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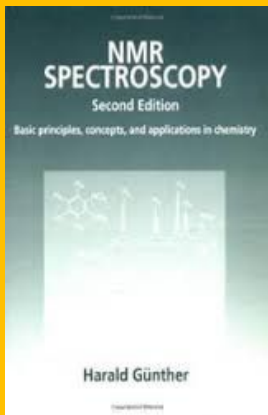
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**Пятница, 9:30–11:05, к. 4017**

# Contents

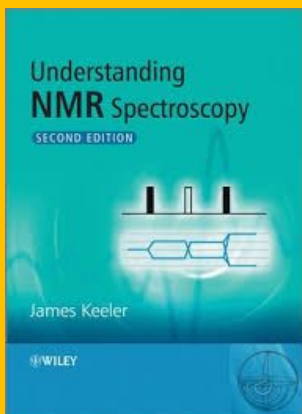
1. Physical background of NMR
2. Chemical shielding
3. Chemical exchange
4. Dipolar interaction
5. Scalar coupling
6. Relaxation
7. Quadrupolar interaction

# Books



Harald Günther

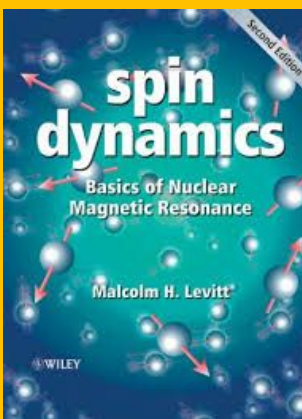
**NMR Spectroscopy: Basic Principles, Concepts, and Applications in Chemistry**



James Keeler

**Understanding NMR Spectroscopy**

<http://www-keeler.ch.cam.ac.uk/lectures/Irvine/>



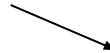
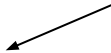
Malcolm H. Levitt

**Spin Dynamics**

## **Discovery of spin and magnetic resonance effect**

# Stern-Gerlach experiment

electrons move on orbits,  
producing angular momentum and magnetic dipole moment



**Lorenz and Zeeman theory:**  
all orientations of magnetic dipoles are allowed

**Bohr and Sommerfeld theory:**  
only few orientations of magnetic dipoles are allowed

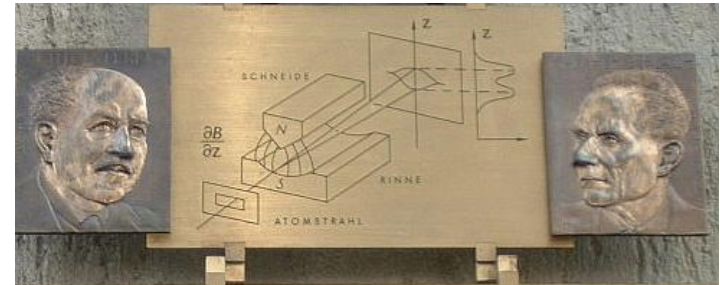
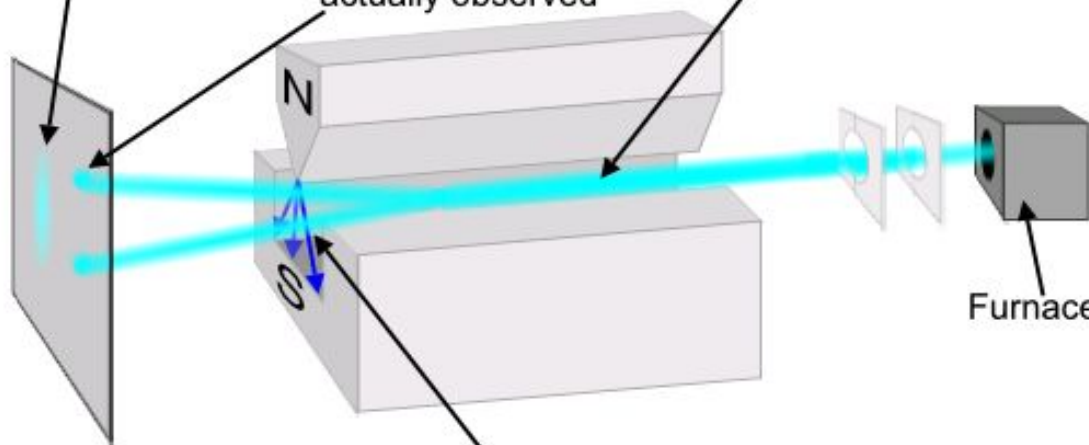
Classical prediction

