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: $\langle \hat{A} \rangle = \mathrm{Tr}\{\hat{\sigma}\hat{A}\}$.

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

  Hamiltonian

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

- 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

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

- At thermal equilibrium:

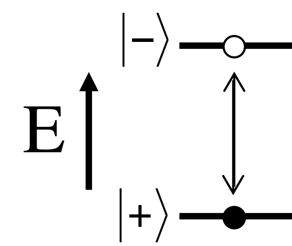
$$\hat{H}_0 = -\omega_0 \hat{I}_z \quad \text{and} \quad \underset{\text{(high temp approx)}}{\hat{\sigma}_0 = \tfrac{1}{2}\hat{E} + \tfrac{\hbar\gamma B_0}{4kT}\hat{I}_z} \quad \left(\left|\varphi\right\rangle = c_+\left|+\right\rangle + c_-\left|-\right\rangle\right)$$

- Most convenient basis set is the eigenkets of $\hat{H}_0$: $\{\underset{\text{“spin up”}}{\left|+\right\rangle}, \underset{\text{“spin down”}}{\left|-\right\rangle}\}$

matrix representation

$$\underline{\sigma} = \begin{pmatrix} \overline{|c_+|^2} & \overline{c_+ c_-^*} \\ \overline{c_+^* c_-} & \overline{|c_-|^2} \end{pmatrix} \Rightarrow \begin{array}{c|cc} & \left|+\right\rangle & \left|-\right\rangle \\ \hline \left|+\right\rangle & L & I \\ \left|-\right\rangle & I & L \end{array}$$

density matrix



energy diagram

L - “longitudinal magnetization”
  - “spin population” or “single-spin order”

I - “transverse magnetization”
  - zero unless phase coherence between states $\left|+\right\rangle$ and $\left|-\right\rangle$
  - “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: $\hat{\sigma} = L_1\hat{T}_{11} + I_1\hat{T}_{12} + I_2\hat{T}_{21} + L_2\hat{T}_{22}$

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

$\hat{T}_{ij}$: orthonormal basis set called "transition operators"

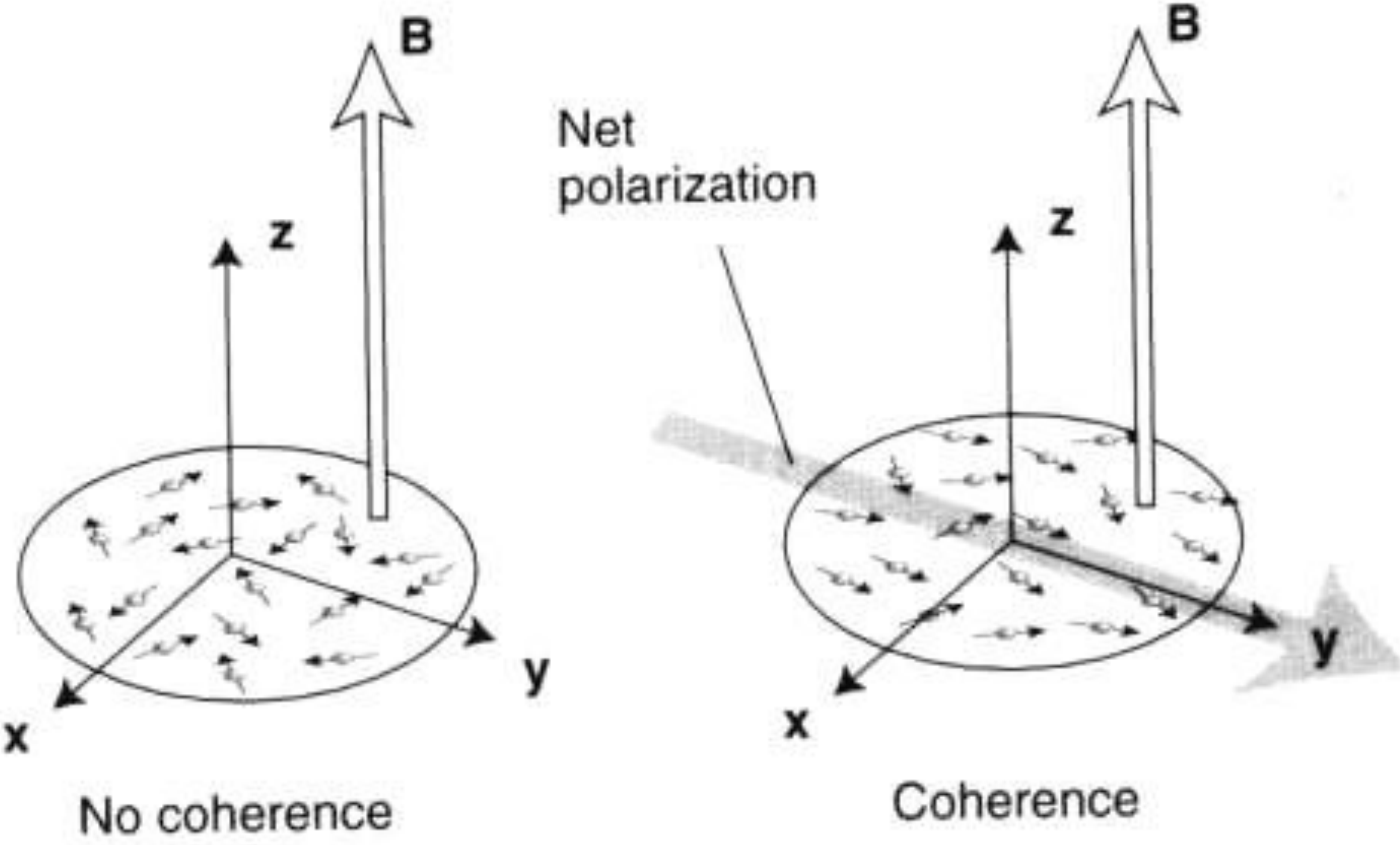
(Anyone remember Problem Set 2?)

