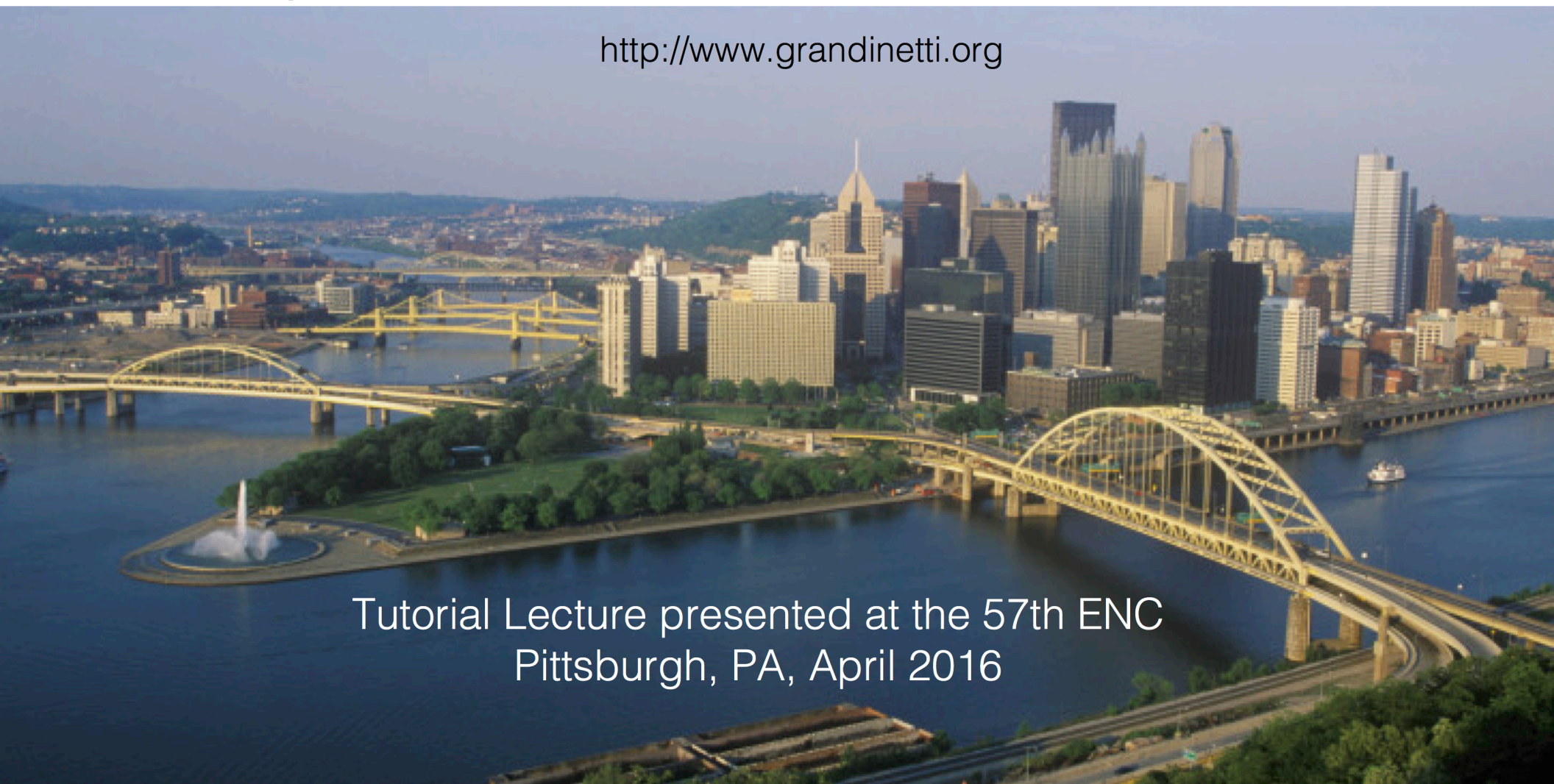


~~phase cycling~~ p pathway selection

Philip J. Grandinetti - Ohio State University

<http://www.grandinetti.org>



Tutorial Lecture presented at the 57th ENC
Pittsburgh, PA, April 2016

Two systematic approaches* for p pathway selection

- (1) exploit Fourier relationship between Δp and pulse phase
 - (A) easy way - via Fourier transform - which no one does
 - (B) hard way - via receiver phase cycling - which everyone does
- (2) use pulsed field gradients to selectively refocus p pathways

*sometimes both (1) and (2) can be combined for even better selection

Two systematic approaches* for p pathway selection

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 - (B) hard way - via receiver phase cycling - which everyone does
- (2) use pulsed field gradients to selectively refocus p pathways
 - see Hurd, "Gradient-enhanced spectroscopy," *J. Magn. Reson.*, **87**, 422 (1990).

Only 40 minutes for this talk, so I'll present (1A) but also post my notes for (1B) for those who want to learn more.

*sometimes both (1) and (2) can be combined for even better selection

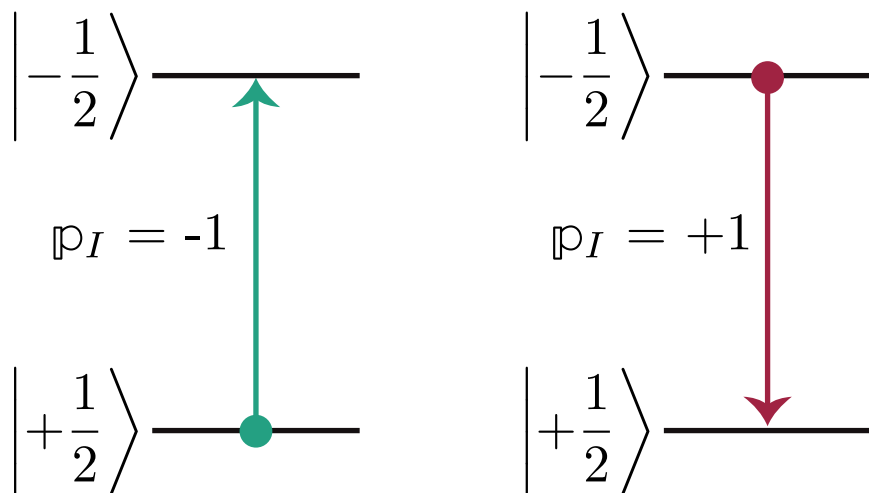
Step One

Identify the spin system,
its energy levels, and all transitions.

Let's look at some examples:

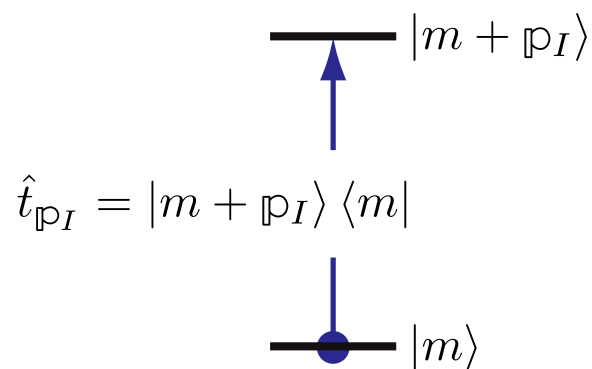
Example 1: Ensemble of Spin 1/2 Nuclei

Only two transitions for spin 1/2 nucleus.



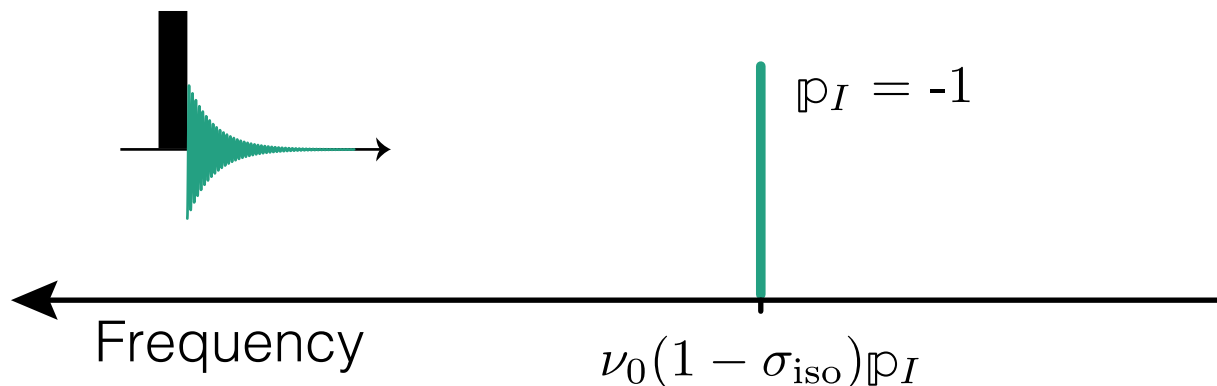
We classify transitions by coherence order

$$p_I(m_i, m_f) = m_f - m_i.$$



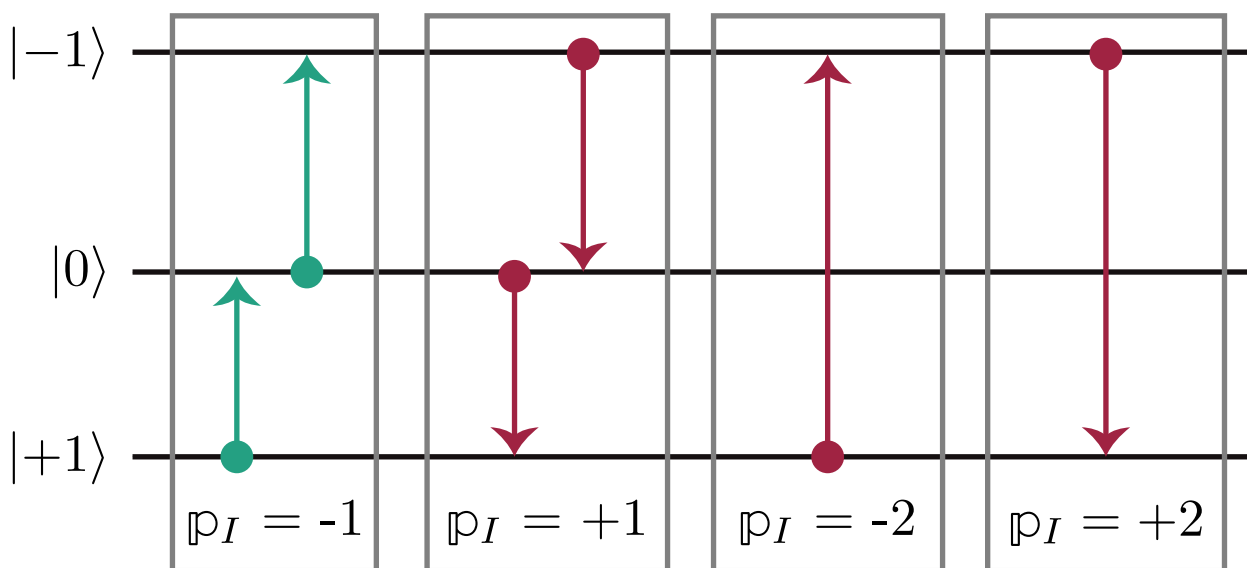
A single transition appears as a single line in a spectrum

Only transitions with $p_I = -1$ are detected.

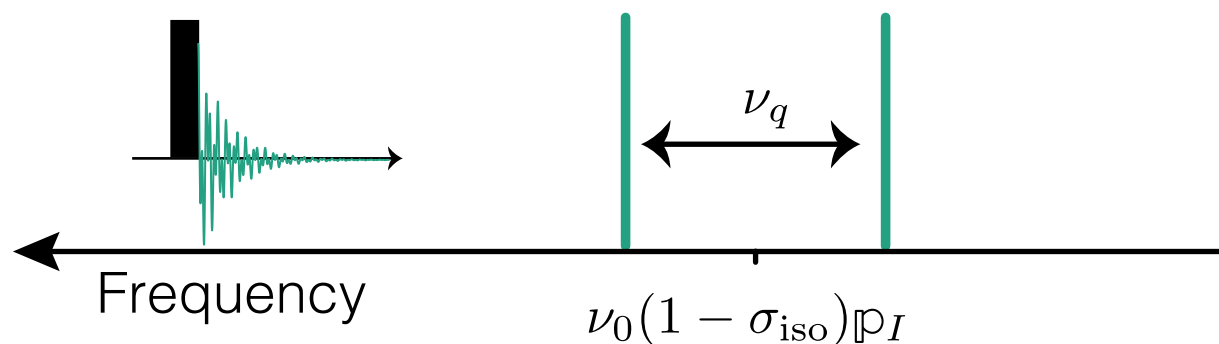


Example 2: Ensemble of Spin 1 Nuclei

Six transitions for spin 1 nucleus.

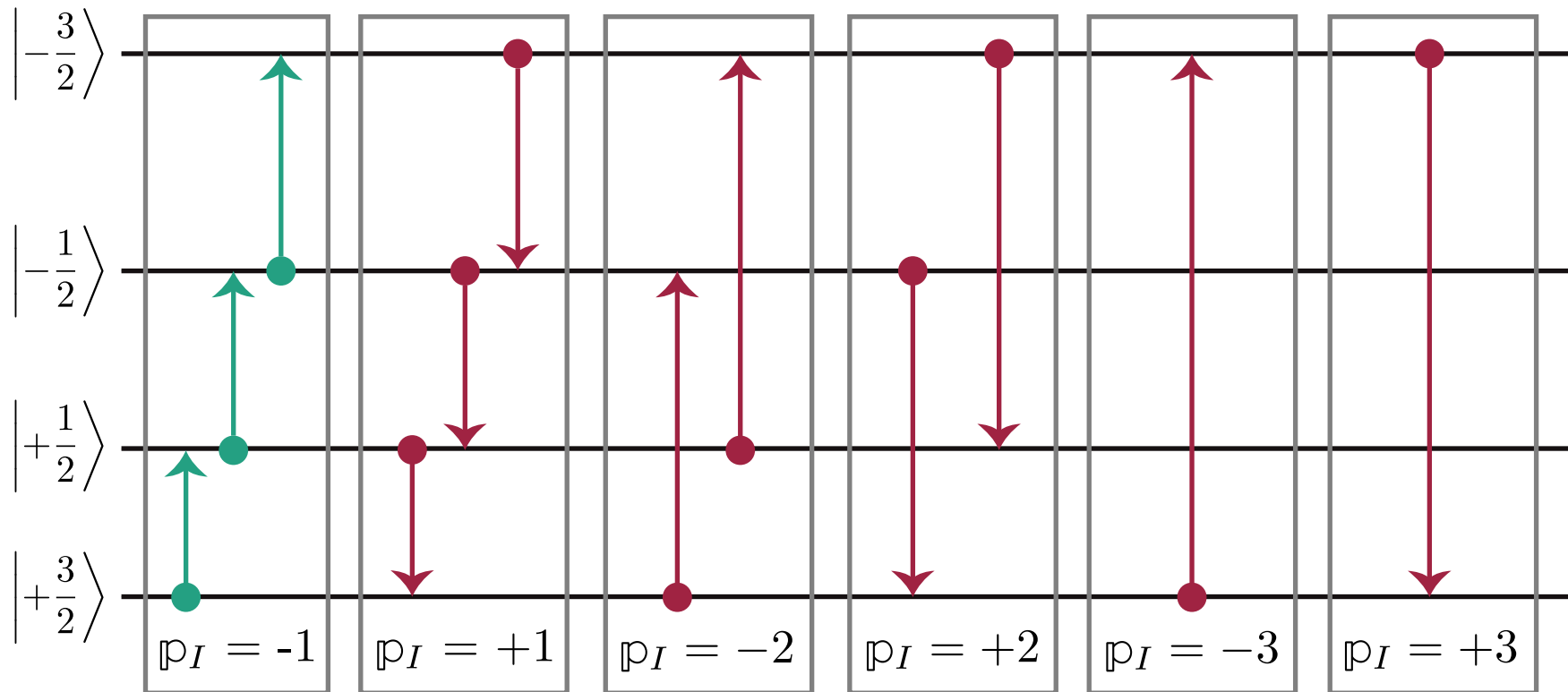


Only transitions with $p_I = -1$ are detected.

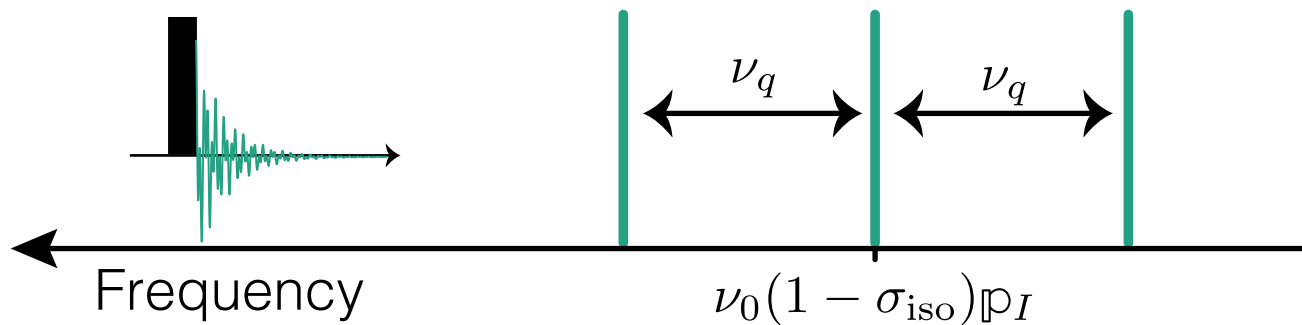


Example 3: Ensemble of Spin 3/2 Nuclei

12 transitions for spin 3/2 nucleus.

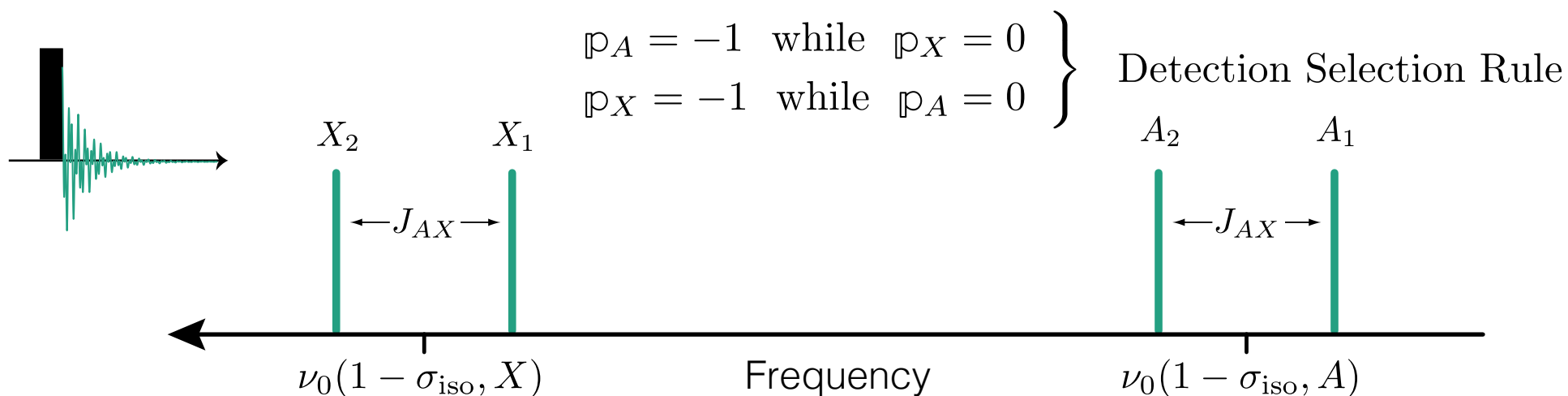
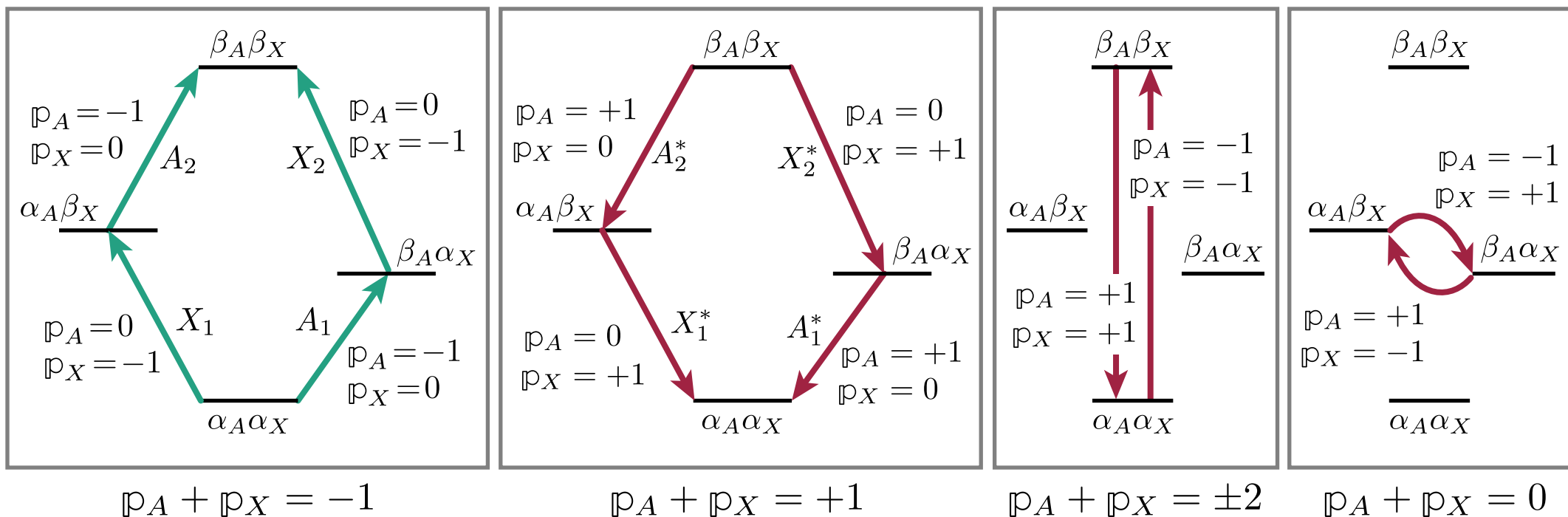


Only transitions with $p_I = -1$ are detected.

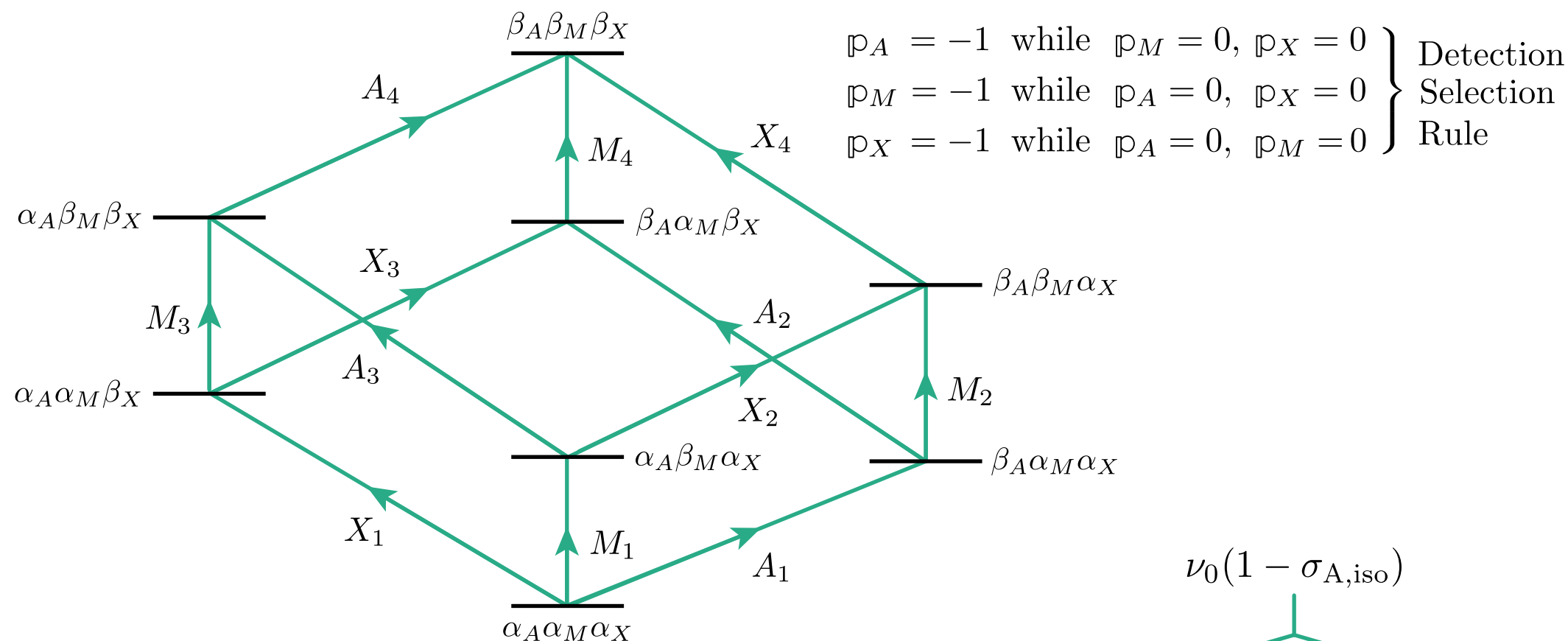


Example 4: Ensemble of two weakly coupling spin 1/2 nuclei

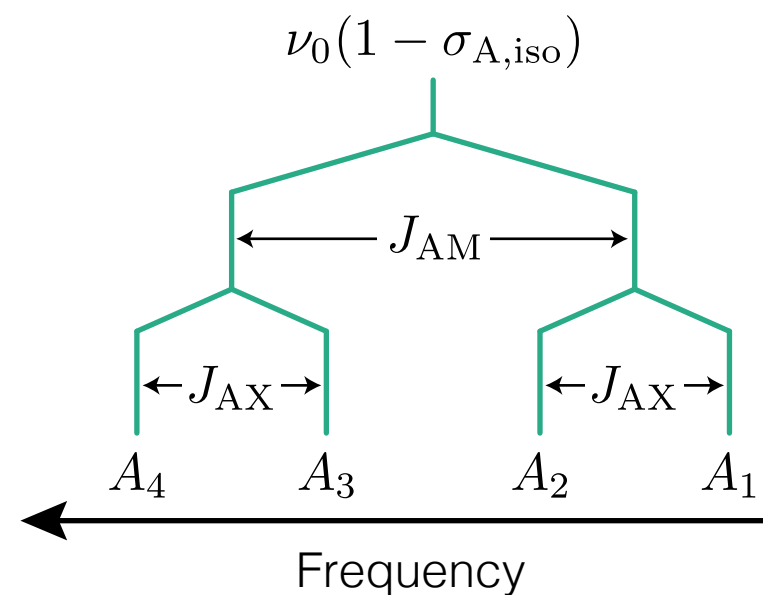
12 transitions for two weakly coupled spin 1/2 nuclei



Example 5: Ensemble of three weakly coupling spin 1/2 nuclei

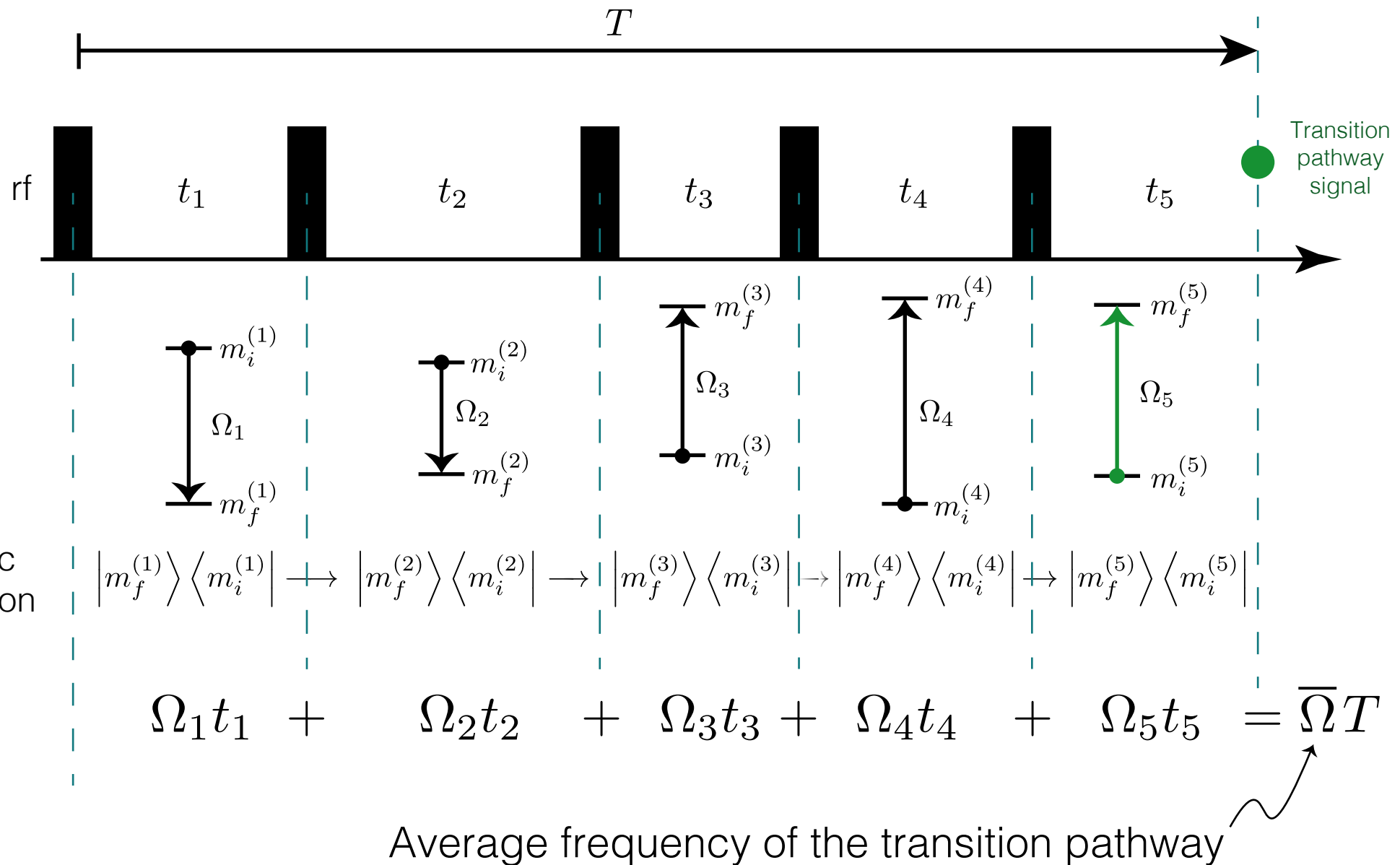


Assignment: Identify all the transitions with $\mathbb{P}_A + \mathbb{P}_M + \mathbb{P}_X = -1$, and determine how many are not directly observable.