What was actually observed

Silver atoms

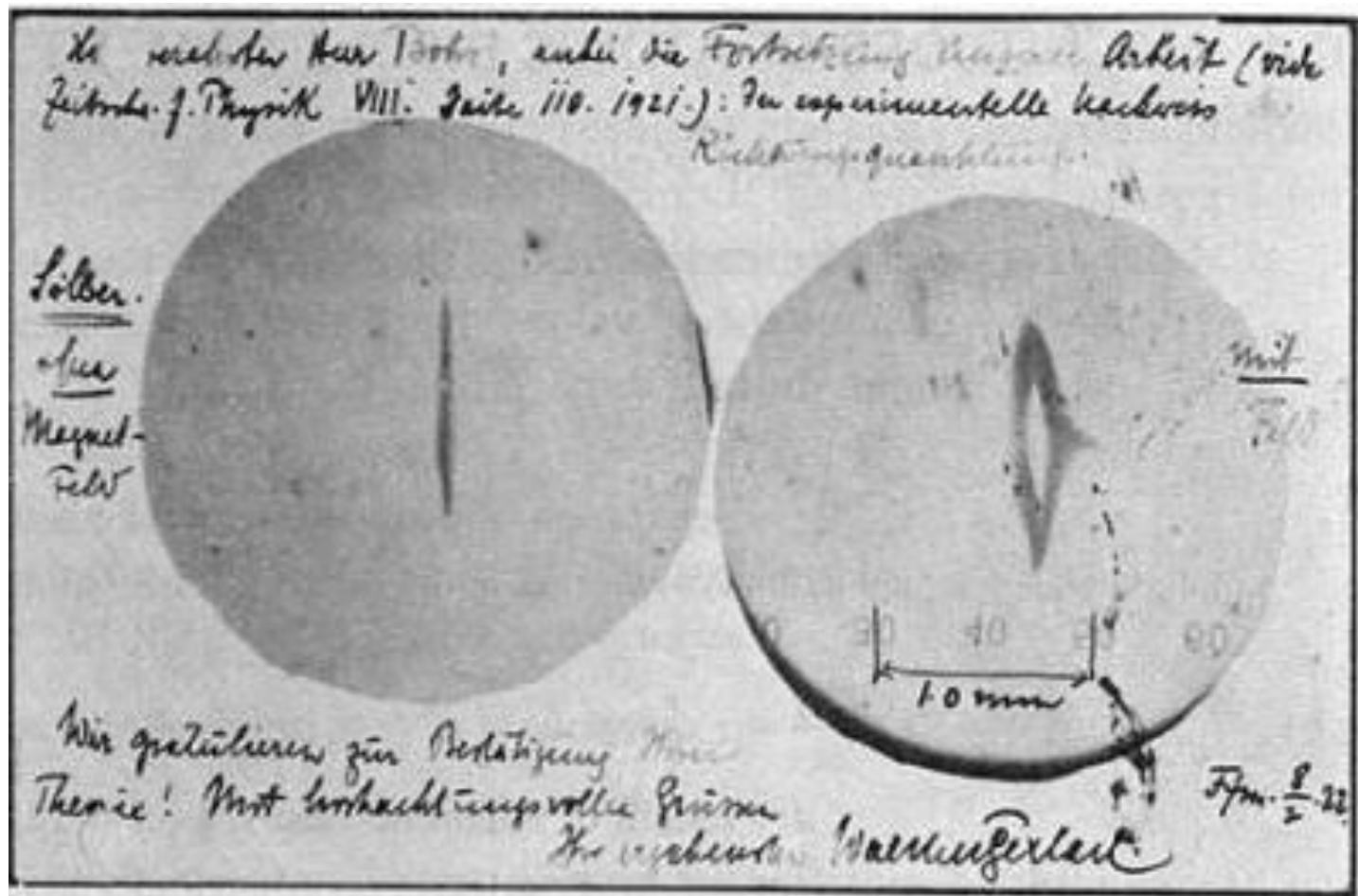
Inhomogeneous magnetic field

Furnace



IM FEBRUAR 1922 WURDE IN DIESEM GEBÄUDE DES PHYSIKALISCHEN VEREINS, FRANKFURT AM MAIN, VON OTTO STERN UND WALTHER GERLACH DIE FUNDAMENTALE ENTDECKUNG DER RAUMQUANTISIERUNG DER MAGNETISCHEN MOMENTE IN ATOMEN GEMACHT. AUF DEM STERN-GERLACH-EXPERIMENT BERUHEN WICHTIGE PHYSIKALISCH-TECHNISCHE ENTWICKLUNGEN DES 20. JHDTS., WIE KERNSPINRESONANZMETHODE, ATOMUHR ODER LASER. OTTO STERN WURDE 1943 FÜR DIESE ENTDECKUNG DER NOBELPREIS VERLIEHEN.