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

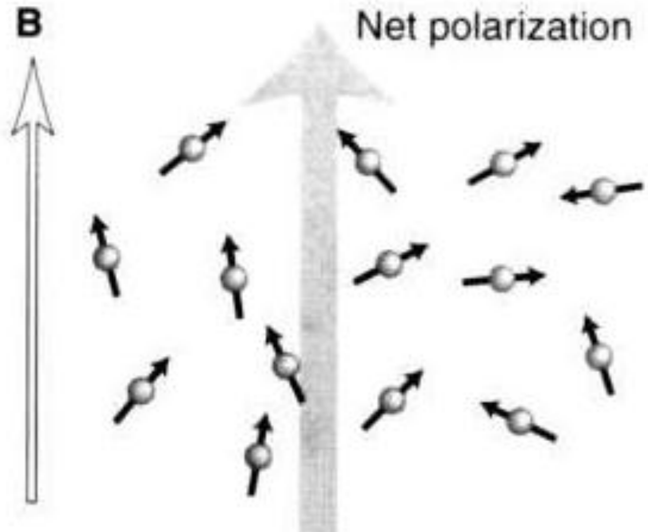
$$\hat{\sigma} = a_1\hat{E} + a_2\hat{I}_x + a_3\hat{I}_y + a_4\hat{I}_z \Rightarrow \left\{\hat{E},\hat{I}_x,\hat{I}_y,\hat{I}_z\right\}$$ "product operator" basis set

Phase Coherence

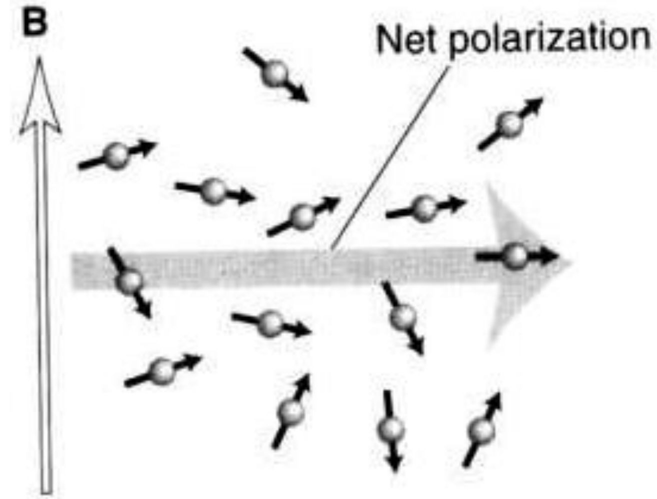
Coherent superposition of quantum states



