# Lecture #10
# Product Operator Formalism I

- Topics
  - Coherence space
  - The three basic rotations
  - Examples
- Handouts and Reading assignments
  - van de Ven: Chapter 2.3 and 2.6
  - Sorenson, et al, "Product Operator Formalism for the Description of NMR Pulse Experiments", *Progress in NMR Spectroscopy*, **16**:163-192, 1983.

# The Spin Density Operator

- Spin density operator, $\hat{\sigma}(t)$, completely describes the state of the system and the expectation of an observable: $\overline{\langle \hat{A} \rangle} = \mathrm{Tr}\{\hat{\sigma}\hat{A}\}$.

- Time evolution of $\hat{\sigma}(t)$: $\dfrac{\partial}{\partial t}\hat{\sigma} = -i\hat{\hat{H}}\hat{\sigma} \Longrightarrow \hat{\sigma}(t) = e^{-i\hat{\hat{H}}t}\hat{\sigma}(0)$

  ($\hat{H}$ time independent)

- Hence, if $\hat{H}$ is piecewise constant:

$$\underbrace{0 \xrightarrow{\hat{H}_1}}_{t_1} \; \underbrace{\xrightarrow{\hat{H}_2}}_{t_2} \; \underbrace{\xrightarrow{\hat{H}_3}}_{t_3} \cdots \; t$$

$$\hat{\sigma}(0) \xrightarrow{\hat{H}_1} \xrightarrow{\hat{H}_2} \xrightarrow{\hat{H}_3} \hat{\sigma}(t_1 + t_2 + t_3)\cdots$$

evolves under $\hat{H}_1$

or $$\hat{\sigma}(0) \xrightarrow{\hat{H}_1(\omega t_1)} \xrightarrow{\hat{H}_2(\omega t_2)} \xrightarrow{\hat{H}_3(\omega t_3)} \hat{\sigma}(t_1 + t_2 + t_3)\cdots$$

rotates round $\hat{H}_1$ for duration $t_1$ (or through an angle $\omega t_1$). Aside: actually rotates around $-\hat{H}_1$

- NMR $\Longrightarrow$ Rotations, Rotations, Rotations!

# Single-Spin Coherence Space

- $\underline{\sigma}$ for a one-spin system can be expressed as:

"vector" in a 4D Liouville space called "coherence space"

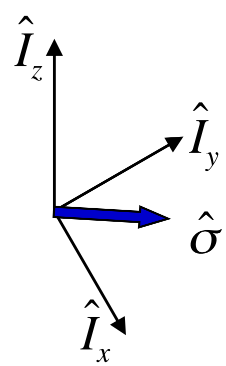
$$\underline{\sigma} = L_1\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + I_1\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} + I_2\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} + L_2\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

In operator form: $\hat{\sigma} = L_1\hat{T}_{11} + I_1\hat{T}_{12} + I_2\hat{T}_{21} + L_2\hat{T}_{22}$ $\Rightarrow$ $\hat{\sigma} \Leftrightarrow \begin{pmatrix} L_1 \\ I_1 \\ I_2 \\ L_2 \end{pmatrix}$

- Alternatively… $\underline{\sigma} = a_1\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + a_2\begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} + a_3\begin{pmatrix} 0 & -\frac{i}{2} \\ \frac{i}{2} & 0 \end{pmatrix} + a_4\begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}$

$\hat{\sigma} = a_1\hat{E} + a_2\hat{I}_x + a_3\hat{I}_y + a_4\hat{I}_z \Rightarrow \{\hat{E}, \hat{I}_x, \hat{I}_y, \hat{I}_z\}$ "product operator" basis set

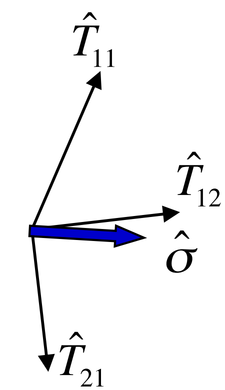
$\hat{\sigma} \Leftrightarrow \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{pmatrix}$ $\Rightarrow$




"vector" expressed in product operator basis

A 3D subspace of coherence space

Alternatively, $\hat{\sigma} \Leftrightarrow \begin{pmatrix} L_1 \\ I_1 \\ I_2 \\ L_2 \end{pmatrix}$ $\Rightarrow$




"vector" expressed in transition operator basis

A 3D subspace of coherence space

# The Master Equation

- Starting with the identity we derived for cyclically commuting operators:

$$e^{i\theta\hat{\hat{A}}}\hat{B} = \hat{B}\cos\theta + i[\hat{A},\hat{B}]\sin\theta \;\Longrightarrow\;$$

Rotation about $\hat{A}$ axis in $\hat{B}\times\left[\hat{A},\hat{B}\right]$ plane

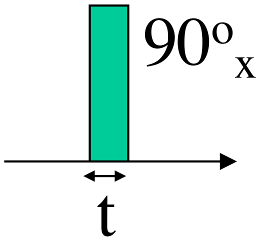
- Noting that $\hat{I}_x$, $\hat{I}_y$, and $\hat{I}_z$ cyclically commute…

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

Then, ignoring relaxation, all possible rotations of $\hat{\sigma}$ during a typical MR experiment can be fully described by the following equation:

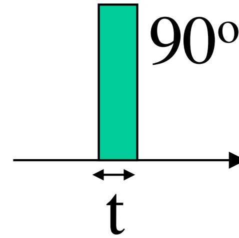
$$\boxed{\hat{I}_p \xrightarrow{\hat{I}_q(\theta)} \begin{cases} \hat{I}_p & \text{if } [\hat{I}_q,\hat{I}_p] = 0 \\ \hat{I}_p\cos\theta - i[\hat{I}_q,\hat{I}_p]\sin\theta & \text{if } [\hat{I}_q,\hat{I}_p] \neq 0 \end{cases}}$$