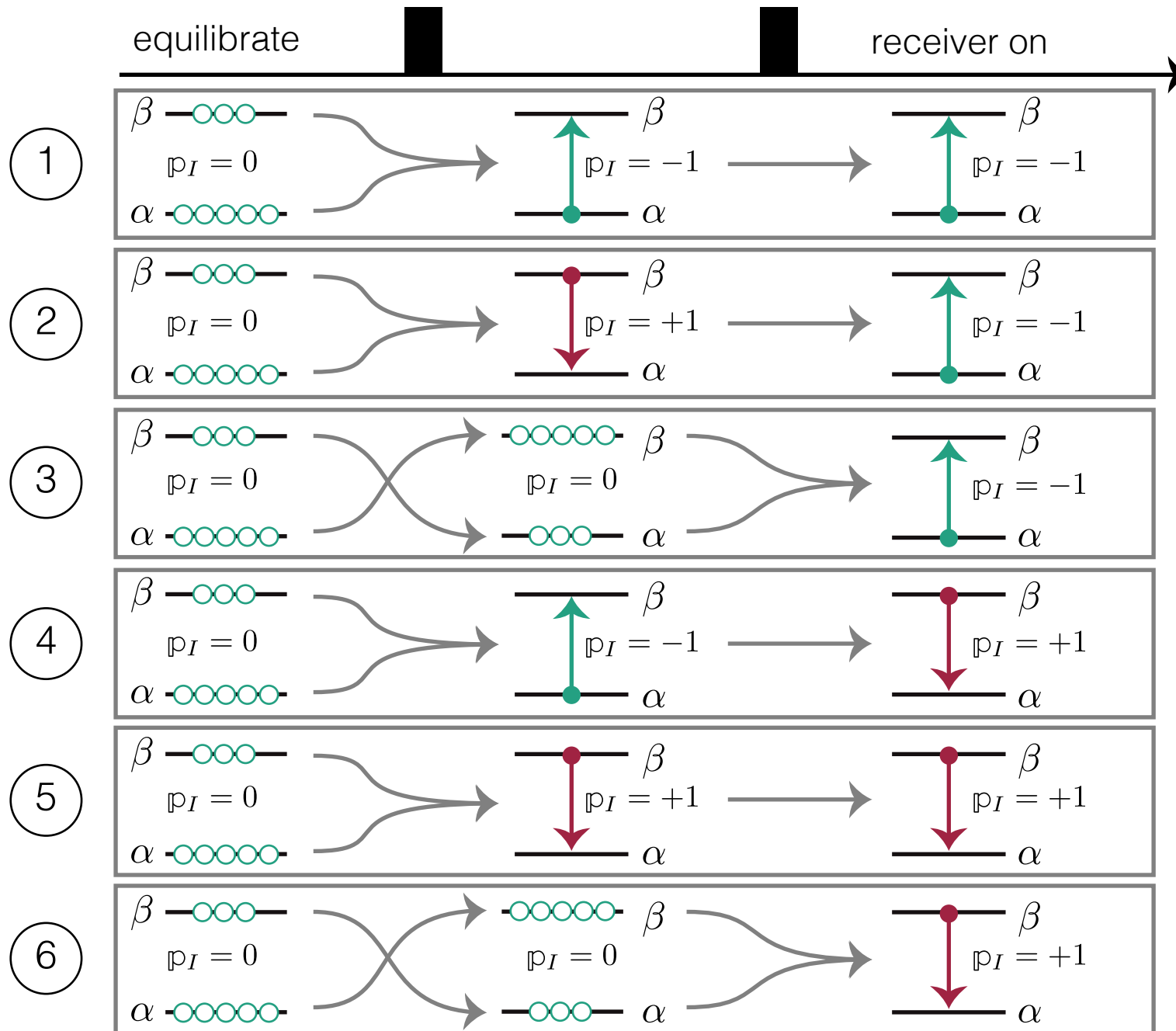
RF pulse transfers coherences between transitions

A pulse sequence generates a pathway of transitions



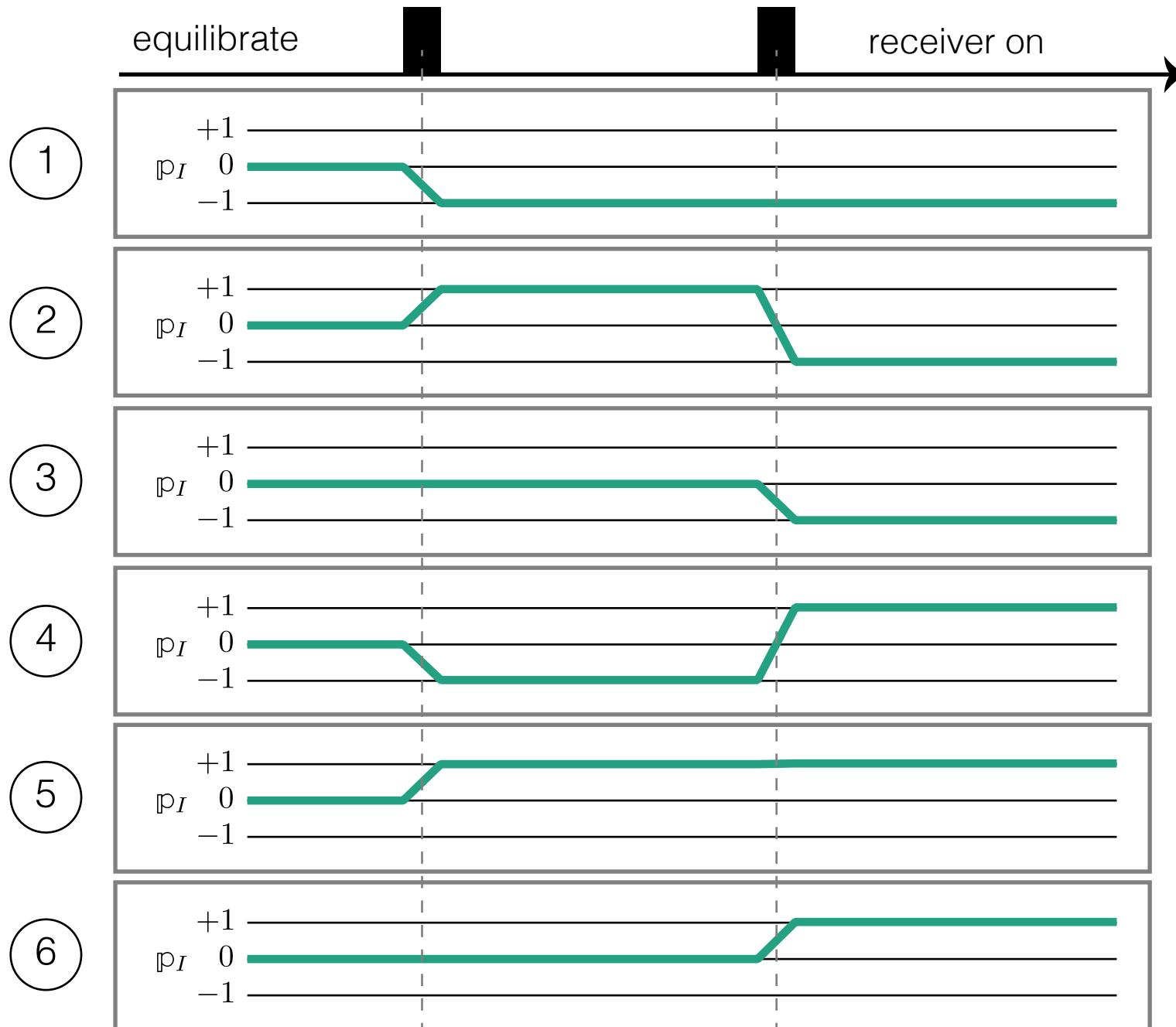
Two Pulse Transition Pathways for Spin 1/2 Case

How many transition pathways are **possible**?



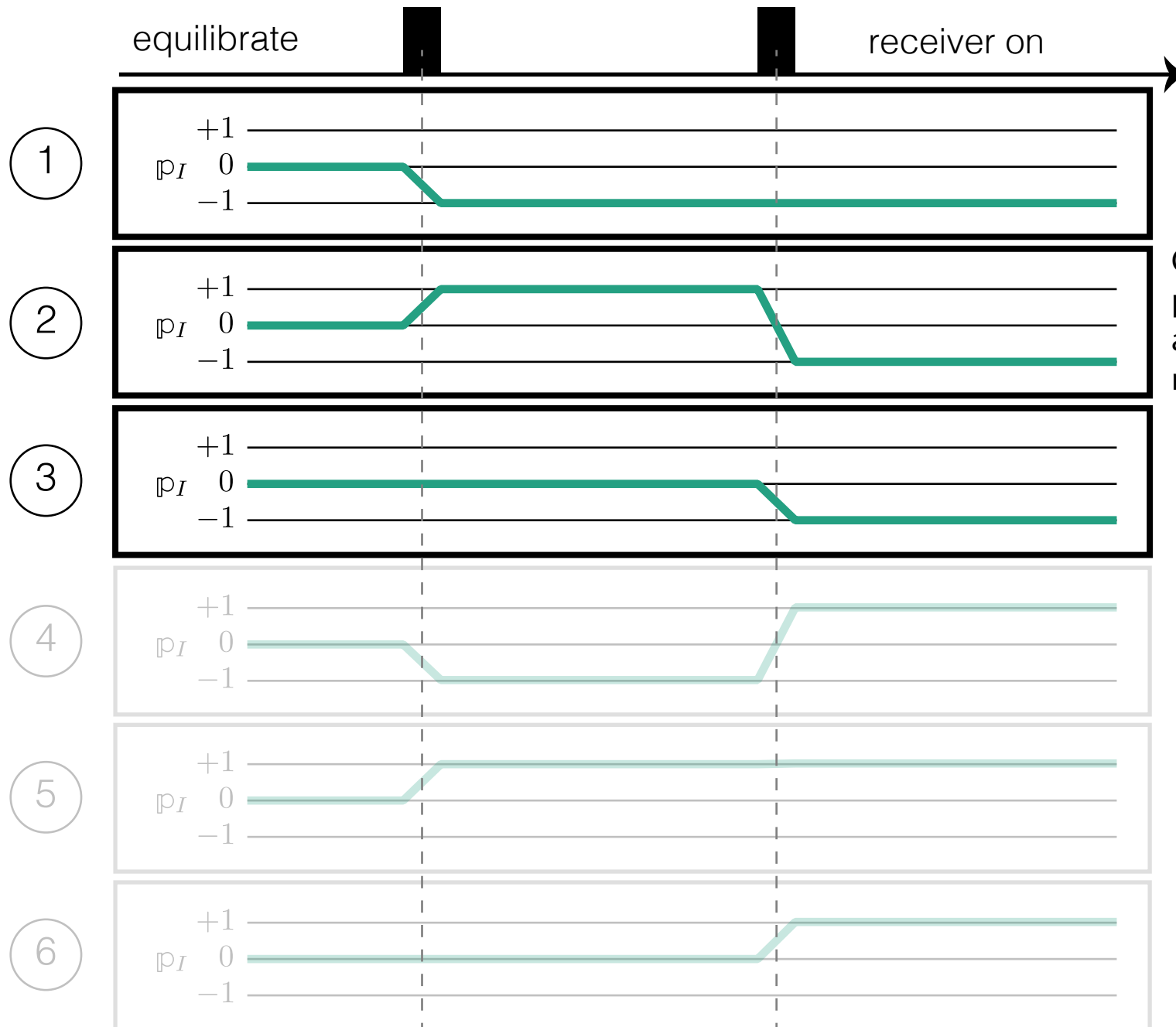
Two Pulse Transition Pathways for Spin 1/2 Case

How many transition pathways are **possible**?



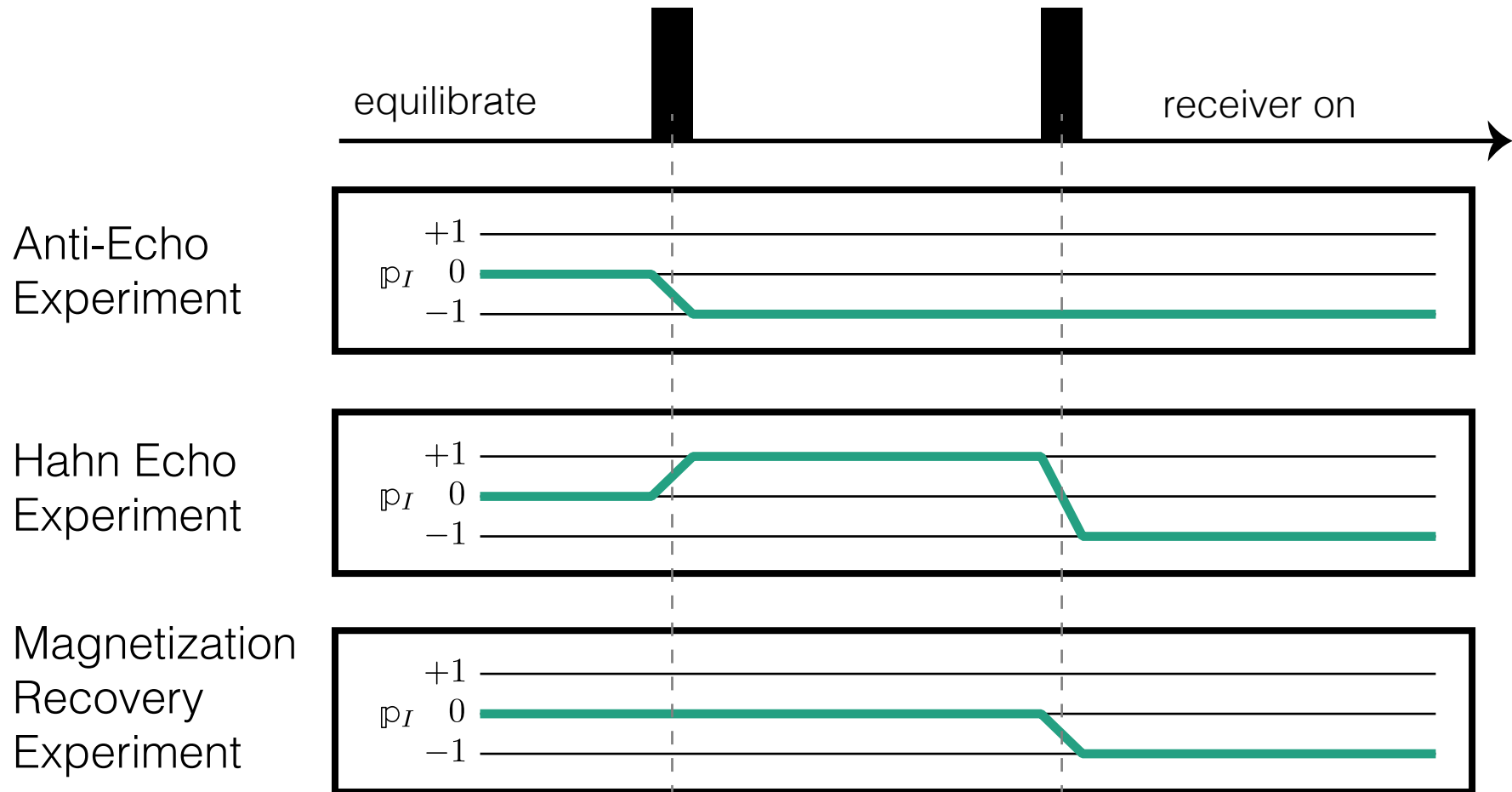
Two Pulse Transition Pathways for Spin 1/2 Case

How many transition pathways are **observable**?



Only signals with pathways at $p = -1$ are observable when receiver is on

Two Pulse Transition Pathways for Spin 1/2 Case

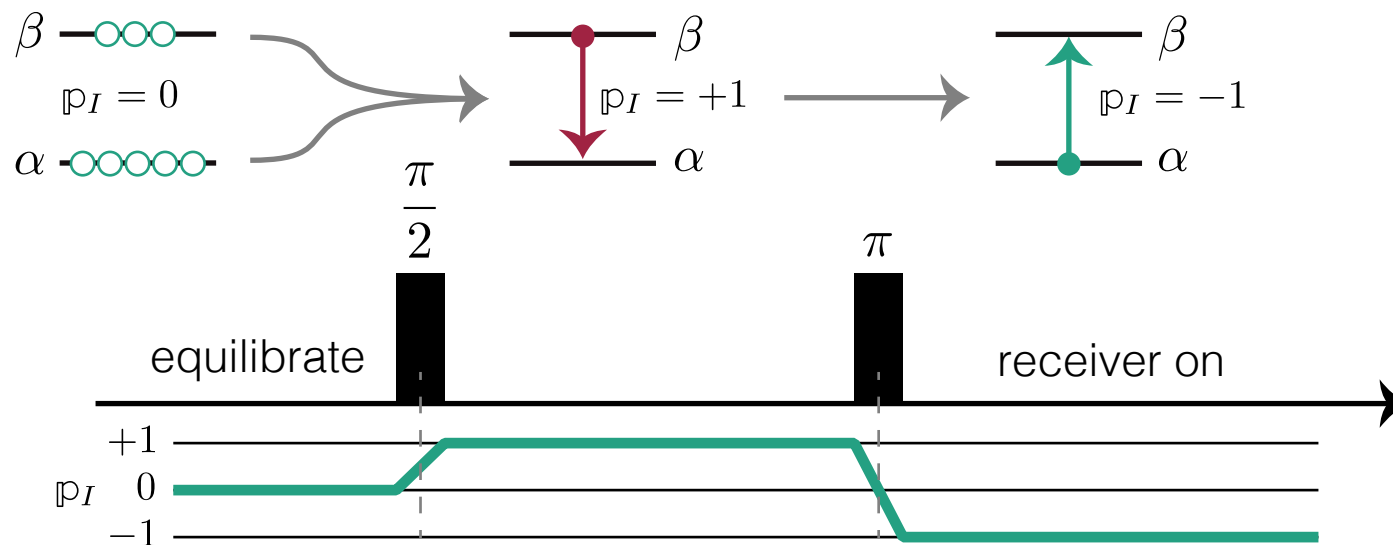


Step Two

Identify the desired transition pathway in the spin system for your pulse sequence and determine its p pathway.

Let's consider two pulse Hahn echo experiment.

Two Pulse Transition Pathways for Spin 1/2 Case



Hahn Echo
Experiment

A perfect π pulse converts $|m_f\rangle\langle m_i|$ completely into $| -m_f\rangle\langle -m_i|$

$$|m_f\rangle\langle m_i| \xrightarrow{\pi} | -m_f\rangle\langle -m_i|$$

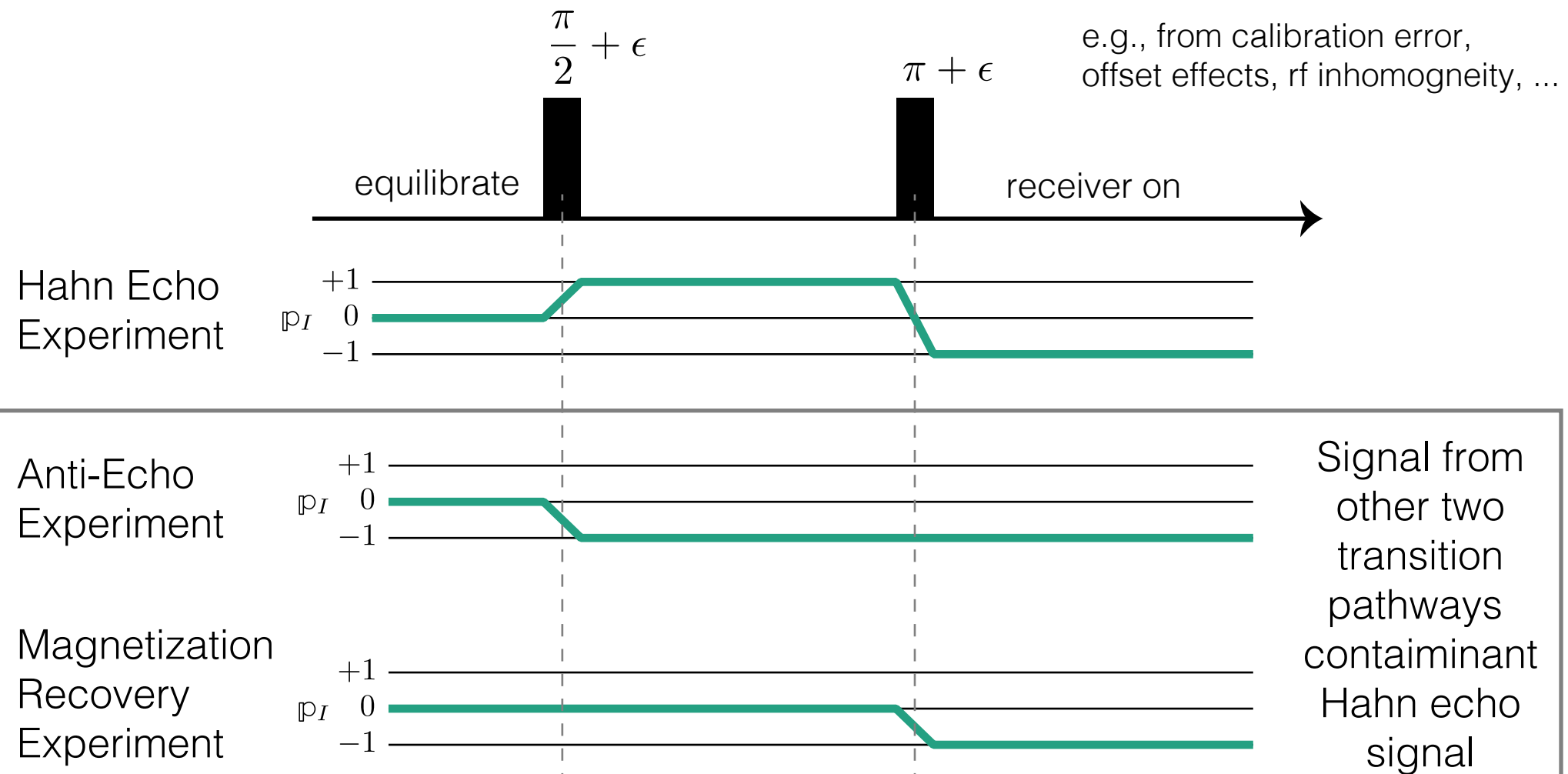
which leads to the general rule:

$$\rho_I \xrightarrow{\pi} -\rho_I$$

Assignment: Show that only the Hahn Echo transition pathway signal is observed when the 2nd pulse is a perfect π pulse

Two Pulse Transition Pathways for Spin 1/2 Case

But what if the two pulses are not perfect $\pi/2$ and π rotations?



How do we eliminate contaminant signals?

Pathway Selection and RF Pulse Phase

When the RF is on, the Hamiltonian is

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

Zeeman Offset, Chem. Shift,
J-Coupling, Dipolar Coupling,
Quadrupolar, ...
(all invariant under z rotation)

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 $|m + p\rangle \langle m|$ transform under an rf pulse of arbitrary phase?

$$\hat{t}_p = |m + p\rangle \langle m|$$

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

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 $\Delta p_1 = p_1 - p_0$

What does all this mean?

A Fourier transform of signal as a function of pulse phase separates signals by their Δp value during the pulse

$$s(\Delta p) = \int_0^{2\pi} s(\phi) e^{i\Delta p \phi} d\phi$$

This idea has been around for a long time in NMR.

Wokaun and Ernst,

“Selective Detection Of Multiple Quantum Transitions In NMR by Two-dimensional Spectroscopy,”
Chemical Physics Letters, **52**, 407 (1977)

Drobny, Pines, Sinton, Weitekamp, Wemmer,

“Fourier Transform Multiple Quantum Nuclear Magnetic Resonance,”
Faraday Symp. Chem. Soc., **13**, 93 (1978)

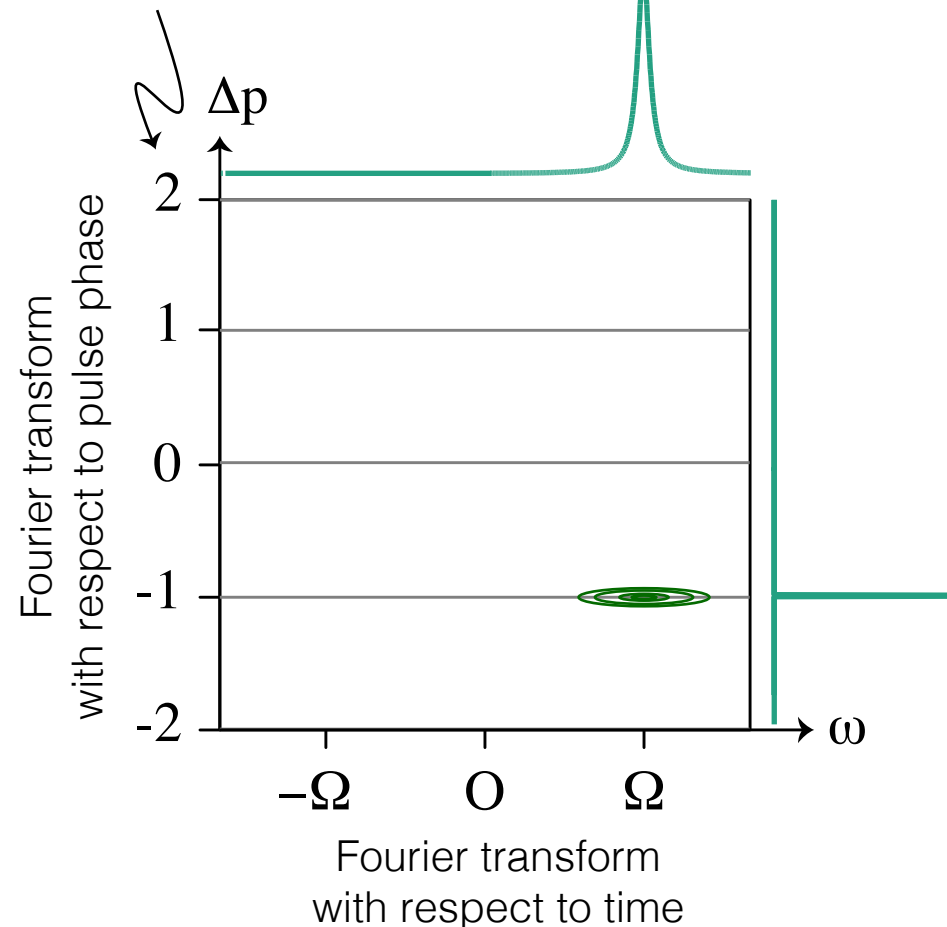
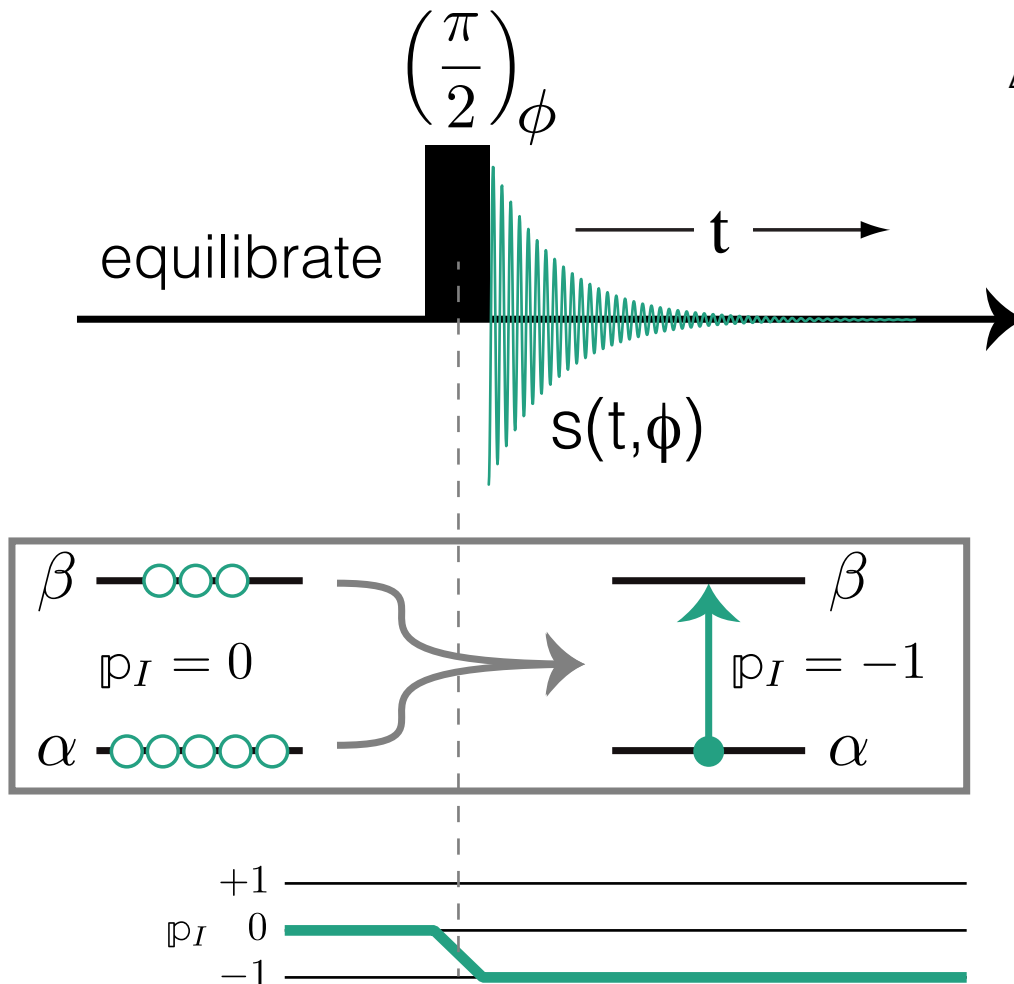
Final Step Three

Acquire signal as a function of pulse phase,
Fourier transform wrt pulse phase,
and select desired p pathway signal.

