SSSC Discovery Series
NMR1

Topics:

- simple spin physics
- net or equilibrium magnetisation
- rotating frame of reference
- a pulse in the rotating frame
- the vector model of nmr spectroscopy
- pulse calibration
- a tour of a spectrometer
- the probe
- the digitizer
- quadrature detection
- magnet shimming
- sensitivity

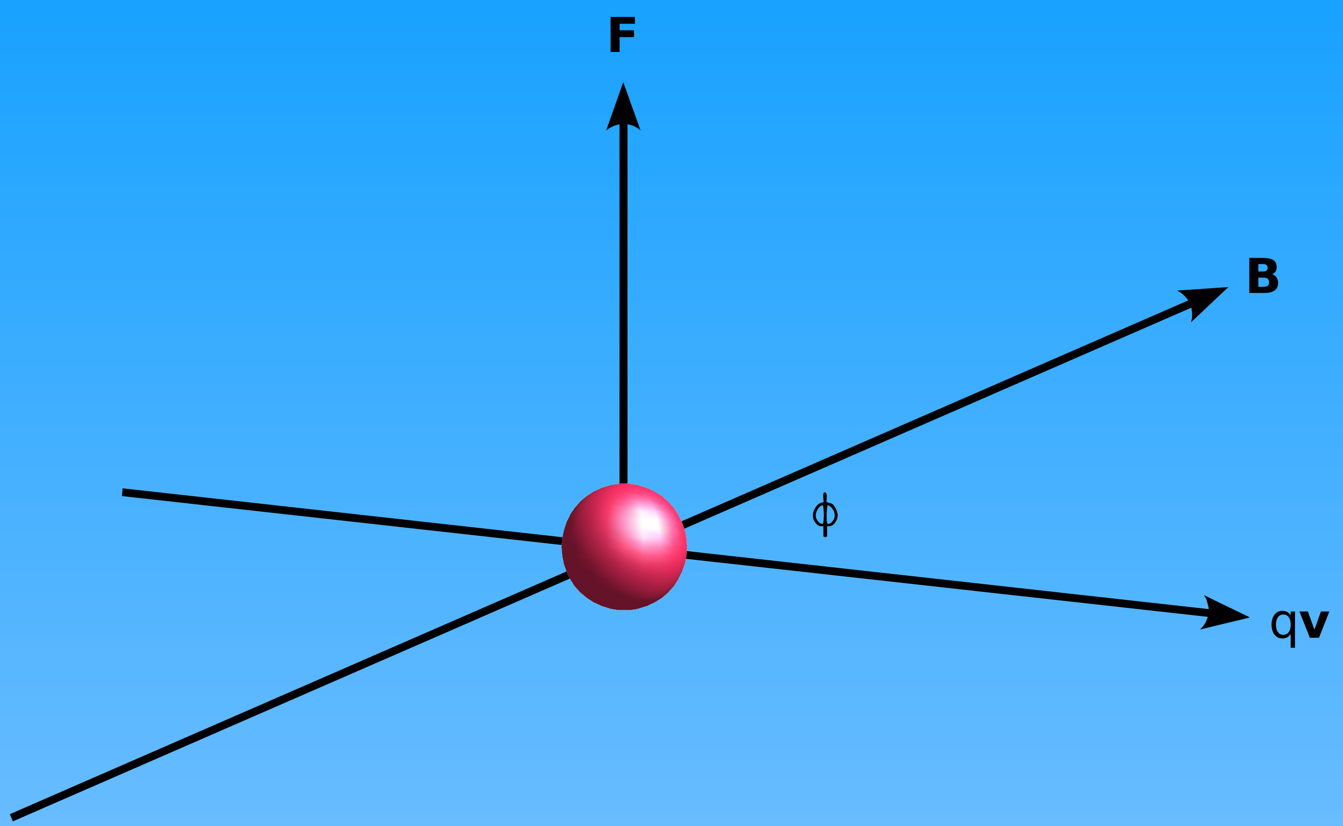
  and ...

- **no** quantum mechanics!

Saskatchewan Structural Sciences Centre
University of Saskatchewan, Canada
SSSC

SSSC NMR Facilities

Motion of a Charged Particle in a Magnetic Field

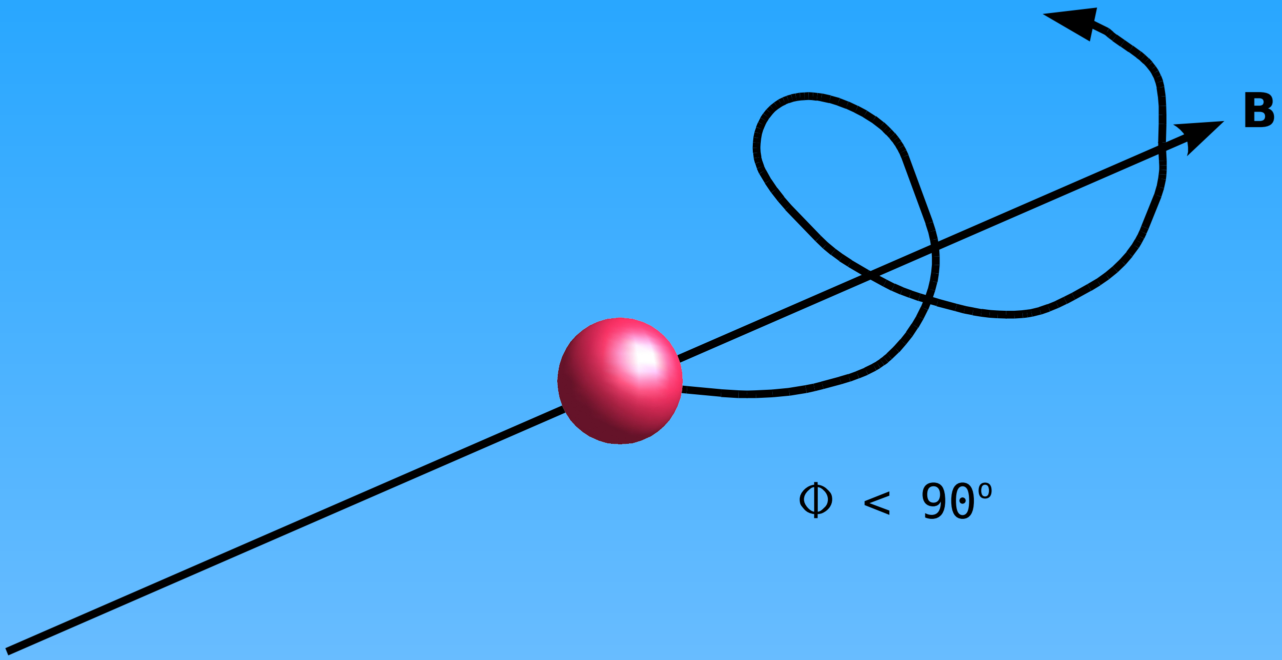


q**v** – particle with charge q moving with velocity **v**
B – magnetic field
F – resultant force

$$\mathbf{F} = q\mathbf{v} \times \mathbf{B}$$

$$F = qvB\sin(\phi)$$

Motion of a Charged Particle in a Magnetic Field



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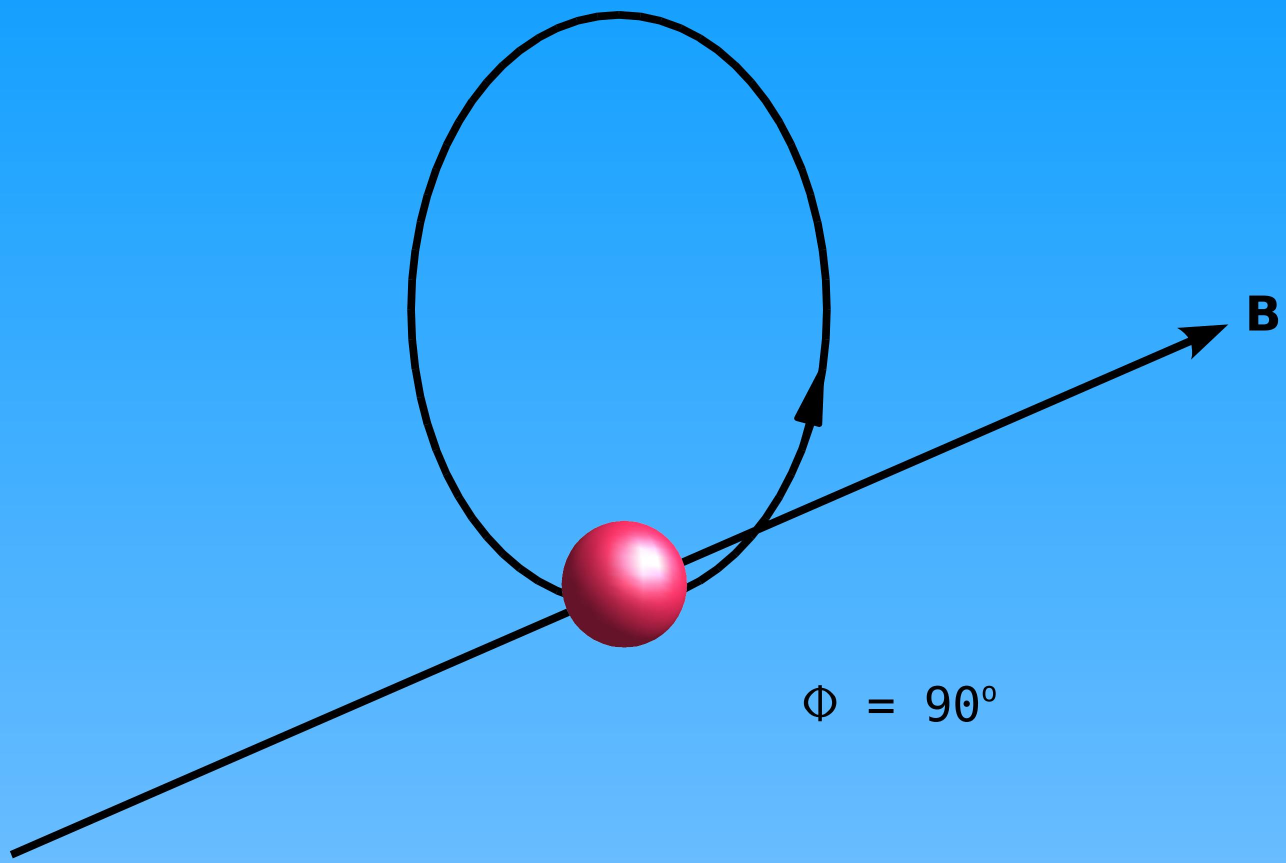

q**v** – particle with charge q moving with velocity **v**
B – magnetic field
F – resultant force

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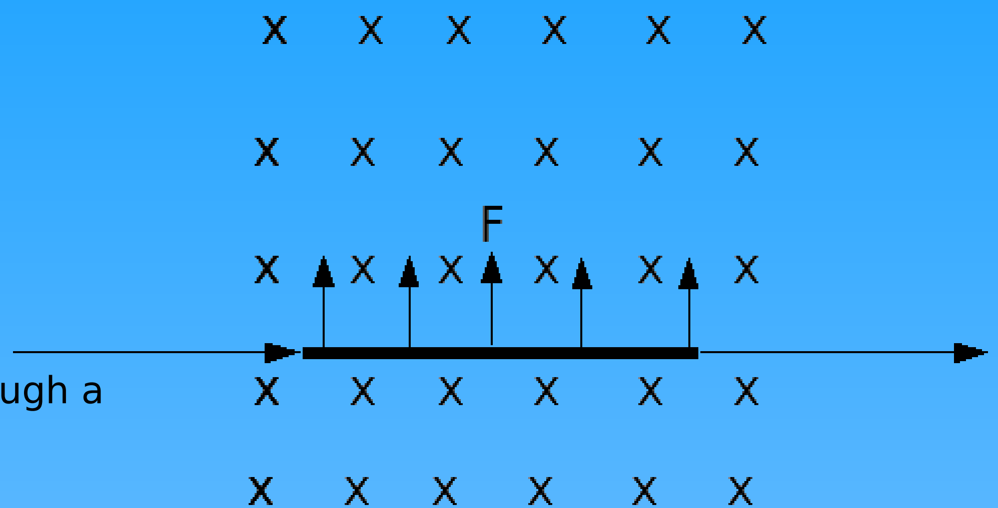
$F = qvB\sin(\phi)$

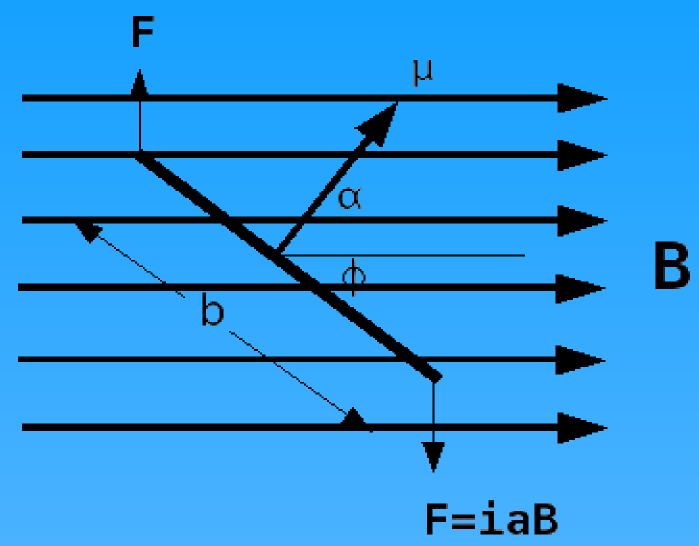
Motion of a Charged Particle Along a Wire in a Magnetic Field



Electron flow through a wire

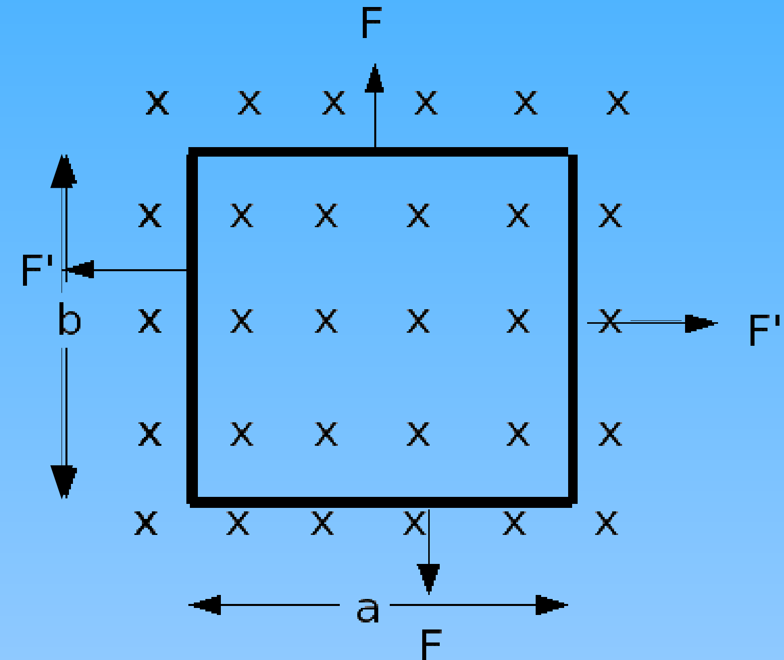
x – magnetic field, B, pointing *away* from the viewer

Magnetic Moment in a Current Loop



$\Gamma = \mu X \mathbf{B}$

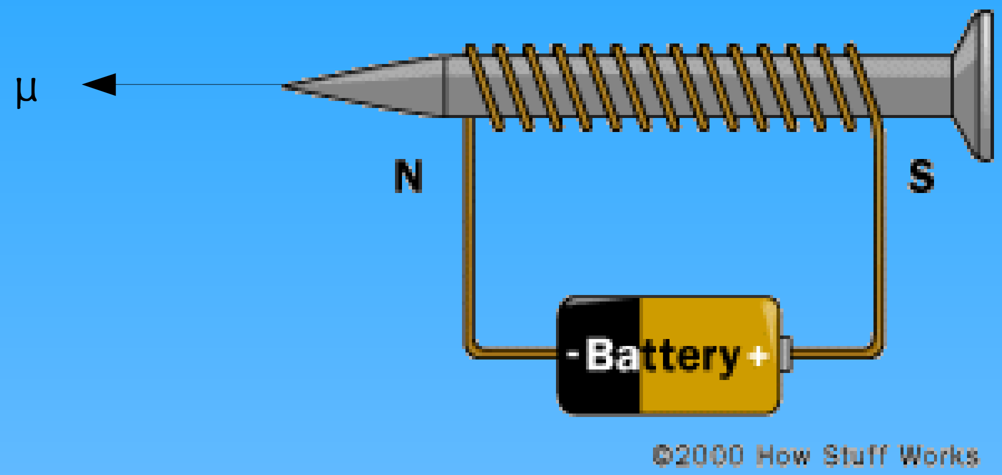
Top view turned 90^{o}



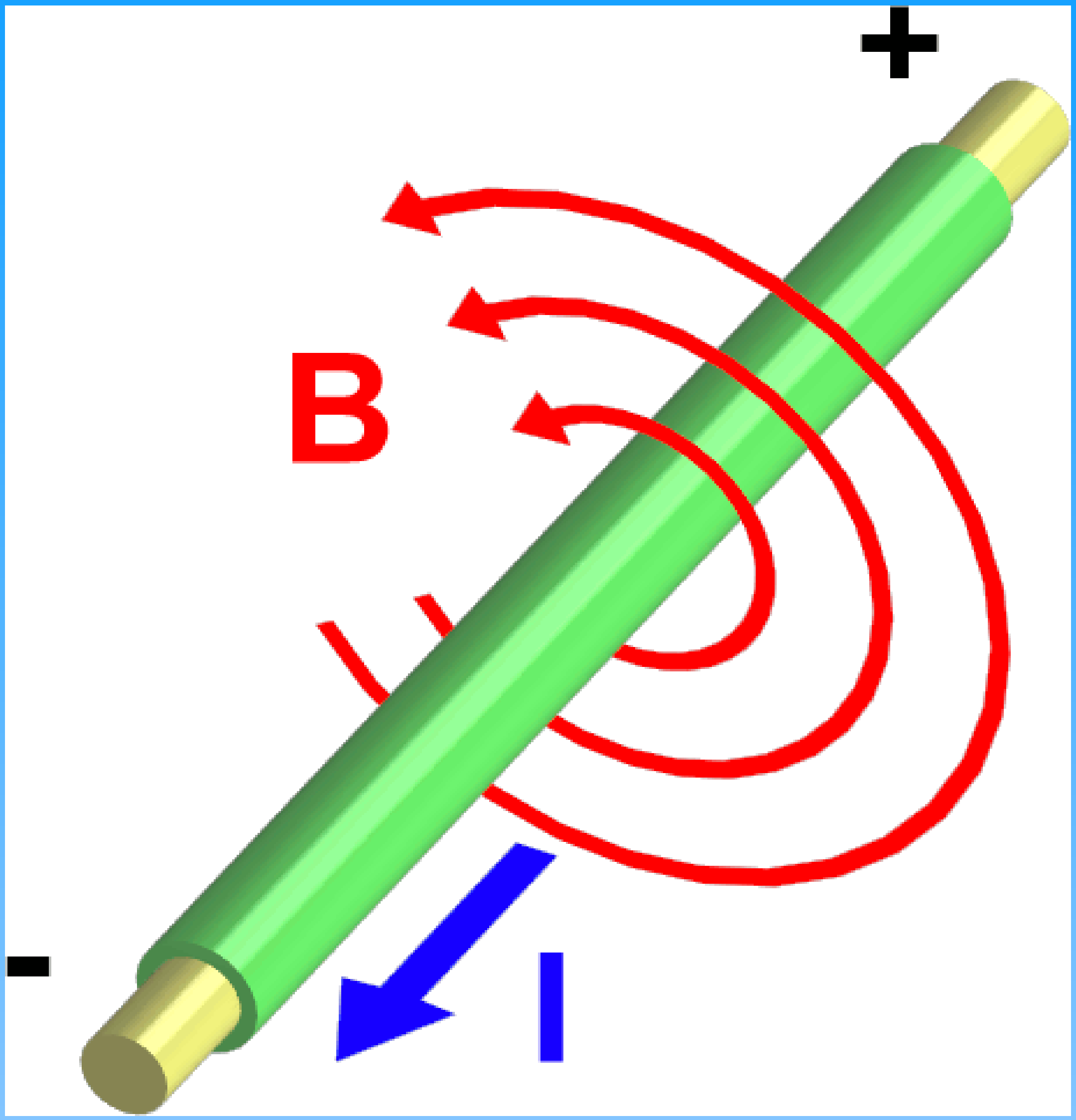
x – magnetic field, B, pointing *away* from the viewer

Magnetic Moment in a Current Loop

An electromagnet utilizes these ideas to produce a magnetic field:

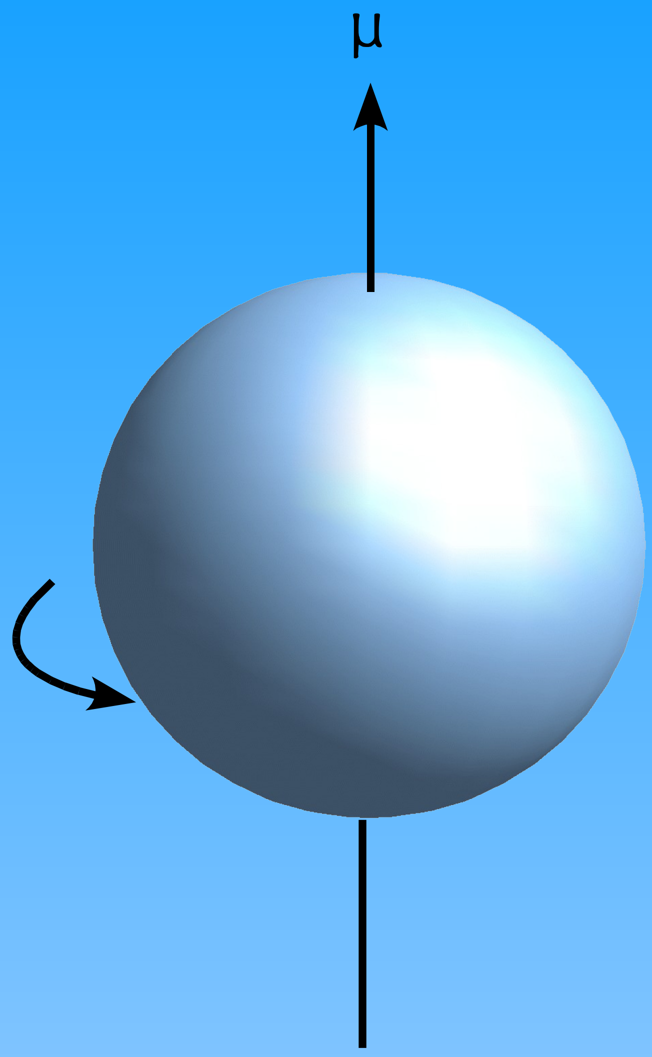


Magnetic Field Around a Current-carrying Wire



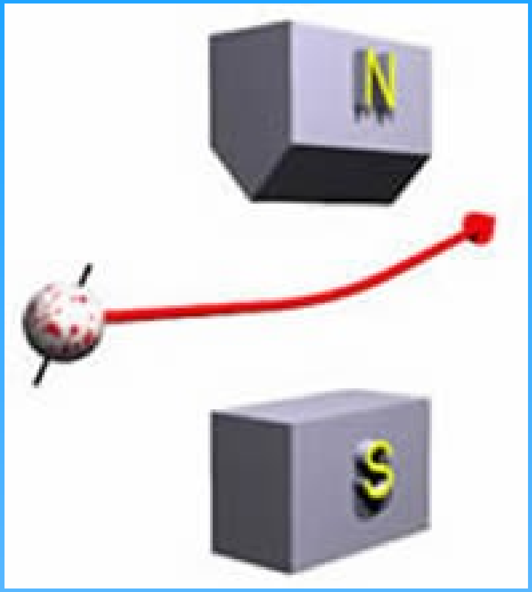
Magnetic field generated by electron flow at right angles to direction of current

Spin

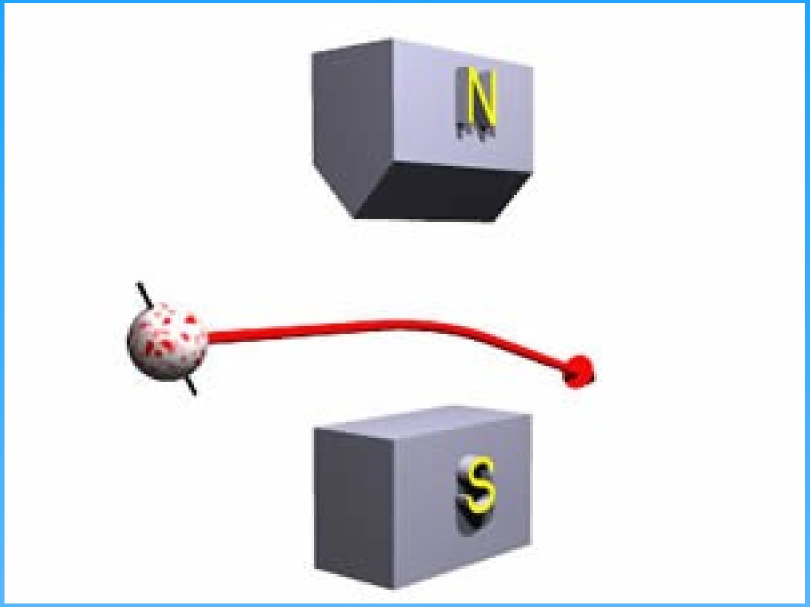


A spinning charge generates a magnetic moment, μ

Spin



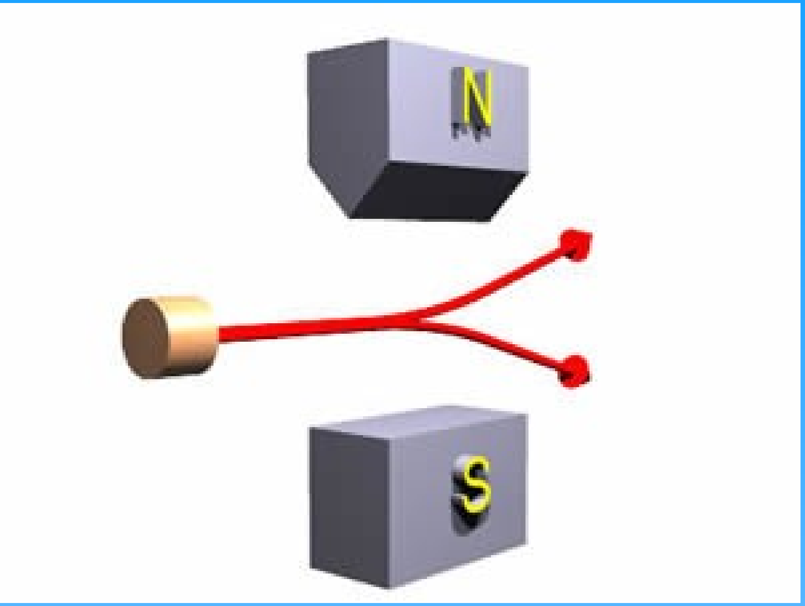
Charged particle spinning clockwise .. spin “up”



Charged particle spinning counterclockwise .. spin “down”

The Stern-Gerlach experiment

Spin



Electron beam through an inhomogenous field.
Evidently, electrons 'spin' and have only two possible spin states.

The Stern-Gerlach experiment

Spin

Like mass and charge, spin or more properly, spin angular momentum is a fundamental or intrinsic property of matter.

Electrons, certain nuclei, muons, photons have "spin" but do **not** actually spin.

Quantum mechanics tells us that particles with spin have $2I + 1$ accessible spin states where I is the "spin" of the particle. For electrons and protons, $I = ½$ so each has two spin states.

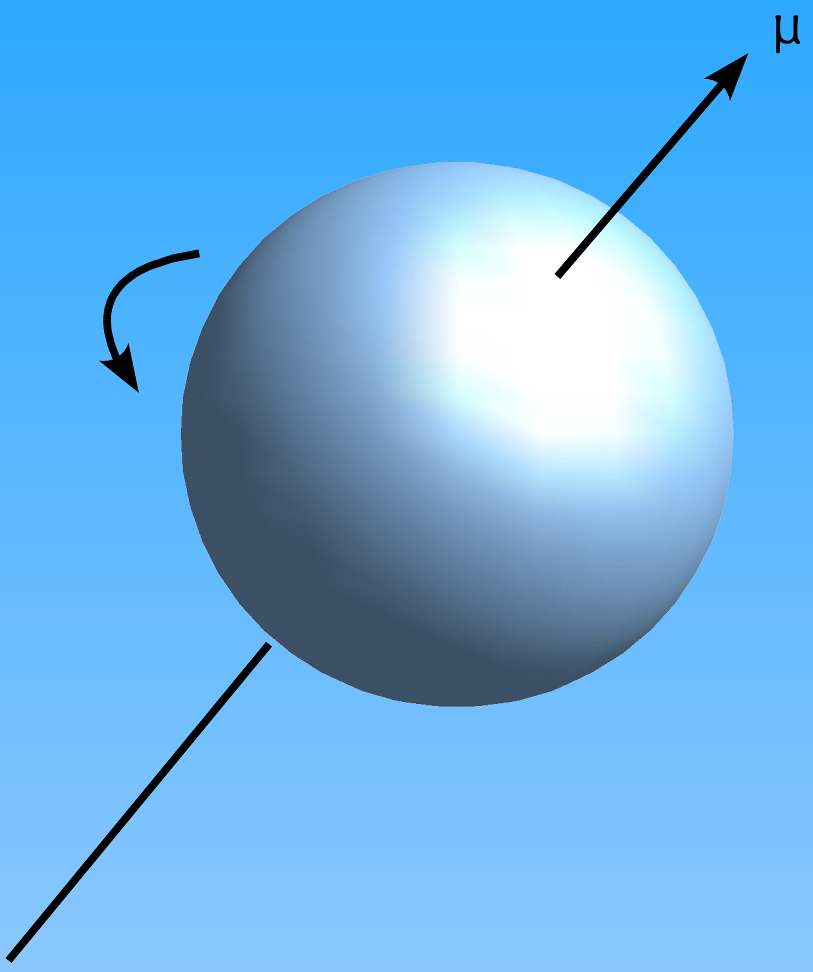
Nuclear spin can be assigned according to the relative numbers of protons and neutrons in the nucleus:

protons/neutrons	
even/even	0 spin
odd/even	half-integer spin (1/2, 3/2, 5/2 ..)
odd/odd	integer spin (1, 2 ..)

Spin

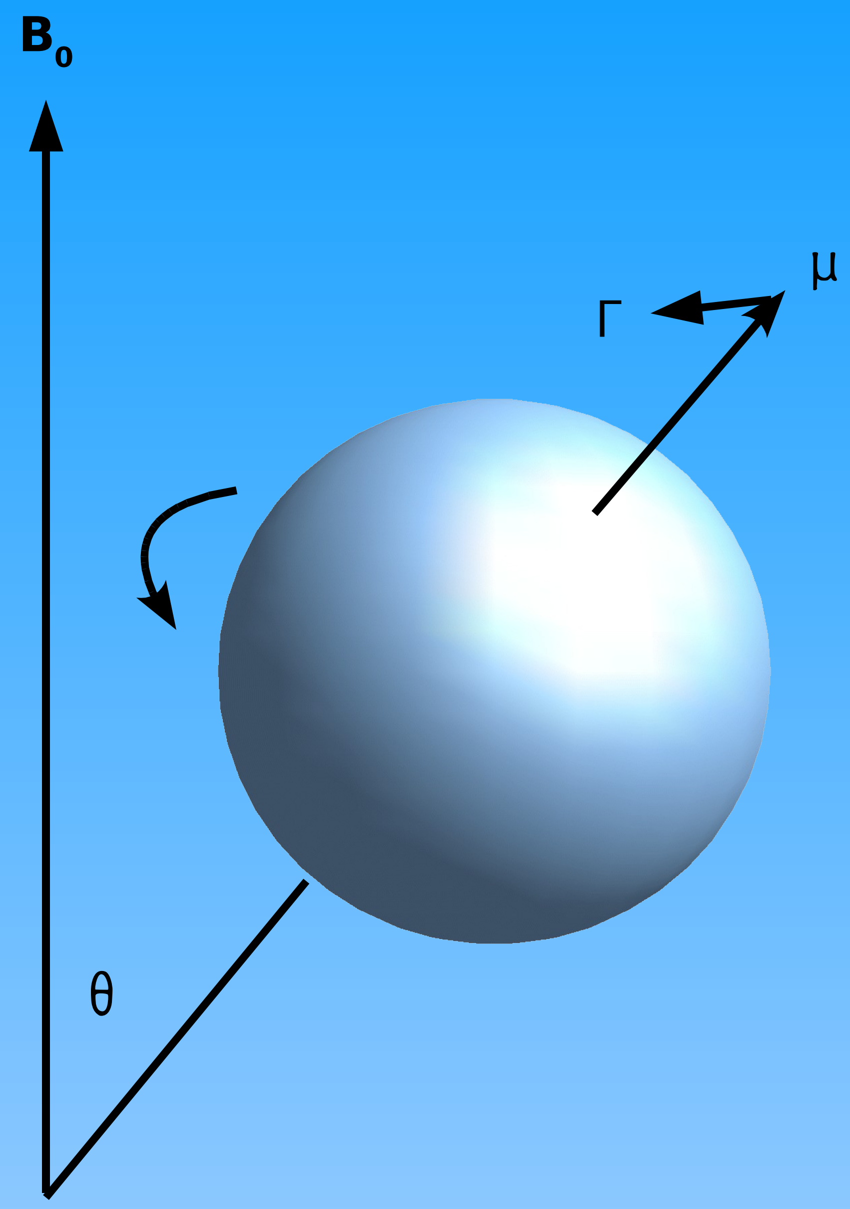
Nuclide	Spin I	Electric quadrupole moment[a] $[eQ]$ $[10^{-28}\ m^2]$	Natural abundance) [%]	Relative sensitivity[b]	Gyromagnetic ratio γ[a] $[10^7\ rad\ T^{-1}\ s^{-1}]$	NMR frequency [MHz][b] $(B_0 = 2.3488\ T)$
^{1}H	1/2	–	99.985	1.00	26.7519	100.0
^{2}H	1	2.87×10^{-3}	0.015	9.65×10^{3}	4.1066	15.351
^{3}H[c]	1/2	–	–	1.21	28.5350	106.664
^{6}Li	1	-6.4×10^{-4}	7.42	8.5×10^{-3}	3.9371	14.716
^{10}B	3	8.5×10^{-2}	19.58	1.99×10^{-2}	2.8747	10.746
^{11}B	3/2	4.1×10^{-2}	80.42	0.17	8.5847	32.084
^{12}C	0	–	98.9	–	–	–
^{13}C	1/2	–	1.108	1.59×10^{-2}	6.7283	25.144
^{14}N	1	1.67×10^{-2}	99.63	1.01×10^{-3}	1.9338	7.224
^{15}N	1/2	–	0.37	1.04×10^{-3}	–2.7126	10.133
^{16}O	0	–	99.96	–	–	–
^{17}O	5/2	-2.6×10^{-2}	0.037	2.91×10^{-2}	–3.6280	13.557
^{19}F	1/2	–	100	0.83	25.1815	94.077
^{23}Na	3/2	0.1	100	9.25×10^{-2}	7.0704	26.451
^{25}Mg	5/2	0.22	10.13	2.67×10^{-3}	–1.6389	6.1195
^{29}Si	1/2	–	4.70	7.84×10^{-3}	–5.3190	19.865
^{31}P	1/2	–	100	6.63×10^{-2}	10.8394	40.481
^{39}K	3/2	5.5×10^{-2}	93.1	5.08×10^{-4}	1.2499	4.667
^{43}Ca	7/2	-5.0×10^{-2}	0.145	6.40×10^{-3}	–1.8028	6.728
^{57}Fe	1/2	–	2.19	3.37×10^{-5}	0.8687	3.231
^{59}Co	7/2	0.42	100	0.28	6.3015	23.614
^{119}Sn	1/2	–	8.58	5.18×10^{-2}	–10.0318	37.272
^{133}Cs	7/2	-3.0×10^{-3}	100	4.74×10^{-2}	3.5339	13.117
^{195}Pt	1/2	–	33.8	9.94×10^{-3}	5.8383	21.499

A “Spinning” Charge in a Magnetic Field



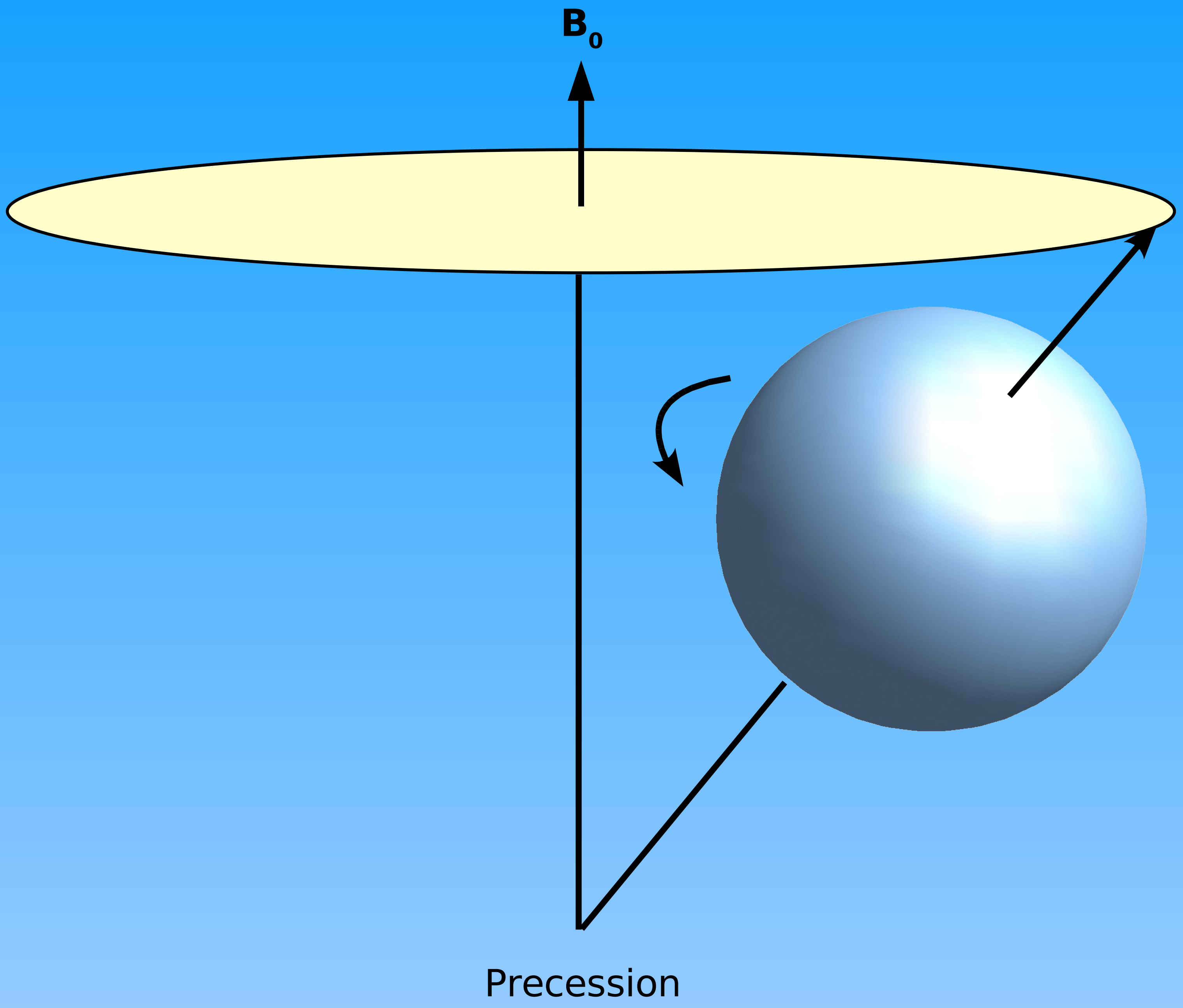
A “Spinning” Charge in a Magnetic Field

Charge experiences a torque, Γ, at right angles to the plane defined by B_0 and μ.



