Density Matrix in Product Operator Form

BCMB/CHEM 8190

Product Operators: Connection to Density Matrix Properties

- We described earlier the equilibrium density matrix (single spin)

$$\hat{\boldsymbol{\rho}}_{eq} = \begin{bmatrix} e^{(-E_n/(k_B T)}/Z & 0 \\ 0 & e^{(-E_n/(k_B T)}/Z \end{bmatrix} = \frac{1}{2}\begin{bmatrix} e^{(-E_n/(k_B T)} & 0 \\ 0 & e^{(-E_n/(k_B T)} \end{bmatrix} = \frac{1}{2}\begin{bmatrix} e^{(\gamma\hbar B_0/(2k_B T)} & 0 \\ 0 & e^{(-\gamma\hbar B_0/(2k_B T)} \end{bmatrix}$$

- It can be reformulated for convenience as a deviation matrix

$$\hat{\boldsymbol{\sigma}}_{eq} = \begin{bmatrix} -E_n/Zk_B T & 0 \\ 0 & -E_n/Zk_B T \end{bmatrix} = \frac{1}{2}\begin{bmatrix} -E_n/k_B T & 0 \\ 0 & -E_n/k_B T \end{bmatrix} = \frac{1}{2}\begin{bmatrix} \gamma\hbar B_0/2k_B T & 0 \\ 0 & -\gamma\hbar B_0/2k_B T \end{bmatrix}$$

$$\rho_{nn} = c_n c_n^* = e^{(-E_n/(k_B T)}/Z \cong 1/Z - E_n/(Zk_{\mathrm{B}}T) = 1/Z + \sigma_{nn}, \text{ where } \sigma_{nn} = -E_n/(Zk_{\mathrm{B}}T)$$

$$\rho_{nn} - 1/Z = \sigma_{nn}$$

$$Z = \sum_n e^{(-E_n/(k_{\mathrm{B}}T)} = \text{number of states} = 2 \text{ for } |\alpha\rangle, |\beta\rangle \text{ basis}$$

- It can further be reduced to constants and a simple matrix

$$\hat{\boldsymbol{\sigma}}_{eq} \equiv \hat{\boldsymbol{\sigma}}_{z,eq} = \frac{\gamma\hbar B_0}{2k_B T}\frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = \delta\frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

Product Operators: Connection to Density Matrix Properties

- We showed that rotation of the equilibrium deviation density matrix about the *x*-axis ($\mathbf{R}_x$ operations) produced the following, which represented *y*-magnetization

$$\hat{\boldsymbol{\sigma}}_y = \delta \begin{bmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{bmatrix} = \frac{\gamma \hbar B_0}{2 k_B T} \frac{1}{2} \begin{bmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{bmatrix}$$

- Likewise, we showed the representation for *x*-magnetization

$$\hat{\boldsymbol{\sigma}}_x = \delta \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = \frac{\gamma \hbar B_0}{2 k_B T} \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

- *These bear a significant resemblance to* $\boldsymbol{I}_x$, $\boldsymbol{I}_y$, *and* $\boldsymbol{I}_z$ *operators*

$$\hat{\boldsymbol{\sigma}}_{z,eq} = \frac{\gamma \hbar B_0}{2 k_B T} \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \qquad \hat{\boldsymbol{I}}_z = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \qquad \hat{\boldsymbol{\sigma}}_{z,eq} = \delta \hat{\boldsymbol{I}}_z$$

$$\hat{\boldsymbol{\sigma}}_y = \frac{\gamma \hbar B_0}{2 k_B T} \frac{1}{2} \begin{bmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{bmatrix} \qquad \hat{\boldsymbol{I}}_y = \frac{1}{2} \begin{bmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{bmatrix} \qquad \hat{\boldsymbol{\sigma}}_y = \delta \hat{\boldsymbol{I}}_y$$

$$\hat{\boldsymbol{\sigma}}_x = \frac{\gamma \hbar B_0}{2 k_B T} \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad \hat{\boldsymbol{I}}_x = \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad \hat{\boldsymbol{\sigma}}_x = \delta \hat{\boldsymbol{I}}_x$$

Expressing σ in a basis set of matrices

- These examples show that some elements of the density matrix represent observables (for instance, *x*-magnetization)
- These examples demonstrate that elements of the density matrix transform to other elements under specific operations
  - for instance, σ_{11} and σ_{22}, (equilibrium (*z*) magnetization), transform to σ_{21} and σ_{12} (transverse magnetization) under $\mathbf{R}_x$ and $\mathbf{R}_y$ operations

- An alternative approach to working with the density matrix is to express the matrix (deviation matrix) as a linear combination of matrix basis functions (**B**)

$$\hat{\sigma}(t) = \sum_n c_n \mathbf{B}_n$$

- Requirements:
  - one basis matrix for each element (4 for single spin density matrix)
  - basis matrices are orthogonal (but not necessarily normalized)
  - basis matrices are Hermitian (self-adjoint)

$$\mathbf{B} = \mathbf{B}^{\dagger} = \mathbf{B}^{T*}$$

Expressing σ in a basis set of matrices

- Requirements:
  - one basis matrix for each element (4 for single spin density matrix)
  - basis matrices are orthogonal (but not necessarily normalized)
  - basis matrices are Hermitian (self-adjoint, **B** = **B**† = **B**^{T*})
- For single spins ½ ($|\alpha\rangle$, $|\beta\rangle$ basis), are 4 matrix basis elements

$$1/2\,\mathbf{E} = \frac{1}{2}\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix} \qquad \mathbf{I}_z = \frac{1}{2}\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix} \qquad \mathbf{I}_x = \frac{1}{2}\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix} \qquad \mathbf{I}_y = \frac{1}{2}\begin{bmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{bmatrix}$$

  - **E** ($\mathbb{1}$) is the identity (unitary) matrix, and has some interesting properties

$$\sum_{n=1}^{N}|n\rangle\langle n| = \mathbf{E} \qquad |\alpha\rangle\langle\alpha| + |\beta\rangle\langle\beta| = \begin{bmatrix}1\\0\end{bmatrix}\begin{bmatrix}1 & 0\end{bmatrix} + \begin{bmatrix}0\\1\end{bmatrix}\begin{bmatrix}0 & 1\end{bmatrix} = \begin{bmatrix}1 & 0\\ 0 & 0\end{bmatrix} + \begin{bmatrix}0 & 0\\ 0 & 1\end{bmatrix} = \begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}$$

$$\mathbf{A}\mathbf{E} = \mathbf{A} \qquad \mathbf{I}_x^2 = \mathbf{I}_y^2 = \mathbf{I}_z^2 = 1/4\ \mathbf{E}$$

- These are orthogonal (for matrices, Tr{$\mathbf{B}_i^\dagger\mathbf{B}_j$} = 0)
  - example: $\mathbf{I}_x$ and $\mathbf{I}_y$

$$\mathrm{Tr}\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}\begin{bmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{bmatrix} = \mathrm{Tr}\begin{bmatrix}\mathrm{i} & 0\\ 0 & -\mathrm{i}\end{bmatrix} = \mathrm{i} + (\text{-}\mathrm{i}) = 0$$

- Matrices are Hermitian (exchange rows and columns, take complex conjugate, original matrix returned): example, $\mathbf{I}_y$

$$\begin{bmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{bmatrix} \text{exchange rows / columns} \rightarrow \begin{bmatrix}0 & \mathrm{i}\\ -\mathrm{i} & 0\end{bmatrix} \text{take complex conjugates} \rightarrow \begin{bmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{bmatrix}$$

Representation of some simple density matrices

- Examine, once again, the equilibrium deviation density matrix

$$\hat{\boldsymbol{\sigma}} = \begin{bmatrix} \boldsymbol{\sigma}_{11} & \boldsymbol{\sigma}_{12} \\ \boldsymbol{\sigma}_{21} & \boldsymbol{\sigma}_{22} \end{bmatrix} = \begin{bmatrix} \boldsymbol{\sigma}_{\alpha\alpha} & \boldsymbol{\sigma}_{\alpha\beta} \\ \boldsymbol{\sigma}_{\beta\alpha} & \boldsymbol{\sigma}_{\beta\beta} \end{bmatrix} \quad \hat{\boldsymbol{\sigma}}_{eq} \equiv \hat{\boldsymbol{\sigma}}_{z,eq} = \frac{\gamma\hbar B_0}{2k_B T}\frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = \delta\frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = \delta\mathbf{I}_z \quad \mathbf{I}_z = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

  - so, the basis set elements are, themselves, density matrices
  - here δ represents a population excess: δ ∝ ½(#α states - #β states)
  - the numeric forms have a simple scalar multiplication relationship to the matrix representation of a particular operator

- Examine, once again, the effect of rotation about the *x*-axis (RF pulse along *x*-axis)

$$\hat{\boldsymbol{\sigma}}(t) = \hat{\mathbf{R}}_{x,\pi/2}\hat{\boldsymbol{\sigma}}_{eq}\hat{\mathbf{R}}_{x,\pi/2}^{-1} = \delta\frac{1}{2}\begin{bmatrix} 0 & \mathrm{i} \\ -\mathrm{i} & 0 \end{bmatrix} = -\delta\mathbf{I}_y \quad \mathbf{I}_y = \frac{1}{2}\begin{bmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{bmatrix}$$

  - a 90° (π/2 radians) pulse on the equilibrium density matrix ($\delta\mathbf{I}_z$) converts it to a density matrix represented by the matrix representation of the $\mathbf{I}_y$ operator ($-\delta\mathbf{I}_y$)

$$\delta\mathbf{I}_z \xrightarrow{90^\circ_x} -\delta\mathbf{I}_y \qquad \mathbf{I}_z \xrightarrow{90^\circ_x} -\mathbf{I}_y$$

  - note that 'product operator' typically refers to multi-spin systems, where the operators are created from products of other operators (see below)
  - however, the idea that density matrices can be expressed as linear combinations of operators representing elements of the density matrix, is a cornerstone of the product operator formalism

Transformation for a pulse on *x*

- Previously, using rotation operators ($\hat{\mathbf{R}}$), we showed the result of a 90° (π/2) RF pulse along the *x*-axis gave -y magnetization

  - the rotation operators are:

$$\hat{\mathbf{R}}_x = \begin{bmatrix} \cos(\omega_1 t/2) & \mathrm{i}\sin(\omega_1 t/2) \\ \mathrm{i}\sin(\omega_1 t/2) & \cos(\omega_1 t/2) \end{bmatrix} \qquad \hat{\mathbf{R}}_x^{-1} = \begin{bmatrix} \cos(\omega_1 t/2) & -\mathrm{i}\sin(\omega_1 t/2) \\ -\mathrm{i}\sin(\omega_1 t/2) & \cos(\omega_1 t/2) \end{bmatrix}$$

  - for 90° (π/2) and 180° (π) pulses, these reduce to:

$$\hat{\mathbf{R}}_{x,\pi/2}^{-1} = \frac{\sqrt{2}}{2}\begin{bmatrix} 1 & \mathrm{i} \\ \mathrm{i} & 1 \end{bmatrix} \qquad \hat{\mathbf{R}}_{x,\pi/2} = \frac{\sqrt{2}}{2}\begin{bmatrix} 1 & -\mathrm{i} \\ -\mathrm{i} & 1 \end{bmatrix} \qquad \hat{\mathbf{R}}_{x,\pi} = \begin{bmatrix} 0 & -\mathrm{i} \\ -\mathrm{i} & 0 \end{bmatrix} \qquad \hat{\mathbf{R}}_{x,\pi}^{-1} = \begin{bmatrix} 0 & \mathrm{i} \\ \mathrm{i} & 0 \end{bmatrix}$$

