7/25/00

2 Spin Case Product Operators

$q=0 \qquad \tfrac{1}{2}\tilde{E}$

$q=1 \qquad \tilde{I}_{1x}, \tilde{I}_{1y}, \tilde{I}_{1z}, \tilde{I}_{2x}, \tilde{I}_{2y}, \tilde{I}_{2z}$

$q=2 \qquad 2\tilde{I}_{1x}\tilde{I}_{2x},\ 2\tilde{I}_{1x}\tilde{I}_{2y},\ 2I_{1x}I_{2z}$

$\qquad\qquad 2I_{1y}I_{2x},\ 2I_{1y}I_{2y},\ 2I_{1y}I_{2z}$

$\qquad\qquad 2I_{1z}I_{2x},\ 2I_{1z}I_{2y},\ 2I_{1z}I_{2z}$

note: 16 operators (pieces of σ)
16 elements in 2 spin σ

3

Physical Meaning of Operators

$\tilde{I}_{1x}, \tilde{I}_{2x}$ are obvious. If σ has this form. x magnetization exists:

$$Tr(\tilde{\sigma}\cdot\gamma\hbar\tilde{I}_x) = Tr(\delta\tilde{I}_{x_1}\cdot\gamma\hbar\tilde{I}_{x_1})$$

$$= \delta\gamma\hbar\, Tr\left[\frac{1}{2}\begin{pmatrix}0&0&1&0\\0&0&0&1\\1&0&0&0\\0&1&0&0\end{pmatrix}\frac{1}{2}\begin{pmatrix}0&0&1&0\\0&0&0&1\\1&0&0&0\\0&1&0&0\end{pmatrix}\right]$$

$$= \frac{\delta\gamma\hbar}{4}\, Tr\begin{pmatrix}1&&&0\\&1&&\\&&1&\\0&&&1\end{pmatrix} = \delta\gamma\hbar$$

TABLE 2.2

Product Operators in the Cartesian Basis for a Two-Spin System

$$\frac{1}{2}\mathbf{E} = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \quad I_z = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \quad S_z = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \quad 2I_zS_z = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

$$I_x = \frac{1}{2}\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix} \quad I_y = \frac{1}{2}\begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{bmatrix} \quad 2I_xS_z = \frac{1}{2}\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix} \quad 2I_yS_z = \frac{1}{2}\begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & i \\ i & 0 & 0 & 0 \\ 0 & -i & 0 & 0 \end{bmatrix}$$

$$S_x = \frac{1}{2}\begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \quad S_y = \frac{1}{2}\begin{bmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{bmatrix} \quad 2I_zS_x = \frac{1}{2}\begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{bmatrix} \quad 2I_zS_y = \frac{1}{2}\begin{bmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & i \\ 0 & 0 & -i & 0 \end{bmatrix}$$

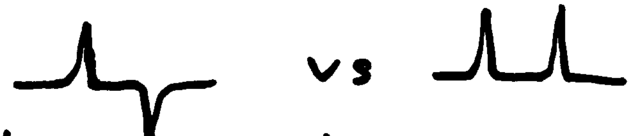
$$2I_xS_x = \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} \quad 2I_yS_y = \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{bmatrix} \quad 2I_xS_y = \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{bmatrix} \quad 2I_yS_x = \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & -i & 0 \\ 0 & i & 0 & 0 \\ i & 0 & 0 & 0 \end{bmatrix}$$

What about $2I_{1x}I_{2z}$?

$$I_{1x} = \frac{1}{2}\begin{bmatrix} 0&0&1&0\\ 0&0&0&1\\ 1&0&0&0\\ 0&1&0&0 \end{bmatrix}, \quad I_{2z} = \frac{1}{2}\begin{bmatrix} 1&&&\\ &-1&&\\ &&1&\\ &&&-1 \end{bmatrix}$$

$$2I_{1x}I_{2z} = \text{product} = \frac{1}{2}\begin{bmatrix} 0&0&1&0\\ 0&0&0&-1\\ 1&0&0&0\\ 0&-1&0&0 \end{bmatrix}$$

note: much like I_{1x} - but. some sign changes. σ_{13}, σ_{24} are lines of A doublet.



x mag of 1 - antiphase wrt. spin 2.

What about $2I_{1x}I_{2x}$? 5

$$2\cdot\frac{1}{2}\frac{1}{2}\begin{bmatrix} 0&0&1&0\\ 0&0&0&1\\ 1&0&0&0\\ 0&1&0&0 \end{bmatrix}\begin{bmatrix} 0&1&0&0\\ 1&0&0&0\\ 0&0&0&1\\ 0&0&1&0 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 0&&&1\\ &&1&\\ &1&&\\ 1&&&0 \end{bmatrix}$$

2Q Zero Q

$$2I_{1y}I_{2y} = \begin{bmatrix} 0&&&-1\\ &&1&\\ &1&&\\ -1&&&0 \end{bmatrix}$$

linear comb. of 2 is pure ZerQ or 2Q coherence.

$$I_{1x}I_{2x} - I_{1y}I_{2y} = 2Q$$

$I_{1x}I_{2y}$, $I_{1y}I_{2x}$ are imaginary comp.

