Signals and Spectra

CHEM 6154 – Nuclear Magnetic Resonance

Marcel Utz

January 26, 2020

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- how acquisition and processing parameters are chosen;
- how imperfections and artefacts affect NMR spectra.

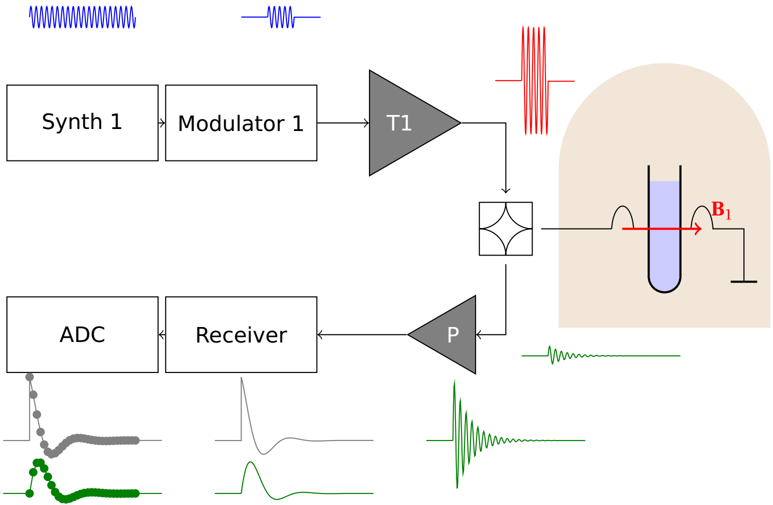
3 | Outline

Detection and Data Processing

Processing NMR Data

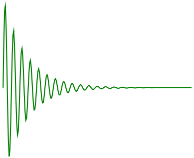
Recapitulation

4 | Block Diagram



5 | Quadrature Detection

NMR Signal



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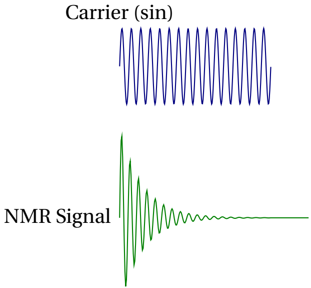

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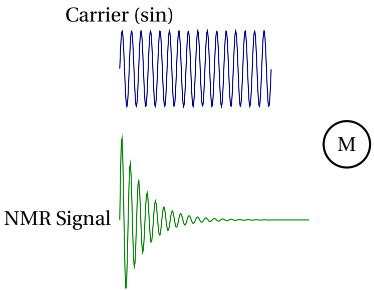

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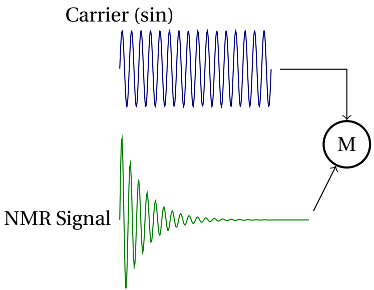

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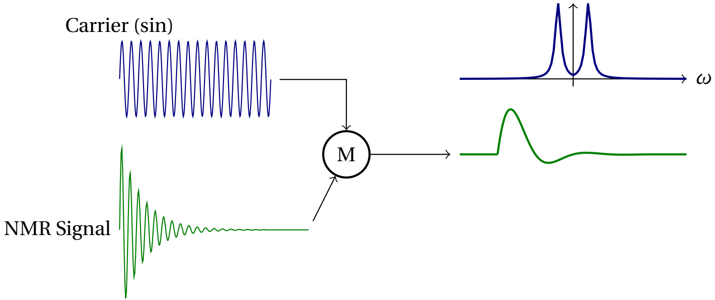