# RF Excitation




$90^{\mathrm{o}}{}_{\mathrm{x}}$ $\hat{H} \cong -\omega_1 \hat{I}_x$

$\omega_1 t = \pi/2$




$90^{\mathrm{o}}{}_{\mathrm{y}}$ $\hat{H} \cong -\omega_1 \hat{I}_y$

$\omega_1 t = \pi/2$

$$\hat{I}_z \xrightarrow{\left(\pi/2\right)_x} \hat{I}_y$$

Typical notation

notation in van de Ven

$$\hat{I}_z \xrightarrow{\hat{I}_x(\pi/2)} \hat{I}_y$$

$$\hat{I}_x \xrightarrow{\hat{I}_x(\pi/2)} \hat{I}_x$$

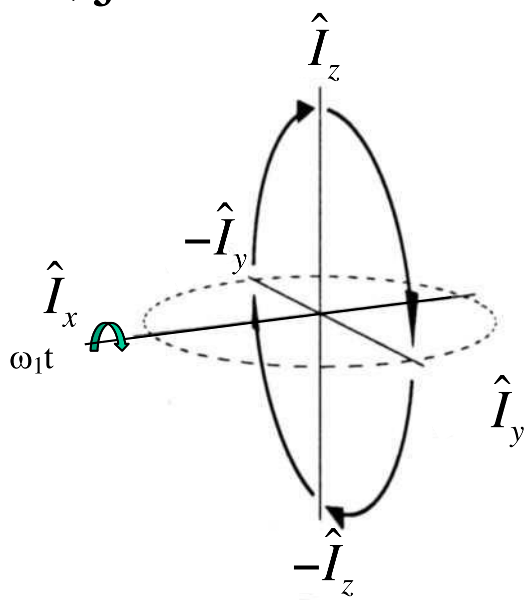
$$\hat{I}_y \xrightarrow{\hat{I}_x(\pi/2)} -\hat{I}_z$$

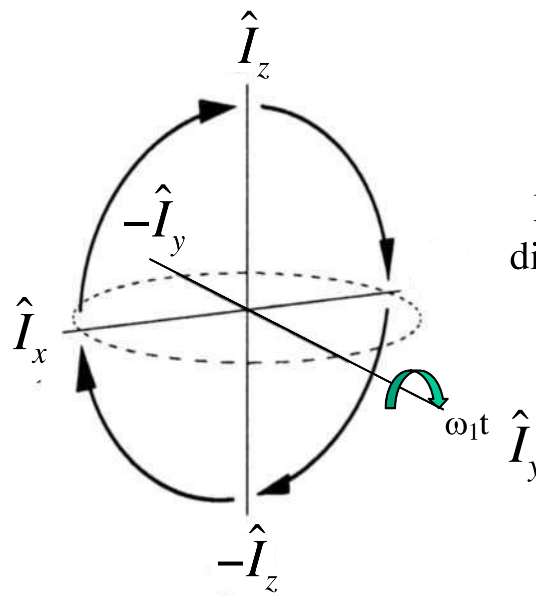
$$\hat{I}_z \xrightarrow{\hat{I}_y(\pi/2)} -\hat{I}_x$$

$$\hat{I}_x \xrightarrow{\hat{I}_y(\pi/2)} \hat{I}_z$$

$$\hat{I}_y \xrightarrow{\hat{I}_y(\pi/2)} \hat{I}_y$$

- In general, just use the master equation:




Note, Sorenson uses a different sign convention ($\omega_0 \equiv -\gamma B_0$).

# Free Precession

- Using the Master Equation and $\hat{H} = -\Omega \hat{I}_z$:

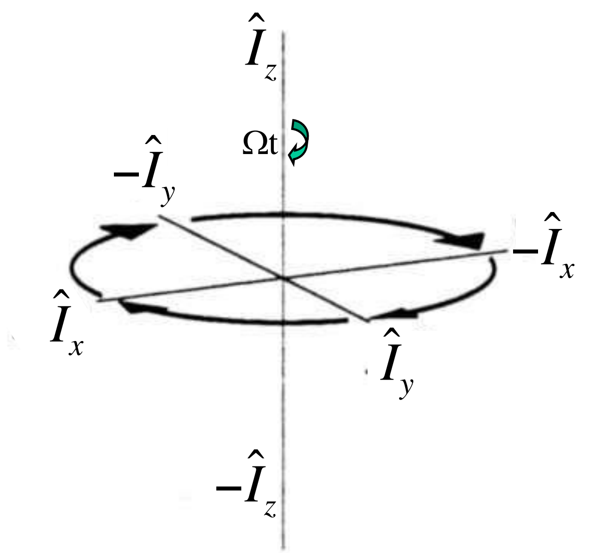
$$\hat{I}_x \xrightarrow{\hat{I}_z(\Omega t)} \hat{I}_x \cos\Omega t - \hat{I}_y \sin\Omega t$$

$$\hat{I}_y \xrightarrow{\hat{I}_z(\Omega t)} \hat{I}_y \cos\Omega t + \hat{I}_x \sin\Omega t$$

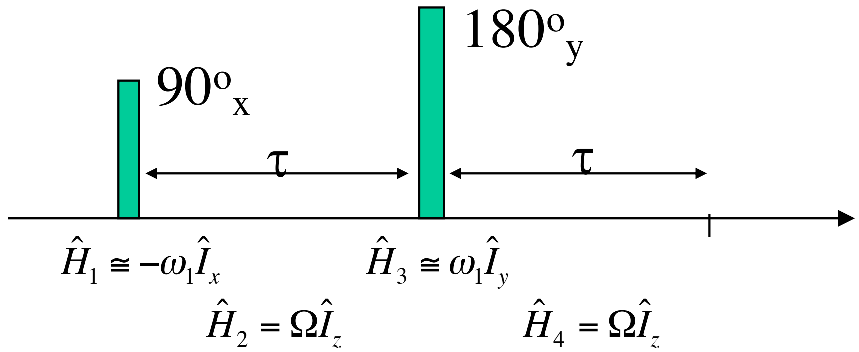
$$\hat{I}_z \xrightarrow{\hat{I}_z(\Omega t)} \hat{I}_z$$

