APPENDIX L: MAGNETIC EQUIVALENCE, THE MULTIPLET FORMALISM

While the PO formalism is basically a shorthand notation for density matrix calculations, we introduce here an even more compact notation (we call it the multiplet formalism) to simplify the PO treatment of CH\textsubscript{n} systems. In such a system \( n \) nuclei out of \( n+1 \) are magnetically equivalent.

The density matrix at thermal equilibrium for a CH\textsubscript{3} system is:

\[
D(0) = -p'[z111] - q'([1z11] + [11z1] + [111z]) \quad \text{(L1)}
\]

We introduce the notation \{1z\} for the sum in parentheses and write \( D(0) \) as:

\[
D(0) = -p'[z111] - q'\{1z\} \quad \text{(L2)}
\]

The notation \{1z\} is not only shorter but it allows us to write the last sum without specifying the number of protons in the system CH\textsubscript{n}. We make the convention that:

\[
\{1z\} = [1z11] + [11z1] + [111z] \quad \text{for CH}_3
\]

\[
\{1z\} = [1z1] + [11z] \quad \text{for CH}_2
\]

\[
\{1z\} = [1z] \quad \text{for CH}
\]

Other examples of the \{ \} notation:

\[
\{1x\} = [1x1] + [11x] \quad \text{for CH}_2
\]

\[
\{yz\} = [zy11] + [z1y1] + [z11y] \quad \text{for CH}_3
\]

The sum \{ \} has always \( n \) terms where \( n \) is the number of magnetically equivalent nuclei. In order to be consistent we have to write \{z1\} as:

\[
\{z1\} = [z111] + [z111] + [z111] = 3[z111] \quad \text{for CH}_3
\]

\[
\{z1\} = 2[z11] \quad \text{for CH}_2
\]

\[
\{z1\} = [z1] \quad \text{for CH}
\]

With this convention we can rewrite (L2) as:
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\[ D(0) = -(p'/n)\{z1\} - q'\{1z\} \quad (L3) \]

an expression valid for any \( n \).

Let us apply a 90°X pulse to \( D(0) \).

\[ D(0) \rightarrow^{90\text{o}X} -(p'/n)\{z1\} + q'\{1y\} \quad (L4) \]

The expression above is easily obtained through the conventional PO rules applied to the expression \( (L1) \) or its equivalents for \( \text{CH}_2 \) or \( \text{CH} \).

The above example may inspire us to hope that any sequence involving a \( \text{CH}_2 \) or \( \text{CH}_3 \) system may be treated as a \( \text{CH} \), just by replacing \([\ ]\) with \(\{\}\). Unfortunately this is not always true. It is important for the user of this formalism to be aware of how far the \(\{\}\) notations can be used and when we have to give up and go back to the explicit \([\ ]\) notation.

**Rule #1**

Not all the POs in the basis set can be included in \(\{\}\) sums. For instance \([1xz]\) is not a legitimate term of such a sum. No more than one of the protons may come in the PO with \( x, y \) or \( z \), the others must participate with a 1.

**Rule #2**

Rotations due to r.f. pulses do not break the \(\{\}\) formalism and can be treated according to the vectorial model. We have done this in \( (L4) \).

**Rule #3**

Likewise, *noncoupled* evolutions (which are merely \( z \)-rotations) can be treated according to the vectorial representation. Example:

\[ \{zx\} \rightarrow^{\text{shift }X}\{zx\} \cos\Omega_X t + \{zy\} \sin\Omega_X t \]

We can satisfy ourselves that this is true in the case of \( \text{CH}_2 \):

\[ \{zx\} = \{z1x\} + \{z1x\} \]

\[ \rightarrow^{\text{shift }X}[z1x] \cos\Omega_X t + [z1x] \sin\Omega_X t + [z1x] \cos\Omega_X t + [z1y] \sin\Omega_X t \]

\[ = \{zx\} \cos\Omega_X t + \{zy\} \sin\Omega_X t \]

**Rule #4**
A coupled evolution usually breaks the \{ \} formalism, since it generates PO's that cannot be included in \{ \} sums. A fortunate exception we can take advantage of is presented by the sums: \{1x\}, \{1y\}, \{zx\}, \{zy\}. The coupled evolution of any of these sums does not break the \{ \} formalism and can be treated according to Section II.7.

**Rule #5**

If the density matrix contains sums as \{x1\}, \{yz\} or \{xy\} and a coupled evolution follows, we have to give up the \{ \} shorthand and go back to the regular PO formalism ([ ] notation).

Even here there is an exception and it is worth talking about because it may save a lot of term writing. The exception works when the coupled evolution we are talking about is the last act of the sequence or is just followed by a decoupled evolution. In this case we are interested in the observable terms only (see Appendix K) and the coupled evolution yields unexpectedly simple results (we observe nucleus A):

\[
\begin{align*}
\{xl\} & \rightarrow cC^n\{xl\} + sC^n\{yl\} + \text{NOT} \\
\{yl\} & \rightarrow -sC^n\{xl\} + cC^n\{yl\} + \text{NOT} \\
\{xz\} & \rightarrow -sC^{n-1}\{xl\} + cC^{n-1}\{yl\} + \text{NOT} \\
\{yz\} & \rightarrow -cC^{n-1}\{xl\} - cC^{n-1}\{yl\} + \text{NOT} \\
\{xx\} & \rightarrow \text{NOT} \\
\{yx\} & \rightarrow \text{NOT} \\
\{xy\} & \rightarrow \text{NOT} \\
\{yy\} & \rightarrow \text{NOT}
\end{align*}
\]

\[
c = \cos \Omega_c t \quad ; \quad C = \cos \pi Jt \quad ; \quad n = \text{number of protons}
\]

\[
s = \sin \Omega_c t \quad ; \quad S = \sin \pi Jt \quad ; \quad \text{NOT} = \text{nonobservable terms}
\]

The above evolution rules can be verified by writing the product operators in the conventional way and calculating the evolution of the CH$_n$ system for $n=1$, 2, and 3, separately.

**Rule #6**
The procedure for retrieving the magnetization components in the \{ \} formalism differs only slightly from that stated in Appendix J.

\[
M_{xC} = -\left( nM_{oC} / p^l \right) \times \text{(coefficient of \{xl\})}
\]

\[
M_{xH} = -\left( M_{oH} / q' \right) \times \text{(coefficient of \{1x\})}
\]

with similar expressions for \( M_y \) and \( M_z \). \( M_{o\text{ff}} \) is the equilibrium magnetization due to all \( n \) magnetically equivalent protons.