V: MANIPULATING SPIN COHERENCES: DECOUPLING, SPECTRAL EDITING AND COHERENCE TRANSFER

V.1 J-COUPPLINGS: IN-PHASE AND ANTI-PHASE COHERENCES

Some time ago (Section I.10) we showed that for an ensemble of isolated spin 1/2 nuclei, the classical magnetization picture and the exact density matrix analysis afforded identical results:

\[ \text{Classical} \]
\[ \{x, y, z\} \text{ rotating frame} \]
\[ \omega \]
\[ M_0 \]
\[ x \]
\[ y \]
\[ z \]

\[ \text{Quantum-mechanical} \]
\[ \{I_x, I_y, I_z\} \text{ basis set (plus } 1 \text{ which is trivial)} \]
\[ I_x \]
\[ I_y \]
\[ I_z \]
\[ \omega \]
\[ a_0 \]
\[ \rho = a_0 \cdot I_z \]

\[ \frac{\pi}{2} \text{ pulse} \]
\[ I_y \]
\[ I_x \]

\[ \text{chemical shift evolution} \]
\[ \phi = -\Delta \omega I_z \]

\[ M(t) = M_0 e^{i\Delta \omega t} \]
\[ \rho(t) = \cos(\Delta \omega t) I_x - i \sin(\Delta \omega t) I_y \]
Thus, both $B_1$ and $\Delta \omega$ produce the following rotations of the spin operators:

**Pulse Rotations**

For rf pulses $\beta = \omega_1 \cdot \mathbf{O}$ along the y-axis:

\[
\begin{align*}
I_z & \quad \xrightarrow{\beta I_y} \quad I_z \cos \beta + I_x \sin \beta \\
I_y & \quad \xrightarrow{\beta I_y} \quad I_y \\
I_x & \quad \xrightarrow{\beta I_y} \quad \cos \beta I_x - \sin \beta I_z
\end{align*}
\]

For rf pulses along the x-axis:

\[
\begin{align*}
I_z & \quad \xrightarrow{\beta I_x} \quad \ldots \quad I_z \cos(\beta) - I_y \sin(\beta) \\
I_y & \quad \xrightarrow{\beta I_x} \quad \ldots \quad I_y \cos(\beta) + I_z \sin(\beta) \\
I_x & \quad \xrightarrow{\beta I_x} \quad I_x
\end{align*}
\]

Due to chemical shift evolution:

\[
\begin{align*}
I_z & \quad \xrightarrow{\Delta \omega t I_z} \quad I_z \\
I_x & \quad \xrightarrow{\Delta \omega t I_z} \quad I_x \cos(\Delta \omega t) + I_y \sin(\Delta \omega t) \\
& \quad = \frac{I_x + e^{i \Delta \omega t} + I_y - e^{-i \Delta \omega t}}{2} \\
I_y & \quad \xrightarrow{\Delta \omega t I_z} \quad I_y \cos(\Delta \omega t) - I_x \sin(\Delta \omega t) = \ldots \\
& \quad \text{Just a vector rotating in } x-y
\end{align*}
\]

Coherent state
Note that $I_x$ is the sum of 2 coherences rotating in opposite directions, which can be distinguished if $I_y$ is also detected.

**EVOLUTIONS OF COUPLED SPINS**

Consider now an ensemble composed by pairs of weakly coupled inequivalent spins. We try to extend this analogy between classical and quantum-mechanical pictures to include these cases.

With respect to pulses and chemical shift, the operators still behave in the same way:

$$I_{1z} + I_{2z} \xrightarrow{\text{Chem. Shift}} I_{1x} + I_{2x}$$

$$I_{1x} + I_{2x} \xrightarrow{\text{Chem. Shift}} I_{1x} \cos(\Delta \omega_1 t) + I_{1y} \sin(\Delta \omega_1 t) + I_{2x} \cos(\Delta \omega_2 t) + I_{2y} \sin(\Delta \omega_2 t)$$

**J-Coupling**

What about the J-coupling? According to the classical picture:

Spin 1 immediately after the pulse

Spin 1 after evolving for a time $t$
The projection along $x$ is the only net observable signal:

\[ \text{FT of thin } \rightarrow \)

\[ M_{x_1}(t) = M_1 \cos \left( \frac{J t}{2} \right) \quad \frac{1}{2} \text{ brings intensity} \]

\[ -\frac{J}{2} \quad +\frac{J}{2} \]

\[ \Delta \omega_1 \]

The projection along $y$ is constantly zero ($M_y(t) = 0$), but only because the number of $|\alpha>$ and $|\beta>$ states of spin 2 throughout the sample are essentially identical.

$M_y$ should actually be described as:

\[ M_{y_1}(t) = M_1 \left[ \left( \cos \alpha_2 \sin \left( \frac{J t}{2} \right) + \cos \beta_2 \sin \left( \frac{J t}{2} \right) \right) \right] \]

Or, since $\left( \cos \alpha_2 - \cos \beta_2 \right) \propto M_{2z}$:

\[
M_{y_1}(t) \propto M_1 \cdot M_{2z} \cdot \sin \left( \frac{J t}{2} \right) \quad \text{\textcolor{red}{CLASSICAL $M_y$ \& $M_y$ \textcolor{red}{SO FAR} \textcolor{red}{BECOMES \textcolor{red}{NEW}}$ \textcolor{red}{DENS. MATR. INTERA\textcolor{red}{L}} \textcolor{red}{NEC.}} \]

\[
M_{y_1}(t) \propto M_1 \cdot M_{2z} \cdot \sin \left( \frac{J t}{2} \right) \quad \text{\textcolor{red}{CLASSICAL $M_y$ \& $M_y$ \textcolor{red}{SO FAR} \textcolor{red}{BECOMES \textcolor{red}{NEW}}$ \textcolor{red}{DENS. MATR. INTERA\textcolor{red}{L}} \textcolor{red}{NEC.}} \]

The full density matrix analysis of this problem gives a very similar answer.