$\Gamma = \mu X \mathbf{B}$

A “Spinning” Charge in a Magnetic Field



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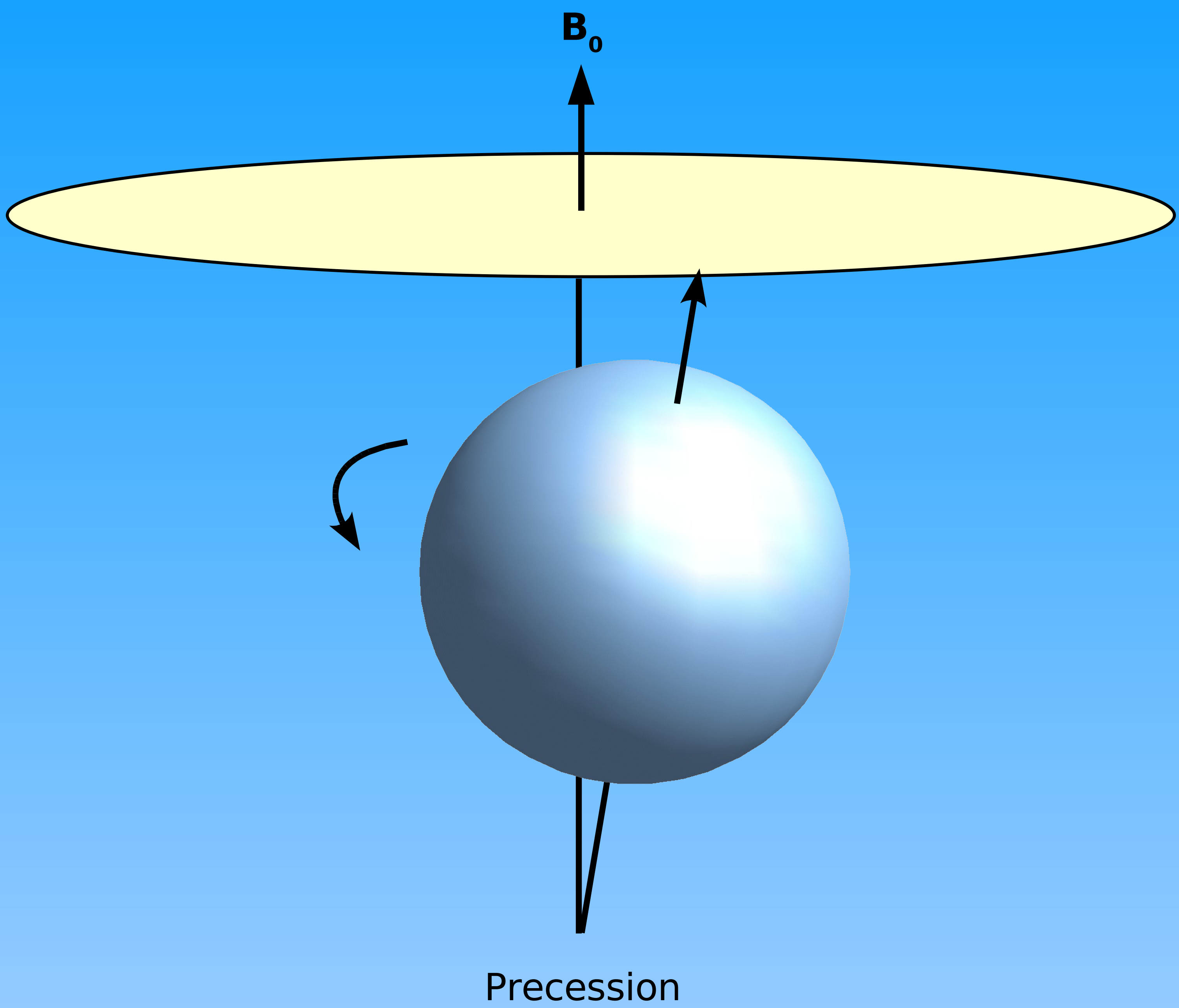

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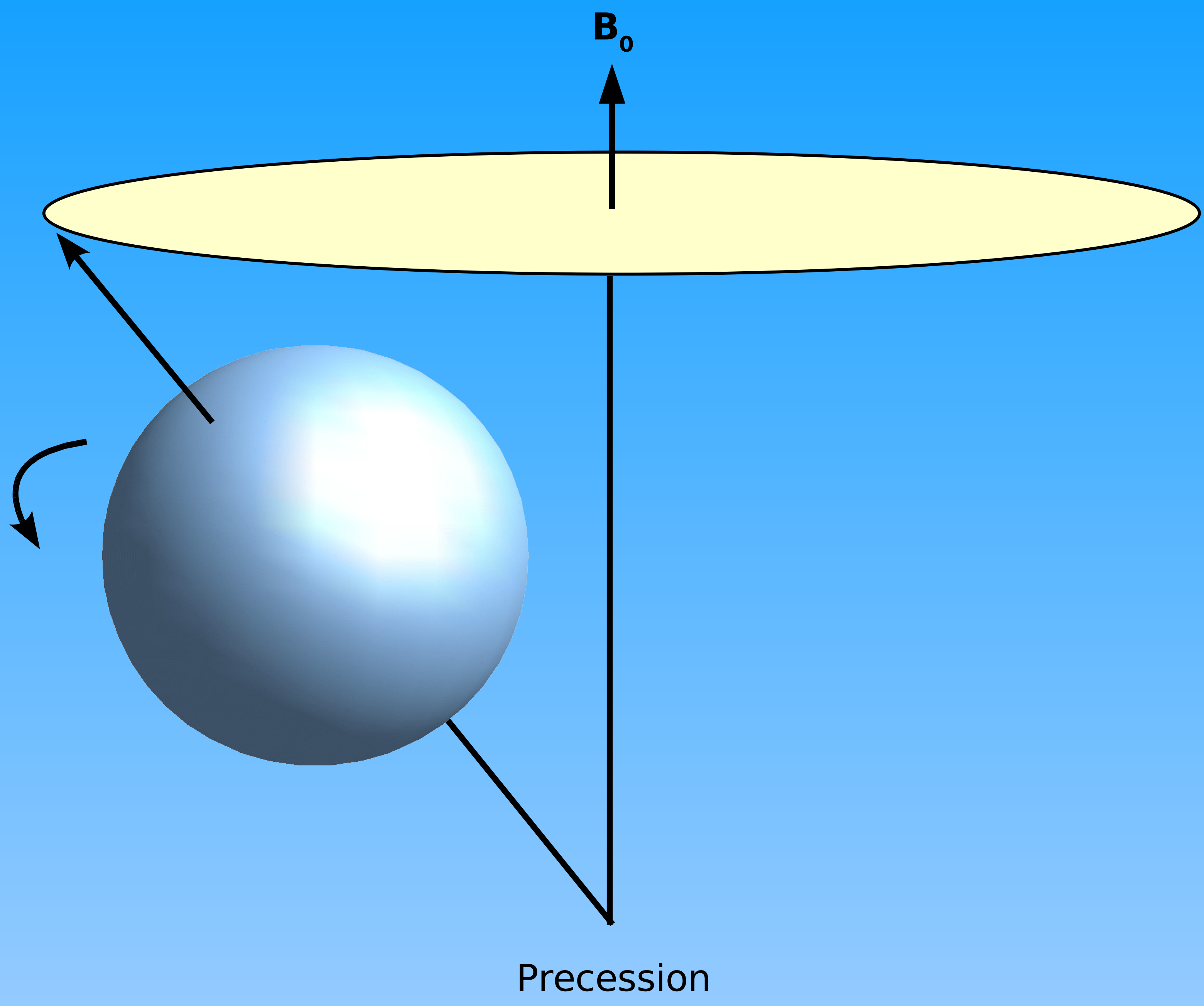

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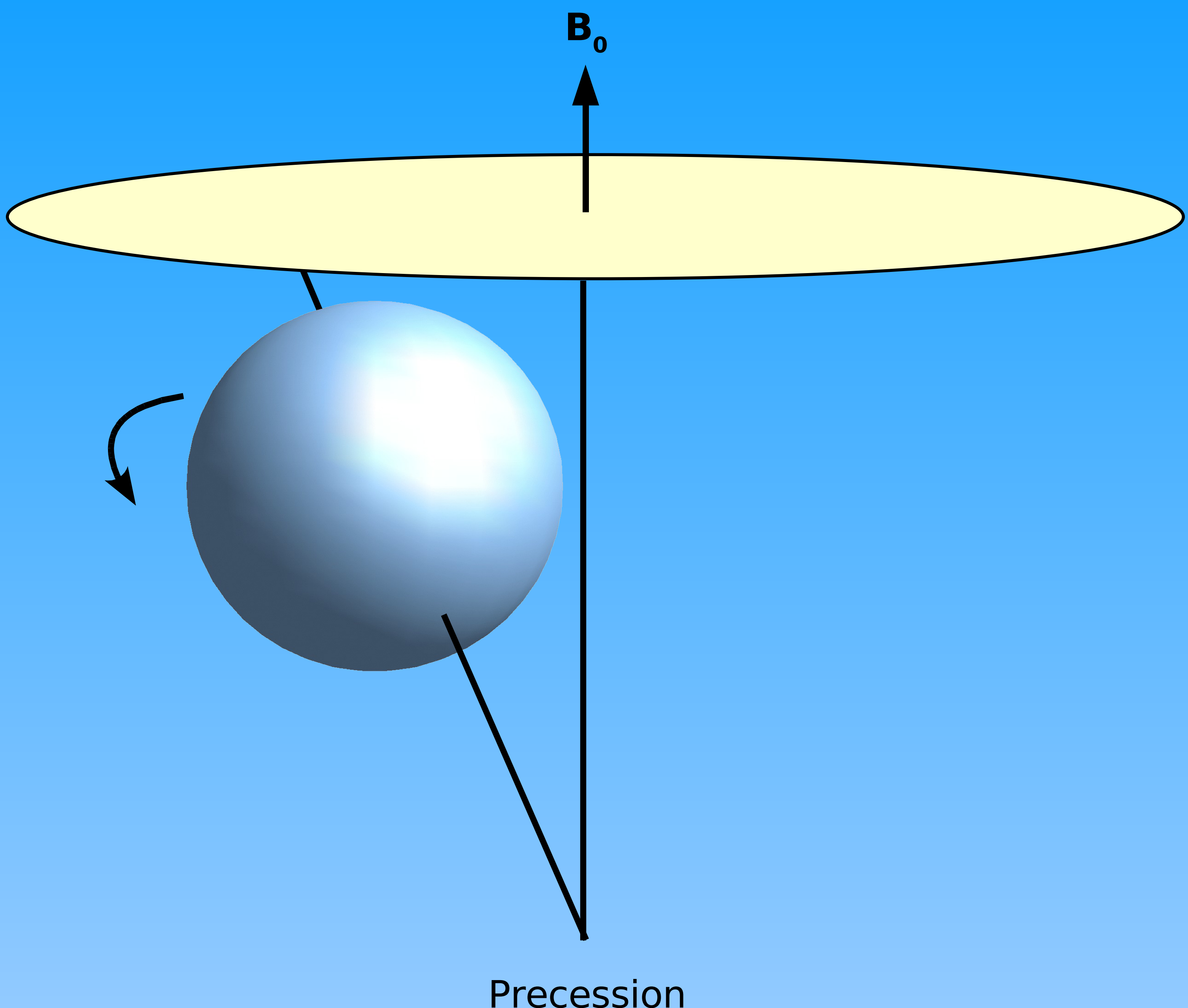
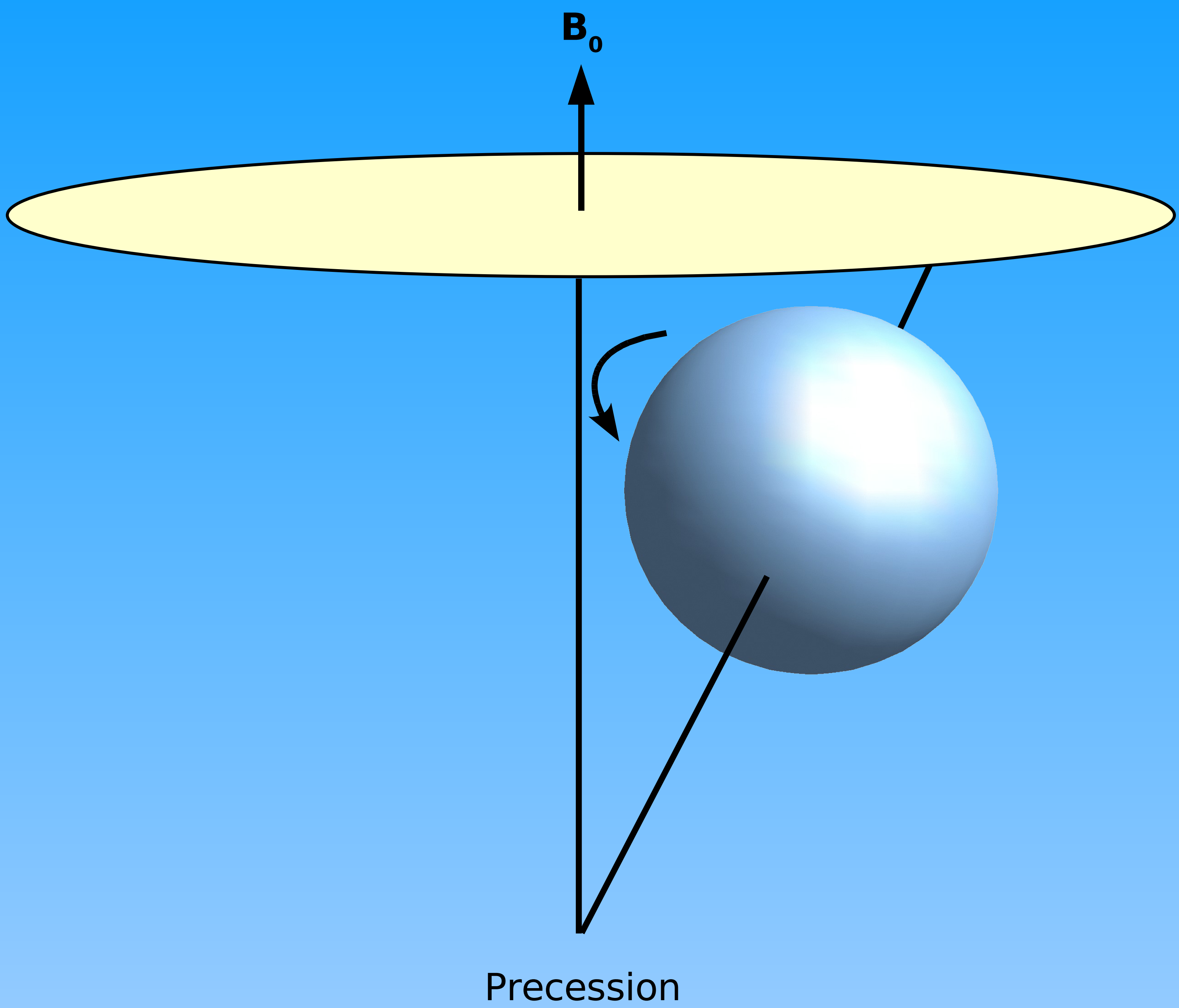
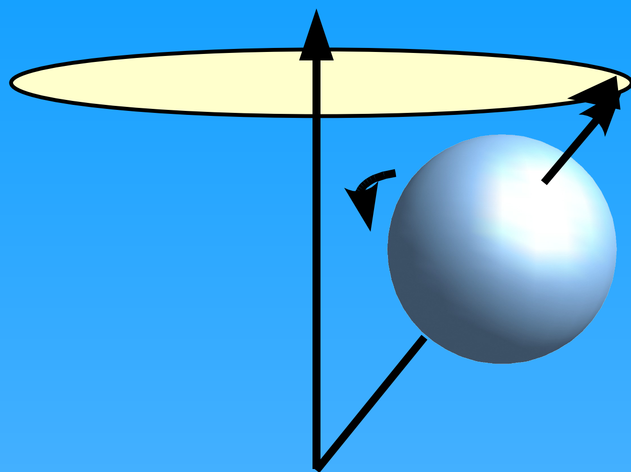
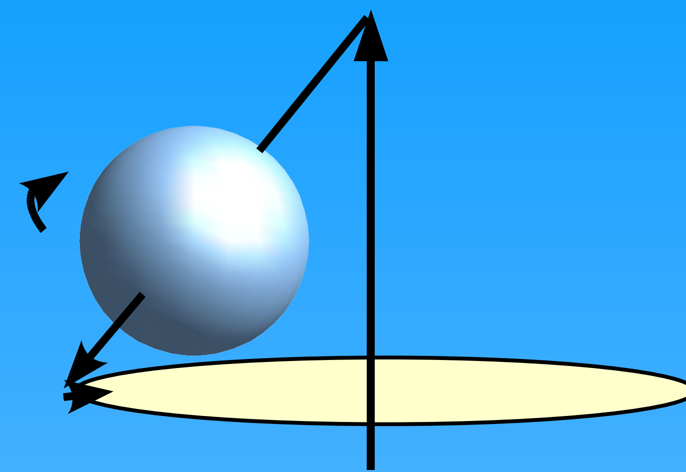


A “Spinning” Charge in a Magnetic Field

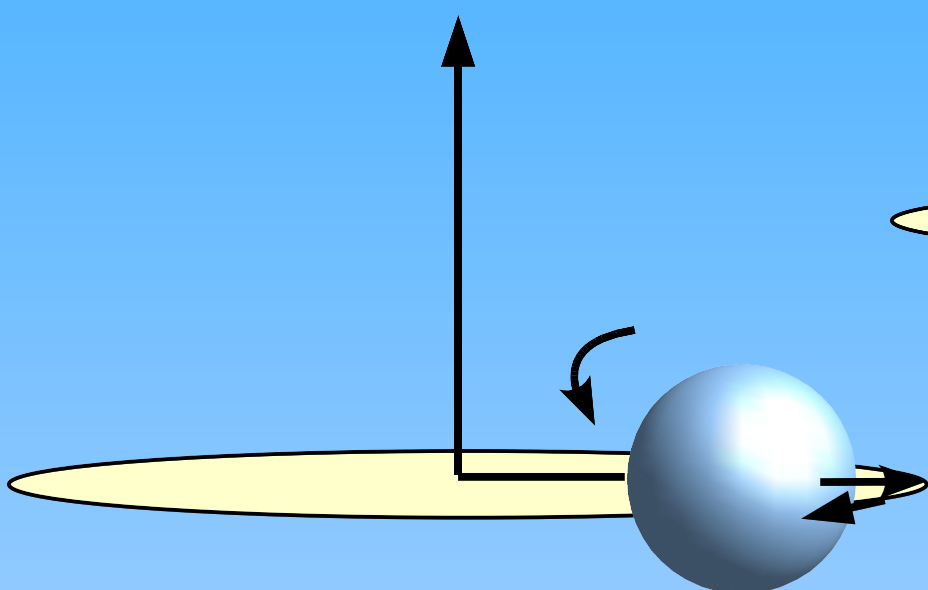


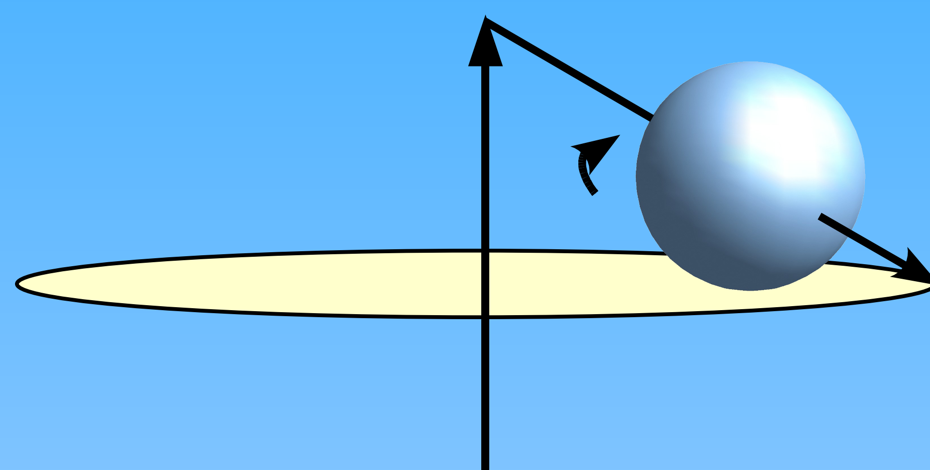
The Equilibrium Magnetisation
Larmor precession





Initially, many spins have randomly oriented precession angles but over time the net sum of magnetic moment vectors points along the same direction as the external field axis.

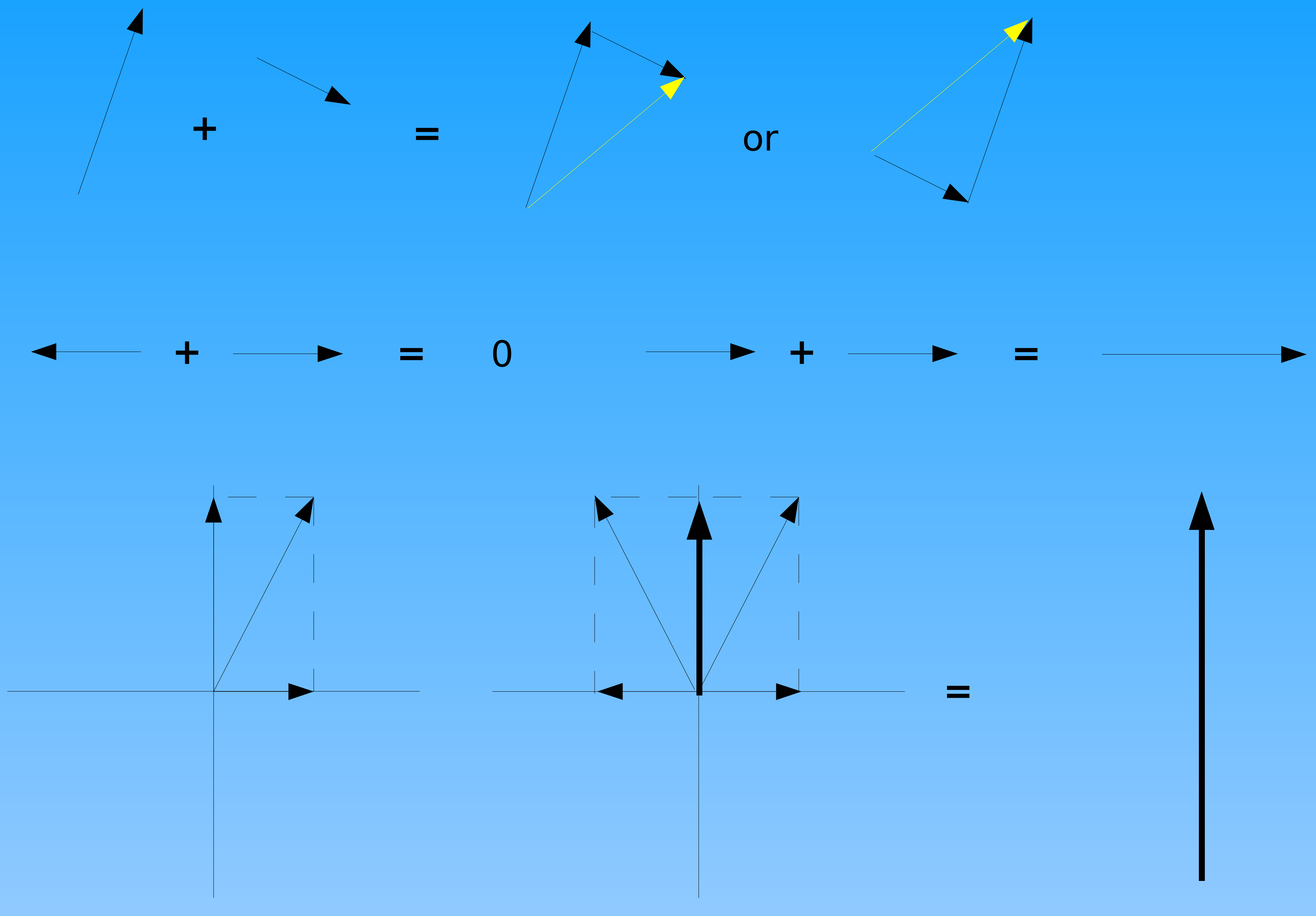




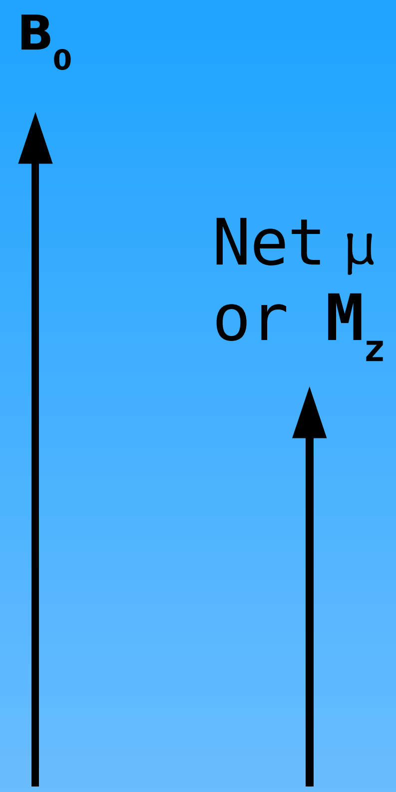
$\omega = \gamma B_0$

ω is Larmor frequency

Vector Addition

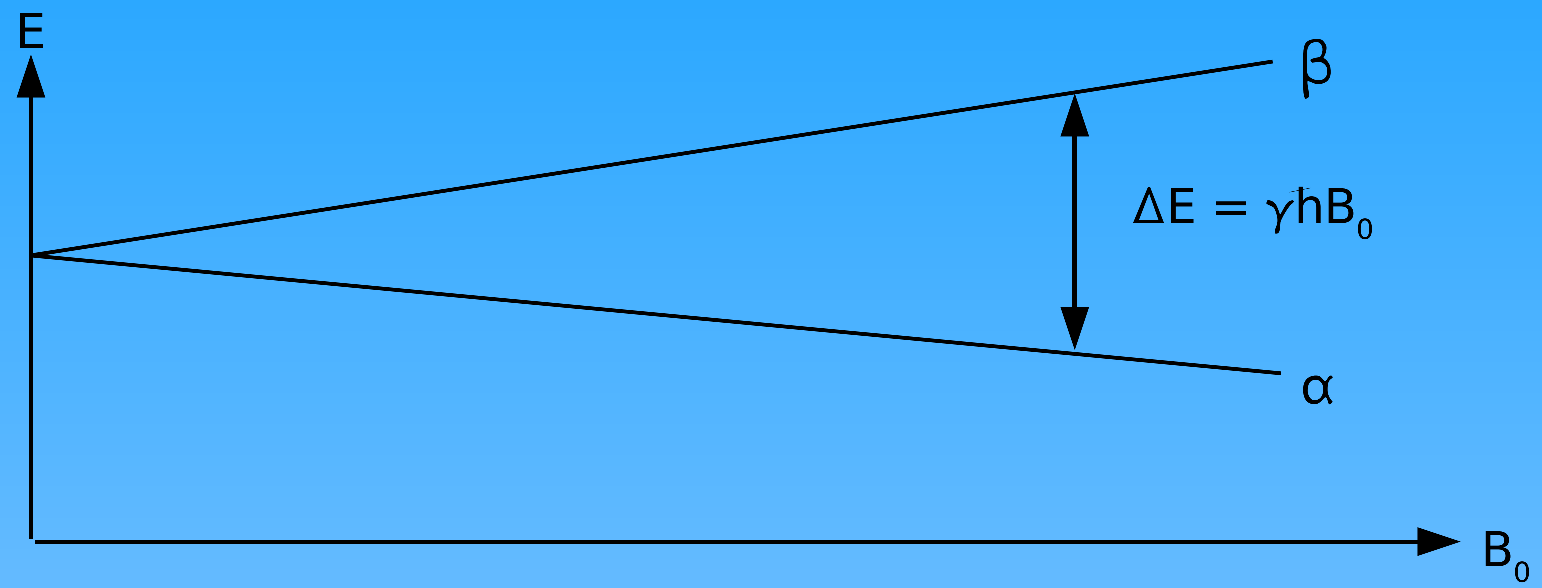


The Equilibrium Magnetisation



The Equilibrium Magnetisation

In a magnetic field, spin states are non-degenerate so for spin = ½ there is an energy difference between the two pure states:



We can calculate a Boltzman equilibrium population difference for ^{1}H in a 500 MHz or 11.75 T field at room temperature:

$$\Delta n = \frac{\gamma \hbar B_0}{2 \mathrm{k}_b T}$$

The Equilibrium Magnetisation

$$\Delta n = \frac{26.7519 \times 10^{7} \cdot 1.0546 \times 10^{-27} \cdot 11.75}{2 \cdot 1.35 \times 10^{-16} \cdot 298}$$

$$= 0.0000806$$

Thus, there is a *slight* excess of spins in the α spin state at equilibrium. Since signal intensity depends on differences in state populations this means that nmr spectroscopy is not very sensitive. Almost all technical advances in nmr spectroscopy are directed towards enhancing sensitivity.

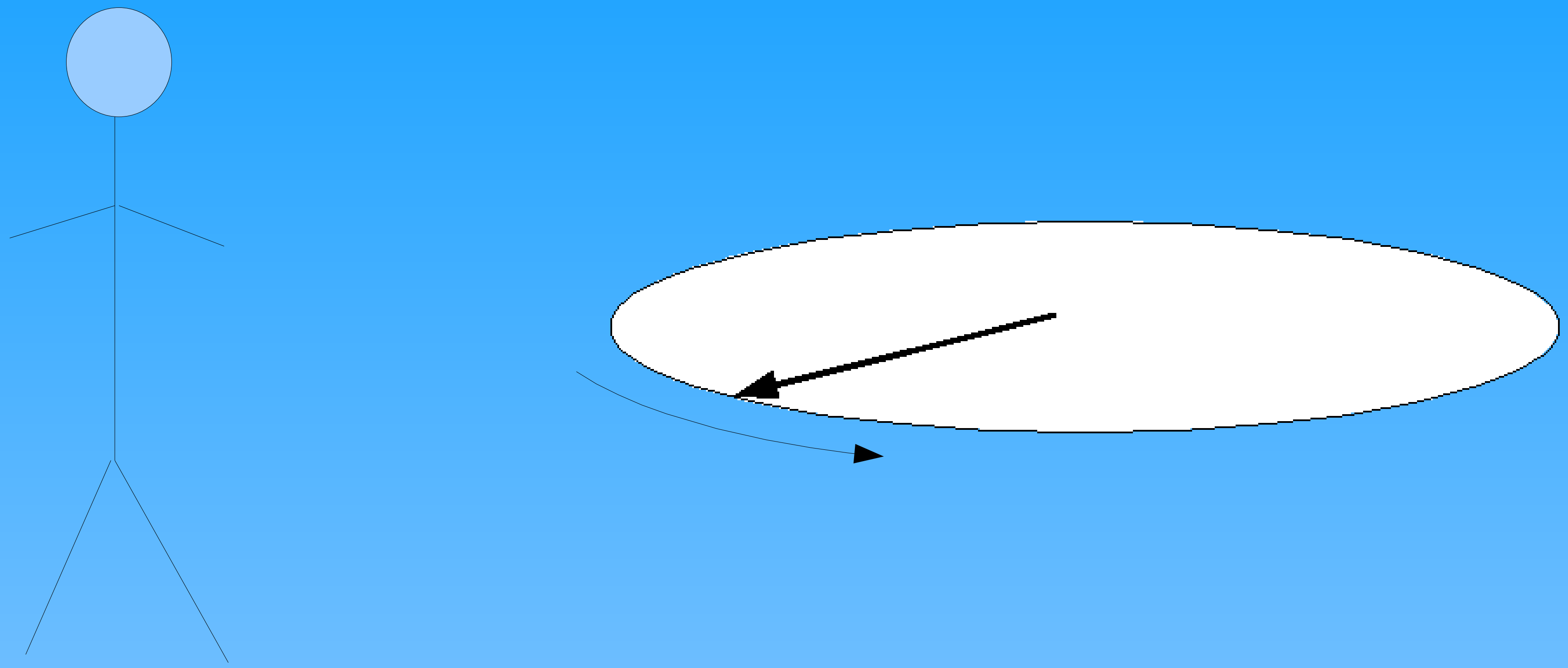
The Equilibrium Magnetisation

Small differences in the local magnetic field caused by shielding of nuclei by electrons causes small differences in Larmor frequencies called *chemical shifts*. Thus, different nuclei in different electronic environments precess at slightly different frequencies.

Because these precession frequencies are field dependent and will change from magnet to magnet, the ppm scale is used which is largely independent of field strength:

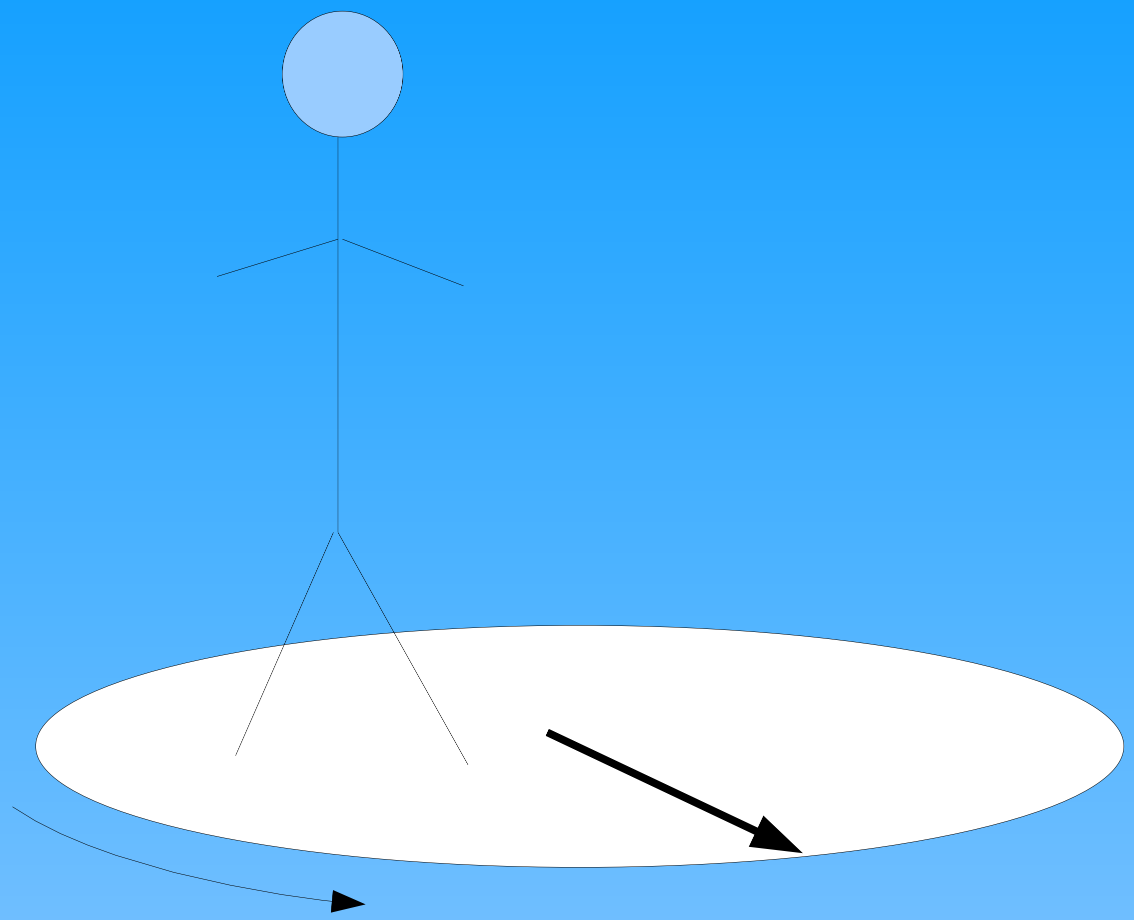
$$\delta = (\nu - \nu_{ref})/\nu_{field}$$

The Rotating Frame of Reference



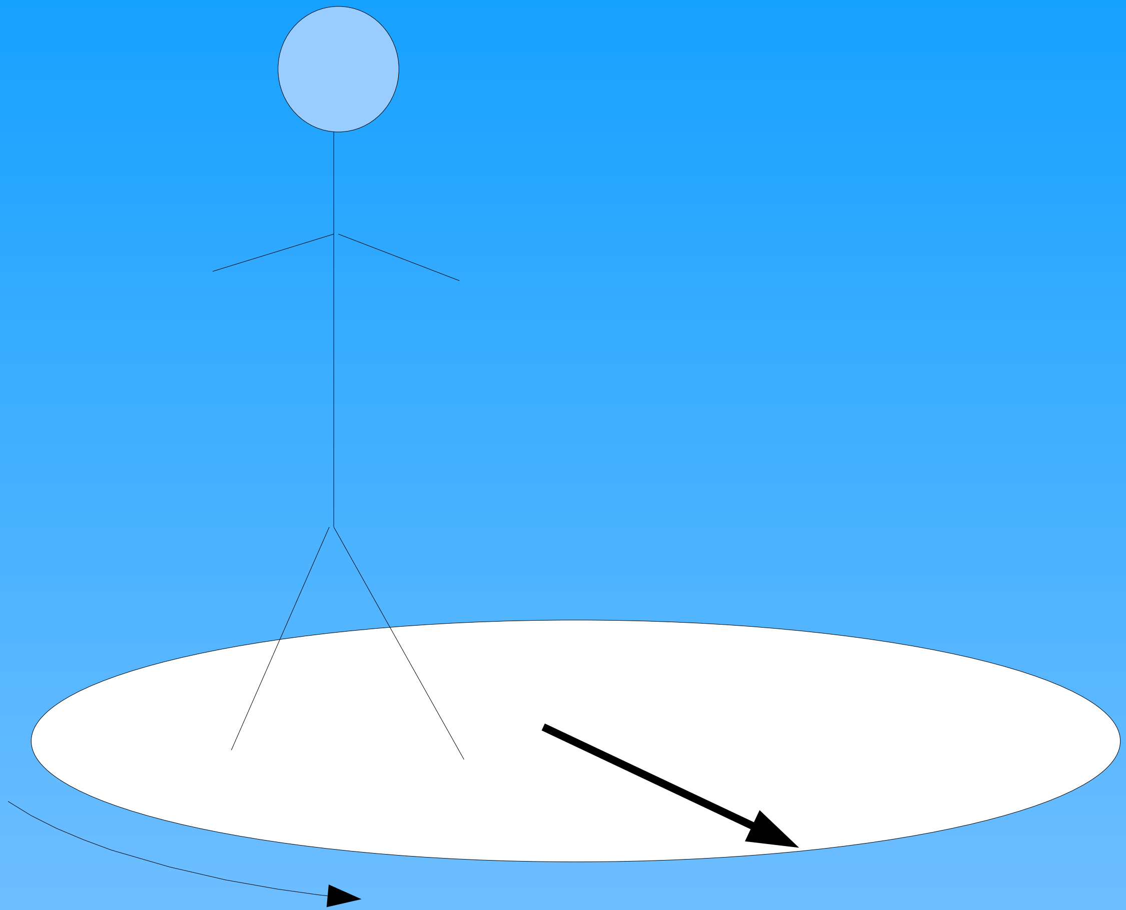
The inertial or laboratory frame of reference

The Rotating Frame of Reference



The rotating frame of reference

The Rotating Frame of Reference



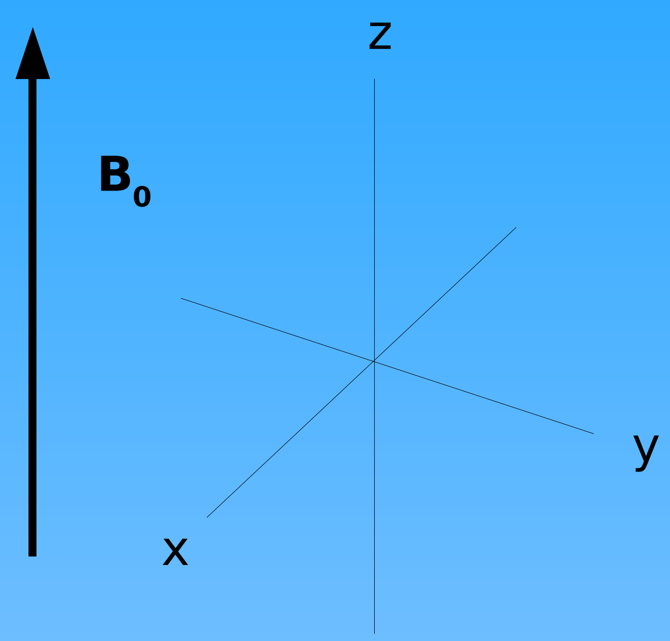
The rotating frame of reference .. no change!

The Rotating Frame of Reference

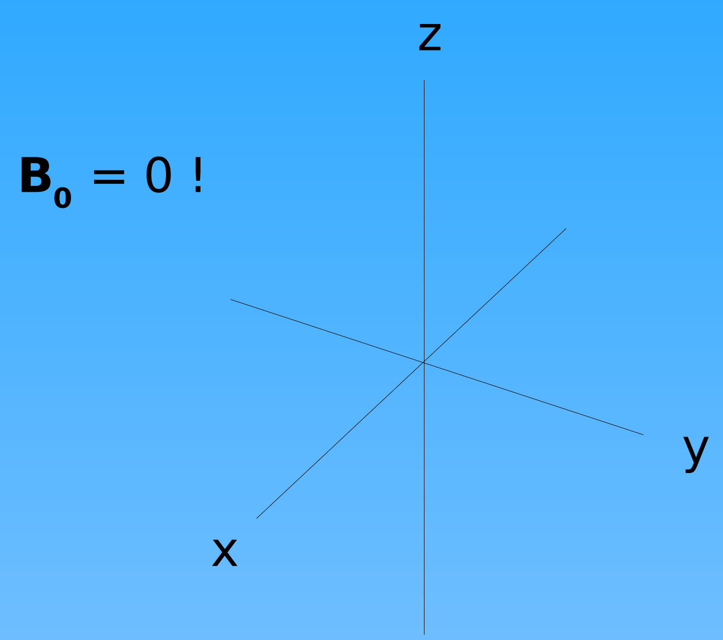
We are all familiar with rotating frames of reference!

