

## APPENDIX 1

# Matrix Algebra of Spin-1/2 and Spin-1 Operators

It is frequently convenient to work with the matrix representation of spin operators in the eigenbase of the Zeeman Hamiltonian. Some results for spin-1/2 and spin-1 systems are given in this Appendix.

### Eigenvectors

Eigenvectors are represented as column matrices (kets) and row matrices (bras), while operators are square matrices. The  $|\alpha\rangle$  and  $|\beta\rangle$  states for spin-1/2 are represented by:

$$|\alpha\rangle \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |\beta\rangle \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (1)$$

while, for spin 1:

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad |0\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad \text{and} \quad |-1\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad (2)$$

### Operators

The matrix representation of spin operators in this eigenbase may be obtained by applying the results of angular momentum theory:

$$\begin{aligned} I_z |I, m\rangle &= m |I, m\rangle \\ I_+ |I, m\rangle &= \sqrt{(I - m)(I + m + 1)} |I, m + 1\rangle, \quad I_+ = I_x + iI_y \\ I_- |I, m\rangle &= \sqrt{(I + m)(I - m + 1)} |I, m - 1\rangle, \quad I_- = I_x - iI_y \\ \mathbf{I}^2 |I, m\rangle &= I(I + 1) |I, m\rangle. \end{aligned} \quad (3)$$

The matrix representation of the operator  $\mathbf{I}^2$  is thus  $I(I + 1)$  times the unit matrix of dimension  $(2I + 1)$ . The other operators are given by:

$$\begin{array}{cc}
 \text{Spin } 1/2 & \text{Spin } 1 \\
 \\
 I_z & \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \\
 \\
 I_x & \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \\
 \\
 I_y & \frac{i}{2} \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \qquad \frac{i}{\sqrt{2}} \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} \\
 \\
 I_+ & \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \qquad \sqrt{2} \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix} \\
 \\
 I_- & \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \qquad \sqrt{2} \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \\
 \\
 \mathbf{I}^2 & \frac{3}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad 2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}
 \end{array} \tag{4}$$

The element  $ij$  of these matrices represents  $\langle i|\mathbf{O}|j\rangle$ ,  $|i\rangle$  being the ket corresponding to  $m = m_i$  ( $m_1 = I, m_2 = I - 1, m_3 = I - 2, \dots$ ).

The matrix representation of eigenvectors and operators in a composite spin system is obtained by working in the appropriate direct product space. Thus, for two spins  $1/2$ ,

$$\begin{array}{cc}
 |\alpha\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} & |\alpha\beta\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} \\
 \\
 |\beta\alpha\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} & |\beta\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}
 \end{array} \tag{5}$$

For such an  $IS$  spin system, we have in the direct product space:

$$\begin{aligned}
 2I_x &= \begin{matrix} & |\alpha\rangle & |\beta\rangle \\ \begin{matrix} (\alpha| \\ (\beta| \end{matrix} & \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \end{matrix} \otimes \mathbf{1}_s = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\
 &= \begin{matrix} & |\alpha\alpha\rangle & |\alpha\beta\rangle & |\beta\alpha\rangle & |\beta\beta\rangle \\ \begin{matrix} (\alpha\alpha| \\ (\alpha\beta| \\ (\beta\alpha| \\ (\beta\beta| \end{matrix} & \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix} \end{matrix} \quad (6)
 \end{aligned}$$

$$\begin{aligned}
 2S_x &= \mathbf{1}_I \otimes \begin{matrix} & |\alpha\rangle & |\beta\rangle \\ \begin{matrix} (\alpha| \\ (\beta| \end{matrix} & \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \end{matrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\
 &= \begin{matrix} & |\alpha\alpha\rangle & |\alpha\beta\rangle & |\beta\alpha\rangle & |\beta\beta\rangle \\ \begin{matrix} (\alpha\alpha| \\ (\alpha\beta| \\ (\beta\alpha| \\ (\beta\beta| \end{matrix} & \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \end{matrix} \quad (7)
 \end{aligned}$$

Note that the order of the spins is chosen arbitrarily; the choice made, however, must be maintained right through. The direct product of two matrices  $A$  and  $B$  is given by:

$$C = A \otimes B = \begin{bmatrix} A_{11}B & A_{12}B & \dots & A_{1n}B \\ \vdots & \vdots & & \vdots \\ A_{n1}B & A_{n2}B & \dots & A_{nn}B \end{bmatrix} \quad (8)$$

The direct product of an  $(m \times m)$  matrix with an  $(n \times n)$  matrix is thus an  $(mn \times mn)$  matrix. Note that the direct product of matrices is therefore very different from matrix multiplication.

Also listed below are the matrix representations of some higher powers of spin operators. These results may be checked by usual matrix multiplication.

$$\begin{array}{cc}
 \text{Spin } 1/2 & \text{Spin } 1 \\
 I_x^2 & \frac{1}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \frac{1}{2} \begin{pmatrix} 1 & 0 & 1 \\ 0 & 2 & 0 \\ 1 & 0 & 1 \end{pmatrix} \\
 I_y^2 & \frac{1}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \frac{1}{2} \begin{pmatrix} 1 & 0 & -1 \\ 0 & 2 & 0 \\ -1 & 0 & 1 \end{pmatrix} \\
 I_z^2 & \frac{1}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}
 \end{array} \quad (9)$$

Spin 1/2	Spin 1
$[I_x, I_y]_+$	$0 \quad i \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}$
$[I_y, I_z]_+$	$0 \quad \frac{i}{\sqrt{2}} \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}$
$[I_z, I_x]_+$	$0 \quad \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}$

Various recursions then follow for  $i = x, y, z$ :

$$\begin{aligned} I_i^n &= \frac{1}{4} I_i^{n-2} \quad (I = 1/2, n \geq 2) \\ I_i^n &= I_i^{n-2} \quad (I = 1, n \geq 3) \end{aligned} \quad (10)$$

For spin 1, the following relations also hold, with  $i = x, y, z$ :

$$\begin{aligned} I_i I_j I_i &= 0 \quad (i \neq j) \\ I_i I_j^2 + I_j^2 I_i &= I_i \quad (i \neq j) \end{aligned} \quad (11)$$

In general, for a spin  $I$ , we have the Cayley identity:

$$[I_z - I][I_z - (I - 1)][I_z - (I - 2)] \dots [I_z + I] = 0$$

and

$$\begin{aligned} I_+^{(2I+1)} &= I_-^{(2I+1)} = 0; \\ I_+^i \left( \prod_{j=-I}^{-I-i} (I_z - j) \right) I_+^i &= 0, \quad i = 1, 2, \dots, I. \end{aligned} \quad (12)$$

Finally, we give below the matrix representation of various bilinear operator products for a two-spin-1/2 situation. The results may be verified by matrix multiplication, working with the representation of the individual single-spin operators in the direct product space of the two spins 1/2.

$$\begin{aligned} I_x S_x &= \frac{1}{4} \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} & I_x S_y &= \frac{i}{4} \begin{bmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} \\ I_y S_x &= \frac{i}{4} \begin{bmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} & I_y S_y &= \frac{1}{4} \begin{bmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{bmatrix} \end{aligned}$$

$$I_z S_z = \frac{1}{4} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \quad I_z S_x = \frac{1}{4} \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{bmatrix} \quad (13)$$

$$I_z S_y = \frac{i}{4} \begin{bmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{bmatrix} \quad I_x S_z = \frac{1}{4} \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix}$$

$$I_y S_z = \frac{i}{4} \begin{bmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix}$$

From the above, it is clear that  $I_x S_x$ ,  $I_y S_y$ ,  $I_x S_y$ , and  $I_y S_x$  represent zero-, and double-quantum coherences in the spin-1/2  $IS$  system.