  - a 90° (π/2) pulse converts equilibrium *z* magnetization to -*y*

$$\hat{\boldsymbol{\sigma}}(t) = \hat{\mathbf{R}}_{x,\pi/2}\hat{\boldsymbol{\sigma}}_{eq}\hat{\mathbf{R}}_{x,\pi/2}^{-1} = \frac{\sqrt{2}}{2}\begin{bmatrix} 1 & -\mathrm{i} \\ -\mathrm{i} & 1 \end{bmatrix}\frac{1}{2}\begin{bmatrix} \delta & 0 \\ 0 & -\delta \end{bmatrix}\frac{\sqrt{2}}{2}\begin{bmatrix} 1 & \mathrm{i} \\ \mathrm{i} & 1 \end{bmatrix} = \frac{1}{4}\begin{bmatrix} 1 & -\mathrm{i} \\ -\mathrm{i} & 1 \end{bmatrix}\begin{bmatrix} \delta & \mathrm{i}\delta \\ -\mathrm{i}\delta & -\delta \end{bmatrix} = \frac{1}{4}\begin{bmatrix} 0 & 2\mathrm{i}\delta \\ -2\mathrm{i}\delta & 0 \end{bmatrix} = \delta\frac{1}{2}\begin{bmatrix} 0 & \mathrm{i} \\ -\mathrm{i} & 0 \end{bmatrix}$$

$$-\hat{\boldsymbol{I}}_y = \frac{1}{2}\begin{bmatrix} 0 & \mathrm{i} \\ -\mathrm{i} & 0 \end{bmatrix}, \text{ so } \delta\frac{1}{2}\begin{bmatrix} 0 & \mathrm{i} \\ -\mathrm{i} & 0 \end{bmatrix} = -\delta\hat{\boldsymbol{I}}_y$$

Transformation for a pulse on *x*

- For an arbitrary pulse angle

$$\hat{\mathbf{R}}_x \mathbf{I}_z \hat{\mathbf{R}}_x^{-1} = \begin{bmatrix} \cos(\omega_1 t/2) & -\mathrm{i}\sin(\omega_1 t/2) \\ -\mathrm{i}\sin(\omega_1 t/2) & \cos(\omega_1 t/2) \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \cos(\omega_1 t/2) & \mathrm{i}\sin(\omega_1 t/2) \\ \mathrm{i}\sin(\omega_1 t/2) & \cos(\omega_1 t/2) \end{bmatrix}$$

$$= \begin{bmatrix} \cos(\omega_1 t/2) & -\mathrm{i}\sin(\omega_1 t/2) \\ -\mathrm{i}\sin(\omega_1 t/2) & \cos(\omega_1 t/2) \end{bmatrix} \begin{bmatrix} \cos(\omega_1 t/2) & \mathrm{i}\sin(\omega_1 t/2) \\ -\mathrm{i}\sin(\omega_1 t/2) & -\cos(\omega_1 t/2) \end{bmatrix} = \begin{bmatrix} \cos^2(\omega_1 t/2) - \sin^2(\omega_1 t/2) & \mathrm{i}2\cos(\omega_1 t/2)\sin(\omega_1 t/2) \\ -\mathrm{i}2\cos(\omega_1 t/2)\sin(\omega_1 t/2) & \sin^2(\omega_1 t/2) - \cos^2(\omega_1 t/2) \end{bmatrix}$$

$$= \begin{bmatrix} \cos(\omega_1 t) & \mathrm{i}\sin(\omega_1 t) \\ -\mathrm{i}\sin(\omega_1 t) & -\cos(\omega_1 t) \end{bmatrix} = \begin{bmatrix} \cos(\omega_1 t) & 0 \\ 0 & -\cos(\omega_1 t) \end{bmatrix} - \begin{bmatrix} 0 & -\mathrm{i}\sin(\omega_1 t) \\ \mathrm{i}\sin(\omega_1 t) & 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\cos(\omega_1 t) - \begin{bmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{bmatrix}\sin(\omega_1 t) = \mathbf{I}_z \cos(\omega_1 t) - \mathbf{I}_y \sin(\omega_1 t)$$

- the result is the same as before: an RF pulse along the x-axis rotates equilibrium *z*-magnetization towards the -*y* axis
- a long pulse exchanges *z*- and *y*-magnetization

- Conventions:
  - the convention here is to specify the sign of the rotation, thus, a positive rotation about the x-axis moves the equilibrium bulk magnetization vector towards the -*y* axis (we'll use this one)
  - the alternate convention is to specify the B_1 direction, thus, a pulse along the +*x* axis will move the equilibrium bulk magnetization vector towards the +*y* axis

Other Transformations

- Pulse on *y* (rotation about *y*-axis) of arbitrary pulse angle

$$\hat{\mathbf{R}}_y \mathbf{I}_z \hat{\mathbf{R}}_y^{-1} = \begin{bmatrix}\cos(\omega_1 t/2) & -\sin(\omega_1 t/2)\\ \sin(\omega_1 t/2) & \cos(\omega_1 t/2)\end{bmatrix}\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}\begin{bmatrix}\cos(\omega_1 t/2) & \sin(\omega_1 t/2)\\ -\sin(\omega_1 t/2) & \cos(\omega_1 t/2)\end{bmatrix}$$

$$= \begin{bmatrix}\cos(\omega_1 t/2) & -\sin(\omega_1 t/2)\\ \sin(\omega_1 t/2) & \cos(\omega_1 t/2)\end{bmatrix}\begin{bmatrix}\cos(\omega_1 t/2) & \sin(\omega_1 t/2)\\ \sin(\omega_1 t/2) & -\cos(\omega_1 t/2)\end{bmatrix} = \begin{bmatrix}\cos^2(\omega_1 t/2) - \sin^2(\omega_1 t/2) & 2\cos(\omega_1 t/2)\sin(\omega_1 t/2)\\ 2\cos(\omega_1 t/2)\sin(\omega_1 t/2) & \sin^2(\omega_1 t/2) - \cos^2(\omega_1 t/2)\end{bmatrix}$$

$$= \begin{bmatrix}\cos(\omega_1 t) & \sin(\omega_1 t)\\ \sin(\omega_1 t) & -\cos(\omega_1 t)\end{bmatrix} = \begin{bmatrix}\cos(\omega_1 t) & 0\\ 0 & -\cos(\omega_1 t)\end{bmatrix} + \begin{bmatrix}0 & \sin(\omega_1 t)\\ \sin(\omega_1 t) & 0\end{bmatrix} = \begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}\cos(\omega_1 t) + \begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}\sin(\omega_1 t) = \mathbf{I}_z \cos(\omega_1 t) + \mathbf{I}_x \sin(\omega_1 t)$$

- Precession of *x*-magnetization (rotation about *z*-axis)

$$\hat{\mathbf{R}}_z \mathbf{I}_x \hat{\mathbf{R}}_z^{-1} = \begin{bmatrix}\cos(\omega_1 t/2) - \mathrm{i}\sin(\omega_1 t/2) & 0\\ 0 & \cos(\omega_1 t/2) + \mathrm{i}\sin(\omega_1 t/2)\end{bmatrix}\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}\begin{bmatrix}\cos(\omega_1 t/2) + \mathrm{i}\sin(\omega_1 t/2) & 0\\ 0 & \cos(\omega_1 t/2) - \mathrm{i}\sin(\omega_1 t/2)\end{bmatrix}$$

$$= \begin{bmatrix}\cos(\omega_1 t/2) - \mathrm{i}\sin(\omega_1 t/2) & 0\\ 0 & \cos(\omega_1 t/2) + \mathrm{i}\sin(\omega_1 t/2)\end{bmatrix}\begin{bmatrix}0 & \cos(\omega_1 t/2) - \mathrm{i}\sin(\omega_1 t/2)\\ \cos(\omega_1 t/2) + \mathrm{i}\sin(\omega_1 t/2) & 0\end{bmatrix} = \begin{bmatrix}0 & \cos^2(\omega_1 t/2) - \mathrm{i}2\sin(\omega_1 t/2)\cos(\omega_1 t/2) - \sin^2(\omega_1 t/2)\\ \cos^2(\omega_1 t/2) + \mathrm{i}2\sin(\omega_1 t/2)\cos(\omega_1 t/2) - \sin^2(\omega_1 t/2) & 0\end{bmatrix}$$

$$= \begin{bmatrix}0 & \cos(\omega_1 t) - \mathrm{i}\sin(\omega_1 t)\\ \cos(\omega_1 t) + \mathrm{i}\sin(\omega_1 t) & 0\end{bmatrix} = \begin{bmatrix}0 & \cos(\omega_1 t)\\ \cos(\omega_1 t) & 0\end{bmatrix} + \begin{bmatrix}0 & -\mathrm{i}\sin(\omega_1 t)\\ \mathrm{i}\sin(\omega_1 t) & 0\end{bmatrix} = \begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}\cos(\omega_1 t) + \begin{bmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{bmatrix}\sin(\omega_1 t) = \mathbf{I}_x \cos(\omega_1 t) + \mathbf{I}_y \sin(\omega_1 t)$$

- Precession of *y*-magnetization (rotation about *z*-axis)

$$\hat{\mathbf{R}}_z \mathbf{I}_y \hat{\mathbf{R}}_z^{-1} = \begin{bmatrix}\cos(\omega_1 t/2) - \mathrm{i}\sin(\omega_1 t/2) & 0\\ 0 & \cos(\omega_1 t/2) + \mathrm{i}\sin(\omega_1 t/2)\end{bmatrix}\begin{bmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{bmatrix}\begin{bmatrix}\cos(\omega_1 t/2) + \mathrm{i}\sin(\omega_1 t/2) & 0\\ 0 & \cos(\omega_1 t/2) - \mathrm{i}\sin(\omega_1 t/2)\end{bmatrix}$$

$$= \begin{bmatrix}\cos(\omega_1 t/2) - \mathrm{i}\sin(\omega_1 t/2) & 0\\ 0 & \cos(\omega_1 t/2) + \mathrm{i}\sin(\omega_1 t/2)\end{bmatrix}\begin{bmatrix}0 & -\mathrm{i}\cos(\omega_1 t/2) - \sin(\omega_1 t/2)\\ \mathrm{i}\cos(\omega_1 t/2) - \sin(\omega_1 t/2) & 0\end{bmatrix} = \begin{bmatrix}0 & -\mathrm{i}\cos^2(\omega_1 t/2) - 2\sin(\omega_1 t/2)\cos(\omega_1 t/2) + \mathrm{i}\sin^2(\omega_1 t/2)\\ \mathrm{i}\cos^2(\omega_1 t/2) - 2\sin(\omega_1 t/2)\cos(\omega_1 t/2) - \mathrm{i}\sin^2(\omega_1 t/2) & 0\end{bmatrix}$$

$$= \begin{bmatrix}0 & -\mathrm{i}\cos(\omega_1 t) - \sin(\omega_1 t)\\ \mathrm{i}\cos(\omega_1 t) - \sin(\omega_1 t) & 0\end{bmatrix} = \begin{bmatrix}0 & -\mathrm{i}\cos(\omega_1 t)\\ \mathrm{i}\cos(\omega_1 t & 0\end{bmatrix} + \begin{bmatrix}0 & \sin(\omega_1 t)\\ \sin(\omega_1 t) & 0\end{bmatrix} = \begin{bmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{bmatrix}\cos(\omega_1 t) - \begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}\sin(\omega_1 t) = \mathbf{I}_y \cos(\omega_1 t) - \mathbf{I}_x \sin(\omega_1 t)$$

Product Operators for Two Spin Case

- We demonstrated earlier construction of operators in matrix form for two-spin systems
  - the example here is for the $\boldsymbol{I}_x$ operator on the A spin in an AX system in the two-spin basis

$$\begin{array}{c|cccc} & \alpha\alpha & \alpha\beta & \beta\alpha & \beta\beta \\ \hline \alpha\alpha & & & & \\ \alpha\beta & & & & \\ \beta\alpha & & & & \\ \beta\beta & & & & \end{array}\quad \begin{bmatrix} \langle\alpha\alpha|\hat{\boldsymbol{I}}_{\mathrm{A}x}|\alpha\alpha\rangle & \langle\alpha\alpha|\hat{\boldsymbol{I}}_{\mathrm{A}x}|\alpha\beta\rangle & \langle\alpha\alpha|\hat{\boldsymbol{I}}_{\mathrm{A}x}|\beta\alpha\rangle & \langle\alpha\alpha|\hat{\boldsymbol{I}}_{\mathrm{A}x}|\beta\beta\rangle \\ \langle\alpha\beta|\hat{\boldsymbol{I}}_{\mathrm{A}x}|\alpha\alpha\rangle & \langle\alpha\beta|\hat{\boldsymbol{I}}_{\mathrm{A}x}|\alpha\beta\rangle & \langle\alpha\beta|\hat{\boldsymbol{I}}_{\mathrm{A}x}|\beta\alpha\rangle & \langle\alpha\beta|\hat{\boldsymbol{I}}_{\mathrm{A}x}|\beta\beta\rangle \\ \langle\beta\alpha|\hat{\boldsymbol{I}}_{\mathrm{A}x}|\alpha\alpha\rangle & \langle\beta\alpha|\hat{\boldsymbol{I}}_{\mathrm{A}x}|\alpha\beta\rangle & \langle\beta\alpha|\hat{\boldsymbol{I}}_{\mathrm{A}x}|\beta\alpha\rangle & \langle\beta\alpha|\hat{\boldsymbol{I}}_{\mathrm{A}x}|\beta\beta\rangle \\ \langle\beta\beta|\hat{\boldsymbol{I}}_{\mathrm{A}x}|\alpha\alpha\rangle & \langle\beta\beta|\hat{\boldsymbol{I}}_{\mathrm{A}x}|\alpha\beta\rangle & \langle\beta\beta|\hat{\boldsymbol{I}}_{\mathrm{A}x}|\beta\alpha\rangle & \langle\beta\beta|\hat{\boldsymbol{I}}_{\mathrm{A}x}|\beta\beta\rangle \end{bmatrix}$$

