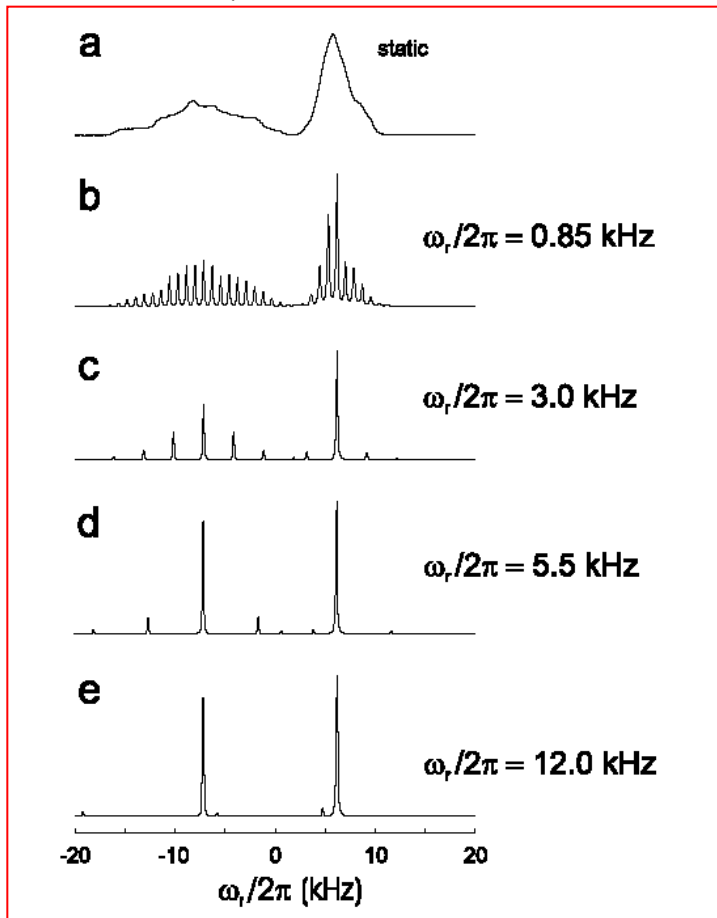
time

Frequency

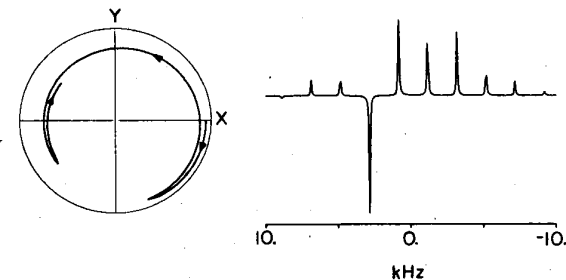


x-y magnetization vectors
of single crystallites after 90° pulse:

The vector representation of the MAS "CSA-only" NMR case



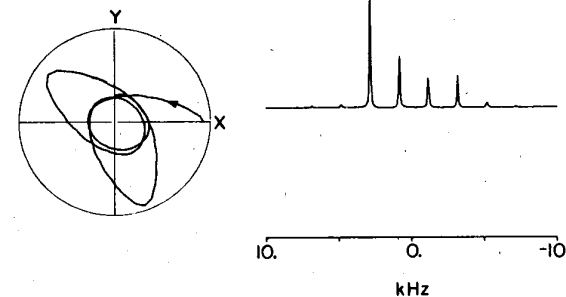
a single crystal



$$\int_0^{2\pi} d\gamma S(\alpha, \beta, \gamma; t)$$

integral over γ only

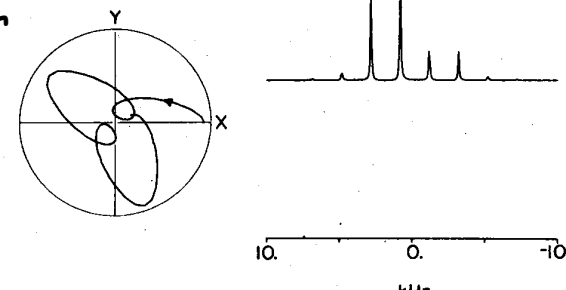
(B)



$$\int_0^{2\pi} d\alpha \int_0^{\pi} \cos \beta d\beta \int_0^{2\pi} d\gamma S(\alpha, \beta, \gamma; t)$$

(C)

