Basic principles of NMR

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PowerPoint 2004

for MacOS

Summary of the lecture

Summary of the lecture

① Bloch vector model

② Basic quantum mechanics

③ Product operator formalism

④ Spin hamiltonian

⑤ NMR building blocks

⑥ Coherence selection - phase cycling

⑦ Pulsed field gradients

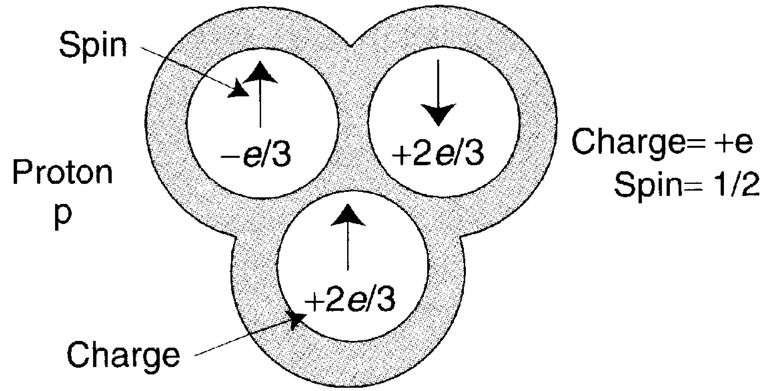
Nuclei observable by NMR

Table 1.1. Properties of some nuclides of importance to NMR.

nuclide	I	gyromagnetic Ratio γ [10^7 rad T^{-1} s^{-1}]	Natural Abundance [%]	NMR frequency [MHz] (B_0=2.3488 T)
^1H	1/2	26.7519	99.985	100.0
^2H	1	4.1066	0.015	15.351
^3H	1/2	28.5350	-.	106.664
^{12}C	0	.	98.9	-.
^{13}C	1/2	6.7283	1.108	25.144
^{14}N	1	1.9338	99.63	7.224
^{15}N	1/2	-2.7126	0.37	10.133
^{19}F	1/2	25.1815	100.	94.077
^{31}P	1/2	10.8394	100.	40.481

Why some nuclei have no spin ?

The proton is composed of 3 quarks stuck together by gluons



	^{12}C	^{13}C	^{14}N
Atomic number	6	6	7
Mass number	6+6	6+7	7+7
Spin quantum number	0	1/2	1

Why some nuclei have no spin ?

Isotopes with odd mass number

(^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P)

→ S = 1/2, 3/2 …

Isotopes with even mass number

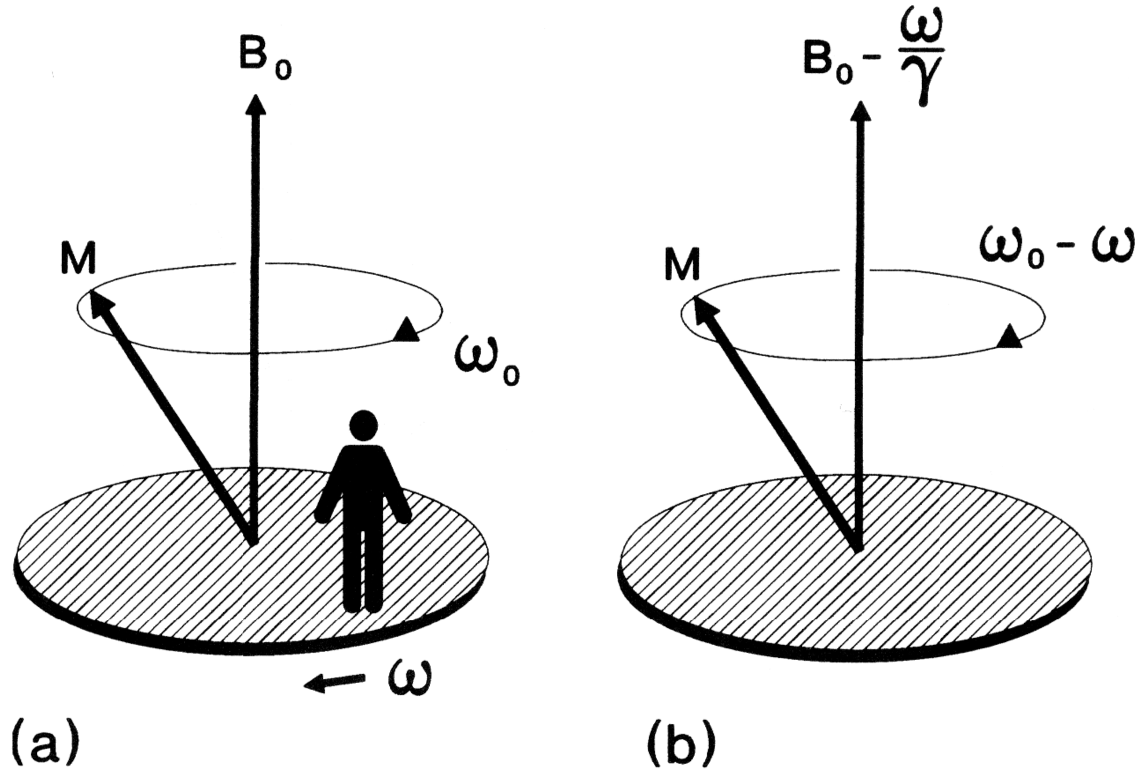
Number of protons and neutron even

→ S = 0

Number of protons and neutron odd

→ S=1, 2, 3 …

Larmor frequency



Laboratory
reference frame

$$\frac{d\vec{M}}{dt} = -\gamma \vec{B}_0 \wedge \vec{M}$$

Rotating
reference frame
at frequency ω

Bloch equations without relaxation

$$\frac{d\dot{\mathbf{M}}}{dt} = -\gamma \vec{B}_0 \wedge \vec{M}$$

B_0 static magnetic field

M macroscopic magnetization

$\wedge$ Cross-product

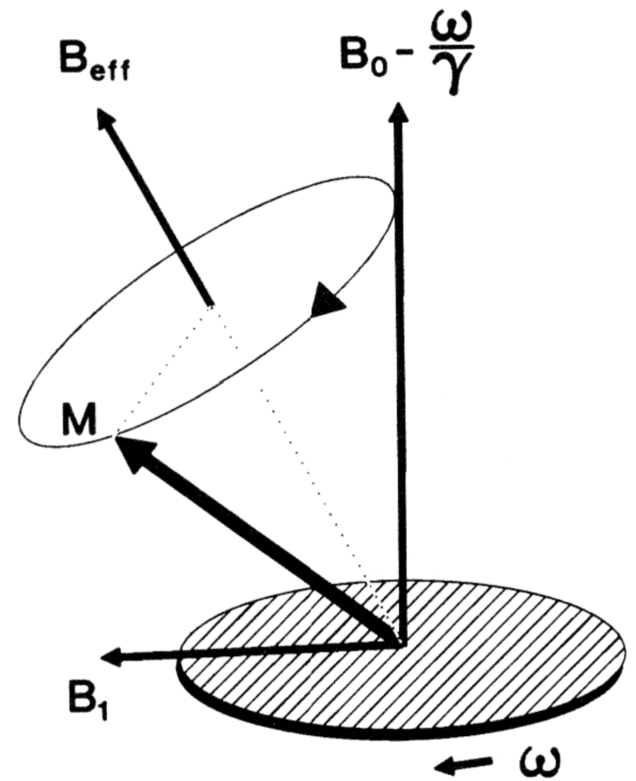
B_1 r.f. magnetic field

$$B_{eff} = \sqrt{B_1^2 + \left(B_0 - \omega / \gamma\right)^2}$$

$$\frac{d}{dt} M_x = -\gamma \left(B_y M_z - B_z M_y\right)$$

$$\frac{d}{dt} M_y = -\gamma \left(B_z M_x - B_x M_z\right)$$

$$\frac{d}{dt} M_z = -\gamma \left(B_x M_y - B_y M_x\right)$$



Bloch equations with relaxation

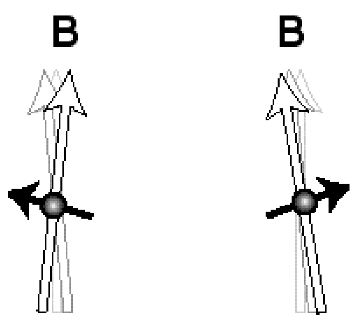
90° pulse ⇨ Magnetization in the XY plane

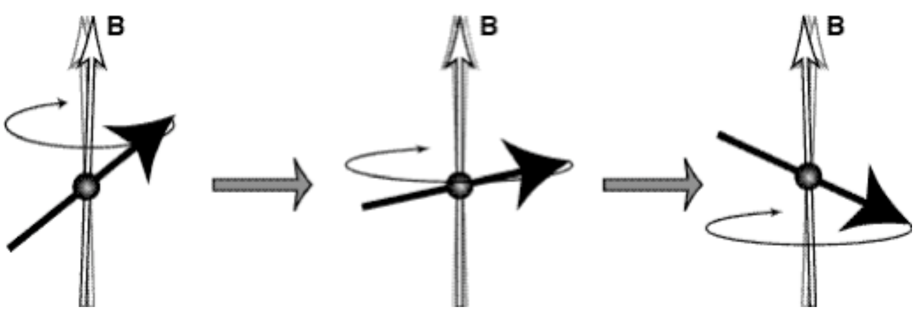
Precession around B_0

Recovery to the equilibrium state ?

Longitudinal magnetization ↗ Transverse magnetization ↘

Spin-lattice relaxation T_1





Thermal motion

⇒ Fluctuating magnetic field

Precession in a fluctuating magnetic field

Non isotropic motion

Magnetization ⇒ Thermal equilibrium

Bloch equations with relaxation

90° pulse ⇨ Magnetization in the XY plane

Precession around B_0

Recovery to the equilibrium state ?

Longitudinal magnetization ↗

Transverse magnetization ↘

Bloch equations with relaxation

90º pulse ⇨ Magnetization in the XY plane

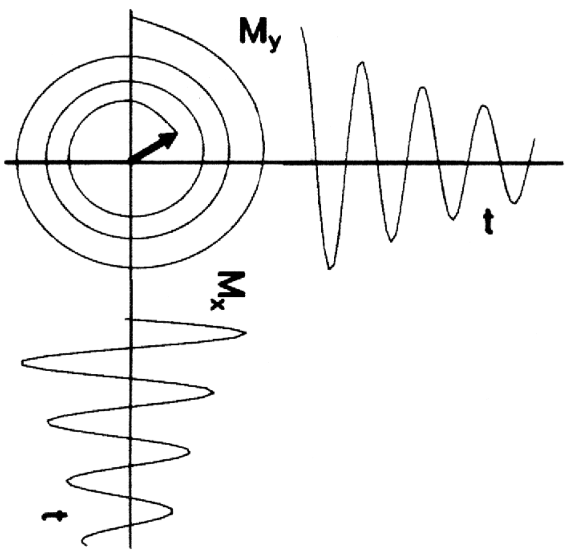
Precession around B_0

Recovery to the equilibrium state ?

Longitudinal magnetization ➚

Transverse magnetization ➘

Spin-spin relaxation T_2



The individual magnetic dipoles all have slightly different precession frequencies

- ✪ True T_2 relaxation
- ✪ B_0 inhomogeneity

Precession in the transverse plane

Bloch equations with relaxation

90° pulse ⇨ Magnetization in the XY plane

Precession around B_0

Recovery to the equilibrium state ?

Longitudinal magnetization ↗

Transverse magnetization ↘

Bloch equations with relaxation

90^o pulse ⇨ Magnetization in the XY plane

Precession around B_0

Recovery to the equilibrium state ?

Longitudinal magnetization ↗

Transverse magnetization ↘

$$\frac{d\dot{M}}{dt} = -\gamma \vec{B}_{eff} \wedge \vec{M}$$

Bloch equations with relaxation

90° pulse ⇨ Magnetization in the XY plane

Precession around B_0

Recovery to the equilibrium state ?

Longitudinal magnetization ↗

Transverse magnetization ↘

$$\frac{d\vec{M}}{dt} = -\gamma \vec{B}_{eff} \wedge \vec{M}$$

Subtitution $\vec{B}_{eff}$ *by* $\left[B_1, 0, \left(B_0 - \omega / \gamma\right)\right]$

Incorporation of T_1 and T_2 relaxation times

Bloch equations with relaxation

90° pulse ⇨ Magnetization in the XY plane

Precession around B_0

Recovery to the equilibrium state ?

Longitudinal magnetization ↗ Transverse magnetization ↘

$$\frac{d\vec{M}}{dt} = -\gamma \vec{B}_{eff} \wedge \vec{M}$$

Bloch equations with relaxation

90° pulse ⇨ Magnetization in the XY plane

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Recovery to the equilibrium state ?

Longitudinal magnetization ↗ Transverse magnetization ↘

$$\frac{d\vec{M}}{dt} = -\gamma \vec{B}_{eff} \wedge \vec{M}$$

$$\frac{d}{dt}M_x = (\omega_0 - \omega)M_y - \frac{1}{T_2}M_x$$

$$\frac{d}{dt}M_y = -(\omega_0 - \omega)M_x - \frac{1}{T_2}M_y + \omega_1 M_z$$

$$\frac{d}{dt}M_z = -\omega_1 M_y - \frac{1}{T_1}(M_z - M_0)$$

Bloch equations with relaxation

90° pulse ⇨ Magnetization in the XY plane

Precession around B_0

Recovery to the equilibrium state ?

Longitudinal magnetization ↗

Transverse magnetization ↘

$$\frac{d\vec{M}}{dt} = -\gamma \vec{B}_{eff} \wedge \vec{M}$$

Longitudinal and transverse relaxation mechanisms are independent

$$\frac{d}{dt}M_x = (\omega_0 - \omega)M_y - \frac{1}{T_2}M_x$$

$$\frac{d}{dt}M_y = -(\omega_0 - \omega)M_x - \frac{1}{T_2}M_y + \omega_1 M_z$$

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Bloch equations with relaxation

90° pulse ⇨ Magnetization in the XY plane

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Recovery to the equilibrium state ?

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Bloch equations with relaxation

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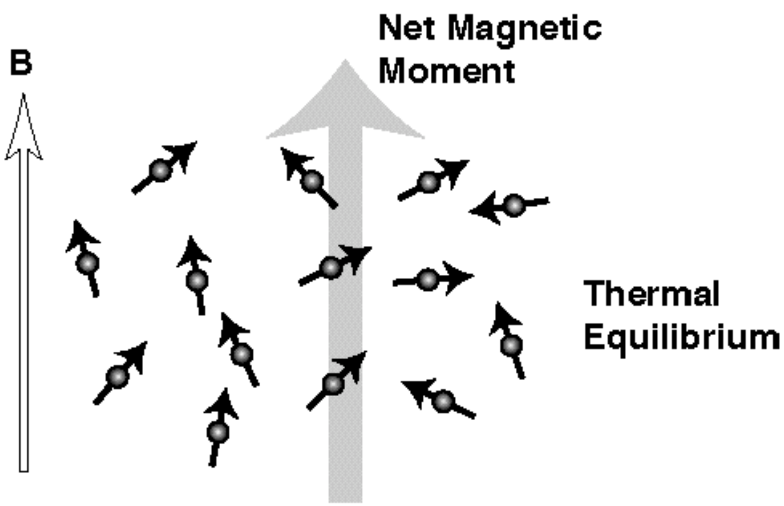
rf pulses connect the z axis with the transverse xy plane

Longitudinal and transverse magnetization



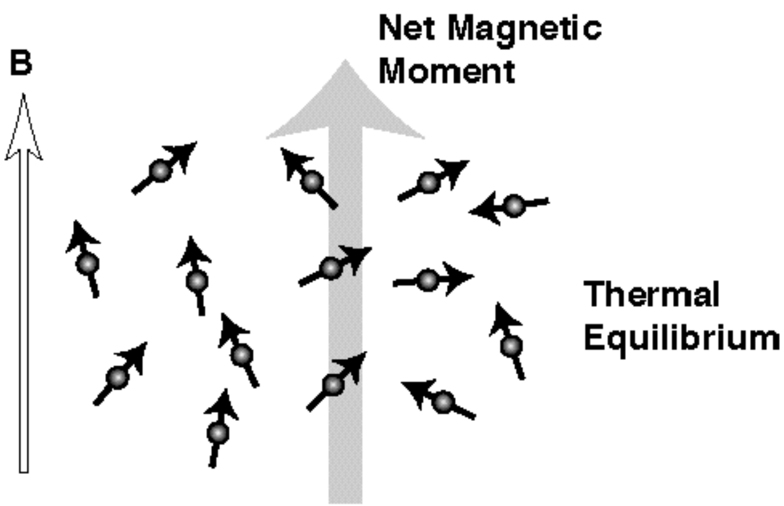
Thermal equilibrium

$$\frac{N_{+1/2}}{N_{-1/2}} = \exp\left(\frac{1/2\,h\,\gamma B_0}{k_B T}\right) / \exp\left(\frac{-1/2\,h\,g B_0}{k_B T}\right)$$

$$\frac{N_{+1/2}}{N_{-1/2}} = \frac{1 + \frac{1/2\,h\,g B_0}{k_B T}}{1 + \frac{-1/2\,h\,\gamma B_0}{k_B T}} \approx 1 + \frac{\eta\gamma B_0}{k_B T}$$

Longitudinal magnetization

Longitudinal and transverse magnetization



Thermal equilibrium

$$\frac{N_{+1/2}}{N_{-1/2}} = \exp\left(\frac{1/2\hbar\gamma B_0}{k_B T}\right) / \exp\left(\frac{-1/2\hbar\gamma B_0}{k_B T}\right)$$

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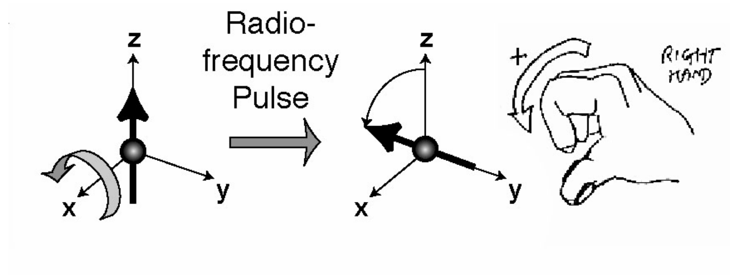
At room temperature « 1

Longitudinal magnetization

Longitudinal and transverse magnetization



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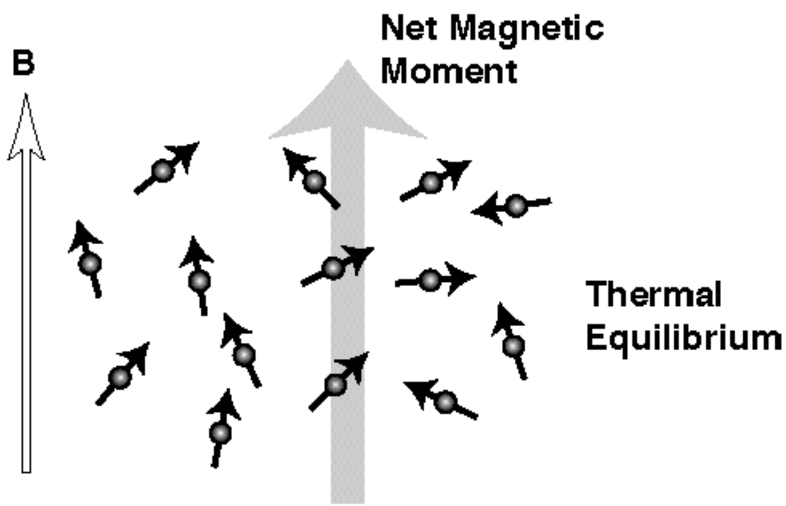
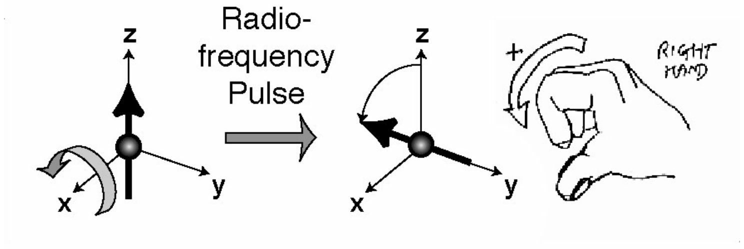


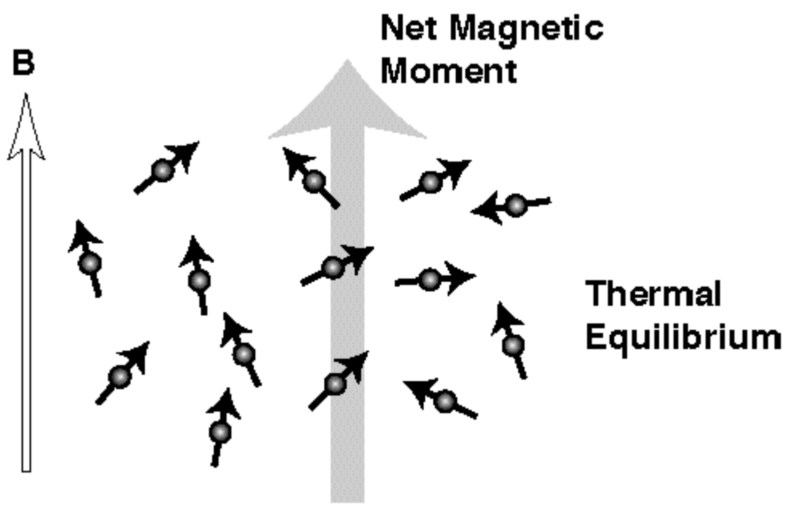
Thermal equilibrium

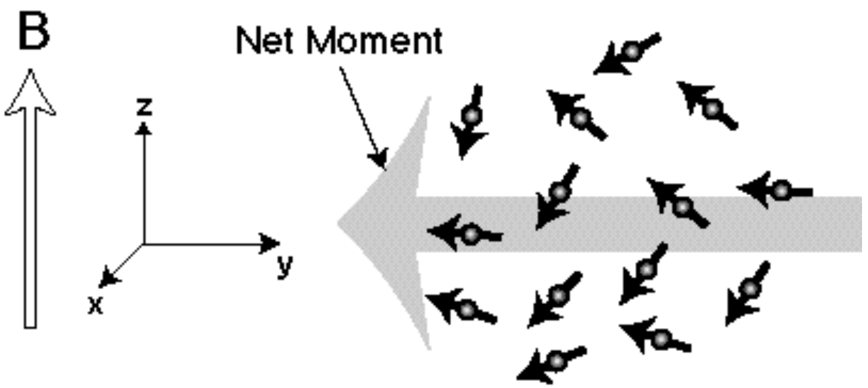
At room temperature « 1

Longitudinal magnetization

Longitudinal and transverse magnetization







Thermal equilibrium

Transverse magnetization

Longitudinal magnetization

Coherence

Bloch equations with relaxation

What are the limitations of the Bloch equations?

Bloch equations with relaxation

What are the limitations of the Bloch equations?

Planes : no collision

Bloch equations with relaxation

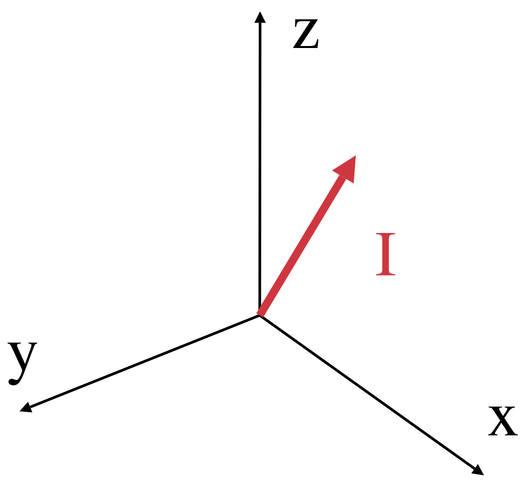
What are the limitations of the Bloch equations?

Planes : no collision

Cars : collision

The limitations of the Bloch equations

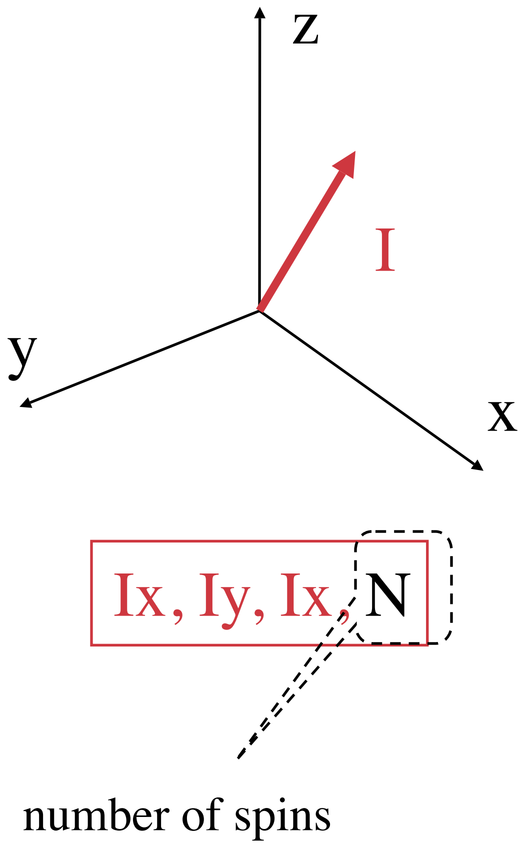
Suitable dimensionality for description



Ix, Iy, Ix, N

The limitations of the Bloch equations

Suitable dimensionality for description



The limitations of the Bloch equations

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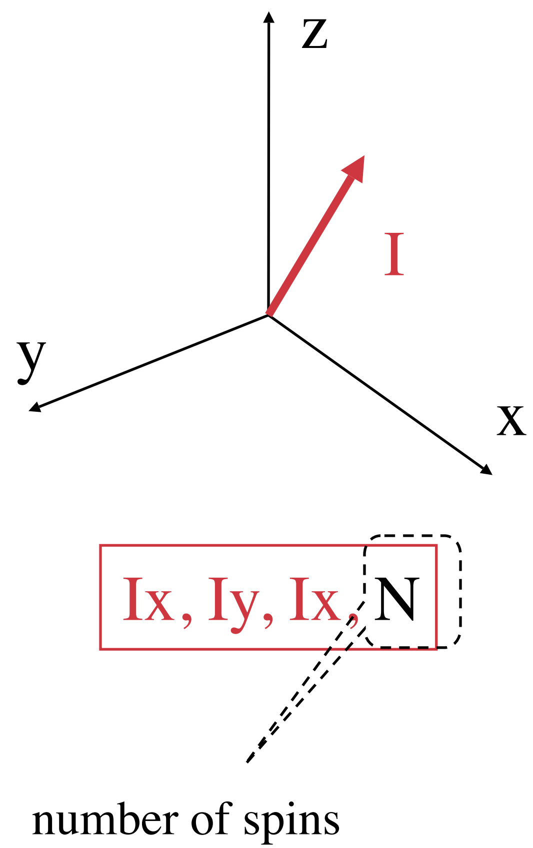

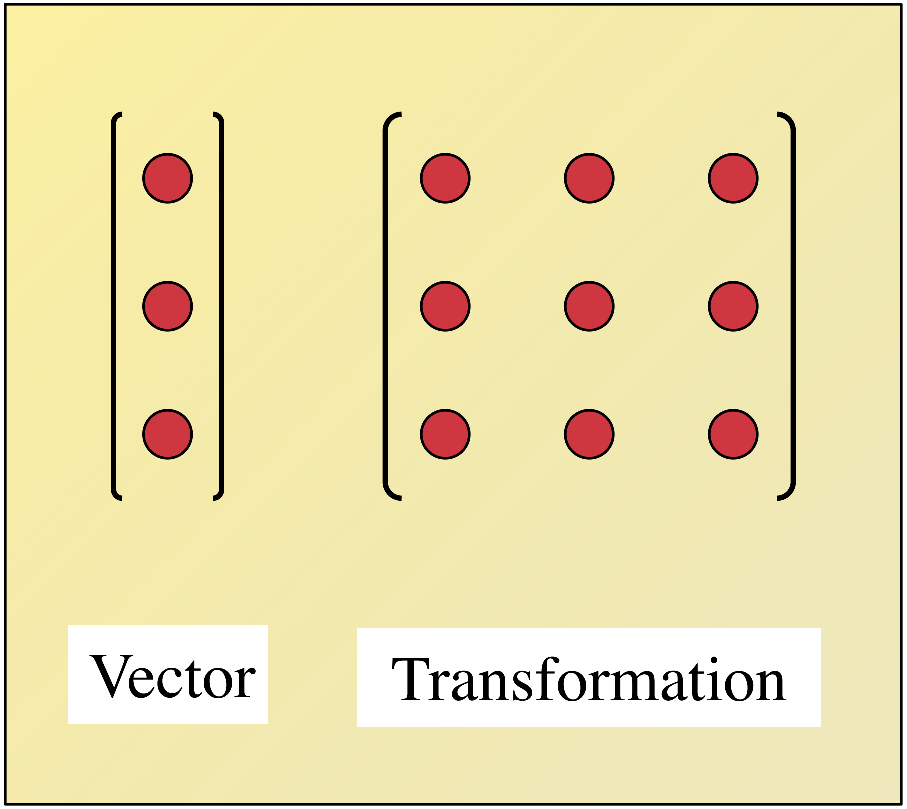

The limitations of the Bloch equations

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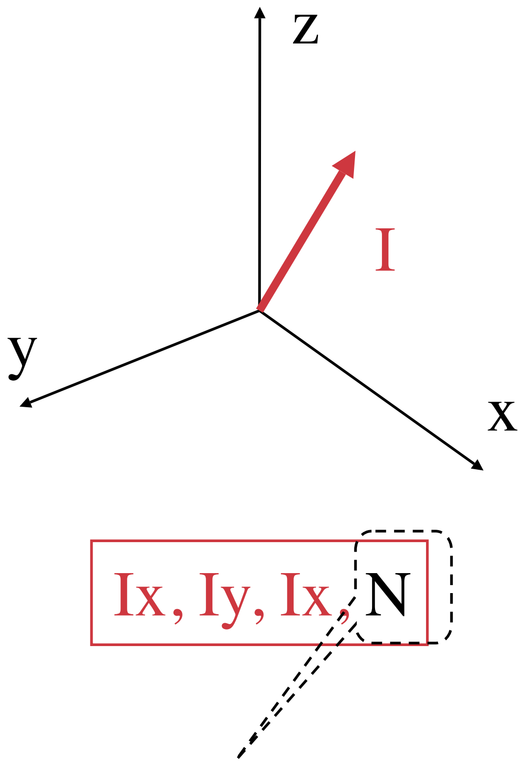
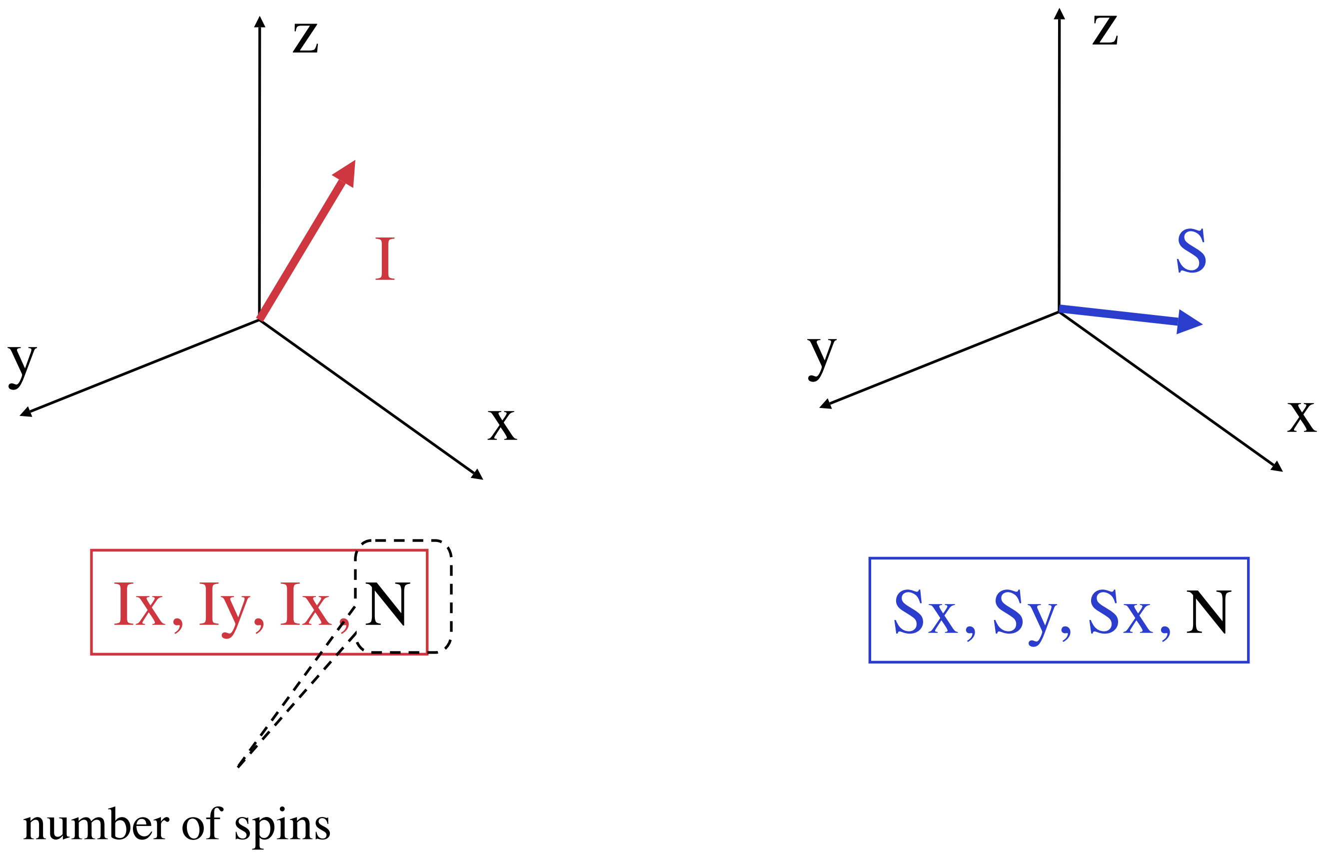


number of spins

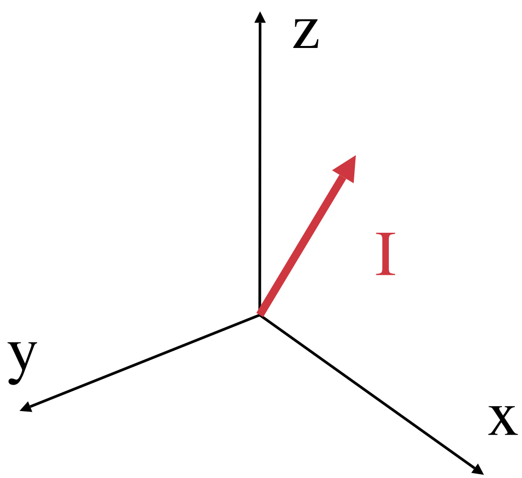
The limitations of the Bloch equations

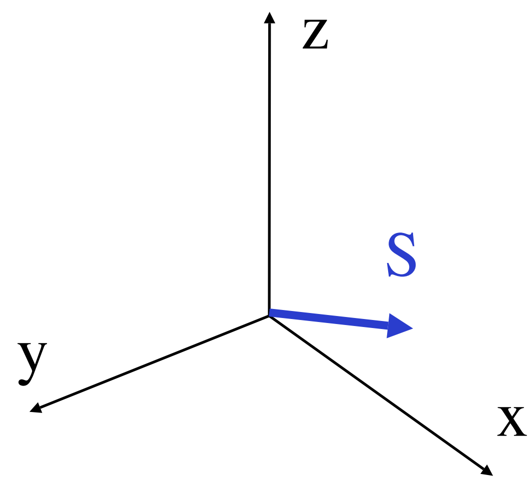
Suitable dimensionality for description



The limitations of the Bloch equations

Suitable dimensionality for description





Ix, Iy, Ix, N

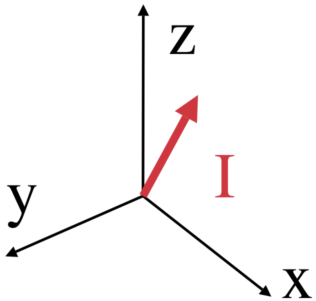
number of spins

Sx, Sy, Sx, N

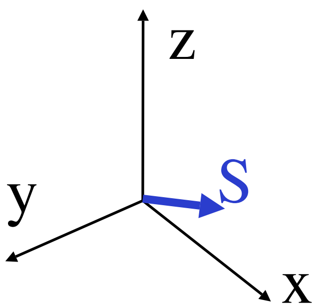
Additional terms if I and S interact

The limitations of the Bloch equations

Suitable dimensionality for description



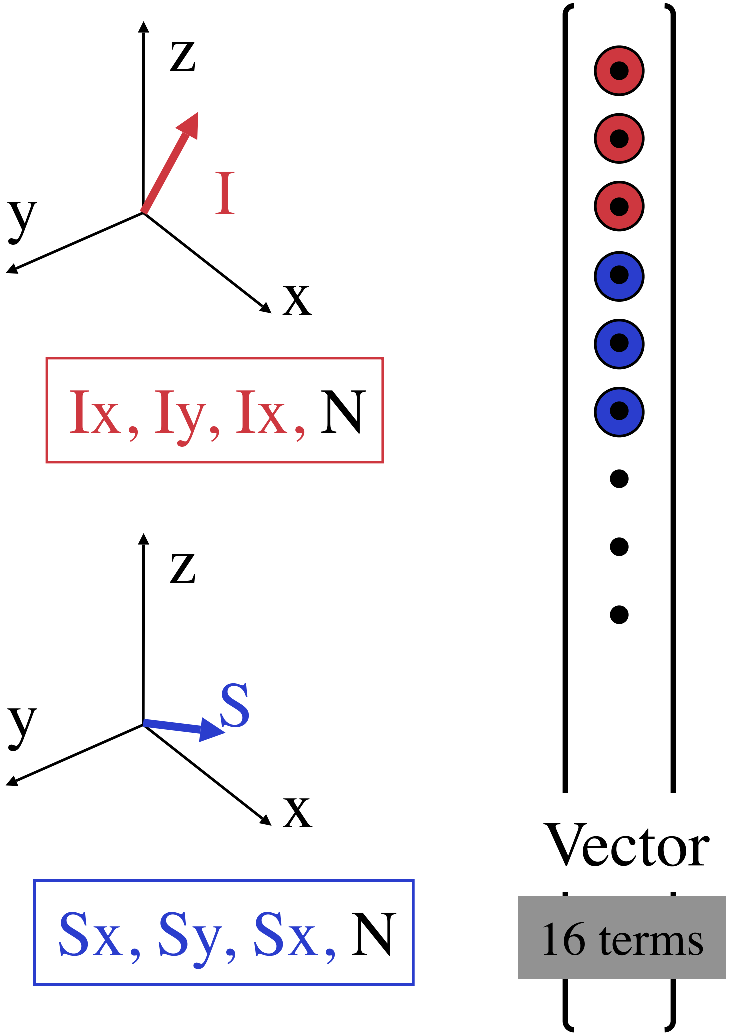
Ix, Iy, Ix, N



Sx, Sy, Sx, N

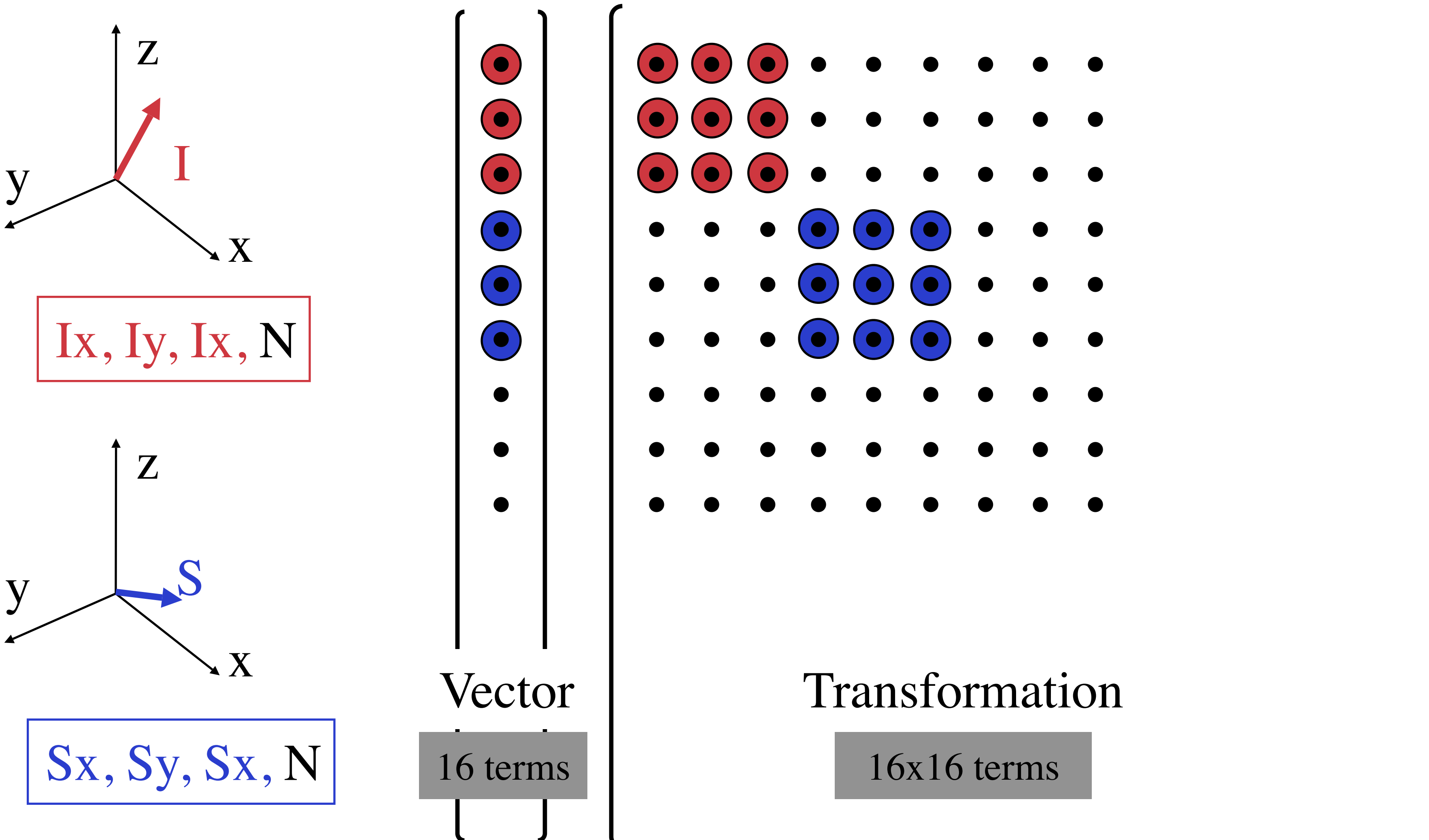
The limitations of the Bloch equations

Suitable dimensionality for description



The limitations of the Bloch equations

Suitable dimensionality for description



Basic Quantum Mechanics

Operator

Performs some operation on a function

Ex: D_x derivative operator $$D_x \; f(x) = \frac{d \; f(x)}{dx}$$

Ex: $\mathbb{1}$ unity operator $\mathbb{1} f(x) = f(x)$

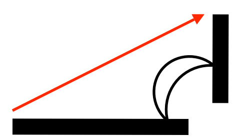
Commutation

The effect of consecutive operations may depends on their order

Drive straight for 100 m

Turn left

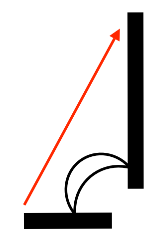
Drive straight for 50 m



Drive straight for 50 m

Turn left

Drive straight for 100 m



$$B\{A(\, f(x) \,)\} \overset{?}{=} A\{B(\, f(x) \,)\}$$

Commutator

$$[A,B] = AB - BA$$

Basic Quantum Mechanics

Matrix representation of operators

!! The matrix representation depend on the basis

$$A = \begin{pmatrix} A_{11} & A_{12} & \bullet & \bullet \\ A_{21} & A_{22} & \bullet & \bullet \\ \bullet & \bullet & \bullet & \bullet \\ \bullet & \bullet & \bullet & \bullet \end{pmatrix}$$

Product of two operators A.B

$$(AB)_{ij} = \sum_k A_{ik} \times B_{kj}$$

Usual law for matrix multiplication

Inverse

$$AB = AB = \mathbb{1}$$

$$A = B^{-1}$$

Adjoint

$$A_{ij} = B_{ji}^*$$

$$A = B^\dagger$$

Hermitian operator

$$A = A^\dagger$$

Unitary operator

$$A^{-1} = A^\dagger$$

Basic Quantum Mechanics

Eigenvalues

Change of basis → Diagonal matrix

$$A = \begin{pmatrix} \lambda_{11} & 0 & \bullet & \bullet \\ 0 & \lambda_{22} & \bullet & \bullet \\ \bullet & \bullet & \lambda_{33} & \bullet \\ \bullet & \bullet & \bullet & \lambda_{44} \end{pmatrix}$$

$$\mathbf{A}\ |v_i> = \lambda_i\ |v_i>$$

Operator

Eigenvector

Eigenvalue

(complex number)

Basic Quantum Mechanics

Eigenvalues

Change of basis ➡ Diagonal matrix

$$A = \begin{pmatrix} \lambda_{11} & 0 & \bullet & \bullet \\ 0 & \lambda_{22} & \bullet & \bullet \\ \bullet & \bullet & \lambda_{33} & \bullet \\ \bullet & \bullet & \bullet & \lambda_{44} \end{pmatrix}$$

$$\mathbf{A}\, |v_i\rangle = \lambda_i\, |v_i\rangle$$

Operator

Eigenvector

Eigenvalue
(complex number)

Orthogonal eigenvectors

Real eigenvalues

Hermitian operator

$$A = A^{\dagger}$$

Basic Quantum Mechanics

Eigenvalues

Change of basis ➡ Diagonal matrix

$$A = \begin{pmatrix} \lambda_{11} & 0 & \bullet & \bullet \\ 0 & \lambda_{22} & \bullet & \bullet \\ \bullet & \bullet & \lambda_{33} & \bullet \\ \bullet & \bullet & \bullet & \lambda_{44} \end{pmatrix}$$

$$\mathbf{A} \, |v_i> = \lambda_i \, |v_i>$$

Operator → $\mathbf{A}$

Eigenvector → $|v_i>$

Eigenvalue (complex number) → λ_i

Hermitian operator

$A = A^\dagger$

Orthogonal eigenvectors

Real eigenvalues

If [A,B] = 0

i.e. A and B commute

∃ Basis such that

A and B diagonal

$$A = \begin{pmatrix} \lambda_{11} & 0 & \bullet & \bullet \\ 0 & \lambda_{22} & \bullet & \bullet \\ \bullet & \bullet & \lambda_{33} & \bullet \\ \bullet & \bullet & \bullet & \lambda_{44} \end{pmatrix}$$

$$B = \begin{pmatrix} \mu_{11} & 0 & \bullet & \bullet \\ 0 & \mu_{22} & \bullet & \bullet \\ \bullet & \bullet & \mu_{33} & \bullet \\ \bullet & \bullet & \bullet & \mu_{44} \end{pmatrix}$$

Basic Quantum Mechanics

Exponential operators

❶ Power of operators

$\mathbf{A}^0 = \mathbb{1}$ $\quad \mathbf{A}^1 = \mathbf{A}$ $\quad \mathbf{A}^2 = \mathbf{AA}$ $\quad \mathbf{A}^3 = \mathbf{AAA}$

Basic Quantum Mechanics

Exponential operators

❶ Power of operators

$\mathbf{A}^0 = \mathbb{1}$ $\mathbf{A}^1 = \mathbf{A}$ $\mathbf{A}^2 = \mathbf{AA}$ $\mathbf{A}^3 = \mathbf{AAA}$

As $[\mathbf{A},\mathbf{A}]=0$ $\mathbf{A}\,|\nu_i> = \lambda_i\,|\nu_i>$ ➡ $\mathbf{A}^n\,|\nu_i> = \lambda_i^n\,|\nu_i>$

All power of an operator have the same eigenvector

Basic Quantum Mechanics

Exponential operators

❶ Power of operators

$\mathbf{A}^0 = \mathbb{1}$ $\mathbf{A}^1 = \mathbf{A}$ $\mathbf{A}^2 = \mathbf{AA}$ $\mathbf{A}^3 = \mathbf{AAA}$

Basic Quantum Mechanics

Exponential operators

❶ Power of operators

$$\mathbf{A}^0 = \mathbb{1} \qquad \mathbf{A}^1 = \mathbf{A} \qquad \mathbf{A}^2 = \mathbf{AA} \qquad \mathbf{A}^3 = \mathbf{AAA}$$

❷ Exponential of operators

For ordinary numbers $\exp(q) = 1 + q + \frac{1}{2!}q^2 + \frac{1}{3!}q^3 + \ldots$

For operators $\exp(A) = 1 + A + \frac{1}{2!}A^2 + \frac{1}{3!}A^3 + \ldots$

! exp(A+B) = exp(A) . exp(B) ***only if*** [A,B]=0

Basic Quantum Mechanics

Exponential operators

❶ Power of operators

$\mathbf{A}^0 = \mathbb{1}$ $\mathbf{A}^1 = \mathbf{A}$ $\mathbf{A}^2 = \mathbf{AA}$ $\mathbf{A}^3 = \mathbf{AAA}$

❷ Exponential of operators

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Basic Quantum Mechanics

Exponential operators

❶ Power of operators

$\mathbf{A}^0 = \mathbb{1} \qquad \mathbf{A}^1 = \mathbf{A} \qquad \mathbf{A}^2 = \mathbf{AA} \qquad \mathbf{A}^3 = \mathbf{AAA}$

❷ Exponential of operators

For ordinary numbers $$\exp(q) = 1 + q + \frac{1}{2!}q^2 + \frac{1}{3!}q^3 + \mathrm{K}$$

For operators $$\exp(A) = 1 + A + \frac{1}{2!}A^2 + \frac{1}{3!}A^3 + \mathrm{K}$$

❸ Complex exponential of operators

For operators $$E = \exp(iA) = 1 + iA + \frac{i^2}{2!}A^2 + \frac{i^3}{3!}A^3 + \mathrm{K}$$

A hermitian $A = A^\dagger$ → E unitary $E^{-1} = E^\dagger$

Basic Quantum Mechanics

Cyclic commutation

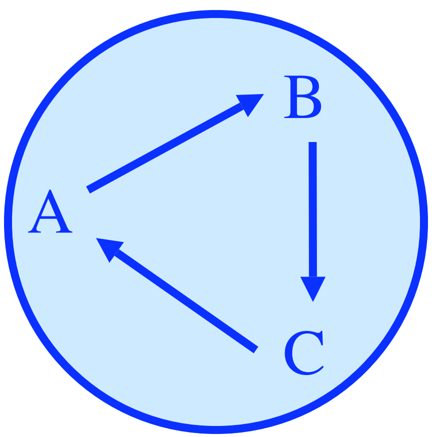
❶ Definition $[\mathbf{A}, \mathbf{B}] = i\mathbf{C}$ $[\mathbf{B}, \mathbf{C}] = i\mathbf{A}$ $[\mathbf{C}, \mathbf{A}] = i\mathbf{B}$

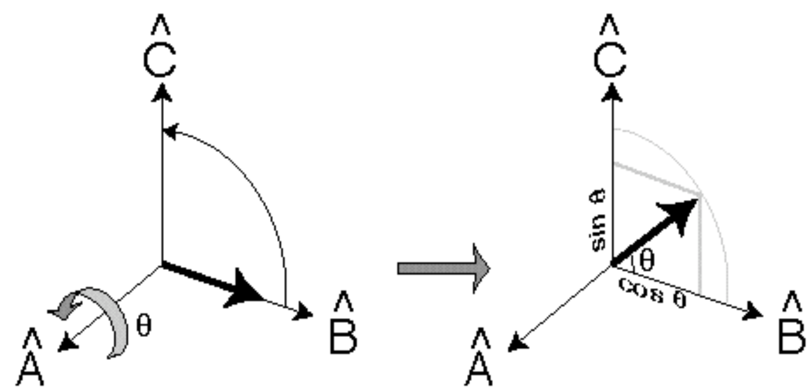
❷ Sandwich formula

Rotation angle

$$\exp(-i\theta\mathbf{A})\,\mathbf{B}\,\exp(i\theta\mathbf{A}) = \mathbf{B}\cos\theta + \mathbf{C}\sin\theta$$

Cyclic permutation

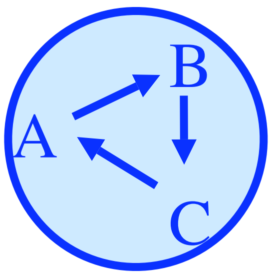




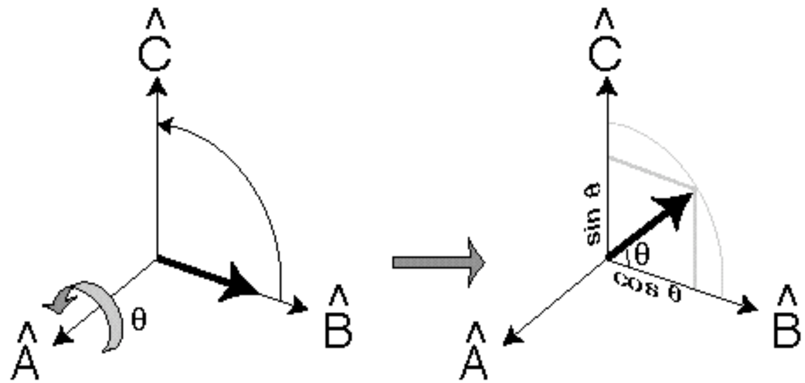
Basic Quantum Mechanics

Cyclic commutation

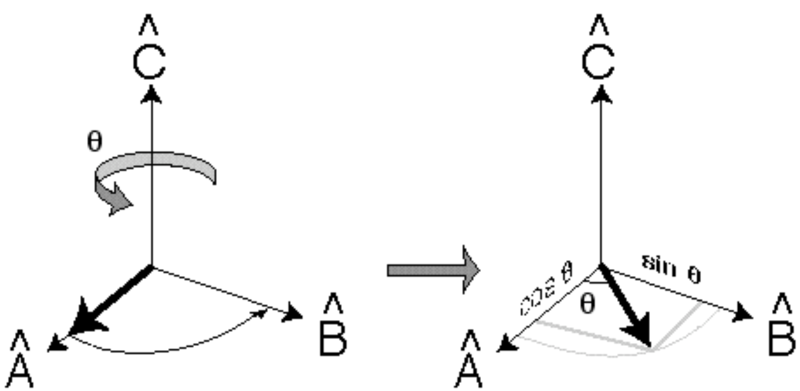
❸ Rotation around the 3 axes



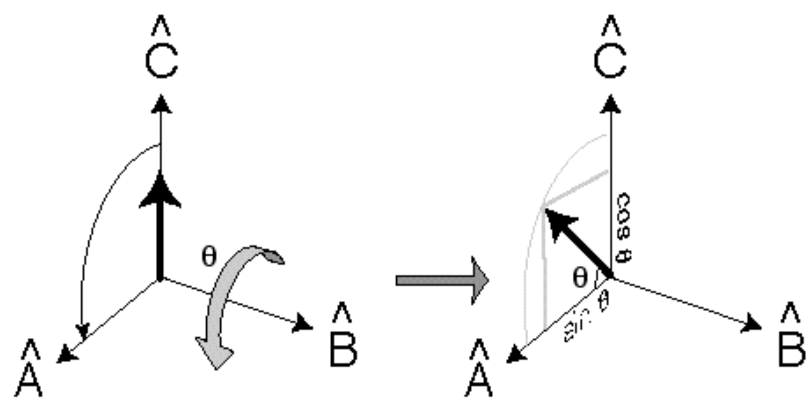
exp (-iθ**A**) **B** exp (iθ**A**) = **B** cos θ + **C** sin θ



exp (-iθ**C**) **A** exp (iθ**C**) = **A** cos θ + **B** sin θ



exp (-iθ**B**) **C** exp (iθ**B**) = **C** cos θ + **A** sin θ



Liouville-von Neumann equation

Classical description

$$\frac{d\vec{M}}{dt} = -\gamma \vec{B}_0 \wedge \vec{M}$$

Magnetic field Magnetization

Liouville-von Neumann equation

Classical description

$$\frac{d\vec{M}}{dt} = -\gamma \vec{B}_0 \wedge \vec{M}$$

Magnetic field

Magnetization

Quantum description

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

Density matrix

Hamiltonian

Liouville-von Neumann equation

Classical description

$$\frac{d\vec{M}}{dt} = -\gamma \vec{B}_0 \wedge \vec{M}$$

Magnetic field — Magnetization

Quantum description

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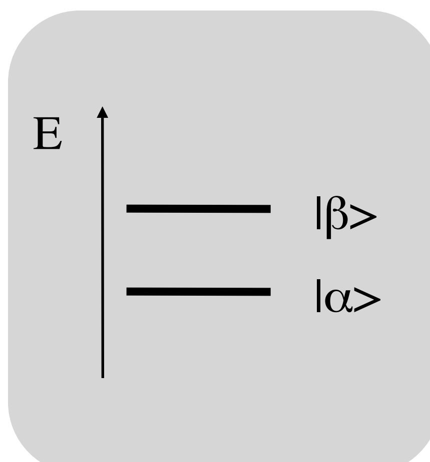
Density matrix — Hamiltonian



Liouville-von Neumann equation

Classical description

$$\frac{d\dot{M}}{dt} = -\gamma \vec{B}_0 \wedge \vec{M}$$

Magnetic field Magnetization

Quantum description

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

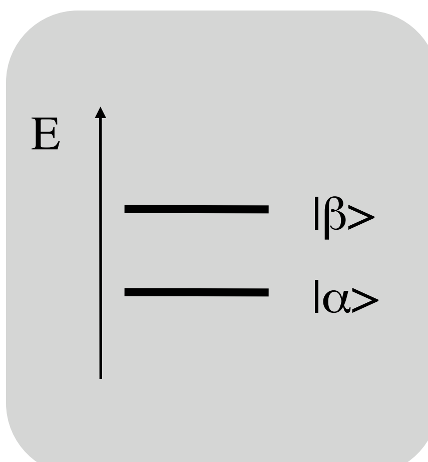
Density matrix Hamiltonian

Single
1/2 spin particle

$|\psi\rangle = c_\alpha |\alpha\rangle + c_\beta |\beta\rangle$

Superposition state

Quantum indeterminacy



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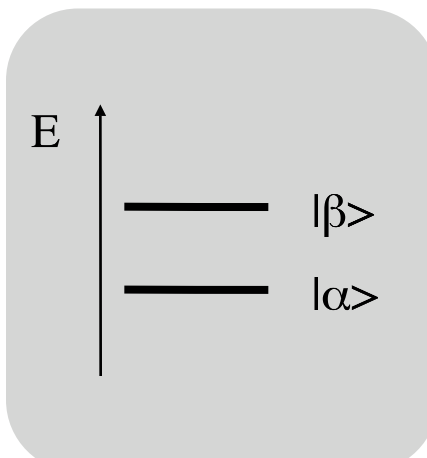


Ensemble of
1/2 spin particles

Density matrix

Ensemble average

$$\sigma = \begin{pmatrix} \sigma_{\alpha\alpha} & \sigma_{\alpha\beta} \\ \sigma_{\beta\alpha} & \sigma_{\beta\beta} \end{pmatrix} = \begin{pmatrix} \overline{c_\alpha c_\alpha^*} & \overline{c_\alpha c_\beta^*} \\ \overline{c_\beta c_\alpha^*} & \overline{c_\beta c_\beta^*} \end{pmatrix}$$

Liouville-von Neumann equation

Quantum description

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

Density matrix

Hamiltonian

Liouville-von Neumann equation

Hamiltonian:

Time-independent part

Static magnetic field B_0

Scalar coupling

Time-dependent part

Radiofrequency field B_1 (pulses)

Quantum description

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

Density matrix — Hamiltonian

Liouville-von Neumann equation

Hamiltonian:

Time-independent part

Static magnetic field B_0

Scalar coupling

Time-dependent part

Radiofrequency field B_1 (pulses)

Transformation that render the pulse Hamiltonian time-independent ?

