Phase cycling in pulse programs

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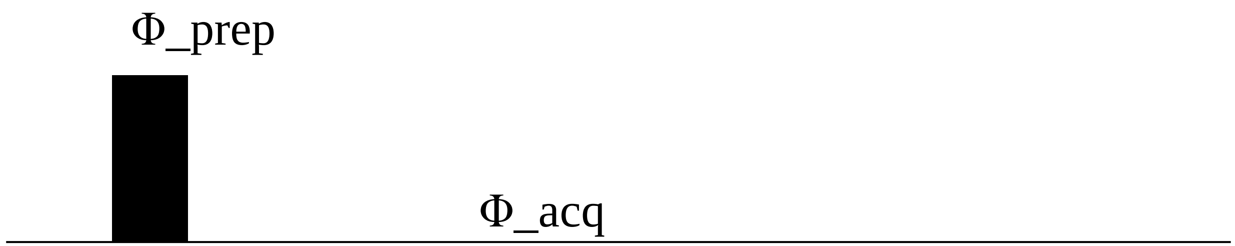
Phase cyclings

In the NMR pulse program, phases of pulses and acquisition are varied scan to scan.

ph1=0 1 2 3
ph31=0 1 2 3

obs_phs_prep = { 0, 90,180,270};
obs_phs_acq = { 0, 90,180,270};



1st scan:	0°	1st scan:	0°
2nd scan:	90 °	2nd scan:	90 °
3rd scan:	180 °	3rd scan:	180 °
4th scan:	270 °	4th scan:	270 °

Phase cyclings

In the NMR pulse program, phases of pulses and acquisition are varied scan to scan.

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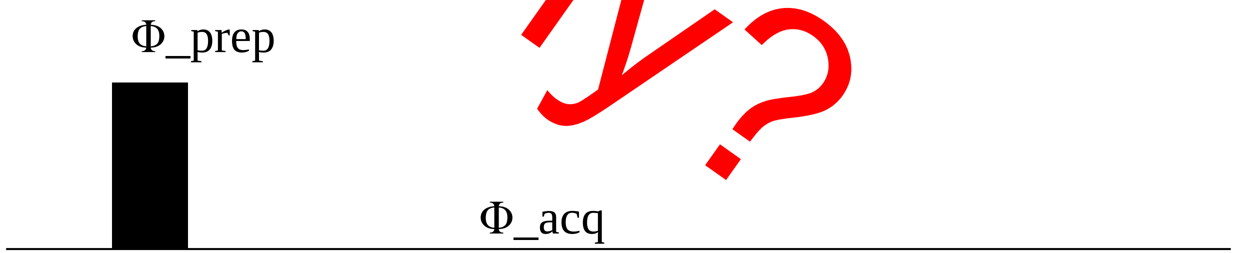
ph31=0 1 2 3

obs_phs_prep = { 0, 90,180,270};
obs_phs_acq = { 0, 90,180,270};

Why?



1st scan:	0°	1st scan:	0°
2nd scan:	90 °	2nd scan:	90 °
3rd scan:	180 °	3rd scan:	180 °
4th scan:	270 °	4th scan:	270 °

references

Phase cycling:
G. Bodenhausen, H. Kogler, R.R. Ernst, J. Magn. Reson. 58 (1984) 370-388.
R.R. Ernst, G. Bodenhausen, A. Wokaun, Principles of Nuclear Magnetic Resonance in One and Two Dimensions, Oxford (1988).

Cogwheel phase cycling:
M.H. Levitt, P.K. Madhu, C.E. Hughes, J. Magn. Reson. 155 (2000) 300-306.

Multiplex phase cycling:
N. Ivchenko, C.E. Hughes, M.H. Levitt, J. Magn. Reson. 160 (2003) 52-58.

contents

Background

Importance of coherence selection

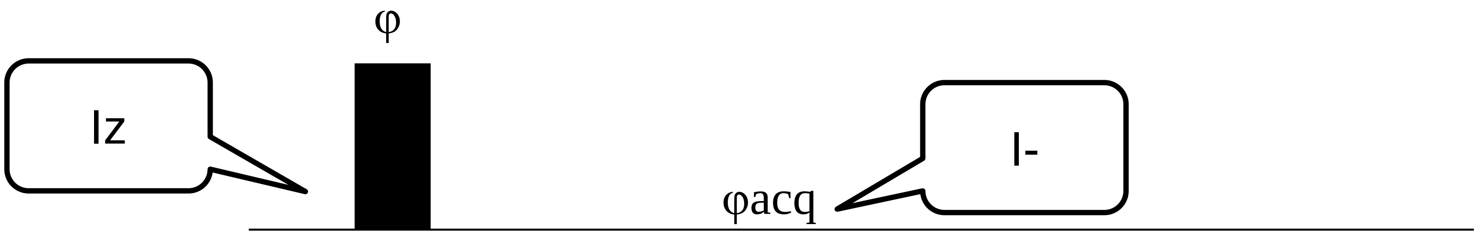
Coherence pathway selection by phase cyclings

Multiple selection, multi-dimension

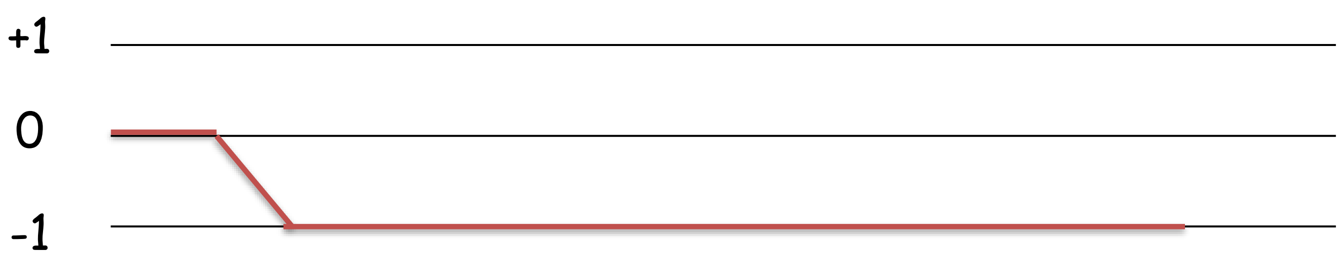
Multiplex and cogwheel phase cycling

Phase cycling in NMR

The same pulse trains are repeatedly applied with changing their phases, then FIDs are added.



1^{st} scan:	0°	1^{st} scan:	0°
2^{nd} scan:	90 °	2^{nd} scan:	90 °
3^{rd} scan:	180 °	3^{rd} scan:	180 °
4^{th} scan:	270 °	4^{th} scan:	270 °



To select coherence pathway

Background: What is coherence order?

Phase cyclings choose a specific coherence.

Coherence is defined by the response with respect to rotation along z-axis.

$$\exp(-i\phi F_z)\sigma^{(p)}\exp(i\phi F_z) = \exp(-ip\phi)\sigma^{(p)}$$

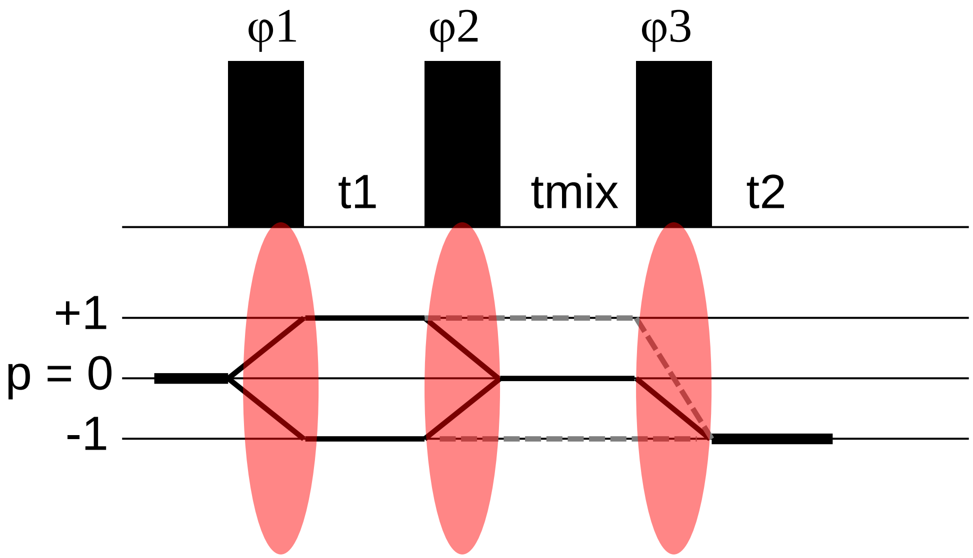
The order of coherence can be calculated by simply adding number of ladder operators. If the operator include *n* I+, *m* I-, and *q* Iz, the coherence order *p* is *n* - *m*.

Examples:

p = 0; Iz, I^+I^- ,I1zI2z etc.
p = +1; I+, I+Iz etc.
p = -1; I-, I1-I2-I1+ etc.
p = +2; I1+I2+ etc.

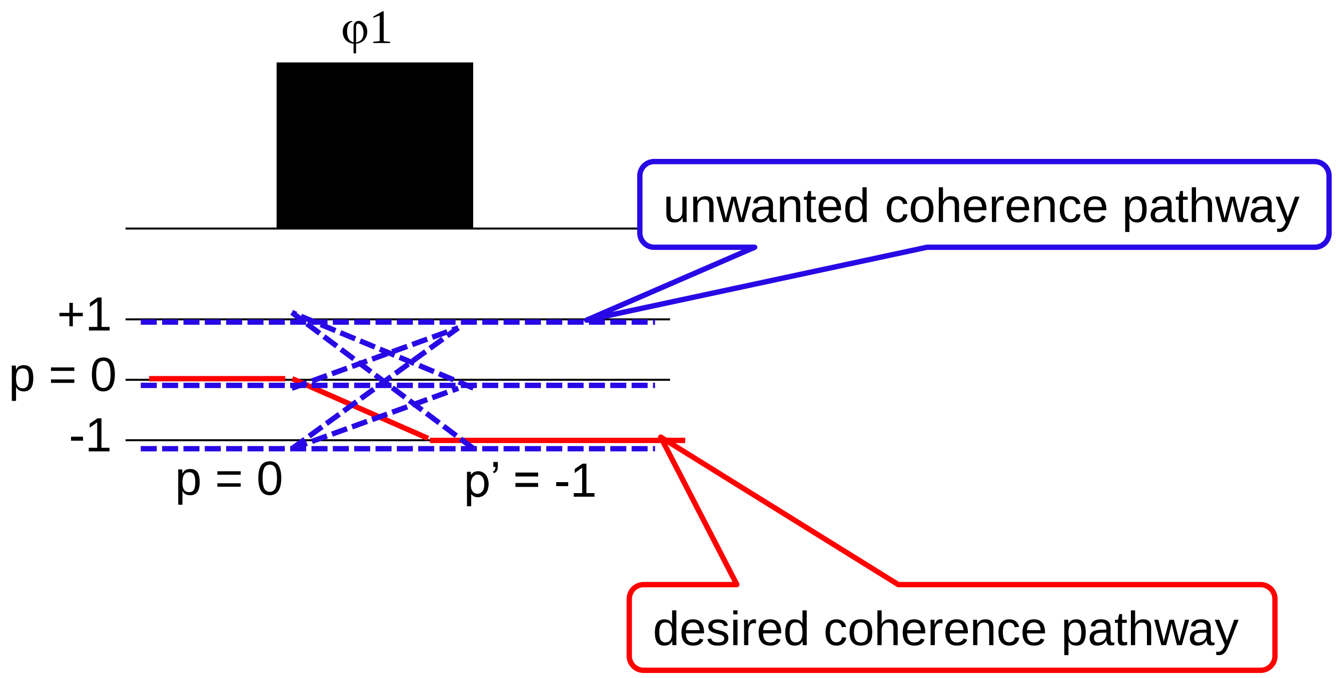
Background: How to change coherence order?

Coherence order does not changes without rf irradiations, (conservative quantity under free evolution)
Coherence can changes under rf irradiation. It can be converted to any coherence order, however, efficiency varies depending on pulses, initial states, spin systems, etc.

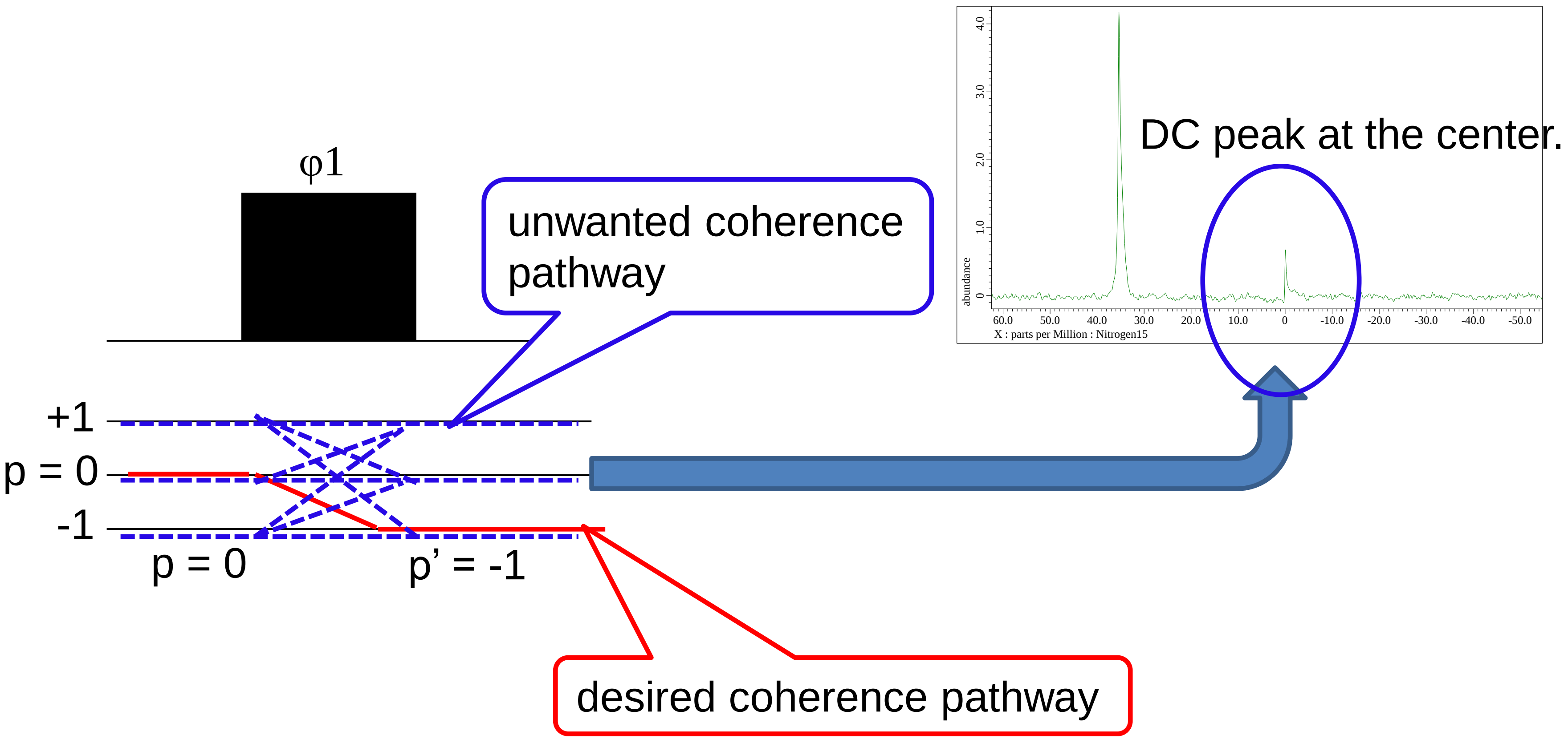


Why should coherence pathway be selected?

As the pulses can introduce any change in coherence order, the unwanted coherence could be involved. Even in a single pulse experiment, 1) initial magnetization could be other than Iz, and 2) p = 0, +1 could be induced after single pulse excitation.



Why should coherence pathway be selected?



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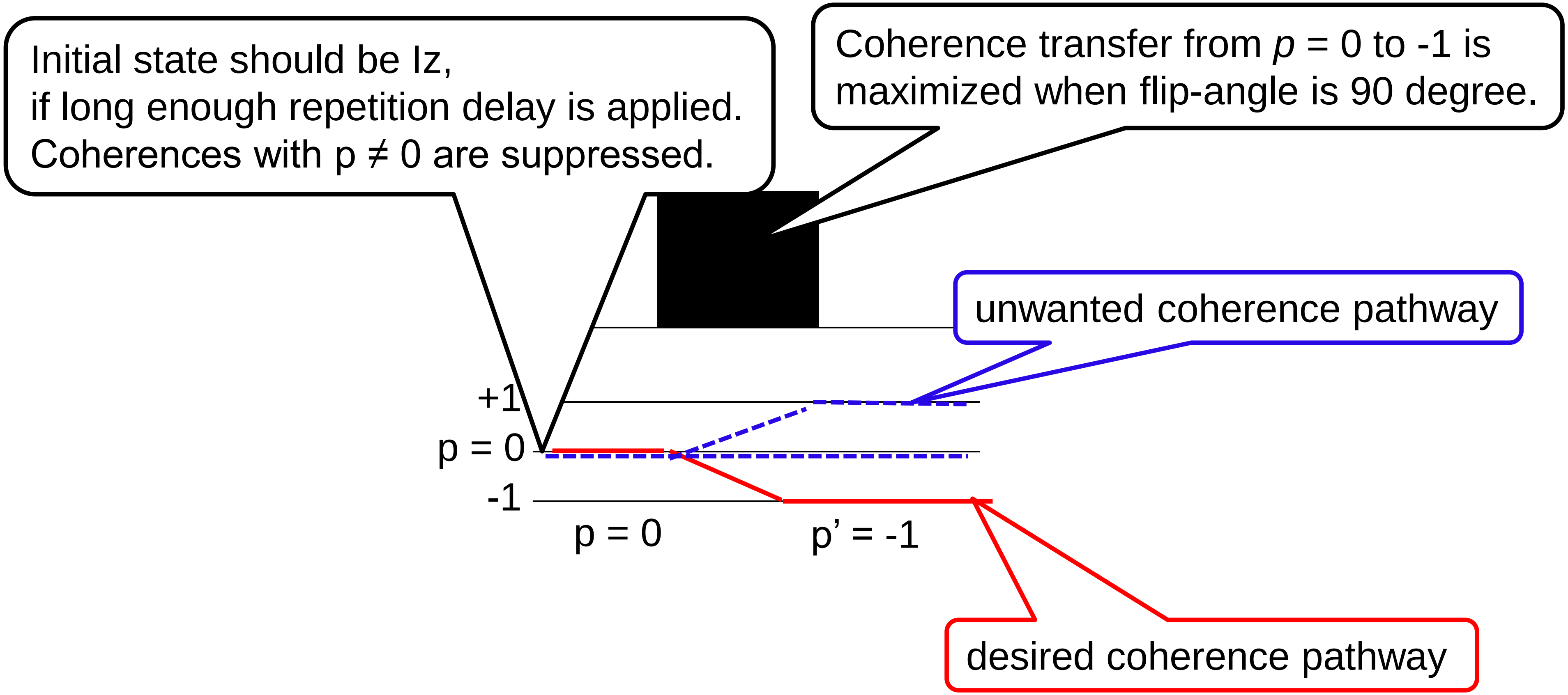
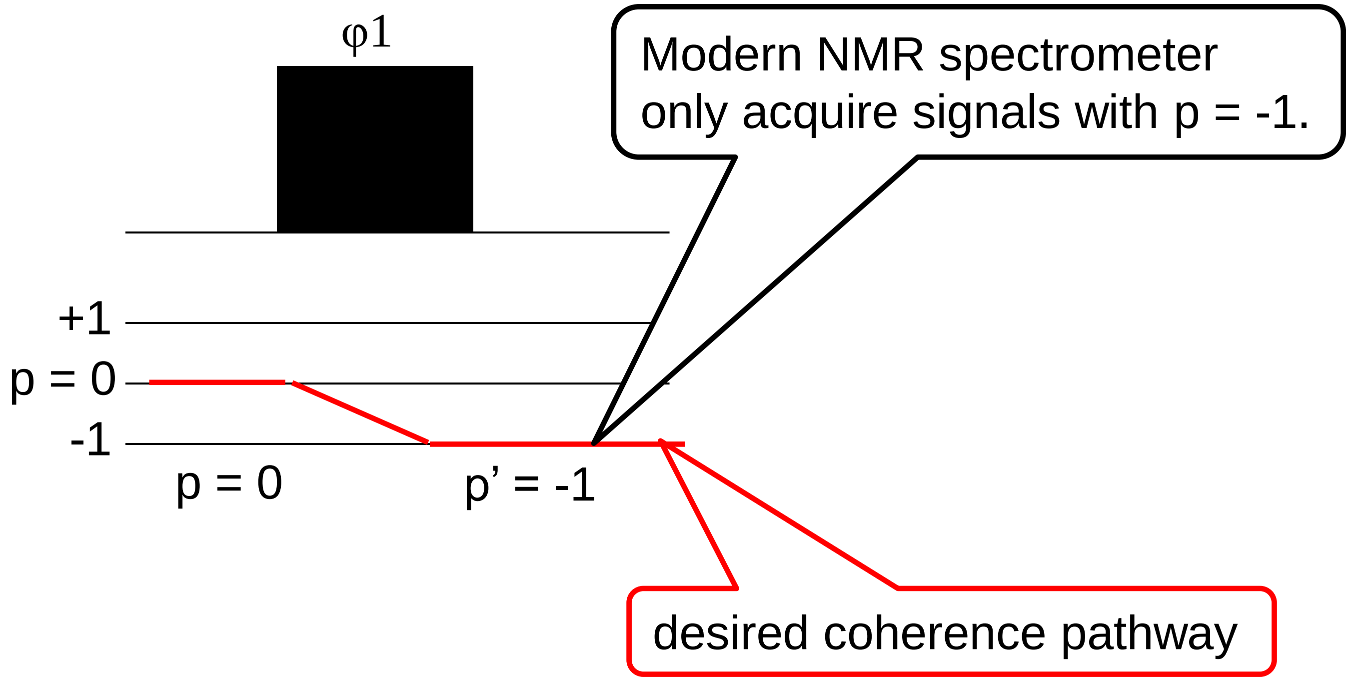
How to minimize the unwanted pathways?

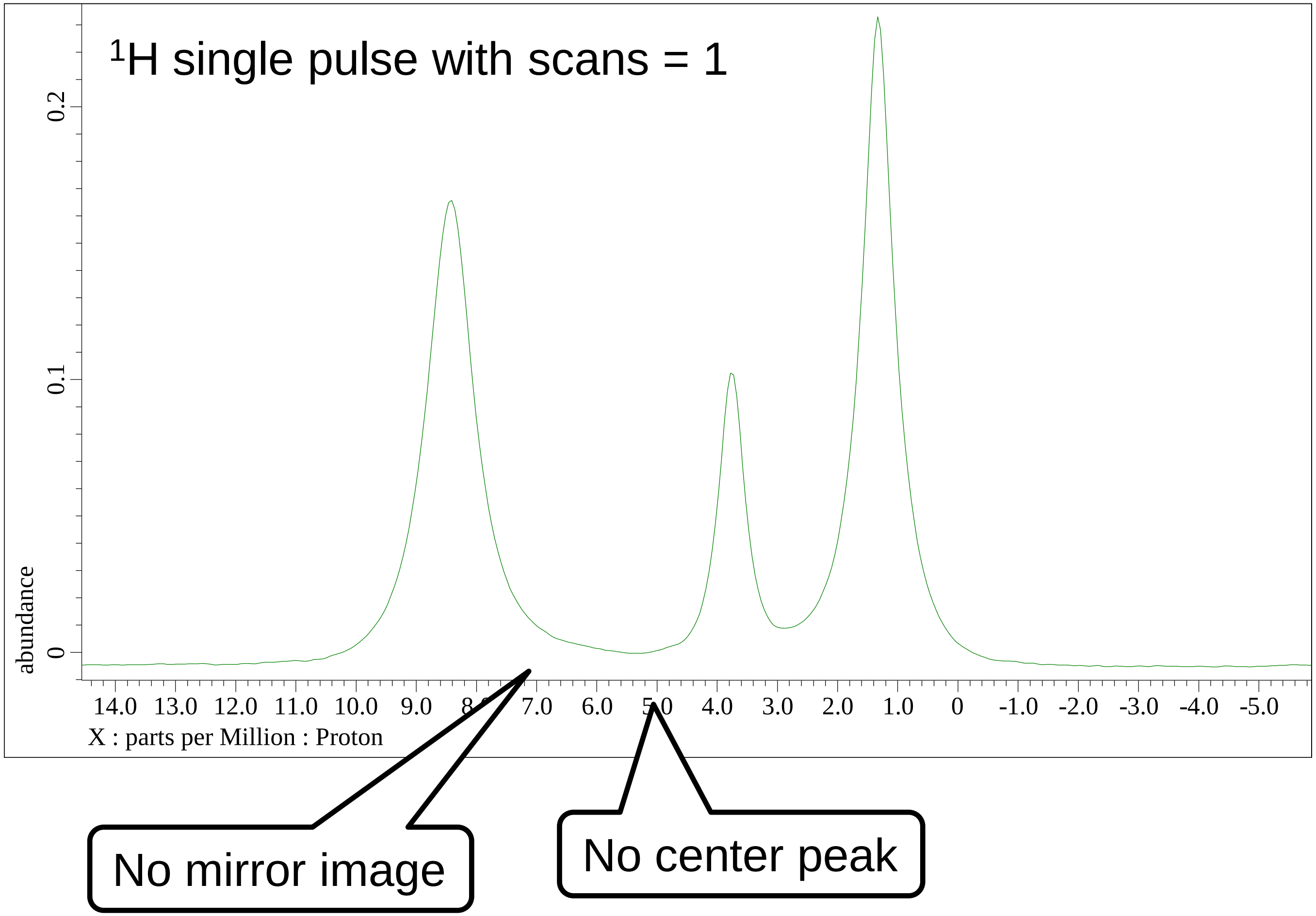


How to minimize the unwanted pathways?