(recall $\hat{\boldsymbol{I}}_x|\alpha\rangle = 1/2\,\beta \quad \hat{\boldsymbol{I}}_x|\beta\rangle = 1/2\,\alpha \quad \hat{\boldsymbol{I}}_y|\alpha\rangle = 1/2\,\mathrm{i}\beta \quad \hat{\boldsymbol{I}}_y|\beta\rangle = -1/2\,\mathrm{i}\alpha \quad \hat{\boldsymbol{I}}_z|\alpha\rangle = 1/2\,\alpha \quad \hat{\boldsymbol{I}}_z|\beta\rangle = -1/2\,\beta$)

$$\hat{\boldsymbol{I}}_{\mathrm{A}x} = \begin{bmatrix} 1/2\langle\alpha\alpha|\beta\alpha\rangle & 1/2\langle\alpha\alpha|\beta\beta\rangle & 1/2\langle\alpha\alpha|\alpha\alpha\rangle & 1/2\langle\alpha\alpha|\alpha\beta\rangle \\ 1/2\langle\alpha\beta|\beta\alpha\rangle & 1/2\langle\alpha\beta|\beta\beta\rangle & 1/2\langle\alpha\beta|\alpha\alpha\rangle & 1/2\langle\alpha\beta|\alpha\beta\rangle \\ 1/2\langle\beta\alpha|\beta\alpha\rangle & 1/2\langle\beta\alpha|\beta\beta\rangle & 1/2\langle\beta\alpha|\alpha\alpha\rangle & 1/2\langle\beta\alpha|\alpha\beta\rangle \\ 1/2\langle\beta\beta|\beta\alpha\rangle & 1/2\langle\beta\beta|\beta\beta\rangle & 1/2\langle\beta\beta|\alpha\alpha\rangle & 1/2\langle\beta\beta|\alpha\beta\rangle \end{bmatrix} = \begin{bmatrix} 0 & 0 & 1/2 & 0 \\ 0 & 0 & 0 & 1/2 \\ 1/2 & 0 & 0 & 0 \\ 0 & 1/2 & 0 & 0 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$

- The matrices for $\boldsymbol{I}_x$, $\boldsymbol{I}_y$, and $\boldsymbol{I}_z$ are

$$\hat{\boldsymbol{I}}_{\mathrm{A}x} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix} \quad \hat{\boldsymbol{I}}_{\mathrm{X}x} = \frac{1}{2}\begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \quad \hat{\boldsymbol{I}}_{\mathrm{Ay}} = \frac{1}{2}\begin{bmatrix} 0 & 0 & -\mathrm{i} & 0 \\ 0 & 0 & 0 & -\mathrm{i} \\ \mathrm{i} & 0 & 0 & 0 \\ 0 & \mathrm{i} & 0 & 0 \end{bmatrix} \quad \hat{\boldsymbol{I}}_{\mathrm{Xy}} = \frac{1}{2}\begin{bmatrix} 0 & -\mathrm{i} & 0 & 0 \\ \mathrm{i} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\mathrm{i} \\ 0 & 0 & \mathrm{i} & 0 \end{bmatrix} \quad \hat{\boldsymbol{I}}_{\mathrm{A}z} = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \quad \hat{\boldsymbol{I}}_{\mathrm{X}z} = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$$

- This process is tedious and not well suited for larger basis sets

Product Operators for Two Spin Case

- A convenient method for constructing matrix forms of operators for two-spin systems uses *direct products* (Kronecker products) of other matrix operators (hence, "product operators")
- The direct product of two matrices is as follows

$$\mathbf{A} = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \quad \mathbf{B} = \begin{bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{bmatrix} \quad \mathbf{A} \otimes \mathbf{B} = \begin{bmatrix} a_{11}\mathbf{B} & a_{12}\mathbf{B} \\ a_{21}\mathbf{B} & a_{22}\mathbf{B} \end{bmatrix} = \begin{bmatrix} a_{11}\begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} & a_{12}\begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} \\ a_{21}\begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} & a_{22}\begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} \end{bmatrix} = \begin{bmatrix} a_{11}b_{11} & a_{11}b_{12} & a_{12}b_{11} & a_{12}b_{12} \\ a_{11}b_{21} & a_{11}b_{22} & a_{12}b_{21} & a_{12}b_{22} \\ a_{21}b_{11} & a_{21}b_{12} & a_{22}b_{11} & a_{22}b_{12} \\ a_{21}b_{21} & a_{21}b_{22} & a_{22}b_{21} & a_{22}b_{22} \end{bmatrix}$$

- for example, we can construct $\mathbf{I}_{1x}$ ($\mathbf{I}_{\mathrm{A}x}$) from $\mathbf{I}_x$ and $\mathbf{E}$ ($\mathbf{I}_x \otimes \mathbf{E}$)

$$1/2\,\mathbf{E} = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \qquad \mathbf{I}_z = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \qquad \mathbf{I}_x = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad \mathbf{I}_y = \frac{1}{2}\begin{bmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{bmatrix}$$

$$\mathbf{I}_{1x} = \mathbf{I}_x \otimes \mathbf{E} = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 0\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} & 1\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \\ 1\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} & 0\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$

Product Operators for Two Spin Case

- The $\mathbf{I}_{1x}$, $\mathbf{I}_{1y}$, and $\mathbf{I}_{1z}$ operators are all constructed this way

$$\mathbf{I}_{1x} = \mathbf{I}_x \otimes \mathbf{E} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix} \qquad \mathbf{I}_{1y} = \mathbf{I}_y \otimes \mathbf{E} = \frac{1}{2}\begin{bmatrix} 0 & 0 & -\mathrm{i} & 0 \\ 0 & 0 & 0 & -\mathrm{i} \\ \mathrm{i} & 0 & 0 & 0 \\ 0 & \mathrm{i} & 0 & 0 \end{bmatrix} \qquad \mathbf{I}_{1z} = \mathbf{I}_z \otimes \mathbf{E} = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$$

- The $\mathbf{I}_{2x}$, $\mathbf{I}_{2y}$, and $\mathbf{I}_{2z}$ operators are constructed as $\mathbf{E}\otimes\mathbf{I}_x$, $\mathbf{E}\otimes\mathbf{I}_x$, $\mathbf{E}\otimes\mathbf{I}_x$
  - for example, we can construct $\mathbf{I}_{2x}$ ($\mathbf{I}_{Xx}$) from and $\mathbf{E}$ and $\mathbf{I}_x$ ($\mathbf{E}\otimes\mathbf{I}_x$)

$$\mathbf{I}_{2x} = \mathbf{E} \otimes \mathbf{I}_x = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 1\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} & 0\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \\ 0\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} & 1\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$$

$$\mathbf{I}_{2x} = \mathbf{E} \otimes \mathbf{I}_x = \frac{1}{2}\begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \qquad \mathbf{I}_{2y} = \mathbf{E} \otimes \mathbf{I}_y = \frac{1}{2}\begin{bmatrix} 0 & -\mathrm{i} & 0 & 0 \\ \mathrm{i} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\mathrm{i} \\ 0 & 0 & \mathrm{i} & 0 \end{bmatrix} \qquad \mathbf{I}_{2z} = \mathbf{E} \otimes \mathbf{I}_z = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$$

Product Operators for Two Spin Case

- Nine operators (**2I**$_{1x}$**I**$_{2x}$, **2I**$_{1x}$**I**$_{2y}$, **2I**$_{1x}$**I**$_{2z}$, **2I**$_{1y}$**I**$_{2x}$, **2I**$_{1y}$**I**$_{2y}$, **2I**$_{1y}$**I**$_{2z}$, **2I**$_{1z}$**I**$_{2x}$, **2I**$_{1z}$**I**$_{2y}$, **2I**$_{1z}$**I**$_{2z}$) are constructed as direct products of **I**$_x$, **I**$_y$, and **I**$_z$
  - for example, we can construct **2I**$_{1y}$**I**$_{2x}$ from **I**$_y$ and **I**$_x$

$$2\mathbf{I}_{1y}\mathbf{I}_{2x} = 2\left\{\mathbf{I}_y \otimes \mathbf{I}_x\right\} = 2\left\{\frac{1}{2}\begin{bmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{bmatrix} \otimes \frac{1}{2}\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}\right\} = \frac{1}{2}\begin{bmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{bmatrix} \otimes \begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix} = \frac{1}{2}\begin{bmatrix}0\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix} & -\mathrm{i}\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}\\ \mathrm{i}\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix} & 0\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}\end{bmatrix} = \frac{1}{2}\begin{bmatrix}0 & 0 & 0 & -\mathrm{i}\\ 0 & 0 & -\mathrm{i} & 0\\ 0 & \mathrm{i} & 0 & 0\\ \mathrm{i} & 0 & 0 & 0\end{bmatrix}$$

$$2\mathbf{I}_{1x}\mathbf{I}_{2x} = 2\left\{\mathbf{I}_x \otimes \mathbf{I}_x\right\} = \frac{1}{2}\begin{bmatrix}0 & 0 & 0 & 1\\ 0 & 0 & 1 & 0\\ 0 & 1 & 0 & 0\\ 1 & 0 & 0 & 0\end{bmatrix} \quad 2\mathbf{I}_{1x}\mathbf{I}_{2y} = 2\left\{\mathbf{I}_x \otimes \mathbf{I}_y\right\} = \frac{1}{2}\begin{bmatrix}0 & 0 & 0 & -\mathrm{i}\\ 0 & 0 & \mathrm{i} & 0\\ 0 & -\mathrm{i} & 0 & 0\\ \mathrm{i} & 0 & 0 & 0\end{bmatrix} \quad 2\mathbf{I}_{1x}\mathbf{I}_{2z} = 2\left\{\mathbf{I}_x \otimes \mathbf{I}_z\right\} = \frac{1}{2}\begin{bmatrix}0 & 0 & 1 & 0\\ 0 & 0 & 0 & -1\\ 1 & 0 & 0 & 0\\ 0 & -1 & 0 & 0\end{bmatrix}$$

$$2\mathbf{I}_{1y}\mathbf{I}_{2x} = 2\left\{\mathbf{I}_y \otimes \mathbf{I}_x\right\} = \frac{1}{2}\begin{bmatrix}0 & 0 & 0 & -\mathrm{i}\\ 0 & 0 & -\mathrm{i} & 0\\ 0 & \mathrm{i} & 0 & 0\\ \mathrm{i} & 0 & 0 & 0\end{bmatrix} \quad 2\mathbf{I}_{1y}\mathbf{I}_{2y} = 2\left\{\mathbf{I}_y \otimes \mathbf{I}_y\right\} = \frac{1}{2}\begin{bmatrix}0 & 0 & 0 & -1\\ 0 & 0 & 1 & 0\\ 0 & 1 & 0 & 0\\ -1 & 0 & 0 & 0\end{bmatrix} \quad 2\mathbf{I}_{1y}\mathbf{I}_{2z} = 2\left\{\mathbf{I}_y \otimes \mathbf{I}_z\right\} = \frac{1}{2}\begin{bmatrix}0 & 0 & -\mathrm{i} & 0\\ 0 & 0 & 0 & \mathrm{i}\\ \mathrm{i} & 0 & 0 & 0\\ 0 & -\mathrm{i} & 0 & 0\end{bmatrix}$$

$$2\mathbf{I}_{1z}\mathbf{I}_{2x} = 2\left\{\mathbf{I}_z \otimes \mathbf{I}_x\right\} = \frac{1}{2}\begin{bmatrix}0 & 1 & 0 & 0\\ 1 & 0 & 0 & 0\\ 0 & 0 & 0 & -1\\ 0 & 0 & -1 & 0\end{bmatrix} \quad 2\mathbf{I}_{1z}\mathbf{I}_{2y} = 2\left\{\mathbf{I}_z \otimes \mathbf{I}_y\right\} = \frac{1}{2}\begin{bmatrix}0 & -\mathrm{i} & 0 & 0\\ \mathrm{i} & 0 & 0 & 0\\ 0 & 0 & 0 & \mathrm{i}\\ 0 & 0 & -\mathrm{i} & 0\end{bmatrix} \quad 2\mathbf{I}_{1z}\mathbf{I}_{2z} = 2\left\{\mathbf{I}_z \otimes \mathbf{I}_z\right\} = \frac{1}{2}\begin{bmatrix}1 & 0 & 0 & 0\\ 0 & -1 & 0 & 0\\ 0 & 0 & -1 & 0\\ 0 & 0 & 0 & 1\end{bmatrix}$$