Quantum description

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

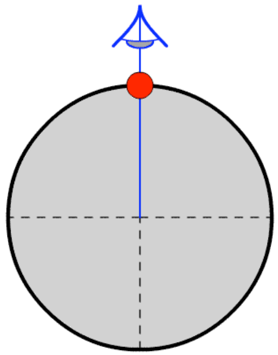
Density matrix — Hamiltonian

Rotating frame

$$\sigma^r = U \, \sigma \, U^{-1}$$

$$\frac{d\sigma^r(t)}{dt} = i \left[\sigma^r(t), H^e\right]$$

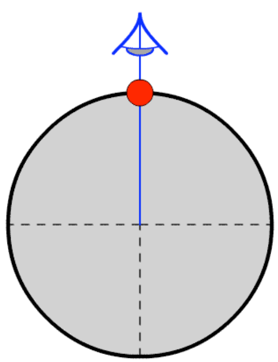
Rotating frame

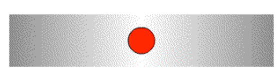


$$\frac{d\sigma(t)}{dt} = i\left[\sigma(t), H(t)\right]$$

Rotating frame

$\sigma^r = U\ \sigma\ U^{-1}$





$$\frac{d\sigma^r(t)}{dt} = i\left[\sigma^r(t), H^e\right]$$

Summary of the lecture

① Bloch vector model

② Basic quantum mechanics

③ Product operator formalism

④ Spin hamiltonian

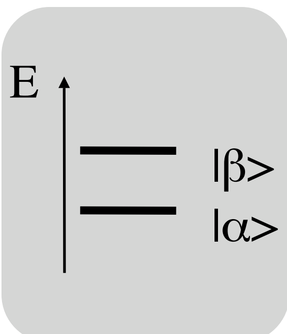
⑤ NMR building blocks

⑥ Coherence selection - phase cycling

⑦ Pulsed field gradients

Matrix representation of the spin operators

We use the |α> and |β> states
of the spin as a basis



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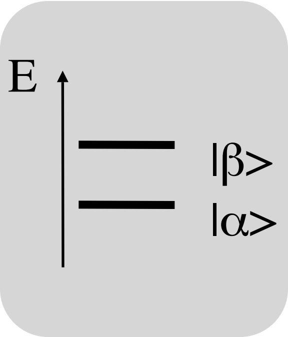

$$I_x = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad I_y = \frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

$$I_z = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

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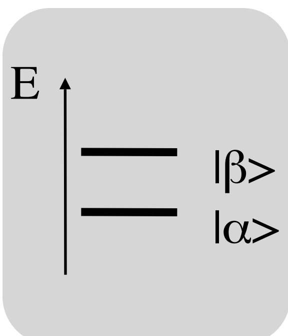

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The spin operators satisfy the commutation relation

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

Matrix representation of the spin operators

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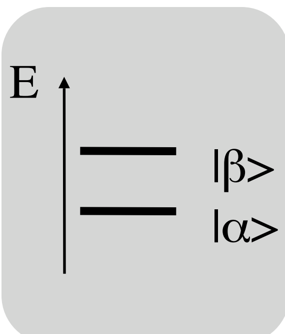

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$$[I_x, I_y] = i\, I_z$$

$$I_x I_y - I_y I_x = \frac{1}{4}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} - \frac{1}{4}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

Matrix representation of the spin operators

We use the |α> and |β> states of the spin as a basis

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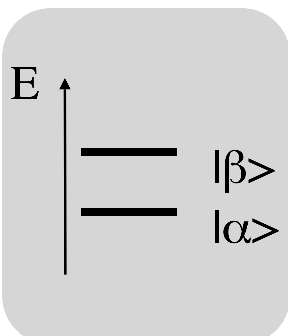

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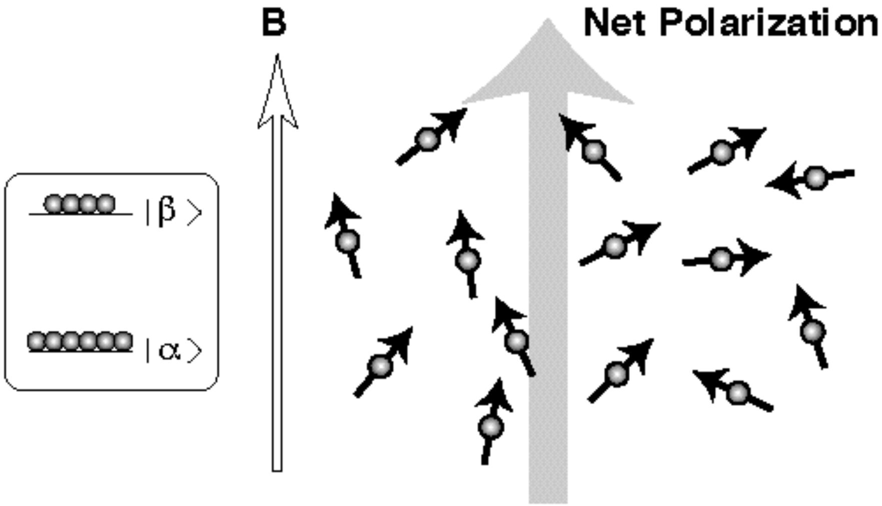
$$I_x I_y - I_y I_x = \frac{1}{4}\begin{bmatrix} i & 0 \\ 0 & -i \end{bmatrix} - \frac{1}{4}\begin{bmatrix} -i & 0 \\ 0 & i \end{bmatrix} = i\frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = i \;\; I_z$$

Matrix representation of the spin operators



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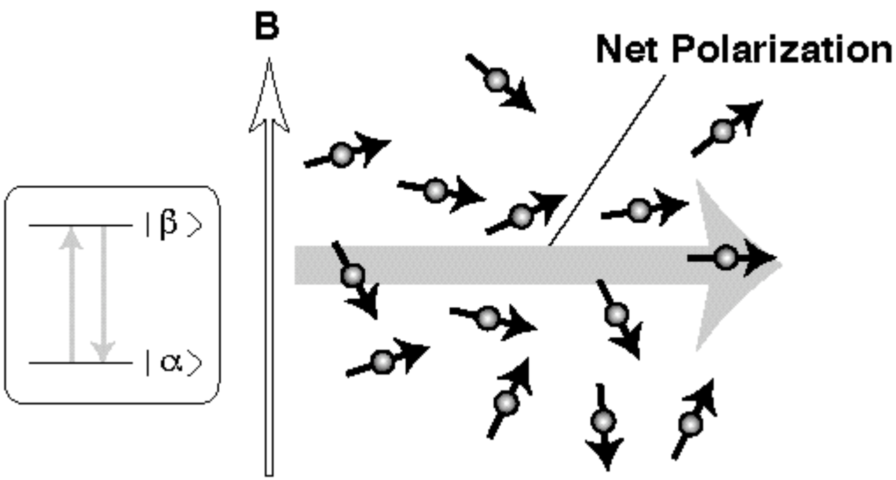

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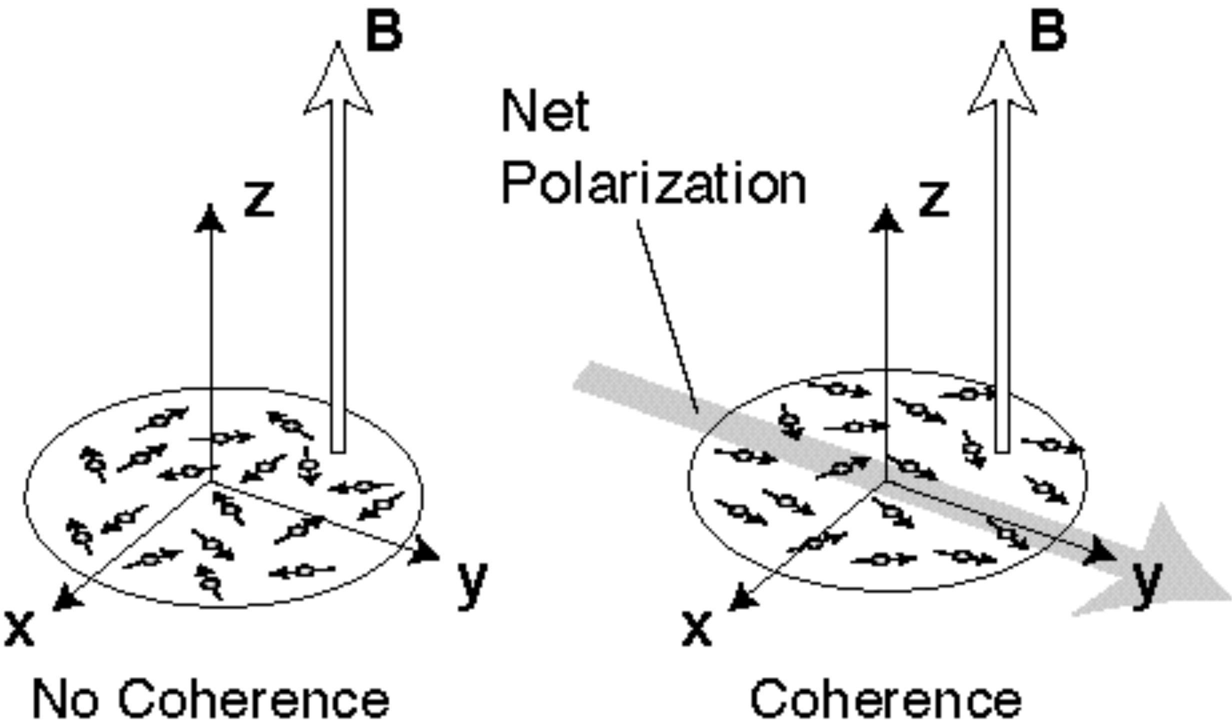

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The transverse coherence has a phase !

Matrix representation of the spin operators

Bras / Kets

Bra notation (1×2 vectors)

$$|\alpha\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad |\beta\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

Ket notation (2×1 vectors)

$$\langle\alpha| = \begin{bmatrix} 1 & 0 \end{bmatrix}$$

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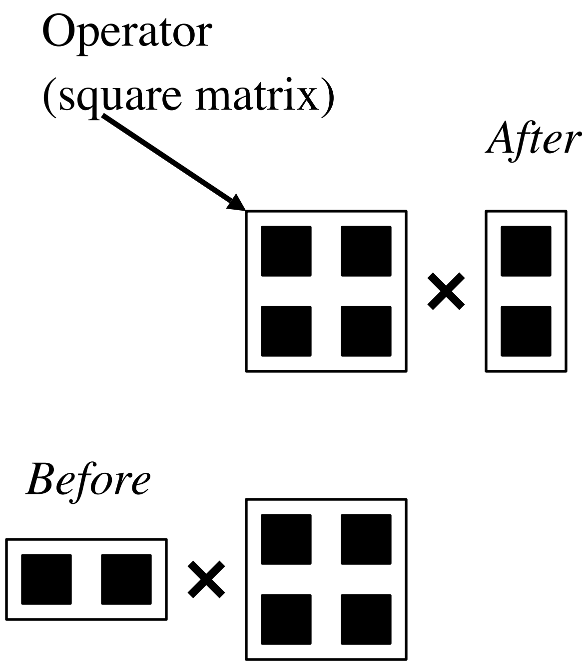

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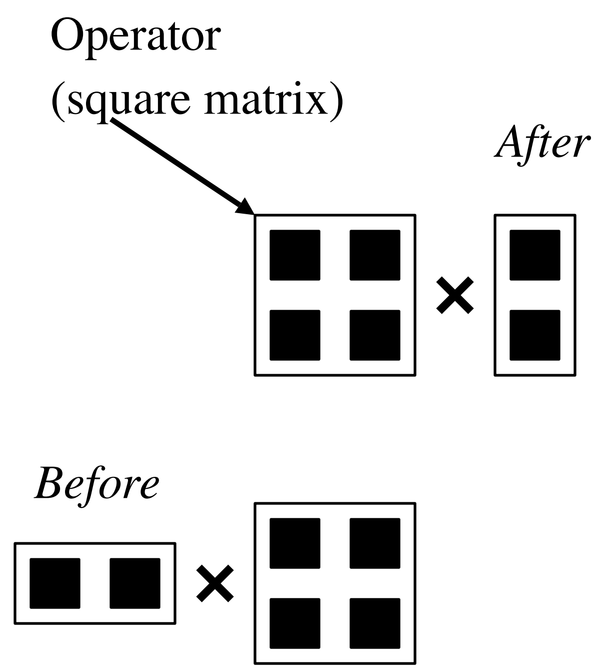
Bra ← adjoint → Ket

$$\langle n| = \{\, |n\rangle \,\}^{\dagger}$$



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Bra ← adjoint → Ket

<nl = { ln> } †

Orthonormal basis

$$\langle\alpha|\alpha\rangle = \begin{bmatrix} 1 & 0 \end{bmatrix} \times \begin{bmatrix} 1 \\ 0 \end{bmatrix} = 1$$

$$\langle\alpha|\beta\rangle = \begin{bmatrix} 1 & 0 \end{bmatrix} \times \begin{bmatrix} 0 \\ 1 \end{bmatrix} = 0$$

$$\langle\beta|\beta = \begin{bmatrix} 0 & 1 \end{bmatrix} \times \begin{bmatrix} 0 \\ 1 \end{bmatrix} = 1$$

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Matrix representation of the spin operators

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Matrix representation using different basis sets can be interconverted using unitary transformation

Multispin systems

Bloch model

Strictly applicable only to a system of non-interacting spins

Quantum mechanics

Direct product space

The two spins are <u>independent</u>

$$|\alpha\rangle = \begin{bmatrix}1\\0\end{bmatrix} \qquad |\beta\rangle = \begin{bmatrix}0\\1\end{bmatrix}$$

$$|\psi\rangle = |\psi_1\rangle \otimes |\psi_2\rangle$$

$|\psi_1\rangle$: basis vector for spin #1

$|\psi_2\rangle$: basis vector for spin #2

Nb of basis vectors = 2^N

Spins	1	2	3
Basis size	2	4	8

$$\psi_1 = |\alpha\alpha\rangle = \begin{bmatrix}1\\0\end{bmatrix} \otimes \begin{bmatrix}1\\0\end{bmatrix}$$

Multispin systems

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Operators

Multispin systems

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Operators

$$I_z + S_z \neq \frac{1}{2}\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix} + \frac{1}{2}\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix} = \begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}$$

Incorrect !

Multispin systems

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Operators

$$I_z^{(2\,spins)} = I_z^{(1\,spin)} \otimes E$$

Multispin systems

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Operators

$$I_z^{(2\,spins)} = I_z^{(1\,spin)} \otimes E = \frac{1}{2}\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix} \otimes \begin{bmatrix}1 & 0\\0 & 1\end{bmatrix} = \begin{bmatrix}1 & 0 & 0 & 0\\0 & 1 & 0 & 0\\0 & 0 & -1 & 0\\0 & 0 & 0 & -1\end{bmatrix}$$

$$S_z^{(2\,spins)} = E \otimes S_z^{(1\,spin)}$$

Multispin systems

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Operators

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Incorrect !

2×2

Dimension

4×4

$$I_z^{(2\,spins)} + S_z^{(2\,spins)} = \begin{bmatrix}1 & 0 & 0 & 0\\0 & 0 & 0 & 0\\0 & 0 & 0 & 0\\0 & 0 & 0 & -1\end{bmatrix}$$

Multispin systems

$|\psi\rangle = |\psi_1\rangle \otimes |\psi_2\rangle$

Operators

$\mathbf{A}\mathbf{B}|ij\rangle = (\mathbf{A} \otimes \mathbf{B})(|i\rangle \otimes |j\rangle) = \mathbf{A}|i\rangle \otimes \mathbf{B}|j\rangle$

Multispin systems

$|\psi\rangle = |\psi_1\rangle \otimes |\psi_2\rangle$

Operators

Product operator

$\mathbf{AB}|ij\rangle = (\mathbf{A}\otimes\mathbf{B})(|i\rangle \otimes |j\rangle) = \mathbf{A}\,|i\rangle \otimes \mathbf{B}|j\rangle$

$\mathbf{A}$ *is an operator that acts on the* i *spin*

$\mathbf{B}$ *is an operator that acts on the* j *spin*

$\mathbf{AB} = (\mathbf{A}\otimes\mathbf{B}) = (\mathbf{A}\otimes\mathbf{E})\,(\mathbf{E}\otimes\mathbf{B})$

Multispin systems

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$\mathbf{AB} = (\mathbf{A}\otimes\mathbf{B}) = (\mathbf{A}\otimes\mathbf{E})\,(\mathbf{E}\otimes\mathbf{B})$

Ex:

$\mathbf{I_z}|\alpha\beta\rangle = (\mathbf{I_z} \otimes \mathbf{E})(|\alpha\rangle \otimes |\beta\rangle) = \mathbf{I_z}\,|\alpha\rangle \otimes \mathbf{E}|\beta\rangle$

$= {}^1/_2\,|\alpha\rangle \otimes |\beta\rangle = {}^1/_2\,|\,\alpha\beta\,\rangle$

$\mathbf{I_z}|\alpha\beta\rangle = {}^1/_2\,|\alpha\beta\rangle$

Multispin systems

$$|\psi\rangle = |\psi_1\rangle \otimes |\psi_2\rangle$$

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A *is an operator that acts on the* i *spin*

B *is an operator that acts on the* j *spin*

$$\mathbf{AB} = (\mathbf{A} \otimes \mathbf{B}) = (\mathbf{A} \otimes \mathbf{E})\,(\mathbf{E} \otimes \mathbf{B})$$

Ex:

$$\mathbf{I_z}|\alpha\beta\rangle = (\mathbf{I_z} \otimes \mathbf{E})(|\alpha\rangle \otimes |\beta\rangle) = \mathbf{I_z}\,|\alpha\rangle \otimes \mathbf{E}|\beta\rangle$$

$$= {}^{1}/_{2}\,|\alpha\rangle \otimes |\beta\rangle = {}^{1}/_{2}\,|\,\alpha\beta\,\rangle$$

$$\mathbf{I_z}|\alpha\beta\rangle = {}^{1}/_{2}\,|\alpha\beta\rangle$$

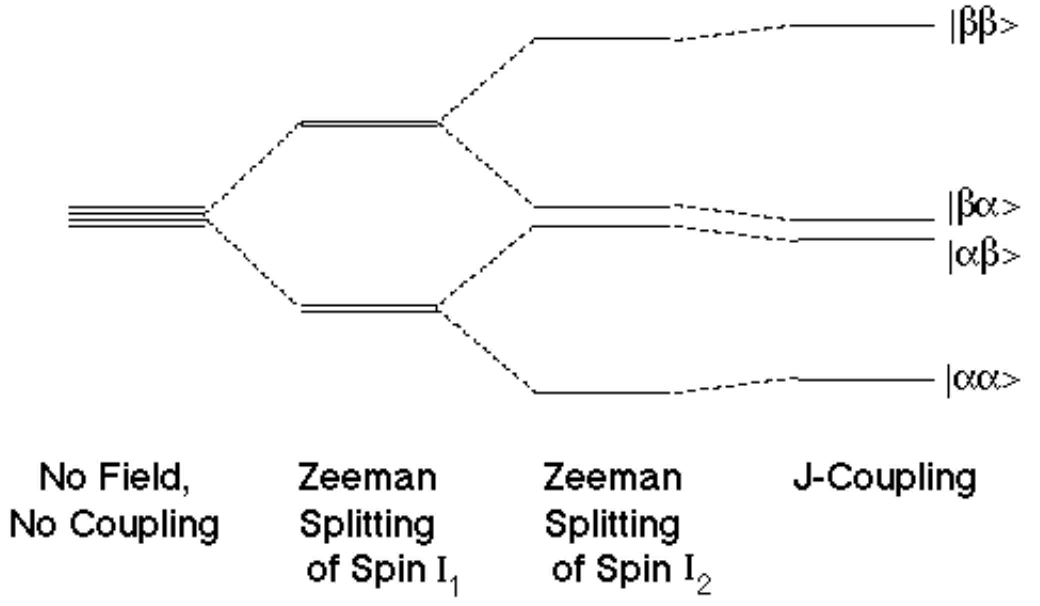
$$\mathbf{I_z}\,\mathbf{S_z}|\,\alpha\beta\,\rangle = (\mathbf{I_z} \otimes \mathbf{S_z})(|\alpha\rangle \otimes |\beta\rangle) = \mathbf{I_z}\,|\alpha\rangle \otimes \mathbf{S_z}\,|\beta\,\rangle$$

$$= {}^{1}/_{2}\,|\alpha\rangle \otimes {}^{-1}/_{2}\,|\beta\rangle = {}^{-1}/_{4}\,|\,\alpha\beta\,\rangle$$

$$\mathbf{I_z}\,\mathbf{S_z}|\,\alpha\beta\,\rangle = {}^{-1}/_{4}\,|\,\alpha\beta\,\rangle$$

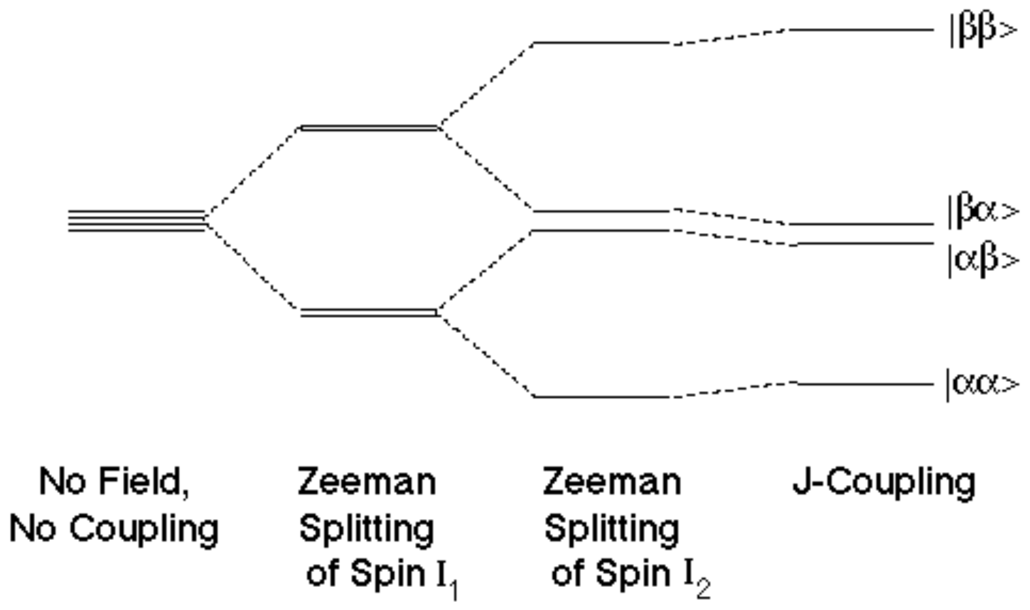
Multispin systems - product operators

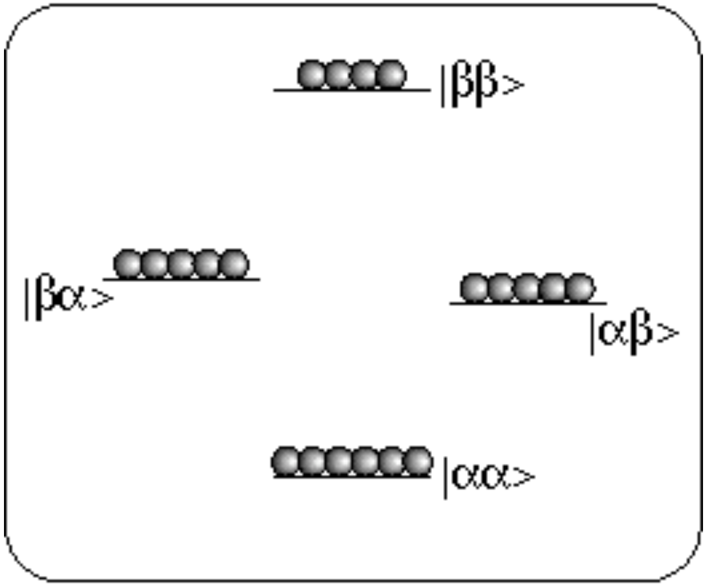
Spectrum of a AX spin system



Multispin systems - product operators

Spectrum of a AX spin system



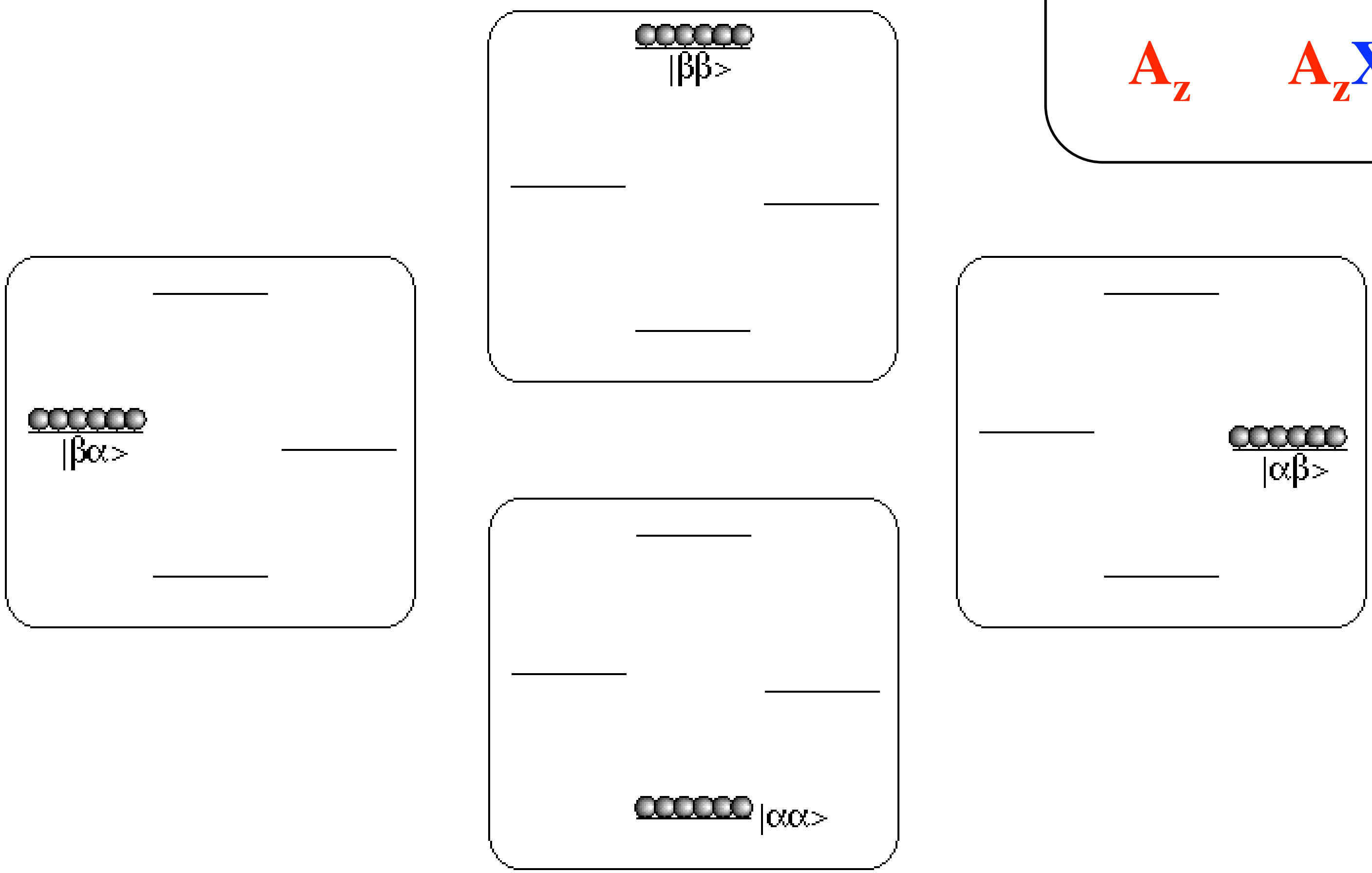


Thermal equilibrium
populations

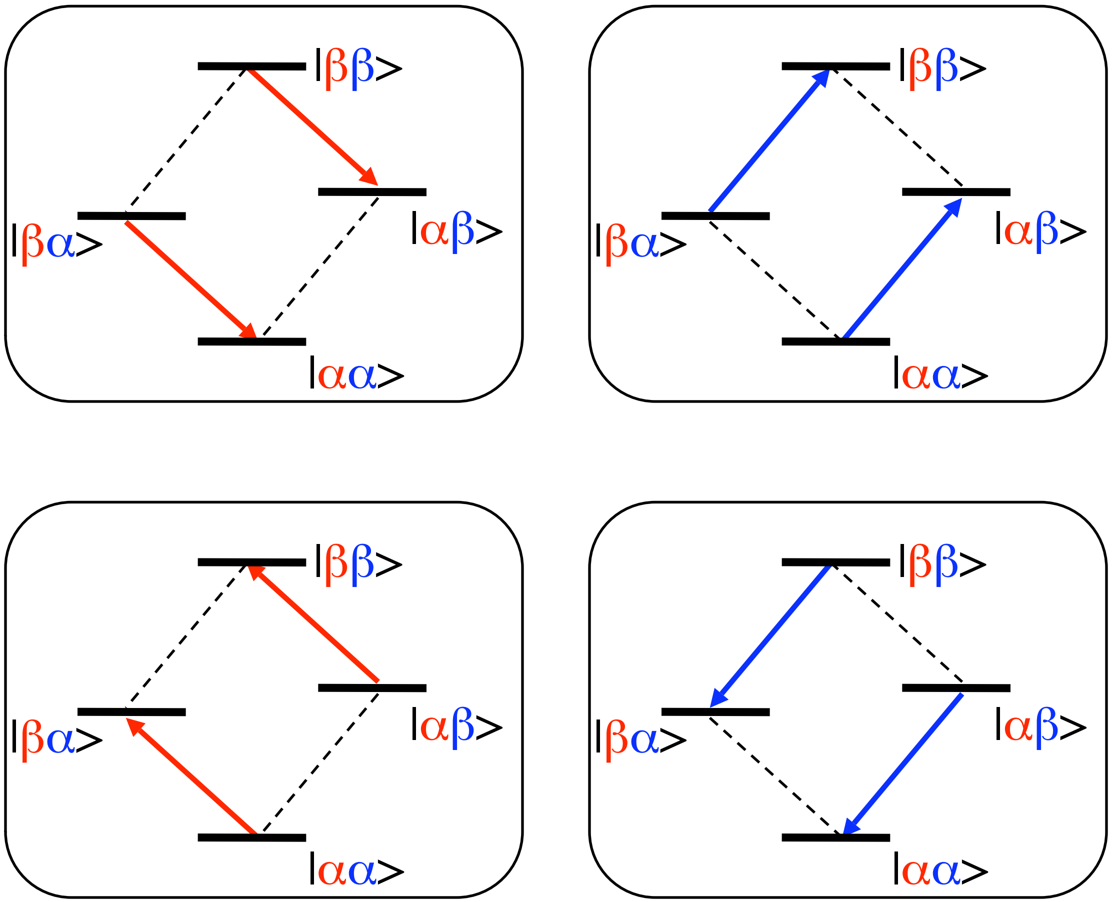
Product operators - coherence /population