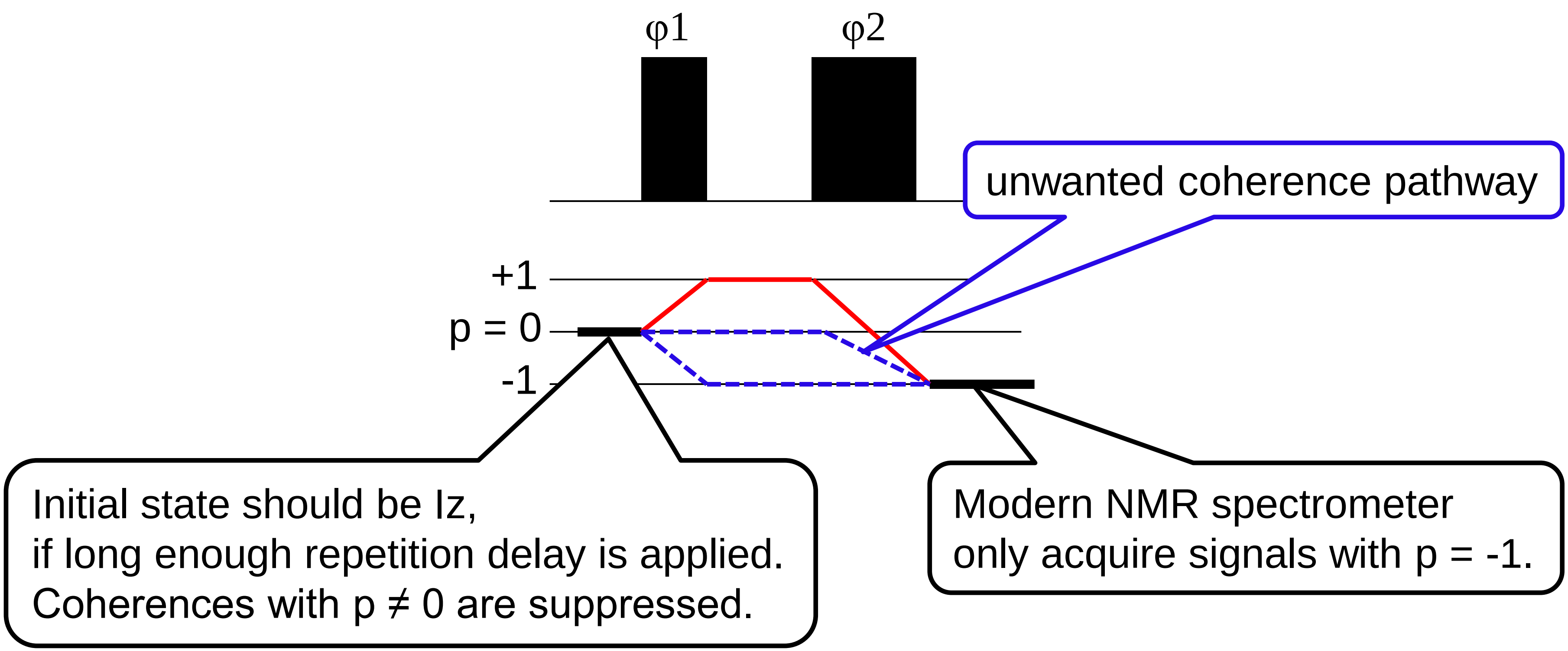
Example1: single pulse

As long as the repetition delay is longer enough than T_2,
modern NMR spectrometer gives signal from desired coherence pathway.



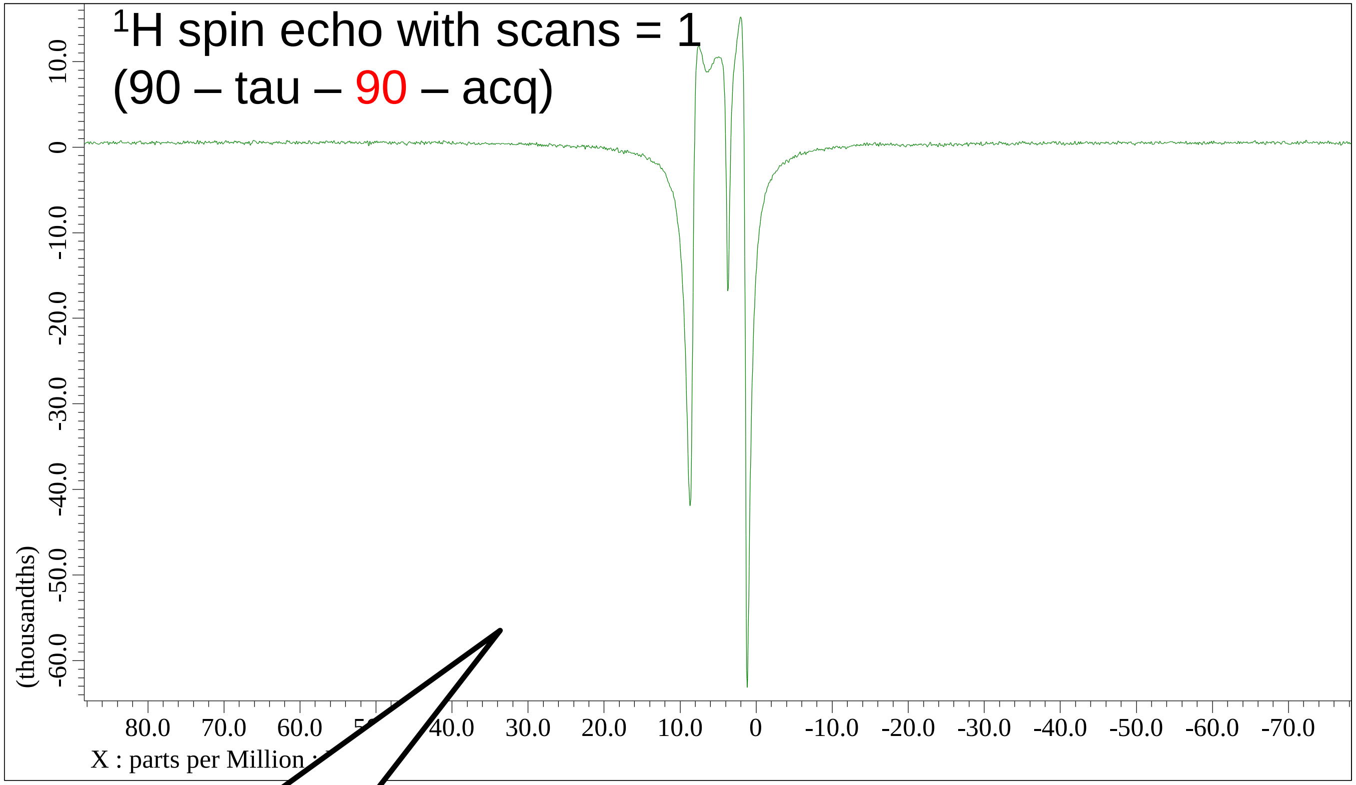
Example2: spin echo

Even with sufficiently long repetition delay and modern NMR spectrometer, unwanted pathway can be observed.



Example2: spin echo

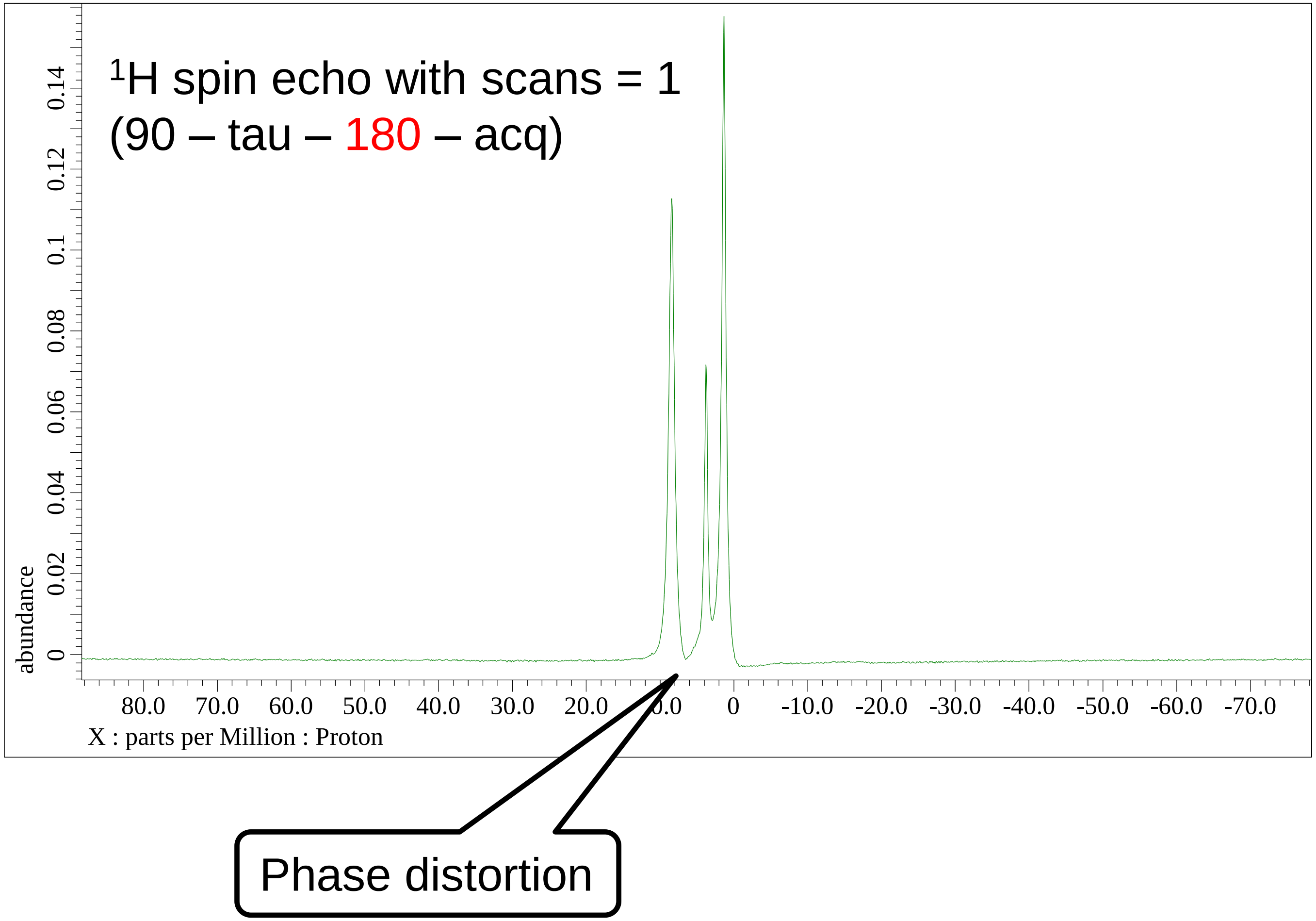
The unwanted coherence pathway results in phase distortion which cannot be corrected by the phi0 and phi1 phasing.



Phase distortion

Example2: spin echo

Phase distortion is minimized by adjusting 90 and 180 degree pulse length.
However, it cannot be fully removed due to B_1 inhomogeneity.



contents

Phase cyclings to select coherence pathway.

A group of pulses are phase cycled according to the following equation, keeping the phases of the other pulses constant:

$$\phi_k = \frac{2\pi k}{N} \qquad k = 0,1,2,\ldots N-1$$

For example,

1st scan:	0°		0°	0°
2nd scan:	90 °		0°	0°
3rd scan:	180 °		0°	0°
4th scan:	270 °	(N=4)	0°	0°

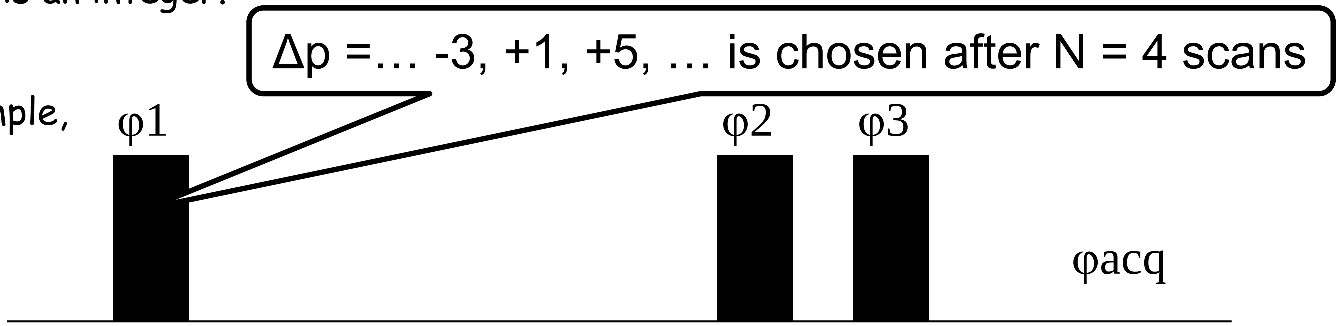
Phase cyclings to select coherence pathway.

If he observation phase is incremented according to

$$\phi_{acq,k} = -2\pi \frac{\Delta p}{N} k = -\Delta p \phi_k \qquad k = 0,1,2,\ldots N-1$$

The coherence pathways which changes the coherence with $\Delta p + mN$ are chosen, where m is an integer.

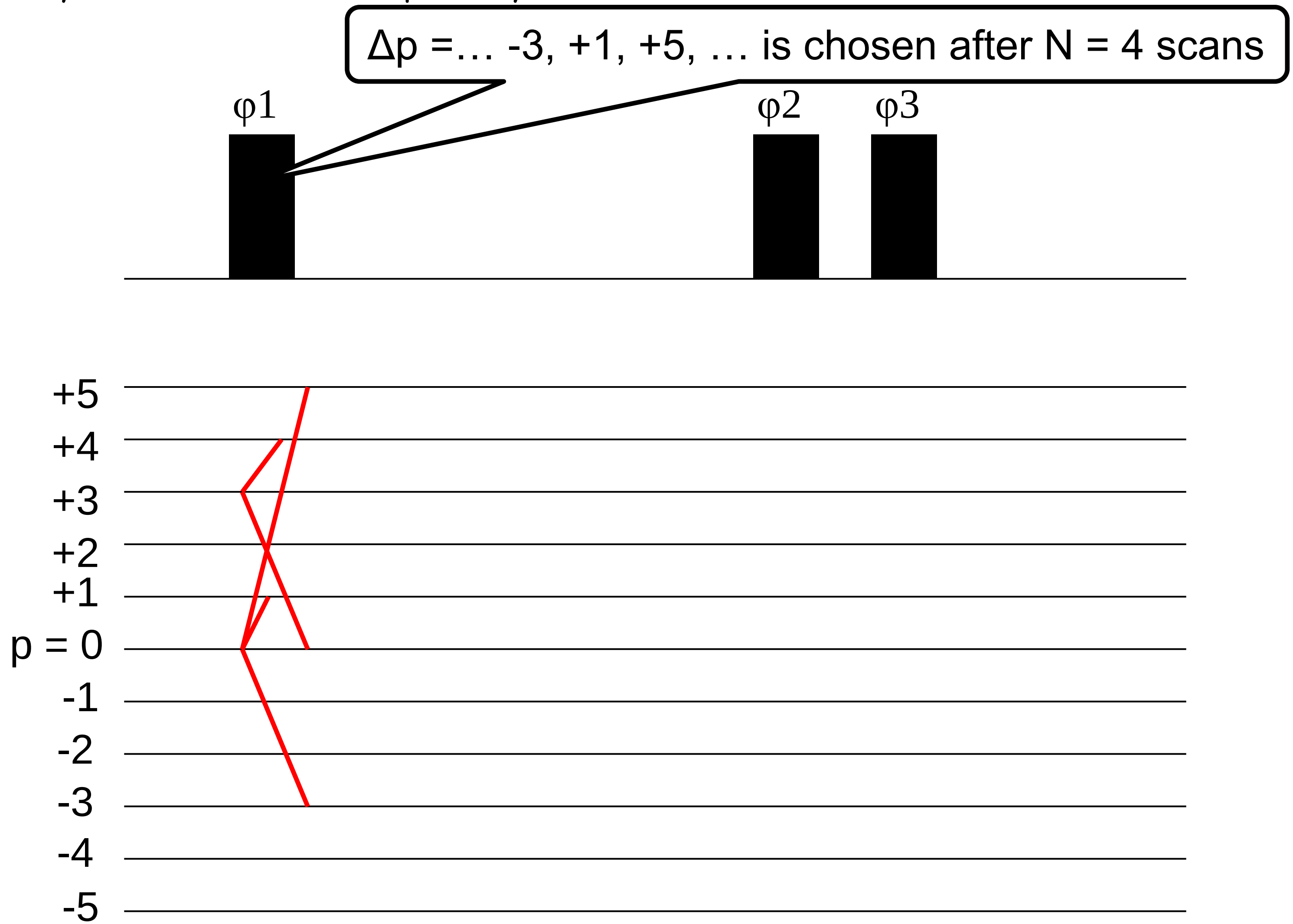
For example,



	φ1		φ2	φ3	φacq	
1st scan:	0°		0°	0°	0°	
2nd scan:	90 °		0°	0°	-90° = 270°	
3rd scan:	180 °		0°	0°	-180° = 180°	
4th scan:	270 °	(N=4)	0°	0°	-270° = 90°	$\Delta p = +1$

Phase cyclings to select coherence pathway.

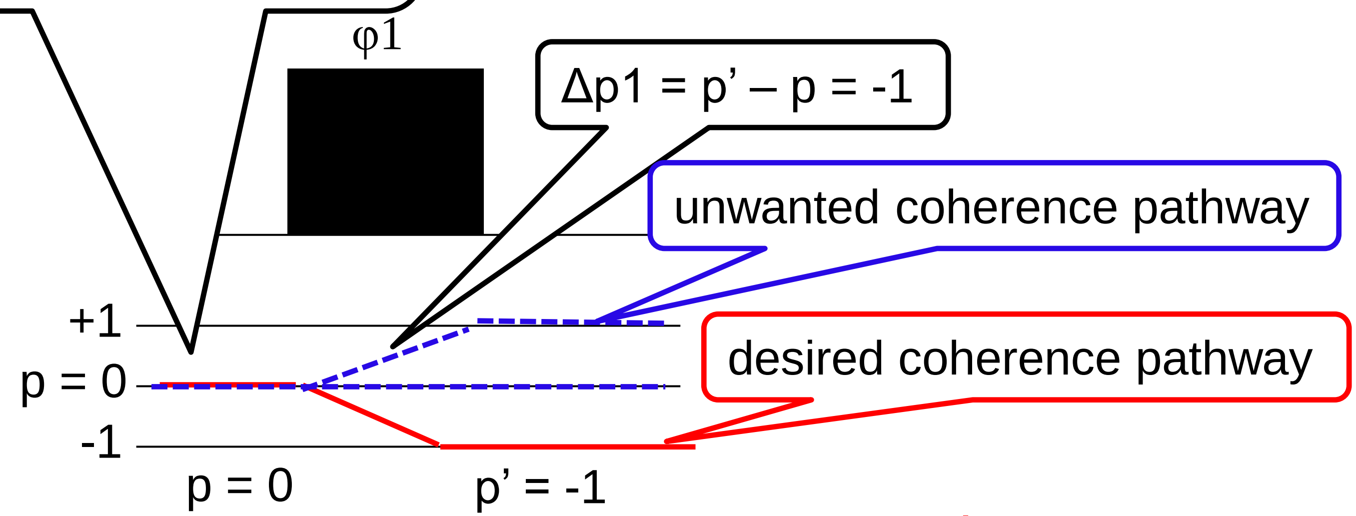
Many different coherence pathways are allowed.



Example 1: single pulse

Traditional CYCLOPS phase cycling chooses Δ = -1.

Initial state should be Iz,
if long enough repetition delay is applied.
Coherences with p ≠ 0 are suppressed.



1st scan:	0°	0°
2nd scan:	90 °	90°
3rd scan:	180 °	180°
4th scan:	270 °	270°

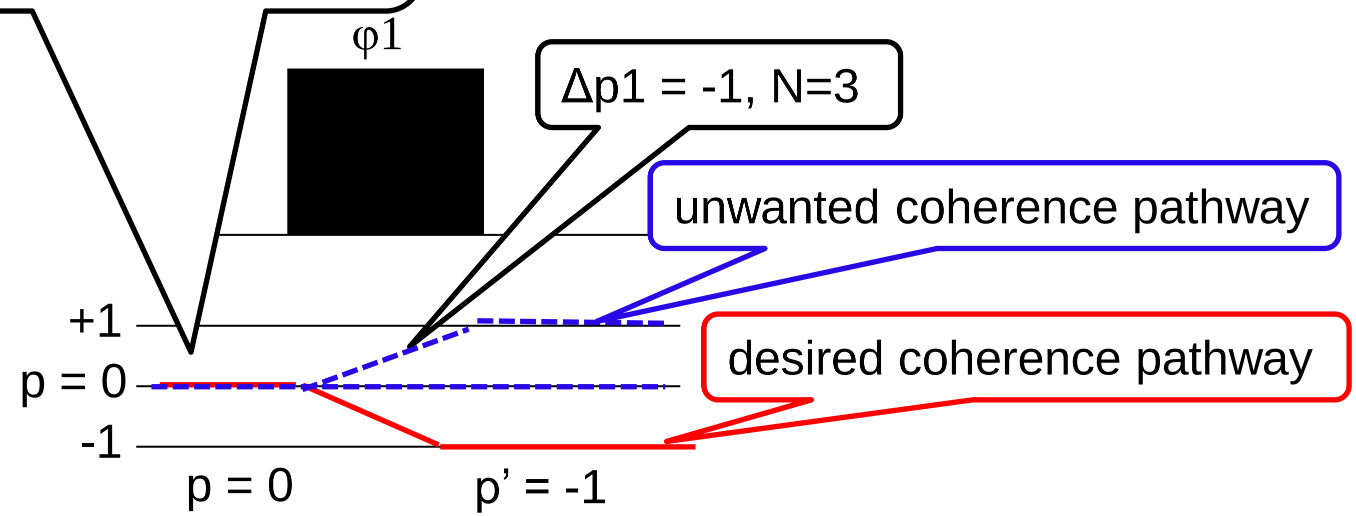
Δp = -5, -1, +3
(N = 4)

$$\phi_{acq,k} = -\Delta p \phi_k$$

Example 1: single pulse

CYCLOPS phase cycling includes too much phase cycling than needed.

Initial state should be Iz,
if long enough repetition delay is applied.
Coherences with p ≠ 0 are suppressed.