The Rotating Frame of Reference

The Rotating Frame of Reference

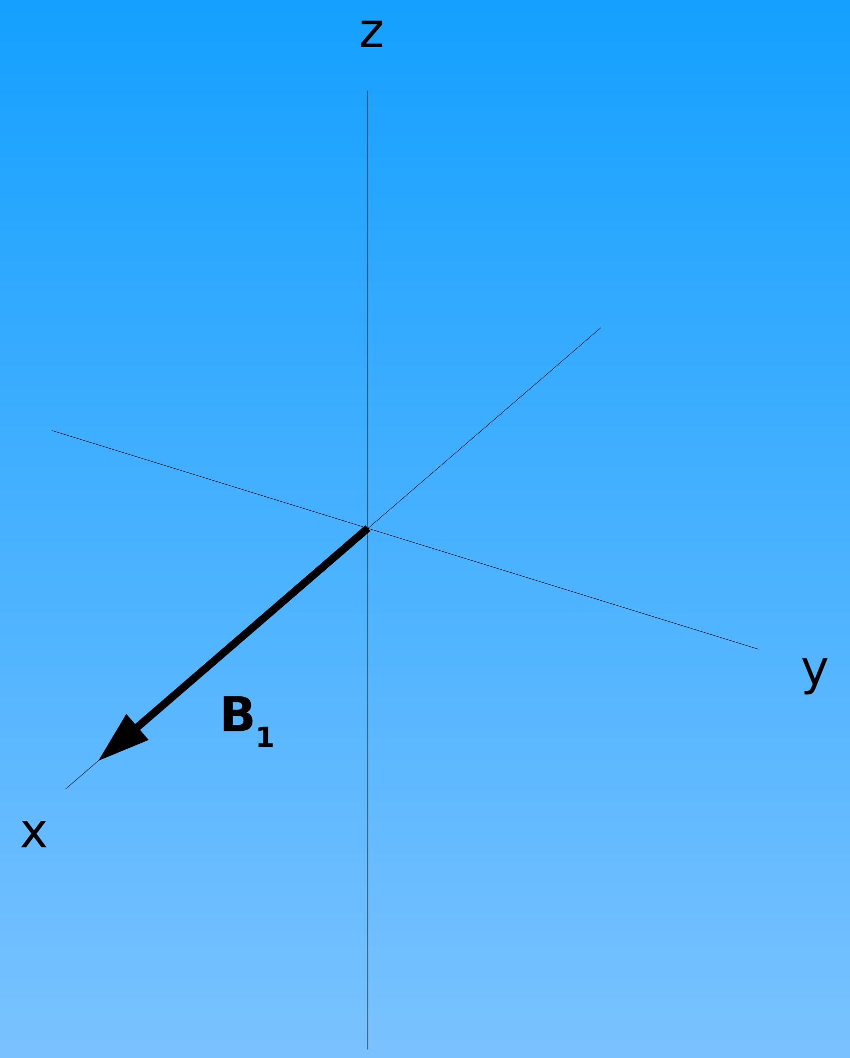


Laboratory frame



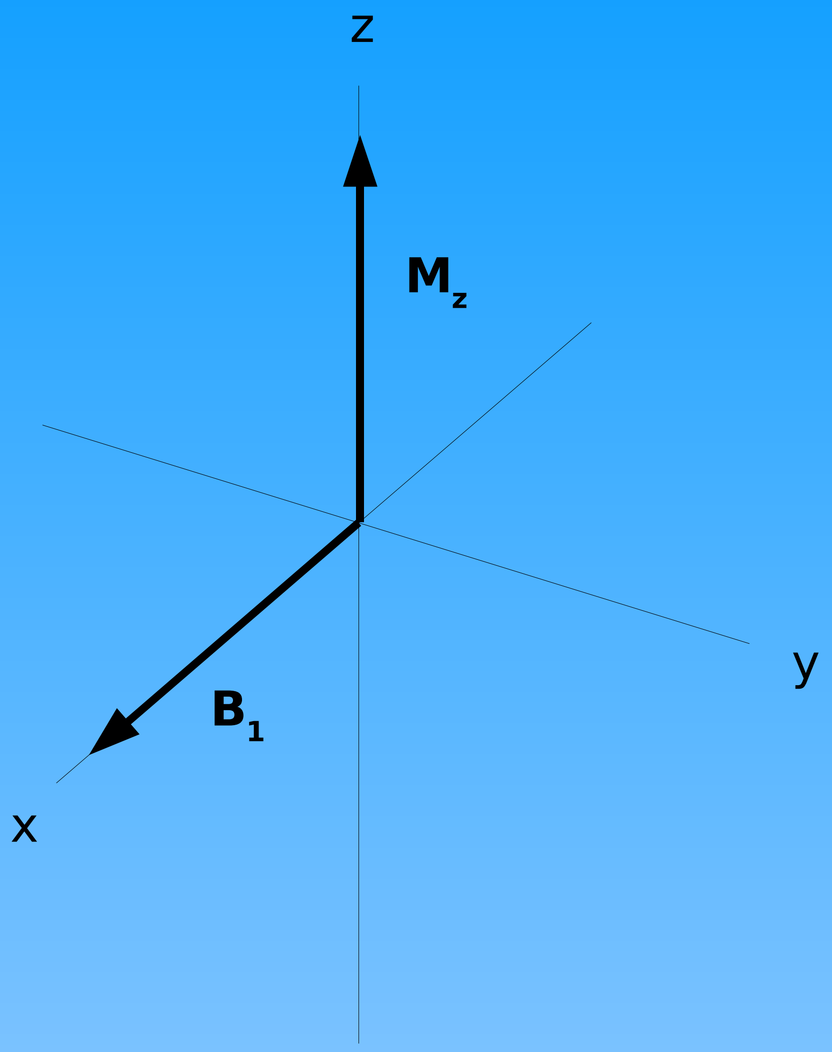
Rotating frame

A Pulse in the Rotating Frame



For an on-resonance pulse, $\mathbf{B_0} = 0$

A Pulse in the Rotating Frame



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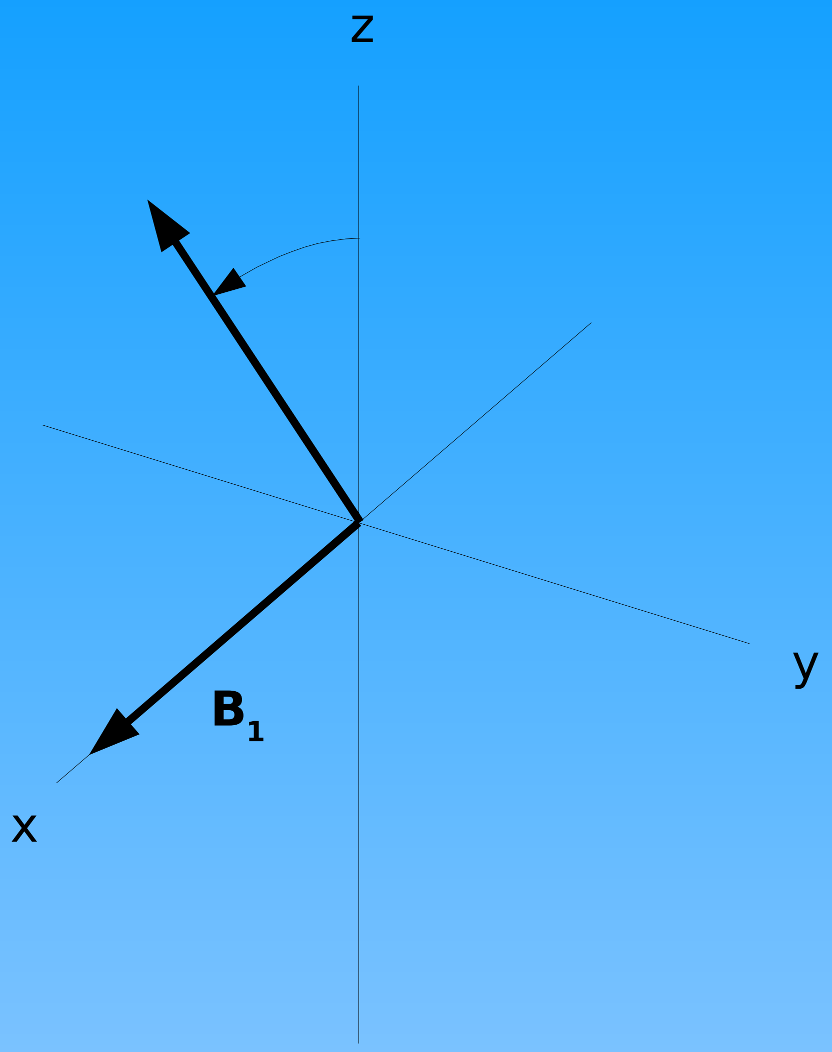

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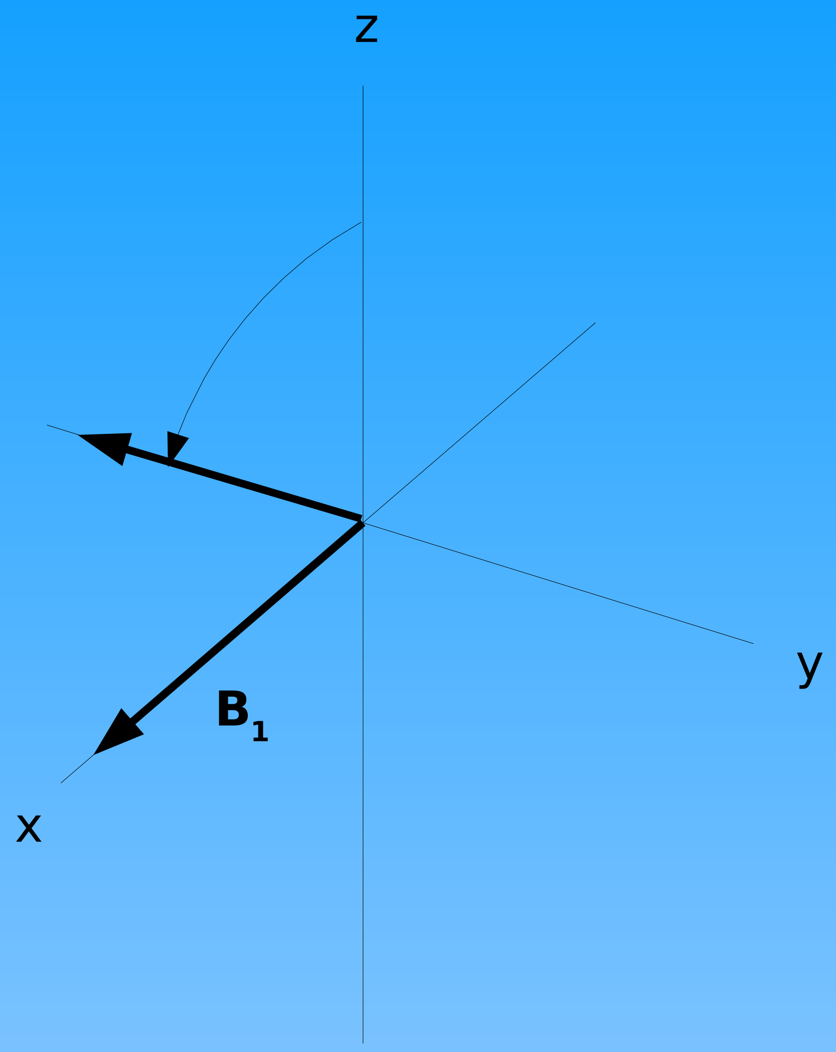

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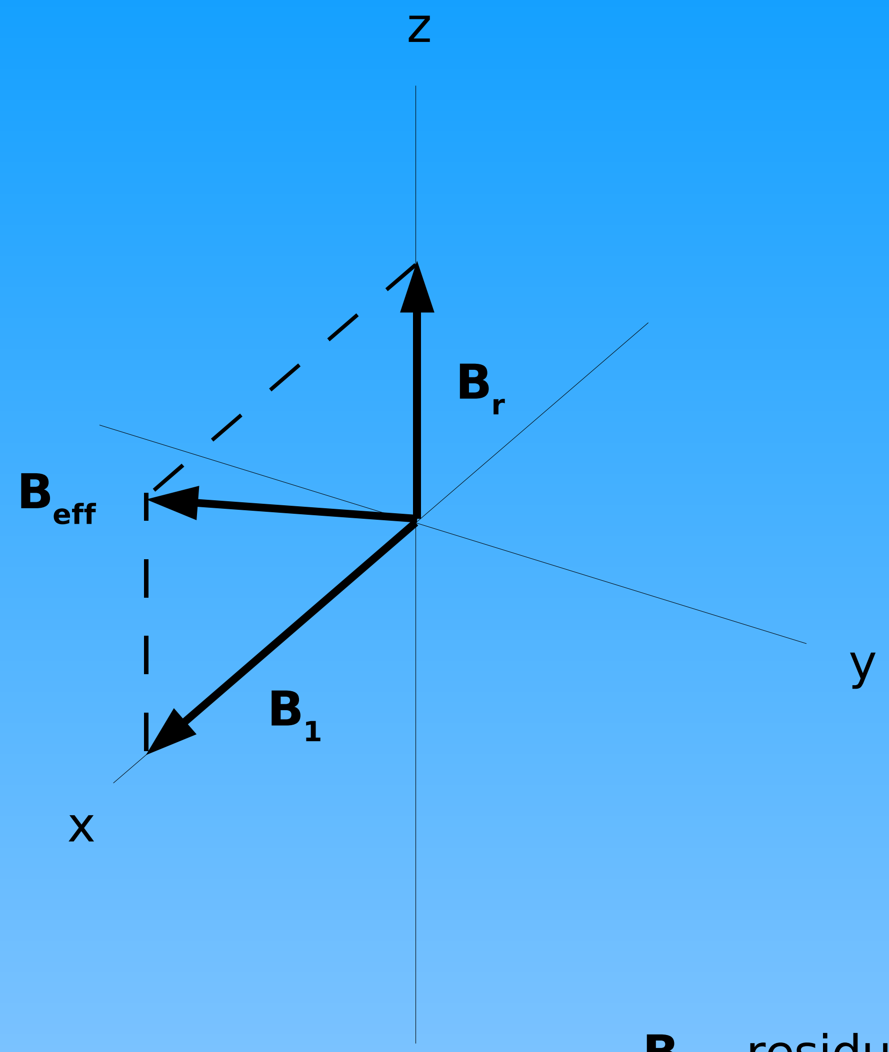
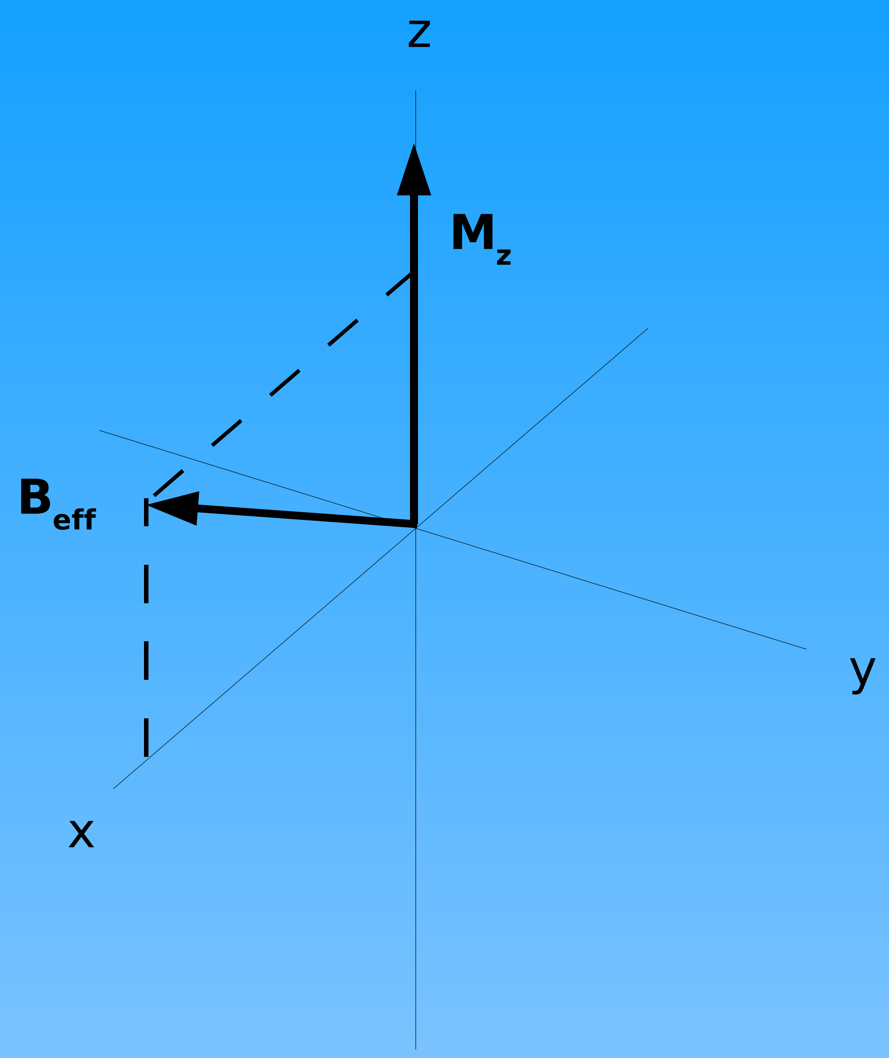


For an off-resonance pulse there is a residual external magnetic field leading to an effective magnetic field

B_r – residual external field
B_1 – rf field
B_{eff} – effective field

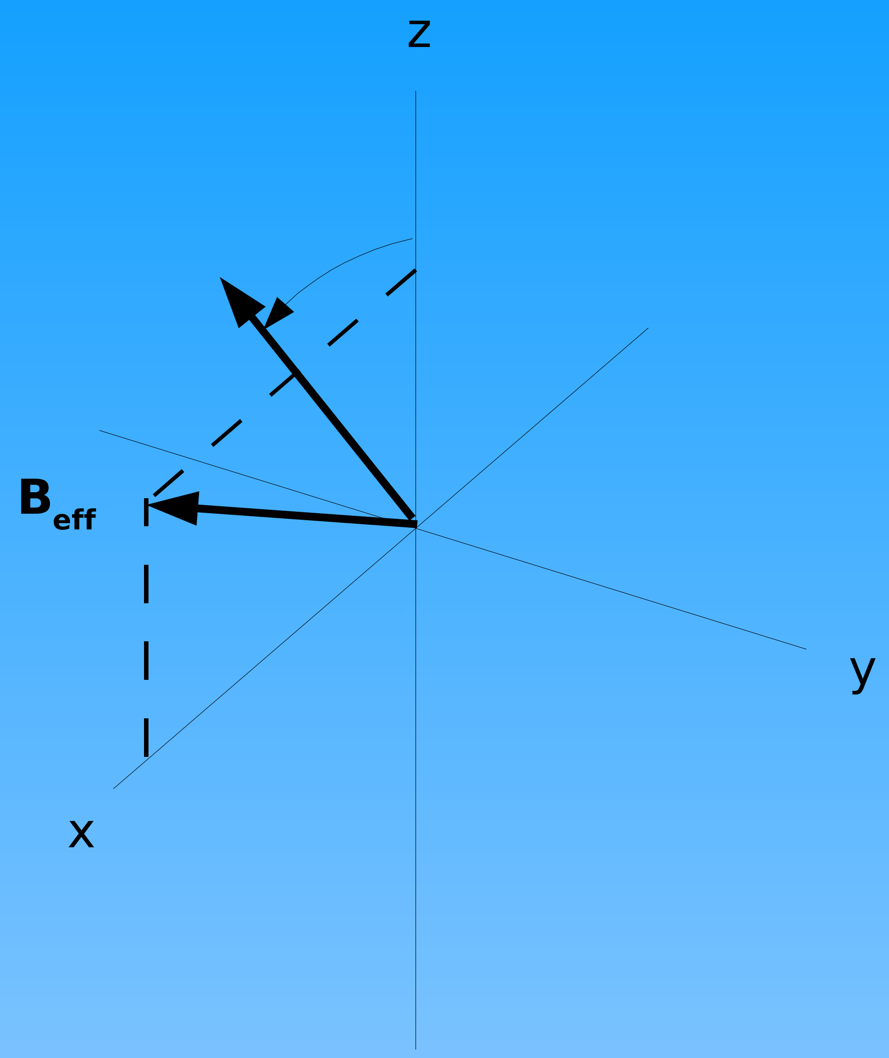
A Pulse in the Rotating Frame



For an off-resonance pulse there is a residual external magnetic field leading to an effective magnetic field

The equilibrium magnetisation precesses about $\mathbf{B}_{\mathbf{eff}}$

A Pulse in the Rotating Frame



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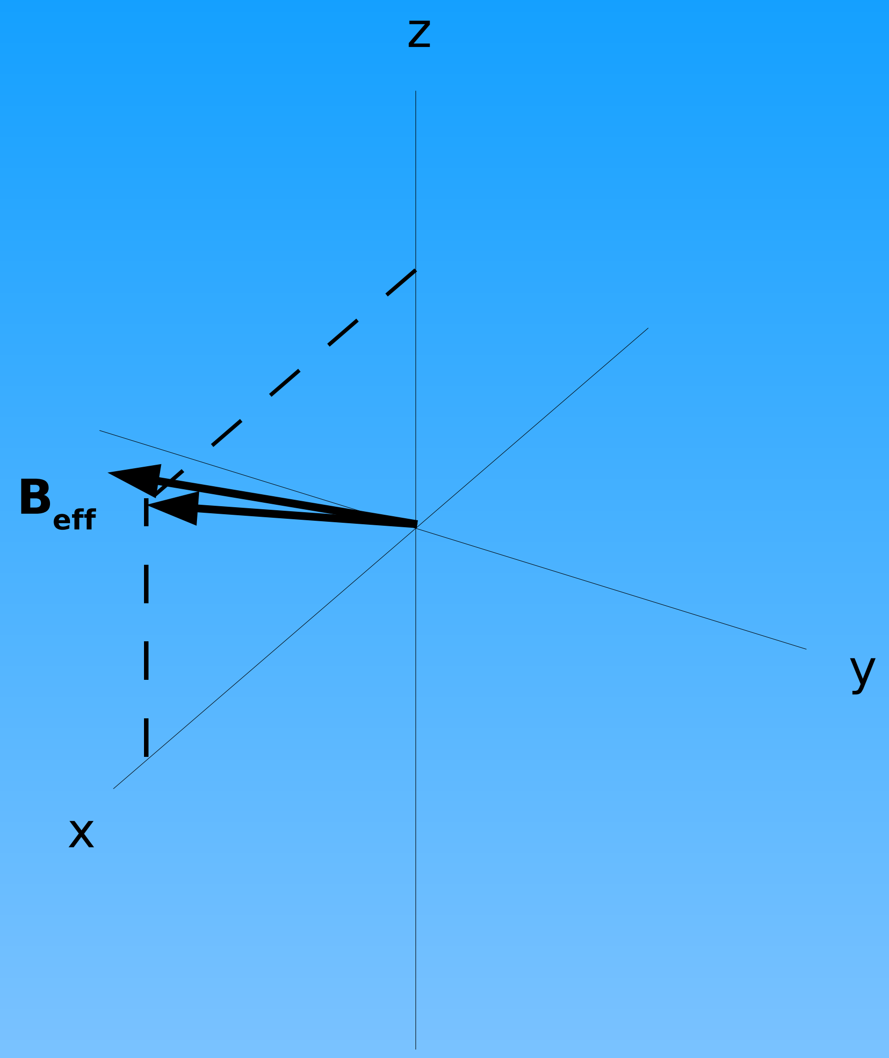

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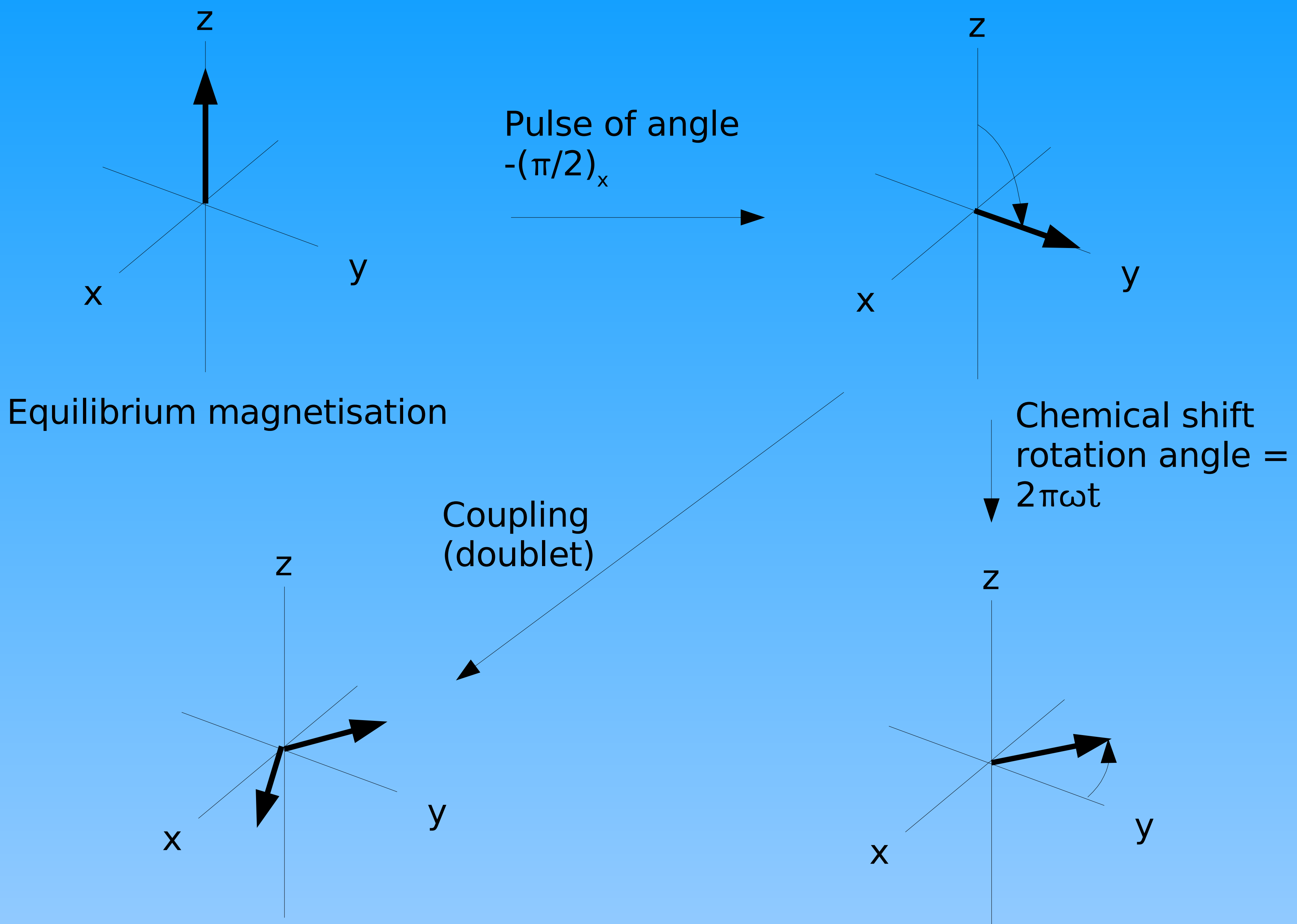
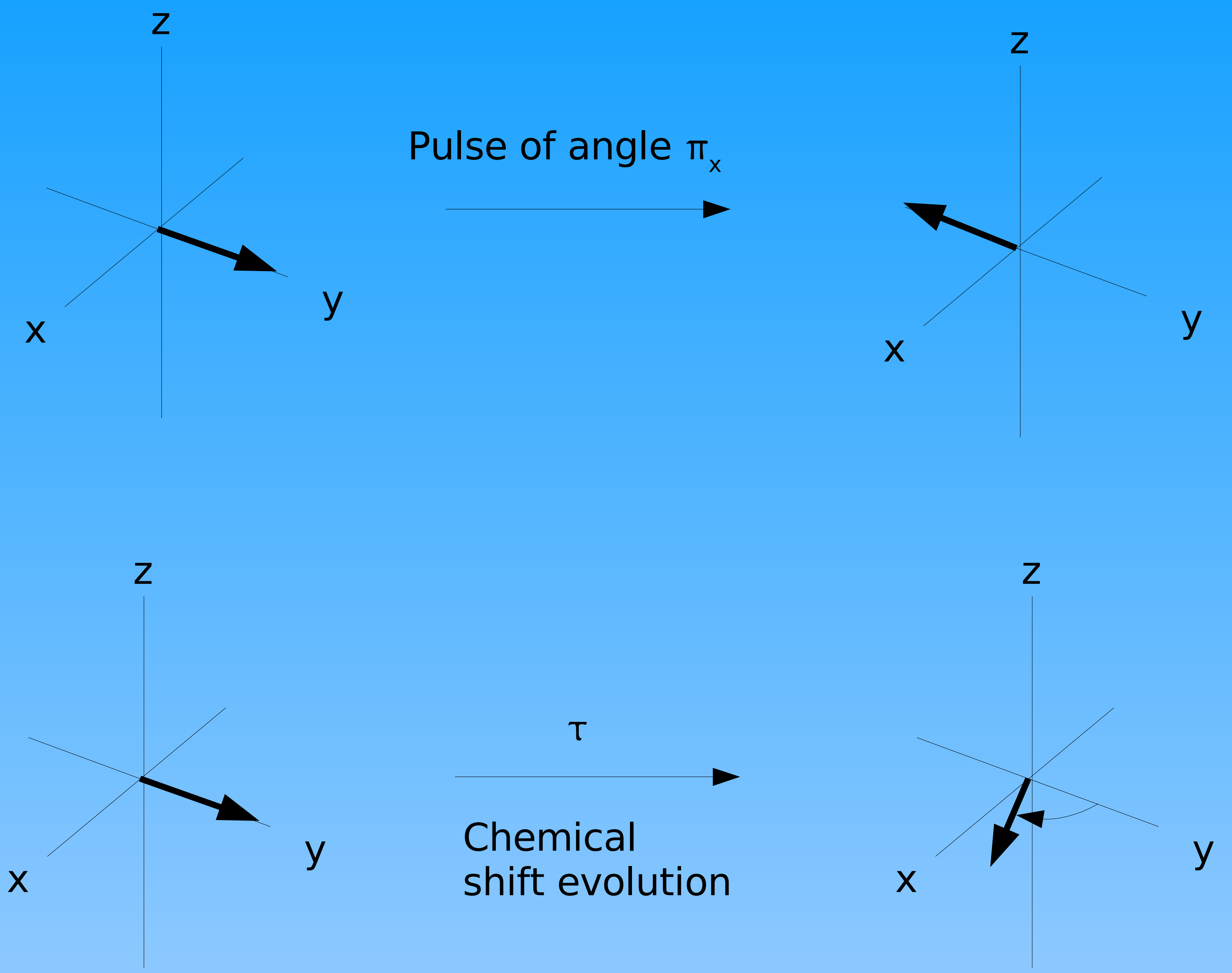
The equilibrium magnetisation precesses about $\mathbf{B}_{eff}$

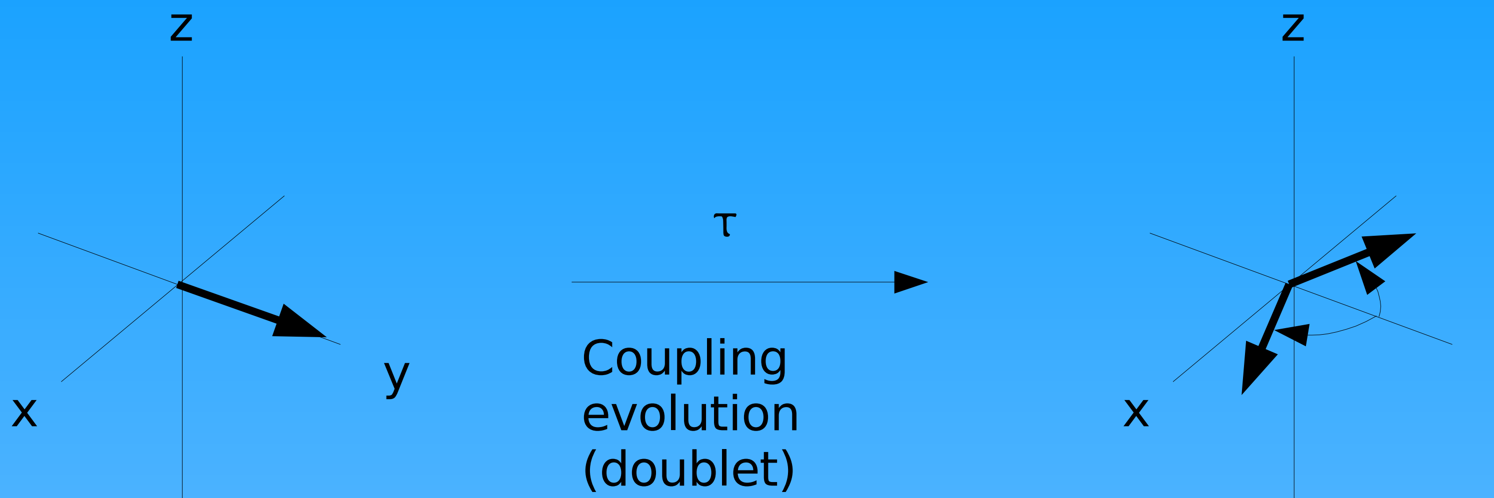
The Vector Model of NMR Spectroscopy

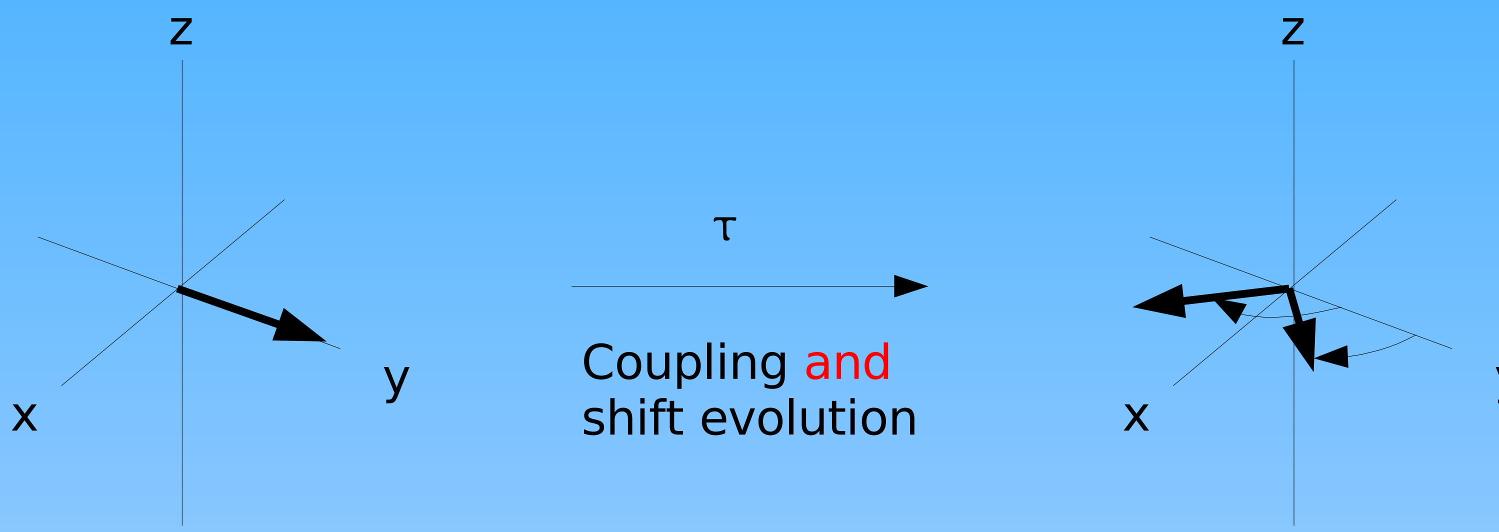


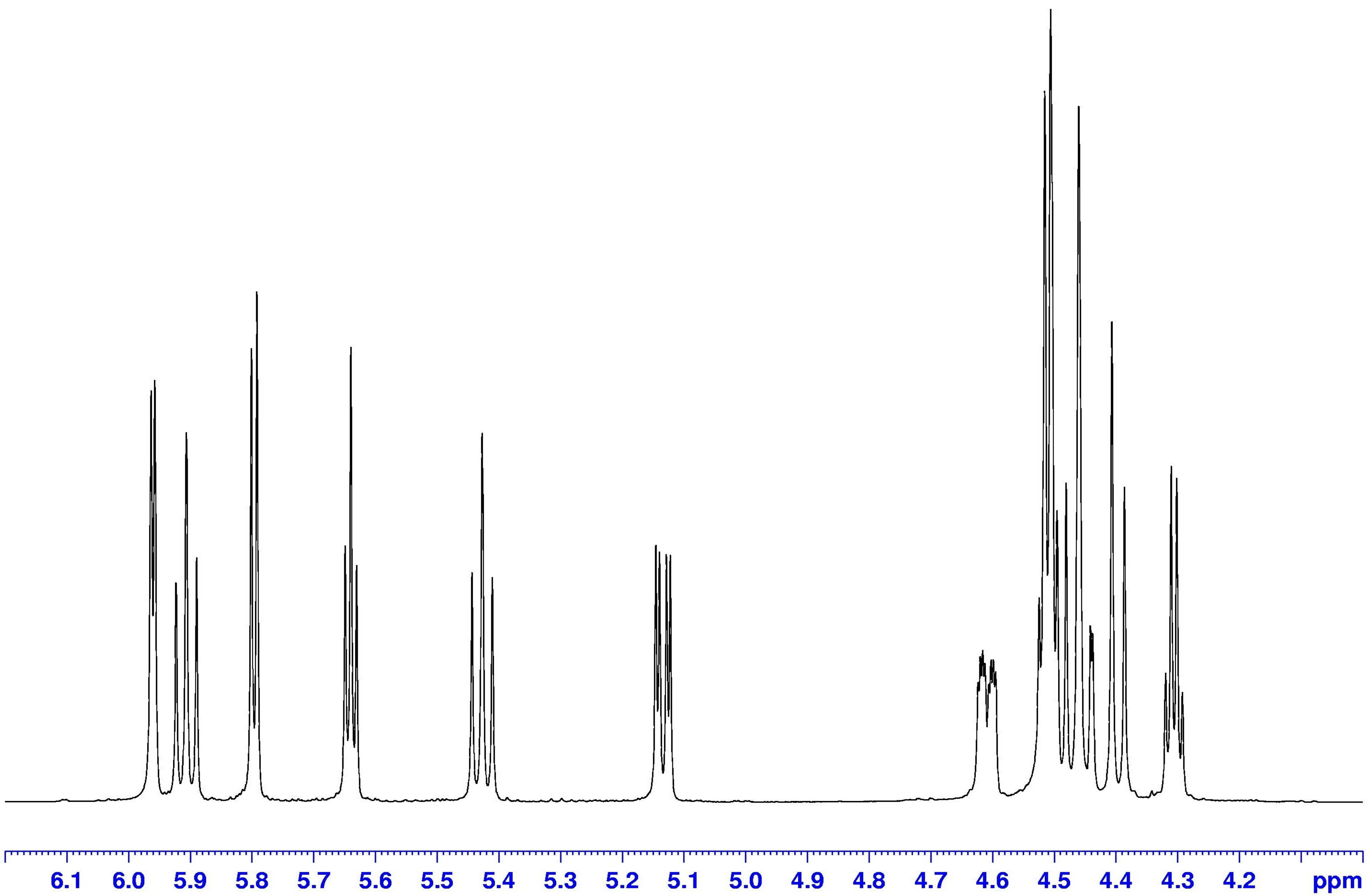
The Vector Model of NMR Spectroscopy



The Vector Model of NMR Spectroscopy

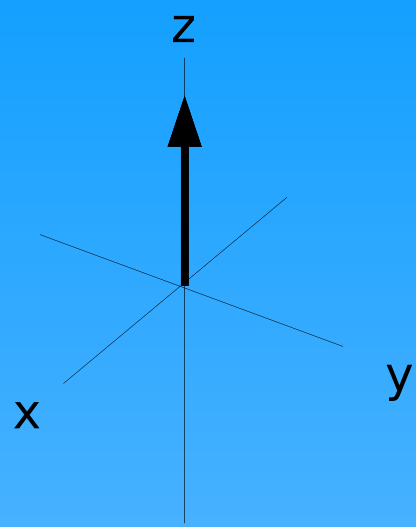




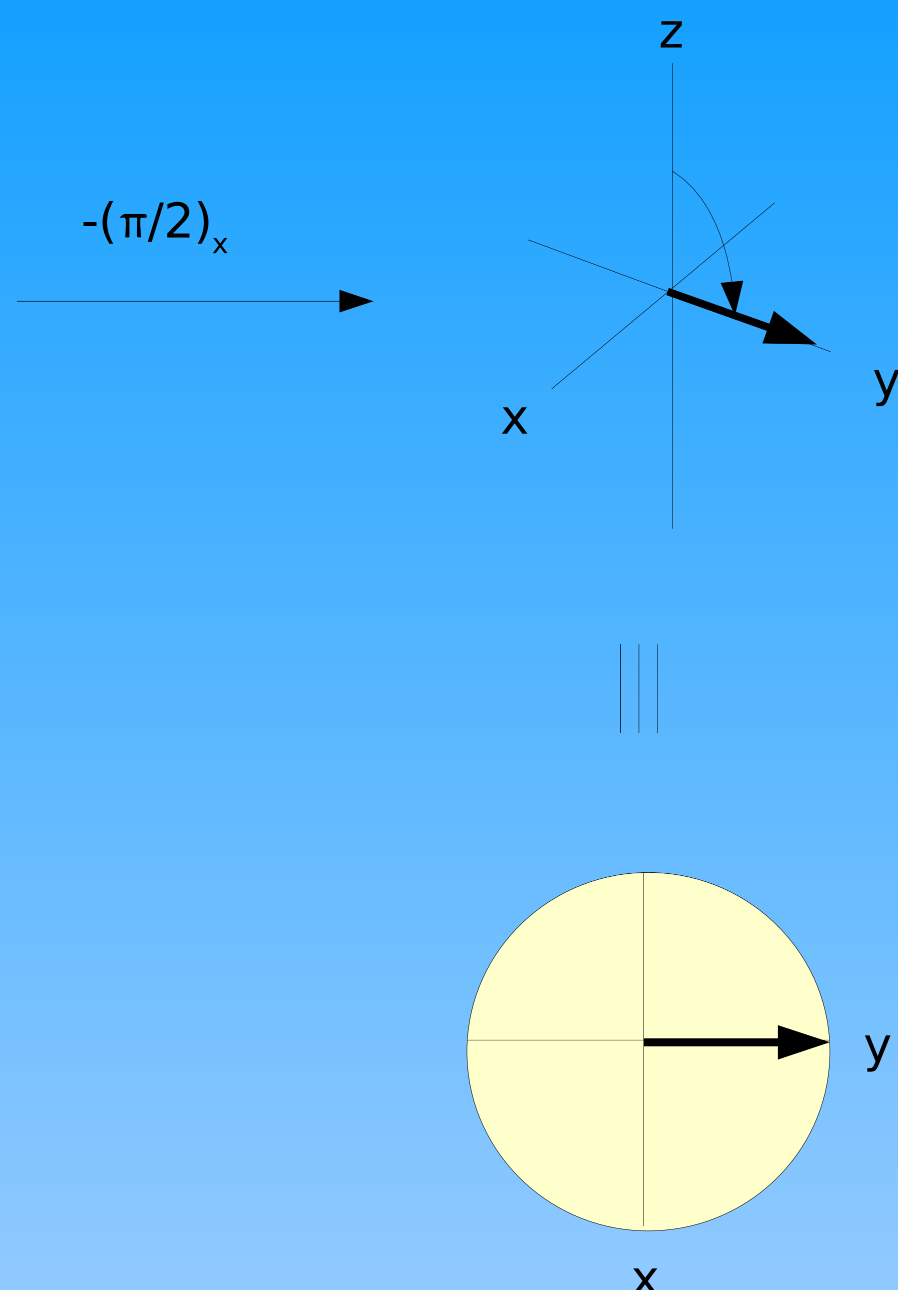


6.1
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
ppm

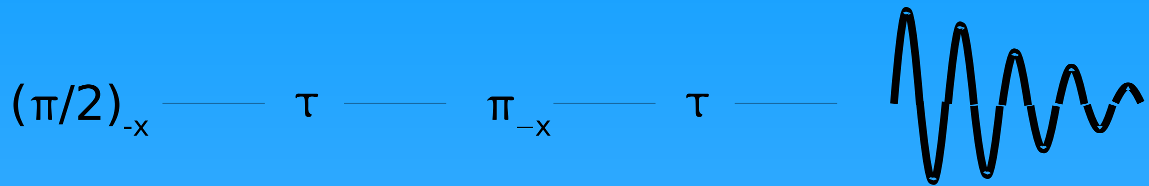
The Vector Model of NMR Spectroscopy



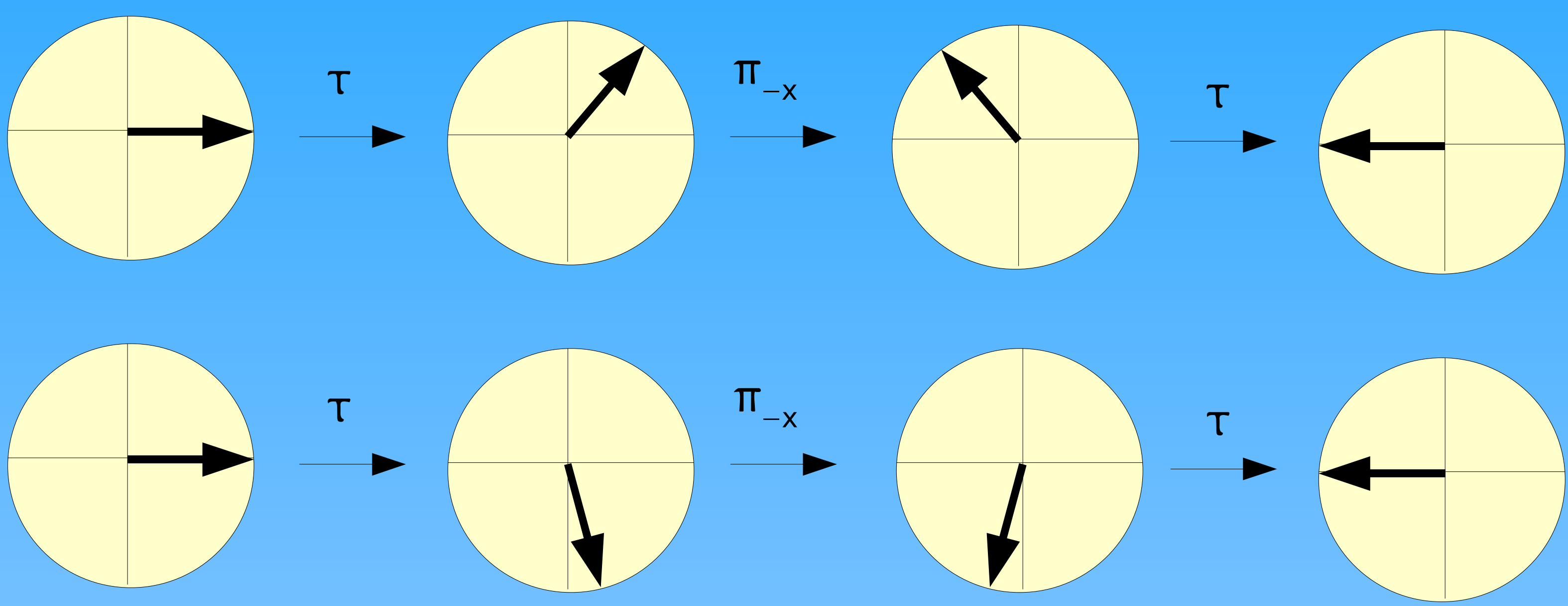
Equilibrium magnetisation



The Vector Model of NMR Spectroscopy
Spin Echo

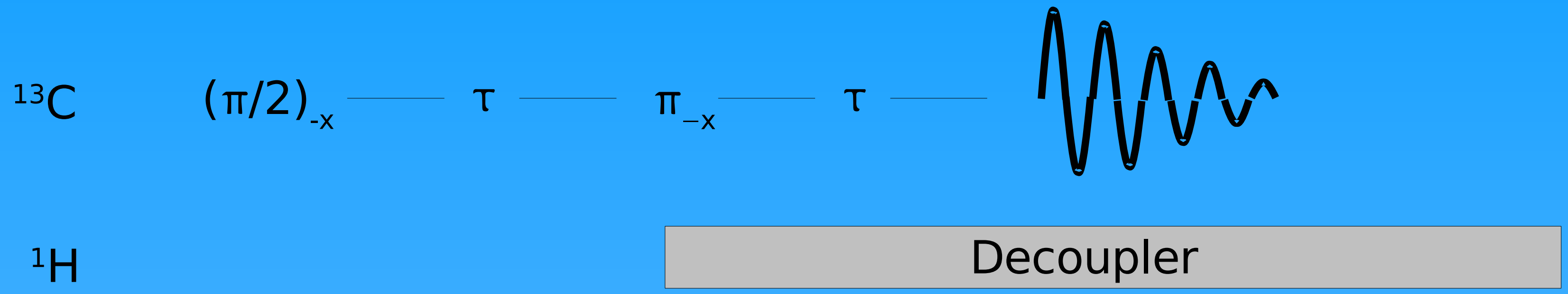


For an off-resonance pulse:



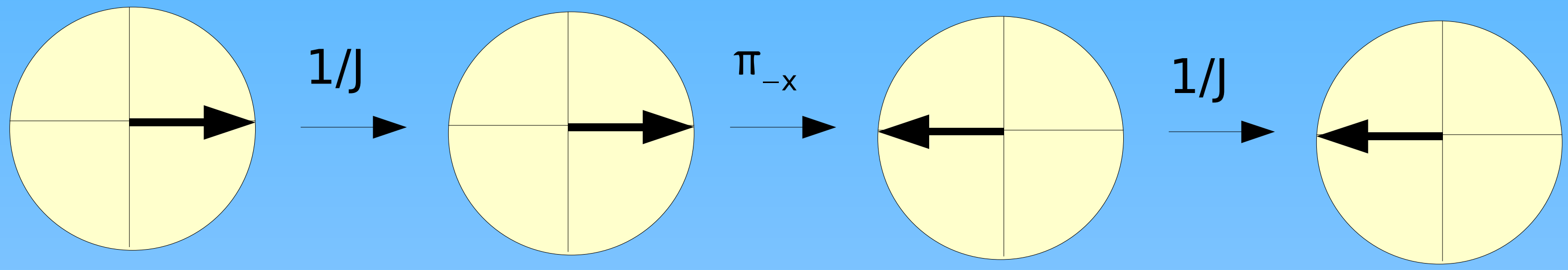
No matter what the chemical shift or the value of τ, the vector ends up in the same spot. This is a 'building block' of many nmr pulse sequences .. used to get rid of chemical shift effects.

