

Lecture #9

Density Operator, Populations, and Coherences

- Topics
 - Single-spin systems
 - Coupled two-spin systems
 - Examples
- Handouts and Reading assignments
 - Levitt, Chapters 10 (optional)

Recap

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

- Time evolution of $\hat{\sigma}(t)$: $\frac{\partial}{\partial t} \hat{\sigma} = -i[\hat{H}, \hat{\sigma}] = -i\hat{H}\hat{\sigma}$
\
Hamiltonian

- If \hat{H} time independent: $\hat{\sigma}(t) = \underbrace{e^{-i\hat{H}t} \hat{\sigma}(0) e^{i\hat{H}t}}_{\text{This lecture we'll focus of this formulation which is typically used for mathematical simulations.}} = \underbrace{e^{-i\hat{H}t} \hat{\sigma}(0)}_{\text{Rotation in operator space (next lecture)}}$

This lecture we'll focus of this formulation which is typically used for mathematical simulations. Rotation in operator space (next lecture)

- Including B_0 , chemical shift, J-coupling, and RF excitation...

$$\hat{H} = -\Omega_I \hat{I}_z - \Omega_S \hat{S}_z + 2\pi J(\hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y + \hat{I}_z \hat{S}_z) - \omega_1^I \hat{I}_x - \omega_1^S \hat{S}_x$$

$\hat{\sigma}$: Single-Spin System

- At thermal equilibrium:

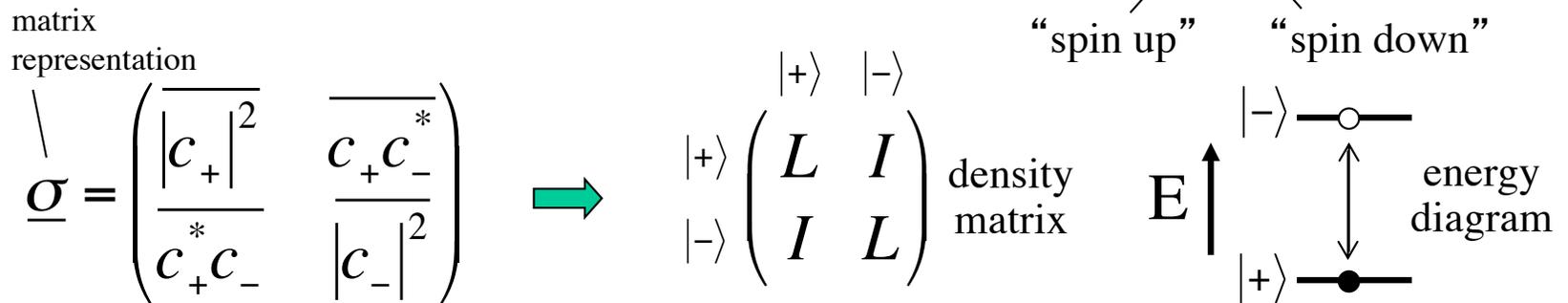
Can you prove $\hat{\sigma}(t) = \hat{\sigma}_0$?



$$\hat{H}_0 = -\omega_0 \hat{I}_z \quad \text{and} \quad \hat{\sigma}_0 = \frac{1}{2} \hat{E} + \frac{\hbar\gamma B_0}{4kT} \hat{I}_z \quad (|\varphi\rangle = c_+|+\rangle + c_-|-\rangle)$$

(high temp approx)

- Most convenient basis set is the eigenkets of \hat{H}_0 : $\{|+\rangle, |-\rangle\}$



L - “longitudinal magnetization”

- “spin population” or “single-spin order”

I - “transverse magnetization”

- zero unless phase coherence between states $|+\rangle$ and $|-\rangle$
- “coherent superposition of quantum states” or “coherence”

$\hat{\sigma}$: Single-Spin System

- $\underline{\sigma}$ could be expressed as:

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

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

\hat{T}_{ij} : orthonormal basis set called “transition operators”
(Anyone remember Problem Set 2?)