Populations

A_z A_zX_z X_z



Product operators - coherence /population

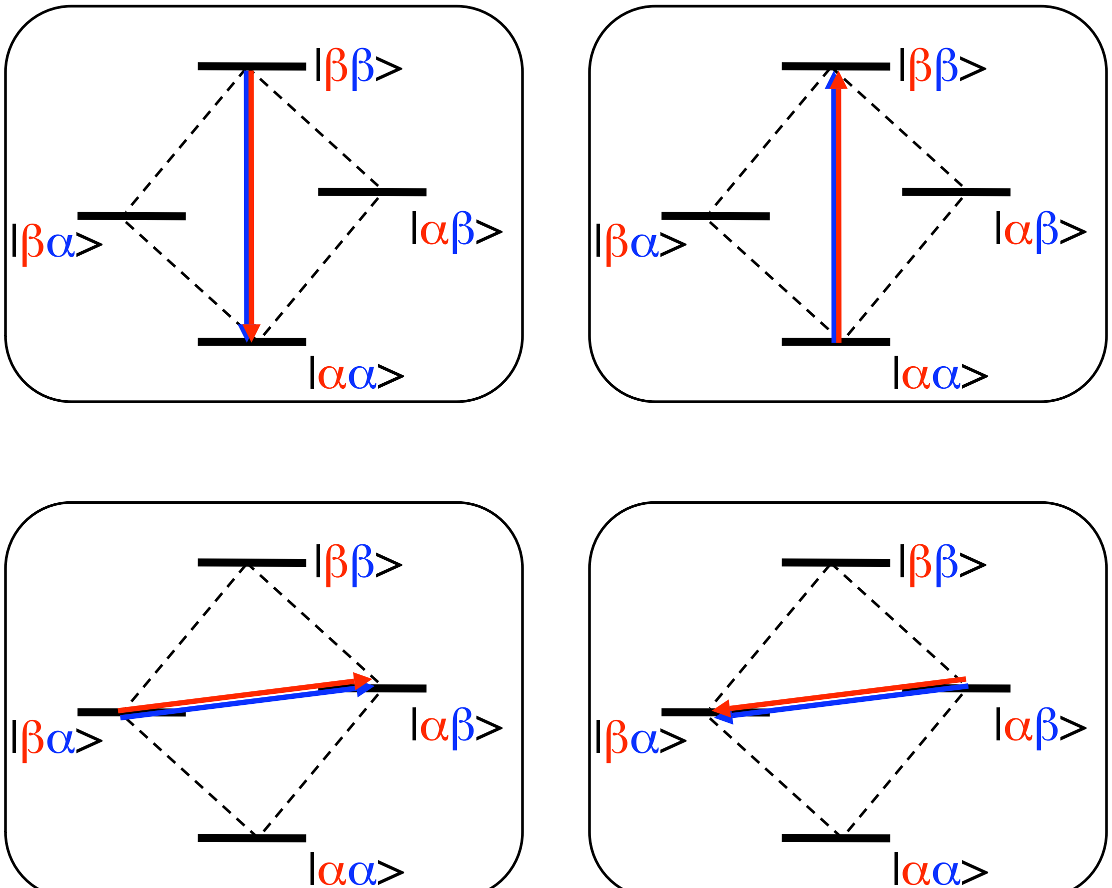


±1 Quantum coherence

A_x X_x

A_y X_y

Product operators - coherence /population



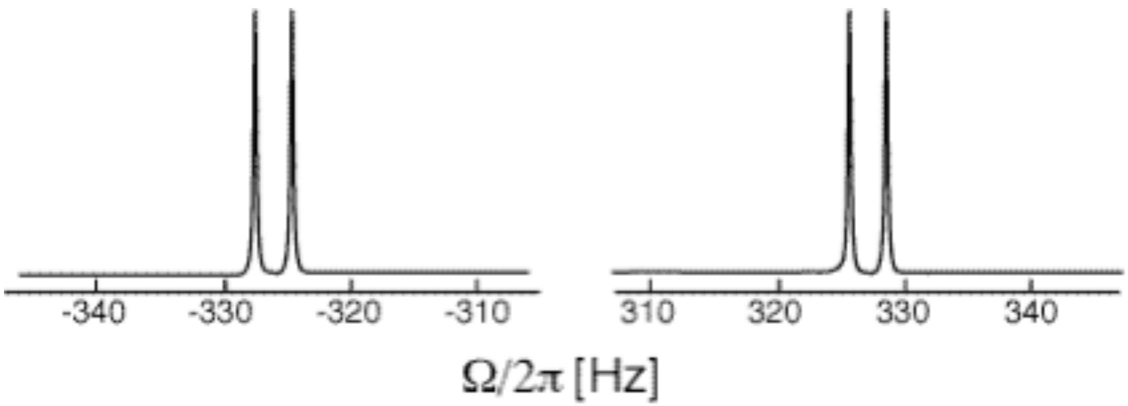
0 / 2 Quantum coherence

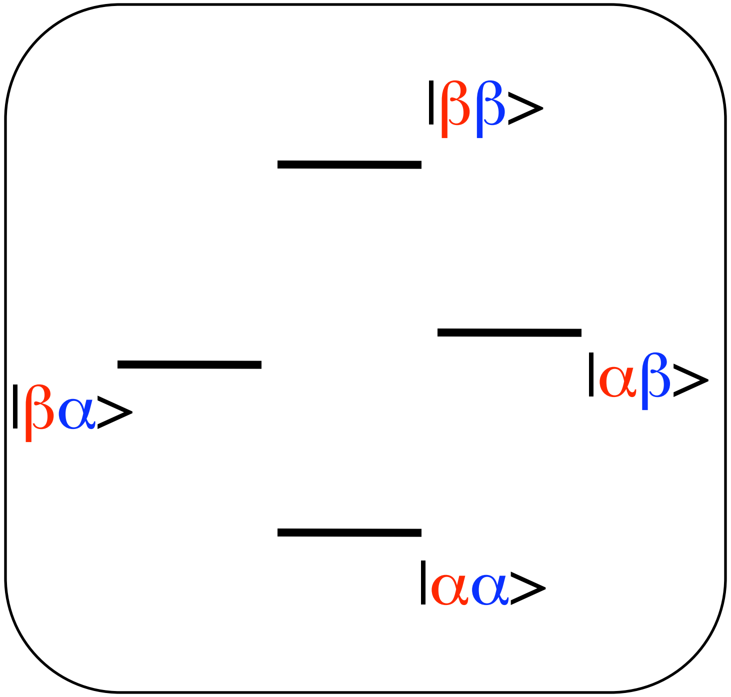
A_xX_y A_xX_x

A_yX_x A_yX_y

Multispin systems - product operators

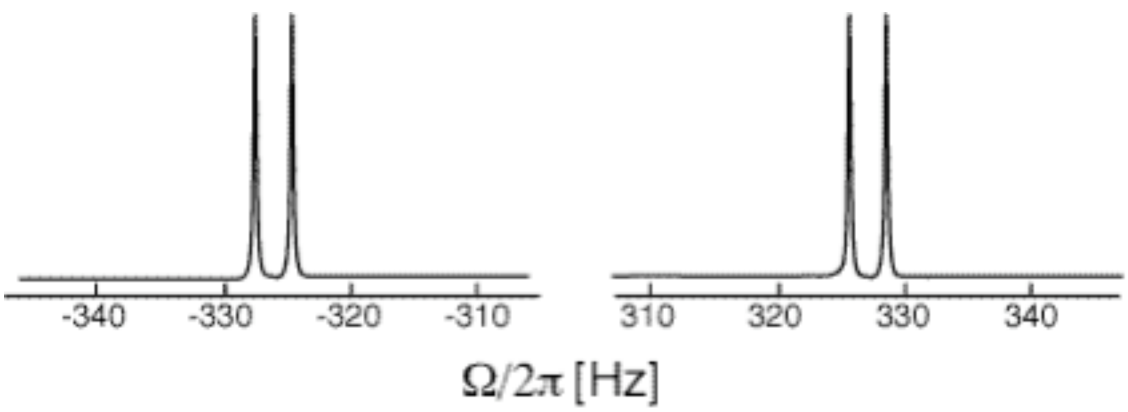
Spectrum of a AX spin system



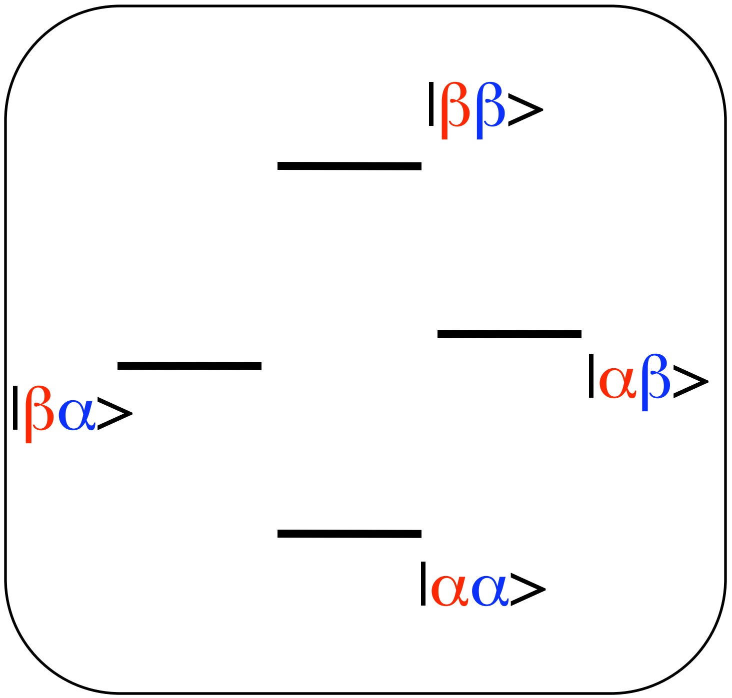


Multispin systems - product operators

Spectrum of a AX spin system

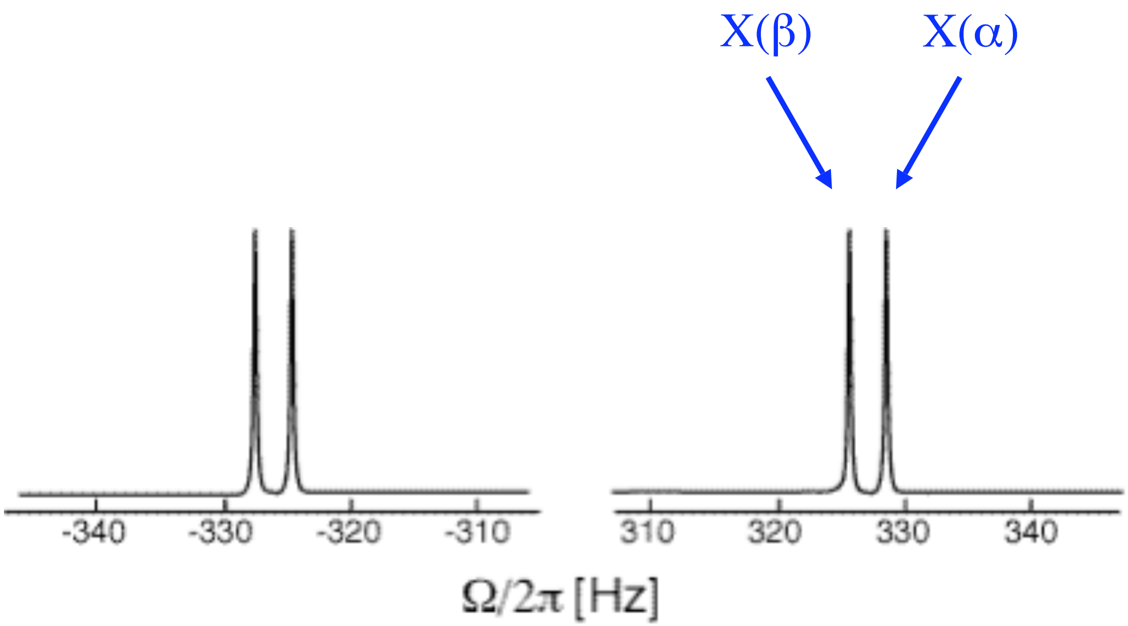


Spectrum of A

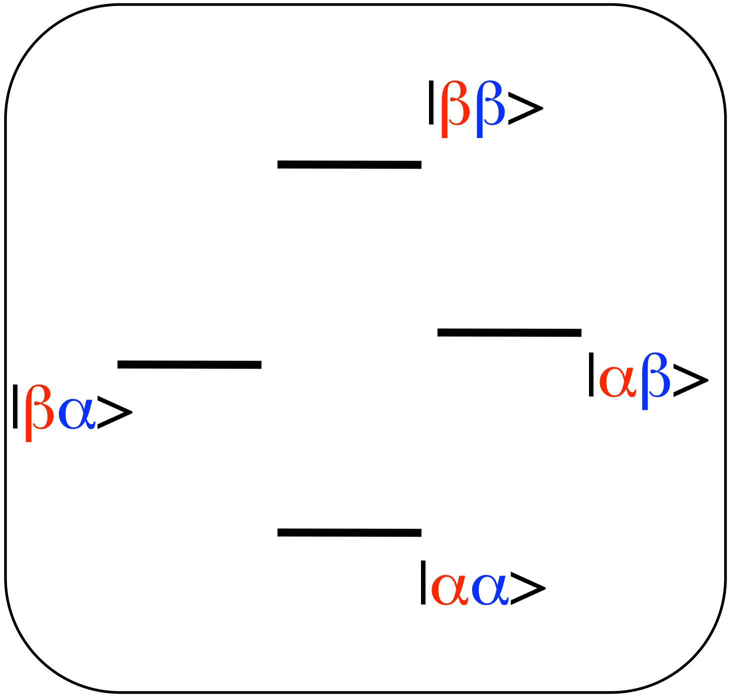


Multispin systems - product operators

Spectrum of a AX spin system

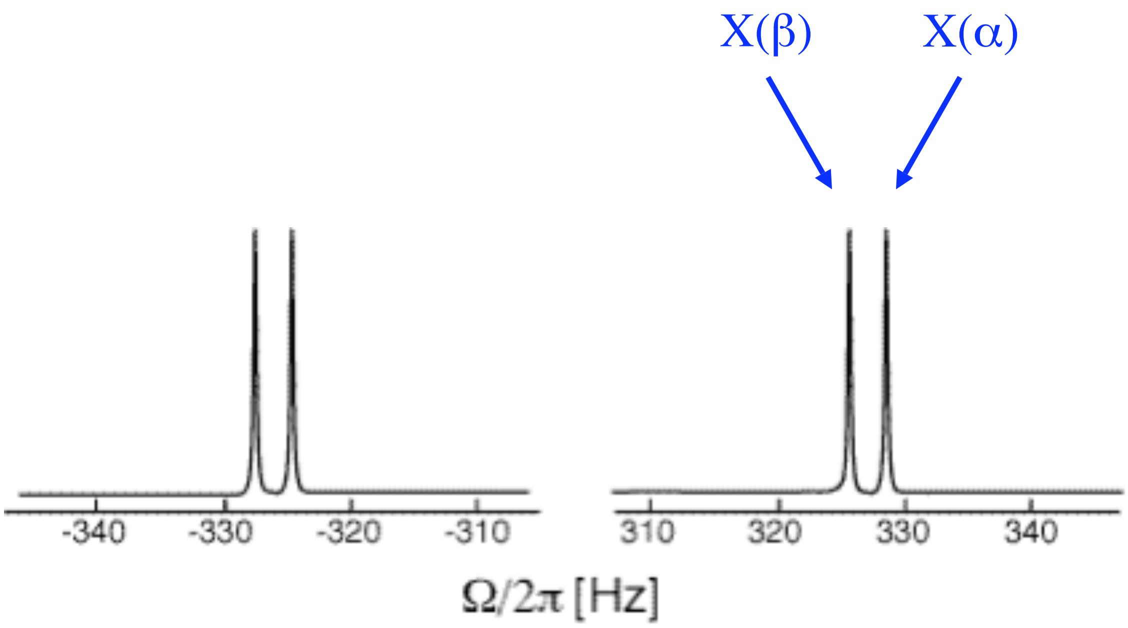


Spectrum of A

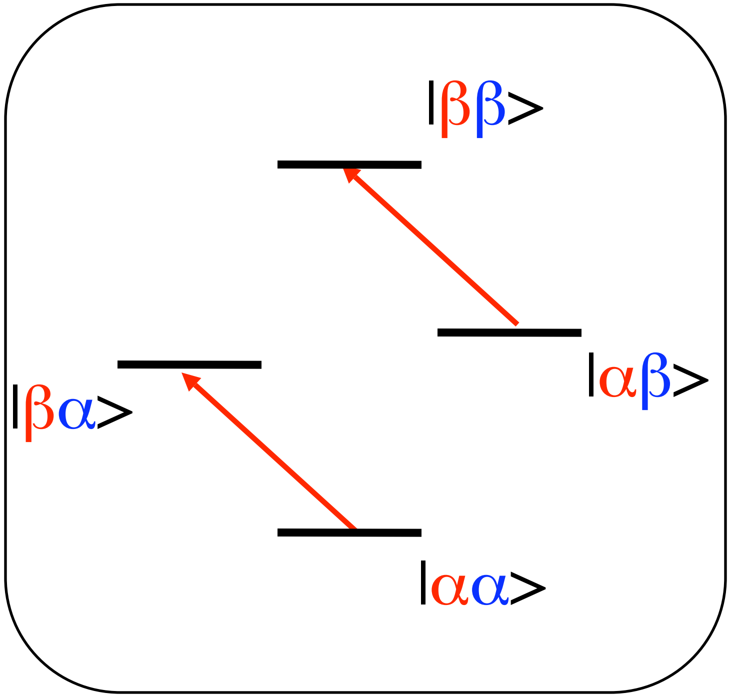


Multispin systems - product operators

Spectrum of a AX spin system

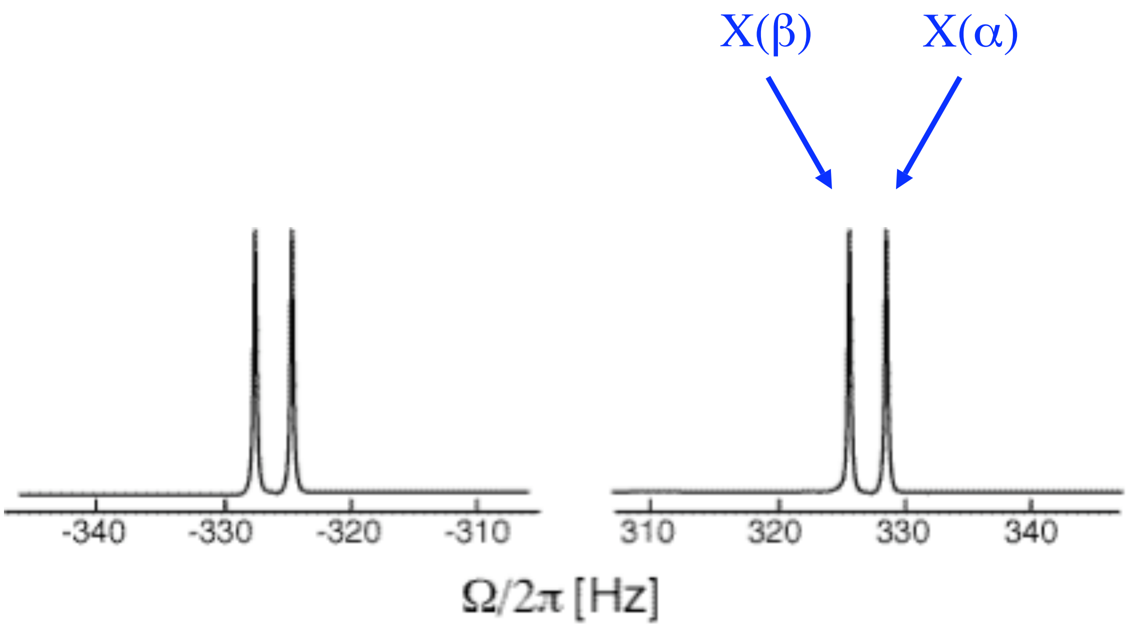


Spectrum of A



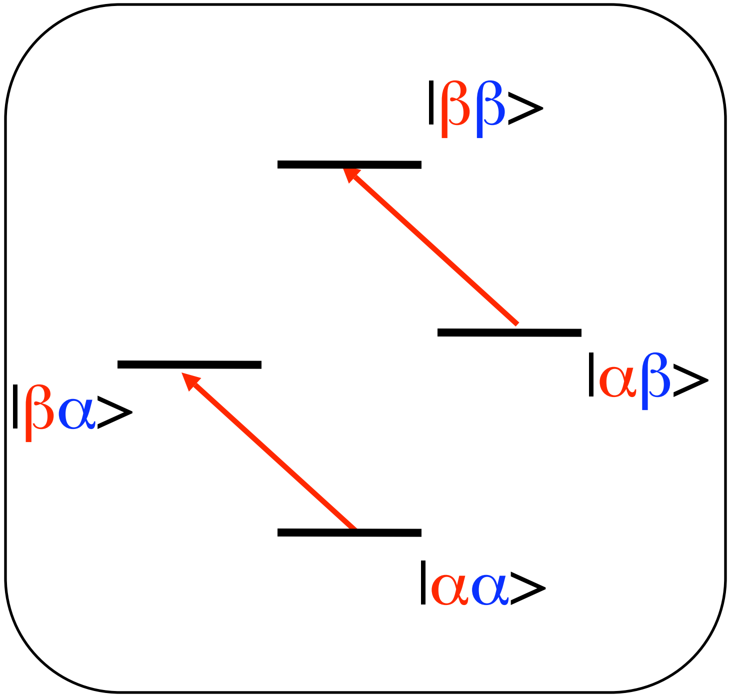
Multispin systems - product operators

Spectrum of a AX spin system



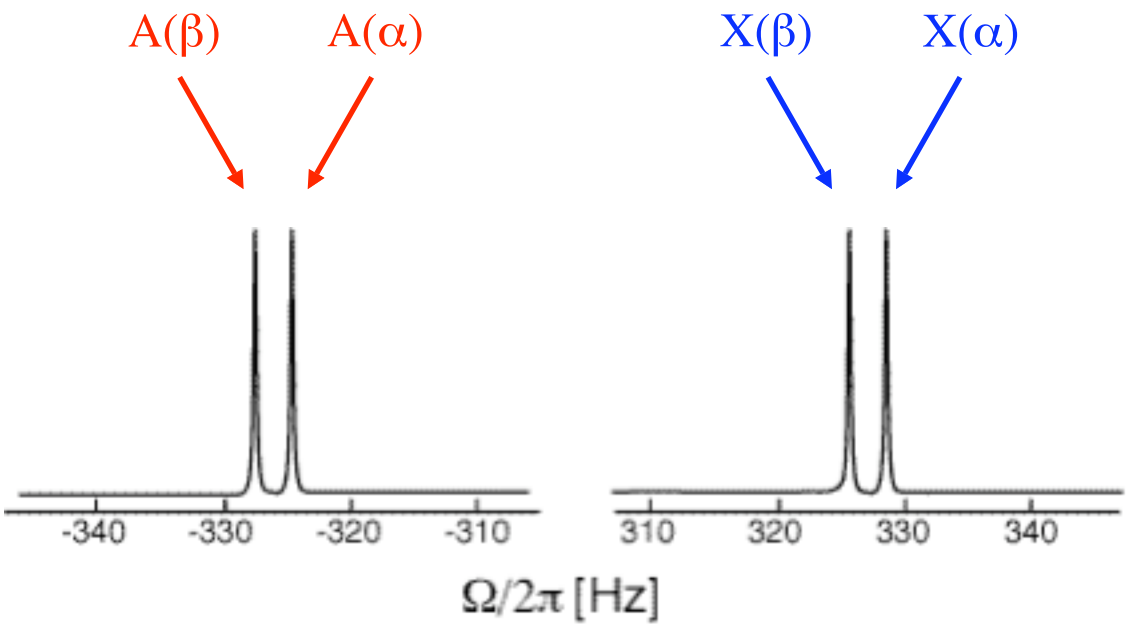
Spectrum of X

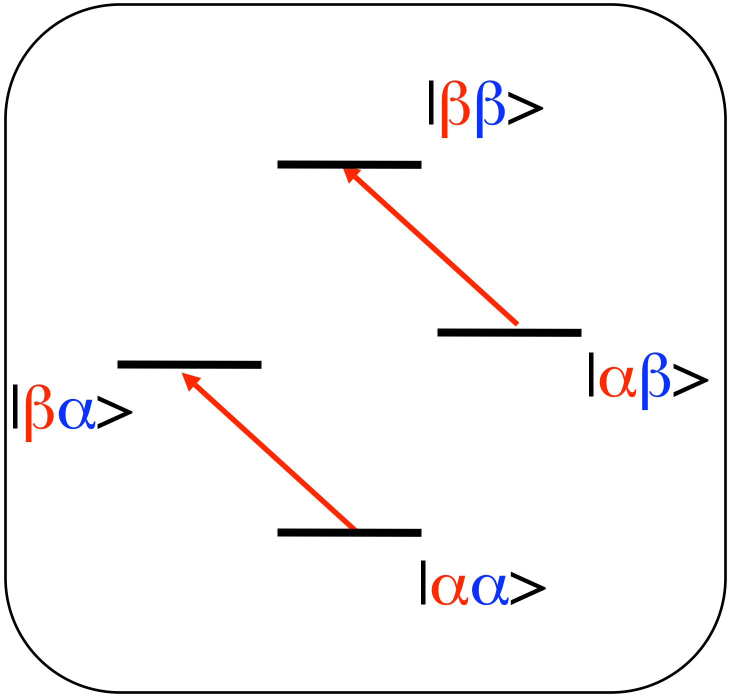
Spectrum of A



Multispin systems - product operators

Spectrum of a AX spin system



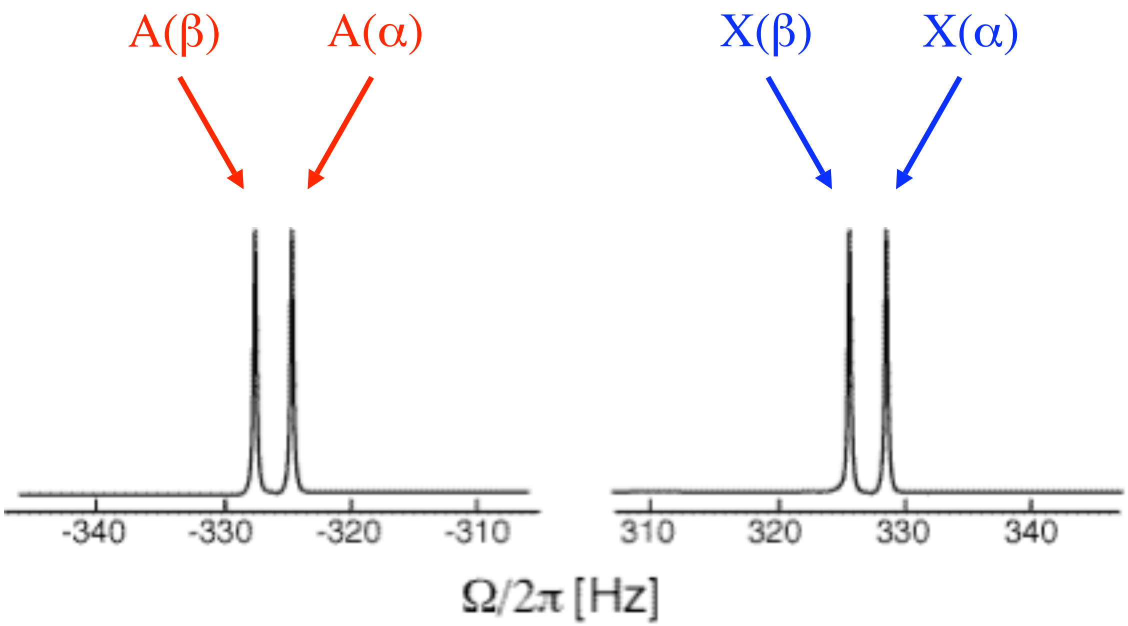


Spectrum of X

Spectrum of A

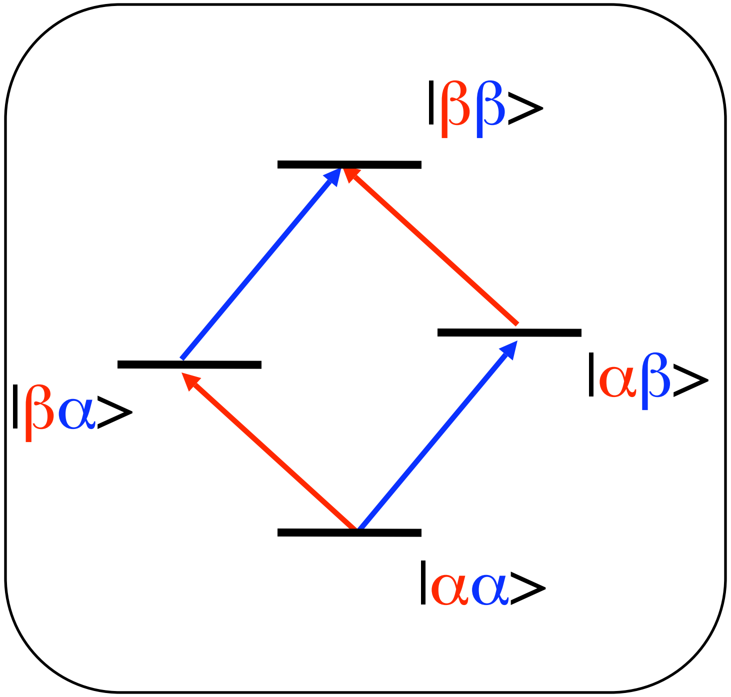
Multispin systems - product operators

Spectrum of a AX spin system

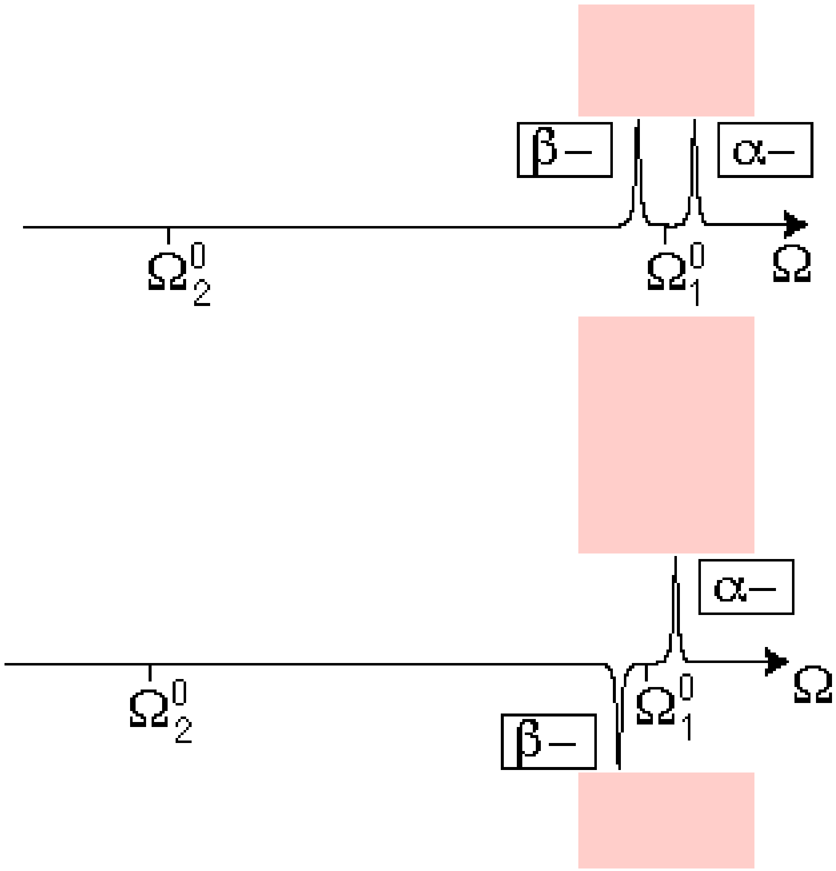


Spectrum of X

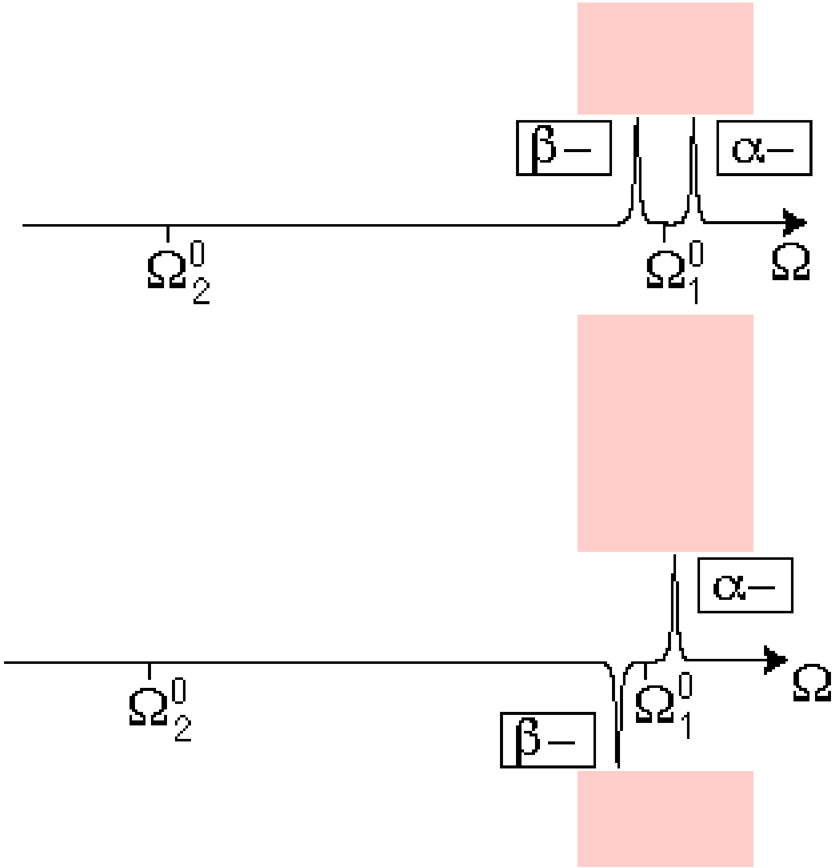
Spectrum of A



Multispin systems - product operators

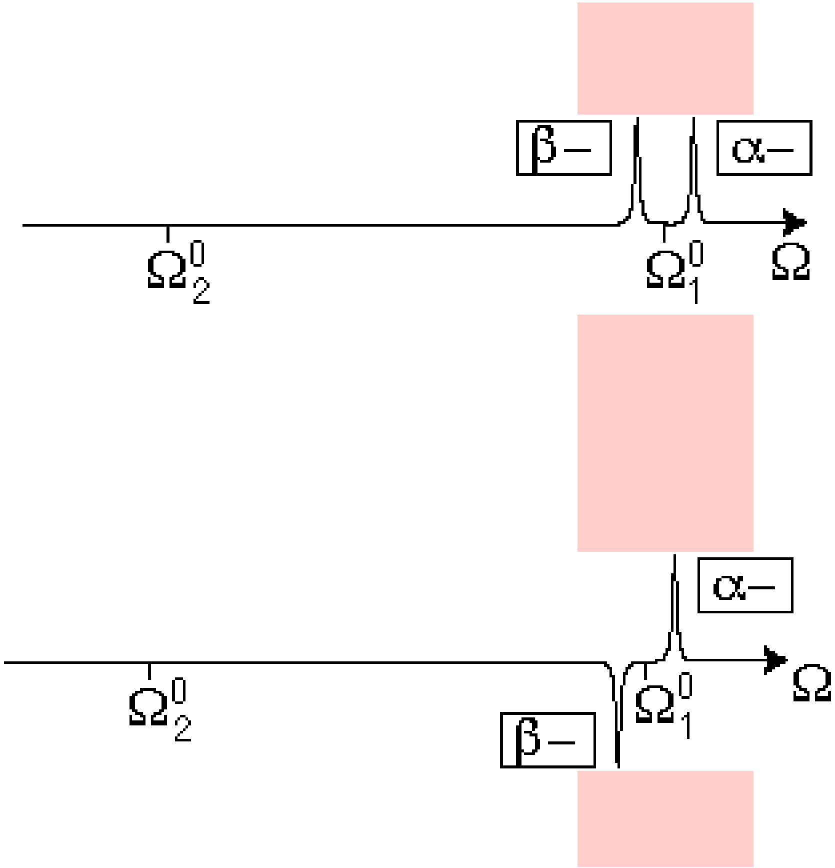


Multispin systems - product operators



Spectrum of A

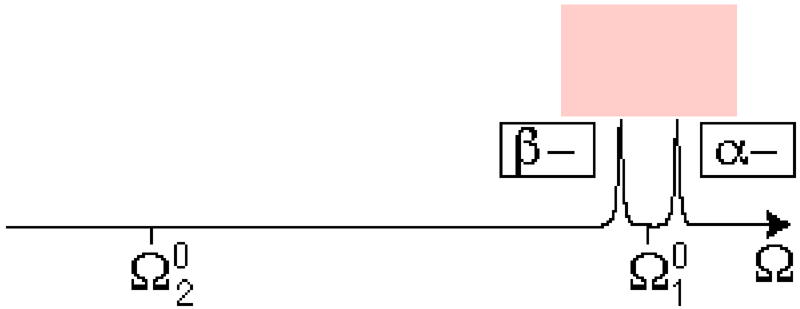
Multispin systems - product operators



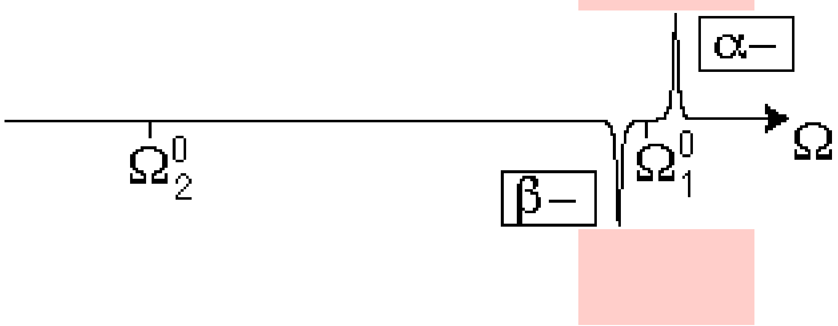
Spectrum of A

In-phase coherence of **A** along y

Multispin systems - product operators



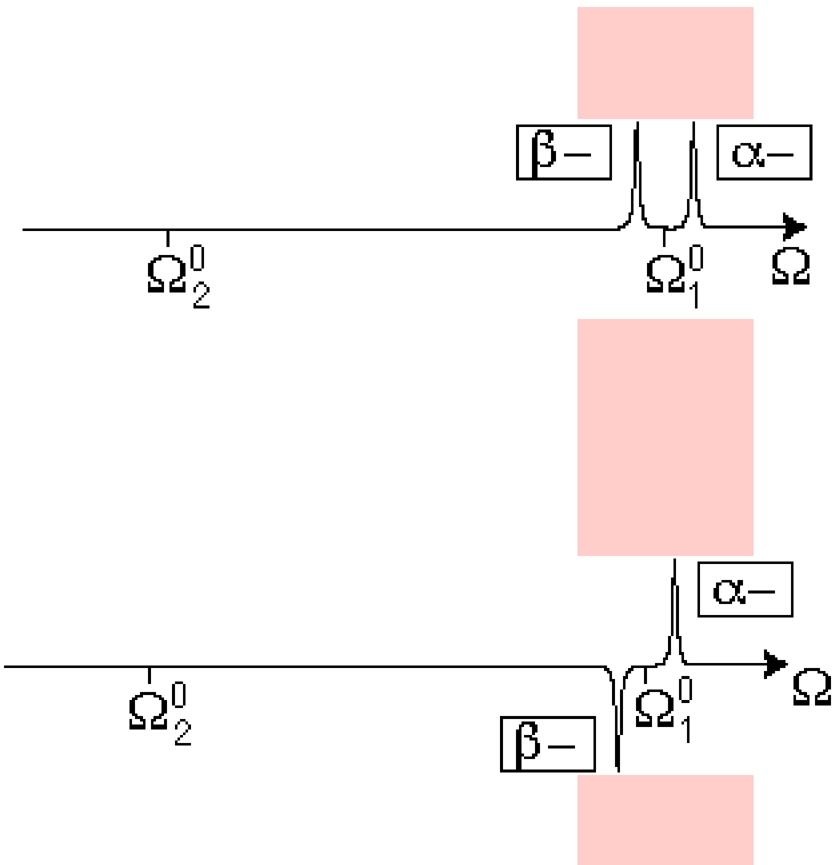
In-phase coherence of **A** along y



Anti-phase coherence of **A** along y

Spectrum of A

Multispin systems - product operators



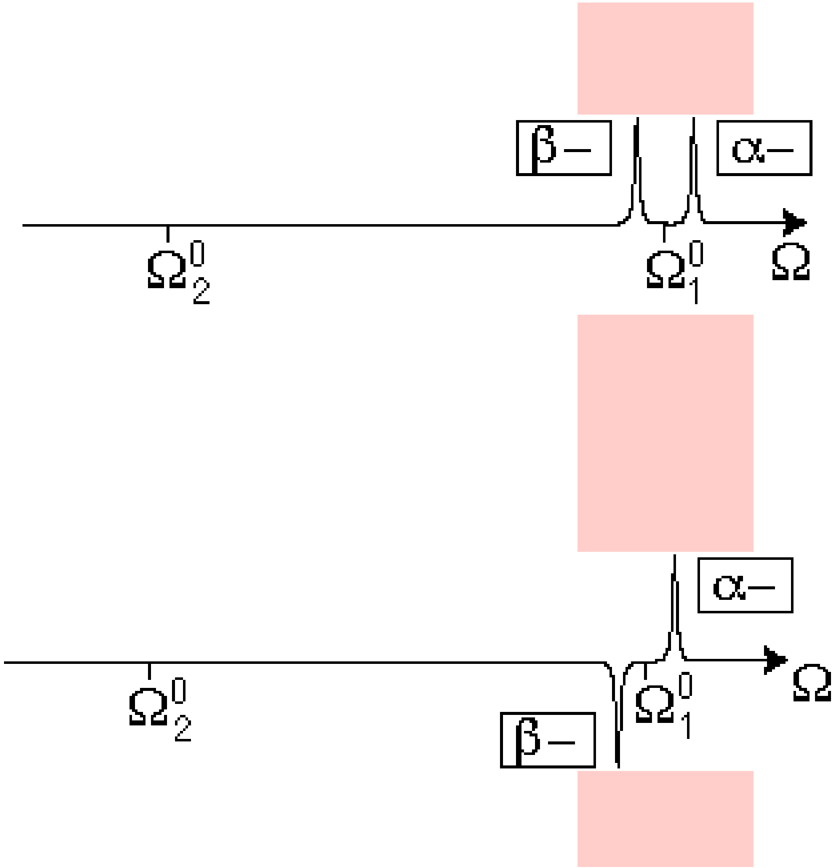
Spectrum of A

In-phase coherence of **A** along y

Anti-phase coherence of **A** along y

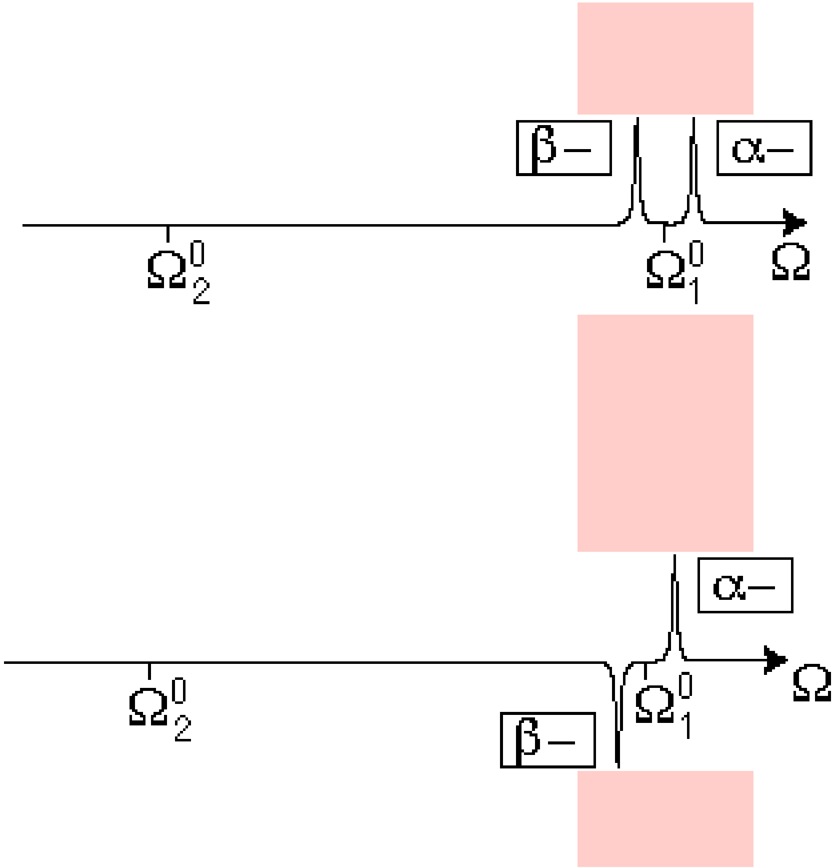
with respect to **X**

Multispin systems - product operators



Spectrum of A

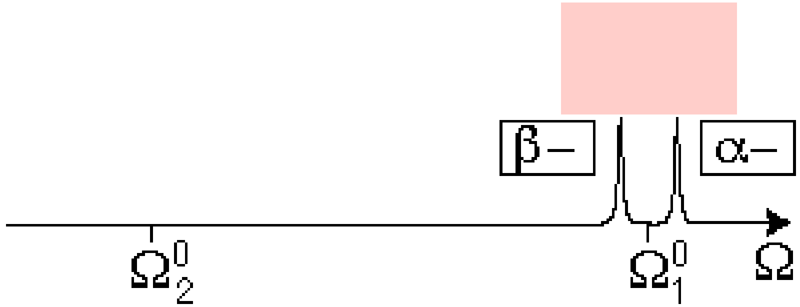
Multispin systems - product operators



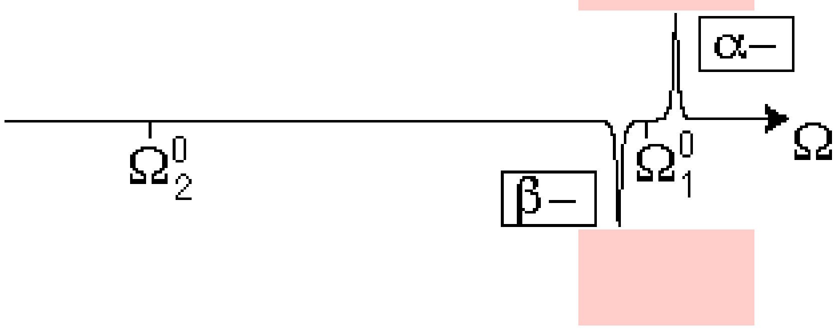
Spectrum of A

$$-A_y = \frac{1}{2i}\begin{bmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$

Multispin systems - product operators



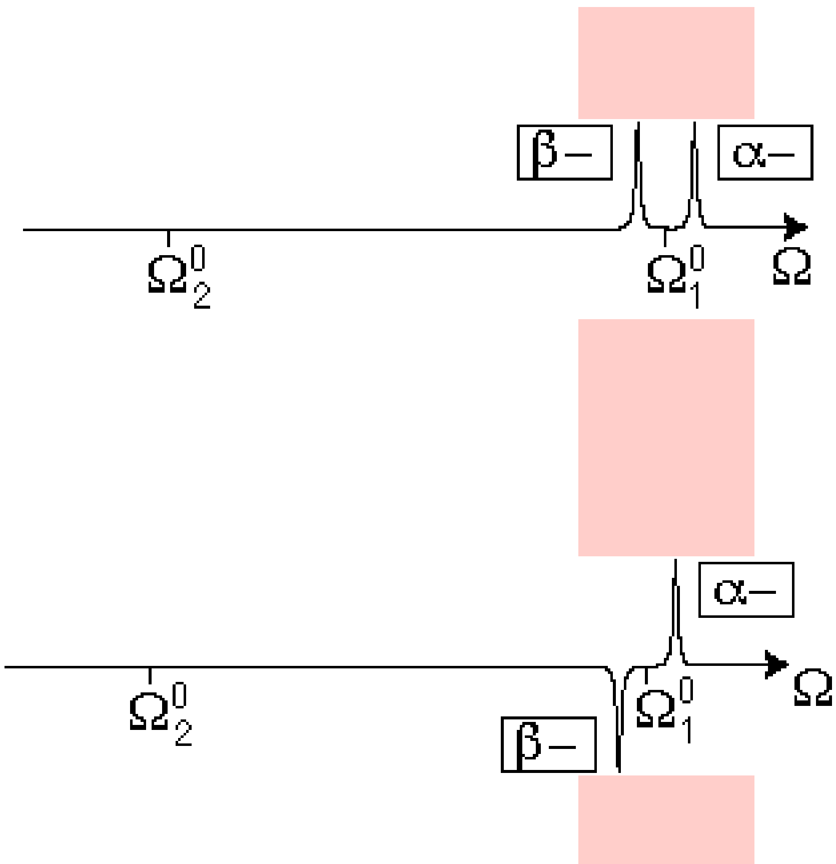
$$-A_y = \frac{1}{2i}\begin{bmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$



$$-2A_yX_z = \frac{1}{2i}\begin{bmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix}$$

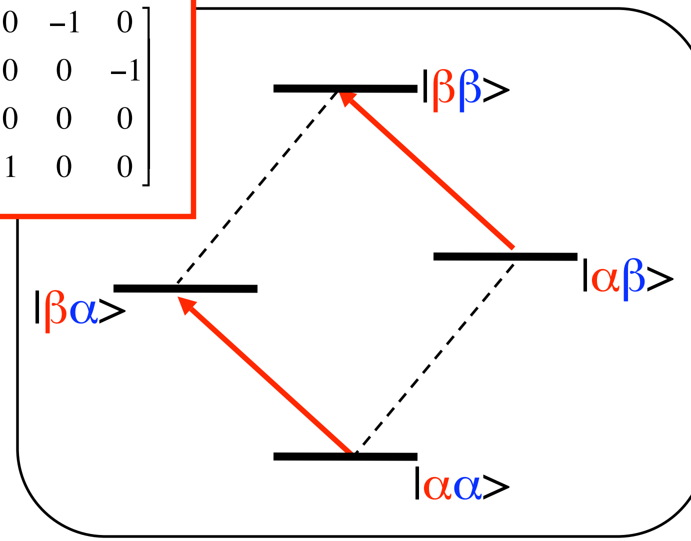
Spectrum of A

Multispin systems - product operators



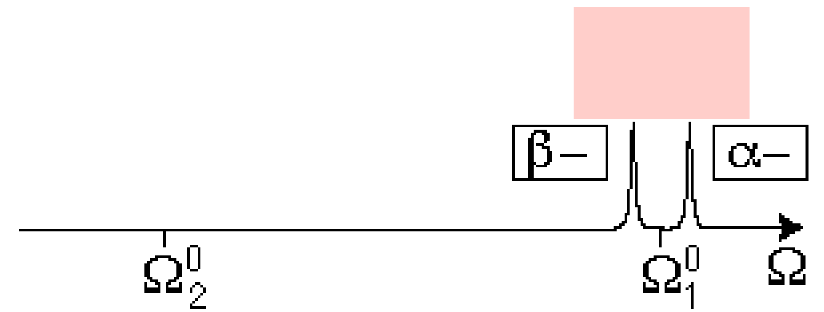
Spectrum of A

$$-A_y = \frac{1}{2i}\begin{bmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$

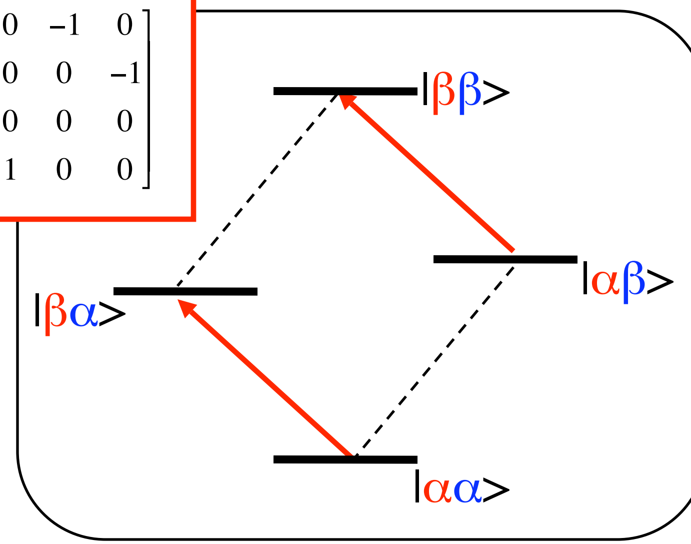


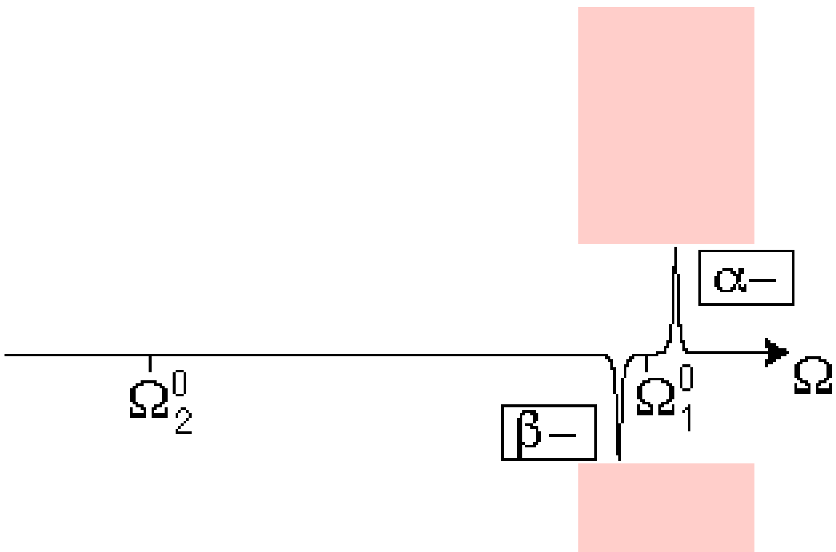
$$-2A_yX_z = \frac{1}{2i}\begin{bmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix}$$

Multispin systems - product operators

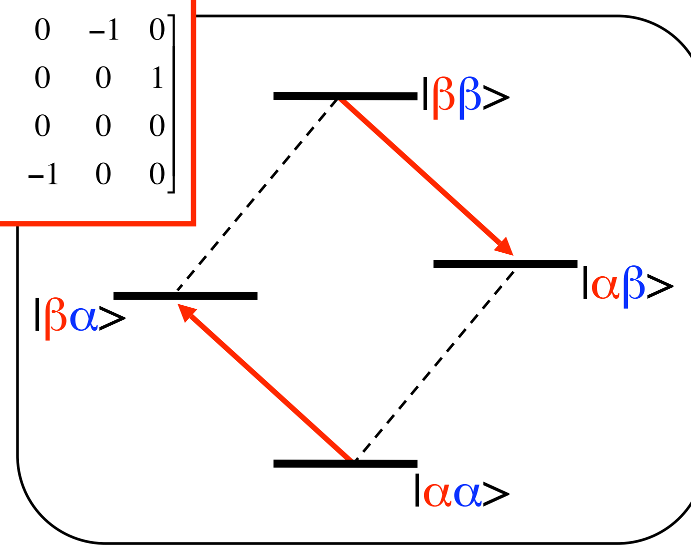


$$-A_y = \frac{1}{2i}\begin{bmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$





$$-2A_yX_z = \frac{1}{2i}\begin{bmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix}$$

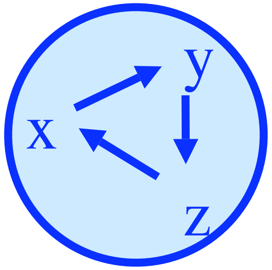


Spectrum of A

Commutation in coherence space

Rule 1:

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



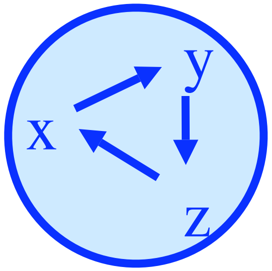
Quantum description

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

Density matrix   Hamiltonian

Commutation in coherence space

Rule 1:



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

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

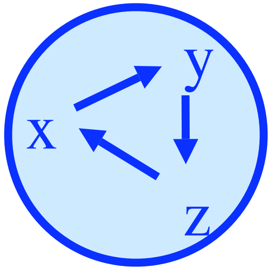
Quantum description

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

Density matrix   Hamiltonian

Commutation in coherence space

Rule 1:



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

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

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

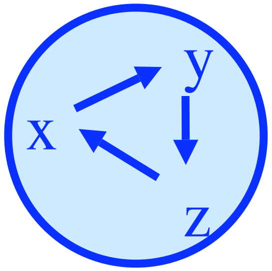
Quantum description

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

Density matrix — Hamiltonian

Commutation in coherence space

Rule 1:



Quantum description

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

Density matrix Hamiltonian

$[I_x,I_y] = i\ I_z$

$[I_y,I_z] = i\ I_x$

$[I_z,I_x] = i\ I_y$

$[S_x,S_y] = i\ S_z$

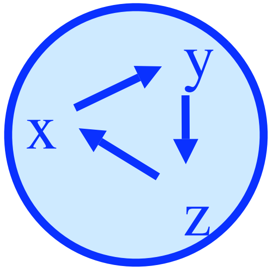
$[S_y,S_z] = i\ S_x$

$[S_z,S_x] = i\ S_y$

Commutation in coherence space

Rule 1:

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



Quantum description

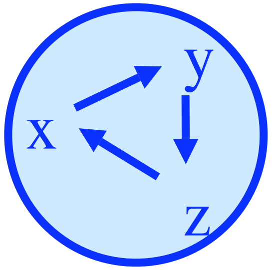
$$\frac{d\sigma(t)}{dt} = i[\sigma(t), H]$$

Density matrix   Hamiltonian

Commutation in coherence space

Rule 1:

$[I_x, I_y] = i\ I_z$



Quantum description

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

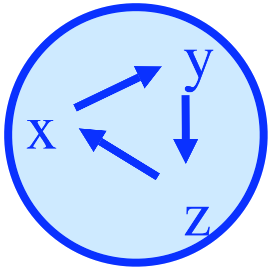
Density matrix   Hamiltonian

Rule 2:

Commutation in coherence space

Rule 1:

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



Quantum description

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

Density matrix   Hamiltonian

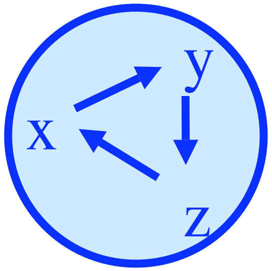
Rule 2:

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

Commutation in coherence space

Rule 1:

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



Quantum description

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

Density matrix   Hamiltonian

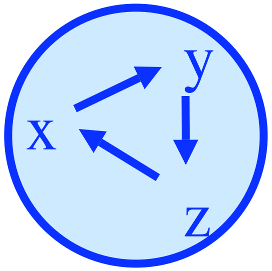
Rule 2:

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

Rule 3:

Commutation in coherence space

Rule 1:



Quantum description

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

Density matrix Hamiltonian

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

Rule 2:

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

Rule 3:

$$[I_p, I_q] = 0 \text{ for } (p,q) = (x,y,z)$$

Commutation in coherence space

Rule 1:

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

Rule 2:

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

Rule 3:

$$[I_p, I_q] = 0 \text{ for } (p,q) = (x,y,z)$$

Commutation in coherence space

Rule 1:

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

Rule 2:

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

Rule 3:

$[I_p, I_q] = 0$ for (p,q) = (x,y,z)

Rule 4:

Commutation in coherence space

Rule 1:

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

Rule 2:

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

Rule 3:

$[I_p, I_q] = 0$ for $(p,q) = (x,y,z)$

Rule 4:

$[I_p\, S_q\, ,\, I_r] = [I_p\, ,\, I_r]\, S_q$

Commutation in coherence space

Rule 1:

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

Rule 2:

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

Rule 3:

$$[I_p, I_q] = 0 \text{ for } (p,q) = (x,y,z)$$

Rule 4:

$$[I_p\, S_q\, ,\, I_r] = [I_p\, ,\, I_r]\, S_q$$

$$[I_p\, S_q\, ,\, I_r] = I_p\, S_q\, I_r - I_r\, I_p\, S_q$$

Commutation in coherence space

Rule 1:

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

Rule 2:

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

Rule 3:

$$[I_p, I_q] = 0 \text{ for } (p,q) = (x,y,z)$$

Rule 4:

$$[I_p S_q\, ,\, I_r] = [I_p\, ,\, I_r]\, S_q$$

$$[I_p S_q\, ,\, I_r] = I_p S_q I_r - I_r I_p S_q$$

Commuting operators

Commutation in coherence space

Rule 1:

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

Rule 2:

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

Rule 3:

$$[I_p, I_q] = 0 \text{ for } (p,q) = (x,y,z)$$

Rule 4:

$$[I_p S_q\, ,\, I_r] = [I_p\, ,\, I_r]\, S_q$$

$$[I_p S_q\, ,\, I_r] = I_p S_q I_r - I_r I_p S_q$$

Commutation in coherence space

Rule 1:

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

Rule 2:

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

Rule 3:

$$[I_p, I_q] = 0 \text{ for } (p,q) = (x,y,z)$$

Rule 4:

$$[I_p S_q\, , I_r] = [I_p\, , I_r]\, S_q$$

$$[I_p S_q\, , I_r] = I_p S_q I_r - I_r I_p S_q$$

$$[I_p S_q\, , I_r] = I_p I_r S_q - I_r I_p S_q$$

Commutation in coherence space

Rule 1:

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

Rule 2:

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

Rule 3:

$$[I_p, I_q] = 0 \text{ for } (p,q) = (x,y,z)$$

Rule 4:

$$[I_p S_q , I_r] = [I_p , I_r]\, S_q$$

Rule 5:

$$[I_p S_q , I_r S_s] =$$

Commutation in coherence space

Rule 1:

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

Rule 2:

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

Rule 3:

$$[I_p, I_q] = 0 \text{ for } (p,q) = (x,y,z)$$

Rule 4:

$$[I_p S_q\, , I_r] = [I_p\, , I_r]\, S_q$$

Rule 5:

$$[I_p S_q\, , I_r S_s\,] =$$

0

if $p \neq r$ and $q \neq s$

Commutation in coherence space

Rule 1:

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

Rule 2:

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

Rule 3:

$$[I_p, I_q] = 0 \text{ for } (p,q) = (x,y,z)$$

Rule 4:

$$[I_p S_q\, ,\, I_r] = [I_p\, ,\, I_r]\, S_q$$

Rule 5:

$$[I_p S_q\, ,\, I_r S_s\,] =$$

0

if $p \neq r$ and $q \neq s$

$^1/_4[S_q\, ,\, S_s\,]$

if $p = r$

Commutation in coherence space

Rule 1:

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

Rule 2:

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

Rule 3:

$[I_p, I_q] = 0$ for (p,q) = (x,y,z)

Rule 4:

$[I_p S_q\, , I_r] = [I_p\, , I_r]\, S_q$

Rule 5:

$[I_p S_q\, , I_r S_s\,] =$

0
if $p \neq r$ and $q \neq s$

$\frac{1}{4}[S_q\, , S_s\,]$
if $p = r$

$\frac{1}{4}[I_p\, , I_r]$
if $q = s$

Commutation in coherence space (summary)

Rule 1:

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

Rule 2:

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

Rule 3:

$$[I_p, I_q] = 0 \text{ for } (p,q) = (x,y,z)$$

Rule 4:

$$[I_p S_q\, ,\, I_r] = [I_p\, ,\, I_r]\, S_q$$

Rule 5:

$$[I_p S_q\, ,\, I_r S_s\,] =$$

- 0 if $p \neq r$ and $q \neq s$
- $\frac{1}{4}[S_q\, ,\, S_s\,]$ if $p = r$
- $\frac{1}{4}[I_p\, ,\, I_r]$ if $q = s$

Table 2.3. Commutators of coherences

Cohe-rence	Commutator with							
	E	I_z	S_z	I_zS_z	I_x	I_y	I_xS_z	I_yS_z
E	0	0	0	0	0	0	0	0
I_z	0	0	0	0	I_y	$-I_x$	I_yS_z	$-I_xS_z$
S_z	0	0	0	0	0	0	0	0
I_zS_z	0	0	0	0	I_yS_z	$-I_xS_z$	I_y	$-I_x$
I_x	0	$-I_y$	0	$-I_yS_z$	0	I_z	0	I_zS_z
I_y	0	I_x	0	I_xS_z	$-I_z$	0	$-I_zS_z$	0
I_xS_z	0	$-I_yS_z$	0	$-I_y$	0	I_zS_z	0	I_z
I_yS_z	0	I_xS_z	0	I_x	$-I_zS_z$	0	$-I_z$	0
S_x	0	0	$-S_y$	$-I_zS_y$	0	0	$-I_xS_y$	$-I_yS_y$
S_y	0	0	S_x	I_zS_x	0	0	I_xS_x	I_yS_x
I_zS_x	0	0	$-I_zS_y$	$-S_y$	I_yS_x	$-I_xS_x$	0	0
I_zS_y	0	0	I_zS_x	S_x	I_yS_y	$-I_xS_y$	0	0
I_xS_x	0	$-I_yS_x$	$-I_xS_y$	0	0	I_zS_x	$-S_y$	0
I_yS_y	0	I_xS_y	I_yS_x	0	$-I_zS_y$	0	0	S_x
I_xS_y	0	$-I_yS_y$	I_xS_x	0	0	I_zS_y	S_x	0
I_yS_x	0	I_xS_x	$-I_yS_y$	0	$-I_zS_x$	0	0	$-S_y$

