as a "refocusing routine" and this brings us directly from $D(1)$ to $D(4)$.

$$\begin{aligned} & D(1) \xrightarrow{180xA} +(p'/n)\{z1\} + q'\{1y\} \\ & \xrightarrow{t_e(\text{shiftX})} (p'/n)\{z1\} + q'\cos\Omega_X t_e \{1y\} - q'\sin\Omega_X t_e \{1x\} \end{aligned} \tag{II.42}$$

D(4)

With the assumption that $\Delta_1 = 1/2J$ (i.e., $\pi J\Delta_1 = \pi/2$) we have

$$\begin{aligned} & D(4) \xrightarrow{\Delta_1(J)} (p'/n)\{z1\} - q'\cos\Omega_X t_e \{zx\} - q'\sin\Omega_X t_e \{zy\} \\ & \xrightarrow{\Delta_1(\text{shift X})} (p'/n)\{z1\} - q'\cos\Omega_X t_e (c'\{zx\} + s'\{zy\}) \\ & \qquad - q'\sin\Omega_X t_e (c'\{zy\} - s'\{zx\}) \end{aligned} \tag{II.43}$$

D(5)

where c', s' have the same meaning as in (II.29), i.e.,

$$c' = \cos\Omega_X \Delta_1 \qquad ; \qquad s' = \sin\Omega_X \Delta_1$$

Using again the trigonometric relations for the sum of two angles as we did in (II.30) we rewrite $D(5)$ as:

$$D(5) = (p'/n)\{z1\} - q'\{zx\}\cos\Omega_X (t_e + \Delta_1) - q'\{zy\}\sin\Omega_X (t_e + \Delta_1) \tag{II.44}$$

$$D(5) \xrightarrow{90xX} (p'/n)\{z1\} - q'\{zx\}\cos\Omega_X (t_e + \Delta_1) - q'\{zz\} \sin\Omega_X (t_e + \Delta_1)$$

D(6)

$$D(6) \xrightarrow{90xA} -(p'/n)\{y1\} + q'\{yx\}\cos\Omega_X (t_e + \Delta_1) + q'\{yz\} \sin\Omega_X (t_e + \Delta_1)$$

D(7) (II.45)

$$D(7) = -(p'/n)\{y1\} + q'\{yz\}\sin\Omega_X (t_e + \Delta_1) + \text{NOT} \tag{II.46}$$

Up to this point we have followed step by step the calculations in Section II.9, while formally replacing [ ] by { } and using p'/n instead of p'. This procedure is always valid for rotations (pulses) and in this case it was allowed for evolutions as stated in Appendix L, rule #4.

For the coupled evolution Δ_2 we can concentrate on the observable terms $\{x1\}$, $\{y1\}$ only and take advantage of the exception stated in Appendix L, rule #5.

$$D(7)\xrightarrow{\Delta_2}-(p'/n)(-sC^n\{x1\}+cC^n\{y1\})$$
$$+q'\sin\Omega_X(t_e+\Delta_1)(-cSC^{n-1}\{x1\}-sSC^{n-1}\{y1\})+\text{NOT} \qquad \text{(II.47)}$$

D(8)

n= number of magnetically equivalent X nuclei (e.g., number of protons in CH_n).

$c=\cos\Omega_A\Delta_2 \qquad C=\cos\pi J\Delta_2$

$s=\sin\Omega_A\Delta_2 \qquad S=\sin\pi J\Delta_2$

In order to separate the effect of shift (c and s) and coupling (C and S) we rewrite D(8) as

$$D(8)=-(p'/n)C^n(c\{y1\}-s\{x1\})-q'\sin\Omega_X(t_e+\Delta_1)SC^{n-1}(c\{x1\}+s\{y1\}) \qquad \text{(II.48)}$$

Here again the second term is the true 2D signal while the first one generates axial peaks in the 2D picture since it does not contain the frequency Ω_X.

The value Δ_2 = 1/2J, which implies S = 1 and C = 0, is not suitable anymore because it nulls the useful 2D signal for any n >1. We will discuss later the optimum value of Δ_2.

