Modern Solid State NMR Techniques for the Study of Disordered Materials

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Literature

Highlight articles

D. Laws, H. M. Bitter, A. Jerschow, Angew. Chem. Int. Ed. 41 (2002), 3096.
M. J. Duer, Ann. Rep. NMR Spectrosc. 43 (2000), 1.

Fundamental Principles (Theory)

A. Abragam, *The Principles of Nuclear Magnetism*, Clarendon Press Oxford (1961).
C. P. Slichter, *Principles of Magnetic Resonance*, Springer Verlag Heidelberg 1978.
B.C. Gerstein, C.R. Dybowski, *Transient Techniques in NMR of Solids*, Academic Press Inc (1985).
M. Mehring, *Principles of High Resolution NMR in Solids*, Springer Verlag Heidelberg (1983)
R.R. Ernst, G. Bodenhausen, A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, Clarendon Press, Oxford (1987)

NMR Applications to Materials Sciences

J. Klinowski, Ed. *New Techniques in Solid State NMR*, Topics in Current Chemistry, 246, Springer-Verlag Heidelberg 2005.
K. Schmidt-Rohr, H.W. Spiess, Multidimensional *Solid-State NMR and Polymers*, Academic Press, London (1996).
M. J. Duer, *Introduction into Solid State NMR Spectroscopy*, Blackwell Publ. 2004

NMR = Nuclear Magnetic Resonance

N: Property of the Atomic Nuclei in Matter

M: Magnetic Property, arising from Spin Angular Momentum

R: Interaction with electromagnetic waves spectroscopy

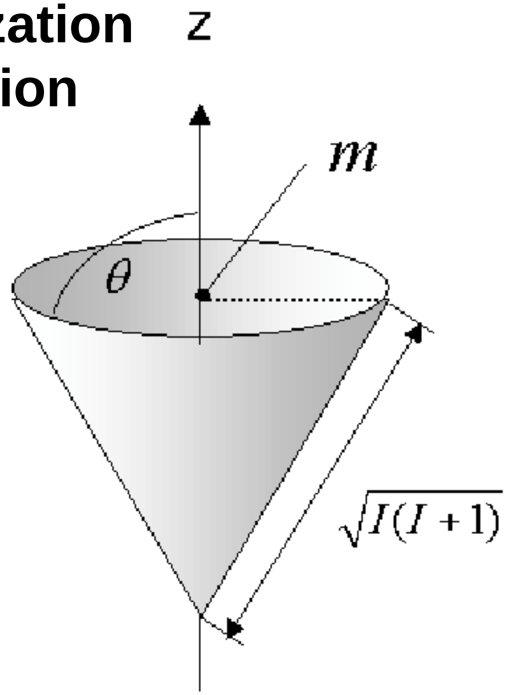
Nuclear Magnetism

Nuclear magnetic moment: $\mu = \gamma \hat{J} = \gamma \hbar \hat{I}$

I, the angular momentum, is subject to quantization laws, concerning both magnitude and orientation

$$\hat{\vec{\mathbf{I}}}^2 |I, m\rangle = \mathrm{I}(\mathrm{I}+1) |I, m\rangle$$

$$\hat{\mathrm{I}}_z |I, m\rangle = \mathrm{m} |I, m\rangle$$



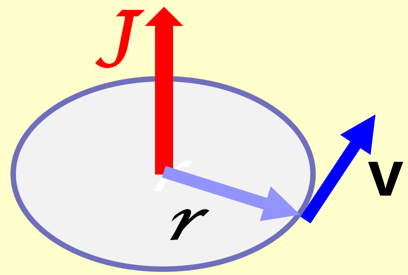
$\cos\theta = m / \sqrt{I(I+1)}$

I: **spin quantum number**

m: **orientational quantum number**
with m=-I,-I+1,…I-1,I
2I +1 orientational states

Relationship Spin-magnetic moment

Classical model: charge q on a circle with radius r



Magnetic moment: **μ = current $\times$ area**

Charge q on a circle: velocity: **$v = 2\pi r/t$ -> $t = 2\pi r/v$**

current = $q/t = qv/2\pi r$
area = πr^2

$\mu = q\, v\, r/2$

Angular momentum: $\boldsymbol{J} = \boldsymbol{p} \times \boldsymbol{r}$ = m **v r**
Magnetic moment: **μ = J q/2m (classical)**
μ = J γ (quantum mechanical)

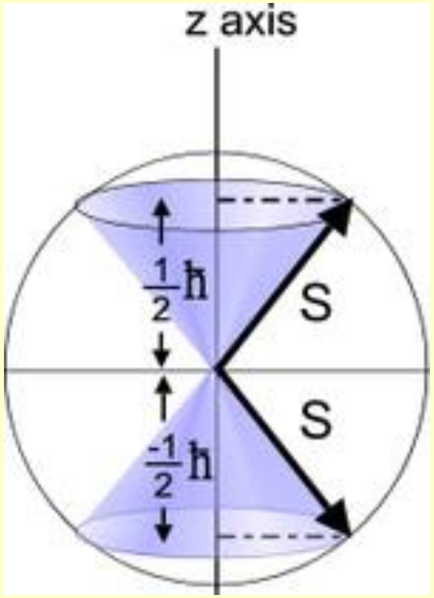
γ: *gyromagnetic ratio* (units $T^{-1}s^{-1}$)

Magnetic moments interact with magnetic fields

Zeeman interaction: $E = - \mu B$

B is called „magnetic flux density" and characterizes the strength of the magnetic field: units 1Tesla = Vs/m^2

Orientational quantization of spin: $|S_z| = m\, h/2\pi$



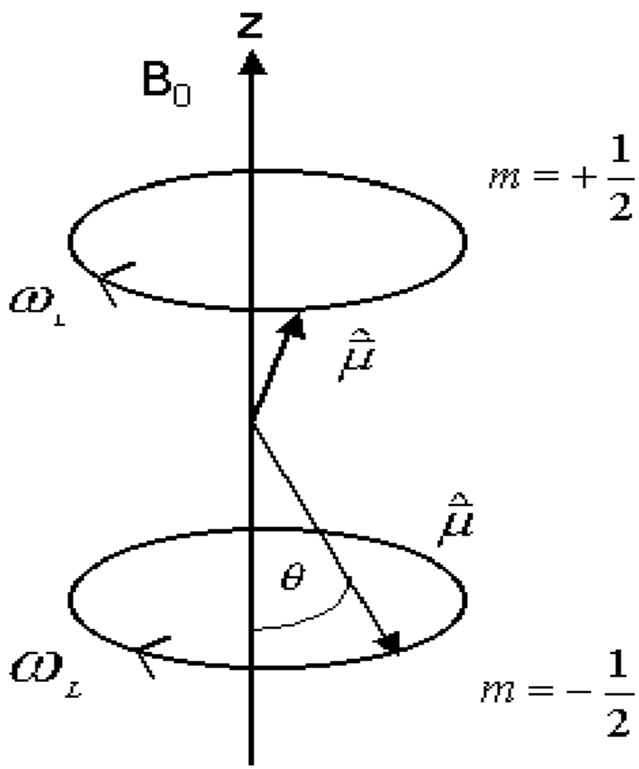
$$F = -dE/dz = -\mu\,(dB/dz)\cos(\mu,B)$$

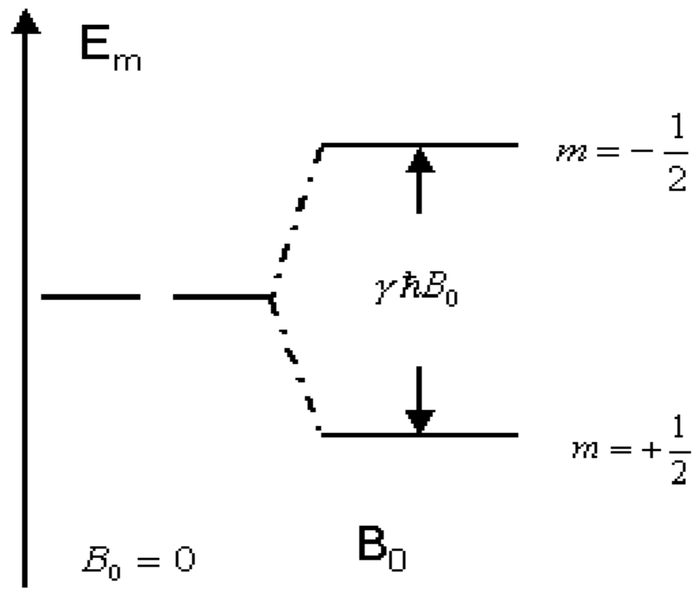
In an inhomogeneous magnetic field (magnetic field gradient) different spin orientations experience forces of different strengths

Case spin-1/2: Two nuclear spin orientations

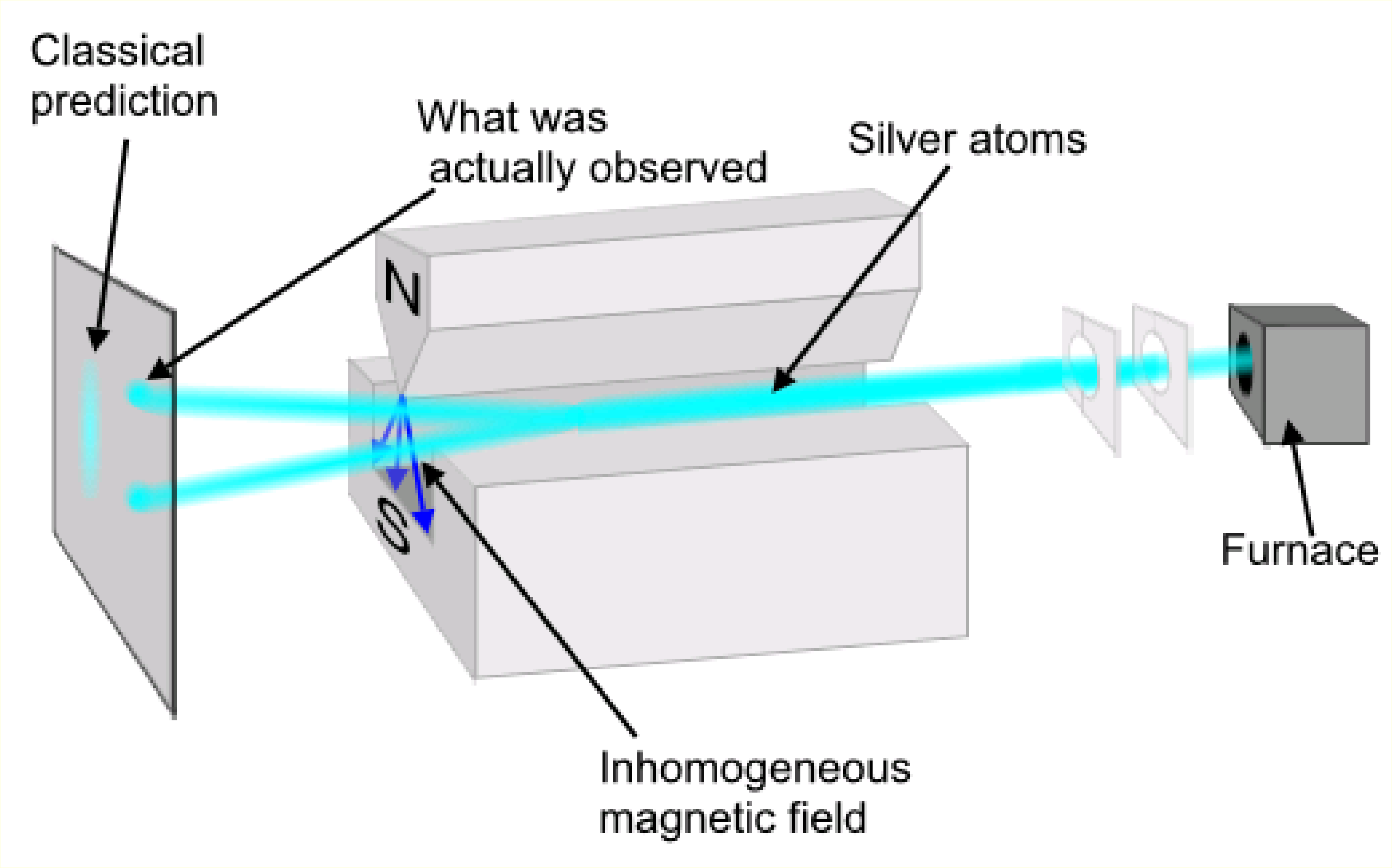
$E(m) = -m\gamma\hbar B_0$ (Zeeman-interaction)