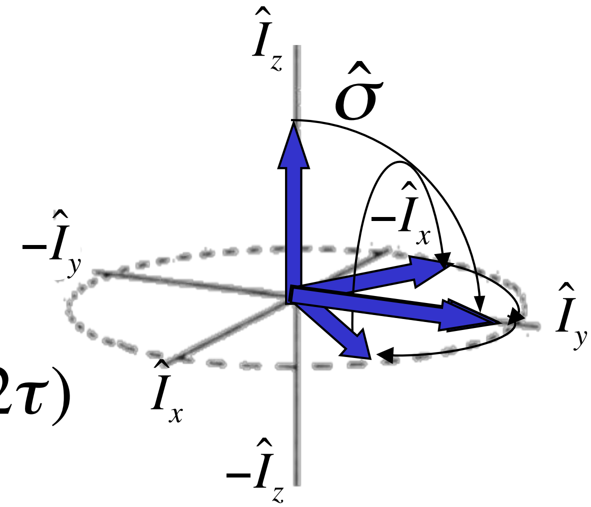
$$\hat{I}_x \xrightarrow{\Omega t} \hat{I}_x \cos\Omega t - \hat{I}_y \sin\Omega t$$

Alternative notation
(axis of rotation not
explicitly given)



# A Spin Echo




$$\hat{\sigma}(0) \xrightarrow{\hat{H}_1} \hat{\sigma}(0^+) \xrightarrow{\hat{H}_2} \hat{\sigma}(\tau) \xrightarrow{\hat{H}_3} \hat{\sigma}(\tau^+) \xrightarrow{\hat{H}_4} \hat{\sigma}(2\tau)$$

$$\hat{I}_z \xrightarrow{\hat{I}_x(\pi/2)} \hat{I}_y$$

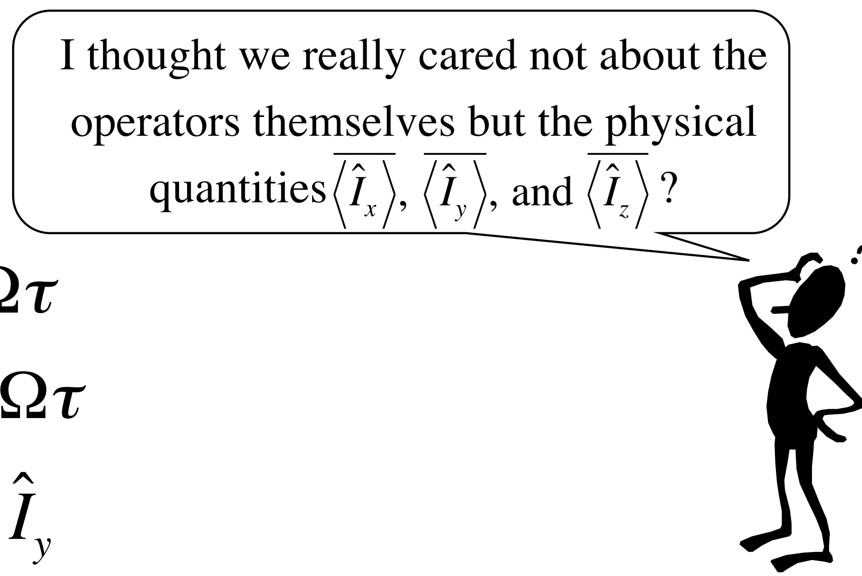
$$\xrightarrow{\hat{I}_z(\Omega\tau)} \hat{I}_y \cos\Omega\tau + \hat{I}_x \sin\Omega\tau$$

$$\xrightarrow{\hat{I}_y(\pi)} \hat{I}_y \cos\Omega\tau - \hat{I}_x \sin\Omega\tau$$

$$\xrightarrow{\hat{I}_z(\Omega\tau)} (\hat{I}_y \cos\Omega\tau + \hat{I}_x \sin\Omega\tau)\cos\Omega\tau$$

$$-(\hat{I}_x \cos\Omega\tau - \hat{I}_y \sin\Omega\tau)\sin\Omega\tau$$

$$= \hat{I}_y \cos^2\Omega\tau + \hat{I}_y \sin^2\Omega\tau = \hat{I}_y$$



# Two-spin Coherence Space

- Product operators form an orthonormal basis in coherence space.

$$\hat{\sigma} = \sum_j \sigma_j \hat{C}_j, \quad \mathrm{Tr}(\hat{C}_j, \hat{C}_k) = \delta_{jk}, \quad \hat{C}_j \in \{\tfrac{1}{2}\hat{E}, \hat{I}_x, \hat{S}_x, \hat{I}_y, \hat{S}_y, \ldots, 2\hat{I}_z\hat{S}_z\}$$

16 terms for a two-spin system

- Remembering that for any physical quantity $C \Rightarrow \overline{\langle \hat{C} \rangle} = \mathrm{Tr}(\hat{\sigma}\hat{C})$

$$\hat{\sigma} = \sum_j \overline{\langle \hat{C}_j \rangle} \hat{C}_j \quad \Longleftrightarrow \quad \begin{pmatrix} 1 \\ \overline{\langle I_x \rangle} \\ \overline{\langle S_x \rangle} \\ \vdots \\ \overline{\langle 2I_zS_z \rangle} \end{pmatrix}$$

Coefficients are the expected values of the corresponding operators!

"vector" in a 16-D coherence (Liouville) space

- MR is all about rotations of $\hat{\sigma}$ in coherence space.
- Given that coherence space is 16-D for a 2-spin system, life can get pretty complicated (not to mention higher-order spin systems).
- Fortunately, we'll only need to deal with sequential rotations in 3-D subspaces.