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

Simplest Case: Single Spin 1/2

“spectral width” determined
by phase increment
 $\Delta\phi = \pi/2$ gives $\Delta p = -2$ to 2

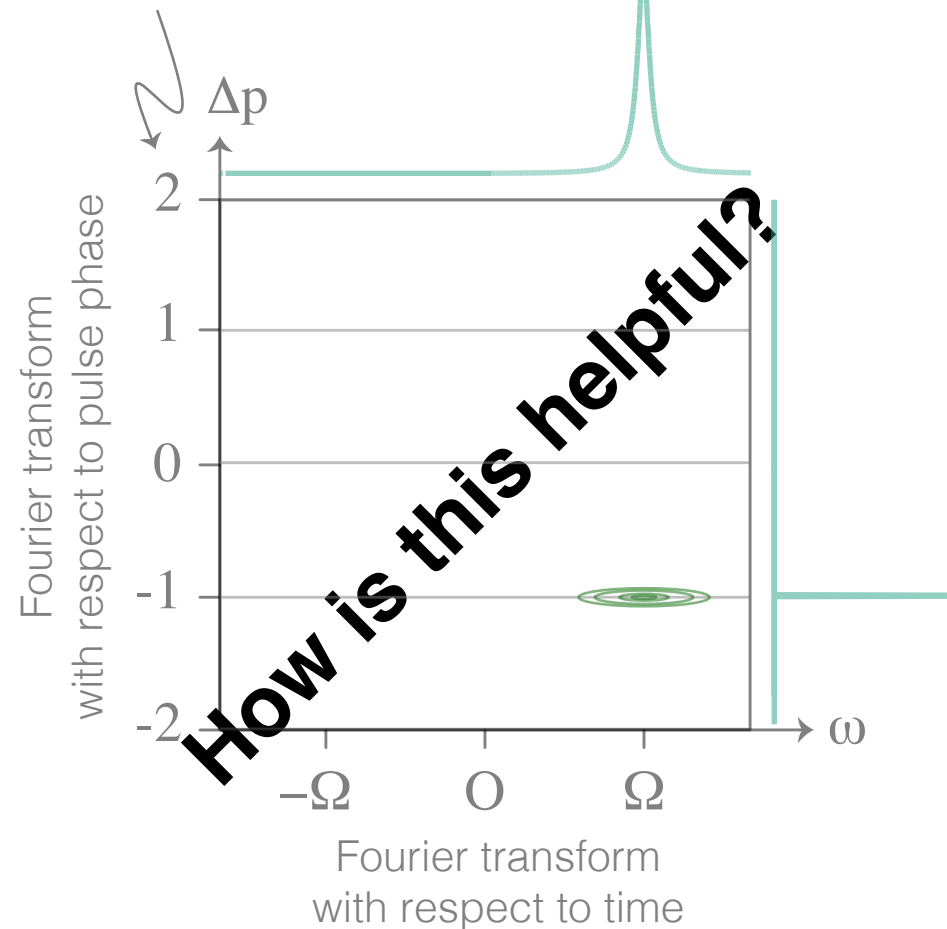
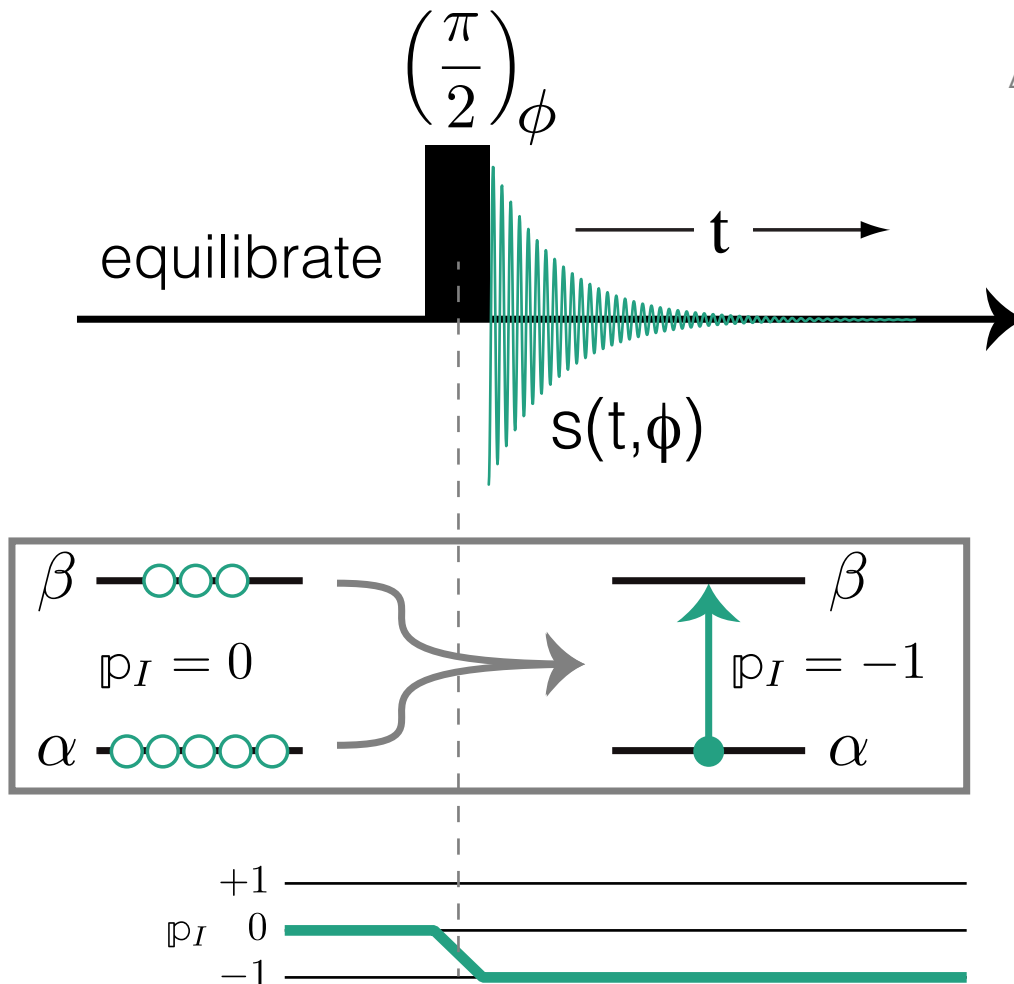


Assignment: What phase increment would give a Δp width of -8 to +8?

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

Simplest Case: Single Spin 1/2

“spectral width” determined
by phase increment
 $\Delta\phi = \pi/2$ gives $\Delta p = -2$ to 2



Assignment: What phase increment would give a Δp width of -8 to +8?

NMR in the 1980s



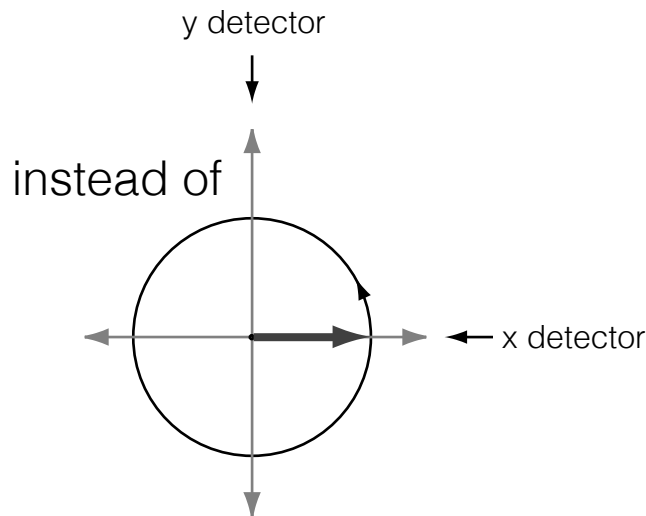
Quadrature Ghosts in the Receiver



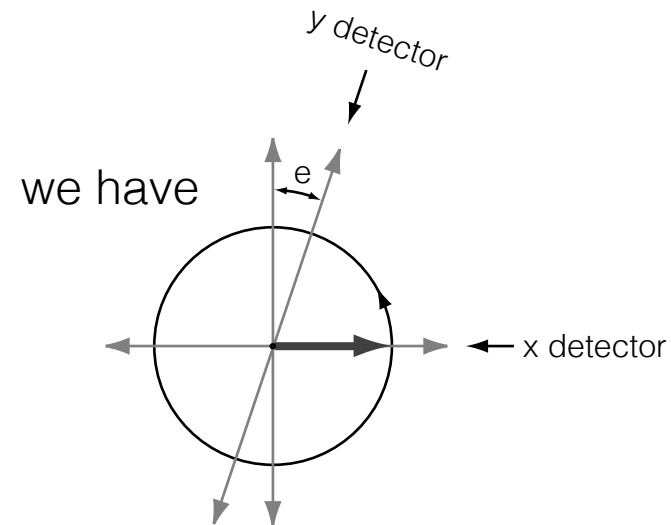
Quadrature Ghosts and Baseline Error

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

Good Receiver



Bad Receiver



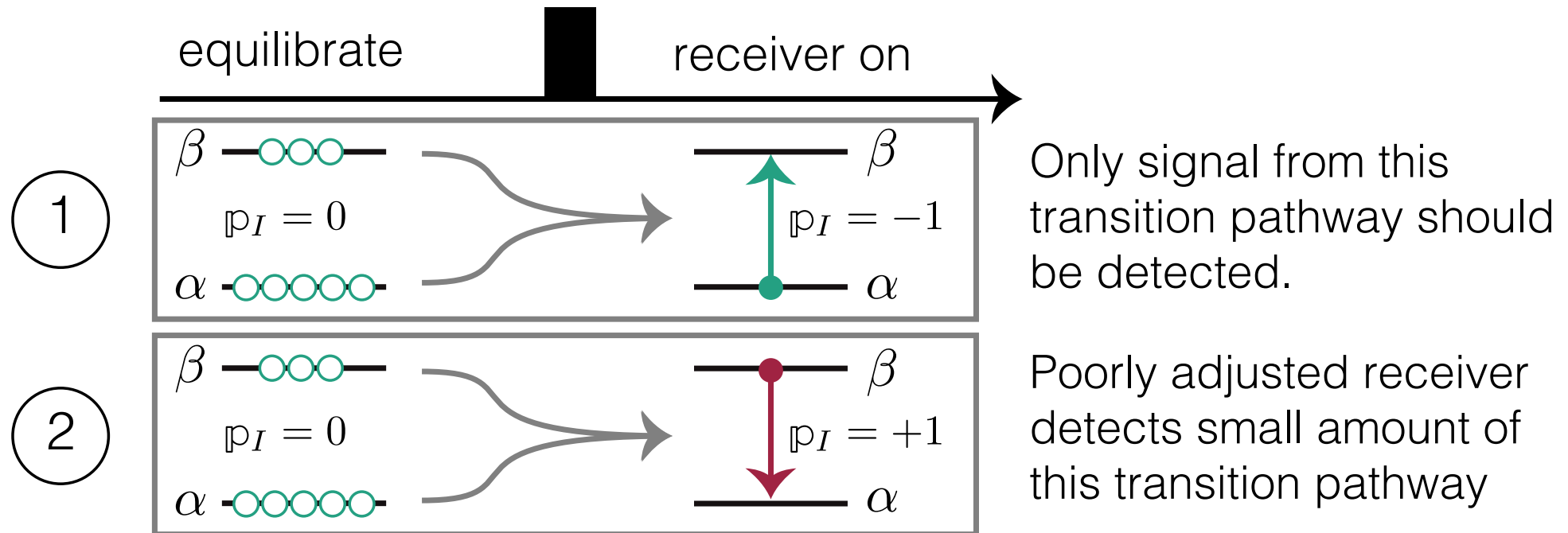
Baseline Error: Even when there's no NMR signal there may be a spurious background signal.

$$S(t) \propto \frac{dM_+}{dt} + \text{constant}$$

causes spike at 0 Hertz

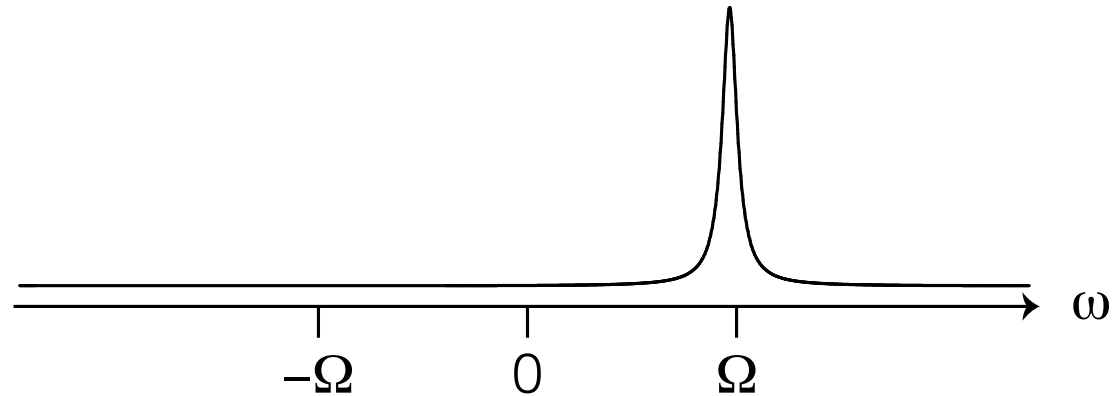
One Pulse and Acquire (as a function of pulse phase)

Simplest Case: Single Spin 1/2

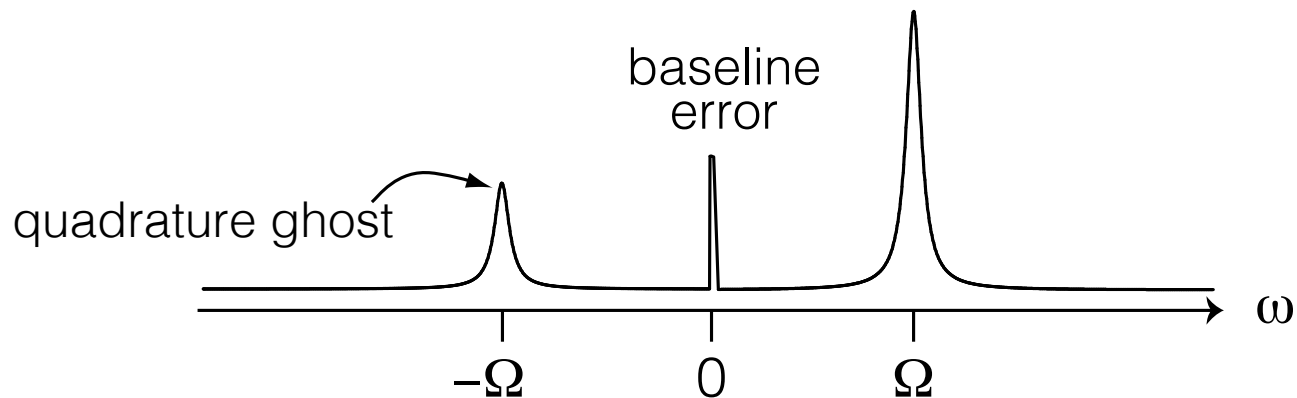


One Pulse and Acquire (on 1980s home-built NMR spectrometer)

You should see this after FT



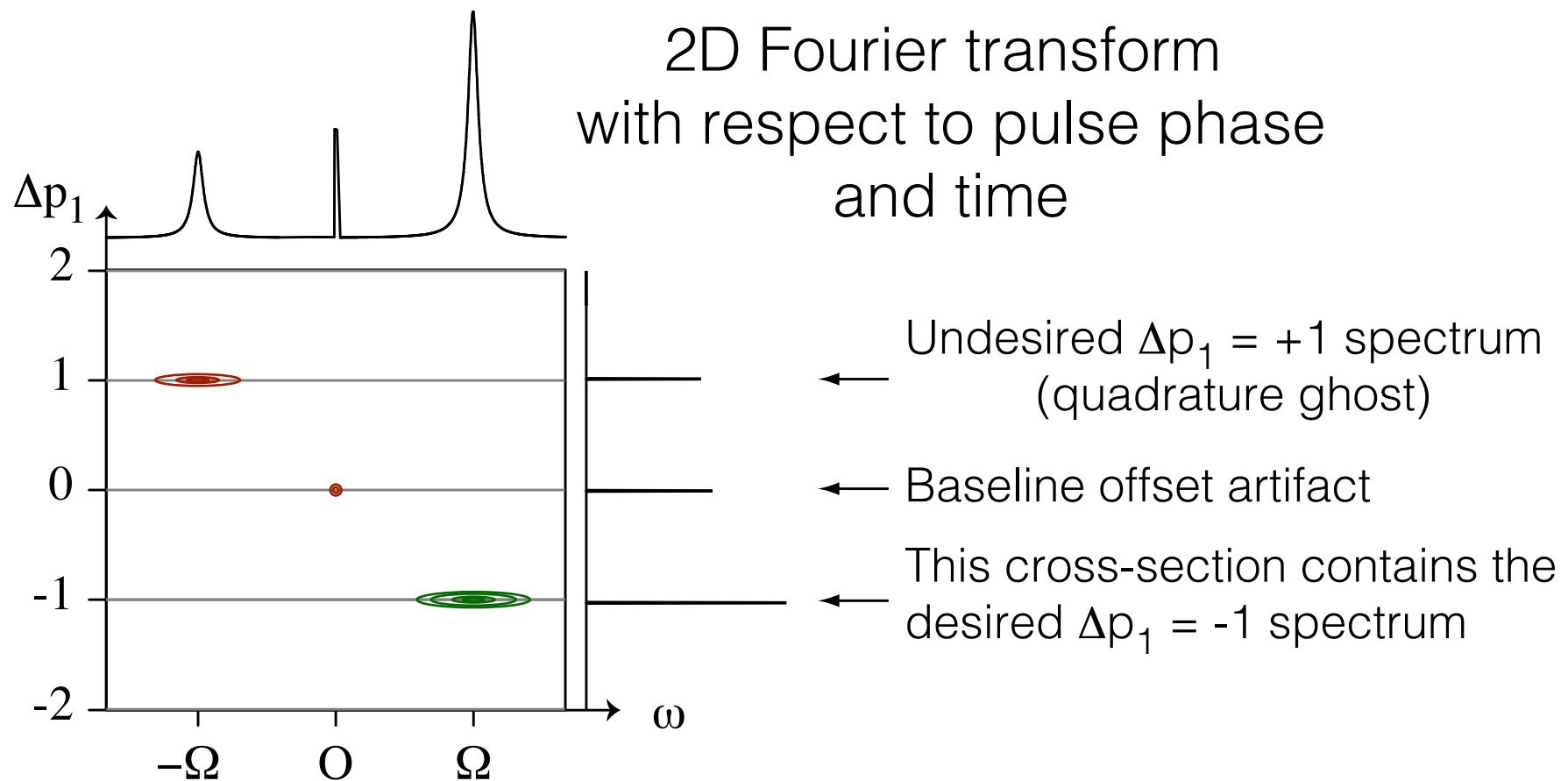
But instead you see this after FT



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

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

How do we separate the desired from undesired signal?

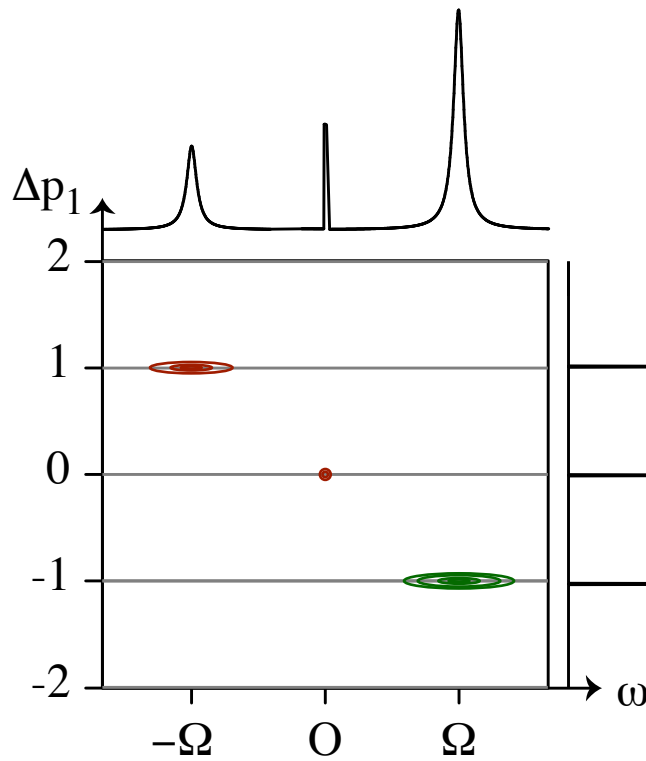


One Pulse and Acquire

(on 1980s home-built NMR spectrometer)

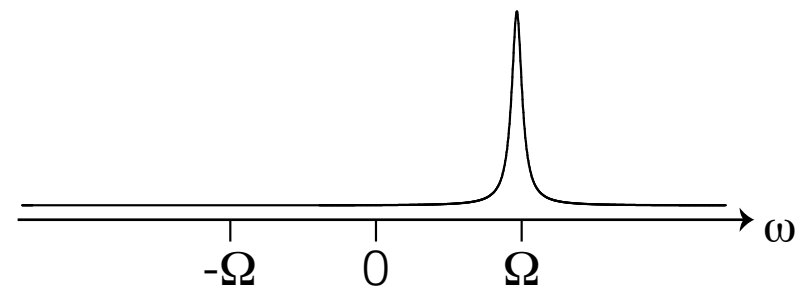
$$S(\phi_1, t) = \underbrace{ae^{i\phi_1}e^{-i\Omega t}}_{\text{desired } \Delta p_1 = -1 \text{ signal}} + \underbrace{be^{-i\phi_1}e^{i\Omega t}}_{\text{undesired } \Delta p_1 = +1 \text{ signal}} + \underbrace{\text{constant}}_{\text{undesired signal}}$$

How do we separate the desired from undesired signal?



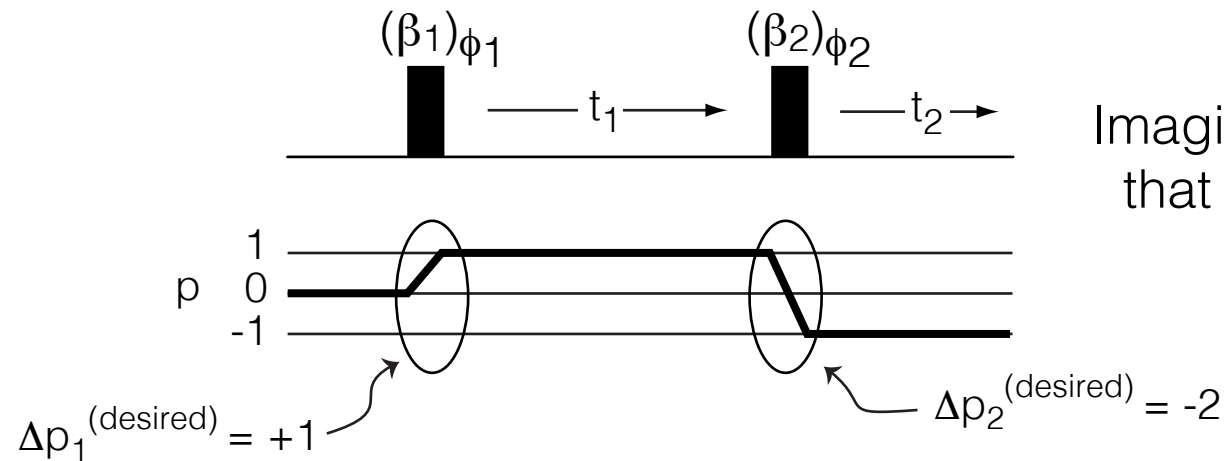
2D Fourier transform
with respect to pulse phase and time

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



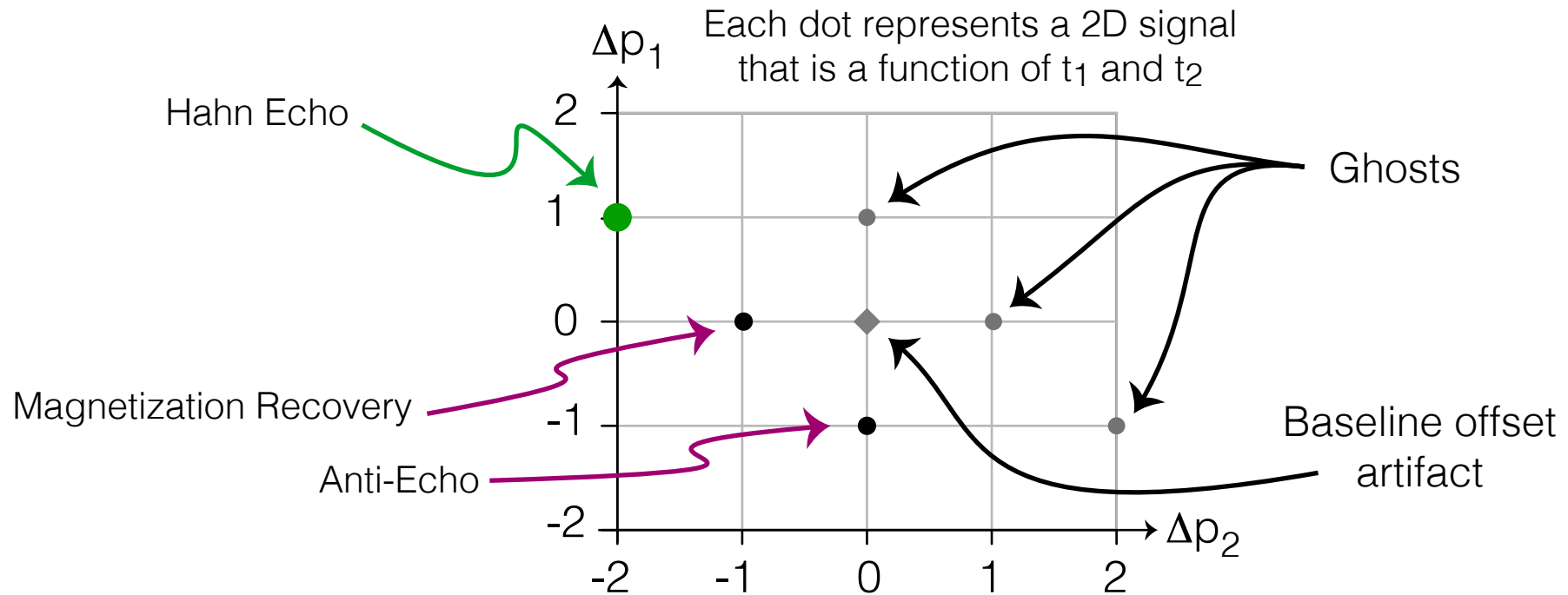
This is the essence of phase cycling: separating signals from different p pathways by their Δp values.