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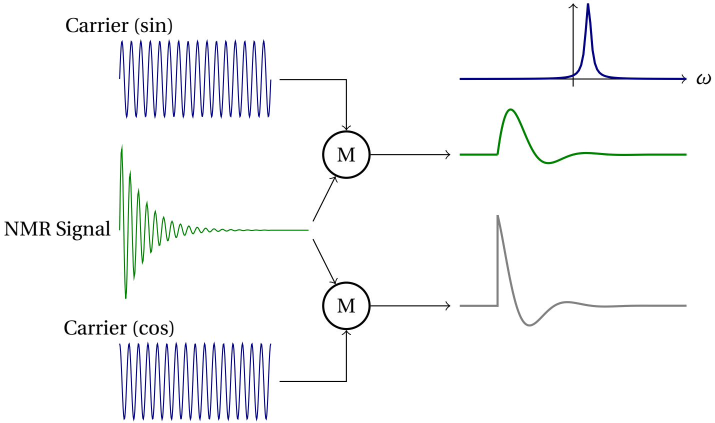
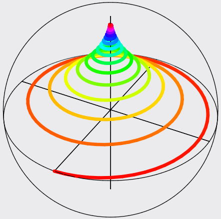


6 | Free induction decay

Magnetisation precession



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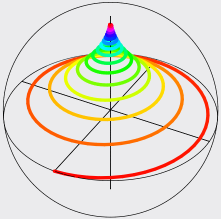

NMR Signal

$$S^{-}(t) = S_x(t) - iS_y(t)$$

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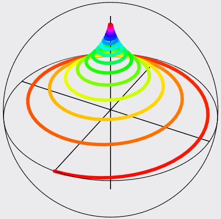

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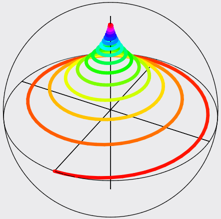

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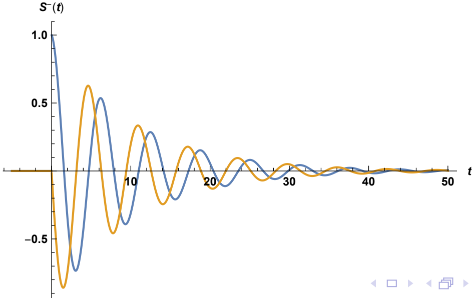
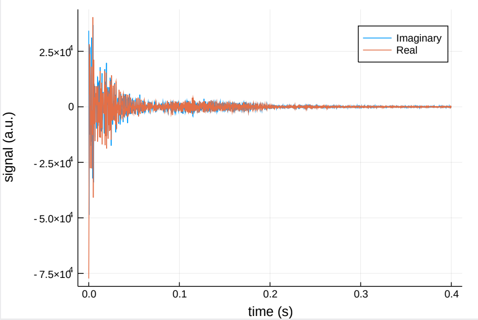
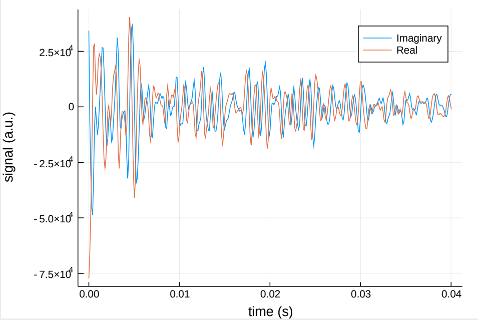


7 | A real example

Raw Spectrometer Data



Zoom



Acquisition parameters

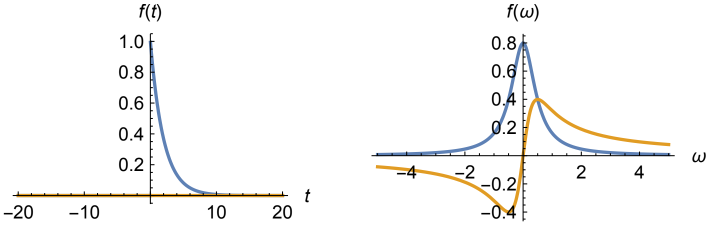
14.1 T magnet, ^{1}H signal, $\pi/2$ pulse, 500 ms acquisition time, microfluidic chip with 2.5 μl cell culture, 8192 complex data points.