Table 2.3. Commutators of coherences

Coherence	Commutator with E	I_z	S_z	I_zS_z	I_x	I_y	I_xS_z	I_yS_z
E	0	0	0	0	0	0	0	0
I_z	0	0	0	0	I_y	$-I_x$	I_yS_z	$-I_xS_z$
S_z	0	0	0	0	0	0	0	0
I_zS_z	0	0	0	0	I_yS_z	$-I_xS_z$	I_y	$-I_x$
I_x	0	[illegible]	[illegible]	[illegible]	0	I_z	0	I_zS_z
I_y	0	[illegible]	[illegible]	[illegible]	$-I_z$	0	$-I_zS_z$	0
I_xS_z	0	$-I_y$	[illegible]	[illegible]	0	I_zS_z	0	I_z
I_yS_z	0	I_x	[illegible]	[illegible]	$-I_zS_z$	0	$-I_z$	0
S_x	0	[illegible]	[illegible]	[illegible]	0	0	$-I_xS_y$	$-I_yS_y$
S_y	0	0	S_x	I_zS_x	0	0	I_xS_x	I_yS_x
I_zS_x	0	0	$-I_zS_y$	$-S_y$	I_yS_x	$-I_xS_x$	0	0
I_zS_y	0	0	I_zS_x	S_x	I_yS_y	$-I_xS_y$	0	0
I_xS_x	0	$-I_yS_x$	$-I_xS_y$	0	0	I_zS_x	$-S_y$	0
I_yS_y	0	I_xS_y	I_yS_x	0	$-I_zS_y$	0	0	S_x
I_xS_y	0	$-I_yS_y$	I_xS_x	0	0	I_zS_y	S_x	0
I_yS_x	0	I_xS_x	$-I_yS_y$	0	$-I_zS_x$	0	0	$-S_y$

Any operator commutes with itself

Table 2.3. Commutators of coherences

Cohe-rence	Commutator with							
	E	I_z	S_z	I_zS_z	I_x	I_y	I_xS_z	I_yS_z
E	0	0	0	0	0	0	0	0
I_z	0	0	0	0	I_y	$-I_x$	I_yS_z	$-I_xS_z$
S_z	0	0	0	0	0	0	0	0
I_zS_z	0	0	0	0	I_yS_z	$-I_xS_z$	I_y	$-I_x$
I_x	0	$-I_y$	0	$-I_yS_z$	0	I_z	0	I_zS_z
I_y	0	I_x	0	I_xS_z	$-I_z$	0	$-I_zS_z$	0
I_xS_z	0	$-I_yS_z$	0	$-I_y$	0	I_zS_z	0	I_z
I_yS_z	0	I_xS_z	0	I_x	$-I_zS_z$	0	$-I_z$	0
S_x	0	0	$-S_y$	$-I_zS_y$	0	0	$-I_xS_y$	$-I_yS_y$
S_y	0	0	S_x	I_zS_x	0	0	I_xS_x	I_yS_x
I_zS_x	0	0	$-I_zS_y$	$-S_y$	I_yS_x	$-I_xS_x$	0	0
I_zS_y	0	0	I_zS_x	S_x	I_yS_y	$-I_xS_y$	0	0
I_xS_x	0	$-I_yS_x$	$-I_xS_y$	0	0	I_zS_x	$-S_y$	0
I_yS_y	0	I_xS_y	I_yS_x	0	$-I_zS_y$	0	0	S_x
I_xS_y	0	$-I_yS_y$	I_xS_x	0	0	I_zS_y	S_x	0
I_yS_x	0	I_xS_x	$-I_yS_y$	0	$-I_zS_x$	0	0	$-S_y$

Table 2.3. Commutators of coherences

Cohe-rence	Commutator with							
	E	I_z	S_z	I_zS_z	I_x	I_y	I_xS_z	I_yS_z
E	0	0	0	0	0	0	0	0
I_z	0	0	0	0	I_y	$-I_x$	I_yS_z	$-I_xS_z$
S_z	0	0	0	0	0	0	0	0
I_zS_z	0	0	0	0	I_yS_z	$-I_xS_z$	I_y	$-I_x$
I_x	0	$-I_y$	0	$-I_yS_z$	0	I_z	0	I_zS_z
I_y	0	I_x	0	I_xS_z	$-I_z$	0	$-I_zS_z$	0
I_xS_z	0	$-I_yS_z$	0	$-I_y$	0	I_zS_z	0	I_z
I_yS_z	0	I_xS_z	0	I_x	$-I_zS_z$	0	$-I_z$	0
S_x	0	0	$-S_y$	$-I_zS_y$	0	0	[illegible]	$-I_yS_y$
S_y	0	0	S_x	I_zS_x	0	[illegible]	[illegible]	I_yS_x
I_zS_x	0	0	$-I_zS_y$	$-S_y$	[illegible]	[illegible]	[illegible]	0
I_zS_y	0	0	I_zS_x	S_x	[illegible]	[illegible]	[illegible]	0
I_xS_x	0	$-I_yS_x$	$-I_xS_y$	0	0	[illegible]	[illegible]	0
I_yS_y	0	I_xS_y	I_yS_x	0	$-I_zS_y$	0	0	S_x
I_xS_y	0	$-I_yS_y$	I_xS_x	0	0	I_zS_y	S_x	0
I_yS_x	0	I_xS_x	$-I_yS_y$	0	$-I_zS_x$	0	0	$-S_y$

[Iz,Ix] ≠ 0
They do not
commute

Table 2.3. Commutators of coherences

Coherence	Commutator with							
	E	I_z	S_z	I_zS_z	I_x	I_y	I_xS_z	I_yS_z
E	0	0	0	0	0	0	0	0
I_z	0	0	0	0	I_y	$-I_x$	I_yS_z	$-I_xS_z$
S_z	0	0	0	0	0	0	0	0
I_zS_z	0	0	0	0	I_yS_z	$-I_xS_z$	I_y	$-I_x$
I_x	0	$-I_y$	0	$-I_yS_z$	0	I_z	0	I_zS_z
I_y	0	I_x	0	I_xS_z	$-I_z$	0	$-I_zS_z$	0
I_xS_z	0	$-I_yS_z$	0	$-I_y$	0	I_zS_z	0	I_z
I_yS_z	0	I_xS_z	0	I_x	$-I_zS_z$	0	$-I_z$	0
S_x	0	0	$-S_y$	$-I_zS_y$	0	0	$-I_xS_y$	$-I_yS_y$
S_y	0	0	S_x	I_zS_x	0	0	I_xS_x	I_yS_x
I_zS_x	0	0	$-I_zS_y$	$-S_y$	I_yS_x	$-I_xS_x$	0	0
I_zS_y	0	0	I_zS_x	S_x	I_yS_y	$-I_xS_y$	0	0
I_xS_x	0	$-I_yS_x$	$-I_xS_y$	0	0	I_zS_x	$-S_y$	0
I_yS_y	0	I_xS_y	I_yS_x	0	$-I_zS_y$	0	0	S_x
I_xS_y	0	$-I_yS_y$	I_xS_x	0	0	I_zS_y	S_x	0
I_yS_x	0	I_xS_x	$-I_yS_y$	0	$-I_zS_x$	0	0	$-S_y$

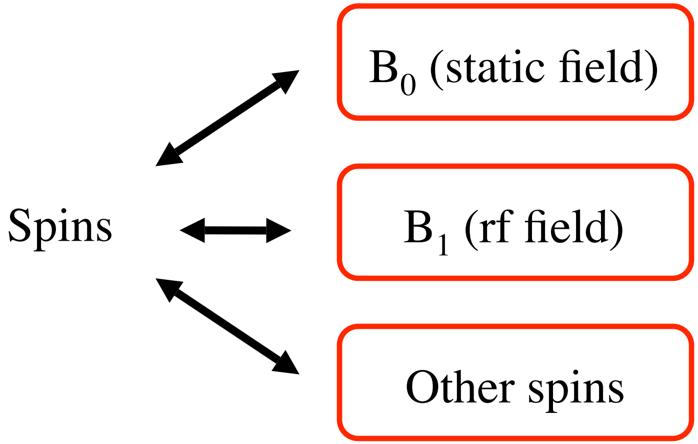
Table 2.3. Commutators of coherences

Coherence	Commutator with							
	E	I_z	S_z	I_zS_z	I_x	I_y	I_xS_z	I_yS_z
E	0	0	0	0	0	0	0	0
I_z	0	0	0	0	I_y	$-I_x$	I_yS_z	$-I_xS_z$
S_z	0	0	0	0	0	0	0	0
I_zS_z	0	0	0	0	I_yS_z	$-I_xS_z$	I_y	$-I_x$
I_x	0	$-I_y$	0	$-I_yS_z$	0	I_z	0	I_zS_z
I_y	0	I_x	0	[illegible]	[illegible]	0	[illegible]	0
I_xS_z	0	$-I_yS_z$	0	[illegible]	[illegible]	[illegible]	[illegible]	I_z
I_yS_z	0	I_xS_z	0	[illegible]	[illegible]	[illegible]	[illegible]	0
S_x	0	0	$-S_y$	[illegible]	[illegible]	[illegible]	[illegible]	$-I_yS_y$
S_y	0	0	S_x	[illegible]	[illegible]	[illegible]	[illegible]	I_yS_x
I_zS_x	0	0	$-I_zS_y$	$-S_y$	I_yS_x	$-I_xS_x$	0	0
I_zS_y	0	0	I_zS_x	S_x	I_yS_y	$-I_xS_y$	0	0
I_xS_x	0	$-I_yS_x$	$-I_xS_y$	0	0	I_zS_x	$-S_y$	0
I_yS_y	0	I_xS_y	I_yS_x	0	$-I_zS_y$	0	0	S_x
I_xS_y	0	$-I_yS_y$	I_xS_x	0	0	I_zS_y	S_x	0
I_yS_x	0	I_xS_x	$-I_yS_y$	0	$-I_zS_x$	0	0	$-S_y$

Table 2.3. Commutators of coherences

Coherence	Commutator with							
	E	I_z	S_z	I_zS_z	I_x	I_y	I_xS_z	I_yS_z
E	0	0	0	0	0	0	0	0
I_z	0	0	0	0	I_y	$-I_x$	I_yS_z	$-I_xS_z$
S_z	0	0	0	0	0	0	0	0
I_zS_z	0	0	0	0	I_yS_z	$-I_xS_z$	I_y	$-I_x$
I_x	0	$-I_y$	0	$-I_yS_z$	0	I_z	0	I_zS_z
I_y	0	I_x	0	I_xS_z	$-I_z$	0	$-I_zS_z$	0
I_xS_z	0	$-I_yS_z$	0	$-I_y$	0	I_zS_z	0	I_z
I_yS_z	0	I_xS_z	0	I_x	$-I_zS_z$	0	$-I_z$	0
S_x	0	0	$-S_y$	$-I_zS_y$	0	0	$-I_xS_y$	$-I_yS_y$
S_y	0	0	S_x	I_zS_x	0	0	I_xS_x	I_yS_x
I_zS_x	0	0	$-I_zS_y$	$-S_y$	I_yS_x	$-I_xS_x$	0	0
I_zS_y	0	0	I_zS_x	S_x	I_yS_y	$-I_xS_y$	0	0
I_xS_x	0	$-I_yS_x$	$-I_xS_y$	0	0	I_zS_x	$-S_y$	0
I_yS_y	0	I_xS_y	I_yS_x	0	$-I_zS_y$	0	0	S_x
I_xS_y	0	$-I_yS_y$	I_xS_x	0	0	I_zS_y	S_x	0
I_yS_x	0	I_xS_x	$-I_yS_y$	0	$-I_zS_x$	0	0	$-S_y$

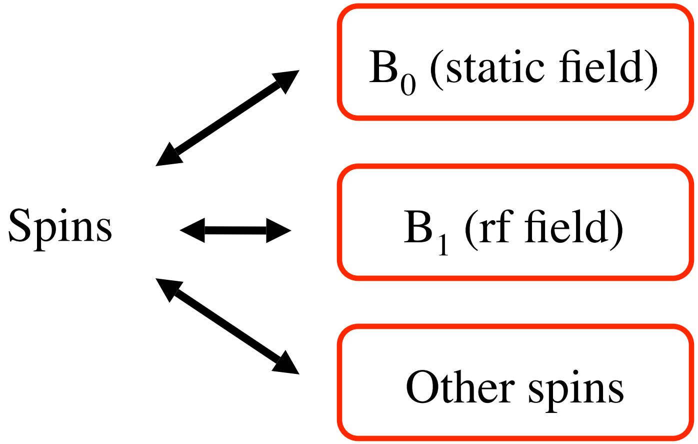
Terms of the spin hamiltonian



Terms of the spin hamiltonian

Zeeman interaction

$$H = -(1 - \sigma_{iso})\, B_0\, I_z$$



Terms of the spin hamiltonian

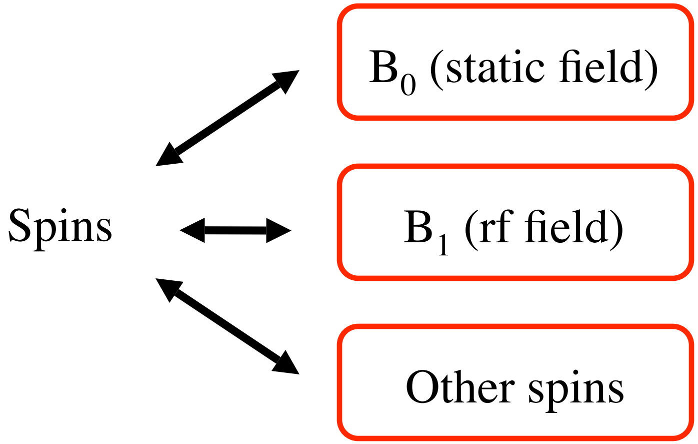
Zeeman interaction

$$H = -(1 - \sigma_{iso})\, B_0\, I_z$$

Shielding tensor

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

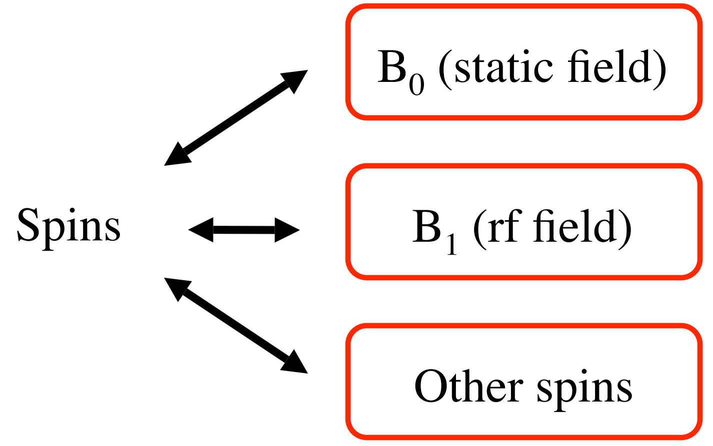
(fast tumbling in liquid)



Terms of the spin hamiltonian

Zeeman interaction

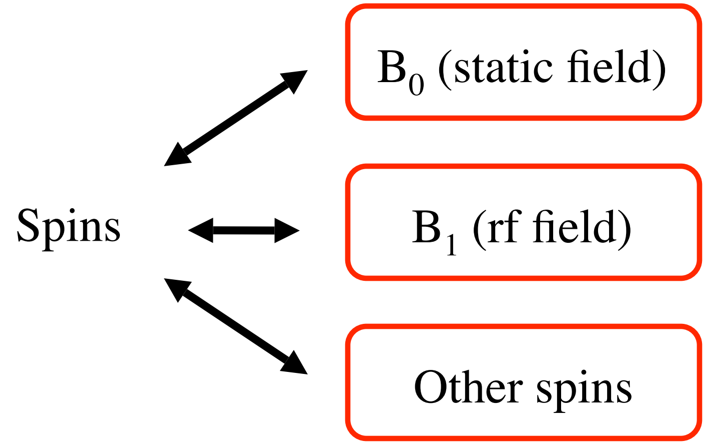
$$H = -(1 - \sigma_{iso})\, B_0\, I_z$$



Terms of the spin hamiltonian

Zeeman interaction

$$H = -(1 - \sigma_{iso}) B_0 I_z$$



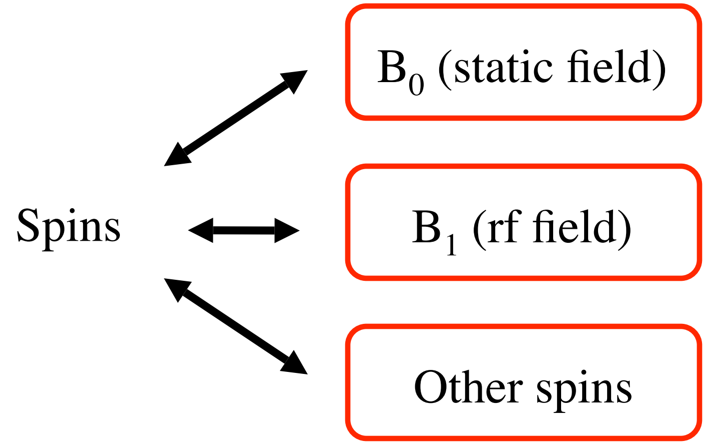
RF field

$$H = -\omega_1[I_x \cos(\omega t) - I_y \sin(\omega t)]$$

Terms of the spin hamiltonian

Zeeman interaction

$$H = -(1 - \sigma_{iso})\, B_0\, I_z$$



RF field

$$H = -\omega_1 [\, I_x \cos(\omega t) - I_y \sin(\omega t)]$$

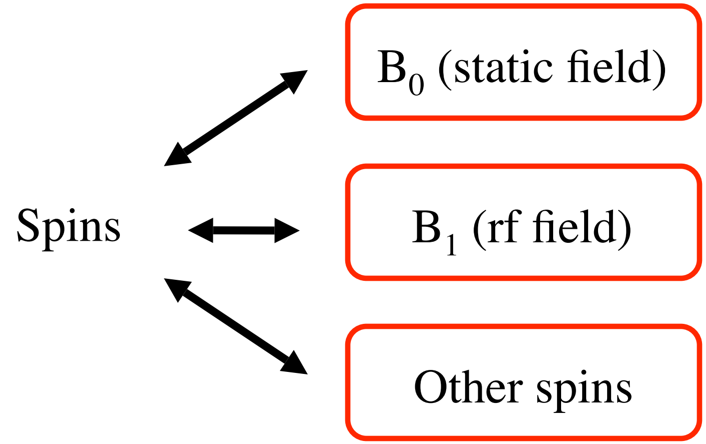
Scalar interaction (J)

$$H = J\, \vec{\mathbf{I}} \,.\, \vec{\mathbf{S}} = J\,(I_x S_x + I_y S_y + I_z S_z)$$

Terms of the spin hamiltonian

Zeeman interaction

$$H = -(1 - \sigma_{iso})\, B_0\, I_z$$



RF field

$$H = -\omega_1 [\, I_x \cos(\omega t) - I_y \sin(\omega t)]$$

Scalar interaction (J)

$$H = J\, \vec{\mathbf{I}} \cdot \vec{\mathbf{S}} = J\,(I_x S_x + I_y S_y + I_z S_z)$$

Dipolar interaction (D)

$\rightarrow 0$ in isotropic liquids

Terms of the spin hamiltonian (conflicts)

RF field

$$H = -\omega_1[\, I_x \cos(\omega t) - I_y \sin(\omega t)]$$

Zeeman interaction

$$H = -\omega_0 I_z$$

Scalar interaction

$$H = J\,\vec{\mathbf{I}}\,.\,\vec{\mathbf{S}} = J\,(I_xS_x + I_yS_y + I_zS_z)$$

Terms of the spin hamiltonian (conflicts)

RF field

$$H = -\omega_1 [\, I_x \cos(\omega t) - I_y \sin(\omega t)]$$

Zeeman interaction

$$H = -\omega_0 I_z$$

$[Iz,Ix] \neq 0$ $[Iz,Iy] \neq 0$

Scalar interaction

$$H = J\, \vec{\mathbf{I}} \cdot \vec{\mathbf{S}} = J\,(I_x S_x + I_y S_y + I_z S_z)$$

Terms of the spin hamiltonian (conflicts)

RF field

$$H = -\omega_1[\, I_x \cos(\omega t) - I_y \sin(\omega t)]$$

Zeeman interaction

$$H = -\omega_0 I_z$$

Scalar interaction

$$H = J\,\vec{\mathbf{I}} \cdot \vec{\mathbf{S}} = J\,(I_x S_x + I_y S_y + I_z S_z)$$

Terms of the spin hamiltonian (conflicts)

RF field

$$H = -\omega_1[\, I_x \cos(\omega t) - I_y \sin(\omega t)]$$

Zeeman interaction

$$H = -\omega_0 I_z$$

$[Iz,IxSx] \neq 0$ $[Iz,IySy] \neq 0$

Scalar interaction

$$H = J\,\vec{\mathbf{I}}\cdot\vec{\mathbf{S}} = J\,(I_xS_x + I_yS_y + I_zS_z)$$

Terms of the spin hamiltonian (solutions)

RF field

During the pulses

$$H = -\omega_1[\, I_x \cos(\omega t) - I_y \sin(\omega t)]$$

Zeeman interaction

$$H = -\omega_0 I_z$$

Scalar interaction

$$H = J\,\vec{\mathbf{I}}\,.\,\vec{\mathbf{S}} = J\,(I_xS_x + I_yS_y + I_zS_z)$$

Terms of the spin hamiltonian (solutions)

RF field

During the pulses

$$H = -\omega_1[\, I_x \cos(\omega t) - I_y \sin(\omega t)]$$

Hypothesis: short pulse
The spins do not precess
during the pulse

Zeeman interaction

$$H = -\omega_0 I_z$$

Scalar interaction

$$H = J\, \vec{\mathbf{I}} \,.\, \vec{\mathbf{S}} = J\,(I_x S_x + I_y S_y + I_z S_z)$$

Terms of the spin hamiltonian (solutions)

RF field

During the pulses

$$H = -\omega_1[\, I_x \cos(\omega t) - I_y \sin(\omega t)]$$

Hypothesis: short pulse
The spins do not precess
during the pulse

Zeeman interaction

$$H = -\omega_0 I_z$$

Scalar interaction

$$H = J\, \vec{\mathbf{I}} \cdot \vec{\mathbf{S}} = J\,(I_x S_x + I_y S_y + I_z S_z)$$

Terms of the spin hamiltonian (solutions)

RF field

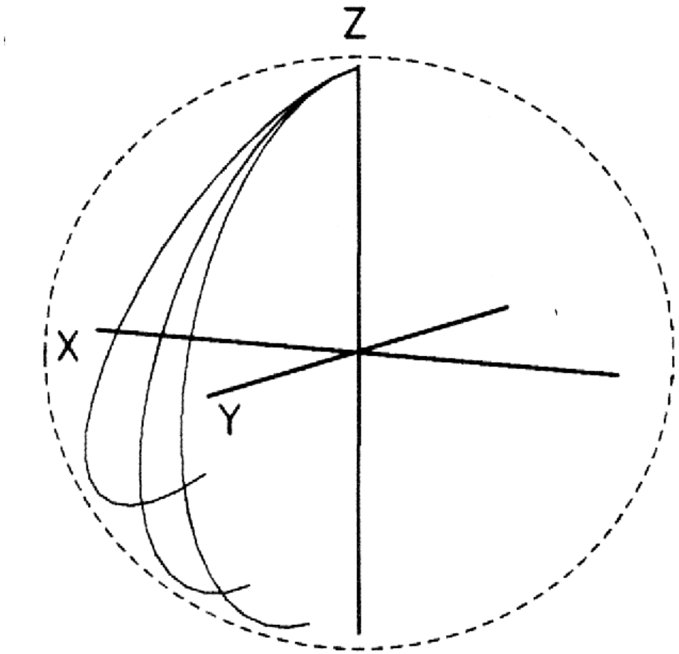
During the pulses

$$H = -\omega_1[\, I_x \cos(\omega t) - I_y \sin(\omega t)]$$

Trajectories of magnetizations

RF field strength = 1000 Hz

Offsets = 100, 250, 500 Hz



Terms of the spin hamiltonian (solutions)

During the free precession

RF field

$$H = -\omega_1[\, I_x \cos(\omega t) - I_y \sin(\omega t)]$$

Zeeman interaction

$$H = -\omega_0 I_z$$

Scalar interaction

$$H = J\, \vec{\mathbf{I}} \cdot \vec{\mathbf{S}} = J\,(I_x S_x + I_y S_y + I_z S_z)$$

Terms of the spin hamiltonian (solutions)

RF field

$H = -\omega_1 [\, I_x \cos(\omega t) - I_y \sin(\omega t)]$

During the free precession

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$H = -\omega_0 I_z$

Hypothesis (1) : weak coupling

$J_{IS} << | \omega_I - \omega_S |$

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$$H = -\omega_0 I_z$$

Hypothesis (2) : the chemical shift evolution is eliminated

Scalar interaction

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Terms of the spin hamiltonian (solutions)

During the free precession

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During the free precession

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~~$H = -\omega_0 I_z$~~

$[IzSz, IxSx] = 0$ ☺

$[IxSx, IySy] = 0$ ☺

$[IzSz, IySy] = 0$ ☺

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$$H = J\, \vec{\mathbf{I}} \cdot \vec{\mathbf{S}} = J\,(I_x S_x + I_y S_y + I_z S_z)$$

Terms of the spin hamiltonian (solutions)

During the free precession

RF field

$H = -\omega_1[\, I_x \cos(\omega t) - I_y \sin(\omega t)]$

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Zeeman interaction

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$[IzSz,IxSx] = 0$ ☺

$[IxSx,IySy] = 0$ ☺

$[IzSz,IySy] = 0$ ☺

Isotropic mixing

Scalar interaction

$$H = J\, \vec{\mathbf{I}} \,.\, \vec{\mathbf{S}} = J\,(I_xS_x + I_yS_y + I_zS_z)$$

Evolution of the spin system

Zeeman interaction

$H = -\omega_0 I_z$

RF field

$H = -\omega_1 [\, I_x \cos(\phi) - I_y \sin(\phi)]$

$\exp(-i\theta \boldsymbol{H})\, \sigma_0 \exp(i\theta \boldsymbol{H})$

$= \sigma_0 \cos\theta + \sigma_1 \sin\theta$

Scalar interaction

$H = J_{IS}\, I_z S_z$

$[\sigma_0 , H] = i\, \sigma_1$

Evolution of the spin system

Zeeman interaction

$$H = -\omega_0 I_z$$

RF field

$$H = -\omega_1[I_x \cos(\phi) - I_y \sin(\phi)]$$

Scalar interaction

$$H = J_{IS} I_z S_z$$

Quantum description

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

Density matrix — Hamiltonian

$$\exp(-i\theta H)\,\sigma_0\,\exp(i\theta H)$$

$$= \sigma_0 \cos\theta + \sigma_1 \sin\theta$$

$$[\sigma_0, H] = i\,\sigma_1$$

Evolution of the spin system (chemical shift)

Zeeman interaction

$$H = -\omega_0 I_z$$

$[Iy,Iz] = i\ Ix$

$[Ix,Iz] = -i\ Ix$

$[Iz,Iz] = 0$

Evolution of the spin system (chemical shift)

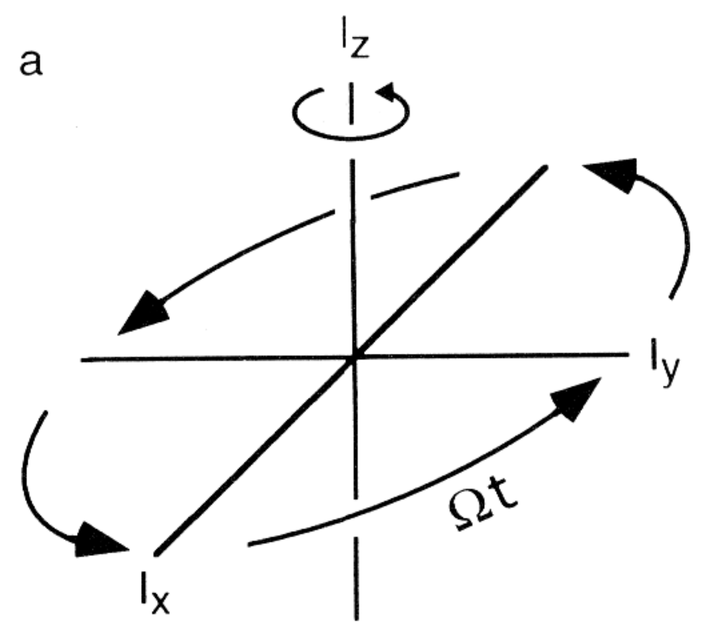
Zeeman interaction

$$H = -\omega_0 I_z$$

[Iy,Iz] = *i* Ix

[Ix,Iz] = –*i* Ix

[Iz,Iz] = 0



Evolution of the spin system (chemical shift)

Zeeman interaction

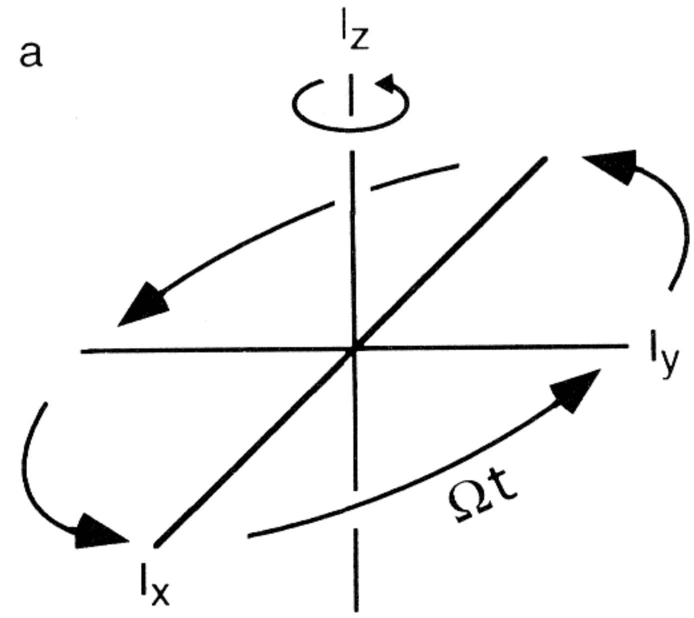
$$H = -\omega_0 I_z$$

$\mathbf{I_x}$

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

$[I_x, I_z] = -i\, I_x$

$[I_z, I_z] = 0$



Evolution of the spin system (chemical shift)

Zeeman interaction

$$H = -\,\omega_0\, I_z$$

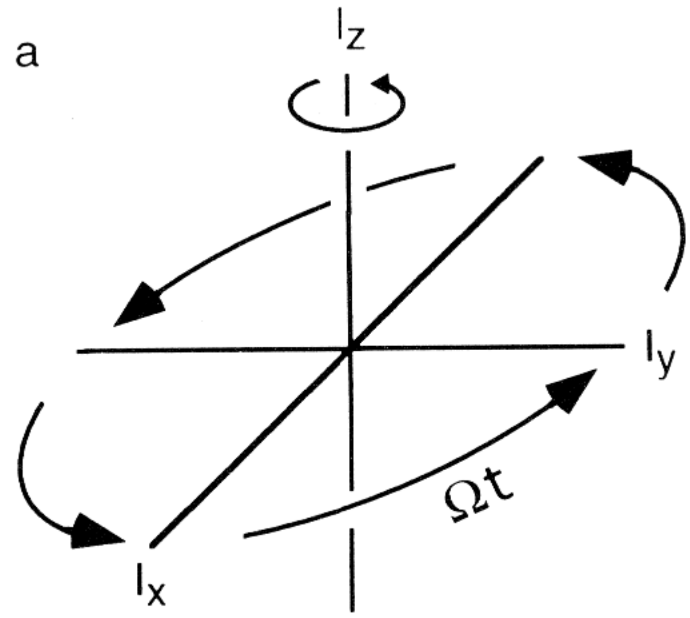
$\mathbf{I_x}$ → $\mathbf{I_x} \cos \omega_0 t$

→ $\mathbf{I_y} \sin \omega_0 t$

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

$[I_x, I_z] = -i\, I_x$

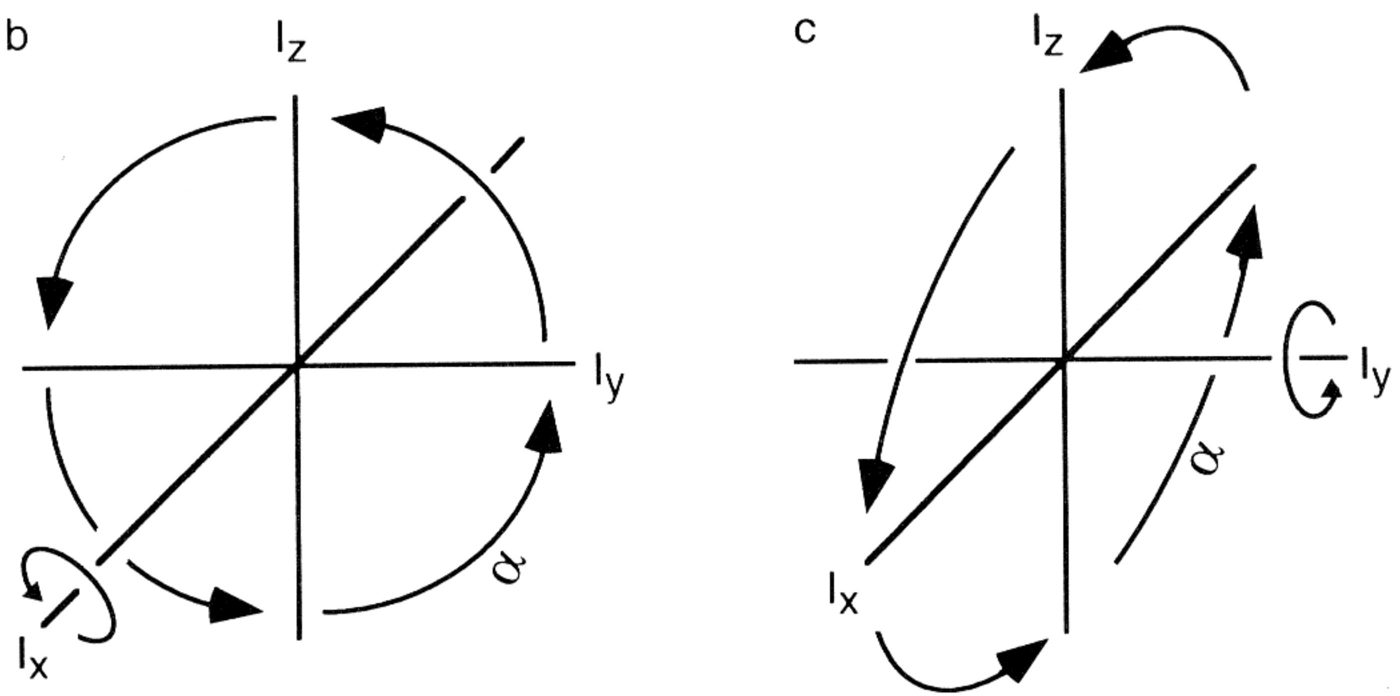
$[I_z, I_z] = 0$



Evolution of the spin system (radiofrequency)

RF field *(rotating frame)*

$$H = -\omega_1[\, I_x \cos(\phi) - I_y \sin(\phi)]$$

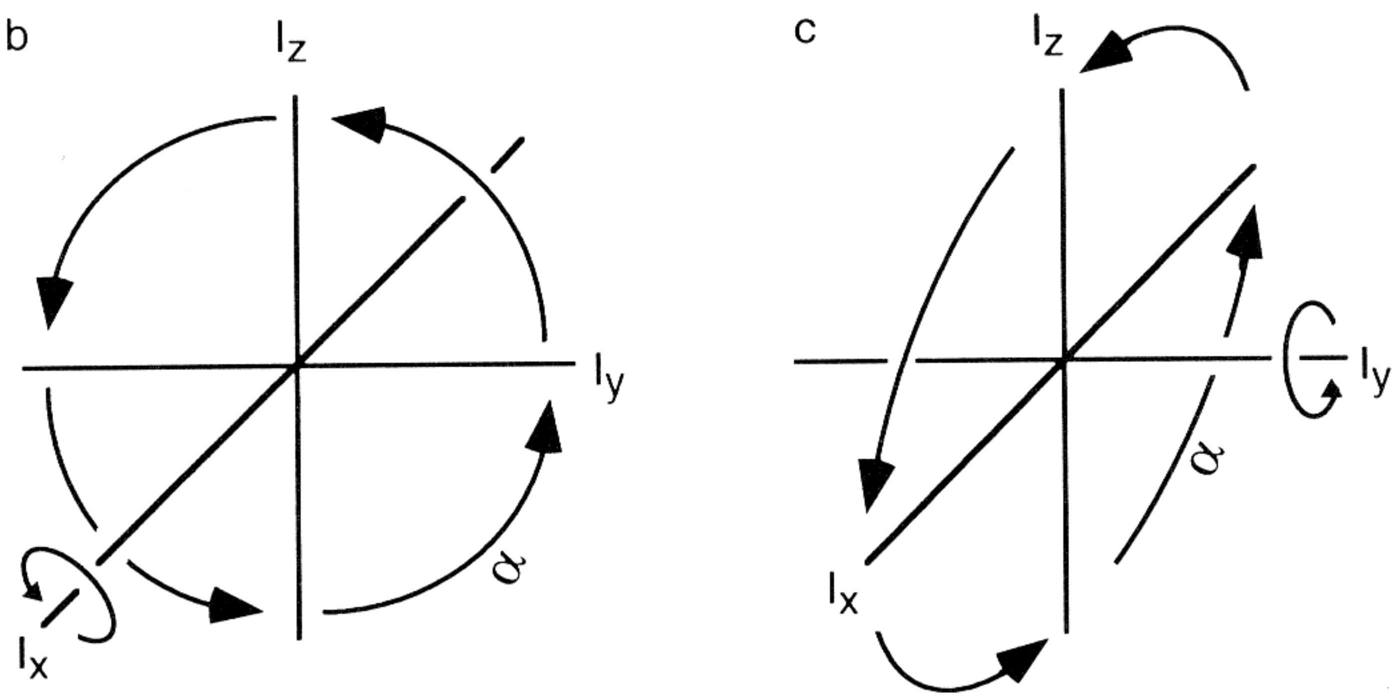


Evolution of the spin system (radiofrequency)

RF field *(rotating frame)*

Phase of the rf

$$H = -\omega_1[\, I_x \cos(\phi) - I_y \sin(\phi)]$$



Evolution of the spin system (radiofrequency)

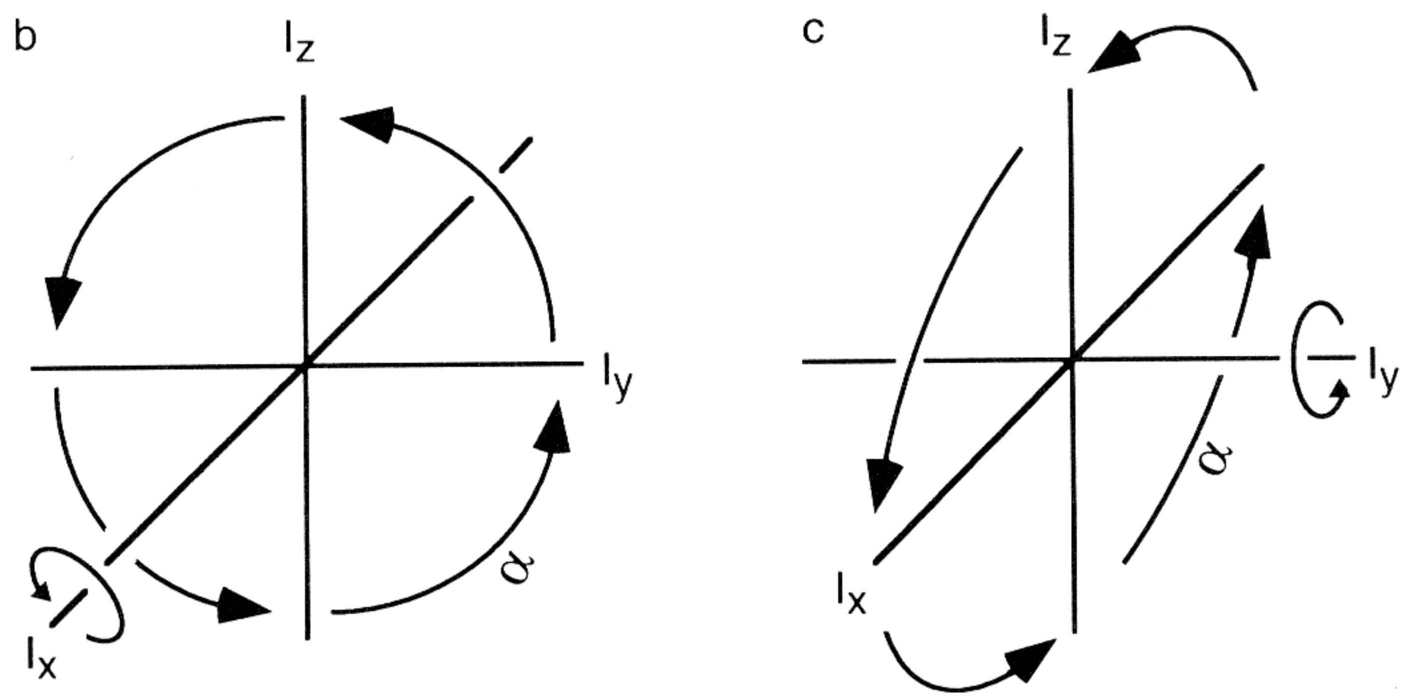
RF field *(rotating frame)*

Phase of the rf

$$H = -\omega_1[\, I_x \cos(\phi) - I_y \sin(\phi)]$$

Pulse around x

$$H = -\omega_1 I_x$$



Evolution of the spin system (radiofrequency)

RF field *(rotating frame)*

Phase of the rf

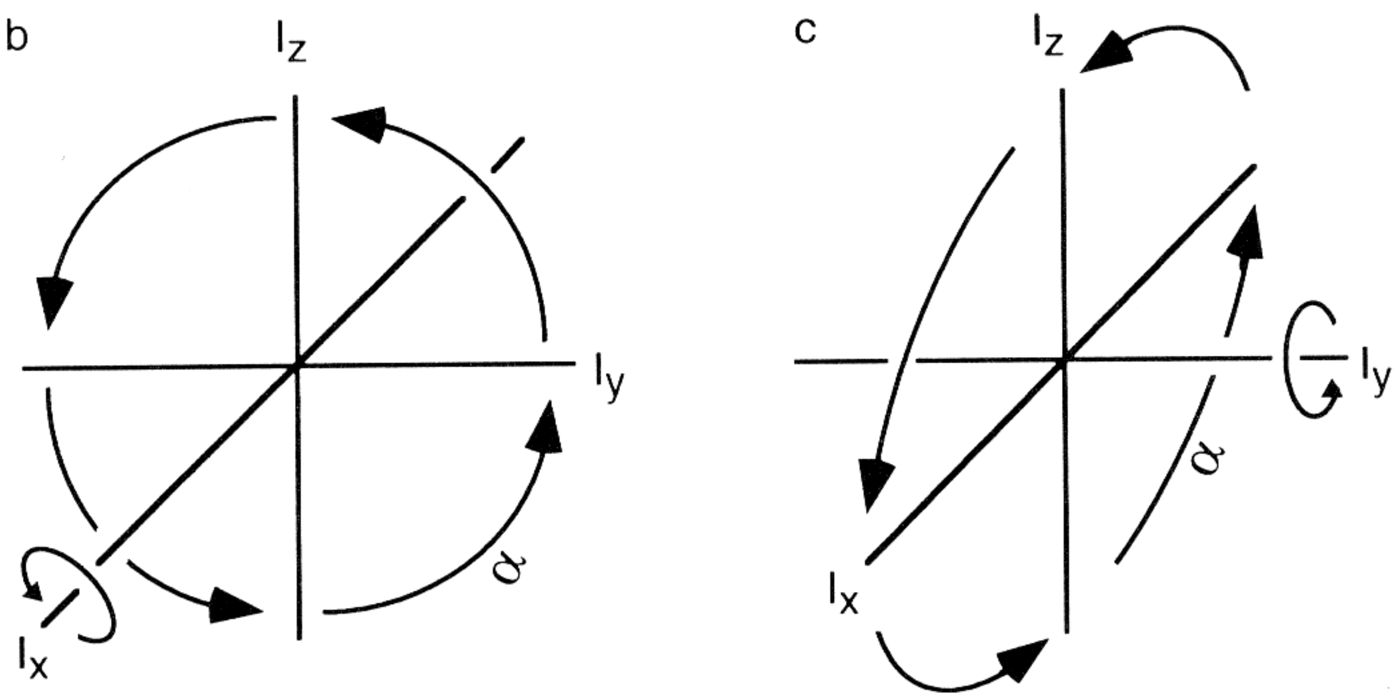
$$H = -\omega_1[\, I_x \cos(\phi) - I_y \sin(\phi)]$$

Pulse around x

$$H = -\omega_1 I_x$$

Pulse around y

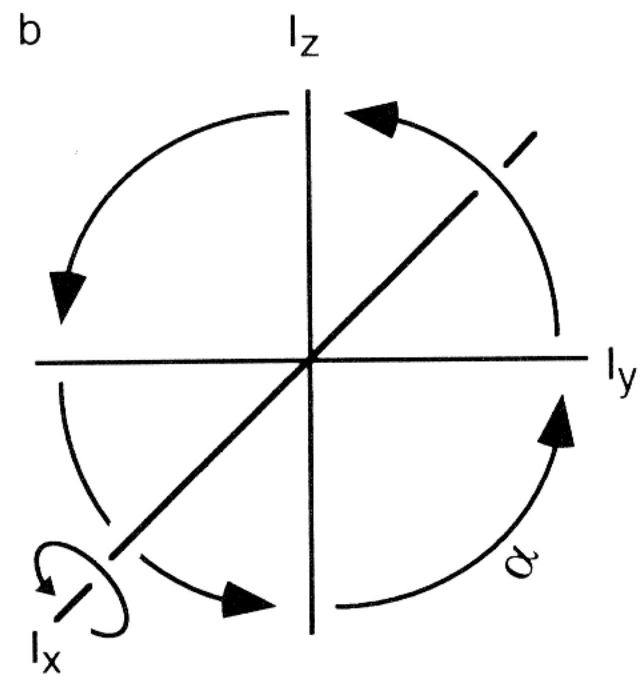
$$H = -\omega_1 I_y$$



Evolution of the spin system (radiofrequency)

RF field *(rotating frame)*

$H = -\omega_1 I_x$

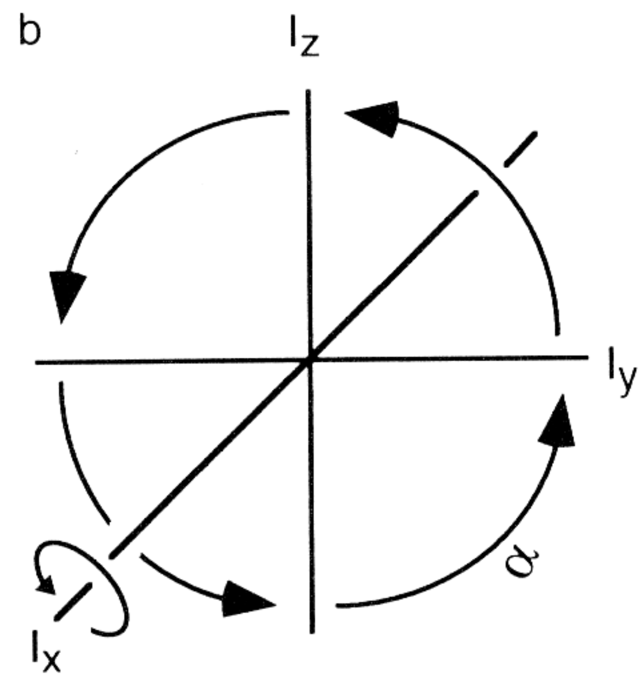


Evolution of the spin system (radiofrequency)

RF field *(rotating frame)*

$$H = -\omega_1 I_x$$

$\mathbf{I_z}$

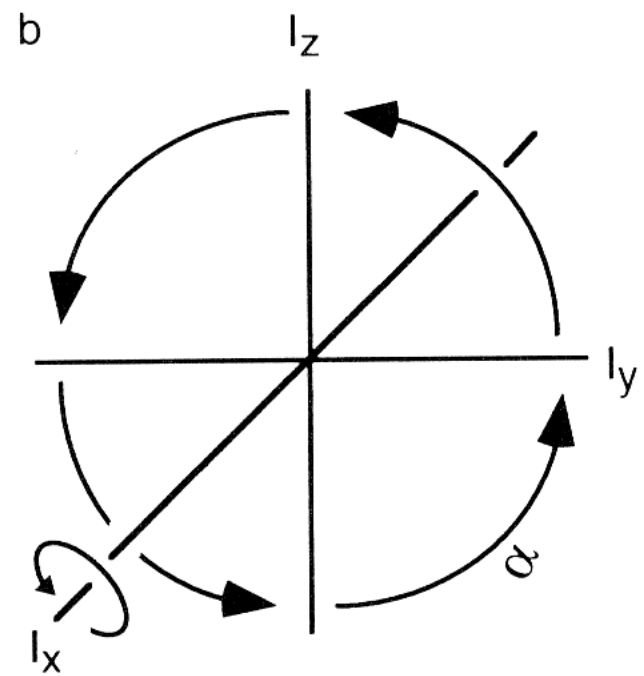


Evolution of the spin system (radiofrequency)

RF field *(rotating frame)*

$$H = -\,\omega_1\, I_x$$

$\mathbf{I_z}$ → $\mathbf{I_z} \cos \omega_1 t$



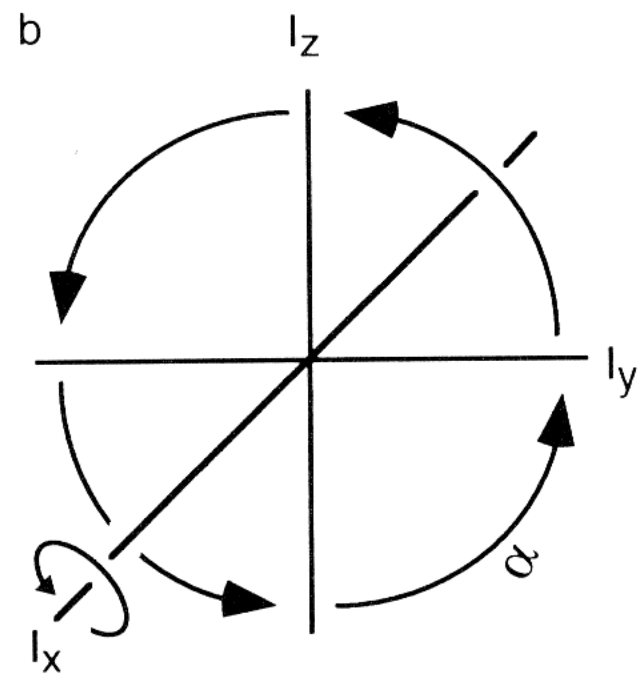
Evolution of the spin system (radiofrequency)

RF field *(rotating frame)*

$$H = -\omega_1 I_x$$

$\mathbf{I_z}$ → $\mathbf{I_z} \cos \omega_1 t$

→ $-\mathbf{I_y} \sin \omega_1 t$



Evolution of the spin system (scalar coupling)

Scalar interaction

$$H = J_{IS}\, I_z S_z$$

Evolution of the spin system (scalar coupling)

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$H = J_{IS}\, I_z S_z$

$[Ix, 2IzSz] = i\ 2IySz$

$[Iy, 2IzSz] = -\ i\ 2IySz$

$[Iz, 2IzSz] = 0$

Evolution of the spin system (scalar coupling)

