Classic description of NMR

Bloch's equations

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

magnetization — State of the spin system

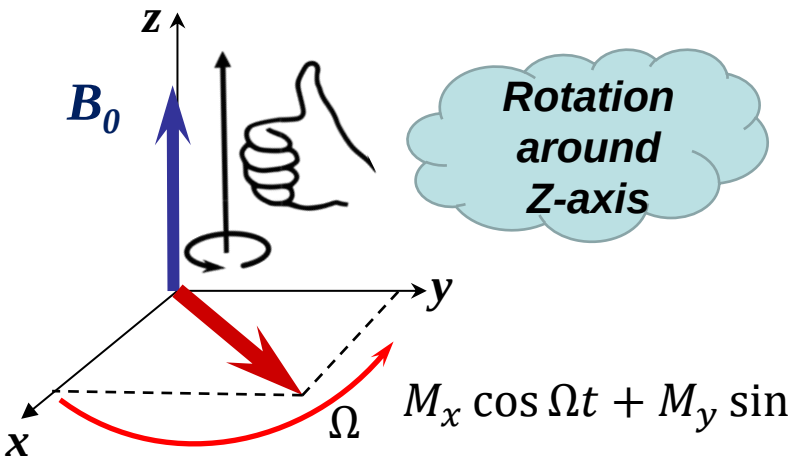
magnetic field — Manipulation with magnetization

Evolution in time – rotation of magnetization

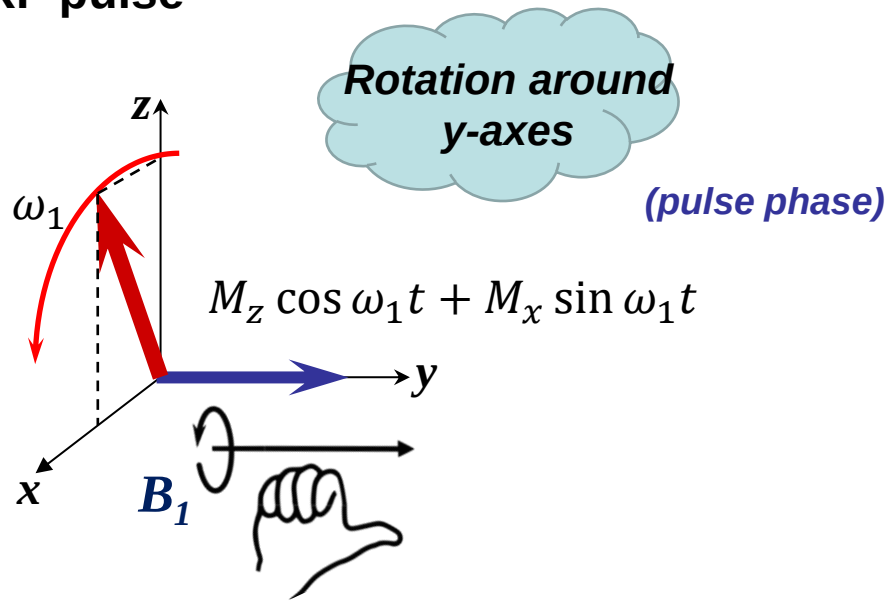
Everything in a rotating coordinate system

Chemical shift

(after subtracting Larmor precession)



RF pulse



Valid only for the set of non-interacting spins 1/2

Modern description of NMR

Quantum description

Liouville-von Neumann

$$\frac{d}{dt}\rho = -i\,[H, \rho]$$

Density matrix — State of the spin system

Hamiltonian — energy operator

Classically

$$E = -\vec{\mu} \cdot \vec{B} = -\gamma \vec{I} \cdot \vec{B} = -\gamma B_0 I_z = \omega_0 I_z$$

Quantum

$$H = \omega_0 \, I_z$$

Hamiltonian (energy operator)

angular momentum operator

Larmor frequency

Density matrix

- Linear combination of angular momentum operators – product operators
- evolution over time – rotation of product operators