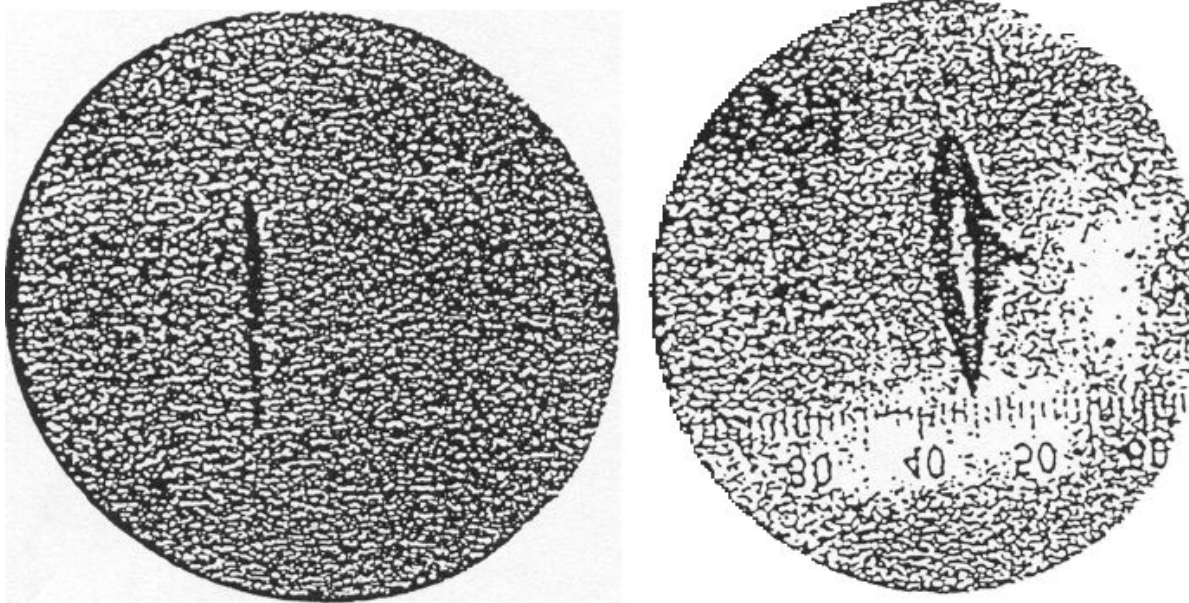
# Stern-Gerlach experiment



“Attached the continuation of our work (Zeitschrift für Physik 8 (1921) 110): The experimental proof of directional quantisation. Silver without magnetic field / with magnetic field. We congratulate on the confirmation of your theory.”

the postcard from Gerlach to Bohr, 8.02.1922

# Stern-Gerlach experiment



Gerlach, W. and O. Stern, "Der experimentelle Nachweis der Richtungsquantelung". *Zeitschrift für Physik* 1922, 9, 349-352.

