Nuclear Magnetic Resonance (NMR):
Spectroscopy and Imaging

VP – Advanced Physics Laboratory
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Experimental investigation in physics

Black-box approach: Investigate the response of an unknown system to external perturbations.

Excitation **Response***

Physical system (black box)

Electrons, protons, nuclei, neutrons, photons, muons, …

Electrons, protons, nuclei, neutrons, photons, positrons

It works, but **too "expensive"** (time, money, effort). Often large-scale facilities required.

Are there **alternative ways** to investigate matter? **Yes!** Use matter itself: nuclei (**NMR**) or e- (**ESR**) as probes.

* Also different, e.g., ARPES: photon in/electron out

Using (nuclear) matter to probe matter!

Nuclear magnetic resonance (NMR): **far reaching impact** in science!

P. Zeeman
1902

F. Bloch*, E. M. Purcell
1952

K. Wüthrich*
2002

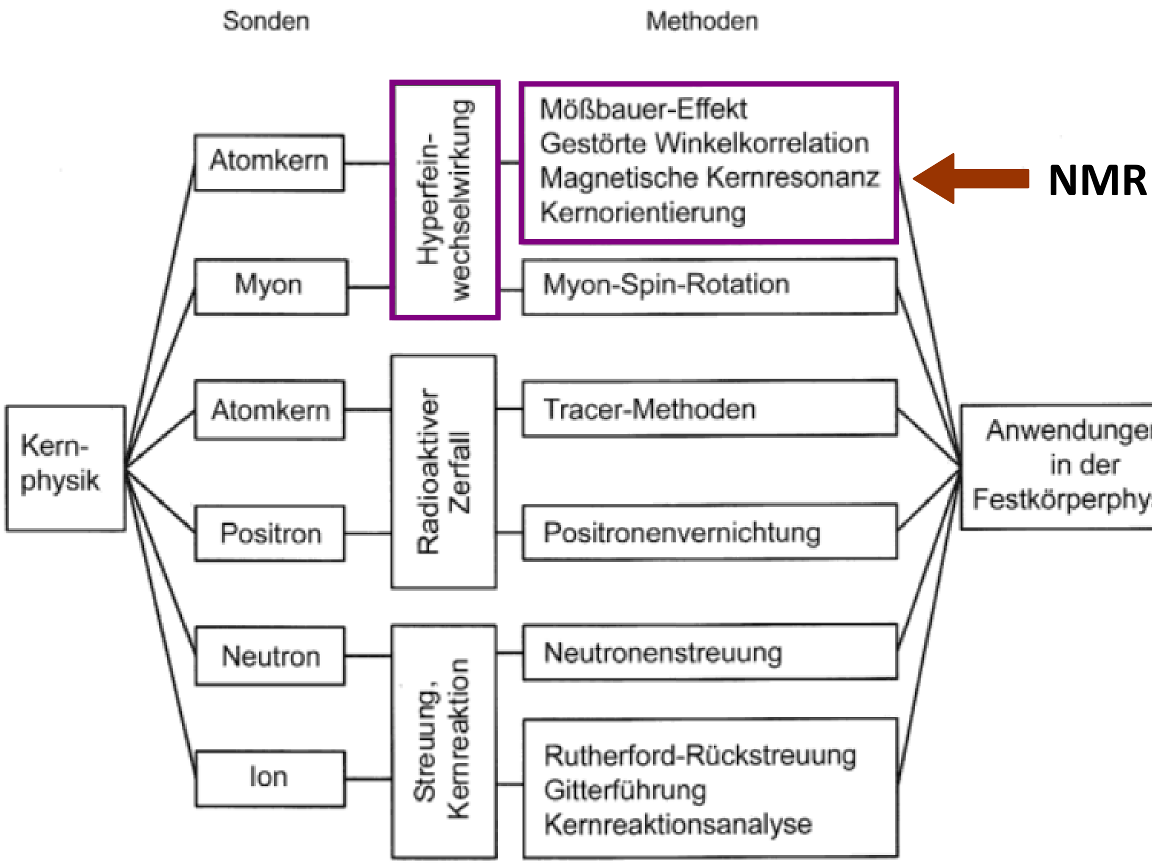
1937
I. Rabi

1991
R. Ernst*

2003
P. Lauterbur, P. Mansfield

* ETH alumni

What is nuclear condensed matter?



