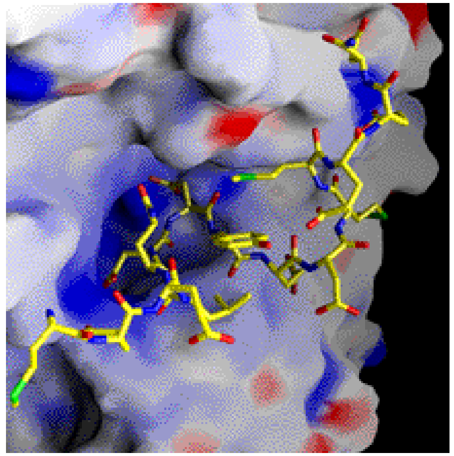
NMR I

- Geschichte der NMR
- Magnetische Moment
- Probe im Magnetfeld
- Besetzungszahlverhältnis
- Übergänge ohne und mit B_1-Feld
- Makroskopische Magnetisierung



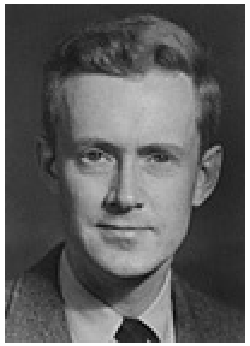
Nobelpreis 1952

F. Bloch
1905-1983

FELIX BLOCH

The principle of nuclear induction

Nobel Lecture, December 11, 1952



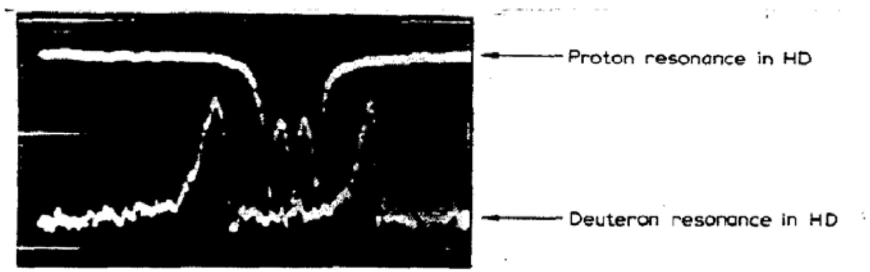
E. Purcell
1912-1997

EDWARD M. PURCELL

Research in nuclear magnetism

Nobel Lecture, December 11, 1952

NMR Proton/Deuteron-Resonanz



$$\frac{\mu(^{2}H)}{\mu(^{1}H)} = 0.307012189 \pm 30$$

Fig. 1. Simultaneous display of deuteron and proton resonances in HD. The proton trace is inverted. (T. F. Wimett, *Massachusetts Institute of Technology.*)

NMR-Protonenspektren

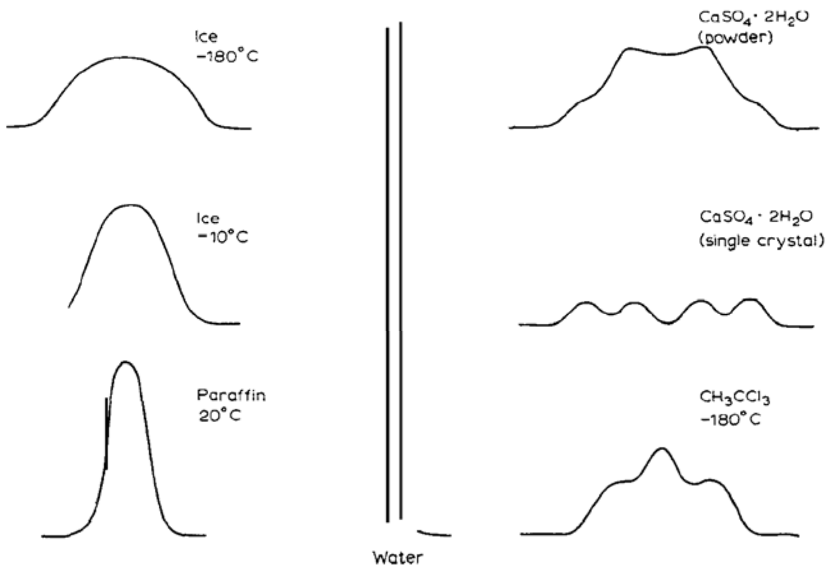


Fig. 3. Line shapes typical of the proton resonance in various substances. The line in water is not drawn to scale; it is actually much narrower and more intense than indicated.

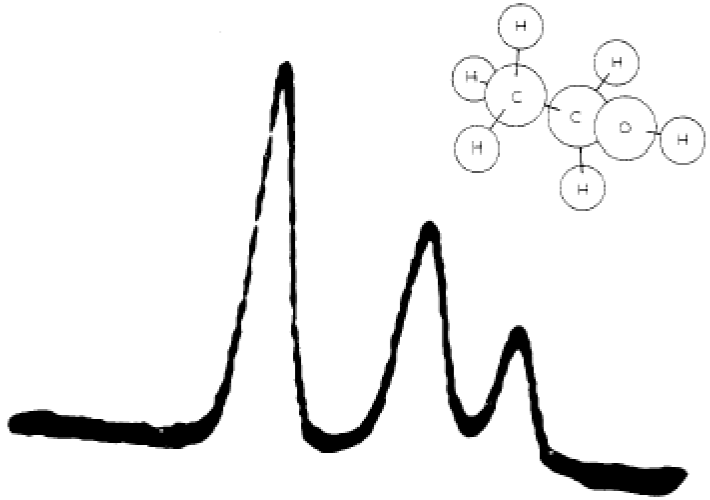


Fig. 6. The proton resonance in ethyl alcohol, observed with high resolution. The three lines arise from the CH_3 hydrogens, from the CH_2 hydrogens, and from the OH hydrogen, respectively.