Operator representations for an  $IS$  system with  $I = 1$ ,  $S = 1/2$  involve  $(6 \times 6)$  matrices. For example,

$$\sqrt{2}I_x = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \otimes \mathbf{1}_S = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$= \begin{matrix} & |1\alpha\rangle & |1\beta\rangle & |0\alpha\rangle & |0\beta\rangle & |-1\alpha\rangle & |-1\beta\rangle \\ \begin{matrix} \langle 1\alpha| \\ \langle 1\beta| \\ \langle 0\alpha| \\ \langle 0\beta| \\ \langle -1\alpha| \\ \langle -1\beta| \end{matrix} & \begin{bmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix} \end{matrix} \quad (14)$$

$$2S_x = \mathbf{1}_I \otimes \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (15)$$

$$= \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix} \quad (16)$$

$$\sqrt{2}I_y = i \begin{bmatrix} 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix} \quad (17)$$

$$2S_y = i \begin{bmatrix} 0 & -1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix} \quad (18)$$

$$I_z = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{bmatrix} \quad (19)$$

$$2S_z = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{bmatrix} \quad (20)$$

## APPENDIX 2

# The Hausdorff Formula

It is frequently necessary to evaluate expressions of the form:

$$R_A = \exp(-i\mathcal{H}t) A \exp(i\mathcal{H}t)$$

which describe the evolution of an operator  $A$  for  $t$  seconds, under the action of a time-independent Hamiltonian  $\mathcal{H}$ . The Baker–Campbell–Hausdorff formula consolidates the series expansion of exponential operators to evaluate such operator evolutions:

$$\begin{aligned} R_A &\equiv \exp(-i\mathcal{H}t) A \exp(i\mathcal{H}t) \\ &= A - (it)[\mathcal{H}, A] + \frac{(it)^2}{2!} [\mathcal{H}, [\mathcal{H}, A]] \\ &\quad - \frac{(it)^3}{3!} [\mathcal{H}, [\mathcal{H}, [\mathcal{H}, A]]] + \dots \end{aligned} \tag{1}$$

Note that this formula involves successive commutators with the Hamiltonian. An NMR problem has a well-defined, finite dimensional operator space associated with it and so the number of independent commutators is limited and the series expansion quickly leads to an operator recursion. It may be noted especially that it is crucial to work with the appropriate basis set of linearly independent operators, and to insure that successive commutators are expressed in this basis set, so that the operator recursions are not lost sight of. Suitable basis set operators for problems involving spin-1/2 and spin-1 systems have been discussed in Chapter 1.

We discuss below briefly some cases of interest.

CASE 1.  $[\mathcal{H}, A] = 0$ .

It follows that  $R_A = A$  since all the commutators vanish. In other words,  $A$  is invariant to evolution under a Hamiltonian with which it commutes. For example consider a spin-1 system, with  $\mathcal{H} = \frac{1}{3}(I_z^2 - I(I+1))$  and  $A = [I_x, I_y]_+$ .

$$\begin{aligned} [\mathcal{H}, A] &\sim [I_z^2, I_x I_y + I_y I_x] \\ &= [I_z^2, I_x I_y] + [I_z^2, I_y I_x] \\ &= iI_z(I_y^2 - I_x^2) + i(I_y^2 - I_x^2)I_z - iI_z(I_x^2 - I_y^2) - i(I_x^2 - I_y^2)I_z \quad (2) \\ &= 2i(I_z(I_y^2 - I_x^2) + (I_y^2 - I_x^2)I_z) \\ &= 2i(I_z - I_z) = 0 \end{aligned}$$

where we have employed the properties of spin-1 operators discussed in Appendix 1, and some properties of commutators to be discussed later in this Appendix. Thus,  $R_A = [I_x, I_y]_+$ .

CASE 2.  $[\mathcal{H}, A] = \alpha A$ .

In this case,  $R_A = A \exp(-i\alpha t)$ . As an example, consider  $\mathcal{H} = \Delta I_z$  and  $A = I_+ = I_x + iI_y$ . Then,  $[\mathcal{H}, A] = i\Delta I_y + \Delta I_x = \Delta A$ . Thus,  $R_A = I_+ \exp(-i\Delta t)$ .

CASE 3.  $[\mathcal{H}, A] = B$ ,  $[\mathcal{H}, B] = kA$ ,  $A \neq \alpha B$ .

This has been termed a problem of order 2. We find,

$$\begin{aligned} R_A &= \left( A + \frac{(it)^2}{2!} kA + \frac{(it)^4}{4!} k^2 A + \dots \right) - \left( itB + \frac{(it)^3}{3!} kB + \dots \right) \\ &= A \left( 1 - \frac{t^2 k}{2!} + \frac{t^4 k^2}{4!} - \dots \right) - iB \left( t - \frac{t^3 k}{3!} + \dots \right) \quad (3) \\ &= A \cos \sqrt{k}t - \frac{1}{\sqrt{k}} iB \sin \sqrt{k}t \end{aligned}$$

Problems of order 2 have been encountered frequently in Chapters 1 and 3 and the corresponding equations of motion,  $R_A$ , have been given there. We consider here a few representative examples.

(1)  $A = I_x$ ,  $\mathcal{H} = 2\pi J I_z S_z$ .

$$\begin{aligned} [\mathcal{H}, A] &= i2\pi J I_y S_z = B; \quad [\mathcal{H}, B] = 4\pi^2 \frac{J^2}{4} I_x \text{ if } S = 1/2 \\ &= 4\pi^2 \frac{J^2}{4} A \end{aligned} \quad (4)$$

Thus,  $R_A = I_x \cos \pi J t + 2I_y S_z \sin \pi J t$ . (5)

(2)  $A = I_x$ ,  $\mathcal{H} = \Delta I_z$ .

$$[\mathcal{H}, A] = i\Delta I_y = B; \quad [\mathcal{H}, B] = \Delta^2 I_x = \Delta^2 A \quad (6)$$

Thus  $R_A = I_x \cos \Delta t + I_y \sin \Delta t$ . (7)



(3)  $A = (I_x - S_x)$ ;  $\mathcal{H} = 2\pi J(I_y S_y + I_z S_z)$  or  $2\pi \bar{J} \mathbf{I} \cdot \mathbf{S}$ .

$$\begin{aligned} \frac{1}{2\pi \bar{J}} [\mathcal{H}, A] &= -iI_z S_y + iI_y S_z + iI_y S_z - iI_z S_y = 2i(I_y S_z - I_z S_y) = B \\ \frac{1}{2\pi \bar{J}} [\mathcal{H}, B] &= 2i \left( \frac{iS_x}{4} - \frac{iI_x}{4} - \frac{iI_x}{4} + \frac{iS_x}{4} \right) = (I_x - S_x) = A, \text{ if } I = S = 1/2 \end{aligned} \quad (8)$$

$$\text{Thus, } R_A = (I_x - S_x) \cos 2\pi \bar{J} t + 2(I_y S_z - I_z S_y) \sin 2\pi \bar{J} t. \quad (9)$$

Problems of order higher than two are encountered, for example, in  $A_M X_N$  systems evolving under a strong coupling Hamiltonian as discussed in Chapter 1 and lead to multiple frequencies of evolution.

## Commutator Algebra

We give here some of the standard results of commutator algebra that are useful in evaluating the Hausdorff formula for specific  $\mathcal{H}$  and  $A$ . These expressions follow from the definition of commutators:

$$[A, B] = (AB - BA) \quad (10)$$

We find:

$$\begin{aligned} [A, B] &= -[B, A] \\ [A, kB] &= k[A, B], k \text{ being a constant.} \\ [AB, C] &= A[B, C] + [A, C]B \\ [A^n, B] &= \sum_{m=0}^{n-1} A^m [A, B] A^{n-m-1}, n \geq 1 \end{aligned} \quad (11)$$

## APPENDIX 3

# Fourier Transformation

In this Appendix we briefly discuss some important properties of the Fourier integral and related issues of sampling, and sensitivity and resolution enhancement by exponential multiplication. We also touch upon the dynamic range problem in FT NMR.

## The Fourier Transform

A time domain function  $f(t)$  with period  $T \rightarrow \infty$  may be represented in the basis set of exponential functions  $\{e^{i\omega_0 t}\}$  ( $\omega_0 = 2\pi/T$ ), which goes over into  $\{e^{i\omega t}\}$  as the period  $T \rightarrow \infty$ . We thus have:

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\omega) e^{i\omega t} d\omega \quad (1)$$

the inverse Fourier transform (FT) of  $F(\omega)$ , with

$$F(\omega) = \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt \quad (2)$$

the Fourier Transform of  $f(t)$ . Note that these prescriptions for  $f(t)$  and its Fourier transform  $F(\omega)$  correspond to an exponential Fourier analysis of a periodic function, in the limit of the period  $T \rightarrow \infty$ . We denote an FT pair by  $f(t) \leftrightarrow F(\omega)$ .  $F(\omega)$  is in general a complex function:

$$F(\omega) = |F(\omega)| e^{i\theta(\omega)} \quad (3)$$

If  $f(t)$  is a real function of  $t$ , the complex conjugate of  $F(\omega)$ , i.e.,  $F^*(\omega) = F(-\omega)$ . Thus

$$F(-\omega) = |F(\omega)| e^{-i\theta(\omega)} \quad (4)$$

The magnitude spectrum  $|F(\omega)|$  is an even function of  $\omega$ , while the phase spectrum  $\theta(\omega)$  is odd. Several properties of the FT follow from the definition, considering the FT pair  $f(t) \leftrightarrow F(\omega)$ .