"Hopefully now even the incredulous Stern will be convinced about directional quantization"

a letter from Pauli to Gerlach, 17.02.1922

# Concept of spin (first proposed in 1925)



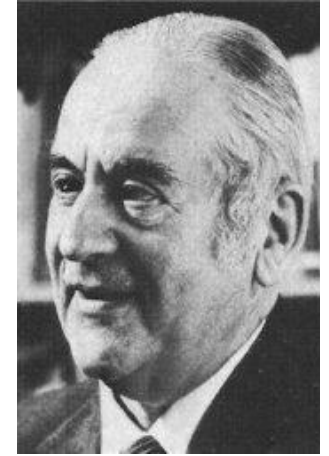
Wolfgang Pauli  
1900-1958



Ralph Kronig  
1904-1995



George Uhlenbeck  
1900-1988



Samuel Abraham Goudsmit  
1902-1978

Tried to explain spin as rotation of the particle, was criticized by Pauli and never published this idea



Did not speak with Pauli before publishing



*Spin (of electron) is two-valued quantum degree of freedom*

Wolfgang Pauli

*Probably nobody really understands spin on a level above the technical mathematical rules*

Malcolm Levitt in „Spin Dynamics“



# Spin and magnetic dipole moment

To have magnetic dipole moment particle needs

- 1) mass
- 2) charge
- 3) spin

Particle	Mass	Charge	Spin	Magnetic dipole moment
Electron	✓	✓	✓	✓
Proton	✓	✓	✓	✓
Neutron	✓	✗	✓	✓
Neutrino	✓	✗	✓	✗
Photon	✗	✗	✓	✗
Graviton (?)	✗	✗	✓	✗
Carbon-12	✓	✓	✗	✗
Carbon-13	✓	✓	✓	✓

**Which elementary particles have no spin?**

Higgs bosons (explain mass of particles)

Squarks (quark partners in the Standard Model)

**existence not confirmed**

Graviscalars (excitation of the gravitational field)

**existence not confirmed**

Axions (introduced to solve the CP-problem)

**existence not confirmed**

# Nuclear spin and nuclear magnetic dipole moment

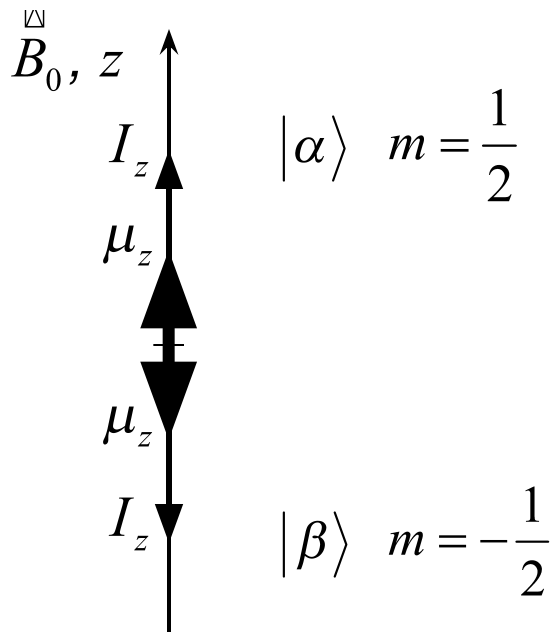
Total spin angular momentum  $I = \sqrt{S(S+1)}\hbar$        $S = \left(0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots\right)$

Projection on z-axis  $I_z = m\hbar$        $m = -S, -S+1, \dots, S-1, S$

Every nucleus with non-zero spin has magnetic moment  $\vec{\mu} = \gamma \vec{I}$

Projection on z-axis  $\mu_z = m\gamma\hbar$        $m = -S, -S+1, \dots, S-1, S$