Quadrupolkerne und Relaxation

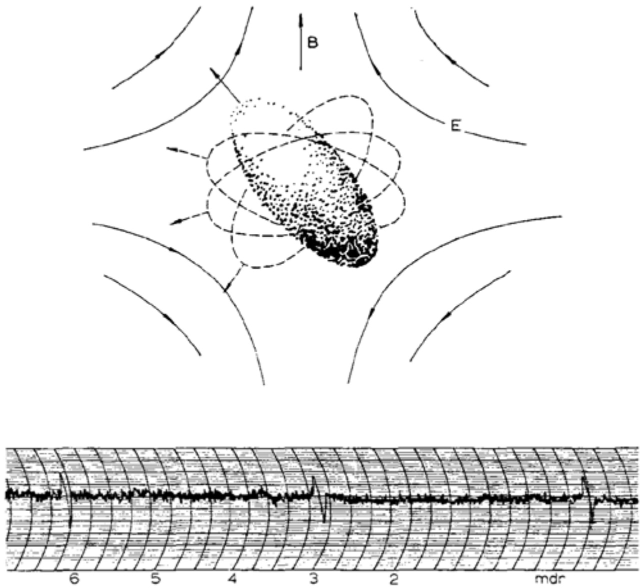


Fig. 4. A nucleus with an electric quadrupole moment in a uniform magnetic field (B) and a non-uniform electric field *(E)*. *Lower trace:* ^{23}Na resonance in a single crystal of $NaNO_3$, showing splitting of magnetic resonance line into a triplet.

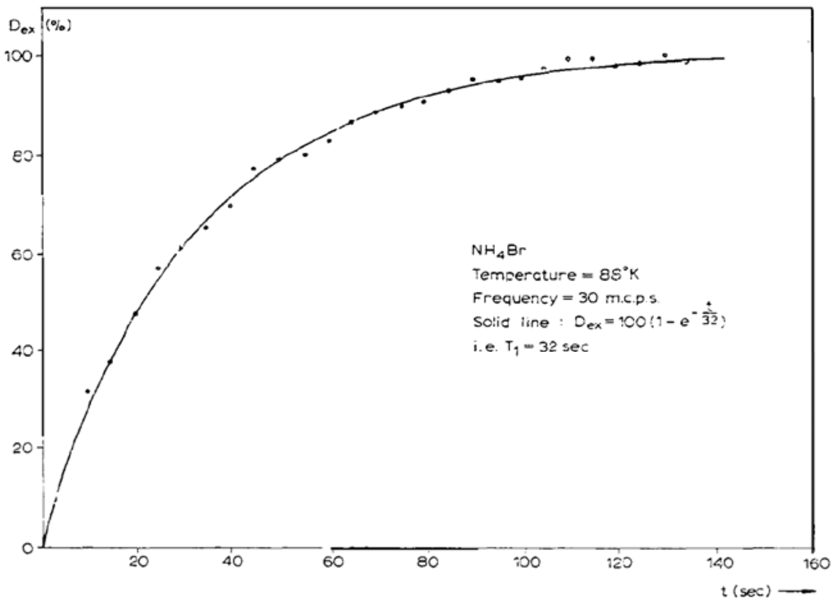
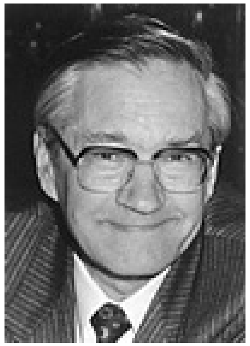
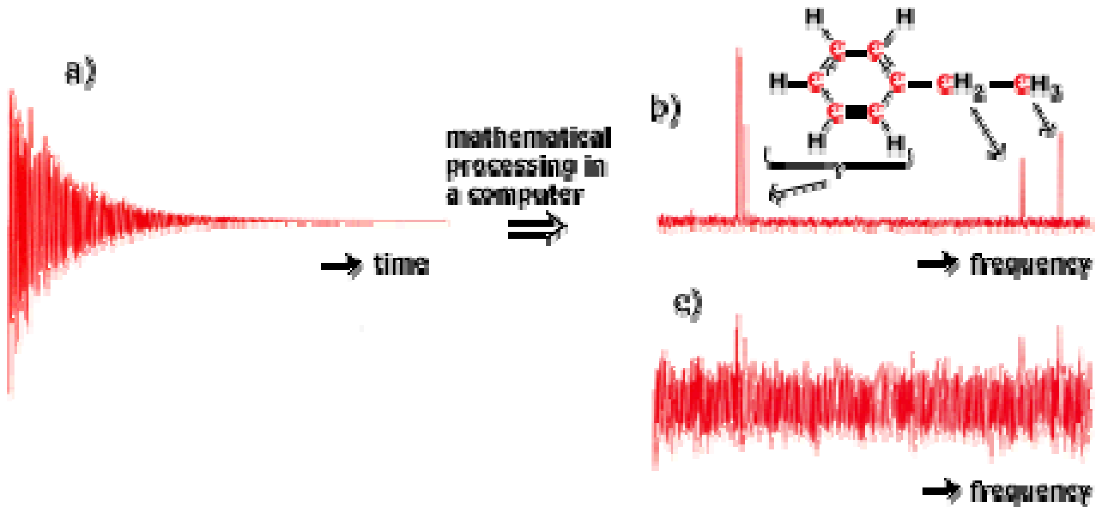


Fig. 5. The gradual approach to equilibrium magnetization. The ordinate is proportional to the intensity of nuclear polarization.