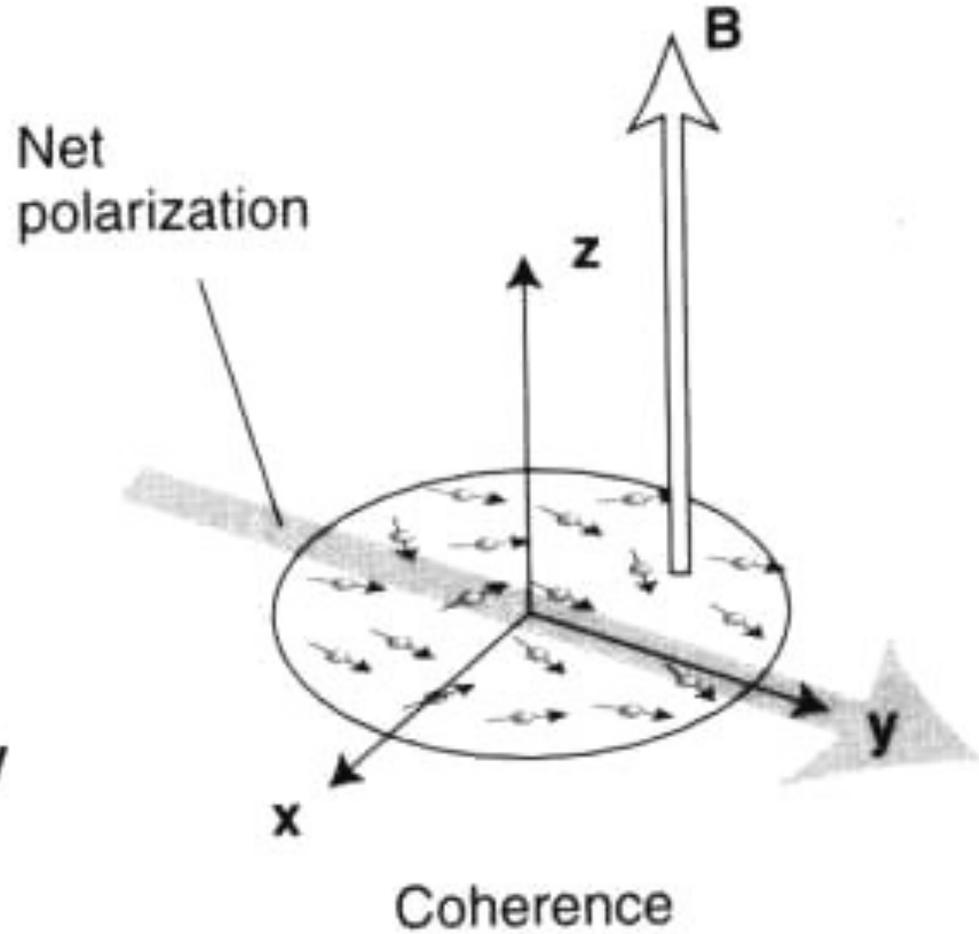
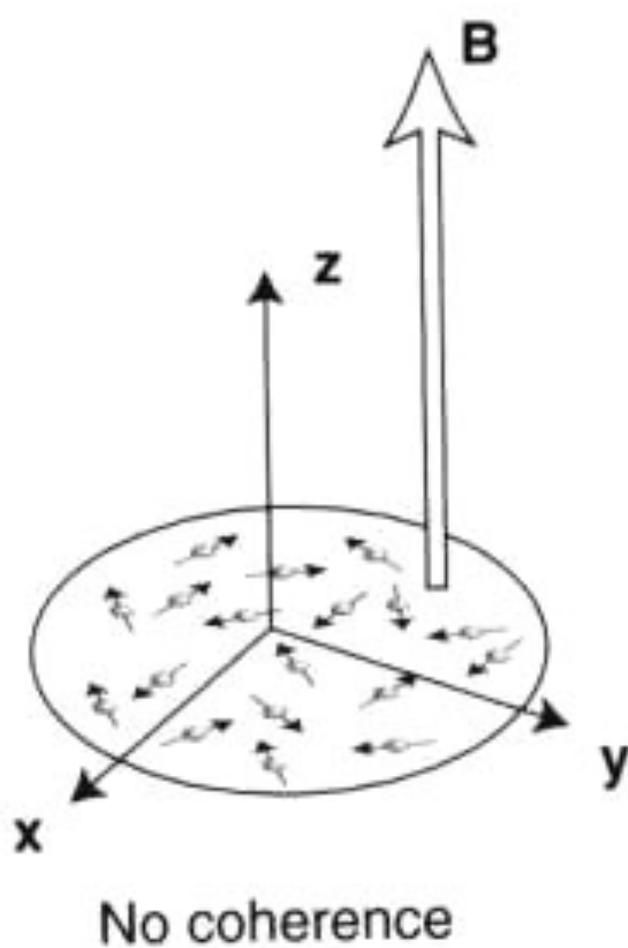
Much of the analysis in Levitt is done in this basis set

