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Tutorial Lecture presented at
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This lecture is not about what NMR can do, but about how to do NMR
A Transition

Final State: $|j\rangle\langle i|$ → $|j\rangle\langle j|$ → Initial State: $|j\rangle\langle i|$ → $|i\rangle\langle i|$ → Outer Products

$|j\rangle\langle j|$
A Transition Pathway

\[ |i\rangle \langle i| \rightarrow |j\rangle \langle i| \]
NMR Transition Frequency is Sum of Components

\[ \Omega(\Theta, i, j) = \sum_k \Omega_k(\Theta, i, j) \]

and each component is the product of three terms:

\[ \Omega_k(\Theta, i, j) = \omega_k \cdot \Xi^{(k)}_L(\Theta) \cdot \xi^{(k)}_l(i, j) \]

for more details see: “Symmetry Pathways in Solid-State NMR”, Prog. NMR Spect., 59, 121-196 (2011)
Relabel spatial function for each rank of $L$

$$
\Xi^{(k)}_{L}(\Theta) \propto R^{(k)}_{L,0}(\Theta)
$$

$\Xi_{L}(\Theta)$

<table>
<thead>
<tr>
<th>$L$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
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</table>
| $S,$ | $P(\Theta),$ | $D(\Theta),$ | $F(\Theta),$ | $G(\Theta),$ ...

Orientation of the sample in magnetic field
Relabel transition function for each rank of $l$

$$\xi_l^{(k)}(i, j) \propto \langle j | \hat{T}_{l,0}^{(k)} | j \rangle - \langle i | \hat{T}_{l,0}^{(k)} | i \rangle$$

Initial state

Final state

$$\xi_l(i, j)$$

$l = 0$ $1$ $2$ $3$

$\mathcal{S}, \ p(i, j), \ \mathcal{D}(i, j), \ \mathcal{F}(i, j), \ldots$

Form of transition function depends on spin system
Values of various symmetry functions can be calculated for each transition

Transition symmetry functions for single spin, \( I \)

\[
\begin{align*}
  s_I(m_i, m_j) &= 0, \\
  p_I(m_i, m_j) &= m_j - m_i,
\end{align*}
\]

Transition functions for a Spin \( I=3/2 \) Nucleus

Values inside solid black circles are negative
Values of various symmetry functions can be calculated for each transition

**Transition symmetry functions for single spin, $I$**

$$d_I(m_i, m_j) = \sqrt{\frac{2}{3}} d_I(m_i, m_j) = m_j^2 - m_i^2,$$

$$f_I(m_i, m_j) = \sqrt{\frac{10}{9}} f_I(m_i, m_j) = \frac{1}{3} \left[ 5(m_j^3 - m_i^3) + (1 - 3I(I + 1))(m_j - m_i) \right]$$

Transition functions for a Spin $I=3/2$ Nucleus

Values inside solid black circles are negative
**First-Order Nuclear Shielding**

\[
\Omega^{(1)}_\sigma = -\omega_0 \sigma_{iso} \left[ S^{\sigma} \cdot p_I(m_i, m_j) \right] \\
-\omega_0 \zeta_\sigma \left[ D^{\sigma}(\Theta) \cdot p_I(m_i, m_j) \right]
\]

*Isotropic contribution* contains the \( S \) spatial function.

**First-Order Quadrupole Coupling**

\[
\Omega^{(1)}_q = \omega_q \left[ D^{\{q\}}(\Theta) \cdot d_I(m_i, m_j) \right]
\]

Notice: \( d_I \) vanishes for all \( m \) to \(-m\) transitions

\[
d_I(m, -m) = 0
\]
Transition Pathway for d Echo

\[ \Omega(i, j) = \Omega_p + \Omega_d \]

\[ \Omega(i, j) = \Omega_p - \Omega_d \]

\[ |i\rangle \rightarrow |j\rangle \langle i|_{t_1} \rightarrow |i\rangle \langle k|_{t_2} \]

\( \Omega_d \) refocuses \( \Omega_p \) modulates
Desired NMR signal can come from multiple transition pathways.