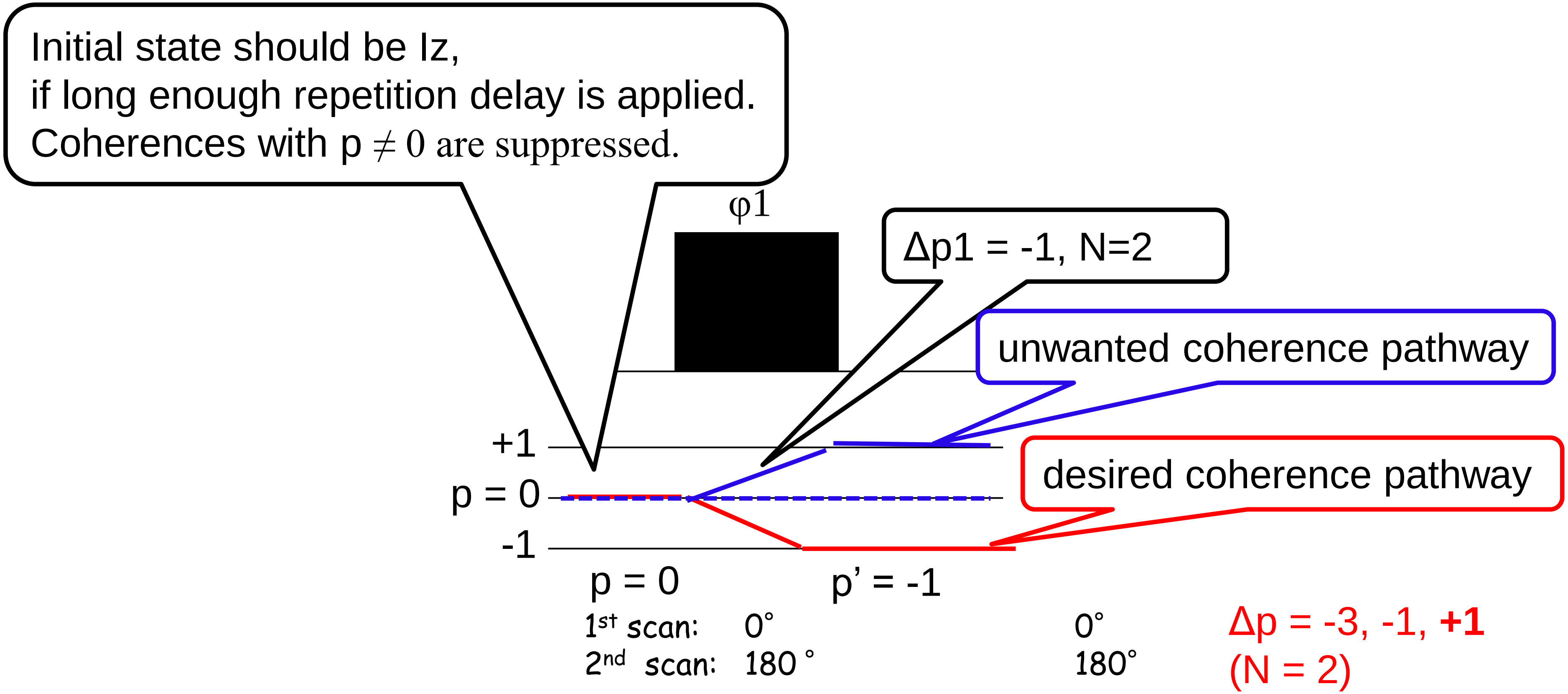
	p = 0	p' = -1
1st scan:	0°	-(-1) 0° = 0 °
2nd scan:	120 °	-(-1) 120° = 120 °
3rd scan:	240 °	-(-1) 240° = 240 °

Δp = -4, -1, +2
(N = 3)

$$\phi_{acq,k} = -\Delta p \phi_k$$

Example 1: single pulse

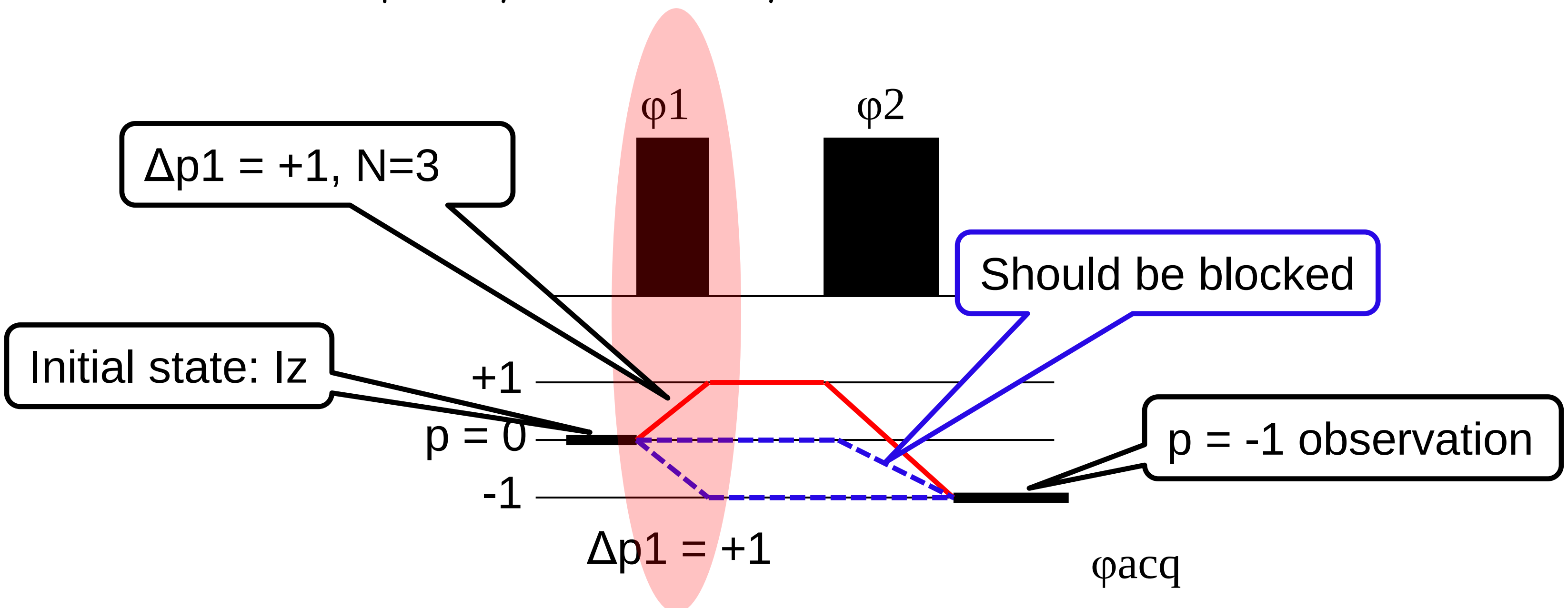
Two step phase cycling introduces mirror image.



$$\phi_{acq,k} = -\Delta p \phi_k$$

Example2: spin echo

There is two way to implement phase cyclings for spin echo. If Δp1 = +1 is chosen, desired pathway is automatically selected.



	φ1	φ2	φacq
1st scan:	0°	0°	0°
2nd scan:	120 °	0°	-(+1)120° = 240°
3rd scan:	240 °	0°	-(+1)240° = 120°

Δp1 = ..-2, +1, +4 … (N = 3)

$$\phi_{acq,k} = -\Delta p \phi_k$$

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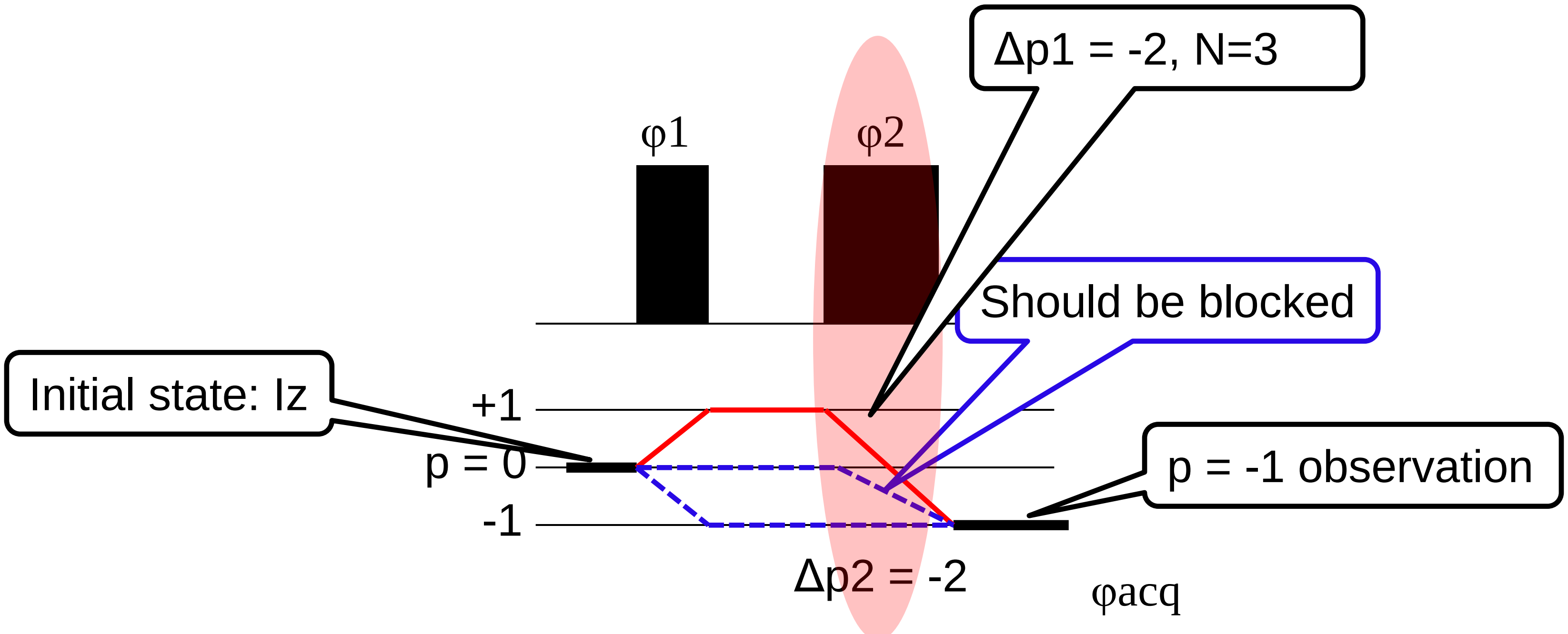
Example2: spin echo

Instead, Δp2 = -2 can be chosen.

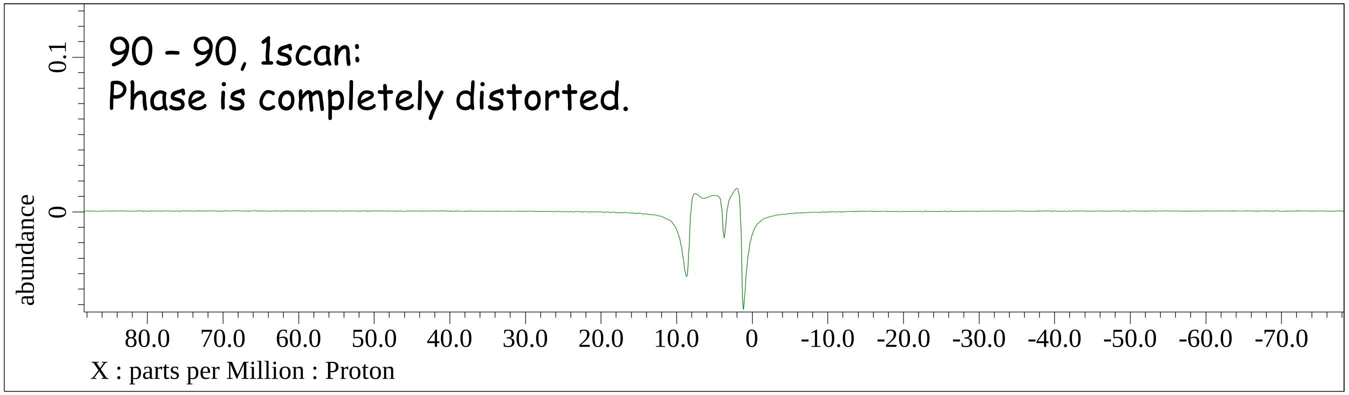


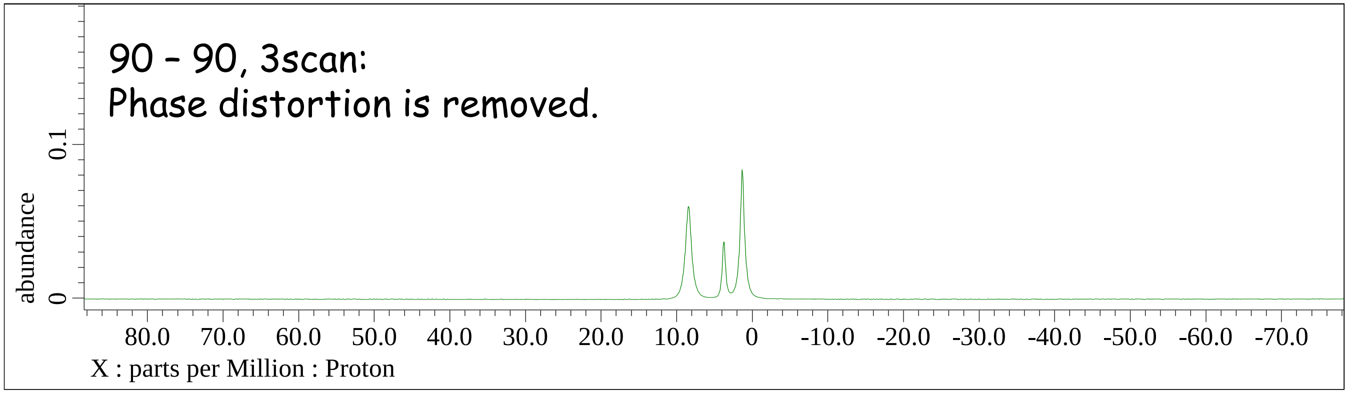
1st scan:	0°	0°	0°
2nd scan:	0 °	120°	-(-2)120° =240°
3rd scan:	0 °	240°	-(-2)240° = 120°

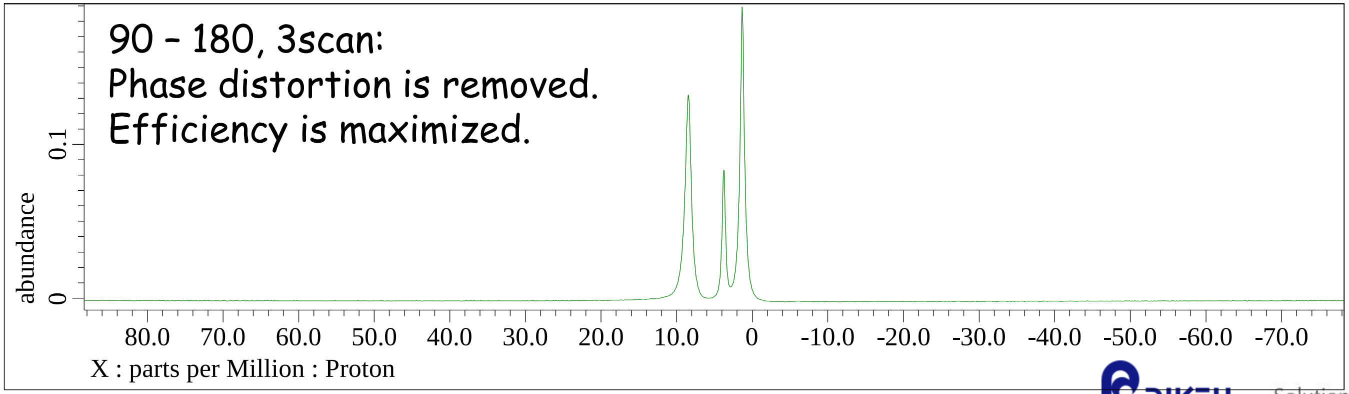
Δp2 = ..-5, -2, +1 … (N = 3)

$$\phi_{acq,k} = -\Delta p \phi_k$$

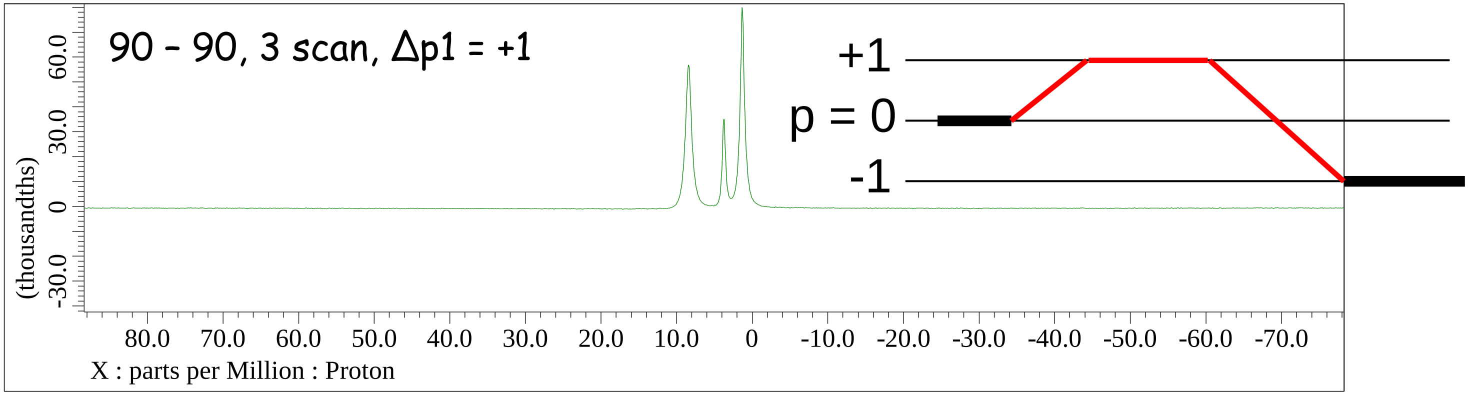
Example2: spin echo

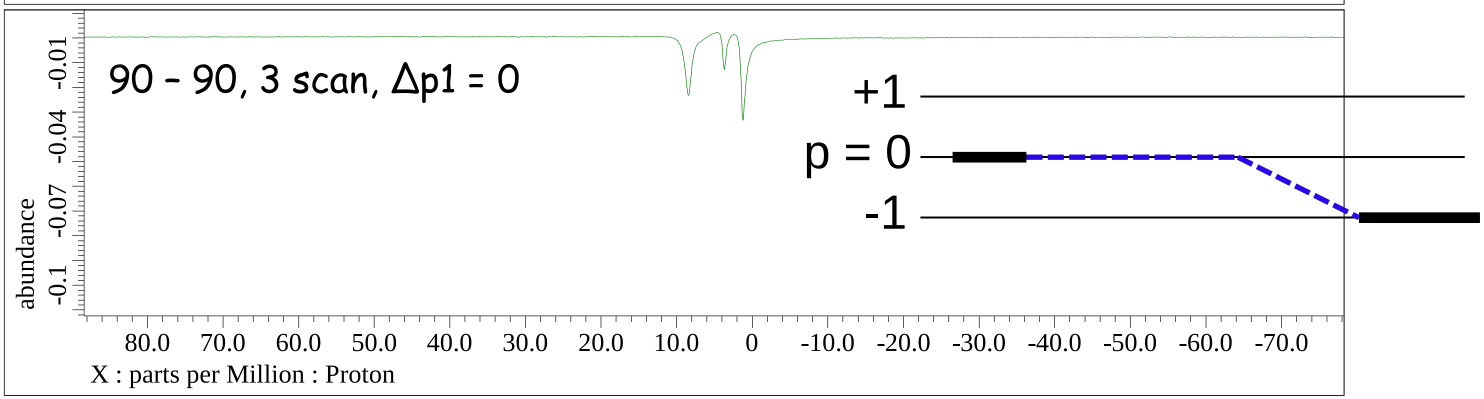


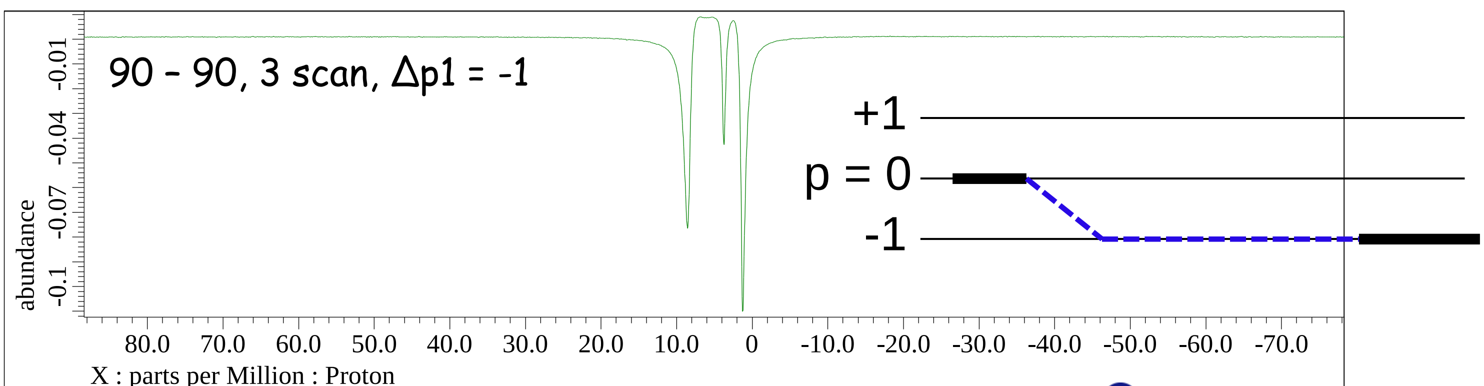




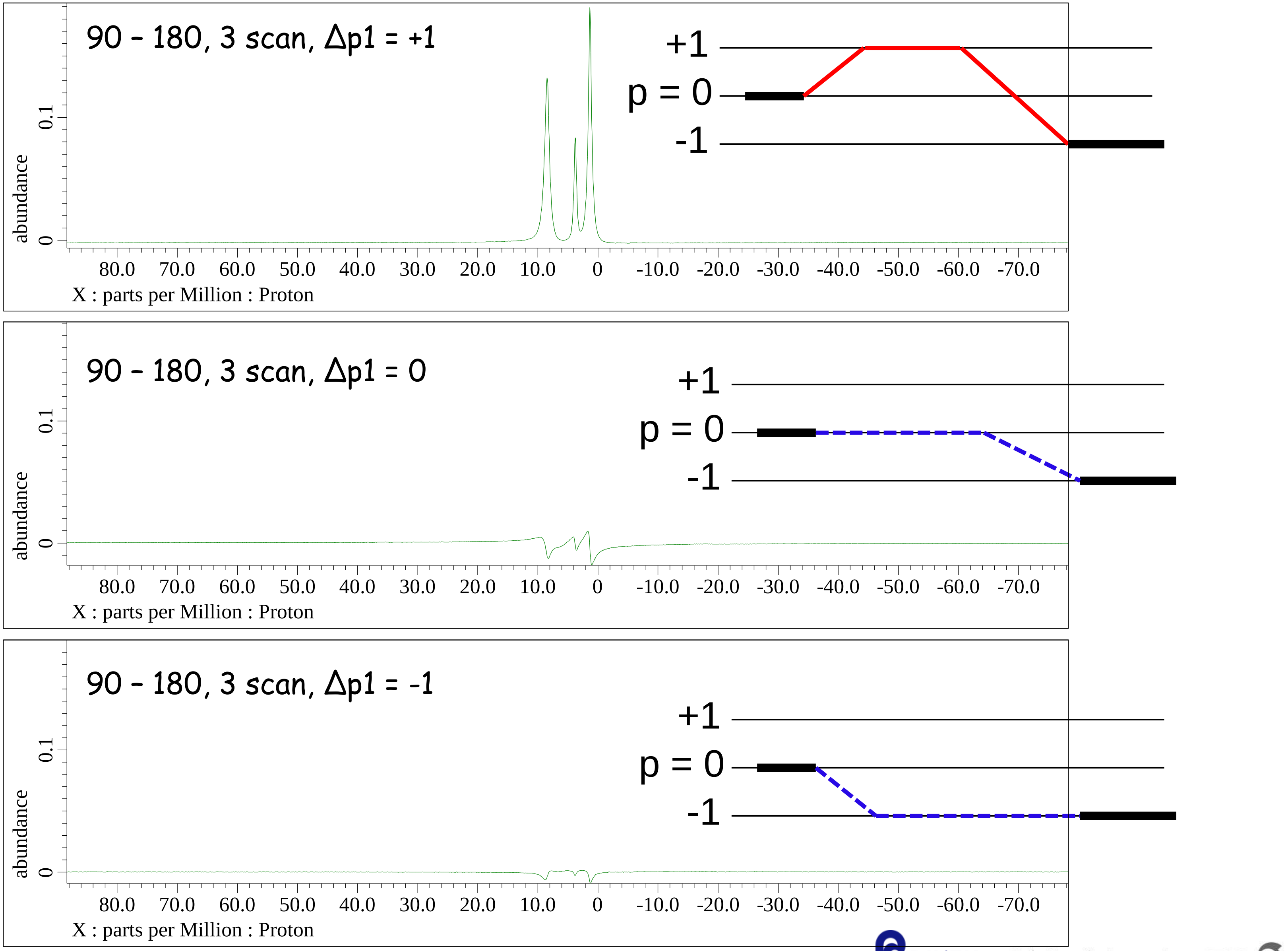
Example2: spin echo







Example2: spin echo



Coherence pathway selection as well as optimization of pulses are required.

contents

Phase cyclings to select multiple coherence pathway.