⇒ The two orientations have different energies, difference depends on B_0 and γ

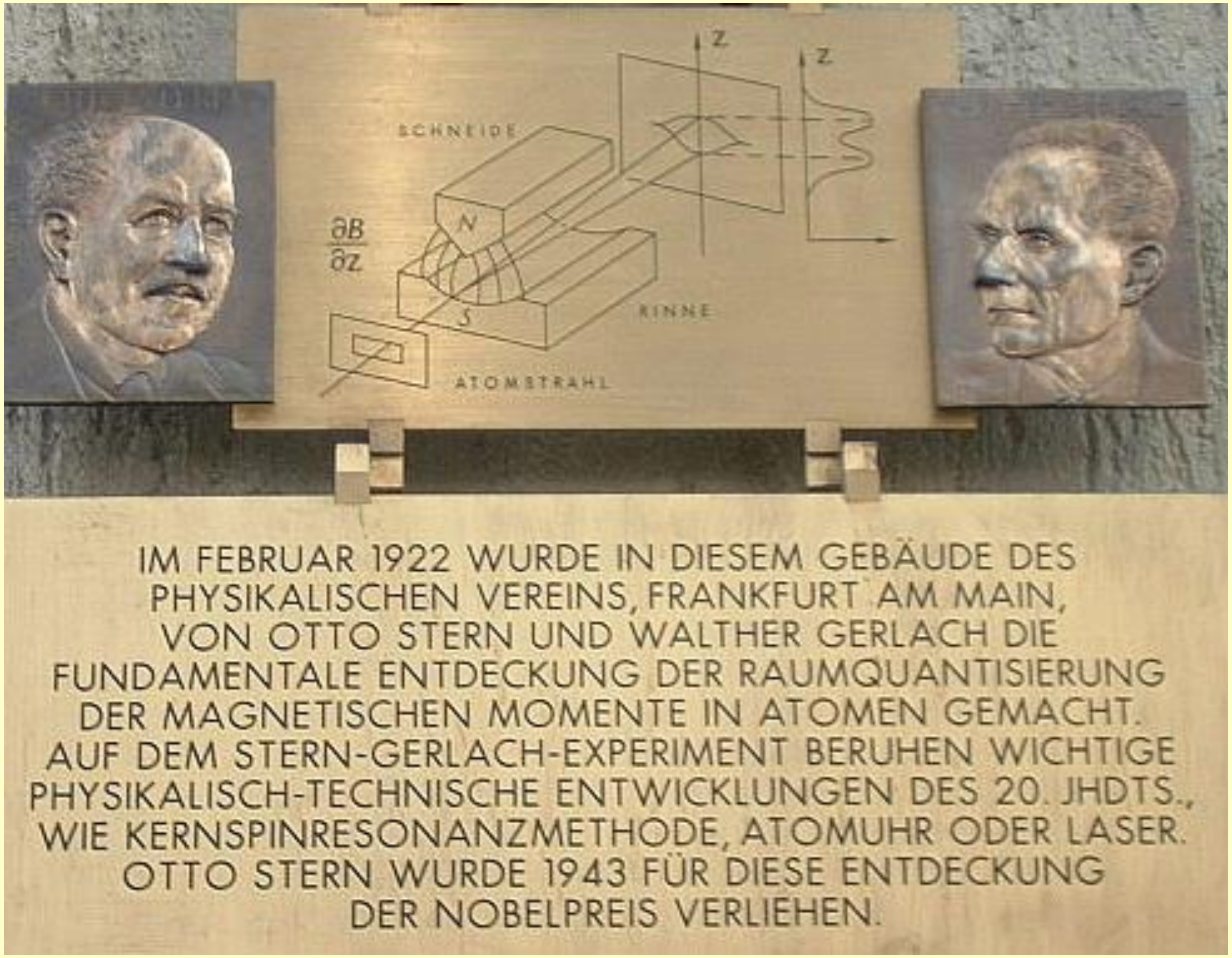




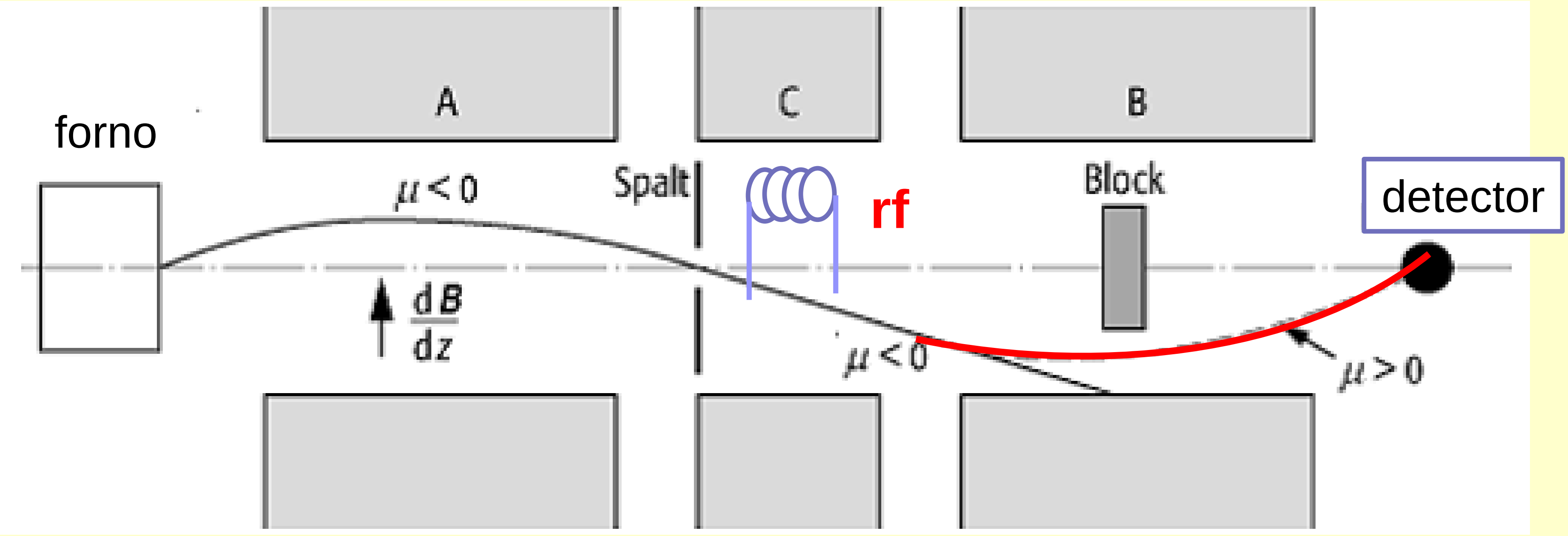
Stern - Gerlach experiment



The Stern – Gerlach experiment, 1922



Experiment of Rabi



Resonance: $\omega = \gamma B_o$

History *

1922 **Stern-Gerlach** Experiment
1938 **Rabi-** Experiment
1945/46 **Purcell/Pound, Bloch**: first NMR in cond. matter
1948 **Bloembergen, Purcell, Pound**: relaxation
1948 **Pake, van-Vleck**: dipolar analysis
1949 **KNIGHT** shift in metals
1950 **Dickinson, Proctor, Yu**: chemical shift
1950-s: commercial spectrometers (VARIAN)
1952 **Gutowsky, Slichter** spin-spin coupling
1950s **Hahn, Slichter**, pulsed NMR, spin echo

* **Nobel laureates**

Important milestones

1958	**Andrew:** magic-angle sample spinning
1966	**Ernst, Anderson**: pulsed Fourier Transf. NMR
early 1970-s	**Lauterbur, Mansfield**: NMR Imaging
early 1970s	**Jeener, Ernst, Bax**: 2-D NMR
1970-s	**Wüthrich**: Protein structure solutions
1975	**Schaefer:** cross-polarization
1980-s	**Spiess:** Polymer dynamics via NMR
1985	**Weitekamp:** Para Hydrogen polarizaiton
1989	**Pines:** Xe- and He Hyperpolarizaiton
1990	**Tycko:** Laser polarization
1990-s	**Griffin, Levitt, S. Vega**: multipulse NMR 1995
	Frydman: High-res. NMR of Q-nuclei
2000:	**Nielsen:** SIMPSON software
2000-s:	High-field magnet technology-> 23.6 T
2000-s:	**Kutzelnigg, Gauss, Schwarz:** DFT-calculations
2000-s	**Griffin, Emsley, Bodenhausen**: DNP/MAS

Nuclear Magnetism

Nuclear magnetic moment: $\mu = \gamma \hat{J} = \gamma \hbar \hat{I}$

I, the angular momentum, is subject to quantization laws, concerning both magnitude and orientation

$$\hat{\vec{\mathbf{I}}}^2 |I, m\rangle = \mathrm{I}(\mathrm{I}+1)|I, m\rangle$$

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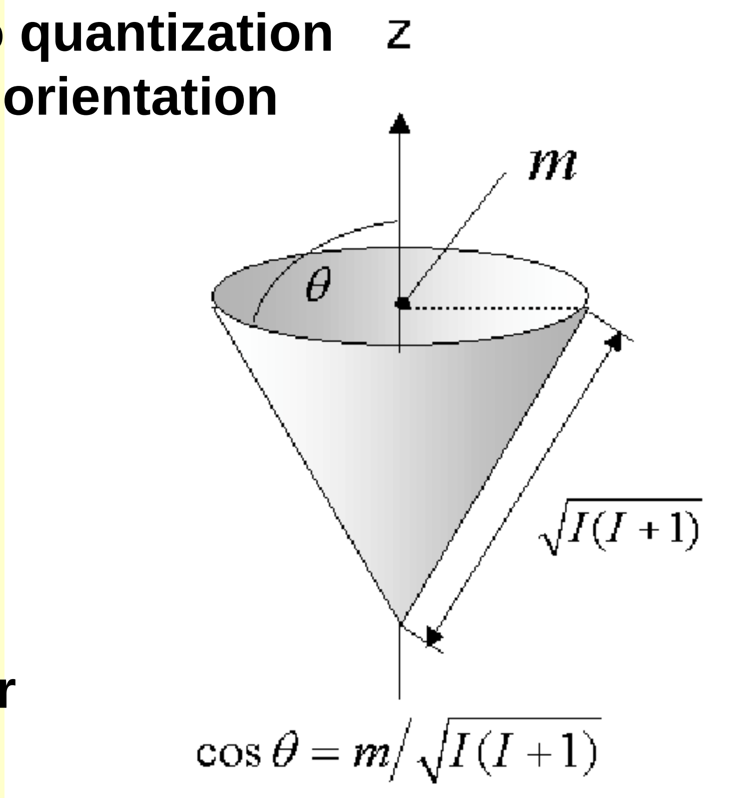
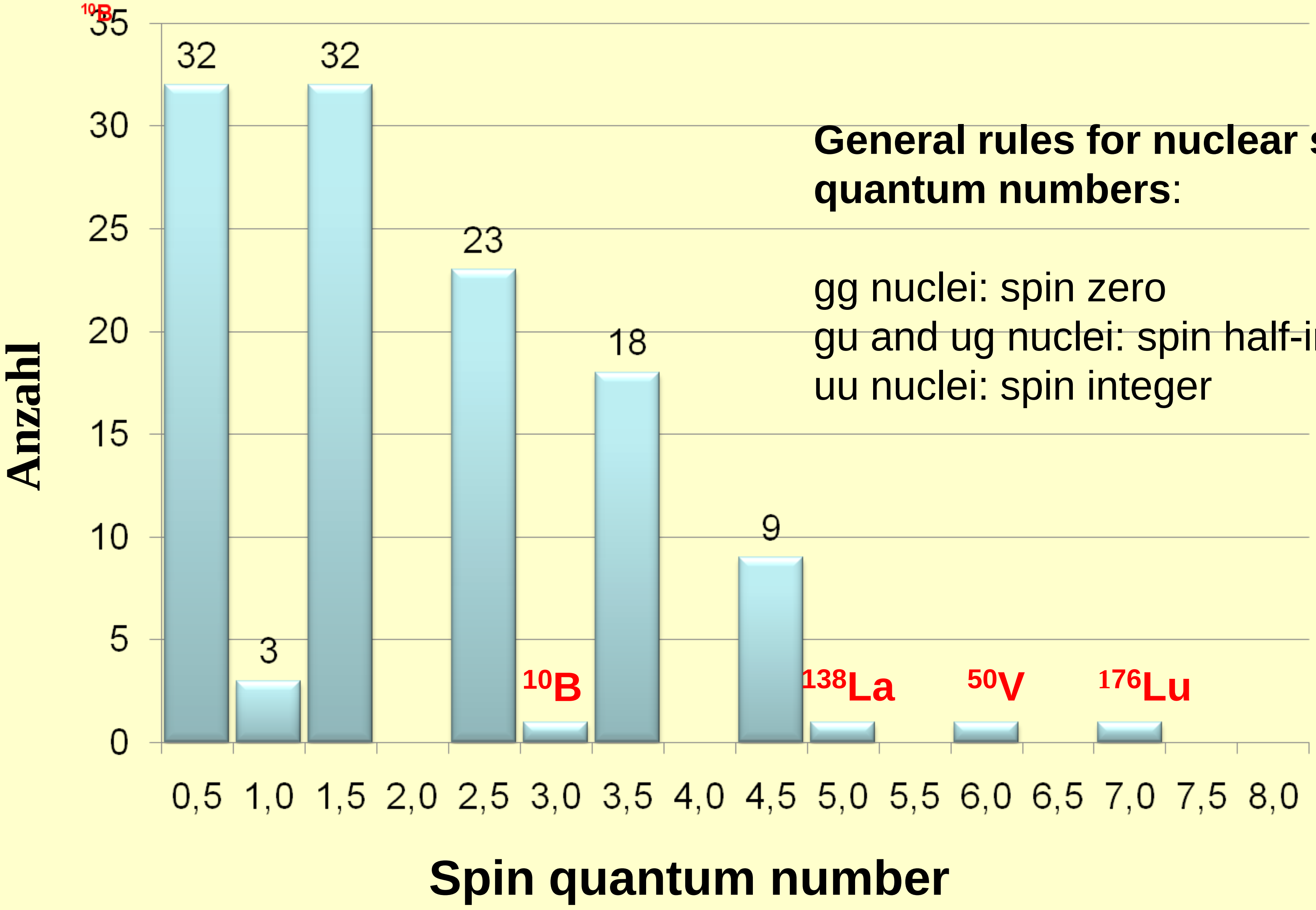


I: **spin quantum number**

m: **orientational quantum number with m=-I,-I+1,…I-1,I**

2I +1 orientational states

Nuclear spin quantum numbers



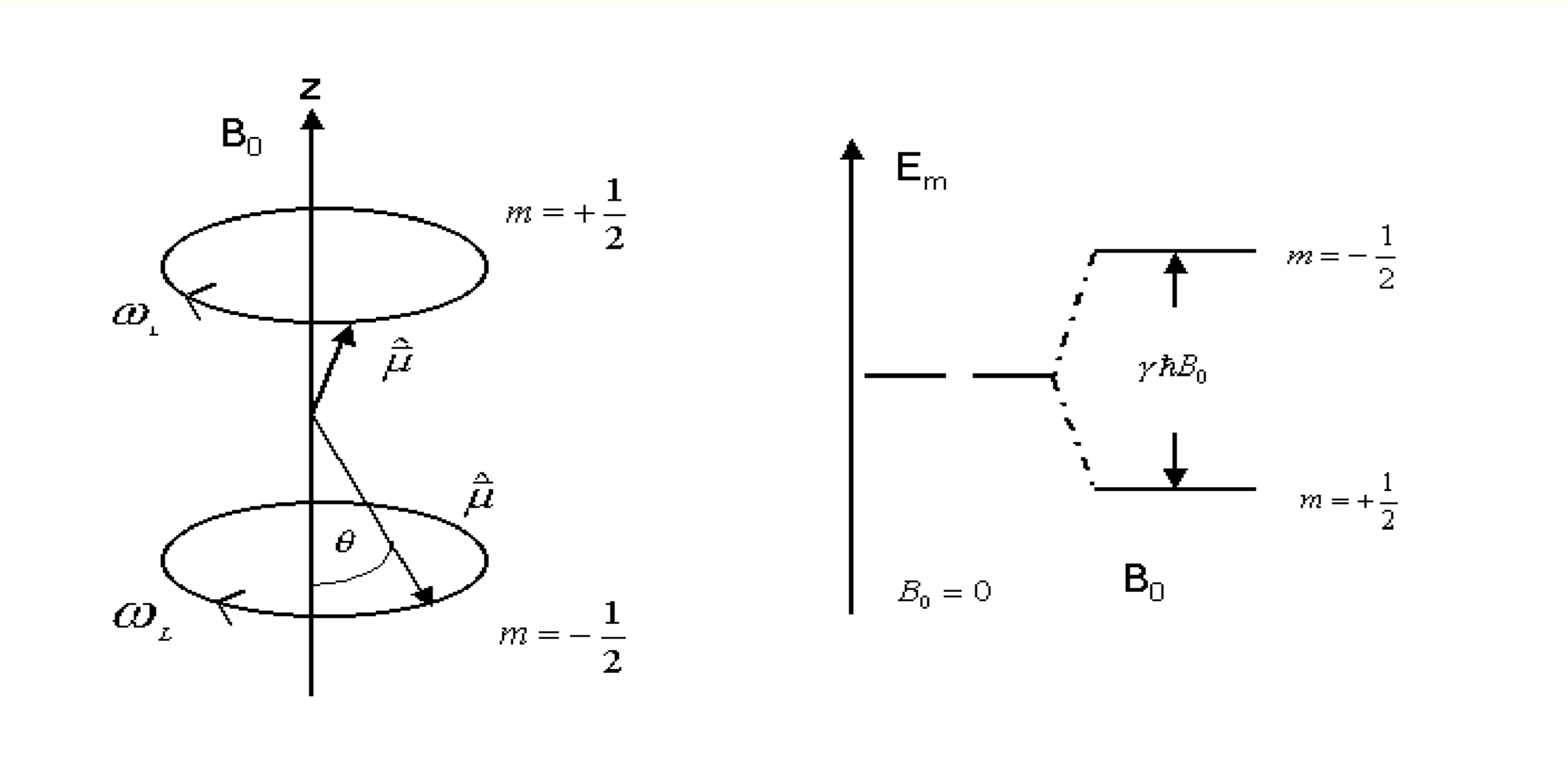
General rules for nuclear spin quantum numbers:

gg nuclei: spin zero
gu and ug nuclei: spin half-integer
uu nuclei: spin integer

Case spin-1/2: Two nuclear spin orientations

$E(m) = -m\gamma h B_0$ (Zeeman-interactions)

