Density Matrix in Product Operator Form

BCMB/CHEM 8190

Product Operators: Connection to Density Matrix Properties

- For small deviations it is convenient to work with a deviation density matrix, $|\sigma| = |\rho| - |E|$ (identity mat)
- $|\sigma|$ is also just a collection of numbers; product operators are specific subsets of these numbers.
- Some subsets are associated with observables; ie. σ_{12}, σ_{21}, σ_{34}, σ_{43}, dictate Mx and My.
- Some sets transform cleanly to other sets under rf pulses; ie. σ_{11}, σ_{22} -> σ_{12}, σ_{21} under a 90°x pulse (actually linear combinations of these)

Expressing σ in a basis set of matrices

- Rationale: collecting elements with common evolution and transformation properties
- $\boldsymbol{\sigma}(t) = \Sigma_s b_s(t) \mathbf{B_S}$
- One option, the cartesian set of spin operators

$\mathbf{B_S} = 2^{(q-1)} \pi_{k=1}^{N} (\mathbf{I_{kv}})^{a(sk)}$

$q = 0 \ldots N$; (# spin operators in product)

$v = x,y,z$; k = nucleus index;

$a(sk) = 1$ for q nuclei, 0 for others ($\mathbf{I^0}$ is identity, $\mathbf{E}$)

Example: a single spin ½ nucleus

- Four element basis set:

  q = 0; ½ **E**

  q = 1; $\mathbf{I_{1X}, I_{1Y}, I_{1Z}}$
- Can represent any density matrix as a linear combination of these (Hemitian; $\boldsymbol{\sigma_{ij} = \sigma_{ij}^*}$; $\boldsymbol{\sigma_{ij}}$ real)

- ½ **E** = $\frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$ $\mathbf{I_Z}$ = $\frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$

- $\mathbf{I_Y}$ = $\frac{1}{2}\begin{bmatrix} 0 & -\mathbf{i} \\ \mathbf{i} & 0 \end{bmatrix}$ $\mathbf{I_X}$ = $\frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$

Representation of some simple density matrices

- What about σ_{eq}?

$$\boldsymbol{\sigma}_{\mathbf{eq}} = \tfrac{1}{2}\begin{bmatrix} \delta & 0 \\ 0 & -\delta \end{bmatrix} = \delta \mathbf{I}_{\mathbf{Z}}$$

- What about σ after a $\pi/2$ pulse on +X axis?

$$\boldsymbol{\sigma}(\pi/2) = \tfrac{1}{2}\begin{bmatrix} 0 & -\delta\mathbf{i} \\ \delta\mathbf{i} & 0 \end{bmatrix} = \delta \mathbf{I}_{\mathbf{Y}}$$

- Note the simple conversion of one product operator (part of a density matrix) to another operator (part of a density matrix) under an rf pulse

Transformation for an arbitrary pulse on X

- $\exp(-i\omega_1 t\ \mathbf{I_X})\ \mathbf{I_Z}\ \exp(i\omega_1 t\ \mathbf{I_X}) = \mathbf{I_Z} \cos(\omega_1 t) - \mathbf{I_Y} \sin(\omega_1 t)$
- Note: $\mathbf{H'} = -\gamma B_1\ \mathbf{I_X}\ t$
- Hence, above $\omega_1 t$ for positive B_1 would be negative. Convention is not to specify direction on axis but to do so implicitly by sign of angle. This makes product operator transformations look opposite of our Bloch equation description.
- A positive 90 degree rotation about X converts $\mathbf{I_Z}$ to – $\mathbf{I_Y}$**;** a 90 degree rotation with field in +X direction converts M_Z to M_Y.

Product Operators for Two Spin Case

- q = 0   ½ **E**
- q = 1 $\mathbf{I}_{1X}$, $\mathbf{I}_{1Y}$, $\mathbf{I}_{1Z}$, $\mathbf{I}_{2X}$, $\mathbf{I}_{2Y}$, $\mathbf{I}_{2Z}$
- q = 2 $2\mathbf{I}_{1X}\mathbf{I}_{2X}$, $2\mathbf{I}_{1X}\mathbf{I}_{2Y}$, $2\mathbf{I}_{1X}\mathbf{I}_{2Z}$,

