2

The Product Operator Formalism

1. INTRODUCTION

In this section we will see that the density matrix at equilibrium can be expressed in terms of the spin angular momentum component I_z of each nucleus. Moreover, effects of pulses (rotations) and evolutions of noncoupled spins can also be described in terms of angular momentum components (I_x,I_y,I_z). However, in order to express evolutions of coupled spins, we will need additional "building blocks" besides angular momentum components. We will thus introduce a "basis set" which is composed of "product operators." The latter are either products between angular momentum components or products of angular momentum components with the unit matrix. We will describe this approach and will apply it to several pulse sequences, beginning with 2DHETCOR.

2. EXPRESSING THE DENSITY MATRIX IN TERMS OF ANGULAR MOMENTUM COMPONENTS

We start with the same procedure of describing the density matrix at equilibrium, $D(0)$, as in Part I. In order to generalize the approach to an AX (not only a CH) system we preserve separate Boltzman factors, $1 + p$ and $1 + q$, for nuclei A and X, respectively [see (I.3-5)]:

$$D(0)=\frac{1}{N}\begin{bmatrix}1 & 0 & 0 & 0\\ 0 & 1+p & 0 & 0\\ 0 & 0 & 1+q & 0\\ 0 & 0 & 0 & 1+p+q\end{bmatrix} \qquad \text{(II.1)}$$

N is the number of states (4 for an AX system).

As we did in Part I, we separate the unit matrix from the matrix representing population differences. However, here we choose as a factor for the unit matrix the average population $(1+p/2+q/2)/N$:

$$D(0)=\frac{1+p/2+q/2}{N}\begin{bmatrix}1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\\ 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 1\end{bmatrix}$$

$$+\frac{1}{N}\begin{bmatrix}-p/2-q/2 & 0 & 0 & 0\\ 0 & p/2-q/2 & 0 & 0\\ 0 & 0 & -p/2+q/2 & 0\\ 0 & 0 & 0 & p/2+q/2\end{bmatrix}$$

(II.2)

Again, we ignore the term containing the unit matrix which does not contribute to magnetization.

$$D(0)=\frac{1}{N}\begin{bmatrix}-p/2-q/2 & 0 & 0 & 0\\ 0 & p/2-q/2 & 0 & 0\\ 0 & 0 & -p/2+q/2 & 0\\ 0 & 0 & 0 & p/2+q/2\end{bmatrix}$$

(II.3)

Separation of the p and q terms gives

$$D(0) = -\frac{p}{2N}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} - \frac{q}{2N}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \qquad \text{(II.4)}$$

We recognize in the first term the angular momentum component I_{zA} and, in the second term, I_{zX} [see (C13) and (C15)]. We note that the signs of the magnetic quantum numbers are in the same order as in Figure I.1 of Part I. We can now write $D(0)$ in shorthand:

$$D(0) = -\frac{p}{N} I_{zA} - \frac{q}{N} I_{zX} \qquad \text{(II.5)}$$

3. DESCRIBING THE EFFECT OF A PULSE IN TERMS OF ANGULAR MOMENTA

The rotation operator for a 90° pulse along the x-axis on nucleus X is:

$$R_{90xX} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 0 & i & 0 \\ 0 & 1 & 0 & i \\ i & 0 & 1 & 0 \\ 0 & i & 0 & 1 \end{bmatrix} \qquad \text{(see I.9)}$$

Its reciprocal is:

$$R_{90xX}^{-1} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 0 & -i & 0 \\ 0 & 1 & 0 & -i \\ -i & 0 & 1 & 0 \\ 0 & -i & 0 & 1 \end{bmatrix} \qquad \text{(see I.10)}$$

We postmultiply $D(0)$ from (II.3) with R_{90xX} (R, for brevity).

$$D(0)R = \frac{1}{2N}\begin{bmatrix} -p-q & 0 & 0 & 0 \\ 0 & p-q & 0 & 0 \\ 0 & 0 & -p+q & 0 \\ 0 & 0 & 0 & p+q \end{bmatrix}\frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 0 & i & 0 \\ 0 & 1 & 0 & i \\ i & 0 & 1 & 0 \\ 0 & i & 0 & 1 \end{bmatrix}$$

$$= \frac{1}{2\sqrt{2}N}\begin{bmatrix} -p-q & 0 & -ip-iq & 0 \\ 0 & p-q & 0 & ip-iq \\ -ip+iq & 0 & -p+q & 0 \\ 0 & ip+iq & 0 & p+q \end{bmatrix} \qquad \text{(II.6)}$$