# The Master Equation, revisited

- Once again, we start with our favorite relation for cyclically commuting operators:

$$e^{i\theta \hat{\hat{A}}}\hat{B} = \hat{B}\cos\theta + i[\hat{A},\hat{B}]\sin\theta$$

- Examination of the Appendix listing two-spin product operator commutators (see end of lecture) reveals that the commutators for *all* two-spin product operators are cyclical!

$$i.e.\text{ in superoperator notation: } \hat{\hat{A}}\hat{\hat{A}}\hat{B} = \hat{B}$$

- Hence, ignoring relaxation, all possible rotations of $\hat{\sigma}$ can be fully described by the following equation:

$$\boxed{\begin{array}{l} \hat{C}_p \xrightarrow{\hat{C}_q(\theta)} \begin{cases} \hat{C}_p & \text{if } [\hat{C}_q,\hat{C}_p] = 0 \\ \hat{C}_p\cos\theta - i[\hat{C}_q,\hat{C}_p]\sin\theta & \text{if } [\hat{C}_q,\hat{C}_p] \neq 0 \end{cases} \\ \text{where } \hat{C}_p \text{ and } \hat{C}_q \text{ are any pair of product operators.} \end{array}}$$

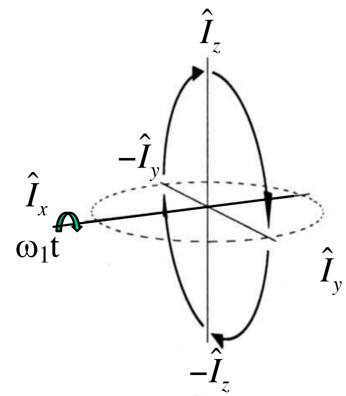
# The 3 Basic Rotations: RF Excitation

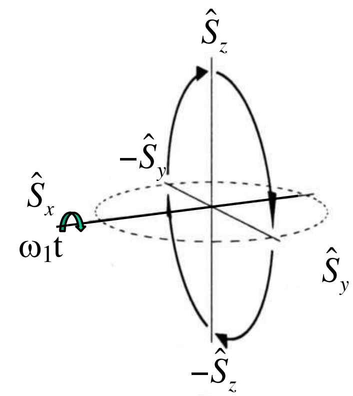
- Rotation axes the same as before for both the *I* and *S* spins.

  For an *x* pulse: $\hat{H} = -\omega_1^I \hat{I}_x - \omega_1^S \hat{S}_x$

  rotation axes

  (note $[\hat{I}_x, \hat{S}_x] = 0$)



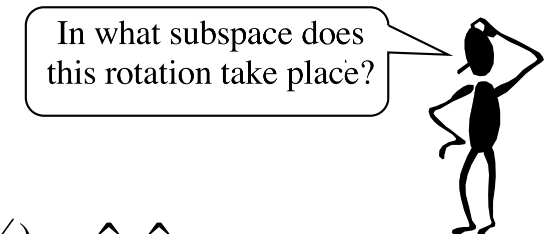

- Examples

$$\hat{I}_z \xrightarrow{\hat{I}_x(\pi/2)} \hat{I}_y$$

$$\hat{S}_z \xrightarrow{\hat{S}_x(\pi)} -\hat{S}_z$$

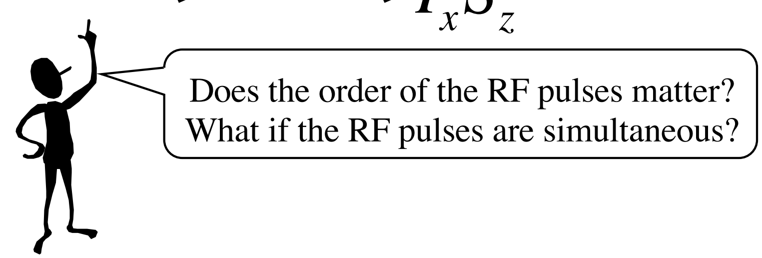
$$\hat{I}_z \xrightarrow{\hat{S}_x(\pi/2)} \hat{I}_z$$

$$\hat{I}_z\hat{S}_z \xrightarrow{\hat{S}_x(\pi/2)} \hat{I}_z\hat{S}_y$$




$$\hat{I}_x\hat{S}_z \xrightarrow{\hat{S}_x(\pi/2)} \xrightarrow{\hat{I}_y(\pi/2)} \hat{I}_z\hat{S}_y$$

$$\hat{I}_x\hat{S}_z \xrightarrow{\hat{I}_y(\pi)} \xrightarrow{\hat{S}_y(\pi)} \hat{I}_x\hat{S}_z$$



# The 3 Basic Rotations: Chemical Shift

- $\hat{H} = -\Omega_I \hat{I}_z - \Omega_S \hat{S}_z + 2\pi J \hat{I}_z \hat{S}_z$

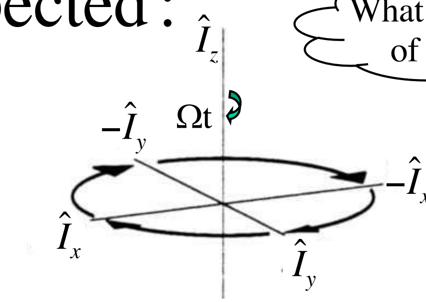
  rotation axes

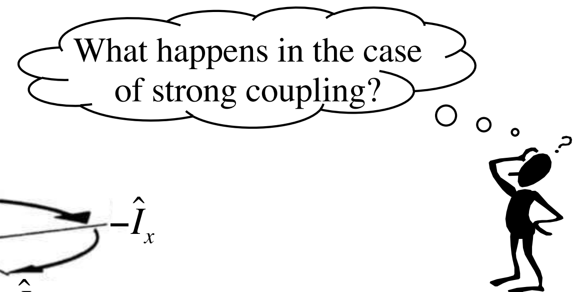
Note: $[\hat{I}_z, \hat{S}_z] = 0 \quad [\hat{I}_z, \hat{I}_z \hat{S}_z] = 0 \quad [\hat{S}_z, \hat{I}_z \hat{S}_z] = 0$