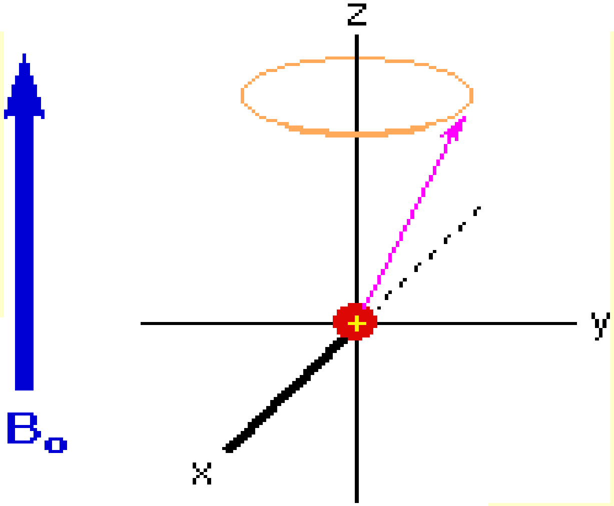
The two orientations have different energies, difference depends on the value of γ

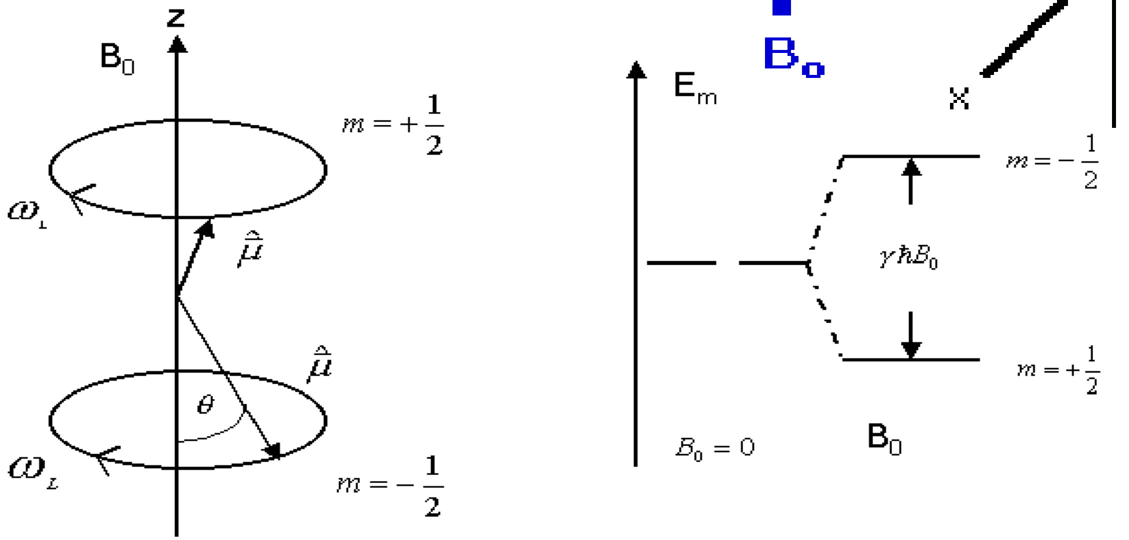


NMR is element selective

Precession

Precession of spins around external field
similar to gyroscope





The precession (Larmor) frequency of the nuclei is given by

$$\omega_p = \gamma B_{eff}$$

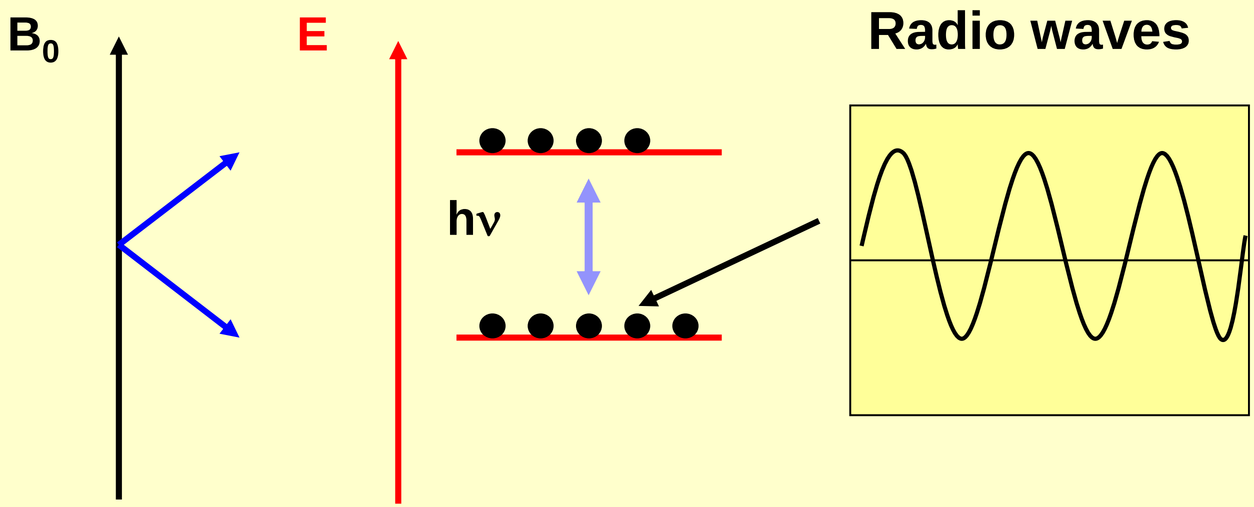
where $B_{eff} = B_0 + B_{int}$

B_{int} contains important structural and chemical information

NMR measures the precession (Larmor) frequency

How is it done ?

By application of a second magnetic field fluctuating with frequency $\omega_o \sim \omega_p$



Resonance absorption occurs if $\omega_0 \sim \omega_p$

Macro-sample: Boltzmann distribution ⇨ Magnetization

$$M_z = \Sigma_i \frac{\mu_i}{V}\left(\frac{A}{m}\right)$$

Calculation of M_z:

$$E/V = \Sigma_i\ B_0 n_i \mu_i / V = \quad M_z B_0$$

where: $\mu_i = m_i \gamma \hbar$ $\qquad n_i = \frac{\exp - E_i/k_B T}{\Sigma_i \exp - E_i/k_B T} N$

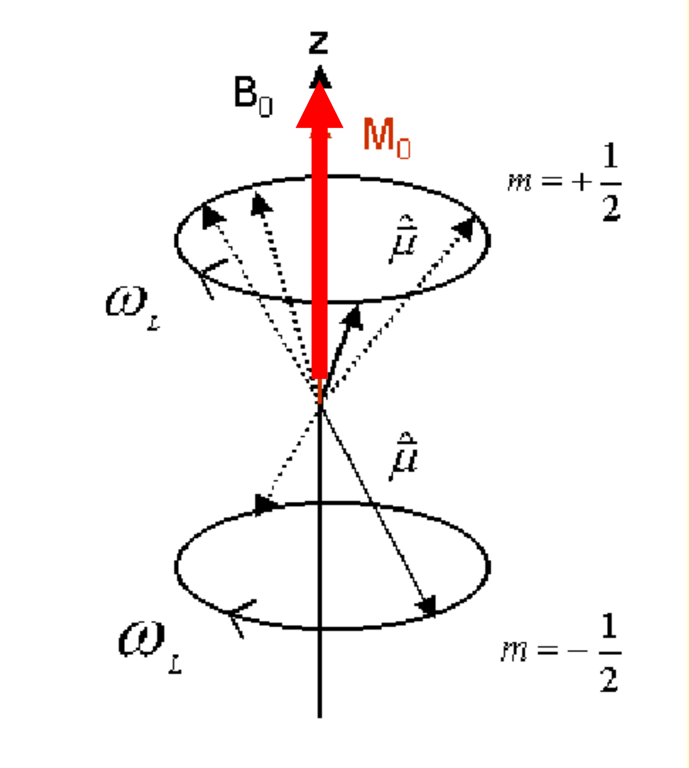
$$\exp - \frac{E_i}{k_B T} \approx 1 - \frac{E_i}{k_B T}$$

(HT approximation)

$$E_i = -\, m_i \gamma \hbar B_0$$

$$\Sigma_i \exp - E_i/k_B T = 2I + 1$$

$$E/V = \Sigma_i \left(1 + \frac{m_i \gamma \hbar B_0}{k_B T}\right) m_i \gamma \hbar \frac{N}{V} \quad = \quad M_z B_0$$



Macroscopic magnetization in z-direction :

$$M_z = M_o = \frac{\boxed{N/V}\,\gamma^2 \hbar^2 I(I+1)}{3kT} B_o$$

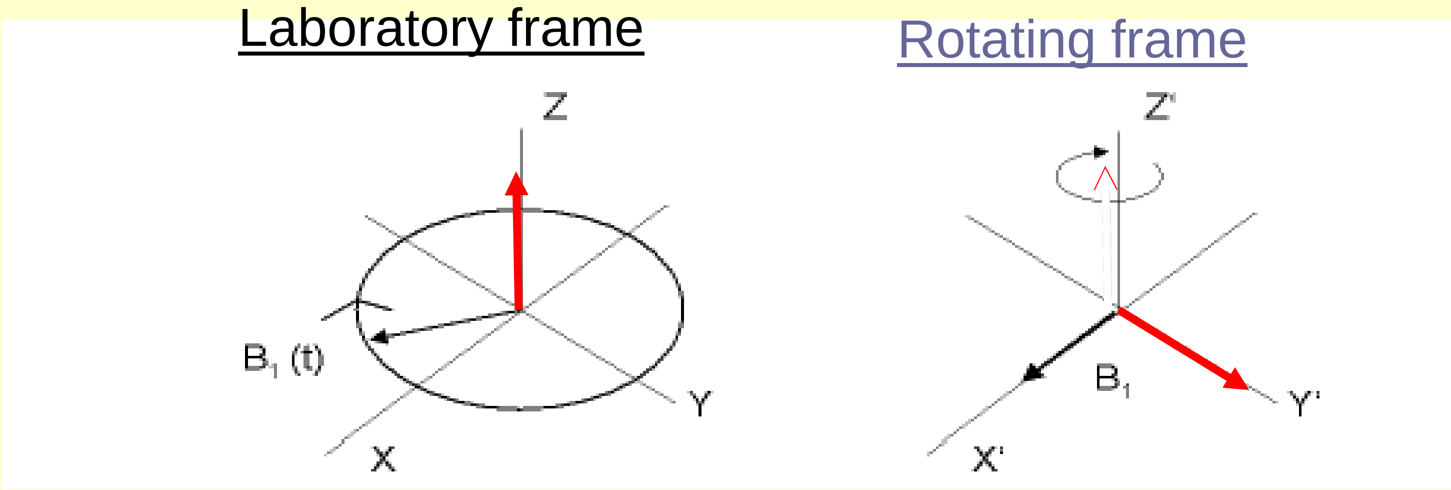
No net magnetization in x- or y-direction

NMR is quantitative

The Rotating Frame

In contrast to the B_0 field, the B_1 field changes direction in time with the frequency ω_0

To simplify the description of the magnetization's time dependence a rotating frame is introduced



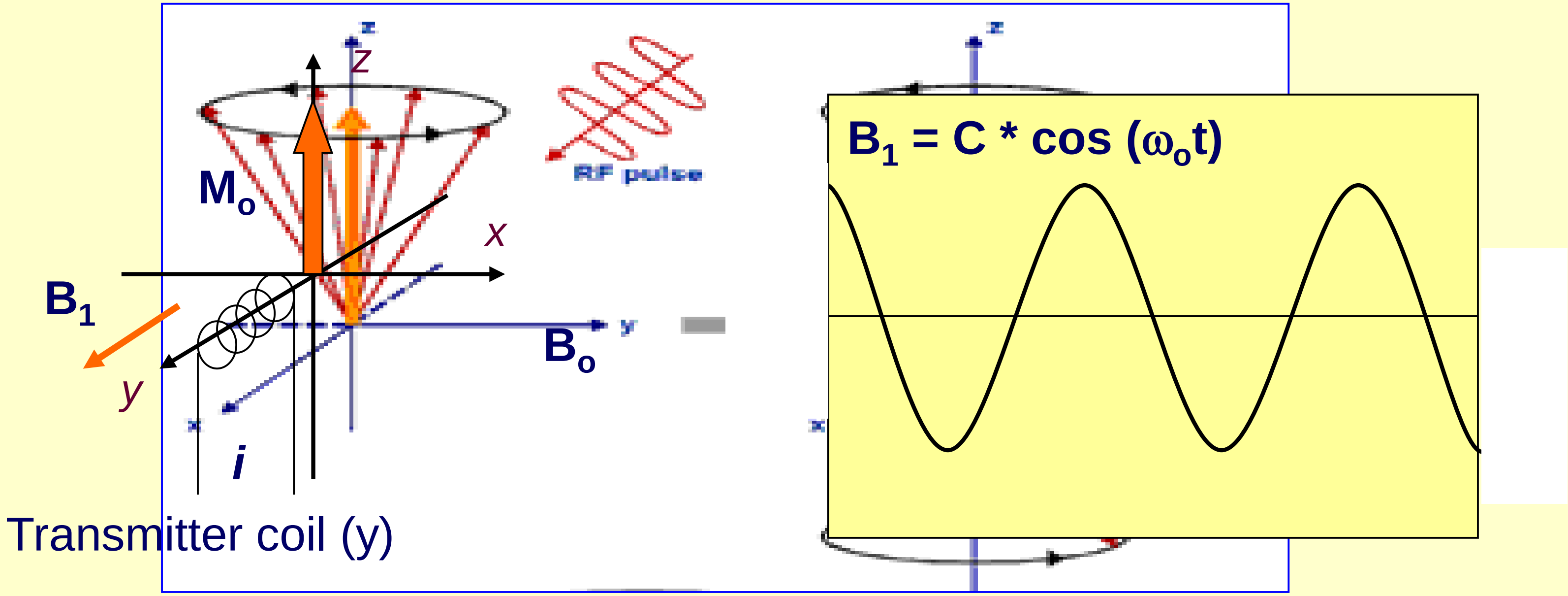
Rotating frame rotates with frequency ω_0 of B_1

90° pulse: **rotates the z-magnetization into the x-y-plane**
180° pulse: **flips the z-magnetization into the –z-direction**

Measuring NMR spectra

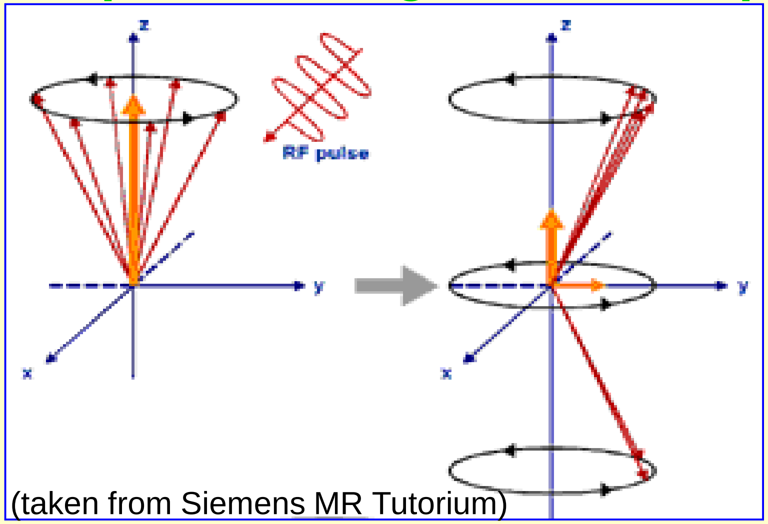
= Detection of Larmor frequencies present in the sample

1. B_1 field is irradiated for a short time t_p along the x,y direction
2. If $\gamma B_1 t_p = \pi/2$ then M_z is flipped by 90 degrees (90° pulse)
3. After the pulse, precession of M induces voltage in the coil.
4. This voltage, oscillating with ω_p, is the NMR signal