Using the operator formalism, we know that after the pulse:

\[ I_0 = I_{1z} + I_{2z} \xrightarrow{\left( \frac{\pi}{2} \right) I_{1y}} I_{1x} + I_{2z} \quad \text{\textcolor{red}{PULSE ON}} \]
The subsequent time evolution of spin 1 will then be given by

\[ \rho_1(t) = e^{-i H_J t} I_{1x} e^{i H_J t} \]

with

\[ \mathcal{H}_J = J \cdot I_{1z} \cdot I_{2z} \]

Solved:  
\[ e^{-i (J I_{2z} t) \cdot I_{1z}} I_{1x} e^{i (J I_{2z} t) \cdot I_{1z}} \]

This is equivalent to a chemical shift evolution of spin 1 with an offset \( \Delta \omega_1 = J I_{2z} \)

\[ \rho_1(t) = I_{1x} \cos (J I_{2z} t) + I_{1y} \sin (J I_{2z} t) \]

\[ \text{(*)} \]

We can evaluate the trigonometric functions by expanding them in power series:

\[ \cos (J I_{2z} t) = 1 - (J I_{2z} t)^2 / 2 + (J I_{2z} t)^4 / 4! - \ldots \approx \cos \left( \frac{J I_{2z} t}{2} \right) \]

\[ \sin (J I_{2z} t) = J I_{2z} t - (J I_{2z} t)^3 / 3! + (J I_{2z} t)^5 / 5! - \ldots \]

and recalling that since \( I_{2z} \cdot I_{2z} = \frac{1}{4} \cdot g_{zz}^2 = \frac{1}{4} \cdot I \)

it follows that

\[ \cos (J I_{2z} t) = \cos \left( \frac{J t}{2} \right) \cdot I \]

\[ \sin (J I_{2z} t) = g_{zz} \cdot \sin \left( \frac{J t}{2} \right) = I_{2z} \sin \left( \frac{J t}{2} \right) \]
Finally, inserting this into (*)

\[ I_{1x} \xrightarrow{J I_{1z}} I_{1x} \cos \left( \frac{J t}{2} \right) + 2 I_{1y} I_{2z} \sin \left( \frac{J t}{2} \right) \]

\[ \text{Resembles a root.} \]

\[ \text{in-phase coherences} \]

\[ \text{anti-phase coherences} \]

Still, the signal \( S(t) \) that we detect from spins 1 in the experiment cannot directly detect the antiphase term:

\[ S(t) = T_n \left[ \rho(t) \cdot I_{1+} \right] \times a_0 \cos \left( \frac{J t}{2} \right) T_n \left( I_{1x} I_{1+} \right) + \]

\[ \sin \left( \frac{J t}{2} \right) T_n \left( 2 I_{1y} I_{2z} I_{1+} \right) = a_0 \cos \left( \frac{J t}{2} \right) \]

\[ T_n(I_{2z}) \to 0 \]

\[ T_n(I_{1z}) \to 0 \]

**Single Linear Rotations**

In the same way as we talked about rotations around the \( I_z \) axis due to chemical shift in the x, y, z-space

\[ [I_x, I_y] = i I_z (t) \]

*This defines a 3D non-commutative space.*

Real reason for rotation: underlying reason why \( I_y \to I_x \)

\[ I_x \to I_y \text{ after time delay under effect of } J \]
Bilinear terms make rotations in a slightly different space.

\[ I_{1z} I_{2z} \rightarrow \begin{cases} J \times J/2 & \text{underlying} \\ I_{1x} \rightarrow I_{1y}, I_{2x} \rightarrow I_{2y} \end{cases} \] (when acted upon by J-coupling)

Of course, \( I_{1z} I_{2z} \) also rotates \( I_{1y} \) or \( I_{2y} \):

\[ \begin{align*} I_{1y} & \rightarrow J I_{1z} I_{2z} \rightarrow I_{1y} \cos \left( J \times J/2 \right) - 2 I_{1x} I_{2z} \sin \left( J \times J/2 \right) \\ I_{2y} & \rightarrow J I_{1z} I_{2z} \rightarrow I_{2y} \end{align*} \]

Moreover, the rotation is also felt by the anti-phase coherences:

\[ \begin{align*} 2 I_{1y} I_{2z} & \rightarrow J I_{1z} I_{2z} \rightarrow 2 I_{1y} I_{2z} \cos \left( J \times J/2 \right) - I_{1x} \sin \left( J \times J/2 \right) \\ \end{align*} \]

Only bilinear couplings can bring into play coherent states between 2 spins.

No couplings \( \rightarrow \) can never achieve these type of antiphase.
We analyze now the evolution of anti-phase coherences under the effect of chemical shifts:

\[ \rho (t) = e^{i \omega s t} e^{-i \omega s t} \]

\[ \rho_{ss} = -i \omega_{s} I \mathbb{I}_{1} \mathbb{I}_{2} \]

\[ \mathbb{I}_{1} \mathbb{I}_{2} \mathbb{I}_{3} \mathbb{I}_{4} = 2 I_{1} I_{2} \cos (\omega s t) + 2 I_{1} I_{2} \sin (\omega s t) \]

where \( \omega_{s} \) is the chemical shift between spins 1 and 2.

