

9. PO TREATMENT OF 2DHETCOR: TWO SPINS (CH)

We consider again the sequence in Figure I.2 applied to a system of two weakly coupled spin 1/2 nuclei A and X. The density matrix at equilibrium (see II.5) is:

$$D(0) = -p'[z1] - q'[1z]$$

where

$$\begin{aligned} p' &= p/2N \\ q' &= q/2N \\ N &= \text{number of states} = 4 \end{aligned}$$

p and q have the same meaning as in (I.3) and (I.4).

$$D(0) \xrightarrow{90_x X} -p'[z1] + q'[1y] \quad (\text{II.27})$$

$$\mathbf{D(1)}$$

We apply the "refocusing routine" treatment to the segment

$$t_e/2 - 180_x A - t_e/2$$

As shown in Section II.8 this routine has the same effect as the $180_x A$ pulse followed by an evolution t_e during which only the shift X is active. The coupling AX is refocused by the $180_x A$ pulse.

$$D(1) \xrightarrow{180_x A} p'[z1] + q'[1y]$$

$$\xrightarrow{t_e(\text{shift X})} p'[z1] + q' \cos W_X t_e [1y] - q' \sin W_X t_e [1x] \quad (\text{II.28})$$

$$\mathbf{D(4)}$$

A coupled evolution Δ_1 follows, which can be handled according to the rules of Section II.7 with

$$\begin{aligned} c' &= \cos \Omega_X \Delta_1 & C &= \cos \pi J \Delta_1 \\ s' &= \sin \Omega_X \Delta_1 & S &= \sin \pi J \Delta_1 \end{aligned}$$

$$D(4) \xrightarrow{\text{shift A}} \text{same}$$

$$\xrightarrow{\text{shift X}} p'[z1] + q' \cos \Omega_X t_e (c'[1y] - s'[1x]) - q' \sin \Omega_X t_e (c'[1x] + s'[1y])$$

$$\xrightarrow{J} p'[z1] + q' \cos \Omega_X t_e (c' C [1y] - c' S [zx] - s' C [1x] - s' S [zy])$$

$$- q' \sin \Omega_X t_e (c' C [1x] + c' S [zy] + s' C [1y] - s' S [zx])$$

$$\mathbf{D(5)}$$

Since $\Delta_1 = 1/2J$ and $\pi J\Delta_1 = \pi/2$, $C = 0$ and $S = 1$

$$D(5) = p'[z1] + q' \cos \Omega_x t_e (-c'[zx] - s'[zy]) - q' \sin \Omega_x t_e (-s'[zx] + c'[zy]) \quad (\text{II.29})$$

Using the trigonometric relations for the sum of two angles [see (A29) and (A30)] we can rewrite $D(5)$:

$$D(5) = p'[z1] + q'[zx](\cos \Omega_x t_e \cos \Omega_x \Delta_1 - \sin \Omega_x t_e \sin \Omega_x \Delta_1) - q'[zy](\cos \Omega_x t_e \sin \Omega_x \Delta_1 + \sin \Omega_x t_e \cos \Omega_x \Delta_1) = p'[z1] - q'[zx] \cos \Omega_x (t_e + \Delta_1) - q'[zy] \sin \Omega_x (t_e + \Delta_1) \quad (\text{II.30})$$

We calculate now the effects of the pulses three and four (in the PO formalism it is simpler to handle them separately):

$$D(5) \xrightarrow{90_{xX}} p'[z1] - q'[zx] \cos \Omega_x (t_e + \Delta_1) - q'[zy] \sin \Omega_x (t_e + \Delta_1) \quad D(6) \\ \xrightarrow{90_{xA}} -p'[y1] + q'[yx] \cos \Omega_x (t_e + \Delta_1) + q'[yz] \sin \Omega_x (t_e + \Delta_1) \quad D(7) \quad (\text{II.31})$$

Since no other r.f. pulse follows we can concentrate on those terms which represent observable magnetization components. We observe nucleus A, therefore we are interested in the product operators $[x1]$ and $[y1]$ which give M_{xA} and M_{yA} . We are also interested in $[yz]$ and $[xz]$ which can evolve into $[x1]$, $[y1]$ during a coupled evolution. All product operators other than the four mentioned above are nonobservable terms (NOT). We can rewrite $D(7)$ as:

$$D(7) = -p'[y1] + q'[yz] \sin \Omega_x (t_e + \Delta_1) + \text{NOT} \quad (\text{II.32})$$

The second term is important for the 2D experiment because it is proton modulated (it contains the frequency Ω_x). It is also enhanced by polarization transfer (i.e., multiplied by q' rather than p').