…hence, rotations can be treated independently.

if $[\hat{A}, \hat{B}] = 0$ then $e^{\hat{A}+\hat{B}} = e^{\hat{A}} e^{\hat{B}} = e^{\hat{B}} e^{\hat{A}}$

- $\{\hat{I}_x, \hat{I}_y, \hat{I}_z\}$ and $\{\hat{S}_x, \hat{S}_y, \hat{S}_z\}$ behave as expected:




$$\hat{I}_x \xrightarrow{\hat{I}_z(\Omega_I t)} \hat{I}_x \cos\Omega_I t - \hat{I}_y \sin\Omega_I t$$

$$\hat{S}_x \xrightarrow{\hat{S}_z(\Omega_S t)} \hat{S}_x \cos\Omega_S t - \hat{S}_y \sin\Omega_S t$$

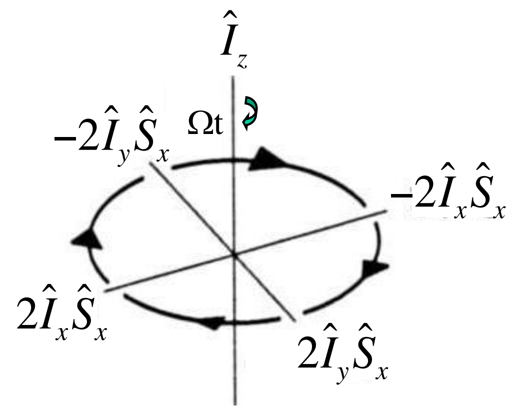
- Product operators, such as $\hat{I}_x \hat{S}_x$, behave similarly.

  For example, under $\hat{H} = -\Omega_I \hat{I}_z$, $\hat{I}_x \hat{S}_p$ rotates in the $\hat{I}_x \hat{S}_p$, $\hat{I}_y \hat{S}_p$ plane where $p$ is $x$, $y$, or $z$.

$$\hat{I}_x \hat{S}_x \xrightarrow{\hat{I}_z(\Omega_I t)} \hat{I}_x \hat{S}_x \cos\Omega_I t - \hat{I}_y \hat{S}_x \sin\Omega_I t$$

$$\hat{I}_x \hat{S}_x \xrightarrow{\hat{S}_z(\Omega_S t)} \hat{I}_x \hat{S}_x \cos\Omega_S t - \hat{I}_x \hat{S}_y \sin\Omega_S t$$

$$\hat{I}_x \hat{S}_x \xrightarrow{\hat{I}_z(\Omega_I t)} \xrightarrow{\hat{S}_z(\Omega_S t)} ?$$



# The Three Basic Rotations: J coupling

- $\hat{H} = -\Omega_I \hat{I}_z - \Omega_S \hat{S}_z + 2\pi J \hat{I}_z \hat{S}_z$

rotation axis

$[\hat{I}_z, \hat{S}_z] = 0 \quad [\hat{I}_z, \hat{I}_z \hat{S}_z] = 0 \quad [\hat{S}_z, \hat{I}_z \hat{S}_z] = 0$

…hence, rotations can be treated independently.

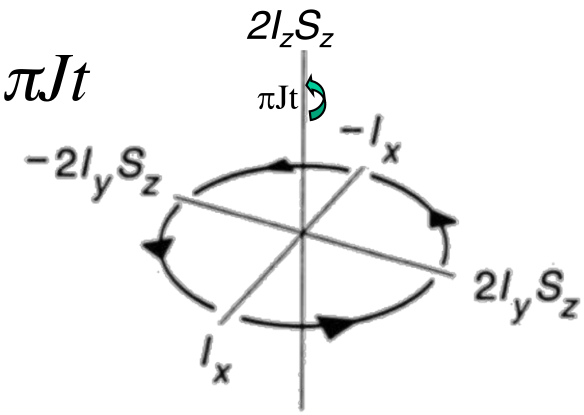
- Using the Master Equation:

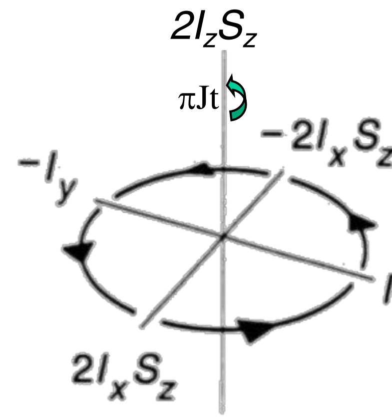
$$\hat{I}_x \xrightarrow{2\hat{I}_z \hat{S}_z (\pi J t)} \hat{I}_x \cos \pi J t + 2\hat{I}_y \hat{S}_z \sin \pi J t$$

$$\hat{I}_y \xrightarrow{2\hat{I}_z \hat{S}_z (\pi J t)} \hat{I}_y \cos \pi J t - 2\hat{I}_x \hat{S}_z \sin \pi J t$$

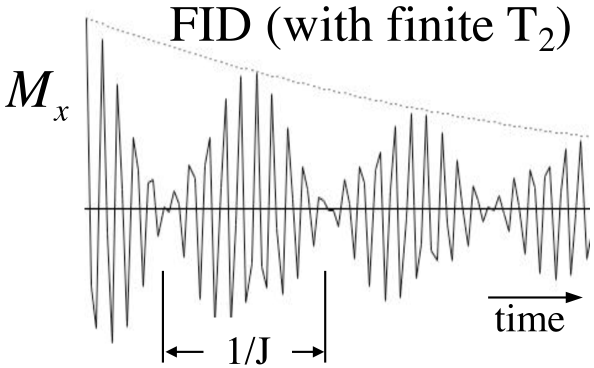
Alternative notation (axis of rotation not explicitly given)

$$\hat{I}_x \xrightarrow{\pi J t} \hat{I}_x \cos \pi J t + 2\hat{I}_y \hat{S}_z \sin \pi J t$$