Conceptual schematic of **nuclear condensed matter** physics

G. Schatz, A. Weidinger, M. Deicher, *Nukleare Festkörperphysik*, 4. Aufl. (Vieweg+Teubner, Wiesbaden, 2010).

NMR advantages in studying matter

Technique		Advantages / Drawbacks
Magnetization meas.	Incr. complexity	Easy, small samples / macroscopic, sensitive to impurities
Magnetic **resonance**		Extreme conditions, small samples / limited local info
Neutron diffraction		Complete (ω,q) spectrum / sample size, large-scale facilities

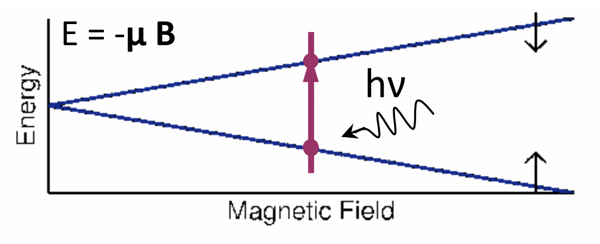
In terms of time/effort/environments/difficulty **NMR** probably offers the **best balance** for the information it can provide.

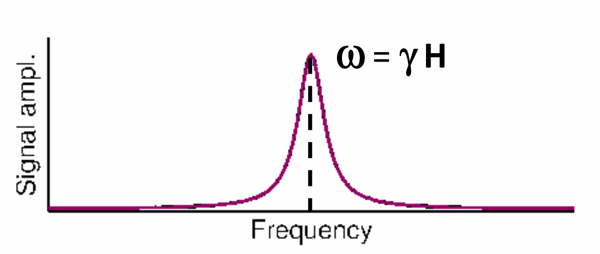
In case of **demanding conditions** (field, pressure, temperature, or sample size) often NMR is **the only technique** available.

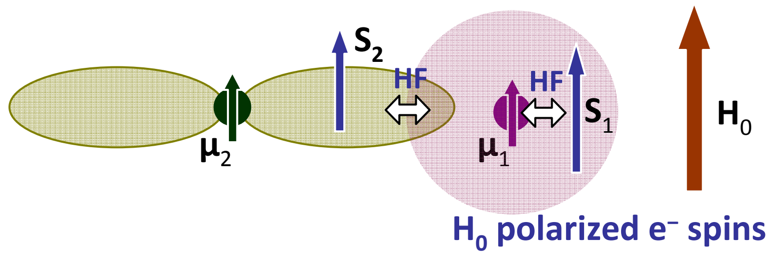
$$\left\{\begin{array}{l} H = 45\ \mathrm{T} \\ p = 10\ \mathrm{GPa} \\ T = 10\ \mathrm{mK} \\ m = 1\ \mathrm{mg} \end{array}\right.$$

NMR I: Static properties (Line shapes)

- **Nuclear magnetic resonance (NMR):** selective absorption of EM radiation by nuclei with nonzero spin placed in an external magnetic field.







- NMR probes **local** magnetic field by means of **hyperfine coupling**

$$\boxed{\omega_{\mathbf{n}} = \gamma_n H_{loc} = \gamma_n\,(H_0 - \mathbf{A}_{\mathbf{n,k}}\,\langle \mathbf{S}_k \rangle)}$$

HF coupl. **Spin polariz.**

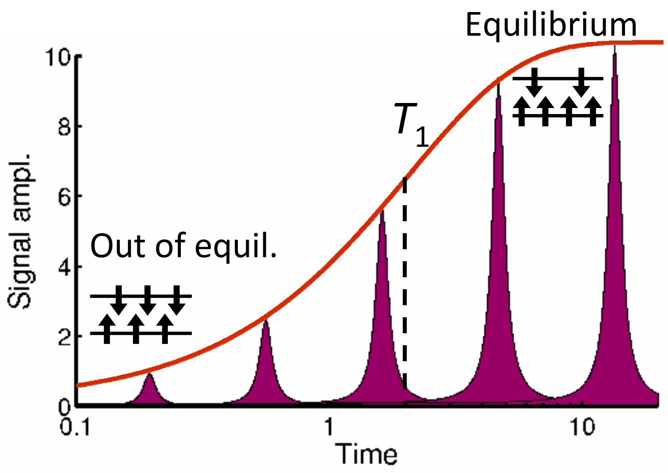
$$\boxed{(\omega_{\mathbf{n}} - \omega_{\mathbf{0}})/\omega_{\mathbf{0}} = K \propto A\chi_{loc}(\omega\approx 0)}$$