The Basic NMR Experiment

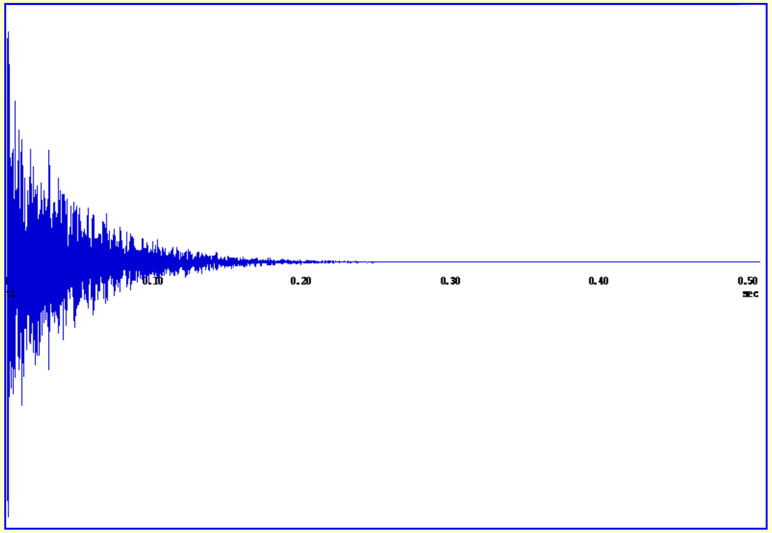
90° pulse -> magnetization flip



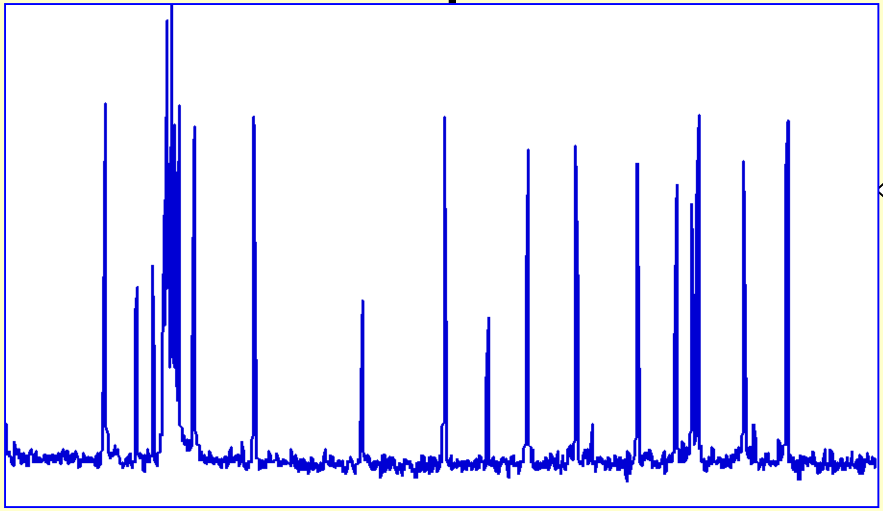
(taken from Siemens MR Tutorium)

Signal-detection

Free Induction Decay



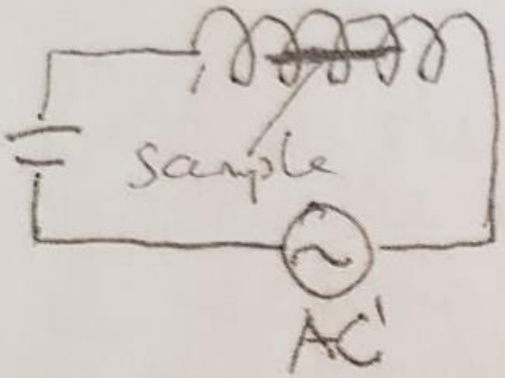
NMR-Spectrum



Fourier-Transformation

$$F(\omega) = \int_{-\infty}^{\infty} f(t) * e^{-i\omega t} dt$$

Como funciona ?

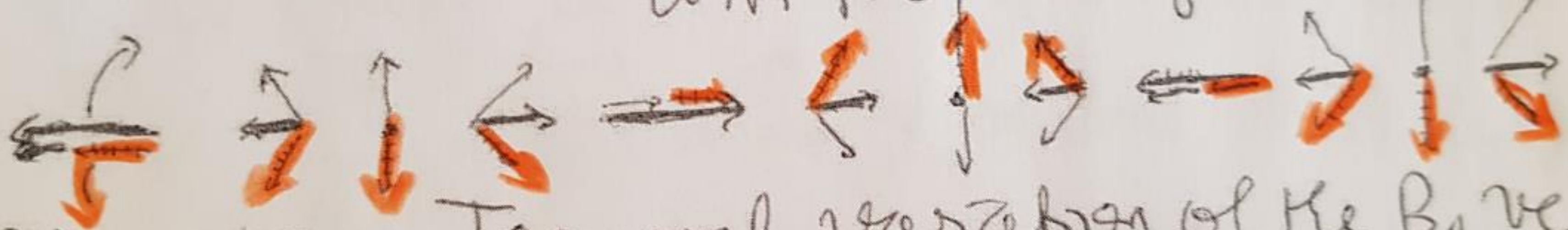


source, frequency w_0 $\omega = \frac{1}{\sqrt{L}}$

Within the coil a linearly po
B_1 field is created and inter
there with the sample. B_1 osc
with frequency w_0

L ⇒

C ⇒

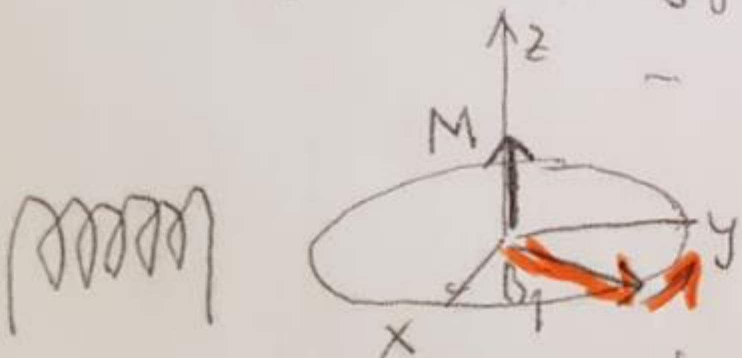


Temporal variation of the B_1 vect
the coil for a linearly polarized field and
position into two circularly polarized comp

$$B_{right}(z,t) = B_1 \cos(kz - w_0 t) + B_1 \sin(kz - w_0 t)$$
$$B_{left}(z,t) = B_1 \cos(kz - w_0 t) - B_1 \sin(kz - w_0 t)$$

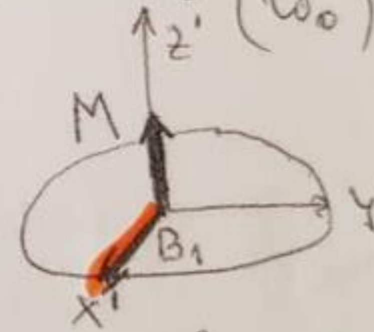
The effect of the B_1 field upon the magnetization is conveniently described in a rotating coordinate system. What moves with the frequency of the applied radio waves, i.e. ω_0 -

<u>Laboratory frame</u>



B_1 vector rotates in the xy plane $\perp$ z

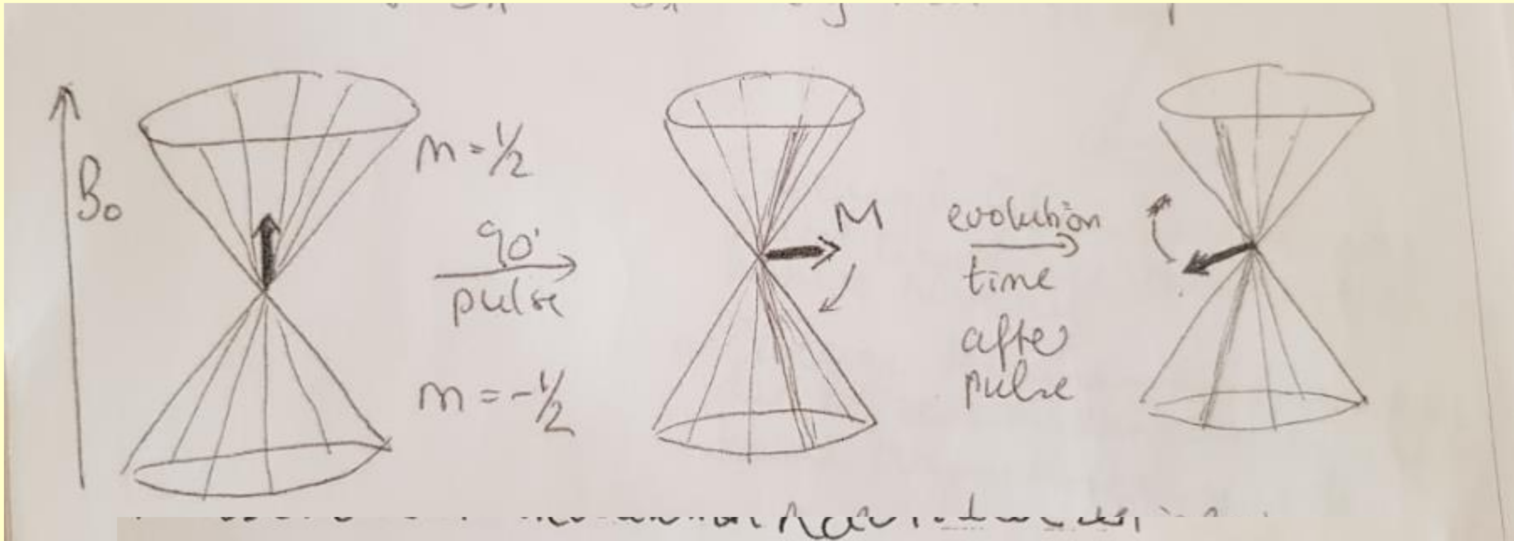
<u>Rotating frame</u> (ω_0)

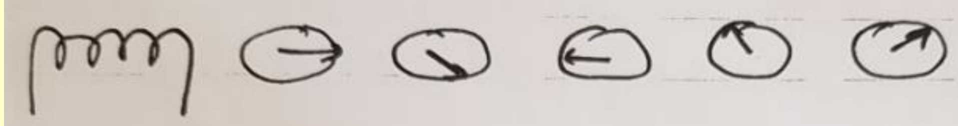


B_1 vector is fixed a
aligned along x' axi

Both in the laboratory frame and in the rota
frame the magnetization is along z. i.e. the
of the magnetiz field B_0. The B_1 ve
the magnetizatio

Signal Detection by electromagnetic induction





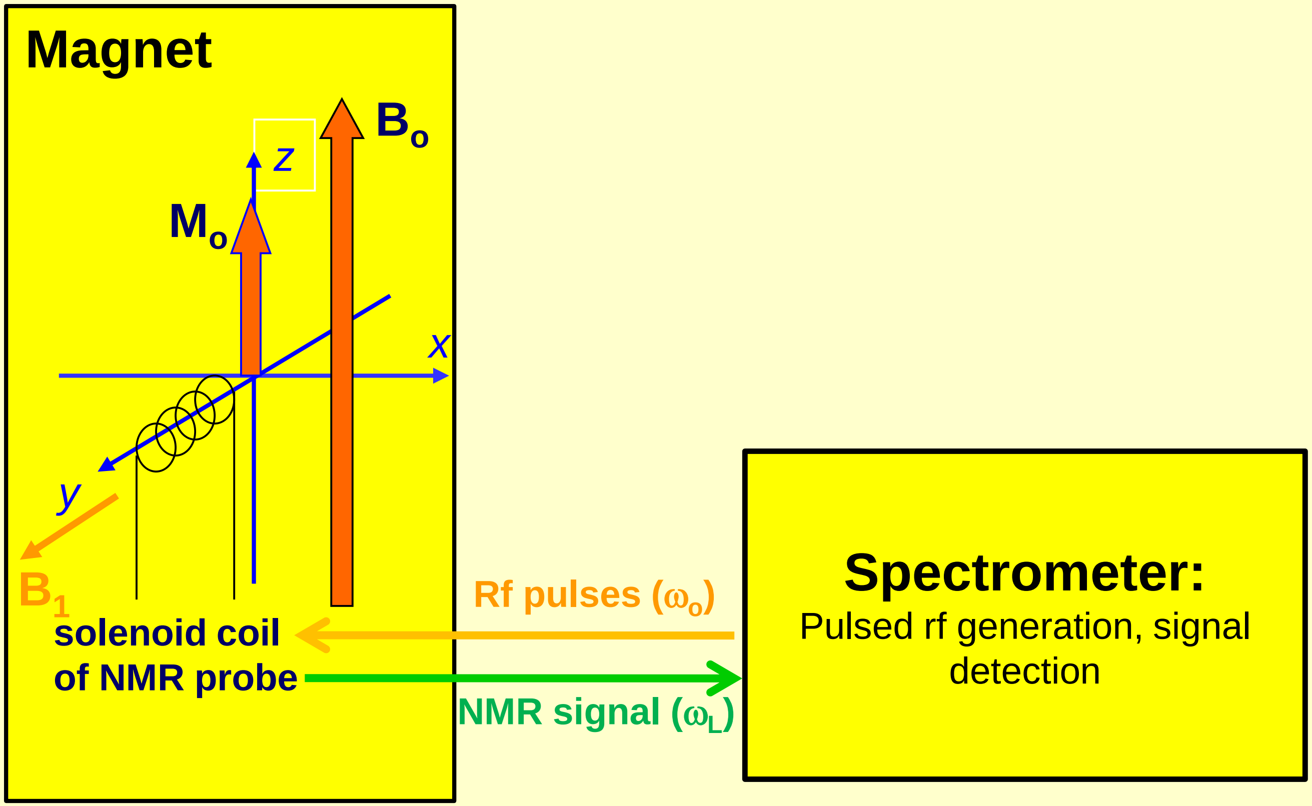
$B_{ind} = \mu_0 \cdot M(t) = \mu_0 M_0 \sin \omega_p t$

$\phi = B_{ind} \cdot A$ (magnetischer Fluß) $\quad U_{ind}(t) = -\frac{d\phi(t)}{dt} n\eta$

$$U_{ind}(t) = -n\eta A \underbrace{\omega_p}_{\sim B_0} \mu_0 \underbrace{M_0}_{\sim B_0} \cos \omega_p t = U_0 \cos \omega_p t$$