Pictorial Representations

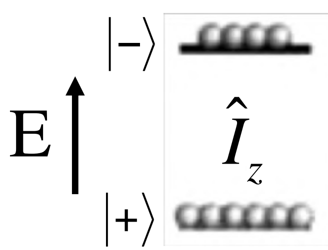


$\hat{I}_z$

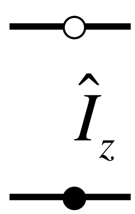


$\hat{I}_x$

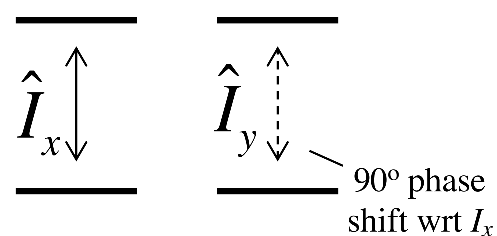
Energy diagrams



or



○ = population deficit
● = population excess



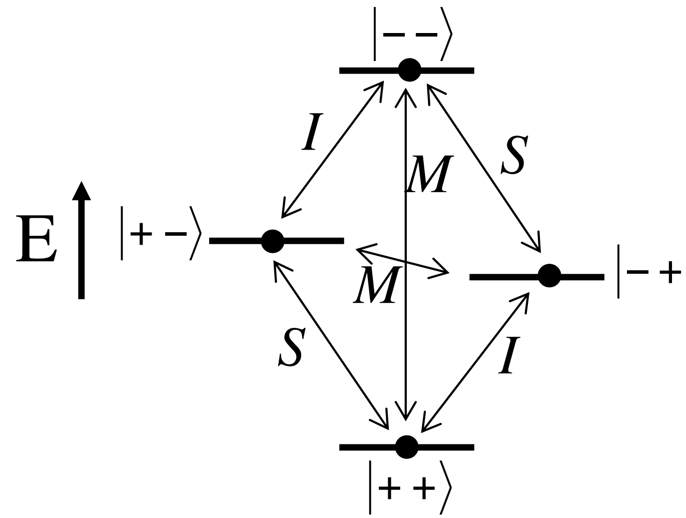
$\hat{\sigma}$: Coupled Two-Spin System

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

Density Matrix

$$\underline{\sigma} \Rightarrow \begin{array}{c|c} & \begin{array}{cccc} |++\rangle & |+-\rangle & |-+\rangle & |--\rangle \end{array} \\ \begin{array}{c} |++\rangle \\ |+-\rangle \\ |-+\rangle \\ |--\rangle \end{array} & \begin{pmatrix} L & S & I & M \\ S & L & M & I \\ I & M & L & S \\ M & I & S & L \end{pmatrix} \end{array}$$

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:

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

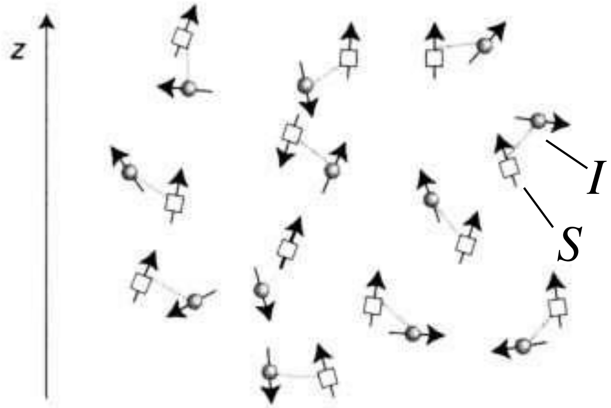
- Unfamiliar terms:

$2\hat{I}_x\hat{S}_z, 2\hat{I}_y\hat{S}_z, 2\hat{I}_z\hat{S}_x, 2\hat{I}_z\hat{S}_y$	Anti-phase single quantum coherences
$2\hat{I}_z\hat{S}_z$	Longitudinal two-spin order
$2\hat{I}_x\hat{S}_x, 2\hat{I}_y\hat{S}_y, 2\hat{I}_x\hat{S}_y, 2\hat{I}_y\hat{S}_x$	Linear combinations of double and zero quantum coherences

Product Operators

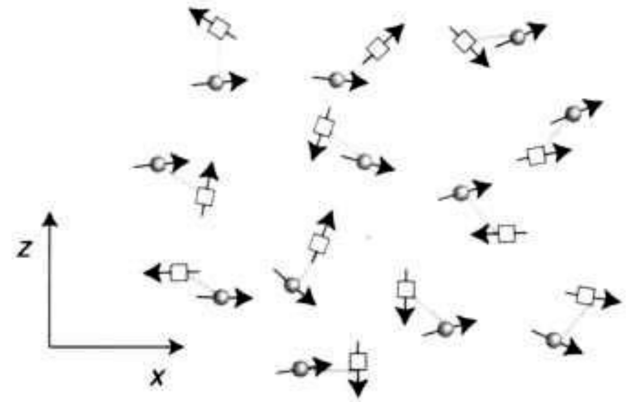
Pictorial Examples (note, we are now considering *pairs* of spins):