### 1. Symmetry

$$F(t) \leftrightarrow 2\pi f(-\omega)$$

If  $f(t)$  is an even function, we have  $F(t) \leftrightarrow 2\pi f(\omega)$

### 2. Linearity

$$a_1 f_1(t) + a_2 f_2(t) \leftrightarrow a_1 F_1(\omega) + a_2 F_2(\omega)$$

for arbitrary constants  $a_1$  and  $a_2$ .

### 3. Scaling

$$f(at) \leftrightarrow \frac{1}{|a|} F\left(\frac{\omega}{a}\right)$$

for a real constant  $a$ .

### 4. Frequency shifting

$$f(t)e^{i\omega_0 t} \leftrightarrow F(\omega - \omega_0)$$

### 5. Time shifting

$$f(t - t_0) \leftrightarrow F(\omega)e^{-i\omega t_0}$$

### 6. Time differentiation and integration

$$\frac{df}{dt} \leftrightarrow i\omega F(\omega)$$

if the FT of  $df/dt$  exists; and

$$\int_{-\infty}^t f(\tau) d\tau \leftrightarrow \frac{1}{i\omega} F(\omega)$$

if  $F(\omega)/\omega$  is bounded at  $\omega = 0$ .

### 7. Frequency differentiation

$$-itf(t) \leftrightarrow \frac{dF}{d\omega}$$

and

$$(-it)^n f(t) \leftrightarrow \frac{d^n F}{d\omega^n}$$

### 8. Convolution

$$f_1(t) * f_2(t) \equiv \int_{-\infty}^{\infty} f_1(\tau) f_2(t - \tau) d\tau \leftrightarrow F_1(\omega) F_2(\omega)$$

Also,

$$\begin{aligned} f_1(t)f_2(t) &\leftrightarrow \frac{1}{2\pi} \int_{-\infty}^{\infty} F_1(v)F_2(\omega - v) dv \\ &\equiv \frac{1}{2\pi} [F_1(\omega) * F_2(\omega)] \end{aligned} \quad (5)$$

Convolutions obey the commutative, associative, and distributive laws.

We list below some useful FT pairs:

$f(t)$	$F(\omega)$
1	$2\pi\delta(\omega)$
$\delta(t)$	1
$u(t)$	$\pi\delta(\omega) + (1/i\omega)$
$e^{-at}u(t)$	$(a + i\omega)^{-1}$
$\cos \omega_0 t$	$\pi[\delta(\omega - \omega_0) + \delta(\omega + \omega_0)]$
$\sin \omega_0 t$	$i\pi[\delta(\omega + \omega_0) - \delta(\omega - \omega_0)]$
$\cos \omega_0 t u(t)$	$\frac{\pi}{2}[\delta(\omega - \omega_0) + \delta(\omega + \omega_0)] + (i\omega/(\omega_0^2 - \omega^2))$
$\sin \omega_0 t u(t)$	$(\omega_0/(\omega_0^2 - \omega^2)) + \frac{\pi}{2i}[\delta(\omega - \omega_0) - \delta(\omega + \omega_0)]$
$e^{-at} \sin \omega_0 t u(t)$	$\omega_0/[(a + i\omega)^2 + \omega_0^2]$
$G_\tau(t)$	$\tau Sa(\omega\tau/2)$
$(\omega_0/2\pi)Sa(\omega_0 t/2)$	$G_{\omega_0}(\omega)$
$e^{-t^2/2\sigma^2}$	$\sigma\sqrt{2\pi}e^{-\sigma^2\omega^2/2}$
$\delta_T(t) \equiv \sum_{n=-\infty}^{\infty} \delta(t - nT)$	$\omega_0\delta_{\omega_0}(\omega) \equiv \omega_0 \sum_{n=-\infty}^{\infty} \delta(\omega - n\omega_0) \left(\omega_0 = \frac{2\pi}{T}\right)$
$e^{-a t }$	$2a(a^2 + \omega^2)$

### Notes

#### 1. The step function

$$\begin{aligned} u(t) &= 1, \quad t > 0 \\ &= 0, \quad t < 0 \end{aligned}$$

#### 2. The Dirac delta function

$$\begin{aligned} \delta(t) &= \lim_{a \rightarrow 0} \frac{d}{dt}(u_a(t)) \\ &= \lim_{a \rightarrow 0} \frac{1}{a}[u(t) - u(t - a)], \end{aligned}$$

where  $u_a(t)$  is a step function with rise time  $t = a$ .

$$\int_{-\infty}^{\infty} \delta(t) dt = 1$$

## 3. The sampling function

$$Sa\left(\frac{\omega\tau}{2}\right) = \sin(\omega\tau/2)/(\omega\tau/2)$$

## 4. The gate function

$$\begin{aligned} G_\tau(t) &= 1, \quad |t| < \tau/2 \\ &= 0, \quad |t| > \tau/2 \end{aligned}$$

It is of particular interest for FT NMR to consider the time-domain functions

$$S_1(t) = u(t)e^{-at} \sin \omega_0 t \text{ and } S_2(t) = u(t)e^{-at} \cos \omega_0 t, \quad (6)$$

which represent a general FID ( $a \geq 0$ ). We find from the definitions that their Fourier transforms are given by:

$$\begin{aligned} S_1(t) &\leftrightarrow \int_{-\infty}^{\infty} u(t)e^{-at} \sin \omega_0 t e^{-i\omega t} dt \\ &= \frac{1}{2} \left[ \frac{(\omega + \omega_0)}{a^2 + (\omega + \omega_0)^2} - \frac{(\omega - \omega_0)}{a^2 + (\omega - \omega_0)^2} \right] \\ &\quad - \frac{i}{2} \left[ \frac{a}{a^2 + (\omega - \omega_0)^2} - \frac{a}{a^2 + (\omega + \omega_0)^2} \right] \end{aligned} \quad (7)$$

The real part, therefore, corresponds to a Lorentzian dispersion signal at  $\omega_0$ , whereas the imaginary part is a Lorentzian absorption at  $\omega_0$  (full width at half height is equal to  $a/\pi$  Hertz), ignoring the responses at  $-\omega_0$ . On the other hand:

$$\begin{aligned} S_2(t) &\leftrightarrow \int_{-\infty}^{\infty} u(t)e^{-at} \cos \omega_0 t e^{-i\omega t} dt \\ &= \frac{1}{2} \left[ \frac{a}{a^2 + (\omega - \omega_0)^2} + \frac{a}{a^2 + (\omega + \omega_0)^2} \right] \\ &\quad - \frac{i}{2} \left[ \frac{(\omega - \omega_0)}{a^2 + (\omega - \omega_0)^2} + \frac{(\omega + \omega_0)}{a^2 + (\omega + \omega_0)^2} \right] \end{aligned} \quad (8)$$

In this case, the real part corresponds to an absorption at  $\omega_0$ , and the imaginary part corresponds to a dispersion.

These results have been employed throughout the book in discussions of lineshapes. In the above expressions,  $a = (T_2^*)^{-1}$ .

Resolution enhancement may be achieved by multiplying  $S_1(t)$  and  $S_2(t)$  by  $\exp(bt)$  ( $b \geq 0$ ), leading to a linewidth of  $(a - b)/\pi$  Hz; sensitivity is reduced in this process because the later, noisy portions of the FID are weighted in preference to the initial portion, which has the maximum signal content.

Sensitivity enhancement, on the other hand, is achieved by multiplying  $S_1(t)$  and  $S_2(t)$  by  $\exp(-bt)$ , ( $b \geq 0$ ), leading to a preferential weighting of the signal-rich initial portion of the FID relative to the noisy FID tail. From the

expressions for the FT of  $S_1(t)$  and  $S_2(t)$ , however, it is clear that in this process resolution is lost, the resulting linewidth being  $(a + b)/\pi$  Hz.