Scalar interaction

$$H = J_{IS}\, I_z S_z$$

x

y

$$[Ix, 2IzSz] = i\; 2IySz$$

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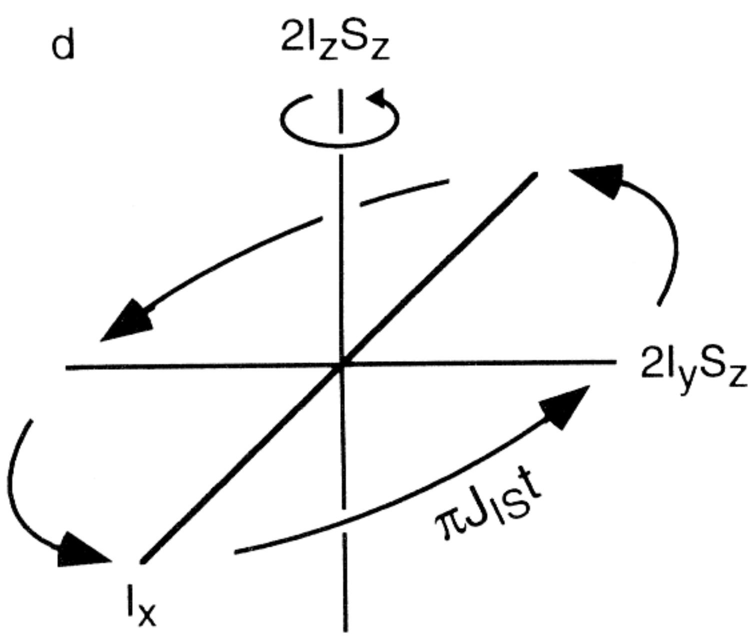

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I_x

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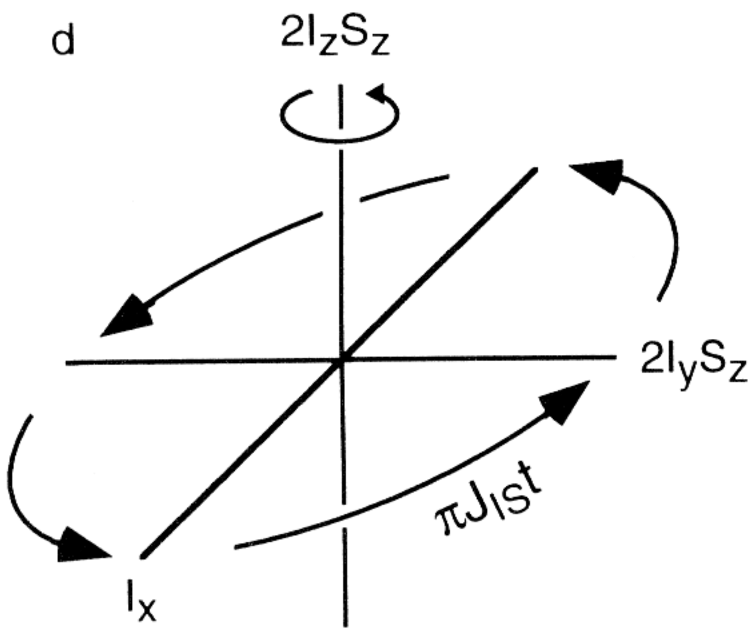
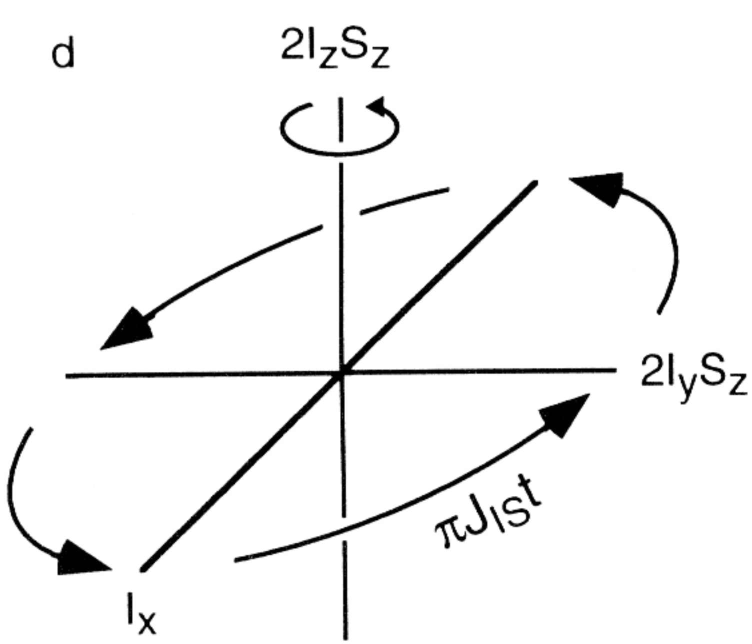


Evolution of the spin system (scalar coupling)

Scalar interaction

$\mathbf{I_x} \rightarrow \mathbf{I_x} \cos \pi J t$

$H = J_{IS}\, I_z S_z$



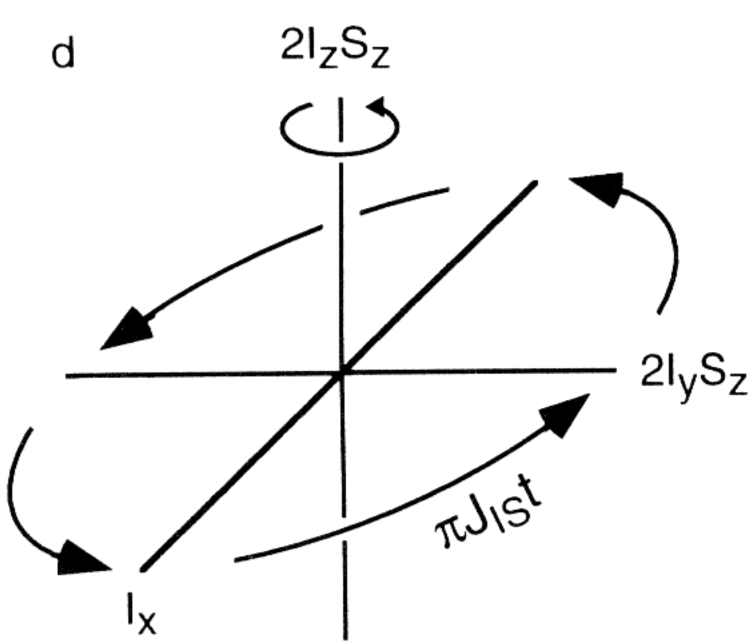
Evolution of the spin system (scalar coupling)

Scalar interaction

$H = J_{IS}\, I_z S_z$

I_x → $I_x \cos \pi J t$

→ $2I_yS_z \sin \pi J t$



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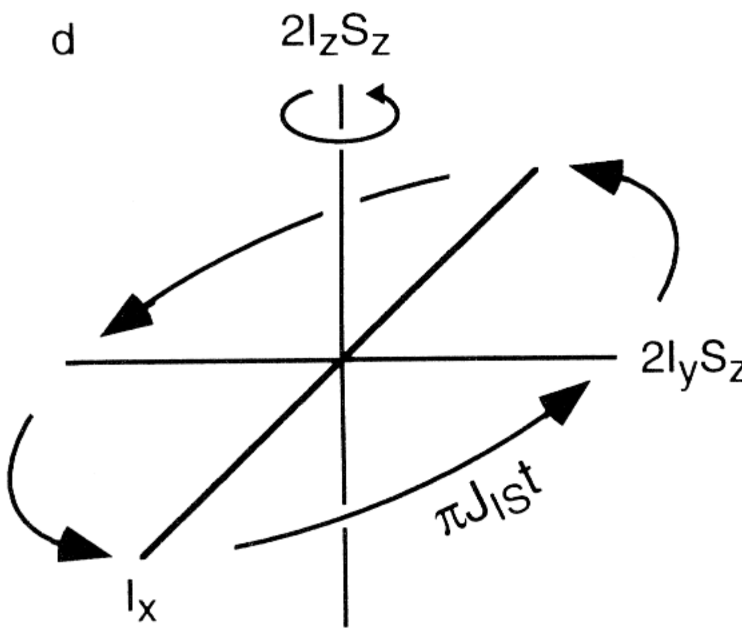

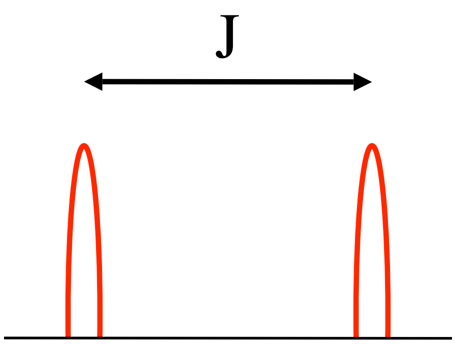

Definition of J
(chemistry)

Evolution of the spin system (scalar coupling)

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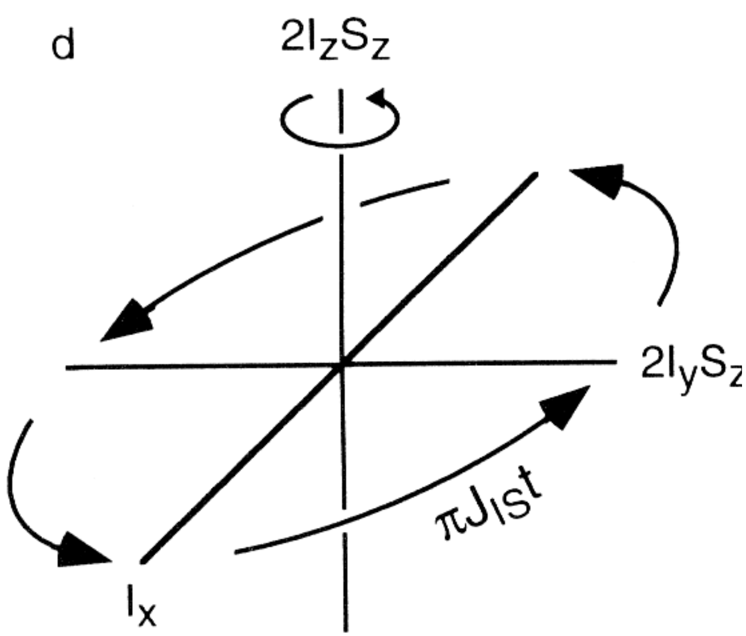
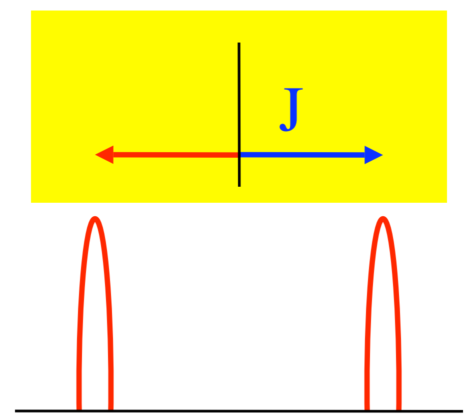




Definition of J
(chemistry)

Summary of the lecture

① Bloch vector model

② Basic quantum mechanics

③ Product operator formalism

④ Spin hamiltonian

⑤ NMR building blocks

⑥ Coherence selection - phase cycling

⑦ Pulsed field gradients

NMR building blocks (1)

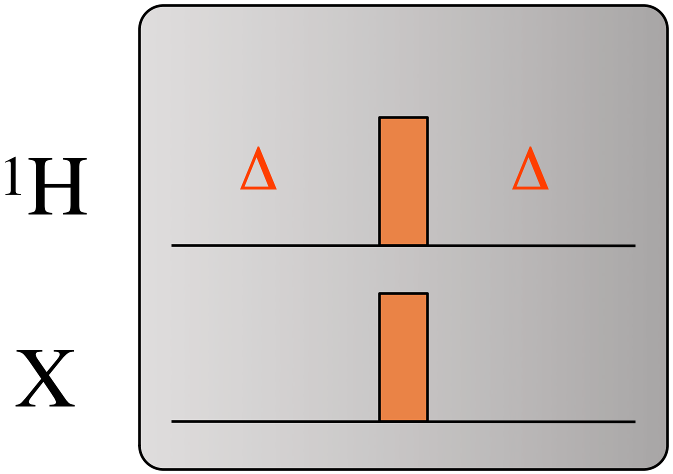
Spin echoes in heteronuclear spin systems

^1H-^{15}N

$^1J \approx 70$ Hz

^1H-^{13}C

$^1J \approx 120$-140 Hz



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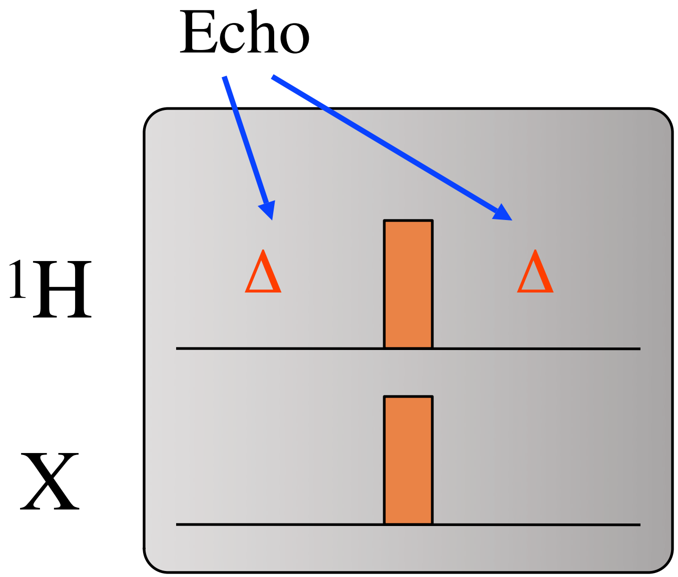

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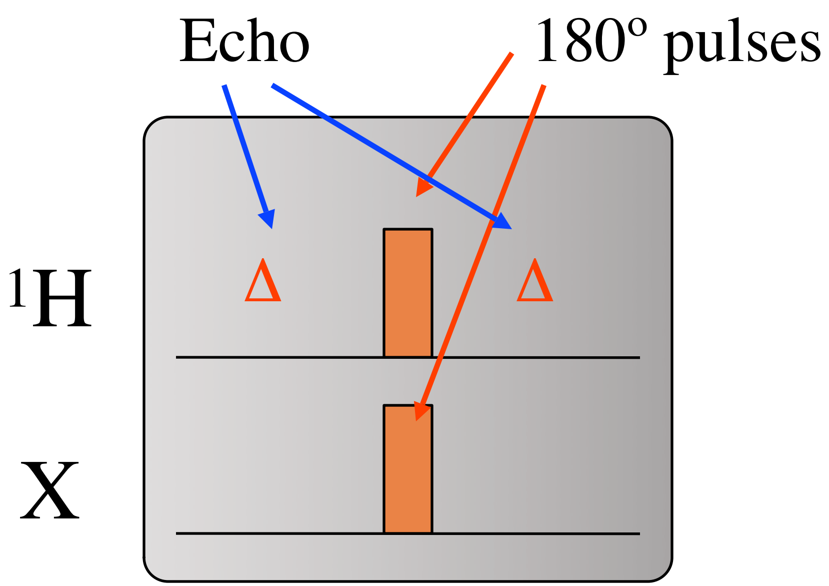

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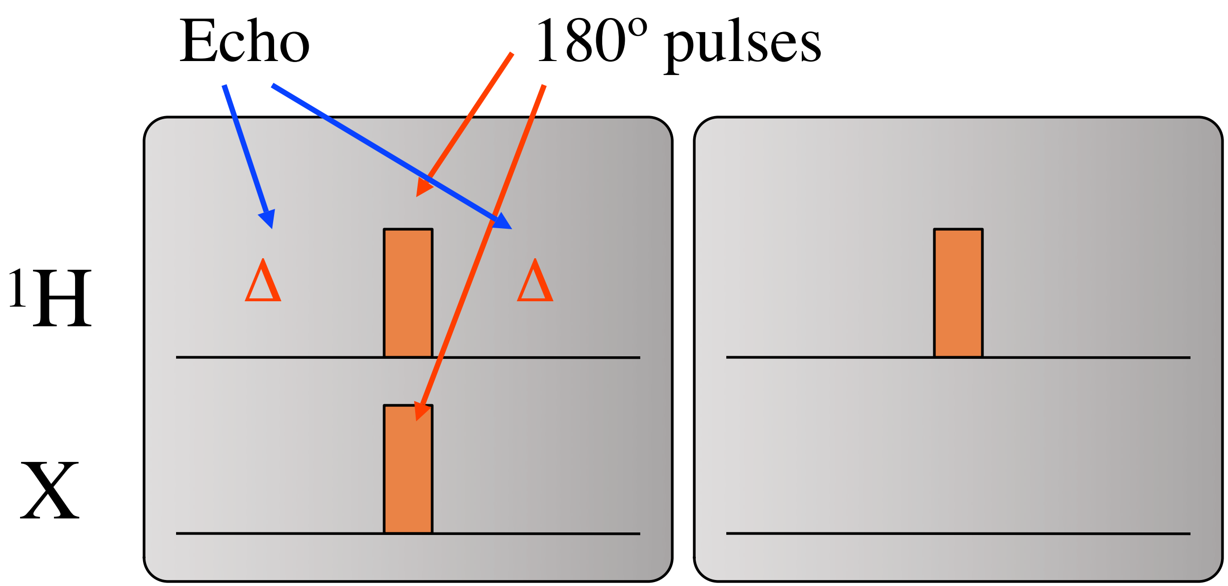

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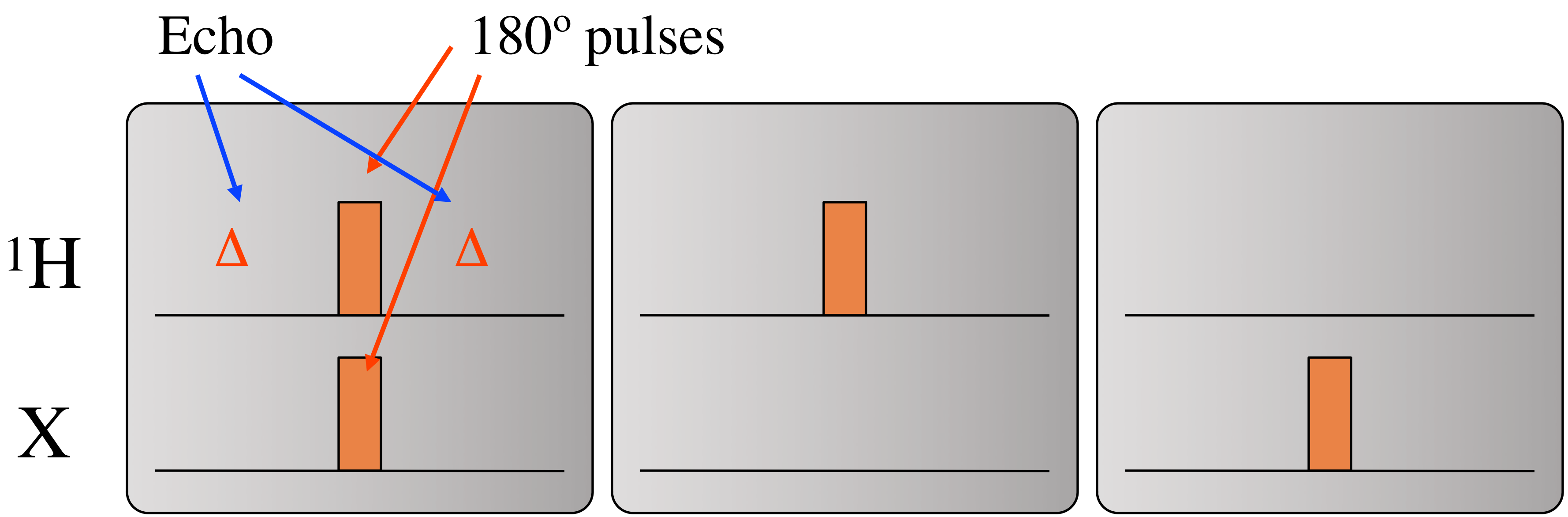

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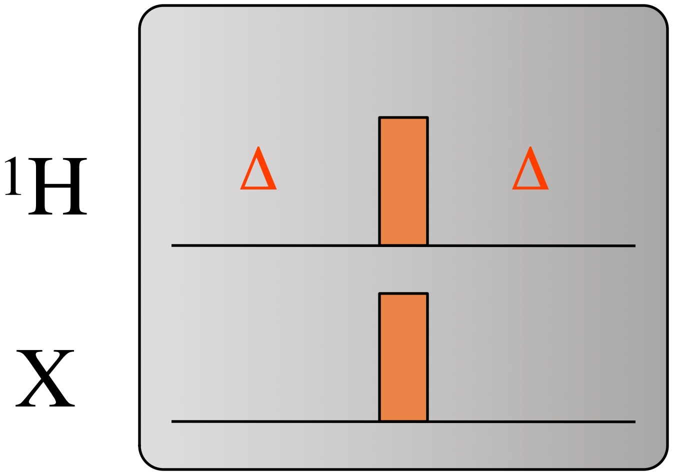

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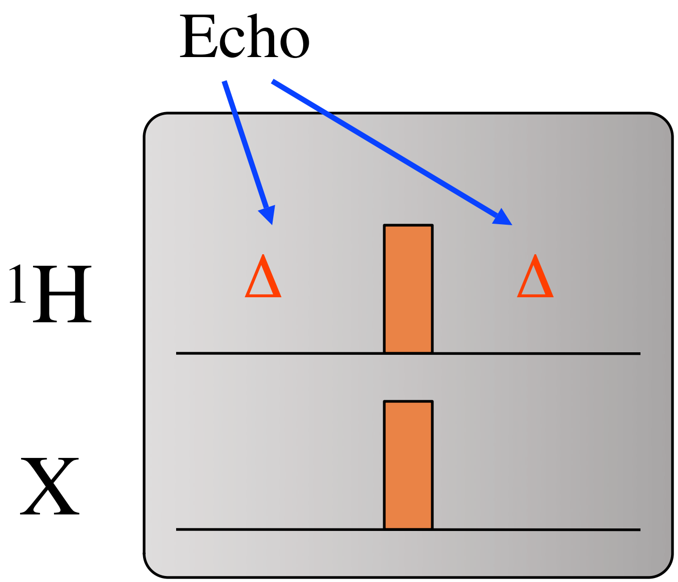

NMR building blocks (1)

Spin echoes in heteronuclear spin systems

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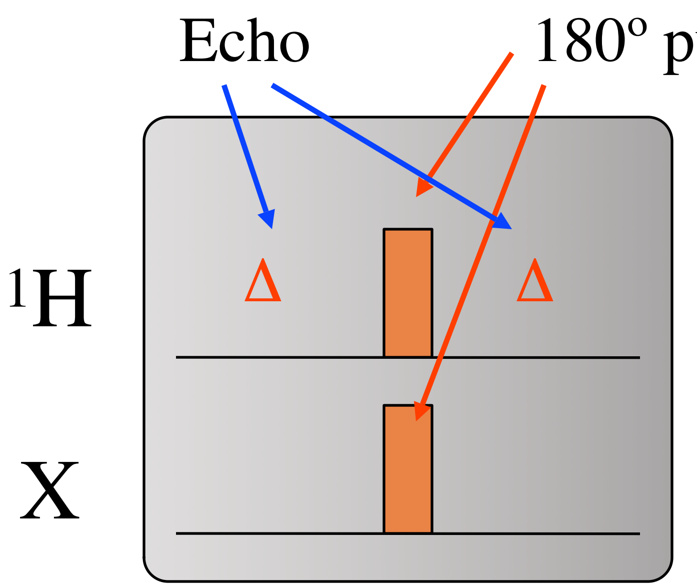

NMR building blocks (1)

Spin echoes in heteronuclear spin systems

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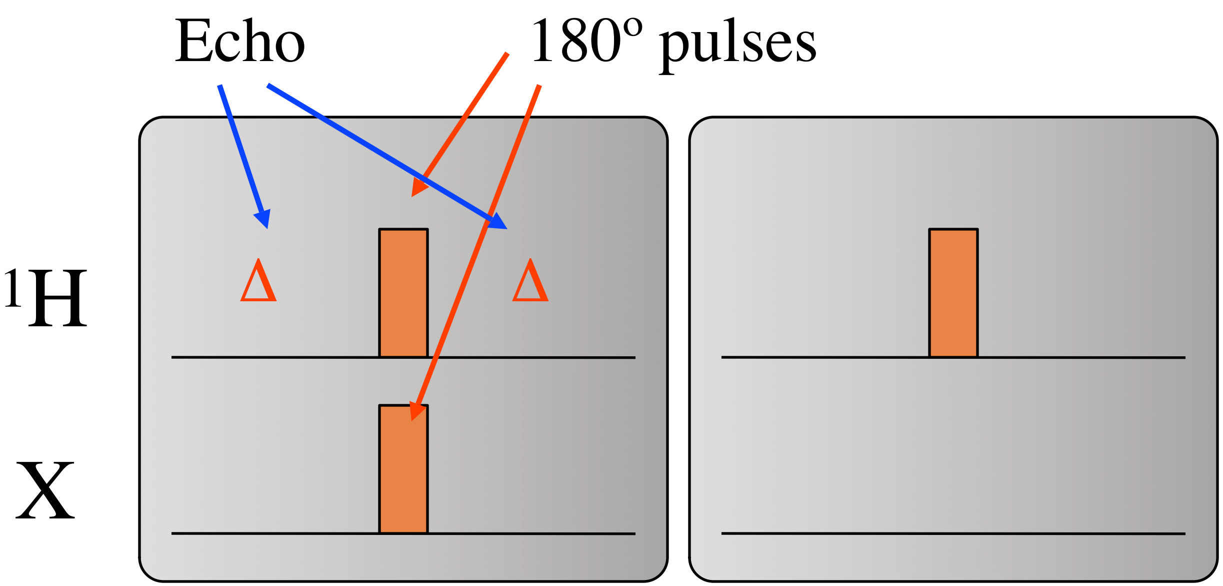

NMR building blocks (1)

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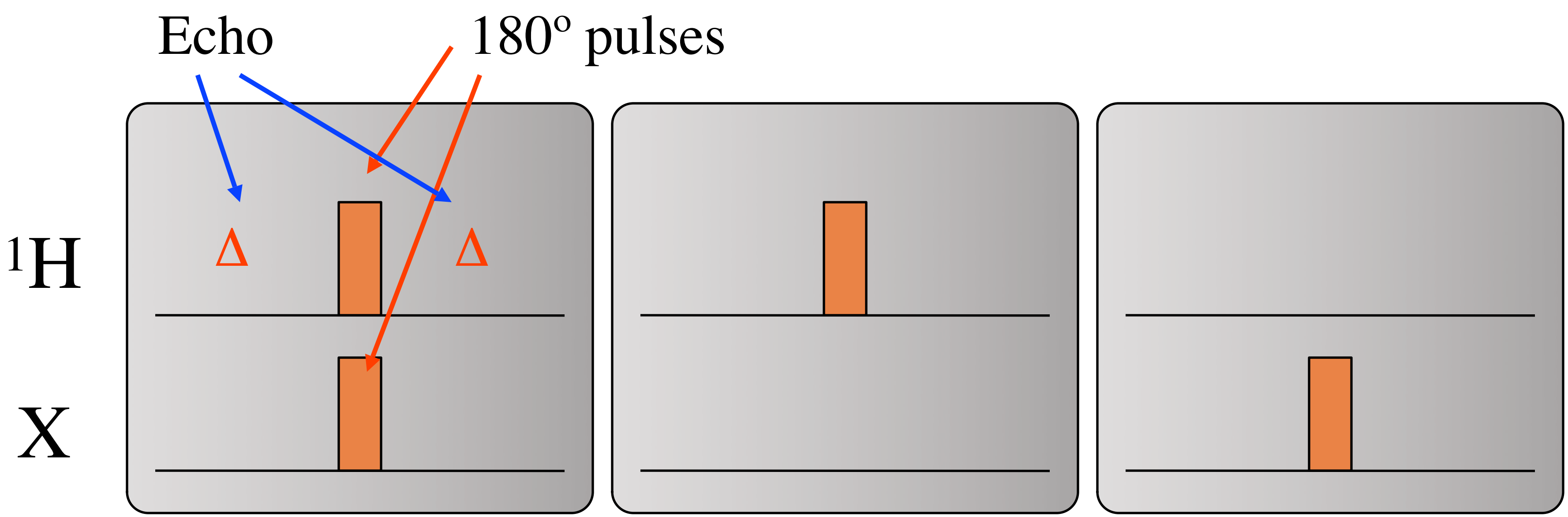
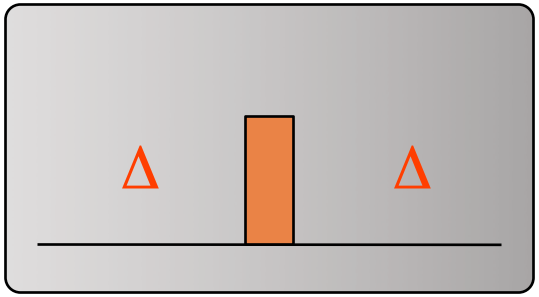


NMR building blocks (2)

Spin echoes in homonuclear spin systems



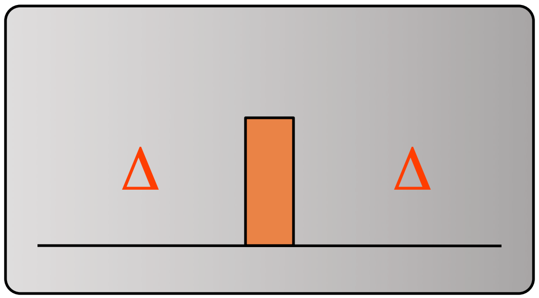
Chemical shift

I_x → $I_x \cos \omega_0 \Delta$

→ $I_y \sin \omega_0 \Delta$

NMR building blocks (2)

Spin echoes in homonuclear spin systems



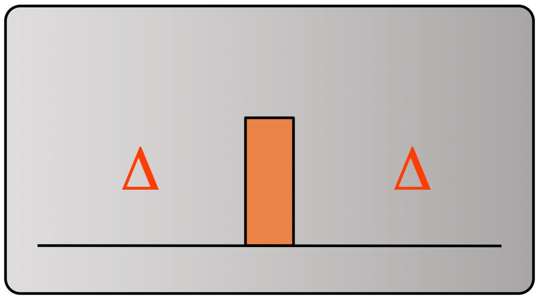
Chemical shift

I_x → $I_x \cos \omega_0\Delta$ → $I_x \cos \omega_0\Delta$

→ $I_y \sin \omega_0\Delta$ → $-I_y \sin \omega_0\Delta$

NMR building blocks (2)

Spin echoes in homonuclear spin systems



Chemical shift

$I_x \rightarrow I_x \cos \omega_0\Delta \rightarrow I_x \cos \omega_0\Delta \rightarrow I_x \cos \omega_0\Delta \cos \omega_0\Delta$

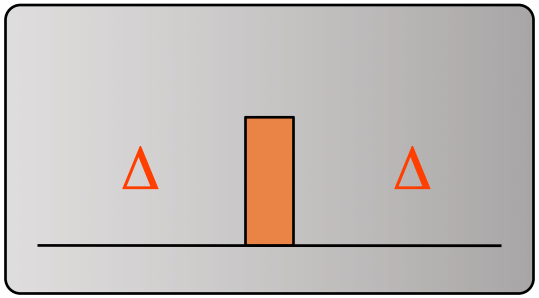
$\rightarrow I_y \cos \omega_0\Delta \sin \omega_0\Delta$

$\rightarrow I_y \sin \omega_0\Delta \rightarrow -I_y \sin \omega_0\Delta \rightarrow -I_y \sin \omega_0\Delta \cos \omega_0\Delta$

$\rightarrow +I_x \sin \omega_0\Delta \sin \omega_0\Delta$

NMR building blocks (2)

Spin echoes in homonuclear spin systems



Chemical shift

$I_x \rightarrow I_x \cos \omega_0\Delta \rightarrow I_x \cos \omega_0\Delta \rightarrow I_x \cos \omega_0\Delta \cos \omega_0\Delta$

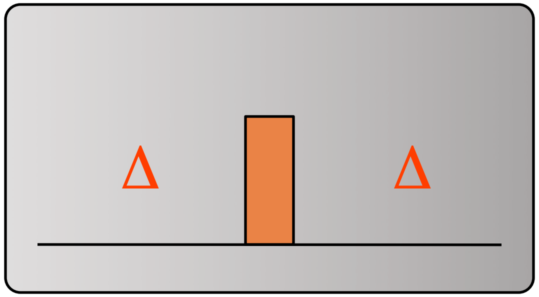
$\rightarrow I_y \cos \omega_0\Delta \sin \omega_0\Delta$

$\rightarrow I_y \sin \omega_0\Delta \rightarrow -I_y \sin \omega_0\Delta \rightarrow -I_y \sin \omega_0\Delta \cos \omega_0\Delta$

$\rightarrow +I_x \sin \omega_0\Delta \sin \omega_0\Delta$

NMR building blocks (2)

Spin echoes in homonuclear spin systems



Chemical shift

$$\mathbf{I_x} \rightarrow \mathbf{I_x} \cos \omega_0\Delta \rightarrow \mathbf{I_x} \cos \omega_0\Delta \rightarrow \mathbf{I_x} \cos \omega_0\Delta \cos \omega_0\Delta$$

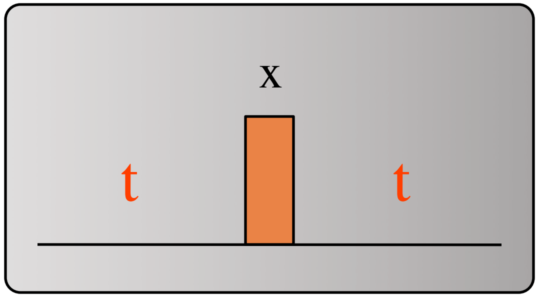
$$\rightarrow \mathbf{I_y} \cos \omega_0\Delta \sin \omega_0\Delta$$

$$\rightarrow \mathbf{I_y} \sin \omega_0\Delta \rightarrow -\mathbf{I_y} \sin \omega_0\Delta \rightarrow -\mathbf{I_y} \sin \omega_0\Delta \cos \omega_0\Delta$$

$$\rightarrow +\mathbf{I_x} \sin \omega_0\Delta \sin \omega_0\Delta$$

NMR building blocks (3)

Spin echoes in homonuclear spin systems



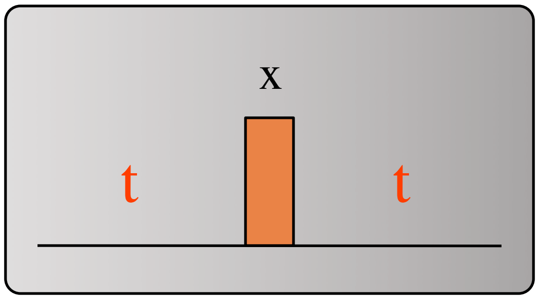
J-coupling

$\mathbf{I_x}$ → $\mathbf{I_x} \cos \pi J t$

→ $\mathbf{2I_yS_z} \sin \pi J t$

NMR building blocks (3)

Spin echoes in <u>homonuclear</u> spin systems



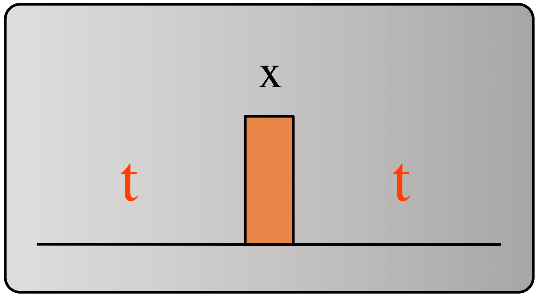
J-coupling

I_x → $I_x \cos \pi J t$

→ $2(-I_y)(\_S_z) \sin \pi J t$

NMR building blocks (3)

Spin echoes in homonuclear spin systems



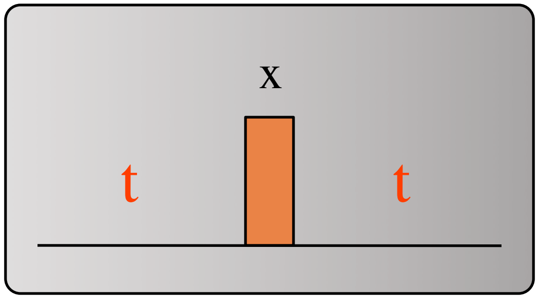
J-coupling

$\mathbf{I_x}$ → $\mathbf{I_x} \cos \pi J t$

→ $\mathbf{2 I_y S_z} \sin \pi J t$

NMR building blocks (3)

Spin echoes in <u>homonuclear</u> spin systems



J-coupling

$I_x \rightarrow I_x \cos \pi Jt \rightarrow I_x \cos \pi Jt \cos \pi Jt$

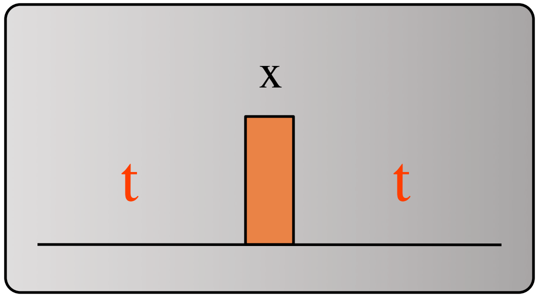
$\rightarrow 2I_yS_z \cos \pi Jt \sin \pi Jt$

$\rightarrow 2I_yS_z \sin \pi Jt \rightarrow 2I_yS_z \sin \pi Jt \cos \pi Jt$

$\rightarrow -I_x \sin \pi Jt \sin \pi Jt$

NMR building blocks (3)

Spin echoes in homonuclear spin systems



J-coupling

I_x → $I_x \cos \pi J t$ → $I_x \cos \pi J t \cos \pi J t - \sin \pi J t \sin \pi J t$

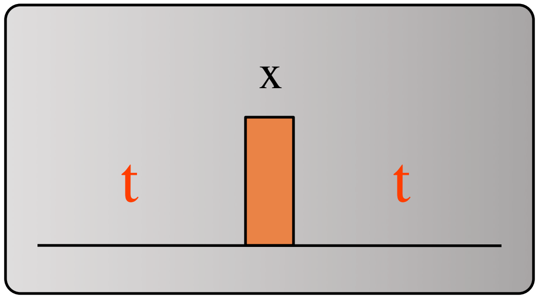
→ $2I_yS_z \cos \pi J t \sin \pi J t$

→ $2I_yS_z \sin \pi J t$ → $2I_yS_z \sin \pi J t \cos \pi J t + \cos \pi J t \sin \pi J t$

→ $-I_x \sin \pi J t \sin \pi J t$

NMR building blocks (3)

Spin echoes in <u>homonuclear</u> spin systems



J-coupling

I_x → $I_x \cos \pi J t$ → $I_x \cos 2\pi J t$

→ $2I_yS_z \sin \pi J t$ → $2I_yS_z \sin 2\pi J t$

[faded]

$I_x \cos \pi J t \cos \pi J t$
$- I_x \sin \pi J t \sin \pi J t$

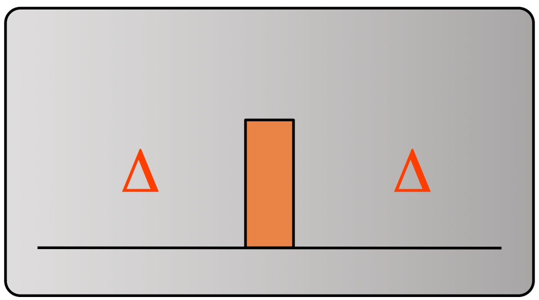
$2I_yS_z \cos \pi J t \sin \pi J t$

$2I_yS_z \sin \pi J t \cos \pi J t$
$+ 2I_yS_z \cos \pi J t \sin \pi J t$

$-I_x \sin \pi J t \sin \pi J t$

NMR building blocks (4)

Spin echoes in homonuclear spin systems



Chemical shift

$\mathbf{I_x}$ → $\mathbf{I_x}$

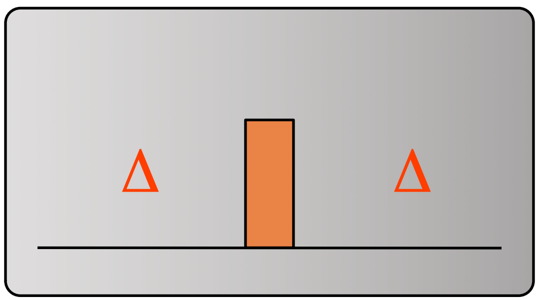
J-coupling

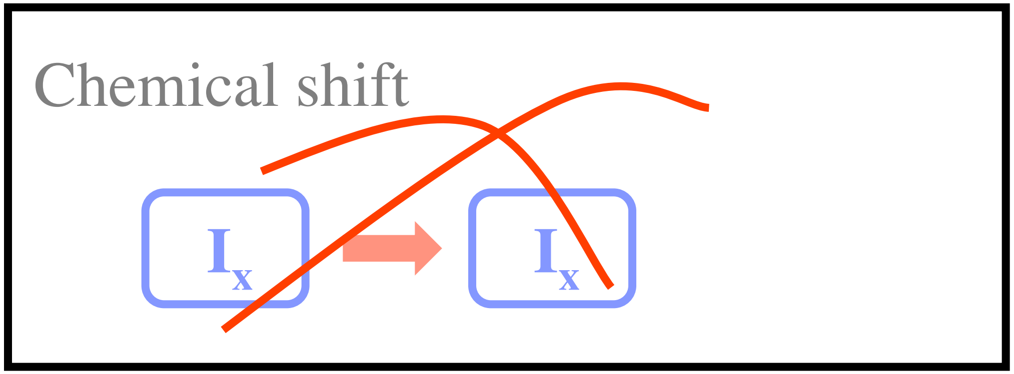
$\mathbf{I_x}$ → $\mathbf{I_x} \cos 2\pi Jt$

→ $\mathbf{2I_yS_z} \sin 2\pi Jt$

NMR building blocks (4)

Spin echoes in homonuclear spin systems





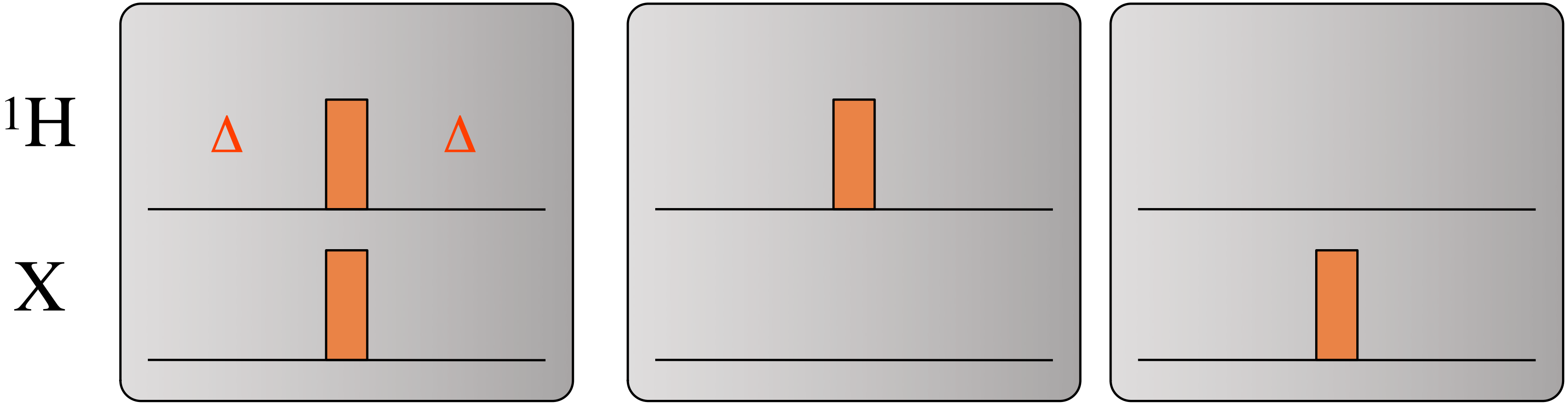
J-coupling

$I_x \rightarrow I_x \cos 2\pi Jt$

$\rightarrow 2I_yS_z \sin 2\pi Jt$

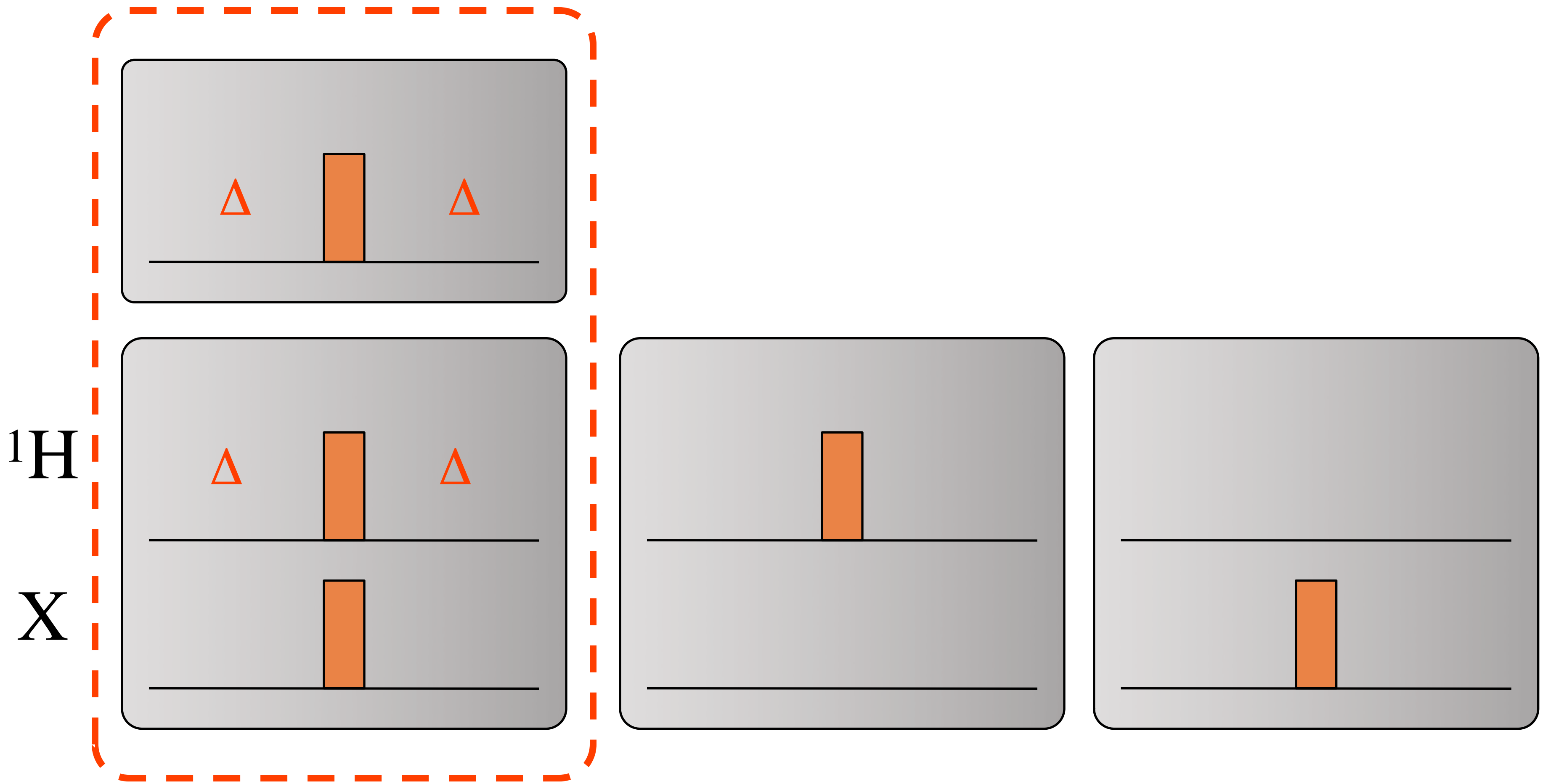
NMR building blocks (5)

Spin echoes in heteronuclear spin systems



NMR building blocks (5)

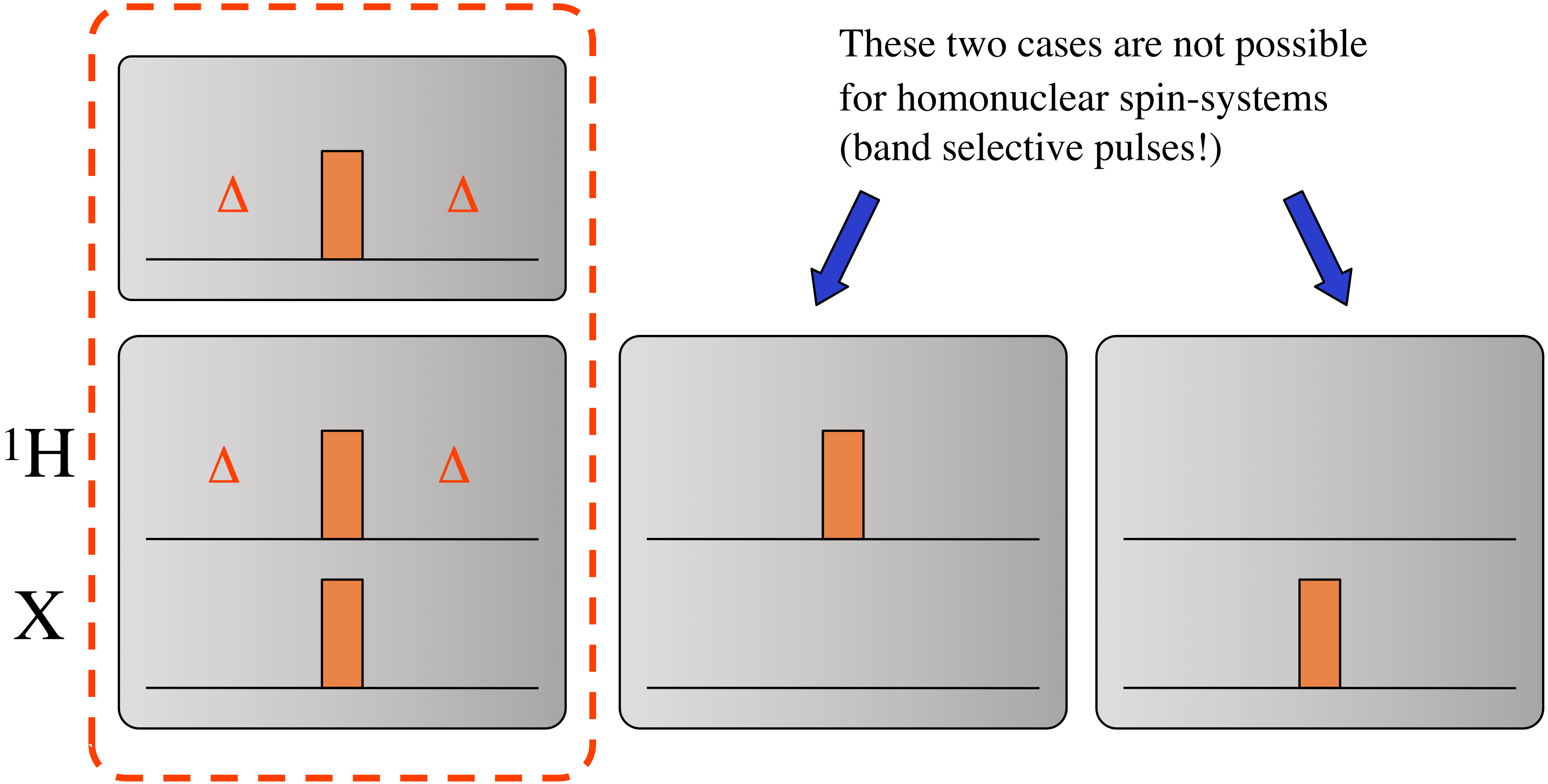
Spin echoes in heteronuclear spin systems



NMR building blocks (5)

Spin echoes in heteronuclear spin systems

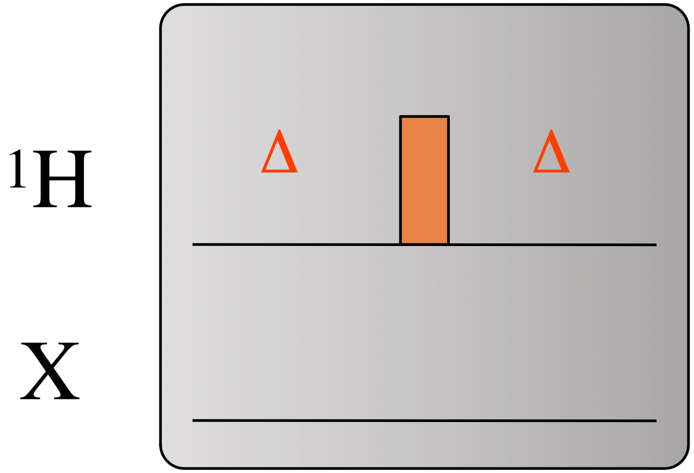
These two cases are not possible for homonuclear spin-systems (band selective pulses!)