$\hat{S}_z$



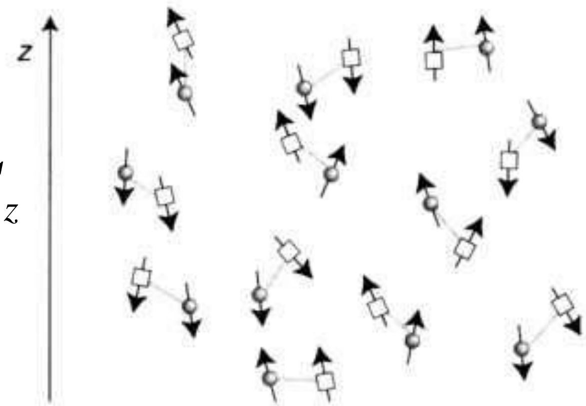
Net tendency for S spins to be +z
No net tendency for I spins in any direction

$\hat{I}_x$



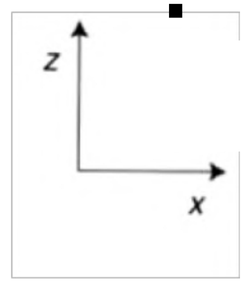
No net tendency for S spins in any direction
Net tendency for I spins to be +x

$2\hat{I}_z\hat{S}_z$

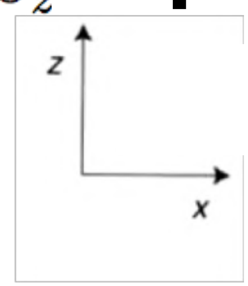


No net tendency for I or S spins to be $\pm$z
If I or S is $\pm$z, increased probability paired spin is $\pm$z

$2\hat{I}_x\hat{S}_z$?

