

Figure II.2. PO and vector representation of rotations.

It must be mentioned at this time that only POs containing  $x$ ,  $y$ , or  $z$  for one spin and 1 for the other(s) represent magnetization components along the corresponding Cartesian axes and have a vector representation. Nevertheless, the rotation applied to all other POs can be treated in the same way as above, by considering separately each factor in the product.

The great advantage over the density matrix formalism is that we can apply this approach to systems larger than two spins without the considerable increase in the computation volume (for  $\text{CH}_3$  the matrix is  $16 \times 16$ , i.e., it has 256 elements). In an AMX system (three spin 1/2 nuclei):

$$\begin{aligned} & \underset{\text{AMX}}{[zzz]} \xrightarrow{90_{yA}} [xzz] \\ & [xzz] \xrightarrow{180_{xM}} -[xzz] \\ & -[xzz] \xrightarrow{180_{xA}} -[xzz] \end{aligned}$$

Nonselective pulses affect more than one nucleus in the system. For example:

$$\begin{aligned} & [zz] \xrightarrow{90_{xAX}} [yy] \\ & [xz] \xrightarrow{90_{xAX}} -[xy] \\ & [zzz] \xrightarrow{90_{yAM}} [xxz] \end{aligned}$$

For rotations  $\alpha$  other than  $90^\circ$  or  $180^\circ$ , nonselective pulses affecting  $n$  nuclei must be handled in  $n$  successive operations. For instance, a nonselective pulse  $\alpha xAX$  applied to the product operator  $[zy]$  is treated in the following sequence:

$$\begin{aligned} & [zy] \xrightarrow{\alpha xA} [zy] \cos \alpha - [yy] \sin \alpha \\ & \xrightarrow{\alpha xX} [zy] \cos^2 \alpha + [zz] \cos \alpha \sin \alpha - [yy] \sin \alpha \cos \alpha - [yz] \sin^2 \alpha \end{aligned}$$

These two operations may be performed in any order.

## 7. TREATMENT OF EVOLUTIONS IN THE PRODUCT OPERATOR FORMALISM

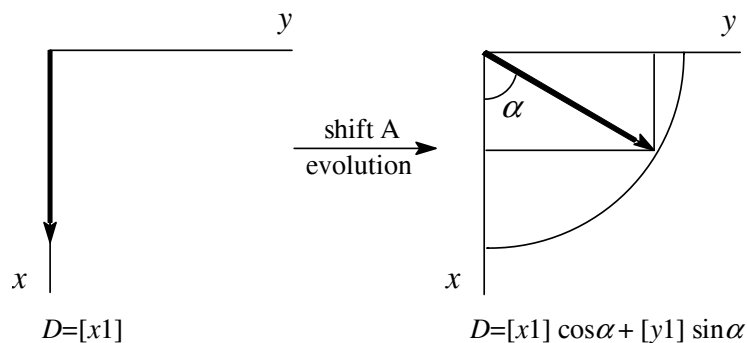
As shown in Appendix F, the evolution of coupled spins is conveniently treated in two steps. Step 1: we consider the system noncoupled (chemical shift evolution only). Step 2: we calculate the effect of coupling.

### Step 1 (shift evolution)

A shift evolution is equivalent to a rotation about the  $z$  axis by an angle  $\alpha = \Omega t$ . Example:

$$[x1] \xrightarrow{\text{shift A}} [x1] \cos \Omega_A t + [y1] \sin \Omega_A t$$

The analogy with the vector representation is shown in Fig. II.3.



**Figure II.3.** PO and vector representation of a coupled evolution. The angle  $\alpha = \Omega_A t$ .

Another example:

$$[zy] \xrightarrow{\text{shift X}} [zy] \cos \Omega_x t - [zx] \sin \Omega_x t$$

The rule of thumb for shift evolution is :

PO after evolution = (PO before evolution)  $\cos \Omega t$  + (PO before evolution in which  $x$  is replaced by  $y$  and  $y$  by  $-x$  for the spin affected by evolution)  $\sin \Omega t$ . The labels 1 and  $z$  are invariant.