The coupled evolution Δ_2 is necessary to render the second term observable. If the decoupled detection started at $t(7)$, the $[yz]$ term would evolve into a combination of $[yz]$ and $[xz]$, none of which is

observable. The observable terms [x1] and [y1] can derive from [yz] only in a coupled evolution.

$$\begin{aligned}
 D(7) &\xrightarrow{\text{shift A}} -p'(c[y1] - s[x1]) + q' \sin \Omega_X(t_e + \Delta_1)(c[yz] - s[xz]) \\
 &\xrightarrow{\text{shift X}} \text{same} \xrightarrow{J} -p'(cC[y1] - cS[xz] - sC[x1] - sS[yz]) \\
 &+ q' \sin \Omega_X(t_e + \Delta_1)(cC[yz] - cS[x1] - sC[xz] - sS[y1]) + \text{NOT} \quad (\text{II.33})
 \end{aligned}$$

D(8)

where

$$\begin{aligned}
 c &= \cos \Omega_A \Delta_2 & C &= \cos \pi J \Delta_2 \\
 s &= \sin \Omega_A \Delta_2 & S &= \sin \pi J \Delta_2
 \end{aligned} \quad (\text{II.34})$$

During the decoupled evolution that follows after $t(8)$, the product operators [x1], [y1] will evolve into combinations of [x1], [y1] while the product operators [xz], [yz] evolve into combinations of [xz], [yz], i.e., they will remain nonobservable. We can therefore retain only [x1], [y1] in the explicit expression of $D(8)$:

$$\begin{aligned}
 D(8) &= -p'(cC[y1] - sC[x1]) + q' \sin \Omega_X(t_e + \Delta_1)(-cS[x1] - sS[y1]) \\
 &+ \text{NOT} \quad (\text{II.35})
 \end{aligned}$$

In order to maximize the proton modulated term, one selects for Δ_2 the value $1/2J$ which leads to $S = 1$ and $C = 0$. This value of Δ_2 represents an optimum in the particular case of the AX system. It will be shown in Section II.10 that for AX_2 and AX_3 (e.g., the methylene and methyl cases) a shorter Δ_2 is to be used. For $\Delta_2 = 1/2J$:

$$D(8) = -q' \sin \Omega_X(t_e + \Delta_1)(\cos \Omega_A \Delta_2 [x1] + \sin \Omega_A \Delta_2 [y1]) + \text{NOT} \quad (\text{II.36})$$

The simplest way to describe the decoupled evolution t_d (from the point of view of the observable A) is a rotation of the transverse magnetization M_{TA} about the z axis. At $t(8)$ we have (see Appendix J):

$$\begin{aligned}
 M_{xA}(8) &= - (M_{oA}/p')(\text{coefficient of [x1]}) \\
 &= (q'/p')M_{oA} \sin \Omega_X(t_e + \Delta_1) \cos \Omega_A \Delta_2 \\
 M_{yA}(8) &= (q'/p')M_{oA} \sin \Omega_X(t_e + \Delta_1) \sin \Omega_A \Delta_2 \\
 M_{TA}(8) &= M_{xA}(8) + iM_{yA}(8) = (q'/p')M_{oA} \sin \Omega_X(t_e + \Delta_1) \exp(i\Omega_A \Delta_2) \quad (\text{II.37})
 \end{aligned}$$

The ratio $q'/p' = \gamma_X/\gamma_A$ represents the enhancement factor through polarization transfer.

By handling the decoupled evolution as a magnetization rotation we get

$$\begin{aligned} M_{TA}(9) &= M_{TA}(8) \exp(i\Omega_A t_d) \\ &= (q'/p') M_{oA} \sin \Omega_X (t_e + \Delta_1) \exp[i\Omega_A (t_d + \Delta_2)] \quad (\text{II.38}) \end{aligned}$$

This is in agreement with the result obtained in Part I through DM calculations. The calculations requested by the PO approach are somewhat less complicated than those of the DM approach. The real advantage will be seen when we apply (see Section II.10) the PO formalism to an AX₂ and AX₃ case (e.g., the 2DHETCOR of a CH₂ or CH₃).

10. PO TREATMENT OF 2DHETCOR: CH₂ AND CH₃

We extend the calculations carried out in section II.9 to an AX₂ or AX₃ system (e.g., a methylene or a methyl). The density matrix at equilibrium is:

$$\begin{aligned} D(0) &= -p'[z11] - q'([1z1] + [11z]) && \text{for AX}_2 \\ D(0) &= -p'[z111] - q'([1z11] + [11z1] + [111z]) && \text{for AX}_3 \end{aligned} \quad (\text{II.39})$$

Instead of following the two cases separately, we use the "multiplet formalism" introduced in Appendix L. The reader should get acquainted with this formalism before proceeding further.

$$D(0) = -(p'/n)\{z1\} - q'\{1z\} \quad (\text{II.40})$$

valid for any AX_n system.

$$D(0) \xrightarrow{90.X} -(p'/n)\{z1\} + q'\{1y\} \quad (\text{II.41})$$

D(1)

As we did in section II.9, we treat the segment $t_e/2 - 180.XA - t_e/2$