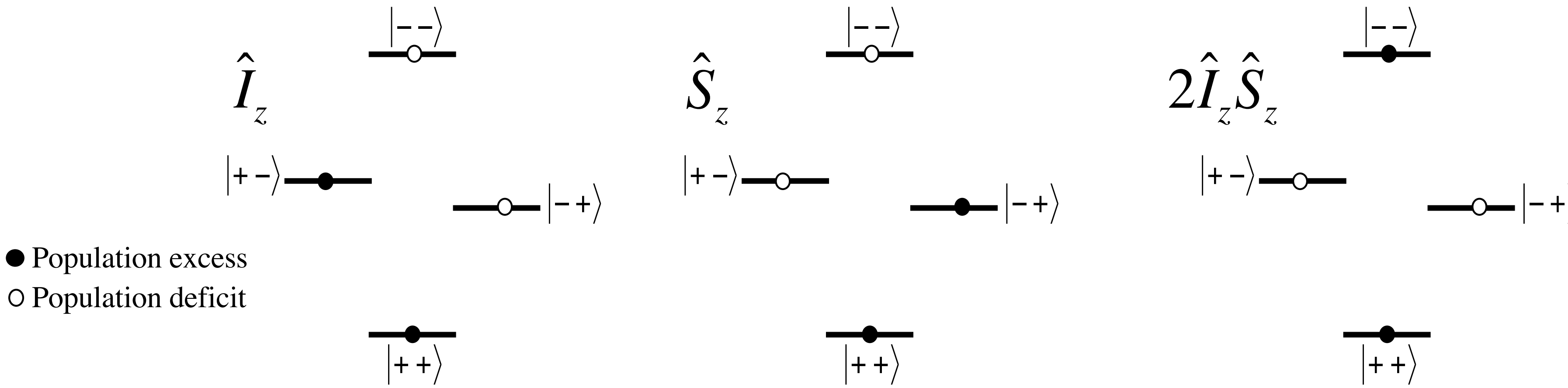


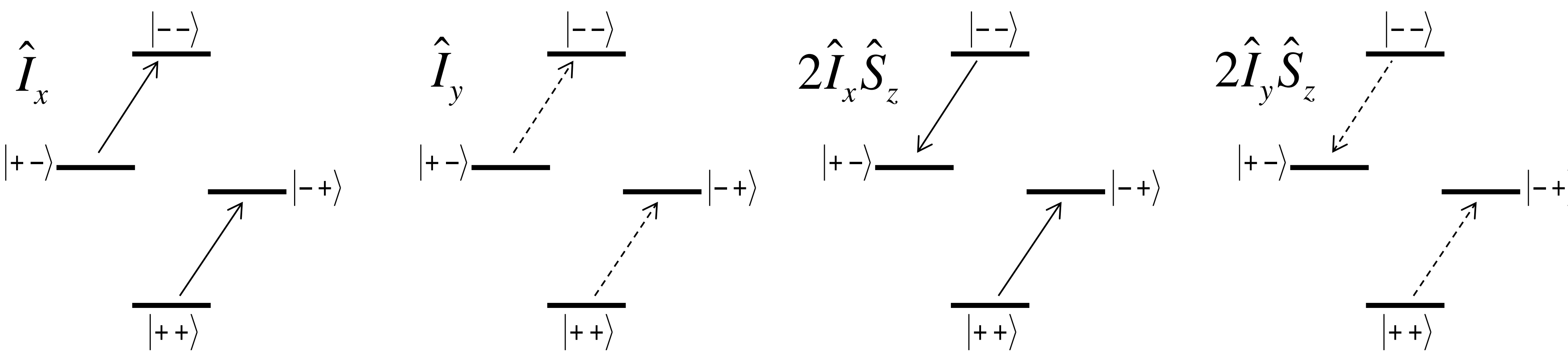
$\hat{I}_x + \hat{S}_z$?



Product Operators

- Some energy diagram representations

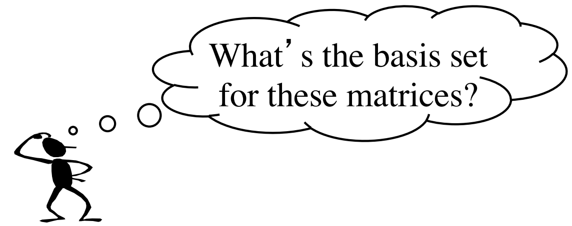




Product Operators: Matrix Representations*

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

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



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

(a_i s complex)

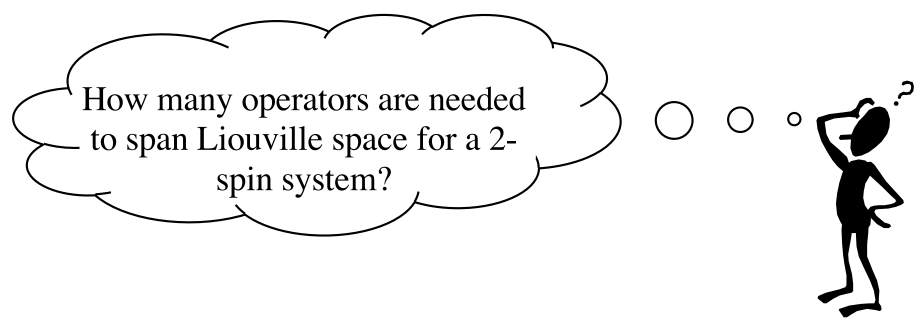
What is $\underline{I}_x$? (Hint: must be 4 x 4)

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

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

An example product operator:

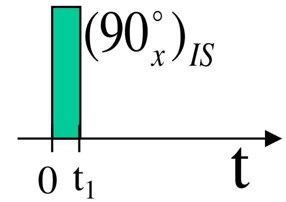
$$\underline{2I_x S_x} = \begin{pmatrix} 0 & 0 & 0 & \frac{1}{2} \\ 0 & 0 & \frac{1}{2} & 0 \\ 0 & \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & 0 & 0 & 0 \end{pmatrix}$$



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

Density Matrix Calculations:

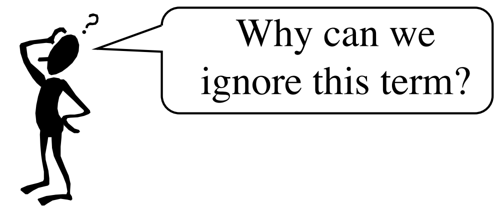
Example: a 2-spin System



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 $\underline{H}$ $\Longrightarrow$ $\underline{H} \approx -\omega_1(\underline{I}_x + \underline{S}_x)$

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

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

Density Matrix Calculations:

Example: a 2-spin System

- t > t_1

  - Step 1: find $\underline{H}$ $\Longrightarrow$ $\underline{H} = -\Omega_I \underline{I_z} - \Omega_S \underline{S_z} + 2\pi J(\underline{I_x S_x} + \underline{I_y S_y} + \underline{I_z S_z})$

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

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

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

(type of secular approximation)

$$-\Omega_I \underline{I_z} - \Omega_S \underline{S_z} + 2\pi J \underline{I_z S_z}$$

Compare this matrix with the energy diagram in previous lecture.