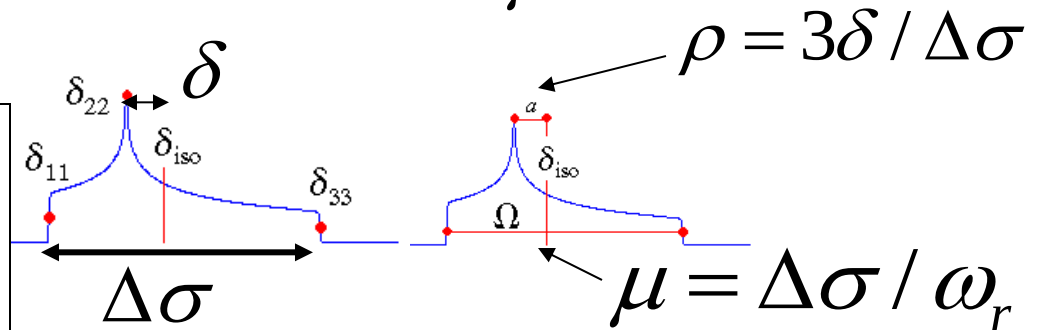
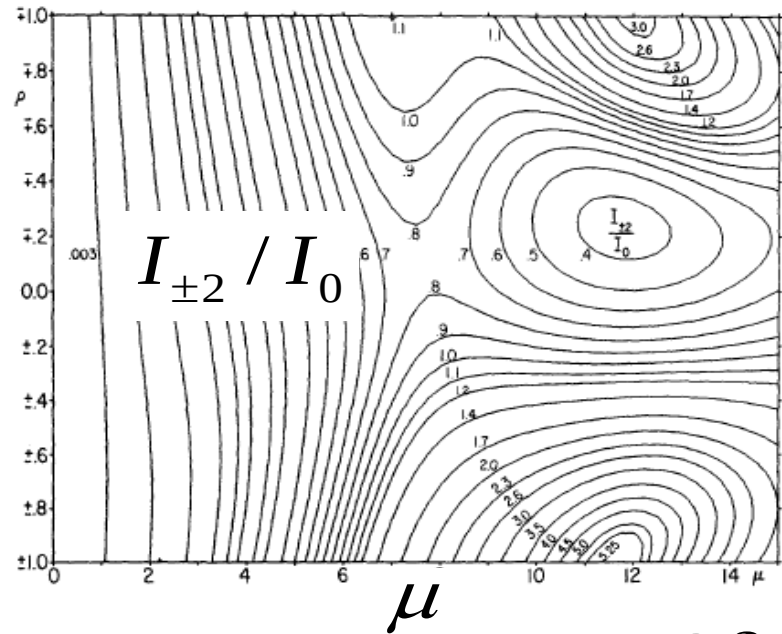
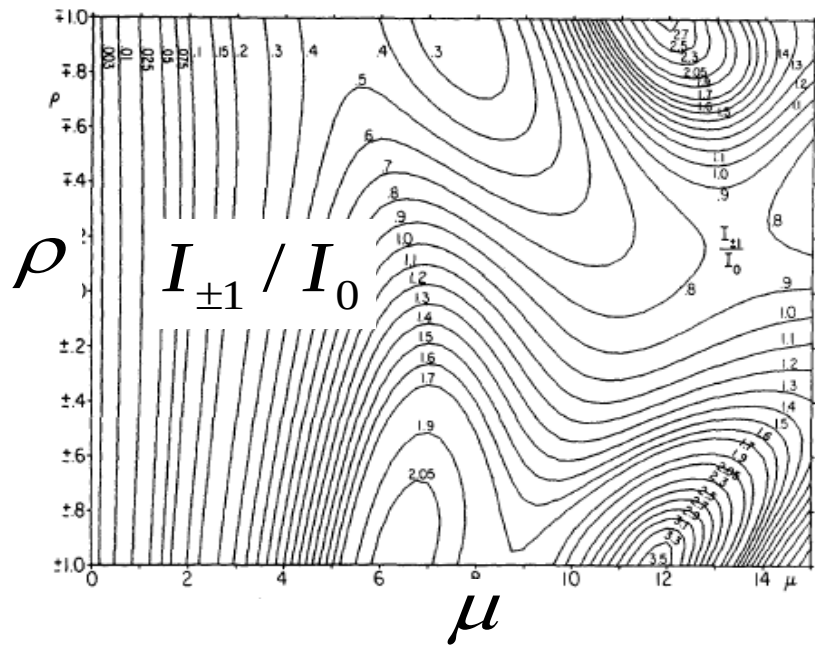
isotropic powder