The Vector Model of NMR Spectroscopy
The APT or Jmod Experiment



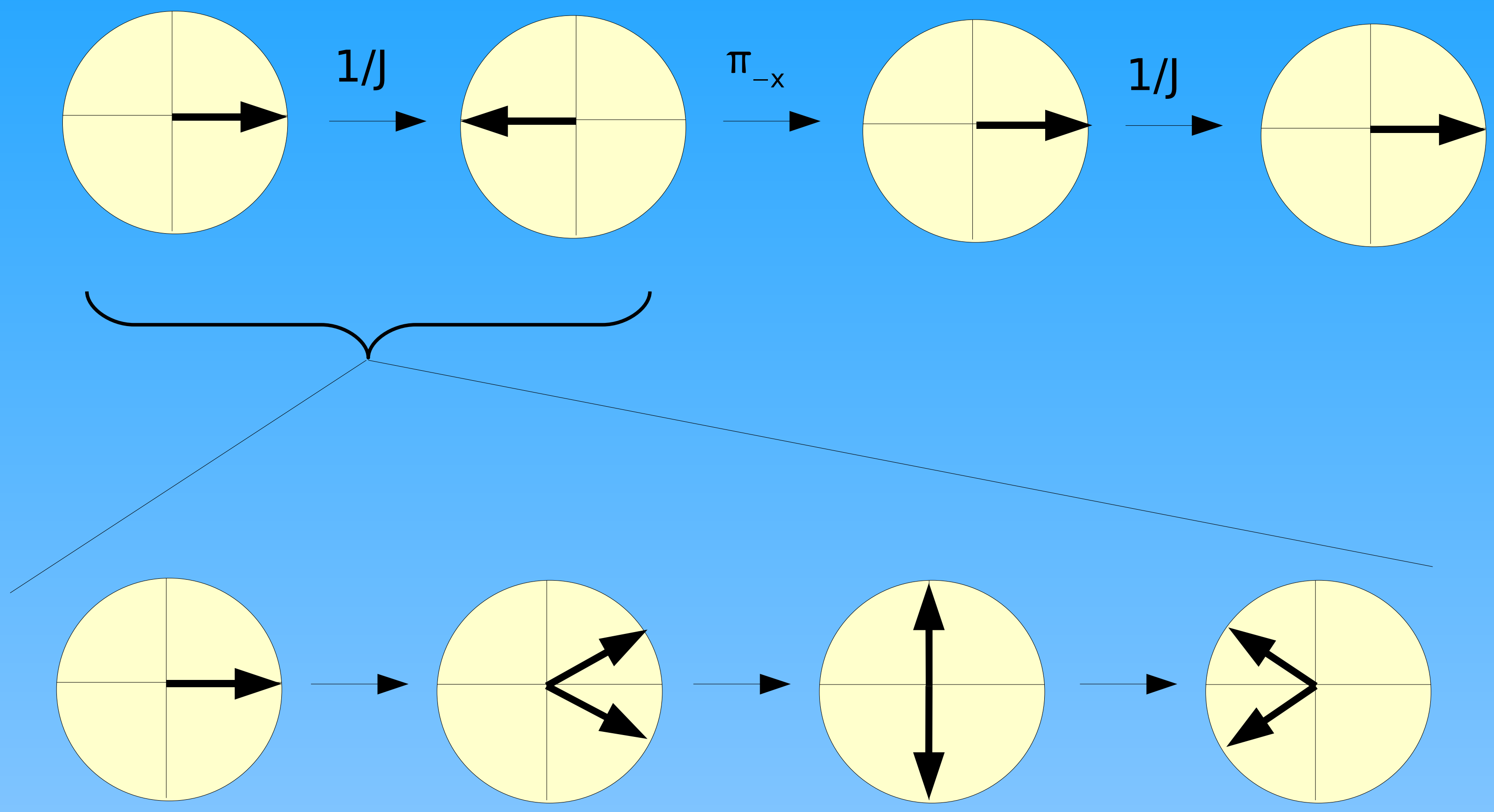
$\tau = 1/J$

For a singlet (quaternary carbon) assuming an on-resonance pulse:



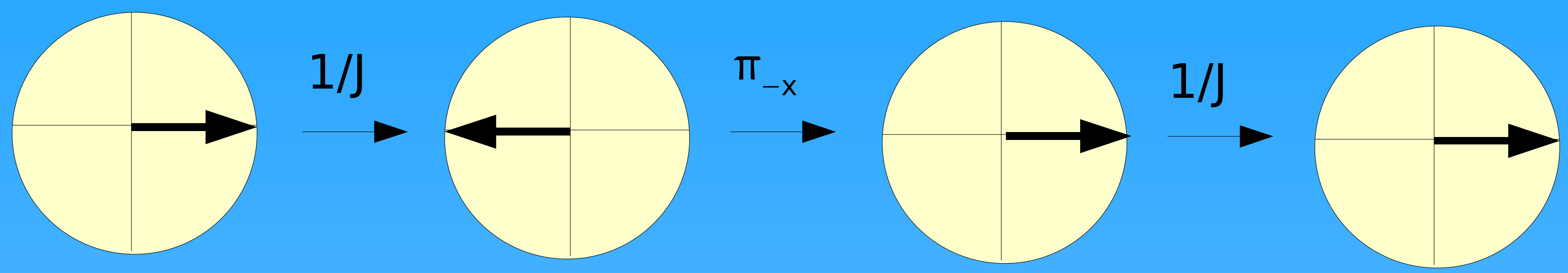
The Vector Model of NMR Spectroscopy
The APT or Jmod Experiment

For a doublet (CH), on-resonance pulse:

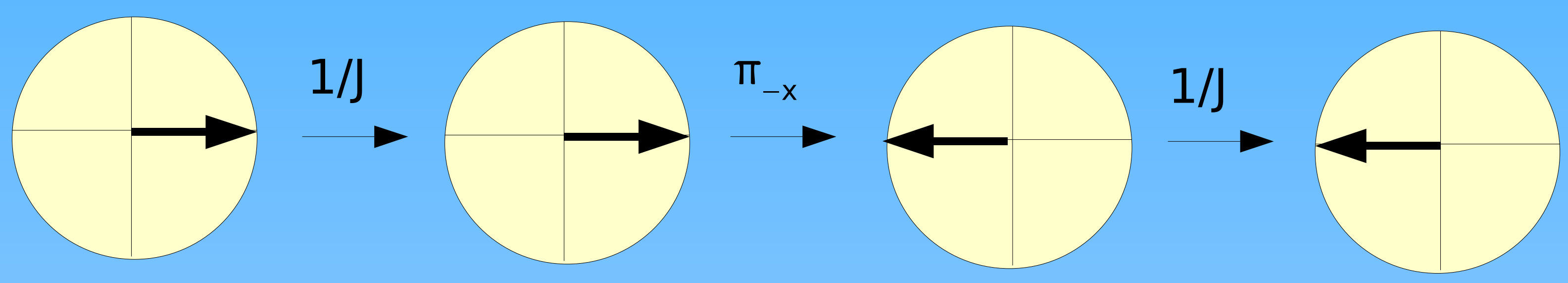


The Vector Model of NMR Spectroscopy
The APT or Jmod Experiment

For a doublet (CH), on-resonance pulse:

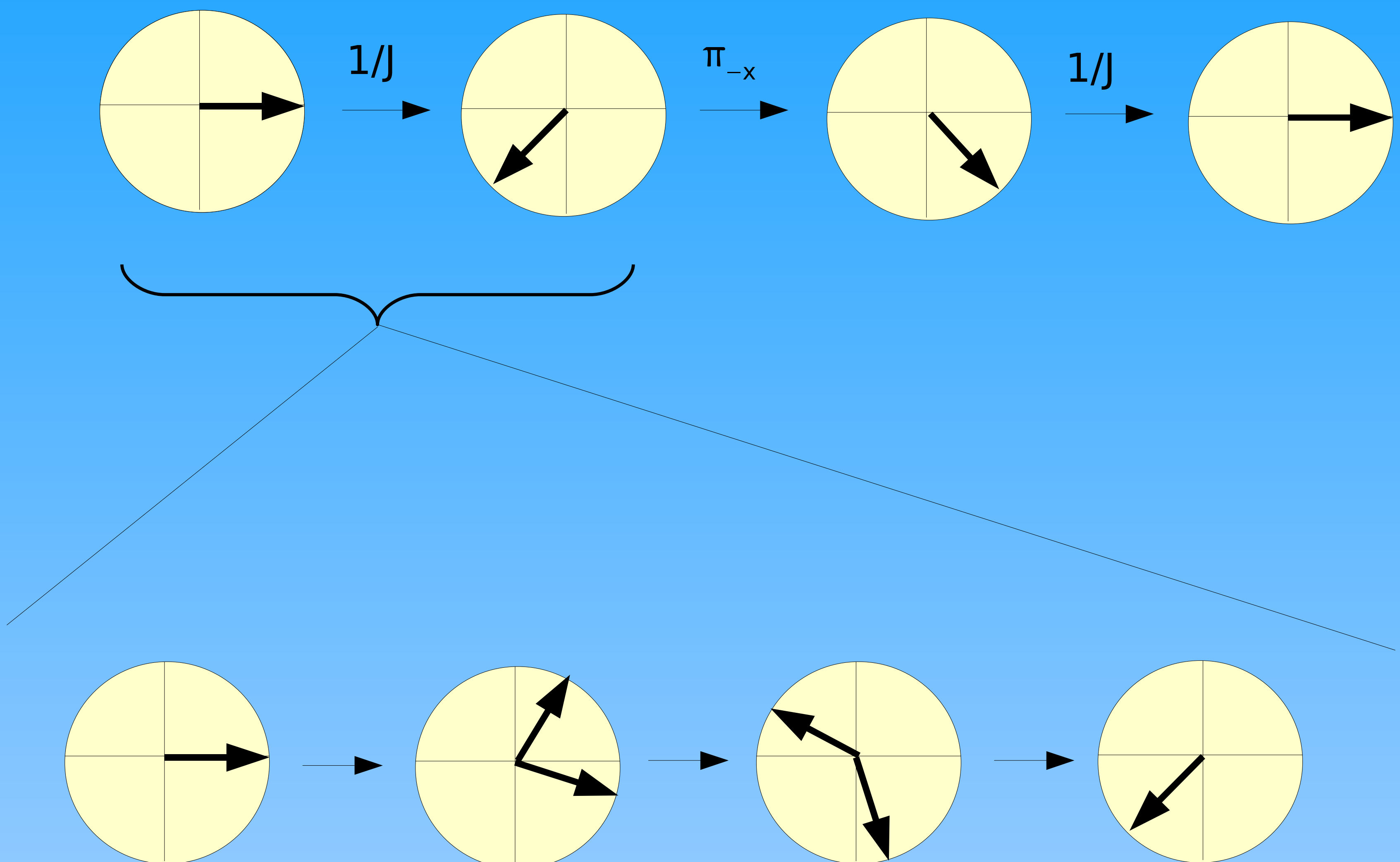


For a triplet (CH_2), on-resonance pulse:

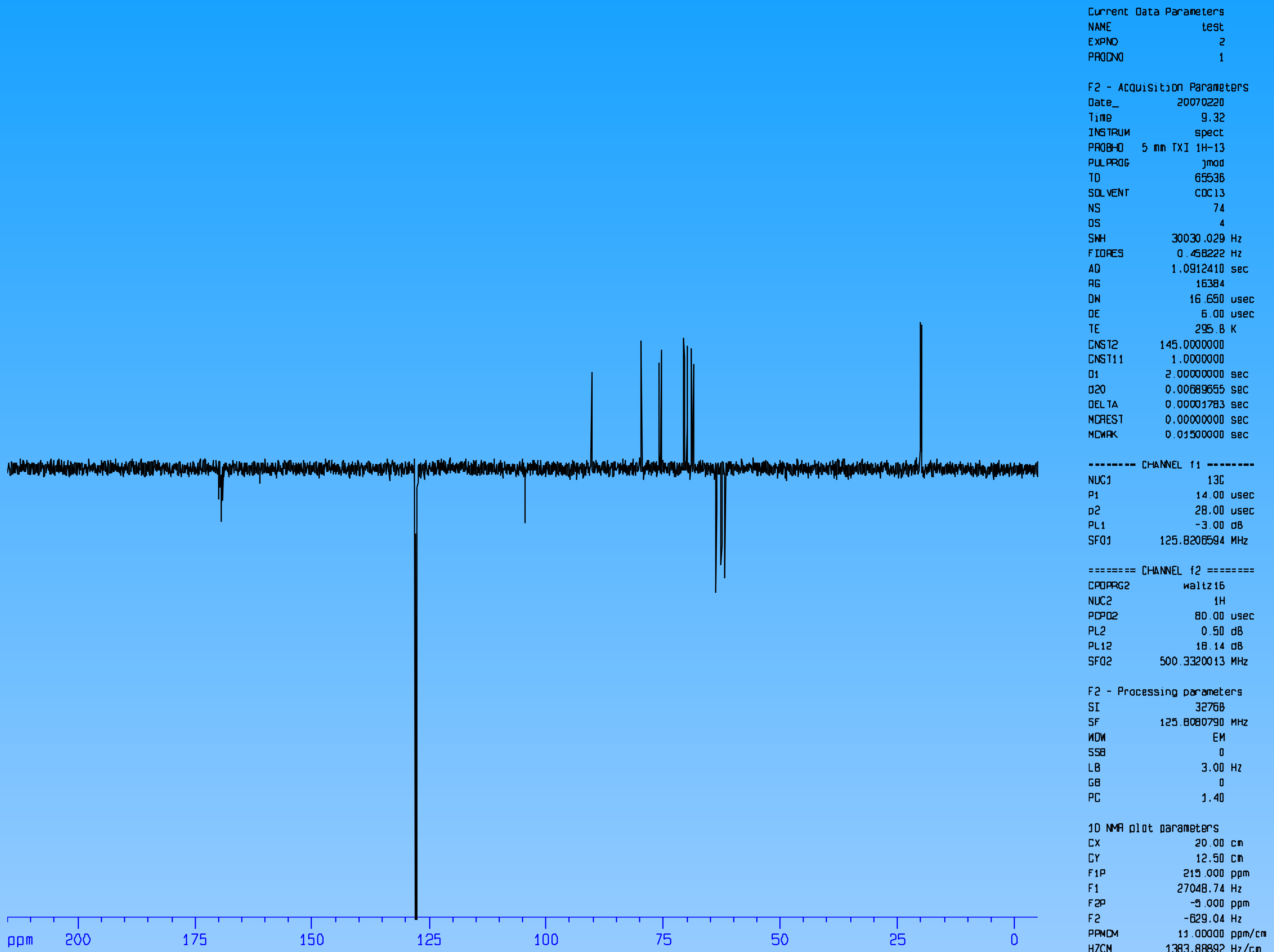


The Vector Model of NMR Spectroscopy
The APT or Jmod Experiment

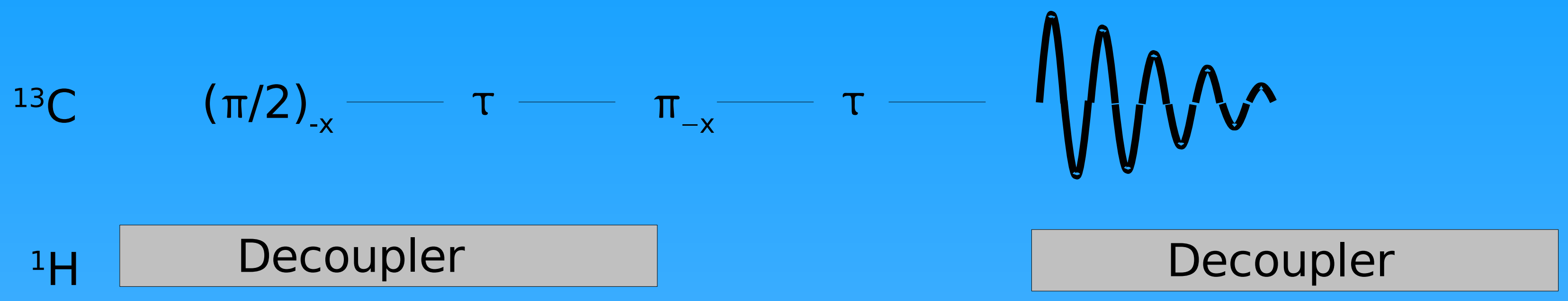
For a doublet (CH), off-resonance pulse:



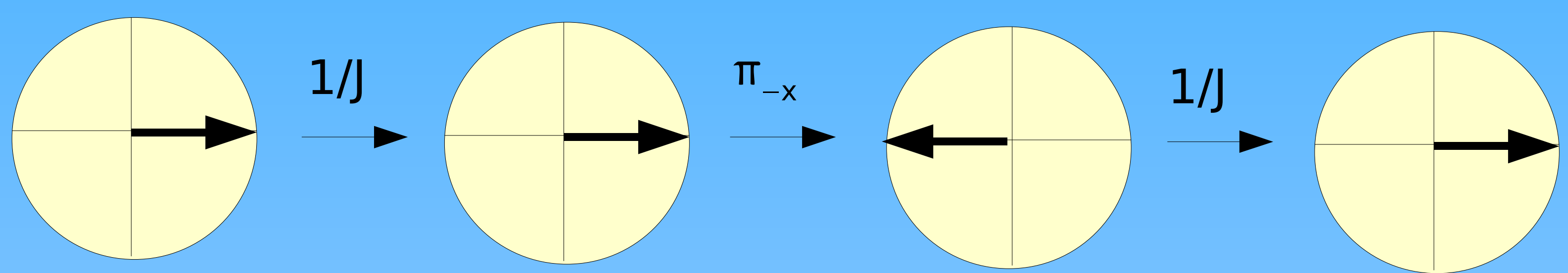
The Vector Model of NMR Spectroscopy
The APT or Jmod Experiment



The Vector Model of NMR Spectroscopy
The APT or Jmod Experiment

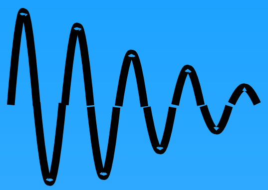


For a doublet (CH):



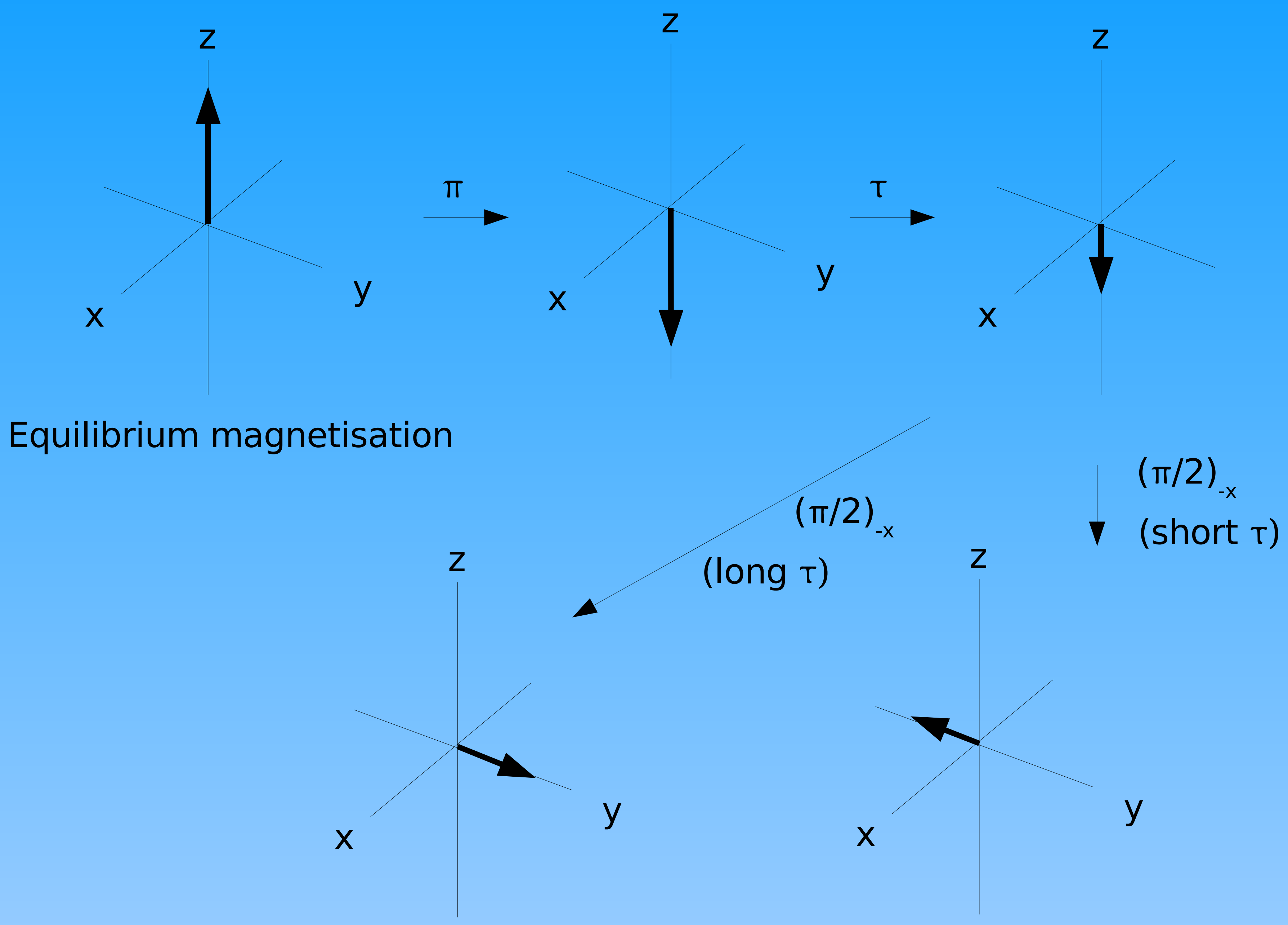
It makes no difference to the outcome of the experiment whether the decoupler is on during the first τ time period and off during the second or the other way around.

The Vector Model of NMR Spectroscopy
Inversion Recovery

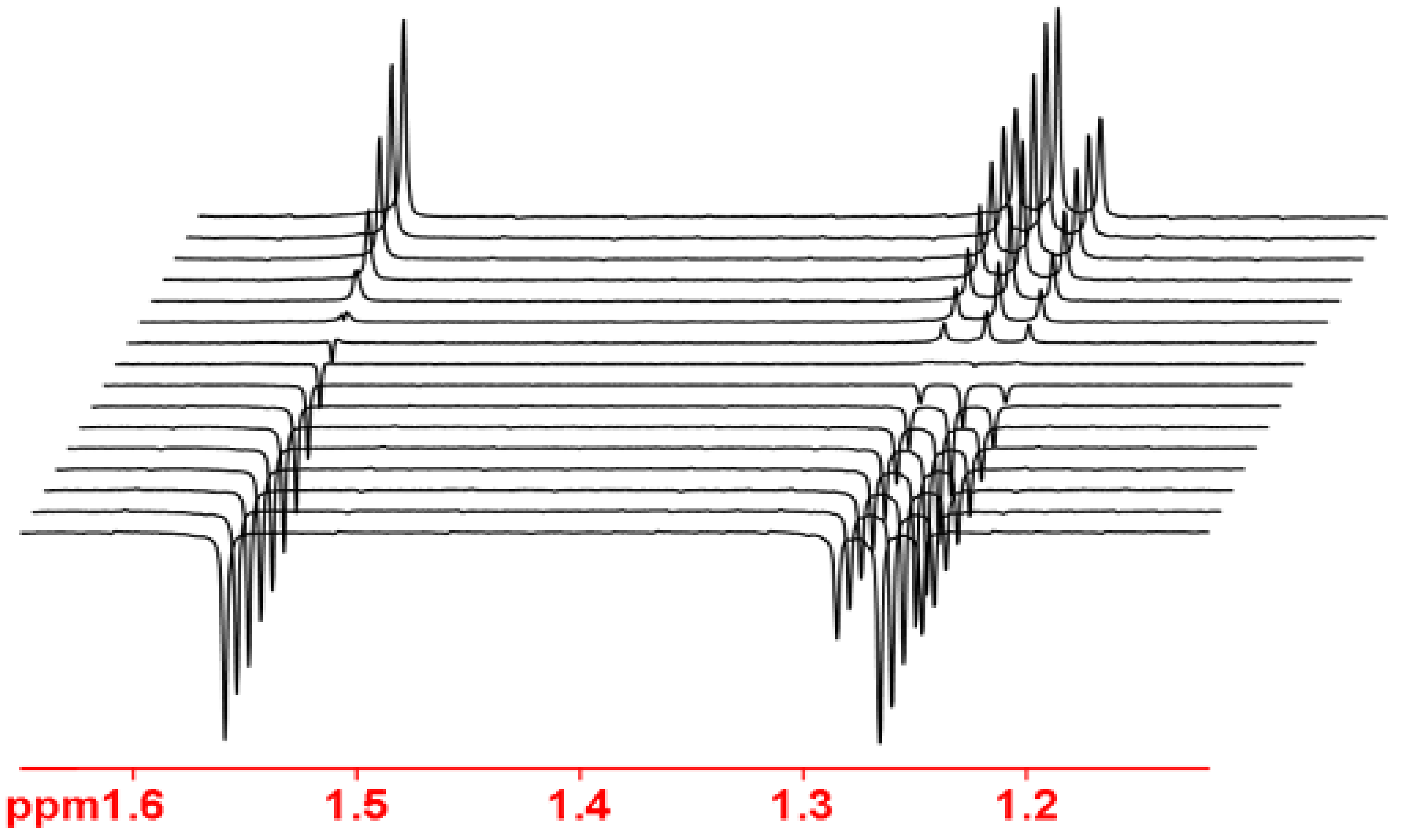
^{1}H π —— τ —— π/2 

τ is a *variable* time delay

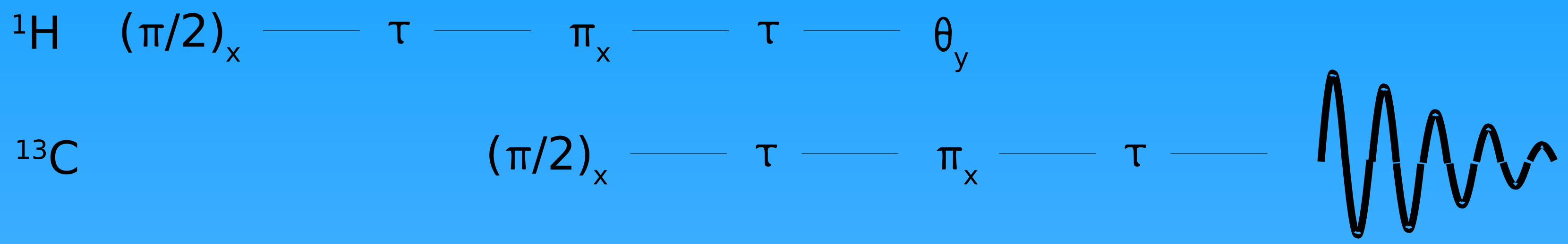
The Vector Model of NMR Spectroscopy
Inversion Recovery

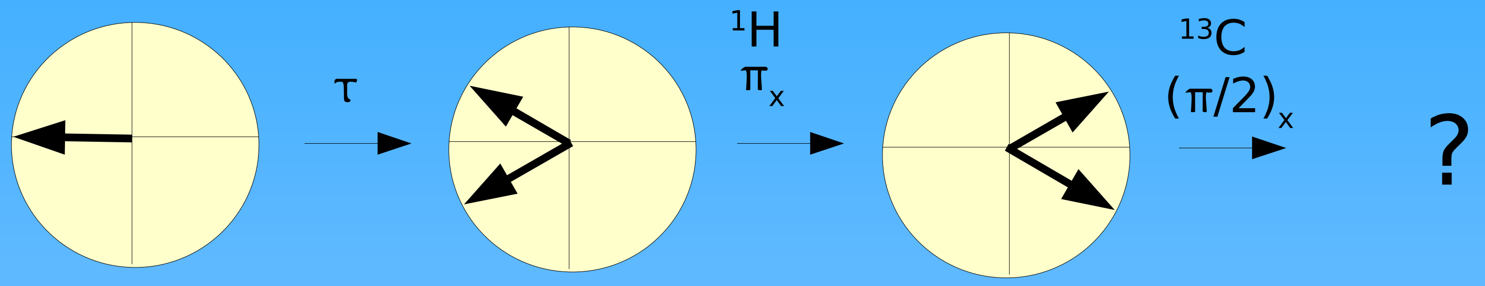


The Vector Model of NMR Spectroscopy
Inversion Recovery



The Vector Model of NMR Spectroscopy
DEPT

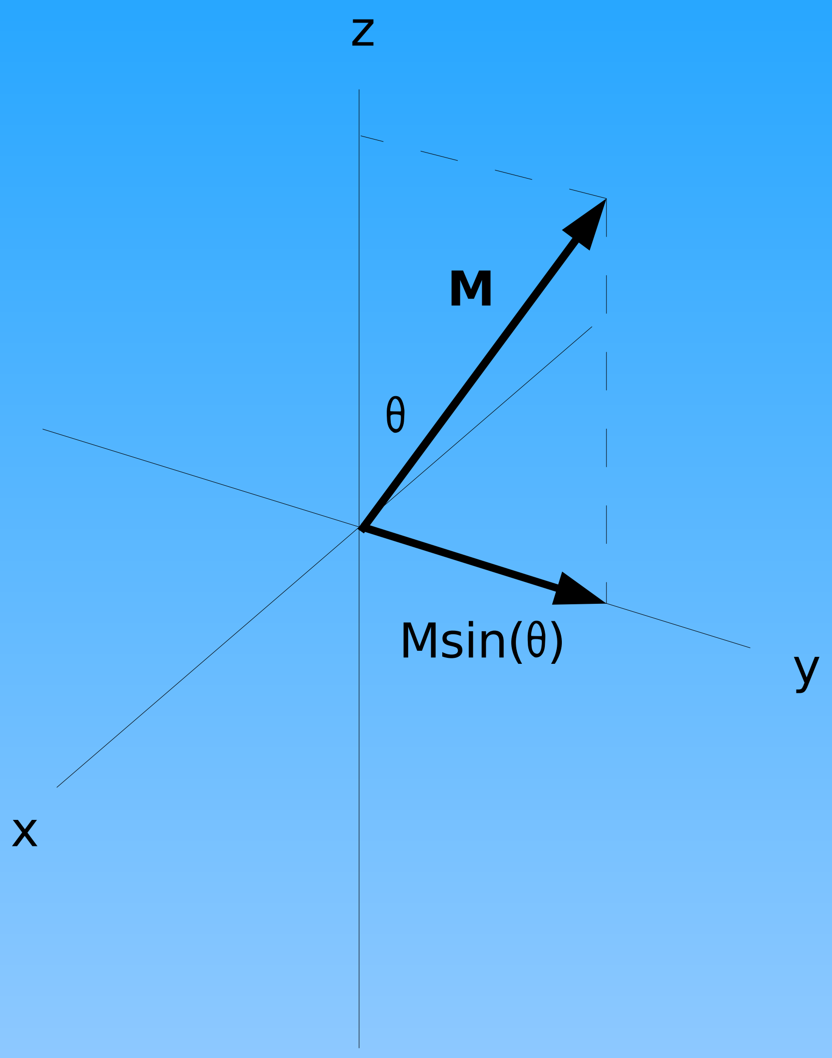




Must use quantum mechanically derived *density matrices* or *product operators* to analyse this pulse sequence.

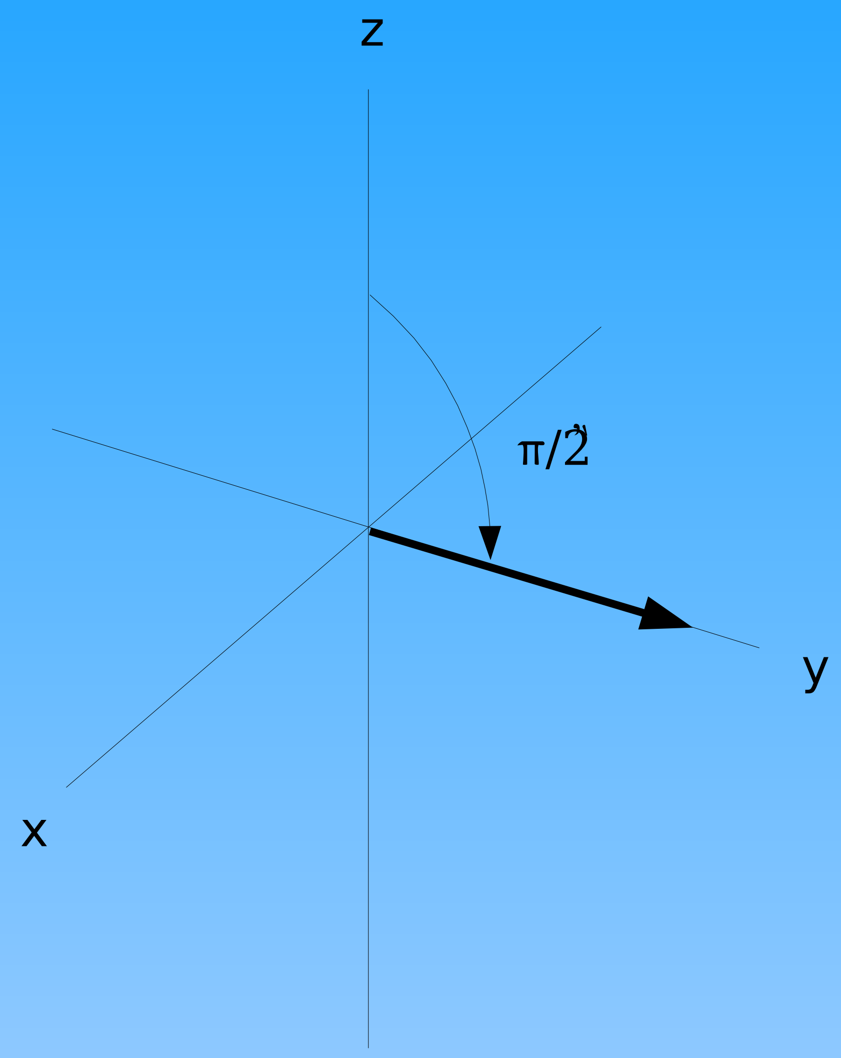
Pulse Calibration

The intensity of an NMR signal is proportional to the *projection* of the magnetisation onto the xy plane:



Pulse Calibration

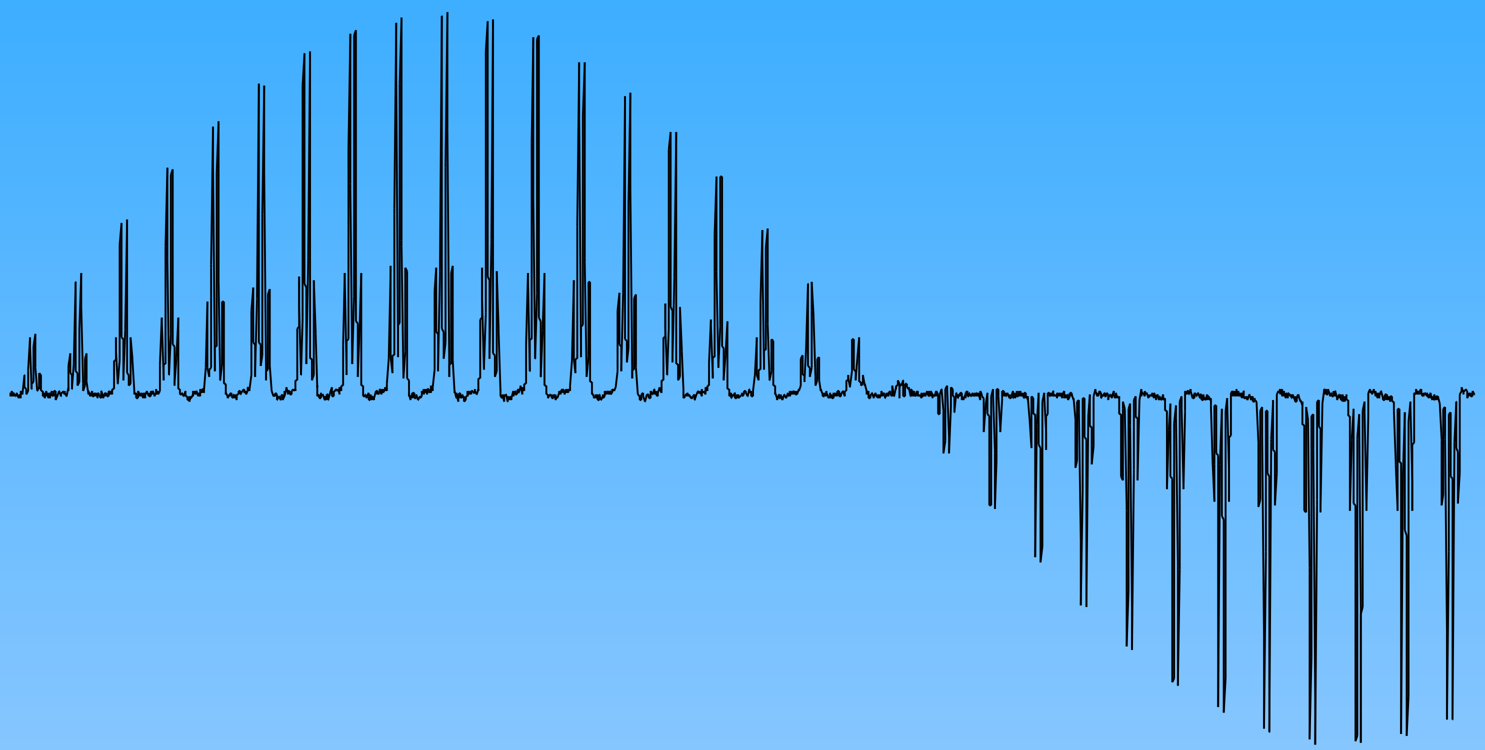
The intensity of the signal will be at a *maximum* when the precession angle is 90 degrees or π/2 radians:



Pulse Calibration

Proton 90 degree calibration
10 us at 0.5 dB

Transmitter frequency must be on-resonance to avoid effective field phase errors. Note that the pulse calibration is performed at a specified power level.