  $2\mathbf{I}_{1Y}\mathbf{I}_{2X}$, $2\mathbf{I}_{1Y}\mathbf{I}_{2Y}$, $2\mathbf{I}_{1Y}\mathbf{I}_{2Z}$,

  $2\mathbf{I}_{1Z}\mathbf{I}_{2X}$, $2\mathbf{I}_{1Z}\mathbf{I}_{2Y}$, $2\mathbf{I}_{1Z}\mathbf{I}_{2Z}$,
- Note: 16 operators (pieces of σ)

  16 elements in 2 spin (4X4) density matrix

Two-Spin Cartesian Product Operators

Howarth et al., JMR 68, 433-452 (1986)

½ E

$$\frac{1}{2}\begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{vmatrix}$$

I1z

$$\frac{1}{2}\begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{vmatrix}$$

I2z

$$\frac{1}{2}\begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{vmatrix}$$

2 I1zI2z

$$\frac{1}{2}\begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{vmatrix}$$

I1x

$$\frac{1}{2}\begin{vmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{vmatrix}$$

I1y

$$\frac{1}{2}\begin{vmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{vmatrix}$$

2 I1xI2z

$$\frac{1}{2}\begin{vmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{vmatrix}$$

2 I1yI2z

$$\frac{1}{2}\begin{vmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & i \\ i & 0 & 0 & 0 \\ 0 & -i & 0 & 0 \end{vmatrix}$$

Two-Spin Cartesian Product Operators (continued)

I2x

$$\frac{1}{2}\begin{vmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{vmatrix}$$

I2y

$$\frac{1}{2}\begin{vmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{vmatrix}$$

2 I1zI2x

$$\frac{1}{2}\begin{vmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{vmatrix}$$

2 I1zI2y

$$\frac{1}{2}\begin{vmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & i \\ 0 & 0 & -i & 0 \end{vmatrix}$$

2 I1xI2x

$$\frac{1}{2}\begin{vmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{vmatrix}$$

2I1yI2y

$$\frac{1}{2}\begin{vmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{vmatrix}$$

2 I1xI2y

$$\frac{1}{2}\begin{vmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{vmatrix}$$

2 I1yI2x

$$\frac{1}{2}\begin{vmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & -i & 0 \\ 0 & i & 0 & 0 \\ i & 0 & 0 & 0 \end{vmatrix}$$

Physical interpretation of Product Operators

I1z + 12z is proportional to equilibrium population
(basis set order: αα, αβ, βα, αα): $\sigma_{11} = \sigma_{\alpha\alpha\alpha\alpha}$ has excess

$$\delta \tfrac{1}{2} \begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{vmatrix} + \delta \tfrac{1}{2} \begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{vmatrix} = \delta \begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{vmatrix}$$

I1x is obvious; if σ is proportional to Ix, x magnetization exists.
$\overline{Mx} = \text{Tr}\,\{|\,\sigma\,|\,\gamma\,(h/2\pi)\,\delta\,|Ix|\} =$

$$\gamma(h/2\pi)\delta/4\ \text{Tr}\{ \begin{vmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{vmatrix} \begin{vmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{vmatrix} \} = \gamma(h/2\pi)\delta/4\ \text{Tr} \begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{vmatrix}$$

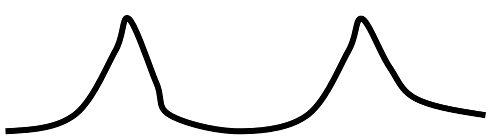
$$= \gamma(h/2\pi)\delta$$

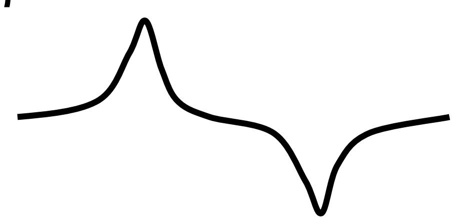
What about 2 I1xI2z?

