Coherence selection and multiple quantum spectroscopy.

- Last time we saw how we can get rid of artifacts by means of cycling the phases of pulses and receivers.

- Apart from artifacts, in more complicated multiple pulse and 2D experiments, the pulses generate magnetization that we don’t want and we have to get rid of somehow.

- In order to understand why we get additional signals (actually, additional magnetization components), we have to introduce the concept of coherence (ugh…).

- Although the math behind it gets trickier and trickier, the basic idea of coherence is pretty simple: A system is coherent when all its elements have something in common, and they keep it with time. We say that such systems have a common phase, or their phase has a definite relationship.

- Strangely enough, a system of spins $1/2$ is coherent after a $\pi/2$ pulse (they all start moving at the same time…).

- In contrast, something is not coherent when there is no relationship between the phase of the components.

- Magnetization in $<z>$ (Boltzmann equilibrium) is not coherent. Every spin is precessing with a random phase...
Coherence (continued)

• Maybe this clarifies things a bit. There is something that we can now explain as loss of coherence and therefore loss of signal.

• We said before that after we apply a $\pi/2$ pulse and wait a while, all magnetization will dephase:

\[ \begin{array}{cc}
\text{y} & \text{x} \\
90 & \text{time}
\end{array} \]

\[ \begin{array}{cc}
\text{y} & \text{x} \\
\text{time} & \equiv
\end{array} \]

• In this case, the magnetic field inhomogeneity causes different spins to have different, *non-related*, phases. The net result is a cancellation of the signal with time.

• Normally, incoherent systems end up giving no signal (and that’s why we stop listening to incoherent people…).
Coherence order

- I’m starting to lose coherence. Now that we more or less know what it refers to, we’ll focus on coherence in NMR.

- We said that a $\pi/2$ pulse generates a coherent system. We can also define the **coherence order ($p$)** of a process as the number of quanta involved in the generation of coherence.

- In a 1-spin system, we have only one transition (it is a 2 state system), which means only a change of one quanta is involved, or a **single-quantum transition**:

\[
\begin{align*}
\beta (+1/2) \\
\alpha (-1/2)
\end{align*}
\]

- The system can have a coherence order of $p$ of + 1 or - 1.

- For a 2-spin system, we have 4 possible states, and we can have **zero-, single-, or double-quantum transitions**:

\[
\begin{align*}
\beta\beta (+1/2, +1/2) \\
(-1/2, +1/2) \alpha\beta \\
\beta\alpha (+1/2, -1/2) \\
\alpha\alpha (-1/2, -1/2)
\end{align*}
\]

\[
\begin{align*}
\text{p = 0} \\
\text{p = ± 1} \\
\text{p = ± 2}
\end{align*}
\]
Coherence order (continued)

• Now we can start analyzing the effects of pulses in different types of coherence. As we said, a $\pi/2$ pulse on equilibrium magnetization ($<z>$), excites the *single-quantum* transitions:

```
\begin{align*}
\beta\beta (\pm 1/2, \pm 1/2) \\
(-1/2, +1/2) \alpha\beta \\
\alpha\alpha (-1/2, -1/2) \\
\beta\alpha (+1/2, -1/2)
\end{align*}
```

• A simple way of putting it (and introducing yet another concept) is to draw the how the coherence evolves as we apply pulses. We call these diagrams *coherence transfer pathways (CTPs)*.

```
\begin{align*}
\text{p} = +1, & & \text{p} = 0, & & \text{p} = -1 \\
\end{align*}
```
Coherence order (…)

• We see that after we generate \( <xy> \) magnetization we have coherence order of + and -1. It does not matter if we are going upwards or downwards.

• We can only see (and detect) this type of coherence, because it is equivalent to having transverse \( <xy> \) magnetization that generates a current in the receiver coil.

• By convention, coherence order -1 is associated with + \( \omega_0 \), and \( p = +1 \) with - \( \omega_0 \). We select the position (and relative direction of rotation) of the rotating frame to detect \( p = -1 \):

![Diagram of coherence order]

- We also see that only pulses change the coherence order. As long as we keep delays smaller than \( T_2 \) & \( T_1 \), things stay where they are.
Coherence order (…)

- So we had our first example of signal that we generate but we choose not to detect: \( p = +1 \). We select the other component of the coherence we generate by selecting the phase of the pulses and receiver (the rotating frame…). The phase has to follow the desired coherence or magnetization component.