## Sampling

In actual practice, most FT NMR spectrometers perform a discrete Fourier transform of the FID to retrieve the frequency spectrum. To this end, the FID, which is an analog voltage waveform, is sampled at regular intervals and digitized for computer handling. The sampling frequency must be sufficiently high to reproduce the frequency spectrum with fidelity. In fact for a band-limited signal with no frequency components above  $\nu_m$  Hz, the sampling frequency should be  $\nu_s \geq 2\nu_m$  to produce the correct spectrum. This result of "Nyquist sampling theorem" may be proved as follows for a function  $f(t)$  which is sampled every  $T$  seconds, generating  $f(t)\delta_T(t)$ , where:

$$\delta_T(t) = \sum_{n=-\infty}^{\infty} \delta(t - nT) \quad (9)$$

For  $f(t) \leftrightarrow F(\omega)$ , we have:

$$f(t)\delta_T(t) \leftrightarrow F(\omega) * \omega_s \delta_{\omega_s}(\omega) \quad (10)$$

Employing the frequency shift property, we find:

$$\begin{aligned} F(\omega) * \delta_{\omega_s}(\omega) &= F(\omega) * \sum_n \delta(\omega - n\omega_s) \\ &= \sum_n F(\omega) * \delta(\omega - n\omega_s) \leftrightarrow \frac{1}{2\pi} \sum_n f(t) e^{in\omega_s t} \end{aligned} \quad (11)$$

$$\begin{aligned} \Rightarrow F(\omega) * \delta_{\omega_s}(\omega) &= \frac{1}{2\pi} \sum_n F(\omega - n\omega_s) \\ \Rightarrow f(t)\delta_T(t) &\leftrightarrow \frac{1}{T} \sum_{n=-\infty}^{\infty} F(\omega - n\omega_s), \end{aligned} \quad (12)$$

which is the function  $F(\omega)$  repeating itself every  $\omega_s$  radians per second; this periodic repetition occurs without overlap as long as  $\omega_s \geq 2\omega_m$ . This implies that the sampling interval (also called dwell time)

$$T = \frac{2\pi}{\omega_s} = \frac{1}{\nu_s} \leq \frac{1}{2\nu_m} \quad (13)$$

If this condition is violated, the overlap of successive  $F(\omega - n\omega_s)$  leads to a frequency  $\nu_s + \Delta\nu$  being represented in the spectrum as  $\nu_s - \Delta\nu$ , which is known as aliasing. Aliased signals in FT NMR spectra may be identified readily because they occur with wrong phases which cannot be corrected by the zero- and first-order phase correction routines.

## Dynamic Range Problem

The detection of very weak signals in the presence of very strong ones is a problem that is often encountered in practical NMR, e.g., in the study of

the  $^1\text{H}$  NMR of biomolecules in  $\text{D}_2\text{O}$ . The small percentage of HDO even in a highly deuterated sample of  $\text{D}_2\text{O}$  can cause considerable problems. In CW NMR, the problem may sometimes be avoided by not exciting the HDO signal at all; in pulsed methods of excitation however, this requires special approaches, such as tailored excitation, described in Chapter 2.

In the presence of very strong resonances, weak resonances in an FID may be detected only if the digitizer resolution and computer word length are sufficiently high. In the frequency domain, single-scan proton spectra can have a dynamic range as high as  $\pm 40,000 : 2$  with a 12-bit digitizer (analog to digital converter, or ADC). The dynamic range increases further with a 16-bit digitizer and can be as high as  $\pm 280,000 : 2$ . In order to utilize the available dynamic range, however, the computer word length should be sufficiently high. For instance, the dynamic range of  $\pm 40,000 : 2$  cannot be availed if the computer word length is only 16 bits ( $\pm 32 \text{ K}$ ).

## APPENDIX 4

# Dipolar Relaxation

The magnetic interaction between nuclear dipoles was the subject of Chapter 6, where the line broadening induced by it in solids was discussed, together with means to counter it. Some consequences of cross-relaxation arising from dipole–dipole interactions in liquids and solids were also described in Chapter 2 and Chapter 6, in the context of sensitivity enhancement by incoherent polarization transfer. In this Appendix, we summarize some basic results for relaxation under dipolar coupling.

The Hamiltonian describing dipolar interaction between two spins  $I$  and  $S$  is given by:

$$\mathcal{H}_d = \frac{\gamma_I \gamma_S \hbar^2}{4\pi^2} \left[ \frac{\mathbf{I} \cdot \mathbf{S}}{r^3} - \frac{3(\mathbf{I} \cdot \mathbf{r})(\mathbf{S} \cdot \mathbf{r})}{r^5} \right] \quad (1)$$

$$\begin{aligned} &= \frac{\gamma_I \gamma_S}{r^3} \left( \frac{\hbar}{2\pi} \right)^2 \left[ I_z S_z + \frac{1}{2}(I^+ S^- + I^- S^+) - 3(\sin^2 \theta \cos^2 \varphi I_x S_x \right. \\ &\quad + \sin^2 \theta \sin^2 \varphi I_y S_y + \cos^2 \theta I_z S_z \\ &\quad + \sin^2 \theta \cos \varphi \sin \varphi (I_x S_y + I_y S_x) \\ &\quad + \sin \theta \cos \theta \sin \varphi (I_x S_z + I_z S_x) \\ &\quad \left. + \sin \theta \cos \theta \cos \varphi (I_y S_z + I_z S_y) \right] \\ &= \left( \frac{\gamma_I \gamma_S \hbar^2}{4\pi^2 r^3} \right) (A + B + C + D + E + F) \end{aligned} \quad (2)$$

with



$$\begin{aligned}
A &= I_z S_z (1 - 3 \cos^2 \theta) \\
B &= -\frac{1}{4}(I^+ S^- + I^- S^+)(1 - 3 \cos^2 \theta) \\
C &= -\frac{3}{2}(I^+ S_z + I_z S^+) \sin \theta \cos \theta e^{-i\varphi} \\
D &= -\frac{3}{2}(I^- S_z + I_z S^-) \sin \theta \cos \theta e^{i\varphi} \\
E &= -\frac{3}{4}I^+ S^+ \sin^2 \theta e^{-2i\varphi} \\
F &= -\frac{3}{4}I^- S^- \sin^2 \theta e^{2i\varphi}
\end{aligned} \tag{3}$$

The structure of this Hamiltonian insures zero-, single-, and double-quantum connectivities. We express  $\mathcal{H}_d$  as a product of a spin operator part and a function of spatial coordinates:

$$\mathcal{H}_d(t) = \mathbf{O}_d f(t)$$

where random motions lead to the time dependence in  $f(t)$ . Employing the standard results of time-dependent perturbation theory to compute the probability of relaxation transitions induced by  $\mathcal{H}_d(t)$  between a pair of levels  $|i\rangle$  and  $|j\rangle$  of the two-spin system, we have, assuming for the fluctuations in  $\mathcal{H}_d$  a stationary random process:

$$\begin{aligned}
W_{ij} &= \frac{1}{T} \frac{4\pi^2}{h^2} |\mathbf{O}_{ij}|^2 \int_0^T dt \int_{-t}^{T-t} \overline{f(t+\tau)f(t)} e^{-2\pi i(E_i - E_j)\tau/h} d\tau \\
&= \frac{1}{T} \frac{4\pi^2}{h^2} |\mathbf{O}_{ij}|^2 \int_0^T dt \int_{-t}^{T-t} G(\tau) e^{-2\pi i(E_i - E_j)\tau/h} d\tau \\
&= \frac{4\pi^2}{h^2} |\mathbf{O}_{ij}|^2 \int_{-\infty}^{\infty} G(\tau) e^{-2\pi i(E_i - E_j)\tau/h} d\tau \\
&= \frac{4\pi^2}{h^2} |\mathbf{O}_{ij}|^2 J(\omega_{ij})
\end{aligned} \tag{4}$$

where  $G(\tau)$  is an autocorrelation function and is generally a rapidly decaying function of  $\tau$ . The transition probability between levels  $i$  and  $j$  under random fluctuations in  $\mathcal{H}_d(t)$  is thus proportional to the spectral density  $J(\omega)$  of the fluctuations at  $\omega_{ij} = (E_i - E_j)$ ;  $J(\omega)$  is the Fourier transform of the correlation function:

$$G(\tau) = \overline{f(t)f(t+\tau)} \tag{5}$$

the statistical average of  $f(t)f(t+\tau)$ .

Three distinct probabilities are to be calculated for zero-, single-, and double-quantum processes, as indicated above. The probabilities are all products of the square of the appropriate matrix element, with the function of spatial coordinates averaged suitably. We find for  $I = S = 1/2$ :

$$\begin{aligned}
W_0 &\sim \frac{1}{16} \overline{(1 - 3 \cos^2 \theta)^2} J(\omega_{23}) = \frac{1}{16} \times \frac{4}{5} J(\omega_{23}) \\
W_{1I} &\sim \frac{9}{16} \overline{\sin^2 \theta \cos^2 \theta} J(\omega_{12}) = \frac{9}{16} \times \frac{2}{15} J(\omega_{12}) \\
W_2 &\sim \frac{9}{16} \overline{\sin^4 \theta} J(\omega_{14}) = \frac{9}{16} \times \frac{8}{15} J(\omega_{14})
\end{aligned} \tag{6}$$

with the spatial coordinates isotropically averaged over the unit sphere. When dealing with white spectral conditions for  $J(\omega)$ , i.e., in the extreme narrowing limit, we therefore have:  $W_0 : 2W_1 : W_2 = 1 : 3 : 6$ . For homonuclear interactions in the “black” spectral limit, on the other hand  $W_1 = W_2 = 0$ , and  $W_0$  alone is nonzero. In general therefore the spectral density at  $\omega = \omega_I$ ,  $\omega_S$ ,  $|\omega_I - \omega_S|$  and  $(\omega_I + \omega_S)$  are all relevant parameters contributing to relaxation under dipolar coupling; for  $T_2$  relaxation  $J(0)$  contributes additionally via the  $A(t)$  term of  $\mathcal{H}_d(t)$ .