We now premultiply this result by R^{-1}

$D(1) = R^{-1}[D(0)\ R]$

$$= \frac{1}{4N}\begin{bmatrix} 1 & 0 & -i & 0 \\ 0 & 1 & 0 & -i \\ -i & 0 & 1 & 0 \\ 0 & -i & 0 & 1 \end{bmatrix}\begin{bmatrix} -p-q & 0 & -ip-iq & 0 \\ 0 & p-q & 0 & ip-iq \\ -ip+iq & 0 & -p+q & 0 \\ 0 & ip+iq & 0 & p+q \end{bmatrix}$$

$$= \frac{1}{4N}\begin{bmatrix} -2p & 0 & -2iq & 0 \\ 0 & 2p & 0 & -2iq \\ 2iq & 0 & -2p & 0 \\ 0 & 2iq & 0 & 2p \end{bmatrix} = \frac{1}{2N}\begin{bmatrix} -p & 0 & -iq & 0 \\ 0 & p & 0 & -iq \\ iq & 0 & -p & 0 \\ 0 & iq & 0 & p \end{bmatrix} \qquad \text{(II.7)}$$

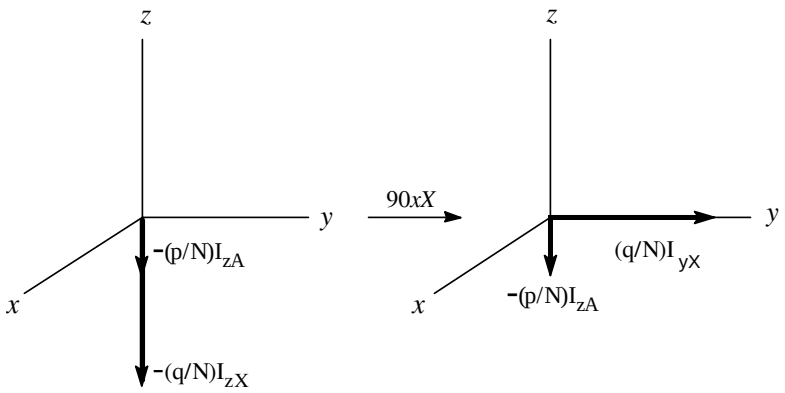
Separation of p and q yields

$$D(1) = \frac{-p}{2N}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} + \frac{q}{2N}\begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{bmatrix} \qquad \text{(II.8)}$$

Comparing the result with (C13) and (C14) we recognize I_{zA} and I_{yX} and we can write

$$D(1) = \frac{-p}{N} I_{zA} + \frac{q}{N} I_{yX} \qquad \text{(II.9)}$$

Relations (II.5) and (II.9) open the way toward the product operator formalism. We succeeded in writing $D(0)$ and $D(1)$ in angular momentum shorthand. Moreover, we foresee the possibility of obtaining the result of pulses without matrix calculations; this can be seen by simply representing the angular momenta in their vector form, as in Figure II.1.



$$-(p/N)I_{zA} - (q/N)I_{zX} \xrightarrow{90xX} -(p/N)I_{zA} + (q/N)I_{yX}$$

Figure II.1. Effect of the 90*xX* pulse.

We note that, because of our convention to take gamma as negative (see Appendix J) the angular momentum vector orientation is opposite to that of the magnetization vector which was used in Part I.

4. AN UNSUCCESSFUL ATTEMPT TO DESCRIBE A COUPLED EVOLUTION IN TERMS OF ANGULAR MOMENTA

Let us calculate the result of a coupled evolution of duration $t_e/2$ starting from $D(1)$. Applying (I.13) to $D(1)$ in (II.7) gives:

$$D(2) = \frac{1}{2N}\begin{bmatrix} -p & 0 & F & 0 \\ 0 & p & 0 & G \\ F* & 0 & -p & 0 \\ 0 & G* & 0 & p \end{bmatrix} \qquad \text{(II.10)}$$

where

$$F = -iq\exp(-i\Omega_{13}t_e/2)$$
$$G = -iq\exp(-i\Omega_{24}t_e/2) \qquad \text{(II.11)}$$

With the notations

$$\Omega_{13} = \Omega_X + \pi J$$
$$\Omega_{24} = \Omega_X - \pi J \qquad \text{(II.12)}$$

the exponentials in (II.11) become

$$\begin{aligned}\exp(-i\Omega_{13}t_e/2) &= \exp[-i(\Omega_X + \pi J)t_e/2] \\ &= \exp(-i\Omega_X t_e/2)\exp(-i\pi J t_e/2) \qquad \text{(II.13)} \\ \exp(-i\Omega_{24}t_e/2) &= \exp[-i(\Omega_X - \pi J)t_e/2] \\ &= \exp(-i\Omega_X t_e/2)\exp(+i\pi J t_e/2)\end{aligned}$$