Density Matrix Calculations:

Example: a 2-spin System

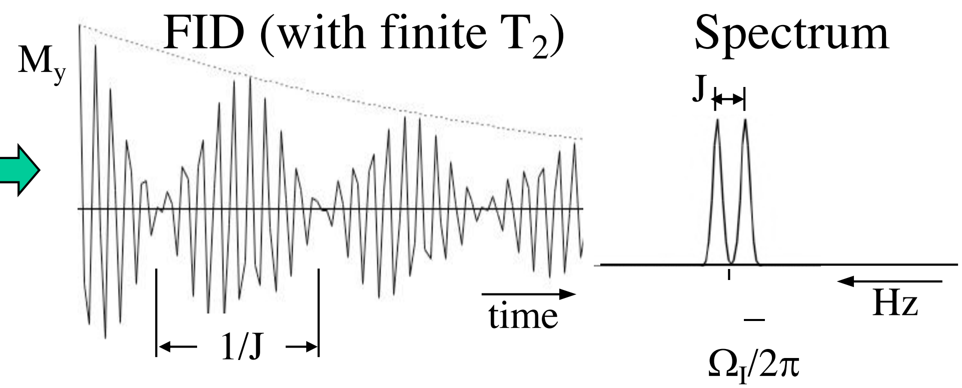
- Step 2: compute $\underline{\sigma}(t) = e^{-i\underline{H}t}\underline{\sigma}(t_1)e^{i\underline{H}t}$ (easy since $\underline{H}$ is diagonal)

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

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

$$\overline{\langle \hat{I}_x \rangle} = \mathrm{Tr}\left(\underline{\sigma}\,\underline{I_x}\right) = \frac{\hbar B_0\gamma}{4kT}\sin\Omega_I t\cos\pi Jt$$

$$\overline{\langle \hat{I}_y \rangle} = \mathrm{Tr}\left(\underline{\sigma}\,\underline{I_y}\right) = \frac{\hbar B_0\gamma}{4kT}\cos\Omega_I t\cos\pi Jt$$



$$\overline{\langle 2\hat{I}_x\hat{S}_z \rangle} = 2\mathrm{Tr}\left(\underline{\sigma}\,\underline{I_x S_z}\right) = -\frac{\hbar B_0\gamma}{4kT}\cos\Omega_I t\sin\pi Jt$$

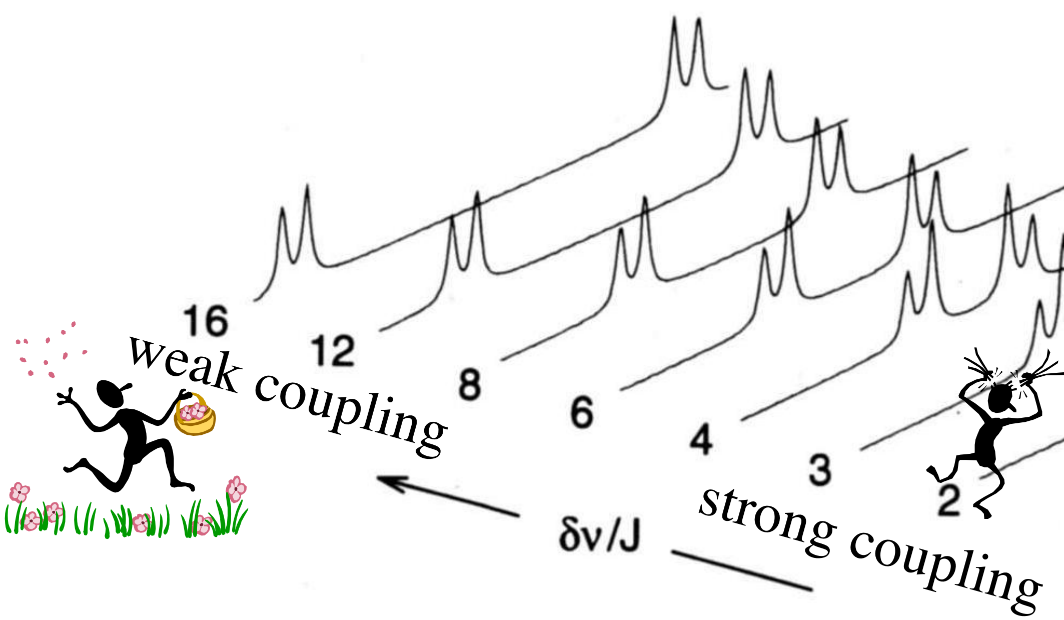
$$\overline{\langle 2\hat{I}_y\hat{S}_z \rangle} = 2\mathrm{Tr}\left(\underline{\sigma}\,\underline{I_y S_z}\right) = \frac{\hbar B_0\gamma}{4kT}\sin\Omega_I t\sin\pi Jt$$

Magnetization oscillates between detectable and undetectable components!