FID (with finite $T_2$)



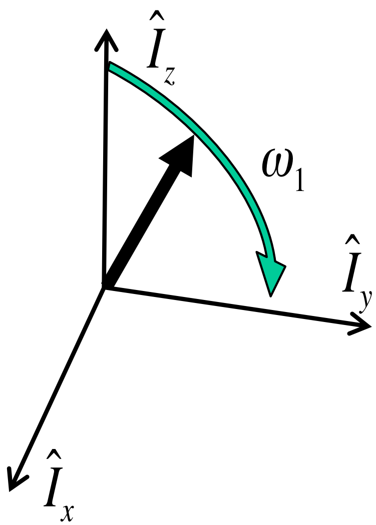

Under J-coupling, transverse magnetization oscillates between in-phase/anti-phase coherences (plot shown with chemical shift $\Omega_I$)

Much easier than direct matrix computations

# Sign Conventions

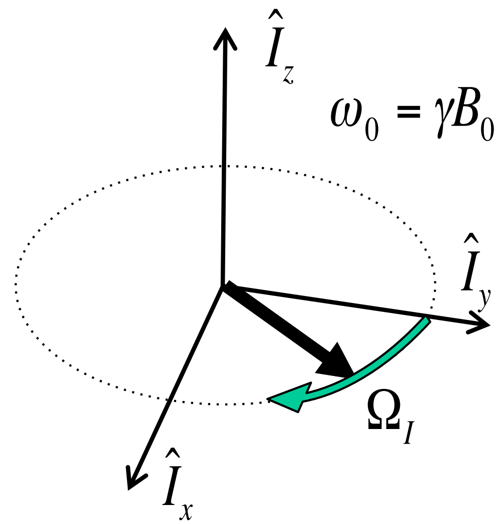
Given: $\hat{\sigma}(t) = e^{-i\hat{H}t}\hat{\sigma}(0)$ and $\hat{H} = -\Omega_I \hat{I}_z - \Omega_S \hat{S}_z + 2\pi J \hat{I}_z \hat{S}_z$

RF excitation



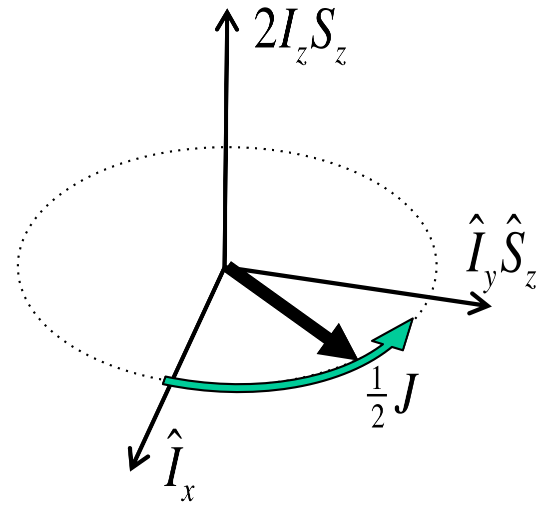

Left-handed rotation

Chemical shift




Left-handed rotation

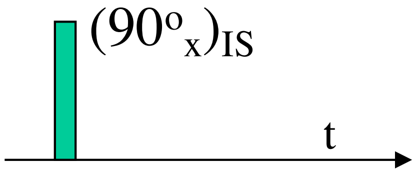
J coupling




Right-handed rotation

(or left-handed rotation with frequency –J/2)

# Example 1: 90-acquire




$$\hat{\sigma}(0) \xrightarrow{\hat{H}_1} \xrightarrow{\hat{H}_2} \hat{\sigma}(t)$$

$$\hat{\sigma}(0) \xrightarrow{\hat{I}_x(\pi/2)} \xrightarrow{\hat{S}_x(\pi/2)} \xrightarrow{\hat{I}_z(\Omega_I t)} \xrightarrow{\hat{S}_z(\Omega_S t)} \xrightarrow{2\hat{I}_z\hat{S}_z(\pi J t)} \hat{\sigma}(t)$$

- Starting with the *I* spin…

$$\hat{I}_z \xrightarrow{\hat{I}_x(\pi/2)} \hat{I}_y \xrightarrow{\hat{S}_x(\pi/2)} \hat{I}_y \xrightarrow{\hat{I}_z(\Omega t)} \hat{I}_y \cos\Omega_I t + \hat{I}_x \sin\Omega_I t \xrightarrow{\hat{S}_z(\Omega t)} \hat{I}_y \cos\Omega_I t + \hat{I}_x \sin\Omega_I t$$

$$\xrightarrow{2\hat{I}_z\hat{S}_z(\pi J t)} (\hat{I}_y \cos\Omega_I t + \hat{I}_x \sin\Omega_I t)\cos\pi J t + \left(2\hat{I}_y\hat{S}_z \sin\Omega_I t - 2\hat{I}_x\hat{S}_z \cos\Omega_I t\right)\sin\pi J t$$

"in-phase coherence" "observable" — "anti-phase coherence" "unobservable"

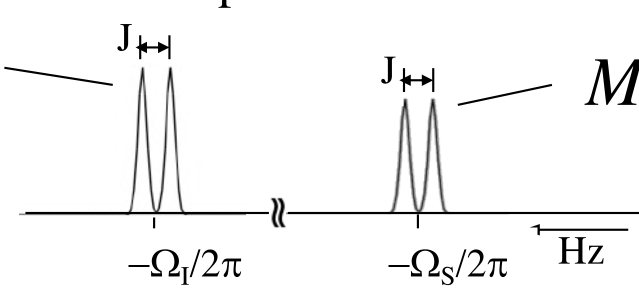
- Similarly for the *S* spin…

$$\xrightarrow{\hat{H}_1} \xrightarrow{\hat{H}_2} (\hat{S}_y \cos\Omega_S t - \hat{S}_x \sin\Omega_S t)\cos\pi J t + (2\hat{I}_z\hat{S}_y \sin\Omega_S t - 2\hat{I}_z\hat{S}_x \cos\Omega_S t)\sin\pi J t$$