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

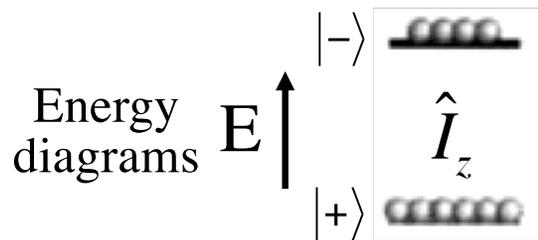
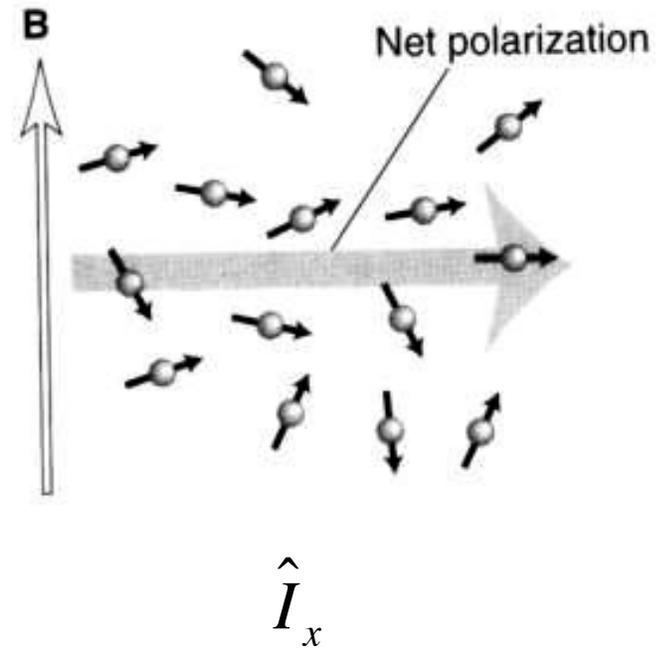
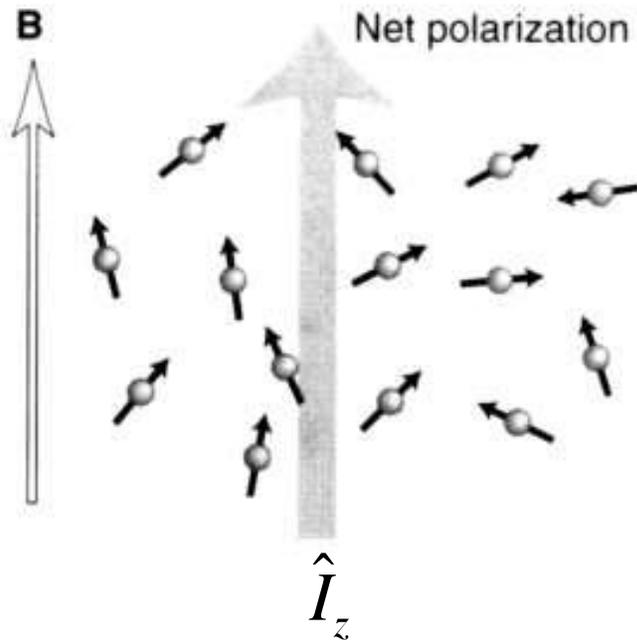
$$\hat{\sigma} = a_1 \hat{E} + a_2 \hat{I}_x + a_3 \hat{I}_y + a_4 \hat{I}_z \rightarrow \{ \hat{E}, \hat{I}_x, \hat{I}_y, \hat{I}_z \} \text{ “product operator” basis set}$$

Phase Coherence

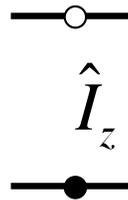
Coherent superposition of quantum states



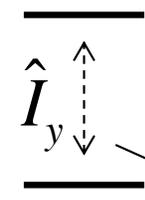
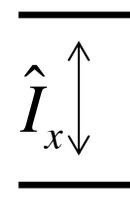
Pictorial Representations



or



○ = population deficit
● = population excess



90° phase shift wrt I_x

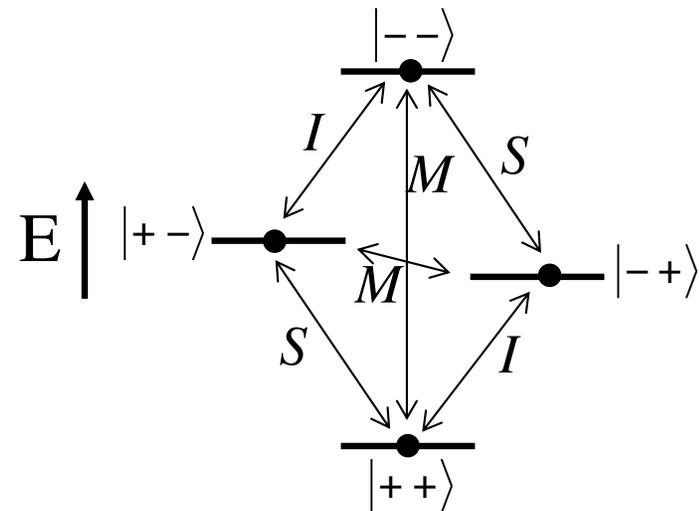
$\hat{\sigma}$: Coupled Two-Spin System

- Eigenkets of \hat{H}_0 : $\{|++\rangle, |+-\rangle, |-+\rangle, |--\rangle\}$

Density Matrix

$$\underline{\sigma} \longrightarrow \begin{matrix} & |++\rangle & |+-\rangle & |-+\rangle & |--\rangle \\ \begin{matrix} |++\rangle \\ |+-\rangle \\ |-+\rangle \\ |--\rangle \end{matrix} & \begin{pmatrix} L & S & I & M \\ S & L & M & I \\ I & M & L & S \\ M & I & S & L \end{pmatrix} \end{matrix}$$

Energy Diagram



Four subspaces:

L - Longitudinal populations

S - Transverse *S* coherences

I - Transverse *I* coherences

M - Multiple quantum (double and zero) coherences

Product Operators

- As with the single-spin case, the product operators form the most convenient basis set.
- For a two spin-system, there are 16 product operators.