Two Pulse (Hahn Echo) Sequence on Spin 1/2



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

After 2D Fourier Transform wrt ϕ_1 and ϕ_2



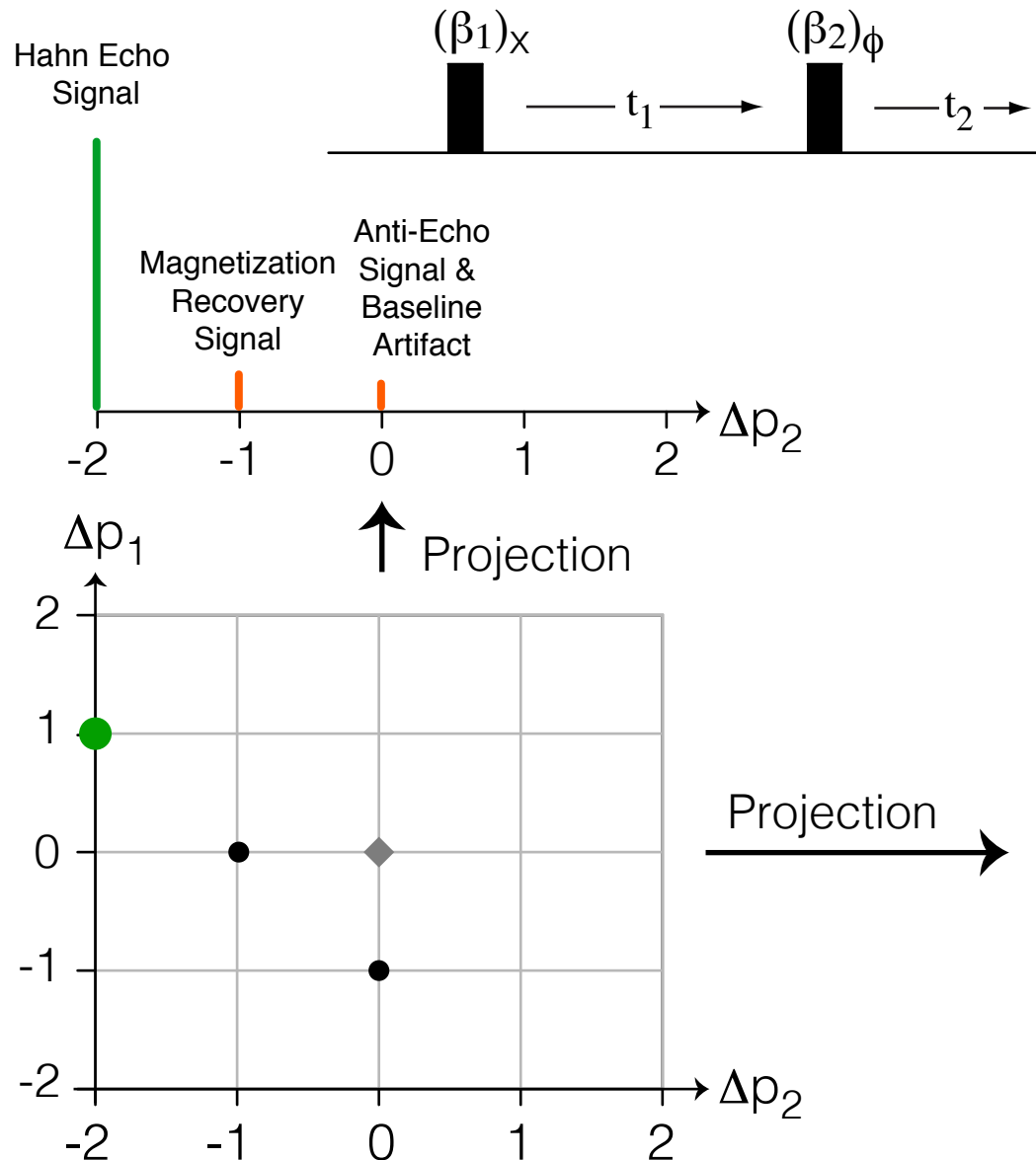
Wait, I need a phase dimension for every pulse?
Isn't that gonna be a lot of dimensions?

There are ways to reduce the number
of phase dimensions needed.

Two Pulse (Hahn Echo) Sequence on Spin 1/2

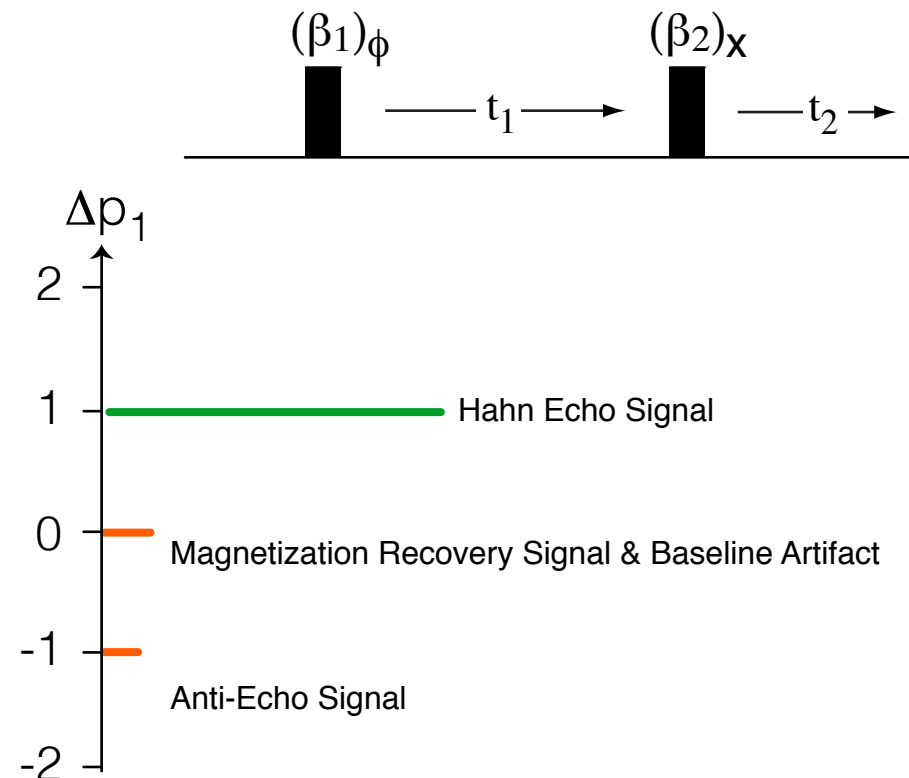
One suggestion

Lock $\phi_1 = 0$ and only vary ϕ_2
to get projection on Δp_2 axis



Another suggestion

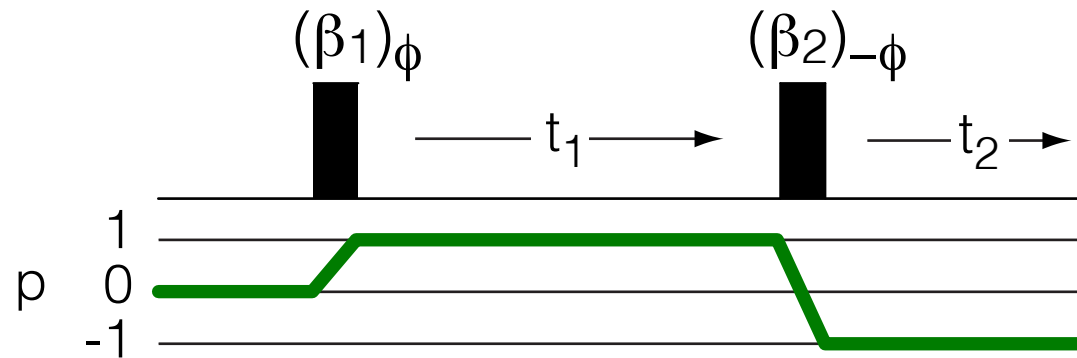
Lock $\phi_2 = 0$ and only vary ϕ_1
to get projection on Δp_1 axis



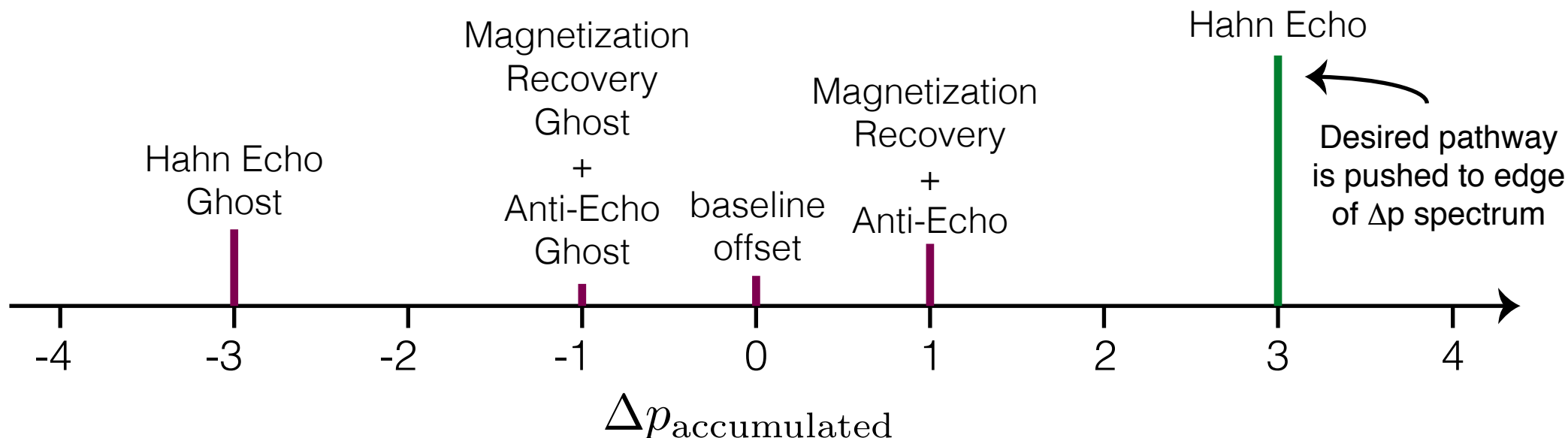
Two Pulse (Hahn Echo) Sequence on Spin 1/2

Another strategy

Use same phase for every pulse except change sign of each pulse phase to match the sign of the desired Δp .



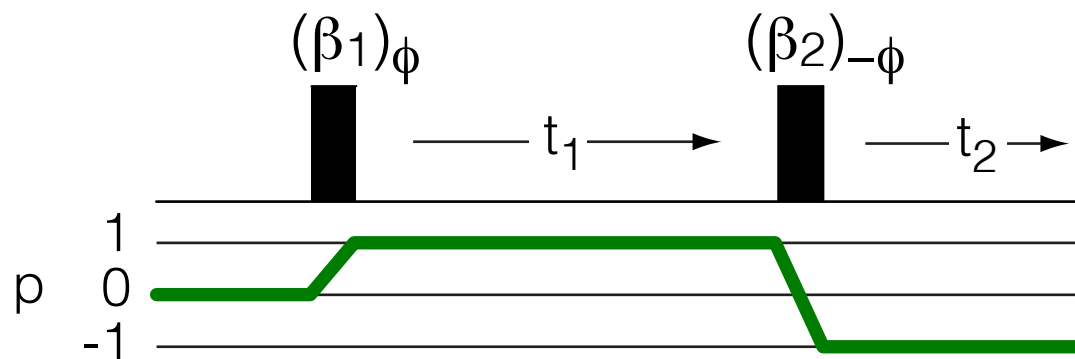
$$\Delta p_1 \phi + \Delta p_2 (-\phi) = (\Delta p_1 - \Delta p_2) \phi = \Delta p_{\text{accumulated}} \phi$$



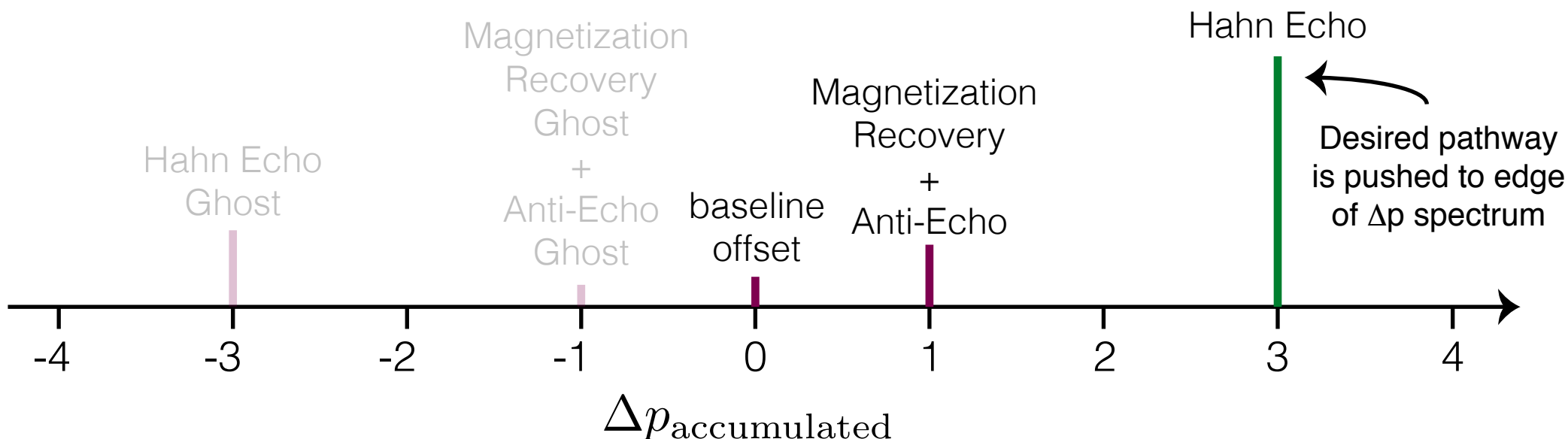
Two Pulse (Hahn Echo) Sequence on Spin 1/2

Another strategy

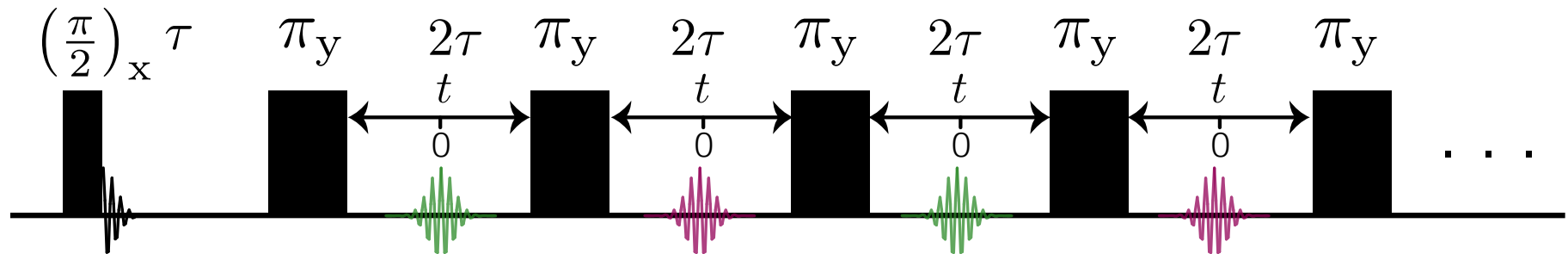
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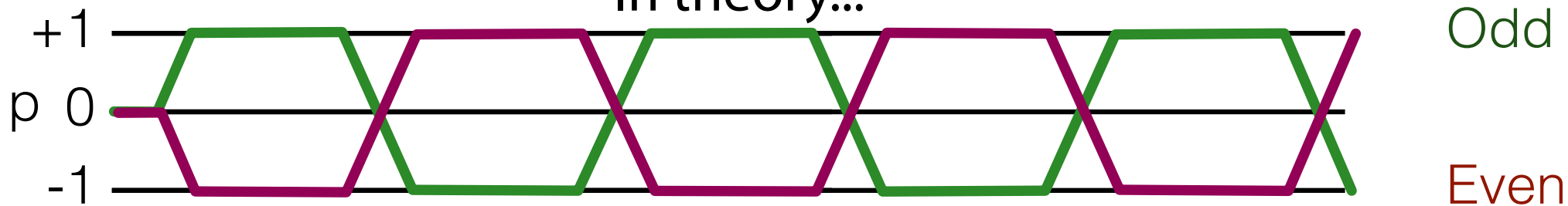
$$\Delta p_1 \phi + \Delta p_2 (-\phi) = (\Delta p_1 - \Delta p_2) \phi = \Delta p_{\text{accumulated}} \phi$$



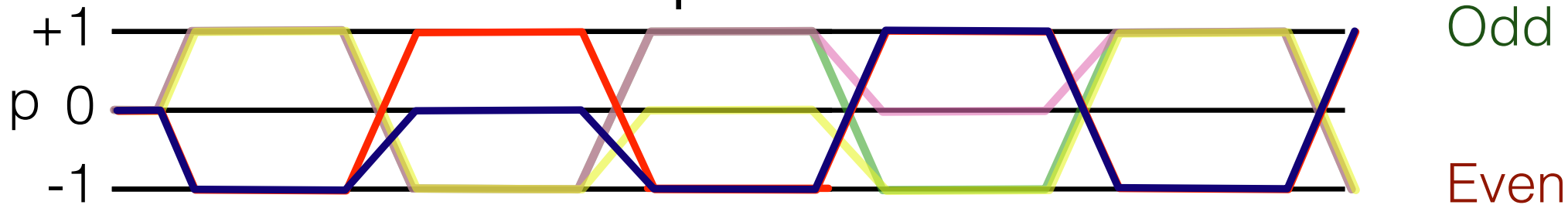
Carr-Purcell-Meiboom-Gill Acquisition



In theory...

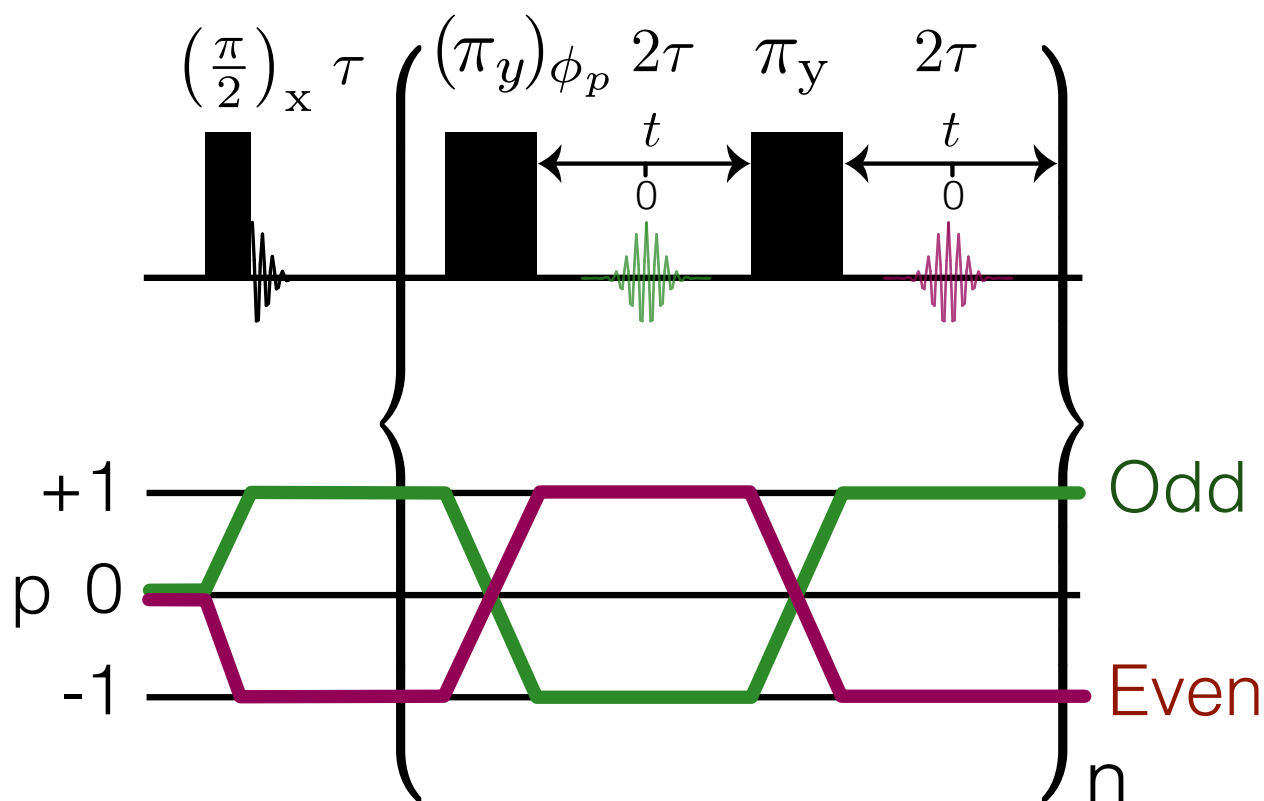


In practice...



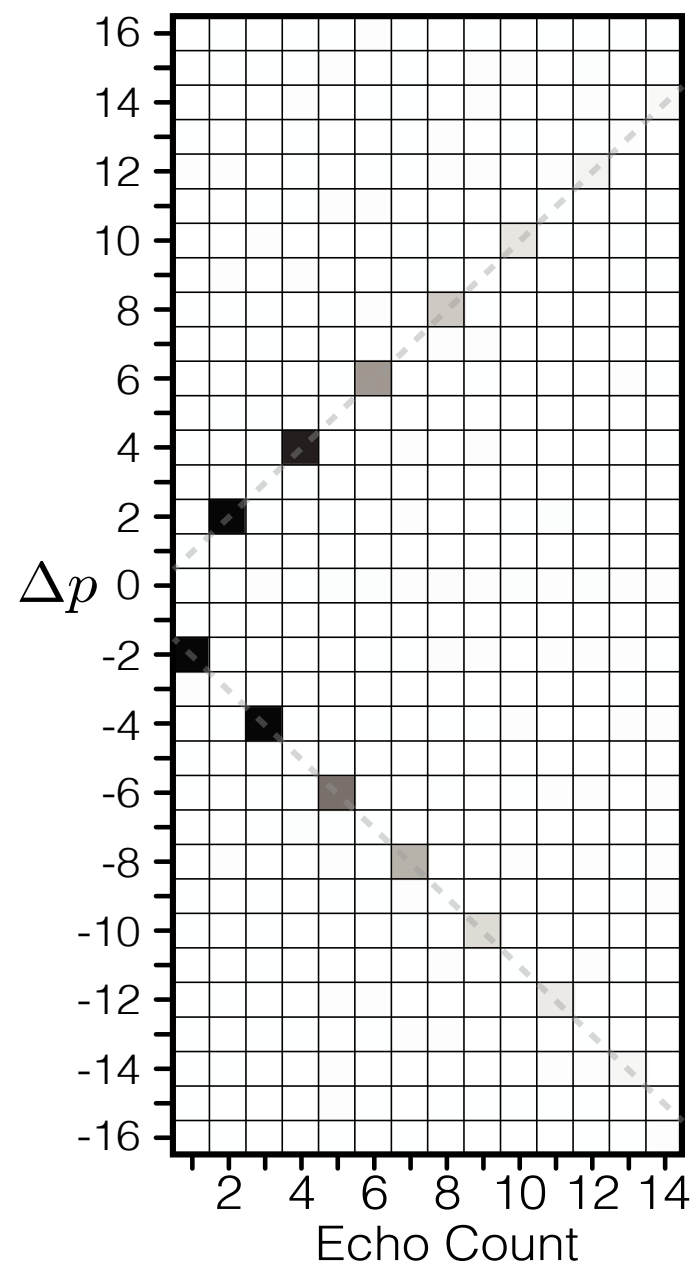
Unless you have perfect pathway selection there will be signal artifacts from undesired pathways which get worse with each π pulse.

Phase Incremented Echo Train Acquisition



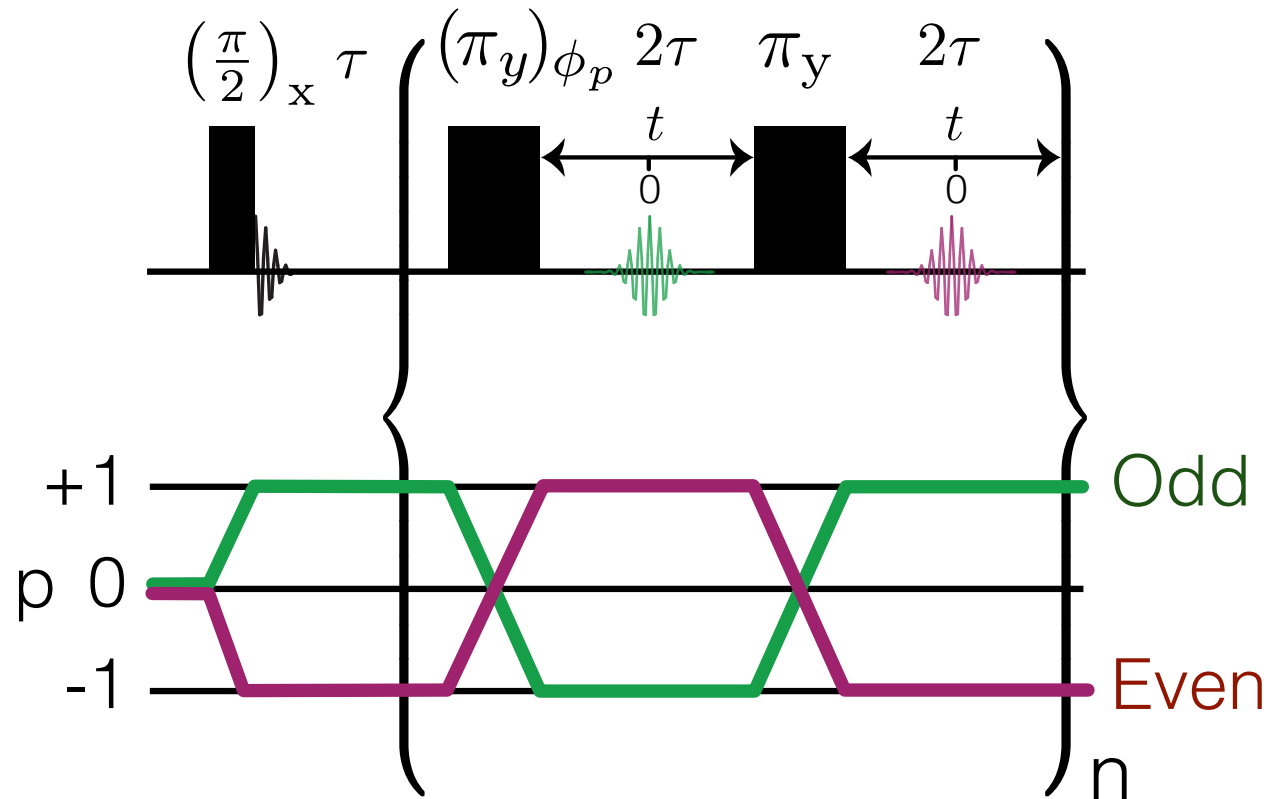
Each time through the loop the Δp of odd echoes accumulate -2 and Δp of even echoes accumulate +2.

Desired pathway echoes are pushed to highest possible $|\Delta p|$ while undesired pathway echoes fall between the two limits.