- With all the constants, the recorded spectrum would look like:

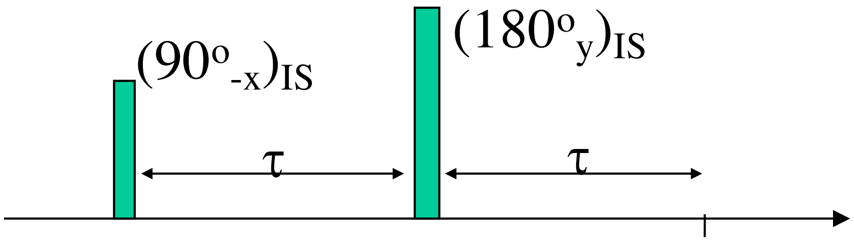
Spectrum

$$M_y^I = \gamma_I^2 \frac{\rho\hbar^2 B_0}{8kT}$$




$$M_y^S = \gamma_S^2 \frac{\rho\hbar^2 B_0}{8kT}$$

# Example 2: Spin Echo




- Continuing from Example 1, the *I* spin term prior to the 180 is:

$$(\hat{I}_y \cos\Omega_I\tau + \hat{I}_x \sin\Omega_I\tau)\cos\pi J\tau + (2\hat{I}_y\hat{S}_z \sin\Omega_I\tau - 2\hat{I}_x\hat{S}_z \cos\Omega_I\tau)\sin\pi J\tau$$

$$\xrightarrow{\hat{I}_y(\pi)} (\hat{I}_y \cos\Omega_I\tau - \hat{I}_x \sin\Omega_I\tau)\cos\pi J\tau + (2\hat{I}_y\hat{S}_z \sin\Omega_I\tau + 2\hat{I}_x\hat{S}_z \cos\Omega_I\tau)\sin\pi J\tau$$

$$\xrightarrow{\hat{I}_z(\Omega\tau)} \xrightarrow{2\hat{I}_z\hat{S}_z(\pi J\tau)} \text{some algebra} \longrightarrow \hat{I}_y \cos 2\pi J\tau - 2\hat{I}_x\hat{S}_z \sin 2\pi J\tau$$

The *S* spin term yields an analogous equation.

We' ll clean this up next lecture.

  – Chemical shift is refocused.
  – J-coupling continues to evolve over the entire 2τ time period.

# Summary

- The three basic rotations define a set of algebraic rules for product operators (weakly coupled spin 1/2 systems).
  - Step 1: Write down the Hamiltonian

    RF excitation: $\hat{H} = -\omega_1^I \hat{I}_x - \omega_1^S \hat{S}_x$ ($x$ pulse)

    Free precession: $\hat{H} = -\Omega_I \hat{I}_z - \Omega_S \hat{S}_z + 2\pi J \hat{I}_z \hat{S}_z$
  - Step 2: Compute the product operator rotations.

- If you want, you can now forget all about quantum mechanics, kets, bras, operators, etc…and just systematically following these algebraic rules to find out what happens in any number of MR pulse sequences. Then use the orthogonal expansion property of $\hat{\sigma}$ to write down $M_x$, $M_y$, and $M_z$.

