Coherence Pathway Selection

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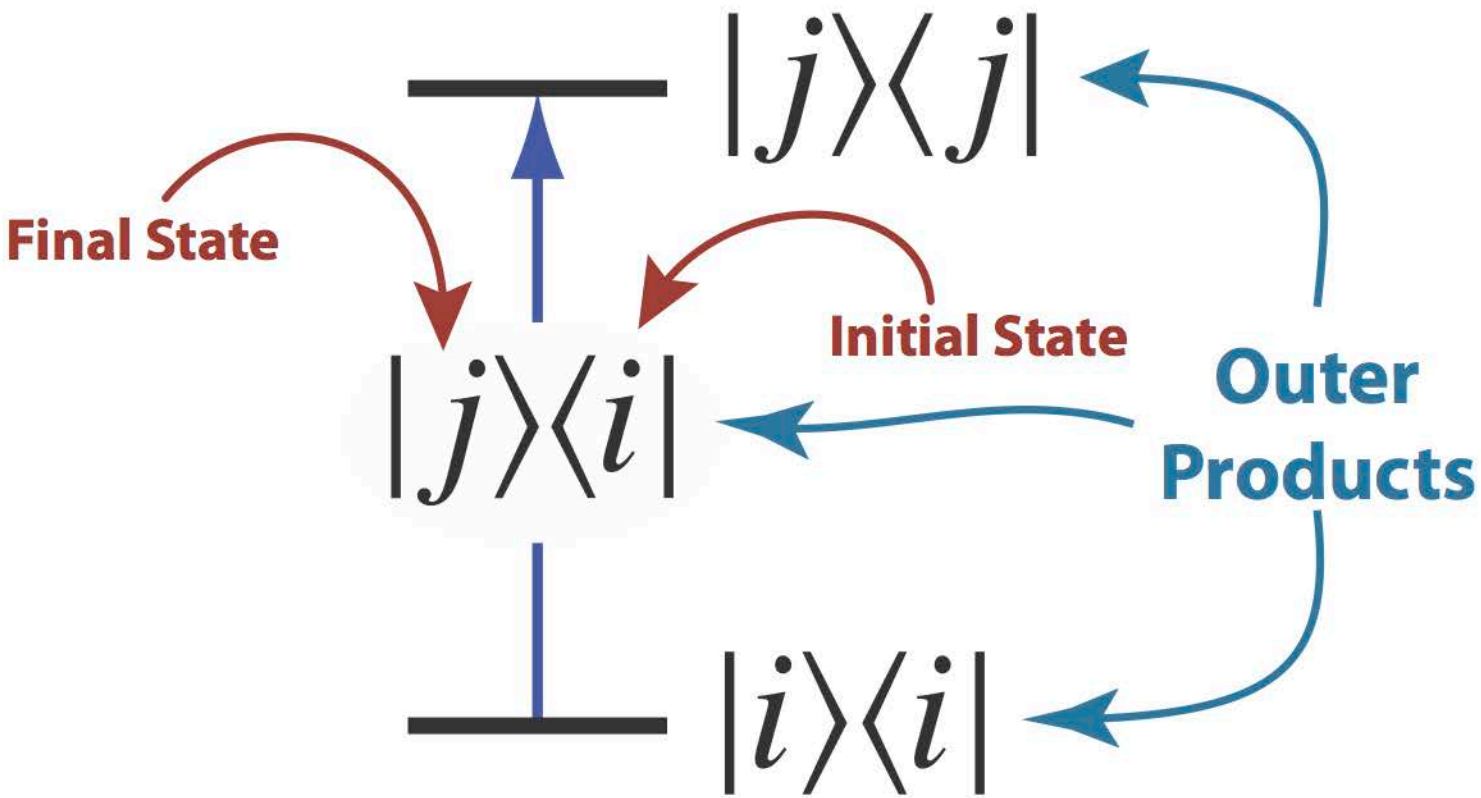
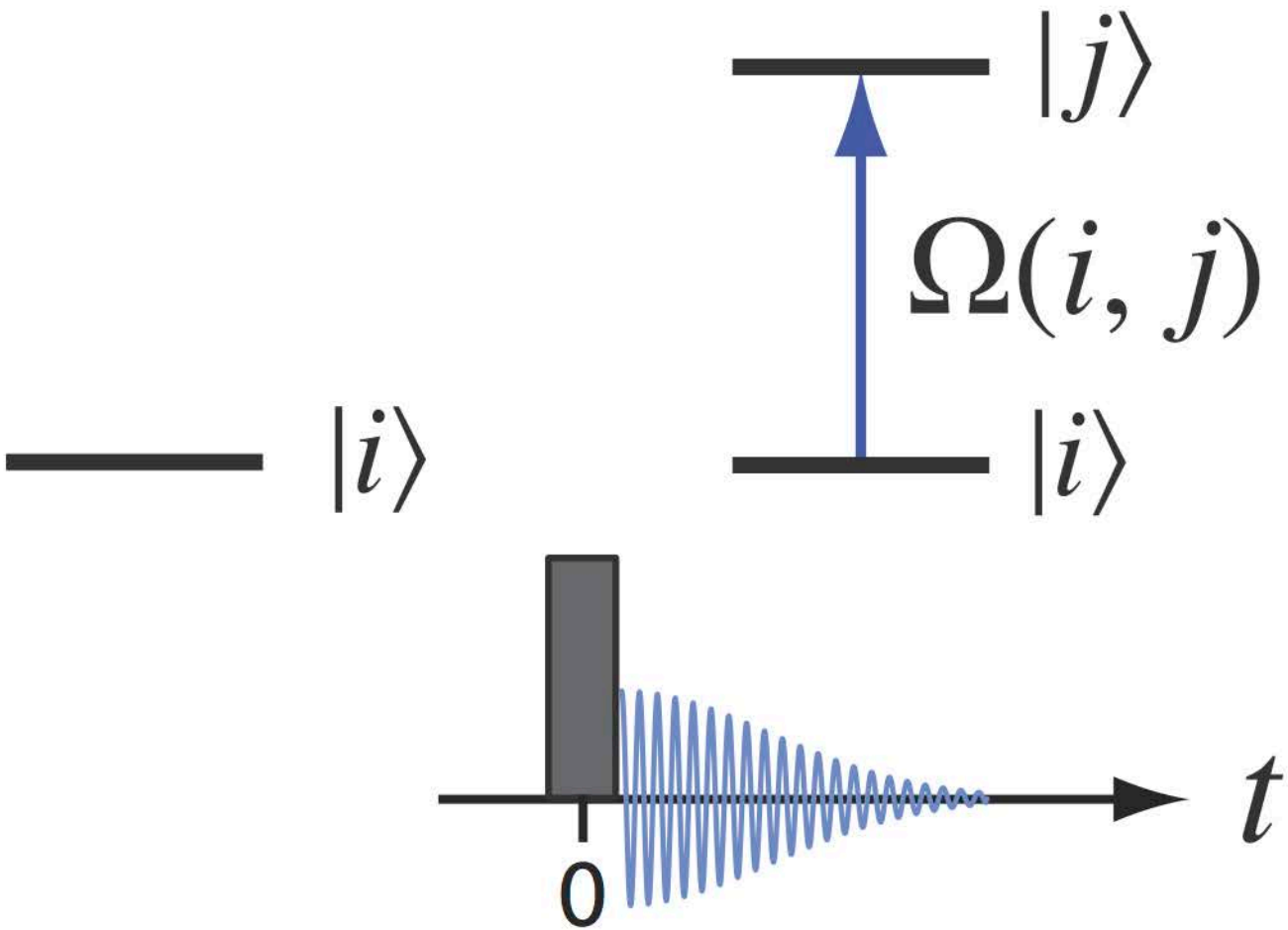
This lecture is not about what NMR can do, but about how to do NMR

A Transition

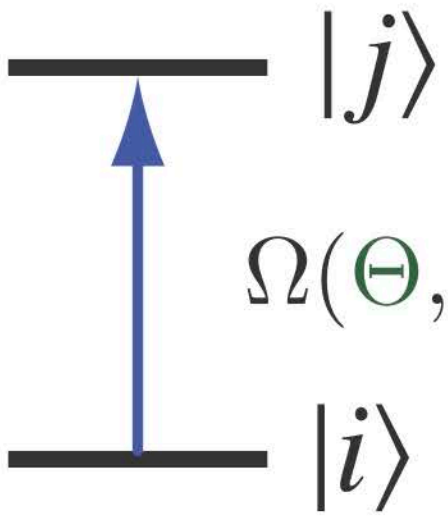


A Transition Pathway



$$|i\rangle\langle i| \rightarrow |j\rangle\langle i|_t$$

NMR Transition Frequency is Sum of Components



$$\Omega(\Theta, i, j) = \sum_k \Omega_k(\Theta, i, j)$$

initial state

final state

Orientation of the sample in magnetic field

and each component is the product of three terms:

$$\Omega_k(\Theta, i, j) = \omega_k \cdot \Xi_L^{(k)}(\Theta) \cdot \xi_l^{(k)}(i, j)$$

Component Strength — **Spatial Function** — **Spin Transition Function**

for more details see : "Symmetry Pathways in Solid-State NMR", *Prog. NMR Spect.*, **59**, 121-196 (2011)

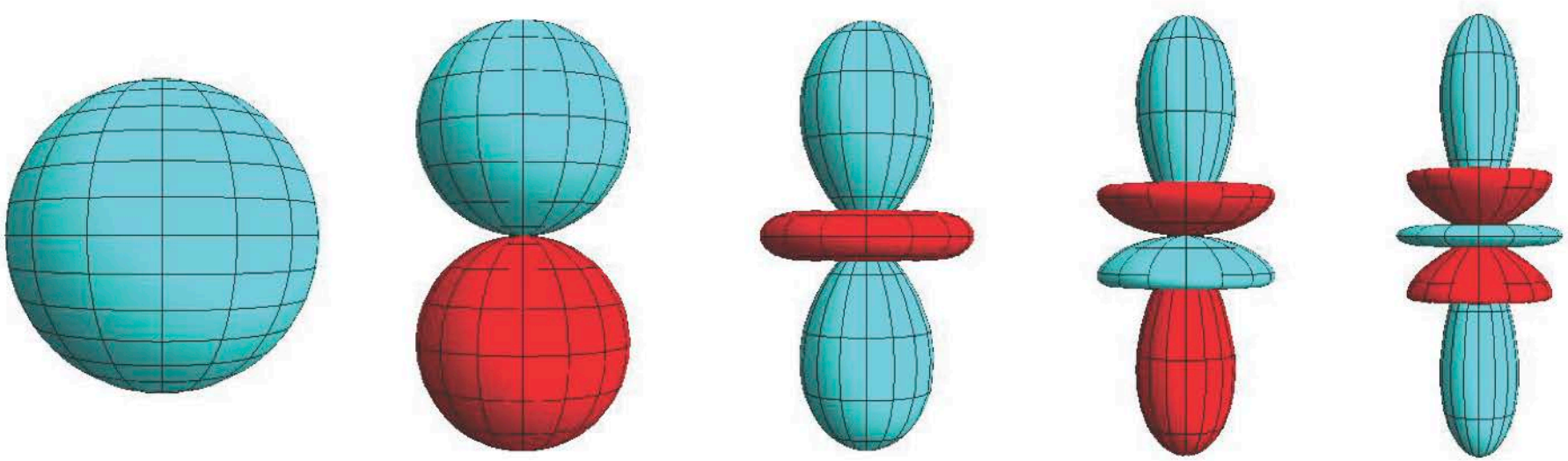
Relabel spatial function for each rank of L

$$\Xi_L^{(k)}(\Theta) \propto R_{L,0}^{(k)}(\Theta)$$

Orientation of the sample in magnetic field

$$\Xi_L(\Theta)$$

$L =$	0	1	2	3	4
	$\mathbb{S}$,	$\mathbb{P}(\Theta)$,	$\mathbb{D}(\Theta)$,	$\mathbb{F}(\Theta)$,	$\mathbb{G}(\Theta)$, ...



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
	$\mathbb{s}$,	$\mathbb{p}(i,\, j)$,	$\mathbb{d}(i,\, j)$,	$\mathbb{f}(i,\, j), \ldots$

Form of transition function depends on spin system

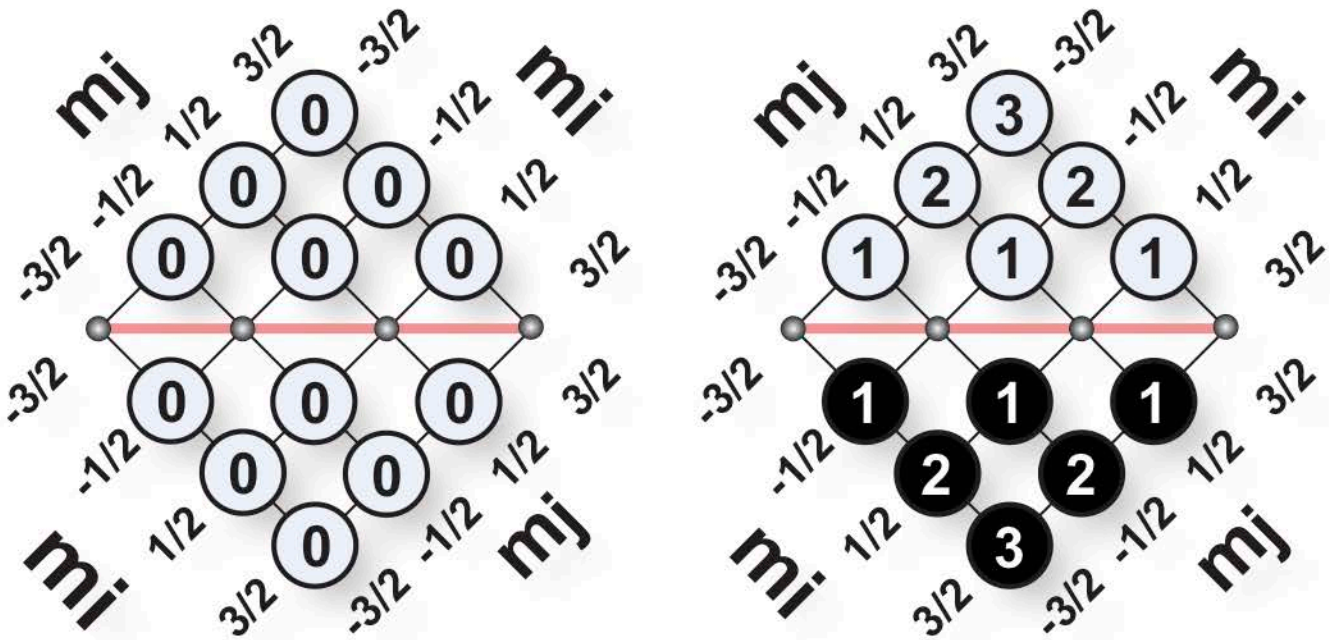
Values of various symmetry functions can be calculated for each transition

Transition symmetry functions for single spin, I

$$s_I(m_i, m_j) = \qquad \mathbb{s}_I(m_i, m_j) = 0,$$

$$p_I(m_i, m_j) = \qquad \mathbb{p}_I(m_i, m_j) = m_j - m_i,$$

$s_I(m_i, m_j)$ $\qquad$ $p_I(m_i, m_j)$



Transition functions for a Spin I=3/2 Nucleus

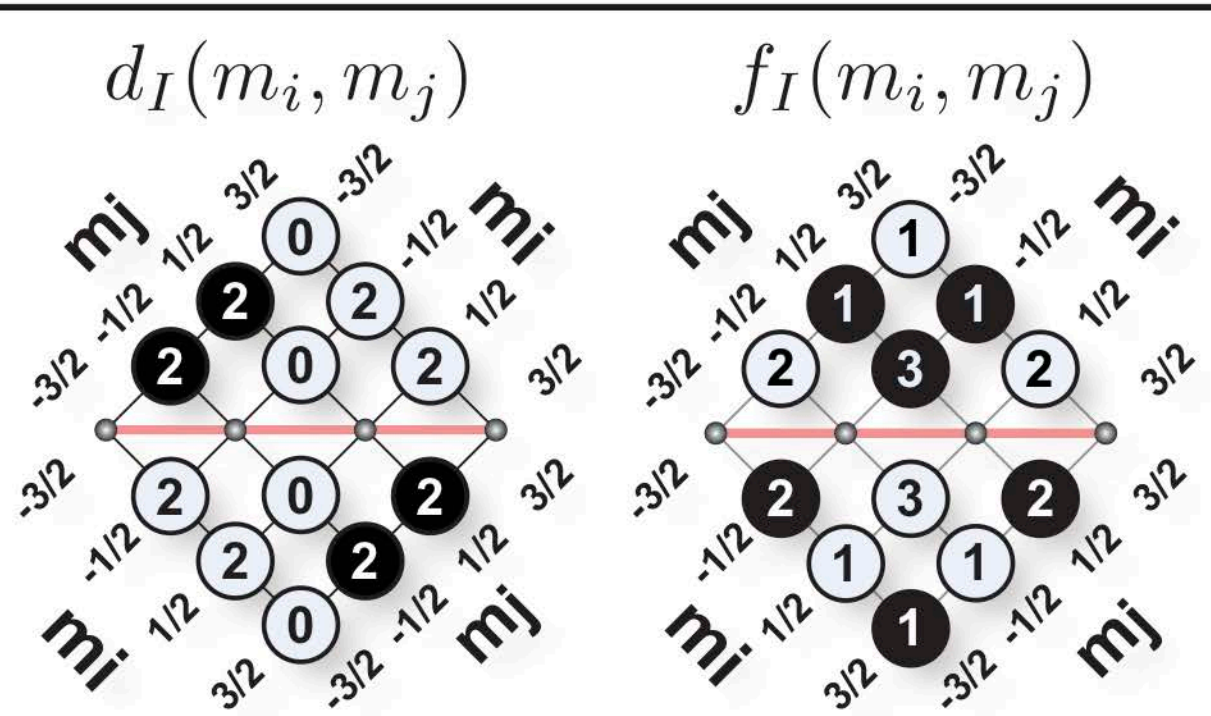
Values inside solid black circles are negative

Values of various symmetry functions can be calculated for each transition

Transition symmetry functions for single spin, I

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

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



Transition functions for a Spin I=3/2 Nucleus

Values inside solid black circles are negative

Rewrite Frequency Contributions using Symmetry Functions

First-Order Nuclear Shielding

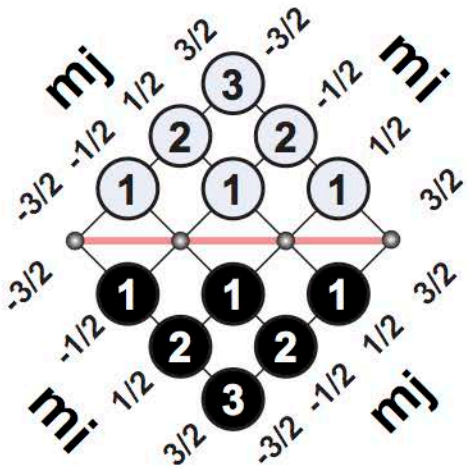
spatial function

transition function

$$\Omega_{\sigma}^{(1)} = -\omega_0 \sigma_{iso} \left[\mathbb{S}^{\{\sigma\}} \cdot \mathbb{p}_I(m_i, m_j) \right]$$
$$-\omega_0 \zeta_{\sigma} \left[\mathbb{D}^{\{\sigma\}}(\Theta) \cdot \mathbb{p}_I(m_i, m_j) \right]$$

Isotropic contribution contains the **S** spatial function.

$$\mathbb{p}(i, j)$$



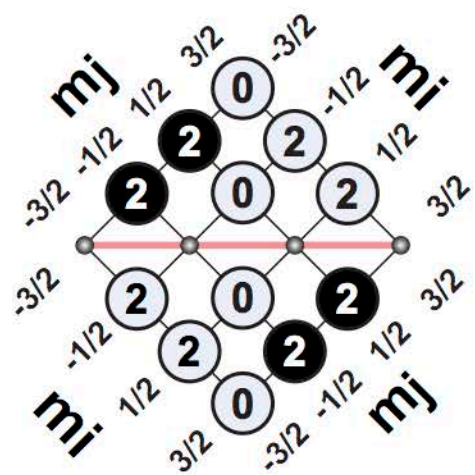
First-Order Quadrupole Coupling

$$\Omega_{q}^{(1)} = \omega_q \left[\mathbb{D}^{\{q\}}(\Theta) \cdot \mathbb{d}_I(m_i, m_j) \right]$$

