## 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 the multiplet formalism) to simplify the PO treatment of $CH_n$ systems.  In such a system $n$ nuclei out of $n+1$ are magnetically equivalent.

The density matrix at thermal equilibrium for a $CH_3$ system is:

$$D(0) = -p'[z111] - q'([1z11] + [11z1] + [111z])  \qquad (L1)$$

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

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

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 $CH_n$. We make the convention that:

$$\{1z\} = [1z11] + [11z1] + [111z] \qquad \text{for } CH_3$$

$$\{1z\} = [1z1] + [11z] \qquad \text{for } CH_2$$

$$\{1z\} = [1z] \qquad \text{for } CH$$

Other examples of the { } notation:

$$\{1x\} = [1x1] + [11x] \qquad \text{for } CH_2$$

$$\{zy\} = [zy11] + [z1y1] + [z11y] \qquad \text{for } CH_3$$

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:

$$\{z1\} = [z111] + [z111] + [z111] = 3[z111] \quad \text{for } CH_3$$

$$\{z1\} = 2[z11] \qquad \text{for } CH_2$$

$$\{z1\} = [z1] \qquad \text{for } CH$$

With this convention we can rewrite (L2) as:

$$D(0) = -(p'/n)\{z1\} - q'\{1z\} \tag{L3}$$

an expression valid for any $n$.

Let us apply a $90xX$ pulse to $D(0)$.

$$D(0) \xrightarrow{\quad 90xX \quad} -(p'/n)\{z1\} + q'\{1y\} \tag{L4}$$

The expression above is easily obtained through the conventional PO rules applied to the expression (L1) or its equivalents for $CH_2$ or CH.

The above example may inspire us to hope that any sequence involving a $CH_2$ or $CH_3$ system may be treated as a 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:

$$\{zx\} \xrightarrow{\quad shift\ X \quad} \{zx\}\cos\Omega_X t + \{zy\}\sin\Omega_X t$$

We can satisfy ourselves that this is true in the case of $CH_2$:

$$\{zx\} = [zx1] + [z1x]$$

$$\xrightarrow{\quad shift\ X \quad} [zx1]\cos\Omega_X t + [zy1]\sin\Omega_X t + [z1x]\cos\Omega_X t + [z1y]\sin\Omega_X$$

$$= \{zx\}\cos\Omega_X t + \{zy\}\sin\Omega_X t$$

### 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):

$$\{x1\} \longrightarrow cC^n\{x1\} + sC^n\{y1\} + NOT$$

$$\{y1\} \longrightarrow -sC^n\{x1\} + cC^n\{y1\} + NOT$$

$$\{xz\} \longrightarrow -sSC^{n-1}\{x1\} + cSC^{n-1}\{y1\} + NOT$$

$$\{yz\} \longrightarrow -cSC^{n-1}\{x1\} - cSC^{n-1}\{y1\} + NOT$$

$$\{xx\} \longrightarrow NOT$$

$$\{yx\} \longrightarrow NOT$$

$$\{xy\} \longrightarrow NOT$$

$$\{yy\} \longrightarrow NOT$$

$$c = \cos \Omega_C t \quad ; \quad C = \cos \pi J t \quad ; \quad n = \text{number of protons}$$

$$s = \sin \Omega_C t \quad ; \quad S = \sin \pi J t \quad ; \quad NOT = \text{nonobservable terms}$$

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.

$$M_{xC} = -\left(nM_{oC} / p'\right) \times \left(\text{coefficient of } \{x1\}\right)$$

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

(L5)

with similar expressions for $M_y$ and $M_z$.  $M_{oH}$ is the equilibrium magnetization due to all $n$ magnetically equivalent protons.