In the presence of both \( J \)- and chemical shift evolution, we can use the fact that to first order

\[ \rho_{ss} = 0 \]

\[ \mathbb{I}_{1} \mathbb{I}_{2} \mathbb{I}_{3} \mathbb{I}_{4} = \mathbb{I}_{1} \mathbb{I}_{2} \]

\[ \mathbb{I}_{1} \mathbb{I}_{2} \mathbb{I}_{3} \mathbb{I}_{4} = \mathbb{I}_{1} \mathbb{I}_{2} \]

\[ \mathbb{I}_{1} \mathbb{I}_{2} \mathbb{I}_{3} \mathbb{I}_{4} = \mathbb{I}_{1} \mathbb{I}_{2} \]

\[ \mathbb{I}_{1} \mathbb{I}_{2} \mathbb{I}_{3} \mathbb{I}_{4} = \mathbb{I}_{1} \mathbb{I}_{2} \]

\[ \mathbb{I}_{1} \mathbb{I}_{2} \mathbb{I}_{3} \mathbb{I}_{4} = \mathbb{I}_{1} \mathbb{I}_{2} \]

\[ \mathbb{I}_{1} \mathbb{I}_{2} \mathbb{I}_{3} \mathbb{I}_{4} = \mathbb{I}_{1} \mathbb{I}_{2} \]

\[ \mathbb{I}_{1} \mathbb{I}_{2} \mathbb{I}_{3} \mathbb{I}_{4} = \mathbb{I}_{1} \mathbb{I}_{2} \]

\[ \mathbb{I}_{1} \mathbb{I}_{2} \mathbb{I}_{3} \mathbb{I}_{4} = \mathbb{I}_{1} \mathbb{I}_{2} \]

\[ \mathbb{I}_{1} \mathbb{I}_{2} \mathbb{I}_{3} \mathbb{I}_{4} = \mathbb{I}_{1} \mathbb{I}_{2} \]

\[ \mathbb{I}_{1} \mathbb{I}_{2} \mathbb{I}_{3} \mathbb{I}_{4} = \mathbb{I}_{1} \mathbb{I}_{2} \]

\[ \mathbb{I}_{1} \mathbb{I}_{2} \mathbb{I}_{3} \mathbb{I}_{4} = \mathbb{I}_{1} \mathbb{I}_{2} \]

\[ \mathbb{I}_{1} \mathbb{I}_{2} \mathbb{I}_{3} \mathbb{I}_{4} = \mathbb{I}_{1} \mathbb{I}_{2} \]

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\[ \mathbb{I}_{1} \mathbb{I}_{2} \mathbb{I}_{3} \mathbb{I}_{4} = \mathbb{I}_{1} \mathbb{I}_{2} \]

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\[ \mathbb{I}_{1} \mathbb{I}_{2} \mathbb{I}_{3} \mathbb{I}_{4} = \mathbb{I}_{1} \mathbb{I}_{2} \]

\[ \mathbb{I}_{1} \mathbb{I}_{2} \mathbb{I}_{3} \mathbb{I}_{4} = \mathbb{I}_{1} \mathbb{I}_{2} \]

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\[ \mathbb{I}_{1} \mathbb{I}_{2} \mathbb{I}_{3} \mathbb{I}_{4} = \mathbb{I}_{1} \mathbb{I}_{2} \]

\[ \mathbb{I}_{1} \mathbb{I}_{2} \mathbb{I}_{3} \mathbb{I}_{4} = \mathbb{I}_{1} \mathbb{I}_{2} \]

\[ \mathbb{I}_{1} \mathbb{I}_{2} \mathbb{I}_{3} \mathbb{I}_{4} = \mathbb{I}_{1} \mathbb{I}_{2} \]

\[ \mathbb{I}_{1} \mathbb{I}_{2} \mathbb{I}_{3} \mathbb{I}_{4} = \mathbb{I}_{1} \mathbb{I}_{2} \]
V.2 THE EFFECTS OF A SECOND PULSE: ZERO- AND DOUBLE-
QUANTUM COHERENCES

Given a system composed by two spins, we have that before the first pulse

\[ \rho = I_{1z} + I_{2z} \]

populations, diagonal elements of \( \rho \)

After the first pulse and in the presence of couplings and chemical shifts, \( \rho \) evolves as a linear combination of

\[ I_{1z}, I_{2z}, I_{1x}, I_{2x}, I_{1y}, I_{2y}, I_{1z}I_{2x}, I_{1x}I_{2z}, I_{1y}I_{2z}, I_{1z}I_{2y} \]

known single-quantum coherences; operators proportional to \( I_{1\pm}, I_{2\pm}, I_{1\pm}I_{2\pm}, I_{1z}I_{2\pm} \)

only contain one of that looks like a single \( I \) coeef'

We investigate now what happens with these 2-spin operators if a second rf pulse is applied. The evolution of the pulse can be

\[ R = e^{i\beta I_{1x}} \quad \text{or} \quad e^{i\beta I_{2x}} \quad \text{selective} \]

\[ R = e^{i\beta I_{1y}} \quad \text{or} \quad e^{i\beta I_{2y}} \quad \text{non-selective} \]

The effect of \( R \) on an anti-phase operator of the form \( I_{1x}I_{2z} \):

\[ 2I_{1x}I_{2z} \xrightarrow{R} 2R I_{1x} R^{-1} R I_{2z} R^{-1} \]

rotate index of one another.