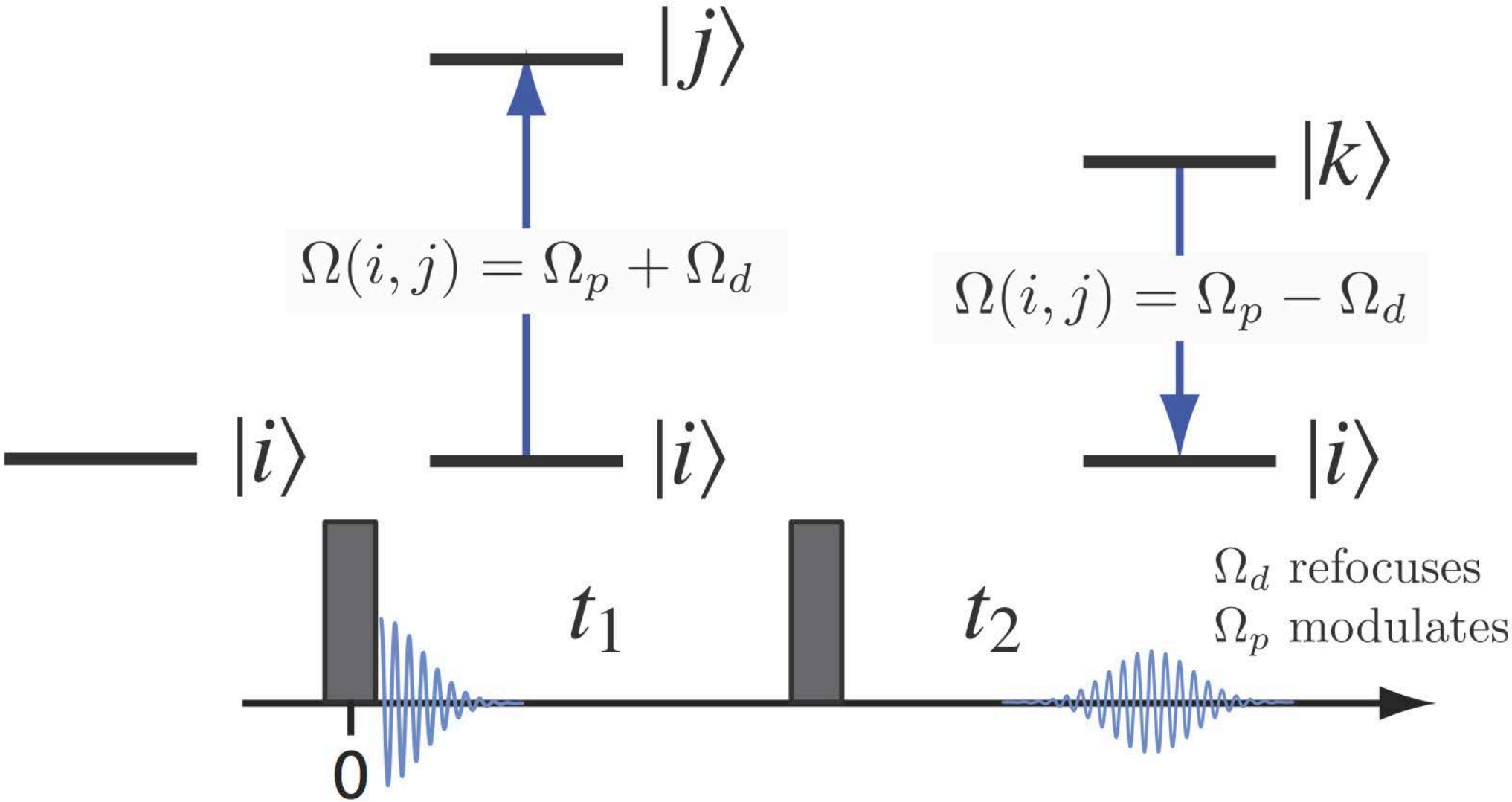
Notice: d_I vanishes for all m to -m transitions

$$\mathbb{d}_I(m, -m) = 0$$

$$\mathbb{d}(i, j)$$



Transition Pathway for d Echo

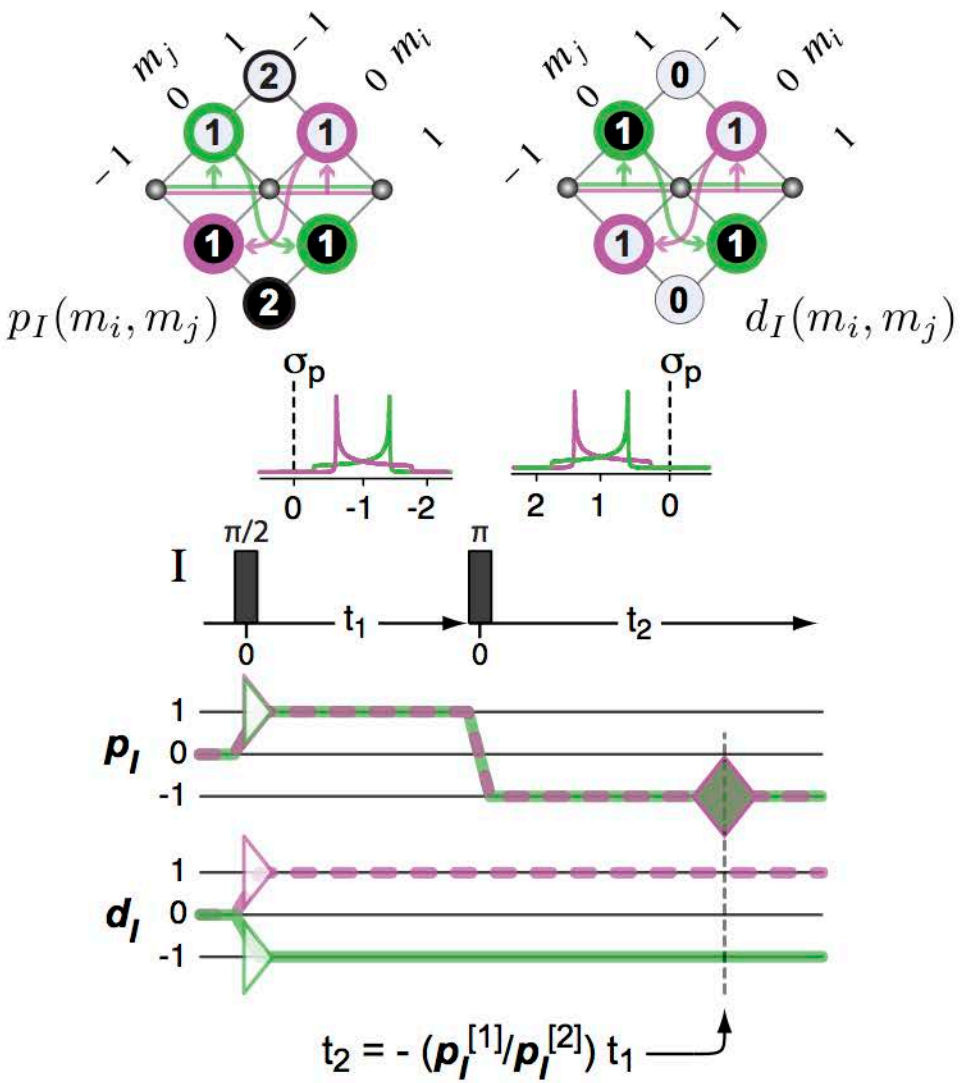


$$|i\rangle\langle i| \rightarrow |j\rangle\langle i|_{t_1} \rightarrow |i\rangle\langle k|_{t_2}$$

Desired NMR signal can come from multiple transition pathways

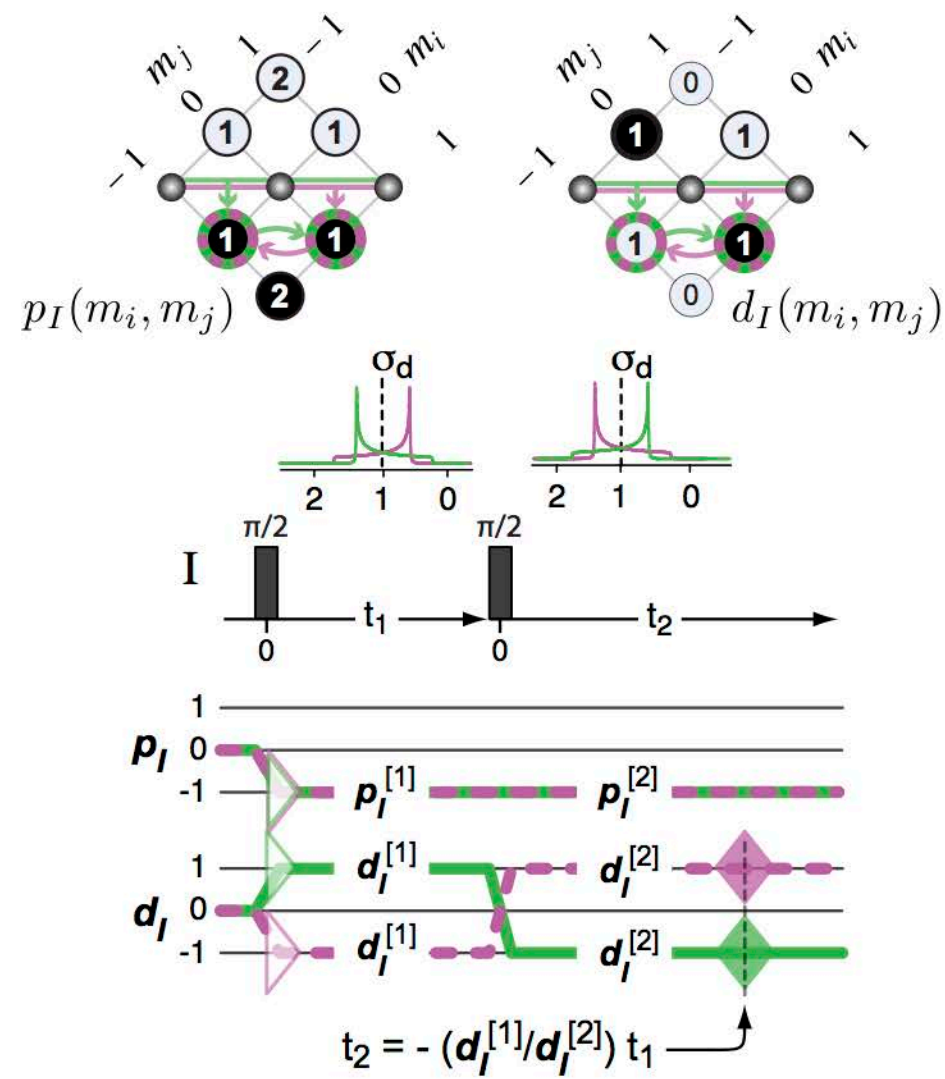
Hahn Echo (p Echo)

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



Solid Echo (d Echo)

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

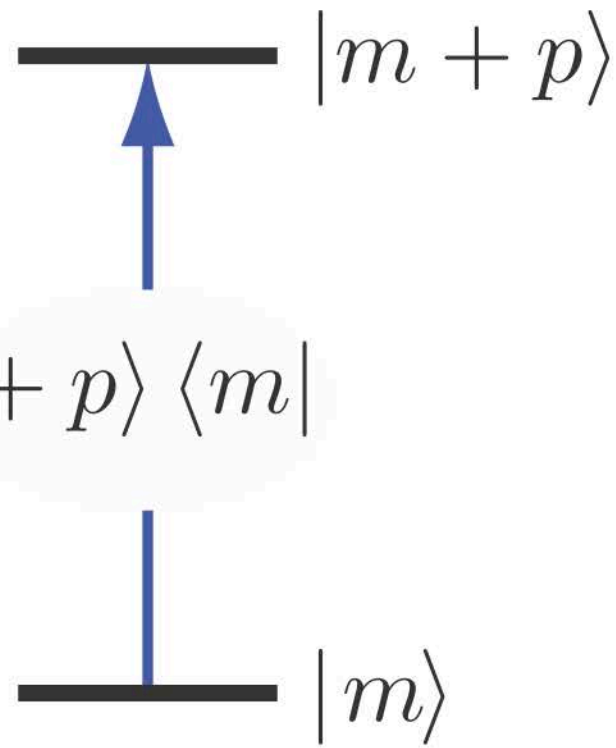


How do we select the right transition pathways and avoid the wrong transition pathways?

Not always possible to
avoid the wrong transition pathways,

but we do have a systematic approach
to avoid the wrong p 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

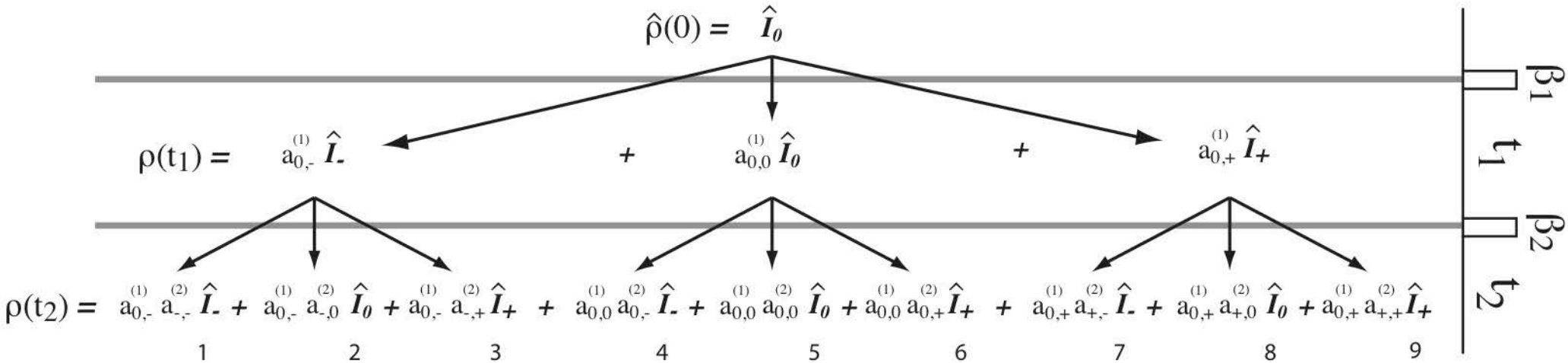
In general: $$\hat{T}_p = \sum_m a_m \hat{t}_p(m)$$

Spin 1/2 Example

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

A Tree of Possible Signals

Generic two pulse NMR experiment on spin 1/2 system

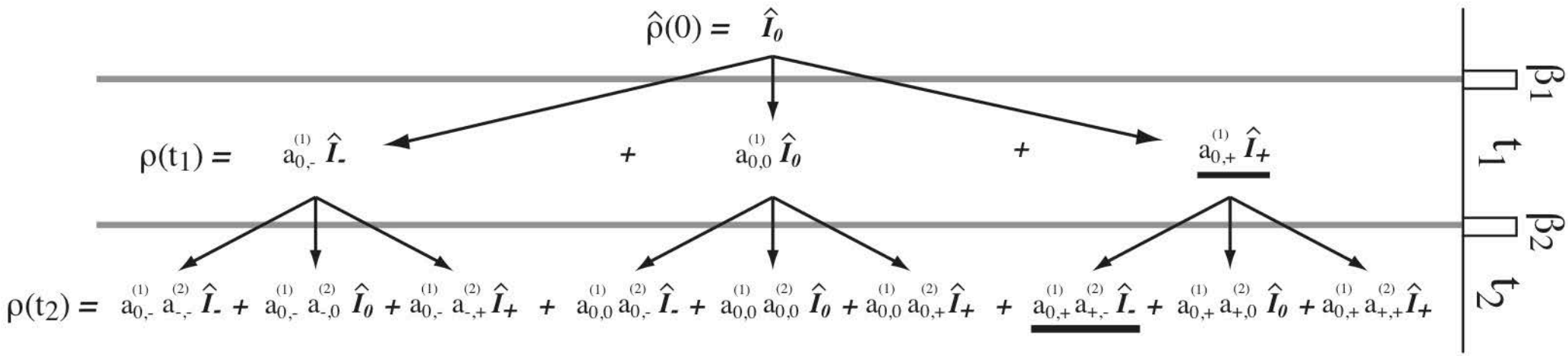


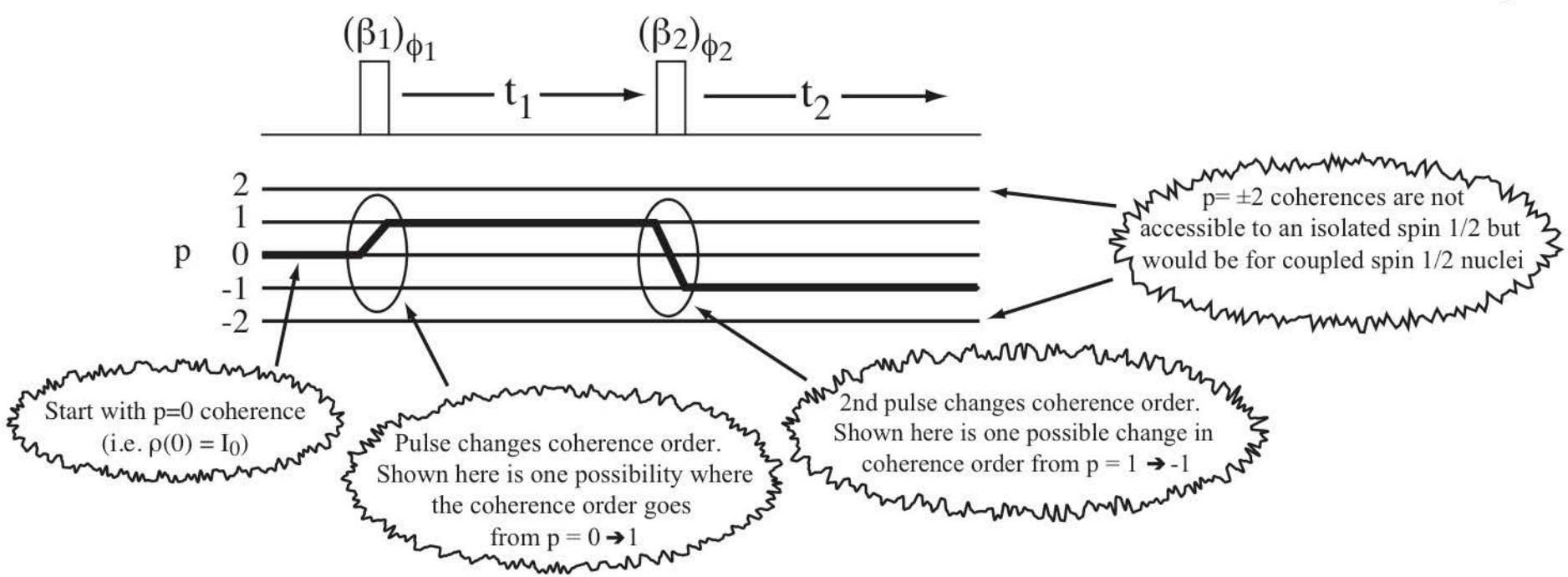
After two pulses there will be 9 different terms in the density operator expansion, each multiplied by coefficients that carry the history of each term.

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

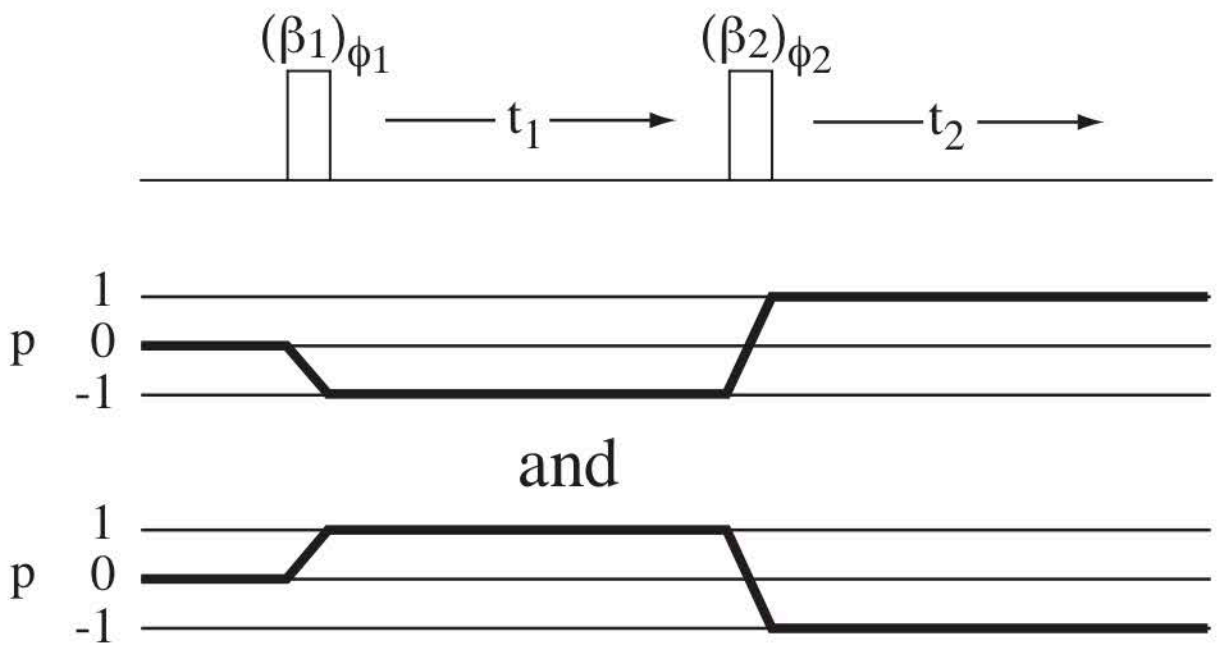




Not all transition pathways are unique

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: $$S(t) = \frac{d}{dt}\mathrm{Tr}\{\tilde{\rho}(t)\hat{I}_+\}$$