- Familiar terms:

$$\frac{1}{2} \hat{E}, \hat{I}_x, \hat{I}_y, \hat{I}_z, \hat{S}_x, \hat{S}_y, \hat{S}_z \quad \text{In-phase single quantum coherences}$$

- Unfamiliar terms:

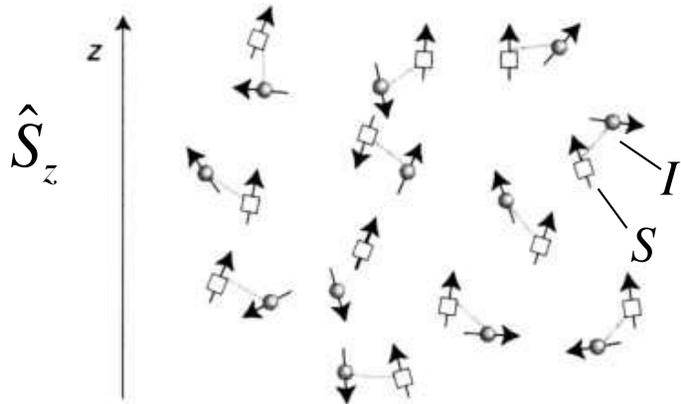
$$2\hat{I}_x\hat{S}_z, 2\hat{I}_y\hat{S}_z, 2\hat{I}_z\hat{S}_x, 2\hat{I}_z\hat{S}_y \quad \text{Anti-phase single quantum coherences}$$

$$2\hat{I}_z\hat{S}_z \quad \text{Longitudinal two-spin order}$$

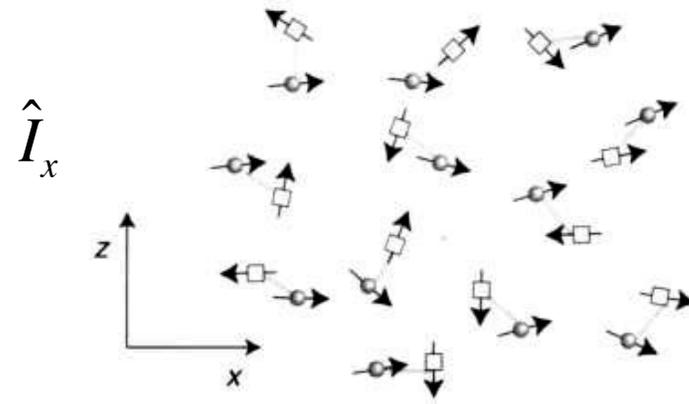
$$2\hat{I}_x\hat{S}_x, 2\hat{I}_y\hat{S}_y, 2\hat{I}_x\hat{S}_y, 2\hat{I}_y\hat{S}_x \quad \text{Linear combinations of double and zero quantum coherences}$$

Product Operators

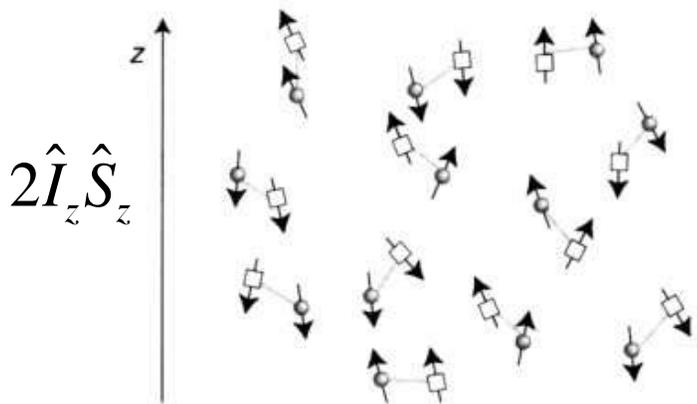
Pictorial Examples (note, we are now considering *pairs* of spins):



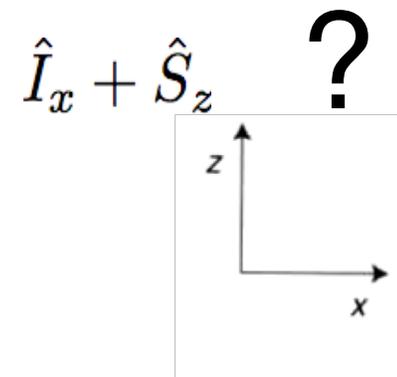
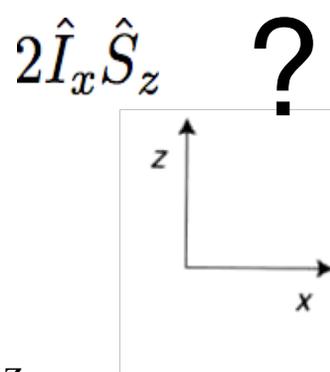
Net tendency for S spins to be +z
No net tendency for I spins in any direction