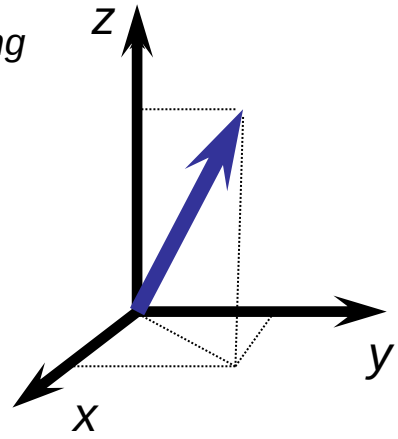
Analogy with the classical vector model

set of non-interacting spins 1/2

$$I_z \rightarrow M_z$$

$$I_x \rightarrow M_x$$

$$I_y \rightarrow M_y$$



Modern description of NMR

Density matrix

- Linear combination of angular momentum operators – product operators

set of non-interacting spins 1/2

$$I_x,\ I_y,\ I_z$$

Equilibrium state *Boltzman distribution* Zeeman Hamiltonian

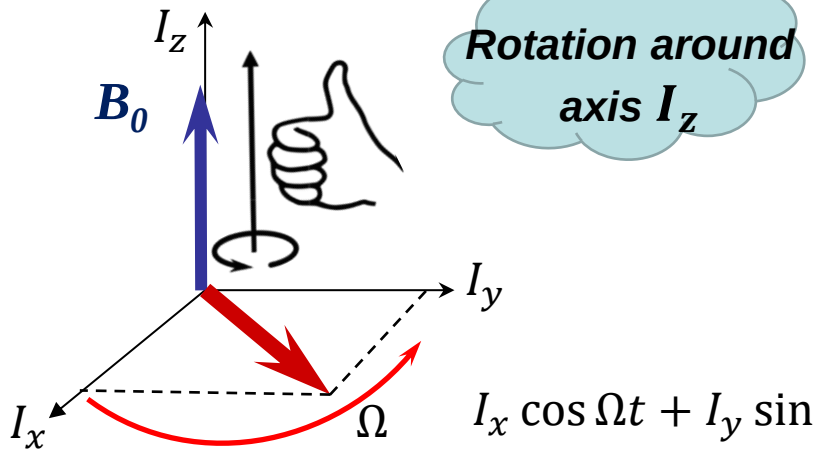
$$\rho_{eq} \sim e^{-\frac{H}{k_B T}} \approx 1 - \left(-\frac{H}{k_B T}\right) = 1 + \frac{\gamma B_0 I_z}{k_B T}$$

Boltzman factor (size of magnetization)

$$\rho_{eq} \sim I_z$$

- evolution over time – rotation of product operators

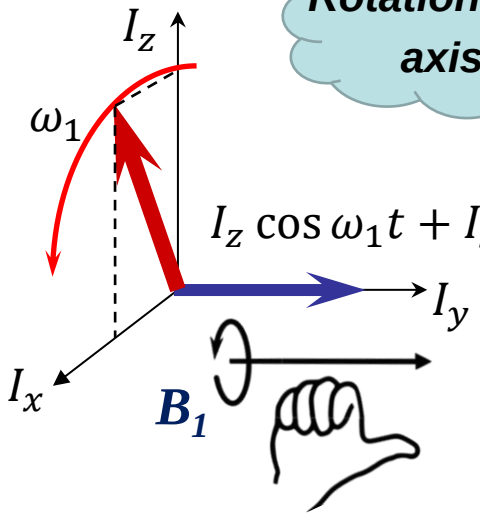
Chemical shift



Rotation around axis I_z

$$I_x \cos \Omega t + I_y \sin \Omega t$$

RF pulse



Rotation around axis I_y

(pulse with phase y)

$$I_z \cos \omega_1 t + I_x \sin \omega_1 t$$

Modern description of NMR

Formalism of Product Operators

basis in spin space (assuming all spin-1/2)

Product operator = 2^{N-1} × operator spin 1 × operator spin 2 × ... × operator spin N