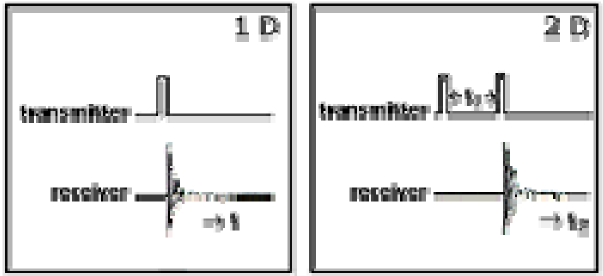
Nobelpreis 1991

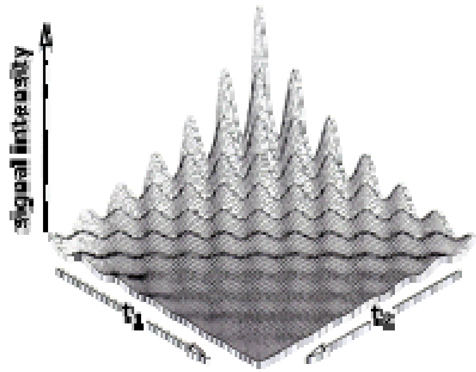


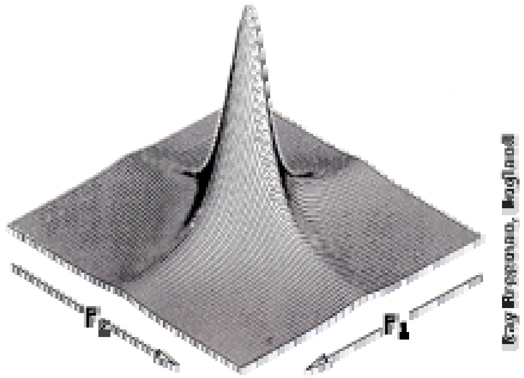
R.R. Ernst



Zweidimensionale-NMR







Nobelpreis 2002

K. Wüthrich
1938

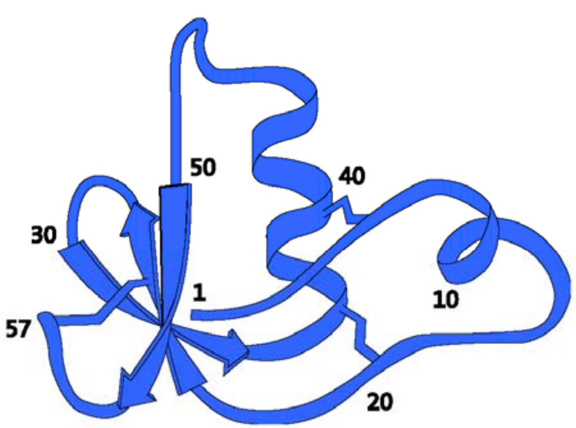


Figure 4a

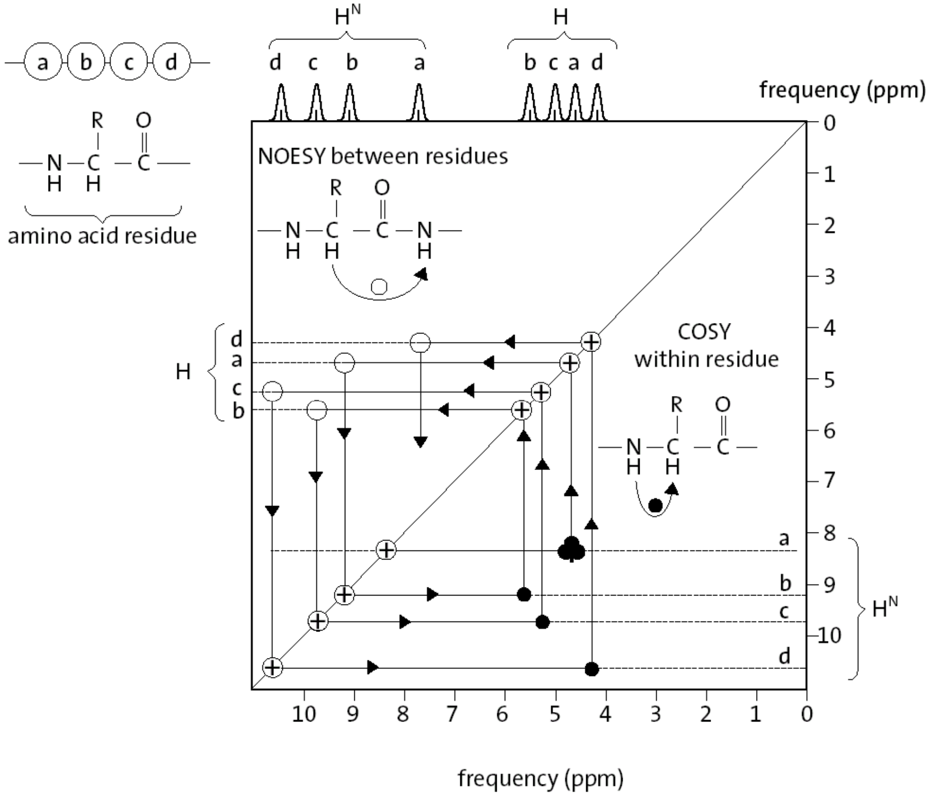
Figure 4b.