In many practical situations the correlation function  $G(\tau)$  may be characterized with a single time constant which is the correlation time  $\tau_c$ :

$$G(\tau) \sim \exp(-|\tau|/\tau_c) \tag{7}$$

$J(\omega)$  now takes the form:

$$\begin{aligned}
J(\omega) &= \int_{-\infty}^{\infty} \exp(-|\tau|/\tau_c) \exp(-i\omega\tau) d\tau \\
&= \frac{2\tau_c}{1 + \omega^2\tau_c^2}
\end{aligned} \tag{8}$$

A plot of  $J(\omega)$  versus  $\omega$  is given in Fig. A.4.1 for three situations:  $\omega_0 < 1/\tau_c$ ,  $\omega_0 \sim 1/\tau_c$  and  $\omega_0 > 1/\tau_c$ ,  $\omega_0$  being the Larmor frequency.

The nuclear Overhauser effect may be derived at once from the relaxation and energy level diagram (Fig. A.4.2) for two spins  $1/2$ , employing the above discussion. Notice that observing  $I$  spins while saturating  $S$ ,  $W_{1I}$  contri-

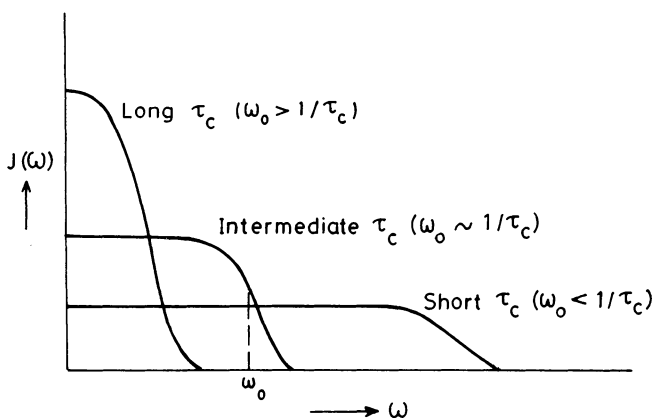


Figure A.4.1. Spectral density  $J(\omega)$  versus frequency  $\omega$ .

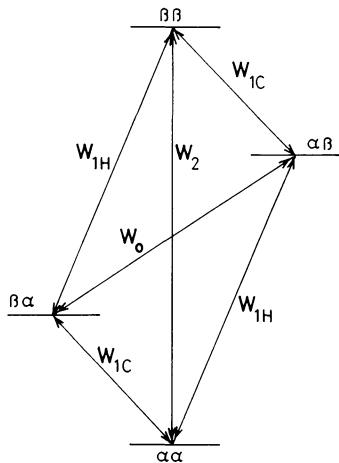


Figure A.4.2. Energy level diagram and relaxation probabilities in a system of two spins  $1/2$ .

butes to establishment of Boltzmann populations, while  $W_2$  and  $W_0$  lead to nonequilibrium populations of opposite sign. This leads at once to the enhancement factor:

$$\frac{\langle I_z \rangle - \langle I_0 \rangle}{\langle I_0 \rangle} = \eta = \frac{(W_2 - W_0)}{(W_0 + 2W_{1I} + W_2)} \frac{\gamma_S}{\gamma_I} \quad (9)$$

In the white spectral limit, therefore,

$$\frac{\langle I_z \rangle - \langle I_0 \rangle}{\langle I_0 \rangle} = \frac{1}{2} \frac{\gamma_S}{\gamma_I} \quad (10)$$

When  $I = {}^{13}\text{C}$  and  $S = {}^1\text{H}$ , for example, upon saturating the proton resonances, the dipole coupled  ${}^{13}\text{C}$ 's attain a polarization which is three times the Boltzmann equilibrium quantity. A negative NOE ( $\sim 5$ ) results for  ${}^{15}\text{N}$  dipolar coupled to protons ( $I = {}^{15}\text{N}$ ,  $S = {}^1\text{H}$ ), since  ${}^{15}\text{N}$  has a negative magnetogyric ratio.

In practical situations, the dipolar interaction between spins may or may not be the dominant mechanism of relaxation; in case other mechanisms such as spin-rotation interaction, chemical shift anisotropy, etc., contribute significantly to the establishment of Boltzmann equilibrium, observed nuclear Overhauser enhancements will be below the maximum derived above:

$$\frac{\langle I_z \rangle - \langle I_0 \rangle}{\langle I_0 \rangle} = \frac{\gamma_S}{\gamma_I} \frac{(W_2 - W_0)}{(W_0 + 2W_{1I} + W_2 + W^0)} \quad (11)$$

where  $W^0$  is the transition probability under other relaxation mechanisms.

In the homonuclear situation, we find:

$$\frac{\langle I_z \rangle - \langle I_0 \rangle}{\langle I_0 \rangle} = \frac{1}{2} \text{ in the white spectral limit} \quad (12)$$

$$= -1 \text{ in the "black" spectral limit}$$

It is interesting to note that in the isotropic phase, negative NOE's can result for a pair of nuclei with the same sign of  $\gamma$ , if  $\tau_c$  is above a threshold value, *provided* the larger  $\gamma$  is not more than 2.38 times the smaller  $\gamma$ . This again corresponds to the situation that  $W_0 > W_2$ , i.e.,  $J(\omega_{23}) \gg J(\omega_{14})$ .

## APPENDIX 5

# Magnus Expansion and the Average Hamiltonian Theory

The time evolution of the density matrix of the system under the influence of the internal Hamiltonians is governed by the von Neumann equation:

$$\dot{\sigma}(t) = -i[\mathcal{H}, \sigma(t)] \quad (1)$$

When the Hamiltonian is time independent then the above equation integrates to:

$$\sigma(t) = U(t)\sigma(0)U^{-1}(t)$$

with:

$$U(t) = \exp(-i\mathcal{H}t) \quad (2)$$

However, when the Hamiltonian is not constant throughout the time interval of interest but can be assumed to change with a proviso that when the total interval is divided into  $n$  subintervals of duration  $\tau_1, \tau_2, \dots, \tau_n$ , the corresponding Hamiltonians  $\mathcal{H}_k (k = 1, \dots, n)$  are constant in the  $k$ th interval we can write  $U(t)$  as:

$$U(t) = \exp(-i\mathcal{H}_n\tau_n) \exp(-i\mathcal{H}_{n-1}\tau_{n-1}) \dots \exp(-i\mathcal{H}_1\tau_1) \quad (3)$$

provided that all the  $\mathcal{H}_k$ 's commute.

If, on the other hand, the Hamiltonian varies continuously we have to express  $U(t)$  in integral form as:

$$U(t) = T \exp(-i \int_0^t \mathcal{H}(t') dt') \quad (4)$$

where  $T$  is the Dyson time ordering operator, which orders the operators of higher time arguments in the expanded exponential to the left.

Magnus expansion is the tool used to express the operator  $U(t_c)$ , (this replaces  $U(t)$ , when dealing with cyclic pulse sequences such as WAHUA-4,

MREV-8, see Chapter 6) in the form of  $\exp(-iFt_c)$ . The form of  $F$  is readily found when we expand  $U(t_c)$  in a power series (under conditions of actions corresponding to infinitesimal rotations):

$$U(t_c) = \left[ 1 + (-i\mathcal{H}_n\tau_n) + \frac{(-i\mathcal{H}_n\tau_n)^2}{2!} + \cdots \right] \times \cdots \\ \left[ 1 + (-i\mathcal{H}_k\tau_k) + \frac{(-i\mathcal{H}_k\tau_k)^2}{2!} + \cdots \right] \times \cdots \\ \left[ 1 + (-i\mathcal{H}_1\tau_1) + \frac{(-i\mathcal{H}_1\tau_1)^2}{2!} + \cdots \right] \times \cdots \quad (5)$$

If the time intervals are so divided as to make  $\mathcal{H}_k\tau_k$  a small quantity of first order we can rewrite the above equation as:

$$U(t_c) = 1 + (-i)[\mathcal{H}_1\tau_1 + \mathcal{H}_2\tau_2 + \cdots + \mathcal{H}_n\tau_n] \\ + \frac{(-i)^2}{2!}[\mathcal{H}_1^2\tau_1^2 + \mathcal{H}_2^2\tau_2^2 + \cdots + \mathcal{H}_n^2\tau_n^2 \\ + 2(\mathcal{H}_2\mathcal{H}_1\tau_2\tau_1 + \mathcal{H}_3\mathcal{H}_2\tau_3\tau_2 + \cdots \\ + \mathcal{H}_n\mathcal{H}_{n-1}\tau_n\tau_{n-1})] + \frac{(-i)^3}{3!}[\mathcal{H}_1^3\tau_1^3 + \mathcal{H}_2^3\tau_2^3 \\ + \cdots 3(\mathcal{H}_2\mathcal{H}_1^2\tau_2\tau_1^2 + \mathcal{H}_2^2\mathcal{H}_1\tau_2^2\tau_1 + \cdots) \\ + 6(\mathcal{H}_3\mathcal{H}_2\mathcal{H}_1\tau_3\tau_2\tau_1 + \mathcal{H}_4\mathcal{H}_3\mathcal{H}_2\tau_4\tau_3\tau_2 + \cdots) \\ \cdots + \cdots] \quad (6)$$

The time ordering operator makes sure that all operators are arranged in ascending order from right to left.