NMR building blocks (6)

Spin echoes in heteronuclear spin systems

X Chemical shift

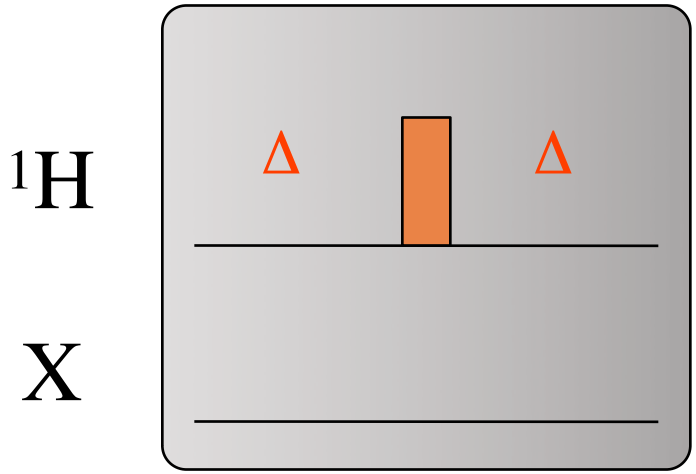


$\mathbf{I_x} \rightarrow \mathbf{I_x} \cos 2\omega_0(2\Delta)$

$\rightarrow \mathbf{I_y} \sin \omega_0(2\Delta)$

NMR building blocks (7)

Spin echoes in heteronuclear spin systems



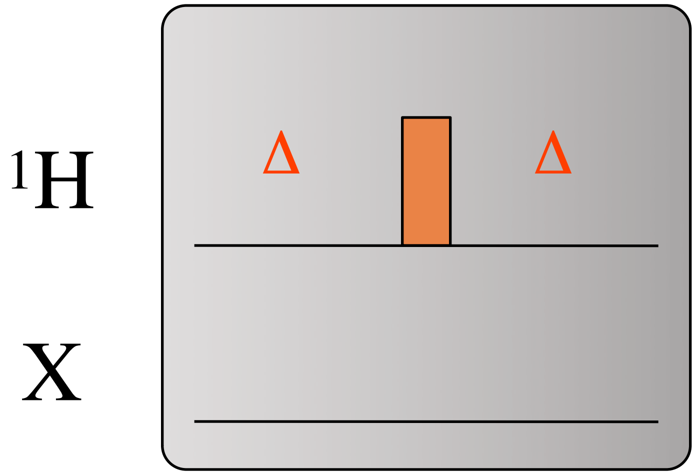
J-coupling

I_x → $I_x \cos \pi J t$

→ $2I_yS_z \sin \pi J t$

NMR building blocks (7)

Spin echoes in heteronuclear spin systems



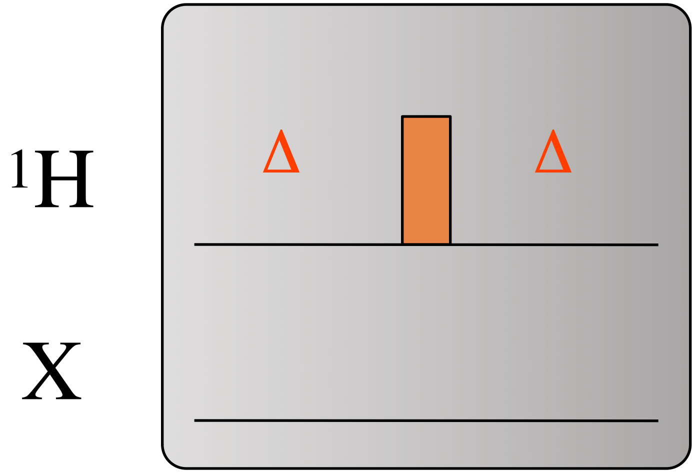
J-coupling

I_x → $I_x \cos \pi Jt$ → $I_x \cos \pi Jt$

→ $2I_yS_z \sin \pi Jt$ → $-2I_yS_z \sin \pi Jt$

NMR building blocks (7)

Spin echoes in heteronuclear spin systems



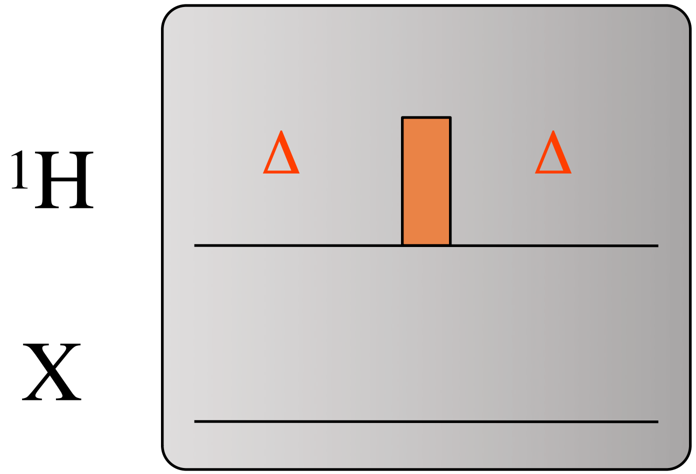
J-coupling

➡ $I_x \cos \pi Jt$

➡ $-2I_yS_z \sin \pi Jt$

NMR building blocks (7)

Spin echoes in heteronuclear spin systems



J-coupling

→ $I_x \cos \pi Jt$

→ $-2I_yS_z \sin \pi Jt$

→ $I_x \cos \pi Jt \cos \pi Jt$

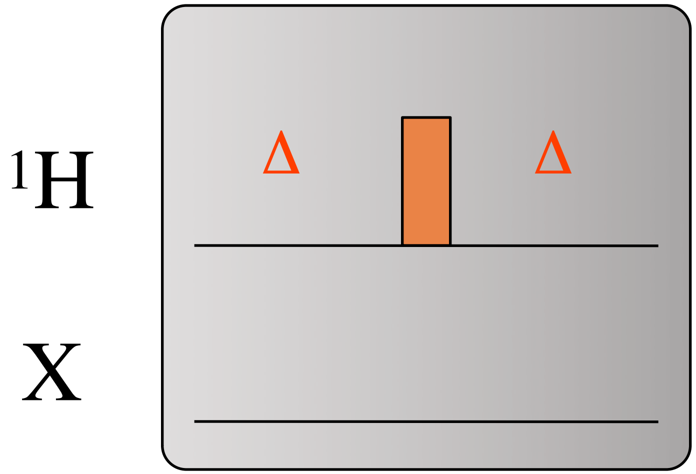
→ $2I_yS_z \cos \pi Jt \sin \pi Jt$

→ $-2I_yS_z \sin \pi Jt \cos \pi Jt$

→ $I_x \sin \pi Jt \sin \pi Jt$

NMR building blocks (7)

Spin echoes in heteronuclear spin systems



J-coupling

$I_x \cos \pi Jt$

$-2I_yS_z \sin \pi Jt$

$I_x \cos \pi Jt \cos \pi Jt$

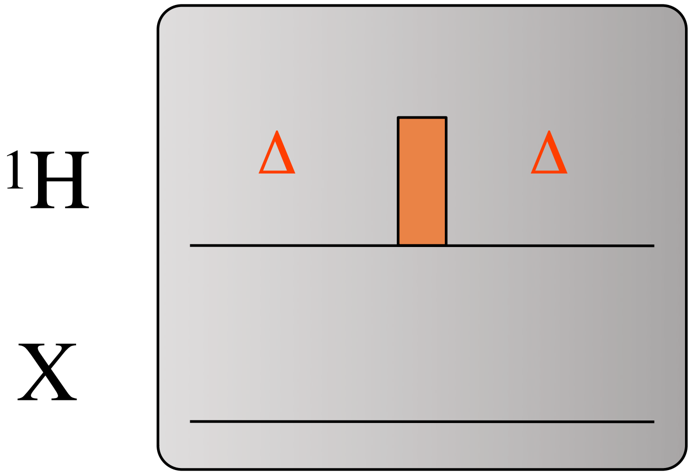
$2I_yS_z \cos \pi Jt \sin \pi Jt$

$-2I_yS_z \sin \pi Jt \cos \pi Jt$

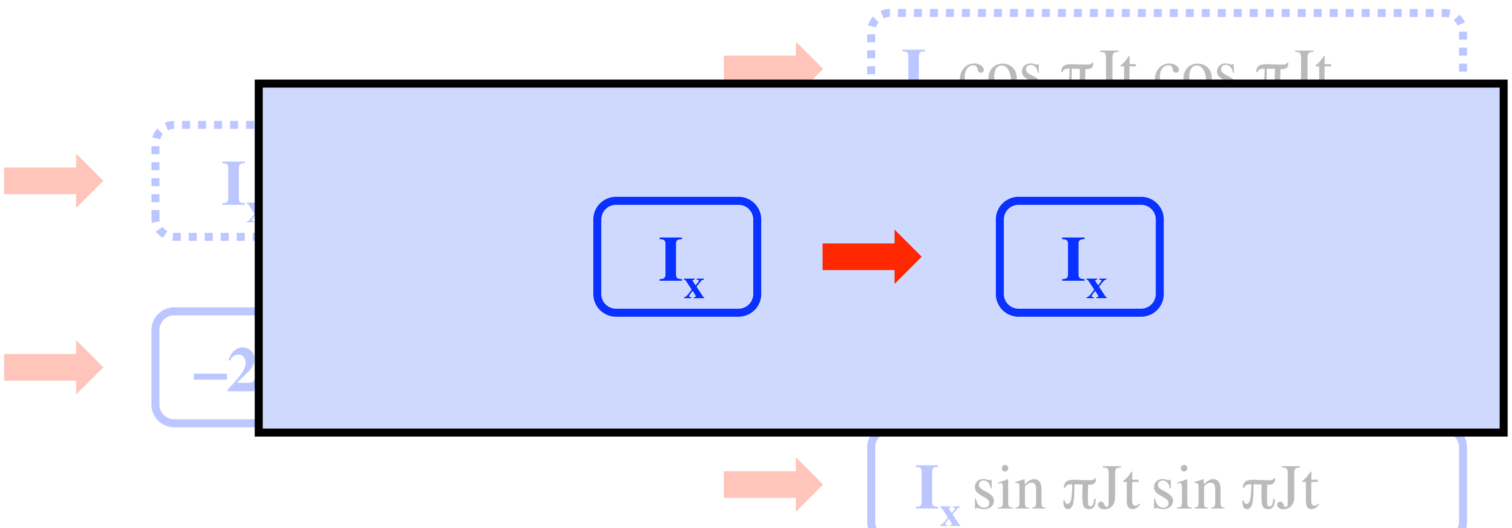
$I_x \sin \pi Jt \sin \pi Jt$

NMR building blocks (7)

Spin echoes in heteronuclear spin systems



J-coupling

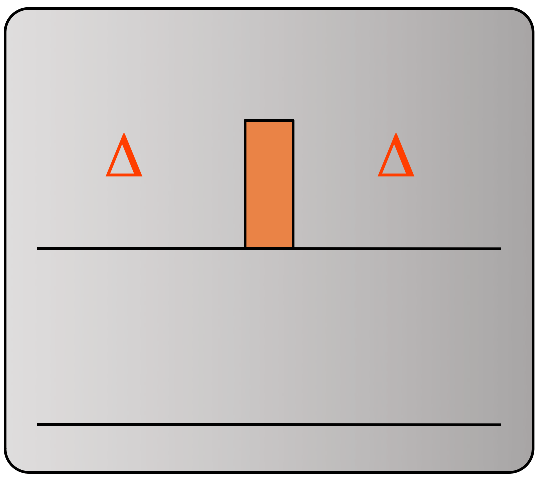


NMR building blocks (8)

Spin echoes in heteronuclear spin systems

^1H

X



Chemical shift

$I_x \rightarrow I_x \cos 2\omega_0(2\Delta)$

$\rightarrow I_y \sin \omega_0(2\Delta)$

J-coupling

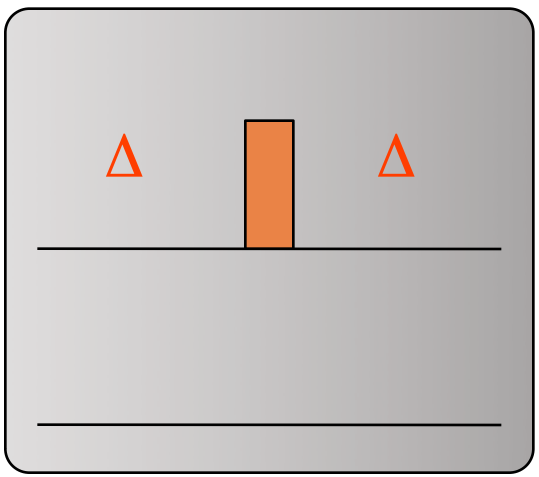
$I_x \rightarrow I_x$

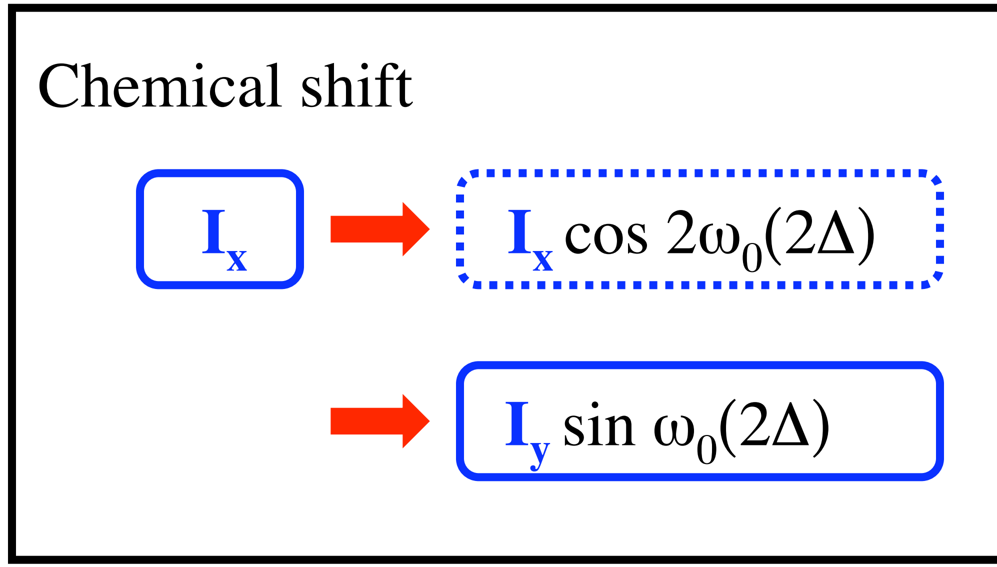
NMR building blocks (8)

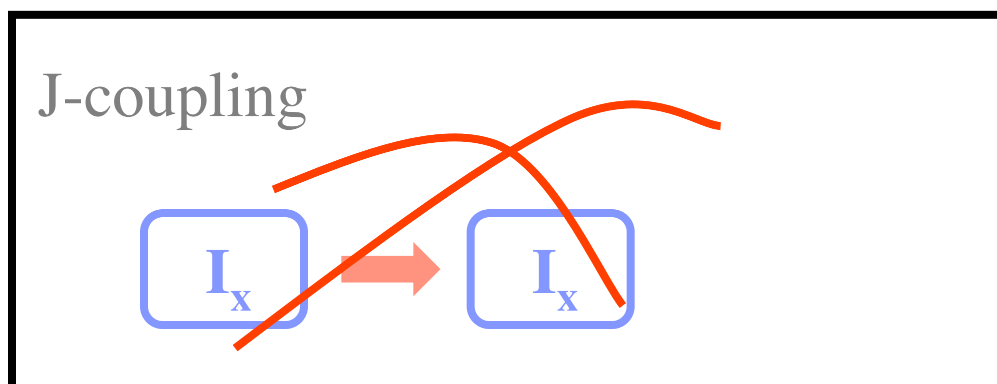
Spin echoes in heteronuclear spin systems

^{1}H

X

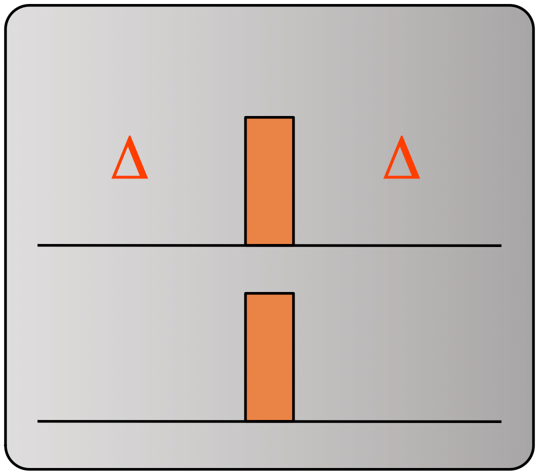






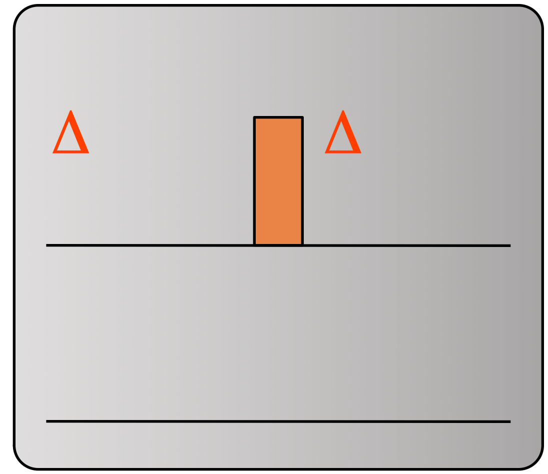
NMR building blocks (9)

Spin echoes in heteronuclear spin systems



^1H

X



J-coupling

$I_x \rightarrow I_x \cos 2\pi Jt$

$\rightarrow 2I_yS_z \sin 2\pi Jt$

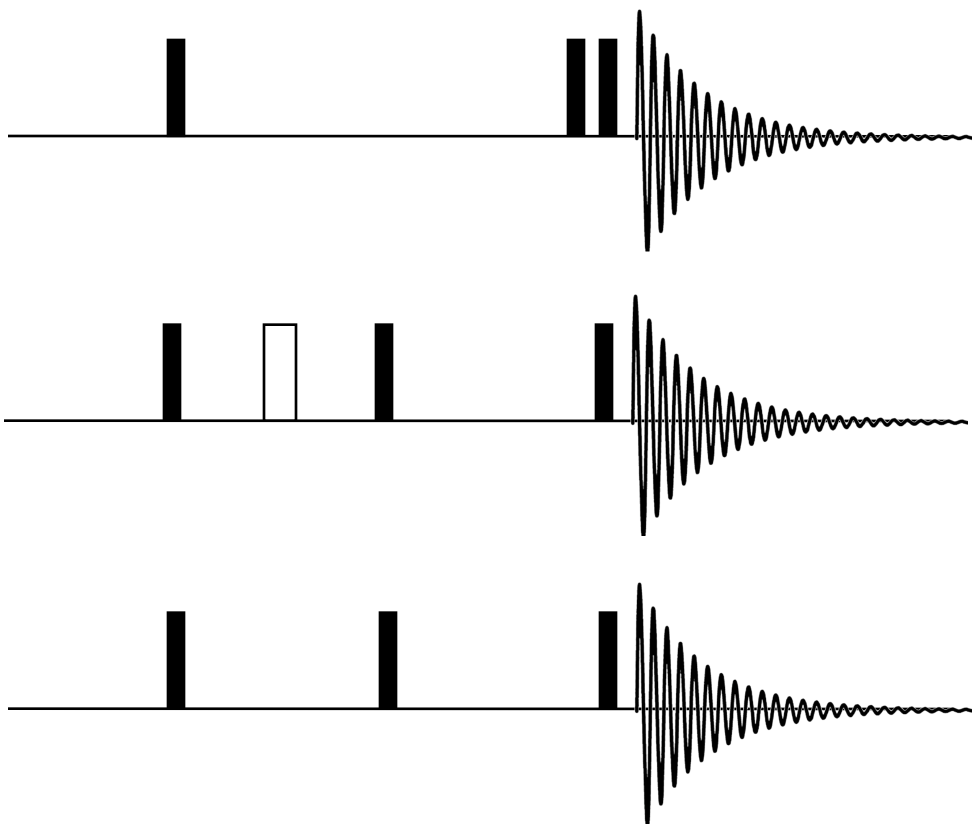
Chemical shift

$I_x \rightarrow I_x \cos 2\omega_0(2\Delta)$

$\rightarrow I_y \sin \omega_0(2\Delta)$

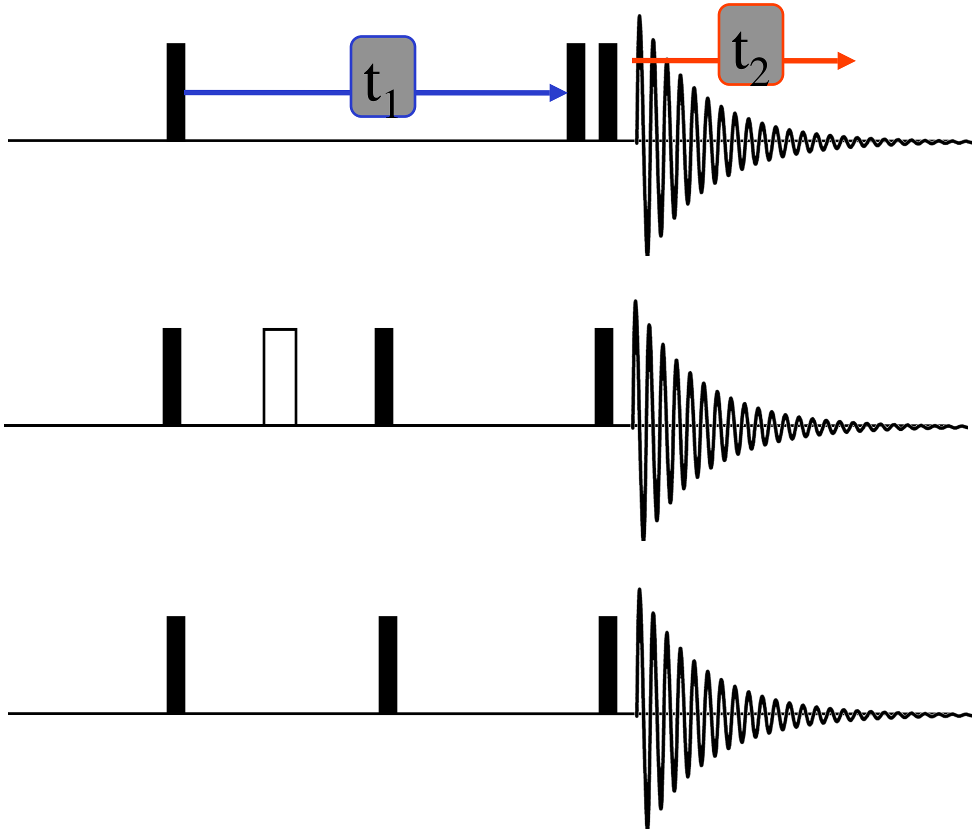
Coherence selection (1)

Pulse sequences with three 90º pulses



Coherence selection (1)

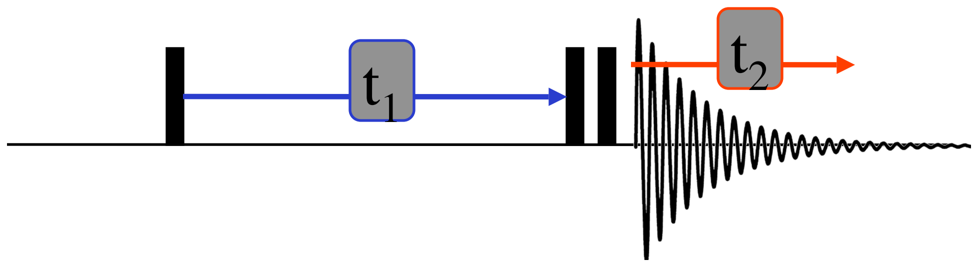
Pulse sequences with three 90º pulses



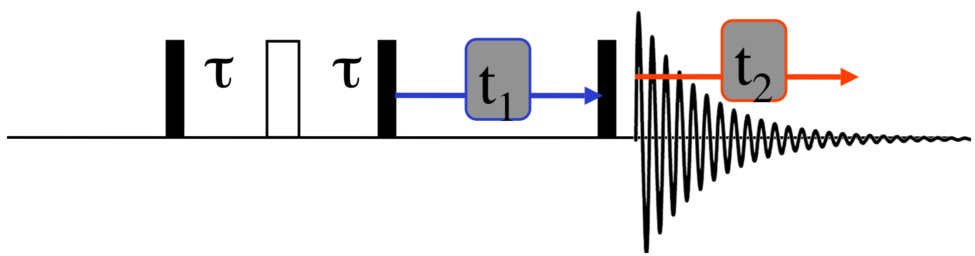
DQF COSY

Coherence selection (1)

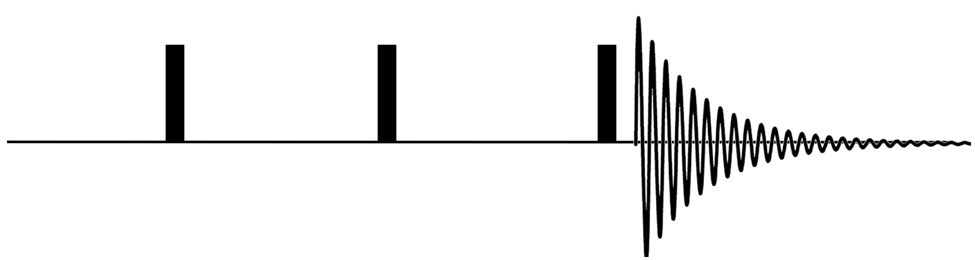
Pulse sequences with three 90º pulses



DQF COSY

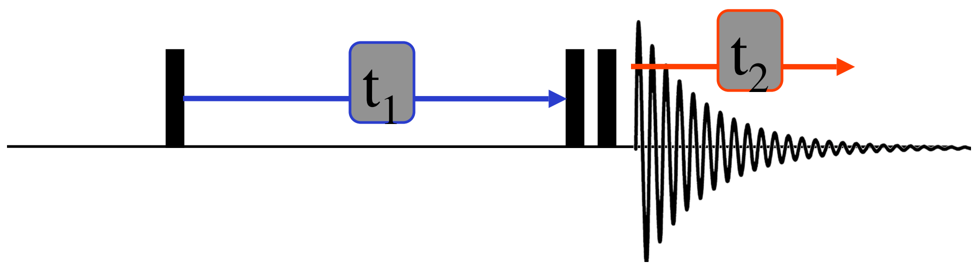


Double quantum spectroscopy

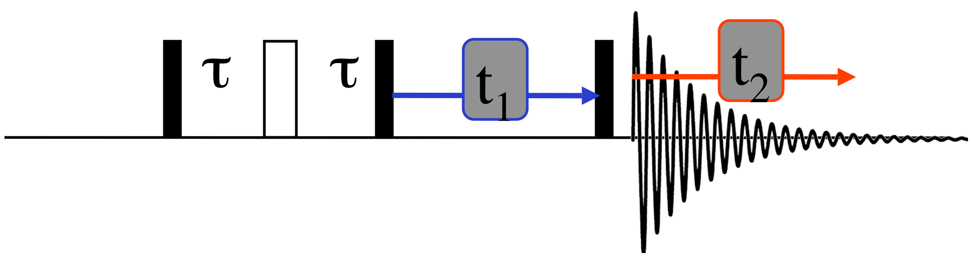


Coherence selection (1)

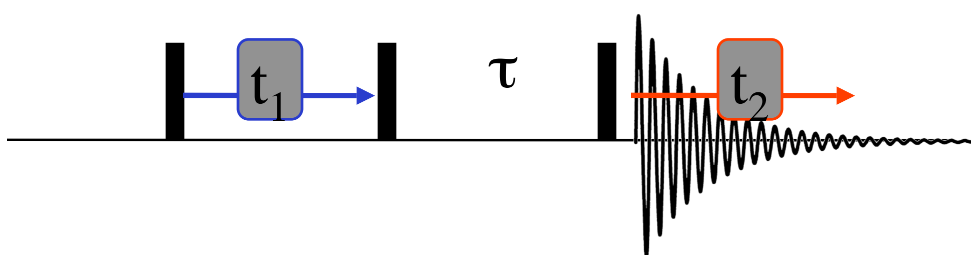
Pulse sequences with three 90º pulses



DQF COSY



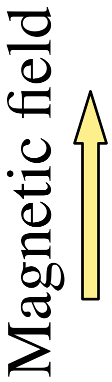
Double quantum spectroscopy

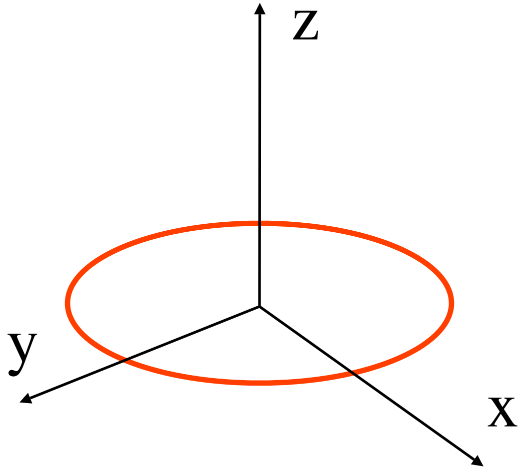


NOESY

Coherence selection (2)

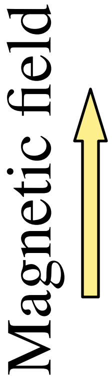
Coherence order

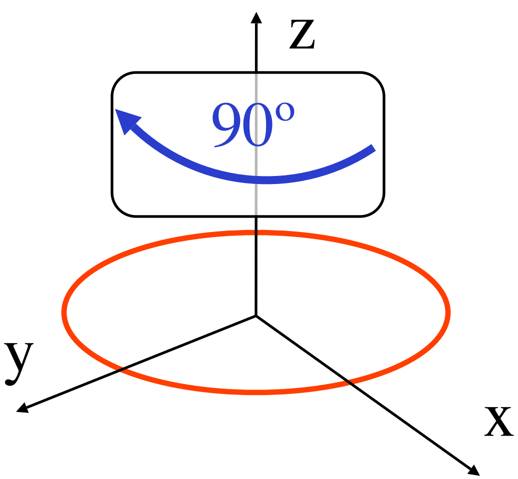




Coherence selection (2)

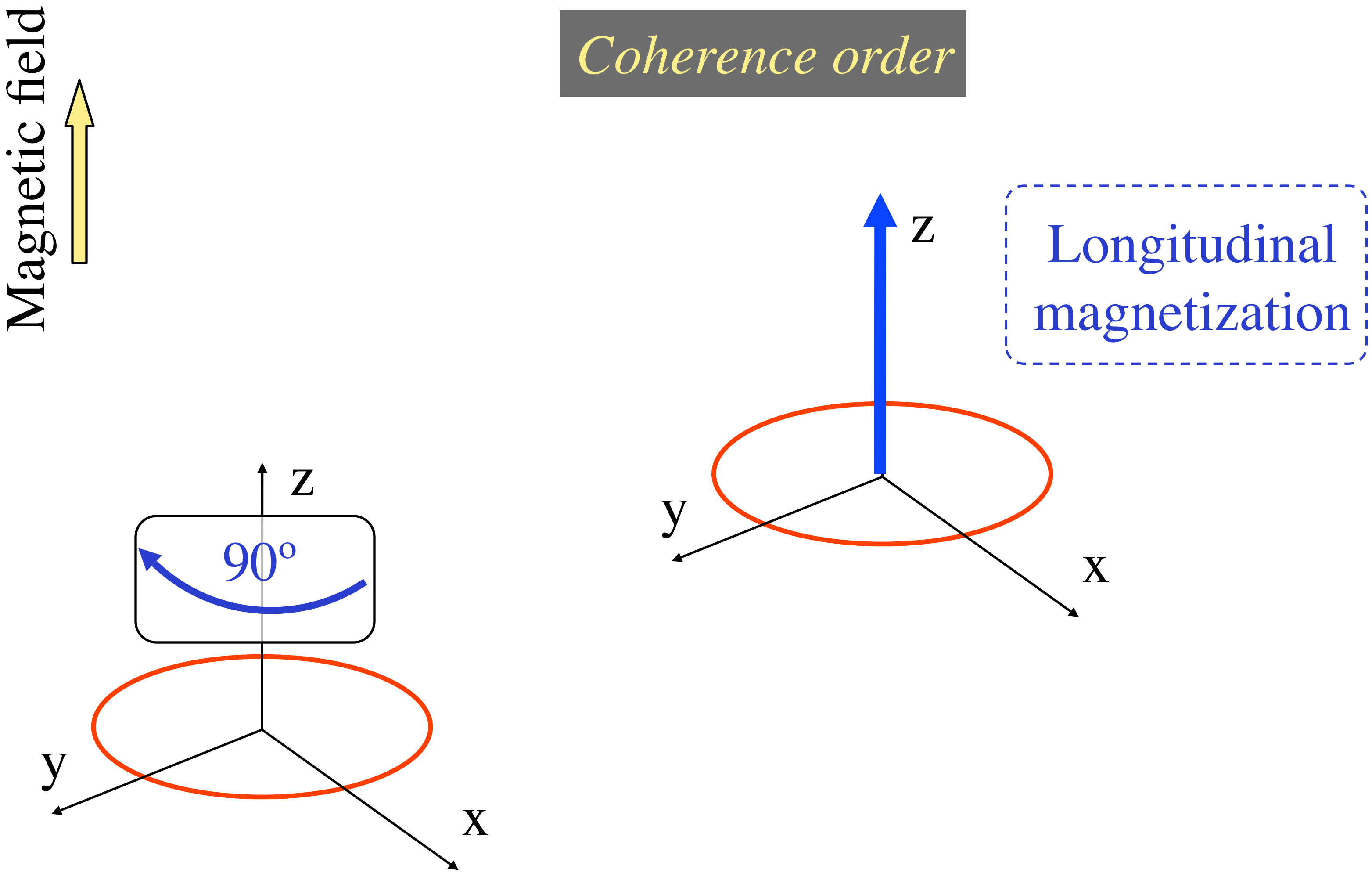
Coherence order



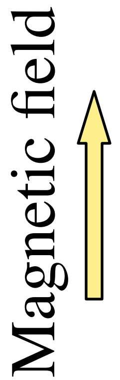


Coherence selection (2)

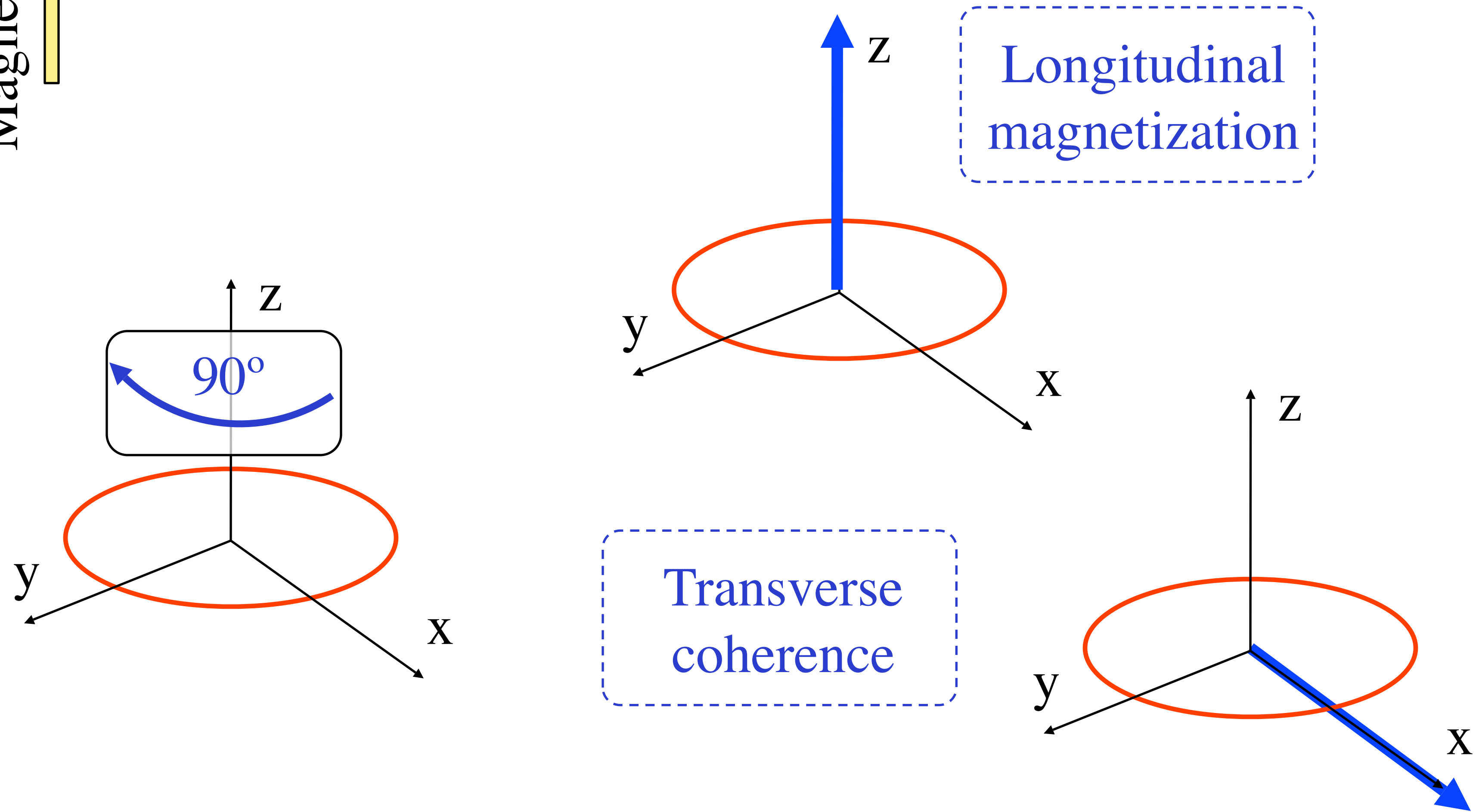
Coherence order



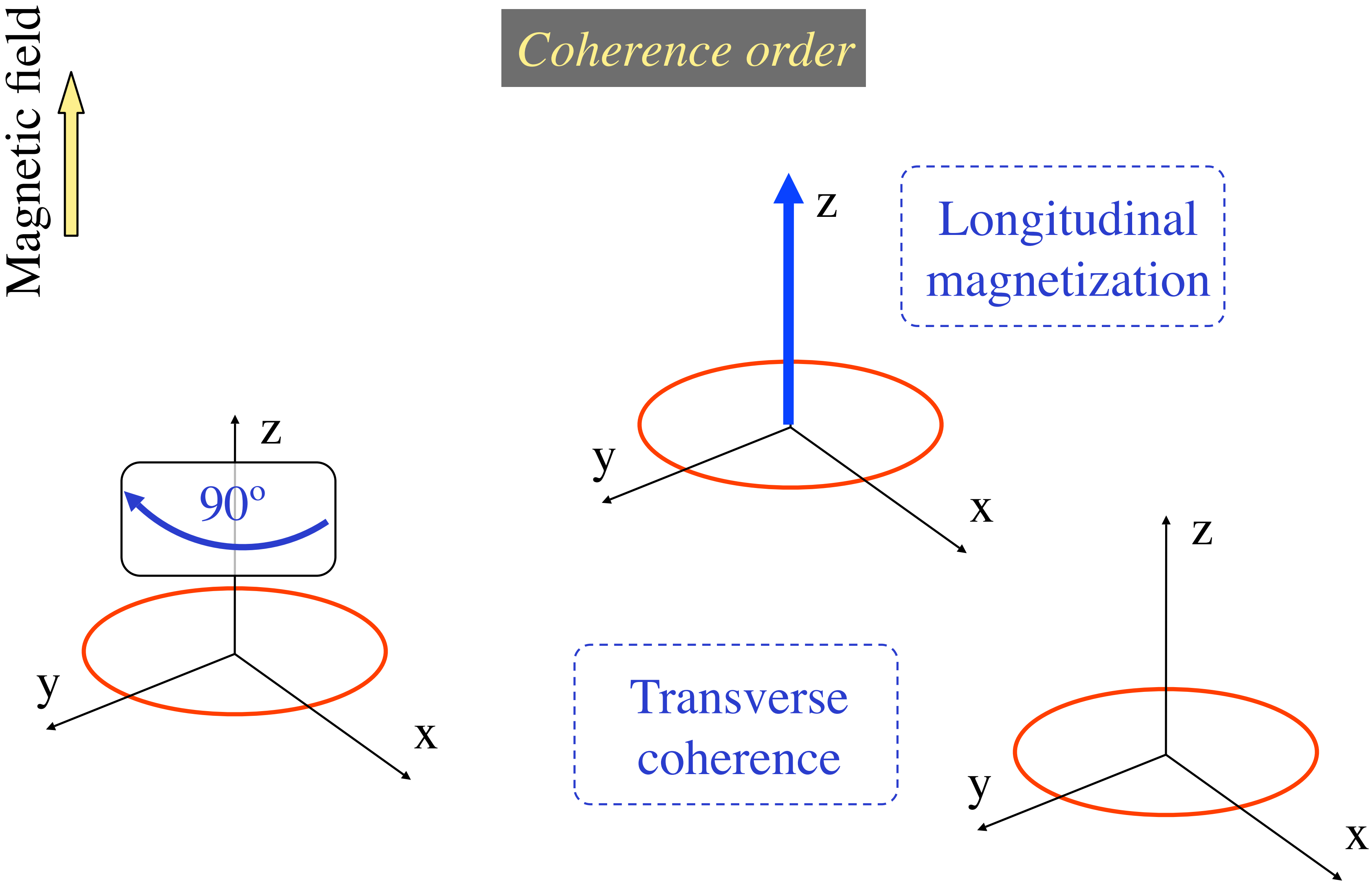
Coherence selection (2)



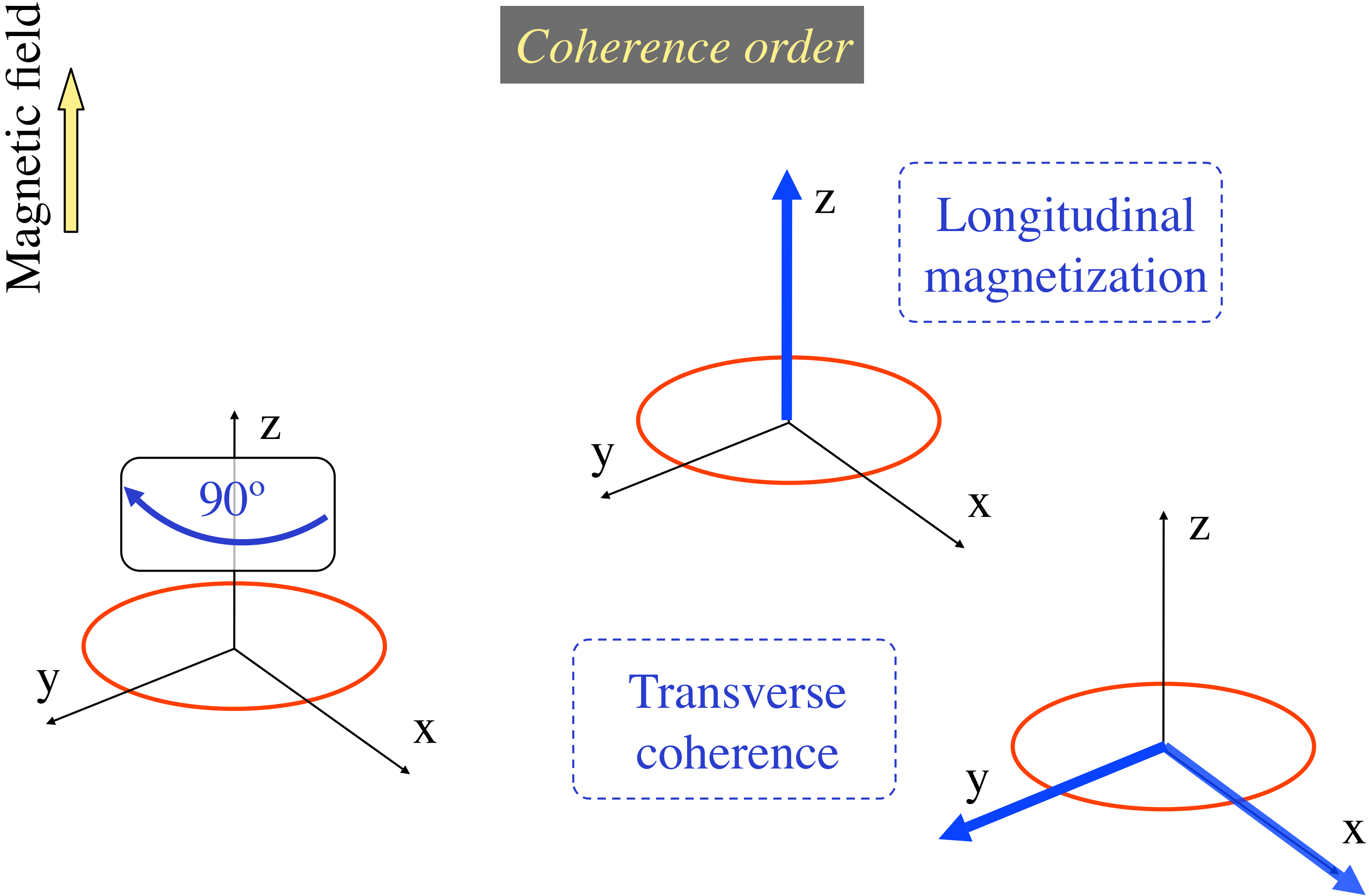
Coherence order



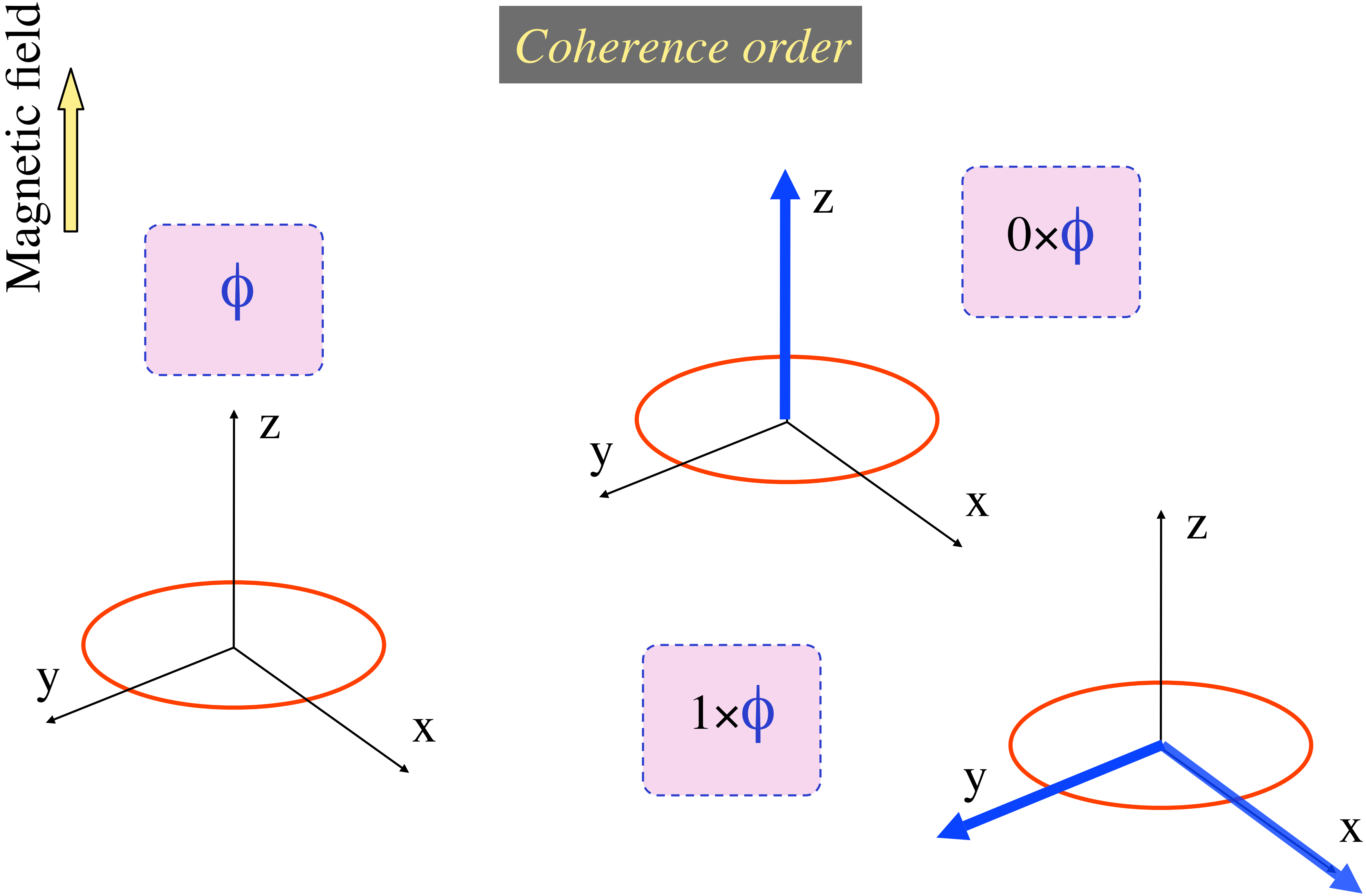
Coherence selection (2)



Coherence selection (2)

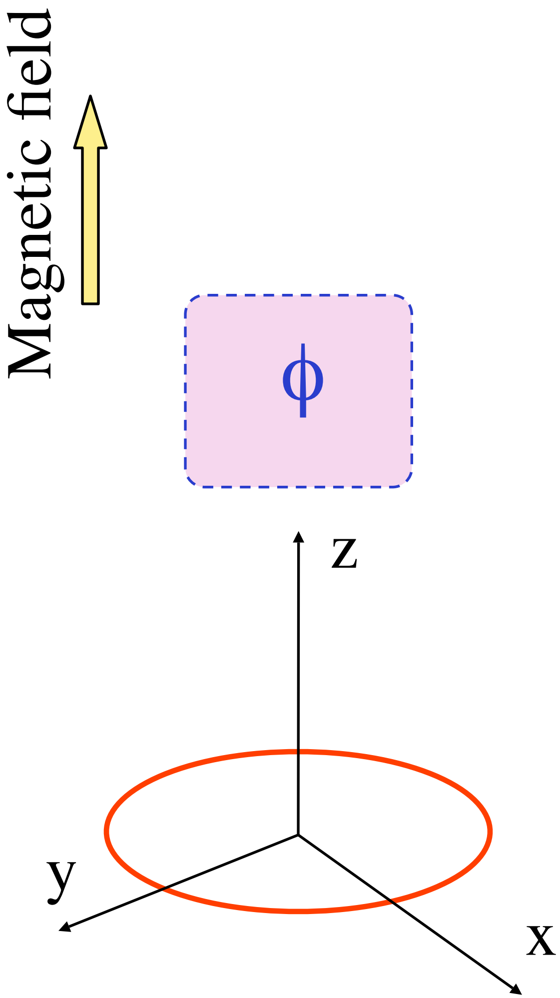


Coherence selection (2)

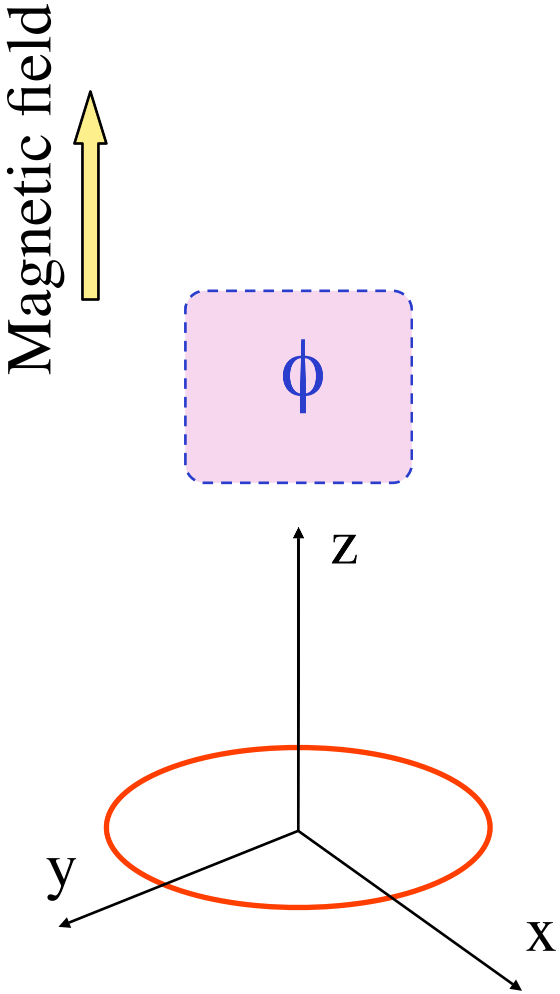


Coherence selection (3)