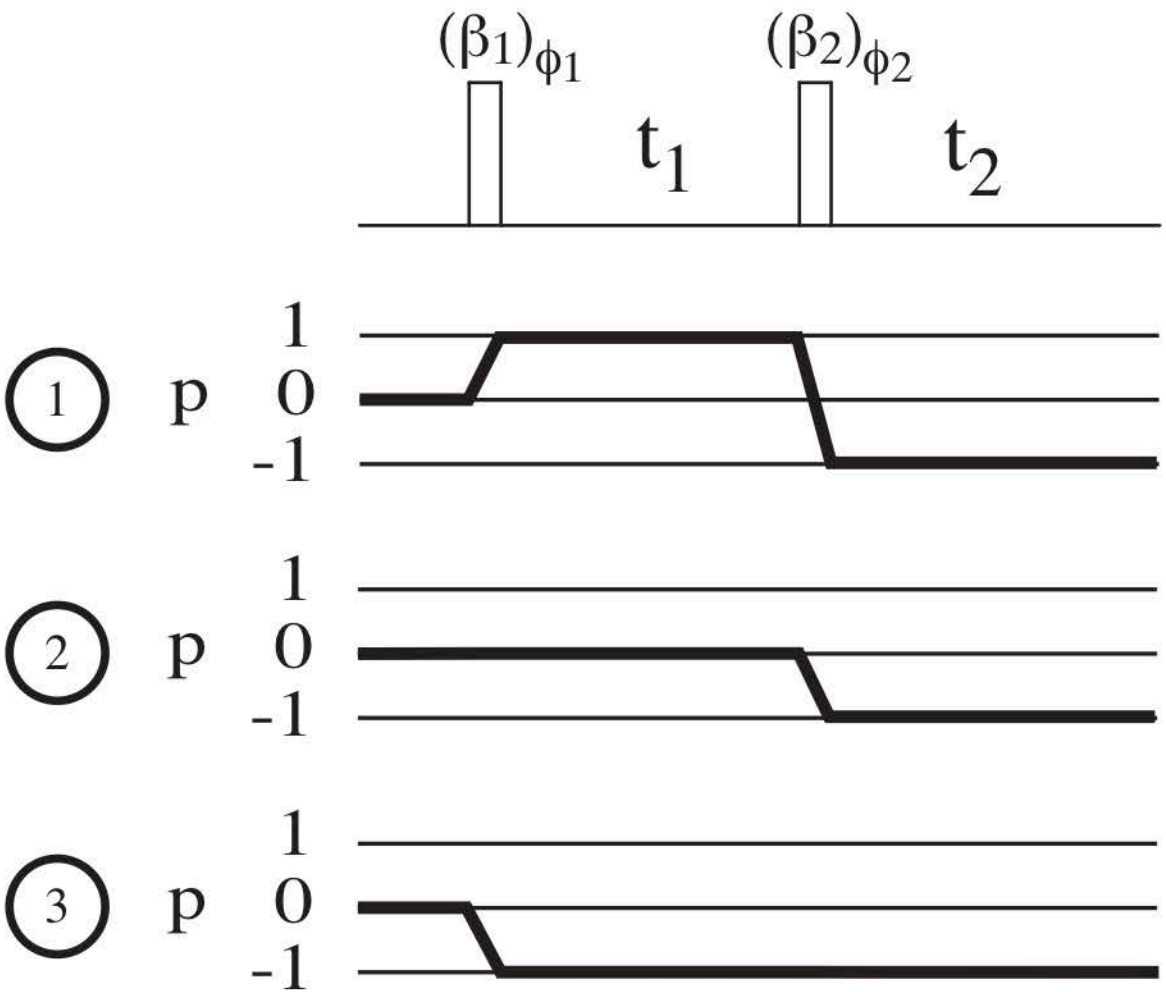
and

$$\boxed{\mathrm{Tr}\{\hat{I}_+\hat{I}_-\} \neq 0,} \quad \mathrm{Tr}\{\hat{I}_0\hat{I}_0\} \neq 0$$

$$\mathrm{Tr}\{\hat{I}_+\hat{I}_+\} = \mathrm{Tr}\{\hat{I}_+\hat{I}_0\} = \mathrm{Tr}\{\hat{I}_0\hat{I}_-\} = \mathrm{Tr}\{\hat{I}_-\hat{I}_-\} = 0$$

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



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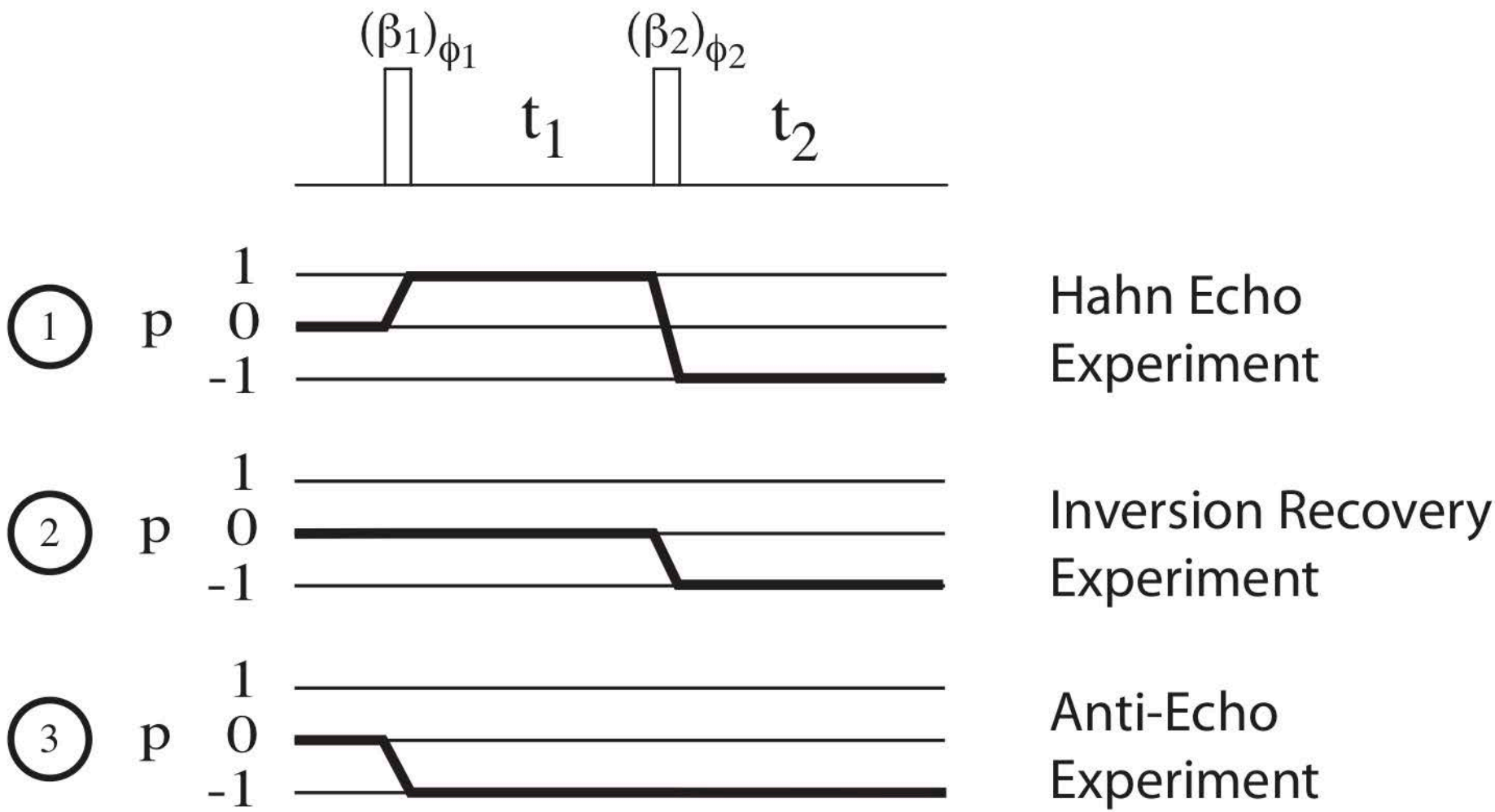

Pathway Selection and RF Pulse Phase

When the RF is on, the Hamiltonian is

$$\tilde{H}(\phi) = \underbrace{-\omega_1(I_x \cos\phi + I_y \sin\phi)}_{\text{rf Hamiltonian}} + \hat{H}'$$

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

An important relationship obeyed by this Hamiltonian is

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

And the same relationship holds for the propagator

$$\boxed{\tilde{U}_\phi(t,0) = e^{-i\phi\hat{I}_z}\tilde{U}_0(t,0)e^{i\phi\hat{I}_z}}$$

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...

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

where $\Delta p_1 = p_1 - p_0$

One Pulse and Acquire (as a function of pulse phase)

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:

$$\tilde{\rho}(t) = \sum_{p_1} c_{p_0,p_1}(t)\hat{I}_{p_1} e^{-i\Delta p_1 \phi} e^{ip_1\Omega t}$$

which consists of three terms:

$$\tilde{\rho}(t) = \underbrace{c_{0,-1}\hat{I}_- e^{i\phi_1} e^{-i\Omega t}}_{\Delta p_1 = -1} + \underbrace{c_{0,0}\hat{I}_0}_{\Delta p_1 = 0} + \underbrace{c_{0,1}\hat{I}_+ e^{-i\phi_1} e^{i\Omega t}}_{\Delta p_1 = +1}$$

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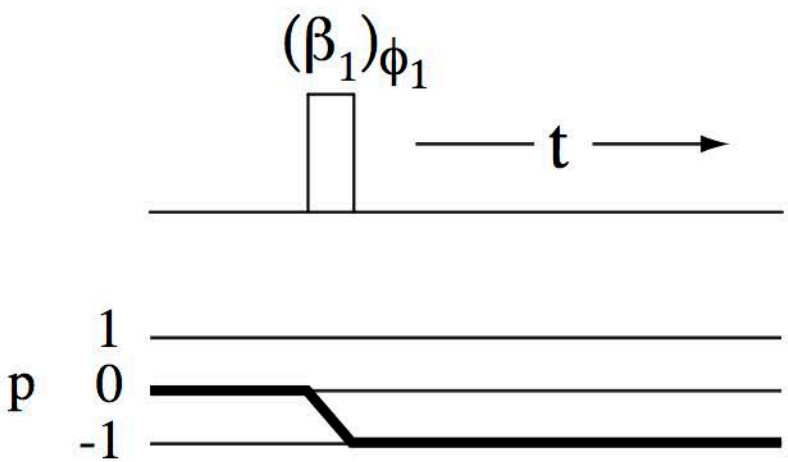
Signal after pulse derives solely from the $\Delta p_1 = -1$ term

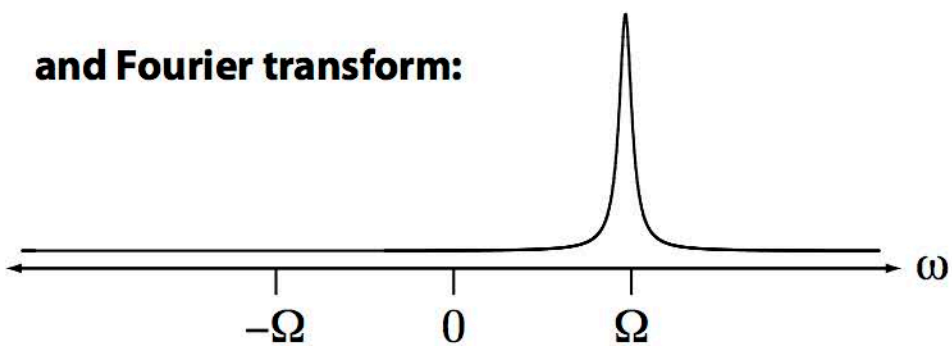
$$S(\phi_1, t) = \mathrm{Tr}\{\tilde{\rho}(t)\hat{I}_+\} = c_{0,-1} e^{i\phi_1} e^{-i\Omega t}$$



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:



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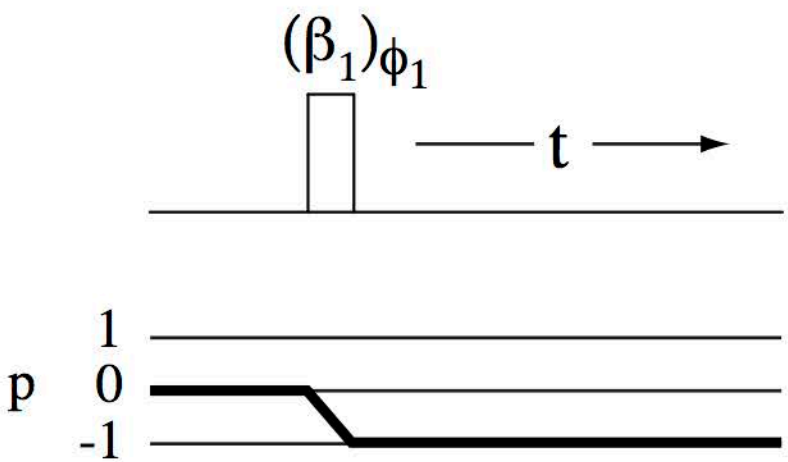

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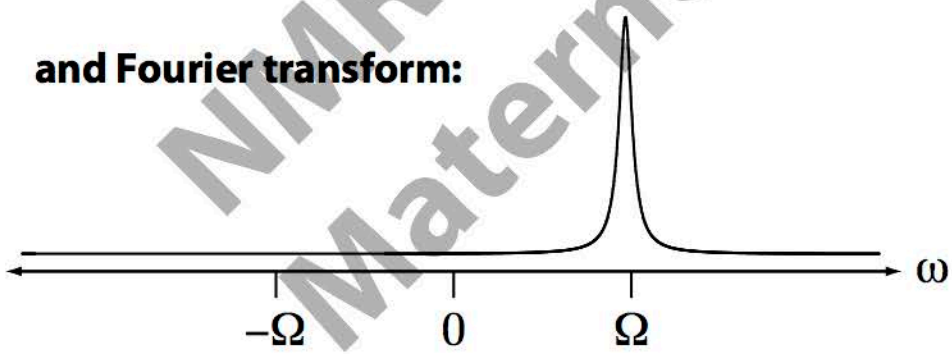

One Pulse and Acquire (as a function of pulse phase)

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 ϕ_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 ϕ_1?

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

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

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

You learn about the change in p during the pulse.

Our one pulse signal on spin 1/2 gives

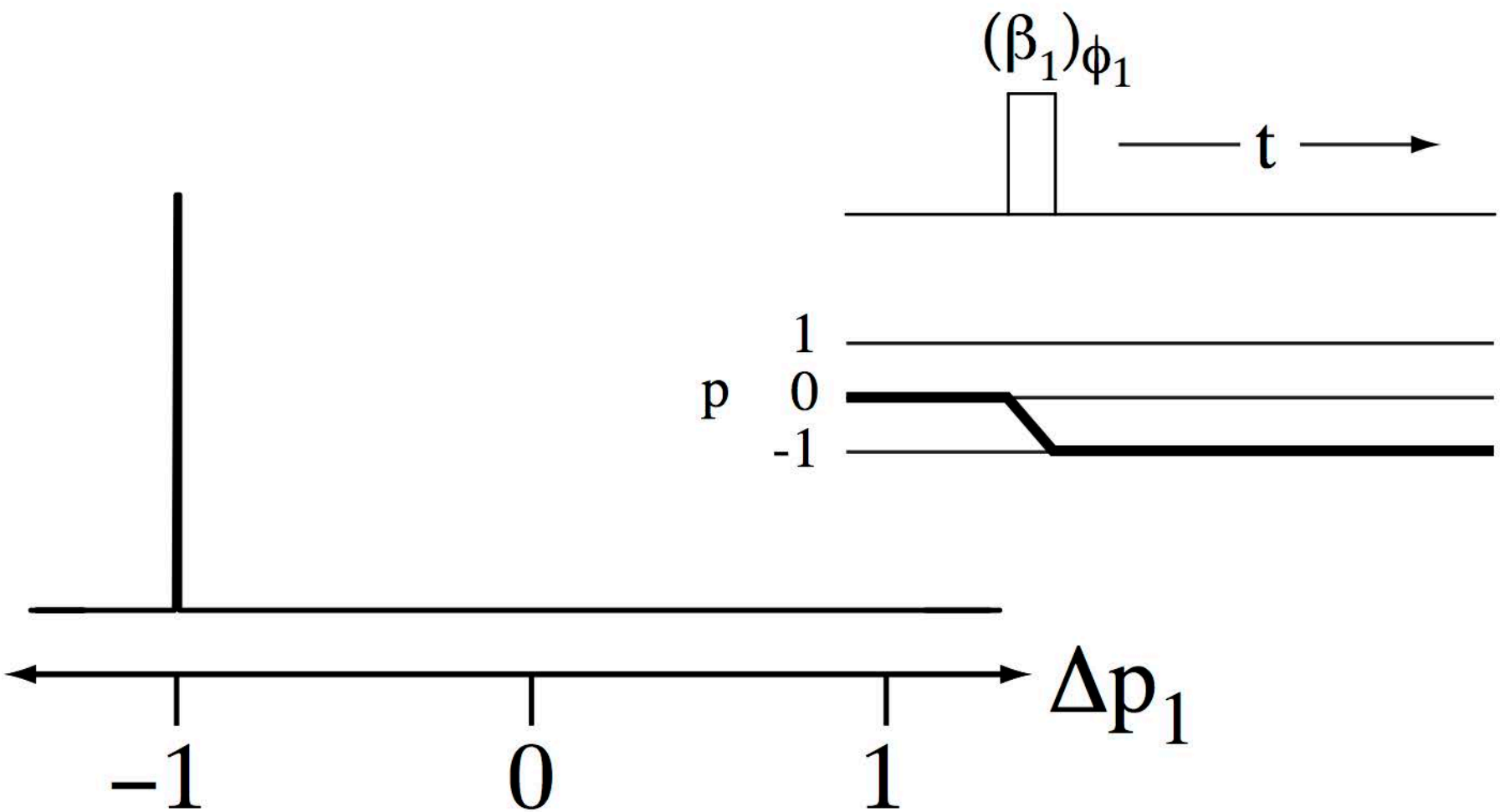
$$\begin{aligned} S(\Delta p_1, t) &= c_{0,-1} e^{-i\Omega t} e^{-t/T_2} \int_{-\infty}^{\infty} e^{i\phi_1} e^{i\Delta p_1 \phi_1} d\phi_1 \\ &= c_{0,-1} e^{-i\Omega t} e^{-t/T_2} \delta(1 + \Delta p_1) \end{aligned}$$

A delta function at $\Delta p_1 = -1$ associated with $p = 0 \rightarrow -1$ during the pulse.

One Pulse and Acquire (as a function of pulse phase)

Simplest Case: Single Spin 1/2

$$S(\Delta p_1, t) = c_{0,-1} e^{-i\Omega t} e^{-t/T_2} \delta(1 + \Delta p_1)$$



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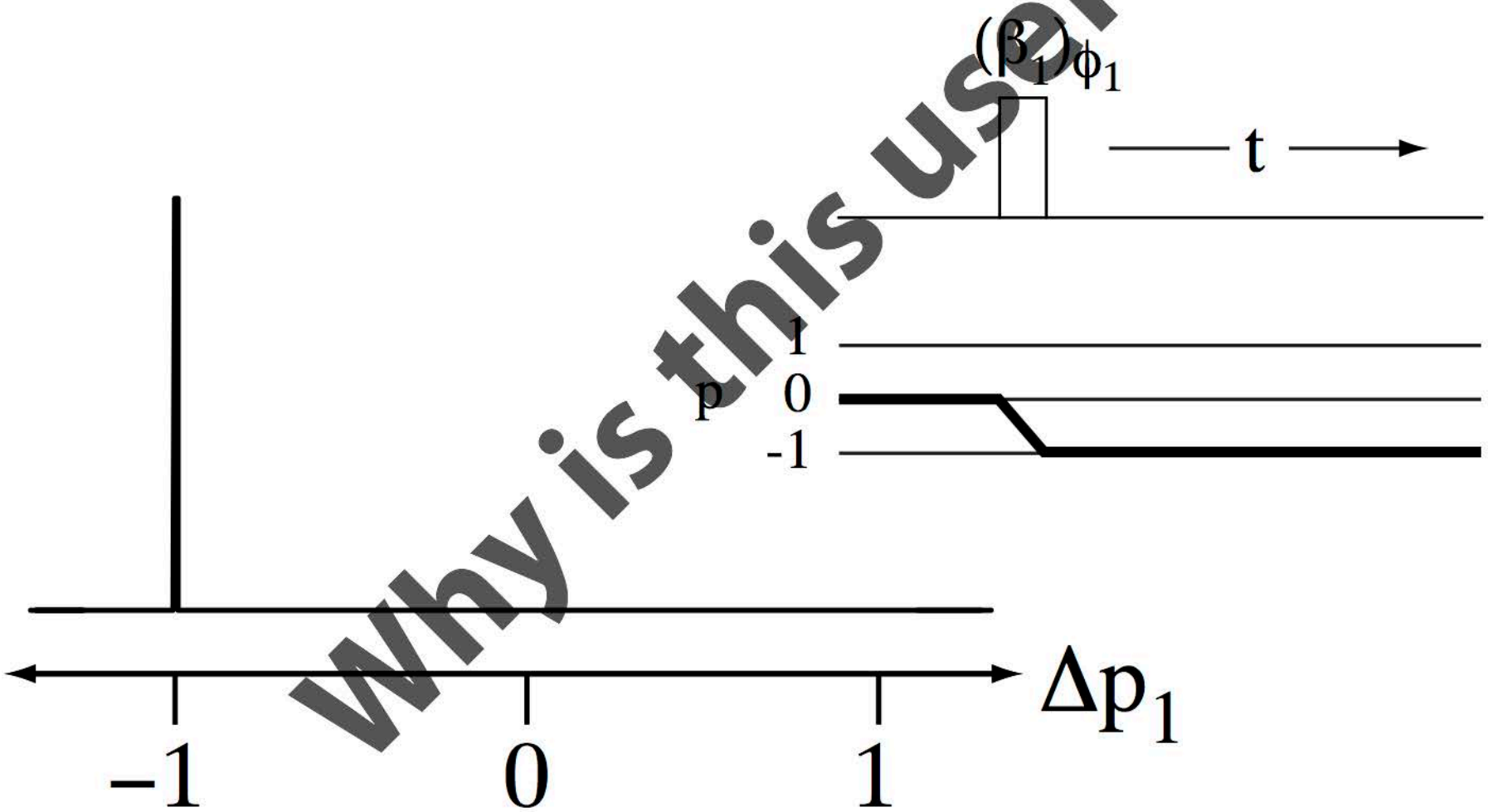
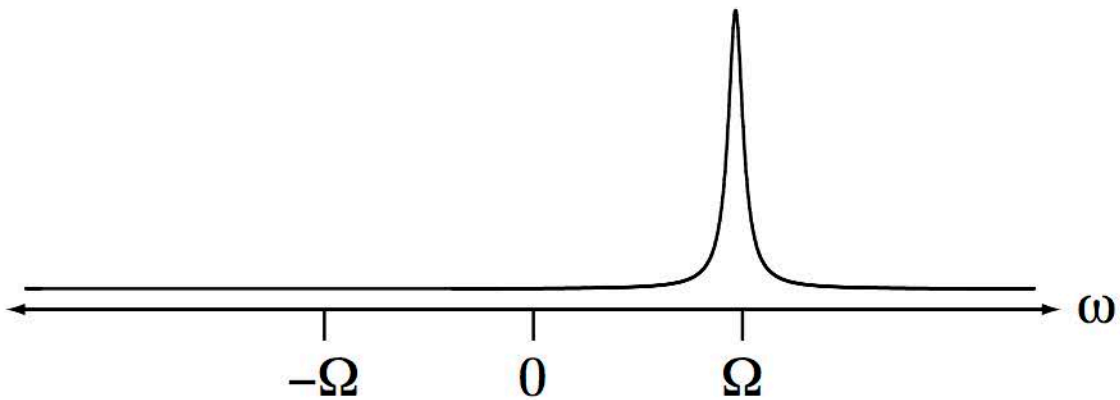


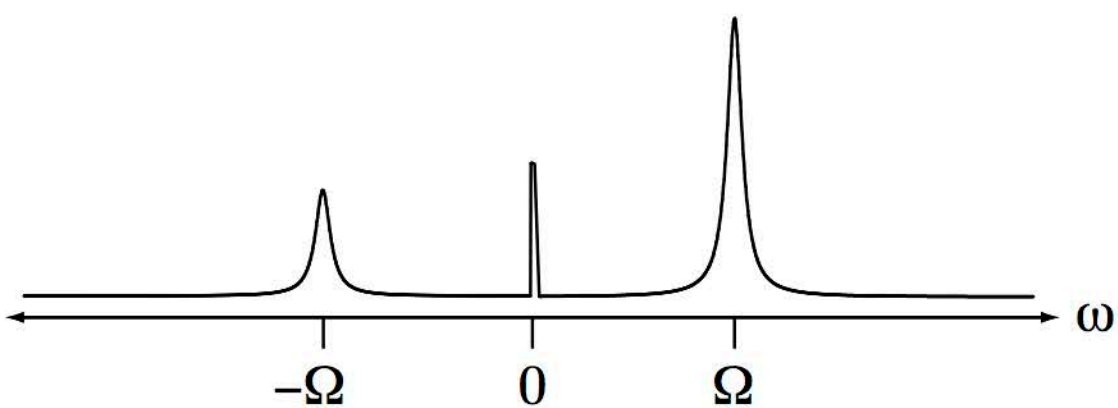
Why is this useful?