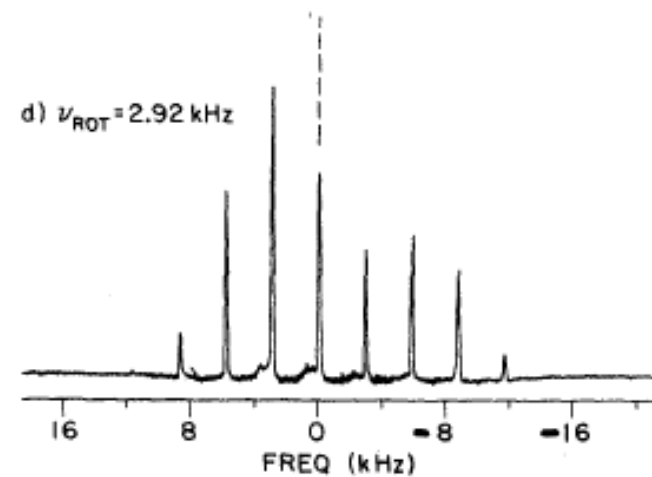
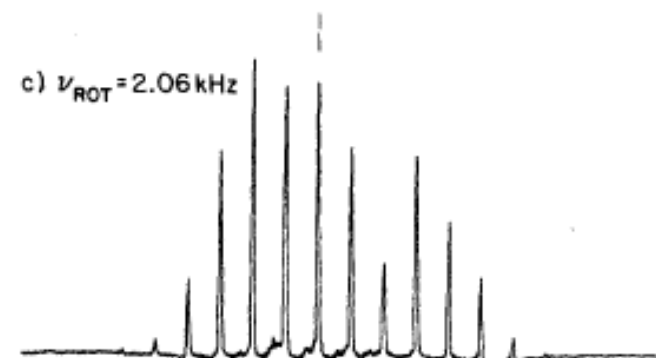
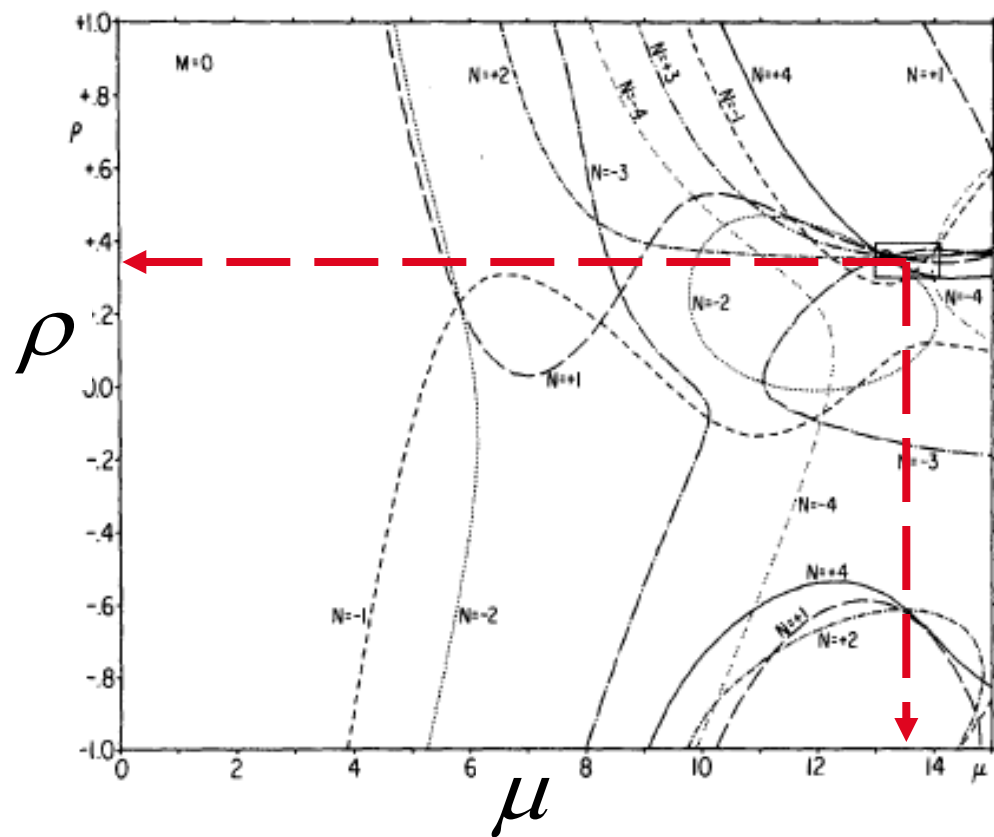


The effect of the heteronuclear dipolar interaction on a spin behaves similarly

Herzfeld-Berger Analysis:

<http://casgm3.anorg.chemie.uni-tuebingen.de/klaus/soft/hba/hba.html>





Cross Polarization Magic Angle Spinning

$$H(t) = \Delta\omega_i I_{zi}^H + \sum_{n=-2}^2 \Delta_{ij}^{H-H} \left\{ \sum_{n=\pm 1, \pm 2} G_{n,ij}^{H-H} e^{in\omega_r t} \right\} \frac{1}{2} (2I_{zi}^H I_{zj}^H - (I_{xi}^H I_{xi}^H + I_{yi}^H I_{yj}^H))$$

$$+ \sum_{n=-2}^2 \Delta_i^{H-C} \left\{ \sum_{n=\pm 1, \pm 2} G_{n,i}^{H-C} e^{in\omega_r t} \right\} I_{zi}^H I_z^C$$

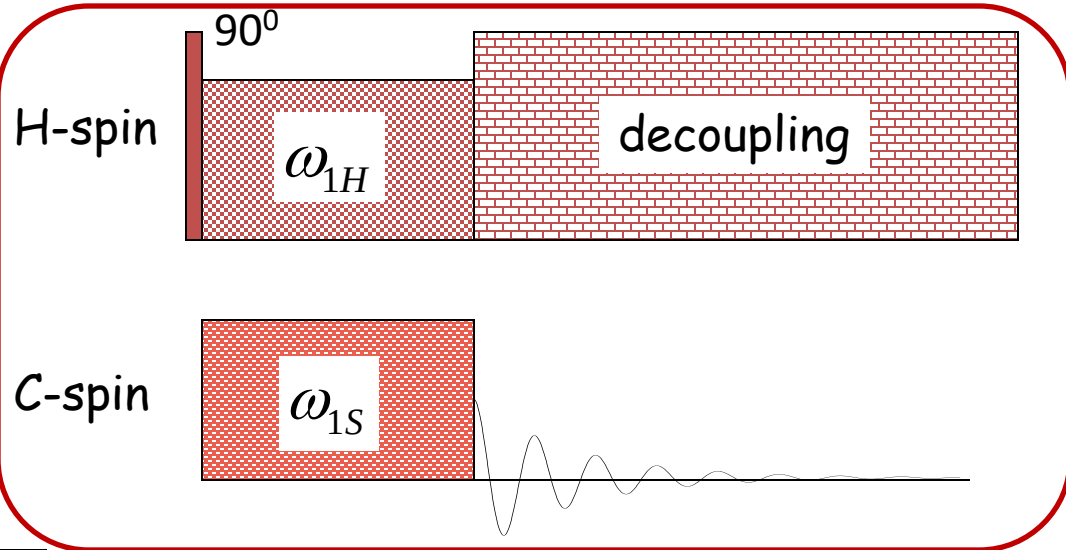
$$+ \omega_{1H} I_x^H + \omega_{1C} I_x^C$$

$$H(t) = \omega_{1H} I_x^H + \omega_{1C} I_x^C + G_{n,i}^{H-C} I_{zi}^H H_z^C e^{in\omega_r t}$$