Static NMR properties

- **Width** of NMR line ➔ **Distribution of $\langle S_z(r)\rangle$**
- **Shift** of NMR line ➔ **Magnetic susceptibility $\chi_{loc}(\omega\approx 0)$**

NMR II: Dynamic properties (Relaxation)

- NMR dynamic properties ➔ **Flow of energy** between spins and surround.
  ➔ Access to **local magnetic field fluctuations**
- Spin-lattice relaxation (T_1) is a direct consequence of the fluctuation-dissipation theorem. Lost energy absorbed by **electron-spin excitations**.



$\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$

Dissipation!

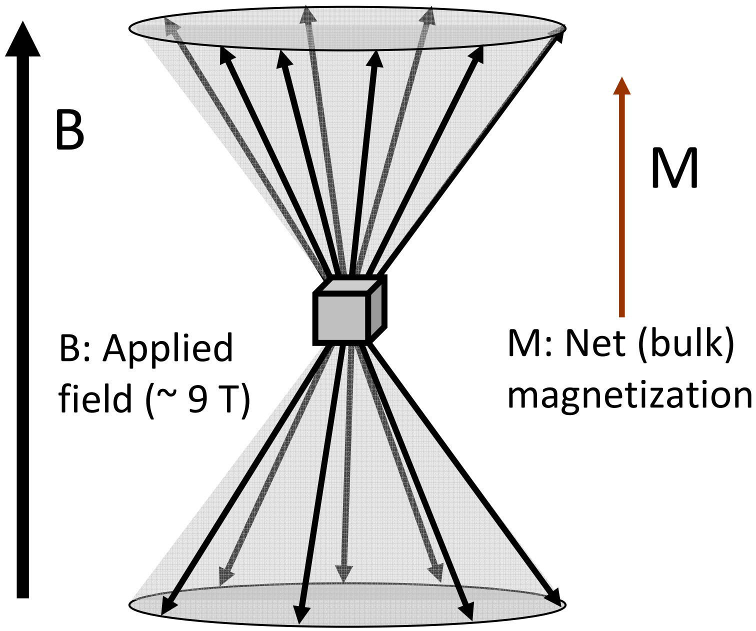
$T_1^{-1} \propto \chi''(q, \omega \approx 0)$

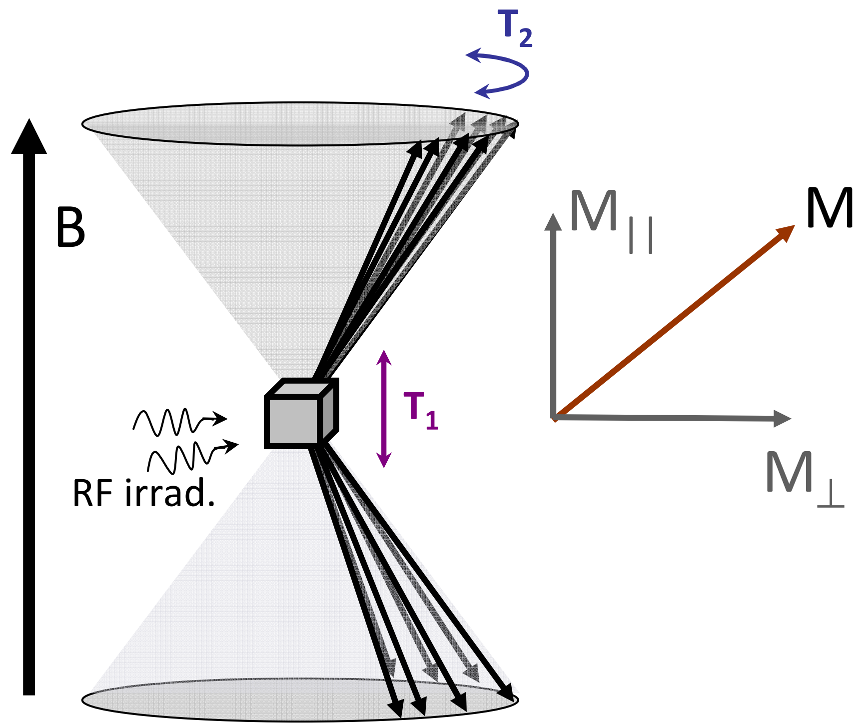
$$\frac{1}{T_1} = \frac{2\gamma_n^2 k_B T}{\gamma_e^2 \hbar^2 N} \sum_{\boldsymbol{q}} \underline{A(\boldsymbol{q})^2} \frac{\chi''(\boldsymbol{q}, \omega_0)}{\omega_0}$$

NMR "form factor"

By measuring $1/T_1$ we are basically exploring the electron spin-spin correlation function ...