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)

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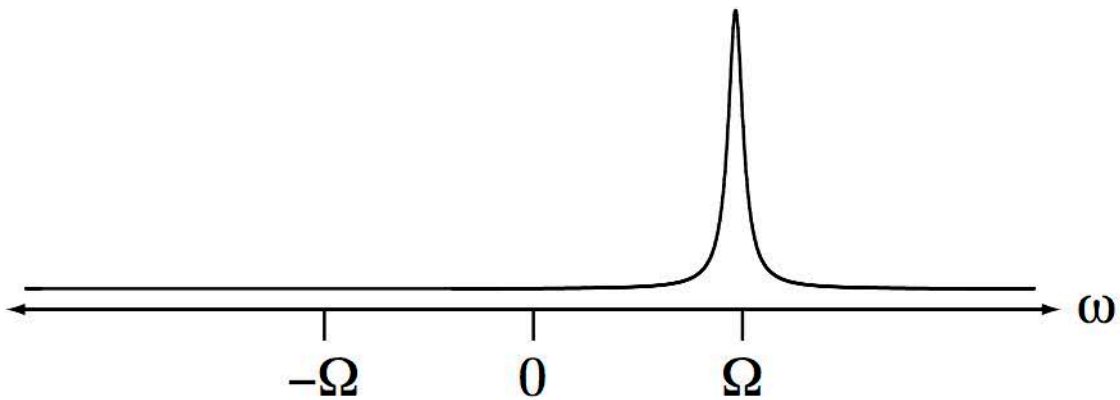

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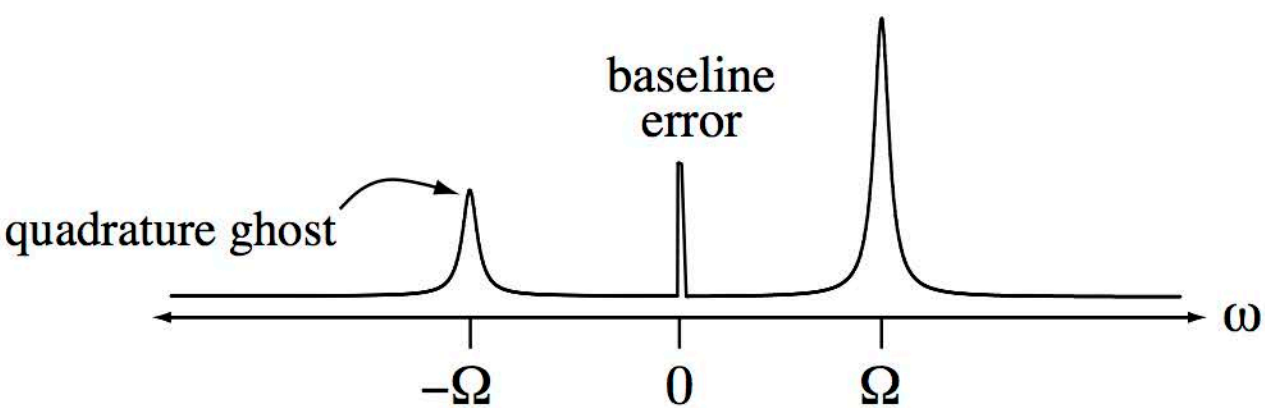


Baseline Error and Quadrature Ghosts

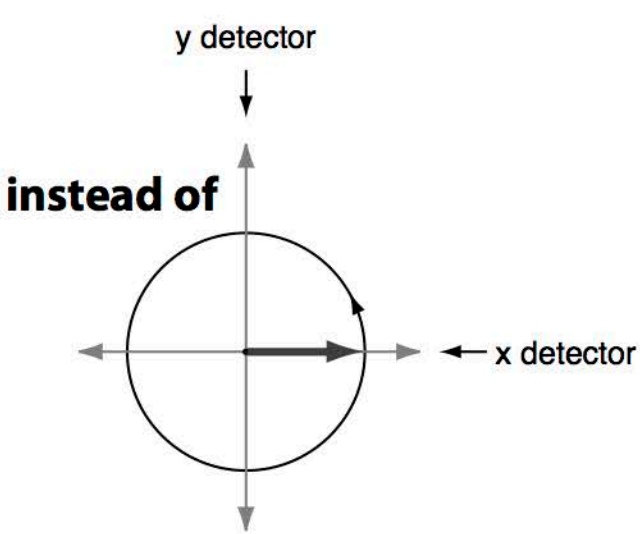
Baseline Error: **Even when there's no signal the receiver records constant value.**

$$S(t) = \mathrm{Tr}\{\tilde{\rho}(t)\hat{I}_+\} + \mathrm{constant}$$

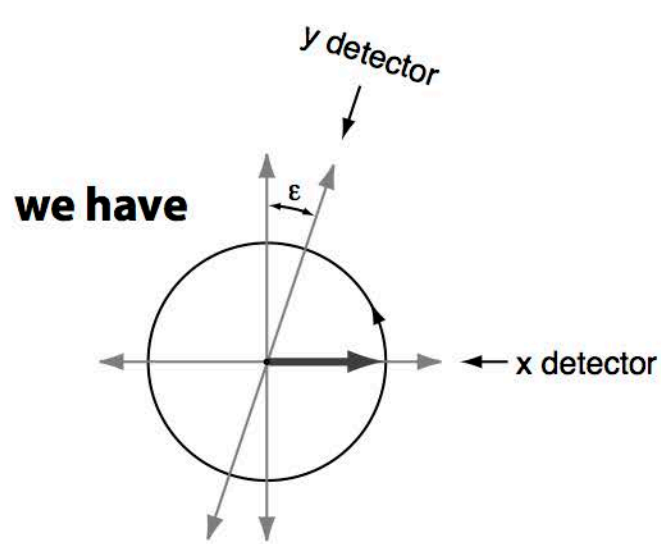
causes spike at 0 Hertz

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

Good Receiver



Bad Receiver



Quadrature Ghosts

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

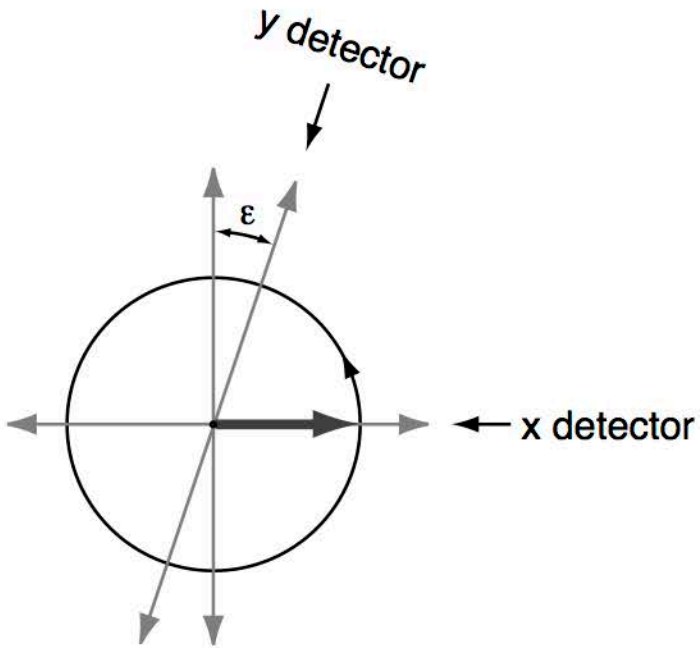
$$\hat{I}_y \cos\epsilon + \hat{I}_x \sin\epsilon,$$

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

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

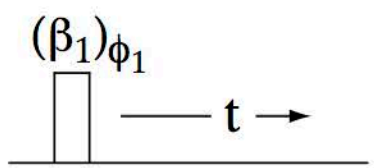
Rewriting this in terms of $\hat{I}_\pm$ we have

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



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

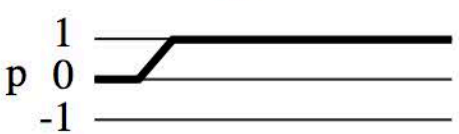
$$S(t) = \left(\frac{1}{2} + \frac{1}{2}e^{i\epsilon}\right) \underbrace{\mathrm{Tr}\{\tilde{\rho}(t)\hat{I}_+\}}_{\text{Original Signal}} + \left(\frac{1}{2} - \frac{1}{2}e^{-i\epsilon}\right) \underbrace{\mathrm{Tr}\{\tilde{\rho}(t)\hat{I}_-\}}_{\text{New Signal}}.$$



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

and

$$S(\phi, t) = \left(\frac{1}{2} + \frac{1}{2}e^{i\epsilon}\right) \underbrace{c_{0,-1}e^{i\phi_1}e^{-i\Omega t}}_{\Delta p_1 = -1 \text{ signal}} + \left(\frac{1}{2} - \frac{1}{2}e^{-i\epsilon}\right) \underbrace{c_{0,+1}e^{-i\phi_1}e^{i\Omega t}}_{\Delta p_1 = +1 \text{ signal}}$$



One Pulse and Acquire
(on 1980s home-built NMR spectrometer)

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

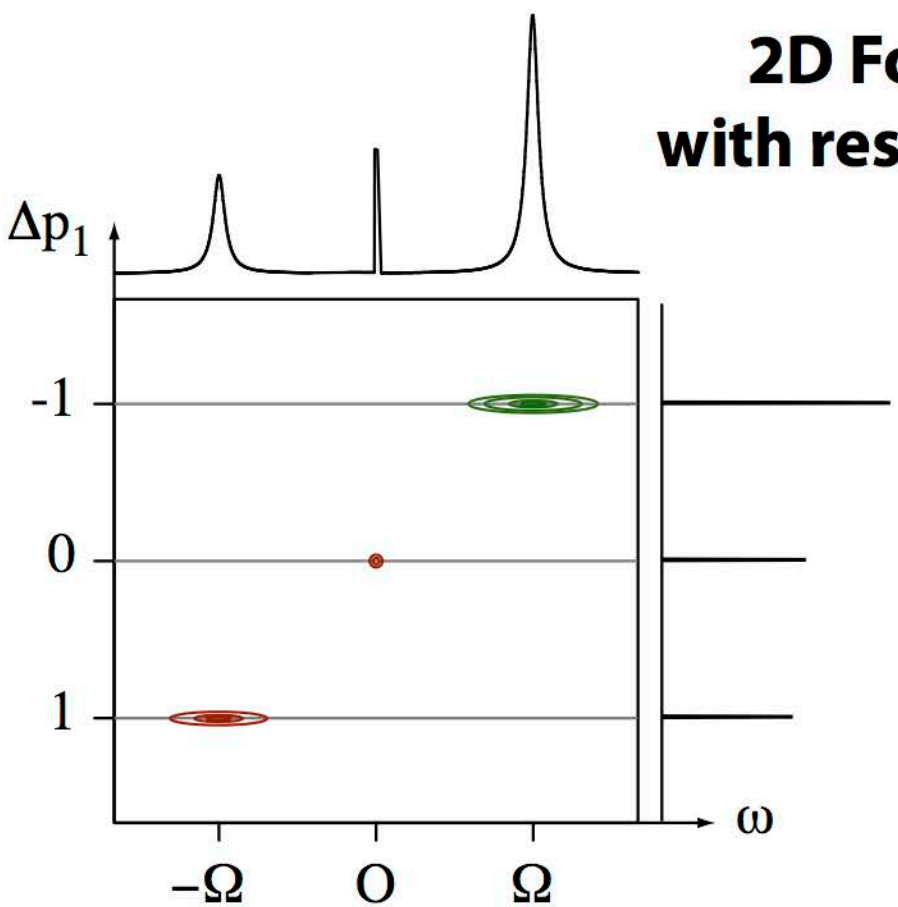
How do we separate the desired from undesired signal?

One Pulse and Acquire
(on 1980s home-built NMR spectrometer)

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

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)

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

How do we separate the desired from undesired signal?

2D Fourier transform
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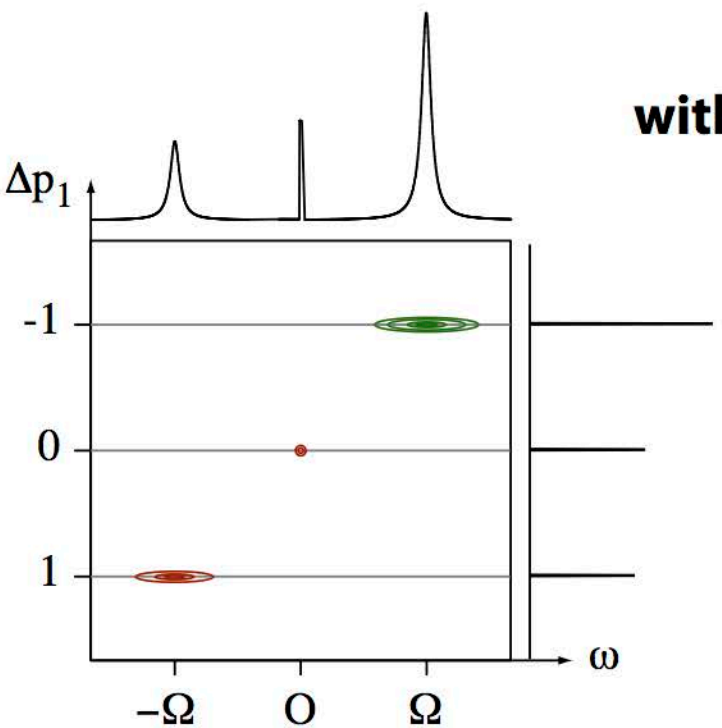
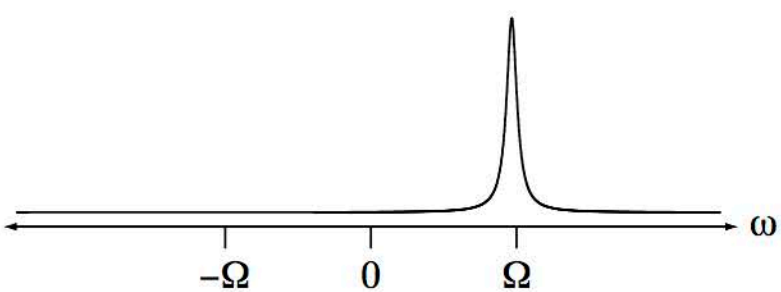


To retrieve the desired spectrum we only need to extract the $\Delta p_1 = -1$ cross section and we're done.



This is the essence of phase cycling: separating signals from different p pathways by their Δp 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

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

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

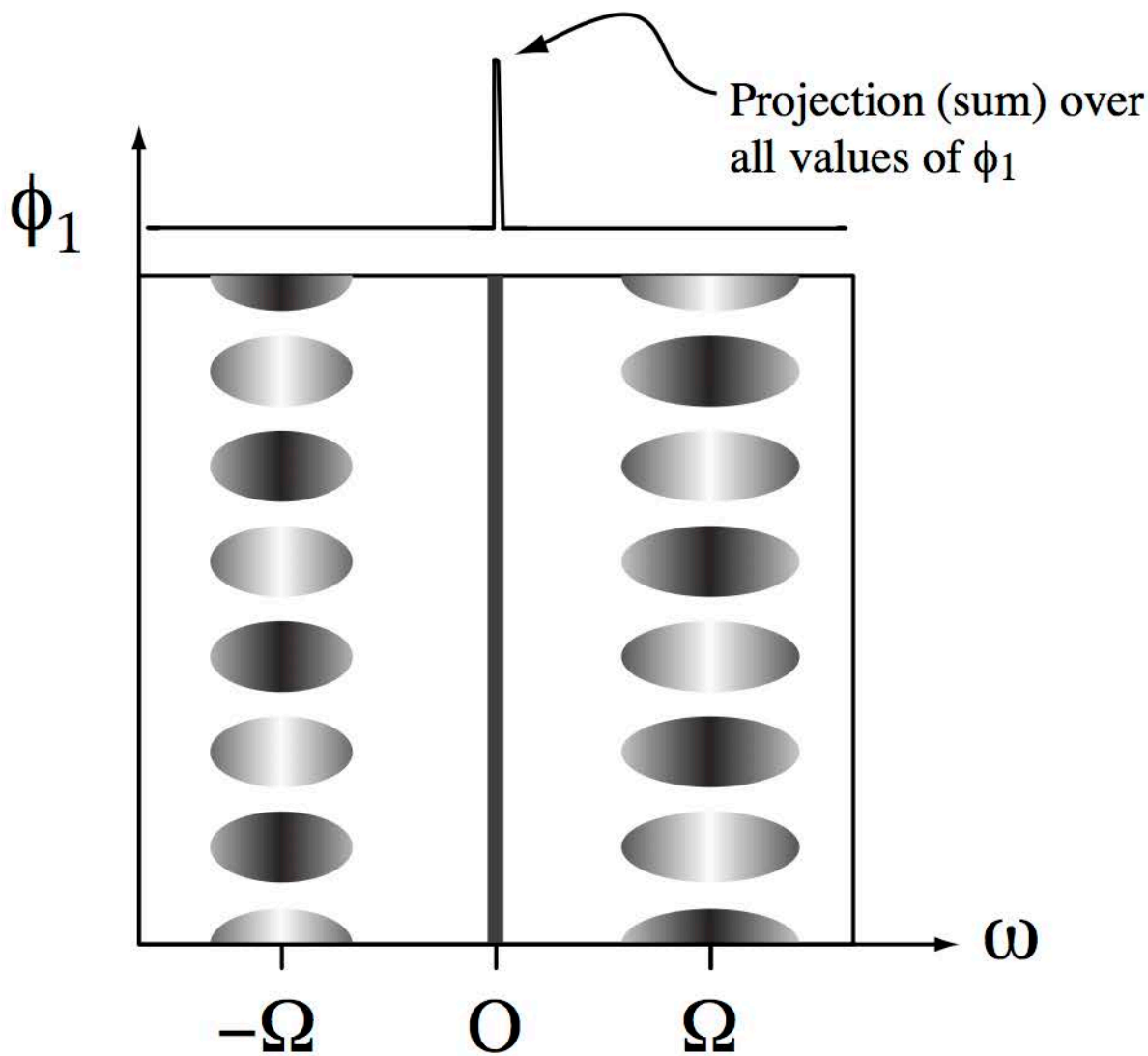
$$\Delta t < \frac{2\pi}{\text{spectral width of frequencies present}}$$

