APPENDIX J: PRODUCT OPERATORS AND MAGNETIZATION COMPONENTS

Finding the magnetization components

Suppose that at a given moment $t(n)$ of the sequence we have the density matrix $D(n)$ expressed in terms of product operators. The x magnetization components for nuclei A, M, X (we take a three-spin system as an example) are given by:

$$M_{xA}(n) = - (M_{oA} / p'_A)\left(\text{coefficient of } [x11] \text{ in } D(n)\right)$$
$$M_{xM}(n) = -(M_{oM} / p'_M)\left(\qquad " \qquad [1x1] \quad " \quad D(n)\right) \quad \text{(J1)}$$
$$M_{xX}(n) = -(M_{oX} / p'_X)\left(\qquad " \qquad [11x] \quad " \quad D(n)\right)$$

with similar expressions for M_y and M_z.

M_{oA}, M_{oM}, M_{oX} are the equilibrium magnetizations for the respective nuclei. The factor p' is related to the Boltzmann factor and has the expression

$$p'_A = p_A / 2N = \hbar\Omega_A / 2NkT \qquad \text{(J2)}$$

with similar expressions for p'_M, p'_X (for two nuclei we adopt p, q instead of p_A, p_X). N = total number of quantum states in the system (degenerate or not). For m nuclei with $I = 1/2$ we have $N = 2^m$.

The quantity $1/N$ represents the average population per state as the total population is normalized to l. The above procedure is justified by the relation (B17), keeping in mind the orthogonality of product operators (relation D1).

Fast and slow magnetization components

In the first part of this book, when deriving the magnetization components from the density matrix elements, we found it instructive to calculate separately the *fast* and *slow* components of the transverse magnetization (see Section I.3.9). This can be achieved in the PO formalism as well.

For an AX system (two spin 1/2 nuclei), one can split the M_{xA} magnetization into M_{x12} (fast) and M_{x34} (slow) as follows:

$$M_{x12} = -\frac{M_{oA}}{2p'}\left(\text{coeff. of } [x1] + \text{coeff. of } [xz]\right)$$

$$M_{x34} = -\frac{M_{oA}}{2p'}\left(\text{coeff. of } [x1] - \text{coeff. of } [xz]\right)$$

with similar relations for M_y.

For nucleus X the fast and slow components are:

$$M_{x13} = -\frac{M_{oA}}{2p'}\left(\text{coeff. of } [1x] + \text{coeff. of } [zx]\right)$$

$$M_{x24} = -\frac{M_{oA}}{2p'}\left(\text{coeff. of } [1x] - \text{coeff. of } [zx]\right)$$

Using Table II.1, one can check that

$$\left([1x] + [zx]\right)/2 \quad \text{and} \quad \left([1x] - [zx]\right)/2$$

represent the matrix elements d_{13} and d_{24}, respectively.

Writing the initial density matrix

We assume usually that, before the pulse sequence starts, all spins are at thermal equilibrium with the lattice.

With the sign convention adopted in this book (vide infra) the density matrix $D(0)$ will be:

$$D(0) = -p'_A[z11] - p'_M[1z1] - p'_X[11z] \tag{J3}$$

This is consistent with

$$M_{zA} = M_{oA} \quad ; \quad M_{xA} = 0 \quad ; \quad M_{yA} = 0$$

and is the same for spins M and X.

If we work in a steady state in which one of the nuclei (let's say nucleus A) does not have enough time to recover from the previous cycle, we can start with

$$D(0) = -\lambda p'_A[z11] - p'_M[1z1] - p'_X[11z] \tag{J4}$$

where $\lambda \leq 1$. If M_{zA} has been brought to zero by the last pulse of the sequence and the start of the next sequence comes after a delay d, then

$$\lambda = 1 - \exp\left(-d/T_{1A}\right)$$

Generally we start a sequence with no transverse magnetization; this implies that d is long enough with respect to T_2 for all nuclei.

Sign convention

Throughout this book the conventional positive sense (right hand rule) has been adopted for all rotations (due to pulses or evolutions). For instance a rotation about Oz brings the magnetization from x to y, to $-x$, to $-y$. A rotation about Ox goes:

$$y \text{ to } z \text{ to } -y \text{ to } -z$$

This is the actual sense of precession when the magnetogyric ratio, γ, is negative. It has been assumed that the main magnetic field B_o is directed upwards (along $+Oz$) and thus at equilibrium the magnetization is directed up and the angular momentum is directed downwards (along $-Oz$) which is also consistent with a negative γ.

This way, the most populated state is the one with the angular momentum negative. Most features of the NMR sequences (one- and two-dimensional) do not depend on the sign of γ for all practical purposes. Commercial NMR spectrometers do not provide specific means to distinguish the sign of γ. Therefore the above rules can be applied for all nuclei in the system, no matter what the sign of their magnetogyric ratio.

If for special purposes the sign of γ has to be taken into account, then for positive γ we have to use left hand rotation rules and start at thermal equilibrium with I_z directed upwards.