These products of operators evolve independently, like single spin operators. Consider model...
Thus for instance

\[
\begin{align*}
2I_{1x}I_{2z} & \xrightarrow{\pi/2 I_1x} 2I_{1x}I_{2z} \\
& \xrightarrow{\pi/2 I_1y} -2I_{1z}I_{2x} \\
& \xrightarrow{\pi/2 I_1z} -2I_{1x}I_{2y} \\
& \xrightarrow{\pi/2 I_2x} 2I_{1x}I_{2z} \\
& \xrightarrow{\pi/2 I_2y} -2I_{1z}I_{2x} \\
& \xrightarrow{\pi/2 I_2z} -2I_{1x}I_{2z}
\end{align*}
\]

\begin{align*}
\text{singly quantum co\-Gs} \\
\text{These operators are new.}
\end{align*}

Overall, a second pulse can create 5 new operators

\[
\begin{align*}
2I_{1x}I_{2x}, 2I_{1y}I_{2y}, 2I_{1x}I_{2y}, 2I_{1y}I_{2x}, 2I_{1z}I_{2z},
\end{align*}
\]

double-quantum coherences

due to

\[
\begin{align*}
\text{zero-quantum coherences}
\end{align*}
\]

come from 2 pulses \& J-couplings. 5 new states \rightarrow 15 new states + zero; \rightarrow 16 \text{ states.}

In total we have these 5 operators, 2 populations \((I_{1x}, I_{2z})\) \& 8 single-quantum operators = 15 operators. If we add the identity operator we have a total of 16 operators \(O_1, O_2, \ldots, O_{16}\); which from a basis set for the 2-spin space. Thus, any \(\frac{1}{2}\) state \(\rho\) representing a two-spin system can be written as:

\[
2I_{1x}I_{2x} = 2 (I_{1x} \pm I_{1y}) (I_{2x} \pm I_{2y}) = I_{1x}I_{2x} \pm I_{1x}I_{2y} \pm I_{1y}I_{2x} \pm I_{1y}I_{2y}
\]

and any full density matrix calculation can be carried out using this \textbf{product operator formalism.}

We investigate how the new product operator terms behave under different interactions.

The zero-quantum coherence does not evolve with \(\mathcal{H}_C\) or \(\mathcal{H}_J\):

\[
[I_{1z}I_{2z}, \mathcal{H}_C] = [I_{1z}I_{2z}, \mathcal{H}_J] = 0: \text{it behaves like populations}
\]
Under the effects of chemical shift, each spin operator in a double-quantum coherence evolves independently:

\[ e^{-i\omega_1 t I_{1z}} e^{-i\omega_2 t I_{2z}} e^{R^{-1}} e^{2I_{1x} t} e^{i\omega_1 t I_{1z}} e^{i\omega_2 t I_{2z}} e^R \]

all the resulting coherences are double-quantum operators

By contrast, the evolution with respect to \( H_J \),

\[ e^{iJ I_{1z} I_{2z} t} e^{i\frac{J}{2} I_{1x} t} e^{i\frac{J}{2} I_{2x} t} = \frac{I_{1x} \cos(Jt/2) + 2I_{1y} I_{2z} \sin(Jt/2)}{I_{2x} \cos(Jt/2) + 2I_{1z} I_{2y} \sin(Jt/2)} \]

\[ = I_{1x} I_{2x} \cos^2(\text{something}) + 4I_{1y} I_{1z} I_{2z} I_{2y} \sin^2(\text{something}) + \cos(\text{something}) \sin(\text{something}) \left[ \frac{2I_{1x} I_{1z} I_{2x} + 2I_{1y} I_{2y}}{2} \right] \]

\[ \Rightarrow I_{1x} I_{2x} \frac{J I_{1z} I_{2z} t}{2} I_{1x} I_{2x} \text{ NOT INTUITIVE} \]

\[ \text{IF} \not\text{ DOESN'T GO ANYWHERE} \]

\[ EJ + E-J \text{ IN THEM} \]

Neither zero nor double-quantum operators evolve due to J-couplings
In an NMR experiment the observed signal $S$ is proportional to $T_n \left( e \cdot I_+ \right)$ only states which have one transverse operator can be detected:

$$T_n \left( I_{1x} \otimes I_+ \right), \quad T_n \left( I_{2x} \otimes I_+ \right) \neq 0$$

$$T_n \left( I_{1y} \otimes I_{2z} \otimes I_+ \right) = T_n \left( I_{1y} \otimes I_{2z} \otimes I_+ \right) = T_n \left( I_{1z} \otimes I_{2z} \otimes I_+ \right) = T_n \left( I_{1x} \otimes I_{2x} \otimes I_+ \right) = 0$$

However, if the spins are coupled, all single-quantum operators can give origin to observable signals:

$$I_{1x} \xrightarrow{\text{J}} I_{1x} \cos \left( \frac{\Delta \omega t}{2} \right) + 2 I_{1y} I_{2z} \sin \left( \frac{\Delta \omega t}{2} \right)$$

$$\uparrow \text{observable}$$

The shape of the signals originated by these coherences:

$I_{1x} \rightarrow e^{i \Delta \omega t \cdot t} \cdot \cos \left( \frac{\Delta \omega t}{2} \right)$: \hspace{1cm} $\rightarrow$ \hspace{1cm} $\rightarrow$

$\uparrow \text{in-phase doublet}$

$\rightarrow$ \hspace{1cm} $\rightarrow$

$\rightarrow$ \hspace{1cm} $\rightarrow$

That's why these operators are called in-phase and anti-phase coherences.
V.3 DOUBLE RESONANCE_PART 1: Π-PULSES AND DECOUPLING

Let's consider a two-spin system I-S composed by a pair of nuclei with widely different chemical shifts (e.g., a spin I = 1H and a spin S = 13C) which are coupled among them. The Hamiltonian in the doubly rotating frame (i.e., rotating frame for I and S) is given by:

\[ H = -\omega_I I_z - \omega_S S_z + J I_z S_z \]

We focus on the signal arising from the S-spins after a (π/2)_S pulse using a classical picture, assuming a π-pulse on the I-spins at time \( \tau \).