8 | The Fourier Transform

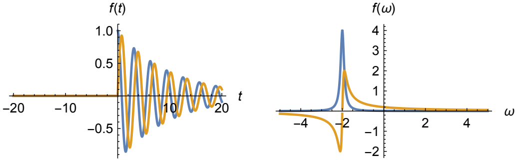
Definition

The Fourier transform $F : f(t) \longrightarrow \hat{f}(\omega)$ is defined by the integral transformation

$$\hat{f}(\omega) = \int_{-\infty}^{\infty} e^{-i\omega t} f(t)\,\mathrm{d}t.$$



9 | Fourier Transform of Oscillatory Functions

Negative frequency	Positive frequency
	

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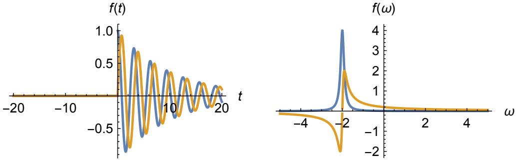

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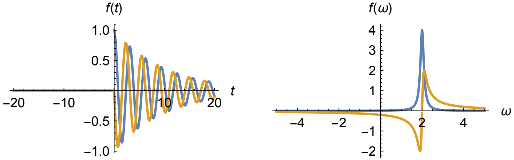

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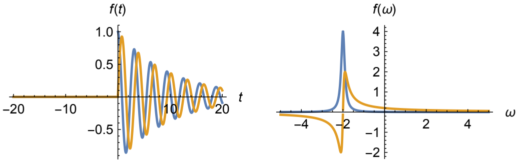

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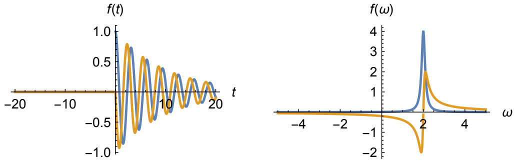
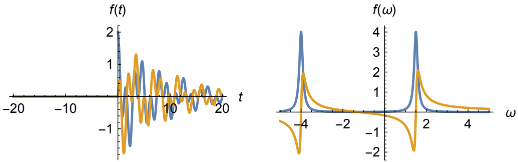
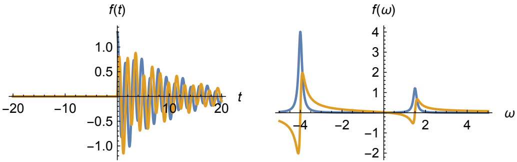


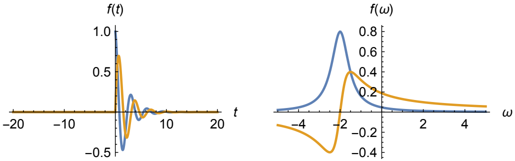
Two frequencies



Unequal intensities



10 | Decay Time and Resolution

Rapid decay	Slow decay
	

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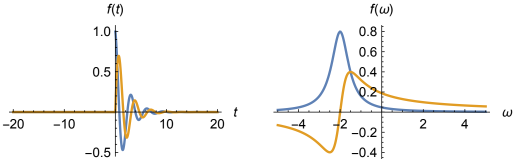
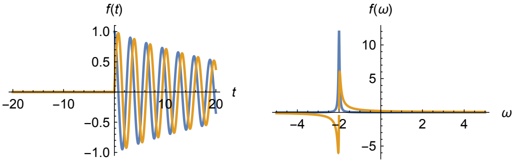


Slow decay



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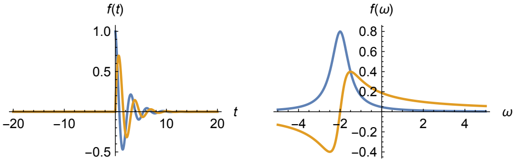
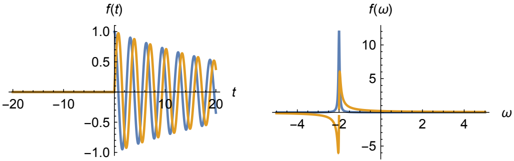
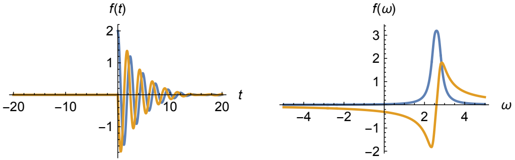