We said we wanted to express  $U(t_c)$  as  $\exp(-iFt_c)$ . We now make the assumption that  $F$  can be written as a sum of Hamiltonians of different order of magnitude (similar to perturbation order); i.e.,

$$F = \bar{\mathcal{H}} + \bar{\mathcal{H}}^{(1)} + \bar{\mathcal{H}}^{(2)} + \cdots \quad (7)$$

This leads to:

$$\exp(-iFt_c) = \exp(-it_c(\bar{\mathcal{H}} + \bar{\mathcal{H}}^{(1)} + \bar{\mathcal{H}}^{(2)} + \cdots)) \\ = 1 + (-it_c)(\bar{\mathcal{H}} + \bar{\mathcal{H}}^{(1)} + \bar{\mathcal{H}}^{(2)} + \cdots) \\ + \frac{(-it_c)^2}{2!}[(\bar{\mathcal{H}})^2 + \bar{\mathcal{H}}\bar{\mathcal{H}}^{(1)} + \bar{\mathcal{H}}^{(1)}\bar{\mathcal{H}} + (\bar{\mathcal{H}}^{(1)})^2 \\ + \bar{\mathcal{H}}\bar{\mathcal{H}}^{(2)} + \bar{\mathcal{H}}^{(2)}\bar{\mathcal{H}} + \bar{\mathcal{H}}^{(2)}\bar{\mathcal{H}}^{(1)} + \cdots] \\ + \frac{(-it_c)^3}{3!}[(\bar{\mathcal{H}})^3 + (\bar{\mathcal{H}})^2\bar{\mathcal{H}}^{(1)} + \bar{\mathcal{H}}^{(1)}(\bar{\mathcal{H}})^2 \\ + \bar{\mathcal{H}}\bar{\mathcal{H}}^{(1)}\bar{\mathcal{H}} + (\bar{\mathcal{H}}^{(1)})^3 + \cdots] \quad (8)$$

Grouping terms that are correct to a given order, the above equation can be rewritten:

$$\begin{aligned} \exp(-iFt_c) = & 1 - it_c \bar{\mathcal{H}} - it_c \bar{\mathcal{H}}^{(1)} + \frac{(-it_c)^2}{2!} (\bar{\mathcal{H}})^2 \\ & - it_c \bar{\mathcal{H}}^{(2)} + \frac{(-it_c)^2}{2!} [\bar{\mathcal{H}} \bar{\mathcal{H}}^{(1)} + \bar{\mathcal{H}}^{(1)} \bar{\mathcal{H}}] + \dots \end{aligned} \quad (9)$$

we shall now equate the terms in the above equation to those given in the expansion of  $U(t_c)$ , leading to:

$$\begin{aligned} \bar{\mathcal{H}} &= 1/t_c (\mathcal{H}_1 \tau_1 + \mathcal{H}_2 \tau_2 + \mathcal{H}_3 \tau_3 + \dots) \\ \bar{\mathcal{H}}^{(1)} &= (-i/(2t_c)) ([\mathcal{H}_2, \mathcal{H}_1] \tau_2 \tau_1 + [\mathcal{H}_3, \mathcal{H}_1] \tau_3 \tau_1 \\ &\quad + [\mathcal{H}_3, \mathcal{H}_2] \tau_3 \tau_2 + \dots) \text{ etc.} \end{aligned} \quad (10)$$

It is obvious that  $t_c \bar{\mathcal{H}}$  must be a quantity of first order,  $t_c \bar{\mathcal{H}}^{(1)}$ , of second order, etc.

As an example, if the  $\mathcal{H}$  takes only two values during a cycle such that during 0 to  $t_c/2$ ,  $\mathcal{H}_1 \tau_1 = A$  and during  $t_c/2$  to  $t_c$ ,  $\mathcal{H}_2 \tau_2 = B$ , then Magnus expansion leads to:

$$\begin{aligned} t_c \bar{\mathcal{H}} &= A + B \\ t_c \bar{\mathcal{H}}^{(1)} &= (-i/2) [B, A] \\ t_c \bar{\mathcal{H}}^{(2)} &= (1/12) \{ [B, [B, A]] + [[B, A], A] \} \end{aligned} \quad (11)$$

From which it follows that, for noncommuting operators  $A$  and  $B$ ,

$$\begin{aligned} \exp(-iB) \exp(-iA) &= \exp \{ -i(A + B) - 1/2 [B, A] \\ &\quad + (i/12) ([B, [B, A]] + [[B, A], A]) + \dots \} \end{aligned} \quad (12)$$

which is the well known Baker–Campbell–Hausdorff formula.

In the limit  $\tau_k \rightarrow 0$ :

$$\bar{\mathcal{H}} = (1/t_c) \int_0^{t_c} \mathcal{H}(t) dt \quad (13)$$

where  $\bar{\mathcal{H}}$  is the *average Hamiltonian* correct to first order. Likewise,

$$\bar{\mathcal{H}}^{(1)} = (-i/2t_c) \int_0^{t_c} dt_2 \int_0^{t_2} dt_1 [\mathcal{H}(t_2), \mathcal{H}(t_1)] \quad (14)$$

For a symmetrical cycle of time-dependent Hamiltonians such that:

$$\begin{aligned} \bar{\mathcal{H}}(t) &= \bar{\mathcal{H}}(t_c - t) \\ U^{-1}(t_c) &= \exp(i\mathcal{H}_1 \tau_1) \exp(i\mathcal{H}_2 \tau_2) \dots \exp(i\mathcal{H}_n \tau_n) \\ &= \exp(-i\mathcal{H}_n \tau_n) \exp(-i\mathcal{H}_{n-1} \tau_{n-1}) \dots \exp(-i\mathcal{H}_1 \tau_1) \\ &= U(-t_c) \end{aligned} \quad (15)$$

For such cycles it is straightforward to show that:

$$\bar{\mathcal{H}}^{(k)} = (-1)^k \bar{\mathcal{H}}^{(k)} \quad (16)$$

and hence:

$$\bar{\mathcal{H}}^{(k)} = 0$$

for  $k$  odd. If, on the other hand, we consider antisymmetrical cycles corresponding to the equality:

$$\bar{\mathcal{H}}(t) = -\bar{\mathcal{H}}(t - t_c)$$

then:

$$\begin{aligned} U(t_c) &= \exp(i\mathcal{H}_1\tau_1)\exp(i\mathcal{H}_2\tau_2)\cdots \times \cdots \exp(i\mathcal{H}_{n-1}\tau_{n-1})\exp(i\mathcal{H}_n\tau_n) \\ &= U^{-1}(t_c) \end{aligned}$$

i.e.,

$$\exp(-iF_a t_c) = \exp(iF_a t_c)$$

Therefore:

$$F_a = 0 \quad (17)$$

Applying the average Hamiltonian theory to the Carr–Purcell sequence corresponding to  $90_y^\circ - \tau - 180_y^\circ - 2\tau - 180_y^\circ 2\tau$ , we can see that the sequence is cyclic with cycle time  $4\tau$ . It is used mainly to suppress the applied field inhomogeneity term:

$$\begin{aligned} \mathcal{H}_{\text{inh}} &= -\gamma \sum_k \Delta B_{0k} I_{kz} \\ &= -\sum_k \Delta \omega_k I_{kz} \end{aligned} \quad (18)$$

where  $\Delta B_{0k}$  is the deviation of the static field from its mean value at the  $k$ th nucleus. In the interaction representation  $I_{kz}$  toggles between  $I_{kz}$  and  $-I_{kz}$  so that for integer cycle times chemical shift evolution and field inhomogeneities are removed. Under  $\delta$  pulse approximation the Hamiltonian commutes at all times and hence no contribution from  $\bar{\mathcal{H}}^{(n)}$  ( $n > 1$ ) exists. For finite pulse width  $t_w$ ,

$$\bar{\mathcal{H}}^{(1)} = \frac{1}{\pi t_w} (1 - (t_w/t_c)) \sum_k (\Delta \omega_k)^2 I_{kz} \neq 0 \quad (19)$$