After the pulse, the state evolves according to the Hamiltonian. After waiting another period \( \tau \) the I-spin echo is observed.

\[ \phi_{cs} = 2 \omega_S \tau \]

We get an echo of decouplings but not of chemical shifts.

C.S. & J could commute if they could confide...
Consider now a system composed of 2 S spins, each one coupled to its I spin, on which we apply a train of (π)_I pulses:

\[ \phi_{cs_1} = \omega_{s_1} \cdot t \]

\[ \phi_{cs_2} = \omega_{s_2} \cdot t \]

If \( \phi \) is short enough, the signal that can be detected corresponds to an I-decoupled S-spectrum. The limit of this sequence is a CW irradiation of the I spins with a B_2 field; in this case the I-S Hamiltonian is:

\[ H_{IS} = -\omega_S S_z - \omega_I I_z + J I_z S_z + \omega_2 \cdot I_x \]

If \( \omega_2 \) is off-resonance, the Hamiltonian is time independent, and can be diagonalized; the resulting S spectrum behaves as follows:

\[ \omega_I = 0: \text{on resonance decoupling} \]

\[ B_2 = J \]

\[ \sqrt{B_2} \to J \to \omega_I \to 0 \]

\[ B_2 = J \]

\[ \omega_I \to 0 \]

\[ B_2 = J \]

\[ \omega_S \]

\[ \omega_I \to B_2 \to J \to \omega_S \]

Unlike other spinning systems, \( \omega_S \) is strong and can be measured in this region.
In the case of $^{13}$C NMR, we thus have the following alternatives:

**Summary**

$^1$H:

- **$^1$H:**
  - no NOE
  - no decoupling

$^{13}$C:

- **$^{13}$C:**
  - with NOE
  - no decoupling
  - with NOE and decoupling

Best $s/n$
Decoupling is very sensitive to the l-spin offset. If $I = ^1H$, at 500 MHz, the $^1H$ dispersion is ca 5000 Hz. The $B_2$ in CW decoupling has to be very large to cover such a frequency range; this is impractical due to probe and sample heating problems. Instead, efficiency can be improved by superimposing on the CW irradiation an rf modulation. Two common choices are noise and square-wave decoupling.

**Regions of decoupling**

- **Noise Decoupling**
  - CW + \[ \text{noise modulation} \]
  - FT
  - **Noise Decoupling**

- **Square Wave Decoupling**
  - CW + \[ \text{square modulation of freq} \]
  - FT
  - **Square Wave Decoupling**

Too little range now decay.
The most efficient way of doing heteronuclear decoupling is using trains of \( \pi \)-pulses, where each \( \pi \)-pulse is a composite pulse: composite pulse decoupling.

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**Fig. 4.7.7.** Comparison of the performance of various decoupling schemes as a function of the offset of the decoupled nuclei. The experimental points indicate the height of the proton-decoupled carbon-13 signal of formic acid, which gives a measure of the line-narrowing efficiency. The amplitude of the decoupling field is \( \gamma B_2/(2\pi) = 1.5 \text{ kHz} \) throughout. (a) MLEV-64 sequence with the composite inversion sequence \( R = (\pi/2)_a(\pi)_a(\pi/2)_b \) of eqn (4.2.55). (b) Frequency-swept square-wave phase modulation. (c) 100-Hz square-wave phase modulation. (d) Noise decoupling with 1-kHz clock rate.

In \(^{13}\text{C} \) NMR however, \( J \) couplings may be useful because they contain structural information:
This information can be partially preserved in decoupled spectra using the attached proton test (APT) experiment. Its pulse sequence:

\[ \frac{\pi}{2} \rightarrow \text{NOE} \rightarrow \pi \rightarrow \text{Dec.} \]

with \( g = \frac{1}{2} J_{\text{average}} \)

Most C-H \( J \approx 125 \text{Hz} \)

\( \tau = 4 \text{ms} \)

\( \frac{\alpha_H}{13C} \rightarrow \beta_H \rightarrow \frac{\alpha_C}{\beta} \rightarrow \frac{\alpha_C}{\beta} \)

The different phases:

C: \[ \text{CH}: \quad \text{CH}_2: \quad \text{CH}_3: \]
V.4 DOUBLE RESONANCE_PART 2: HETERONUCLEAR COHERENCE TRANSFER AND THE INEPT EXPERIMENTS

NOE can be used to transfer populations incoherently from $^1$H to $^{13}$C via relaxation. Coherences can also be transferred from protons to carbons if the $^1$H-$^{13}$C pair is spin-coupled. The simplest pulse sequence capable of achieving this:

Assume no $^1$H (I-spin) or $^{13}$C (S-spin) offset, and no initial $^{13}$C magnetization. The evolution of $C$ in this sequence

$$P_0 = I_z \xrightarrow{\frac{T_2}{2}I_x} I_y \xrightarrow{J I_z S_z \frac{T_2}{2}} I_y \cos\left(\frac{J T_z}{2}\right) - 2I_x S_z \sin\left(\frac{J T_z}{2}\right) \xrightarrow{\frac{T_2}{2}I_y}$$

$$P = Y S \frac{T_2}{2}$$

$$P' = Y S S \frac{T_2}{2}$$

If we tune $T = \frac{1}{2J}$

$$\Rightarrow \text{at } \Theta : I_y \rightarrow 0$$

$$2I_x S_z \rightarrow \text{maximum}$$

Also note that the observable $^{13}$C signal

$\pm$ Another way of looking at it is to note that:

$\pm$
Notice that since we started from I₂, there is an enhancement in the \(^{13}\text{C}\) signal arising from this sequence = \(\gamma_1/\gamma_S\). So