Slow decay



Two frequencies short



Two frequencies long

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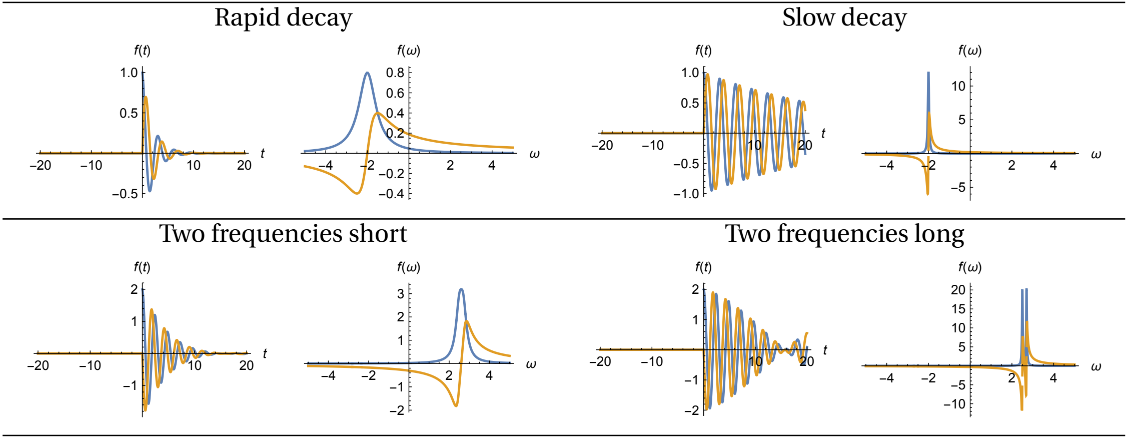


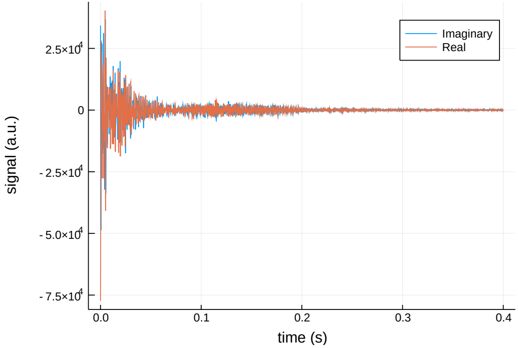
11 | Properties of the Fourier Transform

Linear: $F[g(t)+h(t)] = g(\omega)+h(\omega)$

Complete: $F^{-1}[g(\omega)] = g(t)$

Conservative: $\int_{-\infty}^{\infty} f^*(t) f(t)\, dt = \int_{-\infty}^{\infty} f^*(\omega) f(\omega)\, dt$

12 | Fourier Tranformation of Digitized Data



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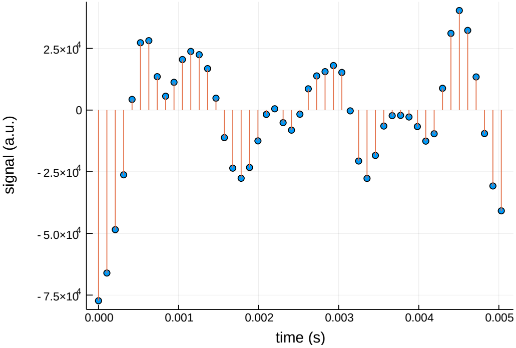

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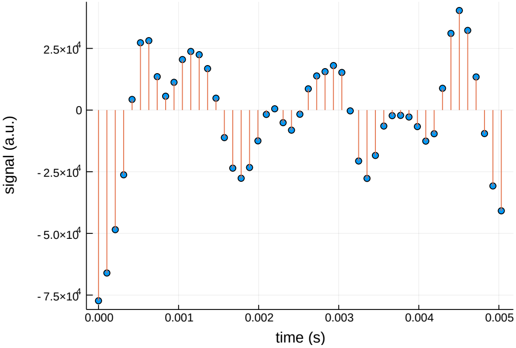

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Digital FID data

- n individual complex data points $f_1, f_2, \ldots, f_n$
- separated by equal intervals δt (time resolution)
- total acquisition time (time window) $\Delta t = n\,\delta t$