Current Data Parameters

NAME	proton_90	
EXPNO	1	
PROCNO	999	

F2 - Acquisition Parameters

Date_	20060811	
Time	10.16	
INSTRUM	spect	
PROBHD	5 mm TXI 1H-13	
PULPROG	zg	
TD	32768	
SOLVENT	C6D6	
NS	1	
DS	0	
SWH	1001.603	Hz
FIDRES	0.030566	Hz
AQ	16.3583355	sec
RG	7.1	
DW	499.200	usec
DE	6.00	usec
TE	297.6	K
D1	10.00000000	sec
MCREST	0.00000000	sec
MCWRK	0.01500000	sec

======== CHANNEL f1 ========

NUC1	1H	
P1	32.00	usec
PL1	0.50	dB
SFO1	500.3312992	MHz

F2 - Processing parameters

SI	131072	
SF	500.3300000	MHz
WDW	no	
SSB	0	
LB	0.00	Hz
GB	0	
PC	1.00	

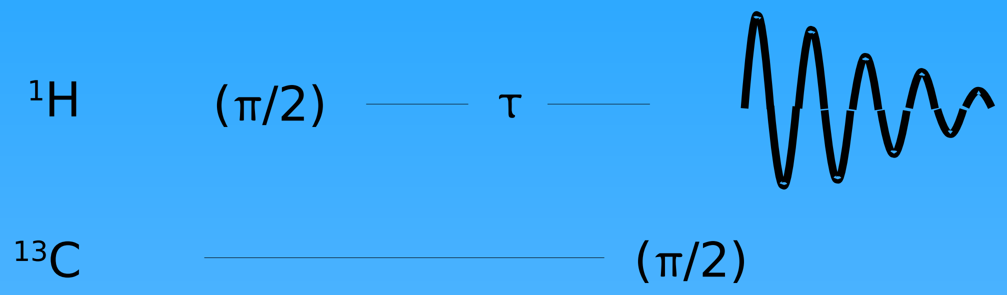
1D NMR plot parameters

CX	20.00	cm
CY	5.00	cm
F1P	3.598	ppm
F1	1800.02	Hz
F2P	2.543	ppm
F2	1272.51	Hz
PPMCM	0.05272	ppm/cm
HZCM	26.37554	Hz/cm

Pulse Calibration
Insensitive Nuclei

How do we do a pulse calibration for ^{13}C or ^{15}N?

We do it indirectly using the TBPDF pulse sequence:
(also commonly known as DECP90)



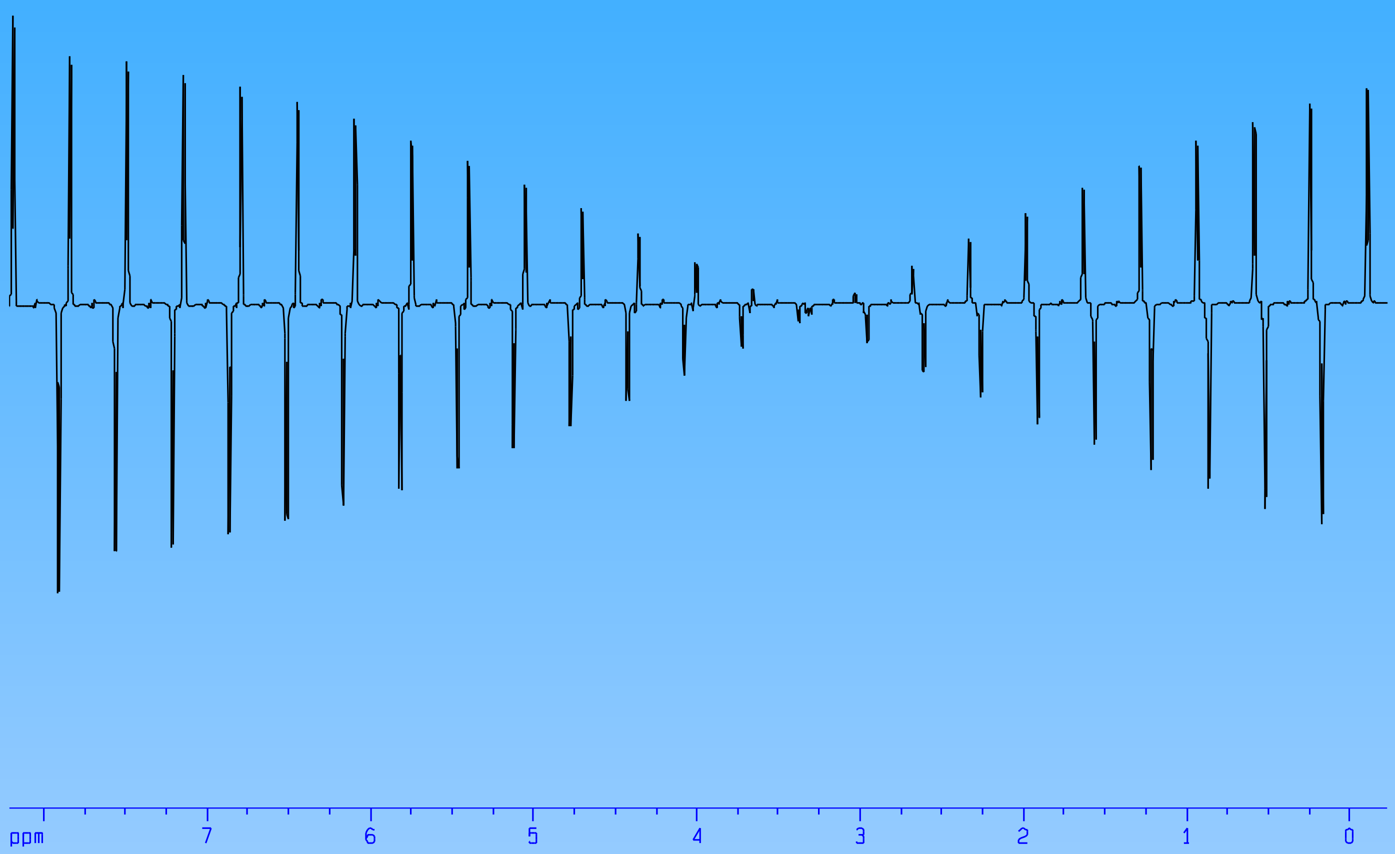
$\tau = 1/(2J)$

Use ^{13}C enriched sample so that ^{13}C coupling in ^{1}H can be easily seen.

At the point at which the ^{13}C pulse is a 90^{o} pulse the antiphase doublet in the spectrum will vanish.

Pulse Calibration
Insensitive Nuclei

13C 90 degree pulse width calibration
14 us at -3 dB



Current Data Parameters
NAME 13C_decoupler
EXPNO 1
PROCNO 999

F2 - Acquisition Parameters
Date_ 20060811
Time 10.32
INSTRUM spect
PROBHD 5 mm TXI 1H-13
PULPROG decp90
TD 16384
SOLVENT Acetone
NS 1
DS 0
SWH 6009.615 Hz
FIDRES 0.366798 Hz
AQ 1.3632820 sec
RG 181
DW 83.200 usec
DE 6.00 usec
TE 297.6 K
CNST2 139.0000000
D1 3.00000000 sec
d2 0.00359712 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

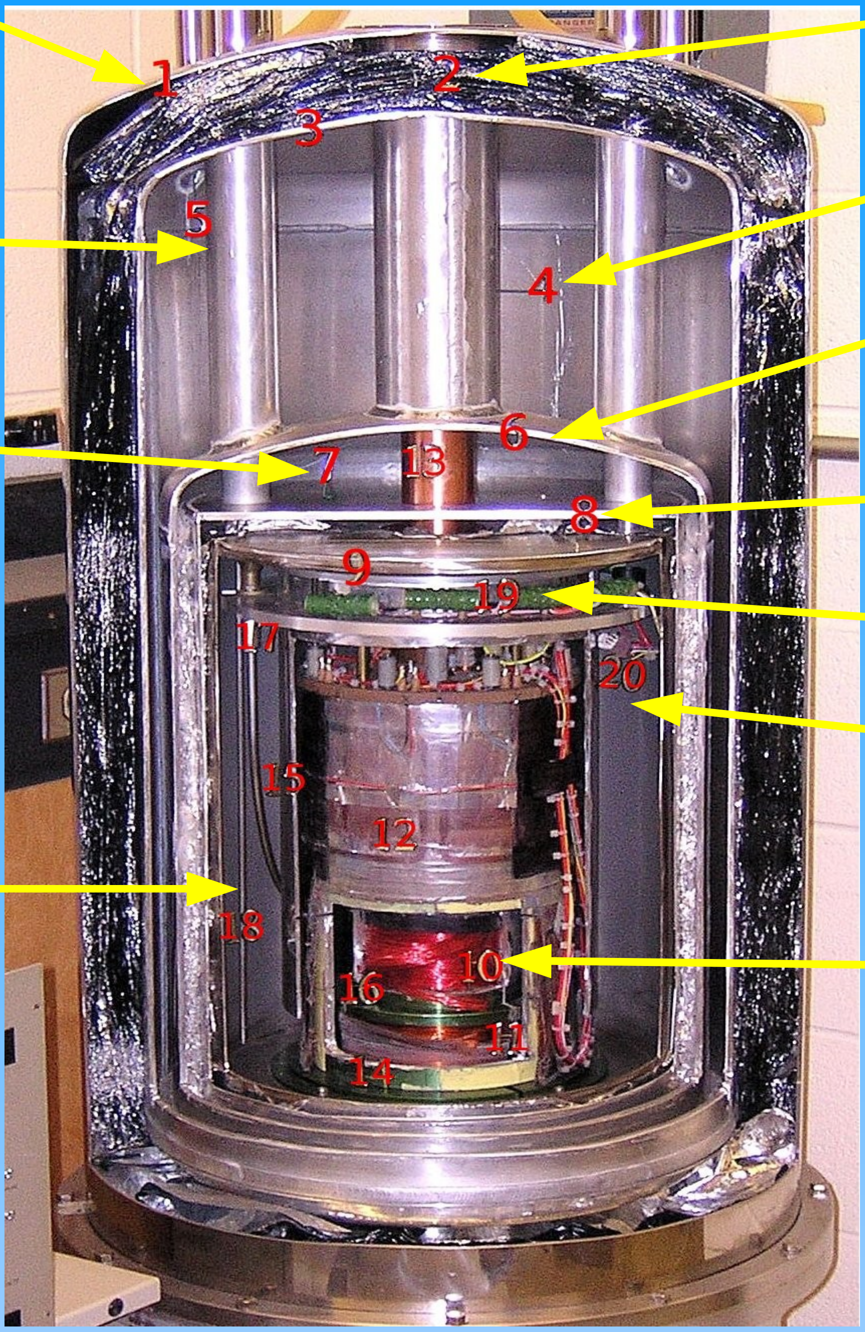
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 0.50 dB
SFO1 500.3315870 MHz

-------- CHANNEL f2 --------
NUC2 13C
P3 24.00 usec
PL2 -3.00 dB
SFO2 125.8142500 MHz

F2 - Processing parameters
SI 32768
SF 500.3304850 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 5.00 cm
F1P 8.208 ppm
F1 4106.80 Hz
F2P -0.230 ppm
F2 -114.96 Hz
PPMCM 0.42190 ppm/cm
HZCM 211.08774 Hz/cm