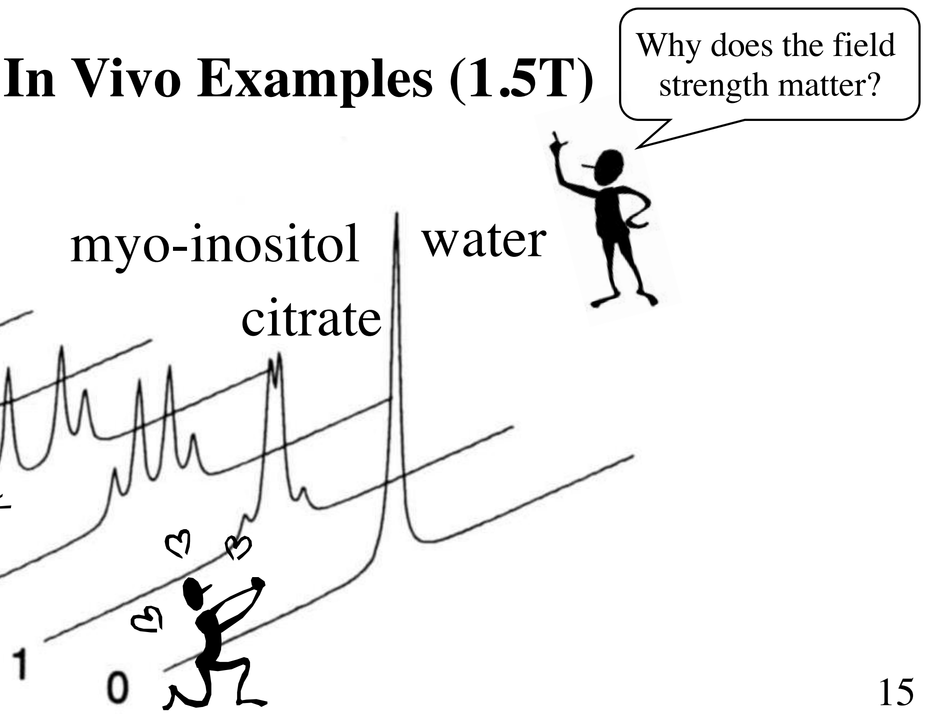
Equivalence and Strong Coupling

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

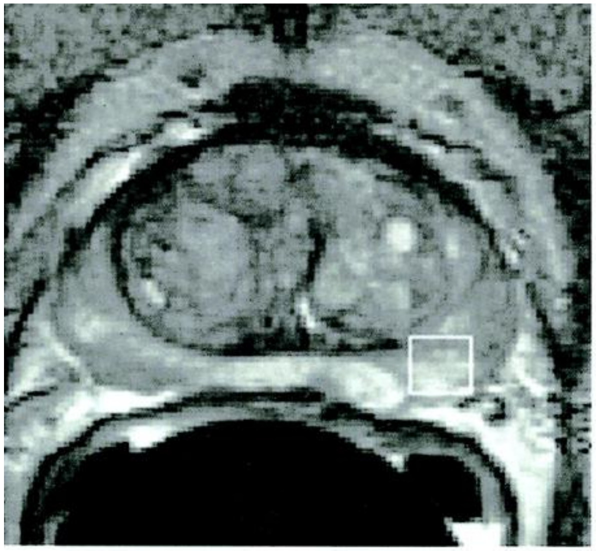
- Case 1: $|\Omega_I - \Omega_S| >> J$ (weak coupling) ➡ two doublets
- Case 2: $\Omega_I = \Omega_S$ (equivalent spins) ➡ one singlet
- General case:



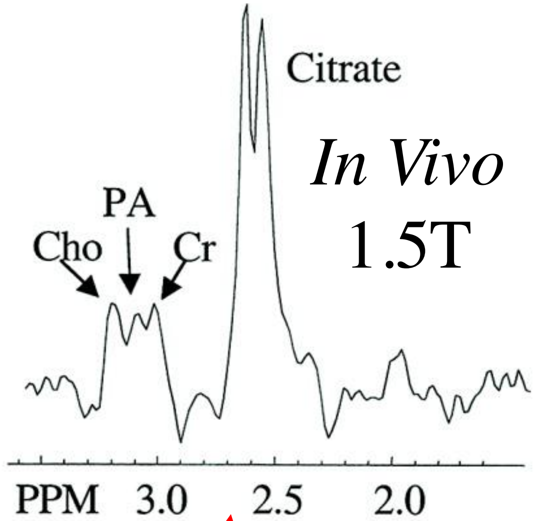
In Vivo Examples (1.5T)