If more than one nucleus in the system is subject to shift evolution, these evolutions have to be treated as separate steps (the order is immaterial). Example:

$$\begin{aligned}
 [xyz] &\xrightarrow{\text{shift A}} [xyz] \cos \Omega_A t + [yyz] \sin \Omega_A t \\
 &\xrightarrow{\text{shift M}} [xyz] \cos \Omega_A t \cos \Omega_M t - [xxz] \cos \Omega_A t \sin \Omega_M t \\
 &\quad + [yyz] \sin \Omega_A t \cos \Omega_M t - [yxz] \sin \Omega_A t \sin \Omega_M t
 \end{aligned} \quad (\text{II.22})$$

The X spin is represented by z in the POs. Therefore the "shift X" does not bring any further change in (II.22).

With the notations

$$\begin{aligned}
 \cos \Omega_A t = c & & \cos \Omega_M t = c' & & \cos \Omega_X t = c'' \\
 \sin \Omega_A t = s & & \sin \Omega_M t = s' & & \sin \Omega_X t = s''
 \end{aligned} \quad (\text{II.23})$$

the relation (II.22) becomes

$$[xyz] \xrightarrow{\text{shift A, M, X}} cc'[xyz] - cs'[xxz] + sc'[yyz] - ss'[yxz]$$

One more example :

$$\begin{aligned}
 [xyy] &\xrightarrow{\text{shift A}} c[xyy] + s[yyy] \\
 &\xrightarrow{\text{shift M}} cc'[xyy] - cs'[xxy] + sc'[yyy] - ss'[yxy] \\
 &\xrightarrow{\text{shift X}} cc'c''[xyy] - cc's''[xyx] - cs'c''[xxy] + cs's''[xxx] \\
 &\quad + sc'c''[yyy] - sc's''[yyx] - ss'c''[yxy] + ss's''[yxx]
 \end{aligned}$$

### Step 2 (J coupling evolution)

According to the rules presented in Appendix F the coupling between two spins is active only when one of the nuclei appears in the PO with an x or y while the other nucleus is represented by z or 1. Examples :

$[xzz]$  – couplings  $J_{AM}$  and  $J_{AX}$  are active, but  $J_{MX}$  is not.  
AMX

$[xyz]$  – couplings  $J_{AX}$  and  $J_{MX}$  are active, but  $J_{AM}$  is not.

Another example:

[xyy] – no coupling is active <sup>1</sup>

For every coupling that is active, the step 2 rule is:

PO after evolution = (PO before evolution)  $\cos \pi J t$  + (PO before evolution with  $x$  replaced by  $y$ ,  $y$  by  $-x$ ,  $1$  by  $z$ , and  $z$  by  $1$ )  $\sin \pi J t$ .

Examples:

$$[xz] \xrightarrow{J_{AX}} C[xz] + S[y1] \quad \text{with} \quad \begin{aligned} C &= \cos \pi J_{AX} t \\ S &= \sin \pi J_{AX} t \end{aligned}$$

$$\begin{aligned} [xyz] &\xrightarrow{J_{AX}} C[xyz] + S[yy1] \\ &\xrightarrow{J_{MX}} CC'[xyz] - CS'[xx1] + SC'[yy1] - SS'[yxx] \end{aligned}$$

$$\text{where} \quad \begin{aligned} C &= \cos \pi J_{AX} t & C' &= \cos \pi J_{AM} t \\ S &= \sin \pi J_{AX} t & S' &= \sin \pi J_{AM} t \end{aligned}$$

Combinations of steps 1 and 2 are illustrated by two examples.

$$\begin{aligned} \text{System AM} \quad [x1] &\xrightarrow{\text{shift A}} c[x1] + s[y1] \\ &\xrightarrow{J_{AM}} cC[x1] + cS[yz] + sC[y1] - sS[xz] \end{aligned} \quad (\text{II.24})$$

$$\begin{aligned} \text{System AMX} \quad [x11] &\xrightarrow{\text{shift A}} c[x11] + s[y11] \\ &\xrightarrow{J_{AM}} cC[x11] + cS[yz1] + sC[y11] - sS[xz1] \\ &\xrightarrow{J_{AX}} cCC'[x11] + cCS'[y1z] + cSC'[yz1] - cSS'[xzz] \\ &\quad + sCC'[y11] - sCS'[x1z] - sSC'[xz1] - sSS'[yzz] \end{aligned} \quad (\text{II.25})$$

Notations for the last two examples:

$$\begin{aligned} c &= \cos \Omega_A t & C &= \cos J_{AM} t & C' &= \cos J_{AX} t \\ s &= \sin \Omega_A t & S &= \sin J_{AM} t & S' &= \sin J_{AX} t \end{aligned} \quad (\text{II.26})$$

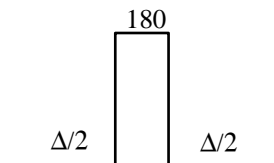
We notice that, in the case of the two spin system, a coupled evolution does not split any PO into more than 4 terms. This is due to the fact that when both shifts are active the coupling is not.