Transformation Properties 6

xpulse by angle α.

$$I_z \xrightarrow{\alpha I_x} I_z \cos\alpha - I_y \sin\alpha$$

$$I_y \xrightarrow{\alpha I_x} I_y \cos\alpha + I_z \sin\alpha$$

$$I_x \xrightarrow{\alpha I_x} I_x$$

free precession:

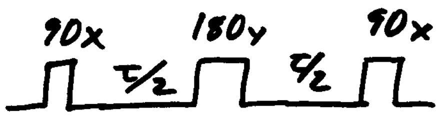
$$I_x \xrightarrow{\Omega I_z t} I_x \cos(\Omega t) + I_y \sin(\Omega t)$$

$$I_x \xrightarrow{2\pi J I_{z1} I_{z2} t} I_x \cos(\pi J t) + 2 I_{y1} I_{z2} \sin(\pi J t)$$

Application of Product Operators: 8

2D 2Q spectrum.

- can we excite a 2Q coherence?
- can we detect (indirectly) a 2Q coherence?

consider: 

with $\tau = \frac{1}{2J}$

$$I_{1z} + I_{2z} \underset{(I_{1x}+I_{2x})}{\xrightarrow{90x}} -I_{1y} - I_{2y} \underset{\text{(180 remove shift evol.)}}{\xrightarrow{J I_{1z} I_{2z} \cdot \tau}} + 2 I_{1x} I_{2z} + 2 I_{1z} I_{2x}$$

$$\xrightarrow{90x} -2 I_{1x} I_{2y} - 2 I_{1y} I_{2x}$$ } ZQ + 2Q evolution ↓ $I_{1x} I_{2x}$ etc

consider: 

after evolution

$$\xrightarrow{90x} -2 I_{1x} I_{2z} - 2 I_{1z} I_{2x}$$ + others.. } 1Q detection on <u>both</u> spin 1+2

JMR 68, 433-452 (1986)

7

TABLE 3

Evolution of the Two-Spin Product Operators

Product operator (P_1)	Evolution caused by $I_{1x} + I_{2x}$	$I_{1y} + I_{2y}$	$I_{1z} + I_{2z}$	$2\, I_{1z} I_{2z}$
$\frac{1}{2}E$	$\frac{1}{2}E$	$\frac{1}{2}E$	$\frac{1}{2}E$	$\frac{1}{2}E$
I_{1z}	$-I_{1y}$	I_{1x}	I_{1z}	I_{1z}
I_{2z}	$-I_{2y}$	I_{2x}	I_{2z}	I_{2z}
$2\, I_{1z} I_{2z}$	$(2\, I_{1y} I_{2y})$	$(2\, I_{1x} I_{2x})$	$2\, I_{1z} I_{2z}$	$2\, I_{1z} I_{2z}$
I_{1x}	I_{1x}	$-I_{1z}$	I_{1y}	$2\, I_{1y} I_{2z}$
I_{1y}	I_{1z}	I_{1y}	$-I_{1x}$	$-2\, I_{1x} I_{2z}$
I_{2x}	I_{2x}	$-I_{2z}$	I_{2y}	$2\, I_{1z} I_{2y}$
I_{2y}	I_{2z}	I_{2y}	$-I_{2x}$	$-2\, I_{1z} I_{2x}$
$2\, I_{1x} I_{2z}$	$-2\, I_{1x} I_{2y}$	$(-2\, I_{1z} I_{2x})$	$2\, I_{1y} I_{2z}$	I_{1y}
$2\, I_{1y} I_{2z}$	$(-2\, I_{1z} I_{2y})$	$2\, I_{1y} I_{2x}$	$-2\, I_{1x} I_{2z}$	$-I_{1x}$
$2\, I_{1z} I_{2x}$	$-2\, I_{1y} I_{2x}$	$(-2\, I_{1x} I_{2z})$	$2\, I_{1z} I_{2y}$	I_{2y}
$2\, I_{1z} I_{2y}$	$(-2\, I_{1y} I_{2z})$	$2\, I_{1x} I_{2y}$	$-2\, I_{1z} I_{2x}$	$-I_{2x}$
$2\, I_{1x} I_{2x}$	$2\, I_{1x} I_{2x}$	$(2\, I_{1z} I_{2z})$	—	$2\, I_{1x} I_{2x}$
$2\, I_{1y} I_{2x}$	$2\, I_{1z} I_{2x}$	$-2\, I_{1y} I_{2z}$	—	$2\, I_{1y} I_{2x}$
$2\, I_{1x} I_{2y}$	$2\, I_{1x} I_{2z}$	$-2\, I_{1z} I_{2y}$	—	$2\, I_{1x} I_{2y}$
$2\, I_{1y} I_{2y}$	$(2\, I_{1z} I_{2z})$	$2\, I_{1y} I_{2y}$	—	$2\, I_{1y} I_{2y}$

Note. The two components of a two-spin operator may each evolve into one or two new components. Hence, each operator P_1 may

(i) remain unchanged (the original operator P_1 is listed in the table);

(ii) evolve into two operators, $P_1 \rightarrow P_1 \cos\theta + P_2 \sin\theta$ (the angle θ is defined as β for x and y rf pulses, $\omega_k t$ for chemical-shift precession, and $\frac{1}{2}J_{12}t$ for scalar coupling. P_2 is listed in the table);

(iii) evolve into four operators (for rf x and y pulses, θ is set to $\frac{1}{2}\pi$ and the single resulting operator given in parentheses. For chemical-shift precession, this simplification is not applicable, and the resulting operators

$$I_{1x}I_{2x} \xrightarrow{\omega_1 I_{1z} t + \omega_2 I_{2z} t} I_{1x}I_{2x}\cos\omega_1 t \cos\omega_2 t + I_{1y}I_{2x}\sin\omega_1 t \cos\omega_2 t + I_{1x}I_{2y}\cos\omega_1 t \sin\omega_2 t + I_{1y}I_{2y}\sin\omega_1 t \sin\omega_2 t$$

are not listed.

MQ (2Q) · β-Me-Gal