Set of non-interacting spins 1/2

$N = 1$

4 basis operators

$I_x, I_y, I_z, \frac{1}{2}\mathbb{1}$

Pauli matrices

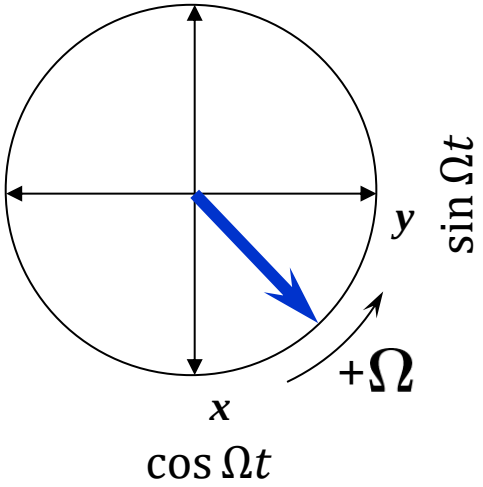
Set of two 1/2 spins with J coupling

$N = 2$

16 basis operators

	$\frac{1}{2}\mathbb{1}$
populations	I_z, S_z
single quantum coherences	I_x, I_y, S_x, S_y
	$2I_xS_z, 2I_yS_z, 2I_zS_x, 2I_yS_z$
multiple quantum coherences	$2I_xS_x, 2I_yS_y, 2I_xS_y, 2I_yS_x$
two-spin order	$2I_zS_z$

Product Operators and NMR spectrum



magnetization $M(t) = M_x \cos \Omega t + M_y \sin \Omega t$

Density matrix $\rho(t) = I_x \cos \Omega t + I_y \sin \Omega t$

Real part

Imaginary part

Quadrature detection

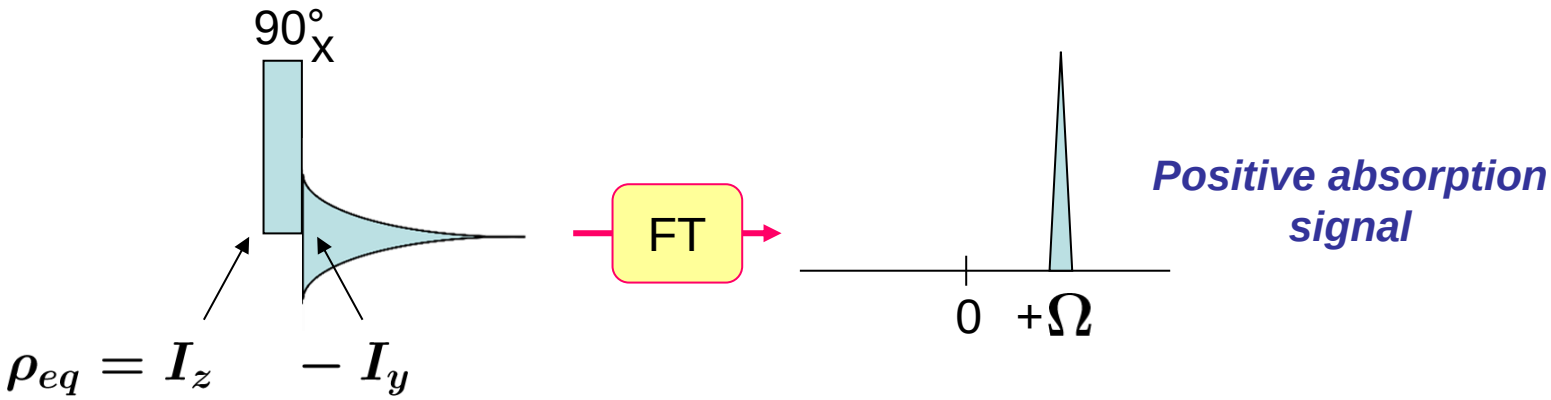
to discriminate the sign of frequency (sense of rotation of „magnetization“)

FID → Projection of density matrix onto operator I_-

$$s(t) = Tr\{I_+ \rho(t)\} = M_0 \exp\left\{i(\Omega t + \varphi) - \frac{t}{T_2}\right\}$$

$$\boldsymbol{I_- = I_x - iI_y}$$

Convention:

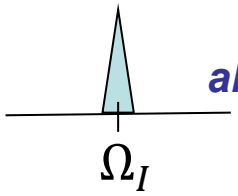


Positive absorption signal

Product Operators and NMR spectrum

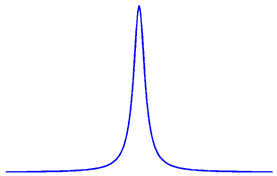
- Only „single quantum coherences“ lead to NMR signal
- We can assign a corresponding spectrum to these operators

Single spin

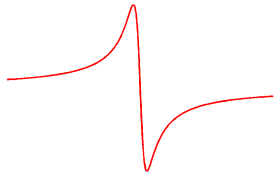
$-I_y$ 

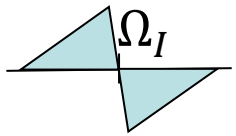
absorpční singlet

Absorption signal



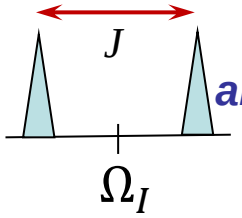
Dispersive signal



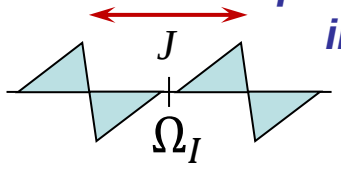
I_x 

dispersive singlet

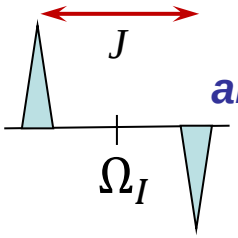
Pair of spins with J coupling

$-I_y$ 

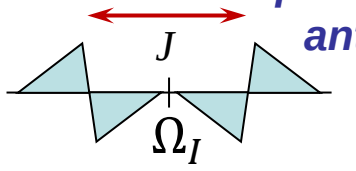
absorption doublet, in-phase

I_x 

dispersion doublet, in-phase

$-2I_yS_z$ 

absorption doublet, anti-phase

$2I_xS_z$ 

dispersion doublet, anti-phase

Product Operators and NMR Spectrum

Pair of spins with J coupling

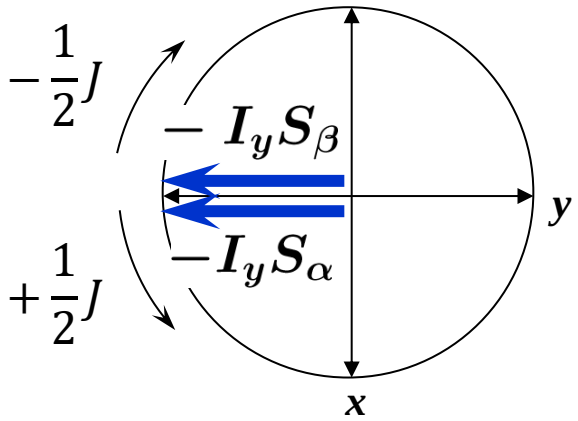
$$\mathbb{1} = I_\alpha + I_\beta$$

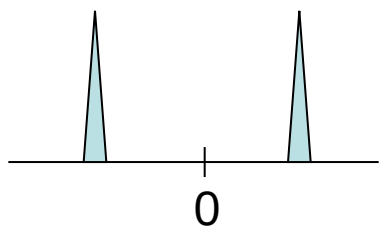
$$I_z = \frac{1}{2}(I_\alpha - I_\beta)$$