If transfer pathway at more than one set of pulses should be chosen, the phase cycling can be implemented by nested way (independently).

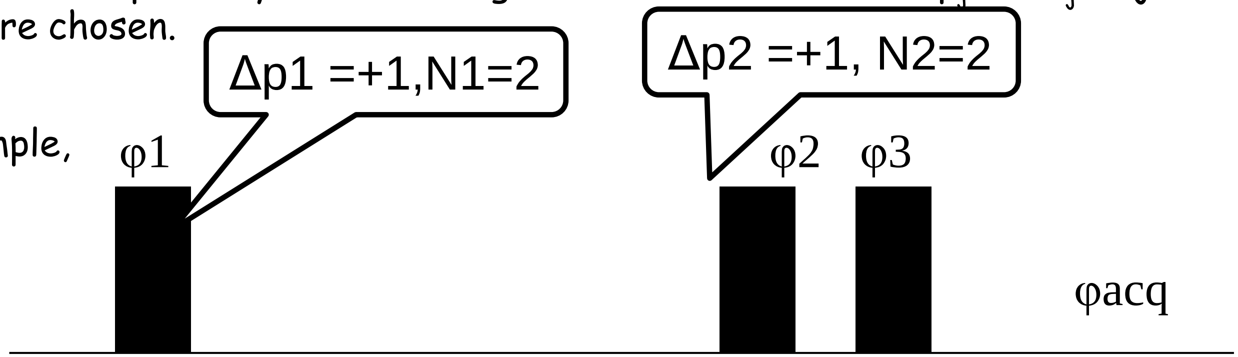
$$\phi_{j,k_j} = \frac{2\pi k_j}{N_j} \qquad k_j = 0,1,2,\ldots N_j - 1$$

The acquisition phase should be incremented according to

$$\phi_{acq,k} = -\sum_j 2\pi \frac{\Delta p_j}{N_j} k_j = -\sum_j \Delta p_j \phi_{j,k_j} \qquad k_j = 0,1,2,\ldots N_j - 1$$

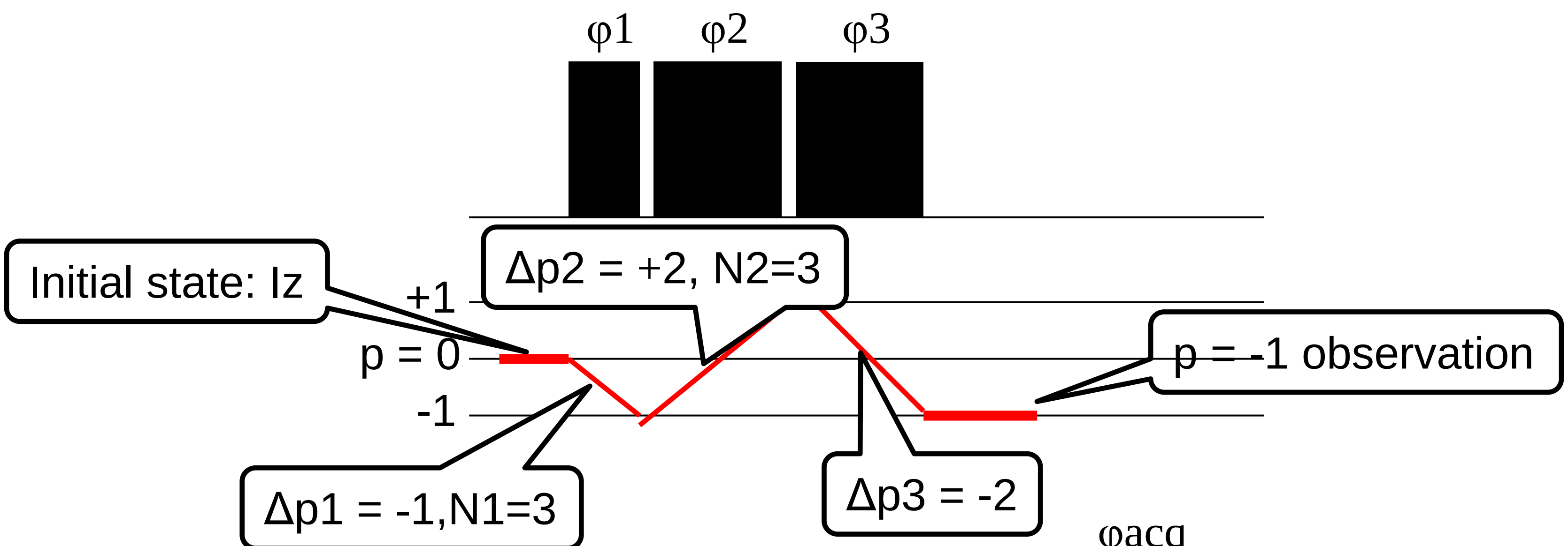
The coherence pathways which changes the coherence with $\Delta p_j + mN_j$ at j-th pulses are chosen.

For example,



	φ1		φ2	φ3	φacq
1st scan:	0°		0°	0°	-((+1)0° +(+1)0°)= 0°
2nd scan:	180 °		0°	0°	-((+1)180° +(+1)0°)= 180°
(3rd scan:	0 °)		180°	0°	-((+1)0° +(+1)180°)= 180°
(4th scan:	180 °)	(N1=2)	180°	0°	-((+1)180° +(+1)180°)= 0°

Example3: DEPTH2 (background suppression)



N_1=3	N_2=3		φacq
0°	0°	0°	0°
120 °	0 °		120°
240 °	0 °		240 °
	120°		120 °
	120 °		240°
	120 °		0 °
	240°		240 °
	240 °		0°
	240 °		120 °

$$\phi_{acq,k} = -\sum_j \Delta p_j \phi_{j,k_j}$$

Multi-dimensional measurements

Two way to implement phase sensitive detection in the indirect dimension.

Amplitude modulation:

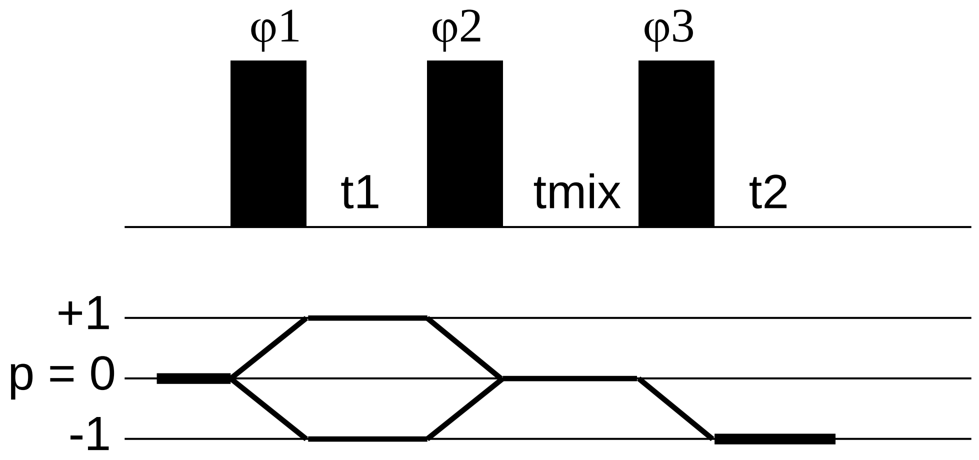
$$S_R(t_1,t_2)=\cos(\omega_1 t_1)e^{-i\omega_2 t_2}$$

$$S_I(t_1,t_2)=\sin(\omega_1 t_1)e^{-i\omega_2 t_2}$$

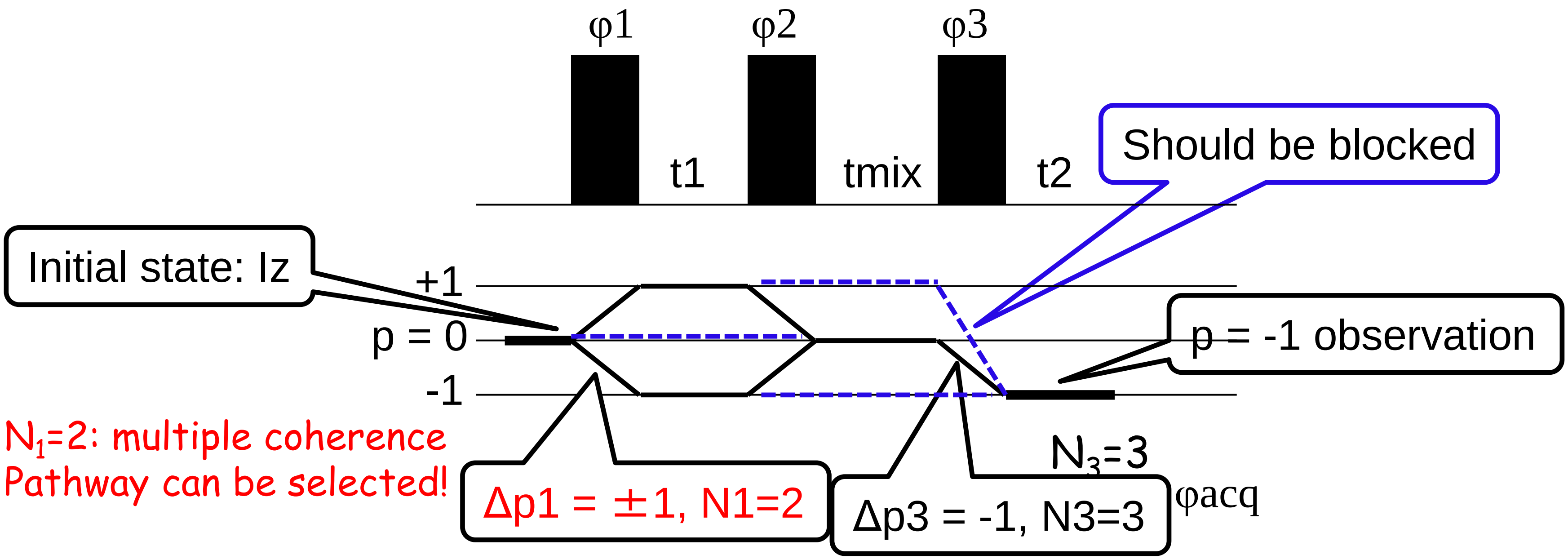
Cosine and sine modulation can be achieved by selecting symmetry pathways in the indirect dimension at the same time.

$$\cos(\omega_1 t_1)=\frac{1}{2}\left[e^{-i\omega_1 t_1}+e^{i\omega_1 t_1}\right]$$

$$\sin(\omega_1 t_1)=\frac{1}{2}\left[-e^{-i\omega_1 t_1}+e^{i\omega_1 t_1}\right]$$



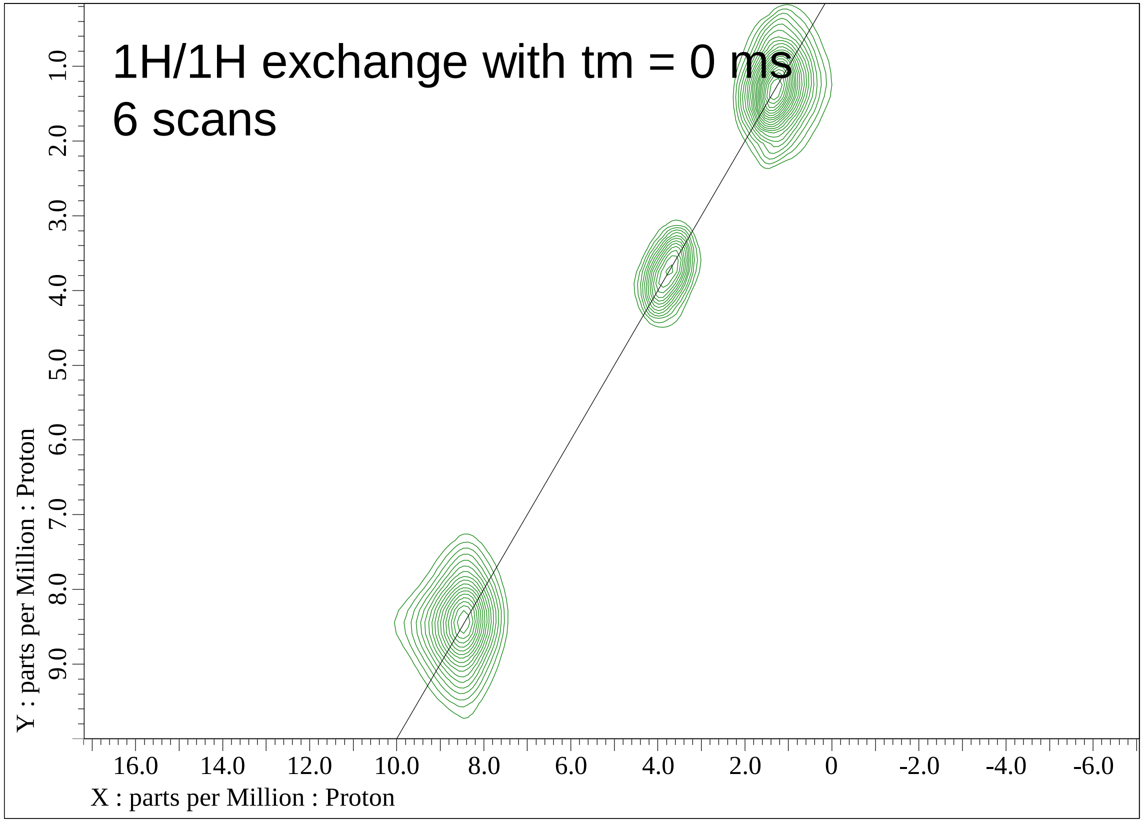
Example4: NOESY (2D exchange)



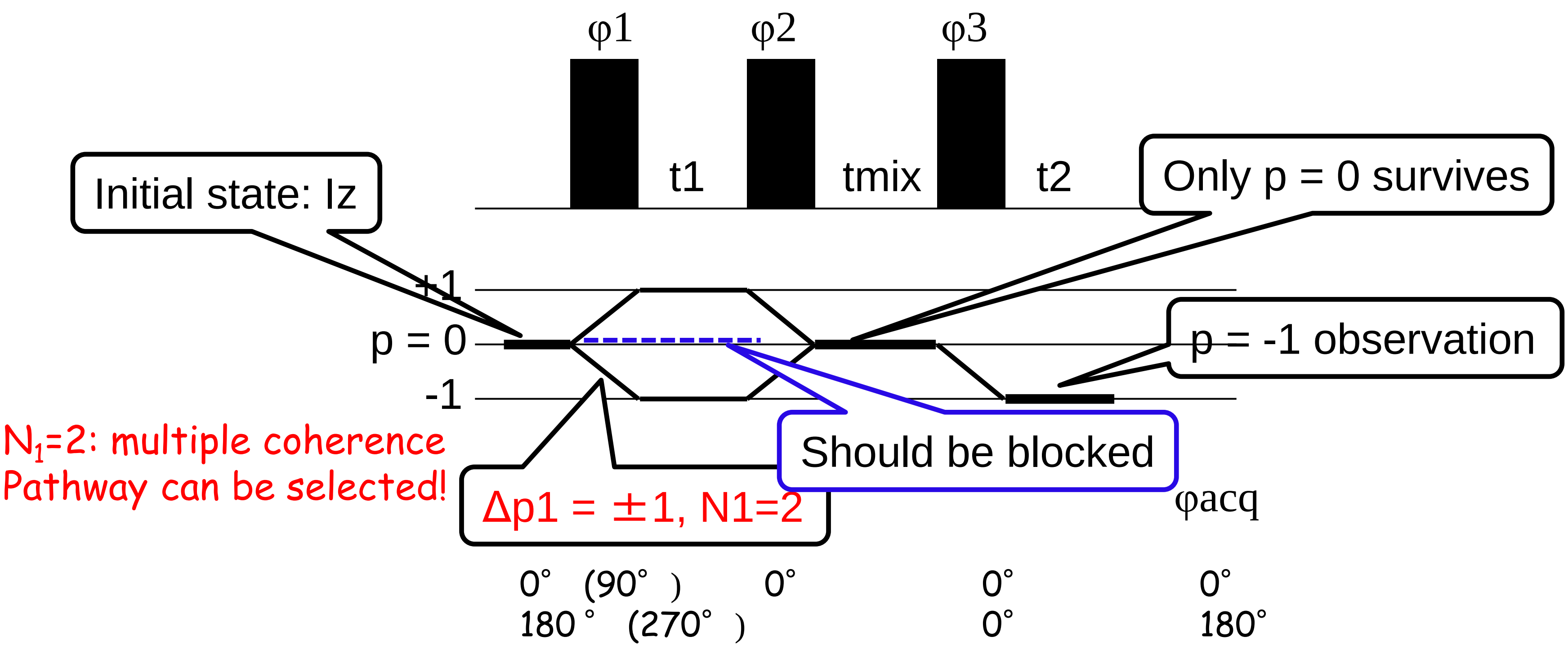
0° (90°)	0°	0°	0°
180° (270°)		0°	180°
		120°	120°
		120°	300°
		240°	240°
		240°	60°

$$\phi_{acq,k} = -\sum_j \Delta p_j \phi_{j,k_j}$$

Example4: NOESY (2D exchange)

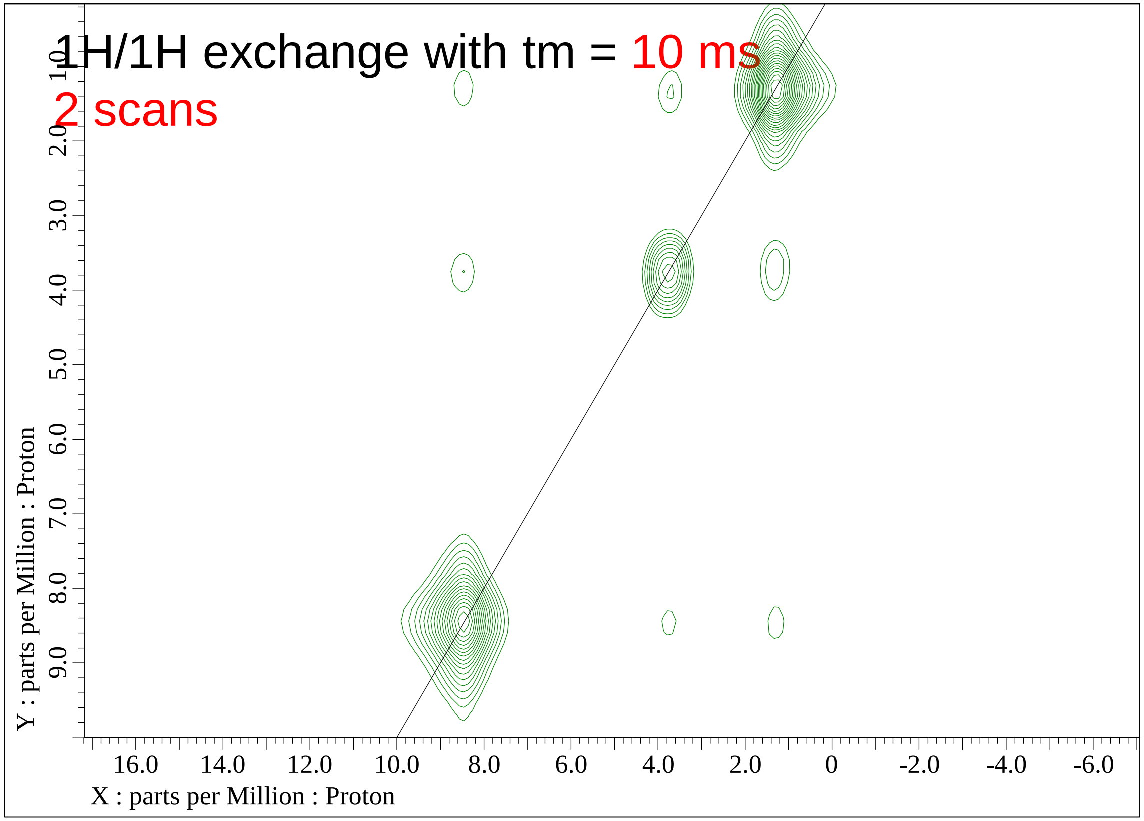


Example4: NOESY (2D exchange)



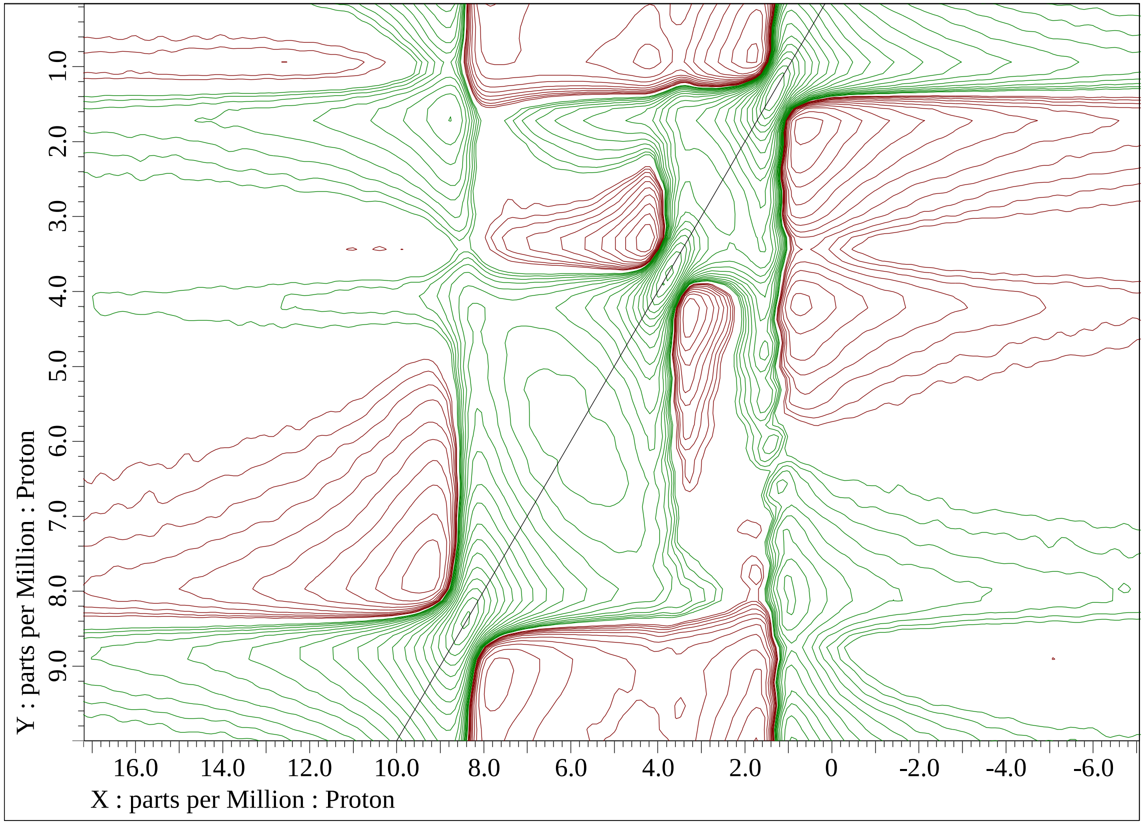
$$\phi_{acq,k} = -\sum_{j} \Delta p_j \phi_{j,k_j}$$

Example4: NOESY (2D exchange)



Example4: NOESY (2D exchange)

1H/1H exchange with tm = 0 ms
2 scans

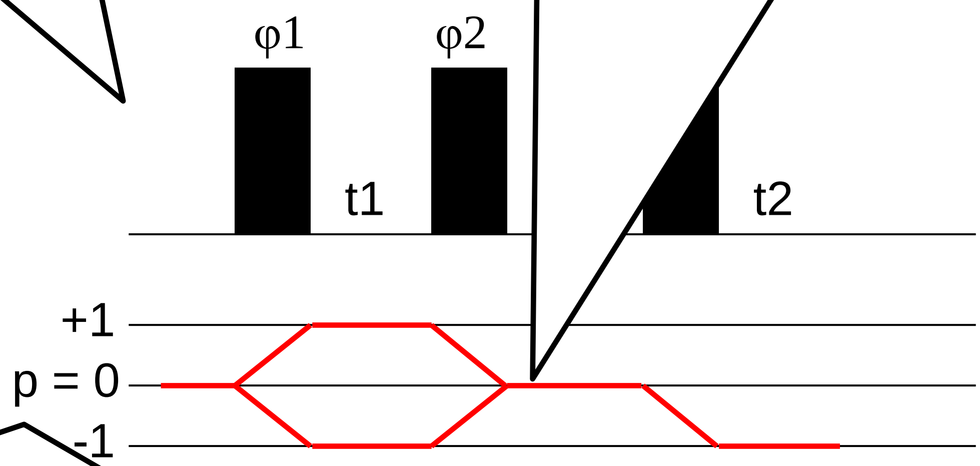


Even with finite tm, pulses in mixing time may cause the same problem.

