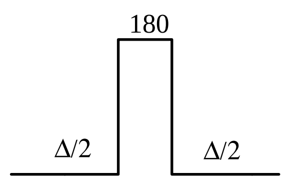
APPENDIX H: DEMONSTRATION OF THE REFOCUSING RULES

We demonstrate here the validity of the rules stated in Section II.8 to handle a refocusing routine:



When handling this segment of a sequence in the conventional way we have to subject the density matrix $D(n)$ to a string of operators representing the $\Delta/2$ evolution (shifts and couplings), the r.f. pulse (R_{180}), then again the $\Delta/2$ evolution. For two nuclei the string would be:

$$R = R_A R_X R_{AX} R_{180} R_{AX} R_X R_A \tag{H1}$$

where R_A, R_X are shift operators and R_{AX} is the coupling operator.

All shift and coupling evolution operators commute with each other. In order to simplify the expression (H1) we have to find out how they commute with R_{180}. Let us concentrate on one nucleus (e.g., nucleus A) and see how R_A commutes with R_{180xA}. According to relation (B51)

$$R_{180xA} = \exp(i\pi I_{xA}) = \cos\frac{\pi}{2}[1] + i\sin\frac{\pi}{2}(2I_{xA}) = 2iI_{xA} \tag{H2}$$

A similar expression can be written for the shift evolution operator R_A which represents a rotation by $\alpha = \Omega_A \Delta/2$ around the z axis.

$$R_A = R_{\alpha A} = \exp(i\alpha I_{zA}) = \cos\frac{\alpha}{2}[1] + i\sin\frac{\alpha}{2}(2I_{zA}) \tag{H3}$$

We want to examine the product of the two operators:

$$R_{180xA}R_{\alpha A} = 2iI_{xA}\left[\cos\frac{\alpha}{2}[1] + i\sin\frac{\alpha}{2}(2I_{zA})\right]$$

Using the anticommutativity of I_x and I_z for I=1/2 stated in (F10) we can rewrite the product as

$$R_{180xA}R_{\alpha A} = \left[\cos\frac{\alpha}{2}[1] - i\sin\frac{\alpha}{2}(2I_{zA})\right]2iI_{xA} = R_{(-\alpha)A}R_{180xA}$$

We notice that $R_{(-\alpha)A}$ is the reciprocal of $R_{\alpha A}$ since their combined action would leave the density matrix unaffected. We can therefore write

$$R_{180xA}R_{\alpha A} = R_{\alpha A}^{-1}R_{180xA} \tag{H4}$$

and this is the commutation rule we needed.

One can check that the rule is the same if instead of R_{180xA} we use R_{180yA} or $R_{180\Phi A}$ (180° rotation about an arbitrary axis in the *xy* plane). For the last case one has use

$$\begin{aligned} R_{180\Phi A} &= R_{(-\Phi)zA}R_{180xA}R_{\Phi zA} = R_{180\Phi A}R_{\Phi zA}^{2} = R_{180xA}R_{(2\Phi)zA} \\ &= 2iI_{xA}\left(\cos\Phi\cdot[1] + i\sin\Phi\cdot 2I_{zA}\right) = \cos\Phi\cdot 2iI_{xA} + i\sin\Phi\cdot(-2iI_{yA}) \\ &= R_{180xA}\cos\Phi + R_{180yA}\sin\Phi \end{aligned}$$

We have used here $I_{xA}I_{zA} = -iI_{yA}/2$ which is a consequence of (E2) and (F9).

Therefore we can write in general

$$R_{180A}R_{A} = R_{A}^{-1}R_{180xA} \tag{H5}$$

On the other hand we have

$$R_{180A}R_{X} = R_{X}R_{180xA} \tag{H6}$$

since operators acting on different nuclei always commute.

A similar pattern can be followed to demonstrate

$$R_{180A}R_{AX} = R_{AX}^{-1}R_{180A} \tag{H7}$$

$$R_{180X}R_{AX} = R_{AX}^{-1}R_{180X} \tag{H8}$$

With these commutation rules we now can rearrange a string like the one in (H1):

$$R = R_A R_X R_{AX} R_{180A} R_{AX} R_X R_A = R_A R_X R_{AX} R_{AX}^{-1} R_X R_A^{-1} R_{180A}$$
$$= R_X^2 R_{180A} = R_{180A} R_X^2$$

Only the shift X is expressed in the final result, while shift A and coupling AX are refocused. Since R_X is the shift evolution for Δ/2,

$$R_X^2$$

is the operator for the full delay Δ.

If the 180° pulse is applied on both nuclei A and X, the rearranging yields:

$$R = R_A R_X R_{AX} R_{180A} R_{180X} R_{AX} R_X R_A = R_A R_X R_{AX} R_{180A} R_{AX}^{-1} R_X^{-1} R_A R_{180X}$$
$$= R_A R_X R_{AX} R_{AX} R_X^{-1} R_A^{-1} R_{180A} R_{180X} = R_{AX}^2 R_{180A} R_{180X} = R_{180A} R_{180X} R_{AX}^2$$

Both shifts are refocused, the coupling only is expressed in the final result. This confirms the refocusing rules stated in Section II.8. There is no difficulty in extending them to more than two nuclei.