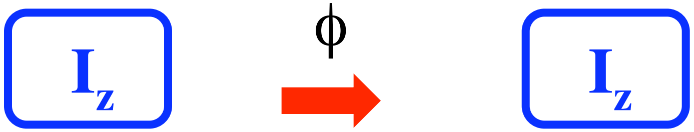
Coherence order



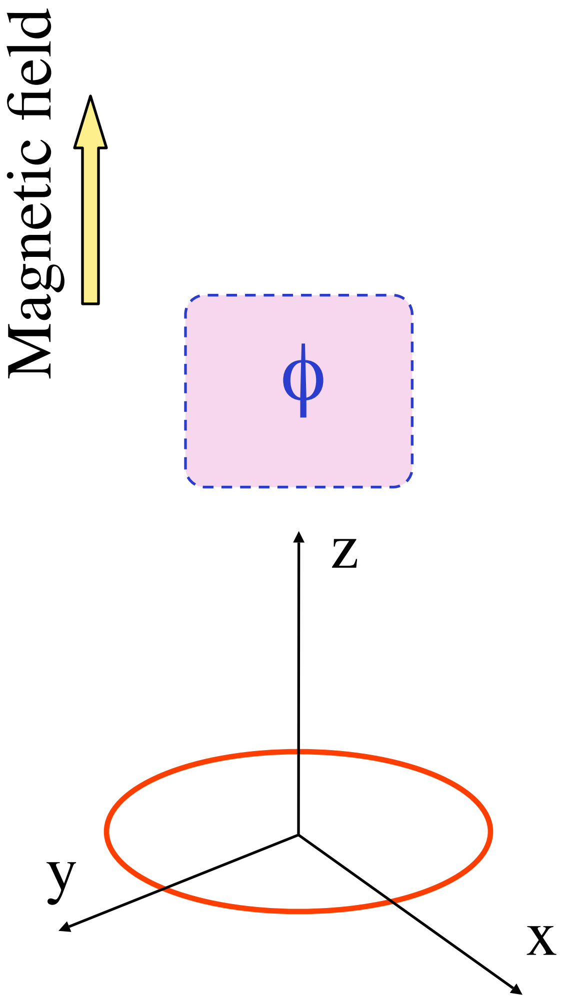
Coherence selection (3)



Coherence order



Coherence selection (3)

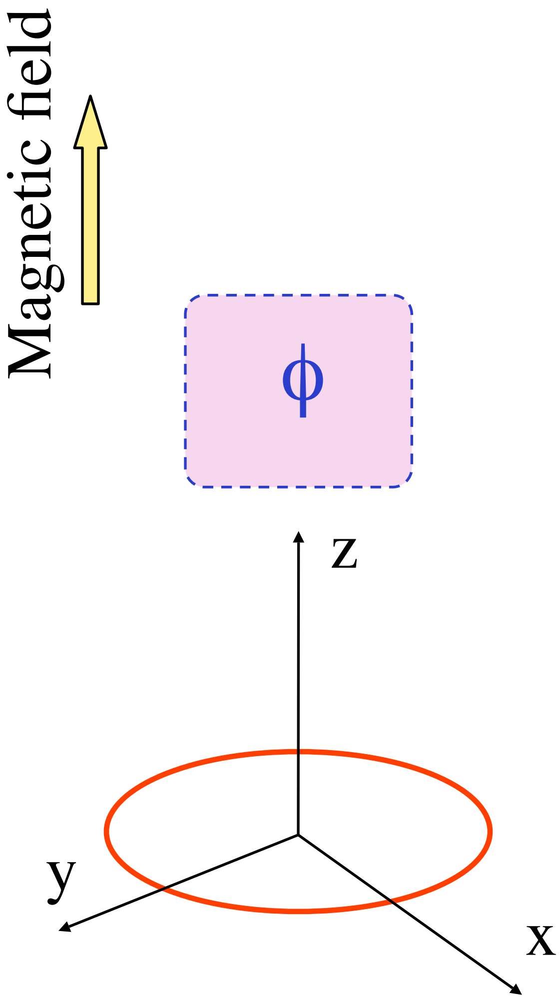


Coherence order

$$I_z \xrightarrow{\phi} I_z$$

$$I_x \xrightarrow{\phi} I_x \cos\phi + I_x \sin\phi$$

Coherence selection (3)



Coherence order

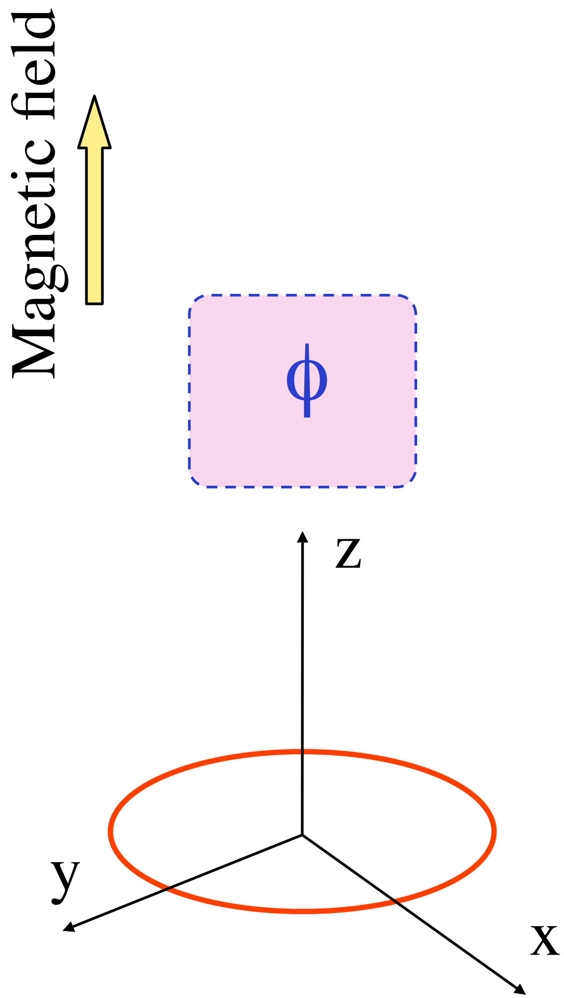
$$I_z \xrightarrow{\phi} I_z$$

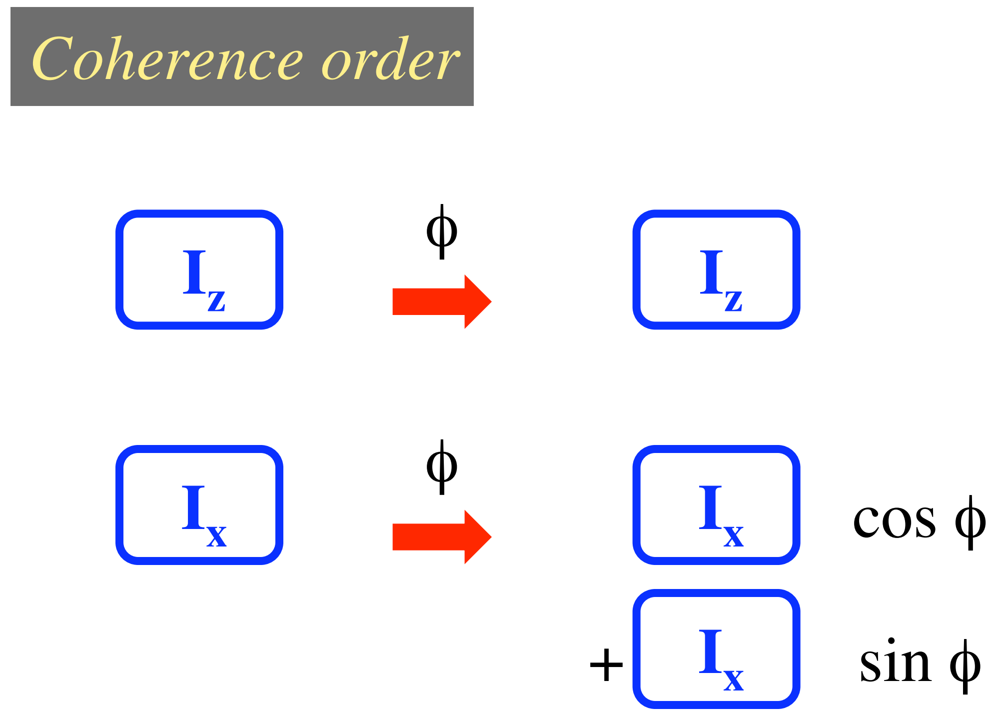
Rising / lowering operators

$$I_+ = I_x + i\, I_x$$

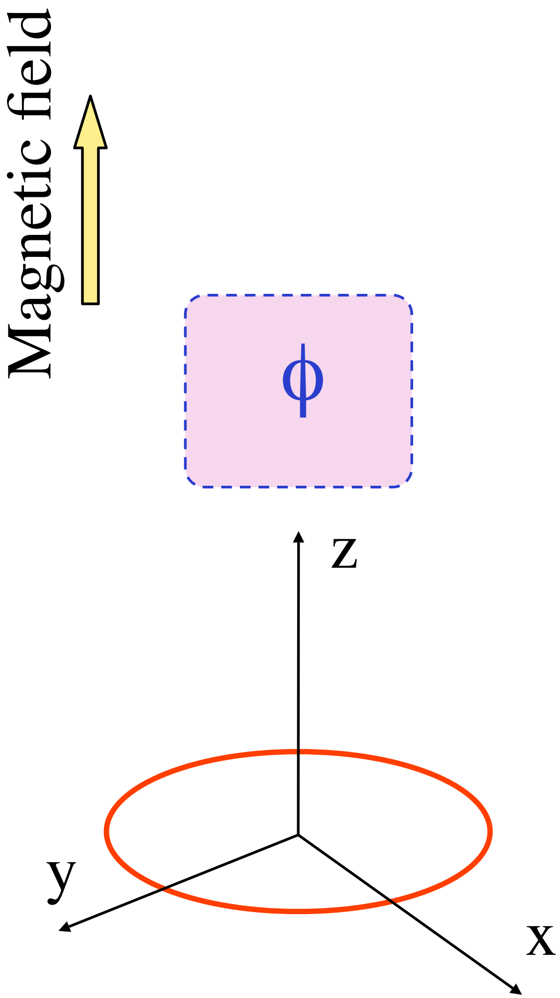
$$I_- = I_x - i\, I_x$$

Coherence selection (3)





Coherence selection (3)



Coherence order

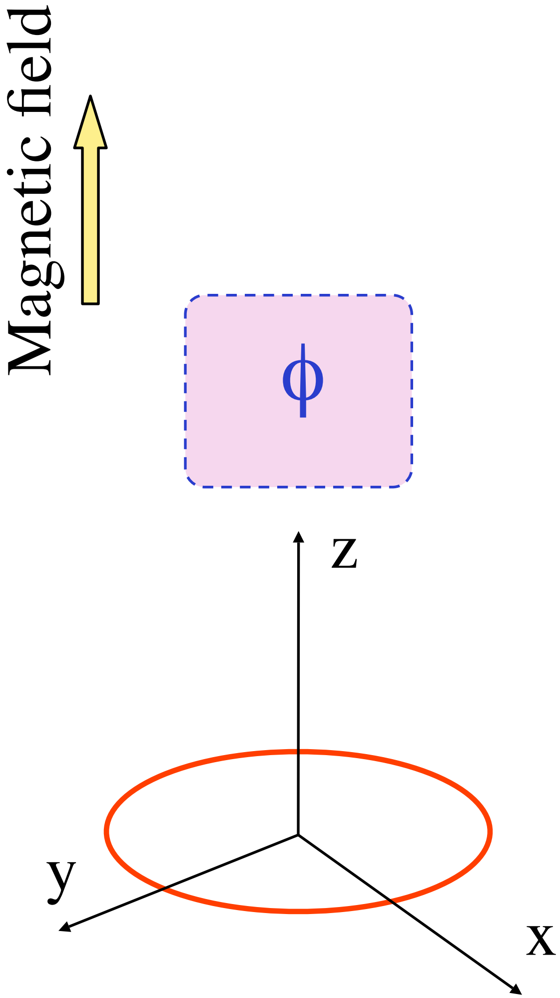
$$I_z \xrightarrow{\phi} I_z$$

$$I_x \xrightarrow{\phi} I_x \cos\phi + I_x \sin\phi$$

$$I_+ \xrightarrow{\phi} I_+ \exp(-\boldsymbol{i}\,\phi)$$

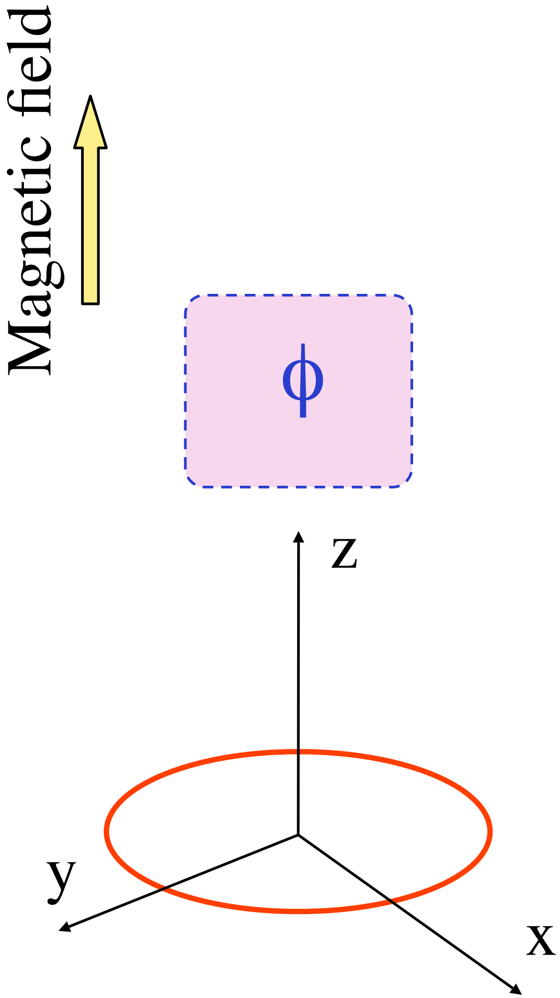
Coherence selection (4)

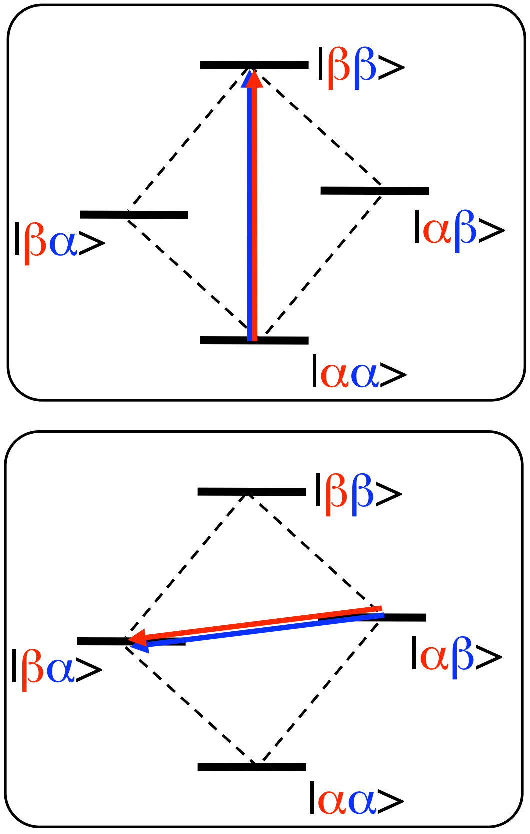
Coherence order



Coherence selection (4)

Coherence order





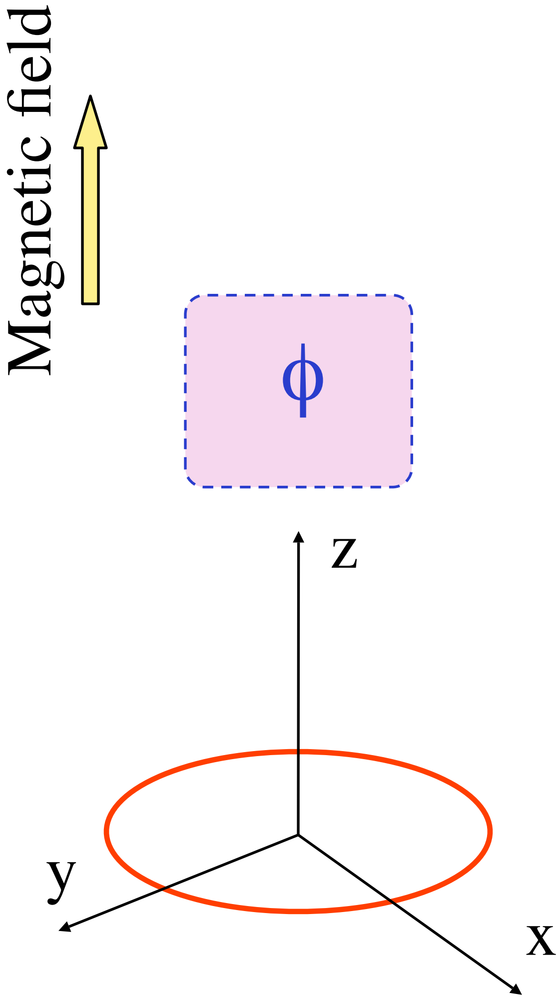
0 / 2 Quantum coherences

$A_x X_y$ $A_x X_x$

$A_y X_x$ $A_y X_y$

Coherence selection (4)

Coherence order

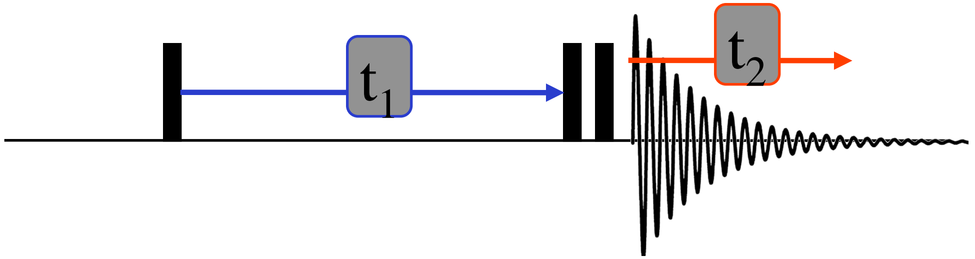


$$2I_xS_x =$$

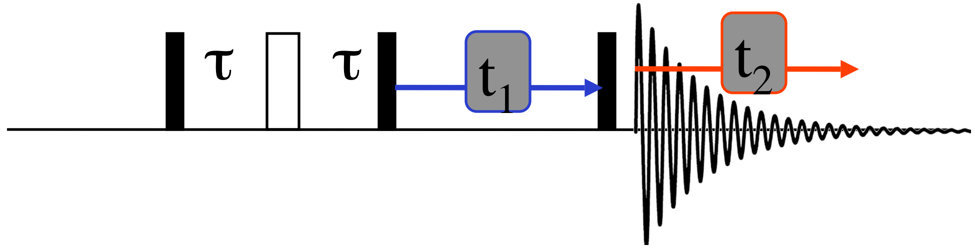
$$1/2\,(\,I_+S_+ + I_-S_- + I_+S_- + I_-S_+\,)$$

Order:	2	2	0	0

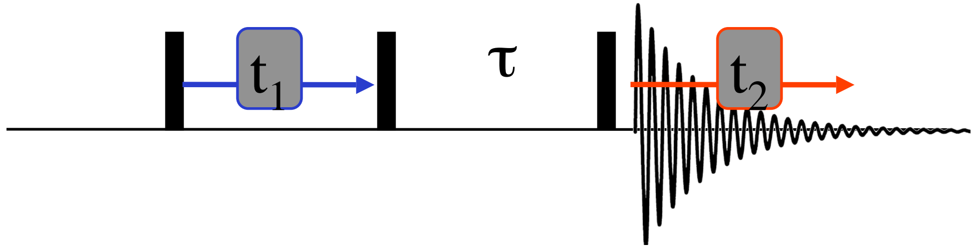
Coherence selection (5)



DQF COSY

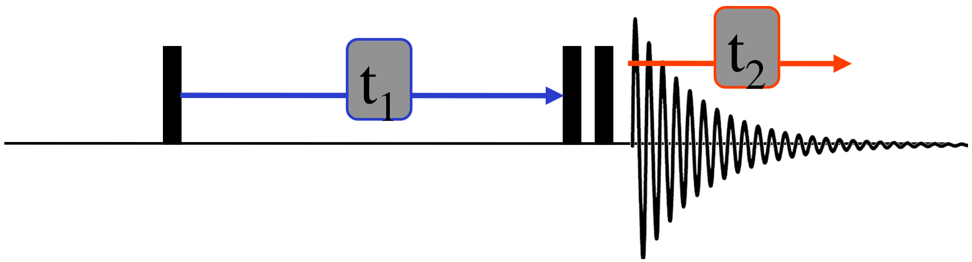


Double quantum spectroscopy

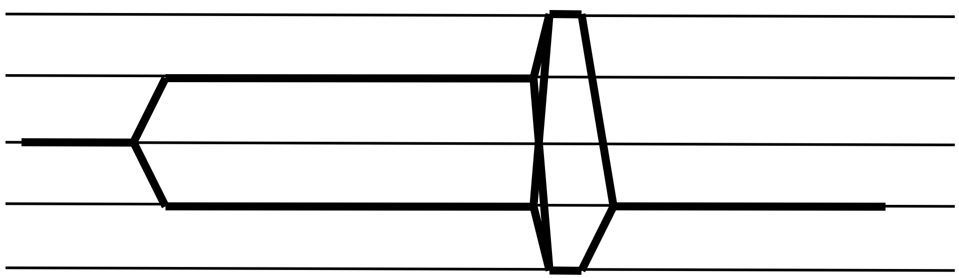


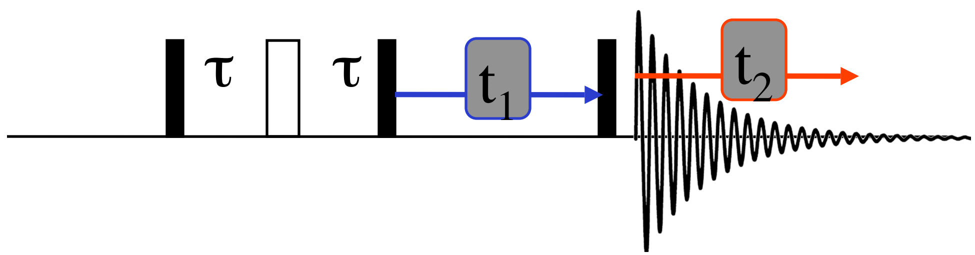
NOESY

Coherence selection (5)

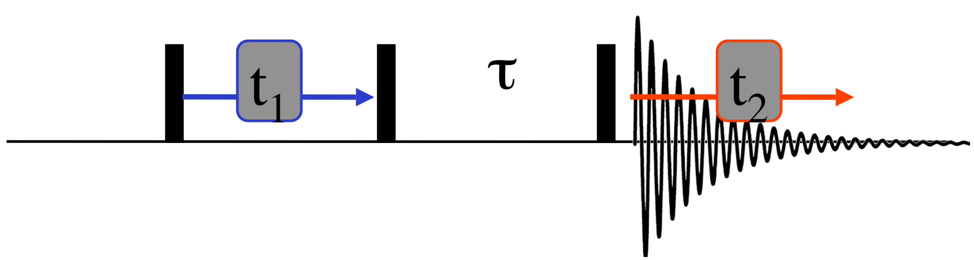


DQF COSY



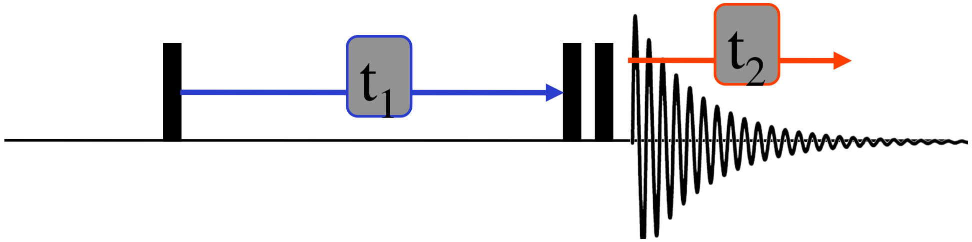


Double quantum spectroscopy

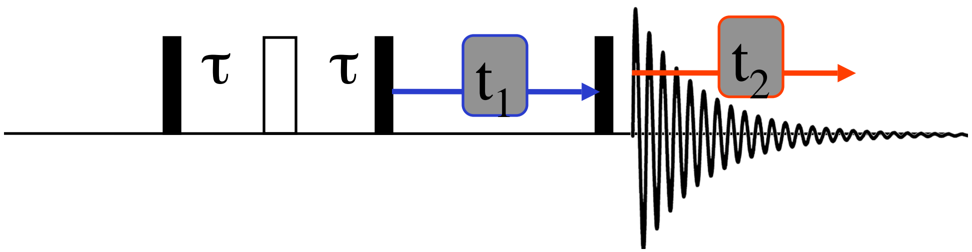


NOESY

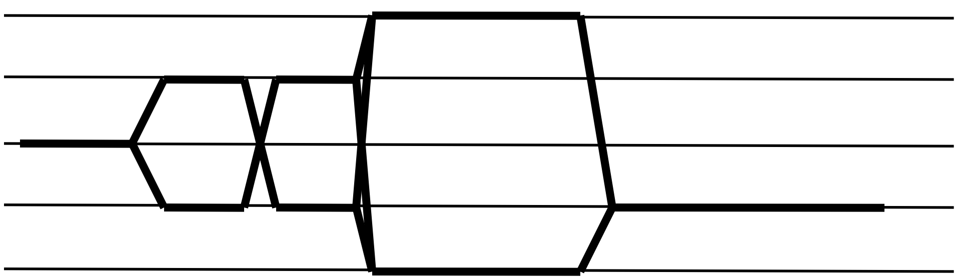
Coherence selection (5)

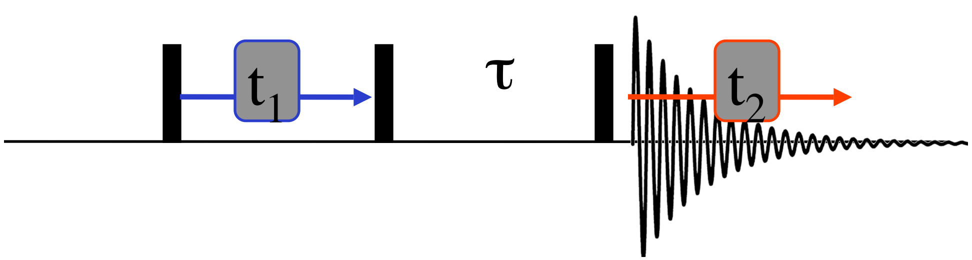


DQF COSY



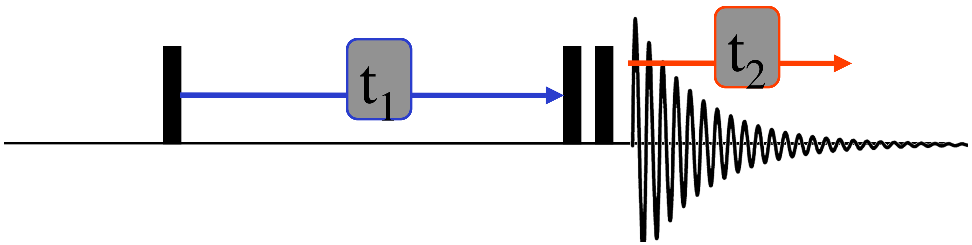
Double quantum spectroscopy



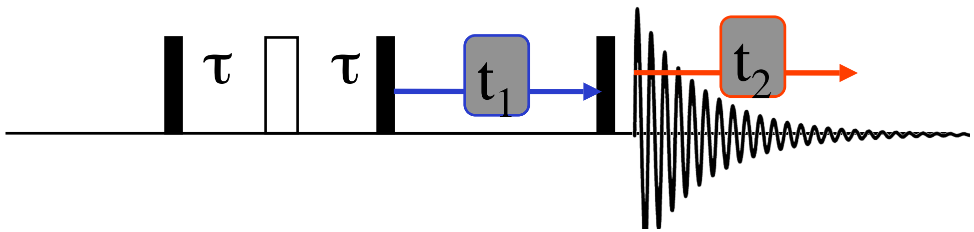


NOESY

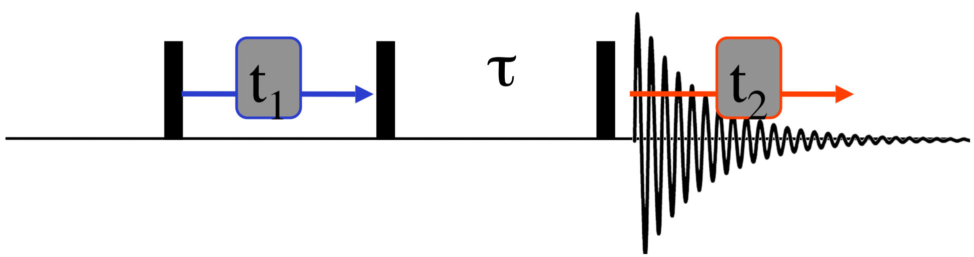
Coherence selection (5)



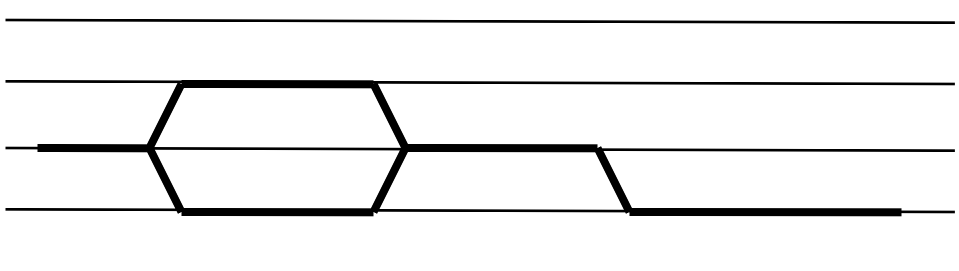
DQF COSY



Double quantum spectroscopy

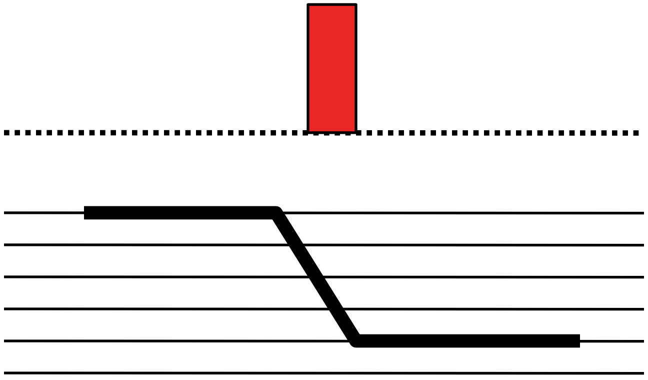


NOESY



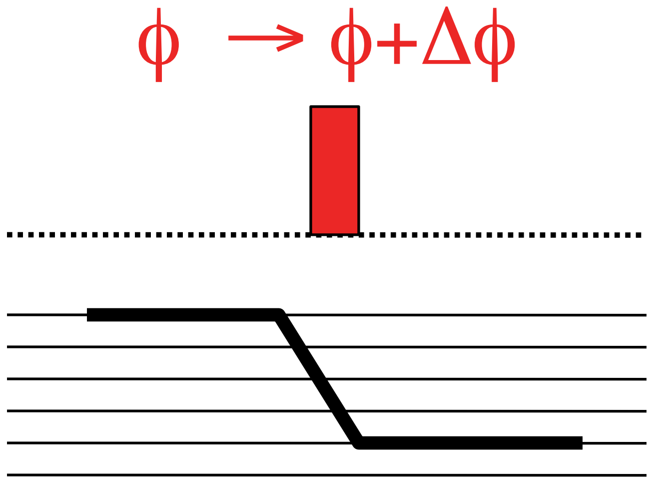
Coherence selection (6)

Phase cycling



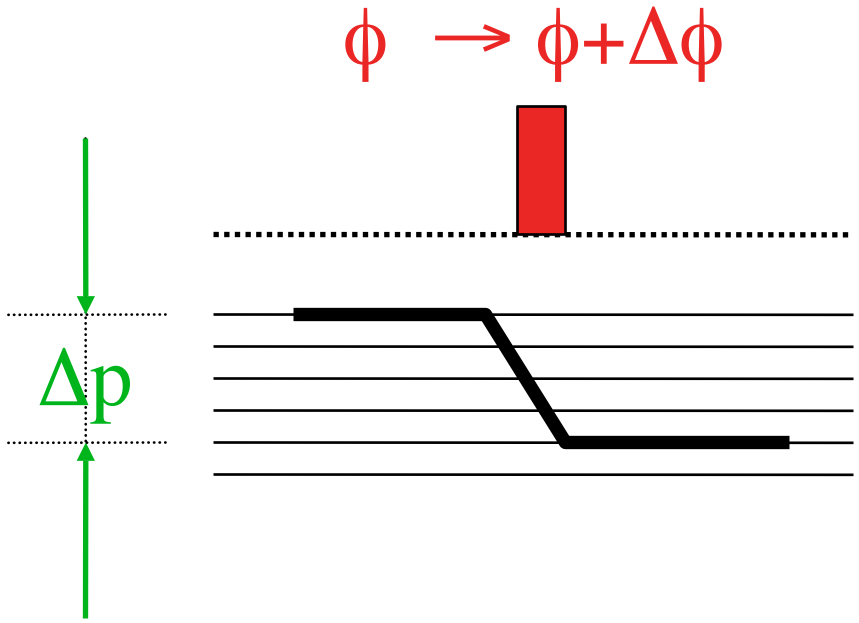
Coherence selection (6)

Phase cycling



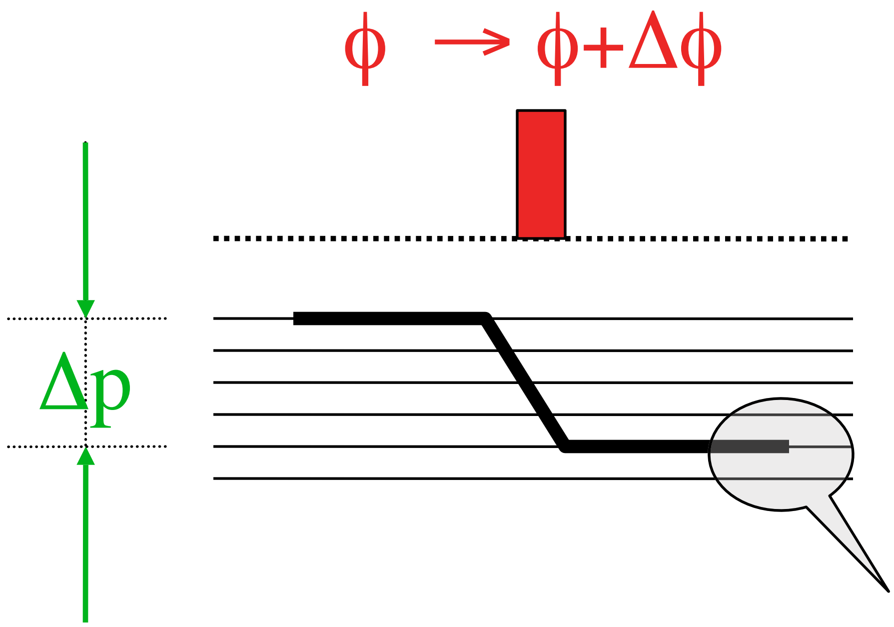
Coherence selection (6)

Phase cycling



Coherence selection (6)

Phase cycling

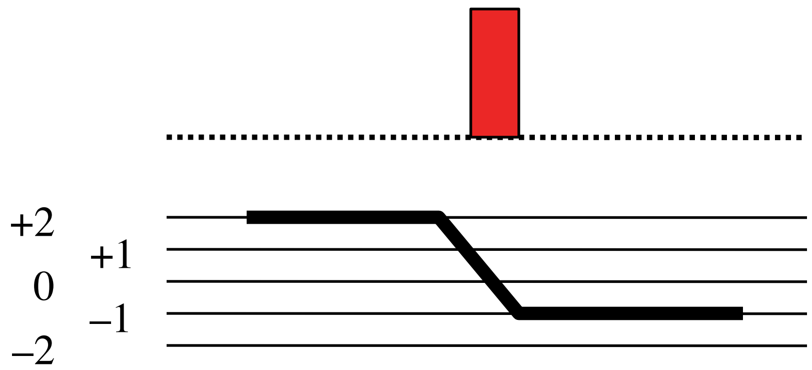


Coherence phase shift:

$\Delta p \times \Delta\phi$

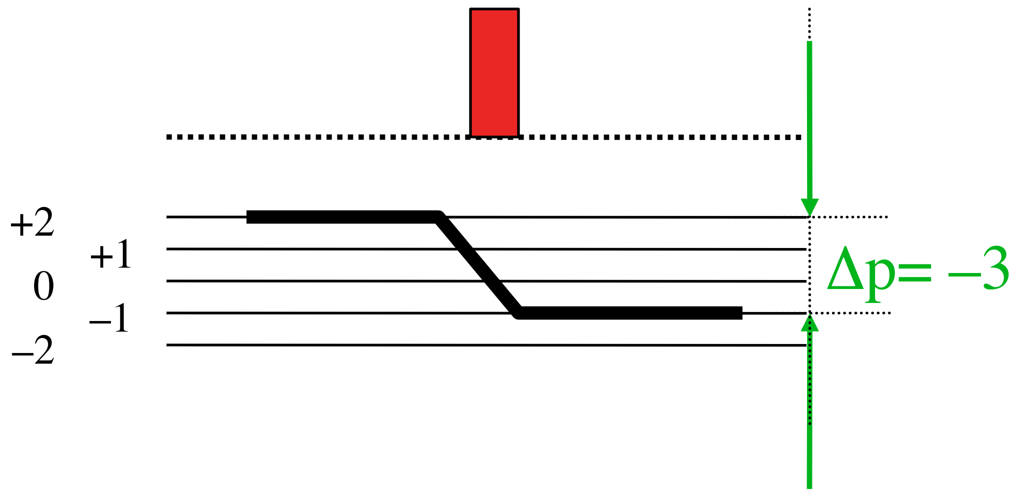
Coherence selection (7)

Phase cycling for the selection of the Δp=–3 coherence pathway



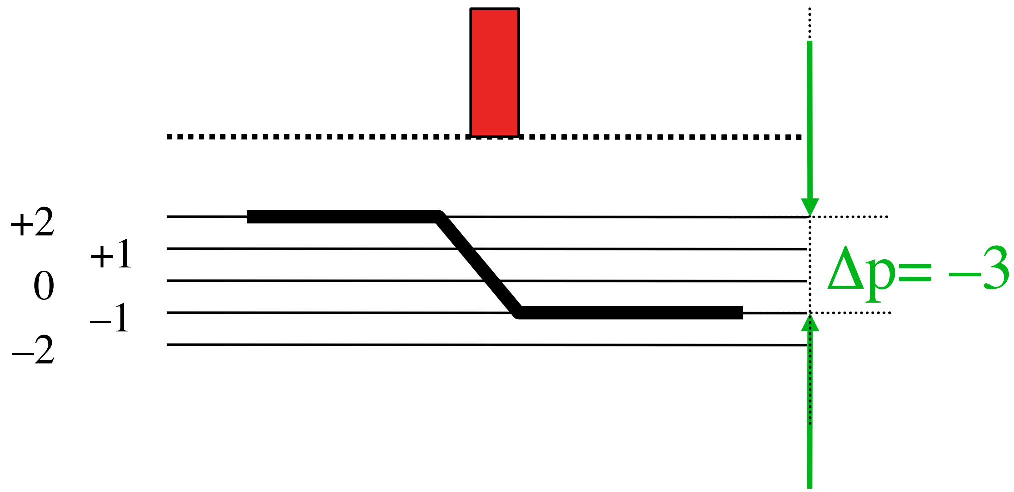
Coherence selection (7)

Phase cycling for the selection of the Δp=–3 coherence pathway



Coherence selection (7)

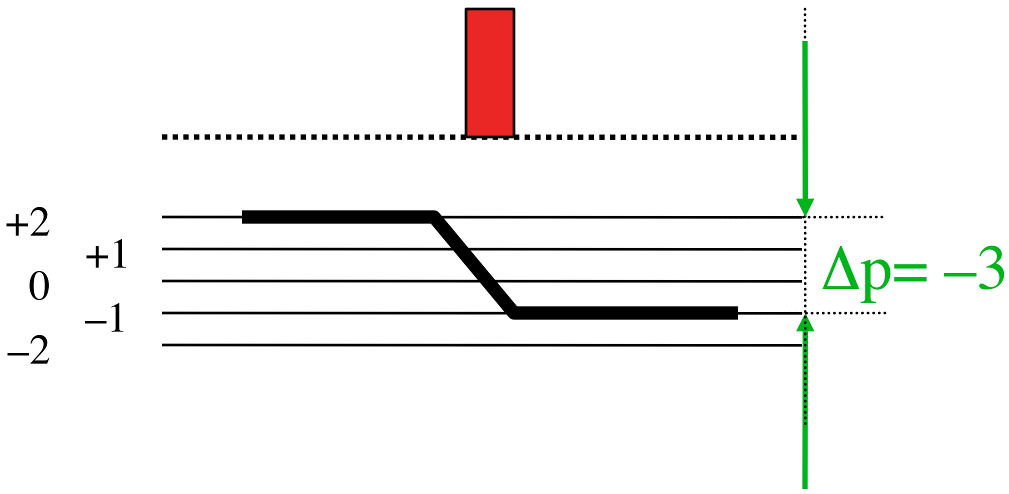
Phase cycling for the selection of the Δp=–3 coherence pathway



Step	Δφ	3 × Δφ	mod 360°
1	0°		
2	90°		
3	180°		
4	270°		

Coherence selection (7)

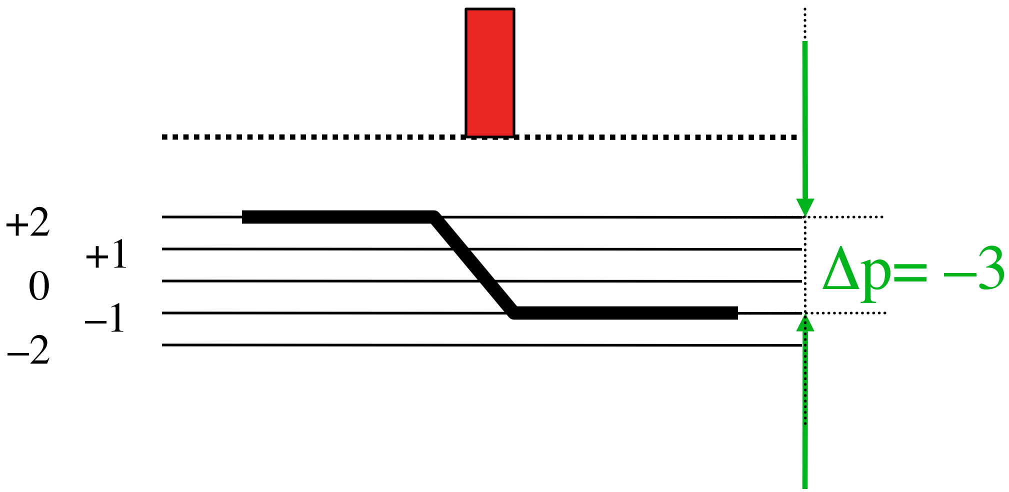
Phase cycling for the selection of the Δp=–3 coherence pathway



Step	Δφ	3 × Δφ	mod 360°
1	0°	0°	0°
2	90°	270°	270°
3	180°	540°	180°
4	270°	810°	90°

Coherence selection (7)

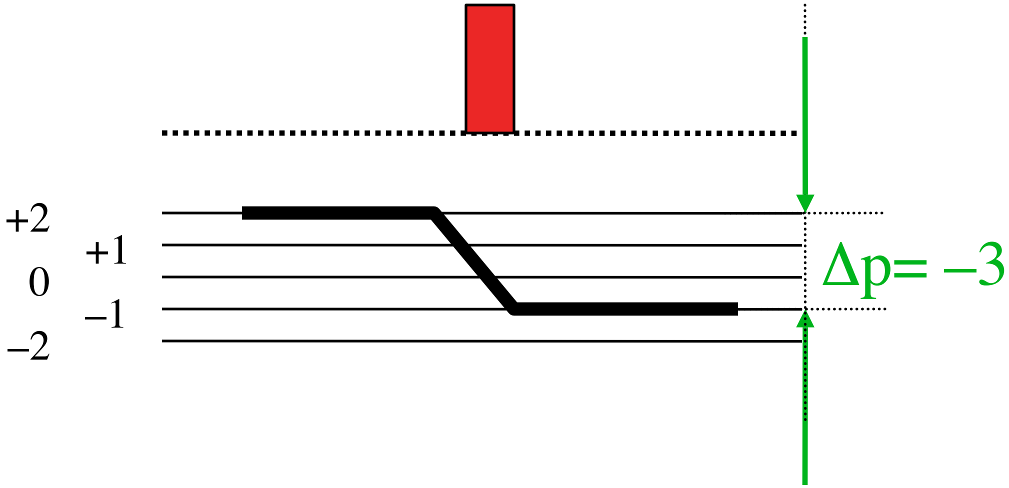
Phase cycling for the selection of the $\Delta p=-3$ coherence pathway



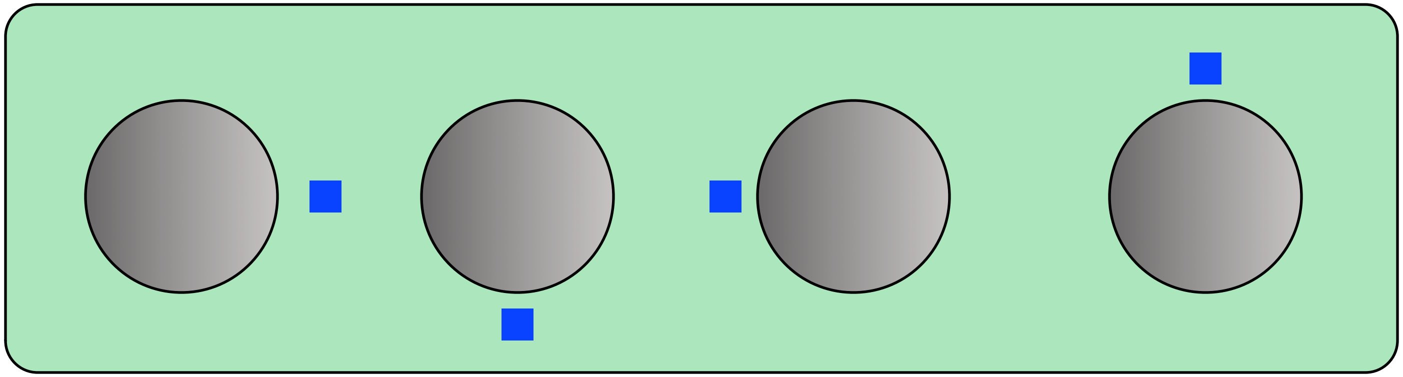
Step	$\Delta\phi$	$3 \times \Delta\phi$	recv phase
1	0°	0°	0°
2	90°	270°	270°
3	180°	540°	180°
4	270°	810°	90°

Coherence selection (7)

Phase cycling for the selection of the Δp=–3 coherence pathway

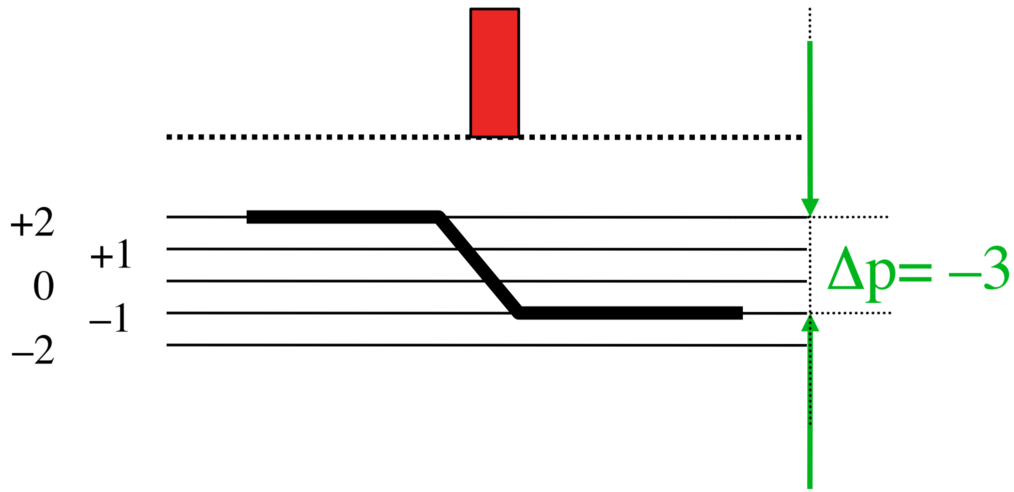


Step	Δφ	3 × Δφ	recv phase
1	0°	0°	0°
2	90°	270°	270°
3	180°	540°	180°
4	270°	810°	90°

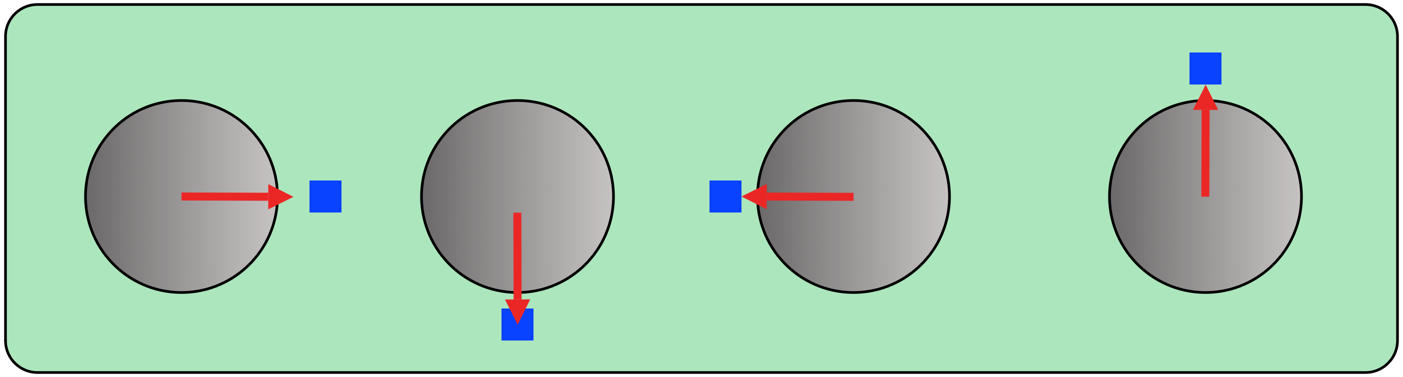


Coherence selection (7)

Phase cycling for the selection of the $\Delta p = -3$ coherence pathway

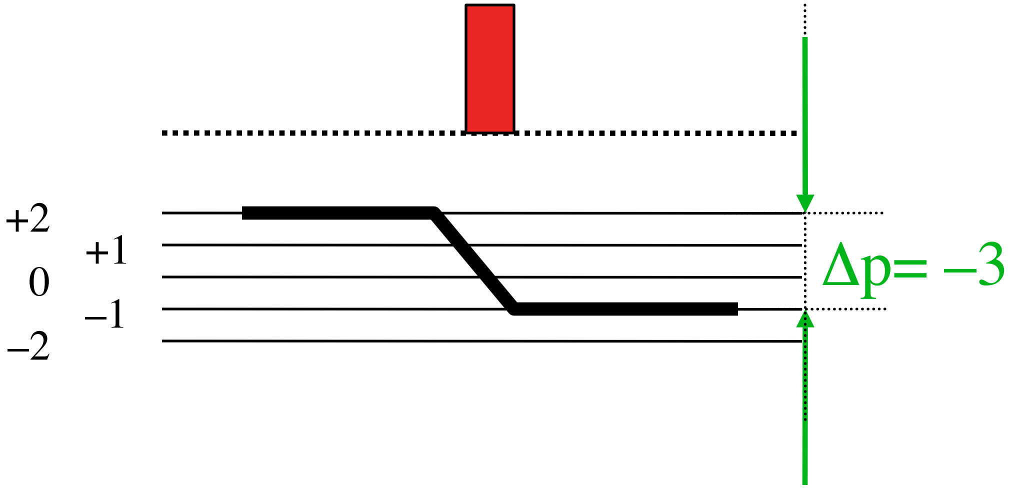


Step	$\Delta\phi$	$3 \times \Delta\phi$	recv phase
1	0°	0°	0°
2	90°	270°	270°
3	180°	540°	180°
4	270°	810°	90°