Example4: NOESY (2D exchange)

3. Draw the desired coherence pathway.
Coherence pathway changes at the pulse.
Free evolution doesn't change coherence order.

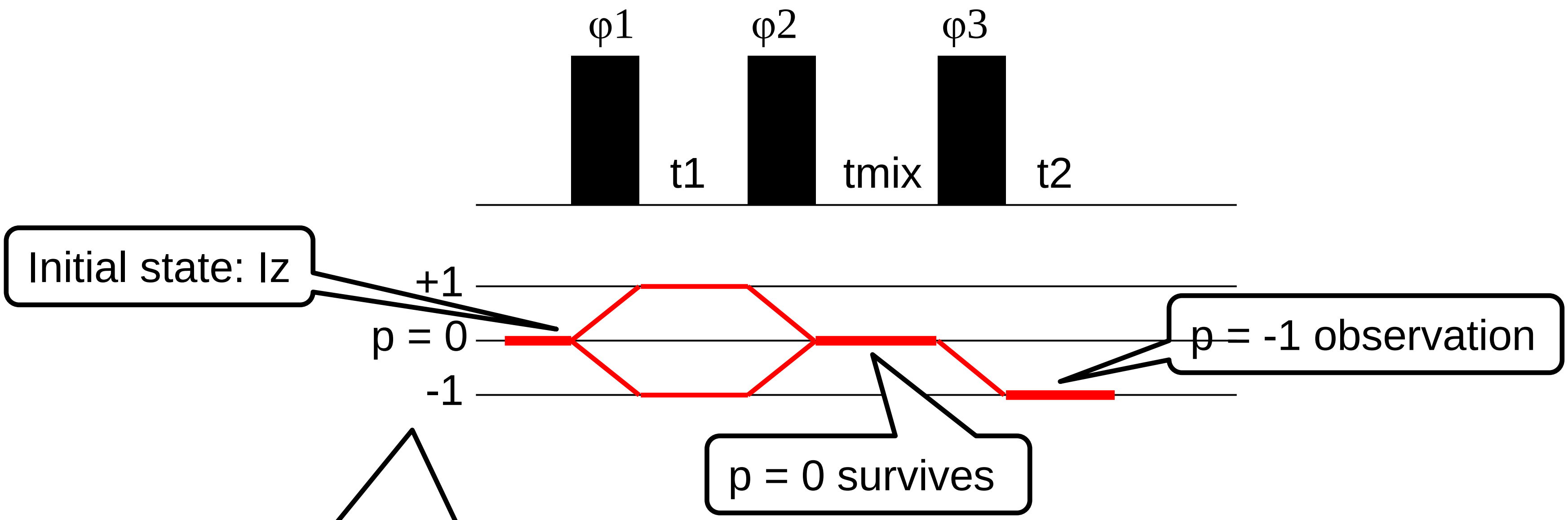
1. draw pulse scheme.



2. Define spin systems: p=-1 to 1 for isolated spin-1/2 systems.

$$\phi_{acq,k} = -\sum_{j} \Delta p_j \phi_{j,k_j}$$

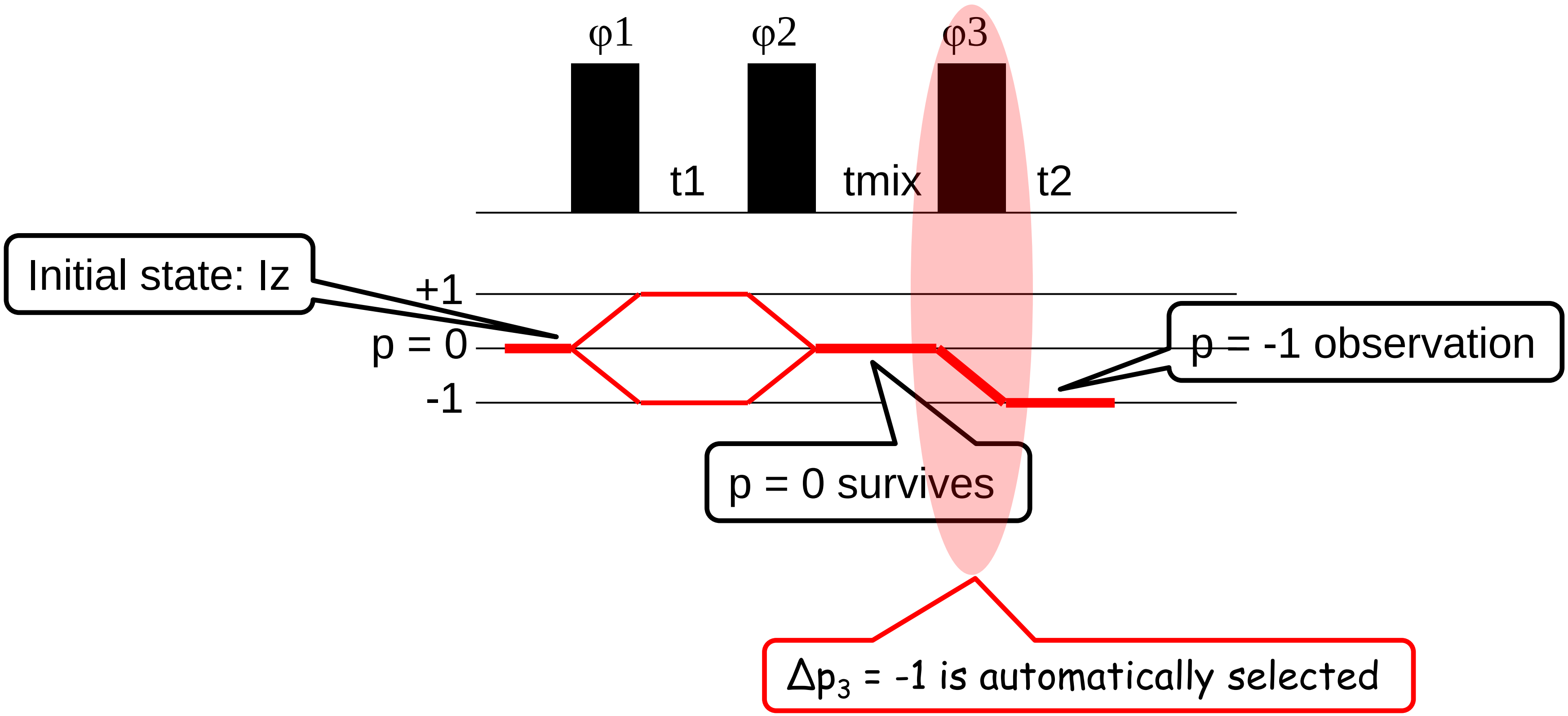
Example4: NOESY (2D exchange)



4. Place the restrictions:
4.1 initial state starts from p = 0.
4.2 only p = -1 is observed.
4.3 coherence other than p = 0 survives during mixing

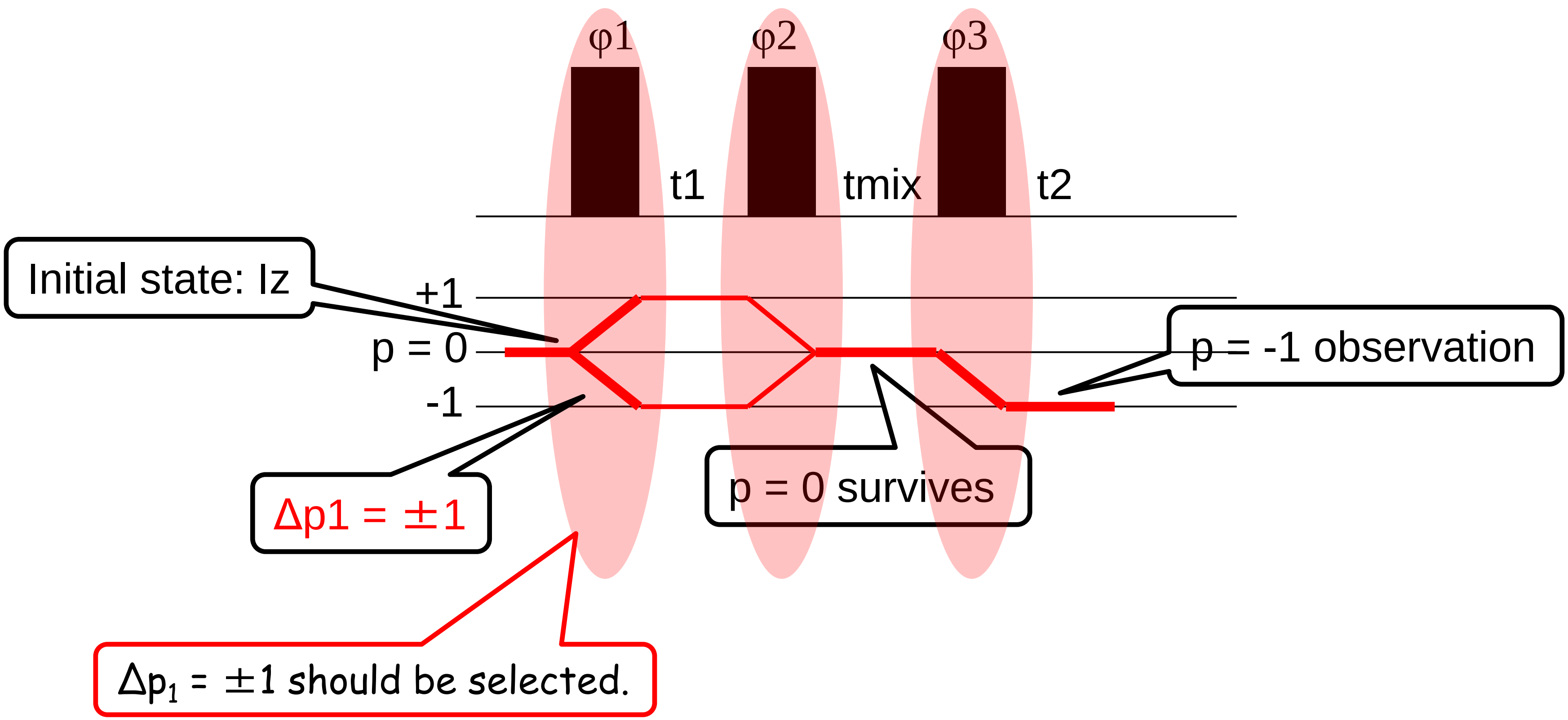
$$\phi_{acq,k} = -\sum_j \Delta p_j \phi_{j,k_j}$$

Example4: NOESY (2D exchange)



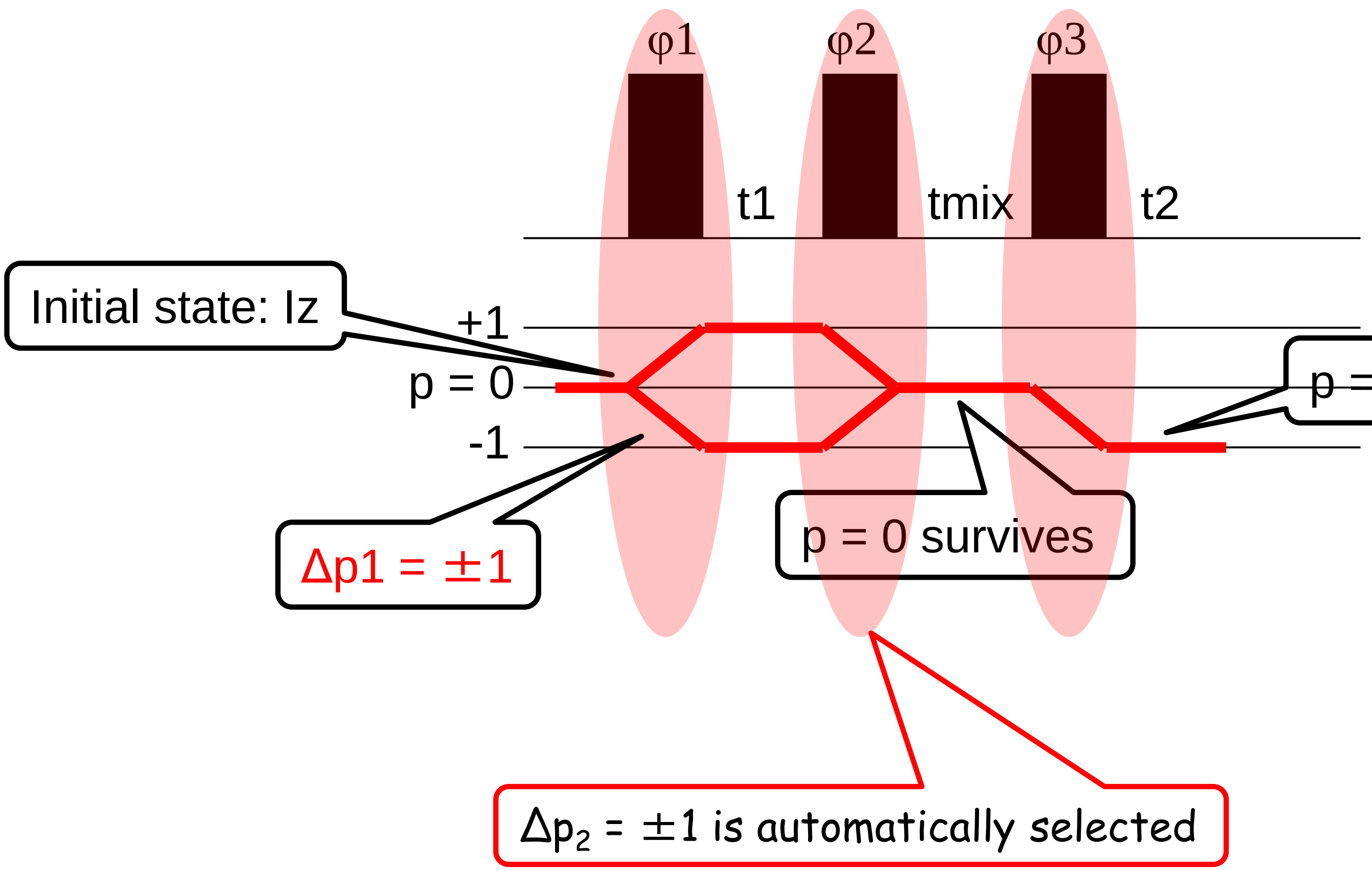
$$\phi_{acq,k} = -\sum_j \Delta p_j \phi_{j,k_j}$$

Example4: NOESY (2D exchange)



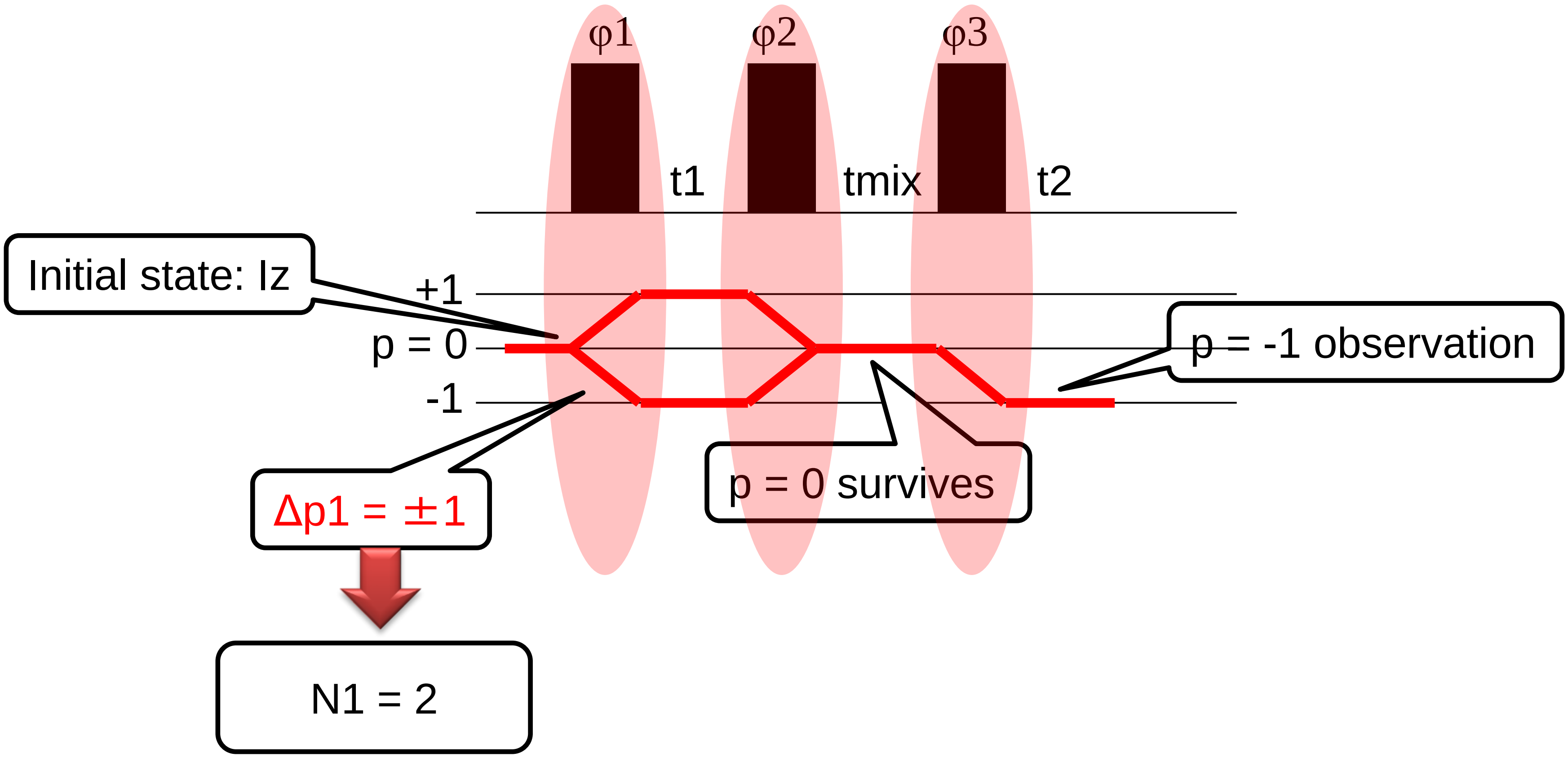
$$\phi_{acq,k} = -\sum_j \Delta p_j \phi_{j,k_j}$$

Example4: NOESY (2D exchange)



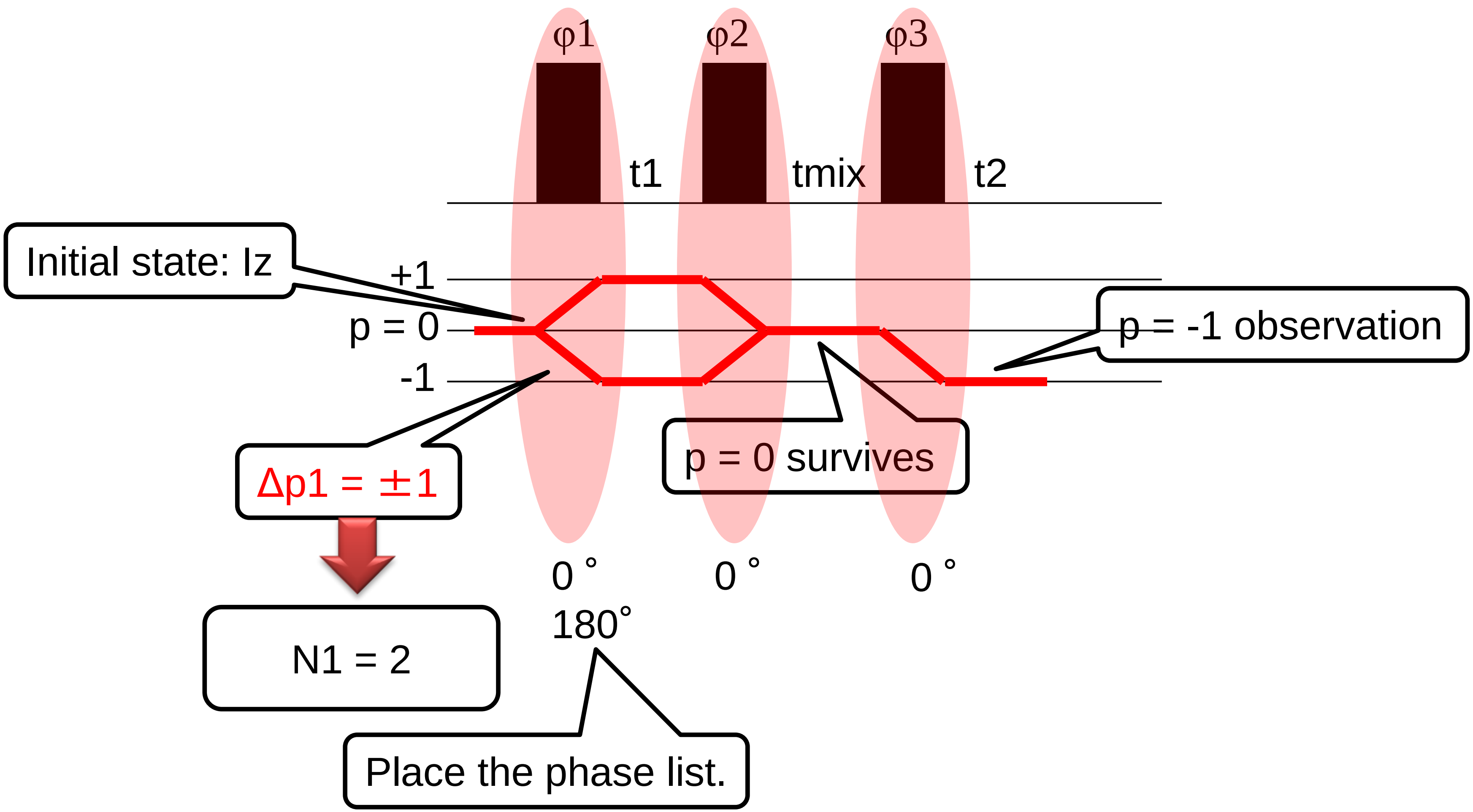
$$\phi_{acq,k} = -\sum_j \Delta p_j \phi_{j,k_j}$$