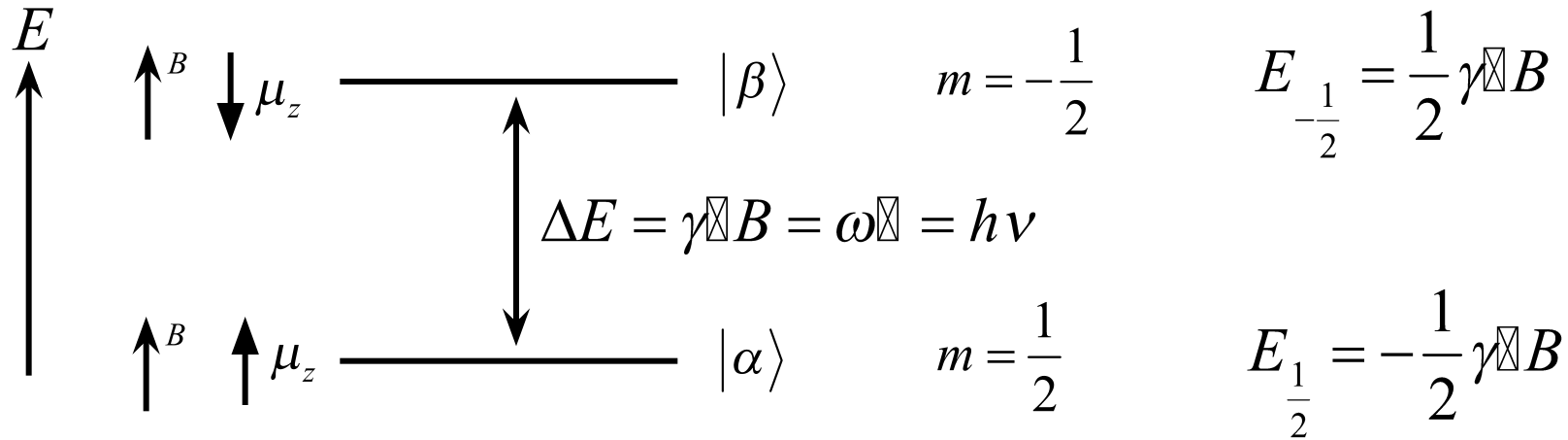
Example for spin  $\frac{1}{2}$  particle



Nucleus	Abundance	Spin S	$\gamma$ / $10^6 \cdot \text{rad} \cdot \text{T}^{-1} \text{s}^{-1}$
$^1\text{H}$	99.985%	1/2	267.5
$^2\text{H}$	0.015%	1	41.1
$^{12}\text{C}$	98.89	0	-
$^{13}\text{C}$	1.11	1/2	67.3
$^{14}\text{N}$	99.63	1	19.3
$^{15}\text{N}$	0.37	1/2	-27.1
$^{16}\text{O}$	99.759	0	-
$^{17}\text{O}$	0.037	5/2	-36.3