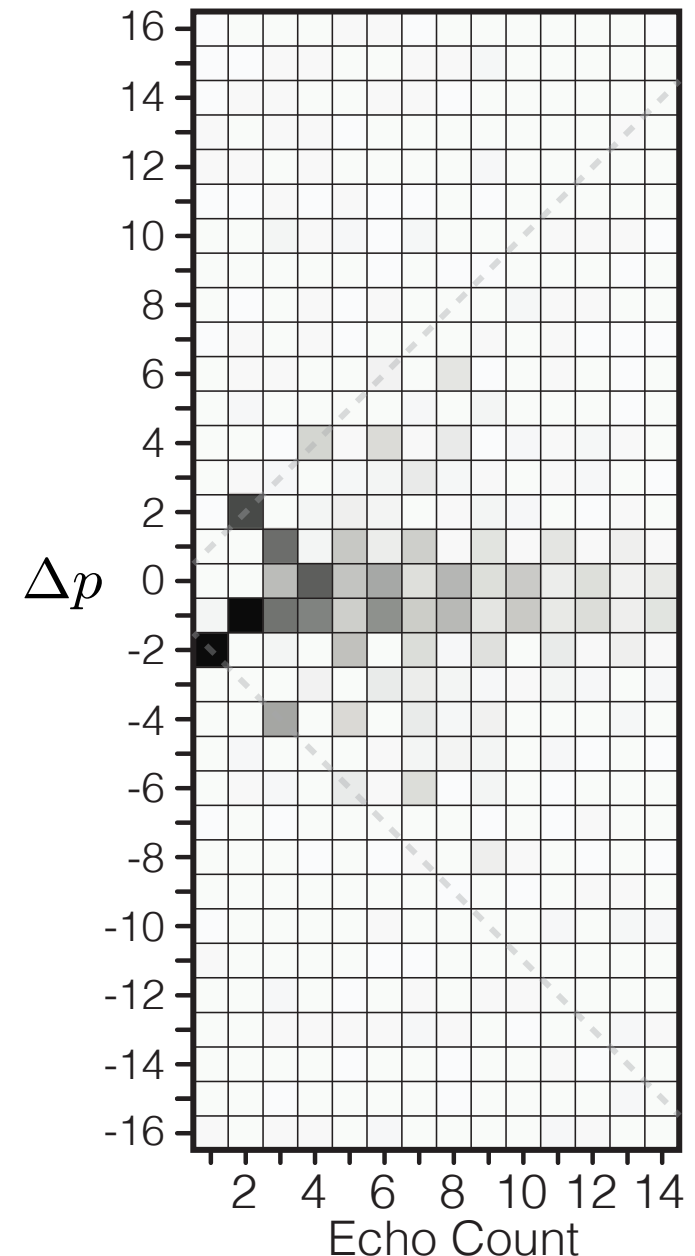
Phase Incremented Echo Train Acquisition

Example: Improper pulse lengths

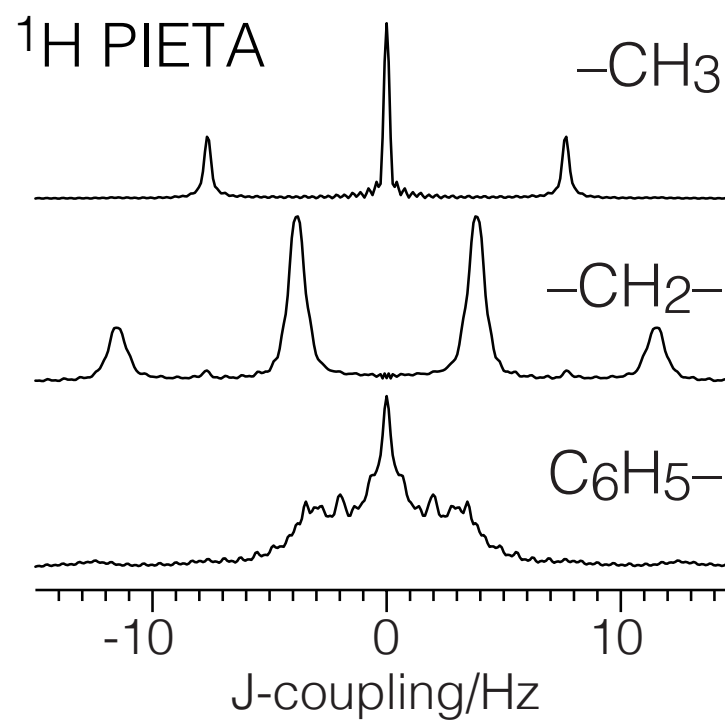
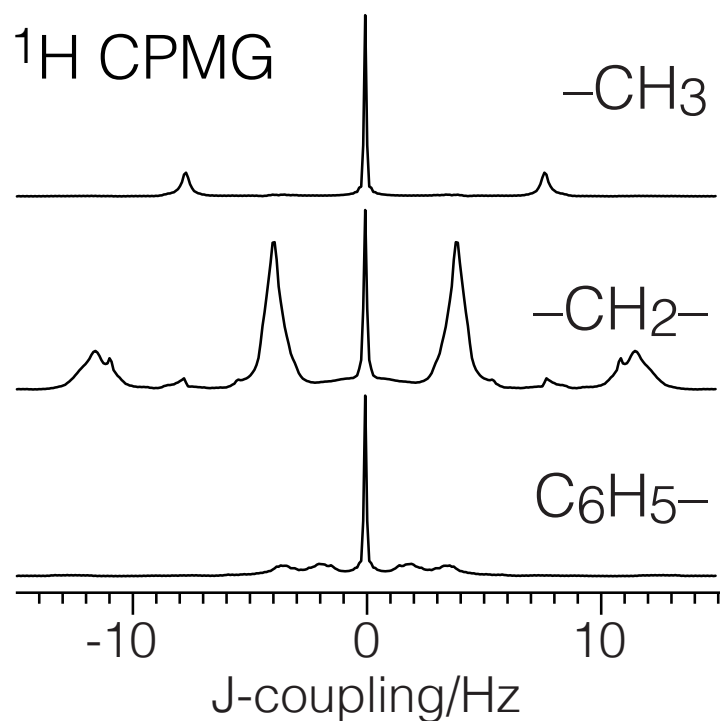
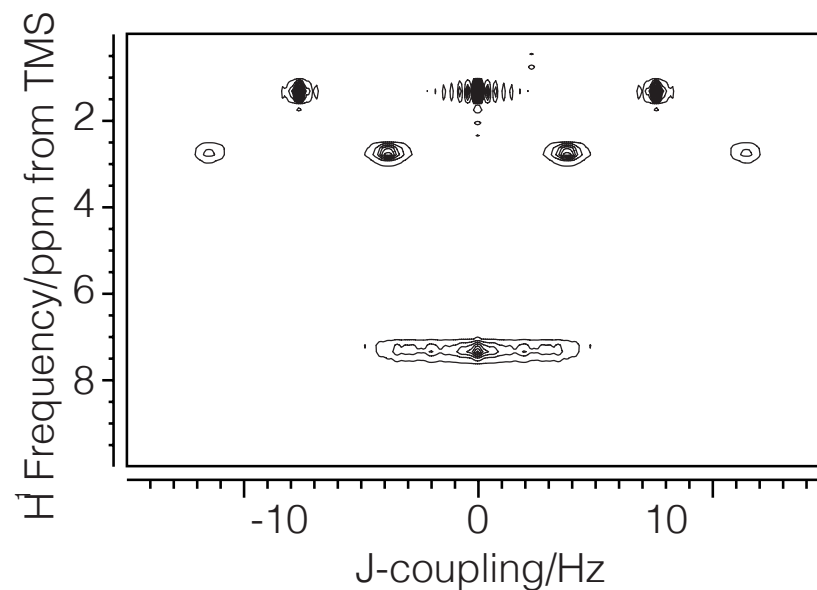
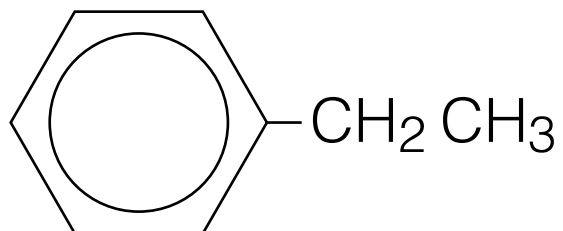


Each time through the loop the Δp of odd echoes accumulate -2 and Δp of even echoes accumulate +2.

Desired pathway echoes are pushed to highest possible $|\Delta p|$ while undesired pathway echoes fall between the two limits.



PIETA measures J Couplings accurately and faster



The p pathway does not
uniquely define experiments

Need to look closer at
NMR transition frequency contributions

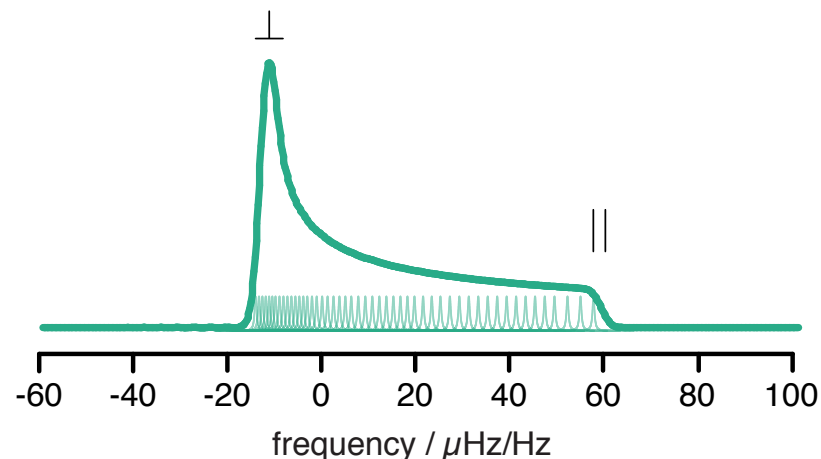
The (Chemical) Shift Frequency Contribution

$$\Omega_{\sigma}^{(1)} = \underbrace{-\omega_0 \sigma_{\text{iso}} \rho_I}_{\text{Larmor Frequency}} \underbrace{-\omega_0 \zeta_{\sigma} \mathbb{D}^{(\sigma)}(\Theta) \rho_I}_{\text{Isotropic Shielding}} \underbrace{-\omega_0 \zeta_{\sigma} \mathbb{D}^{(\sigma)}(\Theta) \rho_I}_{\text{Shielding Anisotropy}}$$

Chemical shift contribution is directly proportional to the p value of a transition

Frequency dependence on the orientation of the shielding tensor PAS relative to B_0

Spatial symmetry function $\rightarrow \mathbb{D}^{\{\sigma\}}(\Theta) = P_2^0(\cos \beta) + \frac{\eta_{\sigma}}{6} P_2^2(\cos \beta) \cos 2\alpha,$



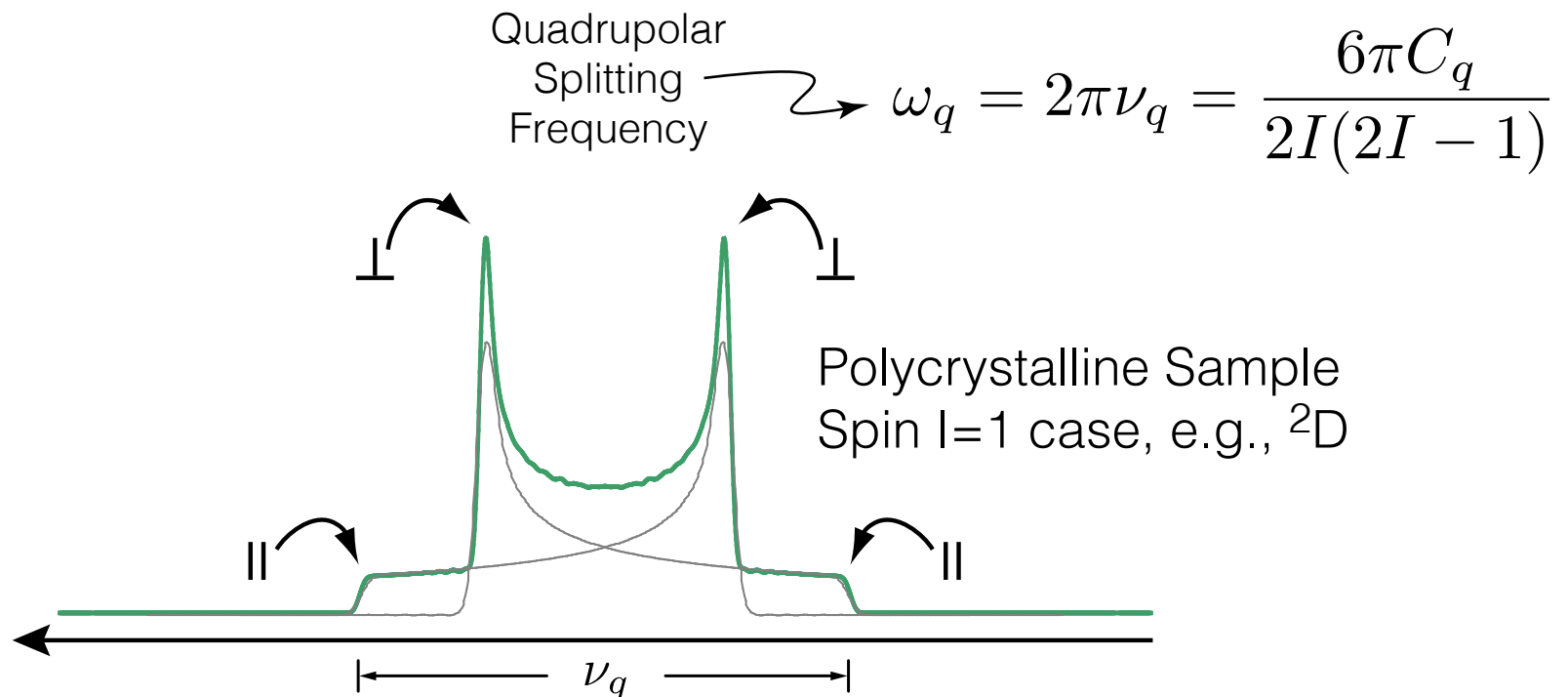
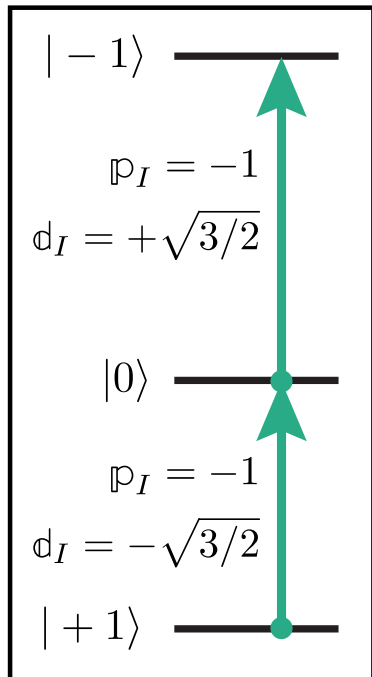
First-Order Quadrupolar Frequency Contribution

$$\Omega_q^{(1)} = \omega_q \mathbb{D}^{\{q\}}(\Theta) \mathfrak{d}_I \leftarrow \text{doesn't depend on } p$$

instead of p we have $\mathfrak{d}_I = \sqrt{\frac{3}{2}}(m_f^2 - m_i^2)$

Anisotropy is described by spatial symmetry function

$$\mathbb{D}^{\{q\}}(\Theta) = \frac{1}{\sqrt{6}} \left[P_2^0(\cos \beta) + \frac{\eta_q}{6} P_2^2(\cos \beta) \cos 2\alpha \right]$$



1st-order quadrupolar frequency is invariant under π pulse

General effect of π pulse on a transition

$$\boxed{|m_f\rangle\langle m_i| \xrightarrow{\pi} |{-m_f}\rangle\langle {-m_i}|}$$

$$\Omega = -\omega_0 \sigma_{\text{iso}} \wp_I - \omega_0 \zeta_\sigma \mathbb{D}^{\{\sigma\}} \wp_I + \omega_q \mathbb{D}^{\{q\}} \mathfrak{d}_I$$

Effect of π pulse on transition symmetry functions

$$\boxed{\wp_I \xrightarrow{\pi} -\wp_I}$$

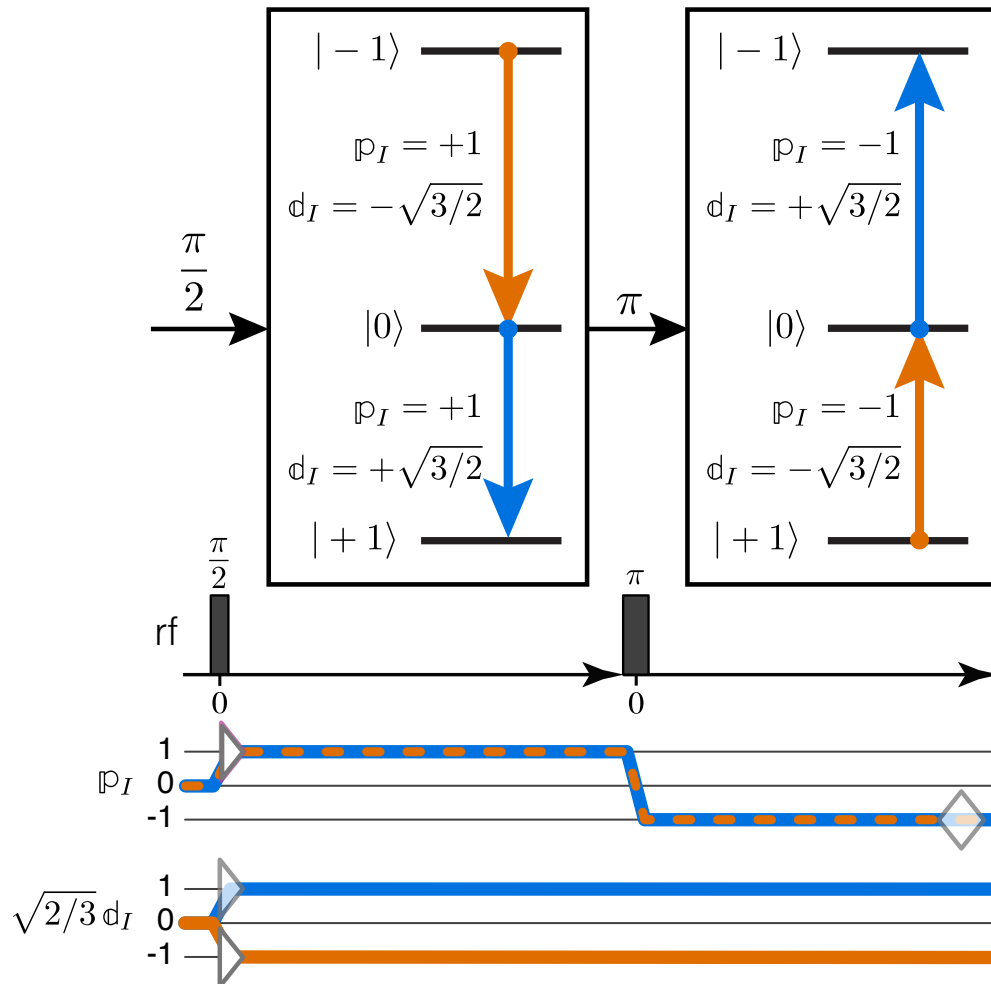
$$\boxed{\mathfrak{d}_I \xrightarrow{\pi} \mathfrak{d}_I}$$

Assignment: Given $\wp_I = m_f - m_i$ and $\mathfrak{d}_I = \sqrt{\frac{3}{2}} (m_f^2 - m_i^2)$ confirm this result.

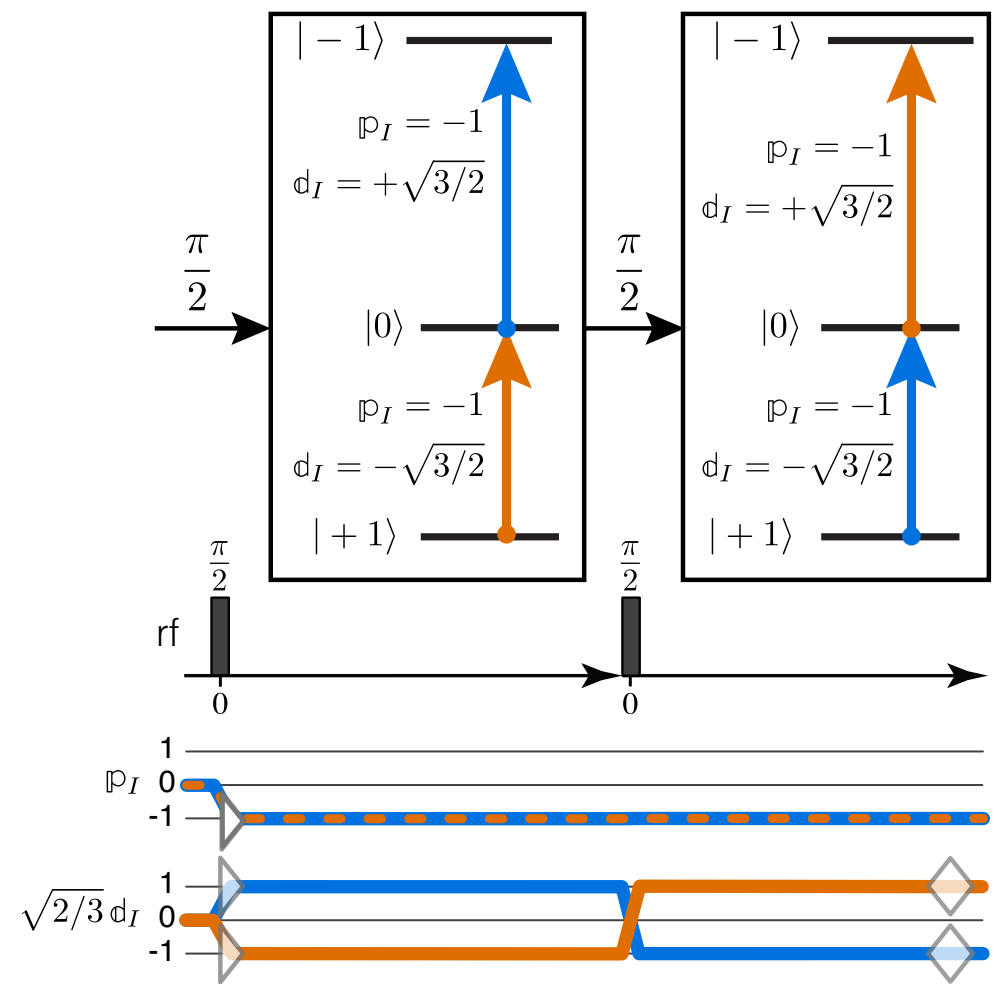
Two pulse pathways in Deuterium

$$\Omega = -\omega_0 \sigma_{\text{iso}} \rho_I - \omega_0 \zeta_\sigma \mathbb{D}^{\{\sigma\}} \rho_I + \omega_q \mathbb{D}^{\{q\}} \rho_I$$

Hahn Echo Sequence



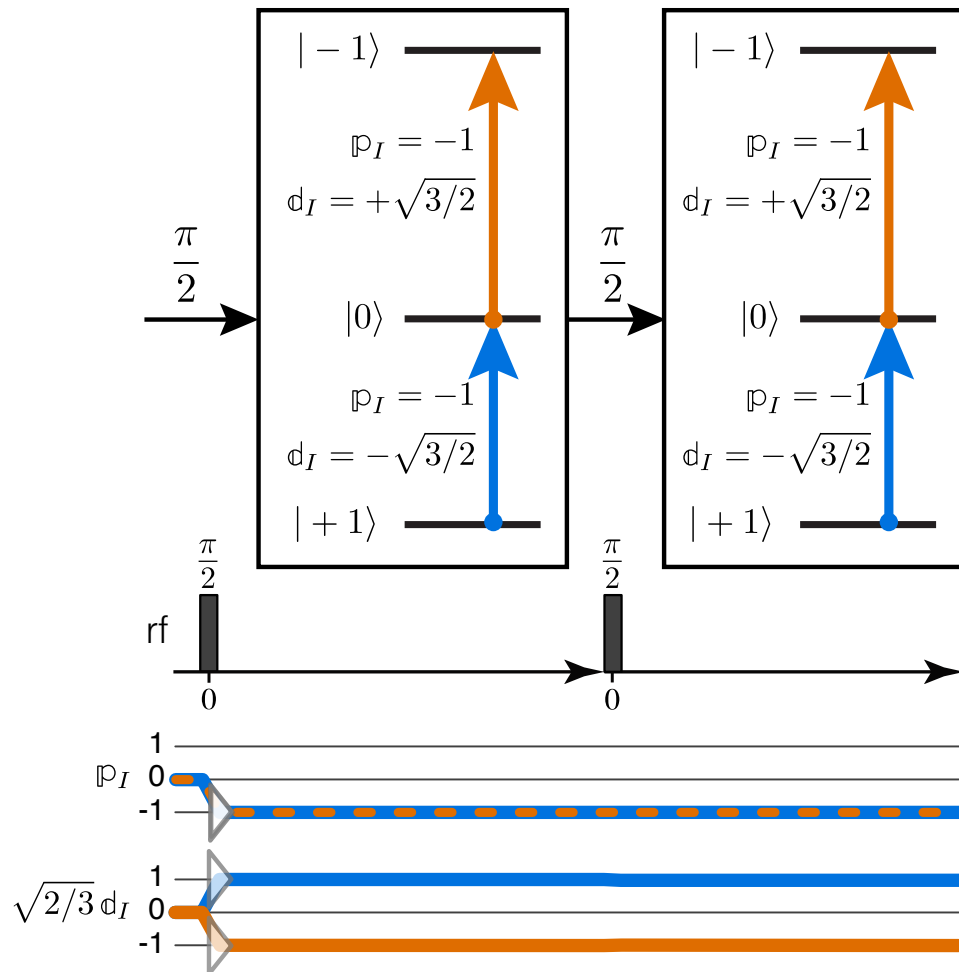
Solid Echo Sequence



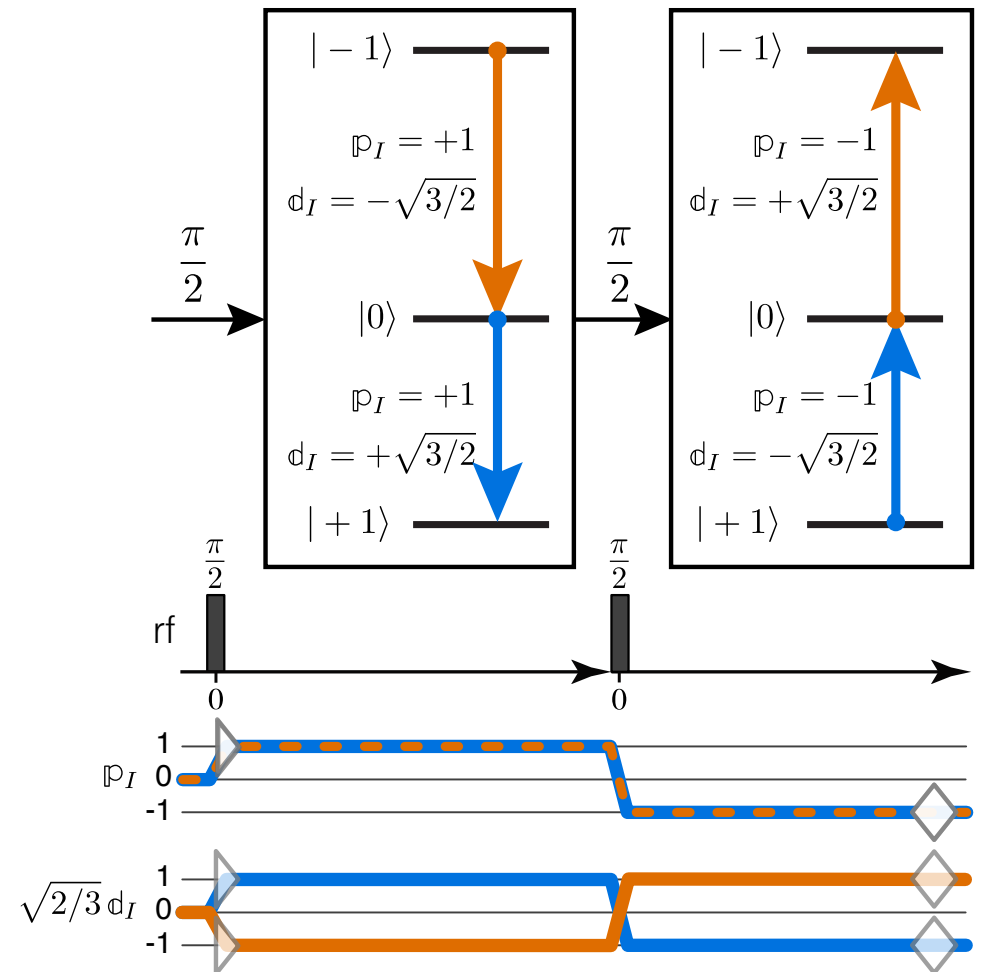
Two pulse pathways in Deuterium

$$\Omega = -\omega_0 \sigma_{\text{iso}} \rho_I - \omega_0 \zeta_\sigma \mathbb{D}^{\{\sigma\}} \rho_I + \omega_q \mathbb{D}^{\{q\}} \rho_I$$