Example4: NOESY (2D exchange)



$$\phi_{acq,k} = -\sum_j \Delta p_j \phi_{j,k_j}$$

Example4: NOESY (2D exchange)



$$\phi_{acq,k} = -\sum_j \Delta p_j \phi_{j,k_j}$$

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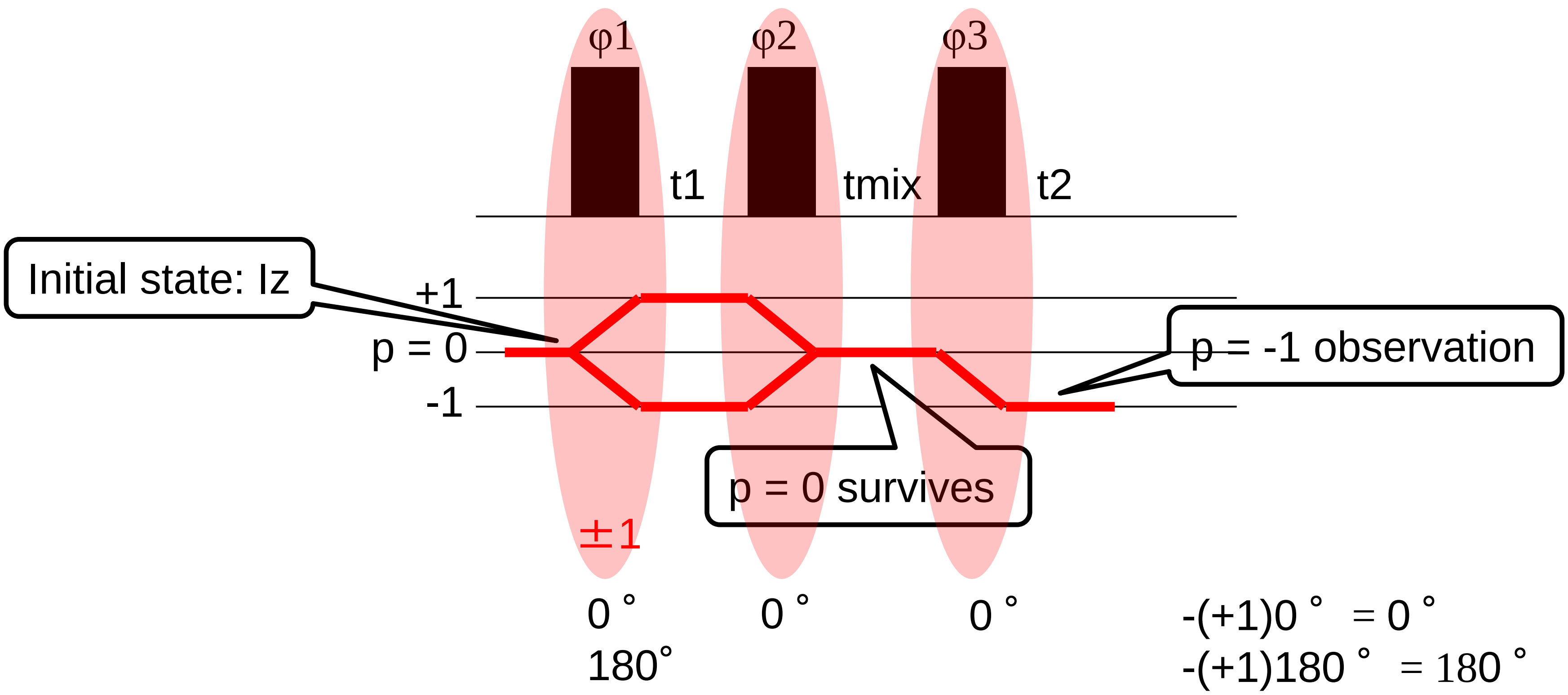
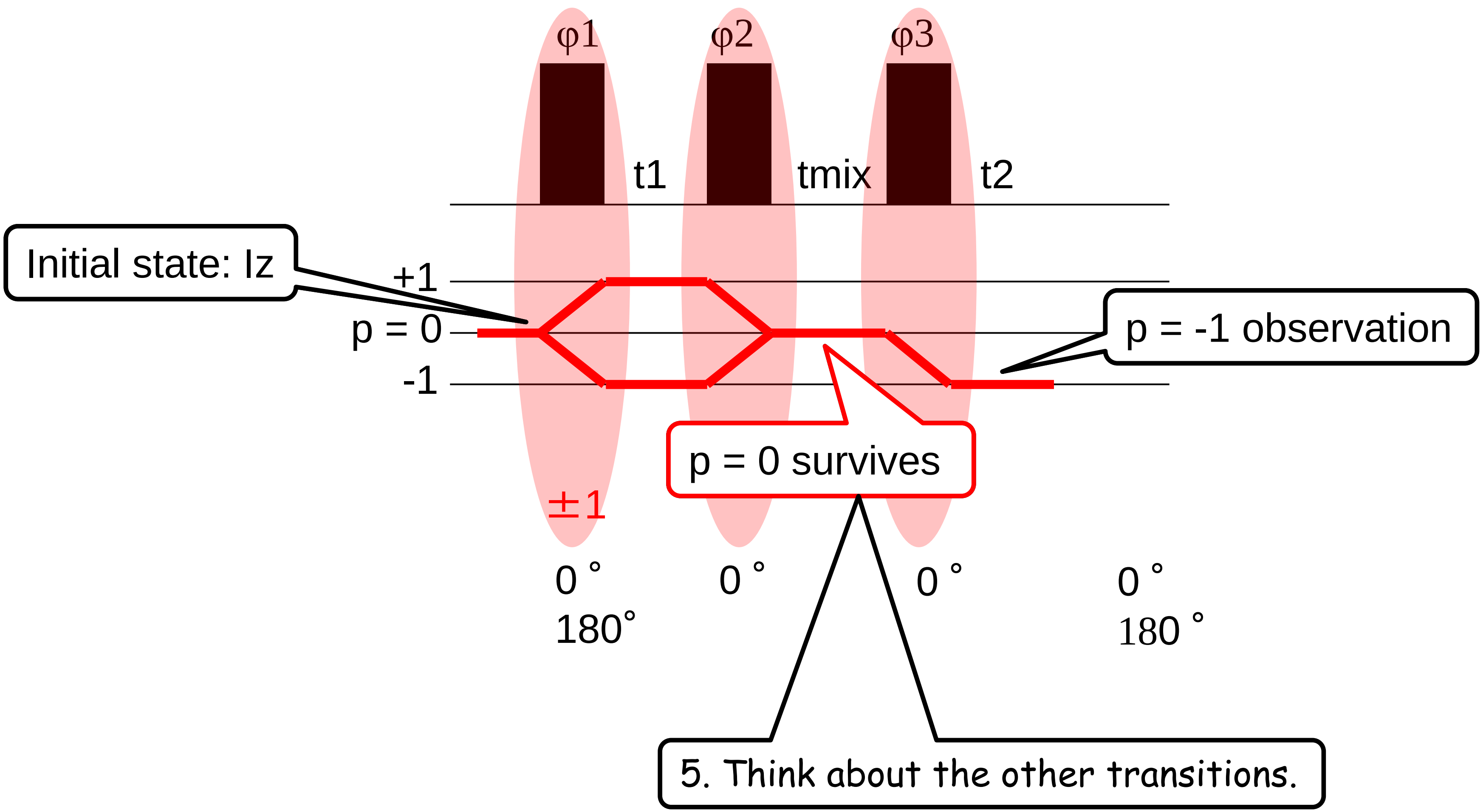
Example4: NOESY (2D exchange)

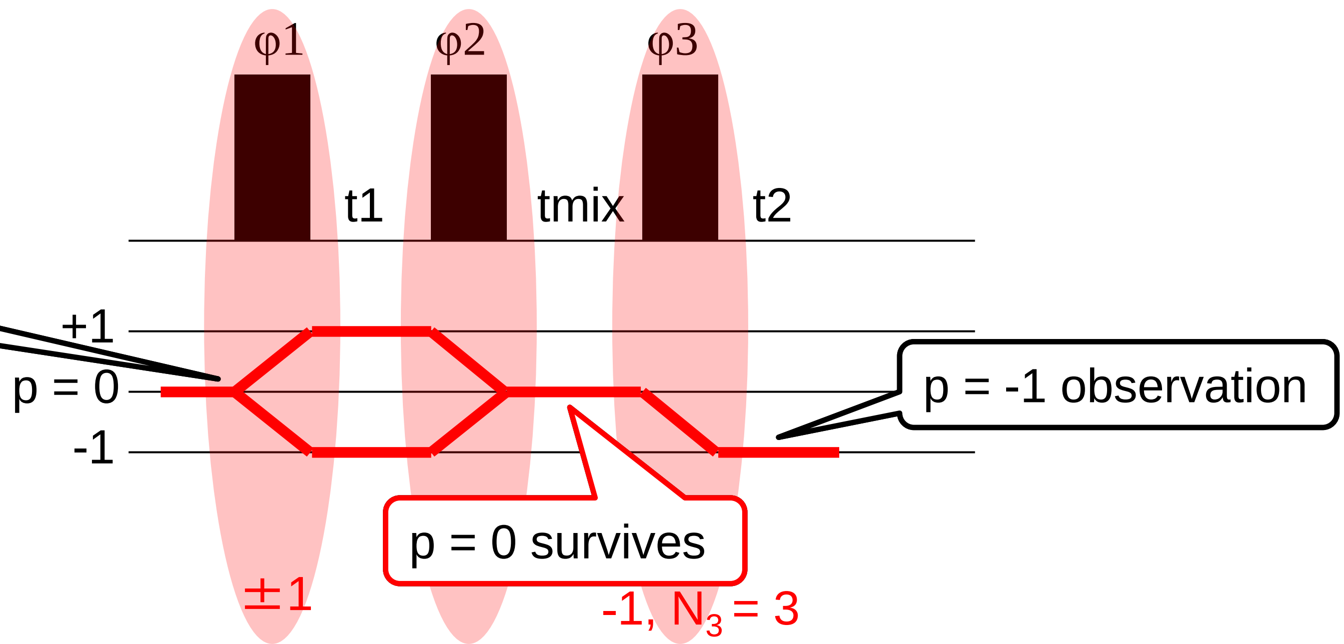


Calculate φ_{acq} according to $\phi_{acq,k} = -\sum_{j} \Delta p_j \phi_{j,k_j}$

Example4: NOESY (2D exchange)



Example4: NOESY (2D exchange)



0° 180°	0°	0°	0° 180°
0° 180°		120°	120° 300°
0° 180°		240°	240° 60°

Multi-dimensional measurements

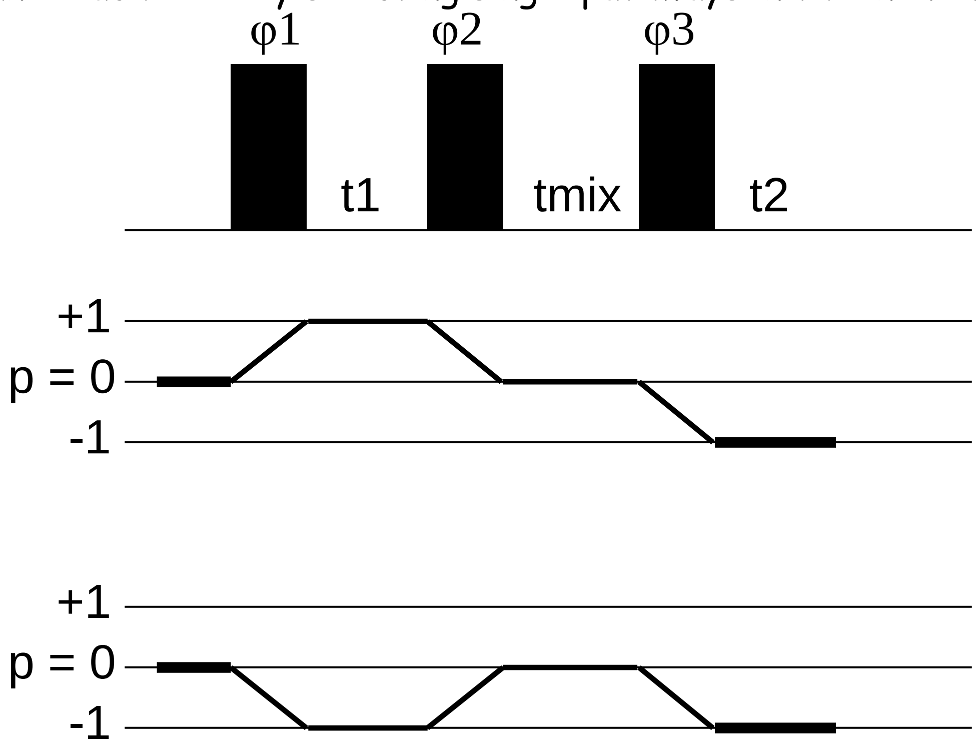
Two way to implement phase sensitive detection in the indirect dimension.

Phase modulation (PN type, echo-antiech):

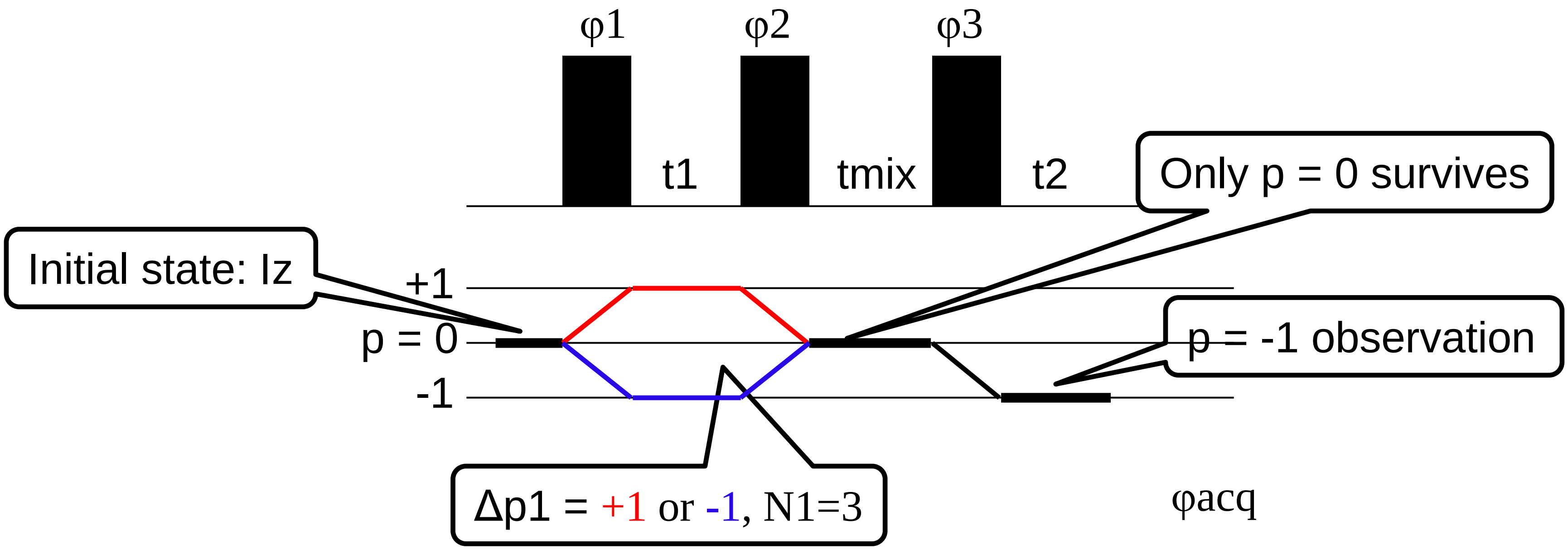
$$S_{echo}\left(t_1,t_2\right)=e^{i\omega_1 t_1}e^{-i\omega_2 t_2}$$

$$S_{antiecho}\left(t_1,t_2\right)=e^{i\omega_2 t_2}e^{-i\omega_2 t_2}$$

Phase modulation can be achieved by selecting single pathways in the indirect dimension.



Example4: NOESY (2D exchange)

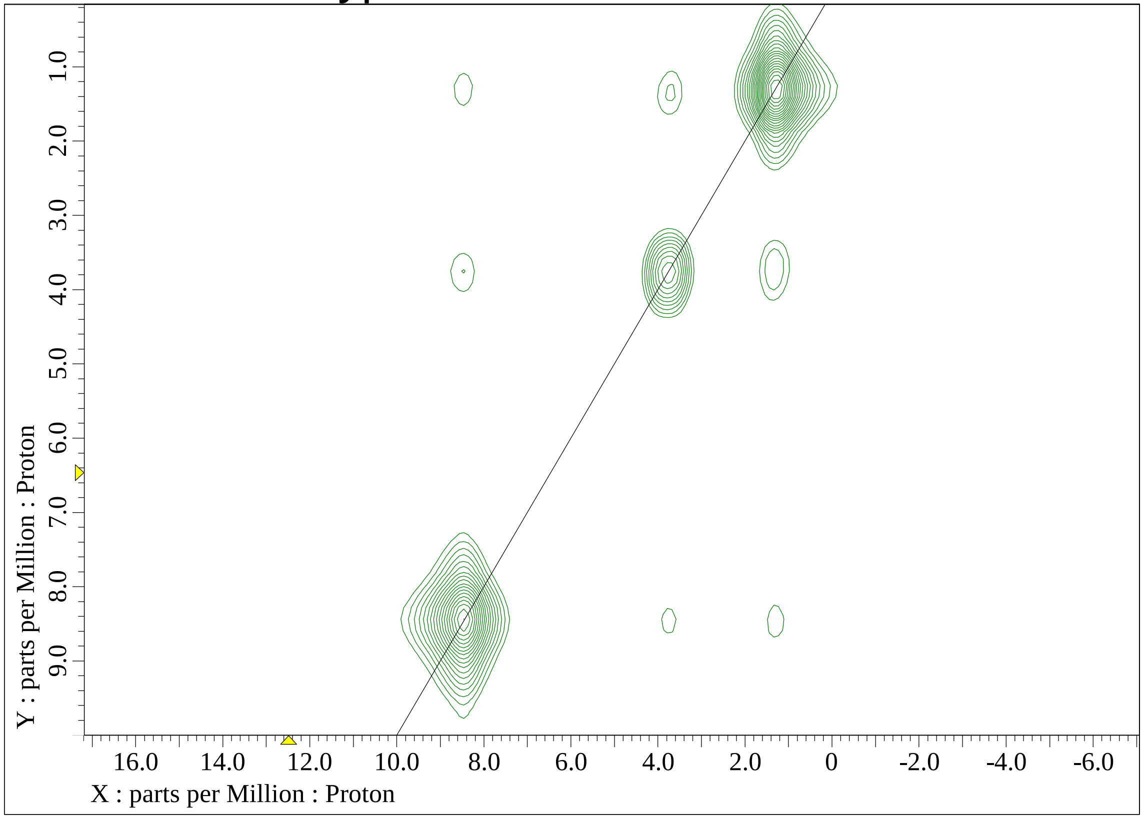


			φacq
0°	0°	0°	0°
120 °		0°	240°
240 °			120°
0°	0°	0°	0°
120 °		0°	120°
240 °			240°

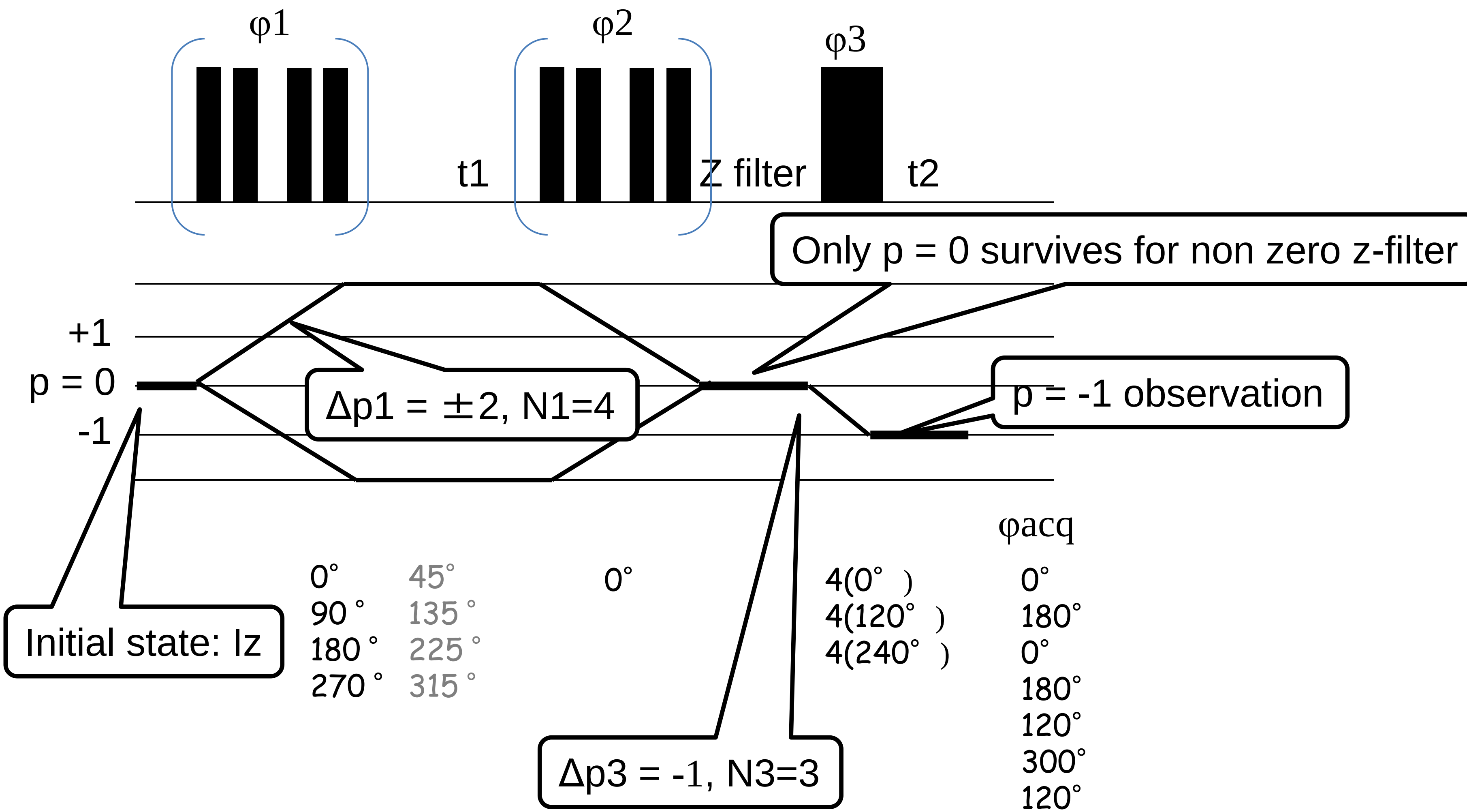
$$\phi_{acq,k} = -\sum_{j} \Delta p_j \phi_{j,k_j}$$

Example4: NOESY (2D exchange)

1H/1H exchange with tm = 10 ms
3 scans, PN-type



Example5: DQ/SQ correlation



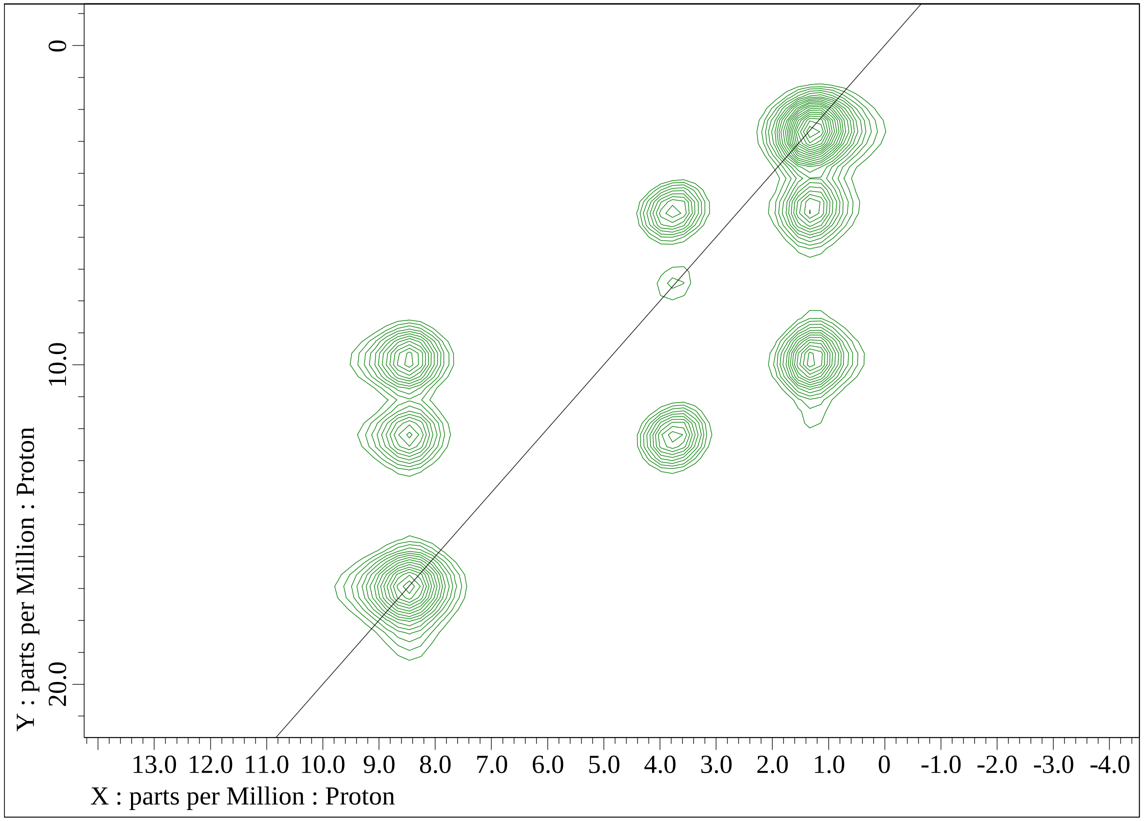
Δp2 = ±2, N2=4 also okay, but more phase cyclings.