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<sup>1</sup> This seemingly surprising situation prompts an explanation. Product operators as [xx], [xy], [xyy] have nonvanishing elements on the secondary diagonal only (which represents zero- and multiple-quantum coherences). Referring to Figure I.1 we see that the evolution frequency for the double-quantum transition (1 → 4) is (A+J/2)+(X-J/2) = X+A. The zero-quantum transition frequency (2 → 3) is X-A. None of them depends on J.

## 8. REFOCUSING ROUTINES

We have seen in the 2DHETCOR section that the  $180^\circ$  pulse caused the decoupling of carbon from proton. In other words, the pulse applied in the middle of the evolution time  $t_e$ , caused the second half to compensate for the coupling effect of the first half. We call this a "refocusing routine." The chemical shift evolution can also be refocused if the pulse is applied on the nucleus that evolves. The routine, as shown below, can be handled in the conventional way (evolution-pulse-evolution) but the partial results are fairly more complicated than the final result.



We suggest here an efficient calculation shortcut in which the entire evolution time,  $\Delta$ , can be placed either before or after the pulse (of course, this cannot be done in the actual sequence).



During the hypothetical delay,  $\Delta$ , the following rules apply:

- a) Only shifts of the nuclei *not* affected by the  $180^\circ$  pulse are taken into account in the evolution  $\Delta$  since all other are refocused.
- b) The coupling between two nuclei is active if both or none of them are affected by the  $180^\circ$  pulse.

The above rules are valid for systems of  $m$  spin  $1/2$  nuclei, part of which may be magnetically equivalent. The  $180^\circ$  rotation is supposed to occur about an axis in the  $xy$  plane (no off-resonance pulse). The phase of the pulse does not affect the validity of the rules but it must be conserved when, in our calculations, we move the pulse from the middle of the interval  $\Delta$  to one of its ends. The rules above are demonstrated in Appendix H.

We now compare the conventional calculation with the short-cut. For example, we assume that the density matrix at time  $t(n)$  is

$$D(n) = p'[x1] + q'[1x]$$

and it is followed by

$$\Delta/2 - 180xA - \Delta/2$$

In the conventional way, i.e., evolution – pulse – evolution, we start with the first evolution,  $\Delta/2$ .

$$\begin{aligned} D(n) &\xrightarrow{\text{shift } A} p'c[x1] + p's[y1] + q'[1x] \\ &\xrightarrow{\text{shift } X} p'c[x1] + p's[y1] + q'c'[1x] + q's'[1y] \\ &\xrightarrow{J} p'cC[x1] + p'cS[yz] + p'sC[y1] - p'sS[xz] \\ &\quad + q'c'C[1x] + q'c'S[zy] + q's'C[1y] - q's'S[zx] = D(n+1) \end{aligned}$$

where

$$\begin{array}{lll} c = \cos \Omega_A \Delta/2 & c' = \cos \Omega_X \Delta/2 & C = \cos \pi J \Delta/2 \\ s = \sin \Omega_A \Delta/2 & s' = \sin \Omega_X \Delta/2 & S = \sin \pi J \Delta/2 \end{array}$$

The 180xA pulse affects only the first label in the POs (nucleus A), changing the sign of y and z and leaving x unchanged.

$$\begin{aligned} D(n+1) &\xrightarrow{180xA} p'cC[x1] - p'cS[yz] - p'sC[y1] - p'sS[xz] \\ &\quad + q'c'C[1x] - q'c'S[zy] + q's'C[1y] + q's'S[zx] = D(n+2) \end{aligned}$$