Product Operators for Two Spin Case

$$1/2\,\mathbf{E} = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

identity matrix:
AE=A

$$\mathbf{I}_{1z} = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \quad \mathbf{I}_{2z} = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$$

z-magnetization

$$\mathbf{I}_{1x} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix} \quad \mathbf{I}_{1y} = \frac{1}{2}\begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{bmatrix} \quad \mathbf{I}_{2x} = \frac{1}{2}\begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \quad \mathbf{I}_{2y} = \frac{1}{2}\begin{bmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{bmatrix}$$

in-phase *x*- and *y*-magnetization

$$2\mathbf{I}_{1x}\mathbf{I}_{2z} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix} \quad 2\mathbf{I}_{1y}\mathbf{I}_{2z} = \frac{1}{2}\begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & i \\ i & 0 & 0 & 0 \\ 0 & -i & 0 & 0 \end{bmatrix} \quad 2\mathbf{I}_{1z}\mathbf{I}_{2x} = \frac{1}{2}\begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{bmatrix} \quad 2\mathbf{I}_{1z}\mathbf{I}_{2y} = \frac{1}{2}\begin{bmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & i \\ 0 & 0 & -i & 0 \end{bmatrix}$$

anti-phase *x*- and
y-magnetization

$$2\mathbf{I}_{1x}\mathbf{I}_{2x} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} \quad 2\mathbf{I}_{1x}\mathbf{I}_{2y} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{bmatrix} \quad 2\mathbf{I}_{1y}\mathbf{I}_{2x} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & -i & 0 \\ 0 & i & 0 & 0 \\ i & 0 & 0 & 0 \end{bmatrix} \quad 2\mathbf{I}_{1y}\mathbf{I}_{2y} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{bmatrix}$$

multiple quantum coherence
(not directly observable)

$$2\mathbf{I}_{1z}\mathbf{I}_{2z} = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

Physical interpretation of Some Product Operators

- Diagonal elements of the density matrix represent populations
- The $\mathbf{I}_{1z}$ and $\mathbf{I}_{2z}$ operators comprise diagonal elements that represent these populations
  - for $\mathbf{I}_{1z}$, the first two diagonal elements represent the population excess for α (1δ) for spin 1, and the second two represent the population deficit for β (-1δ) for spin 1
  - these alternate for spin 2 ($\mathbf{I}_{2z}$)

$$\mathbf{I}_{1z} = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \qquad \begin{bmatrix} \rho_{\alpha\alpha,\alpha\alpha} & \rho_{\alpha\alpha,\alpha\beta} & \rho_{\alpha\alpha,\beta\alpha} & \rho_{\alpha\alpha,\beta\beta} \\ \rho_{\alpha\beta,\alpha\alpha} & \rho_{\alpha\beta,\alpha\beta} & \rho_{\alpha\beta,\beta\alpha} & \rho_{\alpha\beta,\beta\beta} \\ \rho_{\beta\alpha,\alpha\alpha} & \rho_{\beta\alpha,\alpha\beta} & \rho_{\beta\alpha,\beta\alpha} & \rho_{\beta\alpha,\beta\beta} \\ \rho_{\beta\beta,\alpha\alpha} & \rho_{\beta\beta,\alpha\beta} & \rho_{\beta\beta,\beta\alpha} & \rho_{\beta\beta,\beta\beta} \end{bmatrix}$$

$$\begin{bmatrix} \rho_{\alpha\alpha,\alpha\alpha} & \rho_{\alpha\alpha,\alpha\beta} & \rho_{\alpha\alpha,\beta\alpha} & \rho_{\alpha\alpha,\beta\beta} \\ \rho_{\alpha\beta,\alpha\alpha} & \rho_{\alpha\beta,\alpha\beta} & \rho_{\alpha\beta,\beta\alpha} & \rho_{\alpha\beta,\beta\beta} \\ \rho_{\beta\alpha,\alpha\alpha} & \rho_{\beta\alpha,\alpha\beta} & \rho_{\beta\alpha,\beta\alpha} & \rho_{\beta\alpha,\beta\beta} \\ \rho_{\beta\beta,\alpha\alpha} & \rho_{\beta\beta,\alpha\beta} & \rho_{\beta\beta,\beta\alpha} & \rho_{\beta\beta,\beta\beta} \end{bmatrix} \qquad \mathbf{I}_{2z} = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$$

Physical interpretation of Some Product Operators

- The sum of $\mathbf{I}_{1z}$ and $\mathbf{I}_{2z}$ might be expected to represent the total equilibrium population
  - excess and deficit for $\alpha\alpha\alpha\alpha$ and $\beta\beta\beta\beta$, respectively, and these cancel for $\alpha\beta\alpha\beta$ and $\beta\alpha\beta\alpha$

$$\delta\mathbf{I}_{1z} + \delta\mathbf{I}_{2z} = \frac{1}{2}\delta\begin{bmatrix}1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\\ 0 & 0 & -1 & 0\\ 0 & 0 & 0 & -1\end{bmatrix} + \frac{1}{2}\delta\begin{bmatrix}1 & 0 & 0 & 0\\ 0 & -1 & 0 & 0\\ 0 & 0 & 1 & 0\\ 0 & 0 & 0 & -1\end{bmatrix} = \delta\begin{bmatrix}2 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & -2\end{bmatrix}$$

- $\mathbf{I}_{1x}$ should be proportional to *x*-magnetization (M_x)
  - should be able to calculate the magnitude of *x*-magnetization (for spin 1, for instance) knowing the density matrix representation for x magnetization ($\delta\mathbf{I}_{1x}$) and the operator for x ($\boldsymbol{\mu}_{1x}$)

$$\delta\,\mathbf{I}_{1x} = \delta\frac{1}{2}\begin{bmatrix}0 & 0 & 1 & 0\\ 0 & 0 & 0 & 1\\ 1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\end{bmatrix} \qquad \hat{\boldsymbol{\mu}}_{1x} = \gamma\hbar\hat{\boldsymbol{I}}_{1x} = \gamma\hbar\frac{1}{2}\begin{bmatrix}0 & 0 & 1 & 0\\ 0 & 0 & 0 & 1\\ 1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\end{bmatrix} \qquad \delta = \frac{\gamma\hbar B_0}{2k_BT}$$

$$M_x = N\ \mathrm{Tr}\left\{[\hat{\boldsymbol{\sigma}}_{1x}][\hat{\boldsymbol{\mu}}_{1x}]\right\} = N\ \mathrm{Tr}\left\{\delta\frac{1}{2}\begin{bmatrix}0 & 0 & 1 & 0\\ 0 & 0 & 0 & 1\\ 1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\end{bmatrix}\gamma\hbar\frac{1}{2}\begin{bmatrix}0 & 0 & 1 & 0\\ 0 & 0 & 0 & 1\\ 1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\end{bmatrix}\right\} = N\frac{\delta\gamma\hbar}{4}\mathrm{Tr}\begin{bmatrix}1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\\ 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 1\end{bmatrix} = N\delta\gamma\hbar = \frac{N\gamma^2\hbar^2B_0}{2k_BT}$$

Physical interpretation of Some Product Operators

- We can construct *antiphase* operators, such as $\mathbf{2I}_{1x}\mathbf{I}_{2z}$, by direct products (i.e. $2\{\mathbf{I}_x \otimes \mathbf{I}_z\}$) or by simple products ($\mathbf{I}_{1x}\mathbf{I}_{2z}$)

$$2\mathbf{I}_{1x}\mathbf{I}_{2z} = 2\{\mathbf{I}_x \otimes \mathbf{I}_z\} = 2\left\{\frac{1}{2}\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix} \otimes \frac{1}{2}\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}\right\} = \frac{1}{2}\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix} \otimes \begin{bmatrix}1 & 0\\0 & -1\end{bmatrix} = \frac{1}{2}\begin{bmatrix}0\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix} & 1\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}\\1\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix} & 0\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}\end{bmatrix} = \frac{1}{2}\begin{bmatrix}0 & 0 & 1 & 0\\0 & 0 & 0 & -1\\1 & 0 & 0 & 0\\0 & -1 & 0 & 0\end{bmatrix}$$

$$2\mathbf{I}_{1x}\mathbf{I}_{2z} = 2\,\frac{1}{2}\begin{bmatrix}0 & 0 & 1 & 0\\0 & 0 & 0 & 1\\1 & 0 & 0 & 0\\0 & 1 & 0 & 0\end{bmatrix}\frac{1}{2}\begin{bmatrix}1 & 0 & 0 & 0\\0 & -1 & 0 & 0\\0 & 0 & 1 & 0\\0 & 0 & 0 & -1\end{bmatrix} = \frac{1}{2}\begin{bmatrix}0 & 0 & 1 & 0\\0 & 0 & 0 & -1\\1 & 0 & 0 & 0\\0 & -1 & 0 & 0\end{bmatrix}$$

- How might we interpret $\mathbf{2I}_{1x}\mathbf{I}_{2z}$: compare with $\mathbf{I}_x$
  - remember, off-diagonal elements associated with transverse magnetization/coherences, transitions between α and β states
  - for spin 1, elements 1,3 and 3,1 ( ) in $\mathbf{I}_{1x}$ represent $\alpha \leftrightarrow \beta$ transitions with the second spin in the α state, whereas 2,4 and 4,2 ( ) represent $\alpha \leftrightarrow \beta$ transitions with the second spin in the α state

$$\mathbf{I}_{1x} = \frac{1}{2}\begin{bmatrix}0 & 0 & 1 & 0\\0 & 0 & 0 & \boxed{1}\\1 & 0 & 0 & 0\\0 & \boxed{1} & 0 & 0\end{bmatrix} \quad \begin{bmatrix}\rho_{\alpha\alpha,\alpha\alpha} & \rho_{\alpha\alpha,\alpha\beta} & \rho_{\alpha\alpha,\beta\alpha} & \rho_{\alpha\alpha,\beta\beta}\\\rho_{\alpha\beta,\alpha\alpha} & \rho_{\alpha\beta,\alpha\beta} & \rho_{\alpha\beta,\beta\alpha} & \boxed{\rho_{\alpha\beta,\beta\beta}}\\\rho_{\beta\alpha,\alpha\alpha} & \rho_{\beta\alpha,\alpha\beta} & \rho_{\beta\alpha,\beta\alpha} & \rho_{\beta\alpha,\beta\beta}\\\rho_{\beta\beta,\alpha\alpha} & \boxed{\rho_{\beta\beta,\alpha\beta}} & \rho_{\beta\beta,\beta\alpha} & \rho_{\beta\beta,\beta\beta}\end{bmatrix} \quad 2\mathbf{I}_{1x}\mathbf{I}_{2z} = \frac{1}{2}\begin{bmatrix}0 & 0 & 1 & 0\\0 & 0 & 0 & \boxed{-1}\\1 & 0 & 0 & 0\\0 & \boxed{-1} & 0 & 0\end{bmatrix}$$