For the phase alternated sequence  $-\tau - \theta_y - 2\tau - \theta_y - \tau -$  first-order average Hamiltonian is given by:

$$\bar{\mathcal{H}} = (1/2)(\mathcal{H}_x + \mathcal{H}_z) \quad (20)$$

when  $\theta = \pi/2$ . For dipolar interaction:

$$\bar{\mathcal{H}}_D = (1/2)(\mathcal{H}_{Dx} + \mathcal{H}_{Dz}) = -(1/2)\mathcal{H}_{Dy} \quad (21)$$

and for chemical shift interaction:



$$\begin{aligned}\bar{\mathcal{H}}_{\text{CS}} &= \frac{1}{2} \sum_k (\delta_k + \Delta) (-I_{kx} + I_{kz}) \\ &= \frac{1}{\sqrt{2}} \sum_k (\delta_k + \Delta) I_{\langle 101 \rangle}^{(k)}\end{aligned}$$

where:

$$I_{\langle 101 \rangle}^{(k)} = \frac{1}{\sqrt{2}} (-I_{kx} + I_{kz}) \quad (22)$$

with the chemical shifts being scaled by a factor  $(\sqrt{2})^{-1}$ . The cycle is symmetrical and hence all  $\bar{\mathcal{H}}^{(k)}$ ,  $k = \text{odd}$  vanishes. The leading even-order correction term is given by:

$$\bar{\mathcal{H}}^{(2)} = -\frac{\tau^2}{12} \sum_k (\delta_k + \Delta)^3 (2I_{kz} - I_{kx}) \quad (23)$$

When the pulses are  $\theta$  pulses ( $\theta \neq \pi/2$ ),

$$\bar{\mathcal{H}} = \frac{1}{2} \sum_k [I_{kz}(1 + \cos \theta) - I_{kx} \sin \theta] \quad (24)$$

and the corresponding scale factor can be shown to be  $|\cos(\theta/2)|$ . The phase-alternated pulse sequence is used to scale down chemical shifts uniformly.

## APPENDIX 6

# Tensor Representation of Spin Hamiltonians

All interactions that we come across in magnetic resonance spectroscopy—dipolar coupling, chemical shift, spin–spin coupling, quadrupole coupling, etc.,—can be written in compact form using the tensor notation in terms of irreducible spherical tensor operators because the spin-dependent and coordinate-dependent parts transform as second-rank tensors.

The spin operators in the spherical basis and the various spherical harmonics are very similar and it is possible to construct tensor operator equivalents by a systematic substitution of position variables by the corresponding spin components using the equivalent operator formalism. The position operators do commute with each other, while the spin operators need not and to avoid any complication out of this we follow Rose's definition of a tensor operator. The  $m$ th component of an  $l$ th rank tensor is given by:

$$T_{l,m}(\mathbf{I}) = (\mathbf{I} \cdot \nabla)^l r^l Y_{l,m}(r) \quad (1)$$

where the operator  $(\mathbf{I} \cdot \nabla)^l$  operates on the position coordinates of the spherical harmonic  $Y_{l,m}$  and systematically replaces them by the appropriate spin component. The spherical harmonics are given by:

$$Y_{l,m}(\theta, \varphi) = (-1)^{(m+|m|)/2} \left[ \frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!} \right]^{1/2} \times P_{l,m}(\cos \theta) \exp(im\varphi) \quad (2)$$

where  $P_{l,m}(\cos \theta)$  are the associated Legendre polynomials. Equation (1) automatically gives for first-rank tensor elements:

$$\begin{aligned}
T_{1,1} &= -(3/4)I_+/\sqrt{2} \\
T_{1,0} &= (3/4)I_0 \\
T_{1,-1} &= (3/4)I_-/\sqrt{2}
\end{aligned} \tag{3}$$

where  $I_0 = I_z$ ,  $I_+ = I_x + iI_y$ , and  $I_- = I_x - iI_y$ .

The higher rank tensors can be generated from the first-rank tensors by the recursion relation:

$$\begin{aligned}
T_{l,m} &= \left(\frac{4\pi}{3}\right)^{1/2} \left[ \frac{l!(2l+1)!!}{4\pi} \right]^{1/2} \\
&\quad \times \sum_{\mu} C(1, l-1, l; -\mu, \mu+m) \times T_{l-1, \mu+m} T_{1, -\mu}
\end{aligned} \tag{4}$$

where  $C(\dots)$  are the Clebsch–Gordon coefficients. Thus  $T_{2,0}$  is given by:

$$\begin{aligned}
T_{2,0} &= \frac{4\pi}{3} \left(\frac{15}{2\pi}\right)^{1/2} [C(1, 1, 2; -1, 1) T_{1,1} T_{1,-1} \\
&\quad + C(1, 1, 2; 0, 0) T_{1,0} T_{1,0} \\
&\quad + C(1, 1, 2; 1, -1) T_{1,-1} T_{1,1}]
\end{aligned} \tag{5}$$

The second-rank tensors are thus derived to be:

$$\begin{aligned}
T_{2,0} &= \sqrt{\frac{5}{4\pi}} (3I_0^2 - \mathbf{I}^2) \\
T_{2,\pm 1} &= \pm \sqrt{\frac{15}{8\pi}} (I_{\pm} I_0 \pm I_0 I_{\pm}) \\
T_{2,\pm 2} &= \sqrt{\frac{15}{8\pi}} I_{\pm}^2
\end{aligned} \tag{6}$$

The nine components  $T_{ij}$  of a Cartesian second-rank tensor  $\{\mathbf{T}\}$  can be decomposed into a scalar:

$$T_0 = \frac{1}{3} \text{Tr} \{\mathbf{T}\} \tag{8}$$

and an antisymmetric first-rank tensor:

$$\mathbf{T}_1 : T_{ij}^1 = (1/2)(T_{ij} - T_{ji}) \tag{9}$$

of which there will be three components with zero trace and a traceless second-rank tensor;

$$\mathbf{T}_2 : T_{ij}^2 = \frac{1}{2}(T_{ij} + T_{ji}) - \frac{1}{3} \text{Tr} \{\mathbf{T}\} \delta_{ij} \tag{10}$$

having five components. Thus any of the nine elements can be given by:

$$T_{ij} = \frac{1}{3} \text{Tr} \{\mathbf{T}\} \delta_{ij} + T_{ij}^1 + T_{ij}^2 \tag{11}$$

Just as rotation in coordinate space can be represented by Euler rotation

matrices  $R(\alpha\beta\gamma)$  such that:

$$T'_{kq} = R(\alpha\beta\gamma) T_{kq} R^{-1}(\alpha\beta\gamma) \quad (12)$$

the corresponding irreducible spherical tensor components are governed for coordinate space rotation by the Wigner rotation matrices  $\mathcal{D}_{pq}^k(\alpha\beta\gamma)$  (see Table A.6.1). For second-rank tensors one need consider only irreducible spherical tensor operators up to order 2.

Hamiltonians can be expressed as the product of two irreducible tensors  $\mathbf{A}_k$  and  $\mathbf{T}_k$  with components  $A_{kq}$ ,  $T_{kp}$  so that:

$$\mathbf{A}_k \cdot \mathbf{T}_k = \sum_{q=-k}^{+k} (-1)^q A_{kq} T_{k-q} = \sum_{q=-k}^{+k} (-1)^q A_{k-q} T_{kq} \quad (13)$$

Any Hamiltonian involving spin interactions can be expressed as:

$$\mathcal{H} = \mathbf{X} \cdot \mathbf{A} \cdot \mathbf{Y} = \sum_{i,j} A_{ij} X_i Y_j \quad (14)$$

where  $\mathbf{X}$  and  $\mathbf{Y}$  are vectors and  $\mathbf{A}$  is a  $3 \times 3$  matrix. In terms of irreducible spherical tensor operators,

$$\mathcal{H} = \sum_{k=0}^2 \sum_{q=-k}^{+k} (-1)^q A_{kq} T_{k-q} \quad (15)$$

with:

$$T_{ij} = Y_i X_j$$

and:

$$\begin{aligned} T_{00} &= -\frac{1}{3}(T_{xx} + T_{yy} + T_{zz}) \\ T_{10} &= -\frac{i}{\sqrt{2}}(T_{xy} - T_{yx}) \\ T_{1\pm 1} &= -\frac{1}{2}(T_{zx} - T_{xz} \pm i(T_{zy} - T_{yz})) \\ T_{20} &= \frac{1}{\sqrt{6}}(3T_{zz} - (T_{xx} + T_{yy} + T_{zz})) \\ T_{2\pm 1} &= \mp \frac{1}{2}(T_{xz} + T_{zx} \pm i(T_{yz} + T_{zy})) \\ T_{2\pm 2} &= \frac{1}{2}(T_{xx} - T_{yy} \pm i(T_{xy} + T_{yx})) \end{aligned} \quad (16)$$