Coherence transfer: signal enhancement \(\propto \gamma_1/\gamma_S\)  For \(^{13}\text{C}\approx 4; ^{15}\text{N}\approx 10\)

NOE: signal enhancement \(\propto 1 + \gamma_1/2\gamma_S\)  For \(^{13}\text{C}\approx 3; ^{15}\text{N}\approx 4\)

This simple sequence however has its problems. In the presence of chemical shifts:

\[I_x \xrightarrow{(\pi/2)_x} I_y \xrightarrow{J_{I_2}S_z} I_x \xrightarrow{(\pi/2)_y} -I_z \xrightarrow{\text{C tuned}} \text{this is zero} \]

\[I_y \xrightarrow{J_{I_2}S_z} 2I_y S_z \xrightarrow{\text{wasted coherence}} \text{several times} \]

\[I_y \xrightarrow{\text{C tuned}} \text{this is zero} \]

\[I_y \xrightarrow{J_{I_2}S_z} -2I_x S_z \xrightarrow{\text{wasted coherence}} \]

\[C = \cos(\omega_I I_z \tau) \]

\[S = \sin(\omega_I I_z \tau) \]

We have to make I-chemical shifts effectively zero to maximize the S signal, but without affecting the I,S J-coupling. This can be achieved by putting simultaneous I and S \(\pi\)-pulses in the middle of \(\tau\)

\[1\text{H:} \quad (\pi/2)_x \xrightarrow{\pi/2} \pi \xrightarrow{\pi/2} (\pi/2)_y \quad G=1/2J: \text{basic INEPT sequence} \]

\[S\xrightarrow{\text{basic INEPT sequence}} S, S(\frac{\tau}{2}) = \text{Down your path} \]

\[13\text{C:} \quad \text{Use two } \pi \text{ pulses to eliminate (not excite) } L, S \quad \text{I keep J coupling} \]
INEPT: Insensitive Nuclei Enhanced by Polarization Transfer

This sequence still has a problem: \( S_y \propto X_1 \sin(Jt/2) \Rightarrow \text{anti-phase doublet} \)

Coupled spectrum

If \(^1\text{H}-\text{decoupling}\) is immediately after the pair of \((\pi/2)_{1_S}\) pulses, no S signal is observed. To get a fully decoupled spectrum:

Refocused INEPT \((\delta = \frac{1}{2J})\)

Think about \(\text{FT} \cos(\omega t) \Rightarrow \text{FT} S_0\)
Overall, we have the following alternatives for recording a $^{13}$C NMR spectrum (so far!)

Figure 6.9 Permutations on the spectrum of chloroform. It can be seen that the refocused INEPT spectrum shows some loss of intensity as compared with simple INEPT; this is partly due to transverse relaxation during the refocusing period, and partly to imperfections in pulses.

1) Refocused INEPT
2) 'Dec' 
3) No H15 splitting
4) Faster pulses
V.5 MULTISPIN SYSTEMS: INEPT SPECTRAL EDITING AND THE DEPT EXPERIMENT

Let's consider now a system composed by 3 weakly coupled spins \( \{I_1, I_2, I_3\} \).
We have new operators of the type:

\[
2 I_{1x} I_{2z} \quad \frac{J I_{1z} I_{3z}}{t} \quad ?
\]

The result could be

- 3 spins yield all these,
- 2 \( I_{1z} I_{3z} \), 4 \( I_{1z} I_{2z} I_{3z} \) : zero-quantum coherences
- 2 \( I_{1x} I_{2z} \), 4 \( I_{1x} I_{2z} I_{3z} \) : single-quantum coherences
- 2 \( I_{1x} I_{2y} \), 4 \( I_{1x} I_{2y} I_{3z} \) : double-quantum coherences
- 4 \( I_{1x} I_{2x} I_{3x} \), 4 \( I_{1x} I_{2x} I_{3y} \) : triple-quantum coherences

Evolution of \( I_j I_k \) operators under the effects of \( W_j I_{2j} \) or \( J I_{2j} I_{3k} \) remain as in the case of 2 spins. We have to deal now however with new situations, like for instance:

\[
2 I_{1x} I_{2z} \quad \frac{J_{13} I_{1z} I_{3z}}{t} \quad ?
\]

A J-coupl can only give single answers.
The result

\[ P(A) = 2e^{-i\mathcal{J}_{12}I_{1z}I_{3z}t} \left( I_{1x} e^{i\mathcal{J}_{13}I_{1z}I_{3z}t} I_{2z} \right) : \text{only spin 1 evolves} \]

\[ \downarrow \]

\[ 2 \left[ I_{1x} \cos \left( \frac{\mathcal{J}_{13}t}{2} \right) + 2 I_{1y} I_{3z} \sin \left( \frac{\mathcal{J}_{13}t}{2} \right) \right] I_{2z} \Rightarrow \]

\[ \Rightarrow 2 I_{1x} I_{2z} \xrightarrow{\mathcal{J}I_{1z}I_{3z}t} 2 I_{1x} I_{2z} \cos \left( \frac{\mathcal{J}_{13}t}{2} \right) + 4 I_{1y} I_{2z} I_{3z} \sin \left( \frac{\mathcal{J}_{13}t}{2} \right) \]

\[ \text{or with the remaining possibility} \]

\[ 2 I_{1x} I_{2z} \xrightarrow{\mathcal{J}I_{1z}I_{3z}t} 2 I_{1x} I_{2z} \cos \left( \frac{\mathcal{J}_{13}t}{2} \right) + I_{1y} \sin \left( \frac{\mathcal{J}_{13}t}{2} \right) \]

\[ \text{S. Q. D.} \]

\[ \text{Compare with our previous situation} \]