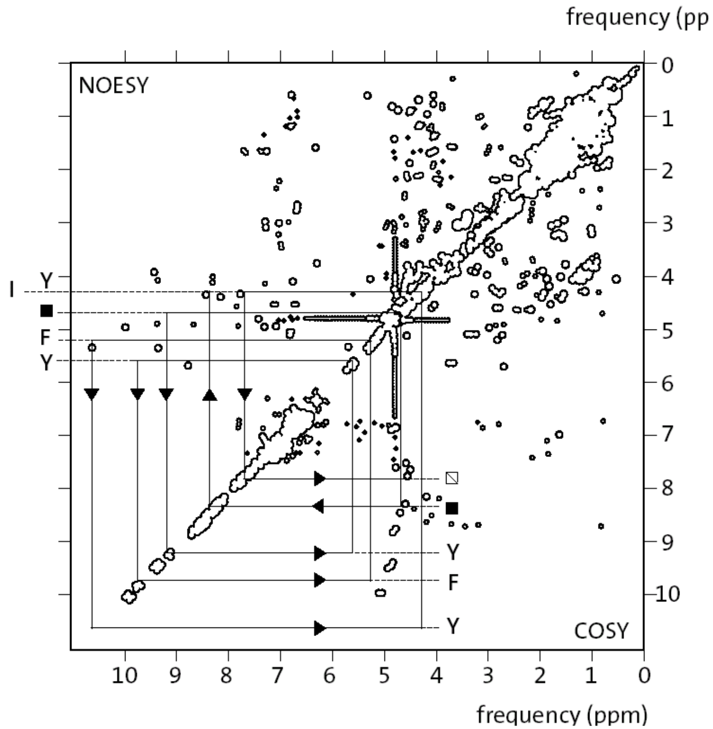
Figure 4.
One of the first three-dimensional NMR solution structures determined by Wüthrich, in 1985. From ref. 23.

a) A schematic view of the topology of the polypeptide backbone of BUSI IIA (bull seminal plasma proteinase inhibitor IIA). The structure was calculated with distance geometry, from numerous distance constraints obtained from two-dimensional NOESY spectra and additional structural constraints such as torsion angles. The structure represents an average of several computed structures that fulfil the structural constraints.

b)A set of five backbone structures of BUSI IIA, calculated with distance geometry using the NOE distance constraints. Such computed structures were used to calculate the average structure presented as Fig. 4a.

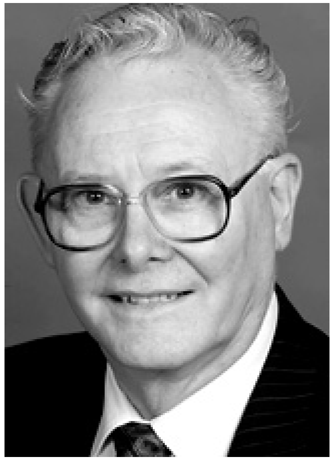
Mehrdimensionale NMR



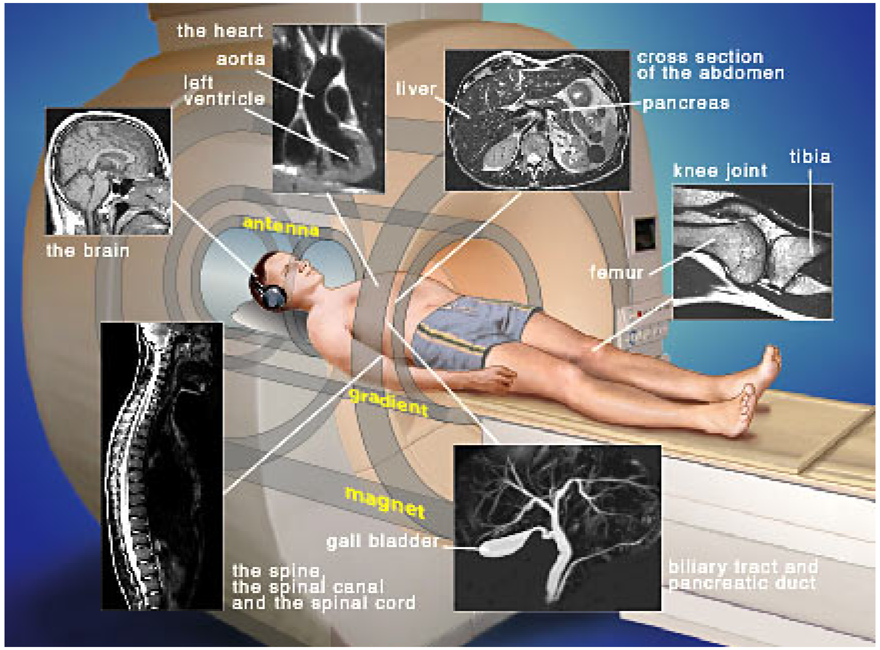


Nobelpreis 2003 (Medizin)

P. C. Lauterbur
1929

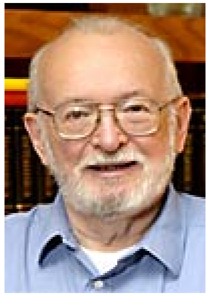


Sir P. Mansfield
1933



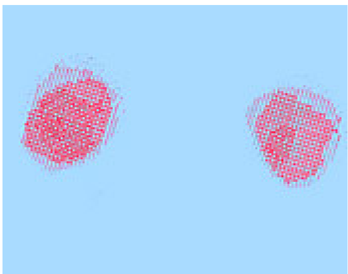
Magnetic Resonance Imaging (MRI)