No net tendency for S spins in any direction
Net tendency for I spins to be +x

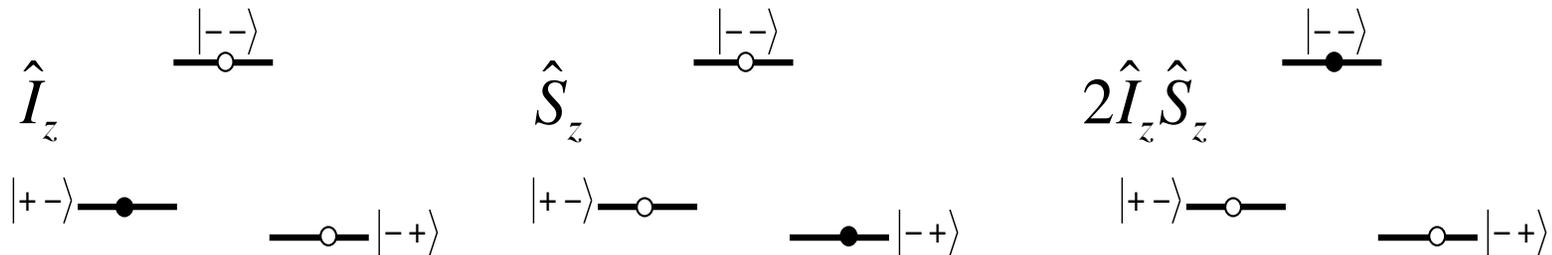


No net tendency for I or S spins to be $\pm z$
If I or S is $\pm z$, increased probability paired spin is $\pm z$

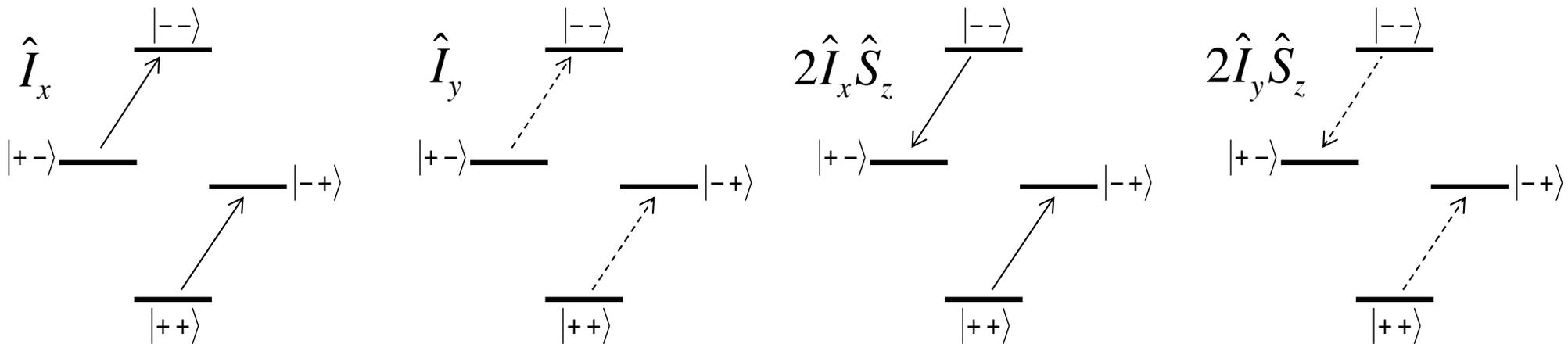
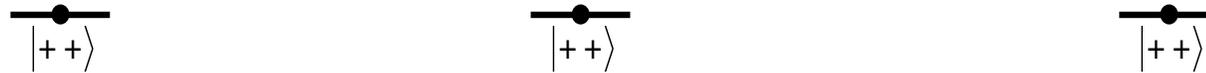


Product Operators

- Some energy diagram representations



● Population excess
○ Population deficit



Product Operators: Matrix Representations*

- One-spin system: $|\psi\rangle = c_+ e^{i\phi_+} |+\rangle + c_- e^{i\phi_-} |-\rangle \Rightarrow \sigma_{nm}(0) = \overline{c_n c_m} e^{-i(\phi_n - \phi_m)}$

$$\underline{I}_x = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \underline{I}_y = \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \underline{I}_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

What's the basis set for these matrices?



- Two-spin system: $|\psi\rangle = a_{++} |++\rangle + a_{+-} |+-\rangle + a_{-+} |-+\rangle + a_{--} |--\rangle$

(a_i s complex)

What is \underline{I}_x ? (Hint: must be 4 x 4)

$$\underline{I}_x = \underbrace{\frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}}_{\text{single-spin } \underline{I}_x} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1/2 & 0 \\ 0 & 0 & 0 & 1/2 \\ 1/2 & 0 & 0 & 0 \\ 0 & 1/2 & 0 & 0 \end{pmatrix}$$

direct product

An example product operator:

$$\underline{2I}_x \underline{S}_x = \begin{pmatrix} 0 & 0 & 0 & 1/2 \\ 0 & 0 & 1/2 & 0 \\ 0 & 1/2 & 0 & 0 \\ 1/2 & 0 & 0 & 0 \end{pmatrix}$$

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

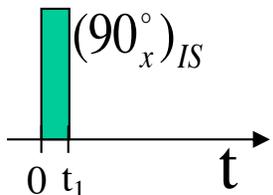
How many operators are needed to span Liouville space for a 2-spin system?