↓

$$H(t) = \omega_{1H} I_z^H + \omega_{1C} I_z^C + G_{n,i}^{H-C} I_{xi}^H H_x^C e^{in\omega_r t}$$

$$\rho(0) = A_H I_{xi}^H \longrightarrow \rho(0) = A_H I_{zi}^H$$



$$H(t) = \begin{pmatrix} \omega_{1H} + \omega_{1C} & & \Delta^{H-C} G_n^* e^{-in\omega_r t} \\ & \omega_{1H} - \omega_{1C} & \Delta^{H-C} G_n^* e^{-in\omega_r t} \\ & \Delta^{H-C} G_n e^{in\omega_r t} & -\omega_{1H} + \omega_{1C} \\ \Delta^{H-C} G_n e^{-in\omega_r t} & & & -\omega_{1H} - \omega_{1C} \end{pmatrix}$$

Schaefer's CPMAS-Hartman-Hahn Condition

$$(\omega_{1H} - \omega_{1C}) = n\omega_r$$

Variable Amplitude CP MAS

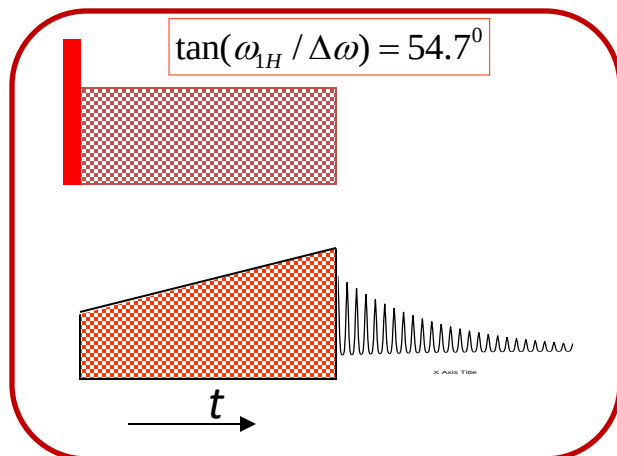
Passing through the H-H Condition

O. Peersen, X. Wu, I. Kustanovich,
S.E. Schmidt, JMR A109, 334 (1993)
S. Zhang, C. Czekaz, W.T. Ford,
JMR A111, 87 (1994)
an others