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

$$\Delta\phi < \frac{2\pi}{\Delta p_{\text{max}} - \Delta p_{\text{min}}}$$

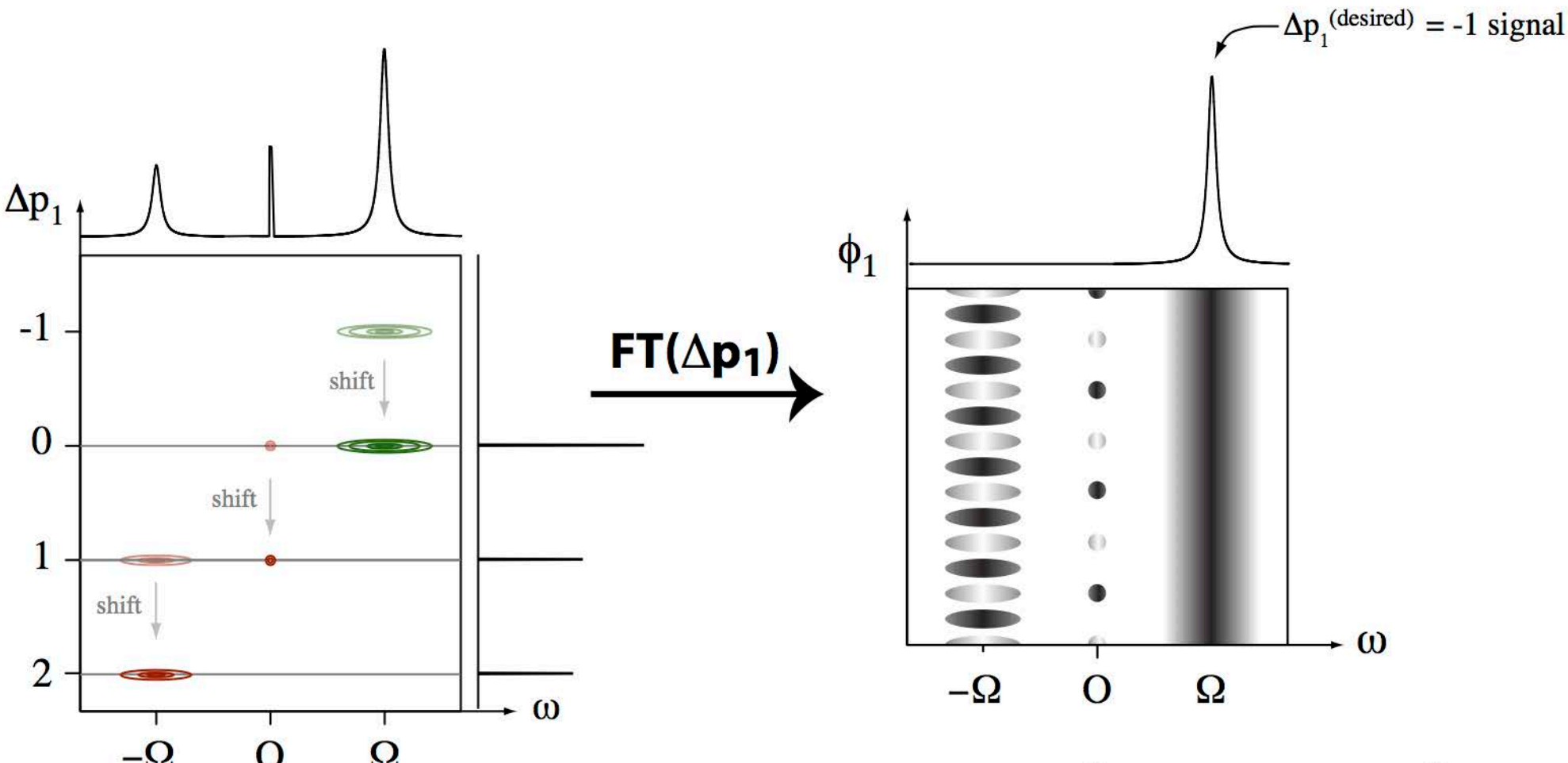
Phase Cycling: Avoiding the FT wrt phase

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



Phase Cycling: Avoiding the FT wrt phase

Shift spectrum along Δp dimension and move desired Δp value to Δp=0.



$$\Delta\phi = \frac{2\pi}{\Delta p_{\max} - \Delta p_{\min} + 1} = \frac{2\pi}{n}$$

Phase Cycling: Avoiding the FT wrt phase

$$S(t+t_s) \quad \overset{FT}{\Longleftrightarrow} \quad S(\omega)e^{-i\omega t_s}, \qquad \text{“time shifting”}$$

$$S(t)e^{i\omega_s t} \quad \overset{FT}{\Longleftrightarrow} \quad S(\omega+\omega_s), \qquad \text{“frequency shifting”}$$

$$S(\phi+\phi_s) \quad \overset{FT}{\Longleftrightarrow} \quad S(\Delta p)e^{-i\Delta p\,\phi_s}, \qquad \text{“}\phi\text{ shifting”}$$

$$S(\phi)e^{i\Delta p_s\,\phi} \quad \overset{FT}{\Longleftrightarrow} \quad S(\Delta p+\Delta p_s), \qquad \text{“}\Delta p\text{ shifting”}$$

Phase Cycling: Avoiding the FT wrt phase

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$$S(\phi+\phi_s) \quad \overset{FT}{\Longleftrightarrow} \quad S(\Delta p)e^{-i\Delta p\,\phi_s}, \qquad \text{“}\phi\text{ shifting”}$$

$$\boxed{S(\phi)e^{i\Delta p_s\,\phi} \quad \overset{FT}{\Longleftrightarrow} \quad S(\Delta p+\Delta p_s), \qquad \text{“}\Delta p\text{ shifting”}}$$

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 ϕ_1 dimension to shift the $\Delta p_{1,\text{desired}}$ signal to $\Delta p_1 = 0$, before projecting over ϕ_1.

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

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

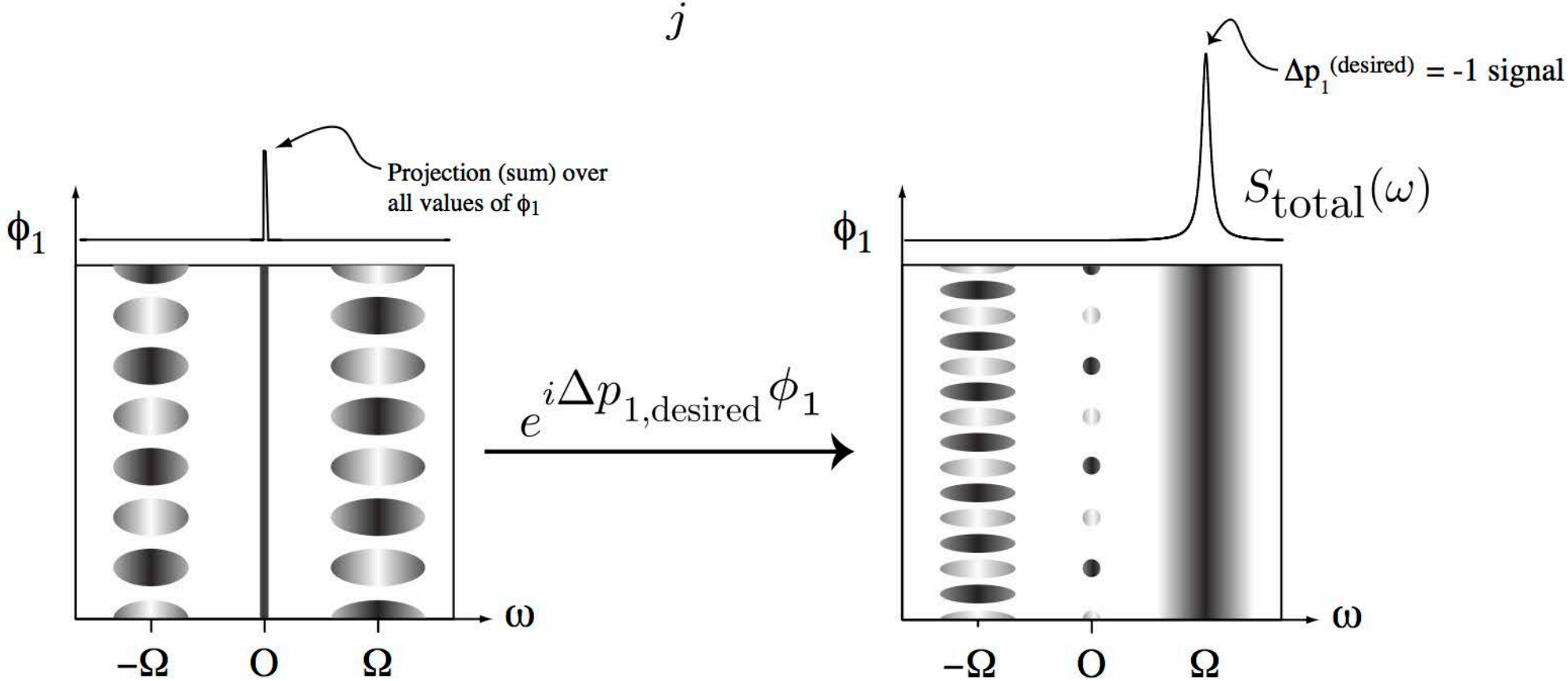
$$\phi_R^{(j)} = -\Delta p_{1,\text{desired}} \phi_1^{(j)}$$

receiver phase

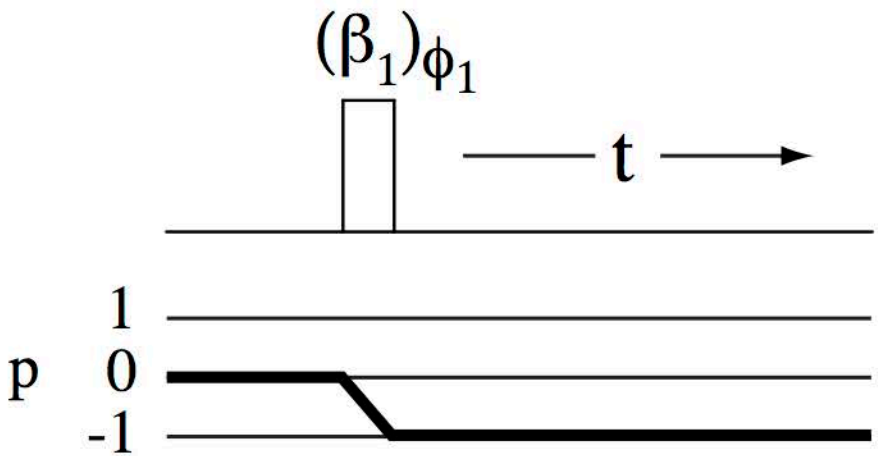
Phase Cycling: Avoiding the FT wrt phase

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



$$\Delta p_{1,\text{desired}} = -1$$

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

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

$$\Delta\phi_1 = 2\pi/3$$

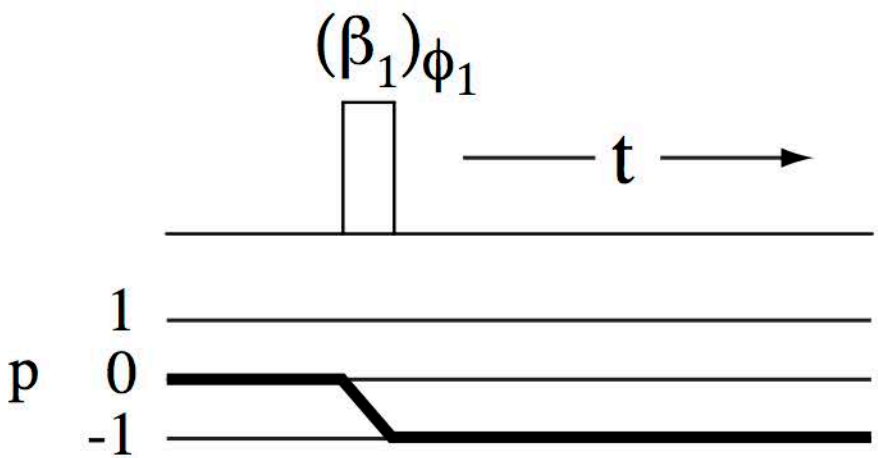
$$\boxed{\begin{array}{rcccc} \phi_1 & = & 0^\circ & 120^\circ & 240^\circ, \\ \phi_R & = & 0^\circ & 120^\circ & 240^\circ. \end{array}}$$

Verify

$$S_{\text{total}}(t) = \sum_j^3 \left(a e^{-i\Omega t} e^{i\phi_1^{(j)}} + b e^{i\Omega t} e^{-i\phi_1^{(j)}} + \text{constant} \right) e^{-i\phi_R^{(j)}},$$

with $\Delta p_{1,\text{desired}} = -1$ reduces to our desired signal, $\boxed{S_{\text{total}}(t) = 3ae^{-i\Omega t}.}$

Phase Cycling: One Pulse & Acquire



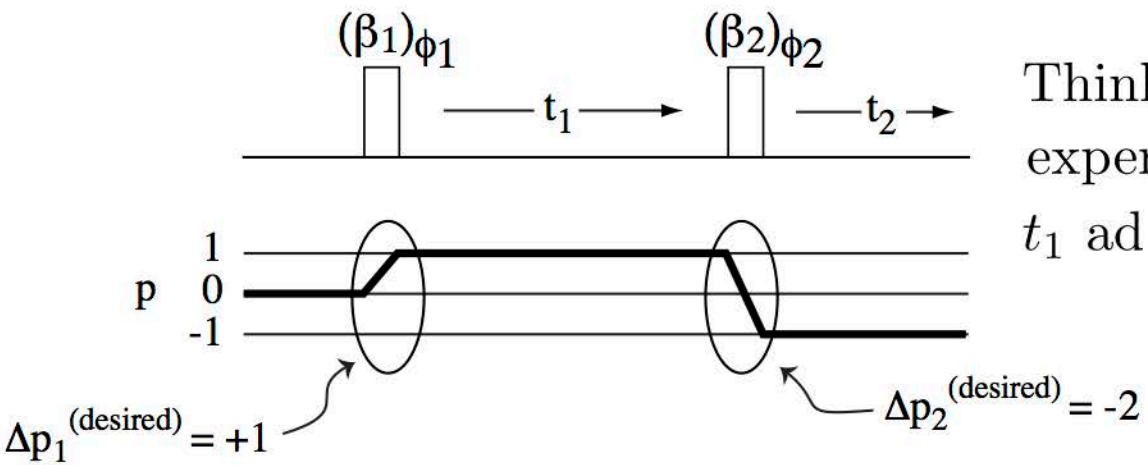
$$\Delta p_{1,\text{desired}} = -1$$

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

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

$$\begin{aligned} \phi_1 &= 0^\circ \quad 90^\circ \quad 180^\circ \quad 270^\circ, \\ \phi_R &= 0^\circ \quad 90^\circ \quad 180^\circ \quad 270^\circ. \end{aligned}$$

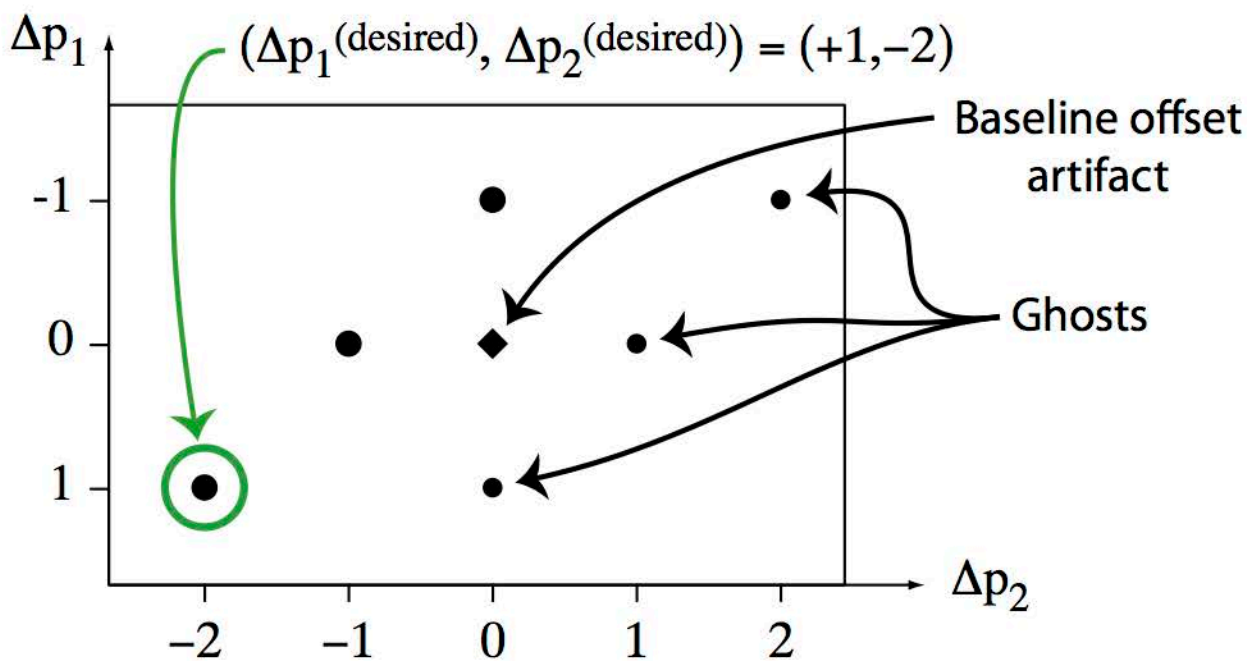
Two Pulse Sequence (Spin 1/2)



Think of this as a four-dimensional experiment that is a function of two times, t_1 ad t_2, and two phases, ϕ_1 and ϕ_2.

After 2D Fourier Transform wrt ϕ_1 and ϕ_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?

Two Pulse Sequence (Spin 1/2)

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

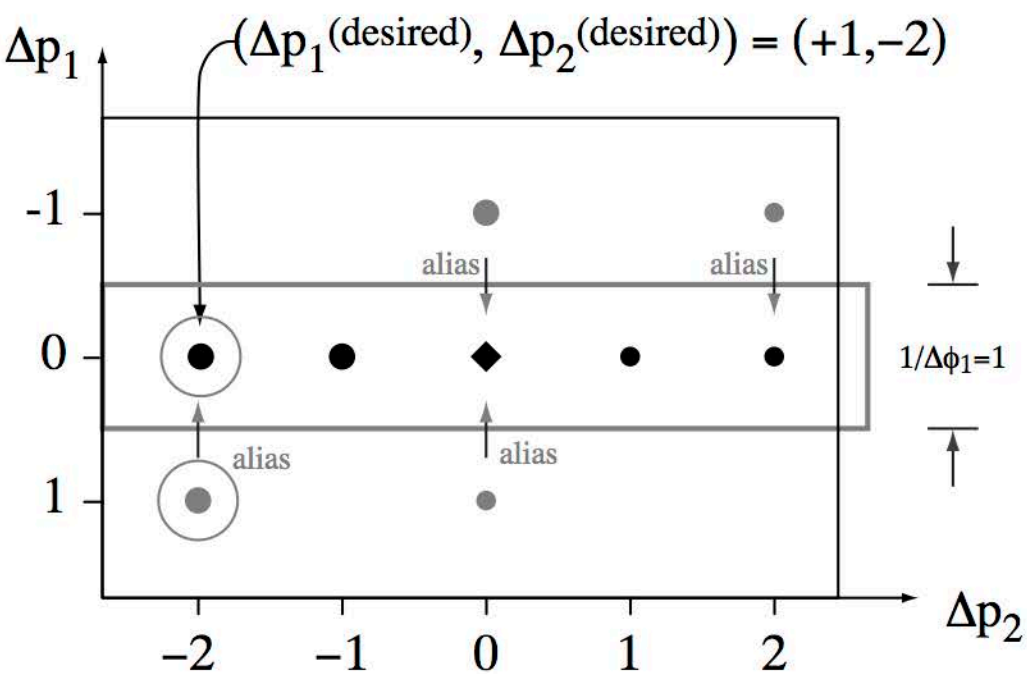
We don't need to separate all signals from each other, only the desired from the undesired. We don't care if undesired signals get aliased onto each other.

Two Pulse Sequence (Spin 1/2)

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 ϕ_1 at all, and let all Δp_1 alias onto $\Delta p_1=0$.