$-I_y$

$$-I_y = -2I_y \frac{1}{2} 1_S$$

$$= -I_y S_\alpha - I_y S_\beta$$

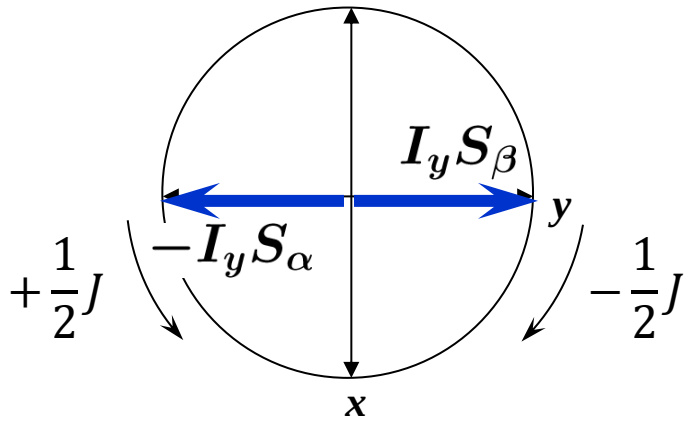


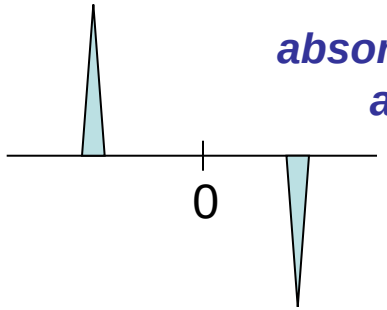


absorption doublet, in-phase

$-2I_y S_z$

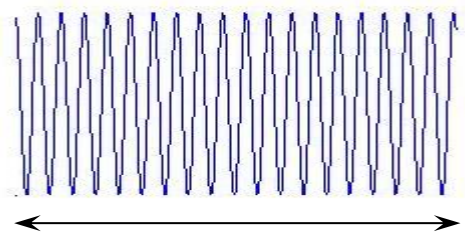
$$-2I_y S_z = -I_y S_\alpha + I_y S_\beta$$





absorption doublet, anti-phase

Product operators and RF pulse



amplitude ω_1

duration τ_p

Flip angle $\varphi = \omega_1 \tau_p$

frequency ω_{rf}

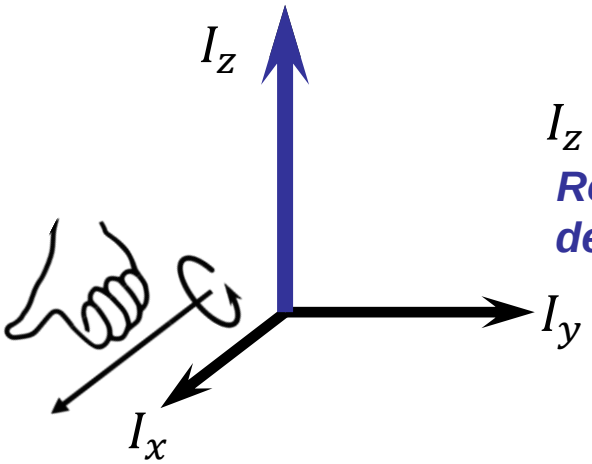
phase α

x, y, -x, -y

Hamiltonian

$$H_{RF} = \omega_1 I_\alpha$$

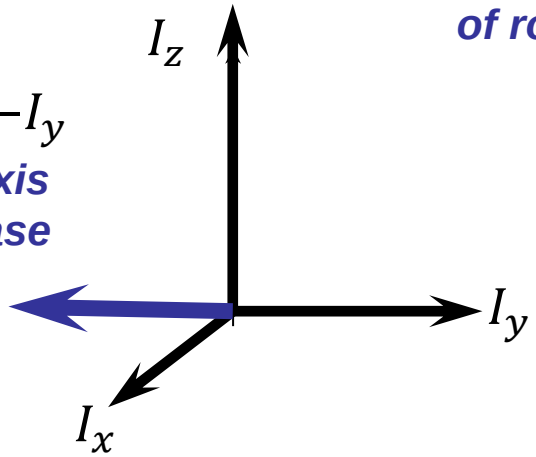
Product operator determining the axis of rotation