No Echo Sequence



Hahn-Solid Echo Sequence



2D COSY in two weakly coupled spin half case

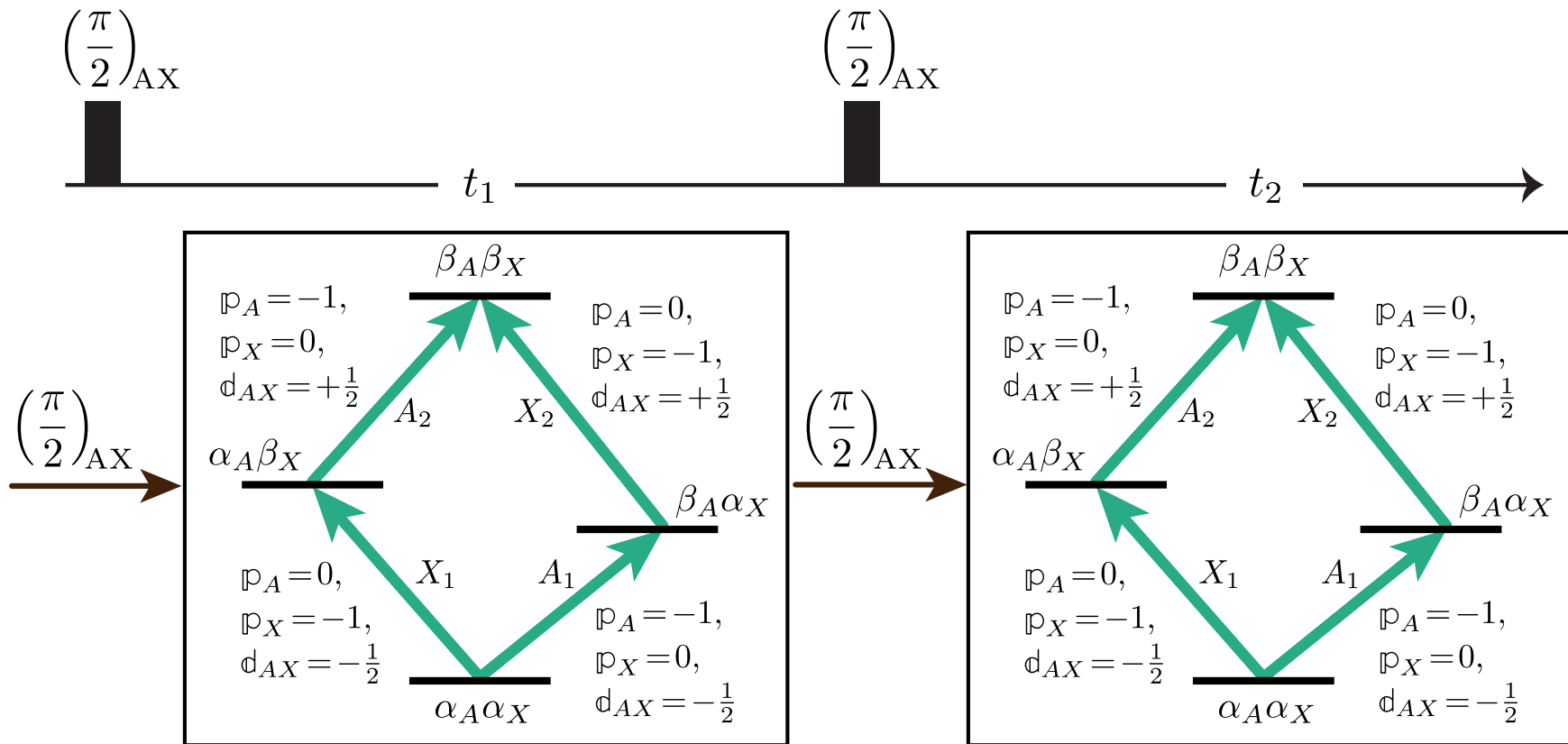
$$\Omega = -(1 - \sigma_{\text{iso},A})\omega_0\rho_A - (1 - \sigma_{\text{iso},B})\omega_0\rho_B + 2\pi J_{AX}(\rho\rho)_{AX}$$

instead of ρ_A or ρ_X
we have

$$(\rho\rho)_{AX} = m_{A,f}m_{X,f} - m_{A,i}m_{X,i}$$

J coupling doesn't
depend on ρ_A or ρ_X

CORrelation SpectroscopY

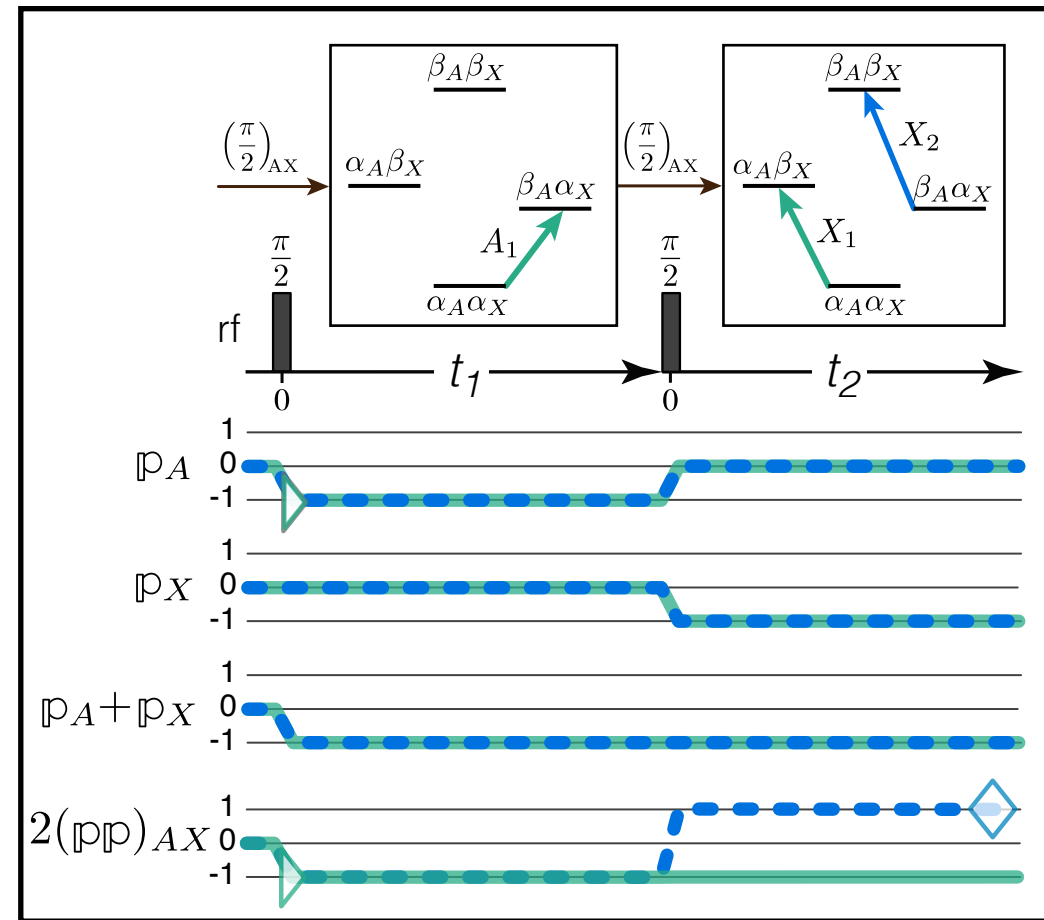
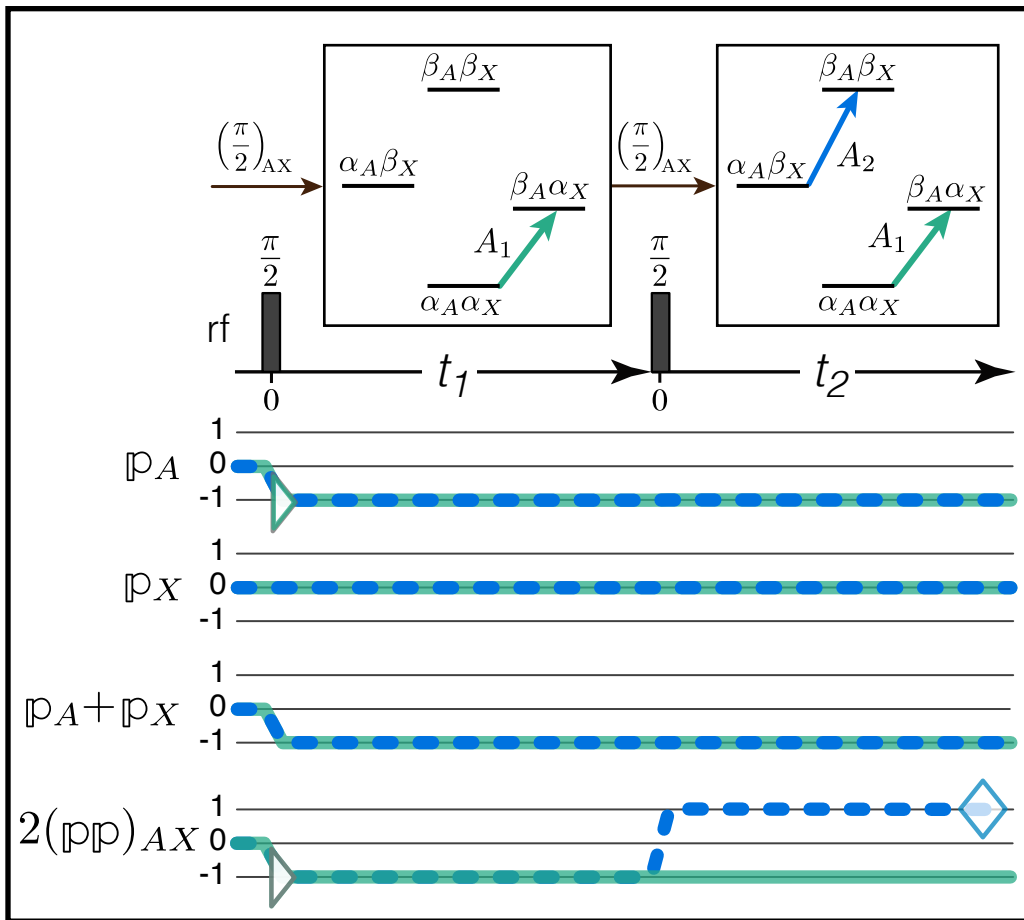


What are the transition pathways?

COSY has 16 transition pathways in two weakly coupled spin half case

$A_1 \rightarrow A_1$ and $A_1 \rightarrow A_2$ pathways

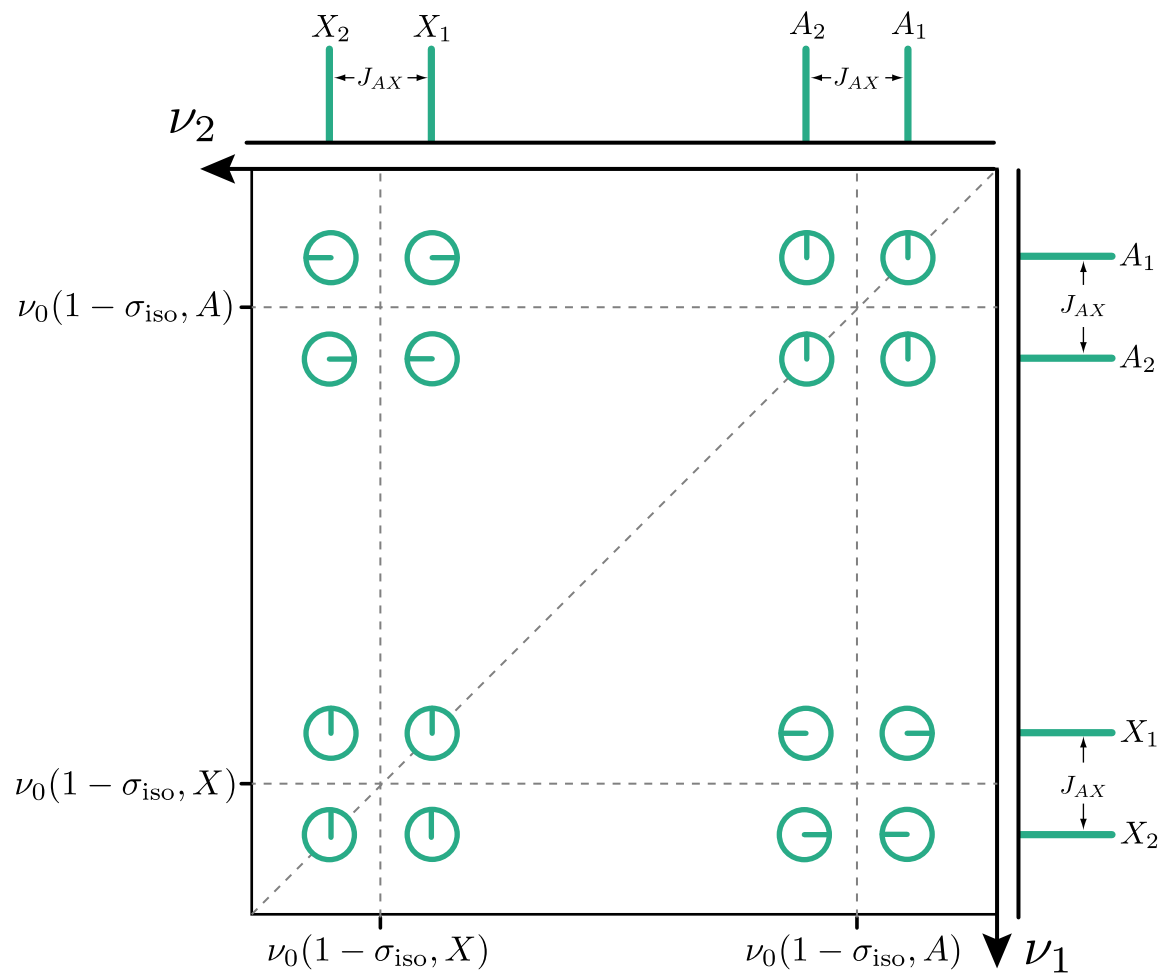
$A_1 \rightarrow X_1$ and $A_1 \rightarrow X_2$ pathways



All 16 transition pathways have the same $p_A + p_X$ pathway of $0 \rightarrow -1 \rightarrow -1$.

Assignment: Identify the remaining 12 transition pathways observed in COSY on this spin system and their p_A , p_X , $p_A + p_X$, and $2(pp)_{AX}$ pathways

COSY has 16 transition pathways in two weakly coupled spin half case



Assignment: Determine the transition pathway and p_A , p_X , $p_A + p_X$, and $2d_{AX}$ pathways associated with each of the 16 resonances observed in this COSY spectrum.

Advanced Assignment: Determine relative phase of the 16 resonances in this COSY spectrum.

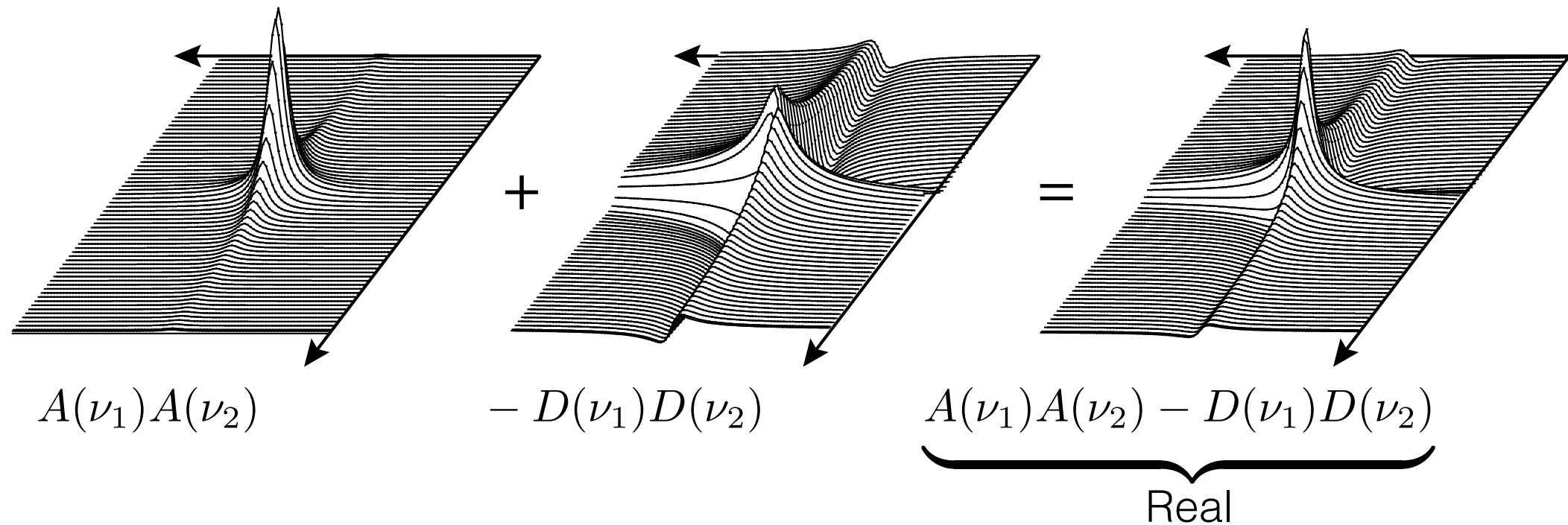
Lineshapes in multidimensional NMR

Path and Anti-Path Selection

Absorption Mode Lineshapes in Two Dimensions

$$S(\nu_1, \nu_2) = \left[\int_0^\infty e^{-i2\pi\nu_A t_1} e^{-|t_1|/T_2} e^{-i2\pi\nu_1 t_1} dt_1 \right] \times \left[\int_0^\infty e^{-i2\pi\nu_X t_2} e^{-|t_2|/T_2} e^{-i2\pi\nu_2 t_2} dt_2 \right]$$

$$= \underbrace{A(\nu_1 - \nu_A)A(\nu_2 - \nu_X) - D(\nu_1 - \nu_A)D(\nu_2 - \nu_X)}_{\text{Real}} + i \underbrace{[A(\nu_1 - \nu_A)D(\nu_2 - \nu_X) + A(\nu_2 - \nu_X)D(\nu_1 - \nu_A)]}_{\text{Imaginary}}$$



Absorption Mode Lineshapes in Two Dimensions

Mathematical Solution: Just extend lower limits to negative infinity.

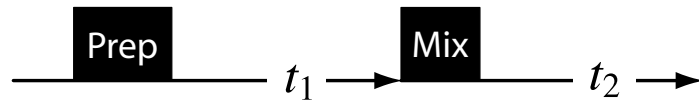
$$\begin{aligned}
 S(\nu_1, \nu_2) &= \left[\int_{-\infty}^{\infty} e^{-i2\pi\nu_A t_1} e^{-|t_1|/T_2} e^{-i2\pi\nu_1 t_1} dt_1 \right] \times \left[\int_{-\infty}^{\infty} e^{-i2\pi\nu_X t_2} e^{-|t_2|/T_2} e^{-i2\pi\nu_2 t_2} dt_2 \right] \\
 &= \underbrace{4A(\nu_1 - \nu_A)A(\nu_2 - \nu_X)}_{\text{Real}},
 \end{aligned}$$

Actually, only need to extend one lower limit to negative infinity

$$\begin{aligned}
 S(\nu_1, \nu_2) &= \left[\int_{-\infty}^{\infty} e^{-i2\pi\nu_A t_1} e^{-|t_1|/T_2} e^{-i2\pi\nu_1 t_1} dt_1 \right] \times \left[\int_0^{\infty} e^{-i2\pi\nu_X t_2} e^{-|t_2|/T_2} e^{-i2\pi\nu_2 t_2} dt_2 \right] \\
 &= \underbrace{2A(\nu_1 - \nu_A)A(\nu_2 - \nu_X)}_{\text{Real}} + \underbrace{i2A(\nu_1 - \nu_A)D(\nu_2 - \nu_X)}_{\text{Imaginary}}.
 \end{aligned}$$

Absorption Mode Lineshapes in Two Dimensions

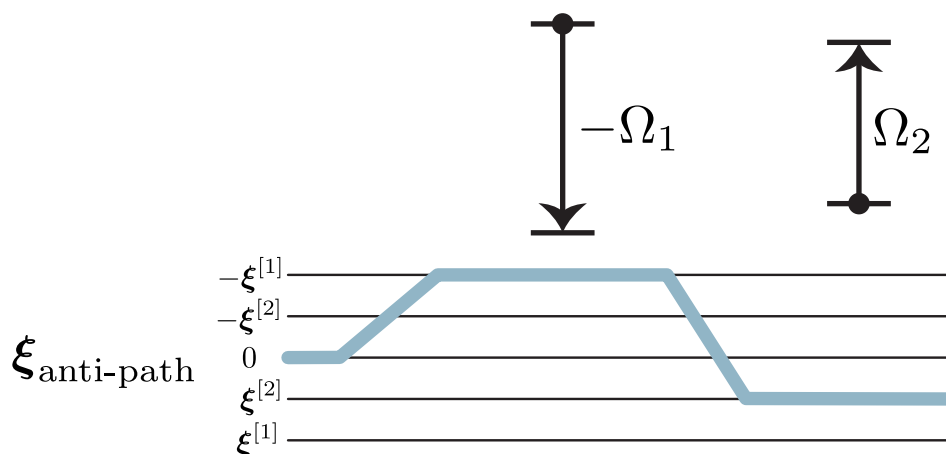
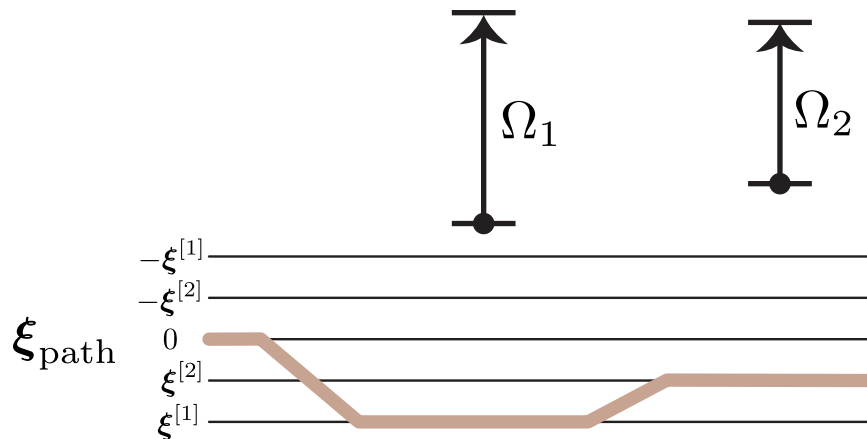
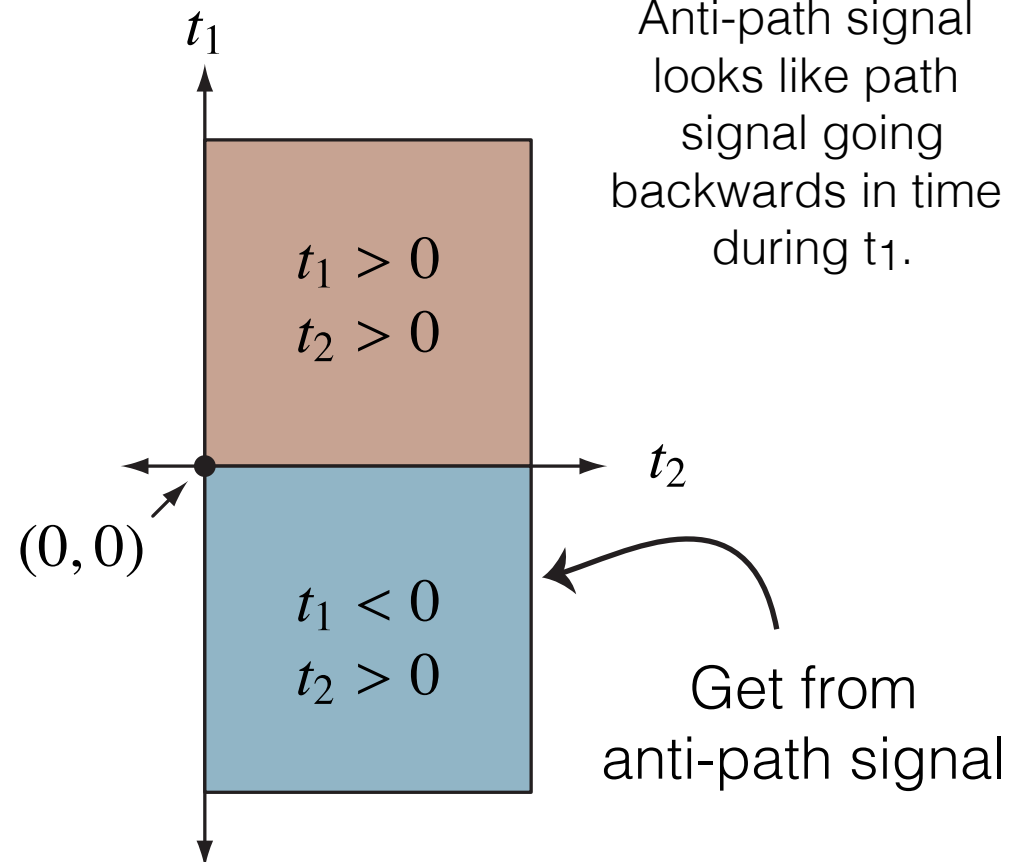
Hypercomplex Approach



$$\Phi_{\text{path}}(t_1, t_2) = \Omega_1 t_1 + \Omega_2 t_2$$

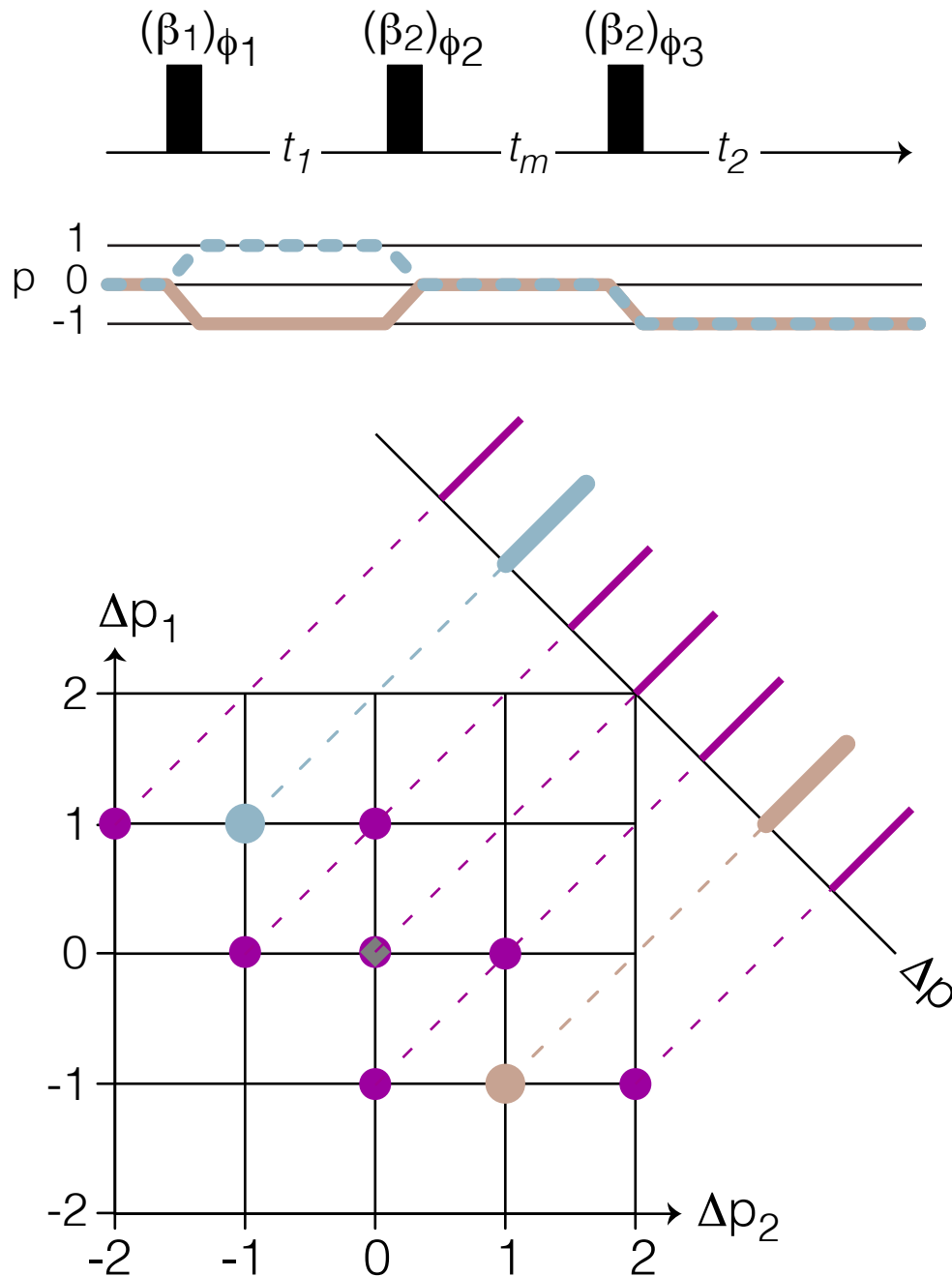
$$\begin{aligned} \Phi_{\text{anti-path}}(t_1, t_2) &= (-\Omega_1)t_1 + \Omega_2 t_2 \\ &= \Omega_1(-t_1) + \Omega_2 t_2 \\ &= \Phi_{\text{path}}(-t_1, t_2) \end{aligned}$$

Anti-path signal
looks like path
signal going
backwards in time
during t_1 .