*Matrix representations of all 2-spin product operators in Appendix at end of this lecture

Density Matrix Calculations:

Example: a 2-spin System

Consider the following homonuclear experiment ($\gamma_I = \gamma_S = \gamma$): 

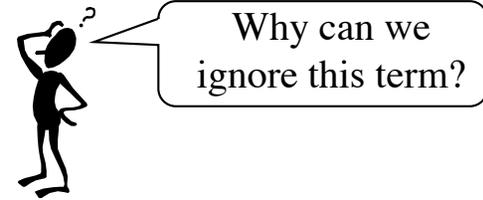
- $t < 0$

from Boltzmann distribution: $\underline{\sigma} = \frac{\hbar B_0 \gamma}{4kT} \overbrace{(\underline{I}_z + \underline{S}_z)}^{\text{total z angular momentum}}$ (ignoring \hat{E} term)

- $0 < t < t_1$

- Step 1: find $\underline{H} \rightarrow \underline{H} \approx -\omega_1(\underline{I}_x + \underline{S}_x)$

- Step 2: compute $\underline{\sigma}(t_1) = e^{-i\underline{H}t_1} \underline{\sigma}(0) e^{i\underline{H}t_1}$ for $\omega_1 t_1 = \pi/2$



$$\underline{\sigma}(t_1) = e^{-i\underline{H}t_1} \underline{\sigma}(0) e^{i\underline{H}t_1} = \text{bunch of algebra} = \frac{\hbar B_0 \gamma}{4kT} \begin{pmatrix} 0 & -i/2 & -i/2 & 0 \\ i/2 & 0 & 0 & -i/2 \\ i/2 & 0 & 0 & -i/2 \\ 0 & i/2 & i/2 & 0 \end{pmatrix}$$

$\underline{I}_y + \underline{S}_y$

Density Matrix Calculations:

Example: a 2-spin System

- $t > t_1$

- Step 1: find \underline{H} $\rightarrow \underline{H} = -\Omega_I \underline{I}_z - \Omega_S \underline{S}_z + 2\pi J(\underline{I}_x \underline{S}_x + \underline{I}_y \underline{S}_y + \underline{I}_z \underline{S}_z)$

$$\underline{H} = \frac{1}{2} \begin{pmatrix} -\Omega_I - \Omega_S + \pi J & 0 & 0 & 0 \\ 0 & -\Omega_I + \Omega_S - \pi J & 2\pi J & 0 \\ 0 & 2\pi J & \Omega_I - \Omega_S - \pi J & 0 \\ 0 & 0 & 0 & \Omega_I + \Omega_S + \pi J \end{pmatrix}$$

Let's consider the case of "weak coupling") $|\Omega_I - \Omega_S| \gg J$.

$$\underline{H} = \frac{1}{2} \begin{pmatrix} -\Omega_I - \Omega_S + \pi J & 0 & 0 & 0 \\ 0 & -\Omega_I + \Omega_S - \pi J & 0 & 0 \\ 0 & 0 & \Omega_I - \Omega_S - \pi J & 0 \\ 0 & 0 & 0 & \Omega_I + \Omega_S + \pi J \end{pmatrix} \quad \text{(type of secular approximation)}$$

$$-\Omega_I \underline{I}_z - \Omega_S \underline{S}_z + 2\pi J \underline{I}_z \underline{S}_z$$

Compare this matrix with the energy diagram in previous lecture.

Density Matrix Calculations:

Example: a 2-spin System

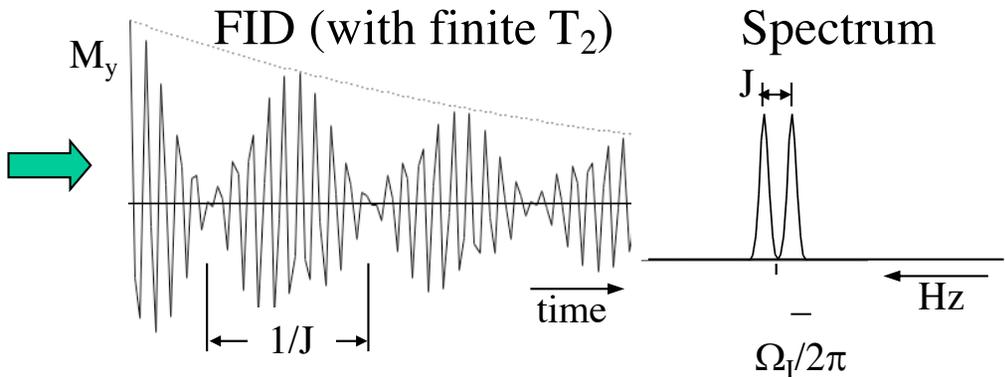
- Step 2: compute $\underline{\sigma}(t) = e^{-i\underline{H}t} \underline{\sigma}(t_1) e^{i\underline{H}t}$ (easy since \underline{H} is diagonal)

$$\underline{\sigma}(t) = e^{-i\underline{H}t} \underline{\sigma}(t_1) e^{i\underline{H}t} = \text{some algebra} = \frac{\hbar B_0 \gamma}{4kT} \frac{1}{2} \begin{pmatrix} 0 & e^{i(\Omega_S - \pi J)t} & e^{i(\Omega_I - \pi J)t} & 0 \\ e^{-i(\Omega_S - \pi J)t} & 0 & 0 & e^{i(\Omega_I + \pi J)t} \\ e^{-i(\Omega_I - \pi J)t} & 0 & 0 & e^{i(\Omega_S + \pi J)t} \\ 0 & e^{-i(\Omega_I + \pi J)t} & e^{-i(\Omega_S + \pi J)t} & 0 \end{pmatrix}$$