**Hahn Echo (p Echo)**

\[ \{ I = 1 \} : \begin{cases} [z_I] \rightarrow |0 \rangle \langle -1| \rightarrow |0 \rangle \langle +1| \\ [z_I] \rightarrow |+1 \rangle \langle 0| \rightarrow |-1 \rangle \langle 0| \end{cases} \]

**Solid Echo (d Echo)**

\[ \{ I = 1 \} : \begin{cases} [z_I] \rightarrow |-1 \rangle \langle 0| \rightarrow |0 \rangle \langle +1| \\ [z_I] \rightarrow |0 \rangle \langle +1| \rightarrow |-1 \rangle \langle 0| \end{cases} \]
How do we select the right transition pathways and avoid the wrong transition pathways?
Not always possible to avoid the wrong transition pathways,

but we do have a systematic approach to avoid the wrong pathways.
Transition in terms of $p$

$$\hat{t}_p(m) = |m + p\rangle \langle m|$$
Group outer products with same value of $p$ into other operators

**In general:**  
\[ \hat{T}_p = \sum_m a_m \hat{t}_p(m) \]

**Spin 1/2 Example**

| $\hat{T}_0$ operators | $\hat{I}_z = \frac{1}{2} \left( |\frac{1}{2}\rangle \langle \frac{1}{2}| - |\frac{-1}{2}\rangle \langle \frac{-1}{2}| \right)$ |
|------------------------|---------------------------------------------------------------------|
|                        | $\hat{E} = |\frac{1}{2}\rangle \langle \frac{1}{2}| + |\frac{-1}{2}\rangle \langle \frac{-1}{2}|$ |
| $\hat{T}_{+1}$ operator | $\hat{I}_+ = |\frac{1}{2}\rangle \langle \frac{-1}{2}|$ |
| $\hat{T}_{-1}$ operator | $\hat{I}_- = |-\frac{1}{2}\rangle \langle \frac{1}{2}|$ |
A Tree of Possible Signals

Generic two pulse NMR experiment on spin 1/2 system

\[ \hat{\rho}(0) = \hat{I}_o \]

\[ \rho(t_1) = a^{(1)}_{0, -} \hat{I}_- + a^{(1)}_{0, +} \hat{I}_+ + a^{(1)}_{0, 0} \hat{I}_o \]

\[ \rho(t_2) = a^{(1)}_{1, -} \hat{I}_- + a^{(1)}_{1, +} \hat{I}_+ + a^{(1)}_{1, 0} \hat{I}_o + a^{(2)}_{0, -} \hat{I}_- + a^{(2)}_{0, +} \hat{I}_+ + a^{(2)}_{0, 0} \hat{I}_o \]

After two pulses there will be 9 different terms in the density operator expansion, each multiplied by coefficients that carry the history of each term.

With each pulse the number of terms in the density operator expansion grows exponentially
One branch

Generic two pulse NMR experiment on spin 1/2 system

\[ \hat{\rho}(0) = \hat{I}_0 \]

\[ \rho(t_1) = a_{0,-}^{(1)} \hat{I}_- + a_{0,0}^{(1)} \hat{I}_0 + a_{0,+}^{(1)} \hat{I}_+ \]

\[ \rho(t_2) = a_{0,-}^{(1)} a_{0,-}^{(2)} \hat{I}_- + a_{0,-}^{(1)} a_{0,0}^{(2)} \hat{I}_0 + a_{0,-}^{(1)} a_{0,+}^{(2)} \hat{I}_+ + a_{0,0}^{(1)} a_{0,0}^{(2)} \hat{I}_0 + a_{0,0}^{(1)} a_{0,+}^{(2)} \hat{I}_+ + a_{0,+}^{(1)} a_{0,-}^{(2)} \hat{I}_- + a_{0,+}^{(1)} a_{0,0}^{(2)} \hat{I}_0 + a_{0,+}^{(1)} a_{0,+}^{(2)} \hat{I}_+ \]

\( p = \pm 2 \) coherences are not accessible to an isolated spin 1/2 but would be for coupled spin 1/2 nuclei.

Start with \( p=0 \) coherence (i.e. \( \rho(0) = I_0 \))

Pulse changes coherence order. Shown here is one possibility where the coherence order goes from \( p = 0 \rightarrow 1 \)

2nd pulse changes coherence order. Shown here is one possible change in coherence order from \( p = 1 \rightarrow -1 \)
Not all transition pathways are unique

A transition pathway can give rise to a signal that is the complex conjugate of another.

Easily identified since they will be mirror images of each other about the 0 level for all symmetries present in the spin system.

If you remove the redundancy of mirror image pathways, then the number of pathways that give rise to unique signals in a two pulse sequence on a spin 1/2 system is five.
Not all transition pathways can be detected

Only pathways that end on the $p = -1$ level are observable

Follows from: \[ S(t) = \frac{d}{dt} \text{Tr}\{\tilde{\rho}(t)\hat{I}_+\} \]

and

\[
\text{Tr}\{\hat{I}_+\hat{I}_-\} \neq 0, \quad \text{Tr}\{\hat{I}_0\hat{I}_0\} \neq 0
\]

\[
\text{Tr}\{\hat{I}_+\hat{I}_+\} = \text{Tr}\{\hat{I}_+\hat{I}_0\} = \text{Tr}\{\hat{I}_0\hat{I}_-\} = \text{Tr}\{\hat{I}_-\hat{I}_-\} = 0
\]
Unique and observable $p$ pathways starting at $p=0$ and ending at $p=-1$ for a spin $1/2$ system in a two pulse sequence.