Signalintensität $\sim B_0^2$

Schematic Experimental Set-up



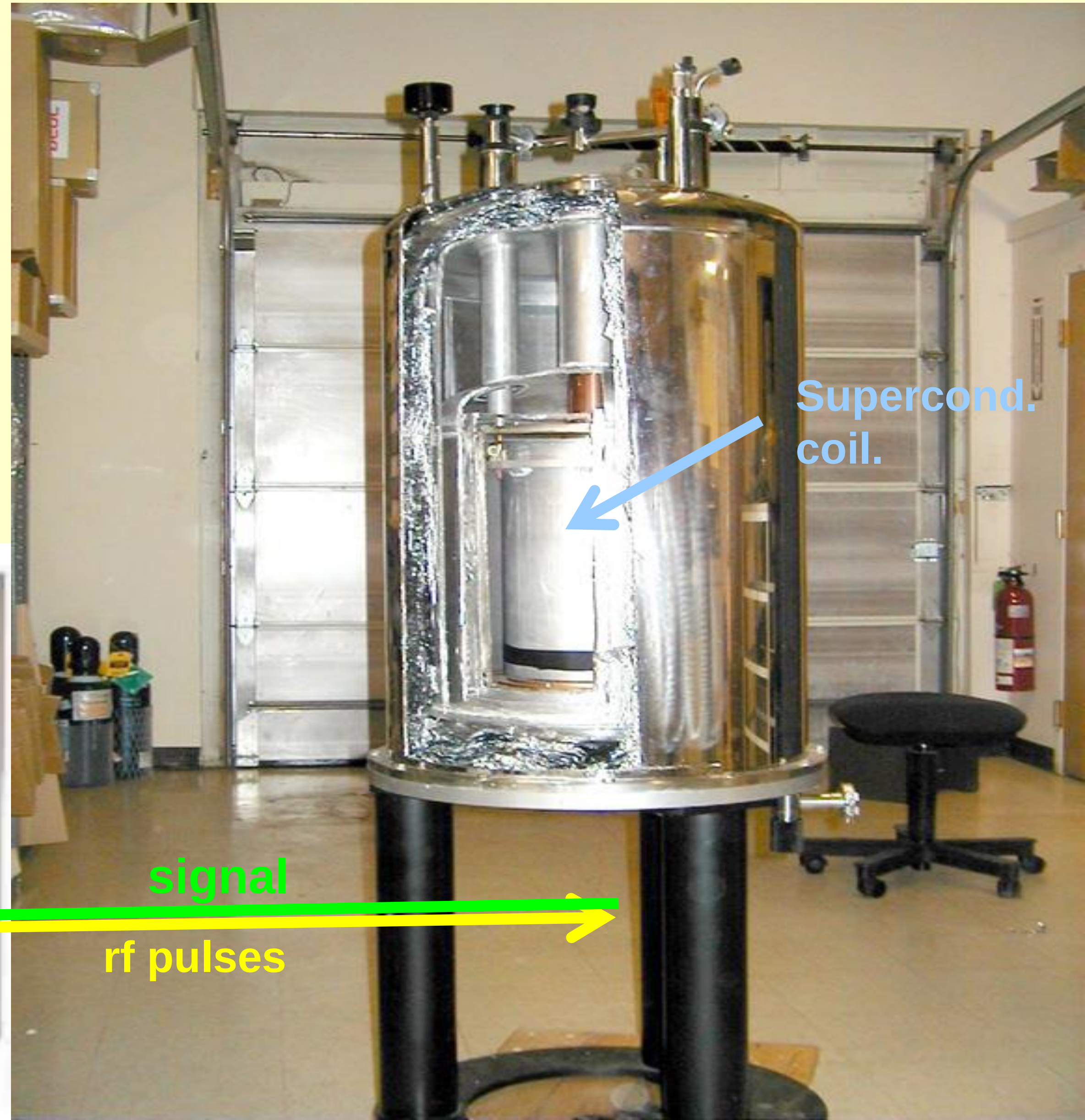
Equipment

magnet

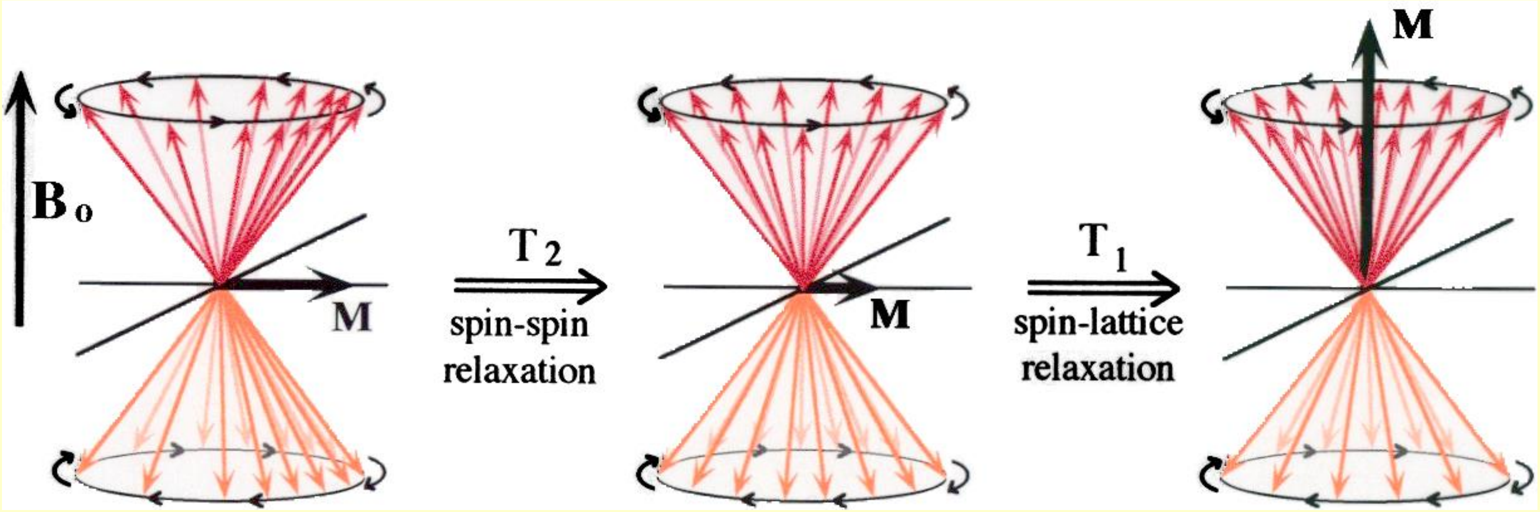
probe

Sample in
coil

Console:
signal excitation
and detection



Relaxation Processes



Transverse relaxation (T_2): dephasing of spins in the x-y plane (distribution of precession frequencies, spin-spin interactions)

Longitudinal relaxation (T_1): build-up of z-magnetization (return to equilibrium, energy exchange with surroundings (lattice)

Four distinct interactions

- magnetic shielding
- Electric quadrupole coupling
- Indirect spin-spin coupling
- magnetic dipole coupling

In the solid state:

anisotropy: $\omega_p \sim 3\cos^2\theta - 1$

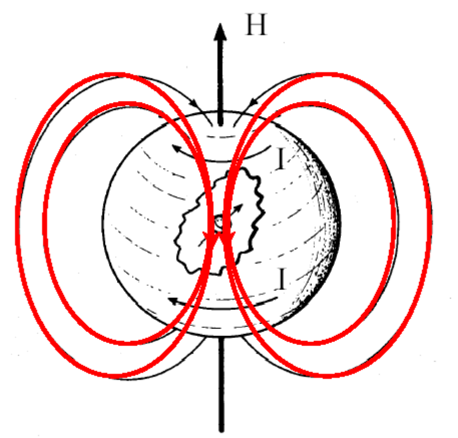
Magnetic Shielding

Resonance frequency (bare nucleus): $\omega_0 = \gamma B_0$

Effective magnetic field at nucleus: $B_{eff} = B_0(1-\sigma)$

Resonance frequency (real sample) $\omega_L = \gamma B_0(1-\sigma)$

Chemical shift $\delta \equiv \dfrac{\omega_L^x - \omega_L^{ref}}{\omega_L^{ref}}$



Effective magnetic field arises from shielding or deshielding of the external magnetic field by electrons

Probe for electronic environment (bonding)

Chemical Shielding Anisotropy

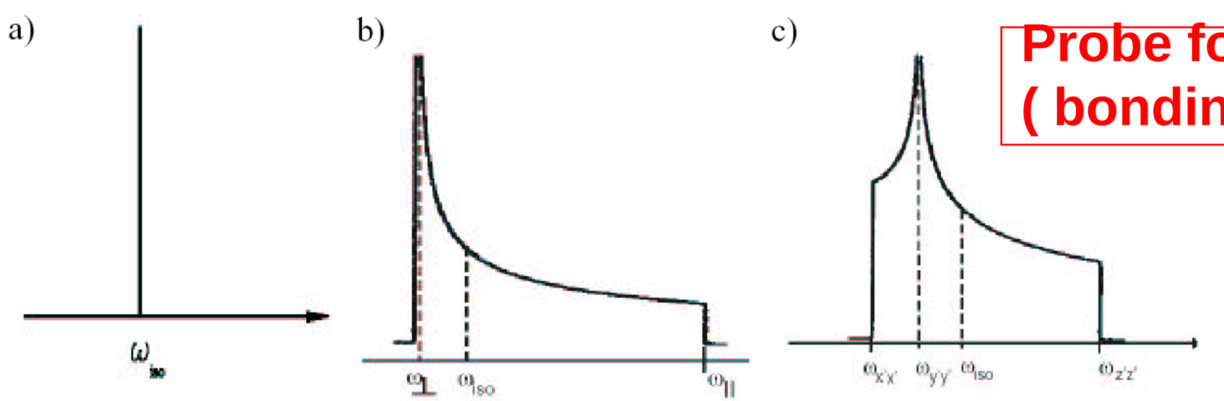
Solid state : chemical shielding is anisotropic:

➔ tensorial description

$$\omega_L = \omega_0 \left[1 - \sigma_{iso} - \frac{1}{3}(\sigma_{z'z'} - \sigma_{x'x'})(3\cos^2\theta - 1) \right]$$

powdered sample

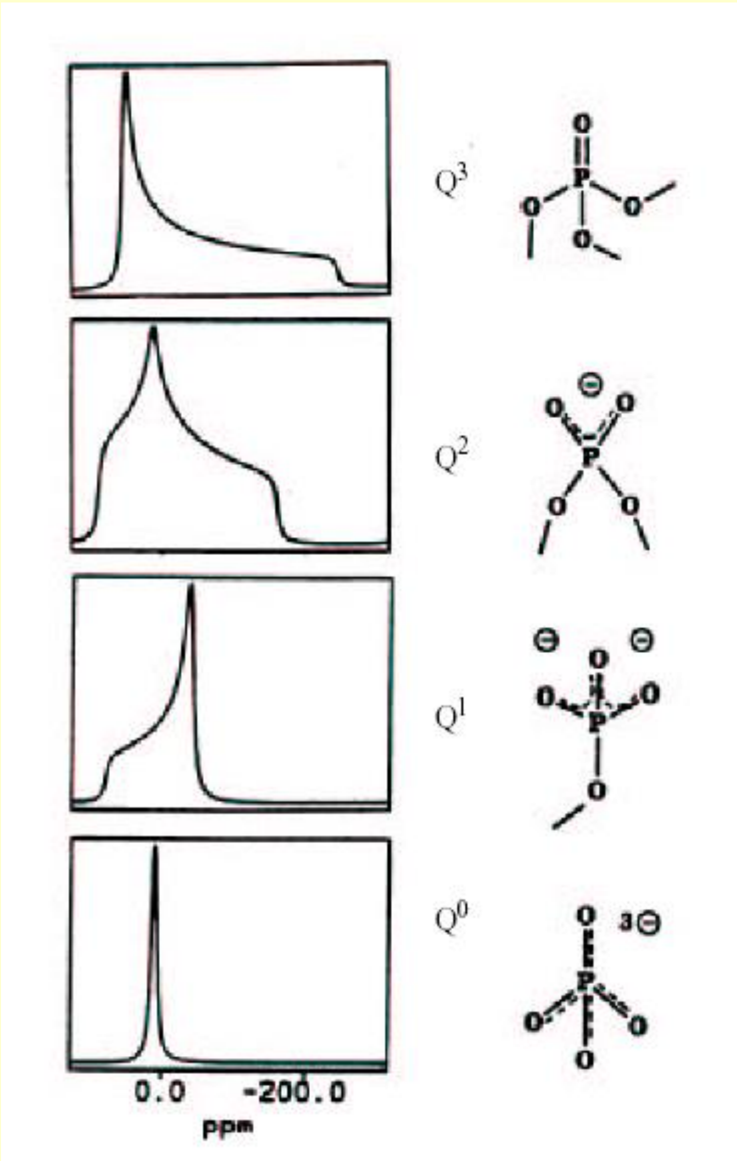
Distribution of orientations

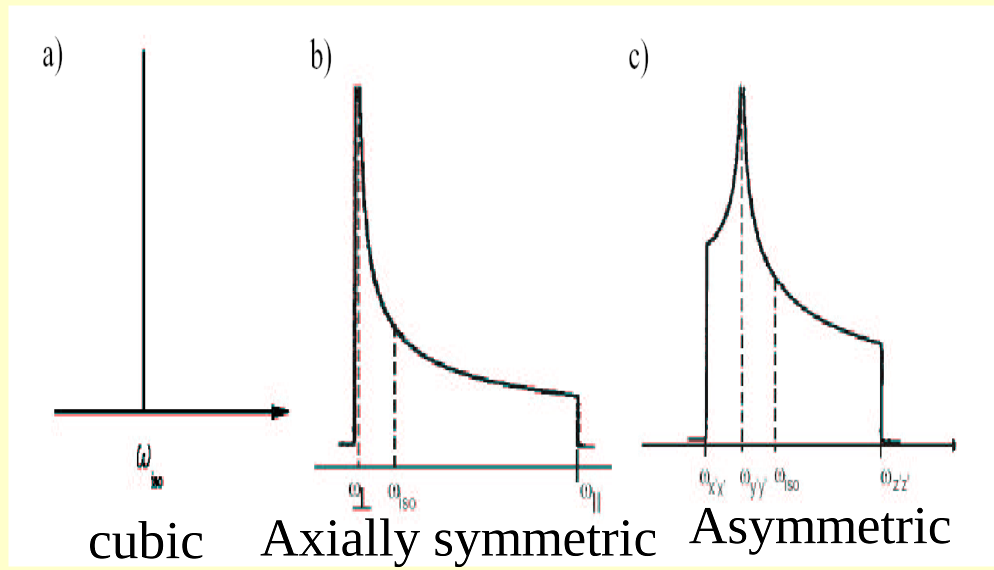


Probe for local symmetry (bonding geometry)

