APPENDIX F: DEMONSTRATION OF THE COUPLED EVOLUTION RULES

Before going into the demonstration we need to point out two limitations:

a. It assumes \( I = 1/2 \) for all nuclei in the system
b. It operates in the weak coupling case:
\[ J \text{ (coupling constant)} \ll \Delta \delta \text{ (chemical shift difference)} \]

Between r.f. pulses the evolution of a two-spin system AX in the rotating frame is governed by the Hamiltonian.
\[ H = h \left( \Omega_{zA} I_{zA} + \Omega_{zX} I_{zX} + 2\pi JJ_{zA} I_{zX} \right) \quad \text{(F1)} \]

The density matrix \( D(n+1) \) at the end of the evolution is related to the initial matrix \( D(n) \) as:
\[ D(n + 1) = \exp(-iHt/h) \cdot D(n) \cdot \exp(iHt/h) \quad \text{(F2)} \]

Since all terms in (F1) commute with each other, we can write the evolution operator as:
\[ \exp(iHt/h) = \exp(i\Omega_{zA} t I_{zA}) \exp(i\Omega_{zX} t I_{zX}) \exp(i2\pi JJ_{zA} I_{zX}) \]
\[ = R_{zA} R_{zX} R_J \]

where the order of the factors is immaterial. Relation (F2) can be rewritten as:
\[ D(n + 1) = R_{zA}^{-1} R_{zX}^{-1} \cdot D(n) \cdot R_{zA} R_{zX} R_J \quad \text{(F3)} \]

In (F3) the actual coupled evolution is formally presented as the result of three independent evolutions due to shift A, shift X, and coupling \( J \), respectively. In fact this is the way the coupled evolutions are handled in the PO formalism: as a succession of shift evolutions and evolutions due to spin-spin coupling (coupling evolutions).

The shift evolutions (noncoupled evolutions) are actually \( z \)-rotations and are easily handled with the vector rotation rules. Example:
\[
\begin{align*}
\text{[xy]} & \xrightarrow{\Omega_{dA} t} [xy] \cos \Omega_{dA} t + [yy] \sin \Omega_{dA} t \\
& \xrightarrow{\Omega_{dX} t} [xy] \cos \Omega_{dA} t \cos \Omega_{dX} t - [xx] \cos \Omega_{dA} t \sin \Omega_{dX} t \\
& \quad + [yy] \sin \Omega_{dA} t \cos \Omega_{dX} t - [yx] \sin \Omega_{dA} t \sin \Omega_{dX} t
\end{align*}
\]

Or, with self-explanatory notations,
The object of this appendix is to derive the rules for calculating
\[ D(n+1) = R_j^{-1}D(n)R_j \]

where
\[ R_j = \exp(i2\pi J_t I_{zA} I_{zX}) \]

and \( D(n) \) may be any of the product operators or a combination thereof.

We have to find first an expression similar to \((B51)\) for the operator \(R_J\). Calculating the powers of \(I_{zA} I_{zX}\) we find
\[ (I_{zA} I_{zX})^n = \frac{1}{4^n}[1] \quad \text{for } n = \text{even} \]
\[ (I_{zA} I_{zX})^n = \frac{1}{4^n}4I_{zA} I_{zX} \quad \text{for } n = \text{odd} \]

and this leads to
\[ R_j = \cos \frac{\pi J_t}{2}[1] + i \sin \frac{\pi J_t}{2}4I_{zA} I_{zX} \]

an expression we can use in calculating \(D(n+1) = R_j^{-1}D(n)R_j\).

It is now the moment to introduce specific product operators for \(D(n)\). We have to discuss three cases.

Case 1. Both nuclei A and X participate in the product operator with \(z\) or \(1\). Example:
\[ D(n) = [zz] = (2I_{zA})(2I_{zX}) \]

In this case \(D(n)\) commutes with both \(I_{zA}\) and \(I_{zX}\) and this gives:
\[ D(n+1) = R_j^{-1}D(n)R_j = D(n)R_j^{-1}R_j = D(n) \]

None of the POs \([zz], [z1], [1z], [11]\) is affected by the coupling evolution. As a matter of fact, all these POs have only diagonal elements and are not affected by any evolution, shift or coupling.