Two Pulses, Three Experiments

$$(\beta_1)_{\phi_1} \quad t_1 \quad (\beta_2)_{\phi_2} \quad t_2$$

1. $p$: 1, 0, -1
2. $p$: 1, 0, -1
3. $p$: 1, 0, -1
Unique and observable \( p \) pathways starting at \( p=0 \) and ending at \( p=-1 \) for a spin 1/2 system in a two pulse sequence.

**Two Pulses, Three Experiments**

\[ (\beta_1)_{\phi_1} \quad t_1 \quad (\beta_2)_{\phi_2} \quad t_2 \]

1. **Hahn Echo Experiment**
   - \( p \): 1, 0, -1
   - 0: 1, 0, -1

2. **Inversion Recovery Experiment**
   - \( p \): 1, 0, -1
   - 0: 1, 0, -1

3. **Anti-Echo Experiment**
   - \( p \): 1, 0, -1
   - 0: 1, 0, -1
Pathway Selection and RF Pulse Phase

When the RF is on, the Hamiltonian is

\[ \tilde{H}(\phi) = -\omega_1 (I_x \cos \phi + I_y \sin \phi) + \tilde{H}' \]

rf Hamiltonian

Zeeman Offset, Chem. Shift, J-Coupling, Dipolar Coupling, Quadrupolar, ...

An important relationship obeyed by this Hamiltonian is

\[ \tilde{H}(\phi) = e^{-i\phi \hat{I}_z} \tilde{H}(0) e^{i\phi \hat{I}_z} \]

And the same relationship holds for the propagator

\[ \tilde{U}_\phi(t, 0) = e^{-i\phi \hat{I}_z} \tilde{U}_0(t, 0) e^{i\phi \hat{I}_z} \]
Pathway Selection and RF Pulse Phase

How does $\hat{T}_p$ transform under an rf pulse of arbitrary phase?

$$\tilde{U}_\phi(t) \hat{T}_p \tilde{U}_\phi^\dagger(t) = \left\{ e^{-i\phi \hat{I}_z} \tilde{U}_0(t) e^{i\phi \hat{I}_z} \right\} \hat{T}_p \left\{ e^{-i\phi \hat{I}_z} \tilde{U}_0^\dagger(t)e^{i\phi \hat{I}_z} \right\}$$

A little bit of math later...

$$\tilde{U}_\phi(t) \hat{T}_{p_0} \tilde{U}_\phi^\dagger(t) = \sum_{p_1} c_{p_0,p_1}(t) \hat{T}_{p_1} e^{-i\Delta p_1 \phi}$$

where $\Delta p_1 = p_1 - p_0$
Simplest Case: Single Spin 1/2

Start with \( \tilde{\rho}(0) = \hat{I}_z = \hat{I}_0 \)

Immediately after rf pulse we have

\[
\tilde{\rho}(0)^+ = \sum_{p_1} c_{p_0,p_1}(t) \hat{I}_{p_1} e^{-i\Delta p_1 \phi}
\]

Then free evolution for a time \( t \):

\[
\tilde{\rho}(t) = \sum_{p_1} c_{p_0,p_1}(t) \hat{I}_{p_1} e^{-i\Delta p_1 \phi} e^{i p_1 \Omega t}
\]

which consists of three terms:

\[
\tilde{\rho}(t) = \underbrace{c_{0,-1} \hat{I}_- e^{i\phi_1} e^{-i\Omega t}}_{\Delta p_1 = -1} + \underbrace{c_{0,0} \hat{I}_0}_{\Delta p_1 = 0} + \underbrace{c_{0,1} \hat{I}_+ e^{-i\phi_1} e^{i\Omega t}}_{\Delta p_1 = +1}
\]
One Pulse and Acquire (as a function of pulse phase)

Simplest Case: Single Spin 1/2

\[ \tilde{\rho}(t) = c_{0,-1} \hat{I}_- e^{i\phi_1} e^{-i\Omega t} + c_{0,0} \hat{I}_0 + c_{0,1} \hat{I}_+ e^{-i\phi_1} e^{i\Omega t} \]

Δ\(p_1 = -1\) \hspace{2cm} Δ\(p_1 = 0\) \hspace{2cm} Δ\(p_1 = +1\)

Signal after pulse derives solely from the \(\Delta p_1 = -1\) term

\[ S(\phi_1, t) = \text{Tr}\{\tilde{\rho}(t) \hat{I}_+\} = c_{0,-1} e^{i\phi_1} e^{-i\Omega t} \]

Sprinkle in some exponential decay

\[ S(\phi_1, t) = c_{0,-1} e^{i\phi_1} e^{-i\Omega t} e^{-t/T_2} \]

and Fourier transform:

\[ \omega \]
One Pulse and Acquire (as a function of pulse phase)