Nobelpreis 2003 (Medizin)

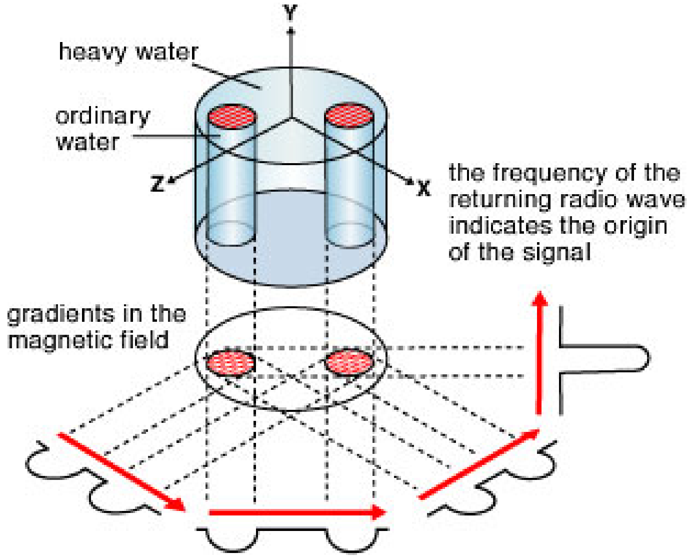


Paul Lauterbur
Born 1929
University of Illinois, Urbana, USA

Paul Lauterbur discovered that two-dimensional images could be produced by introduction of gradients in the magnetic field. In 1973, he described how addition of gradient magnets to the main magnet made it possible to visualize a cross section of tubes with ordinary water surrounded by heavy water.
No other imaging method can differentiate between ordinary and heavy water.



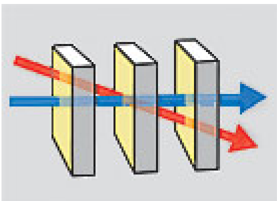
co-ordination of the curves with back-projection calculations results in a transaxial image

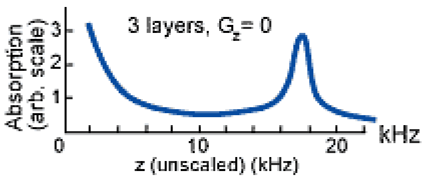


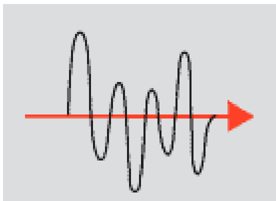
Nobelpreis 2003 (Medizin)

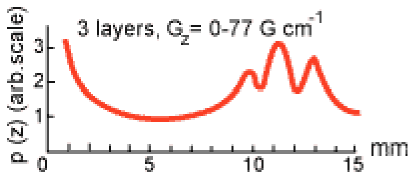
Peter Mansfield
Born 1933
University of Nottingham,
England

Peter Mansfield discovered that use of gradients in the magnetic field gave signals that rapidly and effectively could be analysed and transformed to an image. This was an essential step in order to obtain MR images. Mansfield also showed how extremely rapid imaging could be achieved by very fast gradient variations (socalled echo-planar scanning). This approach became possible in clinical practice a decade later.



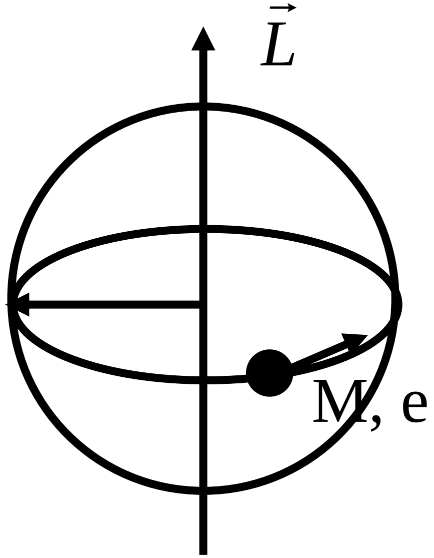






Magnetisches Moment

e = Protonenladung
M = Protonenmasse
R = Kernradius



Rotation von Ladungen erzeugt ein magnetisches Moment.

Magnetisches Moment = Strom × Kreisfläche

$$\mu = e \cdot \nu \times \pi \cdot r^2$$

Magnetisches Moment

Drehimpulsbetrag = Trägheitsmoment × Kreisfrequenz

$$\hbar\sqrt{I(I+1)} \quad = \quad M \cdot r^2 \quad \times \quad 2\pi \cdot \nu$$