cubic **Axially symmetric** **Asymmetric**

Example : ^{31}P NMR of Phosphates

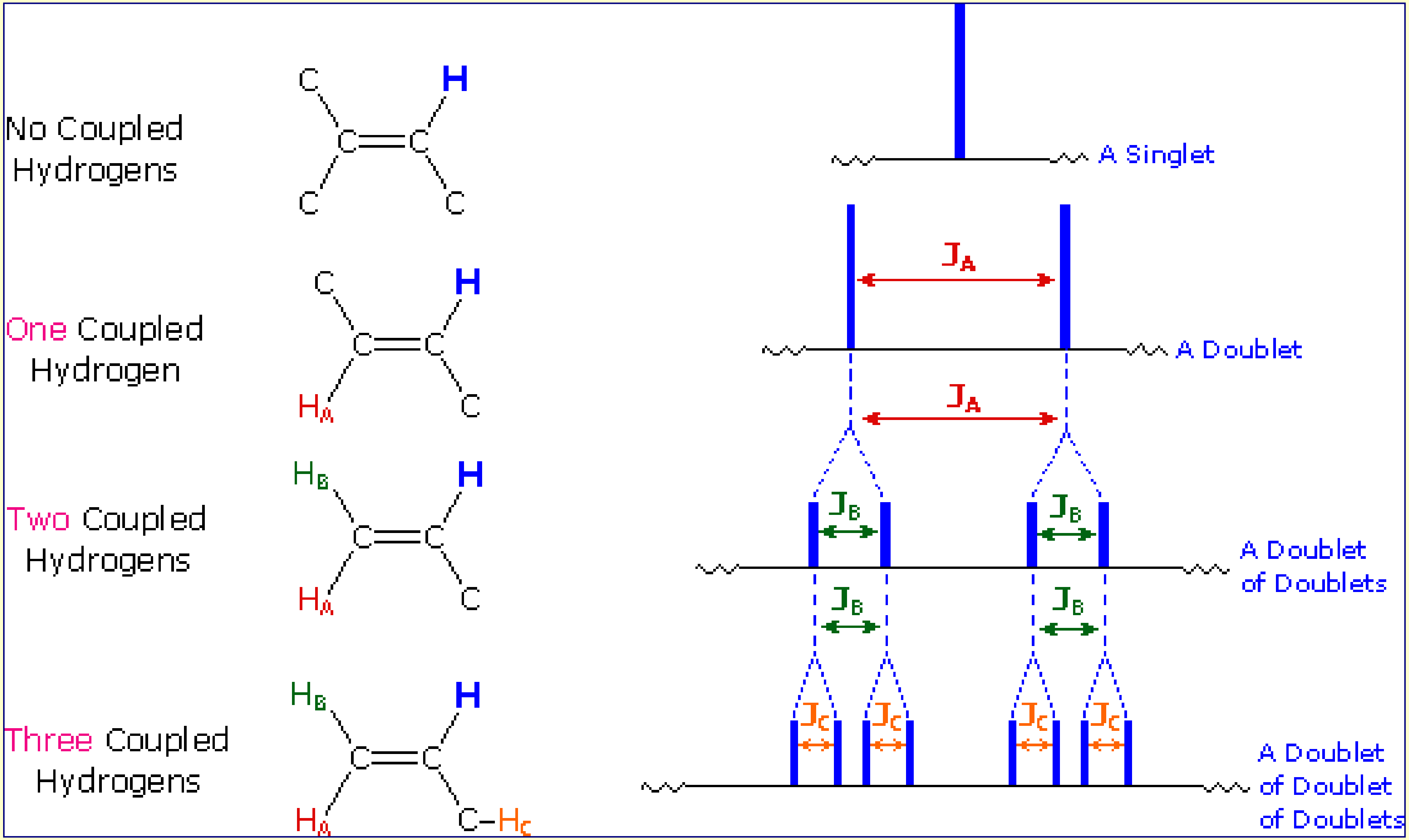




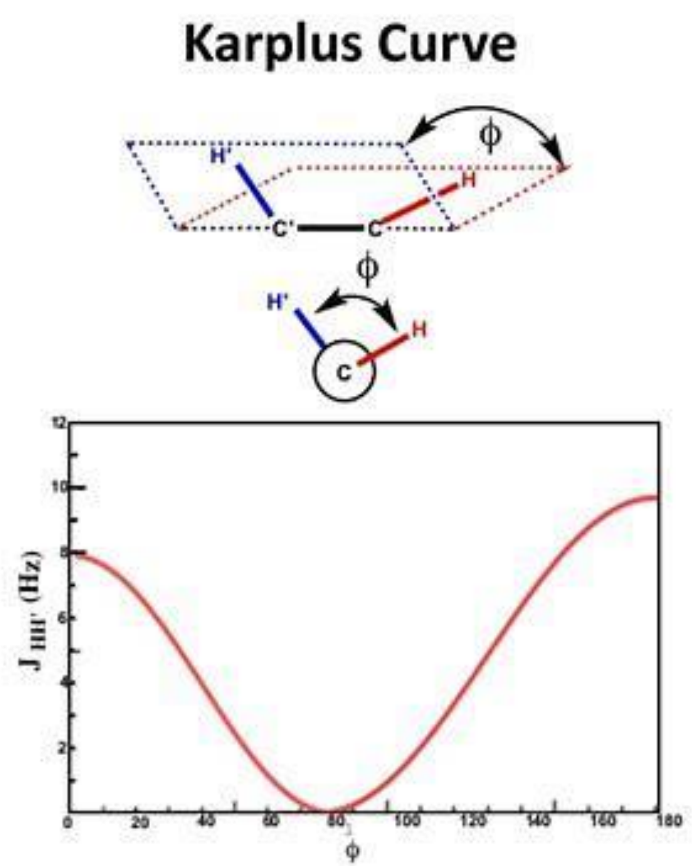
Indirect spin-spin Coupling

- Spin-spin interaction transmitted via polarization of bonding electrons
- HAMILTONIAN $\mathcal{H}_J = 2\pi\, \hat{\mathbf{I}}_1\, \mathfrak{J}\, \hat{\mathbf{I}}_2$ homonuclear
- $\mathcal{H}_J = 2\pi\, \hat{\mathbf{I}}\, \mathfrak{J}\, \hat{\mathbf{S}}$ heteronuclear
- Anisotropy accounted for by tensorial description
- Isotropic component: $\mathbf{J}_{iso}$ (scalar, isotropic coupling constant)
- Anisotropic component: $\Delta\mathbf{J}$, same dependence on spin operators as the through-space dipole-dipole coupling
- Liquid-state and MAS-NMR: only $\mathbf{J}_{iso}$ relevant: $\Pi_i\, 2n_i I_i + 1$ multiplicity rule
- n_i = number of equivalent spins of quantum number I_i the observed nucleus is coupled to

Examples of Spin-Spin Coupling Multiplicities



Karplus-Relation for J-coupling



For ^3J (^1H-^1H) coupling:

$$J(\phi) = C\cos 2\phi + B\cos\phi + A$$

***A* = 4.22, *B* = −0.5, and *C* = 4.5 Hz.**

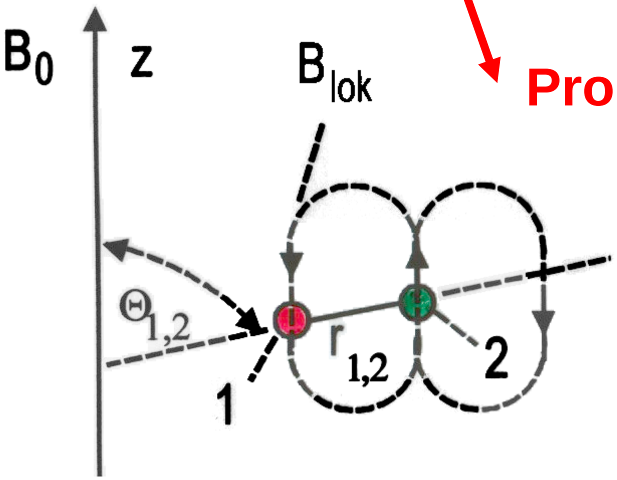
Important for conformational studies (protein folding)

Nobel Prize 2013

Magnetic dipole interactions

Magnetic moments of nearby spins affect the local magnetic field and thus the resonance frequency. „Through-space“ interaction

$$\hat{H}_{DIP}\ (ij) = -\frac{\mu_0}{4\pi}\gamma_i\gamma_j\hbar^2 \boxed{r_{ij}^{-3}} \left[\hat{A}+\hat{B}+\hat{C}+\hat{D}+\hat{E}+\hat{F}\right]$$



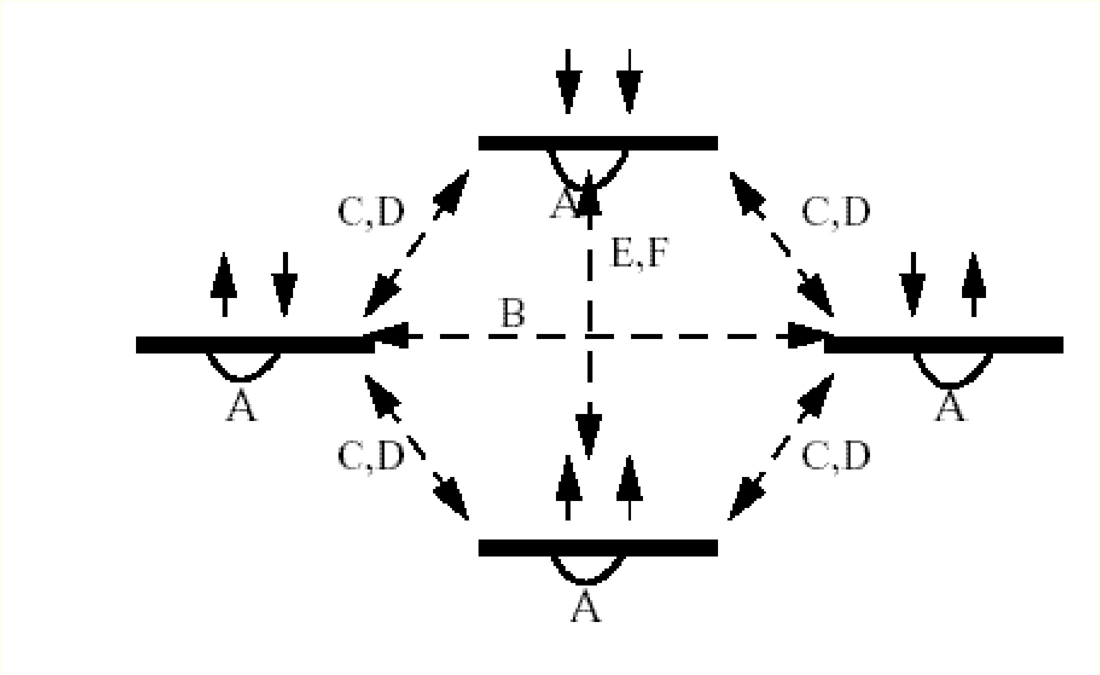
Probe of internuclear distance

$\hat{A} \sim \hat{I}_{z1}\hat{I}_{z2}$ $\qquad$ $\hat{I}_z S_z$

$B \sim \hat{I}^+_1\hat{I}^-_2 + I^-_1 I^+_2$

homo $\qquad$ hetero

Dipolar Hamiltonian Terms

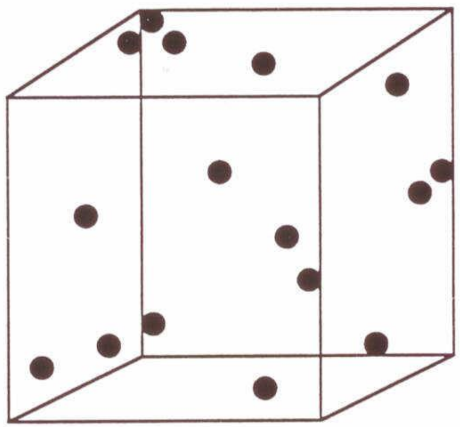


Multi-Spin Interactions: Second Moments

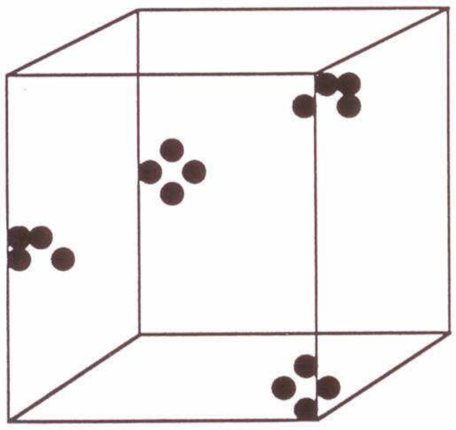
$$M_2 = \frac{4}{15}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_I^2 \gamma_S^2 S(S+1)\hbar^2 \sum_S r_{IS}^{-6}$$

for heteronuclear coupling between spin species I and S

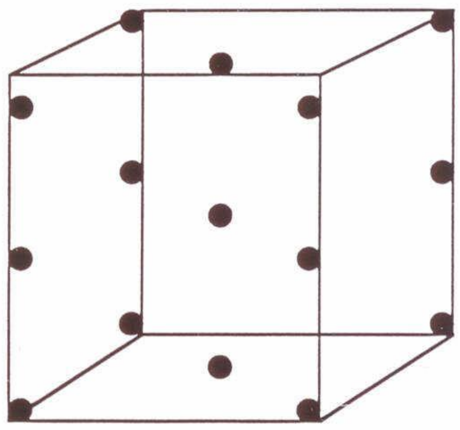
Spatial distribution models in glasses



random

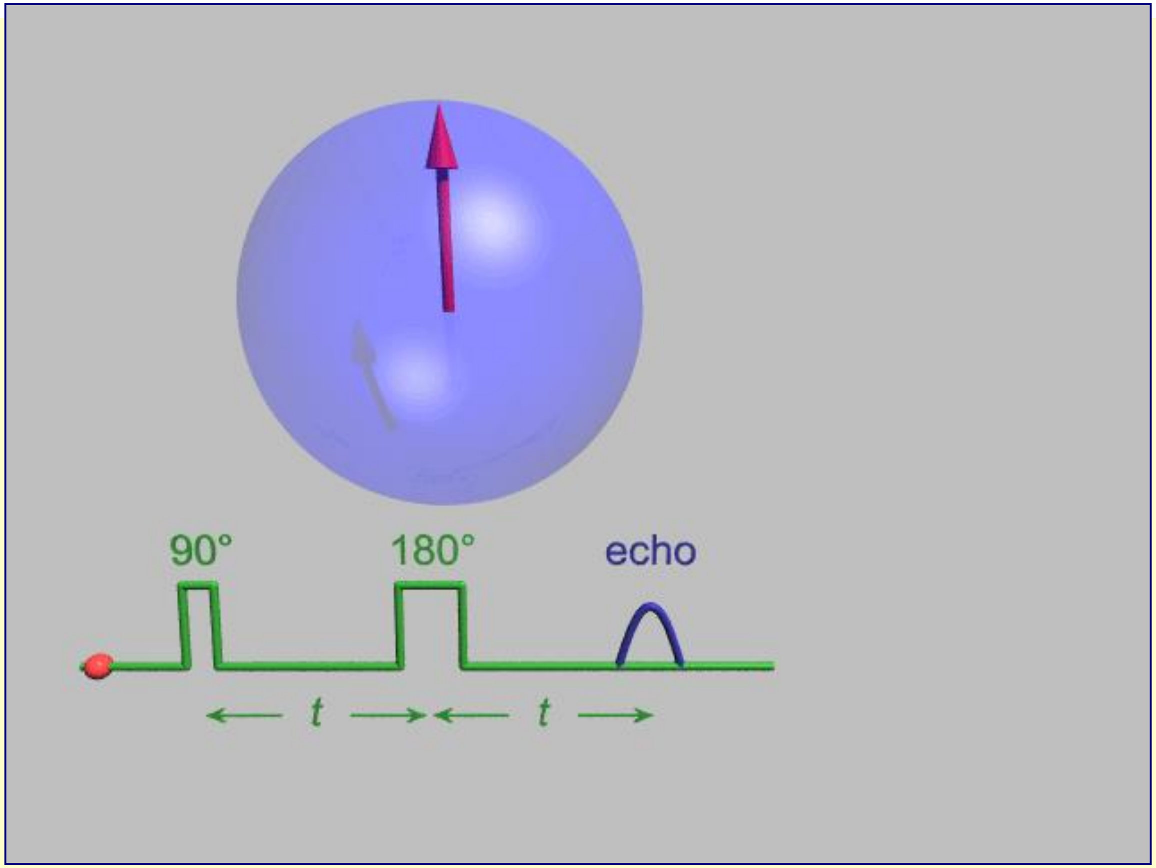


clustered



uniform

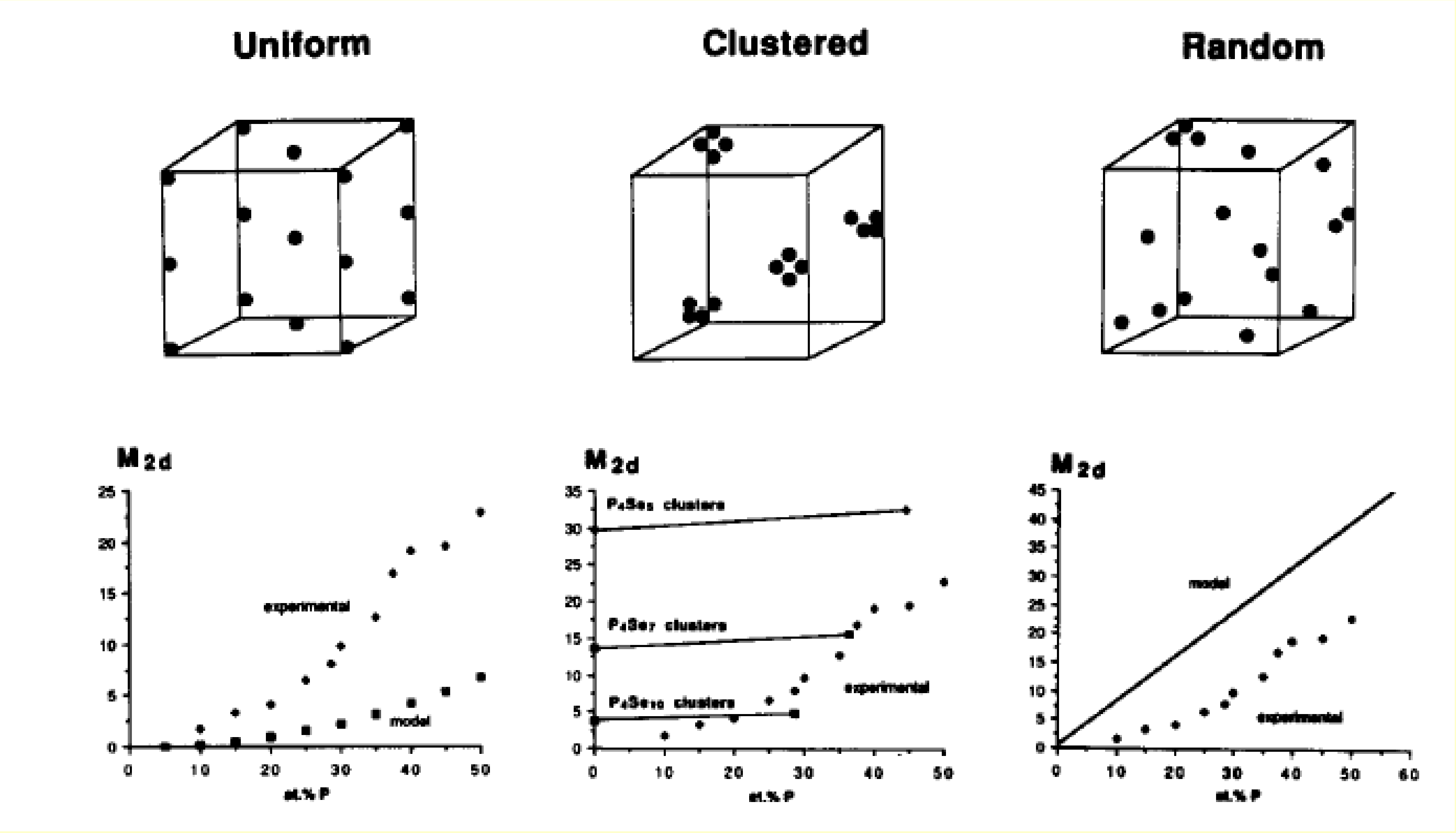
Selective measurement by spin-echo decay