A Tour of a Spectrometer

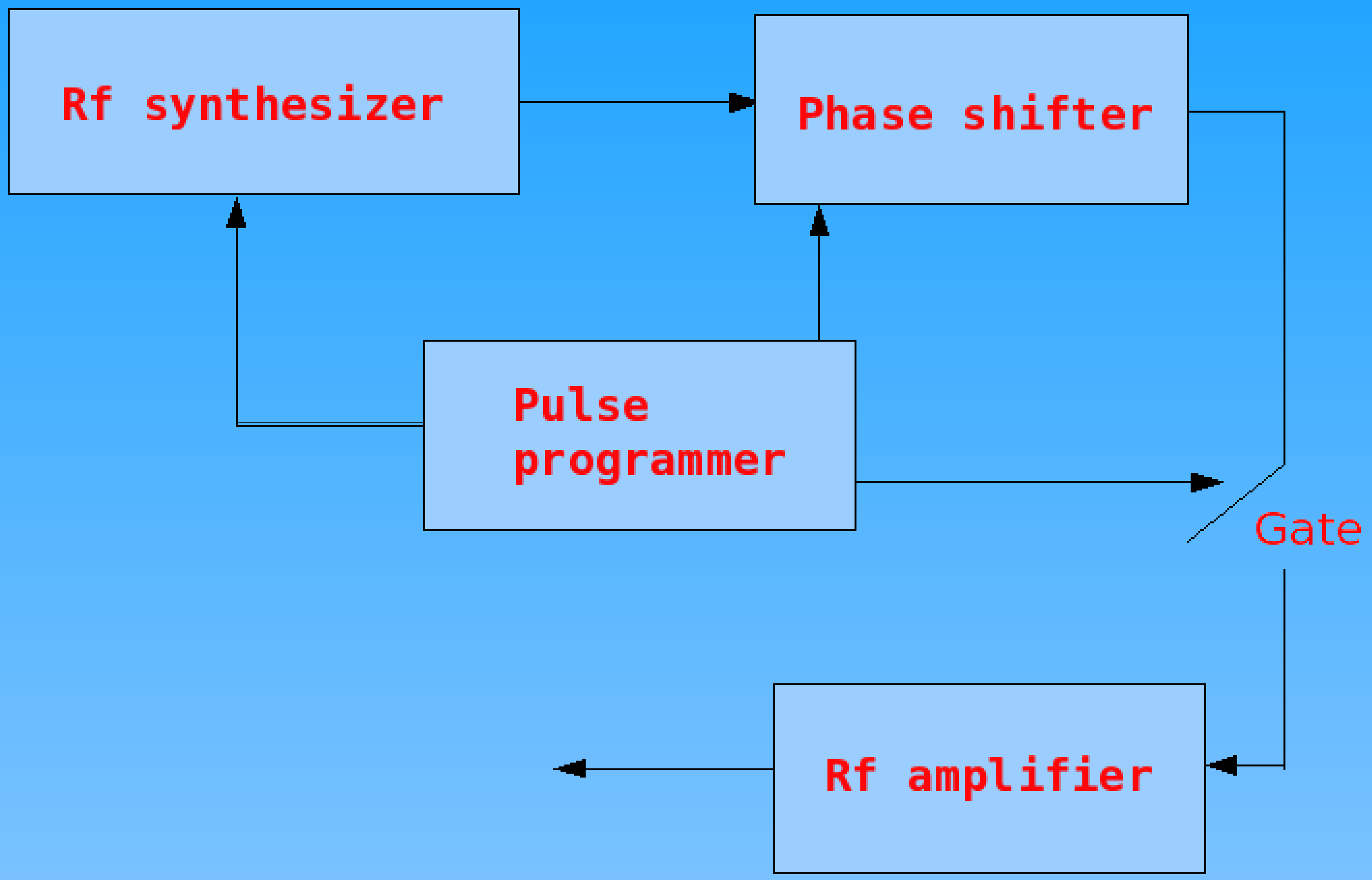


A Tour of a Spectrometer

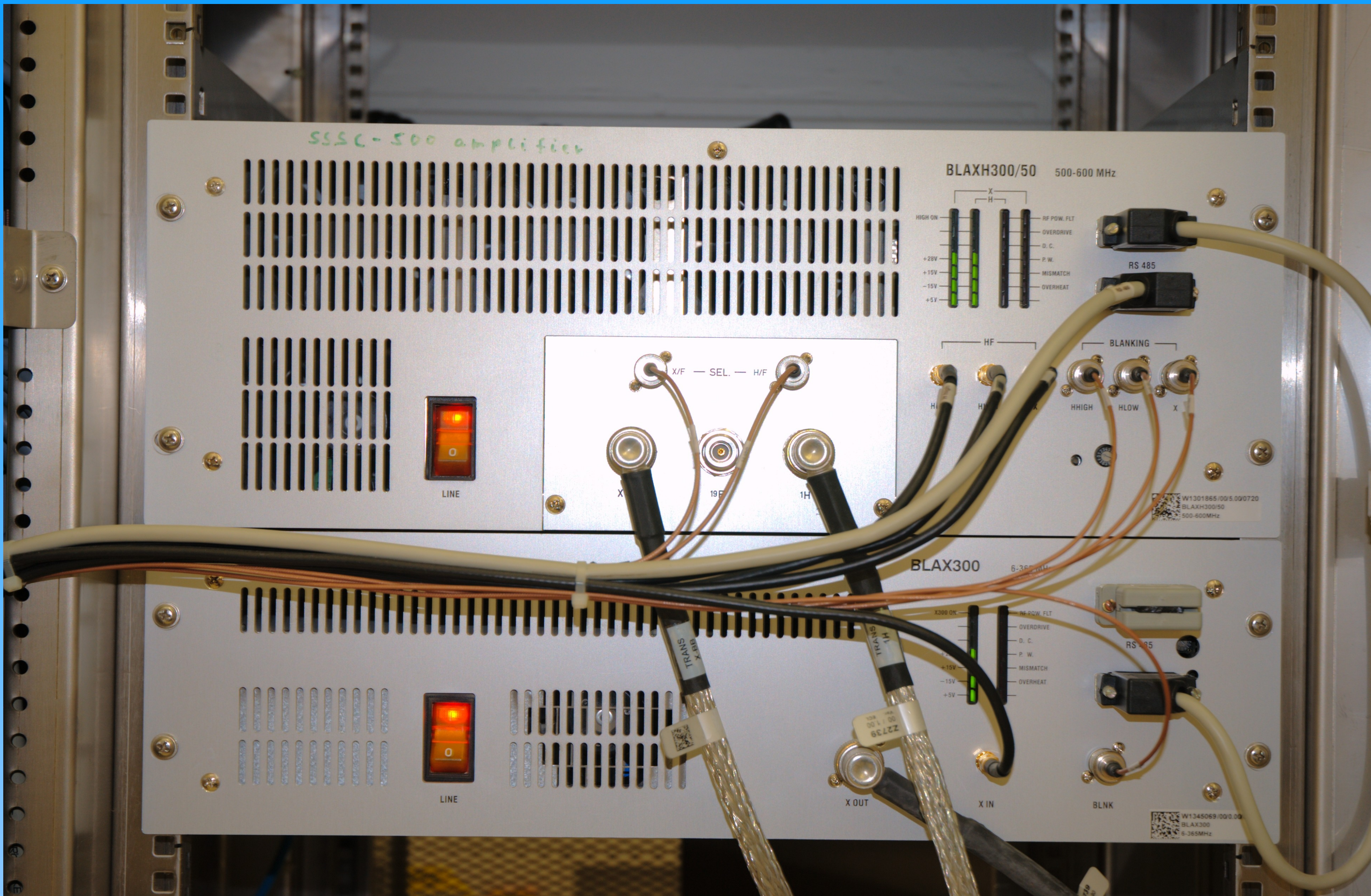
Liquid nitrogen fill

Liquid helium fill

A Tour of a Spectrometer

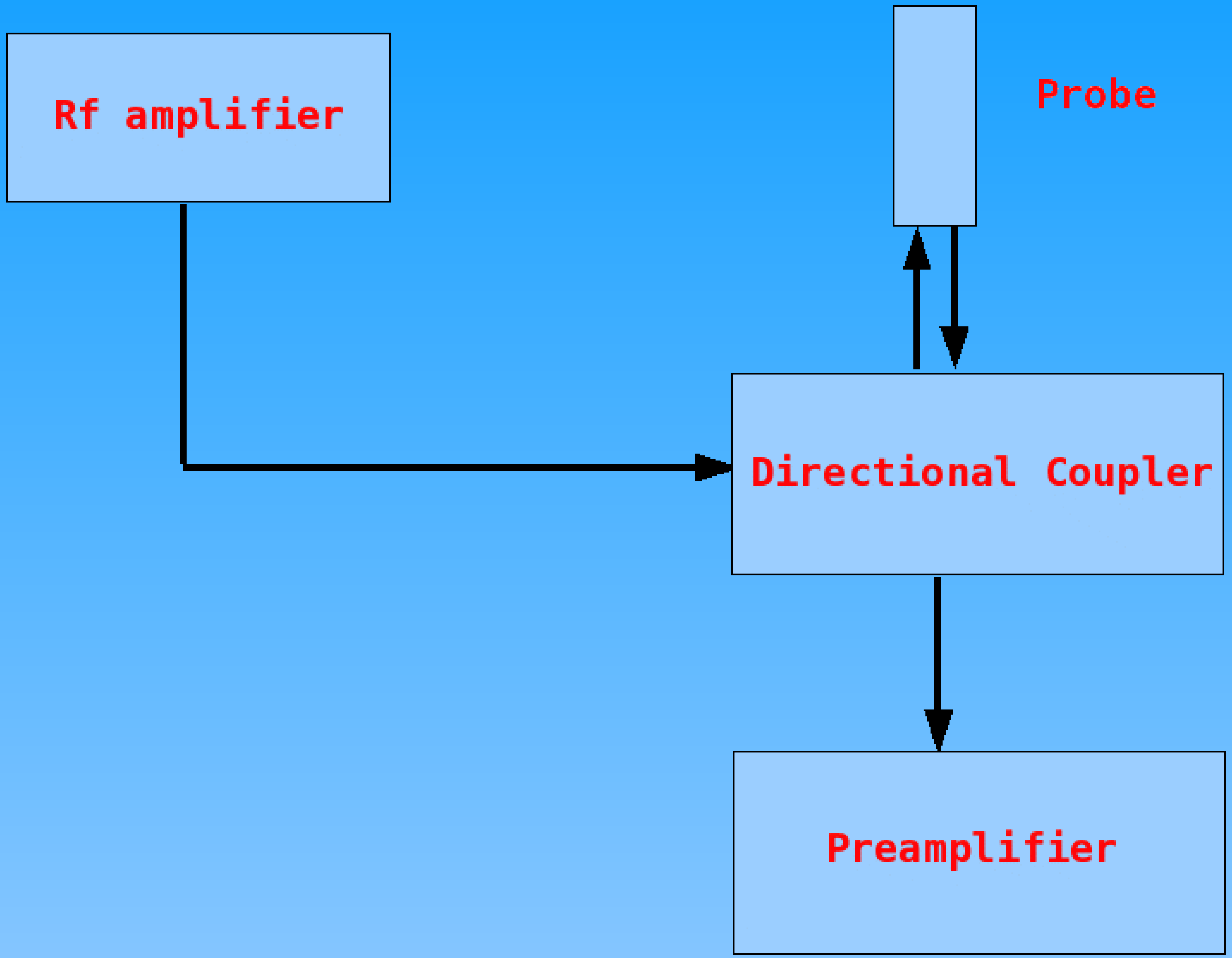


A Tour of a Spectrometer



The rf amplifiers

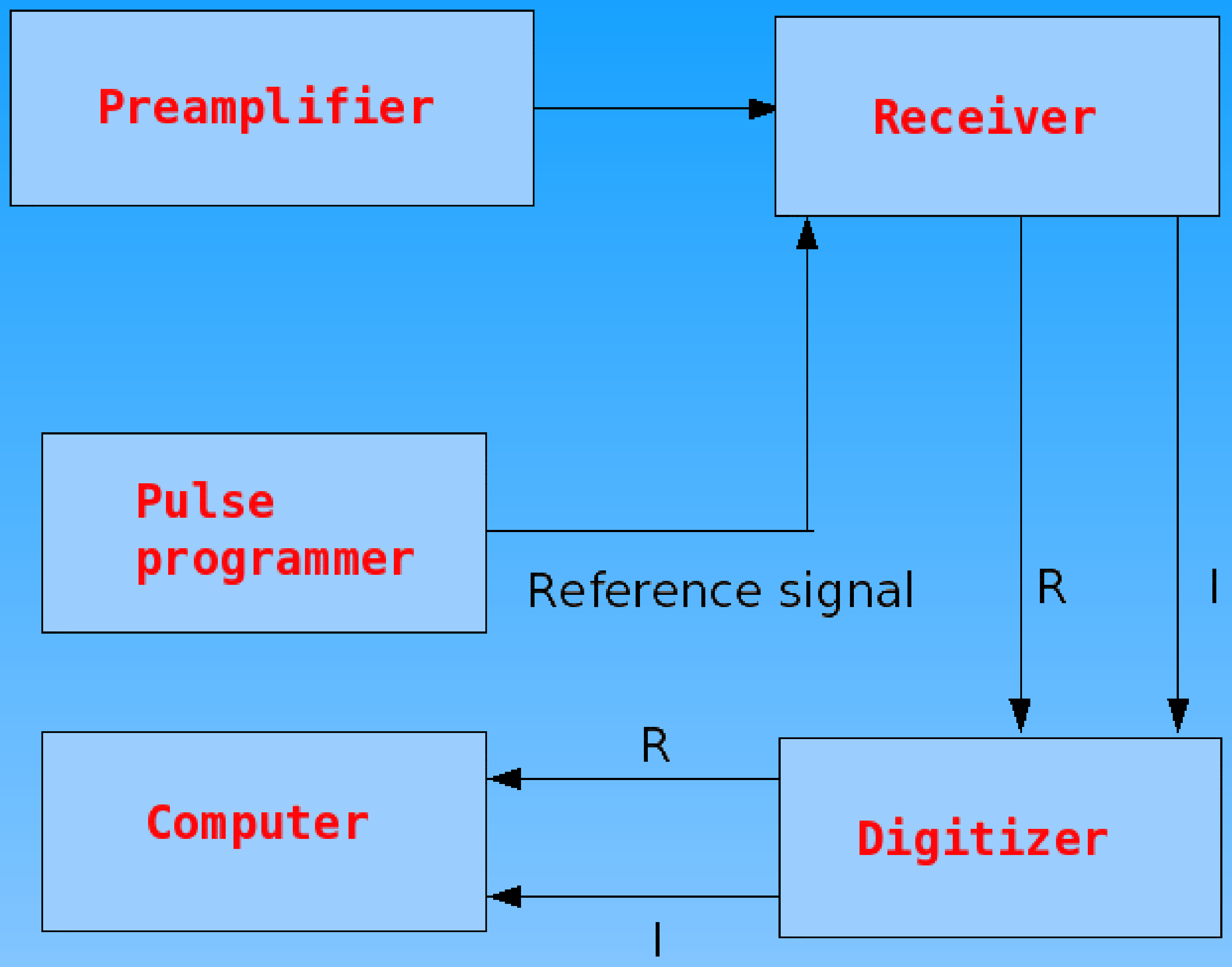
A Tour of a Spectrometer



A Tour of a Spectrometer

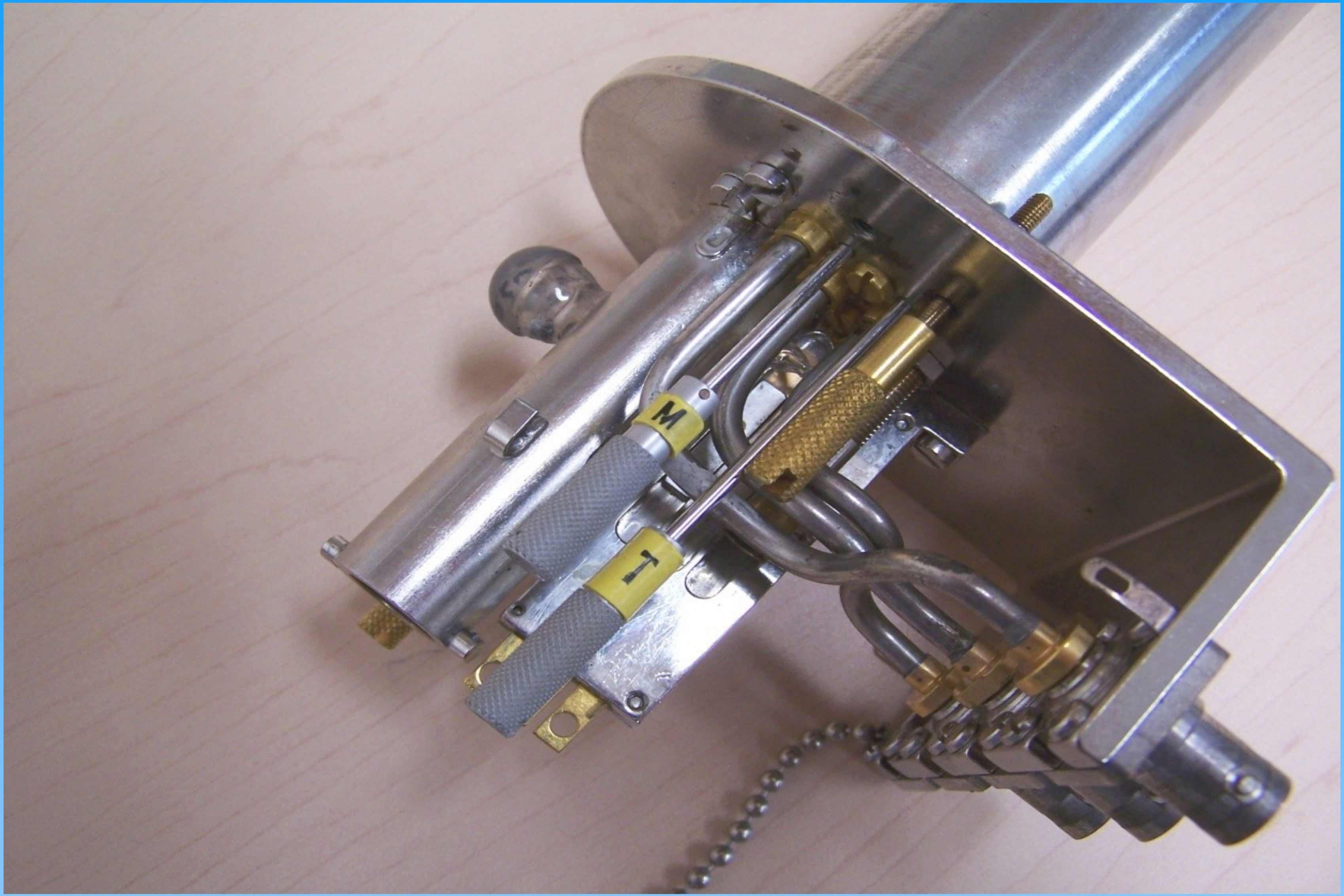
The preamplifiers

A Tour of a Spectrometer

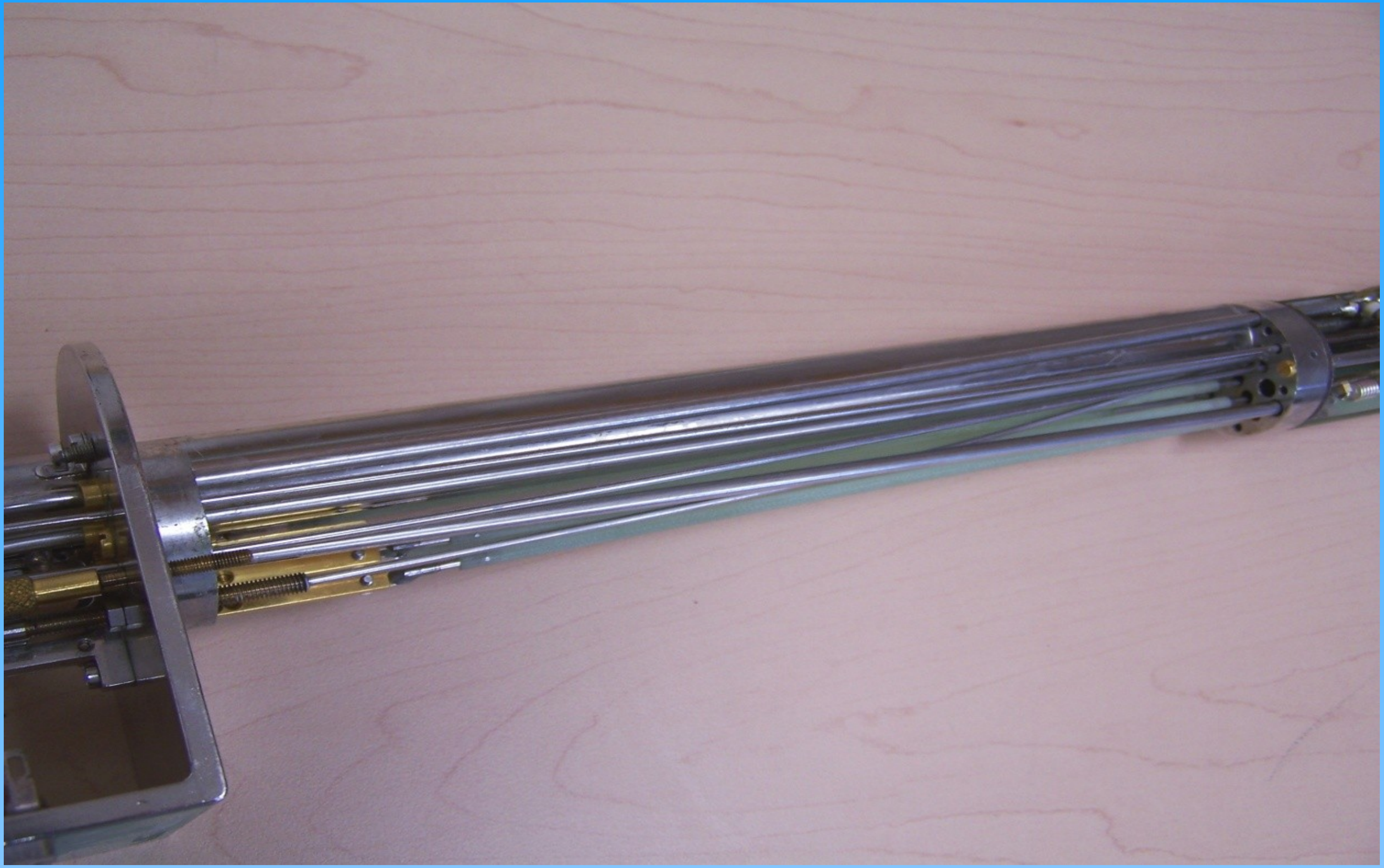


The Probe

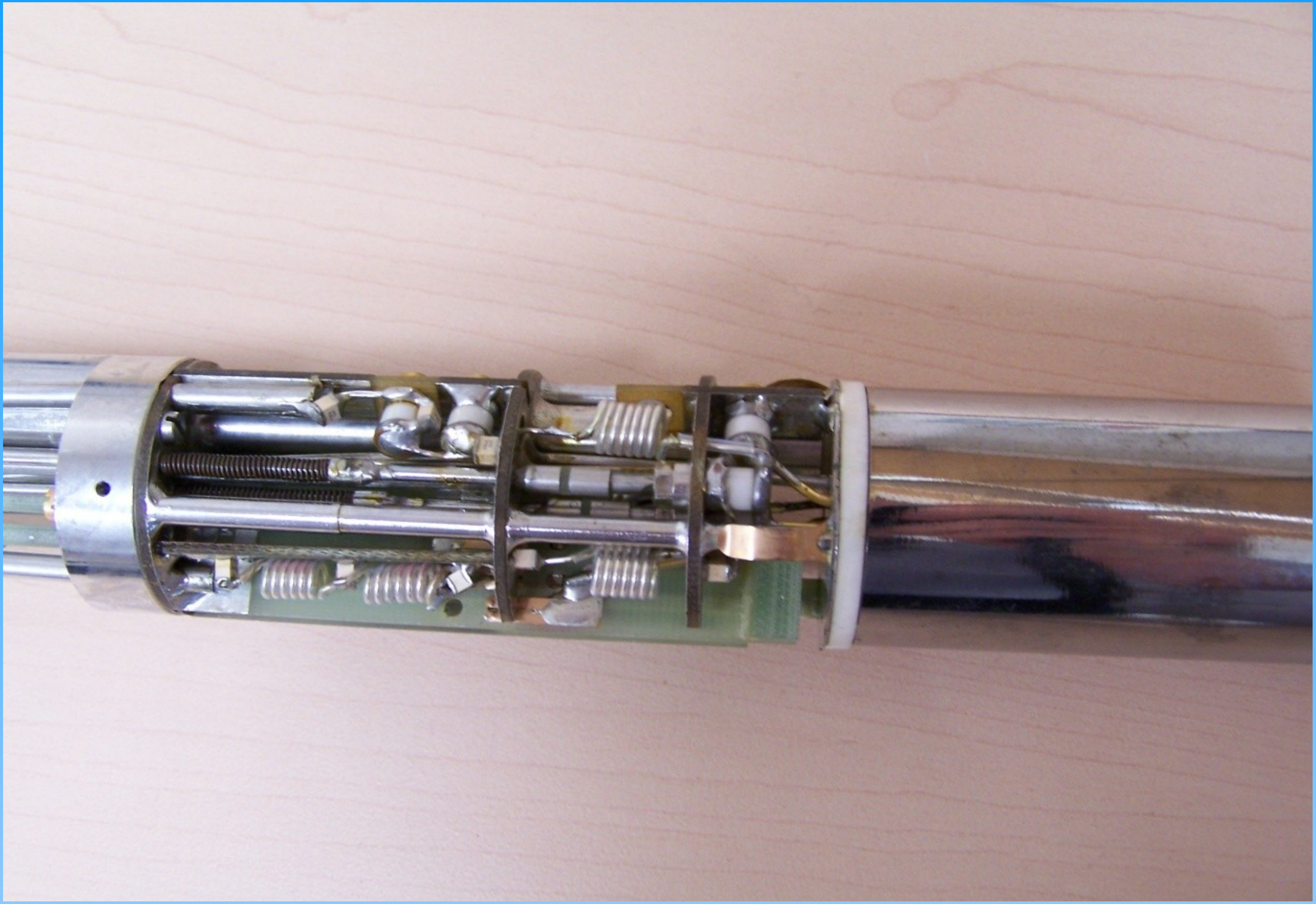
The Probe



The Probe

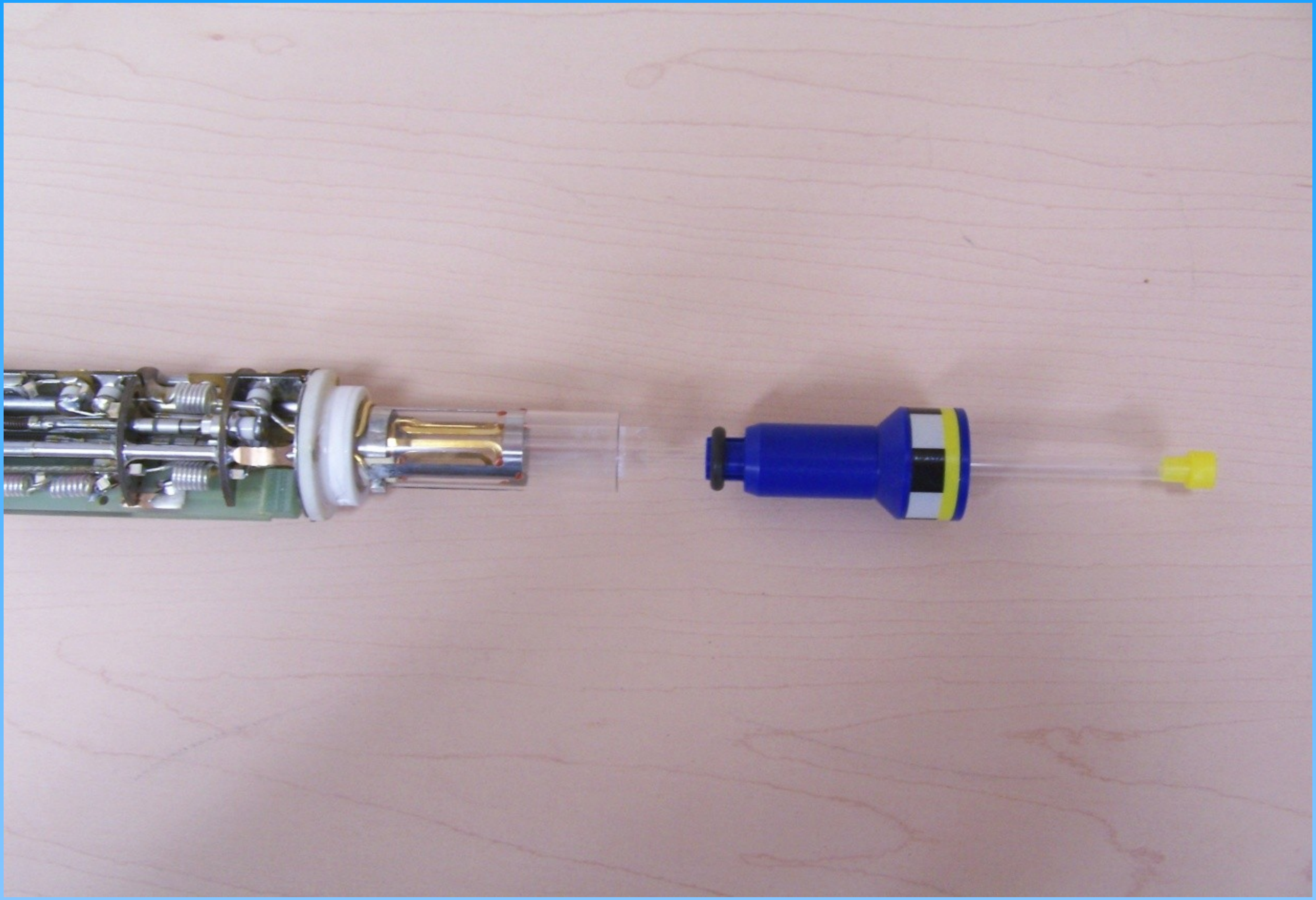


The Probe

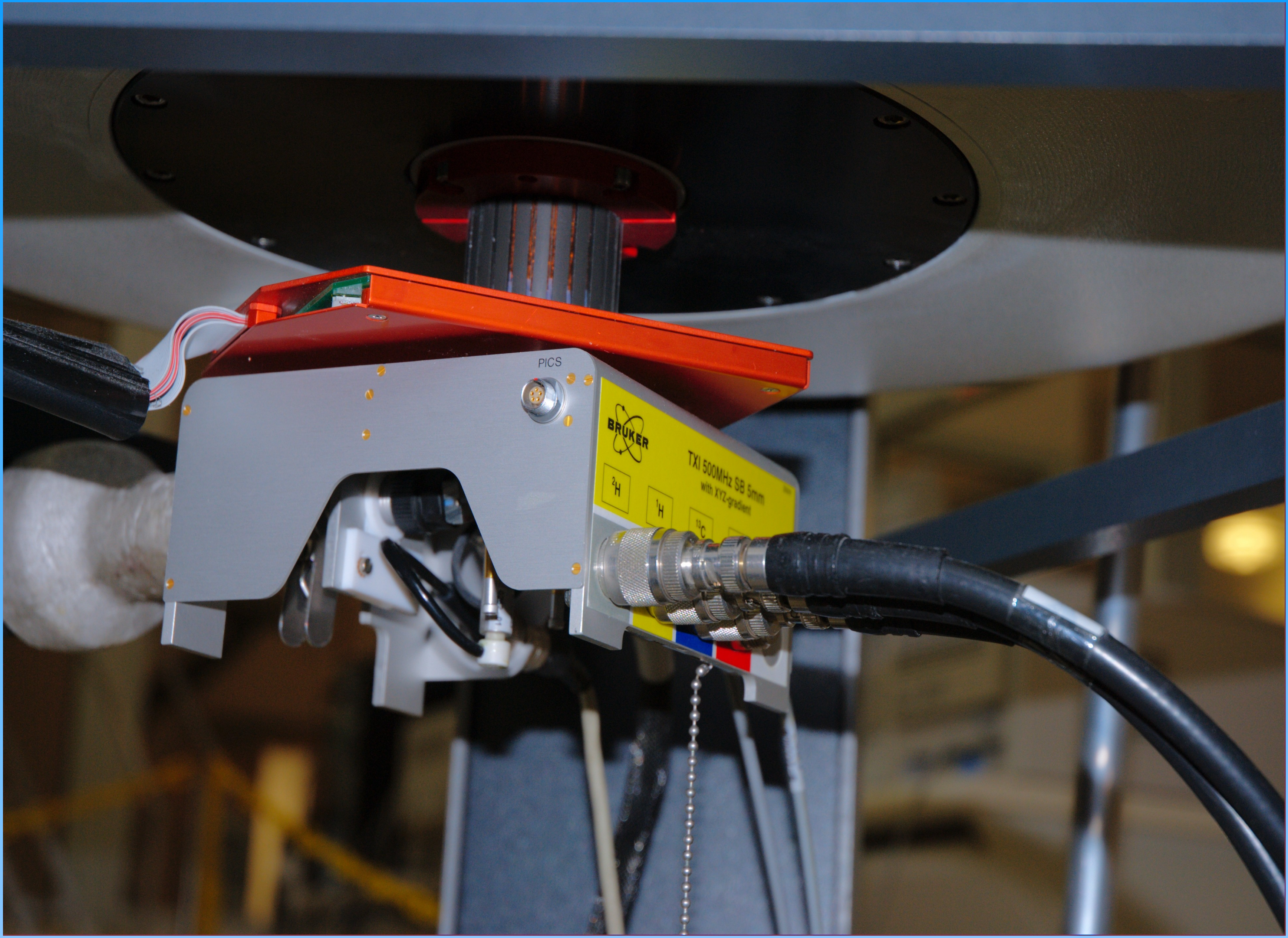


The Probe

The Probe



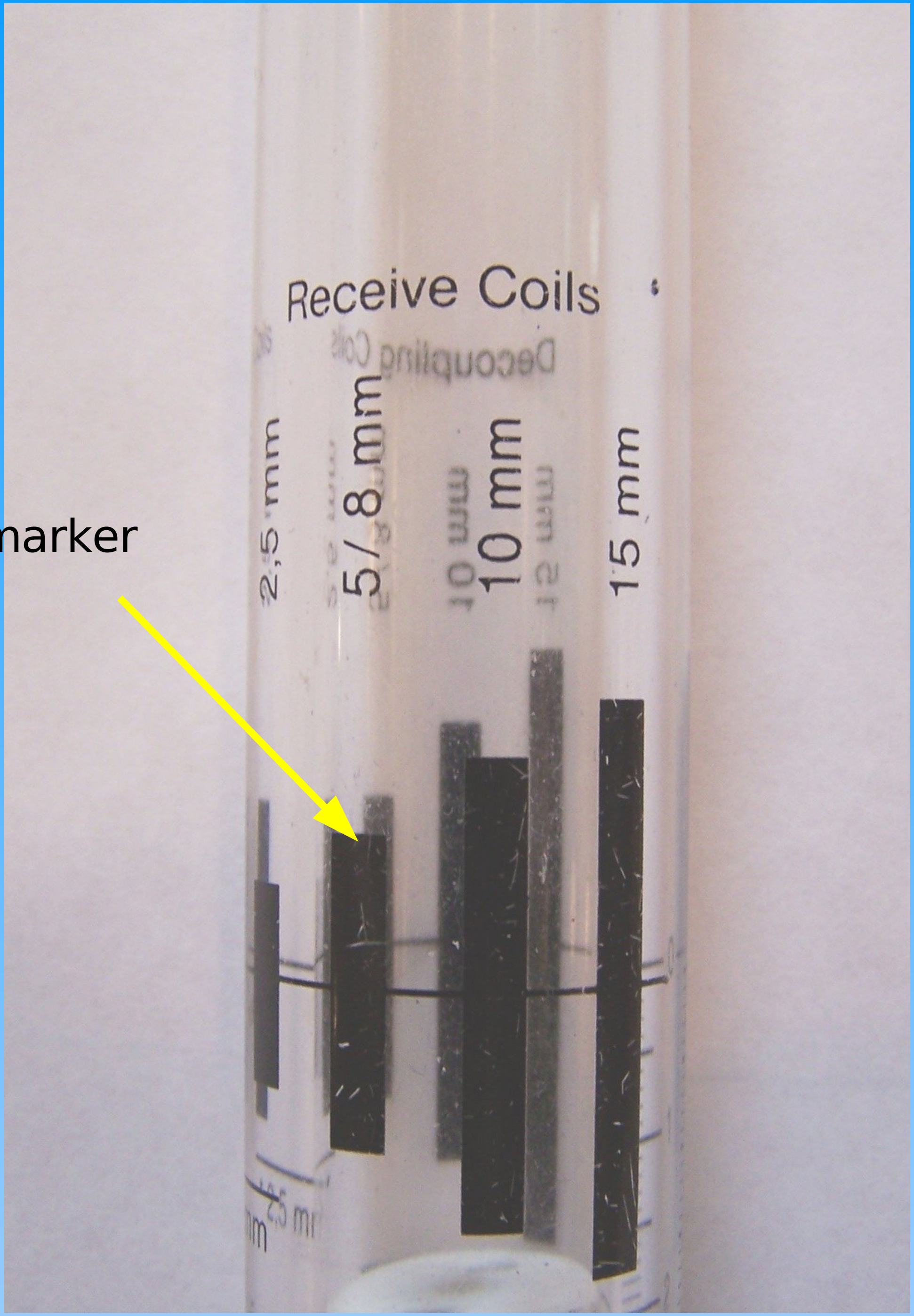
The Probe



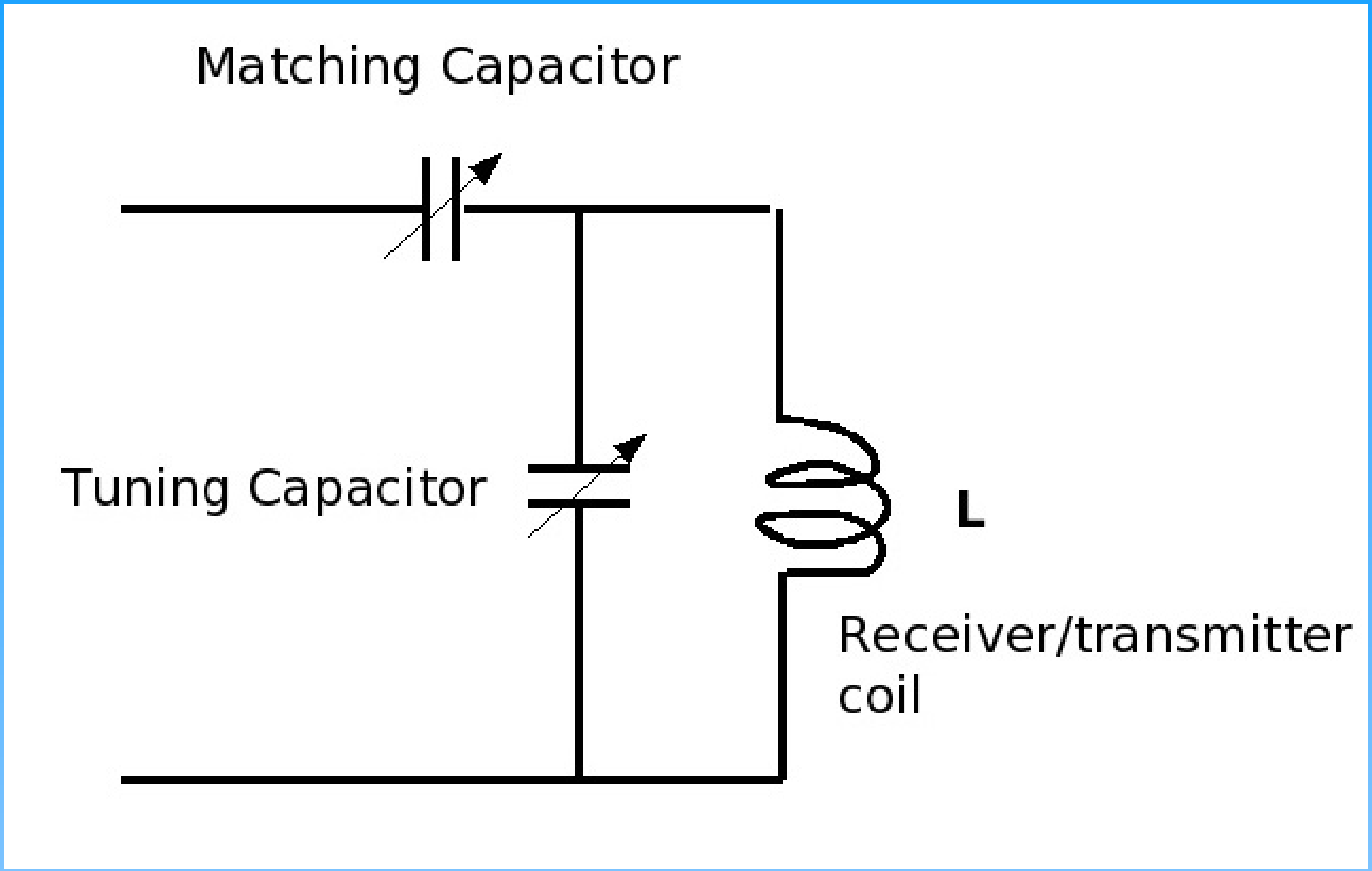
The probe inserted into the magnet

The Probe

Receiver coil position marker



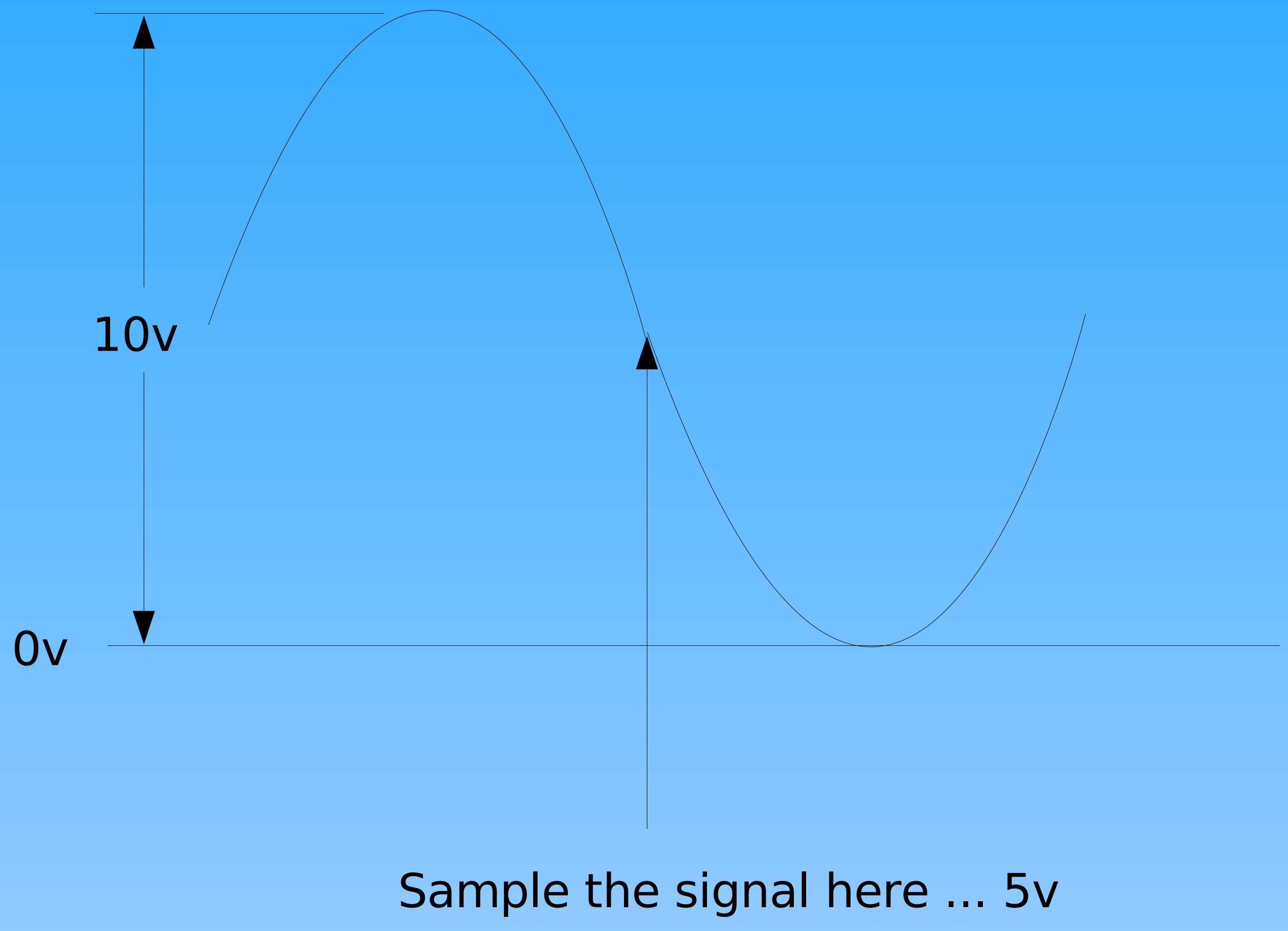
The Probe



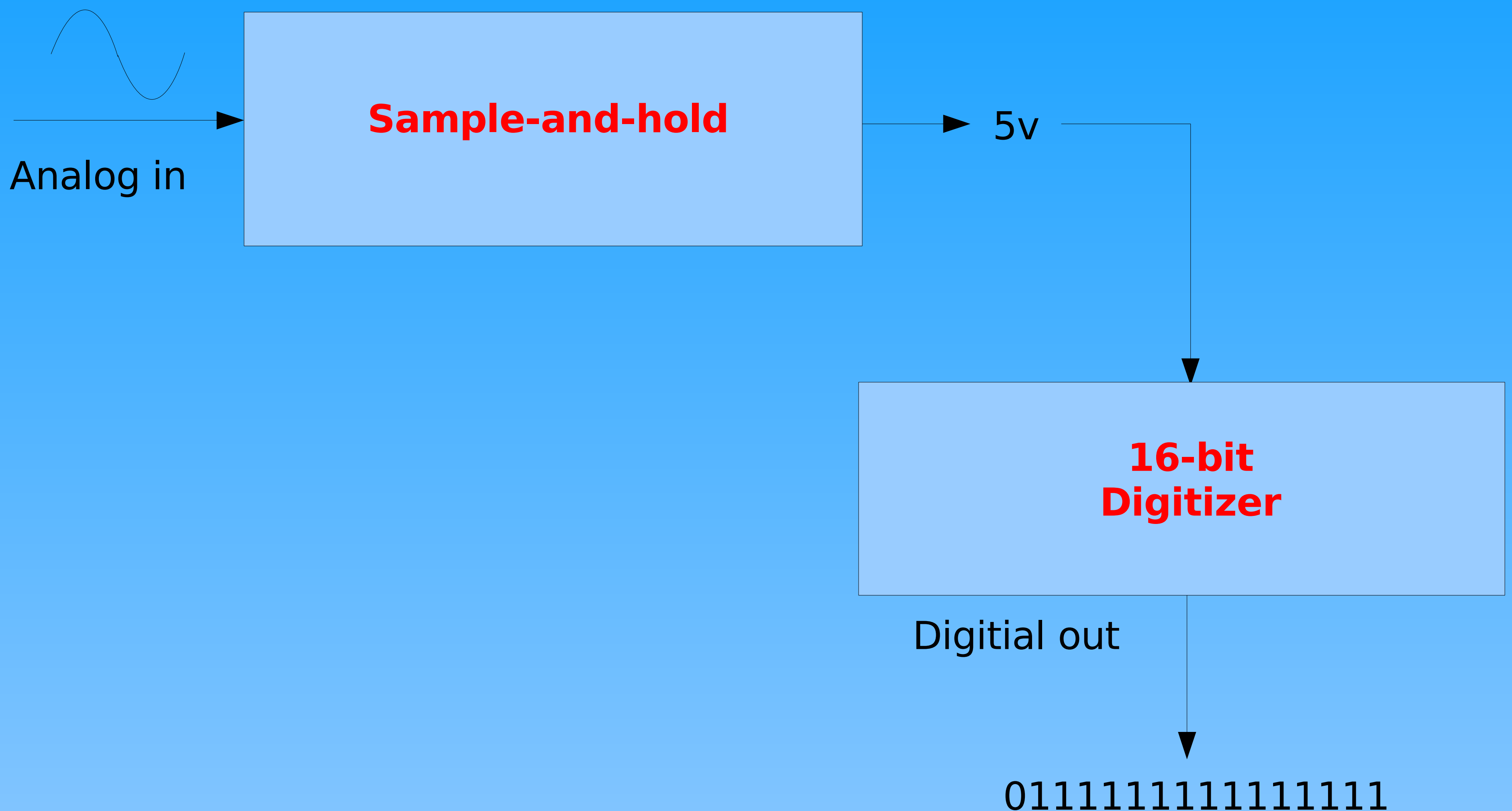
$$\omega_0 = 1/(LC)^{1/2}$$

The Digitizer or ADC

The digitizer consists of two main components, the sample-and-hold unit and the analog-to-digital converter. The analog signal is *continuously* variable in time and the digital signal varies *discontinuously*.



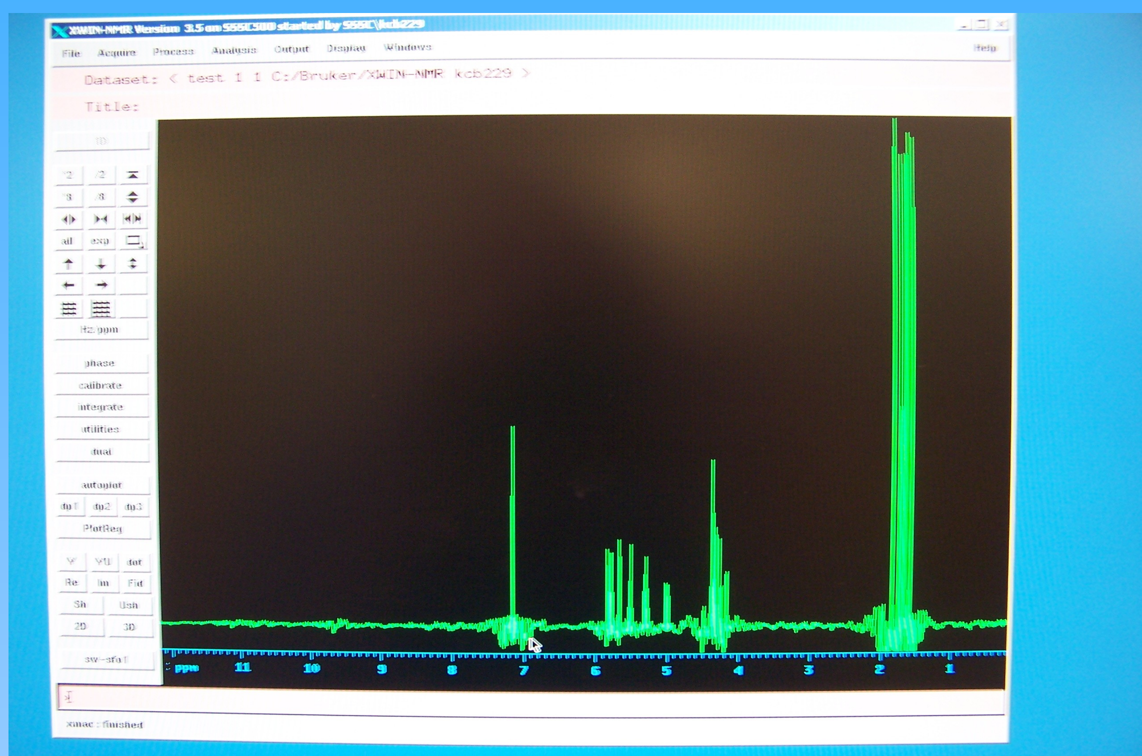
The Digitizer or ADC



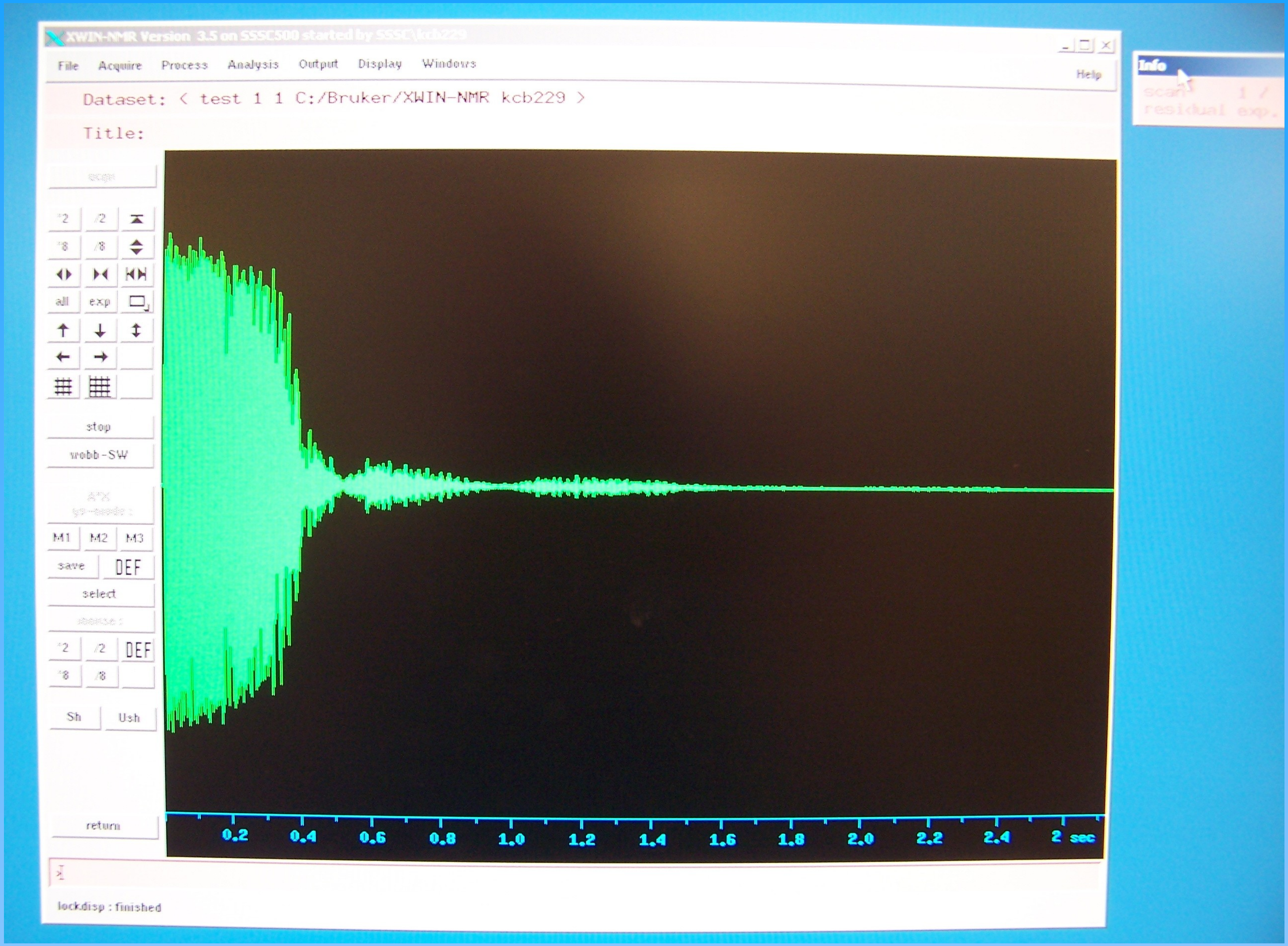
The Digitizer or ADC

A 16-bit digitizer can represent 2^{16}-1 or 65535 different voltages in steps of 10v/65535 or 0.000153v or 0.153 mv. So, 0111111111111111 is equivalent to 32767x0.000153v = 5.0v. 10V would be (obviously) twice this number, 1111111111111111.

What if a voltage larger than 10v goes into the digitizer? It will be cut off or 'clipped' at 10v and the digitizer will output 1111111111111111, the binary number representing 10v. The ultimate result in the nmr spectrum is a distorted baseline.

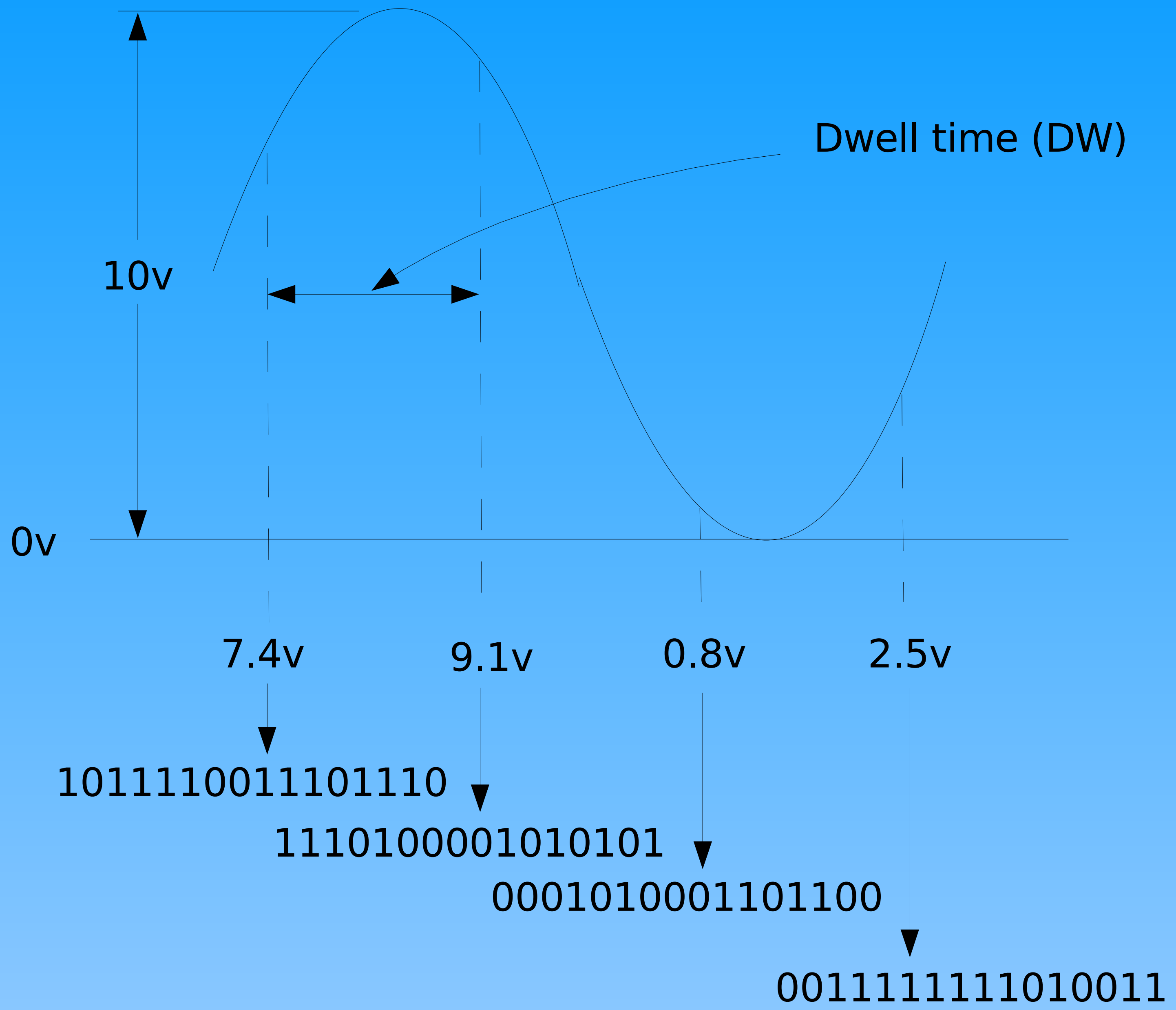


The Digitizer or ADC

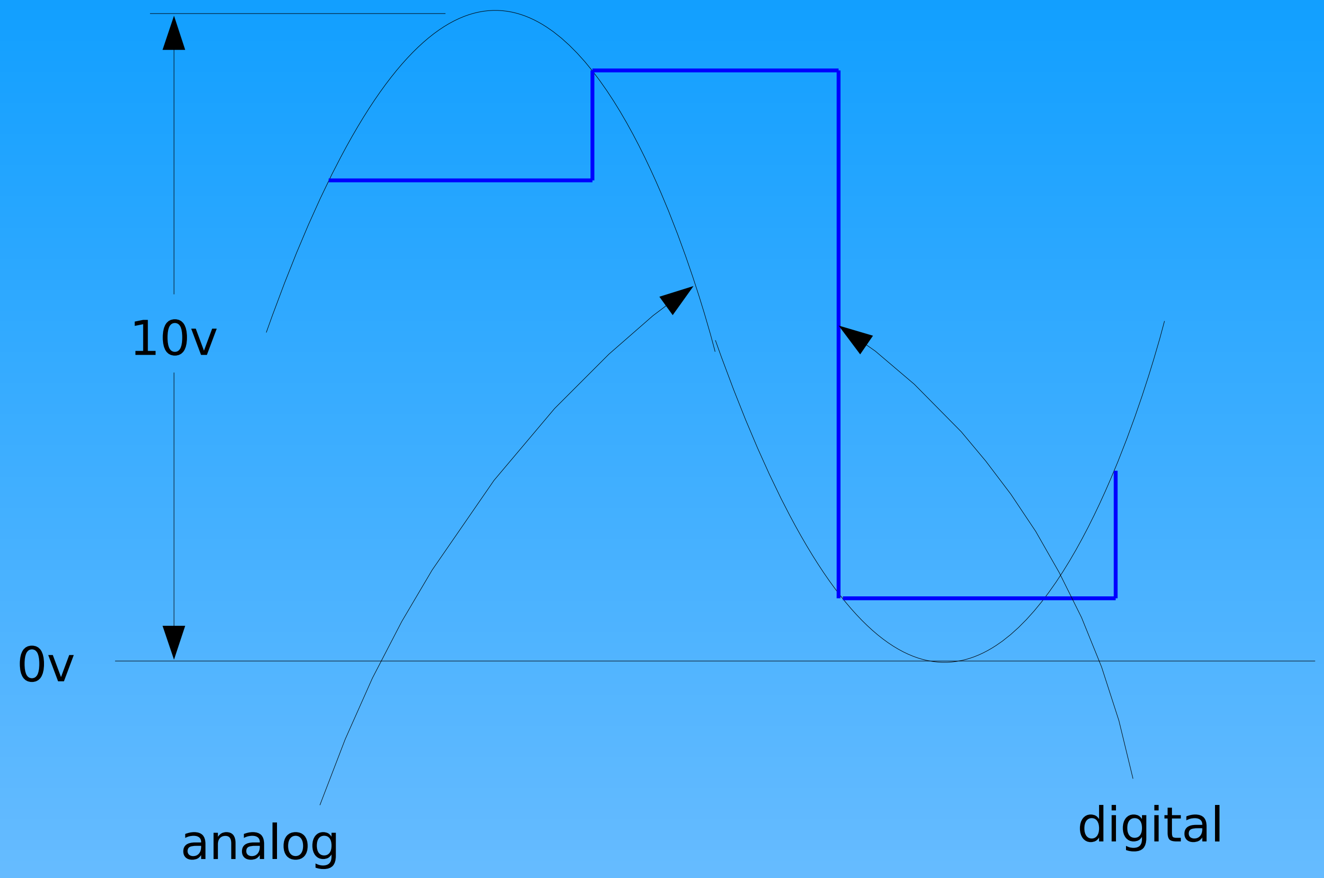


A 'clipped' fid

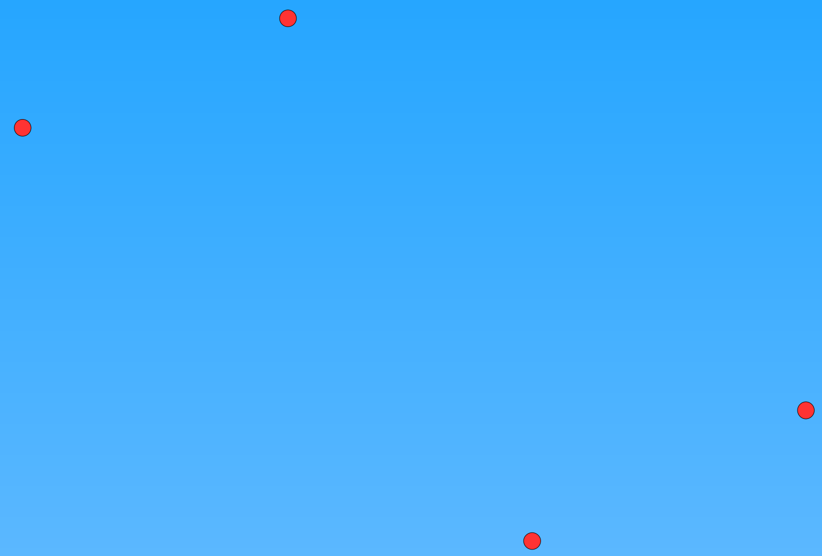
The Digitizer or ADC



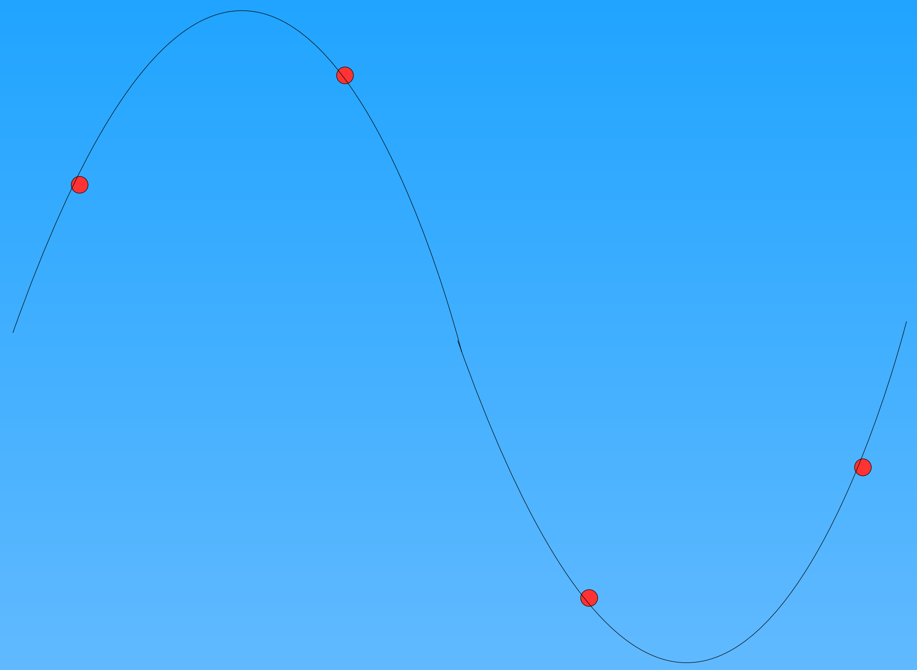
The Digitizer or ADC



The Digitizer or ADC



The Digitizer or ADC



The Digitizer or ADC

The Nyquist theorem says that a cyclically varying signal must be sampled *at least* twice during each cycle in order to be adequately represented digitally. The interval between samples is the dwell time. Thus, the maximum frequency that can be reliably digitized is:

$$\nu_{max} = 1/(2DW)$$

This means that for a proton with a Larmor frequency of approximately 500 Mhz the digitizer must be able to run at 1 Ghz. Digitizers capable of running at this frequency have only recently become available and as it turns out it is not necessary or reasonable to digitize at this frequency.

Since we are only interested in a very narrow range of frequencies for most nucleii, it is not necessary to digitize the entire 500 Mhz frequency range. So, what we do instead is mix the nmr signal which is at megahertz frequency with a reference signal and produce a ***difference*** signal which is then digitized … at a much lower frequency. The frequencies of the nmr signals are then the difference between the reference frequency and their Larmor frequencies.