**Simplest Case: Single Spin 1/2**

\[
\tilde{\rho}(t) = c_{0, -1} \hat{I}_- e^{i\phi_1} e^{-i\Omega t} + c_{0, 0} \hat{I}_0 + c_{0, 1} \hat{I}_+ e^{-i\phi_1} e^{i\Omega t}
\]

- \(\Delta p_1 = -1\)
- \(\Delta p_1 = 0\)
- \(\Delta p_1 = +1\)

Signal after pulse derives solely from the \(\Delta p_1 = -1\) term

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S(\phi_1, t) = \text{Tr}\{\tilde{\rho}(t) \hat{I}_+\} = c_{0, -1} e^{i\phi_1} e^{-i\Omega t}
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Sprinkle in some exponential decay

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Simplest Case: Single Spin 1/2

\[ S(\phi_1, t) = c_0, -1 e^{i\phi_1} e^{-i\Omega t} e^{-t/T_2} \]

What do you get after a Fourier transform with respect to \( \phi_1 \)?
One Pulse and Acquire (as a function of pulse phase)

Simplest Case: Single Spin 1/2

\[ S(\phi_1, t) = c_0, -1 e^{i\phi_1} e^{-i\Omega t} e^{-t/T_2} \]

What do you get after a Fourier transform with respect to \( \phi_1 \)?

\[ S(\Delta p, t) = \int_{-\infty}^{\infty} S(\phi, t) e^{i\Delta p \phi} d\phi, \]

You learn about the change in \( p \) during the pulse.
One Pulse and Acquire (as a function of pulse phase)

Simplest Case: Single Spin 1/2

\[ S(\phi_1, t) = c_0, -1 e^{i\phi_1} e^{-i\Omega t} e^{-t/T_2} \]

What do you get after a Fourier transform with respect to \( \phi_1 \)?

\[ S(\Delta p, t) = \int_{-\infty}^{\infty} S(\phi, t) e^{i\Delta p \phi} d\phi, \]

You learn about the change in \( p \) during the pulse.

Our one pulse signal on spin 1/2 gives

\[ S(\Delta p_1, t) = c_0, -1 e^{-i\Omega t} e^{-t/T_2} \int_{-\infty}^{\infty} e^{i\phi_1} e^{i\Delta p_1 \phi_1} d\phi_1 \]

\[ = c_0, -1 e^{-i\Omega t} e^{-t/T_2} \delta(1 + \Delta p_1) \]

A delta function at \( \Delta p_1 = -1 \) associated with \( p = 0 \rightarrow -1 \) during the pulse.
Simplest Case: Single Spin 1/2

\[ S(\Delta p_1, t) = c_0, -1 e^{-i\Omega t} e^{-t/T_2} \delta(1 + \Delta p_1) \]
One Pulse and Acquire (as a function of pulse phase)

Simplest Case: Single Spin 1/2

\[ S(\Delta p_1, t) = c_0, -1 e^{-i\Omega t} e^{-t/T_2} \delta(1 + \Delta p_1) \]
One Pulse and Acquire
(on 1980s home-built NMR spectrometer)

You should see this after FT

But instead you see this after FT
One Pulse and Acquire (on 1980s home-built NMR spectrometer)

You should see this after FT

But instead you see this after FT

baseline error

quadrature ghost
Baseline Error: Even when there’s no signal the receiver records constant value.

\[ S(t) = \text{Tr}\{\tilde{\rho}(t)\hat{I}_+\} + \text{constant} \]

causes spike at 0 Hertz

Quadrature Ghost: Arises when X and Y detectors in rotating frame are not orthogonal

**Good Receiver**

\[ \text{y detector} \]

instead of

\[ \text{x detector} \]

**Bad Receiver**

\[ \text{y detector} \]

we have

\[ \epsilon \]

\[ \text{x detector} \]
Quadrature Ghosts

In this situation our $\hat{I}_y$ observable becomes

$$\hat{I}_y \cos \epsilon + \hat{I}_x \sin \epsilon,$$

and our complex observable, $\hat{O}$, becomes

$$\hat{O} = \hat{I}_x + i(\hat{I}_y \cos \epsilon + \hat{I}_x \sin \epsilon).$$

Rewriting this in terms of $\hat{I}_\pm$ we have

$$\hat{O} = \hat{I}_+ \left( \frac{1}{2} + \frac{1}{2} e^{i\epsilon} \right) + \hat{I}_- \left( \frac{1}{2} - \frac{1}{2} e^{-i\epsilon} \right).$$