• I -spin transverse magnetization (S -spin terms are similar):

$$\overline{\langle \hat{I}_x \rangle} = \text{Tr}(\underline{\sigma} \underline{I}_x) = \frac{\hbar B_0 \gamma}{4kT} \sin \Omega_I t \cos \pi J t$$

$$\overline{\langle \hat{I}_y \rangle} = \text{Tr}(\underline{\sigma} \underline{I}_y) = \frac{\hbar B_0 \gamma}{4kT} \cos \Omega_I t \cos \pi J t$$



$$\overline{\langle 2\hat{I}_x \hat{S}_z \rangle} = 2\text{Tr}(\underline{\sigma} \underline{I}_x \underline{S}_z) = -\frac{\hbar B_0 \gamma}{4kT} \cos \Omega_I t \sin \pi J t$$

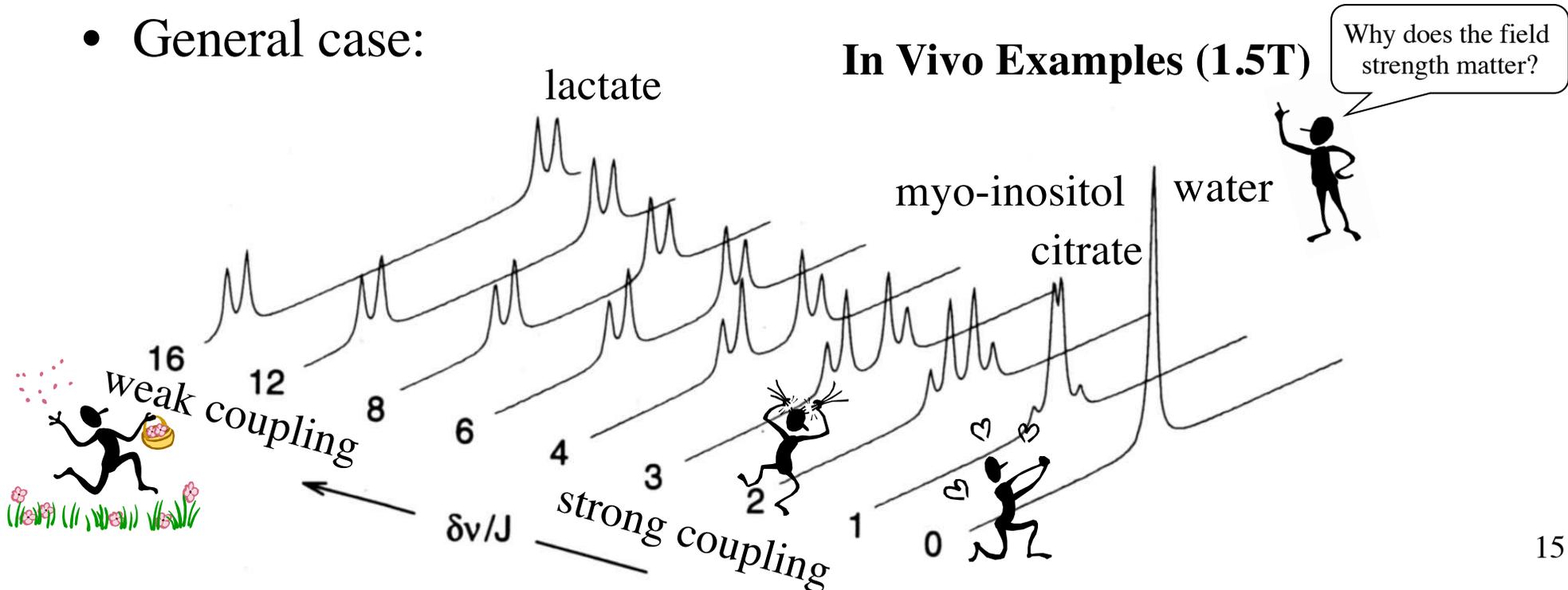
$$\overline{\langle 2\hat{I}_y \hat{S}_z \rangle} = 2\text{Tr}(\underline{\sigma} \underline{I}_y \underline{S}_z) = \frac{\hbar B_0 \gamma}{4kT} \sin \Omega_I t \sin \pi J t$$

Magnetization oscillates between detectable and undetectable components!