Physical interpretation of Some Product Operators

- Same for $\mathbf{2I_{1x}I_{2z}}$
  - for spin 1, elements 1,3 and 3,1 (○) in $\mathbf{2I_{1x}I_{2z}}$ represent $\alpha \leftrightarrow \beta$ transitions with the second spin in the α state, whereas 2,4 and 4,2 (□) represent $\alpha \leftrightarrow \beta$ transitions with the second spin in the α state

$$\mathbf{I}_{1x} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & \boxed{1} \\ 1 & 0 & 0 & 0 \\ 0 & \boxed{1} & 0 & 0 \end{bmatrix} \quad \begin{bmatrix} \rho_{\alpha\alpha,\alpha\alpha} & \rho_{\alpha\alpha,\alpha\beta} & \rho_{\alpha\alpha,\beta\alpha} & \rho_{\alpha\alpha,\beta\beta} \\ \rho_{\alpha\beta,\alpha\alpha} & \rho_{\alpha\beta,\alpha\beta} & \rho_{\alpha\beta,\beta\alpha} & \boxed{\rho_{\alpha\beta,\beta\beta}} \\ \rho_{\beta\alpha,\alpha\alpha} & \rho_{\beta\alpha,\alpha\beta} & \rho_{\beta\alpha,\beta\alpha} & \rho_{\beta\alpha,\beta\beta} \\ \rho_{\beta\beta,\alpha\alpha} & \boxed{\rho_{\beta\beta,\alpha\beta}} & \rho_{\beta\beta,\beta\alpha} & \rho_{\beta\beta,\beta\beta} \end{bmatrix} \quad 2\mathbf{I}_{1x}\mathbf{I}_{2z} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & \boxed{-1} \\ 1 & 0 & 0 & 0 \\ 0 & \boxed{-1} & 0 & 0 \end{bmatrix} \quad 2\mathbf{I}_{1y}\mathbf{I}_{2z} = \frac{1}{2}\begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & i \\ i & 0 & 0 & 0 \\ 0 & -i & 0 & 0 \end{bmatrix}$$

  - for both $\mathbf{I_{1x}}$ and $\mathbf{2I_{1x}I_{2z}}$, these (○ and □) represent the two peaks of a doublet, however, for $\mathbf{2I_{1x}I_{2z}}$, they are opposite in sign
  - peak amplitudes are proportional to these elements, hence, for $\mathbf{2I_{1x}I_{2z}}$, the two peaks of the doublet are opposite in phase (antiphase) to one another

  - same for $\mathbf{I_{1y}}$ and $\mathbf{2I_{1y}I_{2z}}$

Physical interpretation of Some Product Operators

- Elements of four of the basis matrices represent double and zero quantum magnetization
  - the basis matrix $\mathbf{2I}_{1x}\mathbf{I}_{2x}$ is anti-diagonal with values of 1 on the anti-diagonal

$$2\mathbf{I}_{1x}\mathbf{I}_{2x} = 2\left\{\mathbf{I}_x \otimes \mathbf{I}_x\right\} = 2\left\{\frac{1}{2}\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix} \otimes \frac{1}{2}\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}\right\} = \frac{1}{2}\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix} \otimes \begin{bmatrix}0 & 1\\1 & 0\end{bmatrix} = \frac{1}{2}\begin{bmatrix}0\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix} & 1\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}\\ 1\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix} & 0\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}\end{bmatrix} = \frac{1}{2}\begin{bmatrix}0 & 0 & 0 & 1\\0 & 0 & 1 & 0\\0 & 1 & 0 & 0\\1 & 0 & 0 & 0\end{bmatrix}$$

$$2\mathbf{I}_{1x}\mathbf{I}_{2x} = 2\frac{1}{2}\begin{bmatrix}0 & 0 & 1 & 0\\0 & 0 & 0 & 1\\1 & 0 & 0 & 0\\0 & 1 & 0 & 0\end{bmatrix}\frac{1}{2}\begin{bmatrix}0 & 1 & 0 & 0\\1 & 0 & 0 & 0\\0 & 0 & 0 & 1\\0 & 0 & 1 & 0\end{bmatrix} = \frac{1}{2}\begin{bmatrix}0 & 0 & 0 & 1\\0 & 0 & 1 & 0\\0 & 1 & 0 & 0\\1 & 0 & 0 & 0\end{bmatrix} \qquad \mathbf{I}_{1x} = \frac{1}{2}\begin{bmatrix}0 & 0 & 1 & 0\\0 & 0 & 0 & 1\\1 & 0 & 0 & 0\\0 & 1 & 0 & 0\end{bmatrix} \quad \mathbf{I}_{2x} = \frac{1}{2}\begin{bmatrix}0 & 1 & 0 & 0\\1 & 0 & 0 & 0\\0 & 0 & 0 & 1\\0 & 0 & 1 & 0\end{bmatrix}$$

  - anti-diagonal elements associated with zero and double quantum states
  - for both spin 1 and spin 2, elements 1,4 and 4,1 (○) in $2\mathbf{I}_{1x}\mathbf{I}_{2x}$ represent transitions between αα and ββ states (double quantum), whereas elements 2,3 and 3,2 (□) represent transitions between αβ and βα states (zero quantum) (same for $2\mathbf{I}_{1y}\mathbf{I}_{2y}$)

$$2\mathbf{I}_{1x}\mathbf{I}_{2x} = \frac{1}{2}\begin{bmatrix}0 & 0 & 0 & 1\\0 & 0 & \boxed{1} & 0\\0 & \boxed{1} & 0 & 0\\1 & 0 & 0 & 0\end{bmatrix} \qquad \begin{bmatrix}\rho_{\alpha\alpha,\alpha\alpha} & \rho_{\alpha\alpha,\alpha\beta} & \rho_{\alpha\alpha,\beta\alpha} & \rho_{\alpha\alpha,\beta\beta}\\ \rho_{\alpha\beta,\alpha\alpha} & \rho_{\alpha\beta,\alpha\beta} & \boxed{\rho_{\alpha\beta,\beta\alpha}} & \rho_{\alpha\beta,\beta\beta}\\ \rho_{\beta\alpha,\alpha\alpha} & \boxed{\rho_{\beta\alpha,\alpha\beta}} & \rho_{\beta\alpha,\beta\alpha} & \rho_{\beta\alpha,\beta\beta}\\ \rho_{\beta\beta,\alpha\alpha} & \rho_{\beta\beta,\alpha\beta} & \rho_{\beta\beta,\beta\alpha} & \rho_{\beta\beta,\beta\beta}\end{bmatrix} \qquad 2\mathbf{I}_{1y}\mathbf{I}_{2y} = \frac{1}{2}\begin{bmatrix}0 & 0 & 0 & -1\\0 & 0 & \boxed{1} & 0\\0 & \boxed{1} & 0 & 0\\-1 & 0 & 0 & 0\end{bmatrix}$$

Physical interpretation of Some Product Operators

- Zero and double quantum coherences are possible, but not generally observable directly
  - they are not "allowed" for direct detection, but can be detected indirectly (don't induce oscillation in receiver coil, can respond to RF pulses)
  - however, they are "allowed" for other processes, i.e. relaxation (NOE)
  - these are represented by off-diagonal elements, so they do oscillate in the presence of a magnetic field

- Sums/differences of $2\mathbf{I}_{1x}\mathbf{I}_{2x}$ and $2\mathbf{I}_{1y}\mathbf{I}_{2y}$ give pure zero and double quantum matrices

$$2\mathbf{I}_{1x}\mathbf{I}_{2x} + 2\mathbf{I}_{1y}\mathbf{I}_{2y} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} + \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

$$2\mathbf{I}_{1x}\mathbf{I}_{2x} - 2\mathbf{I}_{1y}\mathbf{I}_{2y} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} - \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 2 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 \end{bmatrix}$$

- $2\mathbf{I}_{1x}\mathbf{I}_{2y}$ and $2\mathbf{I}_{1y}\mathbf{I}_{2x}$ are similar, just imaginary components

$$2\mathbf{I}_{1x}\mathbf{I}_{2y} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & -\mathrm{i} \\ 0 & 0 & \mathrm{i} & 0 \\ 0 & -\mathrm{i} & 0 & 0 \\ \mathrm{i} & 0 & 0 & 0 \end{bmatrix} \qquad 2\mathbf{I}_{1y}\mathbf{I}_{2x} = \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & -\mathrm{i} \\ 0 & 0 & -\mathrm{i} & 0 \\ 0 & \mathrm{i} & 0 & 0 \\ \mathrm{i} & 0 & 0 & 0 \end{bmatrix}$$

Wavefunctions in the Product Basis

- Like the product operators themselves, the wavefunctions for the product, 2-spin basis can be written as matrices (vectors)
- These are constructed as direct products of the single spin wavefunctions
  - recall

$$\left|\alpha\right\rangle = \begin{bmatrix}1\\0\end{bmatrix} \quad \left|\beta\right\rangle = \begin{bmatrix}0\\1\end{bmatrix} \quad \left\langle\alpha\right| = [1 \;\; 0] \quad \left\langle\beta\right| = [0 \;\; 1] \quad \hat{\boldsymbol{I}}_x\left|\alpha\right\rangle = 1/2\,\beta \quad \hat{\boldsymbol{I}}_z\left|\beta\right\rangle = -1/2\,\beta$$

  - the wavefunctions are

$$\left|\alpha\alpha\right\rangle = \begin{bmatrix}1\\0\end{bmatrix} \otimes \begin{bmatrix}1\\0\end{bmatrix} = \begin{bmatrix}1\begin{pmatrix}1\\0\end{pmatrix}\\0\begin{pmatrix}1\\0\end{pmatrix}\end{bmatrix} = \begin{bmatrix}1\\0\\0\\0\end{bmatrix} \quad \left|\alpha\beta\right\rangle = \begin{bmatrix}1\\0\end{bmatrix} \otimes \begin{bmatrix}0\\1\end{bmatrix} = \begin{bmatrix}1\begin{pmatrix}0\\1\end{pmatrix}\\0\begin{pmatrix}0\\1\end{pmatrix}\end{bmatrix} = \begin{bmatrix}0\\1\\0\\0\end{bmatrix} \quad \left|\beta\alpha\right\rangle = \begin{bmatrix}0\\1\end{bmatrix} \otimes \begin{bmatrix}1\\0\end{bmatrix} = \begin{bmatrix}0\\0\\1\\0\end{bmatrix} \quad \left|\beta\beta\right\rangle = \begin{bmatrix}0\\1\end{bmatrix} \otimes \begin{bmatrix}0\\1\end{bmatrix} = \begin{bmatrix}0\\0\\0\\1\end{bmatrix}$$

- Operating on wavefunctions in the vector form with product operators return the expected results

$$2\mathbf{I}_{1x}\mathbf{I}_{2z}\left|\alpha\beta\right\rangle = \frac{1}{2}\begin{bmatrix}0 & 0 & 1 & 0\\0 & 0 & 0 & -1\\1 & 0 & 0 & 0\\0 & -1 & 0 & 0\end{bmatrix}\begin{bmatrix}0\\1\\0\\0\end{bmatrix} = \frac{1}{2}\begin{bmatrix}0\\0\\0\\-1\end{bmatrix} = -\frac{1}{2}\begin{bmatrix}0\\0\\0\\1\end{bmatrix} = -\frac{1}{2}\left|\beta\beta\right\rangle \qquad 2\mathbf{I}_{1x}\mathbf{I}_{2z}\left|\alpha\beta\right\rangle = -2\frac{1}{2}\frac{1}{2}\left|\beta\beta\right\rangle = -\frac{1}{2}\left|\beta\beta\right\rangle$$

Transformation properties come from rotation operators

- We've examined how rotation operators operate on equilibrium (z) magnetization and transverse magnetization
  - rotation about *x* (*x* pulse) promotes oscillation of *z*- and *y*-magnetization

$$\hat{\mathbf{R}}_x \mathbf{I}_z \hat{\mathbf{R}}_x^{-1} = \mathbf{I}_z \cos(\omega_1 t) - \mathbf{I}_y \sin(\omega_1 t) \qquad \hat{\boldsymbol{H}} t = \omega_1 t \mathbf{I}_x \equiv \alpha \mathbf{I}_x$$

  - rotation about *y* (*y* pulse) promotes oscillation of *z*- and *x*-magnetization

$$\hat{\mathbf{R}}_y \mathbf{I}_z \hat{\mathbf{R}}_y^{-1} = \mathbf{I}_z \cos(\omega_1 t) + \mathbf{I}_x \sin(\omega_1 t) \qquad \hat{\boldsymbol{H}} t = \omega_1 t \mathbf{I}_y \equiv \alpha \mathbf{I}_y$$