- Now, a simple example. A \( \pi \) pulse inverts populations, so its effect in a CTP diagram is an inversion of the coherence:

\[
\begin{align*}
\text{Final change of coherence } \Delta p &= -2 \\
p &= +1 \\
p &= 0 \\
p &= -1
\end{align*}
\]

- There are two things that we have to keep in mind. When we use this type of diagrams, the frequency of the transitions is the *absolute frequency* (laboratory frame).

- We usually design the phase cycling of the pulse sequence from CTPs, so, in general, we only draw orders of coherence that will in the end give the observable signal (\( p = -1 \)) we want to detect.
**Coherence selection**

- We are interested in seeing how is that we use CTPs to determine phase cycling.

- Unless we do a detailed mathematical treatment, we will have to take several leaps of faith and more or less describe what comes next with rules. They more or less make sense.

**Coherence and phase cycles rules**

- Only pulses can change coherence order. Pulses on <z> magnetization (p = 0) generate p = ±1, while pulses on <xy> magnetization can create higher coherence order, depending on the number of coupled spins.

- We can only detect coherence with order ±1, because it correspond to single-quantum transitions, or <xy> magnetization.

- The number of cycles and steps per cycle needed will depend on the order of the coherence we want to select/transfer.

- In order to select or detect a certain component of the coherence order generated by a pulse of phase \( \phi \), the phase of the selecting pulse or receiver is given by:

\[
\text{phase} = - \Delta p \times \phi
\]

where \( \Delta p \) is the coherence change we want to follow generated by the pulse of phase \( \phi \), and \( \phi \) is its phase.
Coherence selection (continued)

- We knew the first two. The last one is the one that allows us to design the phase cycling of a pulse sequence in order to select certain signals, associated with a certain coherence, and discard others.

- It obviously comes from the innards of a quantum-mechanical description by the product operator formalism, and we (me included) are by no means ready for all that mumbo-jumbo.

- Let's see how it works with the simple 90-FID sequence we use to record a simple 1D. The $\pi / 2$ pulse generates $+1$ and $-1$ coherence, and we are interested in the $-1$ component.

- From our rules, if the phase of the pulse is $\phi$, we need the phase of the detector to be $-(-1) \times \phi$, or $\phi$. Remember that we are using QD, so we have another receiver with 90 - $\phi$...
Coherence selection (…)

- Now we can write the phase cycle that will select $p = -1$. If the phase of the pulse is 0 and we use an increment of 90, we end up with **CYCLOPS**:

<table>
<thead>
<tr>
<th>Cycle</th>
<th>90 Pulse</th>
<th>Rcvr 1</th>
<th>Rcvr 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 (x)</td>
<td>0 (x)</td>
<td>90 (y)</td>
</tr>
<tr>
<td>2</td>
<td>90 (y)</td>
<td>90 (y)</td>
<td>180 (-x)</td>
</tr>
<tr>
<td>3</td>
<td>180 (-x)</td>
<td>180 (-x)</td>
<td>270 (-y)</td>
</tr>
<tr>
<td>4</td>
<td>270 (-y)</td>
<td>270 (-y)</td>
<td>0 (x)</td>
</tr>
</tbody>
</table>

- We’ll analyze how both sets of vectors behave under this cycle. For receiver 2 (◯) and $p = -1$ we have:
Coherence selection (…)

- We see that for the coherence we selected to follow, the signal will co-add always with the same sign. The same goes for receiver 1, although we get the dispersive signal…

- Now, for the coherence involving $\Delta p = +1$, we have a different story. The phase shift seen by this path is $-(+1) \phi$, or $-\phi$, (it rotates in the opposite direction) so if we draw a table we have (first two cycles…):

<table>
<thead>
<tr>
<th>Cycle</th>
<th>90 Pulse</th>
<th>Ph Shift</th>
<th>Eq Ph</th>
<th>Rcvr 1</th>
<th>Rcvr 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 (x)</td>
<td>0</td>
<td>0 (x)</td>
<td>0 (x)</td>
<td>90 (y)</td>
</tr>
<tr>
<td>2</td>
<td>90 (y)</td>
<td>-90</td>
<td>270 (-y)</td>
<td>90 (y)</td>
<td>180 (-x)</td>
</tr>
</tbody>
</table>

- Again, looking at receiver 2, for the four cycles:
Coherence selection (...)