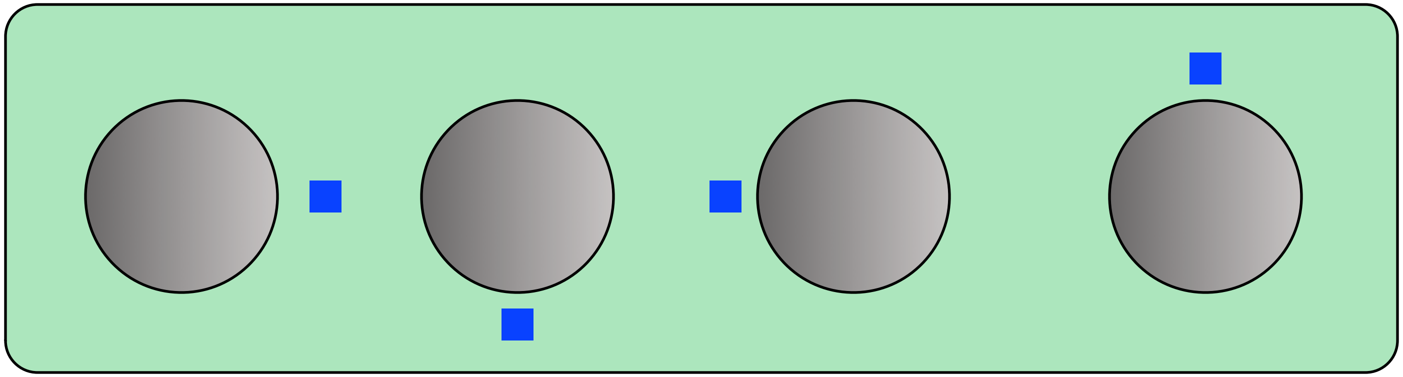


Coherence selection (7)

Phase cycling for the selection of the Δp=–3 coherence pathway

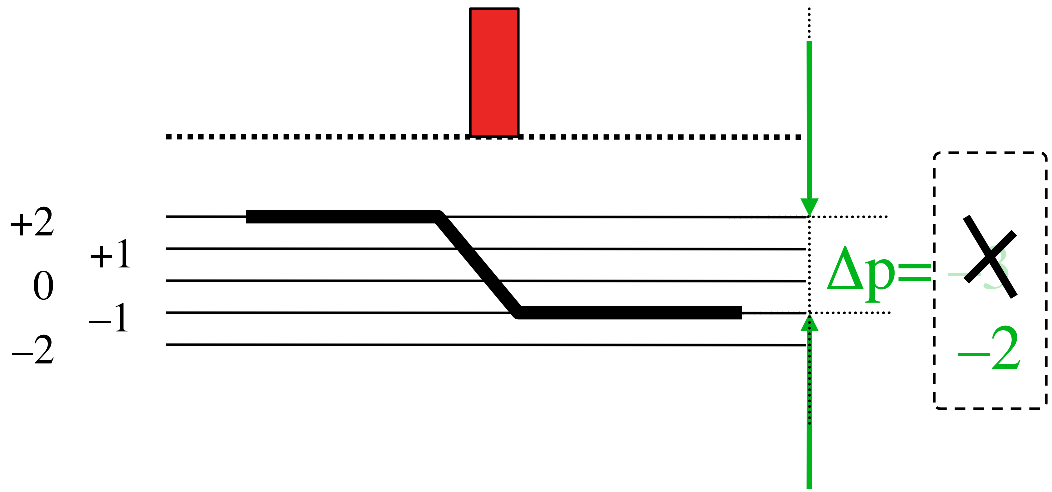


Step	Δφ	3 × Δφ	recv phase
1	0°	0°	0°
2	90°	270°	270°
3	180°	540°	180°
4	270°	810°	90°

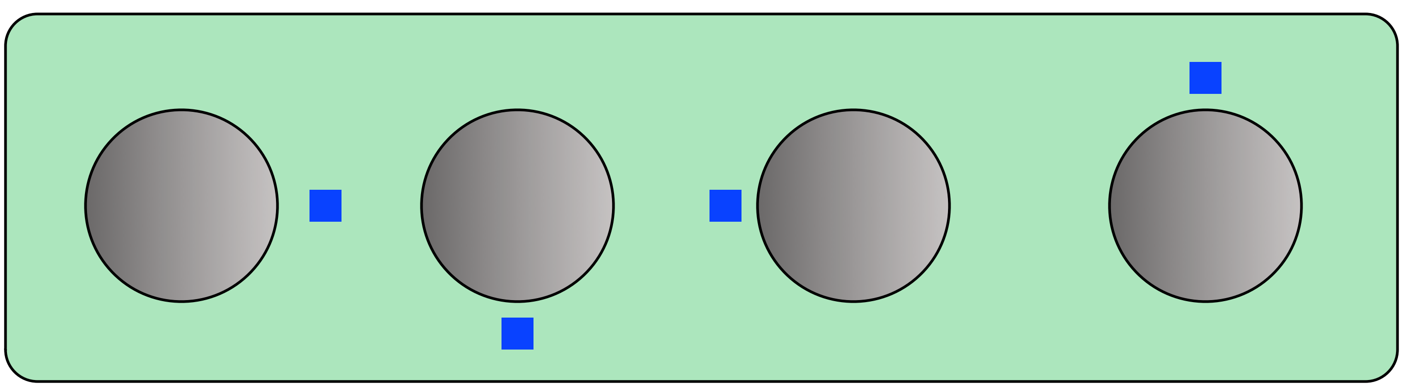


Coherence selection (7)

Phase cycling for the selection of the Δp=–3 coherence pathway

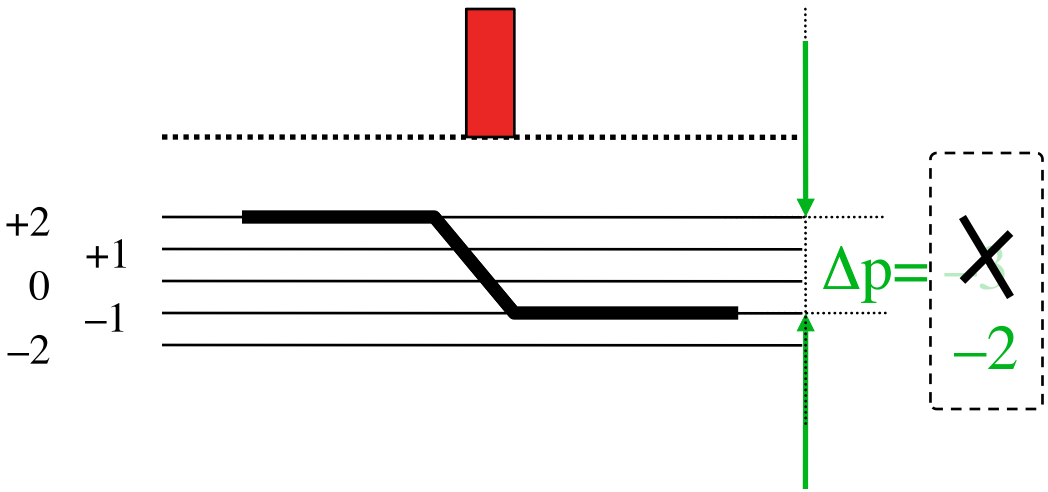


Step	$\Delta\phi$	$2 \times \Delta\phi$	mod 360°
1	0°	0°	0°
2	90°	180°	180°
3	180°	360°	0°
4	270°	540°	180°

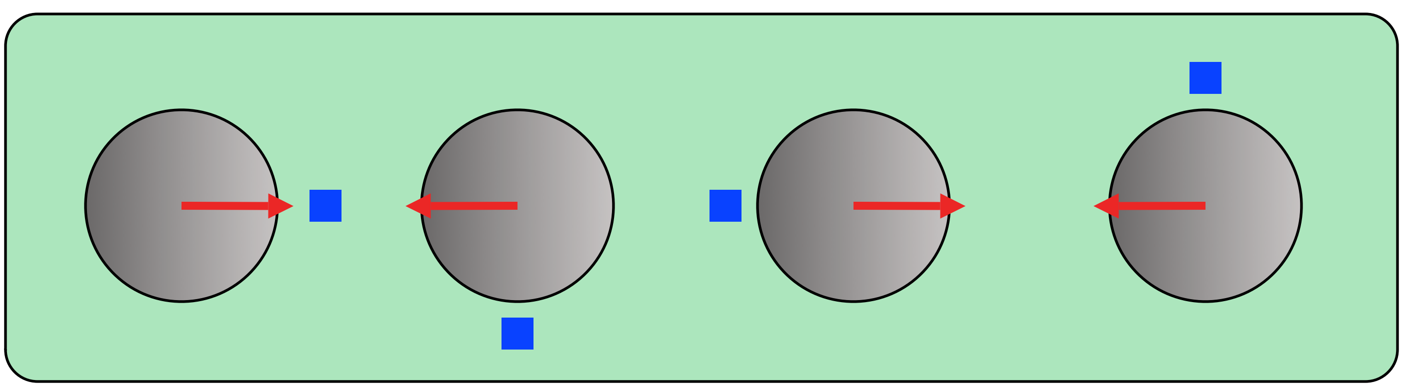


Coherence selection (7)

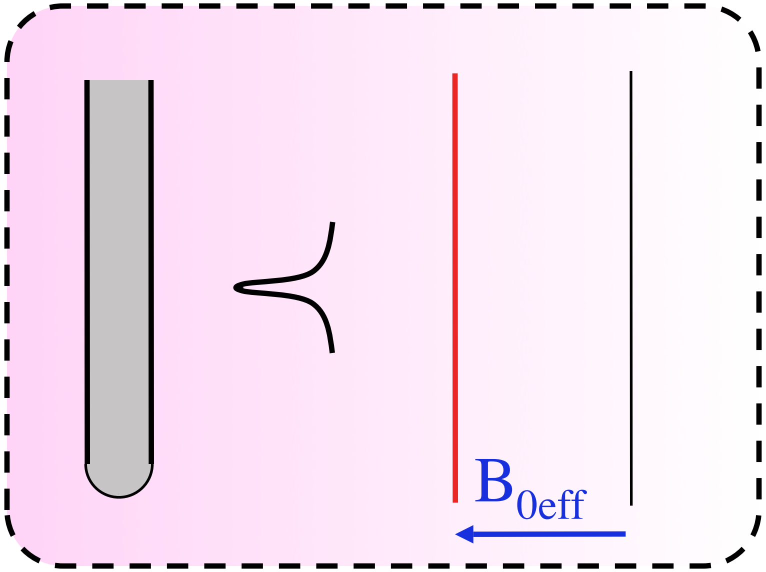
Phase cycling for the selection of the Δp=–3 coherence pathway



Step	$\Delta\phi$	$2 \times \Delta\phi$	mod 360°
1	0°	0°	0°
2	90°	180°	180°
3	180°	360°	0°
4	270°	540°	180°



Pulsed field gradients (1)

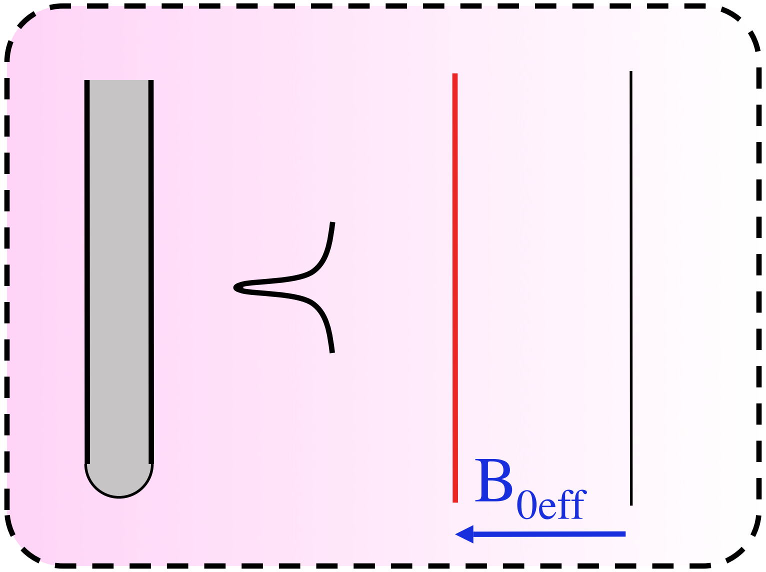


Homogeneous

magnetic field

(well shimmed magnet)

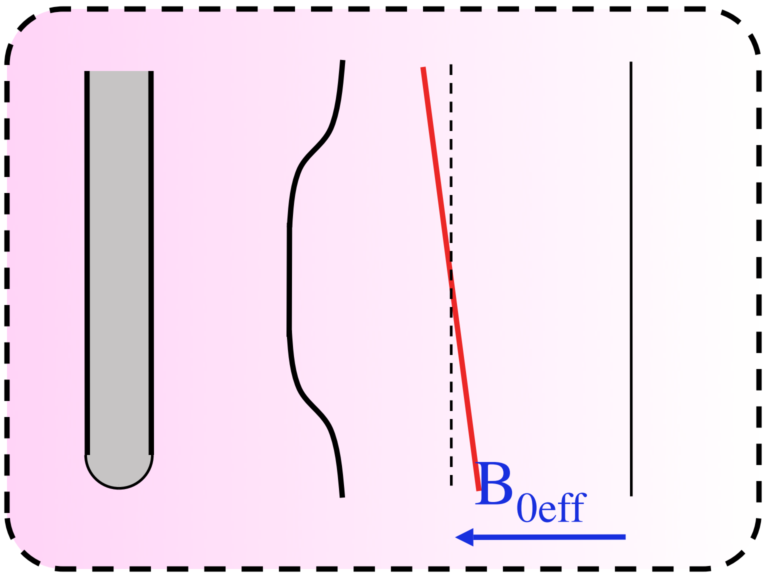
Pulsed field gradients (1)



Homogeneous

magnetic field

(well shimmed magnet)

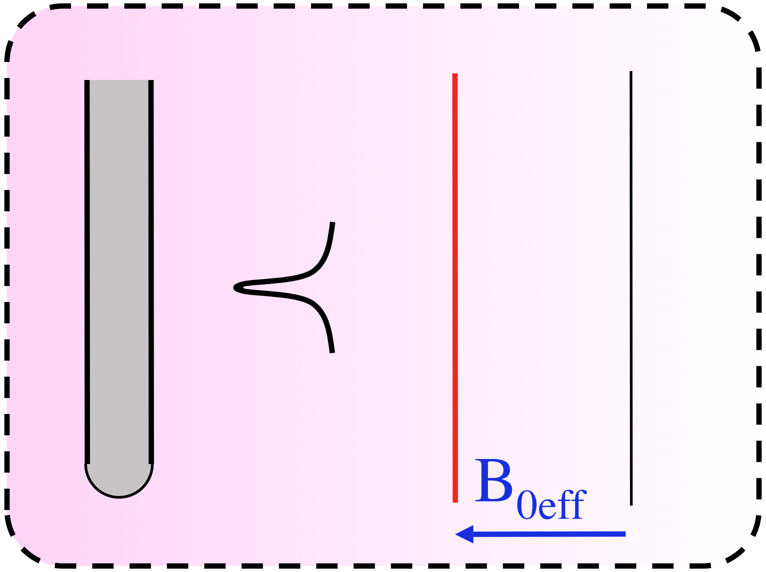


Inhomogeneous

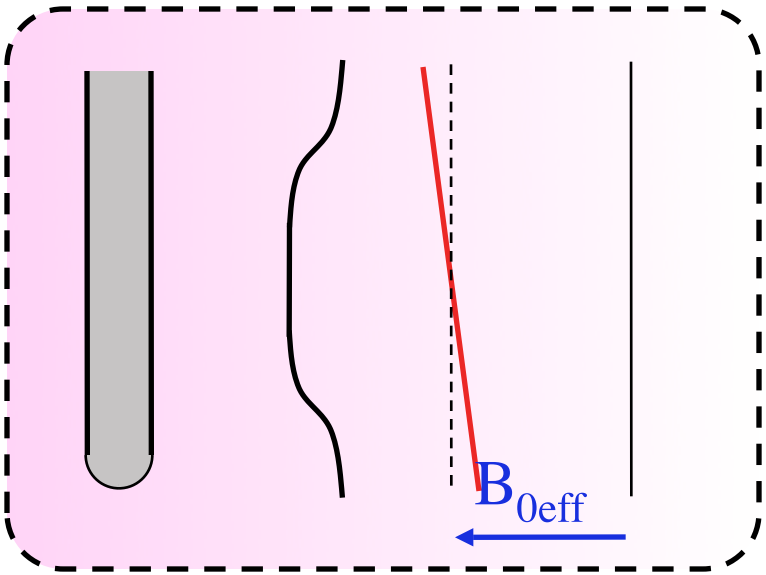
magnetic field

(field gradient)

Pulsed field gradients (1)



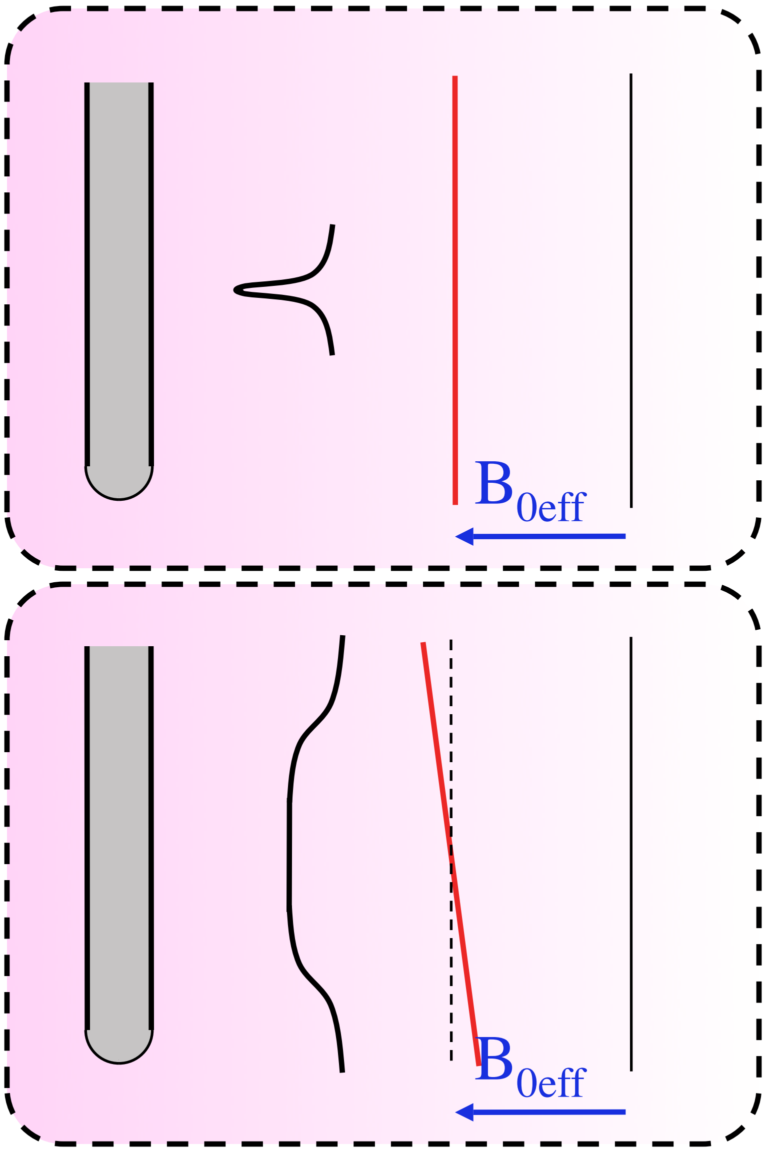
$I_+ \xrightarrow{\omega_0} I_+ \exp(-\boldsymbol{i}\,\omega_0 t)$



$I_+ \xrightarrow{\omega_0 + \gamma\, G(z)}$

$I_+ \exp(-\boldsymbol{i}\,[\,\omega_0 + \gamma\, G(z)]t)$

Pulsed field gradients (1)



$I_+ \xrightarrow{\omega_0} I_+ \exp(-\boldsymbol{i}\,\omega_0 t)$

$I_+ \xrightarrow{\omega_0 + \gamma\, G(z)}$

$I_+ \exp(-\boldsymbol{i}\,[\,\omega_0 + \gamma\, G(z)]t)$

Pulsed field gradients (2)

I_+ $\xrightarrow{\gamma_I G(z)}$

$I_+ \exp(-i\ \gamma_I G(z)t)$

Pulsed field gradients (2)

I_+ $\quad \gamma_I\, G(z)$

I_+ $\quad \exp(-\boldsymbol{i}\ \gamma_I\, G(z)t)$

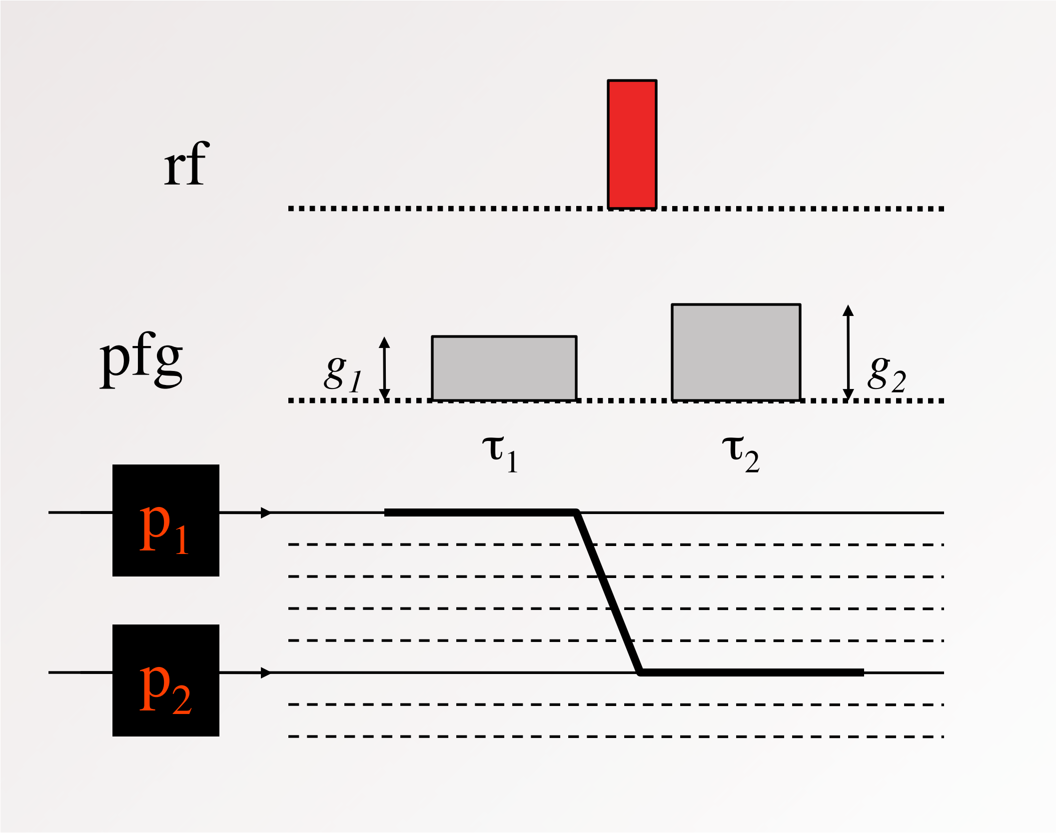
p_I coherence order

associated with spin I

I_+S_+ $\quad (\gamma_I + \gamma_S)G(z)$

I_+S_+ $\quad \exp(-\boldsymbol{i}\ (p_I\, \gamma_I + p_S\, \gamma_S)\ G(z)\ t)$

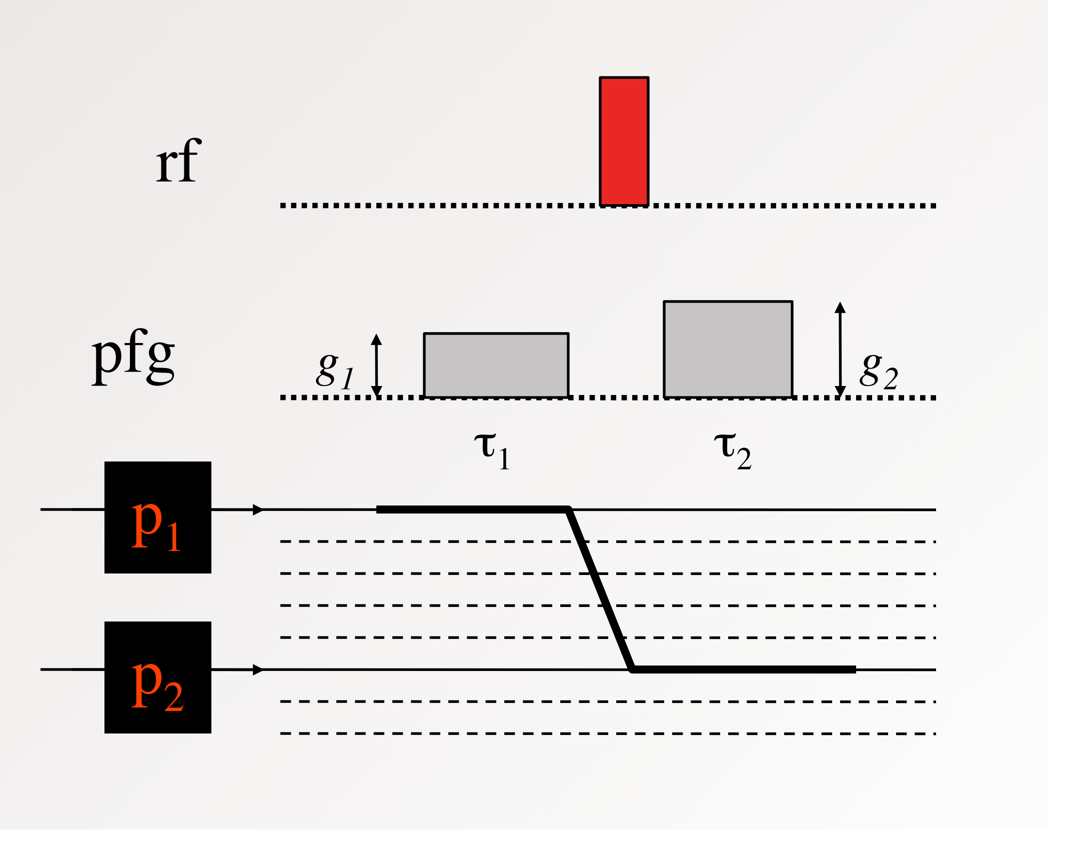
Pulsed field gradients (3)



Pulsed field gradients (3)

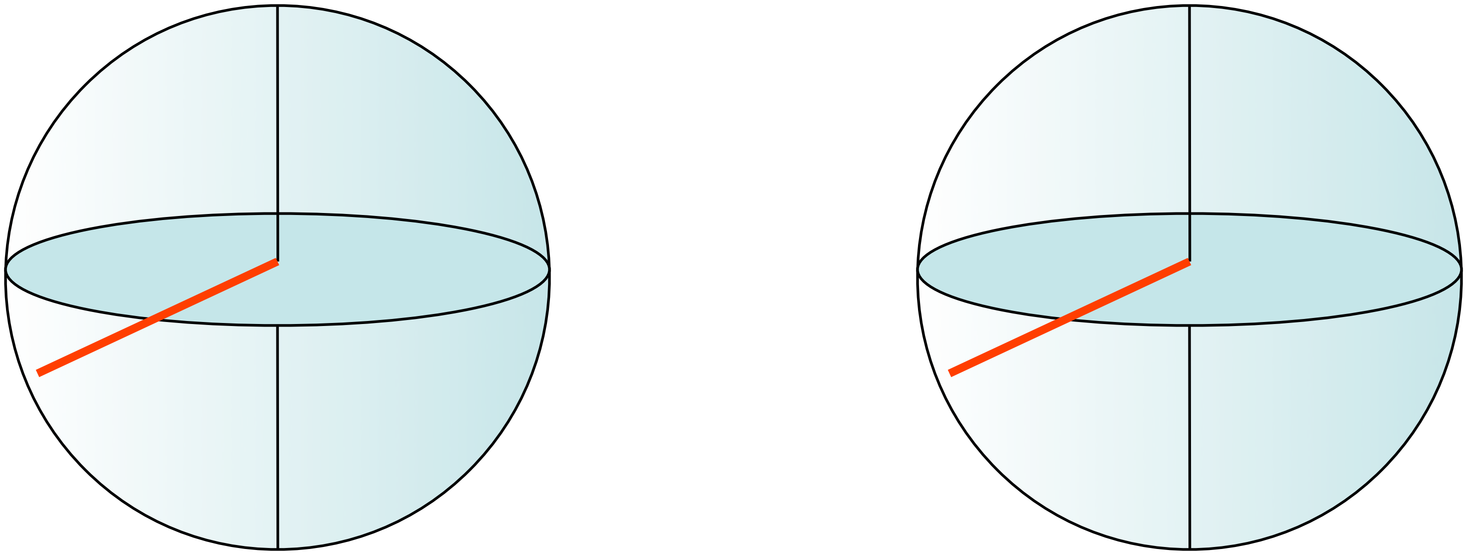
Refocusing condition

$$\frac{g_1\tau_1}{g_2\tau_2} = \frac{-p_1}{-p_2}$$



Pulsed field gradients (4)

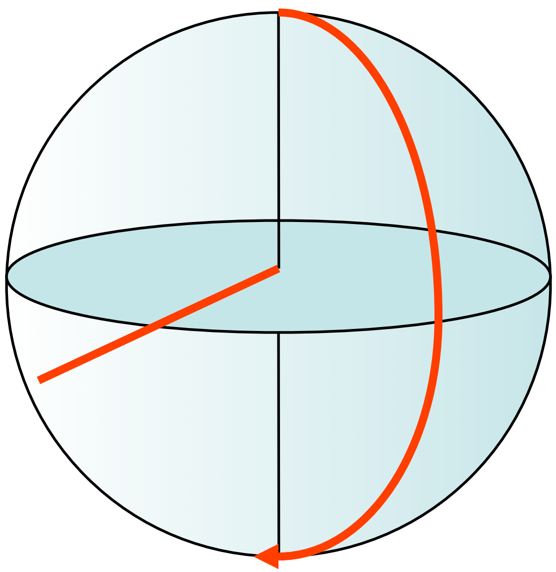
Imperfect 180º pulses



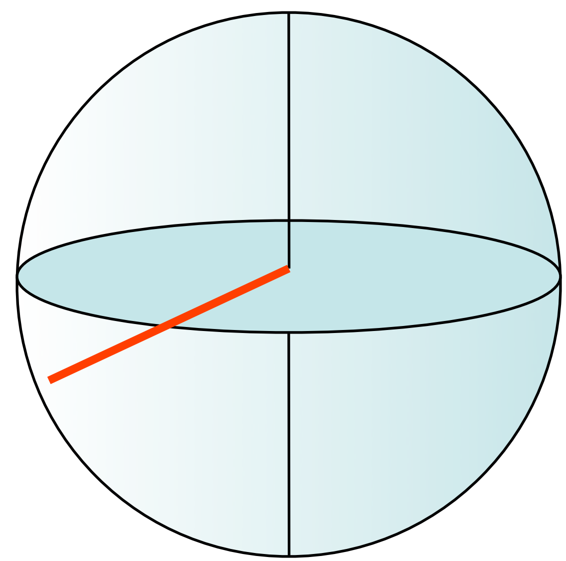
Inversion pulse Refocusing pulse

Pulsed field gradients (4)

Imperfect 180º pulses



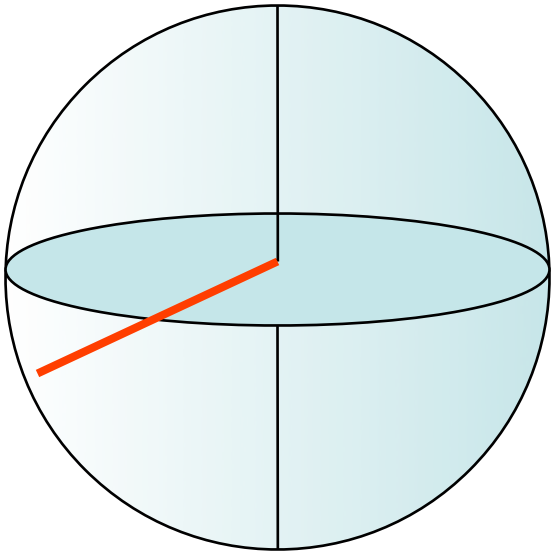
Inversion pulse



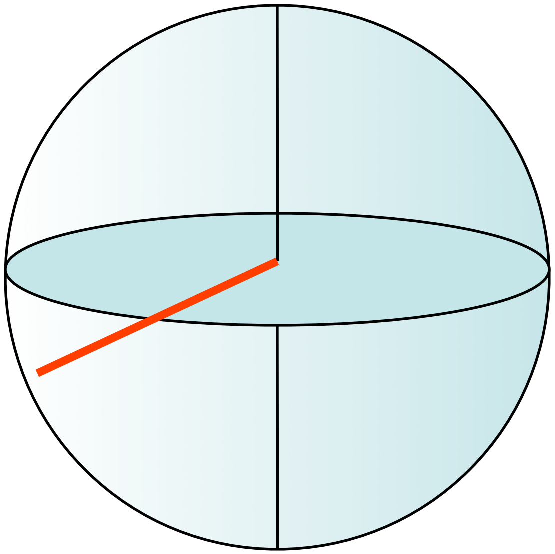
Refocusing pulse

Pulsed field gradients (4)

Imperfect 180º pulses



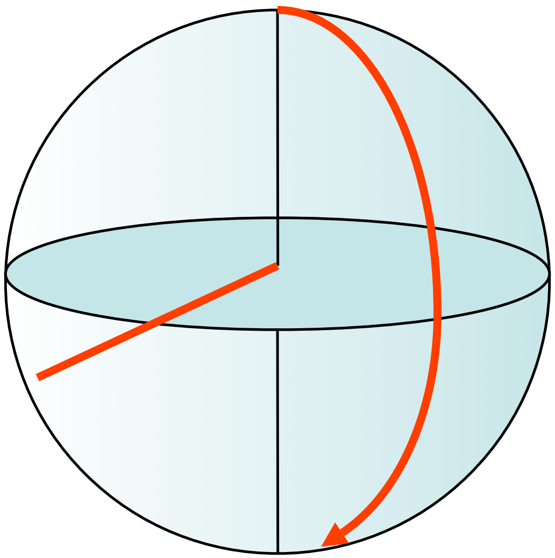
Inversion pulse



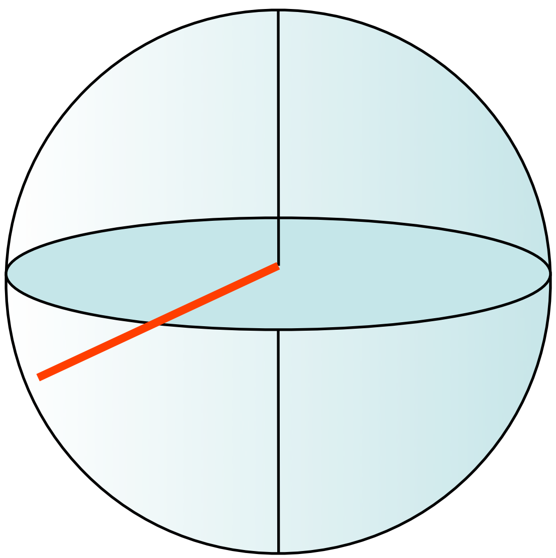
Refocusing pulse

Pulsed field gradients (4)

Imperfect 180º pulses



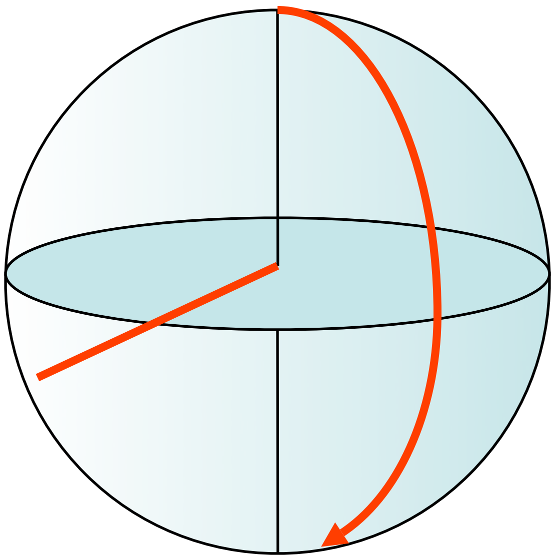
Inversion pulse



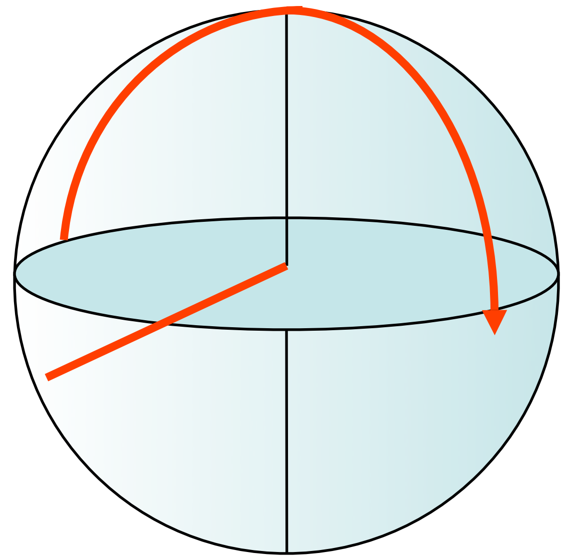
Refocusing pulse

Pulsed field gradients (4)

Imperfect 180º pulses



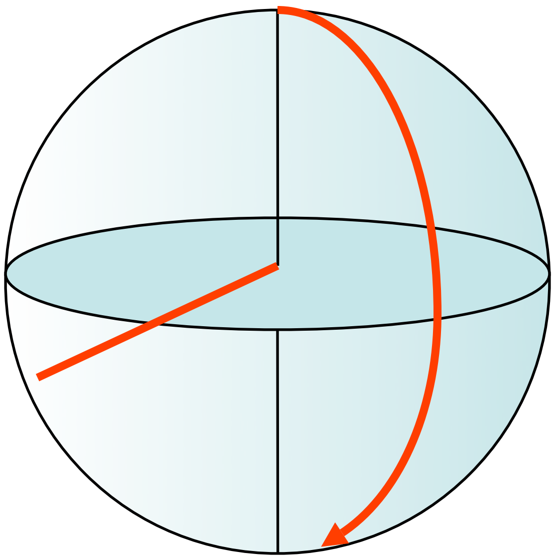
Inversion pulse



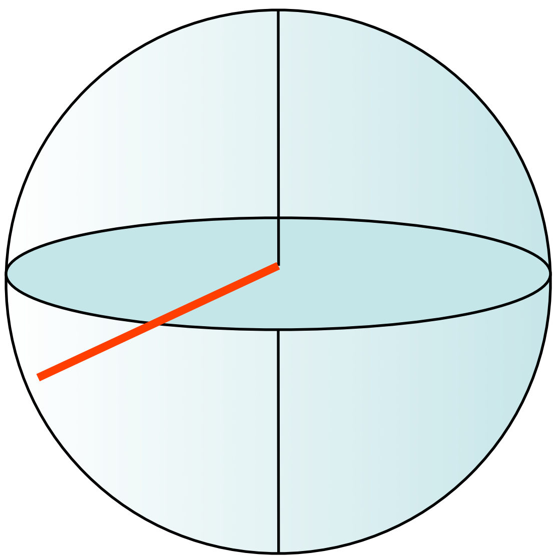
Refocusing pulse

Pulsed field gradients (4)

Imperfect 180º pulses



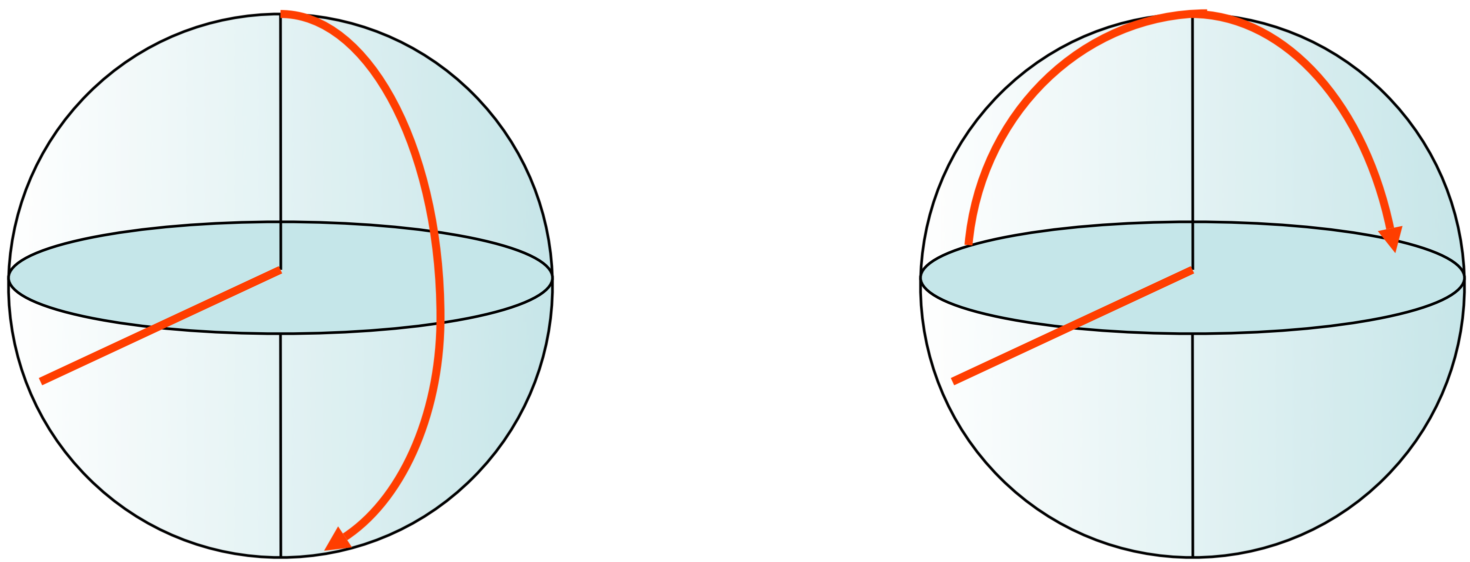
Inversion pulse



Refocusing pulse

Pulsed field gradients (4)

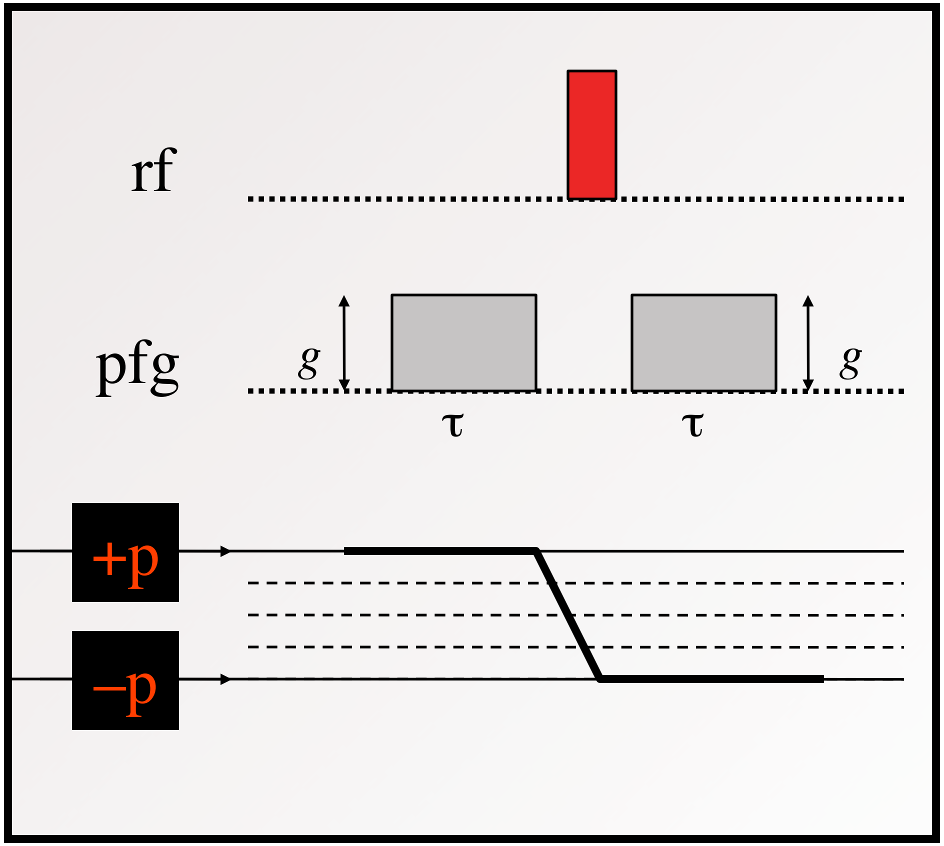
Imperfect 180º pulses

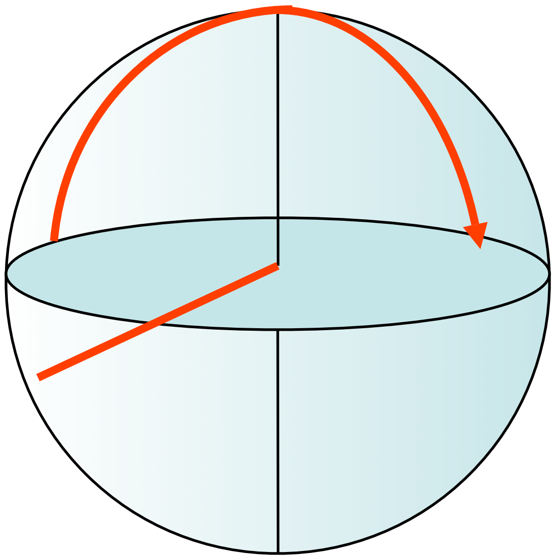


Inversion pulse Refocusing pulse

Pulsed field gradients (4)

Imperfect 180º pulses

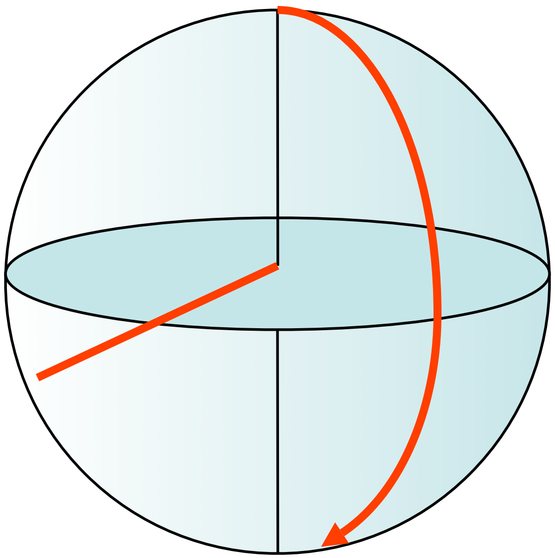




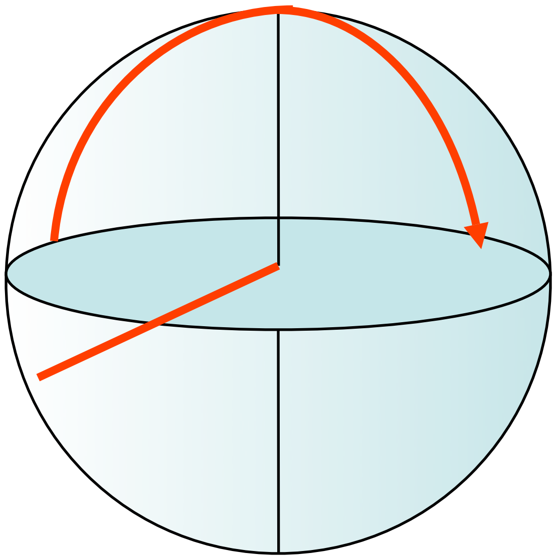
Refocusing pulse

Pulsed field gradients (4)

Imperfect 180º pulses



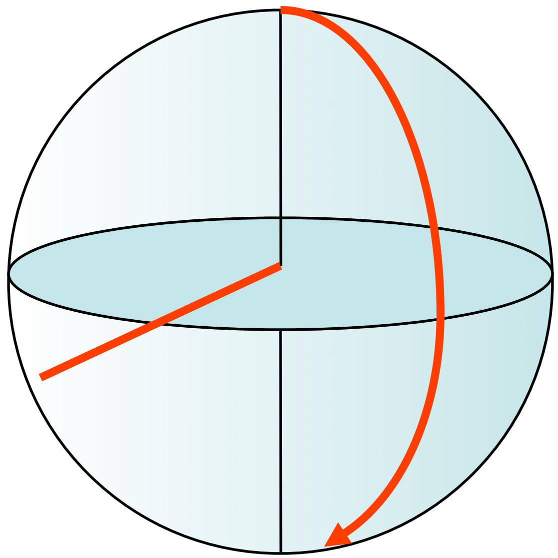
Inversion pulse



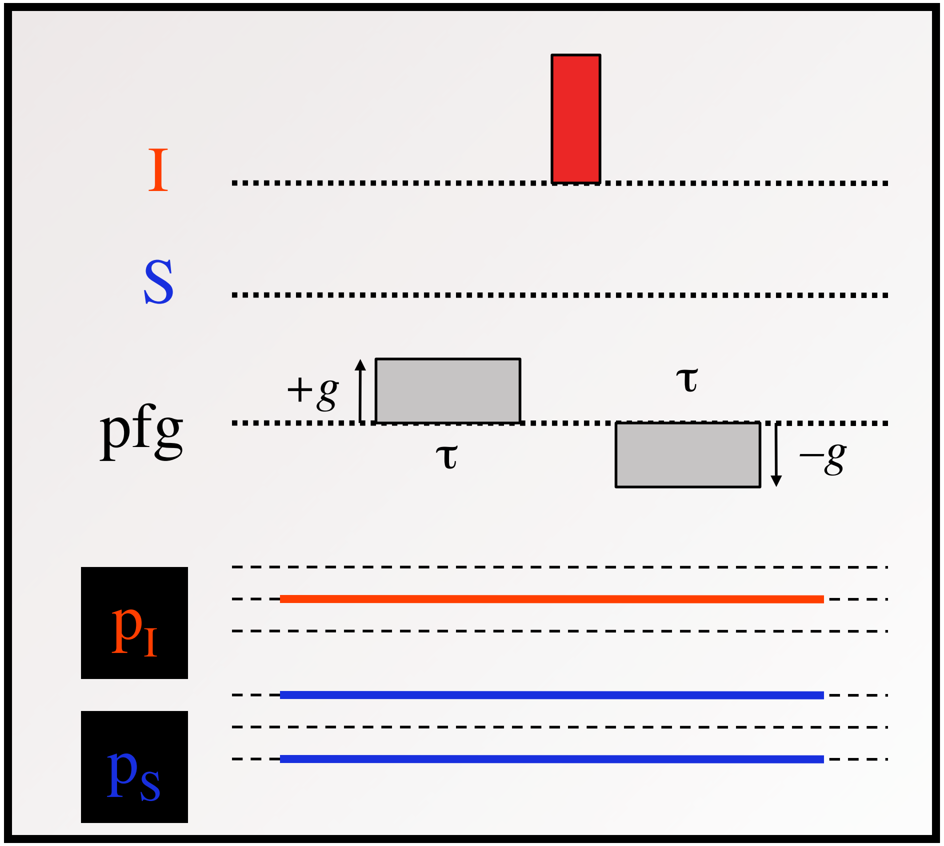
Refocusing pulse

Pulsed field gradients (4)

Imperfect 180º pulses



Inversion pulse



The end…