φacq
0°
180°
0°
180°
120°
300°
120°
300°
240°
60°
240°
60°

$$\phi_{acq,k} = -\sum_j \Delta p_j \phi_{j,k_j}$$

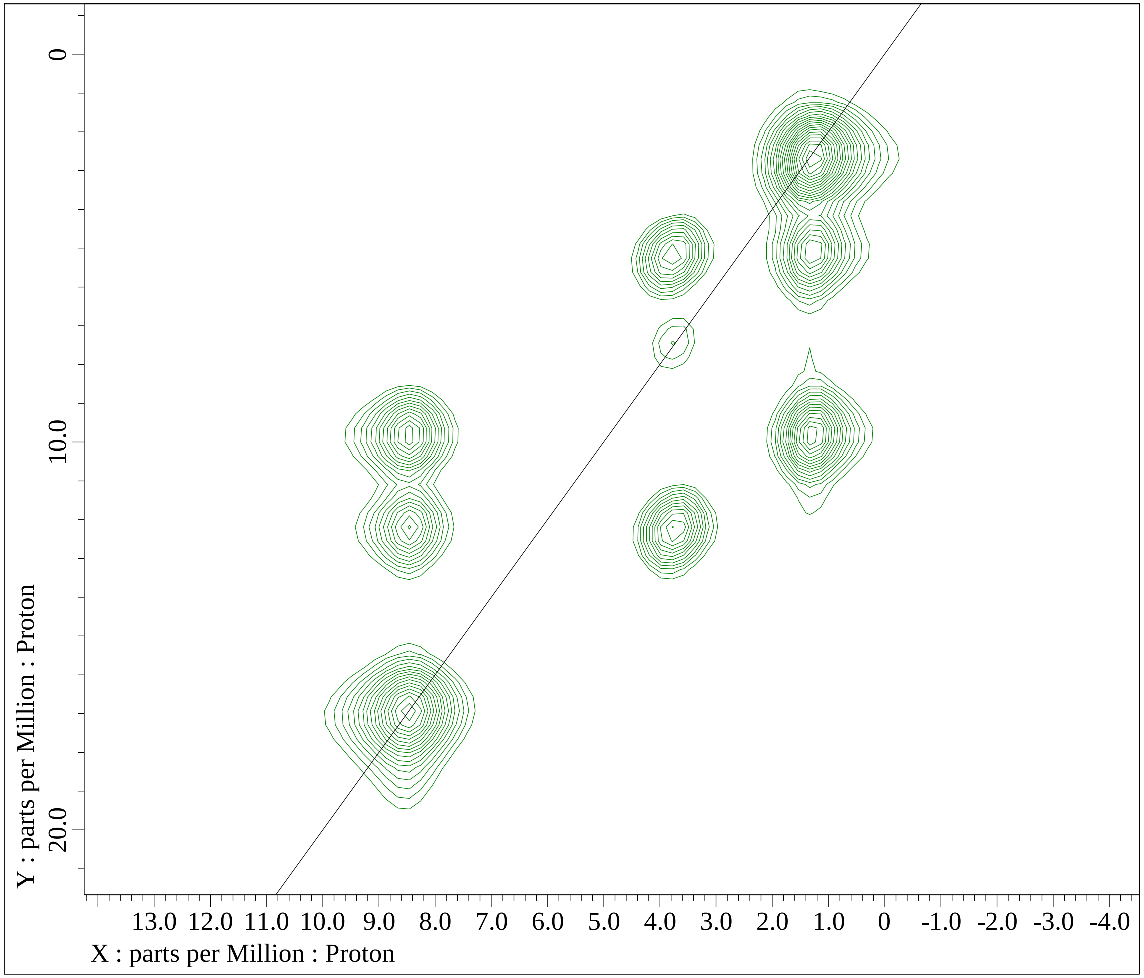
Example5: DQ/SQ correlation

1H DQ/1H SQ correlation with tm = 1 ms
4 scans

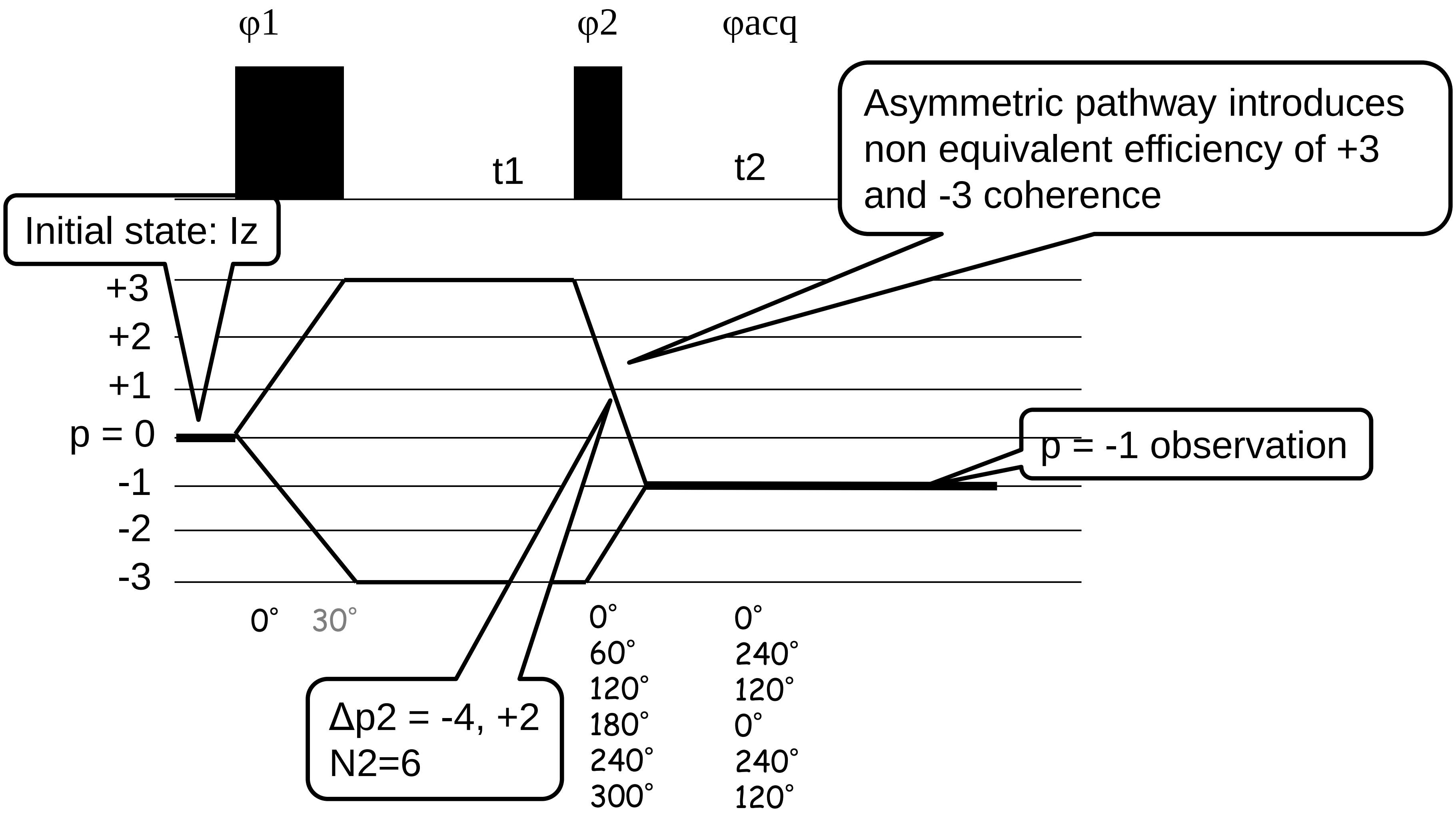


Example5: DQ/SQ correlation

1H DQ/1H SQ correlation with tm = 0 ms
12 scans

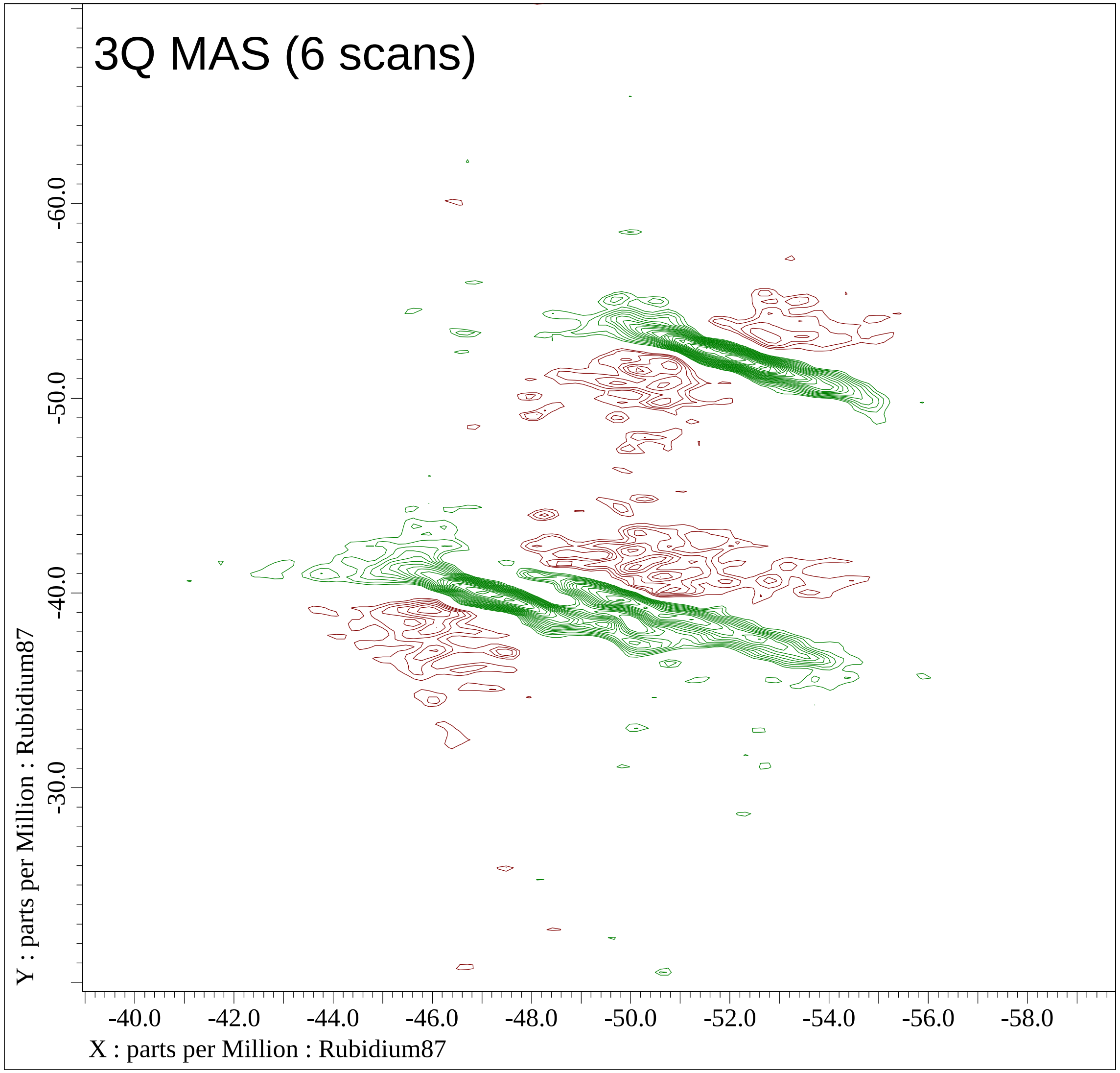


Example6: MQMAS

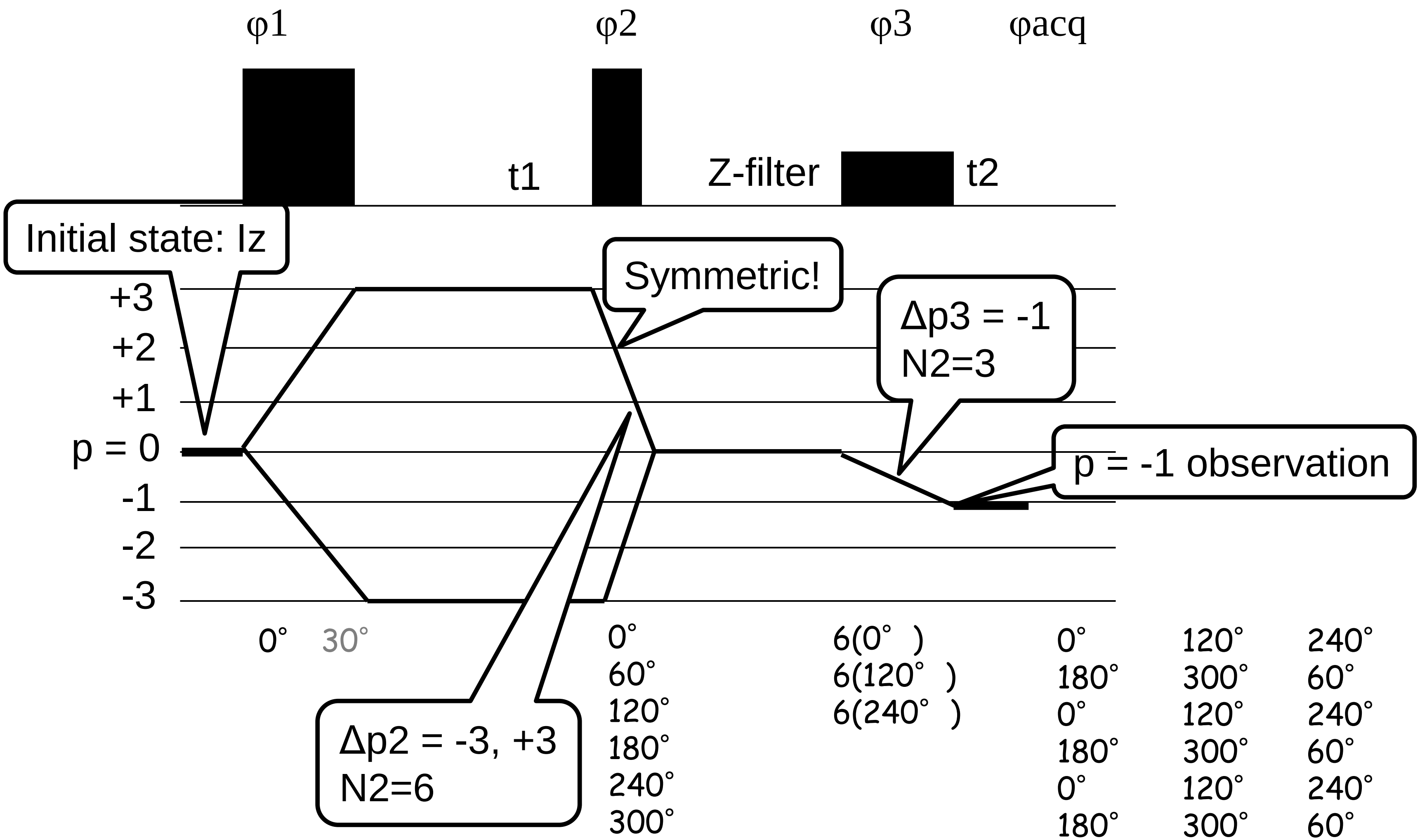


$$\phi_{acq,k} = -\sum_{j} \Delta p_j \phi_{j,k_j}$$

Example6: MQMAS

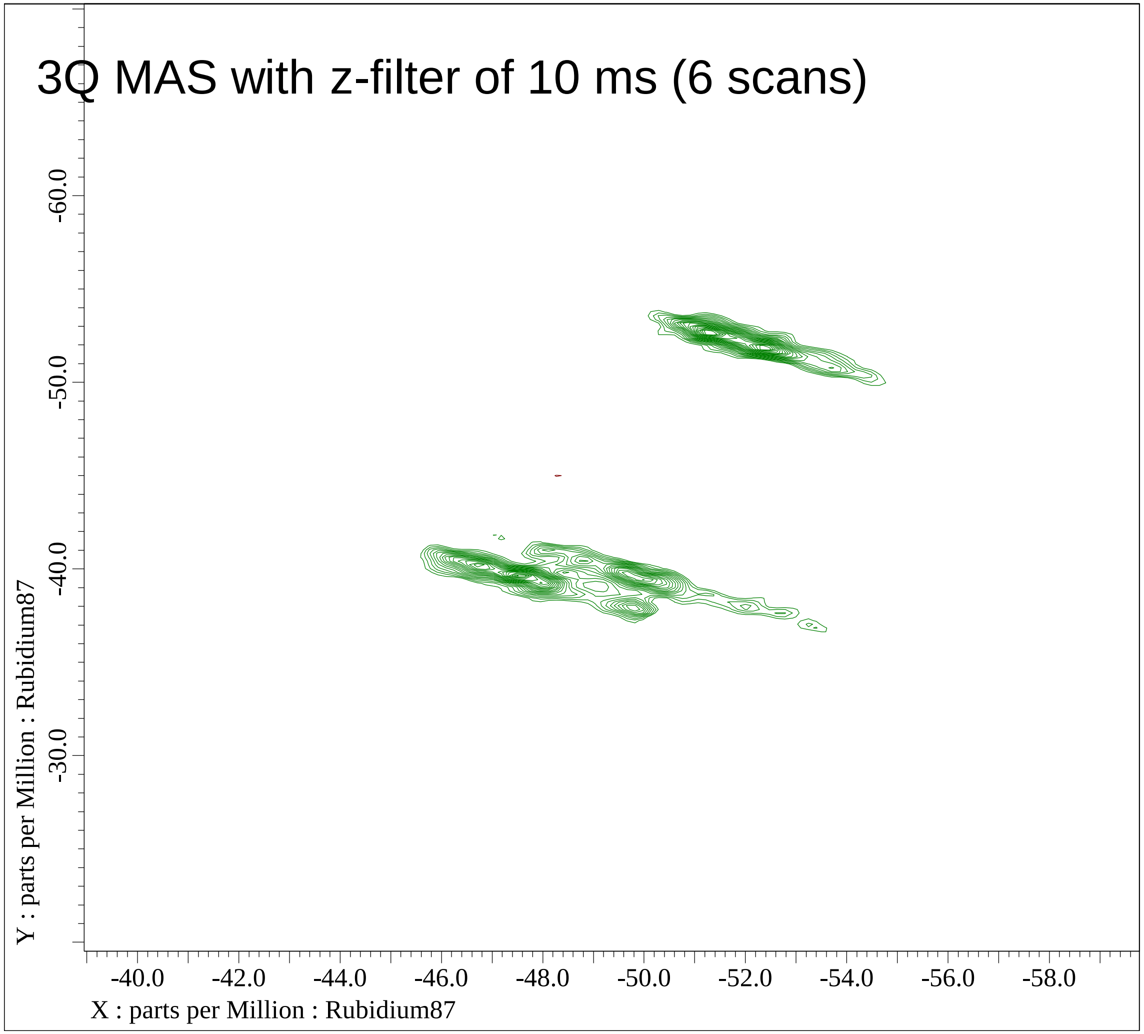


Example7: MQMAS

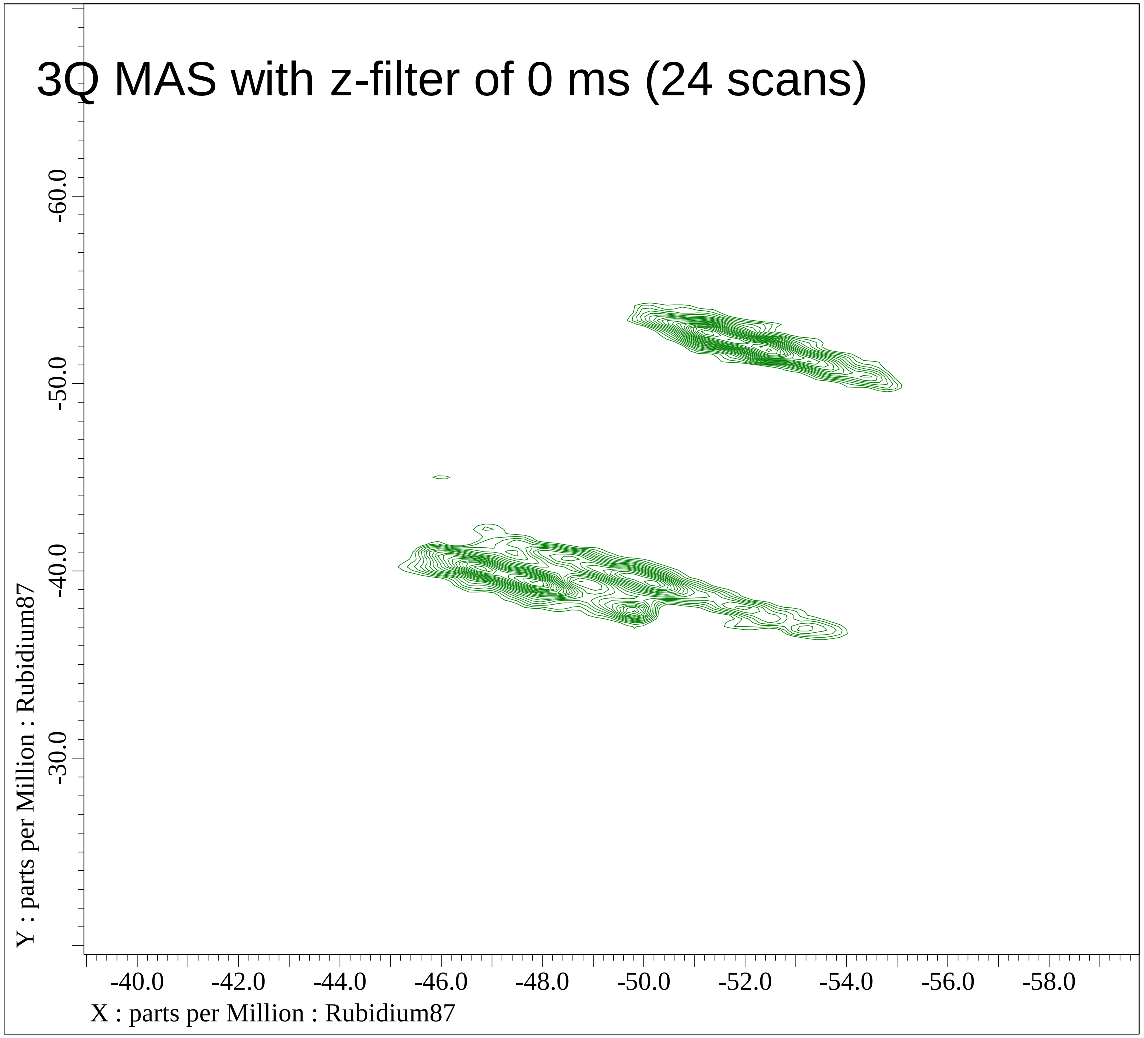


$$\phi_{acq,k} = -\sum_j \Delta p_j \phi_{j,k_j}$$

Example7: MQMAS

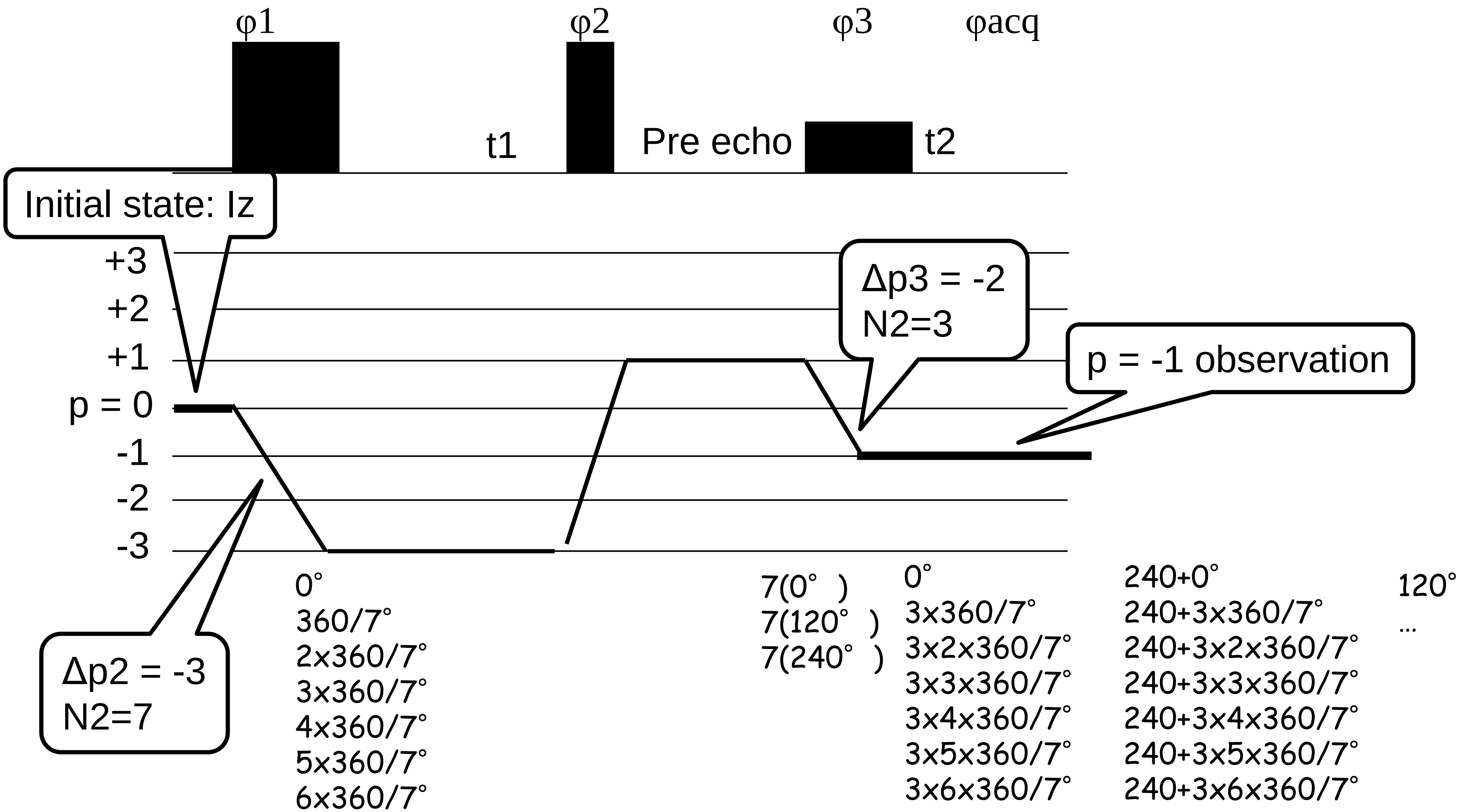


Example7: MQMAS



Example8: MQMAS (shifted-echo whole echo acquisition)

When inhomogeneous broadening is much larger than homogeneous broadening, whole echo acquisition can be applied to obtain pure absorption lineshape.

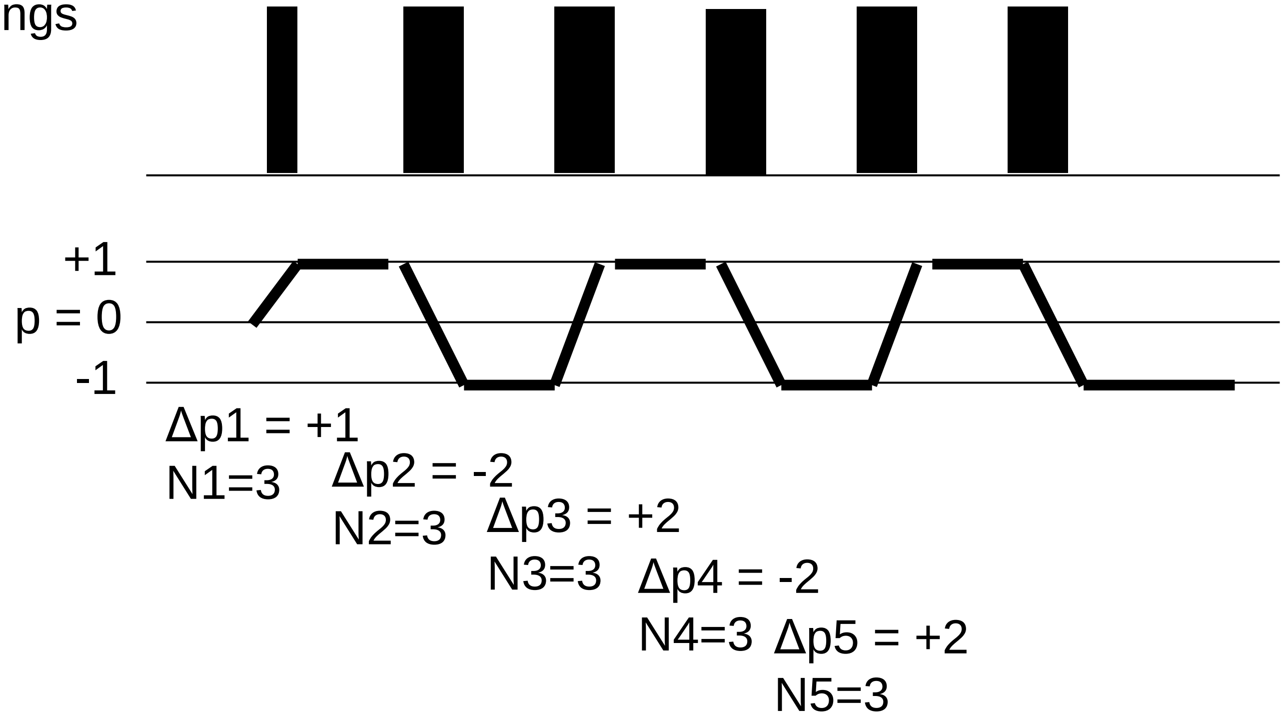


$$\phi_{acq,k} = -\sum_j \Delta p_j \phi_{j,k_j}$$

contents

Cogwheel phase cycling

Total cyclings = N1 x N2 x N3 x N4 x N5 = 243! For nested cycle = 11 for cogwheel phase cyclings



Cogwheel phase cycling:

M.H. Levitt, P.K. Madhu, C.E. Hughes, J. Magn. Reson. 155 (2000) 300-306.