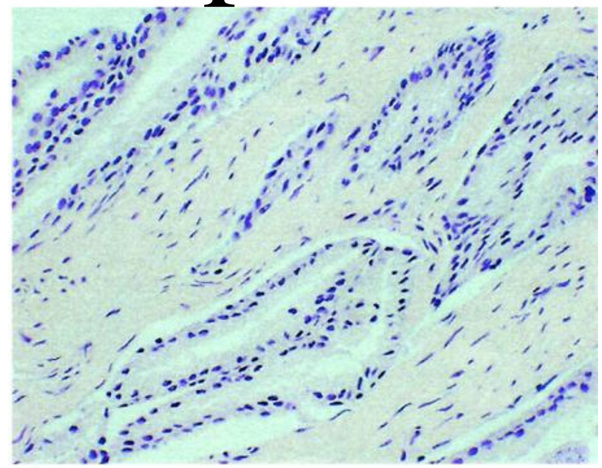


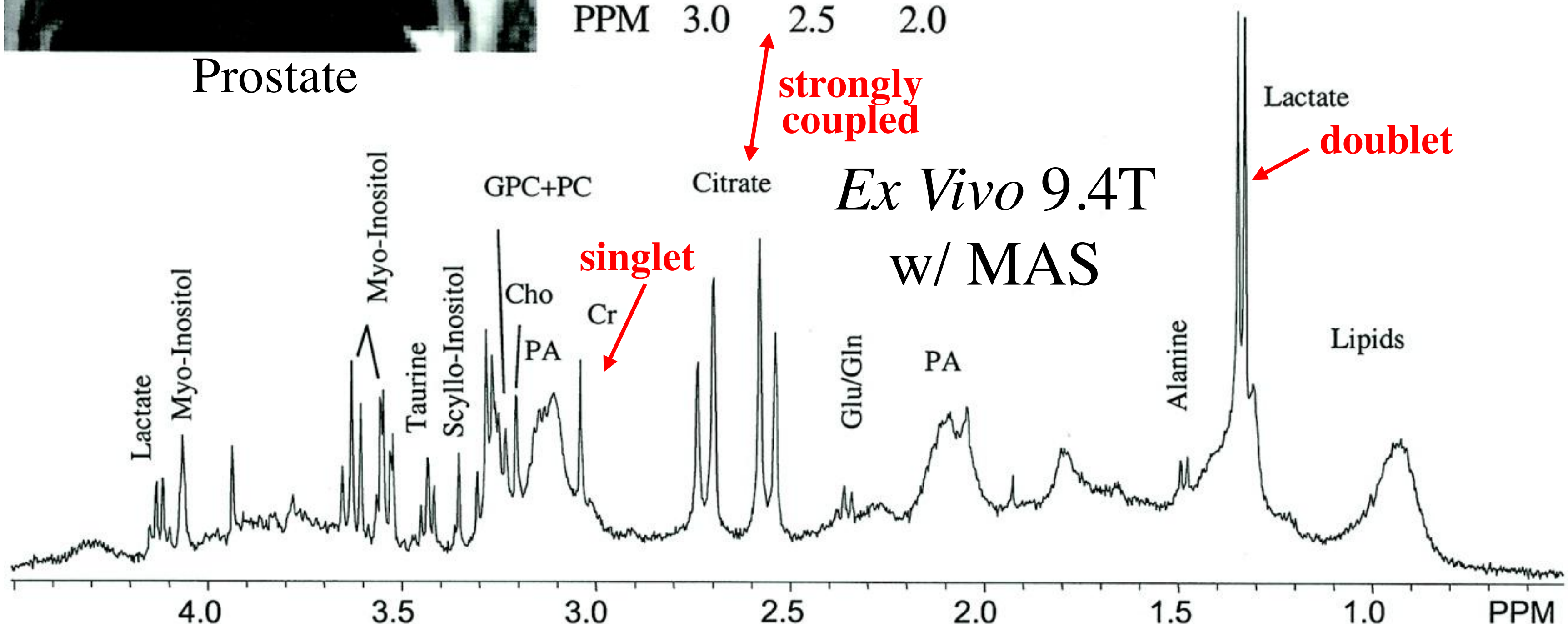
In Vivo/*Ex Vivo* Example



Prostate







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

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

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

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

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