Selective for homonuclear dipole coupling strengths

$$S/S_0 = \exp - (2t^2 M_2)$$

Spatial Atomic Distributions in P-Se Glasses



P-Se vs. P-P- bonding

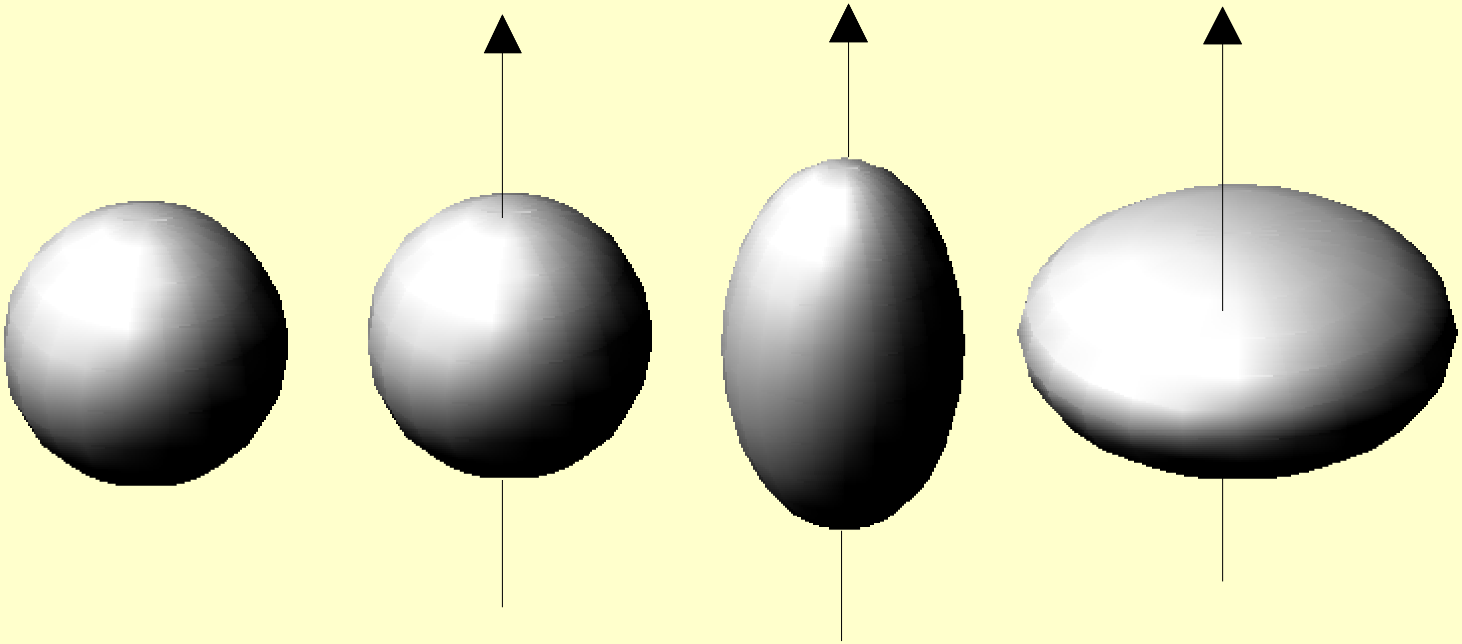
D. Lathrop, H. Eckert, J. Am. Chem. Soc. 111 (1989), 3536

D. Lathrop, H. Eckert, Phys. Rev. B 43 (1991), 7279

Nuclear electric quadrupole moment:

non-spherical distribution of nuclear charge

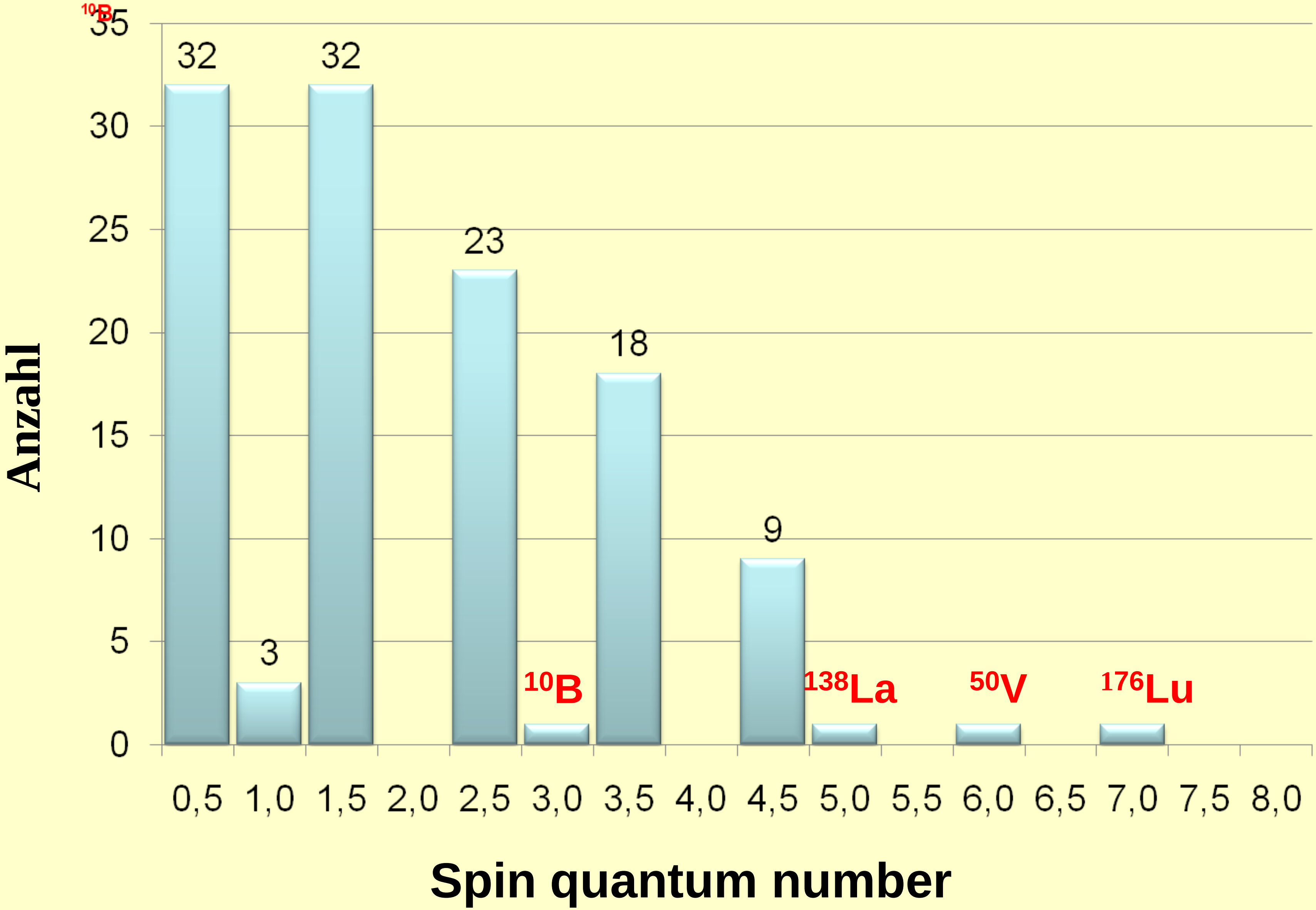
A B C D



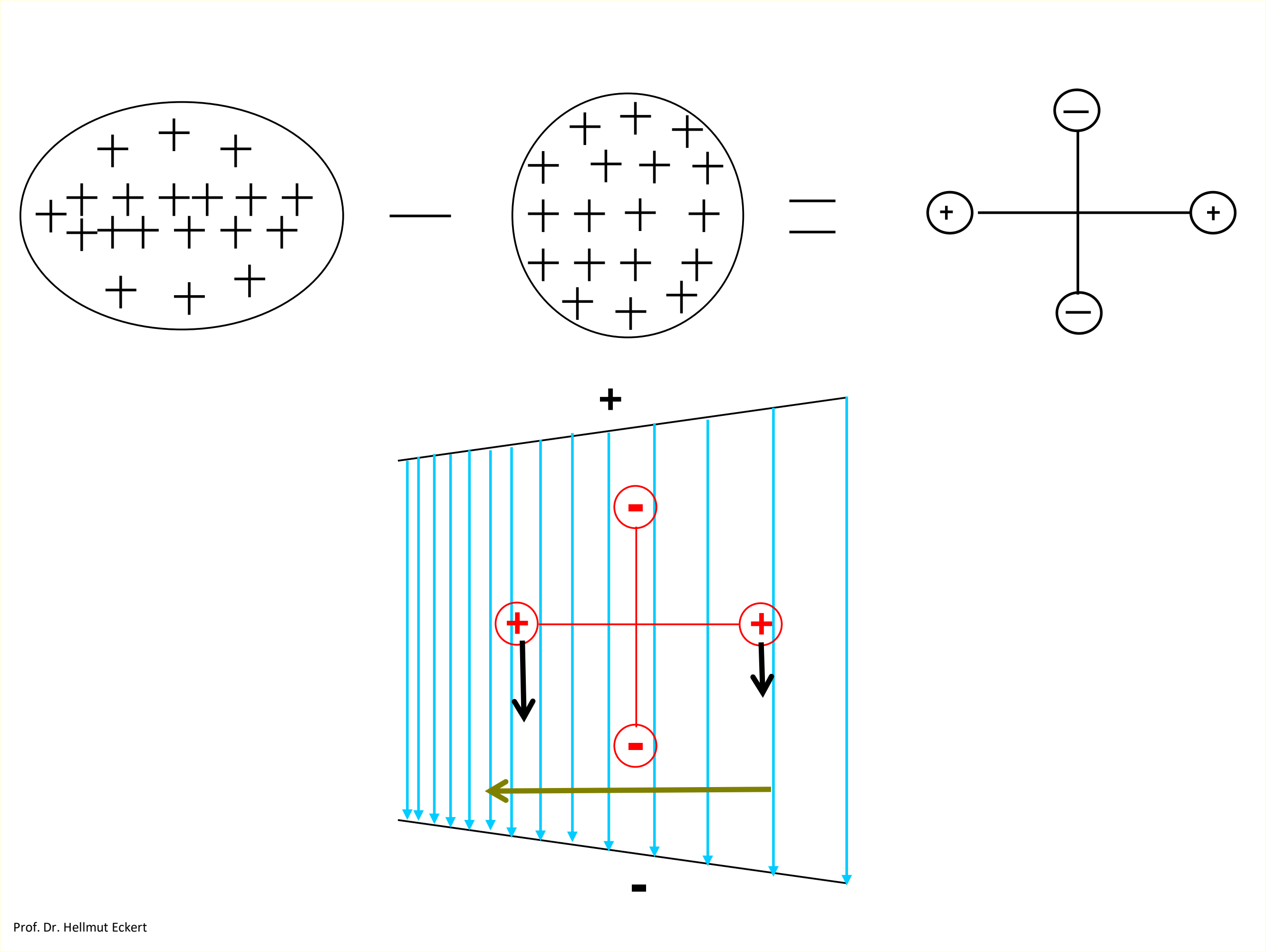
$I = 0$ $I = 1/2$ $I \geqq 1$; $eQ > 0$ $I \geqq 1$; $eQ < 0$

$eQ \sim 10^{-25}$ to 10^{-30} m^2

Nuclear spin values



The physical picture



This quadrupole moment interacts with local electric field gradients created by the bonding environment of the nuclei.