The second evolution  $\Delta/2$  is calculated as follows

$$\begin{aligned} D(n+2) &\xrightarrow{\text{shift } A} p'c^2C[x1] + p'csC[y1] - p'c^2S[yz] + p'csS[xz] \\ &\quad - p'scC[y1] + p's^2C[x1] - p'scS[xz] - p's^2S[yz] \\ &\quad + q'c'C[1x] - q'c'S[zy] + q's'C[1y] + q's'S[zx] \\ &\xrightarrow{\text{shift } X} p'c^2C[x1] + p'csC[y1] - p'c^2S[yz] + p'csS[xz] \\ &\quad - p'scC[y1] + p's^2C[x1] - p'scS[xz] - p's^2S[yz] \\ &\quad + q'c'^2C[1x] + q'c's'C[1y] - q'c'^2S[zy] + q'c's'S[zx] \\ &\quad + q's'c'C[1y] - q's'^2C[1x] + q's'c'S[zx] + q's'^2S[zy] = D(int) \end{aligned}$$

This is an intermediate result, since we still have to consider the effect of  $J$ -coupling. Before doing so, we combine the terms containing the

same PO.

$$\begin{aligned} D(int) &= p'(c^2 + s^2)C[x1] - p'(c^2 + s^2)S[yz] \\ &\quad + q'(c'^2 - s'^2)C[1x] + 2q'c's'C[1y] \\ &\quad - q'(c'^2 - s'^2)S[zy] + 2q'c's'S[zx] \end{aligned}$$

We recognize the expressions for the sine and cosine of twice the angle  $\Omega_X\Delta/2$ , i.e.,  $\Omega_X\Delta$ .

$$\begin{aligned} D(int) &= p'C[x1] - p'S[yz] \\ &\quad + q'\cos\Omega_X\Delta(C[1x] - S[zy]) + q'\sin\Omega_X\Delta(C[1y] + S[zx]) \end{aligned}$$

Further, we calculate the effect of  $J$ .

$$\begin{aligned} D(int) &\xrightarrow{J} p'C^2[x1] + p'CS[yz] - p'SC[yz] + p'S^2[x1] \\ &\quad + q'\cos\Omega_X\Delta(C^2[1x] + CS[zy] - SC[zy] + S^2[1x]) \\ &\quad + q'\sin\Omega_X\Delta(C^2[1y] - CS[zx] + SC[zx] + S^2[1y]) \\ &= p'[x1] + q'\cos\Omega_X\Delta[1x] + q'\sin\Omega_X\Delta[1y] \end{aligned}$$

We now show that this result can be obtained in just two lines by using the shortcut. Following the rules described above, we first apply the  $180_xA$  pulse, then an evolution  $\Delta$  (where only the shift  $X$  is considered, while the shift  $A$  and the coupling  $J$  are ignored).

$$\begin{aligned} D(n) &\xrightarrow{180_xA} p'[x1] + q'[1x] \\ &\xrightarrow{\text{shift } X} p'[x1] + q'\cos\Omega_X\Delta[1x] + q'\sin\Omega_X\Delta[1y] \end{aligned}$$

The first term, representing the  $A$  magnetization, appears unchanged because its evolution during the first delay  $\Delta/2$  has been undone during the second  $\Delta/2$ . The  $X$  magnetization has evolved with the frequency  $\Omega_X$  during the delay  $\Delta$ , but in the end it is not affected by the  $J$ -coupling. This is because its two components, fast and slow, have undergone a change of label in the middle of the delay  $\Delta$ .

In a system of two nuclei ( $A$  and  $X$ ) if the pulse affects nucleus  $A$ , only shift  $X$  is operative. Shift  $A$  and coupling  $J_{AX}$  are refocused (see example above). If the  $180^\circ$  pulse affects both  $A$  and  $X$ , only the coupling is operative. Both shifts are refocused. In a system of more than two nuclei (e.g.,  $AMX$ ), if the pulse affects all nuclei, only the couplings are active. If the pulse affects all nuclei except one (e.g., nucleus  $A$ ), we see the effect of shift  $A$  and of the couplings which do not involve  $A$ , i.e.,  $J_{MX}$ . If the pulse affects only nucleus  $A$ , all shifts except  $A$  and the couplings involving  $A$  ( $J_{AM}$ ,  $J_{AX}$ ) are active.