  - precession of *x*-magnetization (rotation about *z*-axis)

$$\hat{\mathbf{R}}_z \mathbf{I}_x \hat{\mathbf{R}}_z^{-1} = \mathbf{I}_x \cos(\Delta\omega t) + \mathbf{I}_y \sin(\Delta\omega t) \qquad \hat{\boldsymbol{H}}_z = \Delta\omega \mathbf{I}_z \equiv \Omega \mathbf{I}_z$$

  - precession of *y*-magnetization (rotation about *z*-axis)

$$\hat{\mathbf{R}}_z \mathbf{I}_y \hat{\mathbf{R}}_z^{-1} = \mathbf{I}_y \cos(\Delta\omega t) - \mathbf{I}_x \sin(\Delta\omega t) \qquad \hat{\boldsymbol{H}}_z = \Delta\omega \mathbf{I}_z \equiv \Omega \mathbf{I}_z$$

- We can likewise write descriptions for *J* coupling
  - for instance, effect of *J* coupling for *x*-magnetization (spin 1, $\mathbf{I}_{1x}$)

$$\mathbf{I}_{1x} \xrightarrow{2\pi J_{1,2} \mathbf{I}_{1z} \mathbf{I}_{2z} t} \mathbf{I}_{1x} \cos(\pi J_{1,2} t) + \mathbf{2I}_{1y} \mathbf{I}_{2z} \sin(\pi J_{1,2} t) \qquad \hat{\boldsymbol{H}} = 2\pi J_{1,2} \mathbf{I}_{1z} \mathbf{I}_{2z}$$

Simple Operations for Spin System Evolution

- The product operator formalism allows the evolution of a spin system (pulses, delays, coupling) to be followed using the very simple rules described by the rotation operators (and others based on established relationships)

  - pulses

$$\mathbf{I}_x \xrightarrow{\alpha \mathbf{I}x} \mathbf{I}_x$$

result of an x-pulse ($\mathbf{R}_x$, $\hat{H}t=\omega_1 t\mathbf{I}_x$) of an arbitrary pulse angle ($\alpha=\omega_1 t$) on x magnetization ($\mathbf{I}_x$ product operator)

$$\mathbf{I}_y \xrightarrow{\alpha \mathbf{I}x} \mathbf{I}_y \cos(\omega_1 t) + \mathbf{I}_z \sin(\omega_1 t)$$

result of an x-pulse ($\mathbf{R}_x$, $\hat{H}t=\omega_1 t\mathbf{I}_x$) of an arbitrary pulse angle ($\alpha=\omega_1 t$) on y magnetization ($\mathbf{I}_y$ product operator)

$$\mathbf{I}_z \xrightarrow{\alpha \mathbf{I}x} \mathbf{I}_z \cos(\omega_1 t) - \mathbf{I}_y \sin(\omega_1 t)$$

result of an x-pulse ($\mathbf{R}_x$, $\hat{H}t=\omega_1 t\mathbf{I}_x$) of an arbitrary pulse angle ($\alpha=\omega_1 t$) on z magnetization ($\mathbf{I}_z$ product operator)

$$\mathbf{I}_x \xrightarrow{\alpha \mathbf{I}y} \mathbf{I}_x \cos(\omega_1 t) - \mathbf{I}_z \sin(\omega_1 t)$$

result of a y-pulse ($\mathbf{R}_y$, $\hat{H}t=\omega_1 t\mathbf{I}_y$) of an arbitrary pulse angle ($\alpha=\omega_1 t$) on x magnetization ($\mathbf{I}_x$ product operator)

$$\mathbf{I}_y \xrightarrow{\alpha \mathbf{I}y} \mathbf{I}_y$$

result of a y-pulse ($\mathbf{R}_y$, $\hat{H}t=\omega_1 t\mathbf{I}_y$) of an arbitrary pulse angle ($\alpha=\omega_1 t$) on y magnetization ($\mathbf{I}_y$ product operator)

$$\mathbf{I}_z \xrightarrow{\alpha \mathbf{I}y} \mathbf{I}_y \cos(\omega_1 t) + \mathbf{I}_x \sin(\omega_1 t)$$

result of a y-pulse ($\mathbf{R}_y$, $\hat{H}t=\omega_1 t\mathbf{I}_y$) of an arbitrary pulse angle ($\alpha=\omega_1 t$) on z magnetization ($\mathbf{I}_z$ product operator)

  - precession in the transverse plane

$$\mathbf{I}_x \xrightarrow{\Omega \mathbf{I}zt} \mathbf{I}_x \cos(\Delta\omega t) + \mathbf{I}_y \sin(\Delta\omega t)$$

rotation about z ($\mathbf{R}_z$, $\hat{H}_z=\Delta\omega\mathbf{I}_z$) at the rotating frame Larmor frequency($\Omega=\Delta\omega$) of x magnetization ($\mathbf{I}_x$ product operator)

$$\mathbf{I}_y \xrightarrow{\Omega \mathbf{I}zt} \mathbf{I}_y \cos(\Delta\omega t) - \mathbf{I}_x \sin(\Delta\omega t)$$

rotation about z ($\mathbf{R}_z$, $\hat{H}_z=\Delta\omega\mathbf{I}_z$) at the rotating frame Larmor frequency($\Omega=\Delta\omega$) of y magnetization ($\mathbf{I}_y$ product operator)

$$\mathbf{I}_z \xrightarrow{\Omega \mathbf{I}zt} \mathbf{I}_z$$

rotation about z ($\mathbf{R}_z$, $\hat{H}_z=\Delta\omega\mathbf{I}_z$) at the rotating frame Larmor frequency($\Omega=\Delta\omega$) of z magnetization ($\mathbf{I}_z$ product operator)

Simple Operations for Spin System Evolution

- Scalar coupling

  - single-spin operators evolve into two-spin operators

$$\mathbf{I}_{1x} \xrightarrow{2\pi J_{1,2}\mathbf{I}_{1z}\mathbf{I}_{2z}t} \mathbf{I}_{1x}\cos(\pi J_{1,2}t) + \mathbf{2I}_{1y}\mathbf{I}_{2z}\sin(\pi J_{1,2}t)$$

result of scalar coupling ($\hat{\boldsymbol{H}}t$=2π$J_{1,2}\mathbf{I}_{1z}\mathbf{I}_{2z}$) between spins 1 and 2 on *x*-magnetization of spin 1 ($\mathbf{I}_{1x}$ product operator)

$$\mathbf{I}_{1y} \xrightarrow{2\pi J_{1,2}\mathbf{I}_{1z}\mathbf{I}_{2z}t} \mathbf{I}_{1y}\cos(\pi J_{1,2}t) - \mathbf{2I}_{1x}\mathbf{I}_{2z}\sin(\pi J_{1,2}t)$$

result of scalar coupling ($\hat{\boldsymbol{H}}t$=2π$J_{1,2}\mathbf{I}_{1z}\mathbf{I}_{2z}$) between spins 1 and 2 on *x*-magnetization ($\mathbf{I}_{1y}$ product operator)

$$\mathbf{I}_{1z} \xrightarrow{2\pi J_{1,2}\mathbf{I}_{1z}\mathbf{I}_{2z}t} \mathbf{I}_{1z}$$

result of scalar coupling ($\hat{\boldsymbol{H}}t$=2π$J_{1,2}\mathbf{I}_{1z}\mathbf{I}_{2z}$) between spins 1 and 2 on *z*-magnetization ($\mathbf{I}_{1z}$ product operator)

  - two-spin operators evolve into single-spin operators

$$\mathbf{2I}_{1x}\mathbf{I}_{2z} \xrightarrow{2\pi J_{1,2}\mathbf{I}_{1z}\mathbf{I}_{2z}t} \mathbf{2I}_{1x}\mathbf{I}_{2z}\cos(\pi J_{1,2}t) + \mathbf{I}_{1y}\sin(\pi J_{1,2}t)$$

result of scalar coupling ($\hat{\boldsymbol{H}}t$=2π$J_{1,2}\mathbf{I}_{1z}\mathbf{I}_{2z}$) between spins 1 and 2 on antiphase *x*-magnetization of spin 1 ($\mathbf{2I}_{1x}\mathbf{I}_{2z}$ product operator)

$$\mathbf{2I}_{1y}\mathbf{I}_{2z} \xrightarrow{2\pi J_{1,2}\mathbf{I}_{1z}\mathbf{I}_{2z}t} \mathbf{2I}_{1y}\mathbf{I}_{2z}\cos(\pi J_{1,2}t) - \mathbf{I}_{1x}\sin(\pi J_{1,2}t)$$

result of scalar coupling ($\hat{\boldsymbol{H}}t$=2π$J_{1,2}\mathbf{I}_{1z}\mathbf{I}_{2z}$) between spins 1 and 2 on antiphase *y*-magnetization of spin 1 ($\mathbf{2I}_{1y}\mathbf{I}_{2z}$ product operator)

$$\mathbf{2I}_{1z}\mathbf{I}_{2z} \xrightarrow{2\pi J_{1,2}\mathbf{I}_{1z}\mathbf{I}_{2z}t} \mathbf{2I}_{1z}\mathbf{I}_{2z}$$

result of scalar coupling ($\hat{\boldsymbol{H}}t$=2π$J_{1,2}\mathbf{I}_{1z}\mathbf{I}_{2z}$) between spins 1 and 2 on $\mathbf{2I}_{1z}\mathbf{I}_{2z}$ product operator)

Transformations Caused by Various Evolution Operators

- table is for first-order systems

- if the operation leaves the operator unchanged, the original operator is listed as the result (no sine or cosine weighting)

- if the result is different than the operator, then the operator is cosine weighted, and the result sine weighted

-missing values indicate results with four terms (too many to fit in the table, see below)

-results in parentheses indicate results with four terms (too many to fit in the table), but, if evaluated for $\omega_1 t=\pi/2$ (pulses), the result is the entry in the table (in parenthesis)

product operator cos	$\mathbf{R}_x$ I1x + I2x $\sin(\omega_1 t)$	$\mathbf{R}_y$ I1y + I2y $\sin(\omega_1 t)$	precession I1z + I2z $\sin(\Omega t)$	*J* coupling 2 I1zI2z $\sin(\pi J t)$
½ E	½ E	½ E	½ E	½ E
I1z	-I1y	I1x	I1z	I1z
I2z	-I2y	I2x	I2z	I2z
2 I1zI2z	(2 I1yI2y)	(2 I1xI2x)	2 I1zI2z	2 I1zI2x
I1x	I1x	-I1z	I1y	2 I1yI2z
I1y	I1z	I1y	-I1x	-2 I1xI2z
I2x	I2x	-I2z	I2y	2I1zI2y
I2y	I2z	I2y	-I2x	-2 I1zI2x
2 I1xI2z	-2 I1xI2y	(-2 I1zI2x)	2 I1yI2z	I1y
2 I1yI2z	(-2 I1zI2y)	2 I1yI2x	-2 I1xI2z	-I1x
2 I1zI2x	-2 I1yI2x	(-2 I1xI2z)	2 I1zI2y	I2y
2 I1zI2y	(-2 I1yI2z)	2 I1xI2y	-2 I1zI2x	-I2x
2 I1xI2x	2 I1xI2x	(2 I1zI2z)	---	2 I1xI2x
2 I1yI2x	2 I1zI2x	-2 I1yI2z	---	2 I1yI2x
2 I1xI2y	2 I1xI2z	-2 I1zI2y	---	2 I1xI2y
2 I1yI2y	(2 I1zI2z)	2 I1yI2y	---	2 I1yI2y

$$2\mathbf{I}_{1x}\mathbf{I}_{2x} \xrightarrow{\Omega_1 \mathbf{I}z t \Omega_2 \mathbf{I}z t} 2\mathbf{I}_{1x}\mathbf{I}_{2x}\cos(\Omega_1 t)\cos(\Omega_2 t) + 2\mathbf{I}_{1y}\mathbf{I}_{2x}\sin(\Omega_1 t)\cos(\Omega_2 t) + 2\mathbf{I}_{1x}\mathbf{I}_{2y}\cos(\Omega_1 t)\sin(\Omega_2 t) + 2\mathbf{I}_{1y}\mathbf{I}_{2y}\sin(\Omega_1 t)\sin(\Omega_2 t)$$