\[ 2 I_{1x} I_{2z} \xrightarrow{\mathcal{J}I_{1z}I_{2z}t} 2 I_{1x} I_{2z} \cos \left( \frac{\mathcal{J}_{12}t}{2} \right) + I_{1y} \sin \left( \frac{\mathcal{J}_{12}t}{2} \right) \]

\[ \text{or with the remaining possibility} \]

\[ 2 I_{1x} I_{2z} \xrightarrow{\text{evolves}} 2 I_{1x} I_{2z} \]

\[ \text{# easy to understand w/o us} \]

\[ \text{Recall D, O evolves as sum of C.S} \]

\[ \text{Diff?} \]
Moreover there is an additional complication. Recall that although in systems composed by pairs of spins double-quantum states did not evolve:

\[ 2 I_{1x} I_{2y} \xrightarrow{J I_{1z} I_{2z}} 2 I_{1x} I_{2y} \]

these states do evolve in the presence of coupling to a third spin \((J_{13} \neq 0\) for instance):

\[ 2 I_{1x} I_{2y} \xrightarrow{J I_{1z} I_{3z}} 2 I_{1x} I_{2y} \cos \left( \frac{J_{13} t}{2} \right) + 4 I_{1y} I_{2y} I_{3z} \sin \left( \frac{J_{13} t}{2} \right) \]

Consider the INEPT experiment on a 3 spin system \(CH_2\) with \(J_{CH_1} = J_{CH_2} = J\). We focus on the evolution after the second pair of \((\pi/2)\) pulses:

\[ I_{z_1} + I_{z_2} \xrightarrow{(\pi/2)_x} I_{y_1} + I_{y_2} \xrightarrow{(\pi/2)_y} \]

\[ 2 (I_{z_1} + I_{z_2}) \xrightarrow{J I_{1z} S_z} 2 I_{z_1} S_x \cos \left( \frac{J t}{2} \right) + S_y \sin \left( \frac{J t}{2} \right) \]

\[ J I_{z_2} S_z \xrightarrow{(\pi/2)_y} \]

\[ 2 I_{z_1} S_x \cos^2 \left( \frac{J t}{2} \right) + 4 I_{z_1} I_{z_2} S_y \cos \left( \frac{J t}{2} \right) \sin \left( \frac{J t}{2} \right) \]

\[ J I_{z_2} S_z \xrightarrow{(\pi/2)_y} \]

\[ S_y \sin \left( \frac{J t}{2} \right) \cos \left( \frac{J t}{2} \right) - 2 I_{z_2} S_x \sin^2 \left( \frac{J t}{2} \right) \]

\[ \text{Observable?} \]
Out of all these operators, only the term proportional to $S_y$ is observable! Overall, the observable part of the $S$-spin density matrix arising from CH$_n$ groups in an INEPT experiment (with $\theta$ tuned to $\sin \left( \frac{JG}{2} \right) = 1$) is given by:

\[
CH: \quad \rho \propto S_y \sin \frac{JG}{2} \\
CH_2: \quad \rho \propto -2S_y \sin \frac{JG}{2} \cos \frac{JG}{2} \\
CH_3: \quad \rho \propto 3S_y \sin \frac{JG}{2} \cos^2 \frac{JG}{2}
\]

The line shapes:

\[\text{FT} \quad \text{FT} \quad \text{FT}\]

For CH:

\[\frac{J}{2}, -\frac{J}{2}\]

For CH$_2$:

\[* \rightarrow \text{convoluted}\]

For CH$_3$:

\[\frac{3J}{2}, -\frac{3J}{2}\]
The factors multiplying Sy can be used to edit the intensity of the different carbons. To do so, one carries out a number of experiments for different $J_{\text{C-H}}$ values; for instance,

\[
\begin{align*}
\frac{J_{\text{C-H}}}{2} &= \frac{1}{8} \text{ cyc.} & \frac{J_{\text{C-H}}}{2} &= \frac{1}{4} \text{ cyc.} & \frac{J_{\text{C-H}}}{2} &= \frac{3}{8} \text{ cyc.} \\
\text{CH:} & \quad \frac{1}{\sqrt{2}} & 1 & \frac{1}{\sqrt{2}} \\
\text{CH}_2: & \quad 1 & 0 & -1 \\
\text{CH}_3: & \quad 1.5 \frac{1}{\sqrt{2}} & 0 & 1.5 \frac{1}{\sqrt{2}}
\end{align*}
\]

and obtains the subspectra according to

\[
\begin{align*}
\text{CH:} & \quad \text{spectrogram } \left( \frac{J_{\text{C-H}}}{2} = \frac{1}{4} \right) \\
\text{CH}_2: & \quad \text{spectrogram } \left( \frac{J_{\text{C-H}}}{2} = \frac{1}{8} \right) - \text{spectrogram } \left( \frac{J_{\text{C-H}}}{2} = \frac{3}{8} \right) \\
\text{CH}_3: & \quad \text{spectrogram } \left( \frac{J_{\text{C-H}}}{2} = \frac{1}{8} \right) + \text{spectrogram } \left( \frac{J_{\text{C-H}}}{2} = \frac{3}{8} \right) - \sqrt{2} \cdot \text{spectrogram } \left( \frac{J_{\text{C-H}}}{2} = \frac{1}{4} \right)
\end{align*}
\]

The main problem of INEPT is that it works based on the assumption that all $J_{\text{C-H}}$ are equal. This is only partly true, but relatively small dispersions in $J_{\text{C-H}}$ can ruin an INEPT.