In this situation our signal, using $S(t) = \text{Tr}\{\tilde{\rho}(t)\hat{O}\}$ will be

$$S(t) = \left( \frac{1}{2} + \frac{1}{2} e^{i\epsilon} \right) \text{Tr}\{\tilde{\rho}(t)\hat{I}_+\} + \left( \frac{1}{2} - \frac{1}{2} e^{-i\epsilon} \right) \text{Tr}\{\tilde{\rho}(t)\hat{I}_-\}.$$ 

Original Signal

New Signal

Thus, with improper quadrature detection we observe both $p = -1$ and $p = +1$ coherences. In our one pulse experiment we would then obtain

$$S(\phi, t) = \left( \frac{1}{2} + \frac{1}{2} e^{i\epsilon} \right) c_{0,-1} e^{i\phi_1} e^{-i\Omega t} + \left( \frac{1}{2} - \frac{1}{2} e^{-i\epsilon} \right) c_{0,+1} e^{-i\phi_1} e^{i\Omega t}$$

$\Delta p_1 = -1$ signal

$\Delta p_1 = +1$ signal
\[ S(\phi_1, t) = ae^{i\phi_1}e^{-i\Omega t} + be^{-i\phi_1}e^{i\Omega t} + \text{constant}, \]

desired \( \Delta p_1 = -1 \) signal, undesired \( \Delta p_1 = +1 \) signal, undesired signal.

How do we separate the desired from undesired signal?
One Pulse and Acquire (on 1980s home-built NMR spectrometer)

\[ S(\phi_1, t) = ae^{i\phi_1}e^{-i\Omega t} + be^{-i\phi_1}e^{i\Omega t} + \text{constant}, \]

desired \( \Delta p_1 = -1 \) signal \hspace{1cm} \text{undesired} \( \Delta p_1 = +1 \) signal \hspace{1cm} \text{undesired signal}

How do we separate the desired from undesired signal?

2D Fourier transform with respect to pulse phase and time

This cross-section contains the desired \( \Delta p_1 = -1 \) spectrum

Baseline offset artifact

Undesired \( \Delta p_1 = +1 \) spectrum (quadrature ghost)
One Pulse and Acquire (on 1980s home-built NMR spectrometer)

\[ S(\phi_1, t) = ae^{i\phi_1}e^{-i\Omega t} + be^{-i\phi_1}e^{i\Omega t} + \text{constant, undesired signal} \]

How do we separate the desired from undesired signal?

2D Fourier transform with respect to pulse phase and time

To retrieve the desired spectrum we only need to extract the $\Delta p_1 = -1$ cross section and we're done.

This is the essence of phase cycling: separating signals from different $p$ pathways by their $\Delta p$ values.
Sampling the rf phase domain

What sampling interval should you use in the rf phase domain?
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Adopt same approach as in time domain. To avoid aliasing use

$$\Delta t < \frac{2\pi}{\text{spectral width of frequencies present}}$$
Sampling the rf phase domain

What sampling interval should you use in the rf phase domain?

Adopt same approach as in time domain. To avoid aliasing use

$$\Delta t < \frac{2\pi}{\text{spectral width of frequencies present}}$$

$$\Delta \phi < \frac{2\pi}{\text{spectral width of } \Delta p \text{ values present}}$$

$$\Delta \phi < \frac{2\pi}{\Delta p_{\text{max}} - \Delta p_{\text{min}}}$$
Phase Cycling: Avoiding the FT wrt phase

Back to one pulse-acquire example. The 2D signal after FT wrt time looks like

Projection (sum) over all values of $\phi_1$
Phase Cycling: Avoiding the FT wrt phase

Shift spectrum along $\Delta p$ dimension and move desired $\Delta p$ value to $\Delta p=0$.

$$\Delta p^{(\text{desired})} = -1 \text{ signal}$$

$$\Delta \phi = \frac{2\pi}{\Delta p_{\text{max}} - \Delta p_{\text{min}} + 1} = \frac{2\pi}{n}$$
Phase Cycling: Avoiding the FT wrt phase

\[ S(t + t_s) \xleftrightarrow{FT} S(\omega) e^{-i\omega t_s}, \quad \text{“time shifting”} \]

\[ S(t)e^{i\omega_s t} \xleftrightarrow{FT} S(\omega + \omega_s), \quad \text{“frequency shifting”} \]

\[ S(\phi + \phi_s) \xleftrightarrow{FT} S(\Delta p)e^{-i\Delta p \phi_s}, \quad \text{“}\phi\text{ shifting”} \]

\[ S(\phi)e^{i\Delta p_s \phi} \xleftrightarrow{FT} S(\Delta p + \Delta p_s), \quad \text{“}\Delta p\text{ shifting”} \]
Phase Cycling: Avoiding the FT wrt phase

\[ S(t + t_s) \overset{FT}{\leftrightarrow} S(\omega)e^{-i\omega t_s}, \quad \text{“time shifting”} \]

\[ S(t)e^{i\omega_s t} \overset{FT}{\leftrightarrow} S(\omega + \omega_s), \quad \text{“frequency shifting”} \]

\[ S(\phi + \phi_s) \overset{FT}{\leftrightarrow} S(\Delta p)e^{-i\Delta p \phi_s}, \quad \text{“\(\phi\) shifting”} \]

\[ S(\phi)e^{i\Delta p_s \phi} \overset{FT}{\leftrightarrow} S(\Delta p + \Delta p_s), \quad \text{“\(\Delta p\) shifting”} \]
Phase Cycling: Avoiding the FT wrt phase