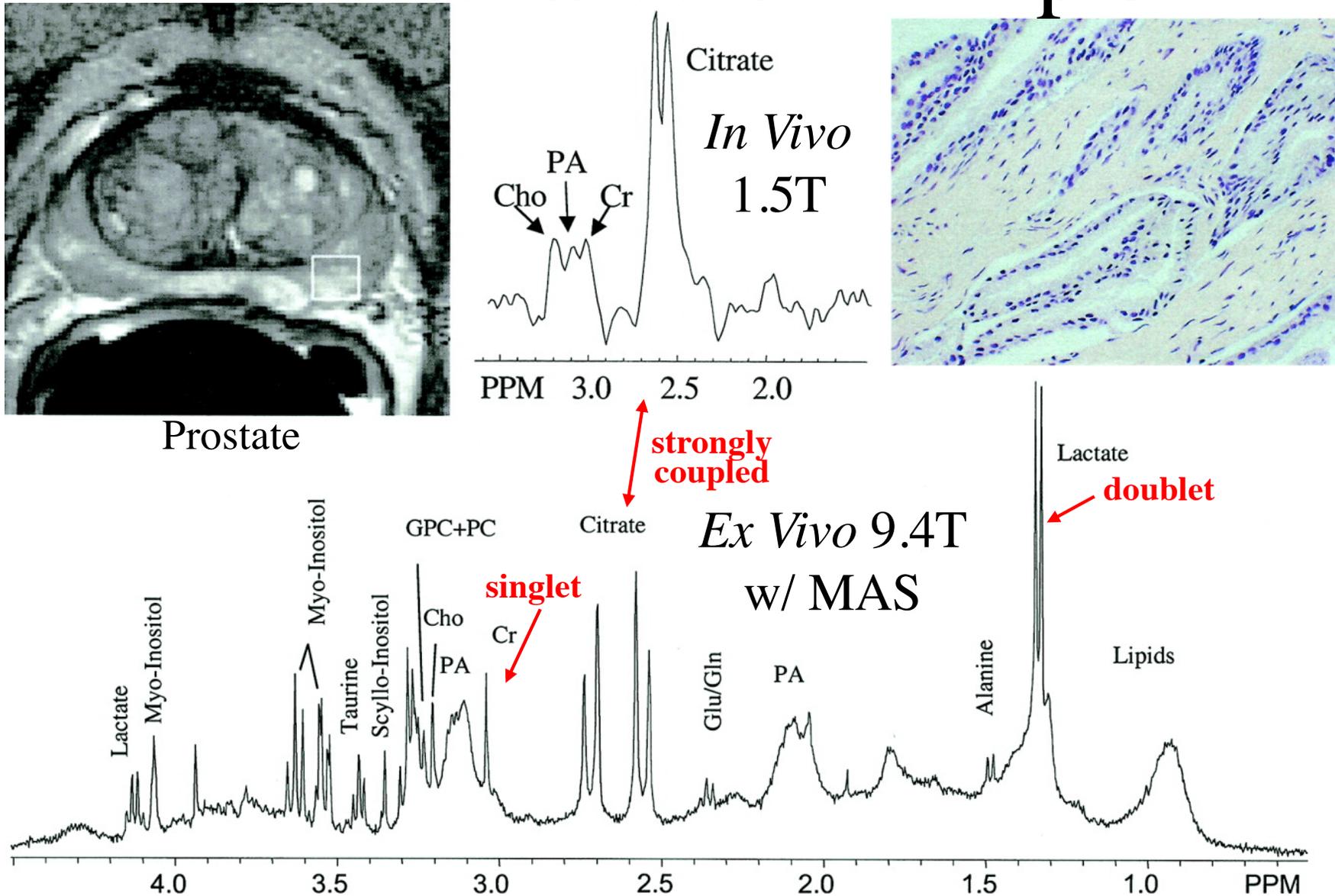
Equivalence and Strong Coupling

$$\underline{H} = \frac{1}{2} \begin{pmatrix} -\Omega_I - \Omega_S + \pi J & 0 & 0 & 0 \\ 0 & -\Omega_I + \Omega_S - \pi J & 2\pi J & 0 \\ 0 & 2\pi J & \Omega_I - \Omega_S - \pi J & 0 \\ 0 & 0 & 0 & \Omega_I + \Omega_S + \pi J \end{pmatrix}$$

- Case 1: $|\Omega_I - \Omega_S| \gg J$ (weak coupling) \rightarrow two doublets
- Case 2: $\Omega_I = \Omega_S$ (equivalent spins) \rightarrow one singlet
- General case:



In Vivo/Ex Vivo Example



Swanson, et al, "Proton HR-MAS spectroscopy and quantitative pathologic analysis of MRI/3D-MRSI-targeted postsurgical prostate tissues", *MRM*, 50:944-954, 2003.

Next lecture:
Product Operator Formulism

Appendix

Matrix Representations of 2-spin Product Operators

$$\underline{I}_x = \frac{1}{2} \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \quad \underline{S}_x = \frac{1}{2} \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \quad 2\underline{I}_x\underline{S}_x = \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \quad 2\underline{I}_y\underline{S}_x = \frac{i}{2} \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$

$$\underline{I}_y = \frac{i}{2} \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \quad \underline{S}_y = \frac{i}{2} \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \quad 2\underline{I}_x\underline{S}_y = \frac{i}{2} \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \quad 2\underline{I}_y\underline{S}_y = \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}$$

$$\underline{I}_z = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \quad \underline{S}_z = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \quad 2\underline{I}_x\underline{S}_z = \frac{1}{2} \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} \quad 2\underline{I}_y\underline{S}_z = \frac{i}{2} \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}$$

$$\frac{1}{2}\underline{E} = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad 2\underline{I}_z\underline{S}_x = \frac{1}{2} \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{pmatrix} \quad 2\underline{I}_z\underline{S}_y = \frac{i}{2} \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix} \quad 2\underline{I}_z\underline{S}_z = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$