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Nyquist Theorem

The *spectral window* is given by the inverse of the time resolution.
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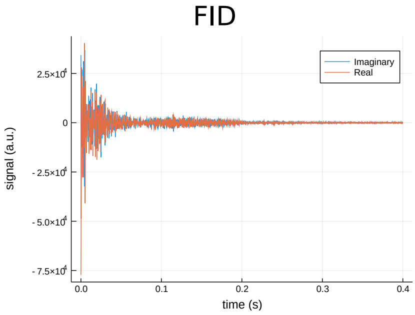
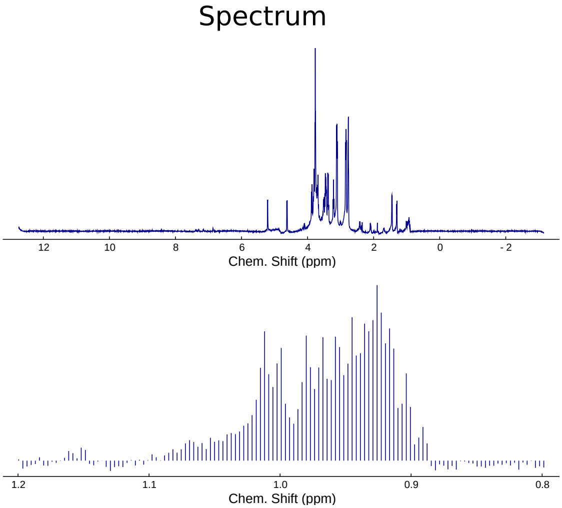
$$\Delta\omega = \frac{2\pi}{\delta t} \qquad \delta\omega = \frac{2\pi}{\Delta t}$$

14 | Example


FID
Imaginary
Real
2.5×10⁴
0
- 2.5×10⁴
- 5.0×10⁴
- 7.5×10⁴
signal (a.u.)
0.0
0.1
0.2
0.3
0.4
time (s)


Spectrum
12
10
8
6
4
2
0
- 2
Chem. Shift (ppm)
1.2
1.1
1.0
0.9
0.8
Chem. Shift (ppm)

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Definition

The *convolution* of two functions f and g is given by

$$[f \otimes g](x) = \int_{-\infty}^{\infty} f(\xi) g(x - \xi) \, \mathrm{d}\xi$$

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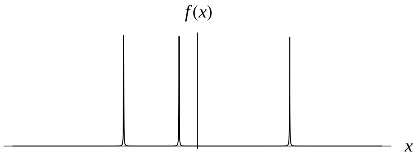

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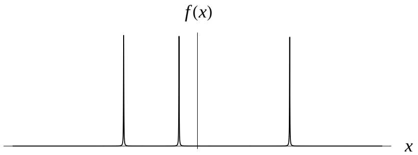

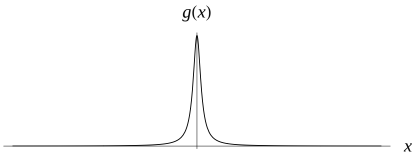

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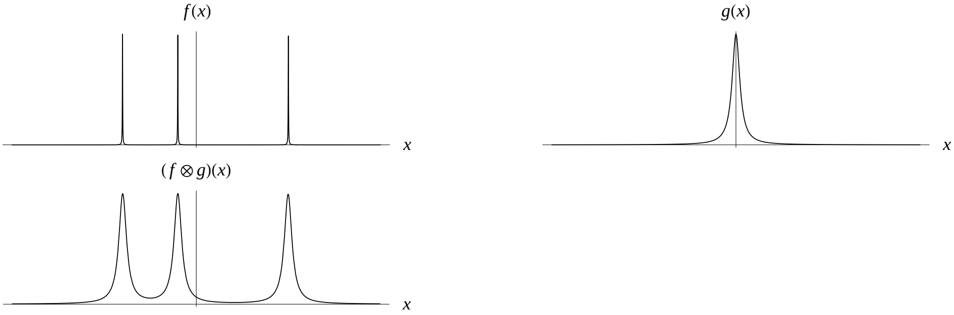

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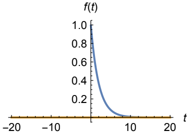

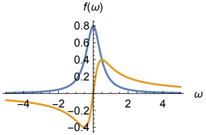

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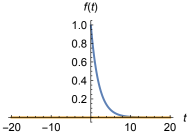

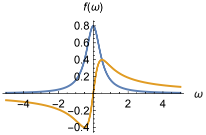

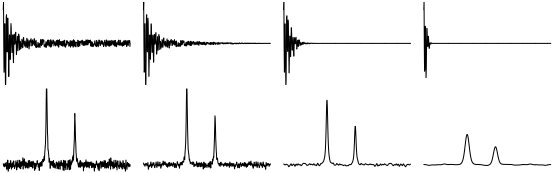

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- ..and this can be used for filtering.