Extract $\Delta p_1, \text{desired}$ signal by applying a 1st-order phase correction to the signal in the $\phi_1$ dimension to shift the $\Delta p_1, \text{desired}$ signal to $\Delta p_1 = 0$, before projecting over $\phi_1$.

$$S_{\text{total}}(t) = \sum_{j=1}^{n_1} S(\phi_1^{(j)}, t)e^{i\Delta p_1, \text{desired}\phi_1^{(j)}}$$

All this can be implemented during signal acquisition by shifting the receiver phase during signal averaging by

$$\phi_R^{(j)} = -\Delta p_1, \text{desired}\phi_1^{(j)}$$

receiver phase
Phase Cycling: Avoiding the FT wrt phase

Implemented with time domain signals during signal acquisition, but easier to visualize in frequency domain

\[ S_{\text{total}}(\omega) = \sum_{j}^{n_1} S(\phi_1^{(j)}, \omega) e^{i \Delta p_1, \text{desired} \phi_1^{(j)}} \]
Phase Cycling: One Pulse & Acquire

\( \Delta p_{1, \text{desired}} = -1 \)

\( \phi_R^{(j)} = -\Delta p_{1, \text{desired}} \phi_1^{(j)} = \phi_1^{(j)} \)

\( n_1 = \Delta p_{1, \text{max}} - \Delta p_{1, \text{min}} + 1 = 3 \)

\( \Delta \phi_1 = \frac{2\pi}{3} \)

\[
\begin{align*}
\phi_1 &= 0^\circ \quad 120^\circ \quad 240^\circ, \\
\phi_R &= 0^\circ \quad 120^\circ \quad 240^\circ.
\end{align*}
\]

Verify

\[
S_{\text{total}}(t) = \sum_{j}^{3} \left( ae^{-i\Omega t} e^{i\phi_1^{(j)}} + be^{i\Omega t} e^{-i\phi_1^{(j)}} + \text{constant} \right) e^{-i\phi_R^{(j)}},
\]

with \( \Delta p_{1, \text{desired}} = -1 \) reduces to our desired signal,

\[
S_{\text{total}}(t) = 3ae^{-i\Omega t}.
\]
Phase Cycling: One Pulse & Acquire

\[ (\beta_1) \phi_1 \]

\[ \Delta p_{1,\text{desired}} = -1 \]

\[ \phi_R^{(j)} = -\Delta p_{1,\text{desired}} \phi_1^{(j)} = \phi_1^{(j)} \]

Historically, 90° phase shifts were easier to implement so n=4 with 90° phase steps are often still used to separate pathways.

<table>
<thead>
<tr>
<th>p</th>
<th>1</th>
<th>0</th>
<th>-1</th>
</tr>
</thead>
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\[ \phi_1 = 0° \quad 90° \quad 180° \quad 270°, \]

\[ \phi_R = 0° \quad 90° \quad 180° \quad 270°. \]
Two Pulse Sequence (Spin 1/2)

Think of this as a four-dimensional experiment that is a function of two times, $t_1$ and $t_2$, and two phases, $\phi_1$ and $\phi_2$.

After 2D Fourier Transform wrt $\phi_1$ and $\phi_2$

Each dot represents a 2D signal that is a function of $t_1$ and $t_2$
Two Pulse Sequence (Spin 1/2)

What is the minimum sampling of rf pulse phases needed to separate desired from undesired signals?
What is the minimum sampling of rf pulse phases needed to separate desired from undesired signals?

We don’t need to separate all signals from each other, only the desired from the undesired. We don’t care if undesired signals get aliased onto each other.
What is the minimum sampling of rf pulse phases needed to separate desired from undesired signals?

We don’t need to separate all signals from each other, only the desired from the undesired. We don’t care if undesired signals get aliased onto each other.

For example, don’t vary $\phi_1$ at all, and let all $\Delta p_1$ alias onto $\Delta p_1=0$.

This works since nothing aliases onto the desired signal.