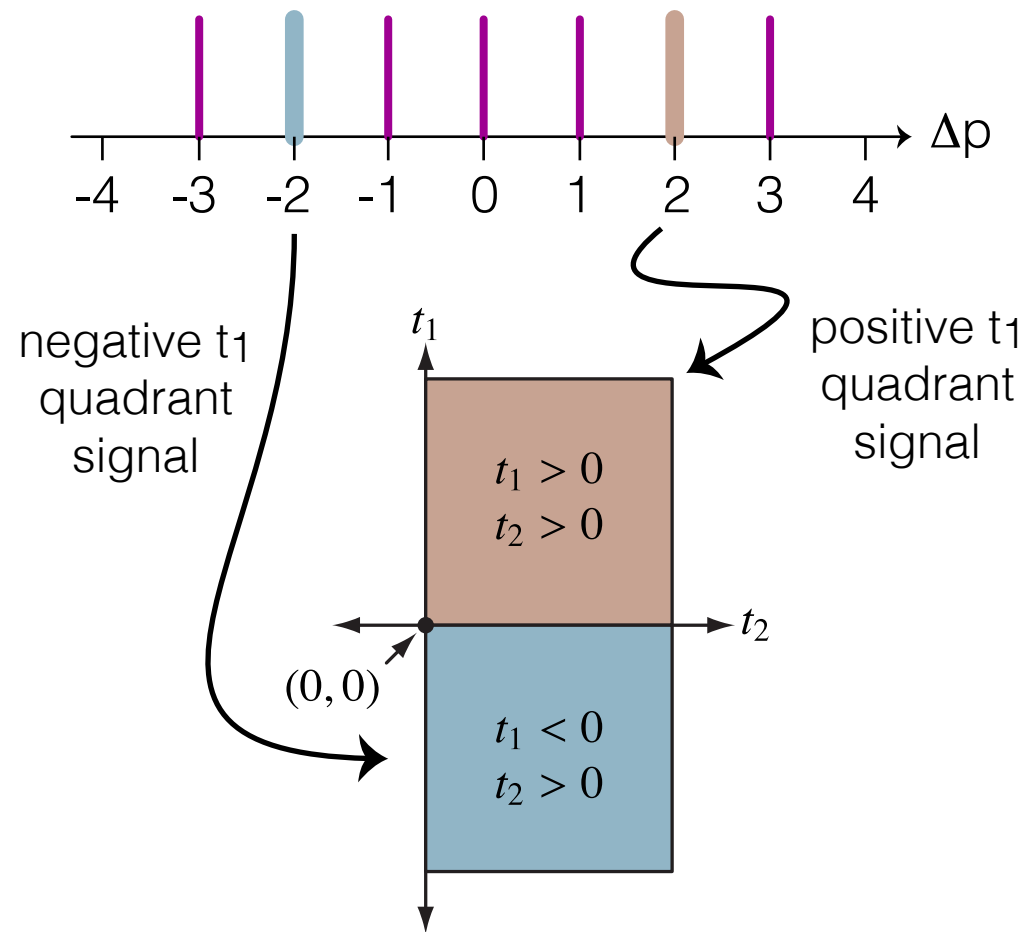


All relevant symmetries must have opposite
sign during t_1 , not just p .

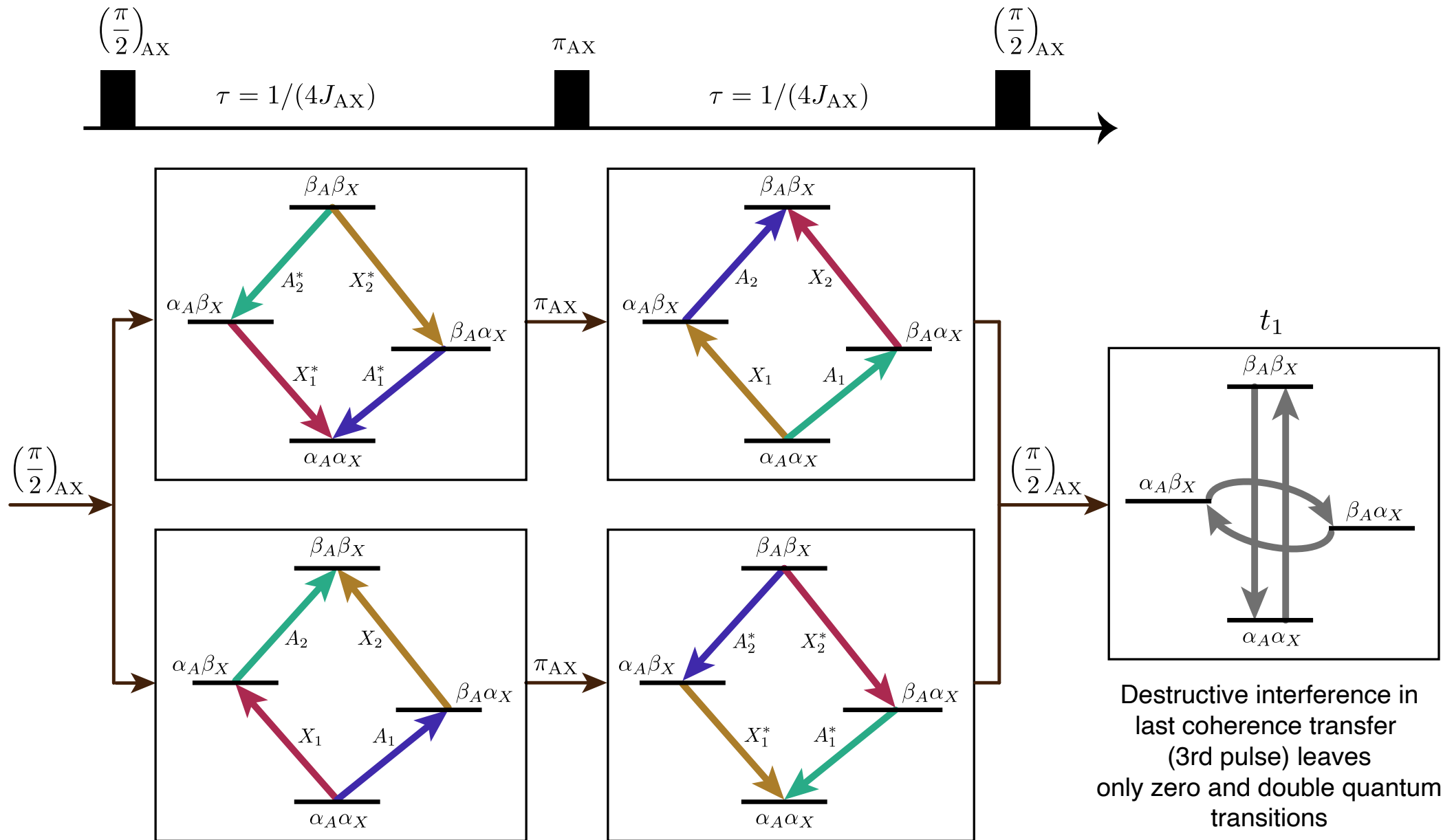
2D EXSY hypercomplex sequence (Spin 1/2)



- (1) Assume no receiver ghosts
 $p = -1$ detected & no need to vary ϕ_3
- (2) Set $\phi = \phi_1 = -\phi_2$
- (3) Vary ϕ in steps of $\pi/4$ from 0 to 2π
- (4) FT wrt ϕ separates pathway signals

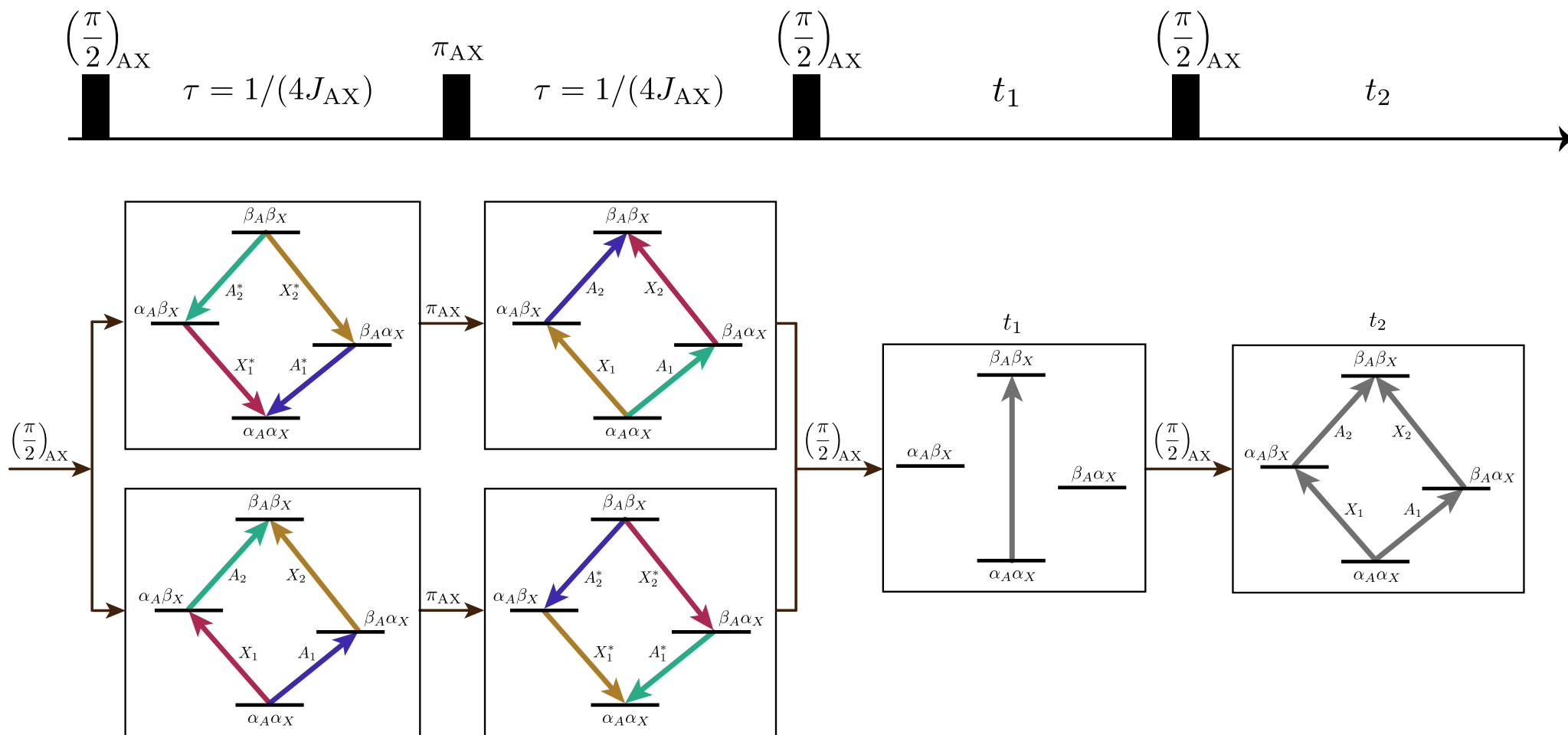


Multiple Quantum Excitation of two weakly coupled spin 1/2



Assignment: Work out the transition pathways and associated p_A , p_X , $(pp)_{AX}$, and $p_A + p_X$ pathways that end at the double quantum transition with $p_A + p_X = -2$.

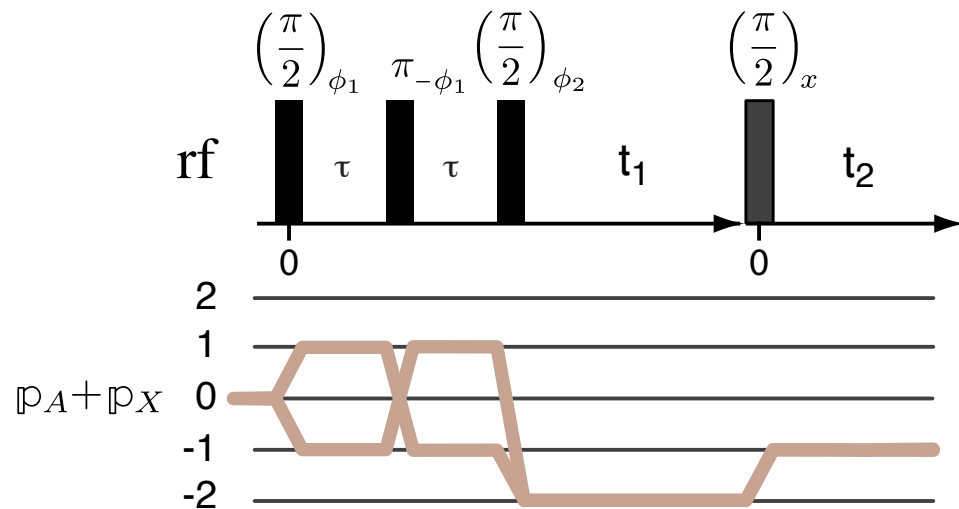
INADEQUATE Transition Pathways



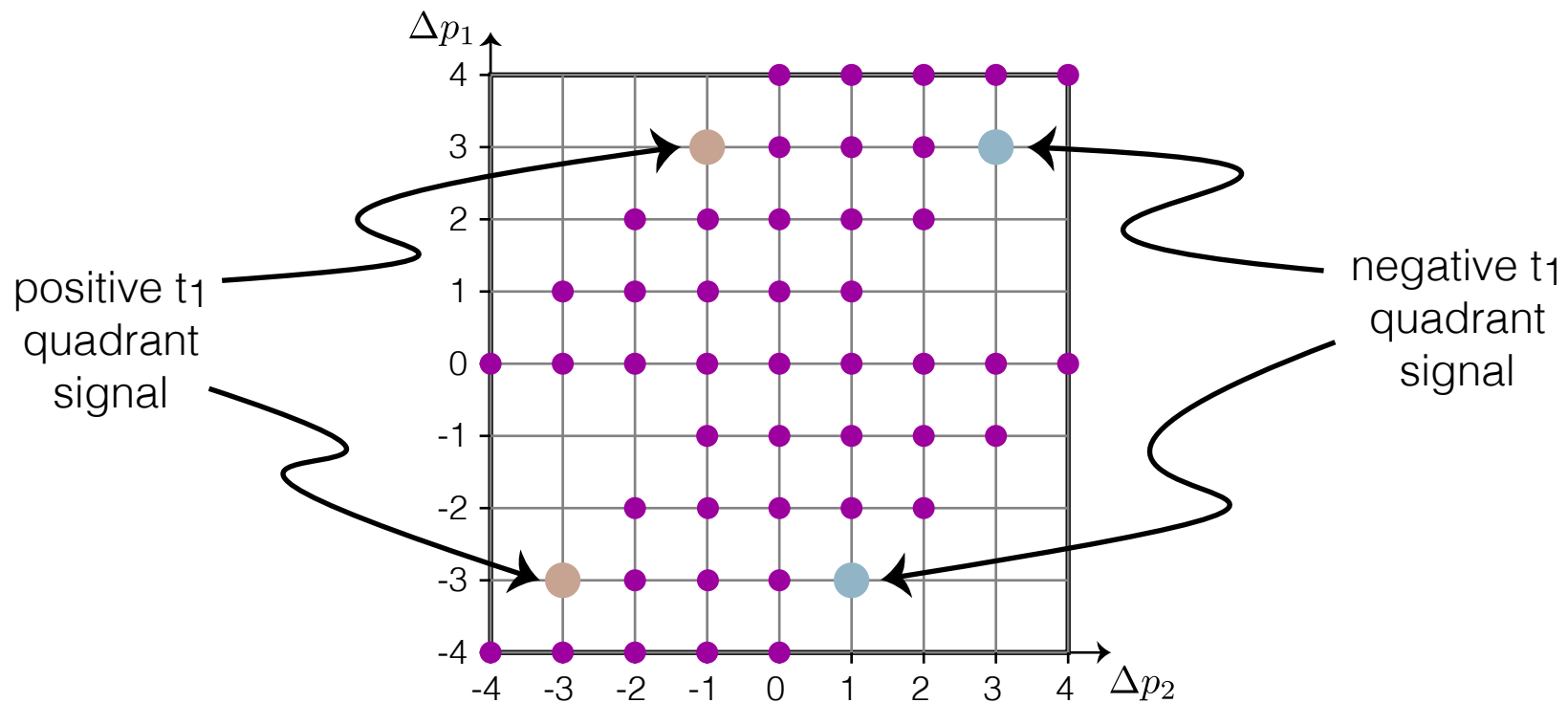
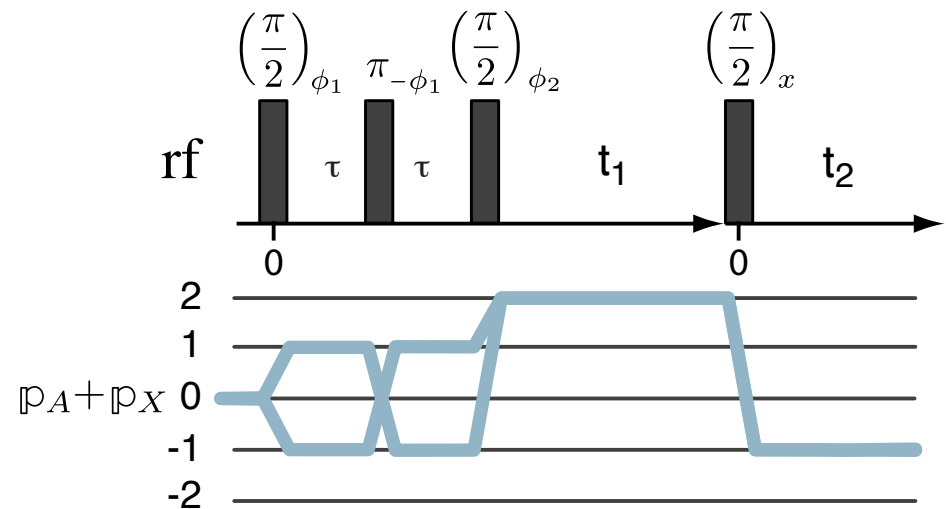
Assignment: Work out the $p_A + p_X$ pathways for the INADEQUATE experiment.

INADEQUATE Phase Dimensions

Positive t_1 quadrant pathways



Negative t_1 quadrant pathways



Why use phase dimensions instead of phase cycling?

- Writing pulse sequences are easier since there's no need to work out a receiver phase cycle that aliases desired pathways together while keeping undesired pathways separate.
(See supplementary notes on phase cycling).

- Δp “spectrum” shows you where your magnetization ends up.
 - Ever watch your signal grow then disappear as a phase cycle completes?
 - Ever wonder where all that signal went?

Phase dimensions allow you to retain this information at no extra cost in time.

Phase cycling throws away information that is useful in determining if your experiment is working correctly.

Further Reading

- Wokaun and Ernst,
“Selective Detection Of Multiple Quantum Transitions In NMR by Two-dimensional Spectroscopy,”
Chemical Physics Letters, **52**, 407 (1977)
- Drobny, Pines, Sinton, Weitekamp, Wemmer,
“Fourier Transform Multiple Quantum Nuclear Magnetic Resonance,”
Faraday Symp. Chem. Soc., **13**, 93 (1978)
- Bain,
“Coherence Levels and Coherence Pathways in NMR. A Simple Way to Design
Phase Cycling Procedures,”
J. Magn. Reson., **56**, 418-427 (1984)
- Bodenhausen, Kogler, Ernst,
“Selection of Coherence-Transfer Pathways in NMR Pulse Experiments,”
J. Magn. Reson., **58**, 370-388 (1984)
- Baltisberger, Walder, Keeler, Kaseman, Sanders, and Grandinetti,
“Phase incremented echo train acquisition in NMR spectroscopy,”
J. Chem. Phys., **136**, 211104 (2012).
- Grandinetti, Trease, and Ash, “Symmetry Pathways in Solid-State NMR”
Prog. NMR Spect. **59**, 121 (2011).

Thanks!



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Ph.D. Students

Symmetry Pathways: Jason Ash (Merck), Nicole Trease (U. Cambridge)

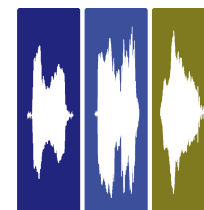
Phase dimensions + Symmetry Pathways: Brennan Walder (EPFL), Deepansh Srivastava (Ohio State U)

Visiting Professor

Phase dimensions + Symmetry Pathways: Jay Baltisberger (Berea College)

RMN

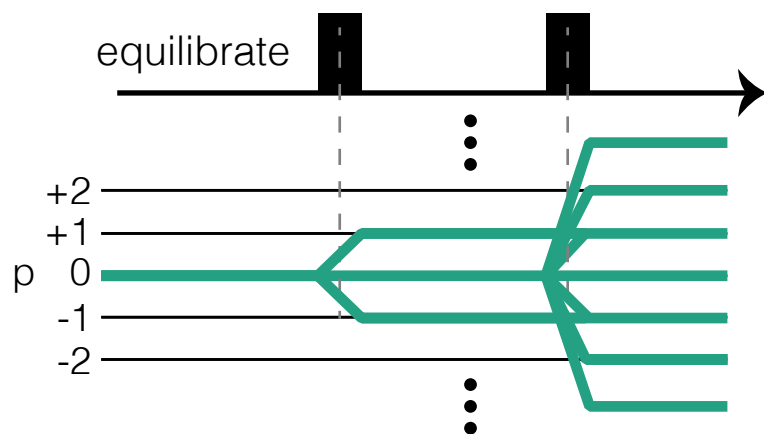
Multidimensional
signal processing on MacOS
Handles arbitrary number of dimensions
(ask for a free promo code)



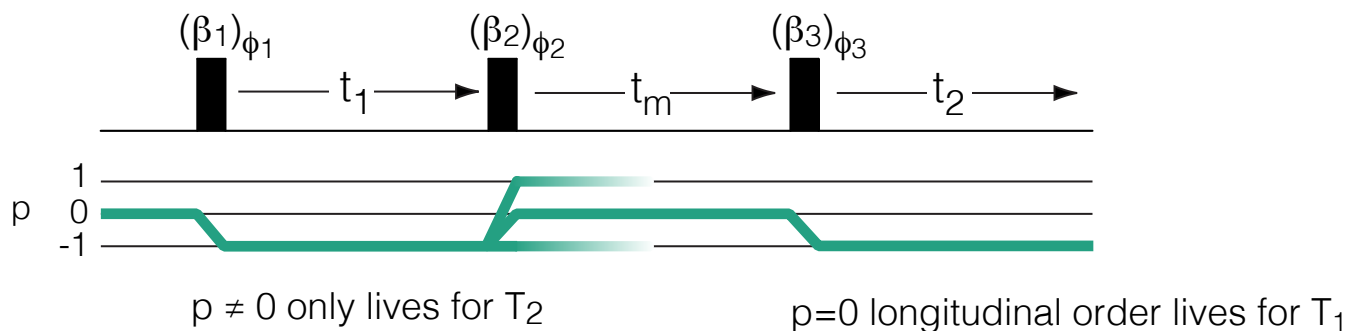
Supplemental Material

Some helpful tips

- When rf strength is much greater than internal (chem. shift, J, dipolar, quadrupolar) couplings then first pulse can only excite observable single quantum transitions



- Use differences between T_1 and T_2 to dephase undesired $p \neq 0$ pathways



Some helpful tips

- Use well calibrated pulse lengths

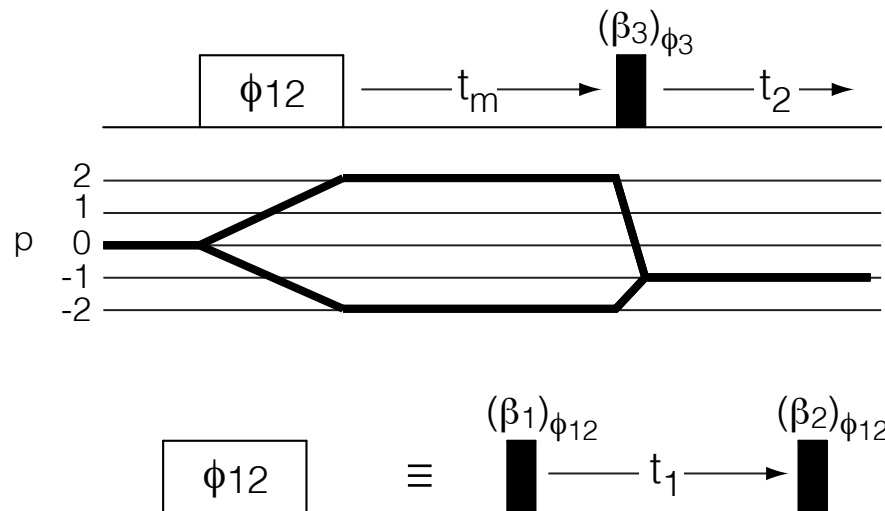
$$p = +1 \xrightarrow{\pi} -1$$

$$p = -1 \xrightarrow{\pi} +1$$

- Use gradients to selectively dephase and rephase pathways
(great for liquids, less so for solids)

Read "Gradient-Enhanced Spectroscopy", Hurd, J. Magn. Reson., 87, 422-428 (1990).

- Get a modern receiver so only $p = -1$ is detected.
- Phase cycle many pulses as one



The hard way

Avoiding the Fourier transform
by cycling the receiver phase.

Pros

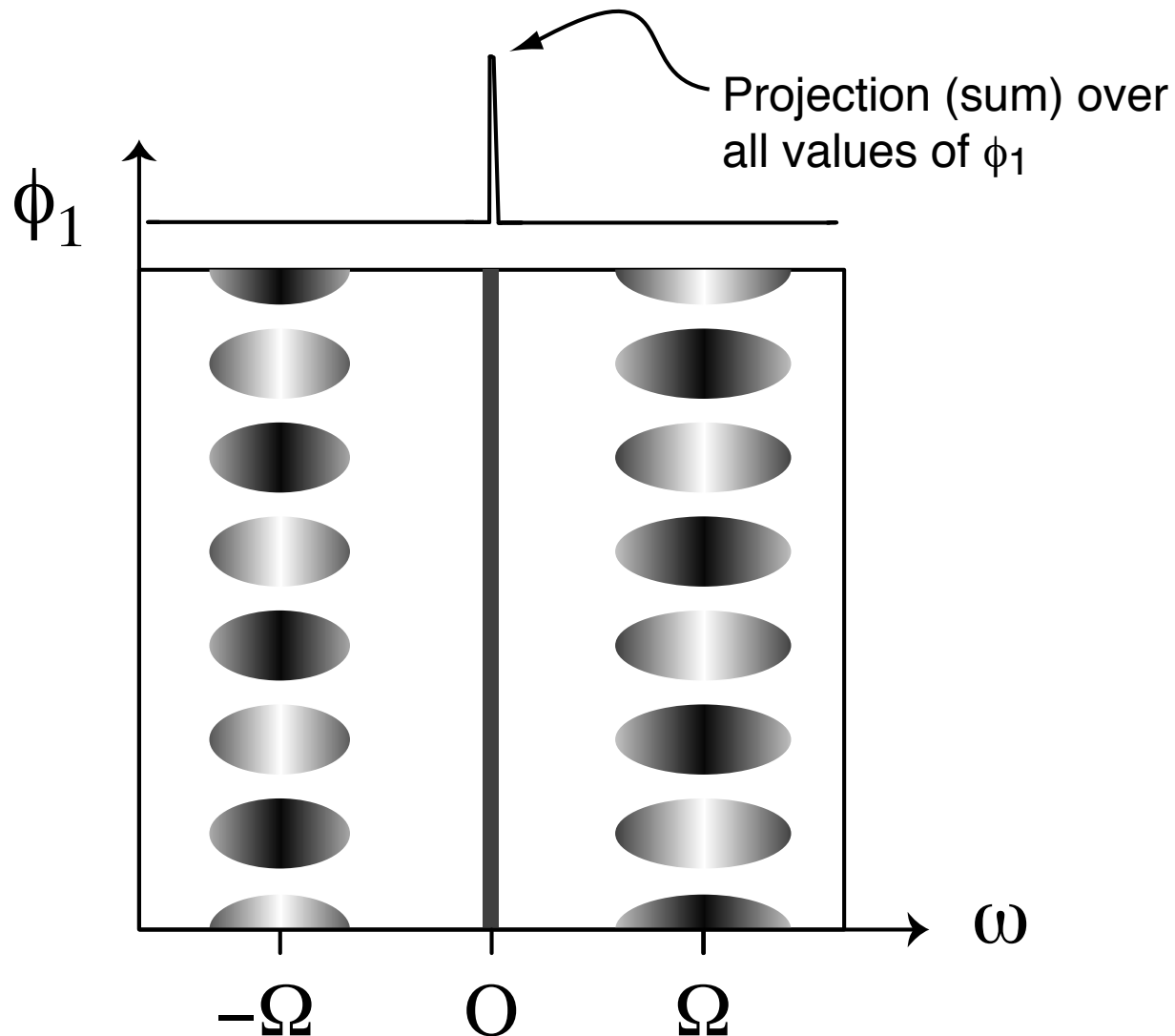
- reduces signal disk space requirements
- avoids extra Fourier transforms

Cons

- Phase cycle design becomes a complicated exercise in spectral folding.
- Information about intensity in undesired pathways is lost.