NMR: Micro- and macroscopic view





Equilibrium: ~1 ppm excess in spin-up state creates a net magnetization

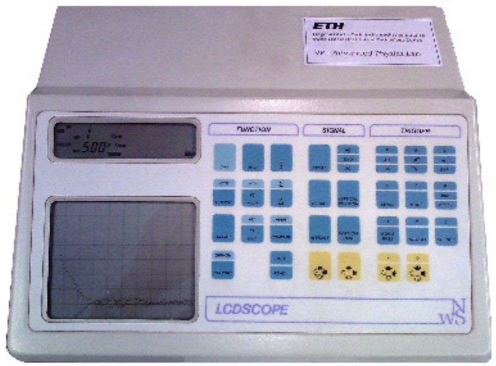
Excitation affects phase and distribution between spin-up and spin-down, rotating bulk magnetization

Equilibrium of spin-up/spin-down: **longitudinal relaxation T_1**
Equilibrium (de-phasing) of spins: **transverse relaxation T_2**

The (new) VP NMR station

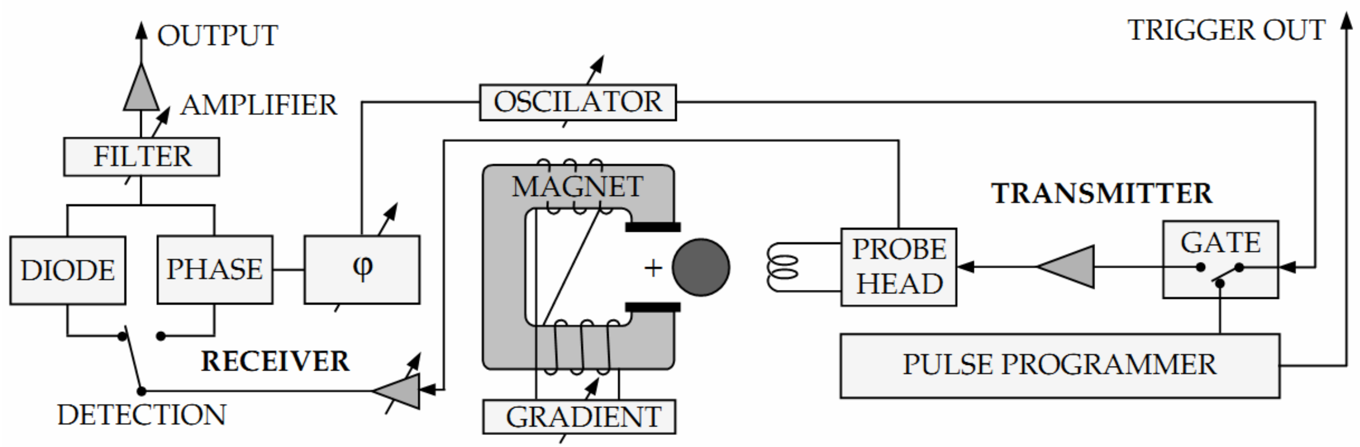
NMR laboratory bench

NMR Spectrometer



LCD Console (Control)

Features of the NMR spectrometer



Spectrometer parameters:

Main field:	0.21 T (AlNiCo magnet)
Homogeneity:	10^{-6} T/cm
Field gradient:	0 – 2×10^{-4} T/cm
Sample size:	8 mm diam., 10 mm height
Frequency:	9 MHz (^{1}H NMR)
RF channels:	0 and 90° (quadrature)
SN ratio (typ.):	100

Wide range of experiments:

Detection of free nuclear precession (FID)

Determination of optimal 90° pulse width

Investigation of (Hahn) spin-echoes

T_1 relaxation time meas. via inversion recovery

T_2 spin-spin relaxation time meas. (Carr-Purcell)