Practical implementation: A. Jerschow and R. Kumar, Calculation of Coherence Pathway Selection and Cogwheel Cycles,
J. Magn. Reson. **160**, 59-64, (2003).https://wp.nyu.edu/jerschow/resources/cccp-complete-calculation-of-coherence-pathways/

Multiplex phase cycling

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Multiplex phase cycling

Natala Ivchenko [a], Colan E Hughes [b, 1], Malcolm H Levitt [a]

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contents

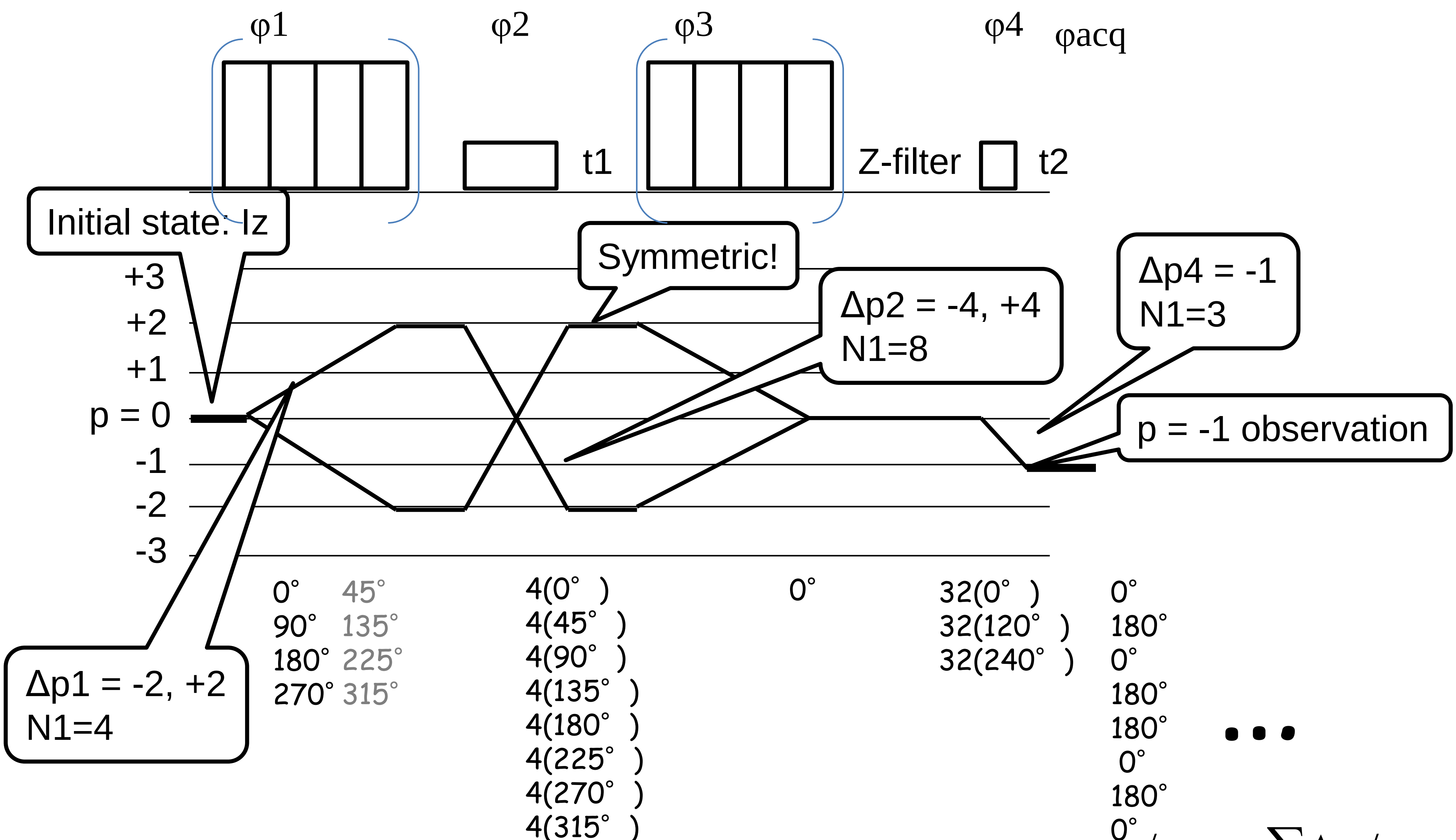
references

Phase cycling:
G. Bodenhausen, H. Kogler, R.R. Ernst, J. Magn. Reson. 58 (1984) 370-388.
R.R. Ernst, G. Bodenhausen, A. Wokaun, Principles of Nuclear Magnetic Resonance in One and Two Dimensions, Oxford (1988).

Cogwheel phase cycling:
M.H. Levitt, P.K. Madhu, C.E. Hughes, J. Magn. Reson. 155 (2000) 300-306.

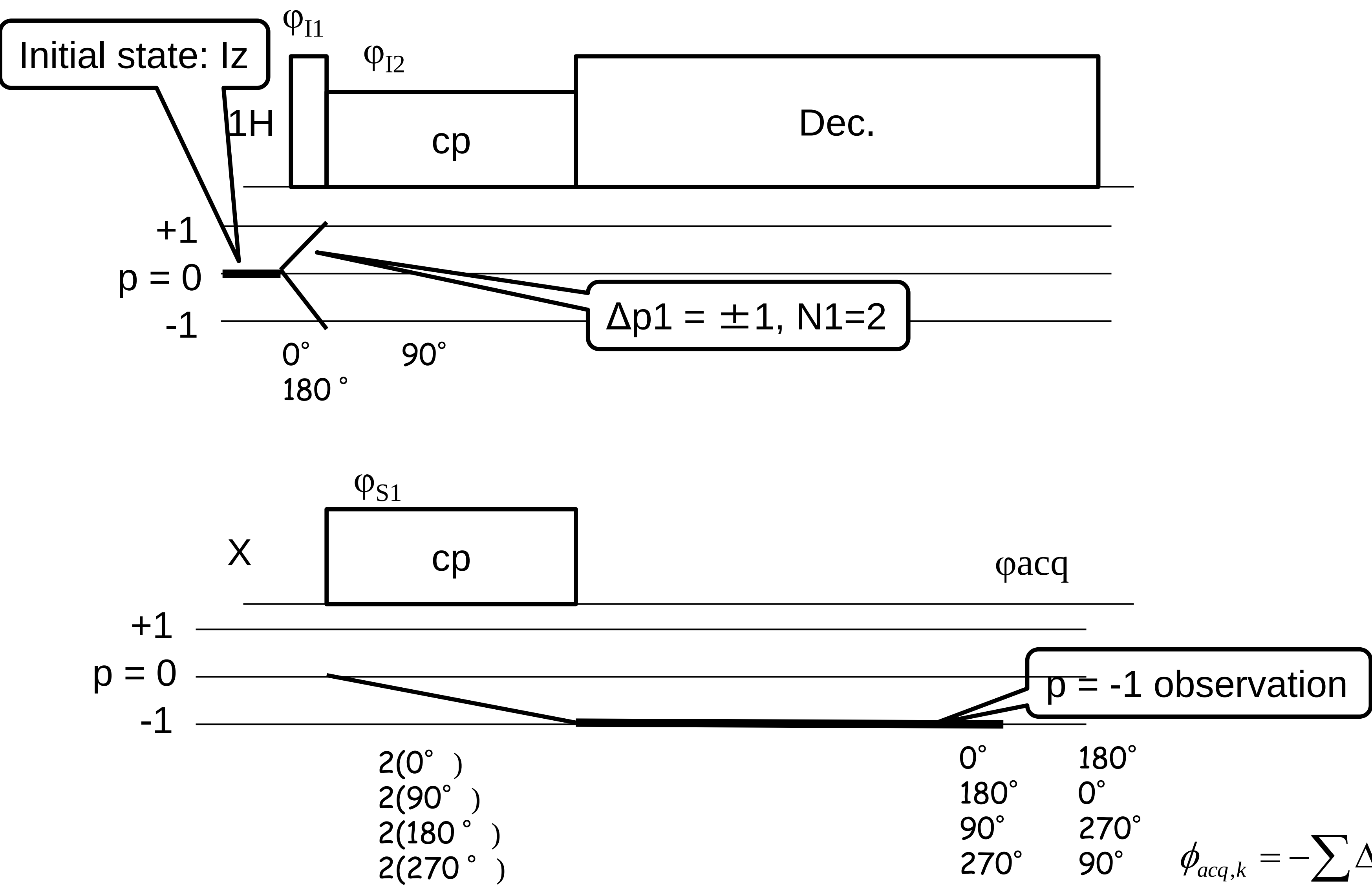
Multiplex phase cycling:
N. Ivchenko, C.E. Hughes, M.H. Levitt, J. Magn. Reson. 160 (2003) 52-58.

Example11: DQ/SQ for half-integer quadrupolar nuclei



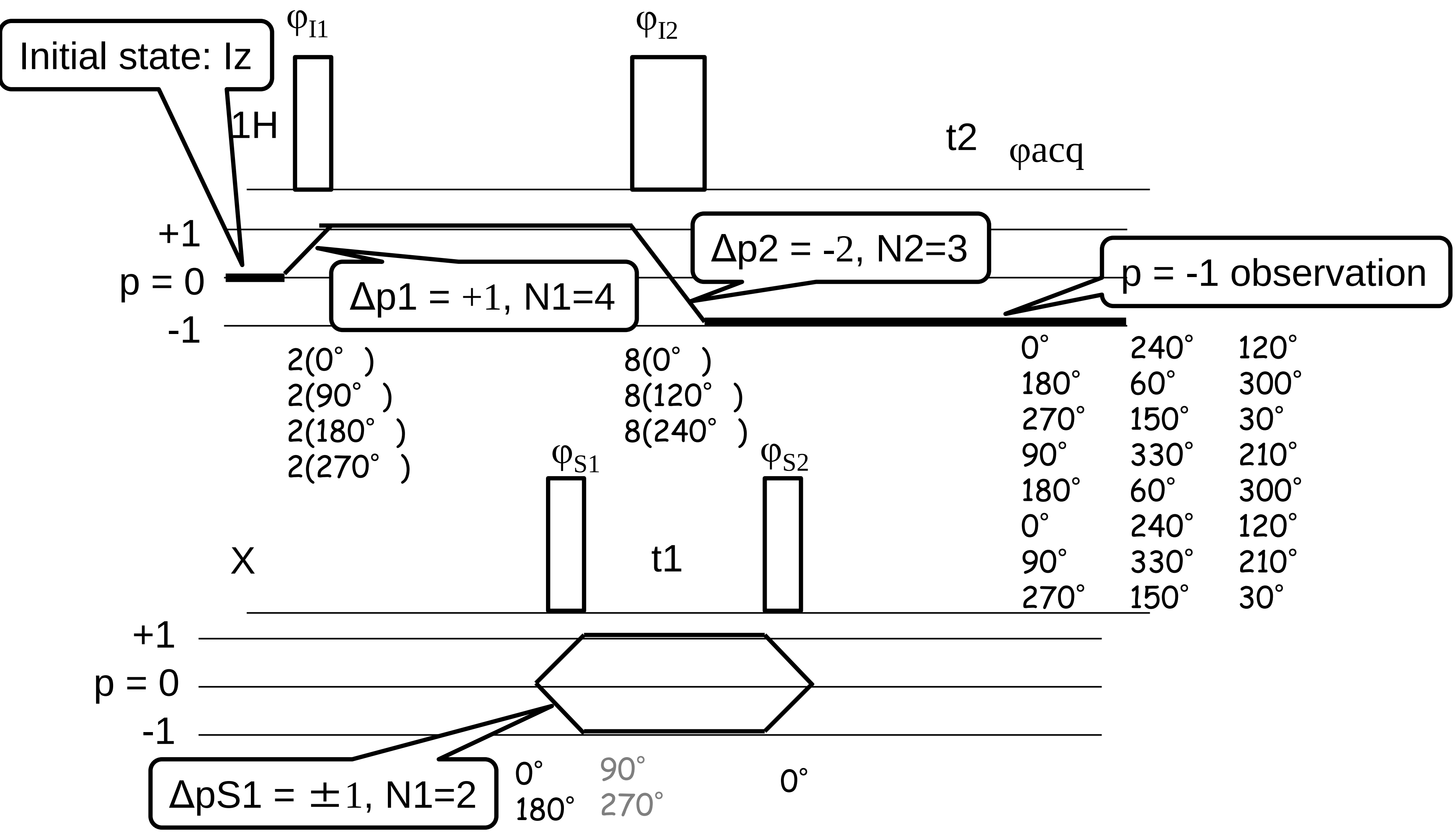
$$\phi_{acq,k} = -\sum_j \Delta p_j \phi_{j,k_j}$$

Example6: CPMAS



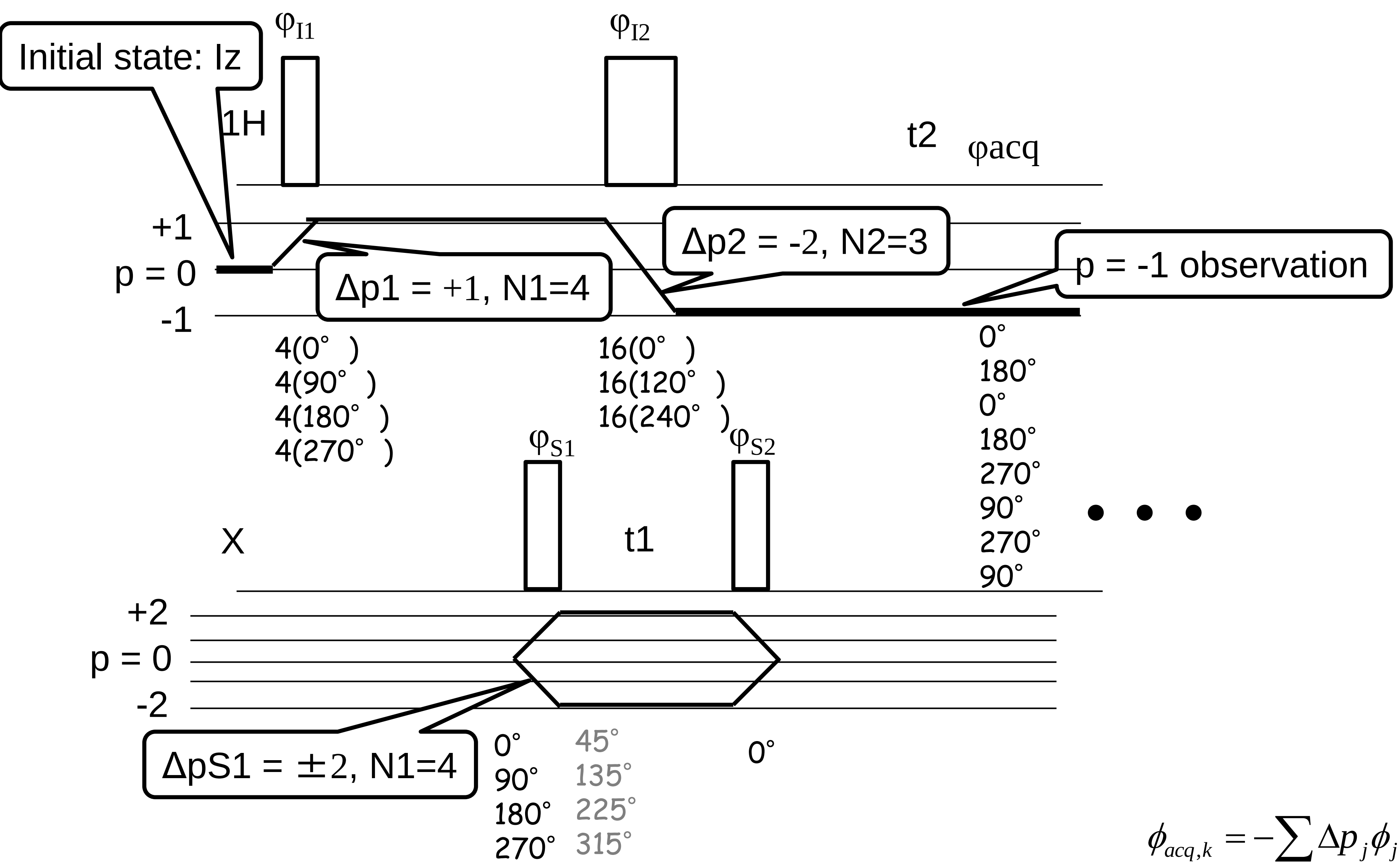
$$\phi_{acq,k} = -\sum_j \Delta p_j \phi_{j,k_j}$$

Example7: HMQC



$$\phi_{acq,k} = -\sum_j \Delta p_j \phi_{j,k_j}$$

Example8: DQ HMQC



$$\phi_{acq,k} = -\sum_j \Delta p_j \phi_{j,k_j}$$