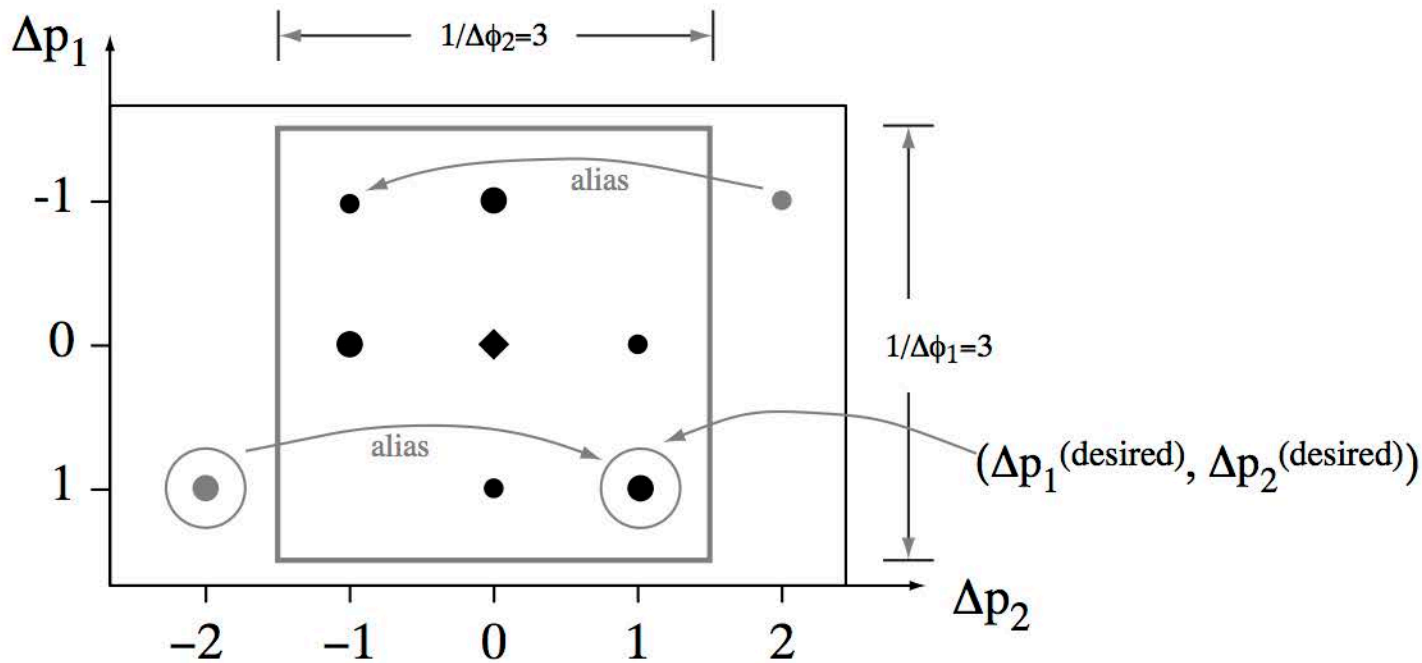


This works since nothing aliases onto the desired signal.

$$
\begin{aligned}
\phi_1 &= 0^\circ, \\
\phi_2 &= 0^\circ \quad 72^\circ \quad 144^\circ \quad 216^\circ \quad 288^\circ, \\
\phi_R &= 0^\circ \quad 144^\circ \quad 288^\circ \quad 72^\circ \quad 216^\circ,
\end{aligned}
$$

Two Pulse Sequence (Spin 1/2)

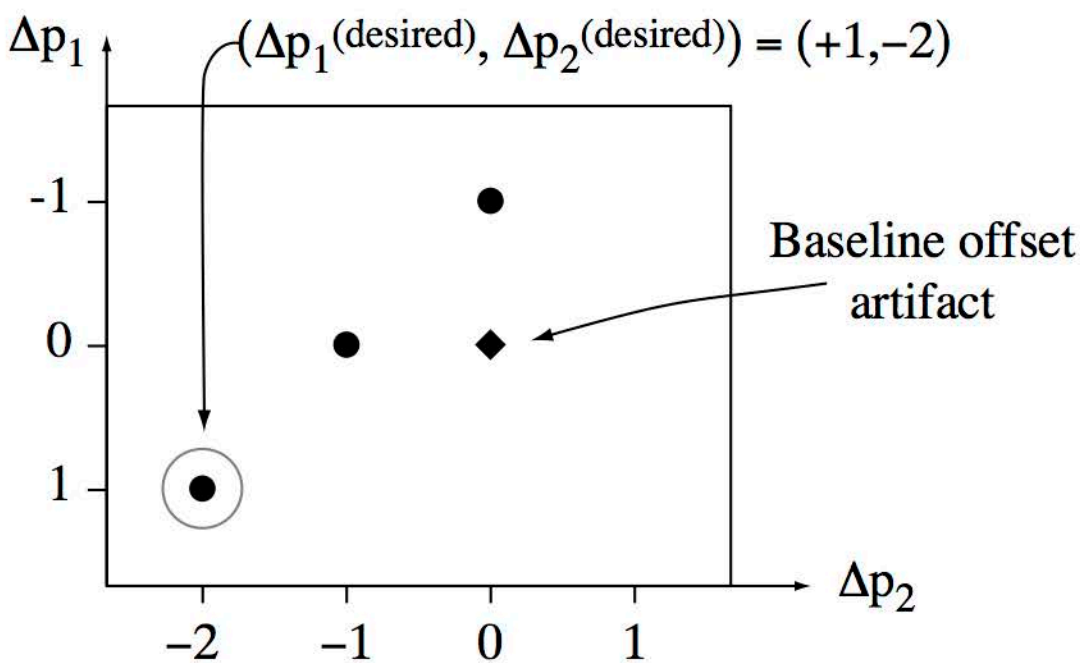
Alternatively, if we phase cycled ϕ_1 with $n_1=3$, then our desired signal would still be unaliased with n_2 as low as $n_2 = 3$.



$$
\begin{array}{lcccccccccc}
\phi_1 & = & 0^\circ & 120^\circ & 240^\circ & 0^\circ & 120^\circ & 240^\circ & 0^\circ & 120^\circ & 240^\circ, \\
\phi_2 & = & 0^\circ & 0^\circ & 0^\circ & 120^\circ & 120^\circ & 120^\circ & 240^\circ & 240^\circ & 240^\circ, \\
\phi_R & = & 0^\circ & 240^\circ & 120^\circ & 240^\circ & 120^\circ & 0^\circ & 120^\circ & 0^\circ & 240^\circ,
\end{array}
$$

Two Pulse Sequence (Spin 1/2)

Without quadrature ghosts we can reduce sampling even more



$$\begin{aligned} \phi_1 &= 0^\circ \quad 120^\circ \quad 240^\circ, \\ \phi_2 &= 0^\circ \\ \phi_R &= 0^\circ \quad 240^\circ \quad 120^\circ, \end{aligned}$$

or

$$\begin{aligned} \phi_1 &= 0^\circ \\ \phi_2 &= 0^\circ \quad 120^\circ \quad 240^\circ, \\ \phi_R &= 0^\circ \quad 240^\circ \quad 120^\circ, \end{aligned}$$

Phase Cycling Two Pulses (Spin 1/2)

General approach is shift the desired signal to the origin of the (Δp_1, Δp_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 ϕ_1 and ϕ_2 to obtain the desired signal:

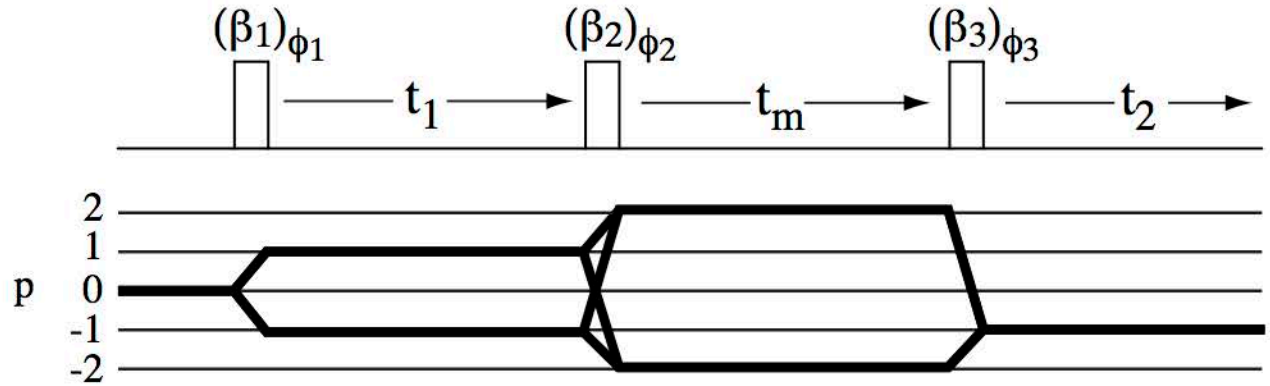
$$S_{\text{total}}(t_1, t_2) = \sum_j^{n_1}\sum_k^{n_2} S(\phi_1^{(j)}, \phi_2^{(k)}, t_1, t_2)e^{-i\phi_R^{(j,k)}}$$

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



$$\Delta p_1^{(\text{desired})} = \pm 1$$

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

$$\Delta p_3^{(\text{desired})} = -3, +1$$

$$\Delta p_1 = \underline{-\mathbf{1}}, (0), \underline{+\mathbf{1}} \qquad n_1 = 2$$

$$\Delta p_2 = \underline{-\mathbf{3}}, (-2), \underline{-\mathbf{1}}, (0), \underline{+\mathbf{1}}, (+2), \underline{+\mathbf{3}} \qquad n_2 = 2$$

$$\Delta p_3 = (-4), \underline{-\mathbf{3}}, (-2), (-1), (0), \underline{+\mathbf{1}}, (+2), (+3), (+4) \qquad n_3 = 4$$

Phase cycling of receiver

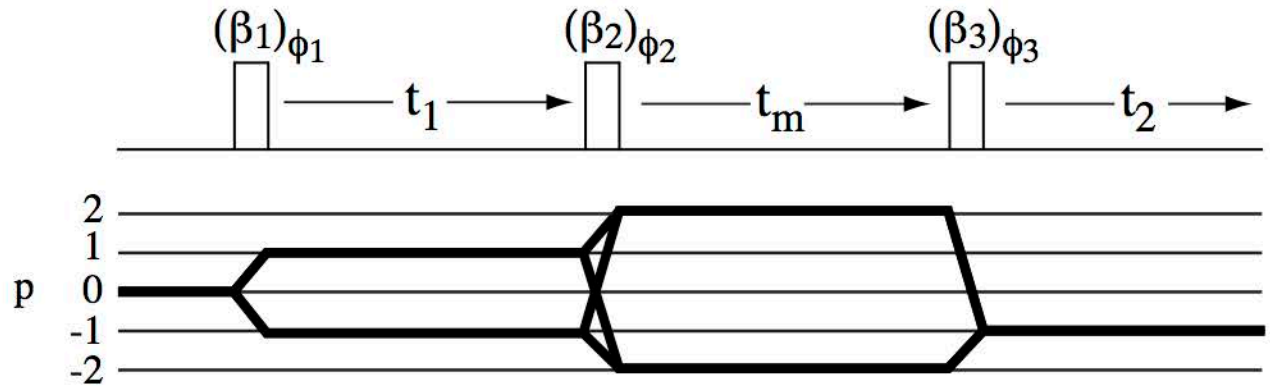
$$\phi_R = -\Delta p_1^{(\text{desired})}\phi_1 - \Delta p_2^{(\text{desired})}\phi_2 - \Delta p_3^{(\text{desired})}\phi_3$$

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 Δp_3



$$\Delta p_1^{(\text{desired})} = \pm 1$$

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

$$\Delta p_1 = \underline{-\mathbf{1}}, (0), \underline{+\mathbf{1}} \qquad n_1 = 2$$

$$\Delta p_2 = \underline{-\mathbf{3}}, (-2), \underline{-\mathbf{1}}, (0), \underline{+\mathbf{1}}, (+2), \underline{+\mathbf{3}} \qquad n_2 = 2$$

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

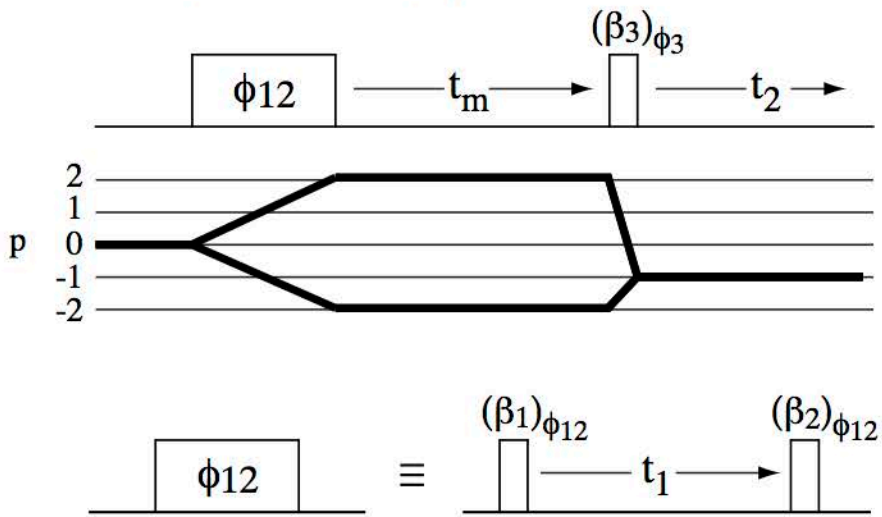
$$\begin{array}{lcllll} \phi_1 & = & 0^\circ & 180^\circ & 0^\circ & 180^\circ, \\ \phi_2 & = & 0^\circ & 0^\circ & 180^\circ & 180^\circ, \\ \phi_R & = & 0^\circ & 180^\circ & 180^\circ & 0^\circ. \end{array}$$

Avoid unnecessary phase dimensions and long phase cycles

- Have a well-tuned receiver so only p = -1 is detected.
- Use knowledge of forbidden Δp 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



$$\phi_R = -\Delta p_{12}^{(desired)}\phi_{12} - \Delta p_3^{(\mathrm{desired})}\phi_3,$$

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

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

use $n_{12} = 4$.

$$\boxed{\begin{array}{lcccccc} \phi_{12} & = & 0^\circ & 90^\circ & 180^\circ & 270^\circ, \\ \phi_R & = & 0^\circ & 180^\circ & 0^\circ & 180^\circ. \end{array}}$$

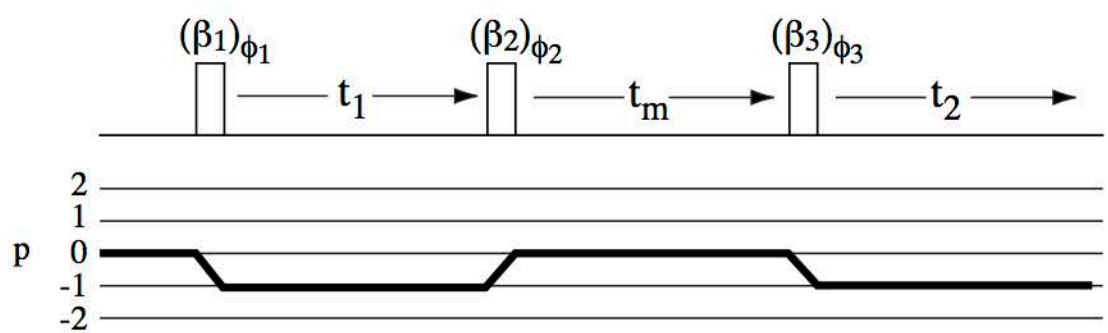
Avoid unnecessary phase dimensions and long phase cycles

- Use well calibrated pulse lengths

$$\hat{I}_+ \xrightarrow{\pi} \hat{I}_-$$
$$\hat{I}_- \xrightarrow{\pi} \hat{I}_+$$
$$\hat{I}_0 \xrightarrow{\pi} -\hat{I}_0$$

$$\hat{I}_0 \xrightarrow{\pi/2} c\left\{\hat{I}_+ \pm \hat{I}_-\right\}, \quad \text{i.e., no } \hat{I}_0 \text{ remaining after a } \pi/2 \text{ pulse.}$$

- Use differences between T_1 and T_2 to dephase undesired pathways



- Use gradients to selectively dephase and rephase pathways

Read ``Gradient-Enhanced Spectroscopy'', R. E. Hurd, *J. Magn. Reson.*, **87**, 422-428 (1990).

Summary

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,

$$\boldsymbol{\phi} = (\phi_1, \phi_2, \ldots, \phi_M). \tag{1}$$

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*,

$$\mathfrak{s}(\boldsymbol{\Delta}\mathbf{p}) = \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \cdots \int_0^{2\pi} d\phi_M \, \mathfrak{s}(\boldsymbol{\phi}) \, e^{i\boldsymbol{\Delta}\mathbf{p}\cdot\boldsymbol{\phi}}, \tag{2}$$

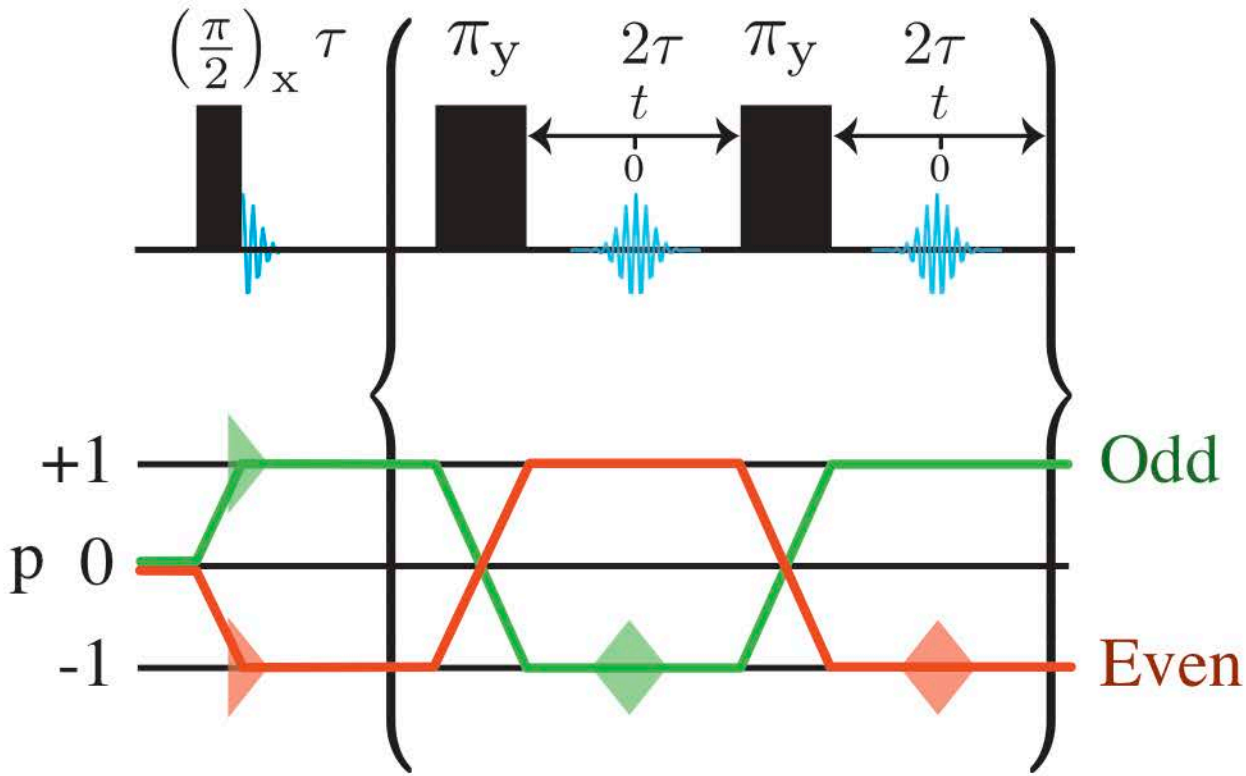
where $\boldsymbol{\Delta}\mathbf{p}$ is a coherence transfer pathway difference vector, with M elements,

$$\boldsymbol{\Delta}\mathbf{p} = (\Delta p_1, \Delta p_2, \ldots, \Delta p_M), \tag{3}$$

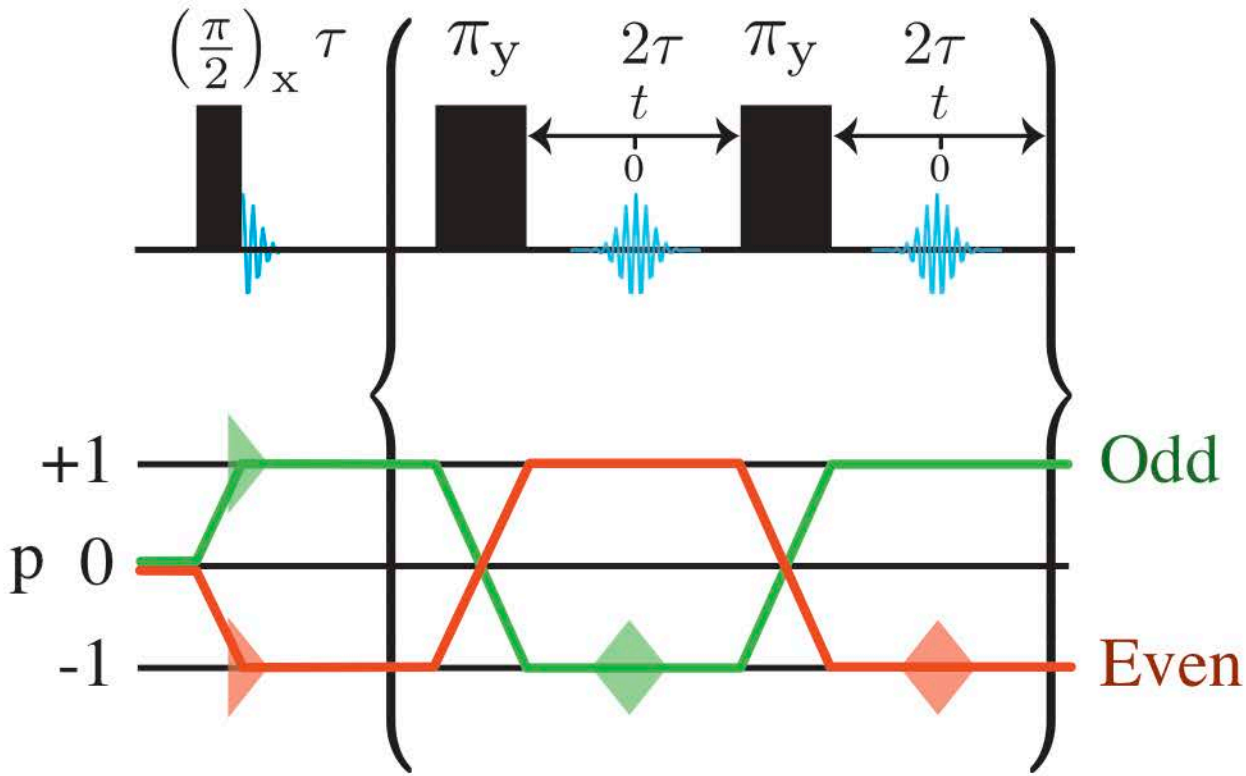
each given by $\Delta p_m = p_m - p_{m-1}$.

- Drobny, Pines, Sinton, Weitekamp, Wemmer, Symp. Faraday Soc. **13**, 93 (1980).
- Bodenhausen, Kogler, and Ernst, *J. Magn. Reson.*, **58**, 370(1984).