The Digitizer or ADC

Instead of digitizing:

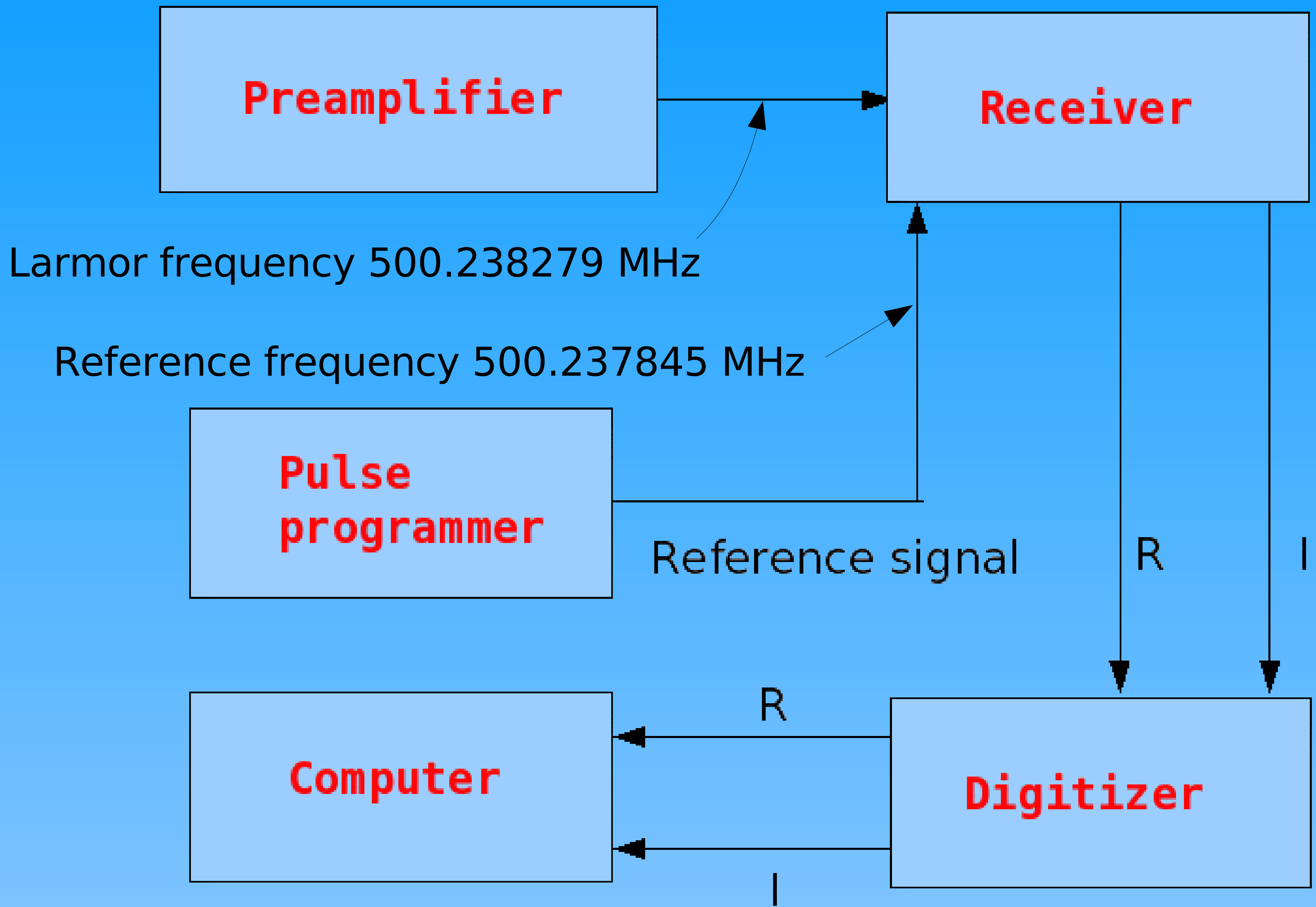
0 Hz 500 Mhz

most of which is wasted since ^{1}H frequencies occur in a very small range of approximately 10000 Hz, we digitize just a small range of *difference* frequencies:

0 Hz 10 Khz

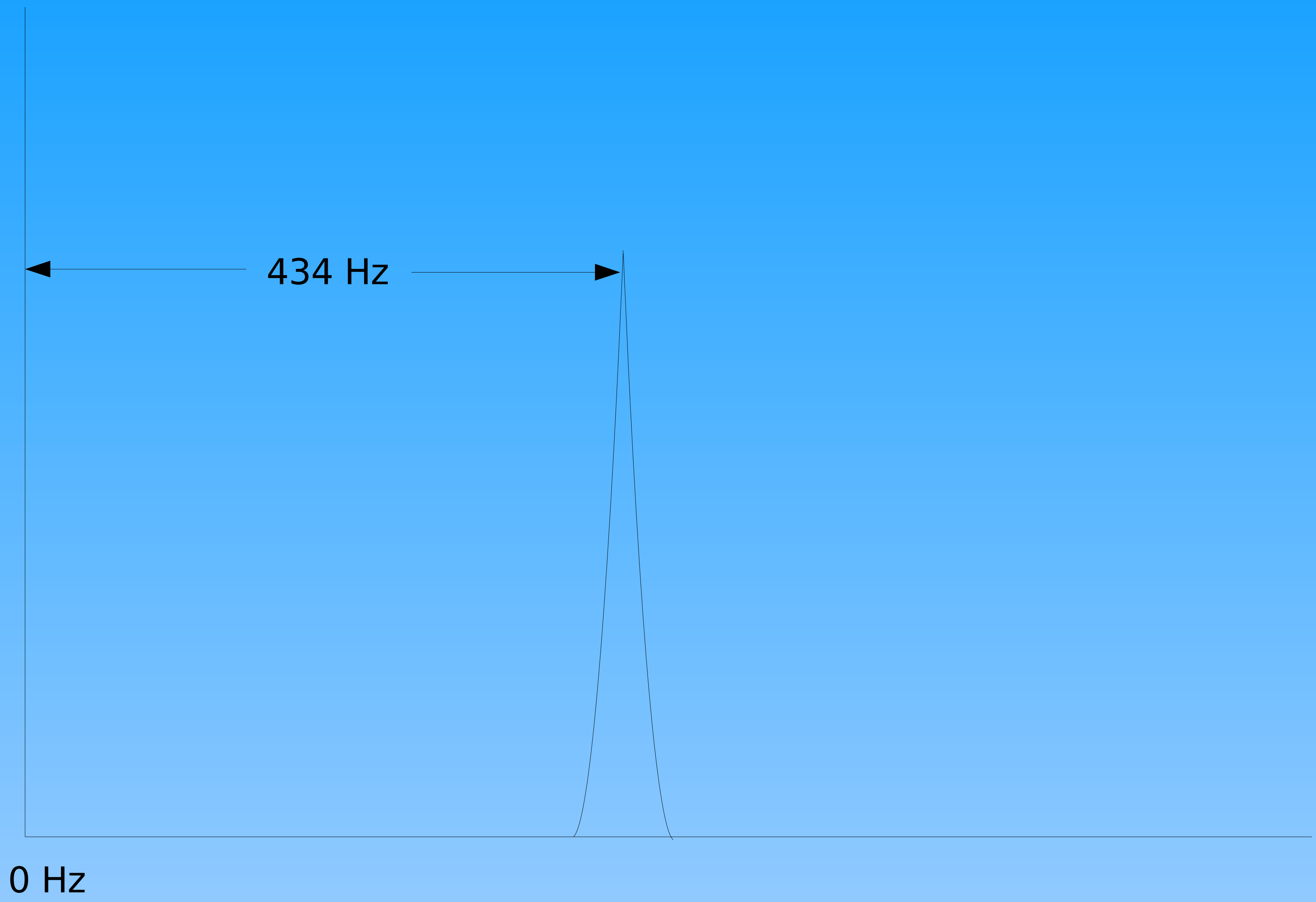
(Remember, these are difference frequencies not absolute frequencies)

The Digitizer or ADC

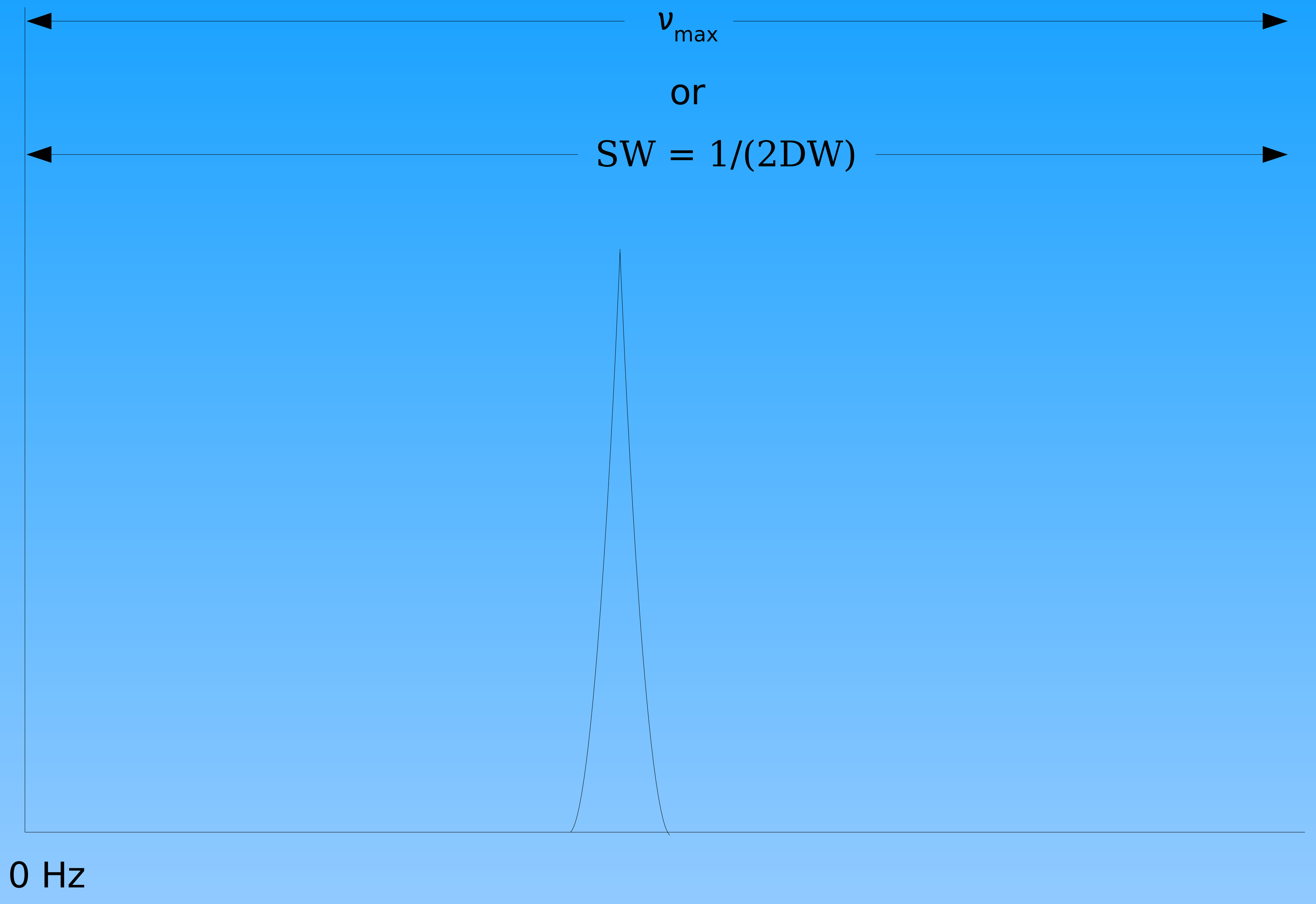


Difference frequency = 500.238279 – 500.237845 = 0.000434 Mhz = 434 Hz

The Digitizer or ADC

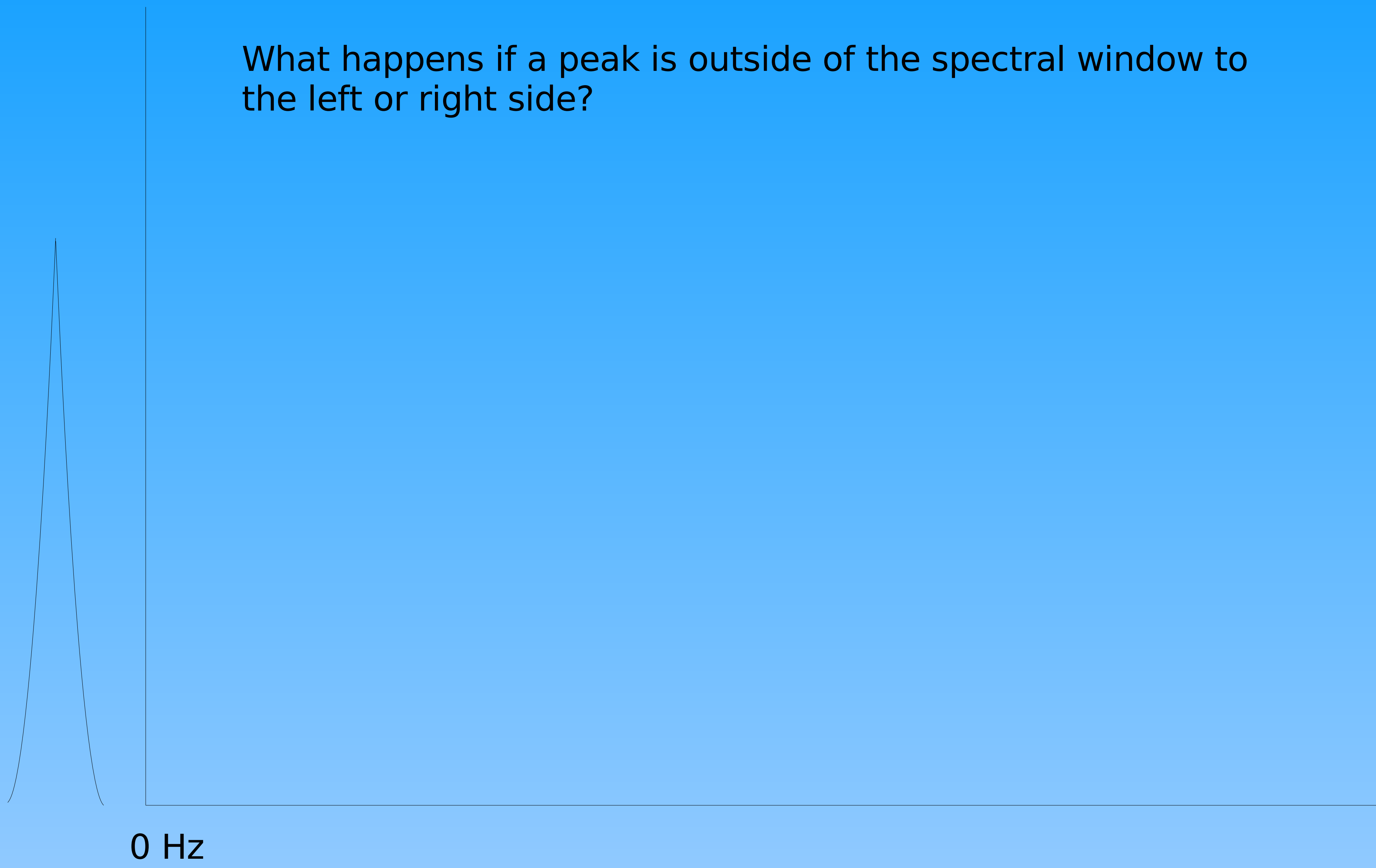


The Digitizer or ADC



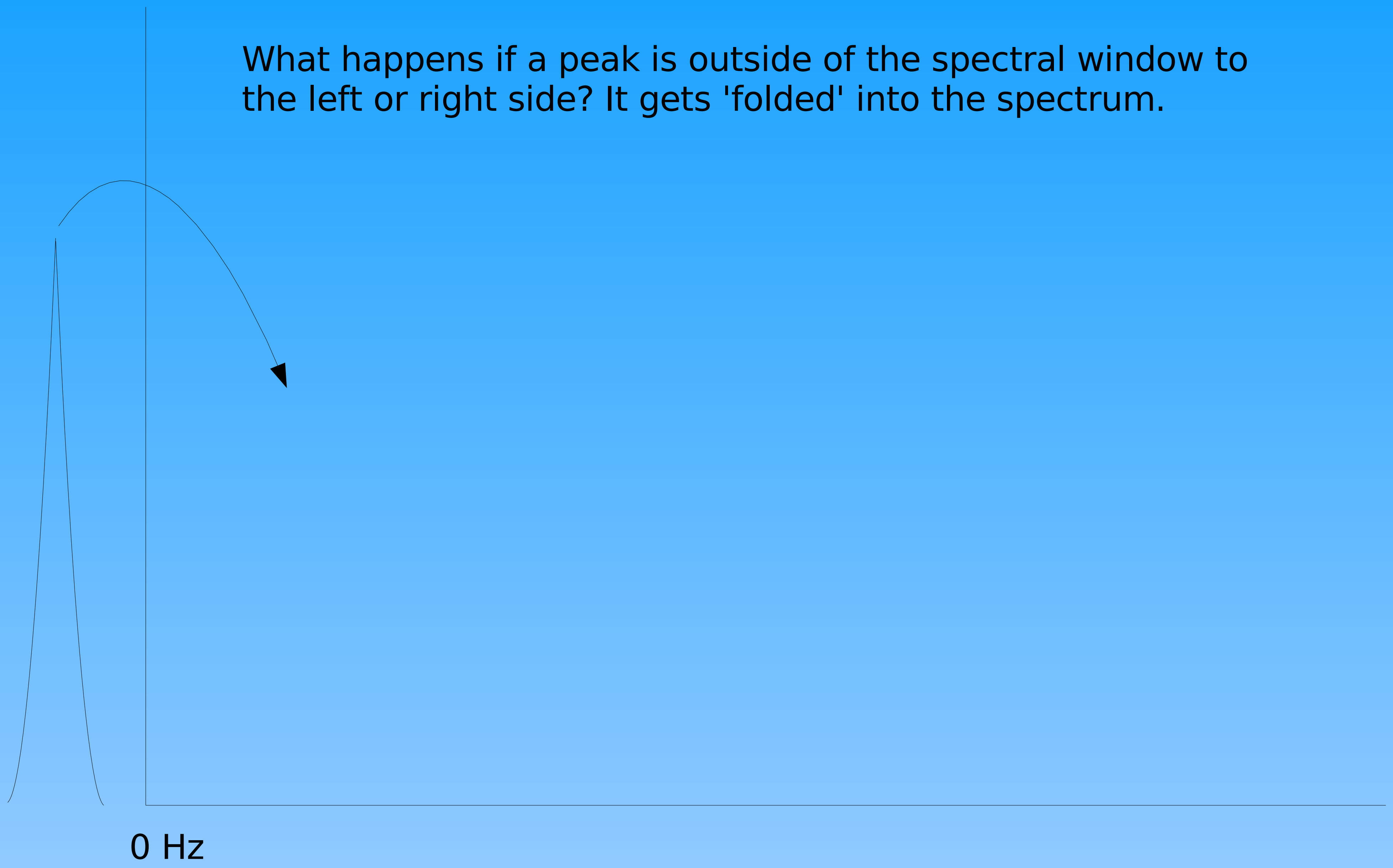
The Digitizer or ADC

What happens if a peak is outside of the spectral window to the left or right side?



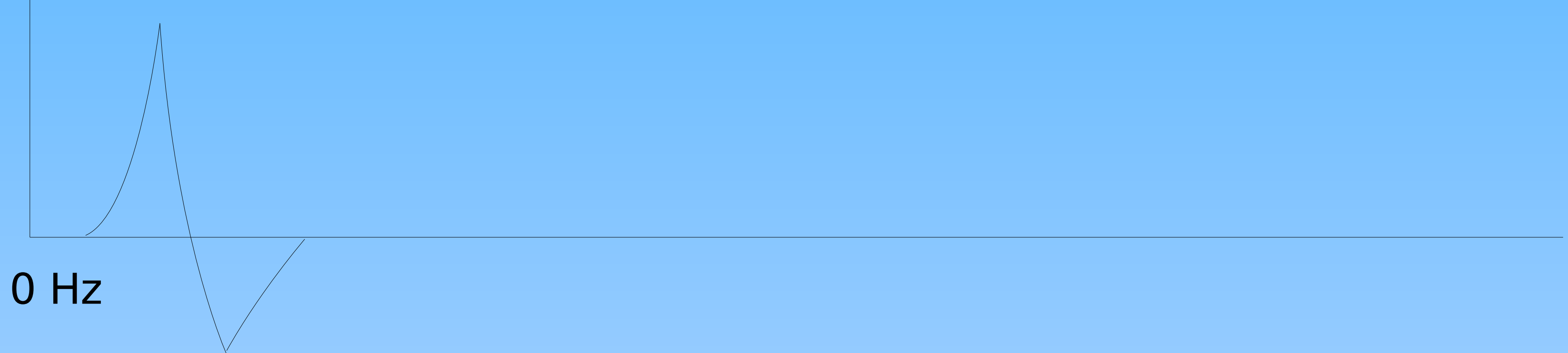
The Digitizer or ADC

What happens if a peak is outside of the spectral window to the left or right side? It gets 'folded' into the spectrum.



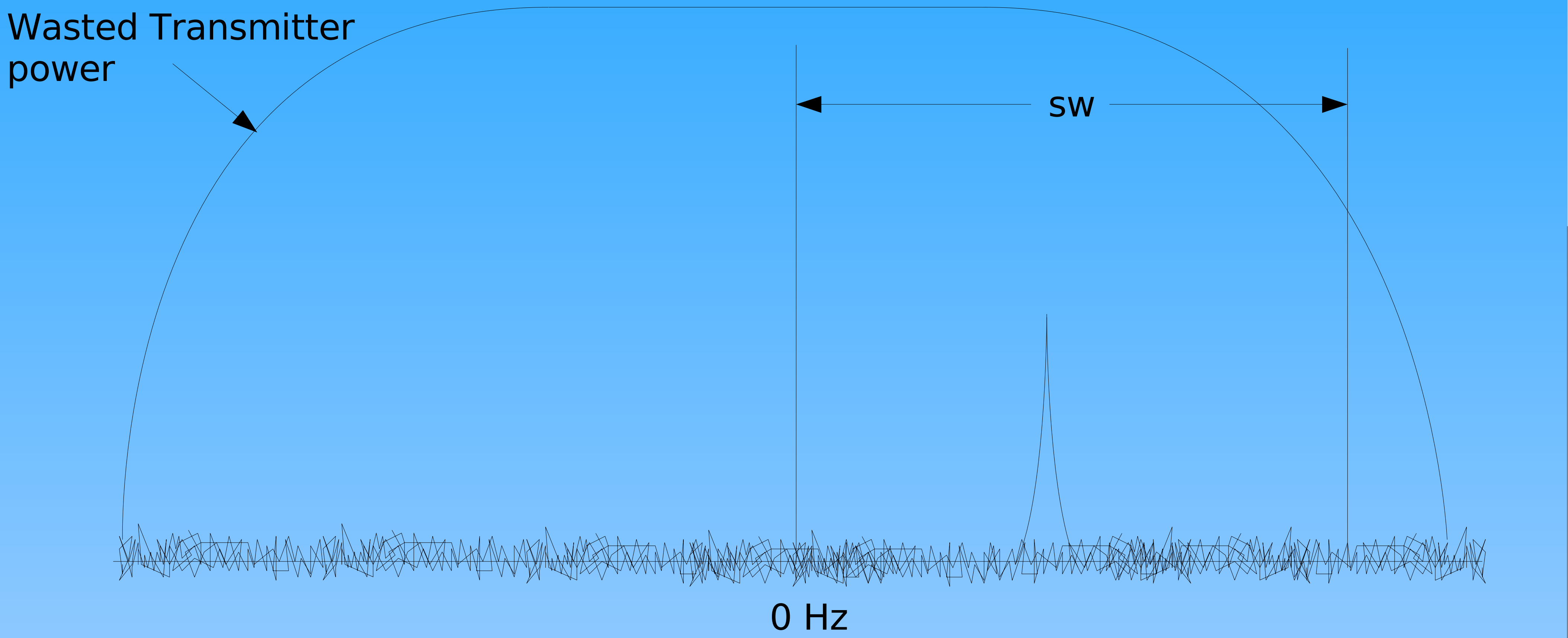
The Digitizer or ADC

The digitizer cannot differentiate between positive and negative frequency differences so the signal is digitized and appears at the wrong place in the spectrum and often it will not be possible to phase correct. In nmr spectroscopy this is called '*folding*' or more generally '*aliasing*'.



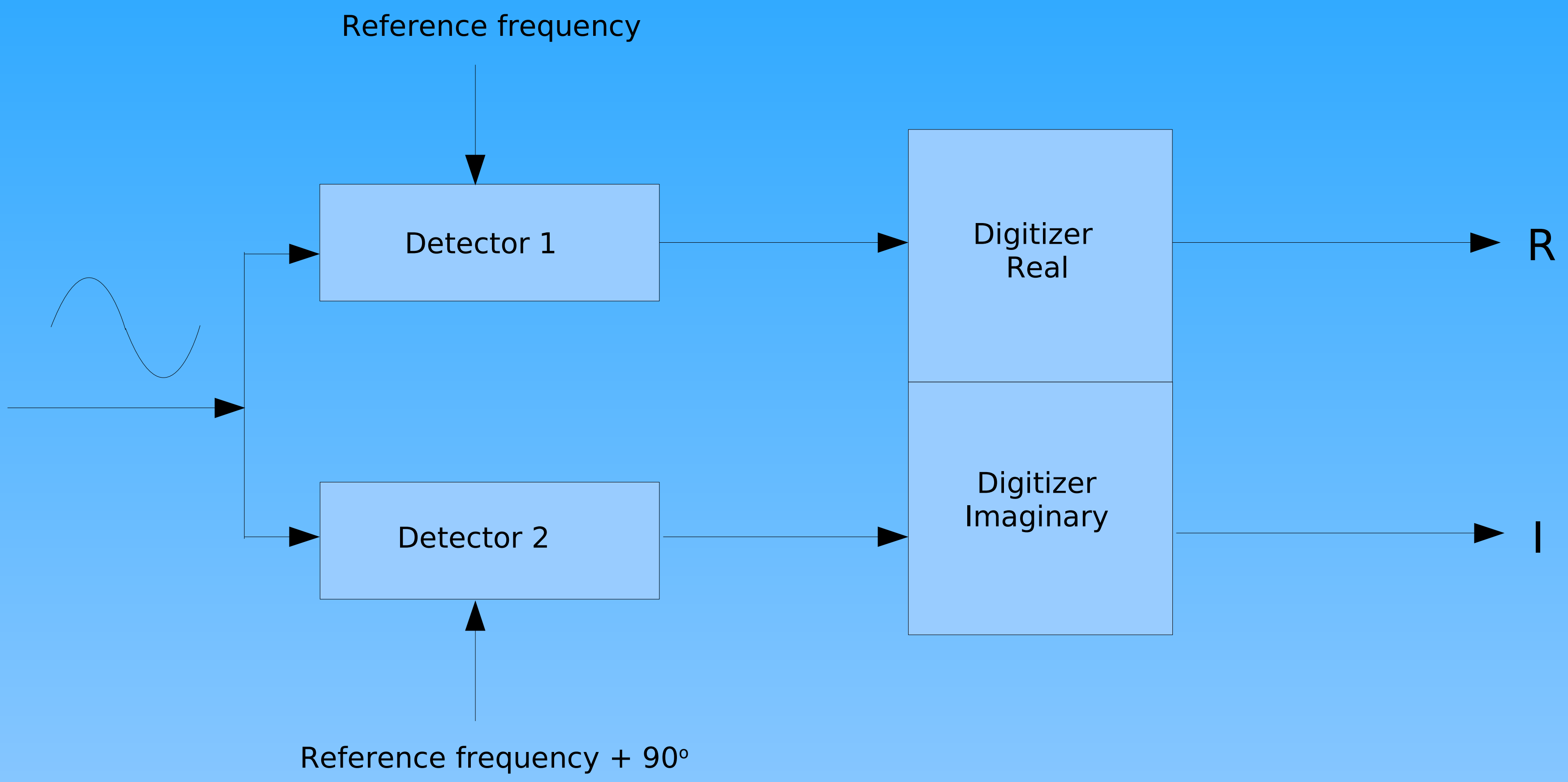
Quadrature Detection

Using the single detector model you have to be careful to position the left side of the spectrum (ie. the transmitter frequency) below the lowest expected frequency and make sure that the spectral window (SW) is large enough so that folding does not occur. These are not major problems as long as you are careful but there are other problems, waste of transmitter bandwidth being the major one.

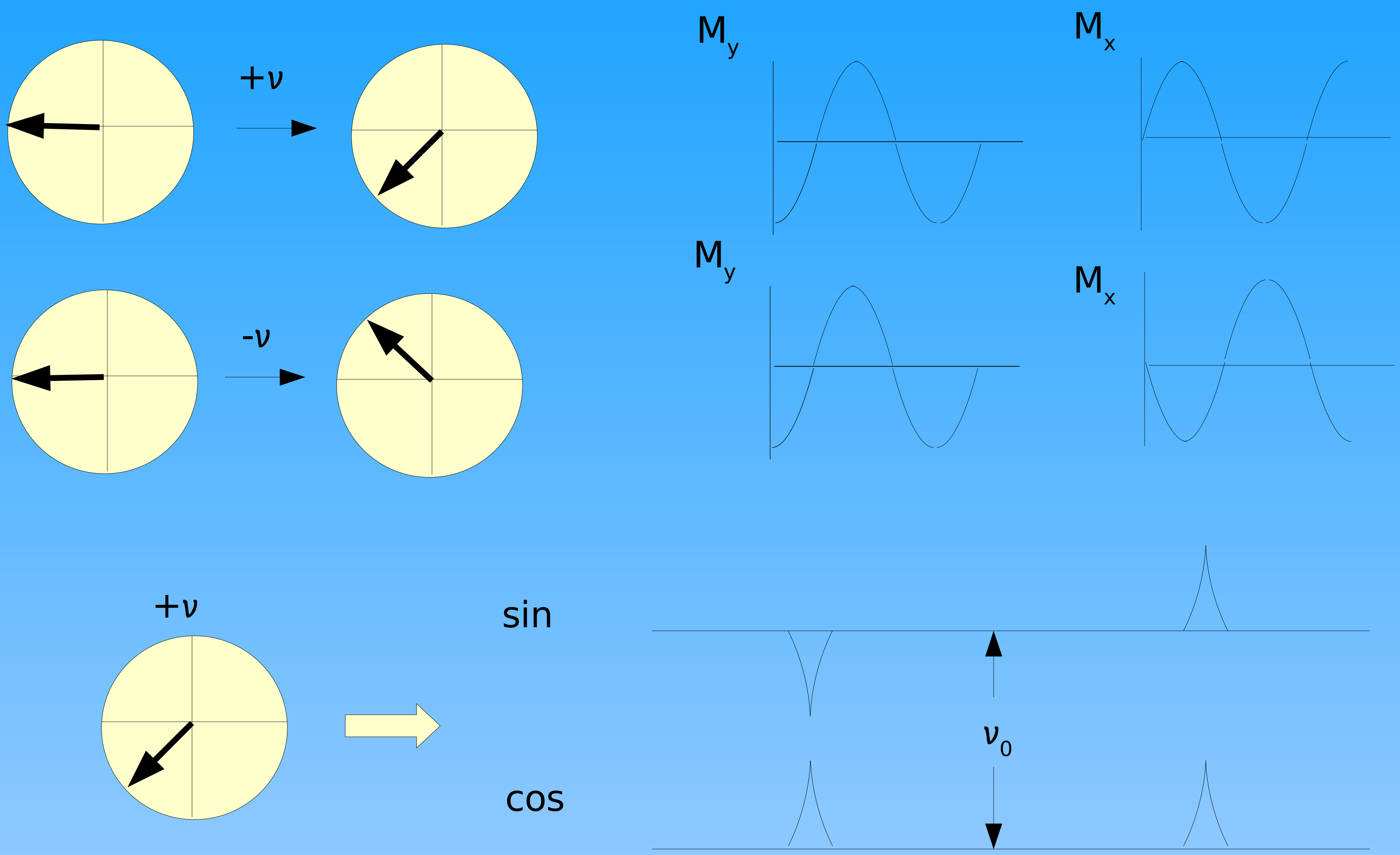


Quadrature Detection

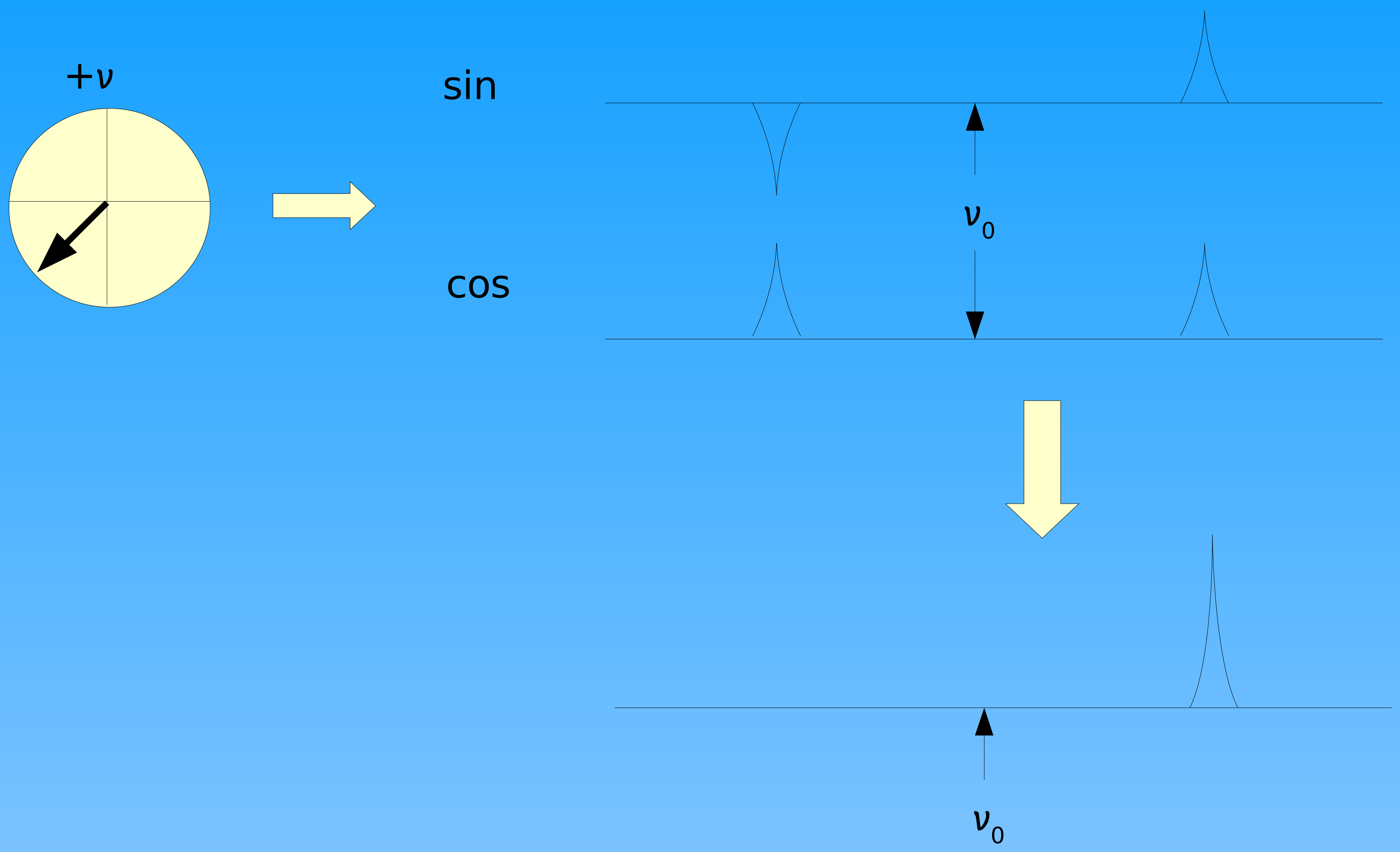
Quadrature detection helps us reduce noise folding, solves the problem with the detection of 'negative' frequencies and reduces wasted transmitter bandwidth. If two phase sensitive detectors are used we can determine the sign of the frequency.



Quadrature Detection

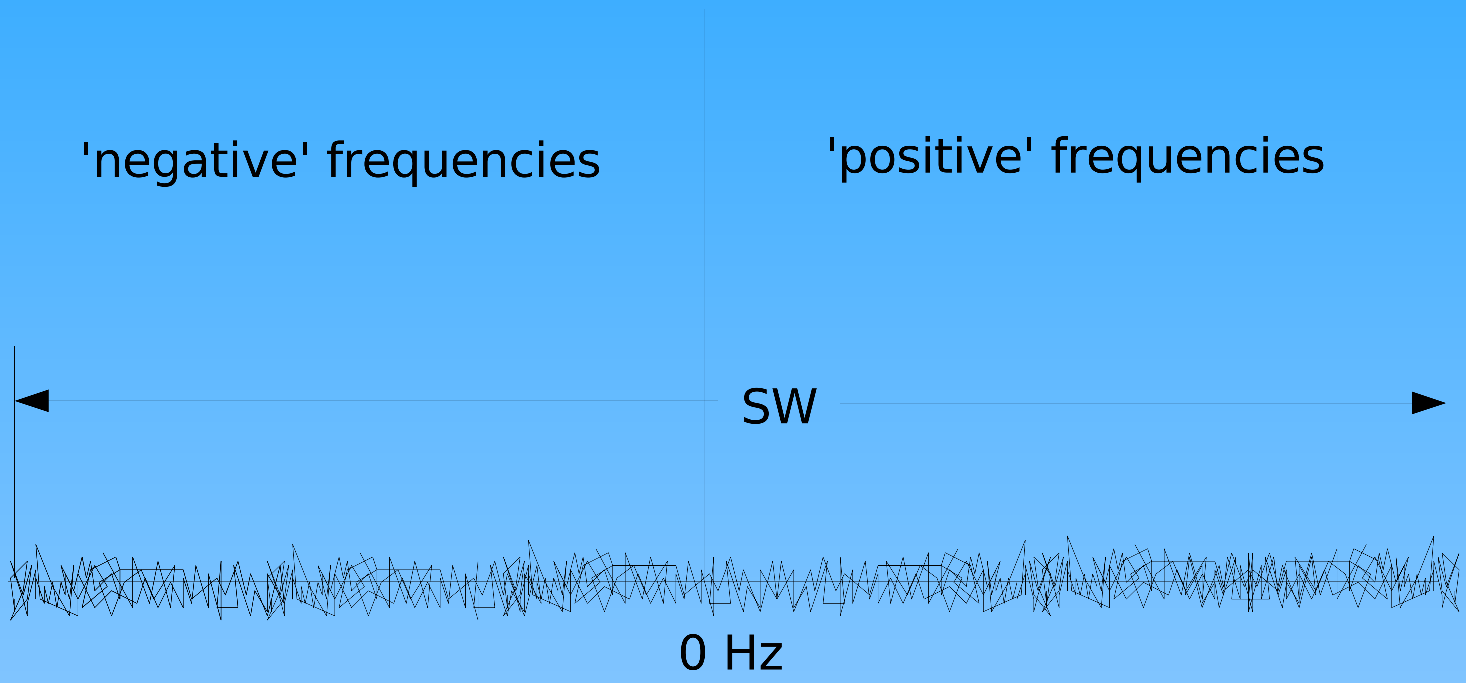


Quadrature Detection



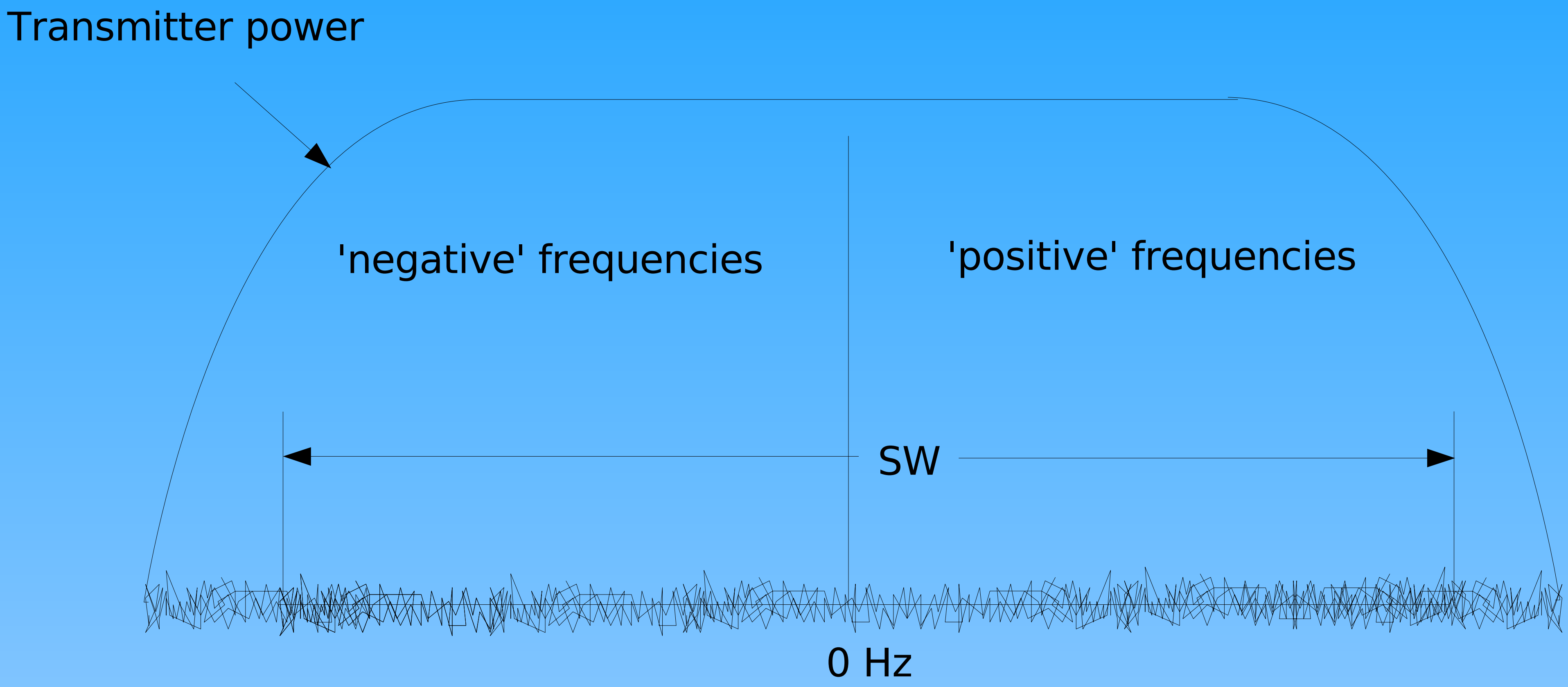
Quadrature Detection

We now place the transmitter frequency in the *center* of the spectrum and position peaks to the left or right of this based on their sign.



Quadrature Detection

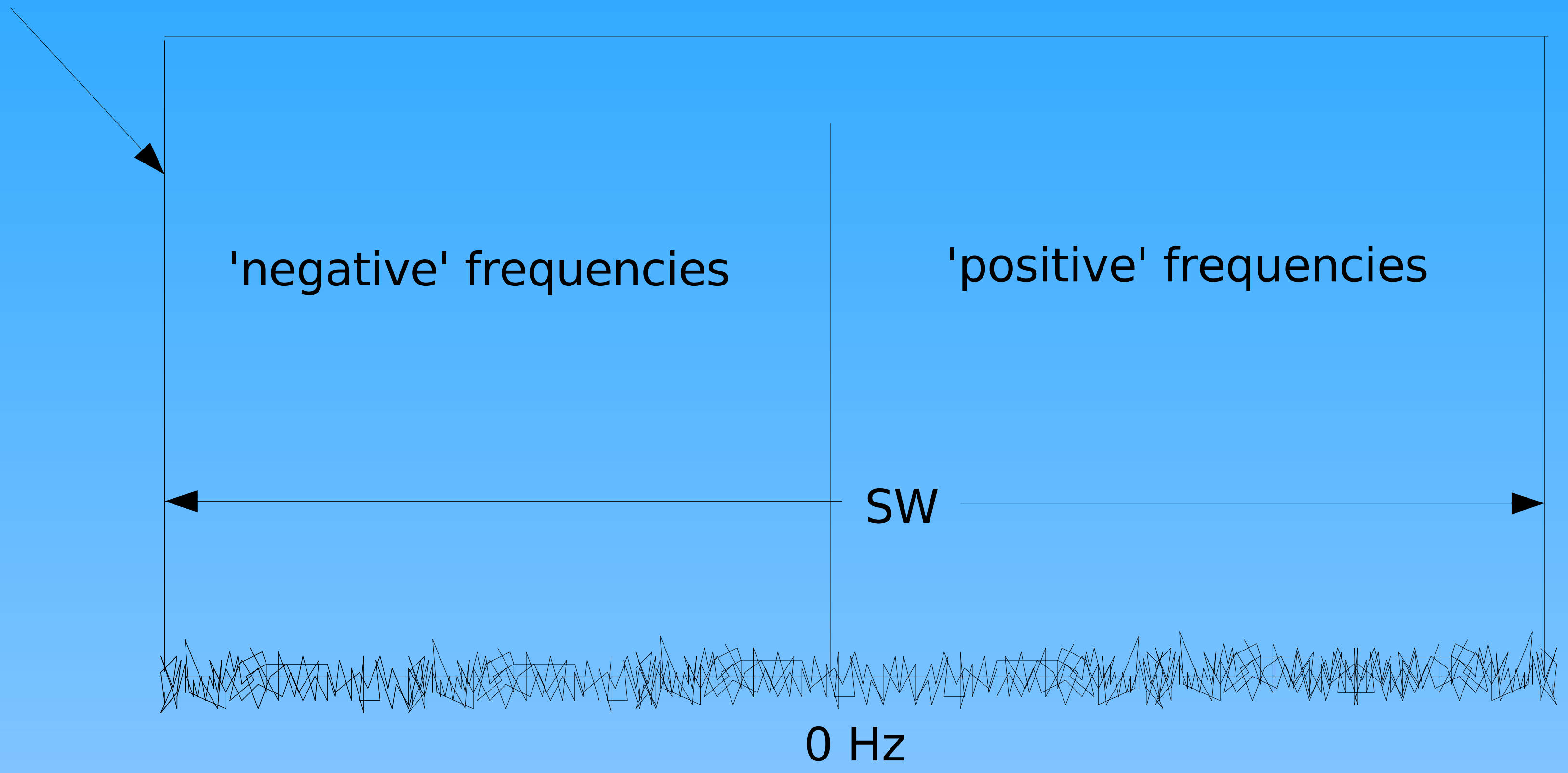
We now place the transmitter frequency in the *center* of the spectrum and position peaks to the left or right of this based on their sign.