In writing the magnetization components we have to follow the procedure stated as rule #6 in Appendix L.

$M_{xA}(8) = -\ (nM_{oA}/p')$(coefficient of $\{x1\}$)

$$=-M_{oA}C^n\sin\Omega_A\Delta_2+nM_{oA}(q'/p')SC^{n-1}\sin\Omega_X(t_e+\Delta_1)\cos\Omega_A\Delta_2$$

$M_{yA}(8) = -\ (nM_{oA}/p')$(coefficient of $\{y1\}$)

$$=M_{oA}C^n\cos\Omega_A\Delta_2+nM_{oA}(q'/p')SC^{n-1}\sin\Omega_X(t_e+\Delta_1)\sin\Omega_A\Delta_2$$

$M_{TA}(8) = M_{xA}(8) + iM_{yA}(8)$

$$=iM_{oA}C^n\exp(i\Omega_A\Delta_2)+nM_{oA}(q'/p')SC^{n-1}\sin\Omega_X(t_e+\Delta_1)\exp(i\Omega_A\Delta_2)$$

$$=M_{oA}[iC^n+n(q'/p')SC^{n-1}\sin\Omega_X(t_e+\Delta_1)]\exp(i\Omega_A\Delta_2) \qquad \text{(II.49)}$$

The decoupled evolution t_d during which the detection takes place is treated the same way it was done in II.9, as a rotation about *Oz*.

$$M_{TA}(9) = M_{TA}(8)\exp(i\Omega_A t_d)$$
$$= M_{oA}[iC^n + n(q'/p')SC^{n-1}\sin\Omega_X(t_e+\Delta_1)]\exp[i\Omega_A(t_d+\Delta_2)] \tag{II.50}$$

The enhancement factor of the 2D term is

$$n(q'/p')SC^{n-1}.$$

Now we can discuss the optimum value of Δ_2. In Figure II.4 the value of the product nSC^{n-1} is plotted versus $\Delta_2 J$ for n = 1, 2 and 3. The optimum Δ_2 values are:

$$\begin{aligned} n=1\ (CH) &\longrightarrow \Delta_2 = 0.5/J \\ n=2\ (CH_2) &\longrightarrow \Delta_2 = 0.25/J \\ n=3\ (CH_3) &\longrightarrow \Delta_2 = 0.196/J \end{aligned} \tag{II.51}$$

A good compromise is Δ_2 = 0.3/*J* for which all three expressions *S*, 2*SC*, and $3SC^2$ have values exceeding 0.8. The bad news is that this Δ_2 value does not cancel the axial peak, represented by the term iC^n in (II.50).

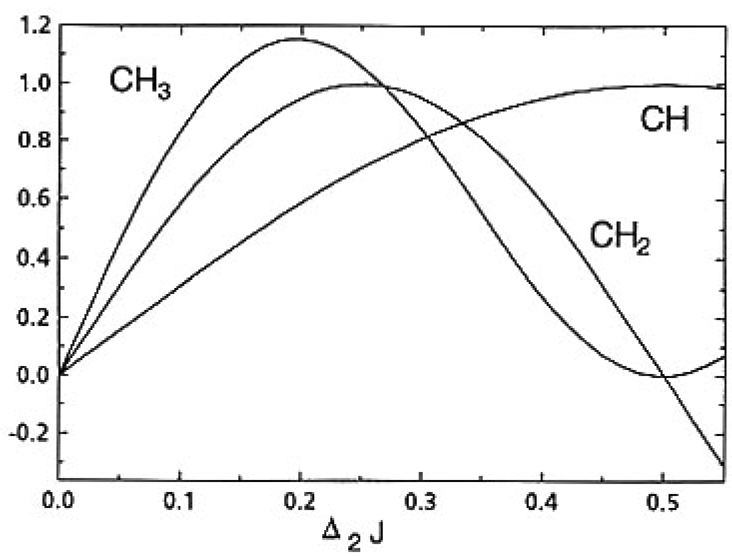

Figure II.4. Dependence of the factor nSC^{n-1} (*S* for CH, 2*SC* for CH_2, and $3SC^2$ for CH_3) on $\Delta_2 J$.