90_x

$I_z \rightarrow -I_y$

Rotation around axis determined by phase of the pulse



Examples

$I_x \xrightarrow{90_x}$

$I_y \xrightarrow{90_x}$

$I_x \xrightarrow{90_y}$

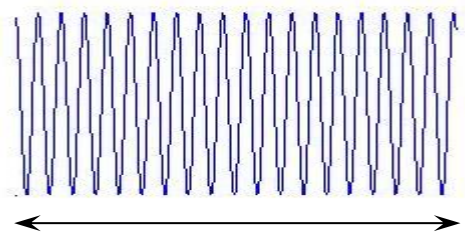
$I_y \xrightarrow{90_y}$

$I_z \xrightarrow{90_y}$

$I_z \xrightarrow{180_x}$

Product operators and RF pulse

amplitude ω_1



duration τ_p

Flip angle $\varphi = \omega_1 \tau_p$

frequency ω_{rf}

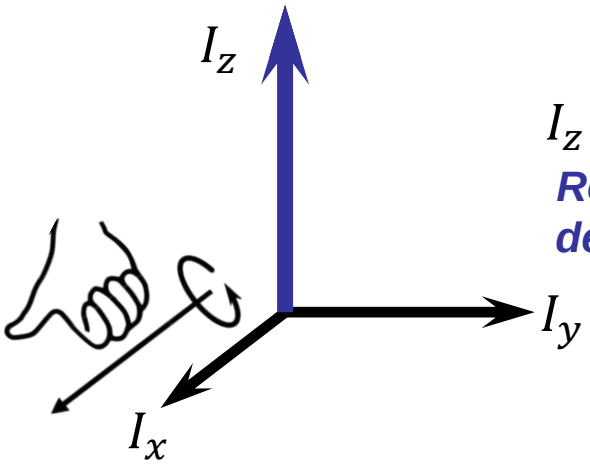
phase α

x, y, -x, -y

Hamiltonian

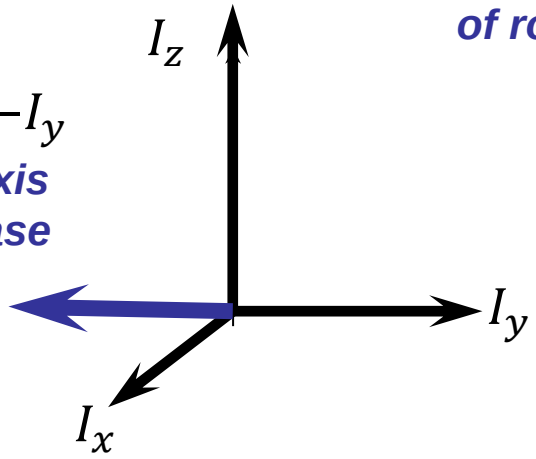
$$H_{RF} = \omega_1 I_\alpha$$

Product operator determining the axis of rotation



$I_z \xrightarrow{90_x} -I_y$

Rotation around axis determined by phase of the pulse



Examples

$I_x \xrightarrow{90_x} I_x$ $\quad I_x \xrightarrow{90_y} -I_z$ $\quad I_z \xrightarrow{90_y} I_x$

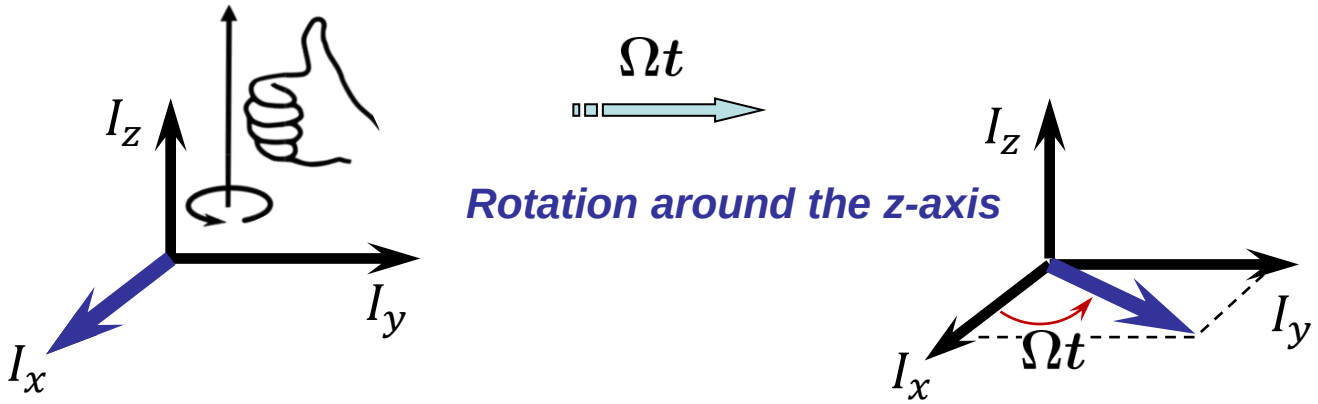
$I_y \xrightarrow{90_x} I_z$ $\quad I_y \xrightarrow{90_y} I_y$ $\quad I_z \xrightarrow{180_x} -I_z$