Daraus folgt:

$$\mu = \frac{e\hbar}{2M}\sqrt{I(I+1)} = \mu_k \sqrt{I(I+1)}$$

Magnetisches Moment

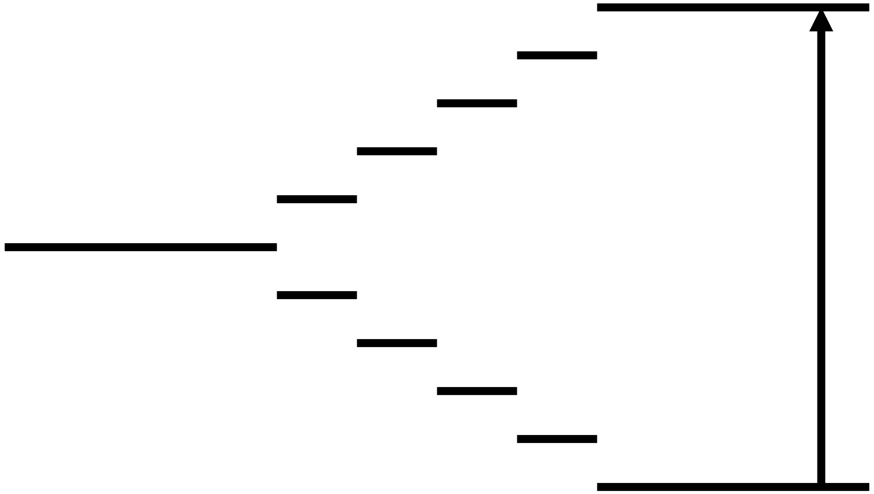
Kernmagneton: $\mu_K = \frac{\mu_B}{1836}$ $\mu_K = \frac{e}{2m_P}\hbar$

$$\mu = g\,\mu_k\,\sqrt{I\left(I+1\right)}$$

Magnetogyrisches Verhältnis: $\gamma = \frac{g_K\,\mu_K}{\hbar}$

Kernmagnetisches Moment: $\mu_z = \gamma \cdot \hbar \cdot I$

Probe im magnetischen Feld



$$m = -1/2$$

$$E_{-} = \frac{\gamma\hbar B_0}{2} = \frac{\hbar\omega}{2}$$

$$\Delta E = \gamma\,\hbar\, B_0$$

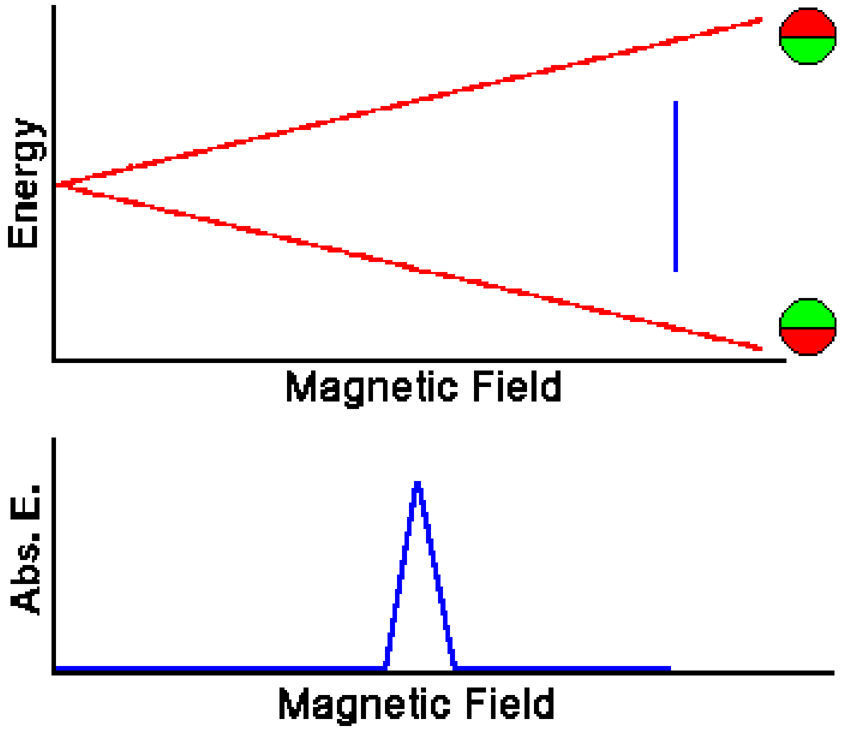
$$m = +1/2$$

$$E_{+} = -\frac{\gamma\hbar B_0}{2} = -\frac{\hbar\omega}{2}$$

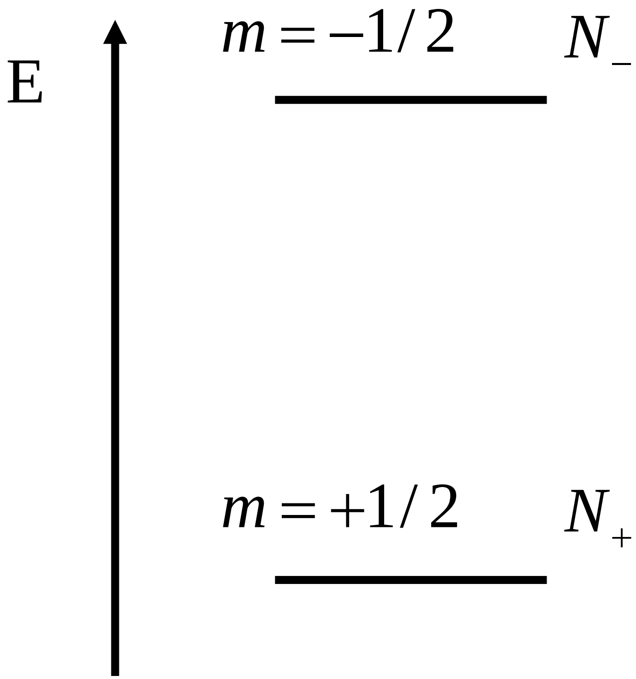
$B_0 = 0$ $B_0 = 2.0\,T$

Probe im magnetischen Feld

Larmorfrequenz: $\omega_0 = \gamma B_0$



Besetzungzahlverhältnis



Besetzungszahlverhältnis:

$$\frac{N_-}{N_+} = \exp(-\Delta E / kT) = \exp(-\gamma\hbar B_0 / kT)$$

$$\gamma\hbar B_0 \approx 10^7 \cdot 10^{-34} \cdot 1 = 10^{-27}\, J$$

$$kT \approx 10^{-21}\, J$$

Übergänge ohne B_1-Feld

$$N = N_+ + N_- \qquad n = N_+ - N_-$$

$$dN_+ / dt = N_- W_\beta - N_+ W_\alpha$$

Gleichgewicht: $dN_+ / dt = 0, \quad also \quad N_-^0 W_\beta - N_+^0 W_\alpha = 0$

$$oder \quad \frac{N_-^0}{N_+^0} = \frac{W_\alpha}{W_\beta}$$

$$\frac{N_-^0}{N_+^0} = \exp\left[\frac{-\gamma \hbar B_0}{kT}\right] = \frac{W_\alpha}{W_\beta} \qquad oder \qquad \frac{W_\beta}{W_\alpha} = \exp\left[\frac{+\gamma \hbar B_0}{kT}\right]$$

Übergänge ohne B_1-Feld

$$N_+^0 - N_-^0 \cong \frac{E_+ - E_-}{kT} = \frac{\Delta E}{kT} = \frac{\gamma\hbar B_0}{kT} = \frac{\mu B_0}{IkT}$$

$$\frac{dn}{dt} = N(W_\beta - W_\alpha) - n(W_\beta + W_\alpha)$$

$$n^0 = N\frac{W_\beta - W_\alpha}{W_\beta + W_\alpha}$$

$$1/T_1 = R_1 = \left(W_\beta + W_\alpha\right)$$

Übergänge ohne B_1-Feld

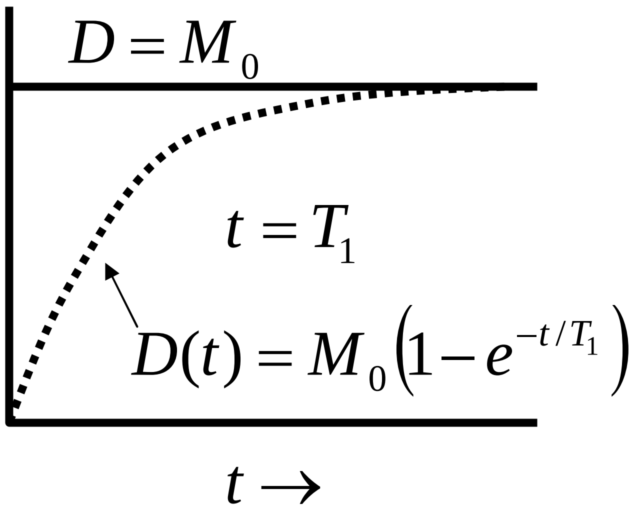
$$\frac{dn}{dt} = R_1\left(n^0 - n\right)$$

$$\frac{1}{n^0 - n}\,dn = R_1 dt$$

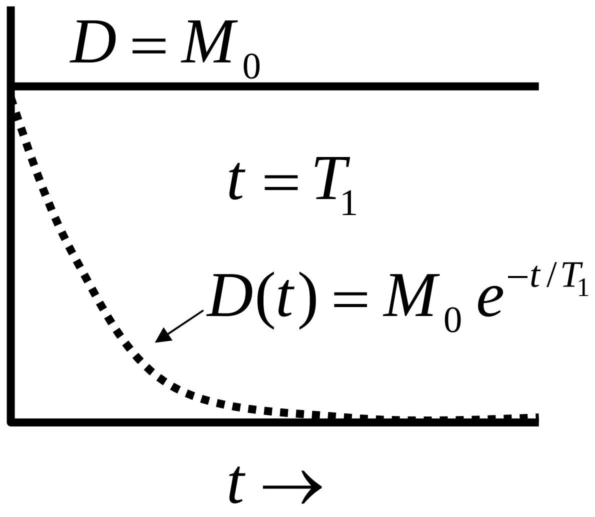
$$-\log_e\left(n^0 - n\right) = R_1 t + A \quad oder \quad n^0 - n = Ae^{-R_1 t}$$

entmagnetisiert: $n = n^0\left[1 - e^{-R_1 t}\right]$ magnetisiert: $n = n^0 e^{-R_1 t}$