We make now the following notations:

$$c = \cos\Omega_X t_e/2 \qquad s = \sin\Omega_X t_e/2$$
$$C = \cos\pi J t_e/2 \qquad S = \sin\pi J t_e/2 \qquad \text{(II.14)}$$

Note that here c and s have different meanings than the ones assigned in Part I (I.31). To make sure, c and s (lower case) represent effects of chemical shift and C and S (upper case) represent effects of J-coupling. Now the exponentials in (II.11) can be written as:

$$\exp(-i\Omega_{13}t_e/2) = (c - is)(C - iS) \qquad \text{(II.15)}$$
$$\exp(-i\Omega_{24}t_e/2) = (c - is)(C + iS)$$

Then F and G become

$$F = -iq(c - is)(C - iS) = -iq(cC - sS) - q(sC + cS)$$
$$G = -iq(c - is)(C + iS) = -iq(cC + sS) - q(sC - cS) \quad \text{(II.16)}$$

and we can rewrite D(2) as

$$\frac{1}{2N}\begin{bmatrix} -p & 0 & \begin{matrix}-iq(cC - sS)\\ -q(sC + cS)\end{matrix} & 0 \\ 0 & p & 0 & \begin{matrix}-iq(cC + sS)\\ -q(sC - cS)\end{matrix} \\ \begin{matrix}iq(cC - sS)\\ -q(sC + cS)\end{matrix} & 0 & -p & 0 \\ 0 & \begin{matrix}iq(cC + sS)\\ -q(sC - cS)\end{matrix} & 0 & p \end{bmatrix} \quad \text{(II.17)}$$

We separate $D(2)$ into five matrices containing the factors p, qcC, qsS, qsC, and qcS:

$$D(2) = -\frac{p}{2N}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} + \frac{q}{2N}cC\begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{bmatrix}$$
$$-\frac{q}{2N}sS\begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & i \\ i & 0 & 0 & 0 \\ 0 & -i & 0 & 0 \end{bmatrix} - \frac{q}{2N}sC\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$
$$-\frac{q}{2N}cS\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix} \quad \text{(II.18)}$$

In (II.18) only three terms, the first, second, and fourth, contain angular momenta [cf.(C12-C15)]. The first term is $-(p/N)I_{zA}$, the second is $(q/N)cCI_{yX}$ and the fourth is $-(q/N)sCI_{xX}$. The third and fifth matrices in (II.18) contain neither angular momenta nor a linear combination of the six components (I_{xA}, I_{yA}, I_{zA}, I_{xX}, I_{yX}, I_{zX}) known to us. This shows that the six angular momentum components shown in parenthesis are not sufficient to express the density matrix after a coupled evolution. In other words they constitute an *incomplete set* of *operators*. We will see in the next section how we can put together a *complete (basis) set* which will allow us to treat coupled evolutions in a shorthand similar to that used for $D(0)$ and $D(1)$. We may use as an analogy the blocks a child would need to build any number of castles of different shapes given in a catalog. For a given castle the child may not need to use all the building blocks, but he knows that none of the castles would require a block he does not have.

5. PRODUCT OPERATORS (PO)

We will call each building block a *basis operator* and will give in Table II.1 a complete set of such operators for the AX system. The bracket notations proposed by us will be defined as we explain how this set was put together.

Table II.1 Basis Operators for 2 Nuclei ($I = 1/2$)

$$[11]=\begin{bmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{bmatrix} \qquad [z1]=\begin{bmatrix}1&0&0&0\\0&-1&0&0\\0&0&1&0\\0&0&0&-1\end{bmatrix}$$

$$[1z]=\begin{bmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{bmatrix} \qquad [zz]=\begin{bmatrix}1&0&0&0\\0&-1&0&0\\0&0&-1&0\\0&0&0&1\end{bmatrix}$$

$$[x1] = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \qquad [y1] = \begin{bmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{bmatrix}$$

$$[xz] = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{bmatrix} \qquad [yz] = \begin{bmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & i \\ 0 & 0 & -i & 0 \end{bmatrix}$$

$$[1x] = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix} \qquad [1y] = \begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{bmatrix}$$

$$[zx] = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix} \qquad [zy] = \begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & i \\ i & 0 & 0 & 0 \\ 0 & -i & 0 & 0 \end{bmatrix}$$

$$[xx] = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} \qquad [xy] = \begin{bmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & -i & 0 \\ 0 & i & 0 & 0 \\ i & 0 & 0 & 0 \end{bmatrix}$$

$$[yx] = \begin{bmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{bmatrix} \qquad [yy] = \begin{bmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{bmatrix}$$

These product operators have been introduced by Ernst and coworkers (see O.W.Sörensen, G.W.Eich, M.H.Levitt, G.Bodenhausen, and R.R.Ernst in *Progress in NMR Spectroscopy*, **16**, 1983, 163-192, and

references cited therein). The operators we use are multiplied by a factor of 2 in order to avoid writing 1/2 so many times.