Product operators and chemical shift

Hamiltonian $\boldsymbol{H_{CS} = -\gamma B_0 (1 + \delta_{iso})\, I_z}$

$H_{CS} = \Omega\, I_z$ — *Product operator determining the axis of rotation*

Rotation frequency



$I_x \xrightarrow{\Omega t}$

$I_y \xrightarrow{\Omega t}$

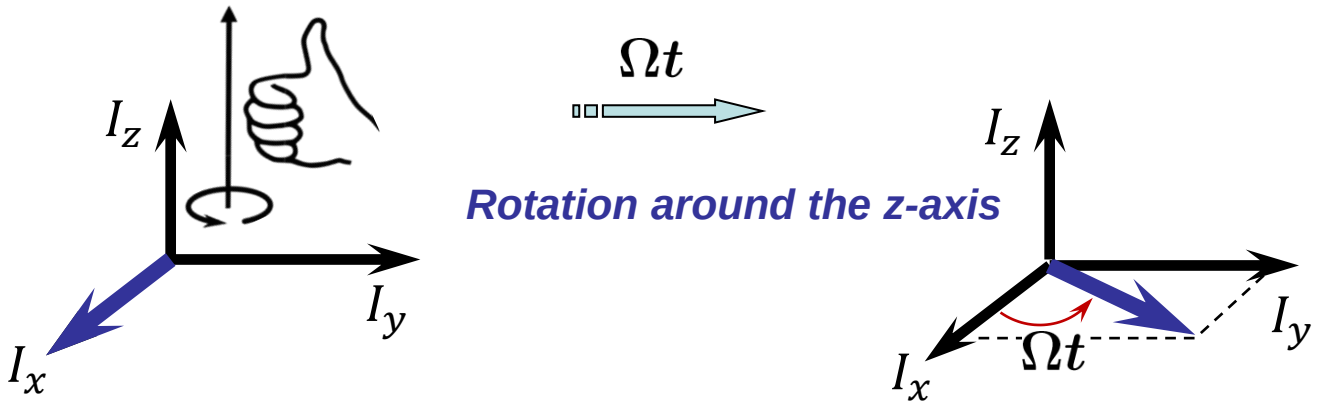
$I_z \xrightarrow{\Omega t}$

Product operators and chemical shift

Hamiltonian $\boldsymbol{H_{CS} = -\gamma B_0 (1 + \delta_{iso})\, I_z}$

$H_{CS} = \Omega\, I_z$ → ***Product operator determining the axis of rotation***