$\phi_1 = 0^\circ,$
$\phi_2 = 0^\circ 72^\circ 144^\circ 216^\circ 288^\circ,$
$\phi_R = 0^\circ 144^\circ 288^\circ 72^\circ 216^\circ,$
Alternatively, if we phase cycled $\phi_1$ with $n_1=3$, then our desired signal would still be unaliased with $n_2$ as low as $n_2 = 3$.

\[
\begin{array}{cccccccc}
\phi_1 & = & 0^\circ & 120^\circ & 240^\circ & 0^\circ & 120^\circ & 240^\circ & 0^\circ & 120^\circ & 240^\circ, \\
\phi_2 & = & 0^\circ & 0^\circ & 0^\circ & 120^\circ & 120^\circ & 120^\circ & 240^\circ & 240^\circ & 240^\circ, \\
\phi_R & = & 0^\circ & 240^\circ & 120^\circ & 240^\circ & 120^\circ & 0^\circ & 120^\circ & 0^\circ & 240^\circ, \\
\end{array}
\]
Without quadrature ghosts we can reduce sampling even more. The desired change vectors are $(\Delta p_1^{\text{(desired)}}, \Delta p_2^{\text{(desired)}}) = (+1, -2)$. The baseline offset artifact is shown in the diagram.

Here are the phase configurations:

- Case 1:
  \[ \phi_1 = 0^\circ \quad 120^\circ \quad 240^\circ, \]
  \[ \phi_2 = 0^\circ \]
  \[ \phi_R = 0^\circ \quad 240^\circ \quad 120^\circ, \]

- Case 2:
  \[ \phi_1 = 0^\circ \]
  \[ \phi_2 = 0^\circ \quad 120^\circ \quad 240^\circ, \]
  \[ \phi_R = 0^\circ \quad 240^\circ \quad 120^\circ, \]
Phase Cycling Two Pulses (Spin 1/2)

General approach is shift the desired signal to the origin of the \((\Delta p_1, \Delta p_2)\) spectrum. This is accomplished by multiplying signal by 1st-phase correction

\[
S(\phi_1^{(j)}, \phi_2^{(k)}, t_1, t_2) e^{-i\phi_R^{(j,k)}}
\]

where \(\phi_R^{(j,k)} = -\Delta p_1^{(\text{desired})} \phi_1^{(j)} - \Delta p_2^{(\text{desired})} \phi_2^{(k)}\)

Then sum (project) signal over all values of \(\phi_1\) and \(\phi_2\) to obtain the desired signal:

\[
S_{\text{total}}(t_1, t_2) = \sum_j \sum_k S(\phi_1^{(j)}, \phi_2^{(k)}, t_1, t_2) e^{-i\phi_R^{(j,k)}}
\]

For \((\Delta p_1^{(\text{desired})}, \Delta p_2^{(\text{desired})}) = (+1, -2)\) the receiver phase varies according to \(\phi_R^{(j,k)} = -\phi_1^{(j)} + 2\phi_2^{(k)}\)

Phase Cycling eliminates phase dimensions and reduces signal dimensionality: Useful idea in old days when computers were slow and memory was limited.
Intentional aliasing of signals

\[ \Delta p_1^{(desired)} = \pm 1 \]
\[ \Delta p_2^{(desired)} = \pm 1, \pm 3 \]
\[ \Delta p_3^{(desired)} = -3, +1 \]

\[ \Delta p_1 = -1, (0), +1 \quad n_1 = 2 \]
\[ \Delta p_2 = -3, (-2), -1, (0), +1, (+2), +3 \quad n_2 = 2 \]
\[ \Delta p_3 = (-4), -3, (-2), (-1), (0), +1, (+2), (+3), (+4) \quad n_3 = 4 \]

Phase cycling of receiver

\[ \phi_R = -\Delta p_1^{(desired)} \phi_1 - \Delta p_2^{(desired)} \phi_2 - \Delta p_3^{(desired)} \phi_3 \]

One possible Receiver Eq.
With aliasing other valid equations give same result

\[ \phi_R = -\phi_1 - \phi_2 + 3\phi_3 \]
Intentional aliasing of signals

If receiver doesn’t have quadrature ghosts then don’t need to select $\Delta p_3$

$$\Delta p_1^{(desired)} = \pm 1$$
$$\Delta p_2^{(desired)} = \pm 1, \pm 3$$

$$\Delta p_1 = -1, (0), +1$$
$$n_1 = 2$$

$$\Delta p_2 = -3, (-2), -1, (0), +1, (+2), +3$$
$$n_2 = 2$$

$$\phi_R = -\phi_1 - \phi_2$$

$$\phi_1 = 0^\circ \ 180^\circ \ 0^\circ \ 180^\circ,$$
$$\phi_2 = 0^\circ \ 0^\circ \ 180^\circ \ 180^\circ,$$
$$\phi_R = 0^\circ \ 180^\circ \ 180^\circ \ 0^\circ.$$
Avoid unnecessary phase dimensions and long phase cycles

- Have a well-tuned receiver so only $p = -1$ is detected.