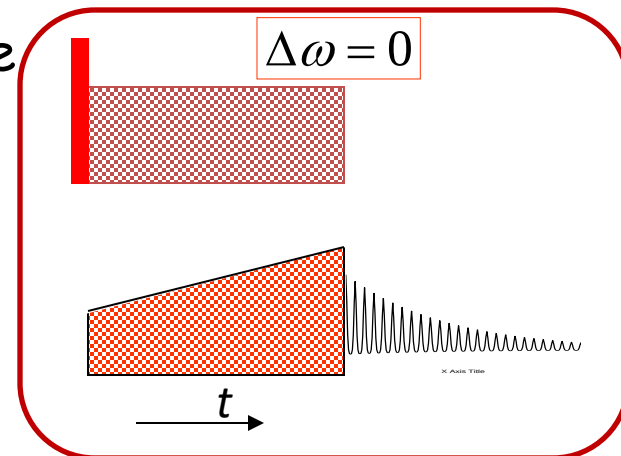
LG-CPMAS

Inhomogeneous B_1
Appr. Adiabatic passage

VA-CPMAS

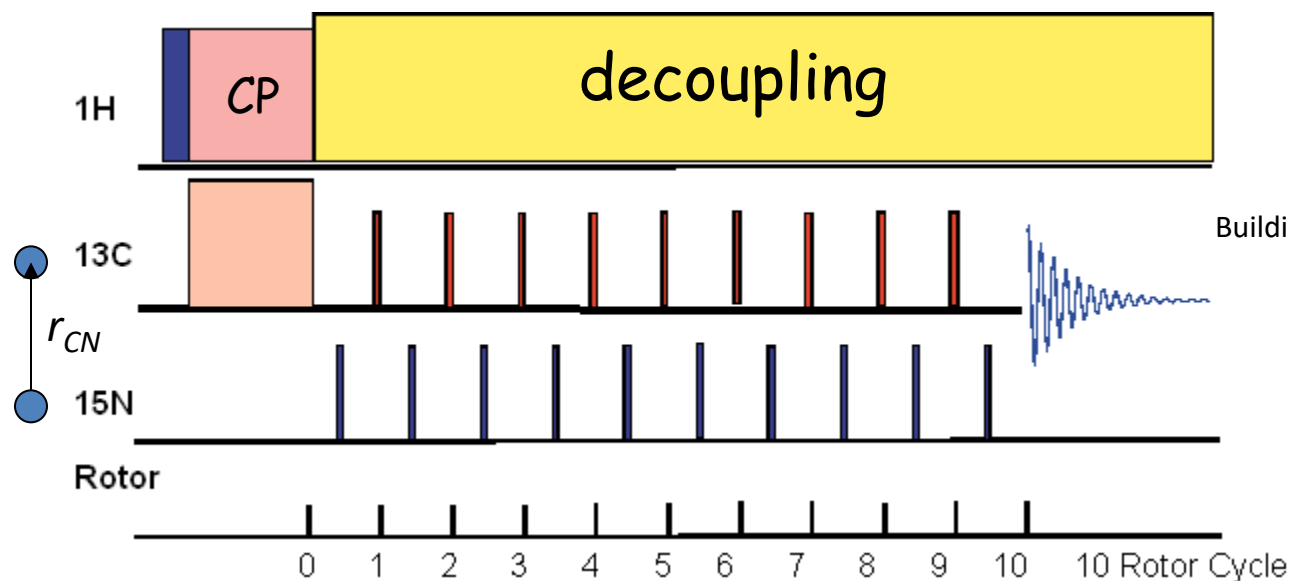


$$|\omega_{1I} - \omega_{1S}(t)| = n\omega_r$$

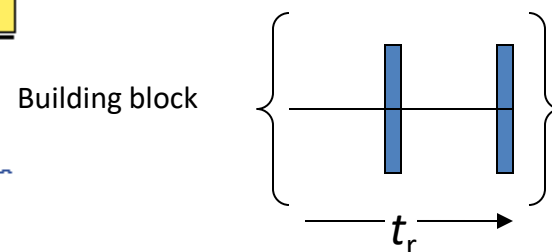


REDOR:

J. Mag. Res. 81 196 - 200 (1989) Terry Gullion and Jacob Schaefer.



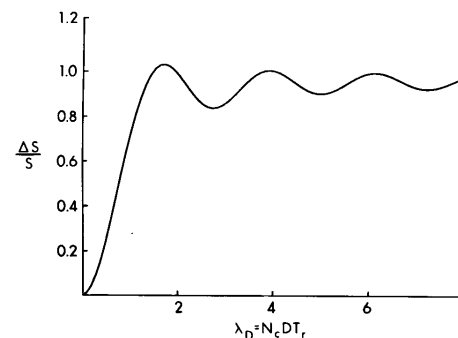
REDOR decay+Hahn echo



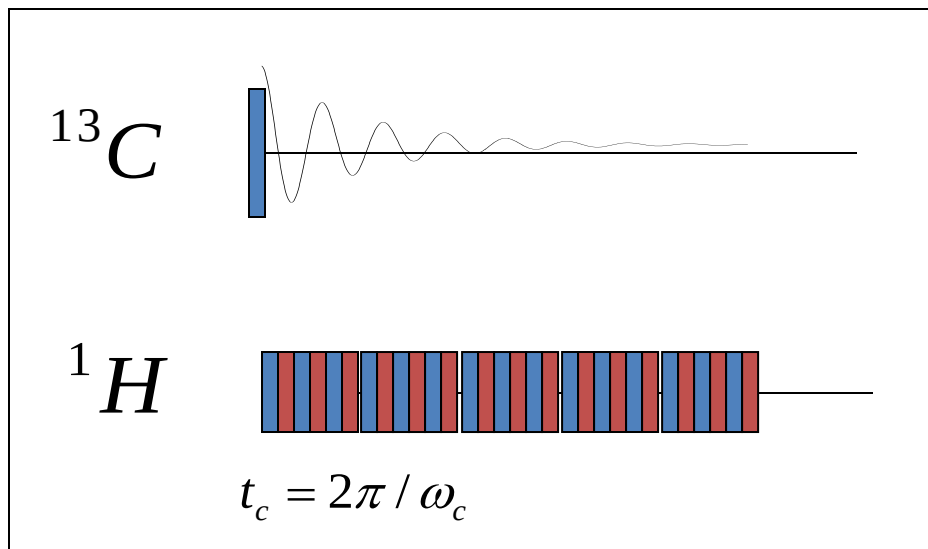
$$\frac{\Delta S}{S} = \frac{S_0(nt_r) - S_{\text{REDOR}}(nt_r)}{S_0(nt_r)} = (1 - F_{\text{REDOR}}(nt_r \omega_D))$$

universal curve:

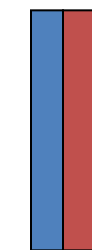
PAN, GULLION, AND SCHAEFER



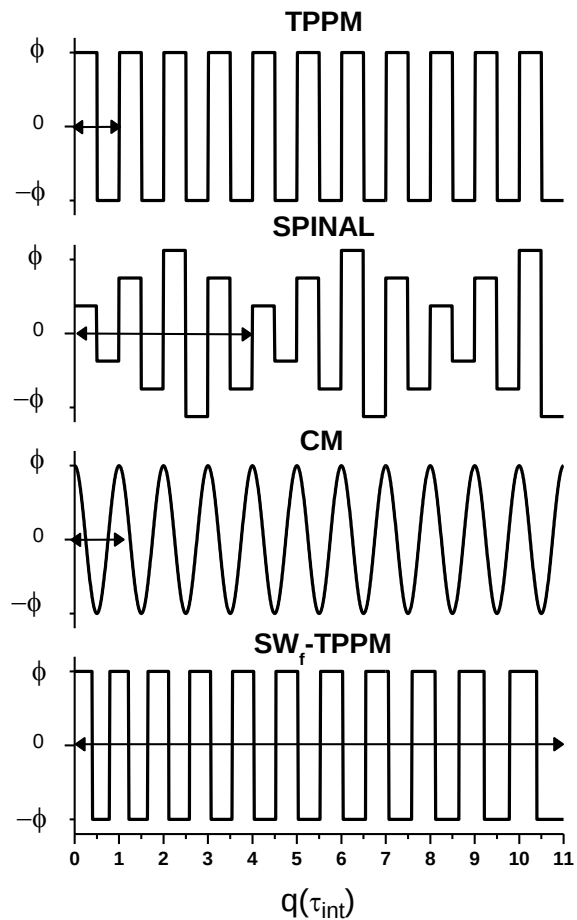
Heteronuclear TPPM decoupling



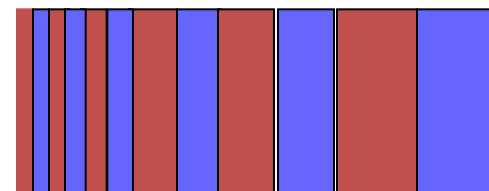
$$\varphi \geq 180^\circ$$



$$\pm \varphi$$



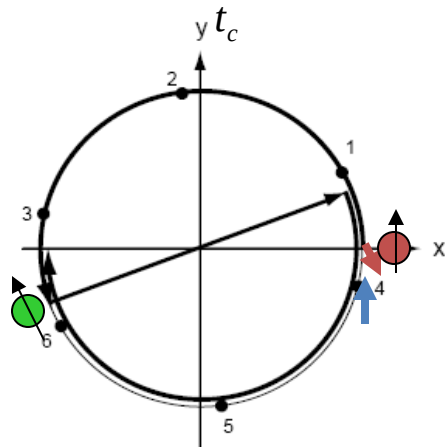
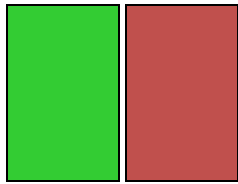
$$\omega_1$$



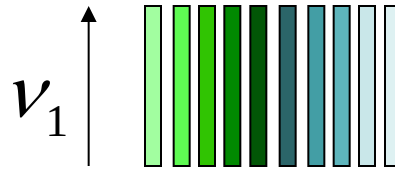
†

Homonuclear decoupling

FSLG

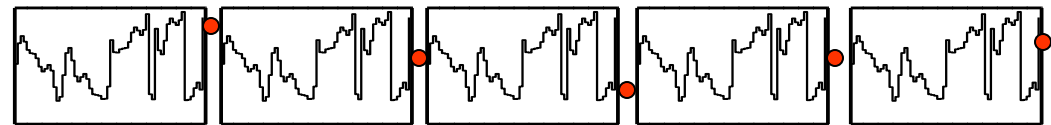
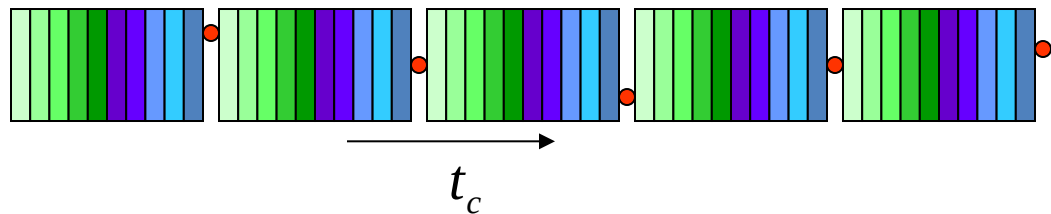