Carr-Purcell-Meiboom-Gill Acquisition

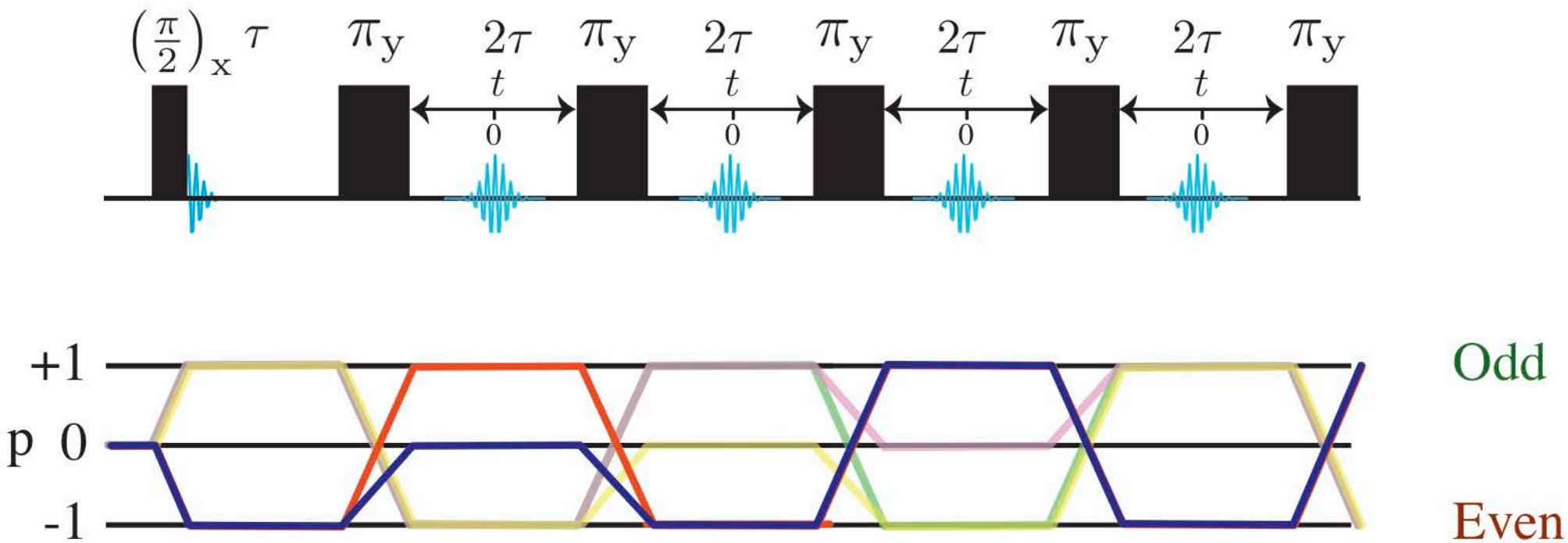


Carr-Purcell-Meiboom-Gill Acquisition



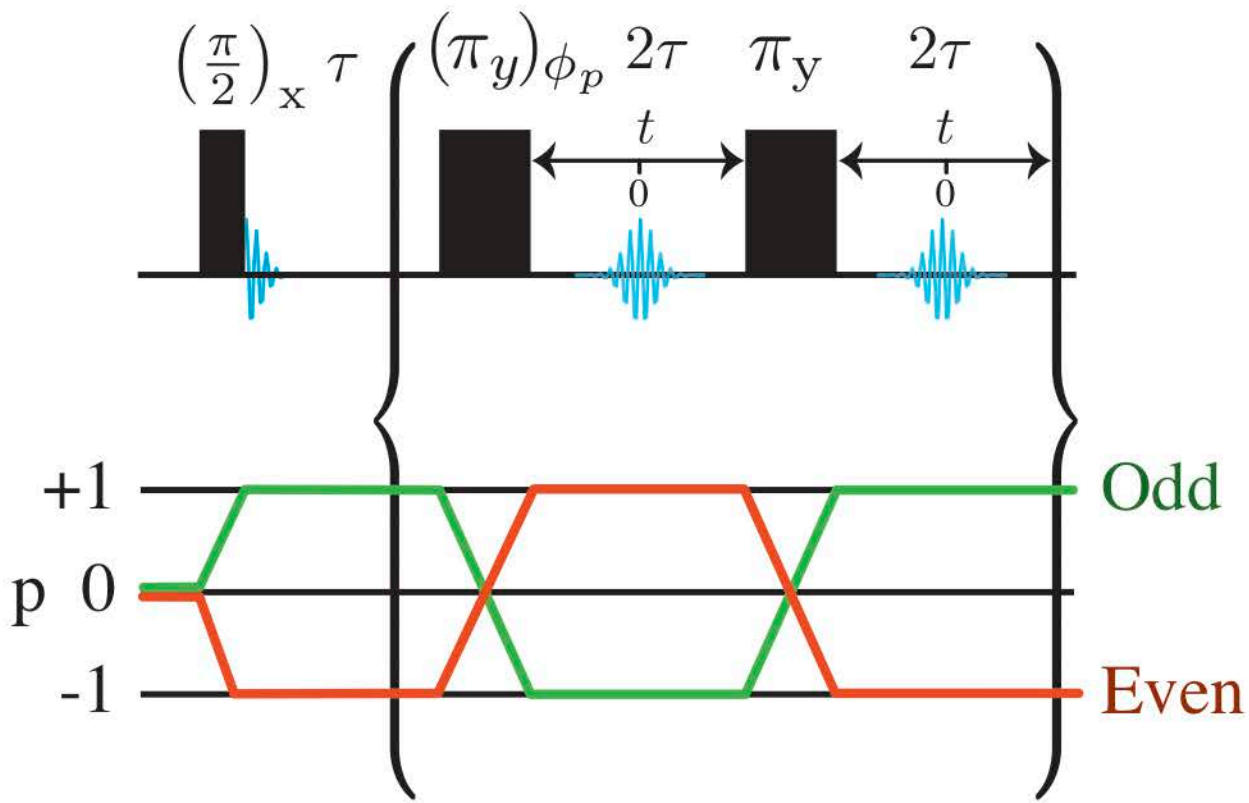
What's wrong with CPMG Acquisition?

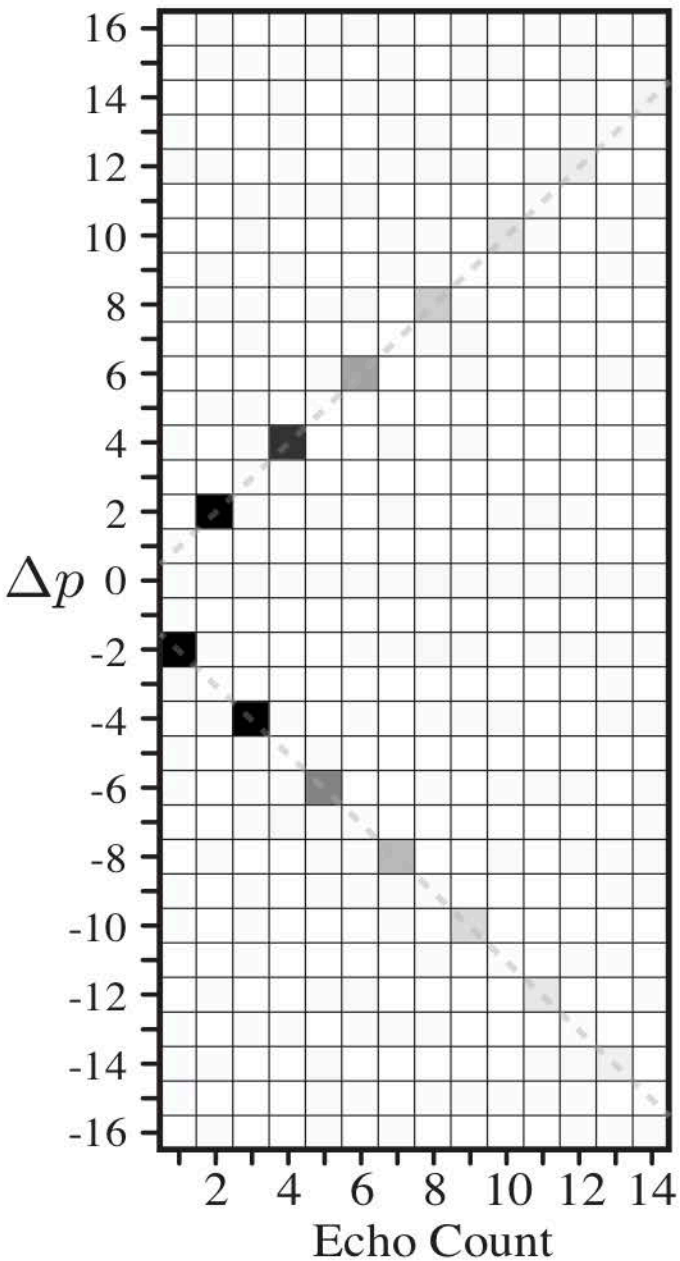
Carr-Purcell-Meiboom-Gill Acquisition



Unless you have perfect pathway selection you can have signal artifacts.

Phase Incremented Echo Train Acquisition

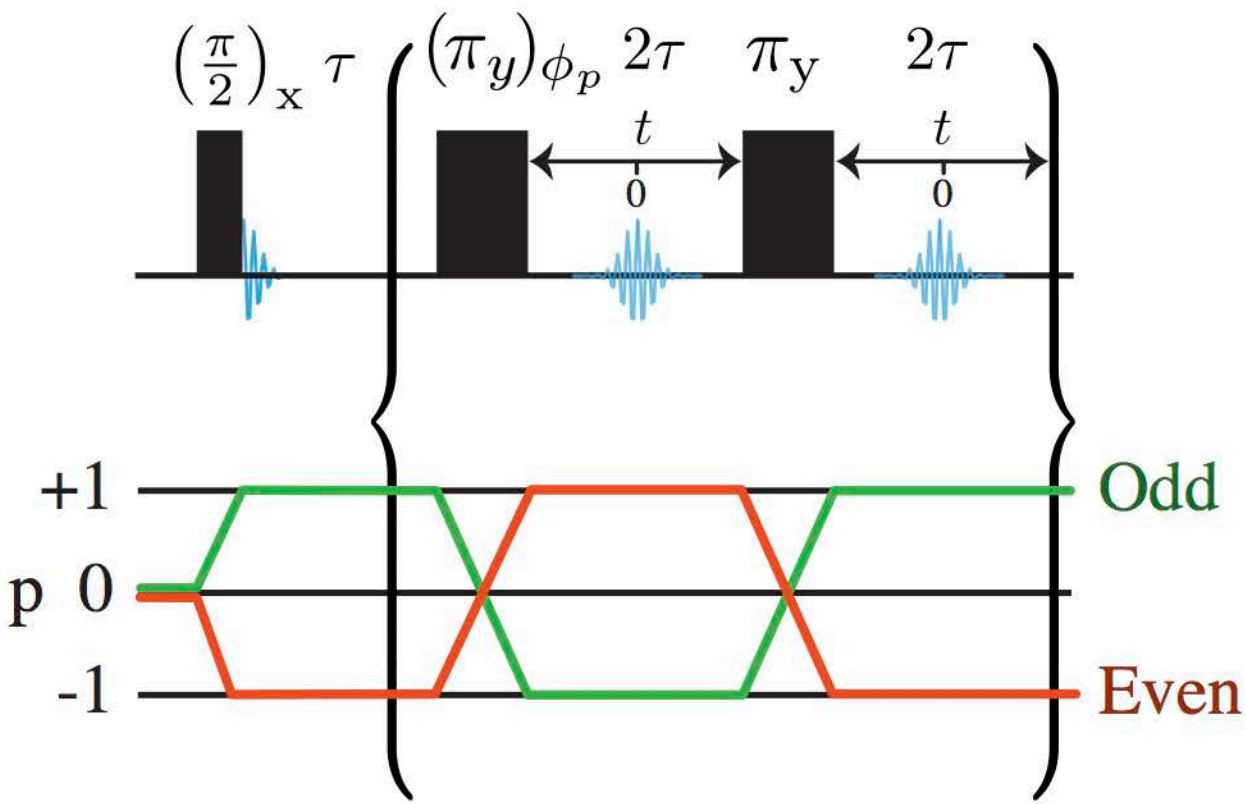


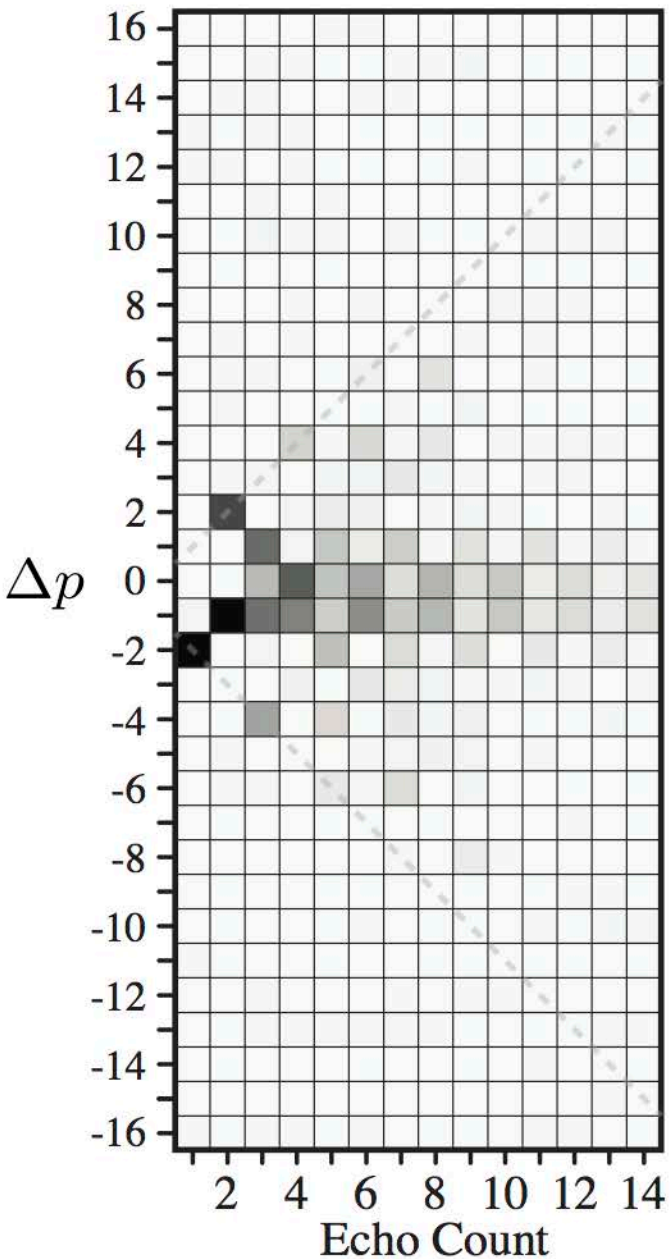


Simple Idea: A Fourier Transform with respect to pulse phase reveals the accumulated coherence change.

Baltisberger et al, *J. Chem. Phys.* **136** , 211104-1-4 (2012).
Phase incremented echo train acquisition in NMR spectroscopy

Phase Incremented Echo Train Acquisition
Example: Improper pulse lengths

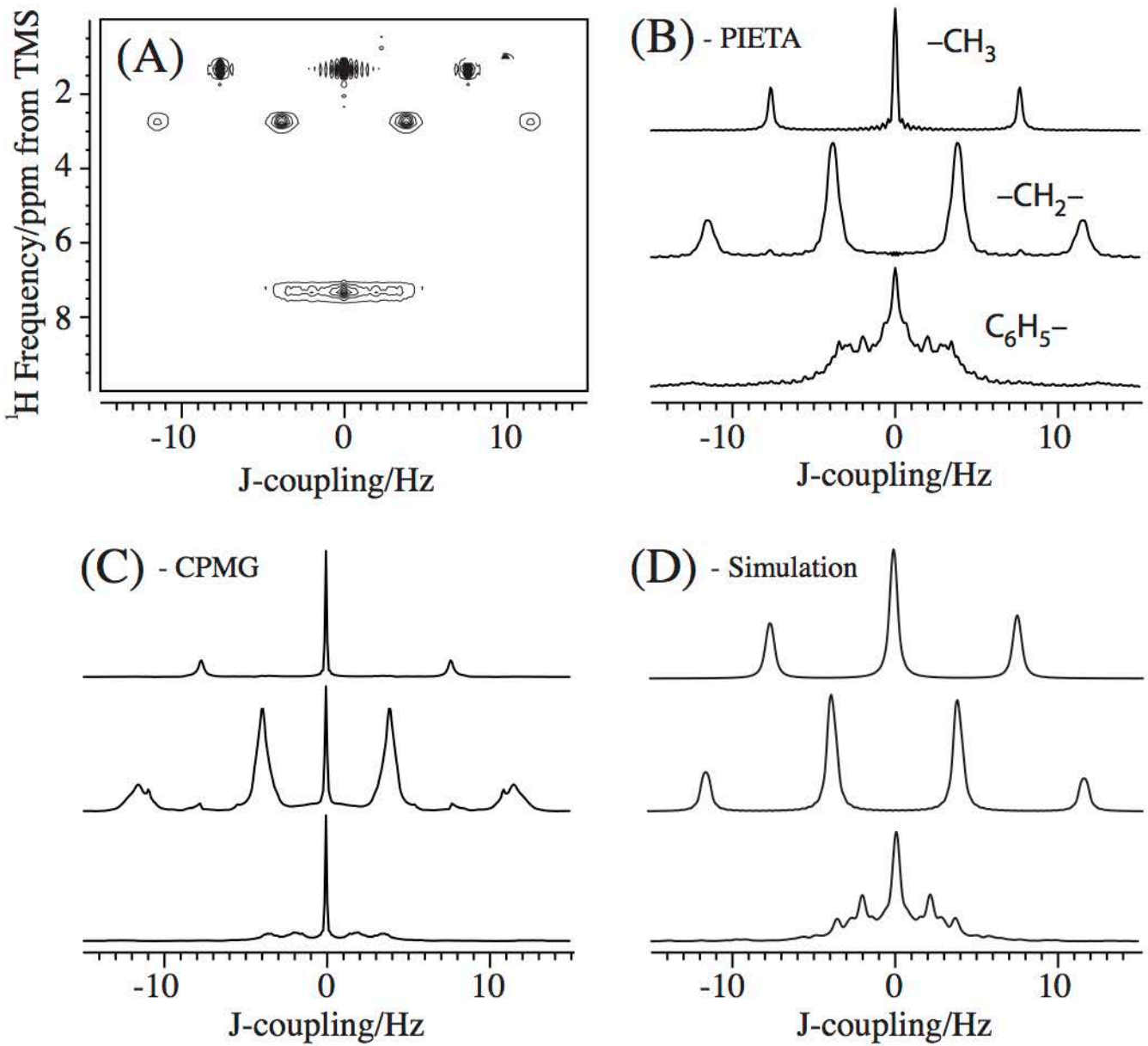




Simple Idea: A Fourier Transform with respect to pulse phase reveals the accumulated coherence change.

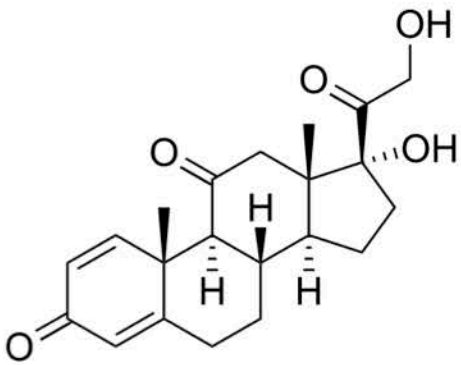
Baltisberger et al, *J. Chem. Phys.* **136** , 211104-1-4 (2012).
Phase incremented echo train acquisition in NMR spectroscopy

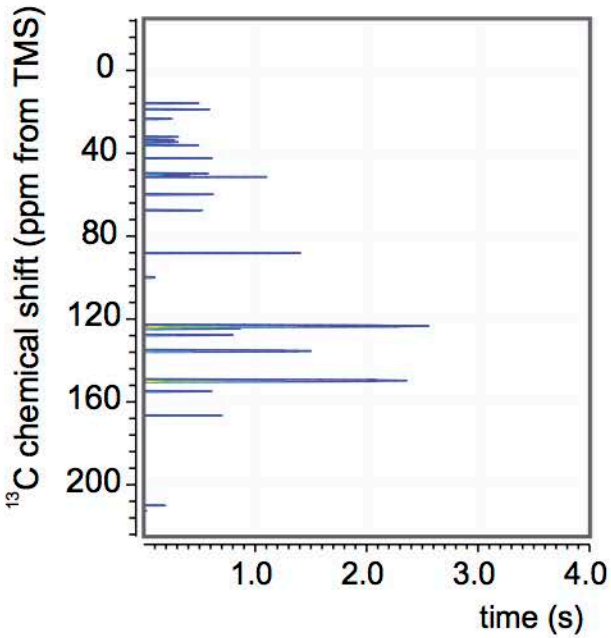
PIETA measures J Couplings accurately and faster

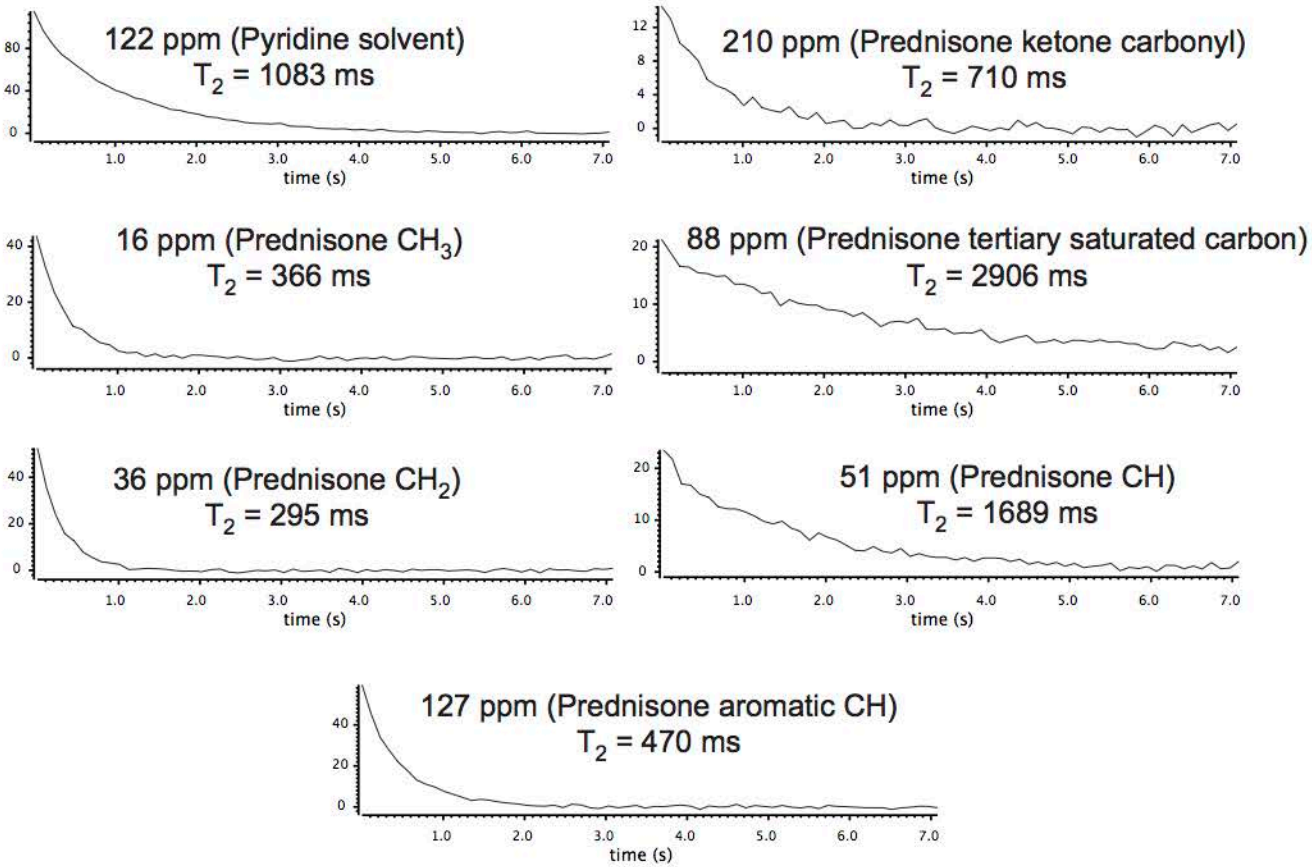


PIETA measures T_2 values accurately and faster

Prednisone ^{13}C T_2 times measured in a PIETA experiment.