# Nuclear spin 1/2 in magnetic field

$$E_m = -m\gamma\hbar B$$



Zeeman effect discovered in 1896, Nobel Prize in 1902

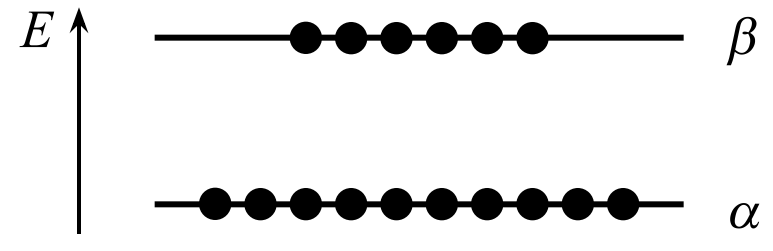
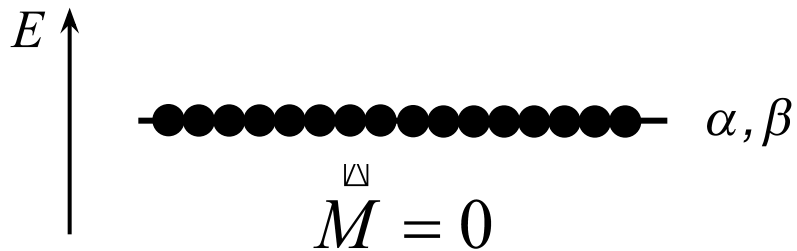
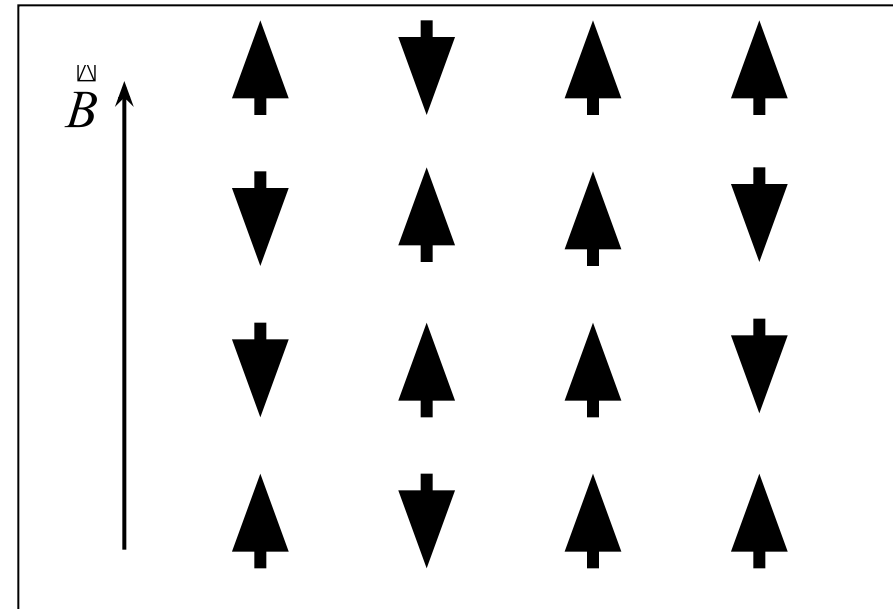
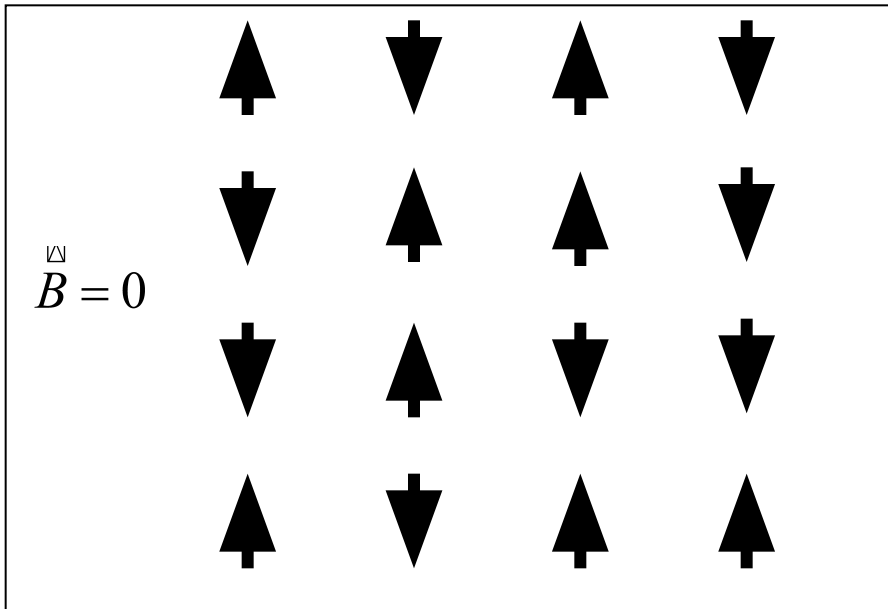


Pieter Zeeman  
1865-1943



Hendrik Antoon Lorentz  
1853-1928

# Ensemble of nuclear spins 1/2 in magnetic field



$$\vec{M} = \text{const} \cdot (x_\alpha - x_\beta)$$

# Nobel Prizes in physics for the discovery of NMR

1944



Isidor Isaac Rabi  
1898-1988  
Columbia U., NY, USA

work of 1938  
NMR in beam

1952



Felix Bloch  
1905-1983  
Stanford U., CA, USA

work of 1945-46  
NMR in bulk

1952



Edward Mills Purcell  
1912-1997  
Harvard U., MA, USA

*A winter of our first experiments... looking on snow with new eyes. There the snow lay around my doorstep – great heaps of protons quietly precessing in the Earth's magnetic field. To see the world for a moment as something rich and strange is the private reward of many a discovery...*