\[\frac{5\pi}{2} \text{ for all } \text{ C's} \approx 100\%\]

\[\text{have problem with large } \text{ C's}\]
There is a second polarization transfer procedure whose efficiency is independent of the strength of J couplings, and which therefore affords a much better quality in the subspectral editing: Distortionless Enhancement by Polarization Transfer (DEPT). The pulse sequence of DEPT:

\[ \text{H:} \quad (T_z)_{y} \quad \pi \quad \theta_{x} \quad \text{Dec} \quad \text{with } \theta \text{ tuned to } \frac{1}{2J} \]

\[ \text{C:} \quad \text{acq} \]

Let's analyze the evolution of \( \rho \) for an Si_\( n \) group (CH\(_3\), etc.). Since the only effect of the \( \pi \) pulses is to refocus the chemical shifts (which we ignore anyway); we have that

\[ m \chi_{z} I_{z} \xrightarrow{\pi/2 \ I_{y}} m \chi_{x} I_{x} \xrightarrow{J I_{z} S_{z} \theta} m 2 \chi_{x} I_{y} S_{x} \]

\[ \pi/2 \ S_{y} \xrightarrow{\pi I} m 2 \chi_{x} I_{y} S_{x} \]

\[ \text{multiple-quantum coherence} \]

DEPT gets rid of extra J-coult problem.
To analyze the evolution of this last term, we analyze the fate of each one of its components:
Let's compare INEPT with DEPT:

\[
m\gamma_{I}^Z S_{IJ} \sin \frac{J_{I}^Z}{2} \cos^{-1} \frac{J_{I}^Z}{2} \]

\[
\text{INEPT (InS): } m\gamma_{I}^Z I_{z} \rightarrow m\gamma_{I}^Z I_{x} \rightarrow m\gamma_{I}^Z 2 I_{y} S_{z} \rightarrow m\gamma_{I}^Z 2 I_{z} S_{x}
\]

\[
\text{DEPT (InS): } m\gamma_{I}^Z I_{z} \rightarrow m\gamma_{I}^Z I_{x} \rightarrow m\gamma_{I}^Z 2 I_{y} S_{z}
\]

The "transfer functions" of both experiments are very similar, but in INEPT the tuning depends on \( J \) whereas in DEPT it is a function of a pulse angle.

Editing can then be carried out like in INEPT, with \( \theta' = \frac{\pi}{4}, \frac{\pi}{2}, \frac{3\pi}{4} \)

---

**Fig. 4.5.6.** Editing of proton-decoupled carbon-13 spectra of a mixture of brucine and 2-bromothiazole, which has a spread of \( J \)-couplings from ca. 125 to 192 Hz. Note the clean separation of the signals associated with \( \text{CH}_2 \) groups and the absence of cross-talk.
V.6 PROBLEMS

1) Using the full 4 x 4 density matrixes representing the space of a pair of spins, demonstrate the following evolutions:

a) \[ I_{1z} + I_{2z} = F_Z \xrightarrow{\frac{\pi}{2}} F_X = I_{1x} + I_{2x} \]

b) \[ F_X \xrightarrow{\Delta \omega_1 I_{1z} + \Delta \omega_2 I_{2z}, t} I_{1x} \cos(\Delta \omega_1 t) + I_{1y} \sin(\Delta \omega_1 t) + I_{2x} \cos(\Delta \omega_2 t) + I_{2y} \sin(\Delta \omega_2 t) \]

c) \[ I_{1x} \xrightarrow{J I_{1z} I_{2z}, t} I_{1x} \cos(Jt/2) + 2 I_{1y} I_{2z} \sin(Jt/2) \]

d) \[ 2 I_{1y} I_{2z} \xrightarrow{J I_{1z} I_{2z}, t} 2 I_{1y} I_{2z} \cos(Jt/2) - I_{1x} \sin(Jt/2) \]

2) Complete the following rotation table:

\[ I_{1z} \xrightarrow{J I_{1z} I_{2z}, t} \]
\[ I_{1y} \xrightarrow{J I_{1z} I_{2z}, t} \]
\[ 2 I_{1y} I_{2z} \xrightarrow{J I_{1z} I_{2z}, t} \]
\[ 2 I_{1x} I_{2z} \xrightarrow{J I_{1z} I_{2z}, t} \]
\[ I_{1x} \xrightarrow{J I_{1z} I_{2z}, t} \Delta \omega_1 I_{1z}, t \]
\[ I_{1x} \xrightarrow{\Delta \omega_1 I_{1z}, t} J I_{1z} I_{2z}, t \]

(194)
3) Write the matrix expression for the 16 elements of the two-spin product operator base.

4) Write the product operator base of a system composed by 3 spins 1/2.

5) Using the product operator formalism, calculate \( p(2\tau) \) for the following pulse sequence

\[
\begin{array}{c}
\text{I} \quad \frac{\pi}{2} \quad \text{I} \\
\text{S} \quad \text{II}
\end{array}
\]

\( p(2\tau) = ? \)

6) Calculate the frequency and intensities of the S-spin transitions in the I-decoupled Hamiltonian

\[
\mathcal{H}_{IS} = -\omega_S S_z - \omega_I I_z + J I_z S_z + \omega_2 I_x
\]

Demonstrate that for \( \omega_I = 0 \) (on-resonance I irradiation), \( \omega_2 >> J \), the S signal is decoupled from the I spins

7) Calculate the classical \(^{13}\text{C}\) magnetizations of -CH\(_3\), -CH\(_2\), -CH- and -C- groups at time 2\(\tau\) in the APT pulse sequence.

8) Calculate \( \rho_{\text{C}} \) at the beginning of the acquisition period in the refocused INEPT sequence for a C-H pair.

9) Calculate the signals arising from the \(^{13}\text{C}\) spins of -C-, -CH-, -CH\(_2\)-, and -CH\(_3\) groups in an INEPT experiment.