Note: we can generate 2 I1xI2z from I1x and I2z by multiplication

$$\frac{1}{2}\begin{vmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{vmatrix} \bullet \frac{1}{2}\begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{vmatrix} = \begin{vmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{vmatrix}$$

Result is much like I1x, but with reversal of some signs.
We can associate elements with particular lines; $\sigma_{13} = \sigma_{\alpha\alpha\beta\alpha}$
This is transition of the first spin with second α. $\sigma_{24} = \sigma_{\alpha\beta\beta\beta}$
is a transition of the first with the second spin β: first doublet

| I1x | = 

| 2 I1xI2z | = 

What about $2\mathbf{I}_{1X}\mathbf{I}_{2X}$?

$$2 \bullet \tfrac{1}{2} \bullet \tfrac{1}{2} \bullet \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix} \bullet \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} = \tfrac{1}{2} \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}$$

Two Q, Zero Q

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

- Linear combination of 2 is pure Zero Q or Two Q

  $2\mathbf{I}_{1X}\mathbf{I}_{2X} + 2\mathbf{I}_{1X}\mathbf{I}_{2X}$ = Two Q
- $2\mathbf{I}_{1X}\mathbf{I}_{2y}$, $2\mathbf{I}_{1Y}\mathbf{I}_{2X}$, are imaginary components

Transformation properties come from rotation operators

- X pulse by angle $\omega_1 t = \alpha$

  $\mathbf{I_Z} \ \text{-}(\mathbf{I_X})\rightarrow \ \mathbf{I_Z} \cos(\omega_1 t) - \mathbf{I_Y} \sin(\omega_1 t)$

  $\mathbf{I_Y} \ \text{-}(\mathbf{I_X})\rightarrow \ \mathbf{I_Y} \cos(\omega_1 t) + \mathbf{I_Z} \sin(\omega_1 t)$

  $\mathbf{I_X} \ \text{-}(\mathbf{I_X})\rightarrow \ \mathbf{I_X}$

- Free precession:

  $\mathbf{I_X} \ \text{-}(\Delta\omega \mathbf{I_X})\rightarrow \ \mathbf{I_X} \cos(\Delta\omega t) + \mathbf{I_Y} \sin(\Delta\omega t)$

  $\mathbf{I_X} \ \text{-}(2\pi J \ \mathbf{I_{1Z}} \, \mathbf{I_{2Z}}) \rightarrow \ \mathbf{I_X} \cos(\pi J t) + \mathbf{I_{1Y}} \, \mathbf{I_{2Z}} \sin(\pi J t)$

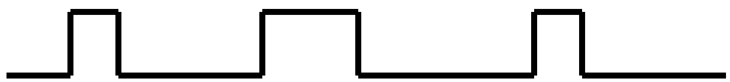
Transformations Caused by Various Evolution Operators

Product Oper.	I1x + I2x	I1y +I2y	I1z +I2z	2 I1zI2z
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	-I1x	I1y	2 I1yI2z
I1y	I1z	I1y	-I1x	-2 I1xI2z
I2x	I2x	-I2x	I2y	2I1zI2x
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

Evolution is to 2, 4( ), or more ---. Coefficient is sin of β, ½ Jt, or ωt.

Application of Product Operators: 2D, 2Q Spectrum

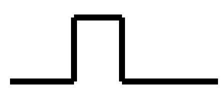
- Can we excite a 2Q coherence? Can we detect it?
- Consider: 90_X $\tau/2$ 180_Y $\tau/2$ 90_X with τ = ¼ J



(removes chem shift)

- $\mathbf{I}_{1Z} + \mathbf{I}_{2Z}$ $-(\mathbf{I}_X+\mathbf{I}_X, 90)\rightarrow$ $-\mathbf{I}_{1Y} - \mathbf{I}_{2Y}$ $-(J\mathbf{I}_{1Z}\mathbf{I}_{2Z}, \tau)\rightarrow$

  $2\mathbf{I}_{1X}\mathbf{I}_{2Z} + 2\mathbf{I}_{1Z}\mathbf{I}_{2X}$ $-(\mathbf{I}_X+\mathbf{I}_X, 90)\rightarrow$ $-2\mathbf{I}_{1X}\mathbf{I}_{2Y} + 2\mathbf{I}_{1Y}\mathbf{I}_{2X}$

  ZQ and 2Q evolution -- also gives $-2\mathbf{I}_{1X}\mathbf{I}_{2X}$ etc
- Consider detection:  90_X
- $2\mathbf{I}_{1X}\mathbf{I}_{2Y}$ $-(\mathbf{I}_X+\mathbf{I}_X, 90)\rightarrow$ $-2\mathbf{I}_{1X}\mathbf{I}_{2Z}$ + others –> 1Q detect

Example: β-Me-Galactose