Relaxation

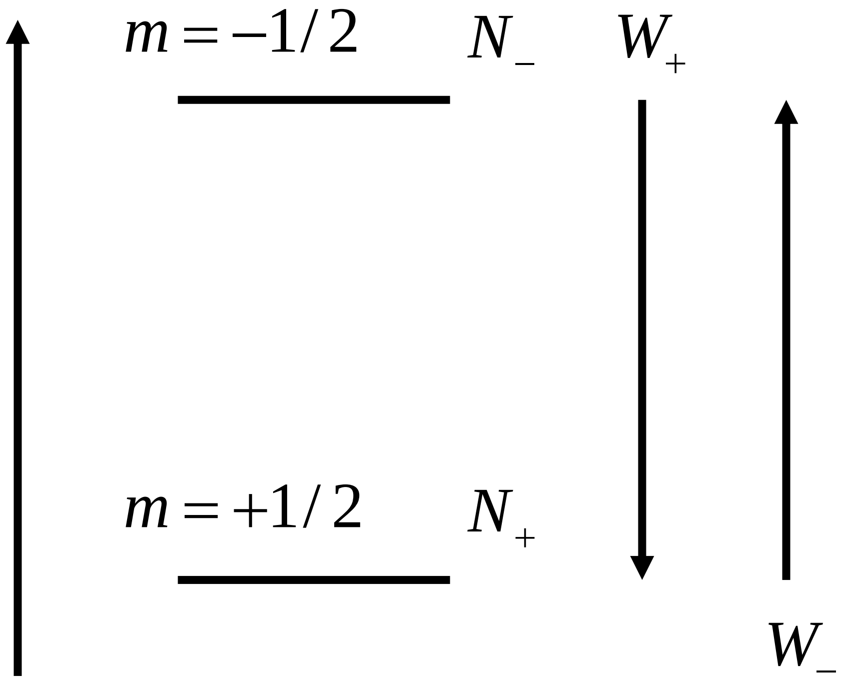


$D = M_0$
$t = T_1$
$D(t) = M_0\left(1 - e^{-t/T_1}\right)$
$t \rightarrow$



$D = M_0$
$t = T_1$
$D(t) = M_0\, e^{-t/T_1}$
$t \rightarrow$

Übergänge mit B_1-Feld

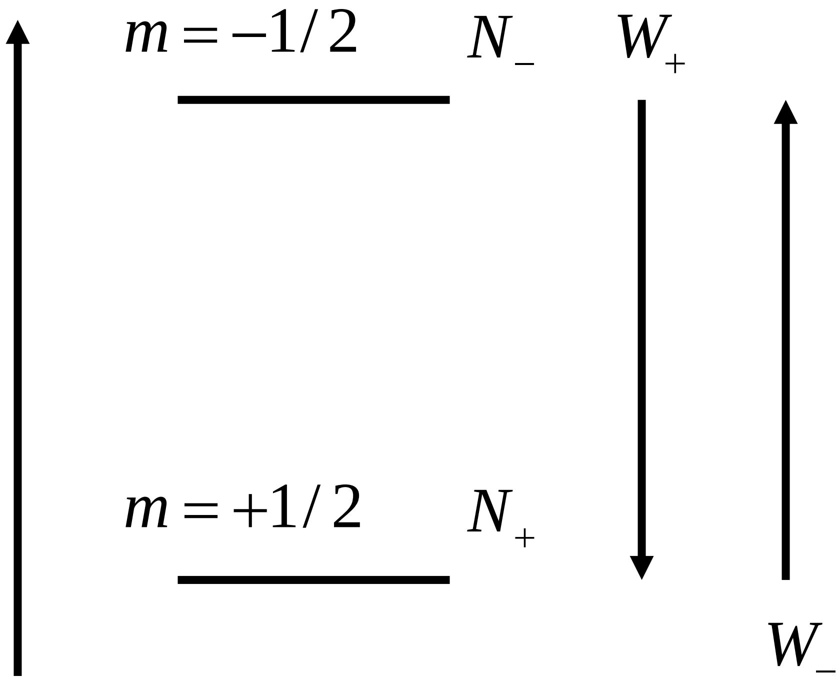


$$\nu = \frac{\Delta E}{h}$$

$$W_- = W_+ = W \approx H_1^{0\,2}$$

$$\frac{dN_+}{dt} = W\left(N_- - N_+\right)$$

Übergänge mit B_1-Feld



$$N = N_+ + N_- \qquad n = N_+ - N_-$$

$$N_+ = 1/2(N + n)$$

$$N_- = 1/2(N - n)$$

$$\frac{dn}{dt} = -2Wn$$

$$n = n(0)e^{-2Wt}$$

Übergänge mit B_1-Feld

B_1-Feld entzogene Energie: $$\frac{dE}{dt} = N_+ W h\omega - N_- W h\omega = h\omega W n$$

$$\frac{dn}{dt} = -2Wn + (n - n^0) R_1$$

im stationären Zustand $$\frac{dn}{dt} = 0: \qquad n = \frac{n^0}{1 + 2WT_1}$$

Makroskopische Magnetisierung

Magnetisierung in Z-Richtung: $$M_z = \sum_i N_i \mu_{zi}$$

Boltzmann-Statistik: $$\frac{N_i}{N} = \frac{\exp(-E_i / kT)}{\sum_i \exp(-E_i / kT)}$$

Entwicklung der e-Funktion: $$\frac{\exp(-E_i / kT)}{\sum_i \exp(-E_i / kT)} \approx \frac{1 - E_i / kT}{\sum_i (1 - E_i / kT)}$$

Makroskopische Magnetisierung

$$\mu_z = \gamma \hbar m \qquad\qquad E_m = -\gamma \hbar B_0 m$$

$$\frac{M_z}{N} = \frac{\sum_m \gamma\hbar m(1+\gamma\hbar B_0 m/kT)}{\sum_m (1+\gamma\hbar B_0 m/kT)}$$

$$= \frac{\sum_m (\gamma\hbar m kT + \gamma^2\hbar^2 B_0 m^2)}{\sum_m (kT + \gamma\hbar B_0 m)}$$

$$= \frac{\gamma^2\hbar^2 B_0 \sum_m m^2}{kT\sum_m 1}$$

Makroskopische Magnetisierung

$$\sum_m 1 = 2I + 1 \qquad \sum_m m^2 = \frac{1}{3} I(I+1)(2I+1)$$

$$\frac{M_z}{N} = \frac{\gamma^2 \hbar^2 I(I+1) B_0}{3kT}$$

Curiesches Gesetz:
$$M_z = \frac{N\gamma^2 \hbar^2 I(I+1)}{3kT} B_0$$
$$= \chi_K H_0$$

Kernsuszeptibilität