The corresponding elements of the  $\mathbf{A}$  tensor are given by replacing  $T$  by spin operators. For symmetric tensors,

$$\mathcal{H} = A_{00} T_{00} + A_{20} T_{20} - (A_{2,-1} T_{21} + A_{21} T_{2-1}) \quad (17)$$

Table A.6.1. Wigner Rotation Matrix  $D_{m'm}^2(\alpha, \beta, \gamma)$ 

$m'$	$m$	2	1	0	-1	-2
2		$\frac{(1 + \cos \beta)^2}{4} e^{2i(\alpha + \gamma)}$	$\frac{1 + \cos \beta}{2} \sin \beta e^{i(2\gamma + \alpha)}$	$\sqrt{\frac{3}{8}} \sin^2 \beta e^{2i\gamma}$	$\frac{1 - \cos \beta}{2} \sin \beta e^{i(2\gamma - \alpha)}$	$\frac{(1 - \cos \beta)^2}{4} e^{2i(\gamma - \alpha)}$
1		$-\frac{1 + \cos \beta}{2} \sin \beta e^{i(2\alpha + \gamma)}$	$\left[ \cos^2 \beta - \frac{1 - \cos \beta}{2} \right] e^{i(\alpha + \gamma)}$	$\sqrt{\frac{3}{8}} \sin 2\beta e^{i\gamma}$	$\left[ \frac{1 + \cos \beta}{2} - \cos^2 \beta \right] e^{i(\gamma - \alpha)}$	$\frac{1 - \cos \beta}{2} \sin \beta e^{i(\gamma - 2\alpha)}$
0		$\sqrt{\frac{3}{8}} \sin^2 \beta e^{2i\alpha}$	$-\sqrt{\frac{3}{8}} \sin 2\beta e^{i\alpha}$	$\frac{3 \cos^2 \beta - 1}{2}$	$\sqrt{\frac{3}{8}} \sin 2\beta e^{-i\alpha}$	$\sqrt{\frac{3}{8}} \sin^2 \beta e^{-2i\alpha}$
-1		$-\frac{1 - \cos \beta}{2} \sin \beta e^{i(2\alpha - \gamma)}$	$\left[ \frac{1 + \cos \beta}{2} - \cos^2 \beta \right] e^{i(\alpha - \gamma)}$	$-\sqrt{\frac{3}{8}} \sin^2 \beta e^{-i\gamma}$	$\left[ \cos^2 \beta - \frac{1 - \cos \beta}{2} \right] e^{-i(\alpha + \gamma)}$	$\frac{1 + \cos \beta}{2} \sin \beta e^{-i(2\alpha + \gamma)}$
-2		$\frac{(1 - \cos \beta)^2}{4} e^{2i(\alpha - \gamma)}$	$-\frac{1 - \cos \beta}{2} \sin \beta e^{i(\alpha - 2\gamma)}$	$\sqrt{\frac{3}{8}} \sin^2 \beta e^{-2i\gamma}$	$-\frac{1 + \cos \beta}{2} \sin \beta e^{-i(\alpha + 2\gamma)}$	$\frac{(1 + \cos \beta)^2}{4} e^{-2i(\alpha + \gamma)}$

with:

$$A_{2\pm 1} = \mp (A_{xz} \pm iA_{yz})$$

For dipolar (D) and quadrupolar (Q) interaction the corresponding elements are:

$$\begin{aligned} A_{00} &= -\frac{1}{3} \text{Tr } \mathbf{D} \\ A_{10} &= A_{1\pm 1} = 0 \\ A_{20} &= (3/\sqrt{6})\mathbf{D}_{zz} \\ A_{2\pm 1} &= \mp (\mathbf{D}_{xz} \pm i\mathbf{D}_{yz}) \\ A_{2\pm 2} &= \frac{1}{2}(\mathbf{D}_{xx} - \mathbf{D}_{yy} \pm 2i\mathbf{D}_{xy}) \end{aligned} \quad (18)$$

and:

$$\begin{aligned} T_{20} &= (1/\sqrt{6})(3I_z S_z - \mathbf{I} \cdot \mathbf{S}) \\ T_{2\pm 1} &= \mp \frac{1}{2}(I_z S_{\pm} + I_{\pm} S_z) \\ T_{2\pm 2} &= (1/2)I_{\pm} S_{\pm} \end{aligned} \quad (19)$$

Table A.6.2 gives the various interactions in terms of spin operators corresponding to the  $T_{l,m}$ 's.

Table A.6.3 summarizes the transformation properties under spin operator space rotation (cf., Chapter 6, multiple-pulse line-narrowing sequences) of operators that are not rejected by truncation (i.e., that correspond to first-order in perturbation).

As can be seen  $I$ -spin homonuclear bilinear spin operators and single spin

Table A.6.2.  $T_{lm}$ 's Corresponding to Various Interactions

Interaction	$\lambda$	$I_{\alpha} A_{\beta}^{\lambda}$	$T_{00}$	$T_{20}$	$T_{2\pm 1}$	$T_{2\pm 2}$
Shielding	CS	$I_{\alpha}^i B_{\beta}$	$I_0^i B_0$	$\sqrt{\frac{2}{3}} I_0^i B_0$	$\frac{1}{\sqrt{2}} I_{\pm}^i B_0$	0
Spin rotation	SR	$I_{\alpha}^i J_{\beta}$	$\mathbf{I}^i \cdot \mathbf{J}$	$\frac{1}{\sqrt{6}} (3I_0^i J_0 - \mathbf{I}^i \cdot \mathbf{J})$	$\frac{1}{\sqrt{2}} (I_{\pm 1}^i J_0 + I_0^i J_{\pm 1})$	$I_{\pm 1}^i J_{\pm 1}$
Quadrupole	Q	$I_{\alpha}^i I_{\beta}^i$	$(\mathbf{I}^i)^2$	$\frac{1}{\sqrt{6}} (3(I_0^i)^2 - (\mathbf{I}^i)^2)$	$\frac{1}{\sqrt{2}} (I_{\pm 1}^i I_0^i + I_0^i I_{\pm 1}^i)$	$(I_{\pm 1}^i)^2$
Dipole indirect Spin-spin	D J	$I_{\alpha}^i I_{\beta}^k$	$\mathbf{I}^i \cdot \mathbf{I}^k$	$\frac{1}{\sqrt{6}} (3I_0^i I_0^k - \mathbf{I}^i \cdot \mathbf{I}^k)$	$\frac{1}{\sqrt{2}} (I_{\pm 1}^i I_0^k + I_0^i I_{\pm 1}^k)$	$I_{\pm 1}^i I_{\pm 1}^k$

Table A.6.3. Transformation of  $T_{lm}$ 's in  $I$ -spin Space

Interaction	$T_{l0}^\lambda$	After truncation	Transforms in $I$ -spin space according to:	
			$l =$	$m =$
Shielding	$T_{00}^{\text{CS}}$	$I_0^i B_0$	1	0
	$T_{20}^{\text{CS}}$	$\sqrt{\frac{2}{3}} I_0^i B_0$	1	0
Quadrupolar	$T_{20}^{\text{Q}}$	$\frac{1}{\sqrt{6}} (3(I_0^i)^2 - (\mathbf{I}^i)^2)$	2	0
Direct and indirect between $\mathbf{I}^i$ and $\mathbf{I}^k$	$T_{00}^J$	$\mathbf{I}^i \cdot \mathbf{I}^k$	0	0
	$T_{20}^{\text{D},J}$	$\frac{1}{\sqrt{6}} (3I_0^i I_0^k - \mathbf{I}_0^i \cdot \mathbf{I}_0^k)$	2	0
Direct and indirect between $\mathbf{I}^i$ and $\mathbf{S}^k$	$T_{00}^J$	$I_0^i S_0^k$	1	0
	$T_{20}^{\text{D},J}$	$\sqrt{\frac{2}{3}} I_0^i S_0^k$	1	0

quadrupolar operators are identical in their transformation properties in both full space and  $I$  spin subspace. However, operators that are linear in  $I$  space transform differently in full space and  $I$ -spin subspace and this aids in selective averaging by multiple-pulse sequences.

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