# Next Lecture: Product Operator Formalism II

# Appendix
## 2-spin Product Operator Commutators

| | $\hat{I}_x$ | $\hat{I}_y$ | $\hat{I}_z$ | $\hat{S}_x$ | $\hat{S}_y$ | $\hat{S}_z$ | $2\hat{I}_x\hat{S}_x$ | $2\hat{I}_x\hat{S}_y$ | $2\hat{I}_x\hat{S}_z$ | $2\hat{I}_y\hat{S}_x$ | $2\hat{I}_y\hat{S}_y$ | $2\hat{I}_y\hat{S}_z$ | $2\hat{I}_z\hat{S}_x$ | $2\hat{I}_z\hat{S}_y$ | $2\hat{I}_z\hat{S}_z$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\hat{I}_x$ | $0$ | $i\hat{I}_z$ | $-i\hat{I}_y$ | $0$ | $0$ | $0$ | $0$ | $0$ | $0$ | $i2\hat{I}_z\hat{S}_x$ | $i2\hat{I}_z\hat{S}_y$ | $i2\hat{I}_z\hat{S}_z$ | $-i2\hat{I}_y\hat{S}_x$ | $-i2\hat{I}_y\hat{S}_y$ | $-i2\hat{I}_y\hat{S}_z$ |
| $\hat{I}_y$ | $-i\hat{I}_z$ | $0$ | $i\hat{I}_x$ | $0$ | $0$ | $0$ | $-i2\hat{I}_z\hat{S}_x$ | $-i2\hat{I}_z\hat{S}_y$ | $-i2\hat{I}_z\hat{S}_z$ | $0$ | $0$ | $0$ | $i2\hat{I}_x\hat{S}_x$ | $i2\hat{I}_x\hat{S}_y$ | $i2\hat{I}_x\hat{S}_z$ |
| $\hat{I}_z$ | $i\hat{I}_y$ | $-i\hat{I}_x$ | $0$ | $0$ | $0$ | $0$ | $i2\hat{I}_y\hat{S}_x$ | $i2\hat{I}_y\hat{S}_y$ | $i2\hat{I}_y\hat{S}_z$ | $-i2\hat{I}_x\hat{S}_x$ | $-i2\hat{I}_x\hat{S}_y$ | $-i2\hat{I}_x\hat{S}_z$ | $0$ | $0$ | $0$ |
| $\hat{S}_x$ | $0$ | $0$ | $0$ | $0$ | $i\hat{S}_z$ | $-i\hat{S}_y$ | $0$ | $i2\hat{I}_x\hat{S}_z$ | $-i2\hat{I}_x\hat{S}_y$ | $0$ | $i2\hat{I}_y\hat{S}_z$ | $-i2\hat{I}_y\hat{S}_y$ | $0$ | $i2\hat{I}_z\hat{S}_z$ | $-i2\hat{I}_z\hat{S}_y$ |
| $\hat{S}_y$ | $0$ | $0$ | $0$ | $-i\hat{S}_z$ | $0$ | $i\hat{S}_x$ | $-i2\hat{I}_x\hat{S}_z$ | $0$ | $i2\hat{I}_x\hat{S}_x$ | $-i2\hat{I}_y\hat{S}_z$ | $0$ | $i2\hat{I}_y\hat{S}_x$ | $-i2\hat{I}_z\hat{S}_z$ | $0$ | $i2\hat{I}_z\hat{S}_x$ |
| $\hat{S}_z$ | $0$ | $0$ | $0$ | $i\hat{S}_y$ | $-i\hat{S}_x$ | $0$ | $i2\hat{I}_x\hat{S}_y$ | $-i2\hat{I}_x\hat{S}_x$ | $0$ | $i2\hat{I}_y\hat{S}_y$ | $-i2\hat{I}_y\hat{S}_x$ | $0$ | $i2\hat{I}_z\hat{S}_y$ | $-i2\hat{I}_z\hat{S}_x$ | $0$ |
| $2\hat{I}_x\hat{S}_x$ | $0$ | $i2\hat{I}_z\hat{S}_x$ | $-i2\hat{I}_y\hat{S}_x$ | $0$ | $i2\hat{I}_x\hat{S}_z$ | $-i2\hat{I}_x\hat{S}_y$ | $0$ | $i\hat{S}_z$ | $-i\hat{S}_y$ | $i\hat{I}_z$ | $0$ | $0$ | $-i\hat{I}_y$ | $0$ | $0$ |
| $2\hat{I}_x\hat{S}_y$ | $0$ | $i2\hat{I}_z\hat{S}_y$ | $-i2\hat{I}_y\hat{S}_y$ | $-i2\hat{I}_x\hat{S}_z$ | $0$ | $i2\hat{I}_x\hat{S}_x$ | $-i\hat{S}_z$ | $0$ | $i\hat{S}_x$ | $0$ | $i\hat{I}_z$ | $0$ | $0$ | $-i\hat{I}_y$ | $0$ |
| $2\hat{I}_x\hat{S}_z$ | $0$ | $i2\hat{I}_z\hat{S}_z$ | $-i2\hat{I}_y\hat{S}_z$ | $i2\hat{I}_x\hat{S}_y$ | $-i2\hat{I}_x\hat{S}_x$ | $0$ | $i\hat{S}_y$ | $-i\hat{S}_x$ | $0$ | $0$ | $0$ | $i\hat{I}_z$ | $0$ | $0$ | $-i\hat{I}_y$ |
| $2\hat{I}_y\hat{S}_x$ | $-i2\hat{I}_z\hat{S}_x$ | $0$ | $i2\hat{I}_x\hat{S}_x$ | $0$ | $i2\hat{I}_y\hat{S}_z$ | $-i2\hat{I}_y\hat{S}_y$ | $-i\hat{I}_z$ | $0$ | $0$ | $0$ | $i\hat{S}_z$ | $-i\hat{S}_y$ | $i\hat{I}_x$ | $0$ | $0$ |
| $2\hat{I}_y\hat{S}_y$ | $-i2\hat{I}_z\hat{S}_y$ | $0$ | $i2\hat{I}_x\hat{S}_y$ | $-i2\hat{I}_y\hat{S}_z$ | $0$ | $i2\hat{I}_y\hat{S}_x$ | $0$ | $-i\hat{I}_z$ | $0$ | $-i\hat{S}_z$ | $0$ | $i\hat{S}_x$ | $0$ | $i\hat{I}_x$ | $0$ |
| $2\hat{I}_y\hat{S}_z$ | $-i2\hat{I}_z\hat{S}_z$ | $0$ | $i2\hat{I}_x\hat{S}_z$ | $i2\hat{I}_y\hat{S}_y$ | $-i2\hat{I}_y\hat{S}_x$ | $0$ | $0$ | $0$ | $-i\hat{I}_z$ | $i\hat{S}_y$ | $-i\hat{S}_x$ | $0$ | $0$ | $0$ | $i\hat{I}_x$ |
| $2\hat{I}_z\hat{S}_x$ | $i2\hat{I}_y\hat{S}_x$ | $-i2\hat{I}_x\hat{S}_x$ | $0$ | $0$ | $i2\hat{I}_z\hat{S}_z$ | $-i2\hat{I}_z\hat{S}_y$ | $i\hat{I}_y$ | $0$ | $0$ | $-i\hat{I}_x$ | $0$ | $0$ | $0$ | $i\hat{S}_z$ | $-i\hat{S}_y$ |
| $2\hat{I}_z\hat{S}_y$ | $i2\hat{I}_y\hat{S}_y$ | $-i2\hat{I}_x\hat{S}_y$ | $0$ | $-i2\hat{I}_z\hat{S}z$ | $0$ | $i2\hat{I}_z\hat{S}_x$ | $0$ | $i\hat{I}_y$ | $0$ | $0$ | $-i\hat{I}_x$ | $0$ | $-i\hat{S}_z$ | $0$ | $i\hat{S}_x$ |
| $2\hat{I}_z\hat{S}_z$ | $i2\hat{I}_y\hat{S}_z$ | $-i2\hat{I}_x\hat{S}_z$ | $0$ | $i2\hat{I}_z\hat{S}_y$ | $-i2\hat{I}_z\hat{S}_x$ | $0$ | $0$ | $0$ | $i\hat{I}_y$ | $0$ | $0$ | $-i\hat{I}_x$ | $i\hat{S}_y$ | $-i\hat{S}_x$ | $0$ |