Case 2. Both nuclei A and X participate in the product operator with an \(x\) or a \(y\). Example:
\[ D(n) = [xy] = (2I_{xA})(2I_{yX}) \]
We can demonstrate that this kind of product operator also is not affected by the coupling evolution. In order to do so we have to take into account that, for $I = 1/2$, the components of the angular momentum are anticommutative:

\[
\begin{align*}
I_x I_y &= -I_y I_x \\
I_y I_z &= -I_z I_y \\
I_z I_x &= -I_x I_z
\end{align*}
\]  

(F9)

The validity of (F9) can be verified on the expressions (C1, C2) of the angular momentum components for $I=1/2$. Using (F8) to calculate $D(n+1)$ we have

\[
D(n+1) = \left[ \cos \frac{\pi J t}{2} I - i \sin \frac{\pi J t}{2} (4 I_{x z A} I_{z x A}) \right] \times (4 I_{x A} I_{y x A})
\]

\[
\times \left[ \cos \frac{\pi J t}{2} I + i \sin \frac{\pi J t}{2} (4 I_{x A} I_{y x A}) \right]
\]

\[
= \cos^2 \left( \frac{\pi J t}{2} \right) \left( 4 I_{x A} I_{y x A} \right) + \sin^2 \left( \frac{\pi J t}{2} \right) \left( 4^2 I_{x A} I_{x A} I_{y A} I_{y A} - I_{x A} I_{y A} I_{x A} I_{y A} \right)
\]

\[
+ i \cos \frac{\pi J t}{2} \sin \frac{\pi J t}{2} \left( 4^2 \right) \left( I_{x A} I_{y A} I_{z A} I_{z A} - I_{x A} I_{y A} I_{z A} I_{z A} \right)
\]

(F10)

Since the angular momentum components of A are commutative with those of X [see(E3)], we can rewrite the last result as

\[
D(n+1) = \cos^2 \left( \frac{\pi J t}{2} \right) \left( 4 I_{x A} I_{y x A} \right) + \sin^2 \left( \frac{\pi J t}{2} \right) \left( 4^2 I_{x A} I_{x A} I_{y A} I_{y A} - I_{x A} I_{y A} I_{x A} I_{y A} \right)
\]

\[
+ i \cos \frac{\pi J t}{2} \sin \frac{\pi J t}{2} \left( 4^2 \right) \left( I_{x A} I_{y A} I_{z A} I_{z A} - I_{x A} I_{y A} I_{z A} I_{z A} \right)
\]  

(F10)

Using (F9) we find out that the last parenthesis in (F10) is null. To calculate the product $I_{z A} I_{x A} I_{y A} I_{z A}$ in (F10) we use the following relations, similar to (E8) :

\[
I_{z A} I_{x A} I_{y A} = -(I_{x A})/4 ; \quad I_{z A} I_{y A} I_{z A} = -(I_{z A})/4
\]

and we reduce (F10) to

\[
D(n+1) = \cos^2 \left( \frac{\pi J t}{2} \right) \left( 4 I_{x A} I_{y x A} \right) + \sin^2 \left( \frac{\pi J t}{2} \right) \left( 4 I_{x A} I_{y x A} \right) = D(n)
\]
All POs in the subset \([xx],[yx],[xy],[yy]\) are not affected by the \(J\) evolution. Unlike the POs in Case 1, they are affected by the shift evolution (see F4). This is consistent with the fact that all the non-vanishing elements of these POs are double-quantum or zero-quantum coherences. The transition frequencies corresponding to these matrix elements do not contain the coupling \(J\).

**Case 3.** The product operator exhibits \(z\) or 1 for one of the nuclei and \(x\) or \(y\) for the other nucleus. Only this kind of product operator is affected by the coupling. Example:

\[
D(n) = [x1] = 2I_{xd}
\]

Calculations similar to those performed in Case 2 lead to:

\[
\begin{align*}
D(n+1) &= \left[ \cos \frac{\pi J_t}{2} [1] - i \sin \frac{\pi J_t}{2} \cdot (4I_{zd}I_{zx}) \right] \times (2I_{xd}) \\
&\times \left[ \cos \frac{\pi J_t}{2} [1] + i \sin \frac{\pi J_t}{2} \cdot (4I_{zd}I_{zy}) \right] \\
&= \cos^2 \frac{\pi J_t}{2} (2I_{xd}) + \sin^2 \frac{\pi J_t}{2} (32I_{zd}I_{zx}I_{xd}I_{zd}I_{zy}) \\
&+ i \cos \frac{\pi J_t}{2} \sin \frac{\pi J_t}{2} (8I_{zd}I_{zx}I_{xd} - 8I_{zd}I_{zx}I_{xd}) \\
&= \cos^2 \frac{\pi J_t}{2} (2I_{xd}) + \sin^2 \frac{\pi J_t}{2} (32I_{zd}I_{xd}I_{zd}I_{zy}^2) \\
&+ i \cos \frac{\pi J_t}{2} \sin \frac{\pi J_t}{2} (8I_{zd}I_{zx}I_{xd} - 8I_{zd}I_{xd}I_{zy}) \\
&= \cos^2 \frac{\pi J_t}{2} (2I_{xd}) - \sin^2 \frac{\pi J_t}{2} (2I_{xd}) \\
&+ i \cos \frac{\pi J_t}{2} \sin \frac{\pi J_t}{2} \left( I_{xd}I_{zd} - I_{zd}I_{xd} \right) (8I_{zx}) \\
&= \cos^2 \frac{\pi J_t}{2} (2I_{xd}) - \sin^2 \frac{\pi J_t}{2} (2I_{zd}) \\
&+ i \cos \frac{\pi J_t}{2} \sin \frac{\pi J_t}{2} (-iI_{zd}) (8I_{zx}) \\
&= \cos \pi J_t (2I_{zd}) + \sin \pi J_t (4I_{yd}I_{zx}) \\
&= \cos \pi J_t [x1] + \sin \pi J_t [yz]
\end{align*}
\]
We have demonstrated that

\[
[x_1] \xrightarrow{J_{\text{coup}l}} [x_1] \cos \pi J t + [yz] \sin \pi J t
\]

After doing similar calculations for all the POs in this category (i.e., \([x_1], [1x], [y_1], [1y], [xz], [zx], [yz], [zy]\)), we can summarize the following rules for the evolution due to the coupling \(J_{AX}\):

a. The coupling evolution operator \(R_J\) affects only those product operators in which one of the nuclei \(A, X\) is represented by \(x\) or \(y\) while the other is represented by 1 or \(z\).

b. The effect of the \(J\) evolution is a rotation of \(x\) (or \(y\)) in the equatorial plane by \(\pi J t\), while \(z\) is replaced by 1 and 1 by \(z\) in the new term. The format is:

PO after \(J\) evolution = \(\cos \pi J t\) (former PO) + \(\sin \pi J t\) (former PO in which \(x\) is replaced by \(y\), \(y\) by \(-x\), \(z\) by 1 and 1 by \(z\)). In systems with more than two nuclei, every nonvanishing coupling like \(J_{AM}\), \(J_{AX}\), \(J_{MX}\), etc., has to be taken into account separately (the order is immaterial).

**Note 1.** From Appendices E and F it results that any rotation (r.f. pulse) or coupled evolution turns a given PO into a linear combination of POs within the basis set. In other words, if the density matrix can be expressed in terms of POs at the start of a sequence we will be able to express it as a combination of POs at any point of the sequence. This confirms that the PO basis set is a complete set.

**Note 2.** Moreover, in a coupled evolution, any \(x\) or \(y\) in the product operator can only become an \(x\) or \(y\). Any \(z\) or 1 can only become a \(z\) or 1. This leads to a natural separation of the basis set (\(N^2\) product operators) into \(N\) subsets of \(N\) operators each.

In the case of \(N = 4\) (two nuclei) the four subsets are:

1) \([11], [12], [z1], [zz]\)
2) \([x1], [y1], [xz], [yz]\)
3) \([1x], [zx], [1y], [zy]\)
4) \([xx], [yx], [xy], [yy]\)

In the case of \(N = 8\) (three nuclei) the eight subsets are:
1) \([111], [z11], [1z1], [zz1], [11z], [z1z], [1zz], [zzz]\)

2) \([x11], [y11], [xz1], [yz1], [x1z], [y1z], [xzz], [yzz]\)

3) \([1x1], [zx1], [1y1], [zy1], [1xz], [1yz], [zxz], [zyz]\)

4) \([xx1], [yx1], [xy1], [yy1], [xxz], [xyz], [xyz], [yyz]\)

5) \([11x], [zl1], [lz1], [zzx], [11y], [zl1], [lzy], [zzy]\)

6) \([x1x], [y1x], [xz1], [y1z], [x1y], [y1z], [xzy], [yzy]\)

7) \([1xx], [zxx], [lxx], [zxy], [1xy], [lzy], [zxy], [lzy]\)

8) \([xxx], [yyx], [yxx], [xxy], [yyx], [xyy], [yyy]\)

Under a coupled evolution, the descendents of a PO are to be found only within its own subset.