PMLG-5

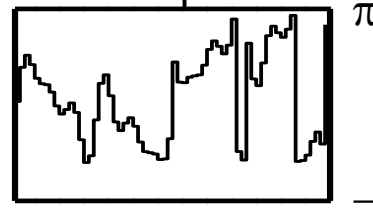


20.78, 62.34, 103.9, 145.46, 187.02
7.02, 325.46, 283.39, 242.34, 200.78

Phase dependence



Phase dependence

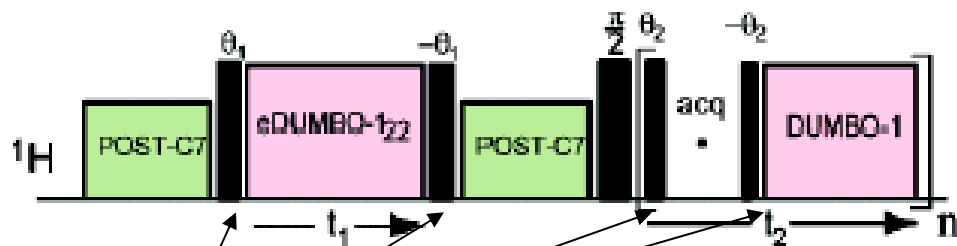
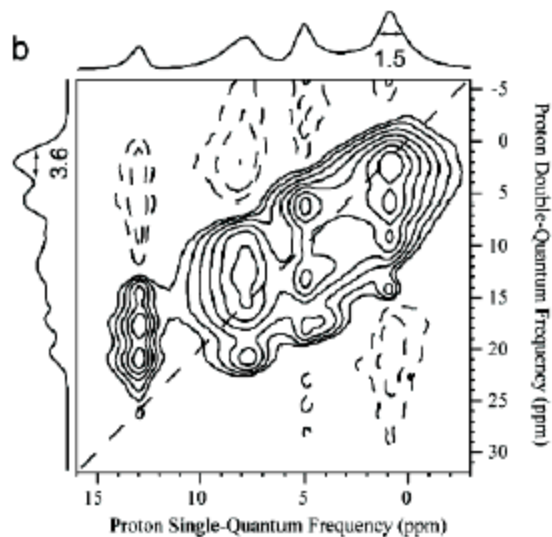
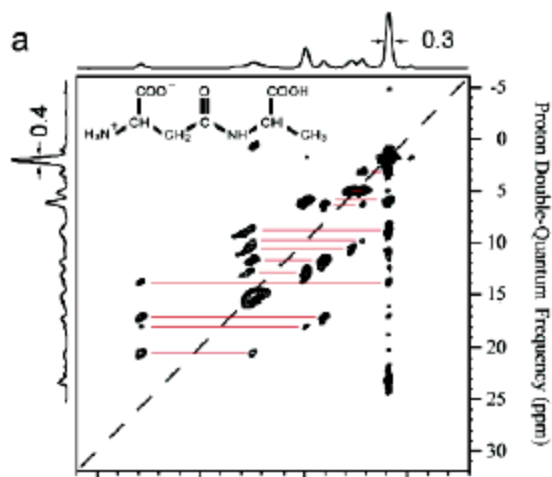


optimized 7 Fourier components
64 pulses

DUMBO

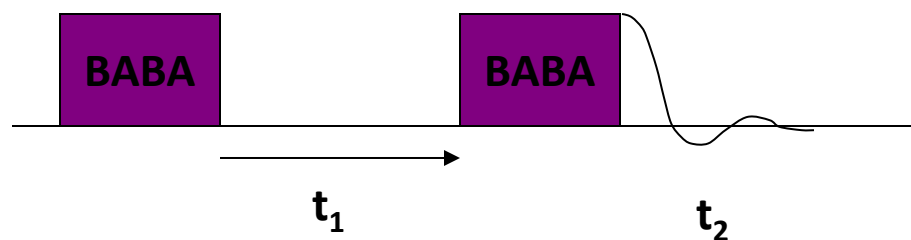
Emsley et al., (2000)

β -AspAla



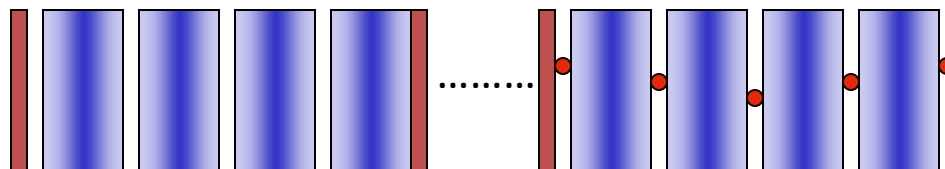
Two-Dimensional ^1H - ^1H Double-Quantum CRAMPS NMR Spectroscopy
 Steven P. Brown, Anne Lesage,
 Benedicte Elena, and Lyndon Emsley

J. AM. CHEM. SOC. 2004, 126, 13230-13231



For BABA see: Schnell, I.; Spiess, H. W. *J. Magn. Reson.* 2001, 151, 153.

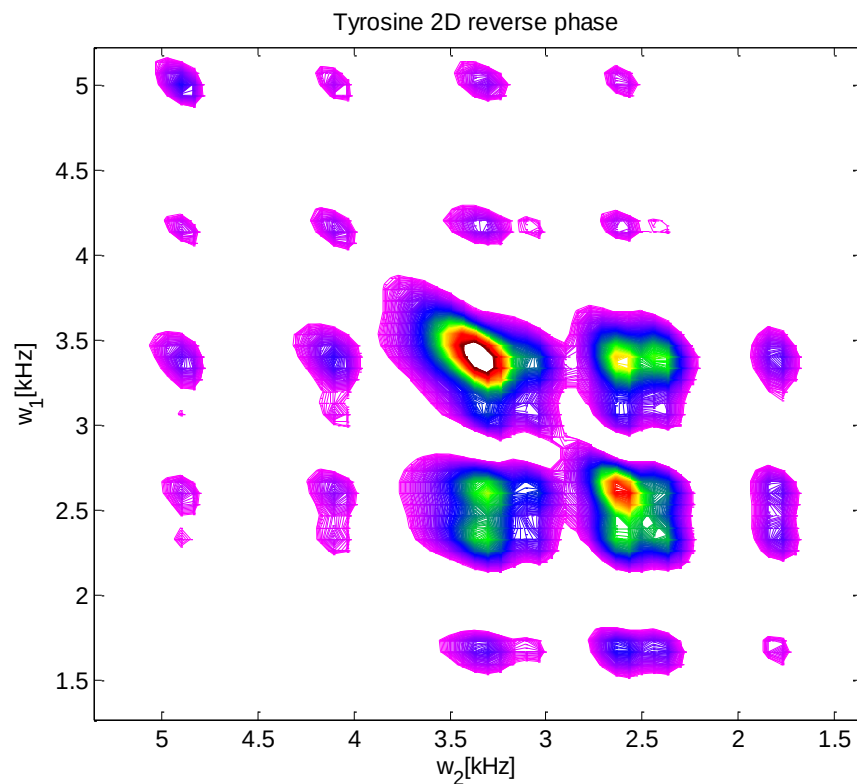
z-axis rotation – no need for “magic-angle” pulses