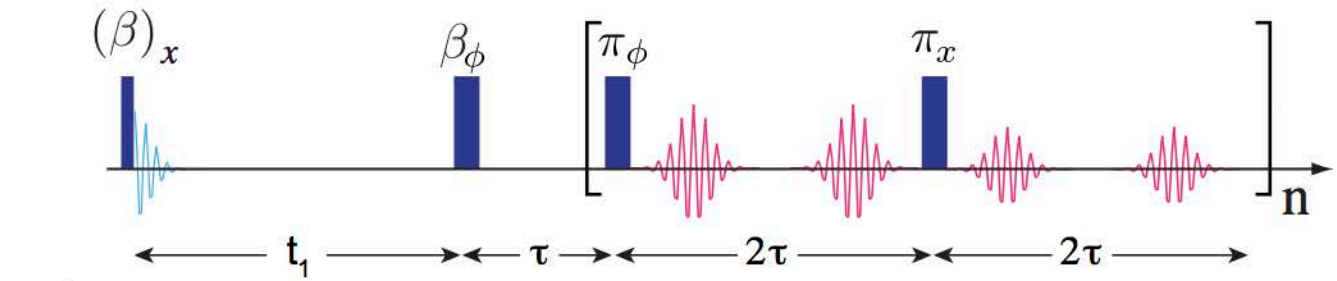


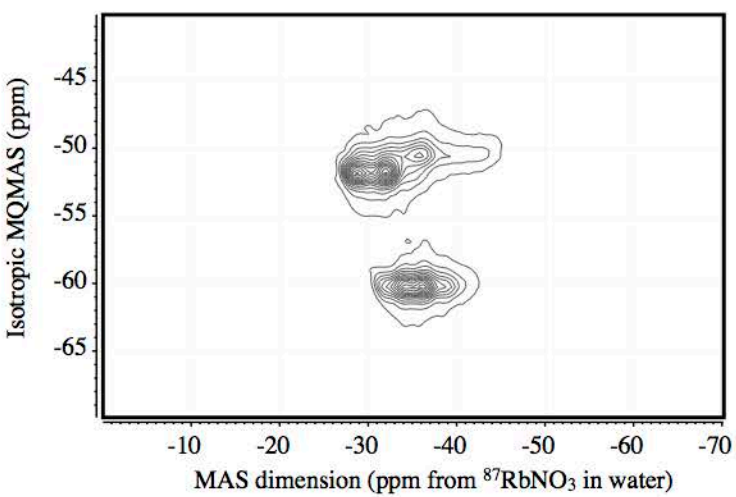


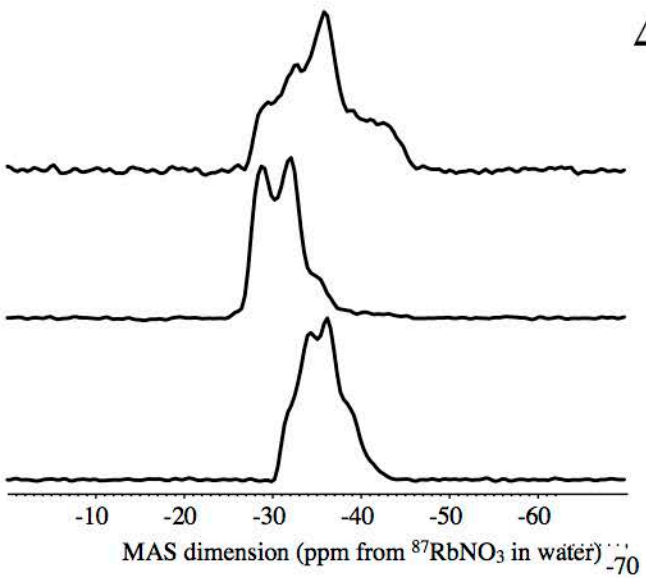


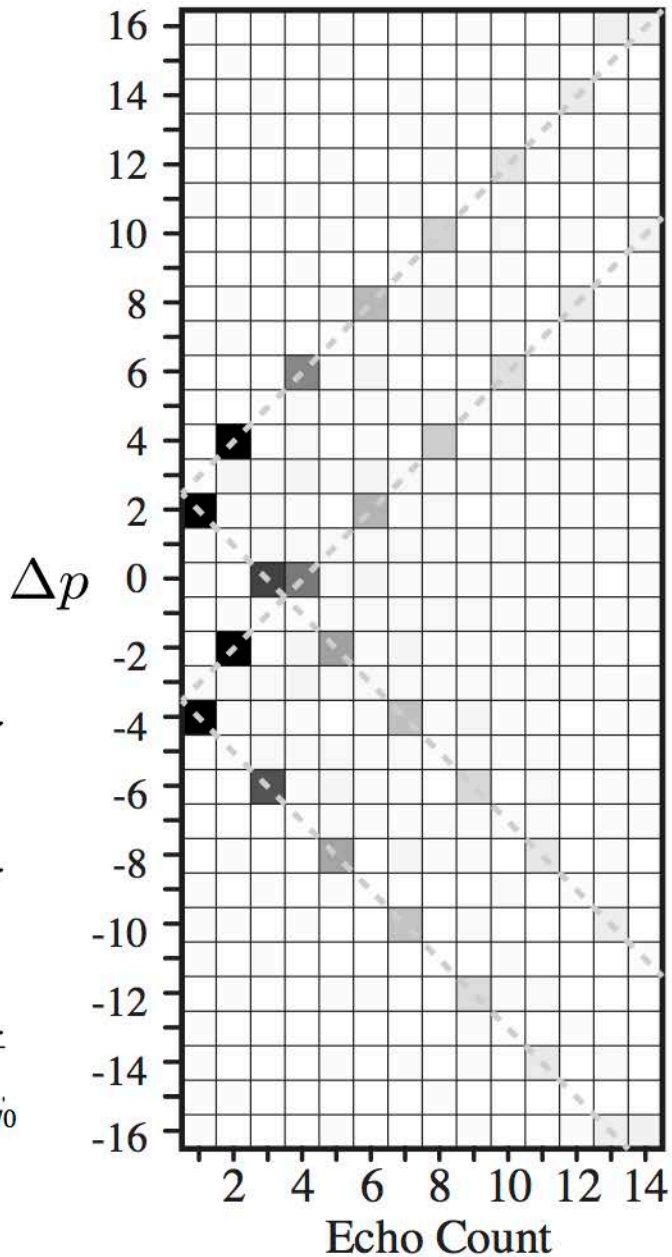
MQ-MAS-PIETA

MQ-MAS & Phase Incremented Echo Train Acquisition



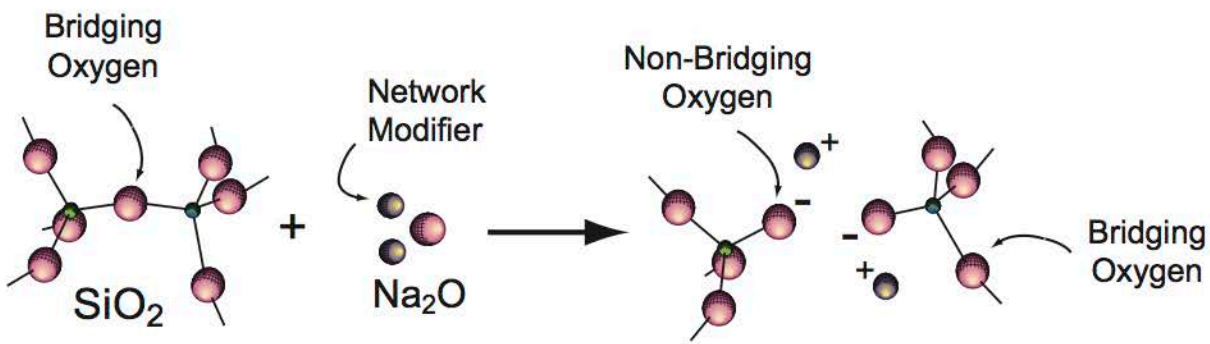


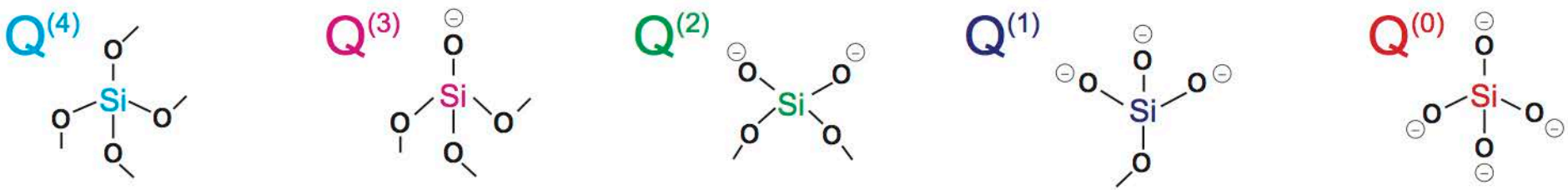




Baltisberger et al, *J. Chem. Phys.* **136** , 211104-1-4 (2012).
Phase incremented echo train acquisition in NMR spectroscopy

Quantifying $Q^{(N)}$ Species Distributions in Silicate Glasses





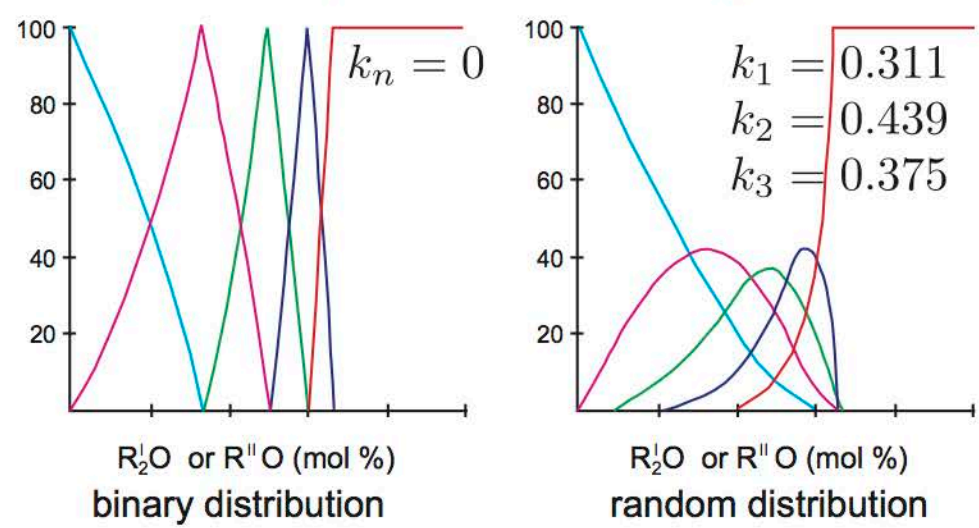
$Q^{(n)}$ Species Disproportionation

$$2\,Q^{(1)} \underset{}{\overset{k_1}{\rightleftharpoons}} Q^{(0)} + Q^{(2)} \qquad k_1 = \frac{[Q^{(2)}]\,[Q^{(0)}]}{[Q^{(1)}]^2}$$

$$2\,Q^{(2)} \overset{k_2}{\rightleftharpoons} Q^{(1)} + Q^{(3)} \qquad k_2 = \frac{[Q^{(3)}]\,[Q^{(1)}]}{[Q^{(2)}]^2}$$

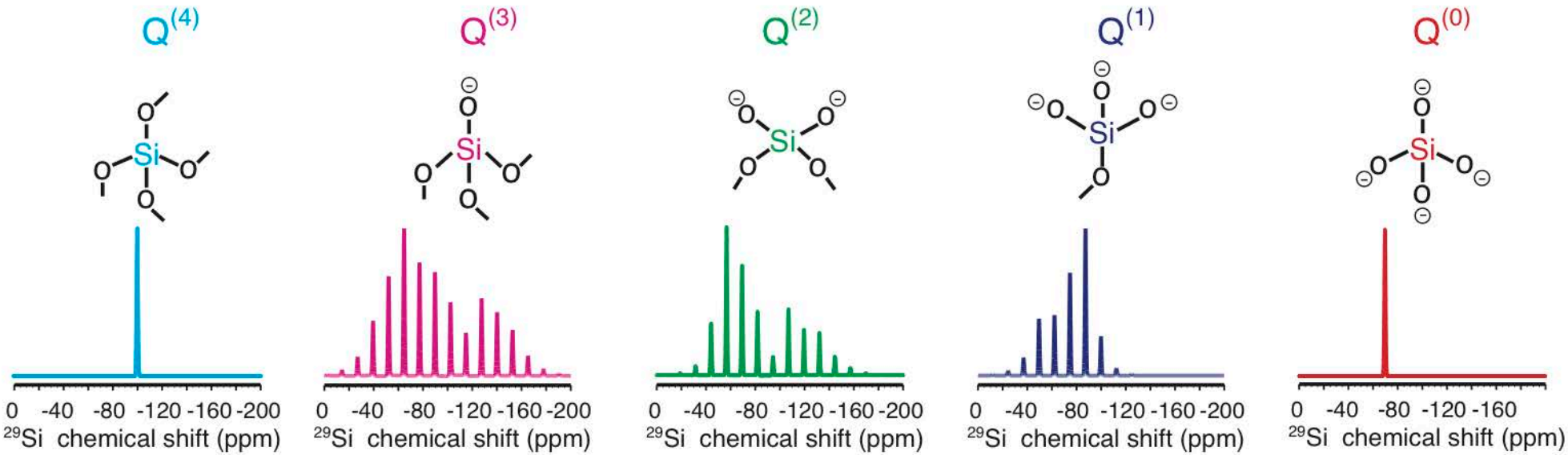
$$2\,Q^{(3)} \overset{k_3}{\rightleftharpoons} Q^{(2)} + Q^{(4)} \qquad k_3 = \frac{[Q^{(2)}]\,[Q^{(4)}]}{[Q^{(3)}]^2}$$

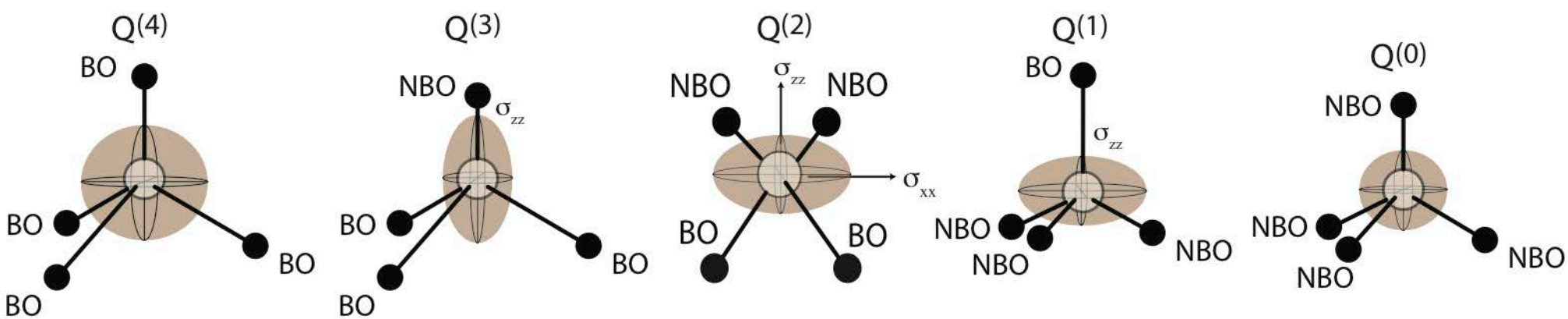
Dupree, Ford, and Holland,
Phys. Chem. Glasses, 28, 78(1987)



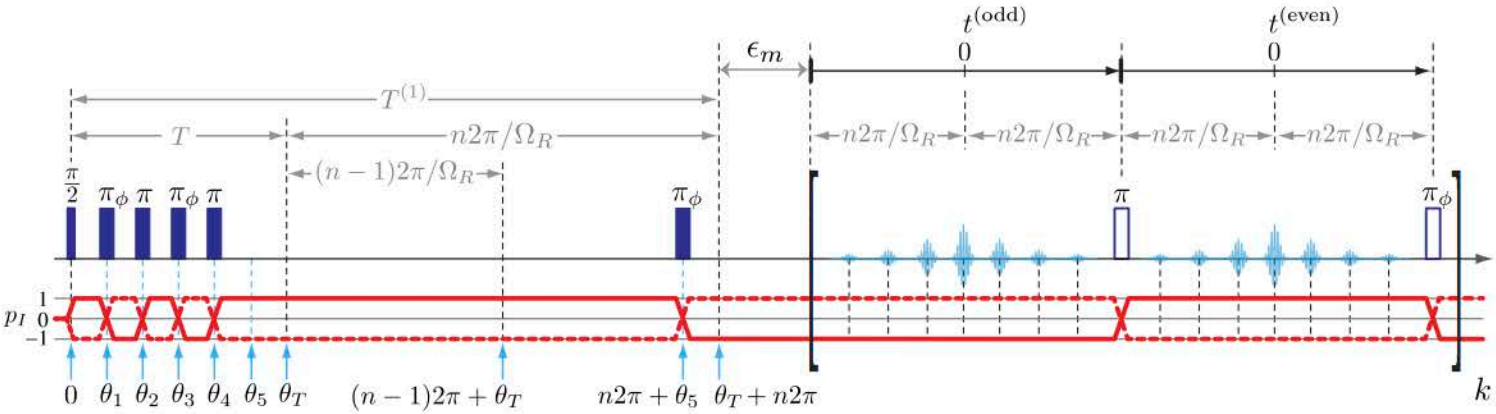
^{29}Si $Q^{(n)}$ Spinning Sideband Patterns

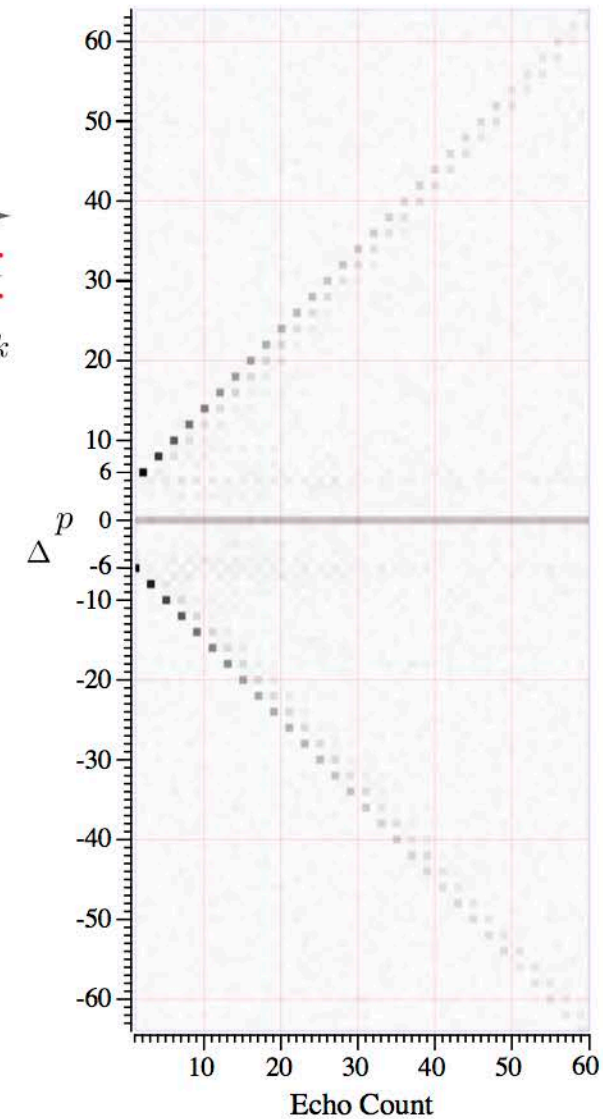
Our Goal: Develop Sensitive 2D PASS approach





2D PASS & PIETA





^{29}Si PASS NMR of Cu(II)-doped mixed potassium/magnesium tetrasilicate glass