$$2\mathbf{I}_{1y}\mathbf{I}_{2x} \xrightarrow{\Omega_1 \mathbf{I}z t \Omega_2 \mathbf{I}z t} 2\mathbf{I}_{1y}\mathbf{I}_{2x}\cos(\Omega_1 t)\cos(\Omega_2 t) - 2\mathbf{I}_{1x}\mathbf{I}_{2x}\sin(\Omega_1 t)\cos(\Omega_2 t) + 2\mathbf{I}_{1y}\mathbf{I}_{2y}\cos(\Omega_1 t)\sin(\Omega_2 t) - 2\mathbf{I}_{1x}\mathbf{I}_{2y}\sin(\Omega_1 t)\sin(\Omega_2 t)$$

$$2\mathbf{I}_{1x}\mathbf{I}_{2y} \xrightarrow{\Omega_1 \mathbf{I}z t \Omega_2 \mathbf{I}z t} 2\mathbf{I}_{1x}\mathbf{I}_{2y}\cos(\Omega_1 t)\cos(\Omega_2 t) + 2\mathbf{I}_{1y}\mathbf{I}_{2y}\sin(\Omega_1 t)\cos(\Omega_2 t) - 2\mathbf{I}_{1x}\mathbf{I}_{2x}\cos(\Omega_1 t)\sin(\Omega_2 t) - 2\mathbf{I}_{1y}\mathbf{I}_{2x}\sin(\Omega_1 t)\sin(\Omega_2 t)$$

$$2\mathbf{I}_{1y}\mathbf{I}_{2y} \xrightarrow{\Omega_1 \mathbf{I}z t \Omega_2 \mathbf{I}z t} 2\mathbf{I}_{1y}\mathbf{I}_{2y}\cos(\Omega_1 t)\cos(\Omega_2 t) - 2\mathbf{I}_{1x}\mathbf{I}_{2y}\sin(\Omega_1 t)\cos(\Omega_2 t) - 2\mathbf{I}_{1y}\mathbf{I}_{2x}\cos(\Omega_1 t)\sin(\Omega_2 t) + 2\mathbf{I}_{1x}\mathbf{I}_{2x}\sin(\Omega_1 t)\sin(\Omega_2 t)$$

Example: Spin-Echo

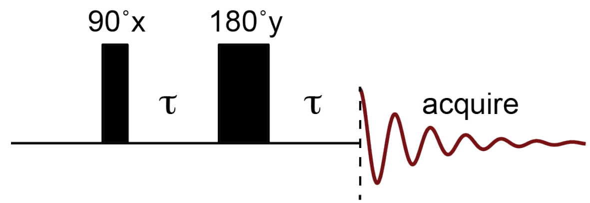
$$\mathbf{I}_z \xrightarrow{\alpha \mathbf{I}x} \mathbf{I}_z\cos(\omega_1 t) - \mathbf{I}_y\sin(\omega_1 t) \qquad \mathbf{I}_y \xrightarrow{\alpha \mathbf{I}x} \mathbf{I}_y\cos(\omega_1 t) + \mathbf{I}_z\sin(\omega_1 t) \qquad \mathbf{I}_x \xrightarrow{\alpha \mathbf{I}y} \mathbf{I}_x\cos(\omega_1 t) - \mathbf{I}_z\sin(\omega_1 t)$$

$$\mathbf{I}_z \xrightarrow{\pi/2\, \mathbf{I}x} -\mathbf{I}_y \qquad \mathbf{I}_y \xrightarrow{\pi \mathbf{I}x} -\mathbf{I}_y \qquad \mathbf{I}_x \xrightarrow{\pi \mathbf{I}y} -\mathbf{I}_x$$

$$\mathbf{I}_x \xrightarrow{\alpha \mathbf{I}x} \mathbf{I}_x \qquad \cos^2(\theta) + \sin^2(\theta) = 1 \qquad \mathbf{I}_y \xrightarrow{\alpha \mathbf{I}y} \mathbf{I}_y$$

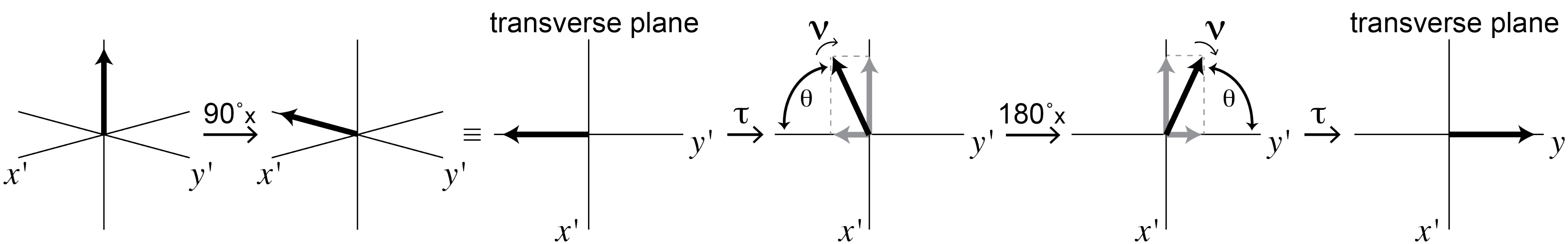
$$\mathbf{I}_y \xrightarrow{\Omega \mathbf{I}zt} \mathbf{I}_y\cos(\Omega t) - \mathbf{I}_x\sin(\Omega t) \qquad \mathbf{I}_x \xrightarrow{\Omega \mathbf{I}zt} \mathbf{I}_x\cos(\Omega t) + \mathbf{I}_y\sin(\Omega t)$$

- Spin-echo: 90° *x* - *t* - 180° *x* - *t*



$$\mathbf{I}_z \xrightarrow{\pi/2\, \mathbf{I}x} -\mathbf{I}_y \xrightarrow{\Omega \mathbf{I}zt} -\mathbf{I}_y\cos(\Omega t) + \mathbf{I}_x\sin(\Omega t) \xrightarrow{\pi \mathbf{I}x} \mathbf{I}_y\cos(\Omega t) + \mathbf{I}_x\sin(\Omega t)$$

$$\mathbf{I}_y\cos(\Omega t) + \mathbf{I}_x\sin(\Omega t) \xrightarrow{\Omega \mathbf{I}zt} \mathbf{I}_y\cos^2(\Omega t) - \mathbf{I}_x\cos(\Omega t)\sin(\Omega t) + \mathbf{I}_x\sin(\Omega t)\cos(\Omega t) + \mathbf{I}_y\sin^2(\Omega t) = \mathbf{I}_y$$



Example: Spin-Echo

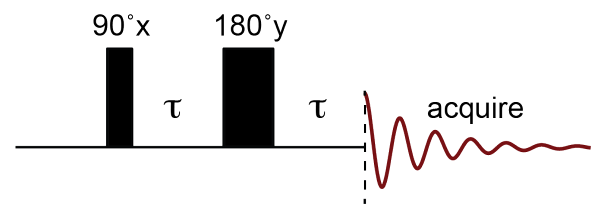
$$\mathbf{I}_z \xrightarrow{\alpha \mathbf{I}x} \mathbf{I}_z\cos(\omega_1 t) - \mathbf{I}_y\sin(\omega_1 t) \qquad \mathbf{I}_y \xrightarrow{\alpha \mathbf{I}x} \mathbf{I}_y\cos(\omega_1 t) + \mathbf{I}_z\sin(\omega_1 t) \qquad \mathbf{I}_x \xrightarrow{\alpha \mathbf{I}y} \mathbf{I}_x\cos(\omega_1 t) - \mathbf{I}_z\sin(\omega_1 t)$$

$$\mathbf{I}_z \xrightarrow{\pi/2\, \mathbf{I}x} -\mathbf{I}_y \qquad \mathbf{I}_y \xrightarrow{\pi \mathbf{I}x} -\mathbf{I}_y \qquad \mathbf{I}_x \xrightarrow{\pi \mathbf{I}y} -\mathbf{I}_x$$

$$\mathbf{I}_x \xrightarrow{\alpha \mathbf{I}x} \mathbf{I}_x \qquad \cos^2(\theta) + \sin^2(\theta) = 1 \qquad \mathbf{I}_y \xrightarrow{\alpha \mathbf{I}y} \mathbf{I}_y$$

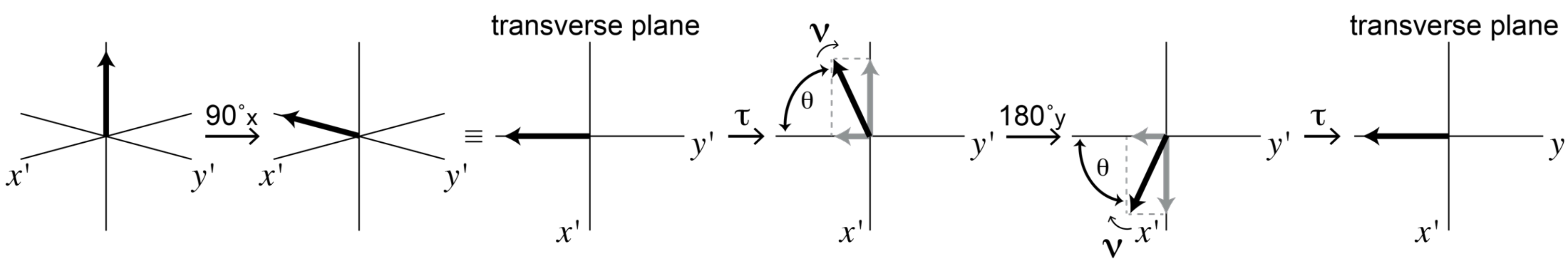
$$\mathbf{I}_y \xrightarrow{\Omega \mathbf{I}zt} \mathbf{I}_y\cos(\Omega t) - \mathbf{I}_x\sin(\Omega t) \qquad \mathbf{I}_x \xrightarrow{\Omega \mathbf{I}zt} \mathbf{I}_x\cos(\Omega t) + \mathbf{I}_y\sin(\Omega t)$$

- Spin-echo: 90° *x* - *t* - 180° *y* - *t*



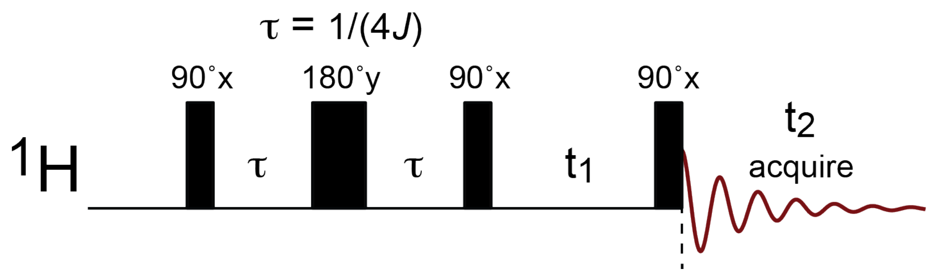
$$\mathbf{I}_z \xrightarrow{\pi/2\, \mathbf{I}x} -\mathbf{I}_y \xrightarrow{\Omega \mathbf{I}zt} -\mathbf{I}_y\cos(\Omega t) + \mathbf{I}_x\sin(\Omega t) \xrightarrow{\pi \mathbf{I}y} -\mathbf{I}_y\cos(\Omega t) - \mathbf{I}_x\sin(\Omega t)$$

$$-\mathbf{I}_y\cos(\Omega t) - \mathbf{I}_x\sin(\Omega t) \xrightarrow{\Omega \mathbf{I}zt} -\mathbf{I}_y\cos^2(\Omega t) + \mathbf{I}_x\cos(\Omega t)\sin(\Omega_1 t) - \mathbf{I}_x\sin(\Omega t)\cos(\Omega t) - \mathbf{I}_y\sin^2(\Omega t) = -\mathbf{I}_y$$



Application of Product Operators: 2D, 2Q Spectrum

- Double quantum coherence can't be detected directly, however, in this "unconventional" example, we'll examine a double quantum spectrum and how two-quantum coherence evolves



- A few things to remember:
  - the spin-echo sequence (τ-180-τ) refocuses chemical shift evolution, so we don't have to consider chemical shift evolution during this period

$$\mathbf{I}_z \xrightarrow{\pi/2\,\mathbf{I}x} -\mathbf{I}_y \xrightarrow{\Omega \mathbf{I}zt \quad \pi \mathbf{I}y \quad \Omega \mathbf{I}zt} -\mathbf{I}_y$$