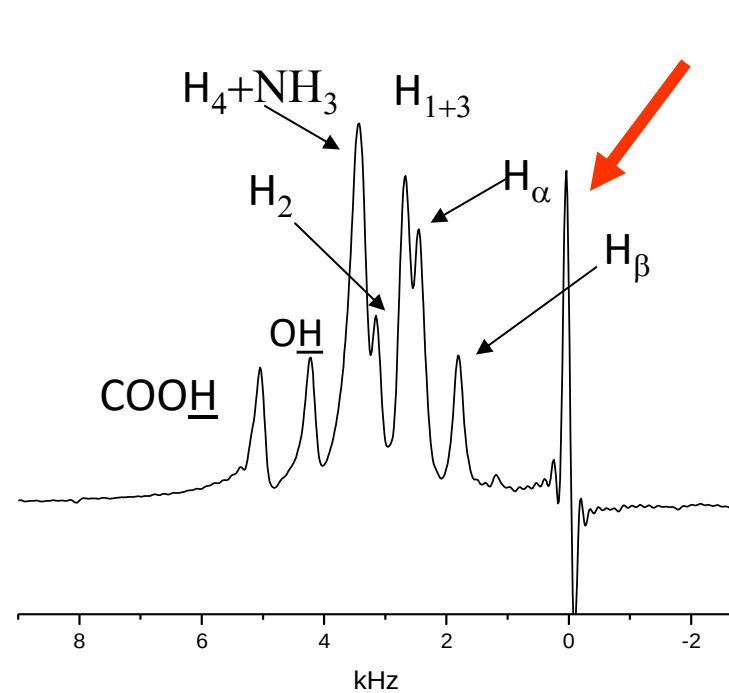
wPMLG5

-

wPMLG5

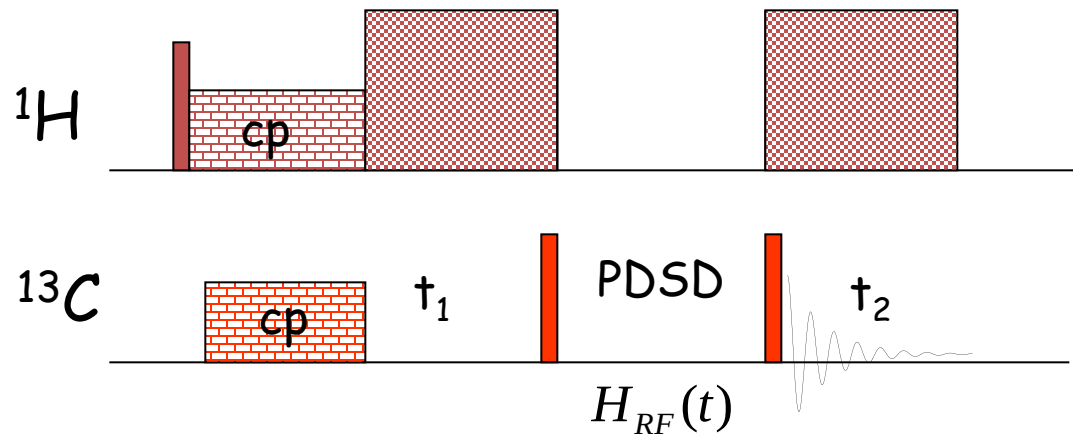


^1H - ^1H correlation spectrum



proton driven spin diffusion

In the mixing time:



RAD\ DARR

$$\omega_1 = \omega_r$$

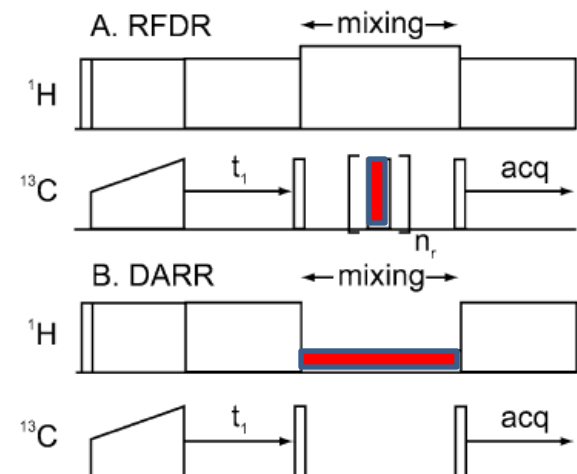


Figure 2. Pulse sequences for the RFDR (A) and DARR (B) experiments. Both sequences begin with VACP using a ramped pulse on the ^{13}C channel. After the evolution period, magnetization is placed along the z-axis with a 90° pulse and mixing occurs longitudinally with either a high power ^1H decoupling pulse in RFDR or a low power ^1H 'recoupling' pulse in DARR. During the DARR mixing period, the ^1H RF field strength is set to the $n = 1$ rotational resonance condition. In the RFDR experiment, mixing is driven by a train of rotor synchronized 180° pulses on the ^{13}C channel. Two pulse phase modulated decoupling is used during acquisition and evolution.