- Use knowledge of forbidden $\Delta p$ values to eliminate phase sampling

  An initial $I_z$ density operator can only be transformed to $p = \pm 1$ or 0 by the first pulse, even if higher $p$ values are accessible to the system.

- Phase cycle many pulses as one

  $\phi_{12} = -\Delta p_{12}^{(desired)} \phi_{12} - \Delta p_{3}^{(desired)} \phi_{3}$,

  $\Delta p_{12} = -2, (-1), (0), (+1), +2$.

  alias $\Delta p_{12} = \pm 2$ together

  use $n_{12} = 4$.

  $\phi_{12} = 0^\circ, 90^\circ, 180^\circ, 270^\circ$,

  $\phi_R = 0^\circ, 180^\circ, 0^\circ, 180^\circ$. 
Avoid unnecessary phase dimensions and long phase cycles

- Use well calibrated pulse lengths
  \[
  \hat{I}_+ \xrightarrow{\pi} \hat{I}_- \\
  \hat{I}_- \xrightarrow{\pi} \hat{I}_+ \\
  \hat{I}_0 \xrightarrow{\pi} -\hat{I}_0
  \]
  \[
  \hat{I}_0 \xrightarrow{\pi/2} c\left\{\hat{I}_+ \pm \hat{I}_-\right\}, \text{ i.e., no } \hat{I}_0 \text{ remaining after a } \pi/2 \text{ pulse.}
  \]

- Use differences between \(T_1\) and \(T_2\) to dephase undesired pathways

- Use gradients to selectively dephase and rephase pathways
  
In an NMR experiment with $M$ phase cycled excitation pulses or excitation pulse blocks, the excitation phases are represented in a vector with $M$ elements,

$$\phi = (\phi_1, \phi_2, \ldots, \phi_M).$$  \hspace{1cm} (1)

The Fourier transform of the excitation phase domain signal as a function of the $M$ excitation phases yields a $M$-dimensional pathway difference domain spectrum,

$$s(\Delta p) = \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \cdots \int_0^{2\pi} d\phi_M s(\phi) e^{i\Delta p \cdot \phi},$$  \hspace{1cm} (2)

where $\Delta p$ is a coherence transfer pathway difference vector, with $M$ elements,

$$\Delta p = (\Delta p_1, \Delta p_2, \ldots, \Delta p_M),$$  \hspace{1cm} (3)

each given by $\Delta p_m = p_m - p_{m-1}$.

Carr-Purcell-Meiboom-Gill Acquisition
Carr-Purcell-Meiboom-Gill Acquisition

What’s wrong with CPMG Acquisition?
Unless you have perfect pathway selection you can have signal artifacts.
**Phase Incremented Echo Train Acquisition**

**Simple Idea:** A Fourier Transform with respect to pulse phase reveals the accumulated coherence change.

*Phase incremented echo train acquisition in NMR spectroscopy*
Phase Incremented Echo Train Acquisition

Example: Improper pulse lengths

Simple Idea: A Fourier Transform with respect to pulse phase reveals the accumulated coherence change.


Phase incremented echo train acquisition in NMR spectroscopy
PIETA measures J Couplings accurately and faster

(A) - CPMG

(B) - PIETA

(C) - Simulation
PIETA measures $T_2$ values accurately and faster.

Prednisone $^{13}$C $T_2$ times measured in a PIETA experiment.
MQ-MAS-PIETA
MQ-MAS & Phase Incremented Echo Train Acquisition

Phase incremented echo train acquisition in NMR spectroscopy
Quantifying $Q^{(n)}$ Species Distributions in Silicate Glasses

\[ 2Q^{(1)} \xleftrightarrow{k_1} Q^{(0)} + Q^{(2)} \]
\[ 2Q^{(2)} \xleftrightarrow{k_2} Q^{(1)} + Q^{(3)} \]
\[ 2Q^{(3)} \xleftrightarrow{k_3} Q^{(2)} + Q^{(4)} \]

\[ k_1 = \frac{[Q^{(2)}][Q^{(0)}]}{[Q^{(1)}]^2} \]
\[ k_2 = \frac{[Q^{(3)}][Q^{(1)}]}{[Q^{(2)}]^2} \]
\[ k_3 = \frac{[Q^{(2)}][Q^{(4)}]}{[Q^{(3)}]^2} \]


\[ k_1 = 0.311 \]
\[ k_2 = 0.439 \]
\[ k_3 = 0.375 \]
29Si $Q^{(n)}$ Spinning Sideband Patterns

Our Goal: Develop Sensitive 2D PASS approach
29Si PASS NMR of Cu(II)-doped mixed potassium/magnesium tetrasilicate glass