  - however, the spin-echo does NOT refocus homonuclear coupling
  - for this sequence we'll be considering τ=1/(4*J*), so

$$\cos(2\pi J\tau) = \cos\left(2\pi J\left(1/(4J)\right)\right) = \cos(\pi/2) = 0 \quad \sin(2\pi J\tau) = \sin\left(2\pi J\left(1/(4J)\right)\right) = \sin(\pi/2) = 1$$

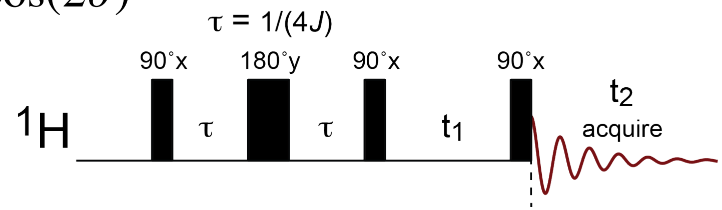
Application of Product Operators: 2D, 2Q Spectrum

$$\mathbf{I}_x \xrightarrow{\pi \mathbf{I}y} -\mathbf{I}_x \quad \mathbf{I}_z \xrightarrow{\pi \mathbf{I}y} -\mathbf{I}_z \qquad 2\mathbf{I}_{1x}\mathbf{I}_{2z} \xrightarrow{2\pi J_{1,2}\mathbf{I}_{1z}\mathbf{I}_{2z}t} 2\mathbf{I}_{1x}\mathbf{I}_{2z}\cos(\pi J_{1,2}t) + \mathbf{I}_{1y}\sin(\pi J_{1,2}t)$$

$$\mathbf{I}_{1y} \xrightarrow{2\pi J_{1,2}\mathbf{I}_{1z}\mathbf{I}_{2z}t} \mathbf{I}_{1y}\cos(\pi J_{1,2}t) - 2\mathbf{I}_{1x}\mathbf{I}_{2z}\sin(\pi J_{1,2}t) \qquad \mathbf{I}_z \xrightarrow{\pi/2\,\mathbf{I}x} -\mathbf{I}_y$$

$$2\sin(\theta)\cos(\theta) = \sin(2\theta) \qquad \cos^2(\theta) - \sin^2(\theta) = \cos(2\theta)$$

- Multiple quantum sequence:



$$\mathbf{I}_{1z} + \mathbf{I}_{2z} \xrightarrow{\pi/2\,\mathbf{I}1x\ \pi/2\,\mathbf{I}2x} -\mathbf{I}_{1y} - \mathbf{I}_{2y} \xrightarrow{2\pi J_{1,2}\mathbf{I}_{1z}\mathbf{I}_{2z}t}$$

$$-\mathbf{I}_{1y}\cos(\pi J_{1,2}\tau) + 2\mathbf{I}_{1x}\mathbf{I}_{2z}\sin(\pi J_{1,2}\tau) - \mathbf{I}_{2y}\cos(\pi J_{1,2}\tau) + 2\mathbf{I}_{1z}\mathbf{I}_{2x}\sin(\pi J_{1,2}\tau)$$

$$\xrightarrow{\pi \mathbf{I}1y\ \pi \mathbf{I}2y} -\mathbf{I}_{1y}\cos(\pi J_{1,2}\tau) + 2\mathbf{I}_{1x}\mathbf{I}_{2z}\sin(\pi J_{1,2}\tau) - \mathbf{I}_{2y}\cos(\pi J_{1,2}\tau) + 2\mathbf{I}_{1z}\mathbf{I}_{2x}\sin(\pi J_{1,2}\tau)$$

$$\xrightarrow{2\pi J_{1,2}\mathbf{I}_{1z}\mathbf{I}_{2z}t} -\mathbf{I}_{1y}\cos^2(\pi J_{1,2}t) + 2\mathbf{I}_{1x}\mathbf{I}_{2z}\cos(\pi J_{1,2}t)\sin(\pi J_{1,2}t) + 2\mathbf{I}_{1x}\mathbf{I}_{2z}\cos(\pi J_{1,2}t)\sin(\pi J_{1,2}t) + \mathbf{I}_{1y}\sin^2(\pi J_{1,2}t)$$

$$-\mathbf{I}_{2y}\cos^2(\pi J_{1,2}\tau) + 2\mathbf{I}_{1z}\mathbf{I}_{2x}\cos(\pi J_{1,2}t)\sin(\pi J_{1,2}\tau) + 2\mathbf{I}_{1z}\mathbf{I}_{2x}\cos(\pi J_{1,2}t)\sin(\pi J_{1,2}\tau) + \mathbf{I}_{2y}\sin^2(\pi J_{1,2}t)$$

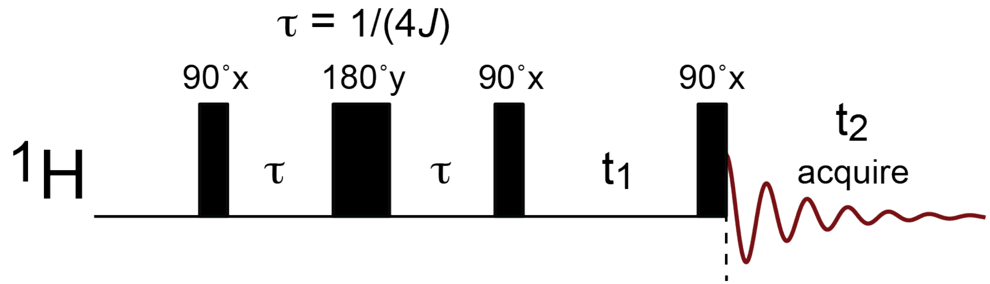
$$= -\mathbf{I}_{1y}\cos(2\pi J_{1,2}t) - \mathbf{I}_{2y}\cos(2\pi J_{1,2}\tau) + 2\mathbf{I}_{1x}\mathbf{I}_{2z}\sin(2\pi J_{1,2}t) + 2\mathbf{I}_{1z}\mathbf{I}_{2x}\sin(2\pi J_{1,2}t) = -0 - 0 + 2\mathbf{I}_{1x}\mathbf{I}_{2z} + 2\mathbf{I}_{1z}\mathbf{I}_{2x}$$

$$2\mathbf{I}_{1x}\mathbf{I}_{2z} + 2\mathbf{I}_{1z}\mathbf{I}_{2x} \xrightarrow{\pi/2\,\mathbf{I}1x\ \pi/2\,\mathbf{I}2x} -2\mathbf{I}_{1x}\mathbf{I}_{2y} - 2\mathbf{I}_{1y}\mathbf{I}_{2x}$$

- so, just after the spin-echo (before the second 90° pulse), we have clean antiphase magnetization, which is converted into multiple quantum magnetization by the second 90° pulse

Application of Product Operators: 2D, 2Q Spectrum

- Evolution during t_1 and detection:



- the $\mathbf{2I_{1x}I_{2y}}$ and $\mathbf{2I_{1y}I_{2x}}$ are terms that are combinations of zero- and two quantum coherence
- during the t_1 period, these terms ($\mathbf{2I_{1x}I_{2y}}$ and $\mathbf{2I_{1y}I_{2x}}$) will oscillate back and forth with others (like $\mathbf{2I_{1x}I_{2x}}$ and the like)

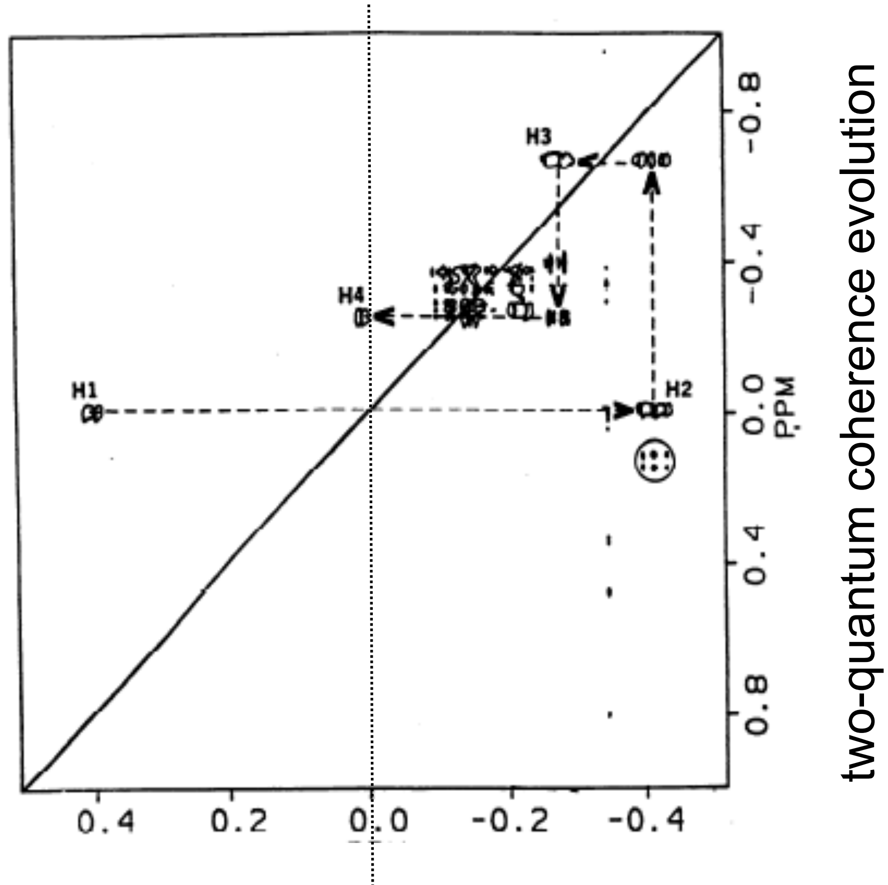
$$-2\mathbf{I}_{1x}\mathbf{I}_{2y} - 2\mathbf{I}_{1y}\mathbf{I}_{2x} \xrightarrow{\Omega_1 \mathbf{I}zt\ \ \Omega_2 \mathbf{I}zt} -2\mathbf{I}_{1x}\mathbf{I}_{2y}\ \ -2\mathbf{I}_{1y}\mathbf{I}_{2x} \ \text{and many others}$$

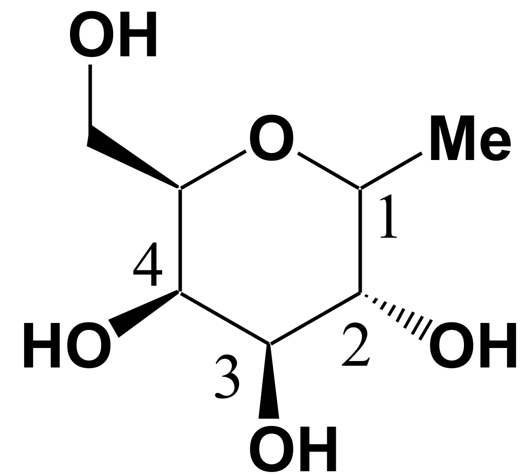
- during the t_1 period, the intensities of these operators are modulated by zero- and two-quantum coherence evolution (as function of time, t_1)

- following the final 90° pulse, these are converted back to single-quantum coherences (transverse anti-phase *x*-magnetization), which are observable (modulated by the frequencies representing the zero- and two-quantum coherences)

$$-2\mathbf{I}_{1x}\mathbf{I}_{2y}\ \ -2\mathbf{I}_{1y}\mathbf{I}_{2x} \xrightarrow{\pi/2\,\mathbf{I}1x\ \ \pi/2\,\mathbf{I}2x} -2\mathbf{I}_{1x}\mathbf{I}_{2z}\ \ -2\mathbf{I}_{1z}\mathbf{I}_{2x} \ \text{and many others}$$

Example: β-Me-Galactose





- 2D spectrum, two-quantum coherences
  - the zero-quantum coherences are filtered out
  - carrier frequency (~center of spectrum) set at 0.0 ppm
  - for coupled peaks, sum of frequencies (*x*-axis) gives shift on *y*-axis (i.e. two-quantum coherences are sums of frequencies of coupled nuclei)
  - information similar to COSY spectrum (cross-peaks are coupled nuclei)