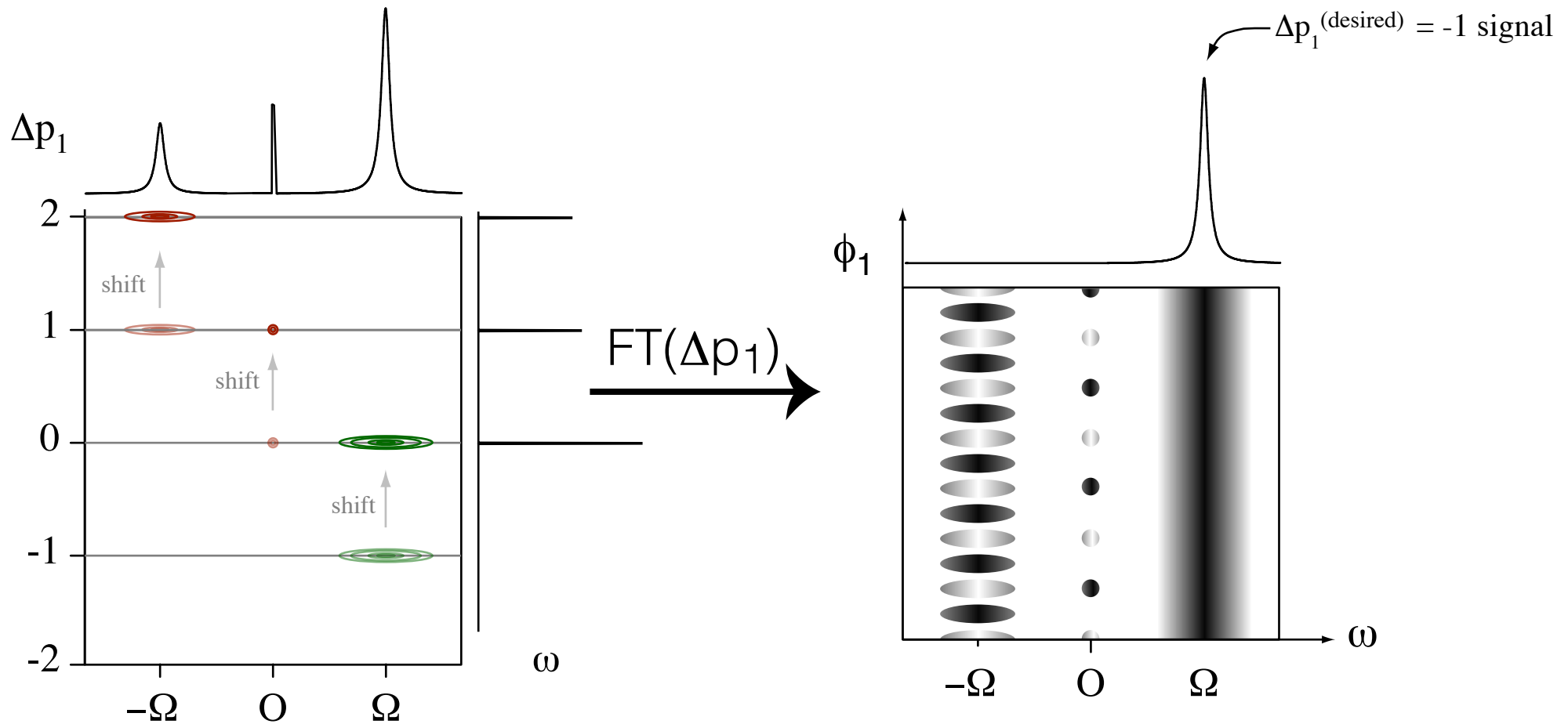
Phase Cycling: Avoiding the FT wrt phase

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 $\Delta p=0$.



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

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

Extract $\Delta p_{1,\text{desired}}$ signal by applying 1st-order phase correction to signal in ϕ_1 dimension to shift $\Delta p_{1,\text{desired}}$ signal to $\Delta p_1 = 0$, before projecting over ϕ_1 .

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

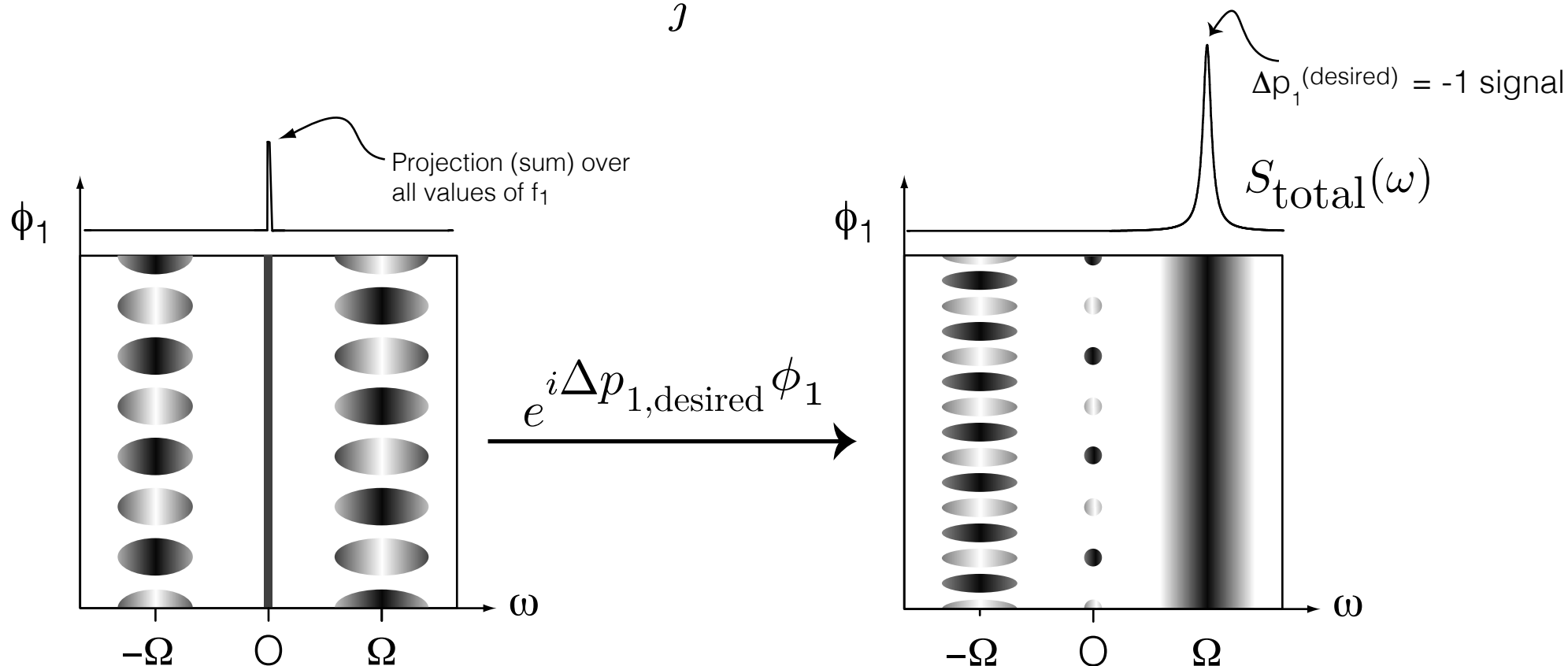
All this can be implemented during signal acquisition by shifting the receiver phase during signal averaging by

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

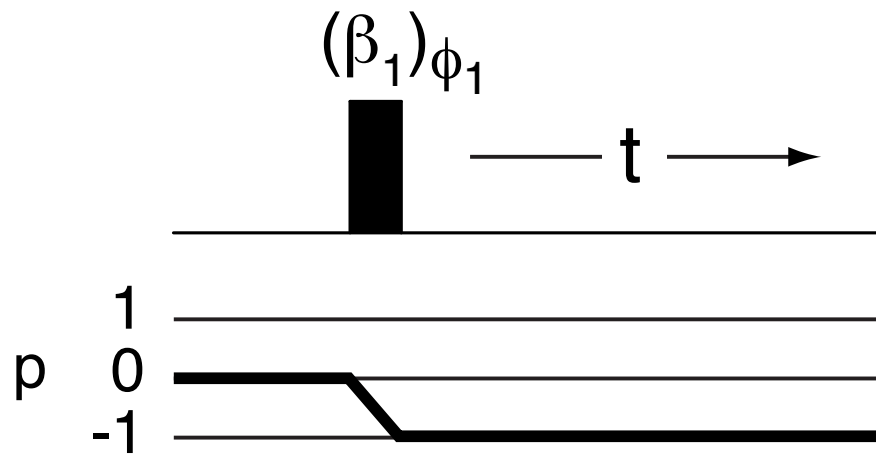
Phase Cycling: Avoiding the FT wrt phase

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



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

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

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

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

$$\phi_1 = 0^\circ \quad 120^\circ \quad 240^\circ,$$

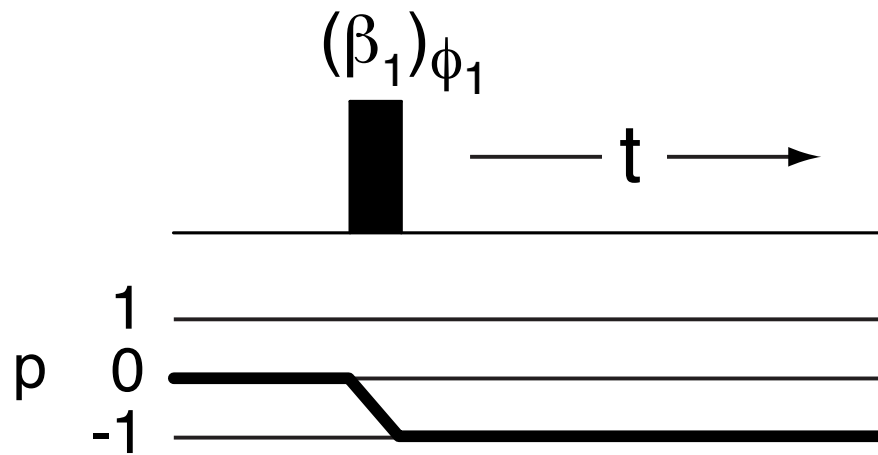
$$\phi_R = 0^\circ \quad 120^\circ \quad 240^\circ.$$

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, $S_{\text{total}}(t) = 3a e^{-i\Omega t}$.

Phase Cycling: One Pulse & Acquire



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

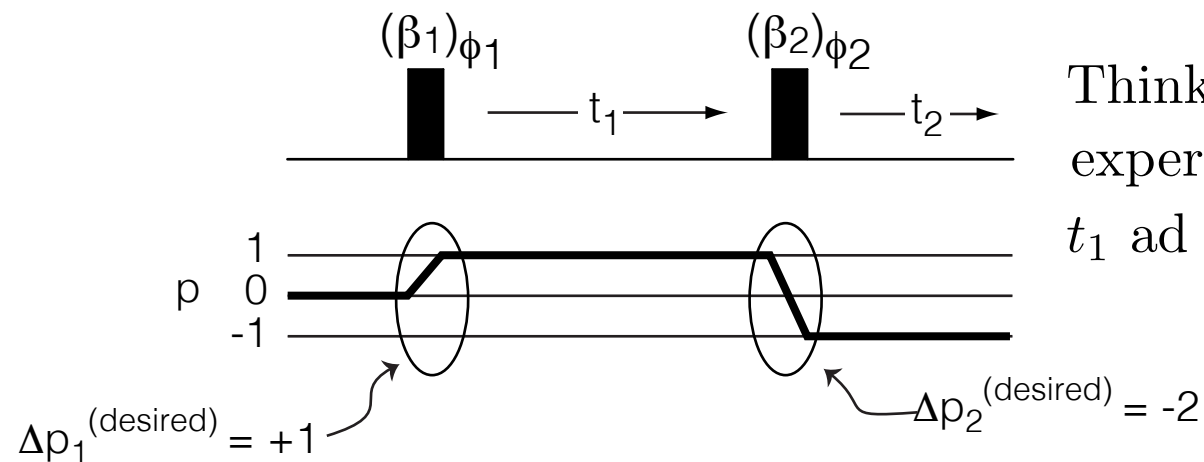
$$\phi_R^{(j)} = -\Delta p_{1,\text{desired}} \phi_1^{(j)} = \phi_1^{(j)}$$

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

$$\phi_1 = 0^\circ \quad 90^\circ \quad 180^\circ \quad 270^\circ,$$

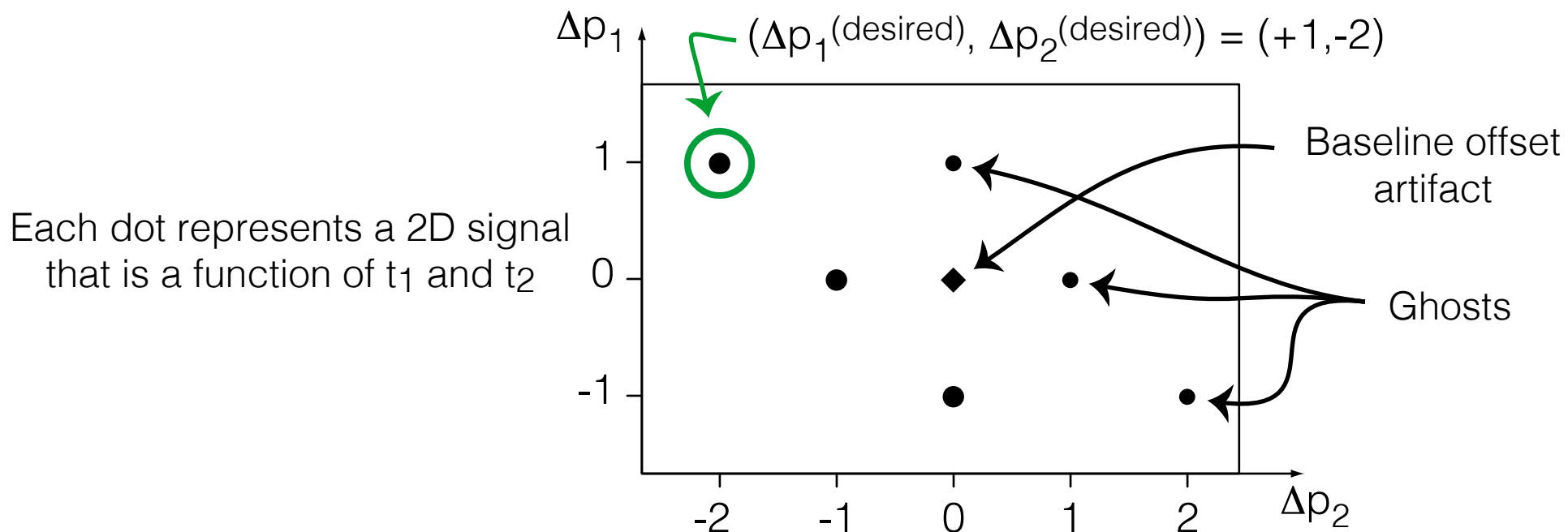
$$\phi_R = 0^\circ \quad 90^\circ \quad 180^\circ \quad 270^\circ.$$

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, ϕ_1 and ϕ_2 .

After 2D Fourier Transform wrt ϕ_1 and ϕ_2

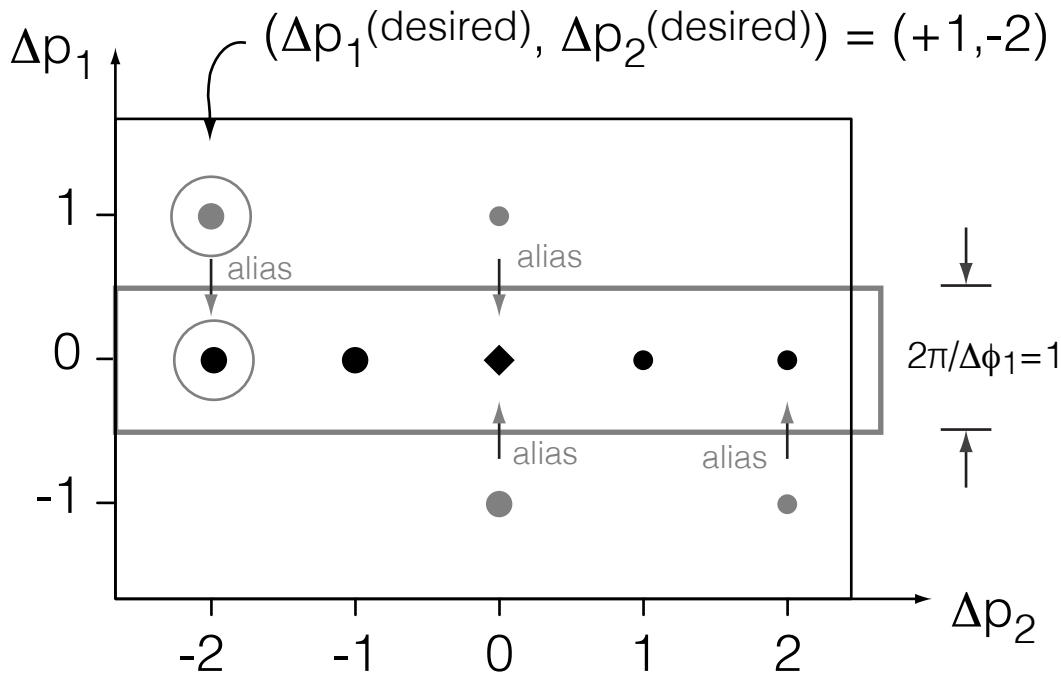


Two Pulse Sequence (Spin 1/2)

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 $\Delta p_1=0$.

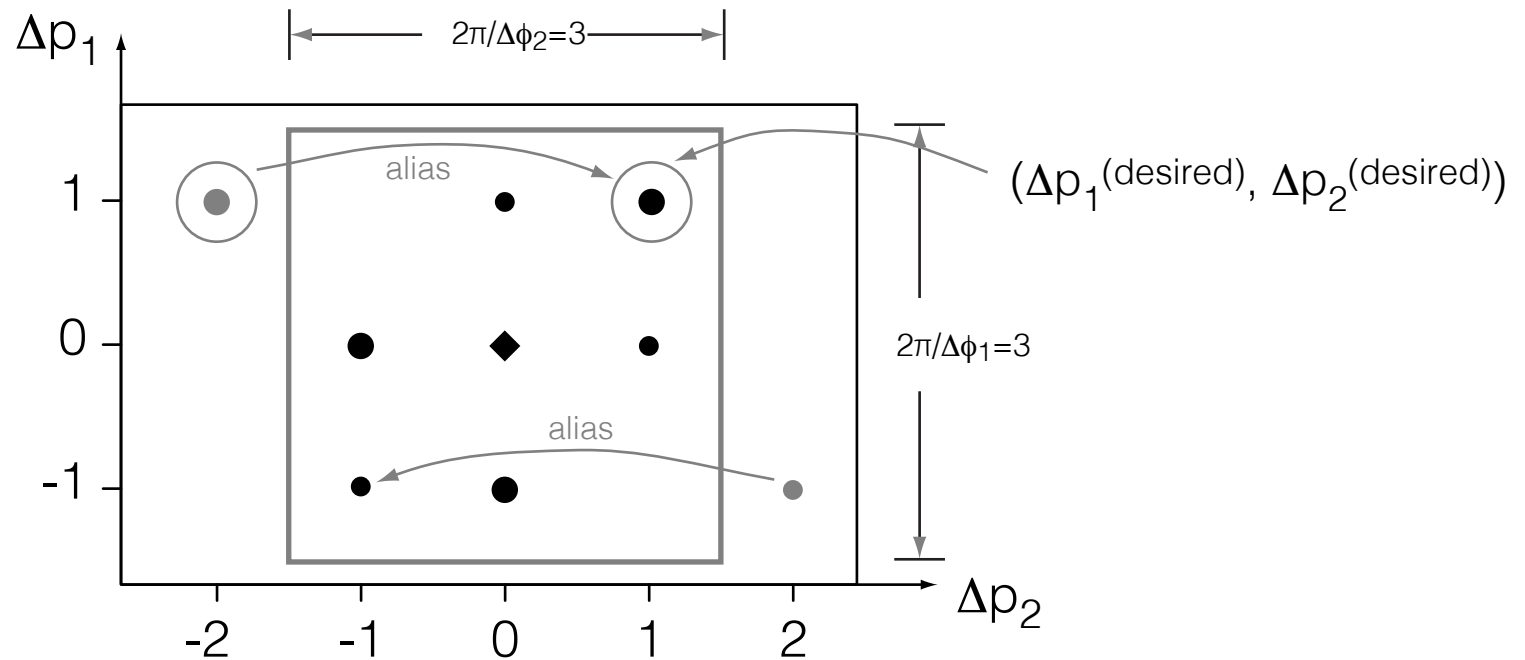


This works since nothing aliases onto the desired signal.

$\phi_1 = 0^\circ,$				
$\phi_2 = 0^\circ$	72°	144°	216°	$288^\circ,$
$\phi_R = 0^\circ$	144°	288°	72°	$216^\circ,$

Two Pulse Sequence (Spin 1/2)

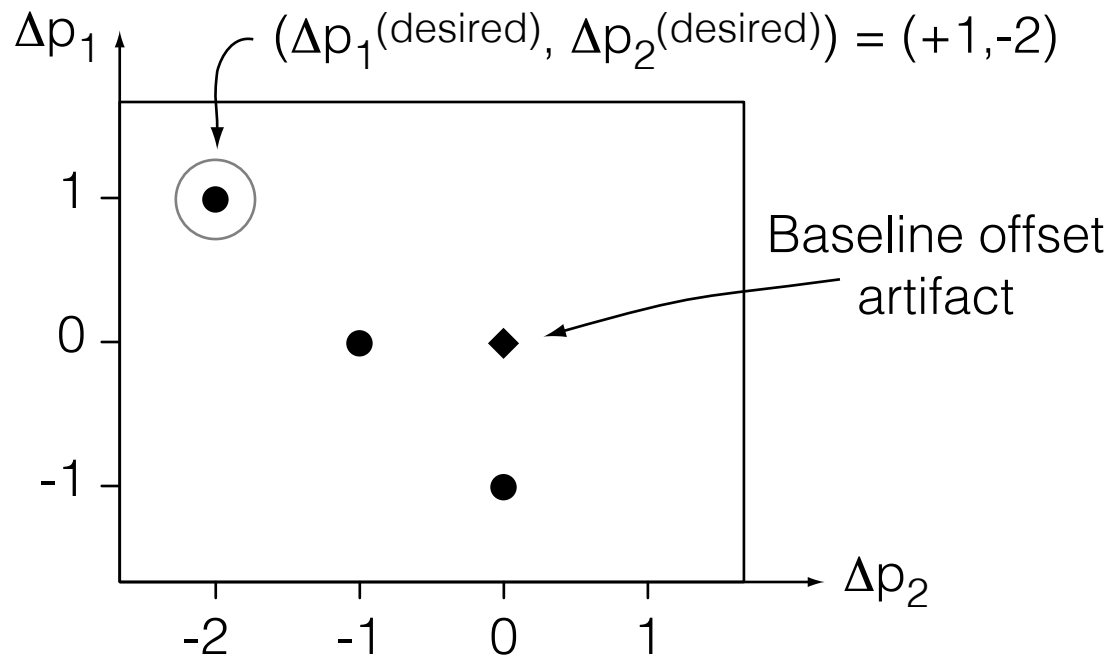
Alternatively, if we phase cycled ϕ_1 with $n_1=3$, then our desired signal would still be unaliased with n_2 as low as $n_2 = 3$.



ϕ_1	=	0°	120°	240°	0°	120°	240°	0°	120°	240° ,
ϕ_2	=	0°	0°	0°	120°	120°	120°	240°	240°	240° ,
ϕ_R	=	0°	240°	120°	240°	120°	0°	120°	0°	240° ,

Two Pulse Sequence (Spin 1/2)

Without quadrature ghosts we can reduce sampling even more



$$\phi_1 = 0^\circ \quad 120^\circ \quad 240^\circ,$$

$$\phi_2 = 0^\circ$$

$$\phi_R = 0^\circ \quad 240^\circ \quad 120^\circ,$$

or

$$\phi_1 = 0^\circ$$

$$\phi_2 = 0^\circ \quad 120^\circ \quad 240^\circ,$$

$$\phi_R = 0^\circ \quad 240^\circ \quad 120^\circ,$$

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

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

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

Then sum (project) signal over all values of ϕ_1 and ϕ_2 to obtain the desired signal:

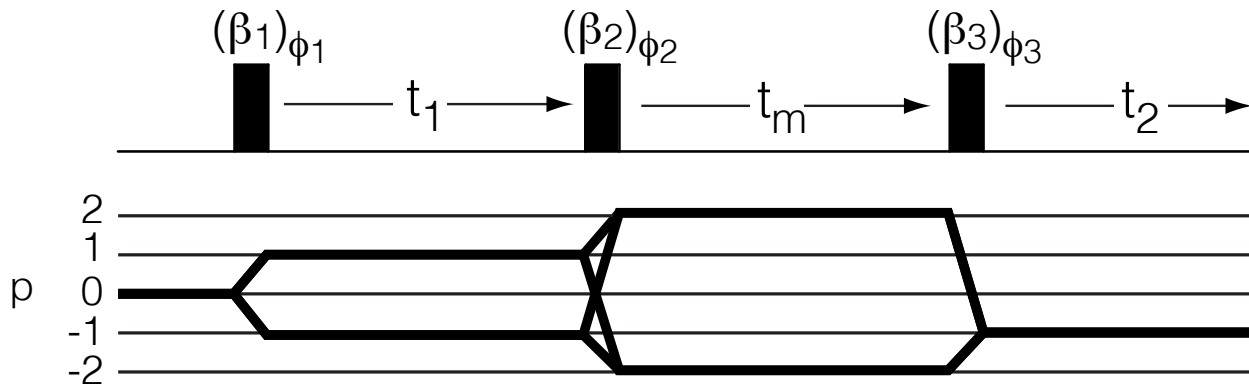
$$S_{\text{total}}(t_1, t_2) = \sum_j^{n_1} \sum_k^{n_2} S(\phi_1^{(j)}, \phi_2^{(k)}, t_1, t_2) e^{-i\phi_R^{(j,k)}}$$

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



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

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

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

$$\Delta p_1 = \underline{-1}, (0), \underline{+1}$$

$$n_1 = 2$$

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

$$n_2 = 2$$

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

Phase cycling of receiver

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

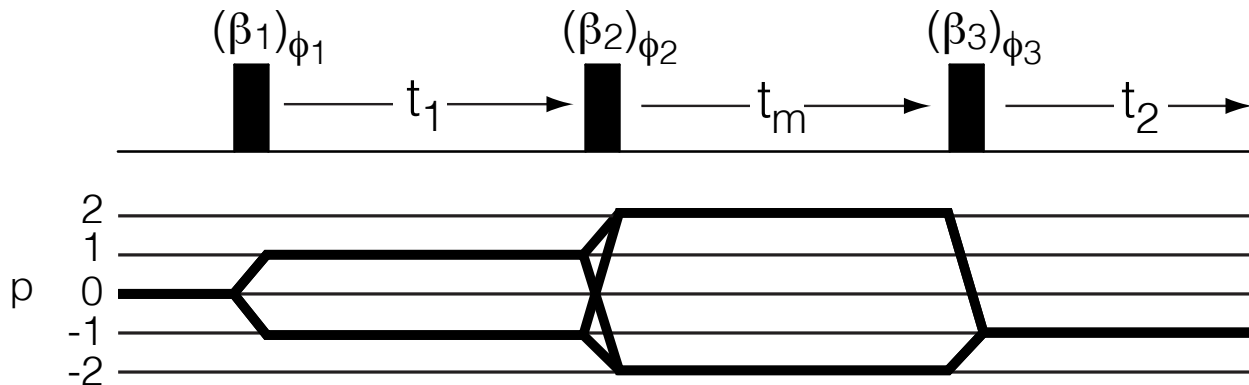
One possible Receiver Eq.

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



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

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

$$\Delta p_1 = \underline{-1}, (0), \underline{+1}$$

$$n_1 = 2$$

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

$$n_2 = 2$$

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

$$\phi_1 = 0^\circ \quad 180^\circ \quad 0^\circ \quad 180^\circ,$$

$$\phi_2 = 0^\circ \quad 0^\circ \quad 180^\circ \quad 180^\circ,$$

$$\phi_R = 0^\circ \quad 180^\circ \quad 180^\circ \quad 0^\circ.$$