APPENDIX E: DEMONSTRATION OF THE ROTATION RULES

We demonstrate here the validity of the PO pulse rotations derived from the vector representation in Section II.6 (correspondence between the vector rotations and the PO formalism).

Demonstration of an αx rotation

We will demonstrate an α rotation around the *x*-axis:

$$I_y \xrightarrow{\alpha x} I_y \cos\alpha + I_z \sin\alpha \qquad \text{(E1)}$$

Other rotations can be demonstrated in a similar way. We start from the rotation operator applied to a density matrix and we make use of the commutation rules for the operators I_x, I_y, I_z, which are:

$$\begin{aligned} I_x I_y - I_y I_x &= iI_z \\ I_y I_z - I_z I_y &= iI_x \\ I_z I_x - I_x I_z &= iI_y \end{aligned} \qquad \text{(E2)}$$

It is necessary to emphasize that the above rules apply not only to an isolated spin but also to every particular nucleus in a multi-nuclear system (with or without coupling). In an AMX system for instance we have for nucleus A:

$$I_{xA} I_{yA} - I_{yA} I_{xA} = iI_{zA} \qquad \text{(and so on)}$$

Angular momentum components of *different* nuclei within a system are commutative. For instance:

$$\begin{aligned} I_{xA} I_{yM} - I_{yM} I_{xA} &= 0 \\ I_{xA} I_{xM} - I_{xM} I_{xA} &= 0 \end{aligned} \qquad \text{(E3)}$$

The rotation operator $R_{\alpha x}$ [see(B45)] has the expression:

$$R_{\alpha x} = \exp(i\alpha I_x) \qquad \text{(E4)}$$

Applied to a density matrix $D(n)$ it will yield:

$$D(n+1) = R_{\alpha x}^{-1} D(n) R_{\alpha x} \qquad \text{(E5)}$$

In (E1) we have assumed that $D(n)$ is equal to I_y, so what we have to demonstrate is:

$$D(n+1) = R_{\alpha x}^{-1} I_y R_{\alpha x} = I_y \cos\alpha + I_x \sin\alpha \tag{E6}$$

In Appendix B we have demonstrated [see (B51)] that

$$R_{\alpha x} = \cos\frac{\alpha}{2}\cdot[1] + i\sin\frac{\alpha}{2}\cdot(2I_x) \tag{E7}$$

Introducing this expression in (E6) gives

$$D(n+1) = \left[\cos\frac{\alpha}{2}\cdot[1] - i\sin\frac{\alpha}{2}\cdot(2I_x)\right] I_y \left[\cos\frac{\alpha}{2}\cdot[1] + i\sin\frac{\alpha}{2}\cdot(2I_x)\right]$$

$$= \cos^2\frac{\alpha}{2}\cdot I_y + 4\sin^2\frac{\alpha}{2}\cdot I_x I_y I_x + 2i\cos\frac{\alpha}{2} 4\sin\frac{\alpha}{2}(I_y I_x - I_x I_y)$$

After using the first relation in (E2) this becomes

$$D(n+1) = \cos^2\frac{\alpha}{2}\cdot I_y + 4\sin^2\frac{\alpha}{2}\cdot I_x I_y I_x + 2i\cos\frac{\alpha}{2} 4\sin\frac{\alpha}{2}(-iI_z)$$

$$= \cos^2\frac{\alpha}{2}\cdot I_y + 4\sin^2\frac{\alpha}{2}\cdot I_x I_y I_x + \sin\alpha\cdot I_z$$

If we use now the relation

$$I_x I_y I_x = -\frac{1}{4} I_y \tag{E8}$$

which will be demonstrated immediately, we get

$$D(n+1) = \cos\alpha\cdot I_y + \sin\alpha\cdot I_z$$

which confirms (E1).

To demonstrate (E8) we postmultiply the first relation in (E2) by I_x and, taking (B48) into account, we obtain

$$I_x I_y I_x - \frac{1}{4} I_y = iI_z I_x \tag{E9}$$

Premultiplying of the first relation in (E1) by I_x yields

$$\frac{1}{4} I_y - I_x I_y I_x = iI_x I_z \tag{E10}$$

Subtracting (E10) from (E9) gives

$$2I_x I_y I_x - \frac{1}{2} I_y = i(I_z I_x - I_x I_z) = i(iI_y) = -I_y$$

or

$$2I_xI_yI_x = -\frac{1}{2}I_y$$

which demonstrates (E8).

Rotation operators applied to product operators

Suppose we have to apply the rotation operator the $R_{\alpha xA}$ to the product operator [*yzy*]. The latter is a shorthand notation for the product.

$$(2I_{yA})(2I_{zM})(2I_{yX})$$

The subscripts *A*, *M*, *X* refer to the different nuclei in the system. Since these subscripts are omitted for simplicity in the product operator label [*yzy*], we have to keep in mind as a convention that the different nuclei of the system appear in the product operators always in the same order: A, M, X.

What we have to calculate is:

$$D(n+1) = \exp(-i\alpha I_{xA}) \cdot 8I_{yA}I_{zM}I_{yX}\exp(i\alpha I_{xA}) \qquad \text{(E11)}$$

We have stated (E3) that I_{xA} commutes with both I_{zM} and I_{yX}. This enables us to rewrite (E11) as:

$$D(n+1) = \exp(-i\alpha I_{xA}) \cdot I_{yA}\exp(i\alpha I_{xA})8I_{zM}I_{yX}$$

and we have reduced the problem to a known one. Using (E6) we get:

$$D(n+1) = 8(\cos\alpha \cdot I_{yA} + \sin\alpha \cdot I_{zA})I_{zM}I_{yX}$$

In shorthand notation:

$$[yzy] \xrightarrow{\alpha xA} [yzy]\cos\alpha + [zzy\}\sin\alpha \qquad \text{(E12)}$$

This can be phrased as follows: A rotation operator affects only one factor in the product operator and leaves the others unchanged. The affected factor parallels the vector rotation rules.

This is true in the case of a *selective pulse*. We have sometimes to handle *nonselective pulses*, affecting two or more nuclei in the system. In such cases, the procedure to follow is to substitute (in the calculations, not in the hardware) the nonselective pulse by a sequence of selective pulses following immediately one after another.

The problem

$$[yzy] \xrightarrow{\alpha xMX}$$

has to be handled as

$$\begin{aligned} [yzy] &\xrightarrow{\alpha xM} [yzy]\cos\alpha - [yyy]\sin\alpha \\ &\xrightarrow{\alpha xX} [yzy]\cos^2\alpha + [yzz]\cos\alpha\sin\alpha \\ &\quad - [yyy]\sin\alpha\cos\alpha - [yyz]\sin^2\alpha \end{aligned} \qquad \text{(E13)}$$

The reader can easily check that the order in which αxM and αxX are applied is immaterial. The procedure described above has to be followed even if the spins affected by the pulse are magnetically equivalent.

The result (E13) may seem unexpectedly complicated for one single pulse. Fortunately, in most practical cases α is either 90^o or 180^o. In these cases, the procedure above leads to exhilariatingly simple results like:

$$[yzy] \xrightarrow{90xMX} -[yyz]$$
$$[yzy] \xrightarrow{180xMX} [yzy]$$
$$[xyz] \xrightarrow{90xAM} [xzz]$$

In these cases it is not necessary to split the non-selective pulse into subsequent selective pulses.