from the Nobel Prize address of Purcell

# Nobel Prizes for the applications of NMR

1991



Richard R. Ernst  
b. 1933  
ETH, Switzerland

2002



Kurt Würthrich  
b. 1938  
ETH, Switzerland

2003



Paul C. Lauterbur  
1929-2007  
U. Of Illinois, IL, US

2003



Peter Mansfield  
b. 1933  
U. Of Nottingham

Multidimensional NMR

MRI

3D structure of biomolecules



Richard R. Ernst

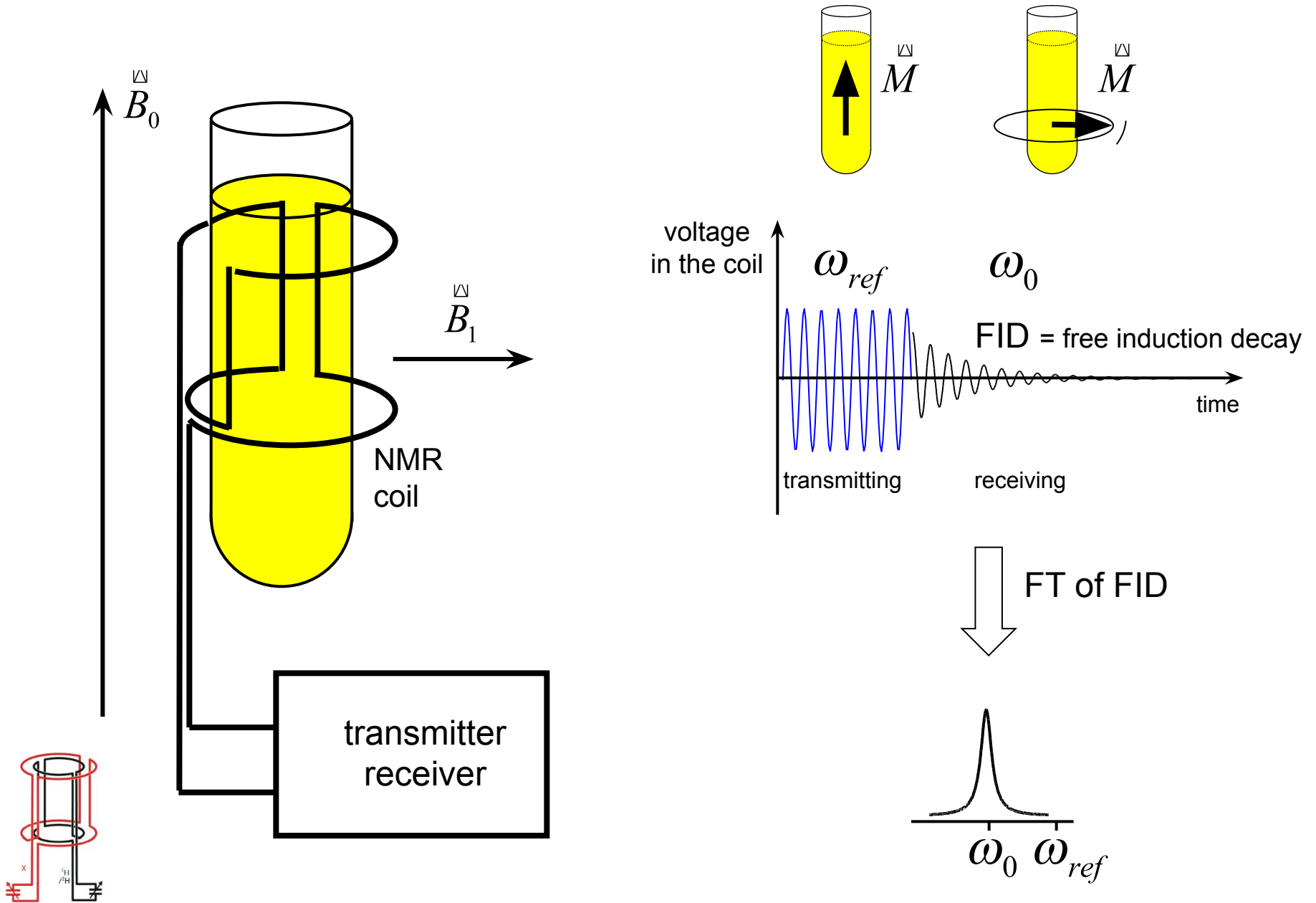
What are the reasons behind NMR's success?... nature has generously provided us with three basic physical properties:

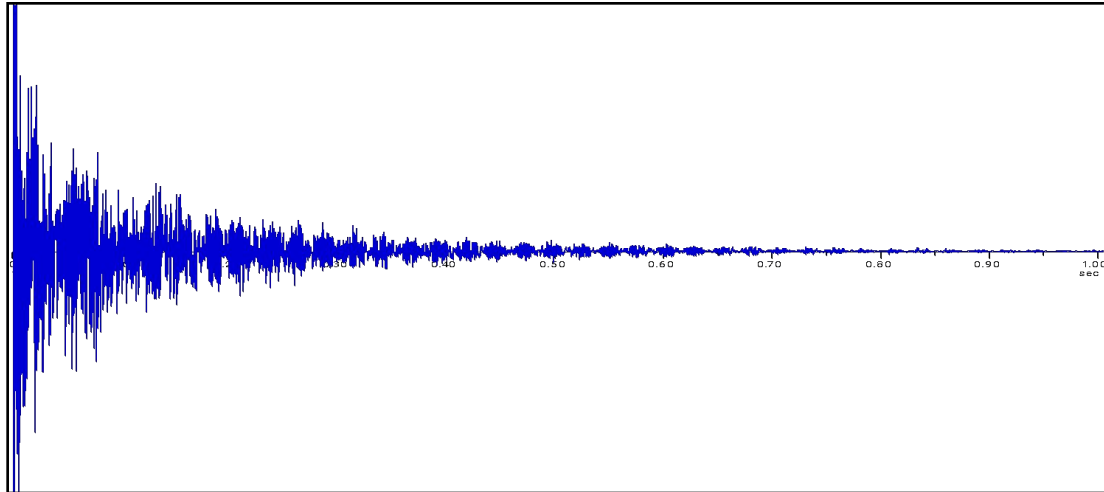
- (1) The nuclear sensors ... are as localized as ever needed, with a diameter as small as 2 fm, allowing for almost unlimited spatial resolution.
- (2) Interactions with the environment at less than 0.2 J/mol are extremely weak, permitting virtually perturbation-free sensing of the surroundings. Nevertheless, the interactions are highly sensitive to the environmental conditions.
- (3) Internuclear pair interactions provide accurate distance information and information on bond angles.

# **Overview of an NMR experiment and design of NMR instruments**

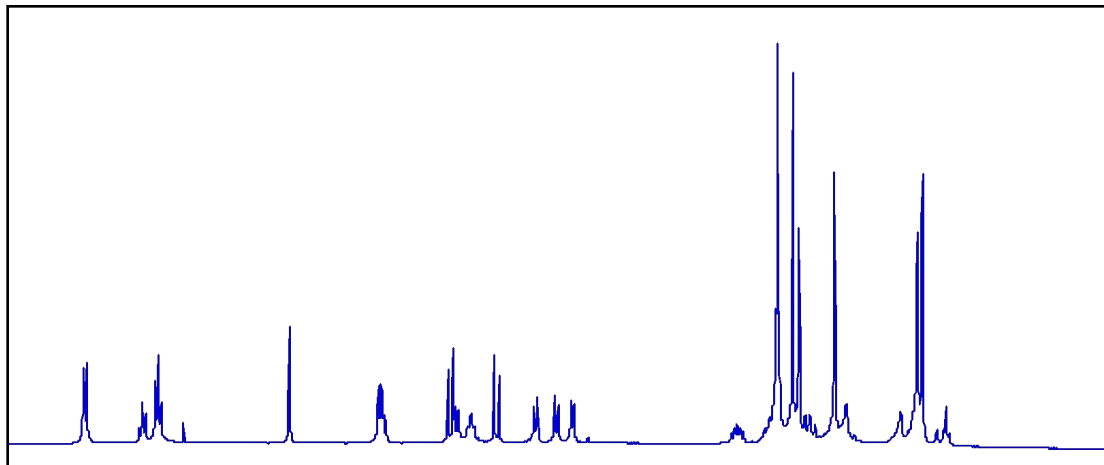


# Brief overview of the NMR experiment





↓ FT *time*



*frequency*