Quadrature Detection

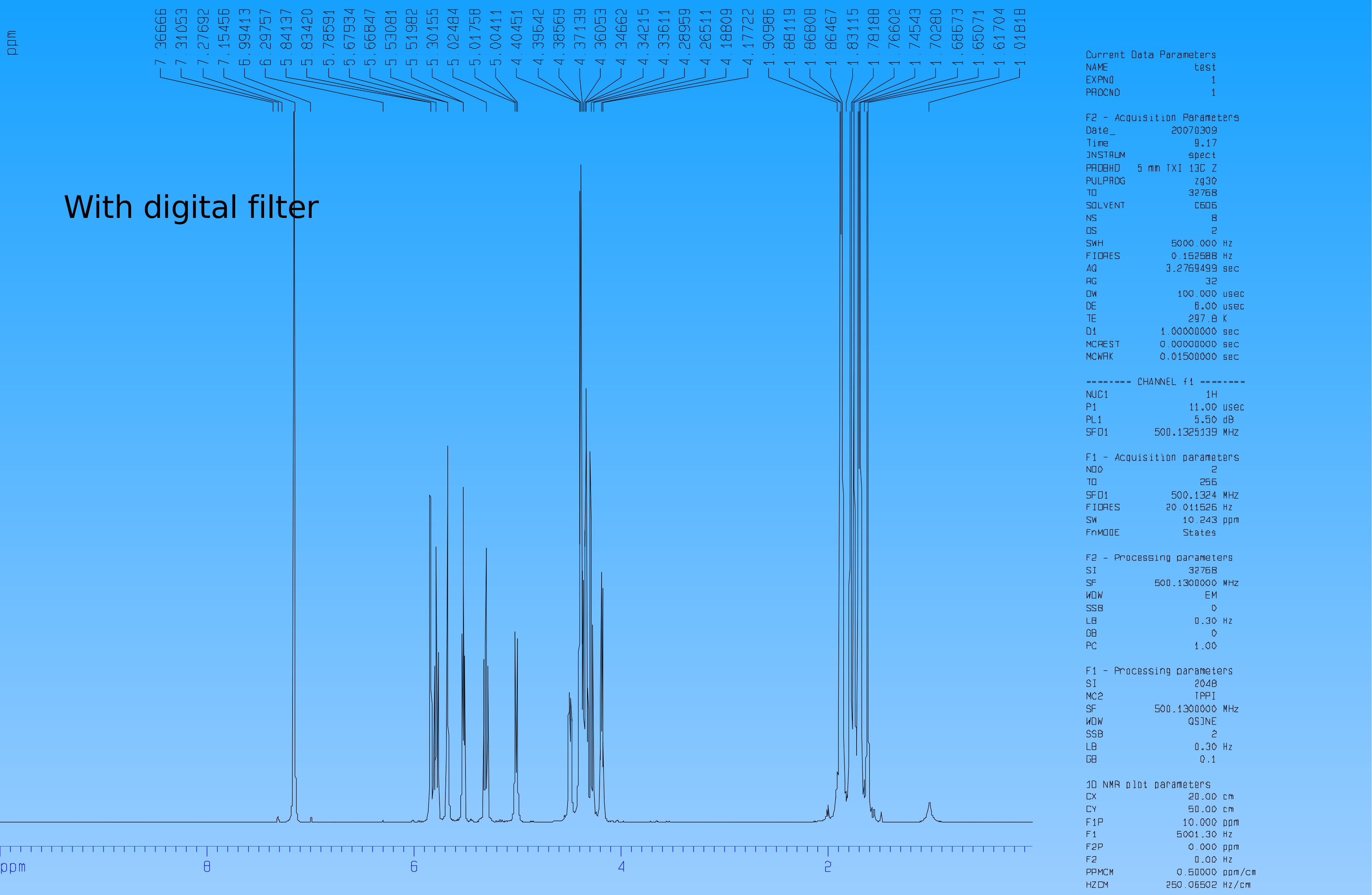
We now place the transmitter frequency in the *center* of the spectrum and position peaks to the left or right of this based on their sign.

Digital filter rolloff .. no noise folding!



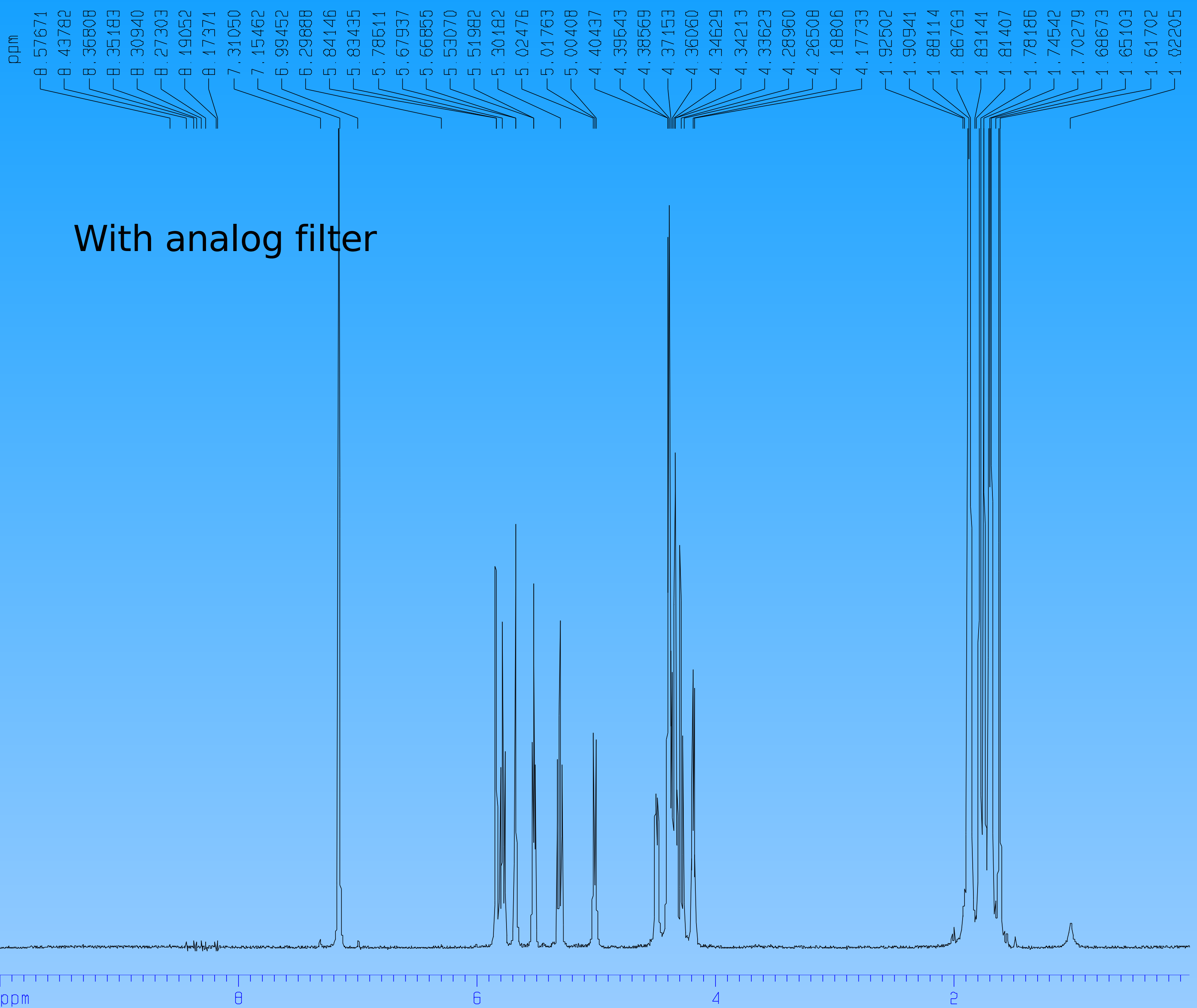
Quadrature Detection

With digital filter



Quadrature Detection

With analog filter



Current Data Parameters
NAME test
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PROCNO 1

F2 - Acquisition Parameters
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Time 9.21
INSTRUM spect
PROBHD 5 mm TXI 13C Z
PULPROG zg30
TD 32768
SOLVENT C6D6
NS 8
DS 2
SWH 5000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2769499 sec
RG 32
DW 100.000 usec
DE 142.86 usec
TE 298.6 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 5.50 dB
SFO1 500.1325139 MHz

F1 - Acquisition parameters
ND0 2
TD 256
SFO1 500.1324 MHz
FIDRES 20.011526 Hz
SW 10.243 ppm
FnMODE States

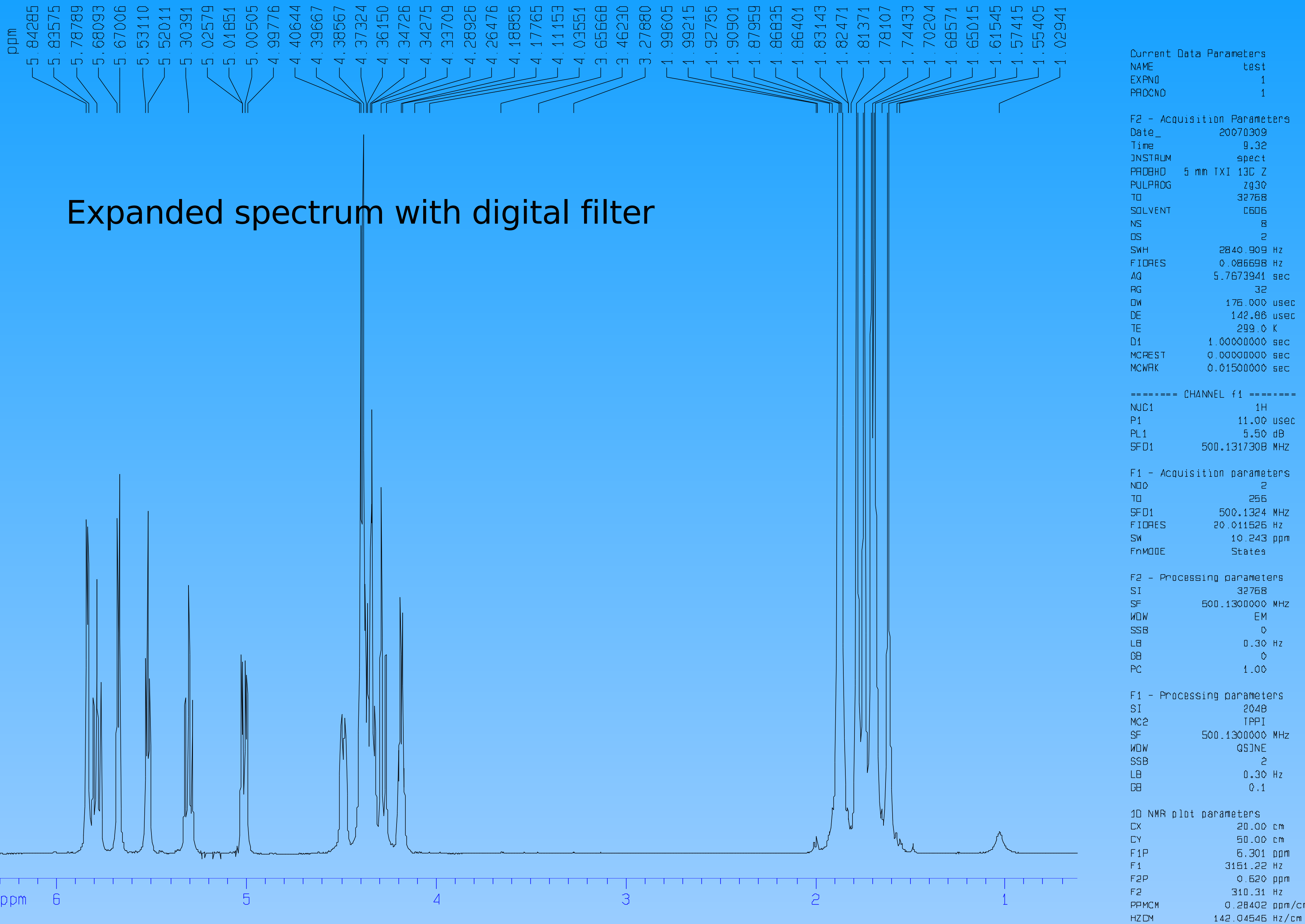
F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 2048
MC2 TPPI
SF 500.1300000 MHz
WDW QSINE
SSB 2
LB 0.30 Hz
GB 0.1

1D NMR plot parameters
CX 20.00 cm
CY 50.00 cm
F1P 10.000 ppm
F1 5001.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.50000 ppm/cm
HZCM 250.06502 Hz/cm

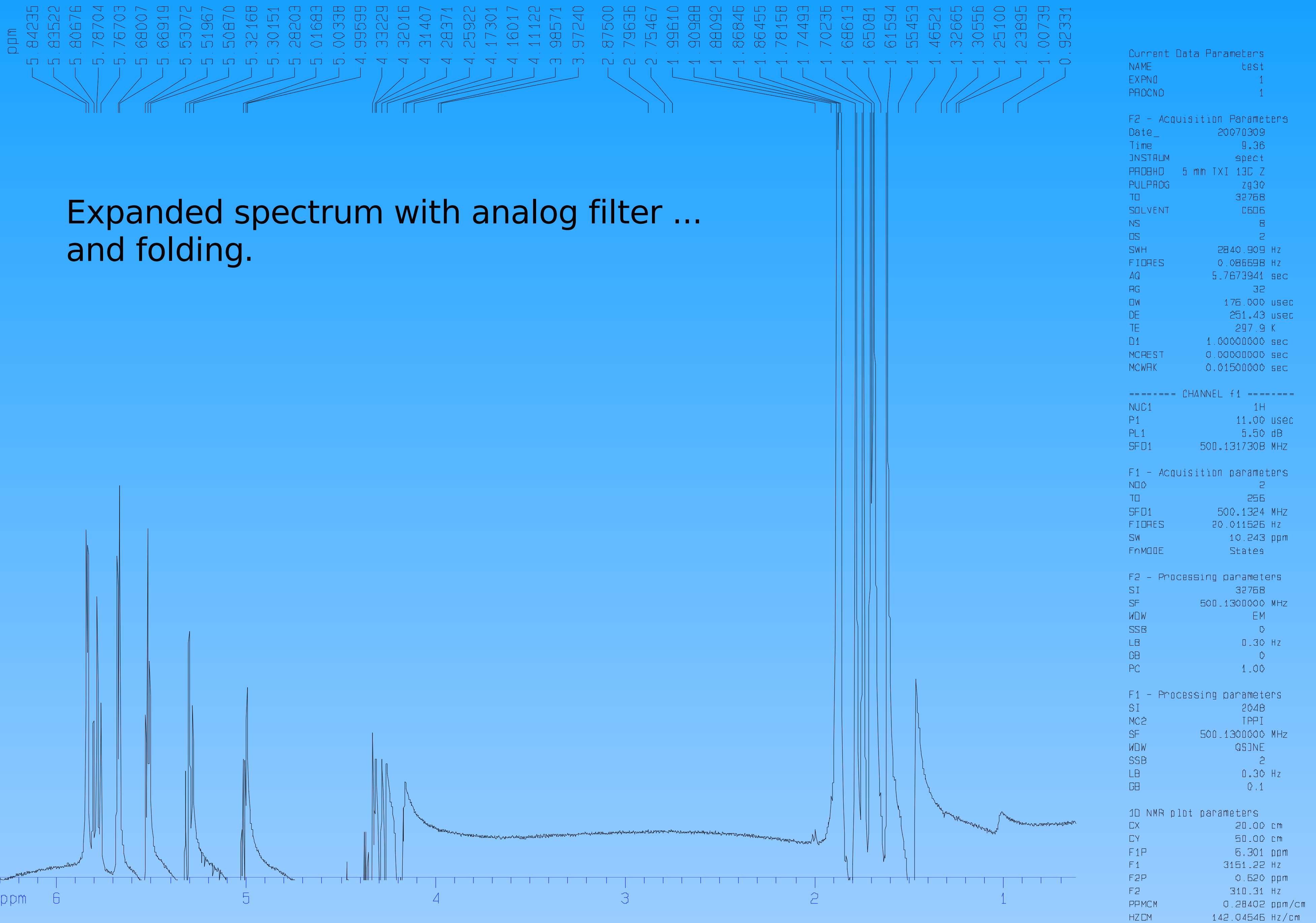
Quadrature Detection

Expanded spectrum with digital filter



Quadrature Detection

Expanded spectrum with analog filter ...
and folding.



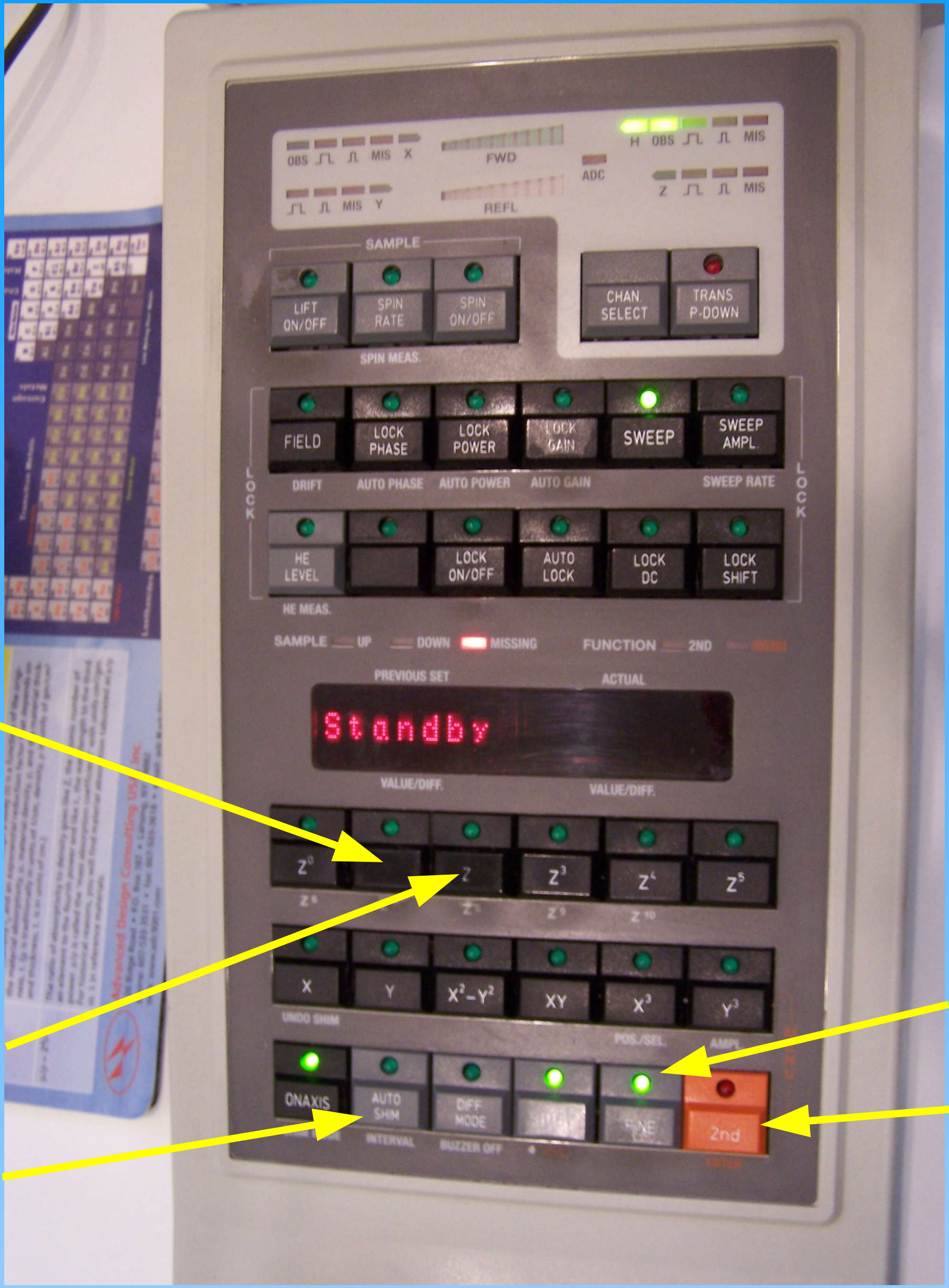
Magnet Shimming

The spectrometer magnet by itself cannot give us the resolution that we require. In order of have our spectral resolution at 1 hz or less we must make fine adjustments to the magnetic field ***homogeneity*** using the room-temperature shim coils.

The field that the sample experiences must be uniform throughout the bulk of the sample or the nuclei in the sample will precess with different Larmor frequencies leading to a broadening of lines and loss of resolution. So, in order to see a line with a linewidth of 0.5 Hz on a 500 MHz the field must not vary by more than 0.5 Hz over the bulk of the sample or by ***1 part per billion***. This is more than the main superconducting magnet is capable of achieving so the field must be adjusted with '**shims**'.

Magnet Shimming

Magnet Shimming



Z shim

Z^2 shim

Autoshim

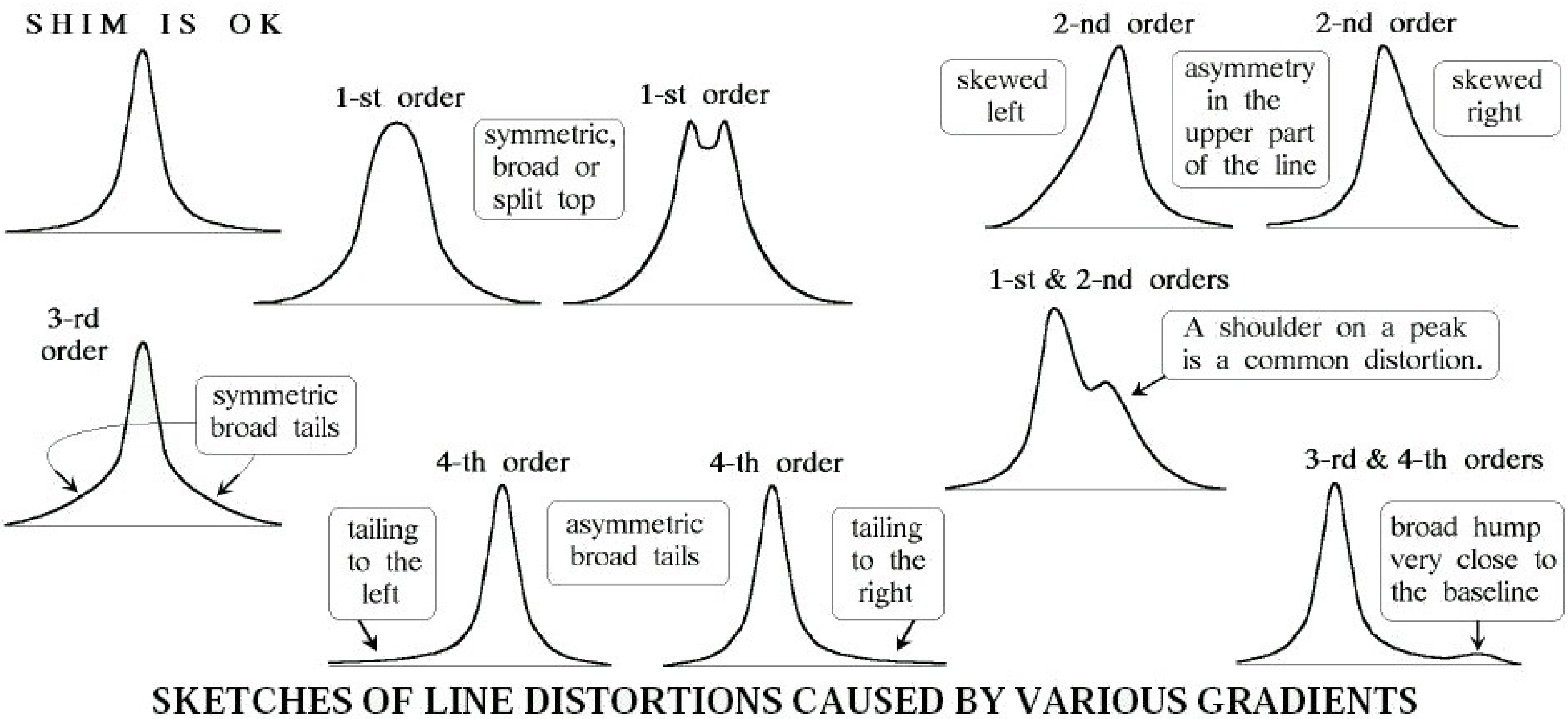
fine/course

2^{nd} function

Magnet Shimming

SHIM CONTROLS ON THE SPECTROMETERS					spinning/ non-spin	high/ low	odd/ even	order
FX-90Q	WM-360	MSL-300	AC-300	AMX-600				
Y	Z	Z	Z	Z	spinning	low	odd	1-st
C	Z^2	Z^2	Z^2	Z^2	spinning	low	even	2-nd
Y^3	Z^3	Z^3	Z^3 Z^5	Z^3 Z^5	spinning spinning	high high	odd odd	3-rd 5-th
F	Z^4	Z^4	Z^4	Z^4	spinning	high	even	4-th
Z X	X Y	X Y	X Y	X Y	non-spin non-spin	low low	odd odd	1-st 1-st
ZX XY YZ X^2-Y^2	XY YZ XZ X^2-Y^2	XY YZ XZ X^2-Y^2	XY YZ XZ X^2-Y^2	XY YZ XZ X^2-Y^2	non-spin non-spin non-spin non-spin non-spin	low low low low low	even even even even even	2-nd 2-nd 2-nd 2-nd 2-nd
X^3 Z^3	X^3 Y^3	X^3 Y^3 XZ^2 YZ^2	X^3 Y^3 XZ^2 YZ^2	X^3 Y^3 XZ^2 YZ^2 ZXY $Z(X^2-Y^2)$	non-spin non-spin non-spin non-spin non-spin non-spin	high high high high high high	odd odd odd odd odd odd	3-rd 3-rd 3-rd 3-rd 3-rd 3-rd
				XZ^3 YZ^3	non-spin non-spin	high high	even even	4-th 4-th
Y	Z				<--- spinning axis for NMR tubes			

Magnet Shimming



Sensitivity

Sensitivity is of primary concern to nmr spectroscopists. NMR is **not** a very sensitive technique to begin with so most technical advances are concerned with increasing sensitivity as measured by the signal-to-noise ratio (S/N).

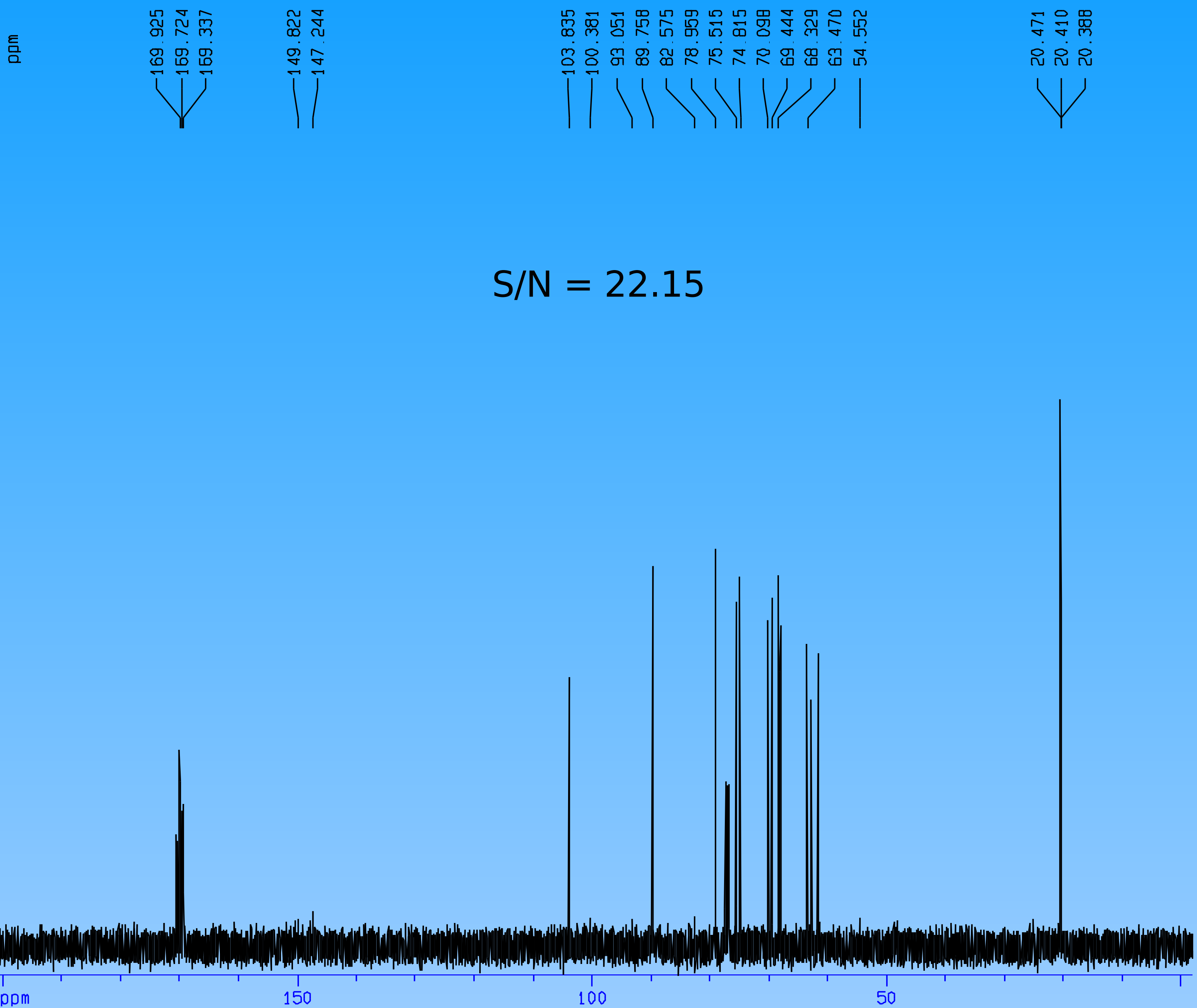
The first major advance was to move from CW spectrometers to FT spectrometers. Instead of scanning through resonances in much the same way as on a uv-vis spectrometer, one can irradiate all resonances simultaneously with a pulse of rf radiation. To this was added the ability to co-add multiple scans together into a computer's memory.

Co-addition of scans results in a S/N enhancement of $N^{1/2}$ where N is the number of scans. Thus, to double the S/N it is necessary to ***quadruple*** the number of scans.

Quadrature detection improves S/N by $2^{1/2}$ as a result of addition of sine and cosine terms.

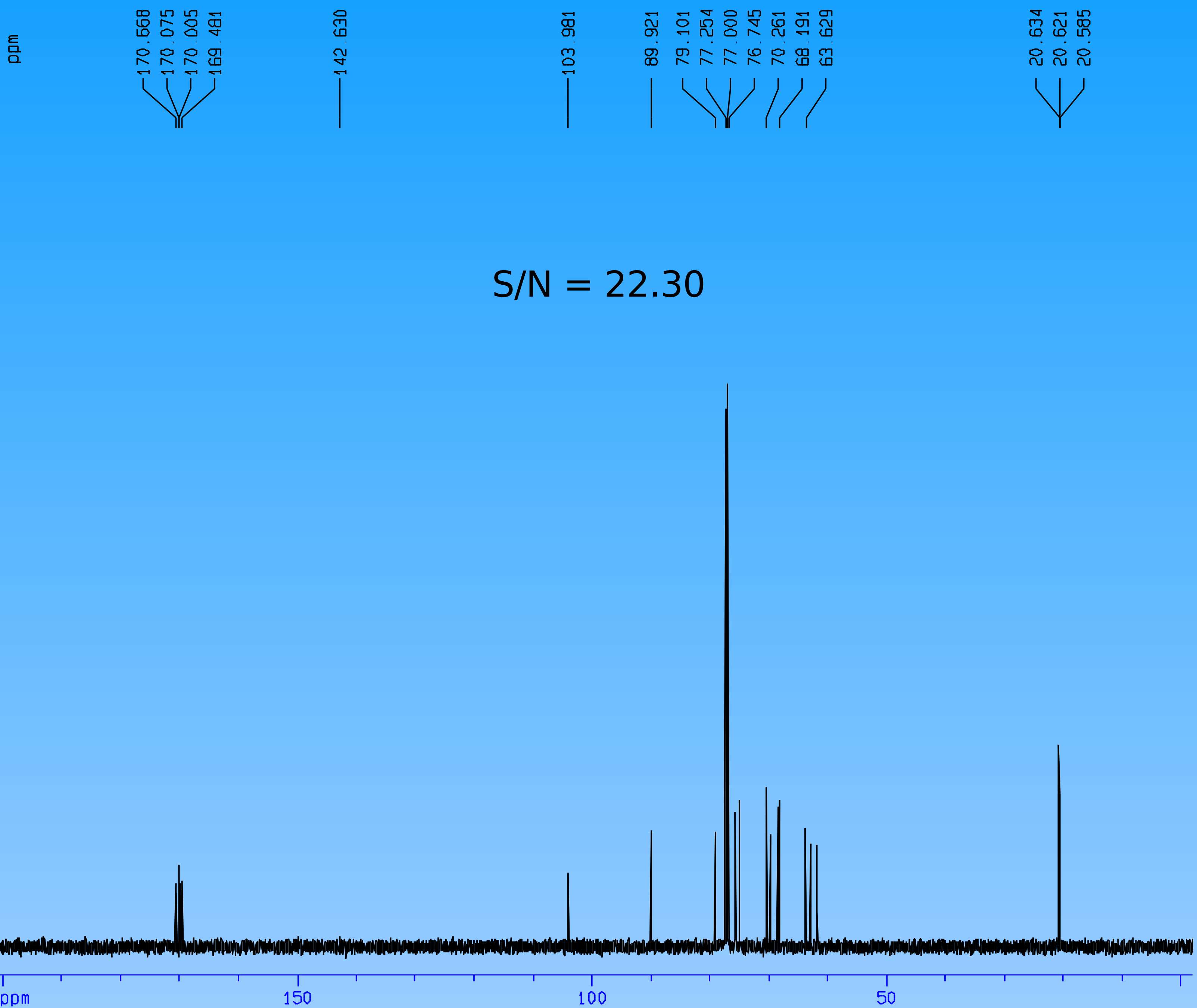
Digital filtering removes folded noise. This is a bit of a double-edged sword in that it increases S/N but it will also remove legitimate peaks outside of the spectral window.

Sensitivity



Current Data Parameters		
NAME	100mgSoAc	
EXPNO	2	
PROCNO	1	
F2 - Acquisition Parameters		
Date_	20020121	
Time	14.13	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg	
TD	65536	
SOLVENT	CDCl3	
NS	8	
DS	4	
SWH	30030.029	Hz
FIDRES	0.458222	Hz
AQ	1.0912244	sec
RG	1149.4	
DW	16.650	usec
DE	6.00	usec
TE	300.0	K
D1	3.00000000	sec
d11	0.03000000	sec
d12	0.00002000	sec
======== CHANNEL f1 ========		
NUC1	13C	
P1	5.10	usec
PL1	-1.00	dB
SFO1	125.7954618	MHz
-------- CHANNEL f2 --------		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	70.00	usec
PL2	-1.00	dB
PL12	14.00	dB
PL13	14.00	dB
SFO2	500.2320009	MHz
F2 - Processing parameters		
SI	32768	
SF	125.7829854	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	
1D NMR plot parameters		
CX	20.00	cm
CY	10.00	cm
F1P	200.418	ppm
F1	25209.17	Hz
F2P	-1.962	ppm
F2	-246.75	Hz
PPMCM	10.11898	ppm/cm
HZCM	1272.79602	Hz/cm

Sensitivity



Current Data Parameters

NAME	11mg5oAc
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20020121
Time	14.19
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg
TD	65536
SOLVENT	CDCl3
NS	454
DS	4
SWH	30030.029 Hz
FIDRES	0.458222 Hz
AQ	1.0912244 sec
RG	1149.4
DW	16.650 usec
DE	6.00 usec
TE	300.0 K
D1	3.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec

======== CHANNEL f1 ========

NUC1	13C
P1	5.10 usec
PL1	-1.00 dB
SFO1	125.7954618 MHz

-------- CHANNEL f2 --------

CPDPRG2	waltz16
NUC2	1H
PCPD2	70.00 usec
PL2	-1.00 dB
PL12	14.00 dB
PL13	14.00 dB
SFO2	500.2320009 MHz

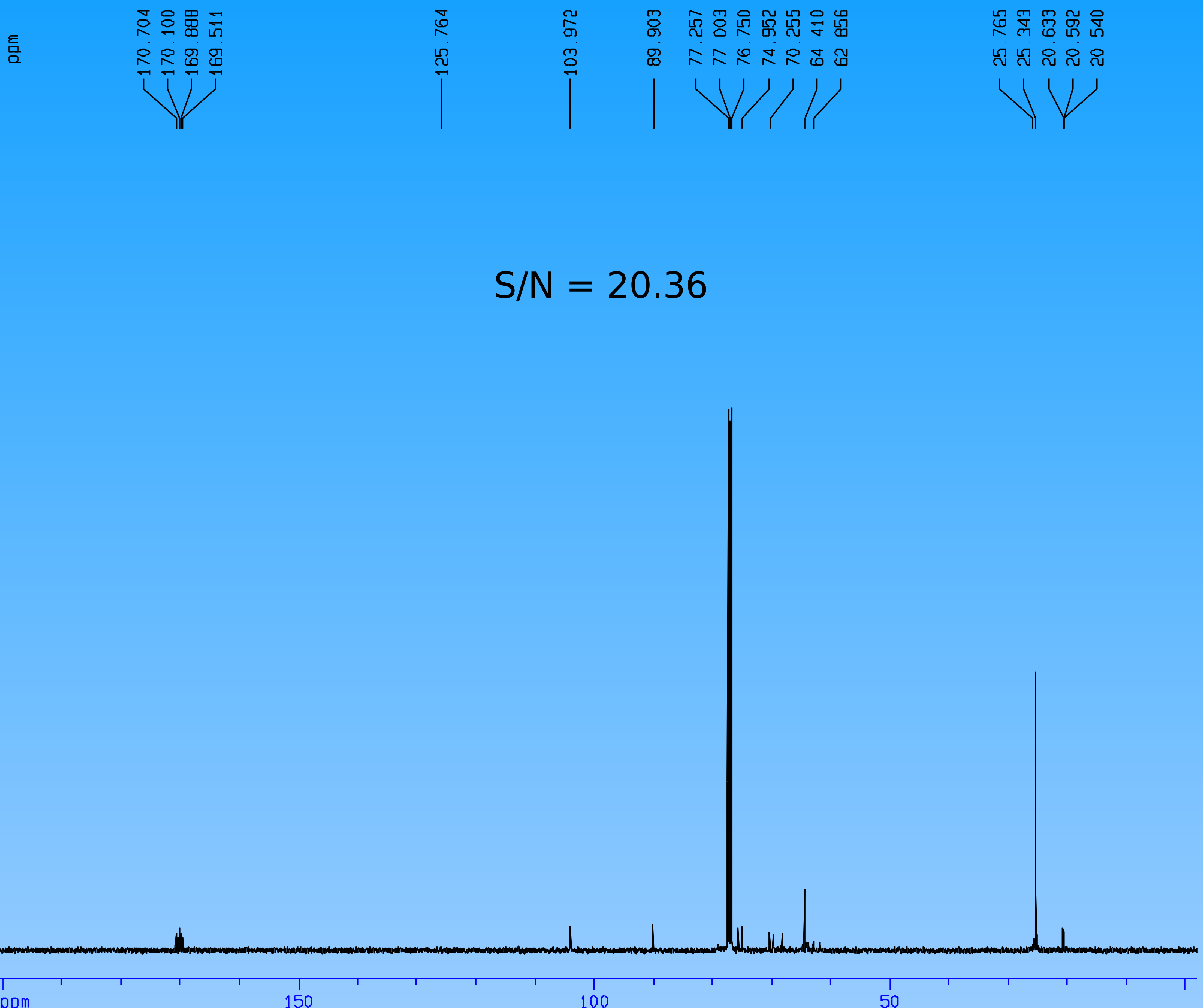
F2 - Processing parameters

SI	32768
SF	125.7829735 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
CY	10.00 cm
F1P	200.418 ppm
F1	25209.16 Hz
F2P	-1.962 ppm
F2	-246.75 Hz
PPMCM	10.11898 ppm/cm
HZCM	1272.79590 Hz/cm

Sensitivity



Current Data Parameters
NAME 2mg5oAc
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020122
Time 9.31
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 3923
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912244 sec
RG 1149.4
DW 16.650 usec
DE 6.00 usec
TE 300.0 K
D1 3.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 5.10 usec
PL1 -1.00 dB
SFO1 125.7954618 MHz

-------- CHANNEL f2 --------
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 -1.00 dB
PL12 14.00 dB
PL13 14.00 dB
SFO2 500.2320009 MHz

F2 - Processing parameters
SI 32768
SF 125.7829735 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 200.418 ppm
F1 25209.16 Hz
F2P -1.962 ppm
F2 -246.75 Hz
PPMCM 10.11898 ppm/cm
HZCM 1272.79590 Hz/cm

References
(all available in the Natural Sciences library except *)

Introductory with little math:

Sanders and Hunter, *Modern NMR Spectroscopy: A Guide for Chemists*.
Derome, *Modern NMR Techniques for chemistry research*.

Intermediate with lots of relatively simple math:

Levitt, *Spin Dynamics.*
Keeler, *Understanding NMR Spectroscopy.*

Advanced .. *insane* math:

Slichter, *Principles of Magnetic Resonance*.
Ernst, Bodenhausen, Wokaun, *Principles of Nuclear Magnetic Resoance in One and Two Dimensions*.

Practical information:

*Braun, Kalinowski, Berger, *200 and More Basic NMR Experiments*.
Fukushima, Roeder, *Experimental Pulse NMR; A Nuts and Bolts Approach*.

My Website:

http://chem4823.usask.ca/nmr/practical_nmr.html