Rotation frequency



$$I_x \xrightarrow{\Omega t} I_x \cos \Omega t + I_y \sin \Omega t$$

$$I_y \xrightarrow{\Omega t} I_y \cos \Omega t - I_x \sin \Omega t$$

$$I_z \xrightarrow{\Omega t} I_z$$

Product operators and J coupling

Hamiltonian

weak J coupling

$2\pi J \ll \Delta\Omega$

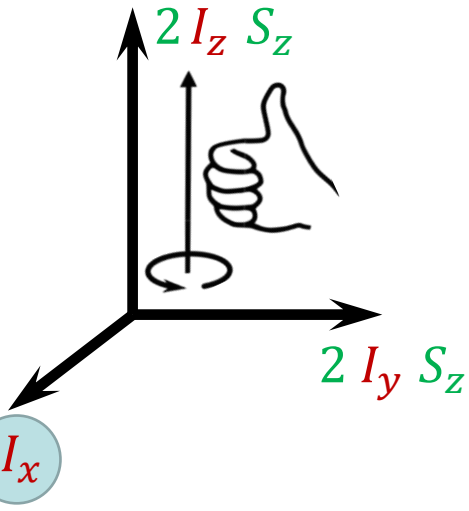
$$H = \pi J \, 2I_z S_z$$

Rotation frequency (rad/s)

Product operator determining the axis of rotation

Rotation in the appropriate subspace

1. Label axes with components of the single spin operator, for example I_x, I_y, I_z
2. On two axes, add the z-component of the second spin operator multiplied by 2, that means $2S_z$
3. Axes labels must contain an operator $2I_z S_z$ and operator to evolve, for example I_x

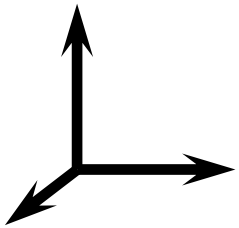


$$I_x \xrightarrow{\pi J t} I_x \cos \pi J t + 2 I_y S_z \sin \pi J t$$

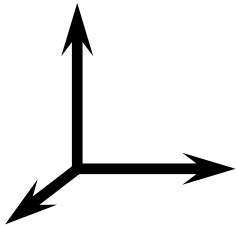
Original operator ***New operator***

Product operators and J coupling

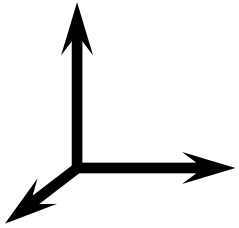
$2I_y S_z \xrightarrow{\pi J t}$



$2I_x S_z \xrightarrow{\pi J t}$

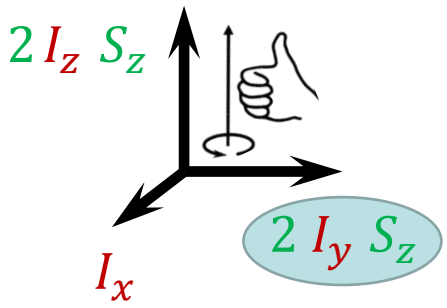


$S_y \xrightarrow{\pi J t}$

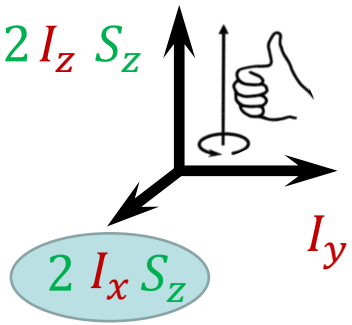


Product operators and J coupling

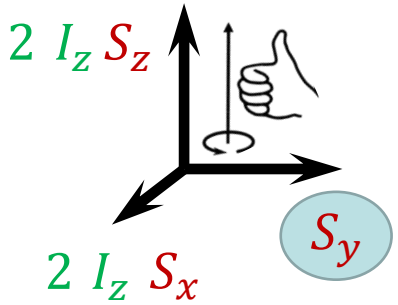
$$2I_yS_z \xrightarrow{\pi Jt} 2I_yS_z\cos\pi Jt - I_x\sin\pi Jt$$



$$2I_xS_z \xrightarrow{\pi Jt} 2I_xS_z\cos\pi Jt + I_y\sin\pi Jt$$



$$S_y \xrightarrow{\pi Jt} S_y\cos\pi Jt - 2I_zS_x\sin\pi Jt$$



- Only „single quantum coherences“ are evolving

  $I_x, I_y, S_x, S_y, 2I_xS_z, 2I_yS_z, 2I_zS_x, 2I_yS_z$

- Other operators do NOT change due to J-couplings

  $I_z, S_z, 2I_zS_z, 2I_xS_x, 2I_yS_y, 2I_xS_y, 2I_yS_x$