Each basis operator is a product of two factors, one for each of the two nuclei (hence, the name "product operator"). The factor corresponding to a given nucleus may be one of its own angular momentum components multiplied by two ($2I_x$, $2I_y$, $2I_z$) or the unit matrix.

For example in the product operator [*zz*] the first factor is $2I_{zA}$ and the second, $2I_{zX}$. Proof:

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \times \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

$$2I_{zA} \quad \times \quad 2I_{zX} \quad = \quad [zz] \qquad \text{(II.19)}$$

Another example:

$$[x1] = 2I_{xA} \cdot [1] = 2I_{xA} = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \qquad \text{(II.20)}$$

The basis set in Table II.1 allows us now to write (II.18) in shorthand because we recognize that the third term in (II.18) contains the product operator [*zy*] and the fifth term contains [*zx*]. Thus,

$$D(2) = -(p2N)[z1] + (q/2N)cC[1y] - (q/2N)sS[zy] - (q/2N)sC[1x] - (q/2N)cS[zx] \qquad \text{(II.21)}$$

If we were to continue now to transform into product operators (PO) all the subsequent density matrices of HETCOR we would, of course, be able to do it, but this would do us no good. The real advantage will consist in finding a way to go from one PO to the next PO

without using matrices. There is a small price to pay for this advantage, namely learning a few rules which show how to obtain a new PO representation after pulses or evolutions. It will be seen later that the PO advantage is much more important when we have to handle systems of more than two spins.

6. PULSE EFFECTS (ROTATIONS) IN THE PRODUCT OPERATOR FORMALISM

The great advantage of expressing the density matrix in terms of product operators is found in the dramatic simplification of calculations needed to describe pulse effects (rotations). Let us illustrate this by a few examples.

(1) 90*xX* pulse applied to *D*(0):

$$-(p/2N)[z1]-(q/2N)[1z] \xrightarrow{90xX} -(p/2N)[z1]+(q/2N)[1y]$$

***D*(0)** ***D*(1)**

This PO operation can be readily visualized in vector representation. Indeed, looking at Figure II.2a we see that, while the angular momentum of X moves from $-$ z to $+y$ (90° rotation), the vector of A remains unaffected.

Let the vector representation guide us now to write another PO operation (see Figure II.2b).

(2) 90*xA* pulse applied to *D*(0):

$$-(p/2N)[z1]-(q/2N)[1z] \xrightarrow{90xA} +(p/2N)[y1]-(q/2N)[1z]$$

***D*(0)** ***D*(1)**

By following the same procedure in examples 3 to 5 we find out that the product operators after any rotation can be written by changing the labels *x,y,z,* of the affected nucleus according to the rotation which took place in the vector representation. Of course, the unit matrix (label "1") always stays the same.

(3) 90*yAX* (nonselective) pulse applied to *D*(0):

$$-(p/2N)[z1]-(q/2N)[1z]\xrightarrow{90\,yAX}-(p/2N)[x1]-(q/2N)[1x]$$
$$\boldsymbol{D(0)} \qquad\qquad \boldsymbol{D(1)}$$

(4) 90xA applied to D(1) above:

$$-(p/2N)[x1]-(q/2N)[1x]\xrightarrow{90\,xA}-(p/2N)[x1]-(q/2N)[1x]$$

(No change, whatsoever)

(5) 90*yA* applied to *D*(1) above:

$$-(p/2N)[x1)-(q/2N)[1x]\xrightarrow{90\,yA}+(p/2N)[z1]-(q/2N)[1x]$$

The validity of this approach is demonstrated in Appendix E.

Many pulse sequences contain rotations other than 90° or 180°. We now proceed to apply our vector rule for an arbitrary angle α (see Figure II.2c). The PO representation of this rotation is

$$-(p/2N)[z1]-(q/2N)[1z]\xrightarrow{\alpha\,xX}-(p/2N)[z1]$$
$$-(q/2N)([1z]\cos\alpha-[1y]\sin\alpha)$$

A few more examples of rotations are given below. This time we ignore the factors p/2N or q/2N.

$$[zz]\xrightarrow{90\,yA}[xz]$$

$$[zz]\xrightarrow{90\,yX}[zx]$$

$$[zz]\xrightarrow{90\,xA}-[yz]$$

$$[xy]\xrightarrow{180\,yA}-[xy]$$

$$[1y]\xrightarrow{90\,xA}[1y]$$

$$[zz]\xrightarrow{\alpha\,yA}[zz]\cos\alpha+[xz]\sin\alpha$$