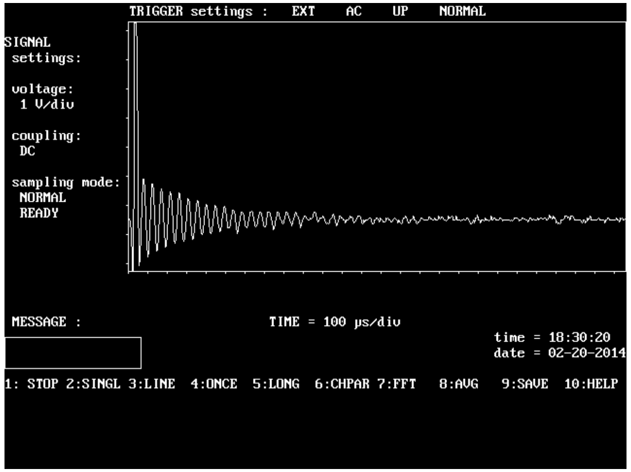
Measurements of molecular diffusion

Magnetic resonance imaging (MRI)

NMR data: screenshots + digital

Data can be saved in different formats:

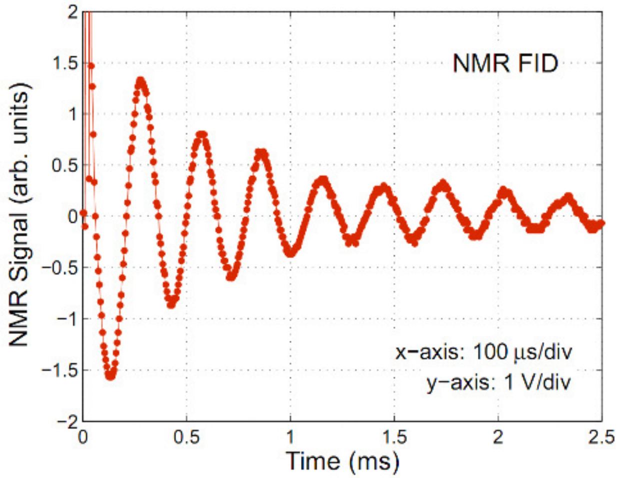
- Screenshots (documentation)
- Digital data (further analysis)



testdata.sig

100 us/div	2 V/div
.005 ms/ch	Volts
0	8.8667
1	8.2000
2	5.8000
3	5.1333
4	5.0000
5	4.9333

Fit + display

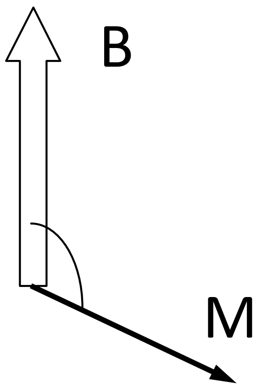


Scope of the experiments

Goal: familiarize with **conceptual** framework + carry out **practical** experiments.

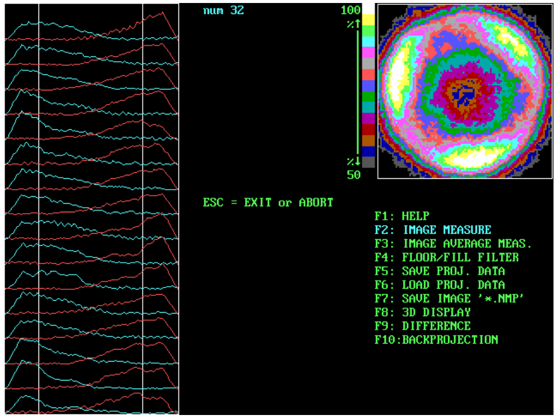
Two experiment categories: **preliminary** (easy) and **research grade** (more difficult).

Preliminary exp.



E.g.: Measure 90° pulse width

Research grade exp.



E.g.: Perform magnetic resonance imaging (MRI)

Conclusion and perspectives

- NMR is among the most **demanding** experiments. Concepts from quantum and statistical physics, electromagnetism, RF techniques should be well mastered **before** starting the experiment.

- Problems with identifying sources of **errors**. Difficulties in (apriori) distinguishing crucial errors from irrelevant ones.

- **High scattering** in student preparation. Some quite independent, others under close guidance. Generally students are satisfied, especially after learning how to overcome difficulties.