- We can clearly see that two cycles add and two subtract, so the net result is no signal. The same goes for receiver 1...

- As an aside, we see that in this simple case, just two cycles do the trick (we are just selecting a $\Delta p$ of $|1|$).

- As we put more pulses into the sequences, the phase cycling tables get bigger and bigger, so we change the notation. We represent 0, 90, 180, and 270 with 0, 1, 2, 3, and we align them in rows for the pulses and the receivers.

- CYCLOPS can be re-written as:

| Pulse: 0 1 2 3 |
| Rcvr 1: 0 1 2 3 |
| Rcvr 2: 1 2 3 0 |

- Another thing that we have to consider in sequences with more pulses is that, as we mentioned before, pulses can (and will) excite multiple-quantum transitions, and therefore they will generate coherence of $p > 1$.

- The coherence ‘fans-out’, and in order to select only the one we need (the one we draw in the CTP), we need to increase the steps per cycle or reduce the phase increments.
Coherence selection (…)

• Now we can try to analyze the phase cycle (not why we need to select this particular path - this is unfortunately quantum mechanics) of more complicated sequences. For example in the COSY experiment we discussed before:

In this case, we need the phase cycle to select the $p = +1$ and then allow the last pulse to re-create coherence of $-1$ from the coherence order we selected to follow.

• Following our rules, the second pulse must select $\Delta p = +1$, so the phase is $- ( +1 ) * \phi$, or $- \phi$, and then the detector must follow $\Delta p = -2$, therefore the phase is $- ( -2 ) * \phi$, or $2 * \phi$. 
Coherence selection (…)

• An appropriate phase cycle for this could be the one below. It is called \textit{EXORCYCLE}:

\[ \Delta p = +1 \quad \Delta p = -2 \]

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Pulse 1</th>
<th>Pulse 2</th>
<th>Eq Ph</th>
<th>Receiver</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 (x)</td>
<td>0 (x)</td>
<td>0 (x)</td>
<td>0 (x)</td>
</tr>
<tr>
<td>2</td>
<td>90 (y)</td>
<td>-90 (-y)</td>
<td>270 (-y)</td>
<td>180 (-x)</td>
</tr>
<tr>
<td>3</td>
<td>180 (-x)</td>
<td>-180 (-x)</td>
<td>180 (-x)</td>
<td>0 (x)</td>
</tr>
<tr>
<td>4</td>
<td>270 (-y)</td>
<td>-270 (y)</td>
<td>90 (y)</td>
<td>180 (-x)</td>
</tr>
</tbody>
</table>

• This would work in selecting \( \Delta p = -2 \), but if we do the analysis for other coherence orders that may be present after the pulses, we would see that we select also \(-2 \pm 4 \times n\), where \( n \) can take values of 0, \( \pm 1, \pm 2, \ldots \)

• What we need to do is to repeat this so that each pulse is independent, which requires that for each of the possible steps in the cycle (0, 1, 2, 3) the other pulses are cycled to. The final phase cycle is:

\[
\begin{align*}
\text{Pulse 1:} & \quad 0 \ 0 \ 0 \ 0 \ 1 \ 1 \ 1 \ 1 \ 2 \ 2 \ 2 \ 2 \ 3 \ 3 \ 3 \ 3 \\
\text{Pulse 2:} & \quad 0 \ 1 \ 2 \ 3 \ 0 \ 1 \ 2 \ 3 \ 0 \ 1 \ 2 \ 3 \ 0 \ 1 \ 2 \ 3 \\
\text{Receiver:} & \quad 0 \ 2 \ 0 \ 2 \ 3 \ 1 \ 3 \ 1 \ 0 \ 2 \ 0 \ 2 \ 1 \ 3 \ 1 \ 3
\end{align*}
\]