-> probe of local symmetry

Electric field gradient

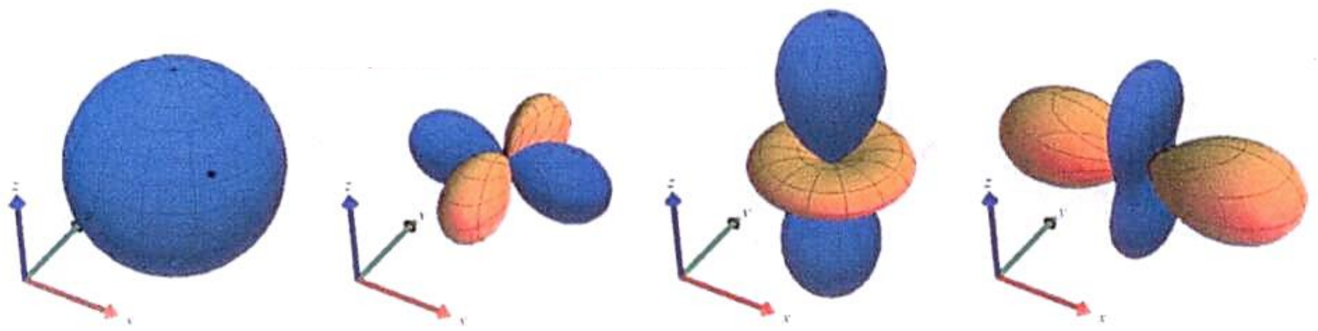
Symmetric second-rank tensor

$$\nabla E_{\alpha,\beta} = \begin{bmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yz} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{bmatrix}$$

diagonal in the principal axis system

$$|V_{z'z'}| \geq |V_{y'y'}| \geq |V_{x'x'}|$$

Laplace equation $V_{x'x'} + V_{y'y'} + V_{z'z'} = 0$



isotropic	axial, η=1	axial, η=0	intermediate, η=1/3
$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} -0.75 & 0 & 0 \\ 0 & -0.75 & 0 \\ 0 & 0 & 1.5 \end{pmatrix}$	$\begin{pmatrix} -1.5 & 0 & 0 \\ 0 & 0.5 & 0 \\ 0 & 0 & 1.0 \end{pmatrix}$

2 parameters:
and

$V_{z'z'} = eq$

Absolute size

$$\eta \equiv \frac{V_{y'y'} - V_{x'x'}}{V_{z'z'}}$$

deviation from cylin-drical symmetry

The Quadrupolar Hamiltonian

$$E_{el} = V(0)\int \rho d\tau + \sum_{\alpha} V_{\alpha} \int x_{\alpha} \rho d\tau + \boxed{\frac{1}{2!}\sum_{\alpha,\beta} V_{\alpha,\beta} \int x_{\alpha} x_{\beta} \rho d\tau} + \ldots\ldots\ldots$$

Coulomb term **dipole term** **quadrupole term**

$$Q_{\alpha\beta} = \int \left(3x_{\alpha}x_{\beta} - \delta_{\alpha\beta} r^2\right)\rho d\tau$$

$$E_Q = \frac{1}{6}\sum_{\alpha,\beta} V_{\alpha\beta} Q_{\alpha\beta}$$

$$\hat{Q}_{\alpha\beta} = \left[\frac{3(\hat{I}_{\alpha}\hat{I}_{\beta} + \hat{I}_{\beta}\hat{I}_{\alpha})}{2} - \delta_{\alpha\beta}\hat{I}^2\right] \cdot \frac{eQ}{I(2I-1)}$$

Expressed in spin coordinate
Wigner-Eckart-Theorem

$$\hat{H}_Q = \frac{e^2 qQ}{4I(2I-1)}\left[\left(3\hat{I}_{z'}^2 - \hat{I}^2\right) + \eta\left(\hat{I}_{y'}^2 - \hat{I}_{x'}^2\right)\right]$$

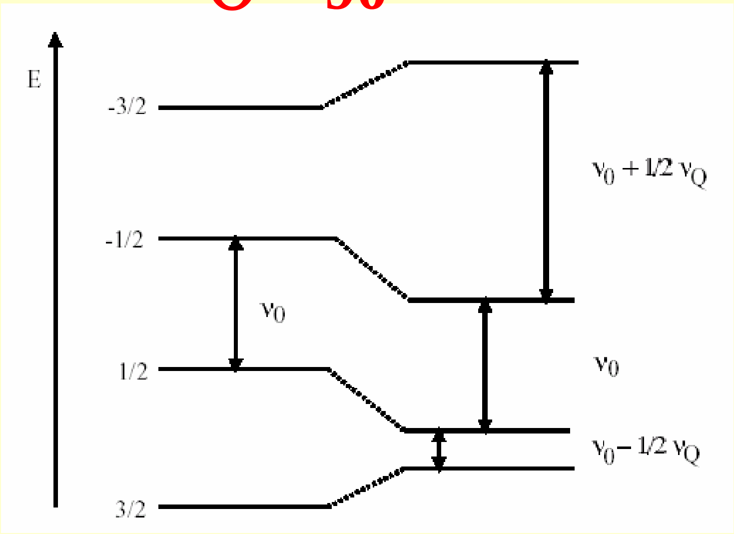
For axially symmetric EFG, the 1st order correction is:

$$\langle m|\hat{H}_Q|m\rangle = \frac{e^2qQ}{4I(2I-1)}\left[3m^2\cos^2\theta + \tfrac{3}{2}I(I+1)\sin^2\theta - \tfrac{3}{2}m^2\sin^2\theta - I(I+1)\right]$$

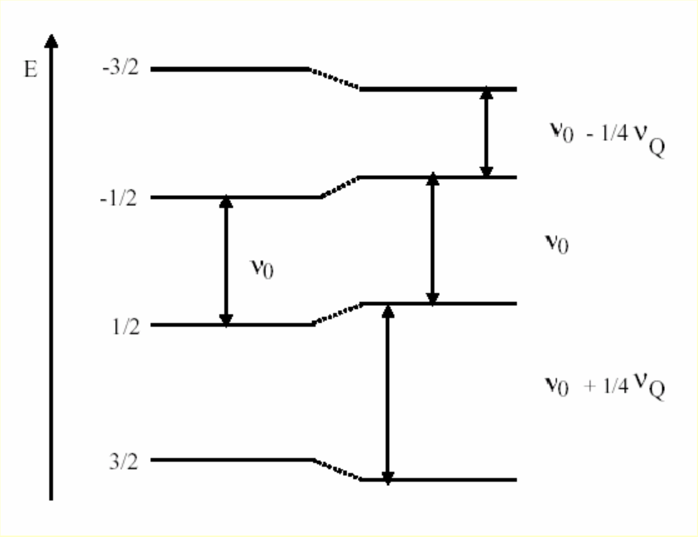
$$E_m^{(1)} = -m\gamma\hbar B_o + \frac{e^2qQ}{4I(2I-1)}\left[3m^2 - I(I+1)\right]\frac{3\cos^2\theta - 1}{2}$$

Energy level diagram for I = 3/2

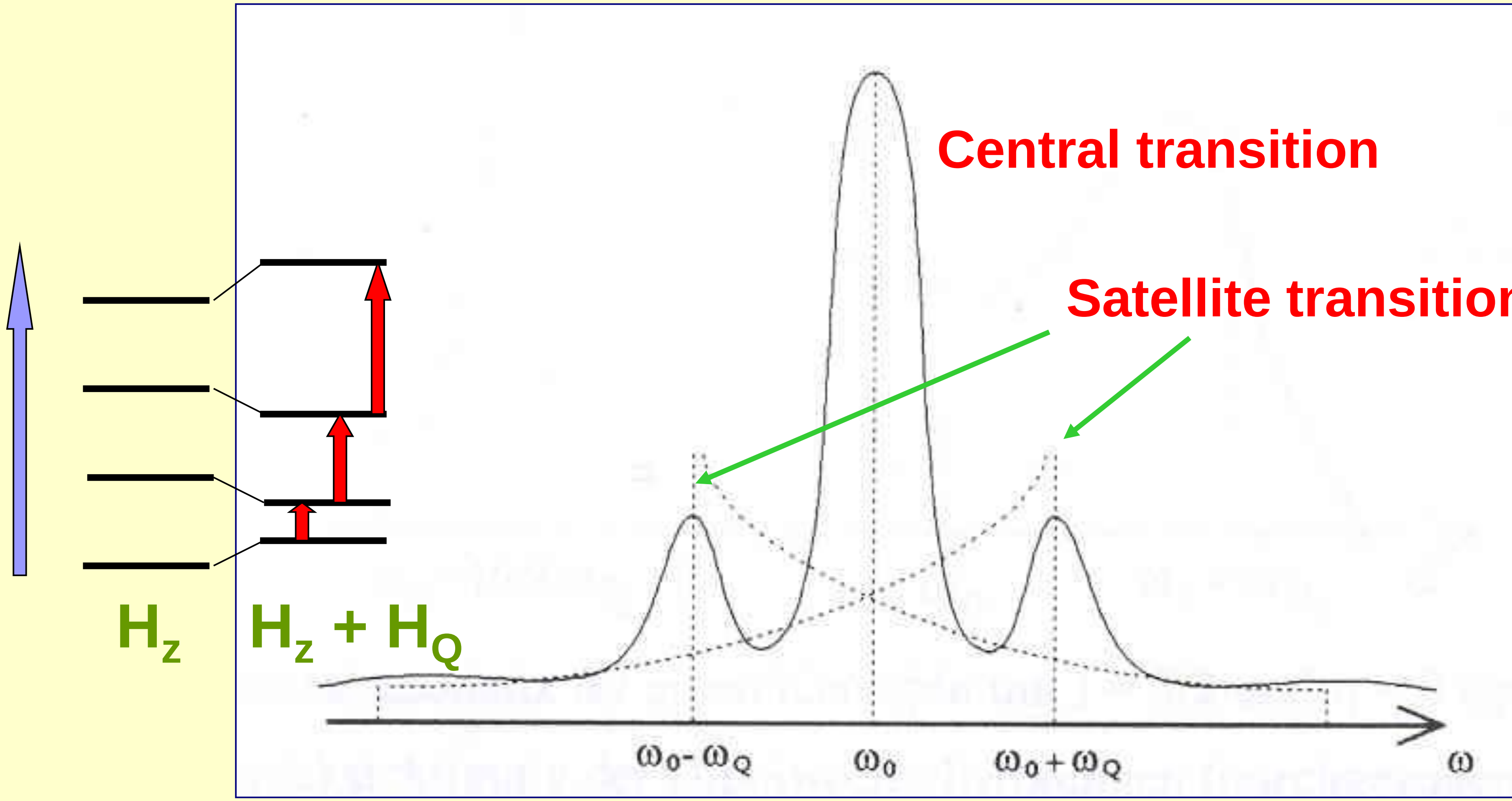
Θ = 90°



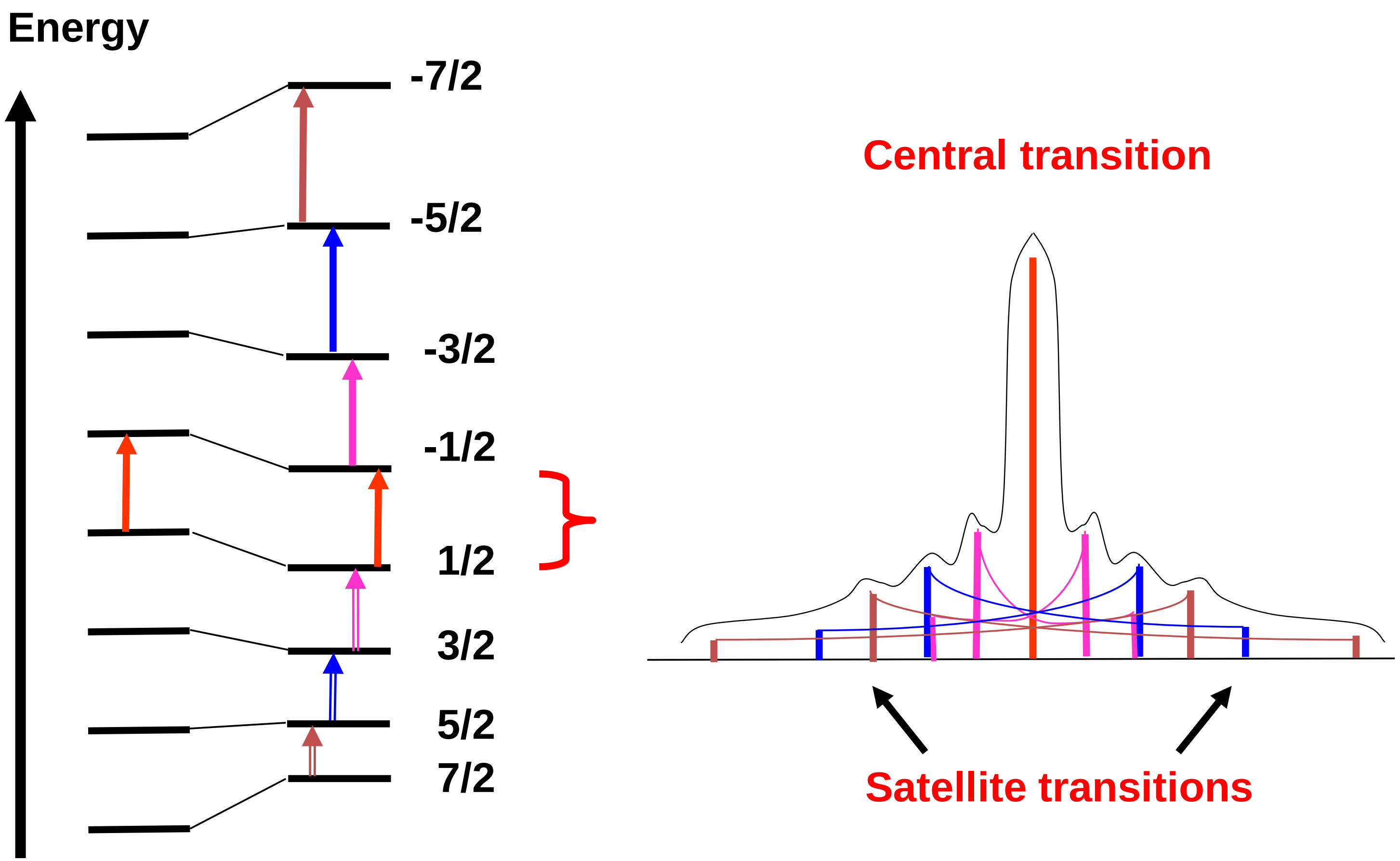
Θ = 0°



Effect of Quadrupolar Interactions on the NMR Lineshape

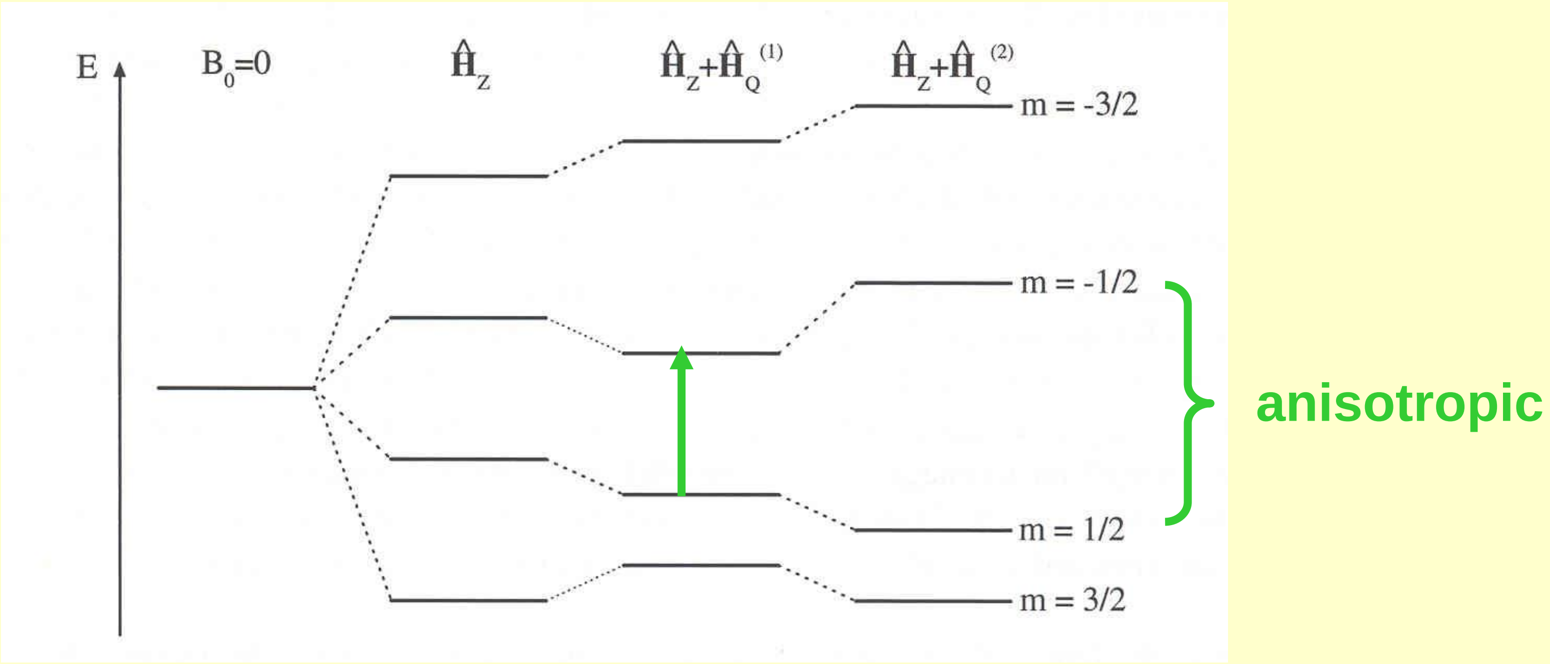


Powder pattern for spin-7/2

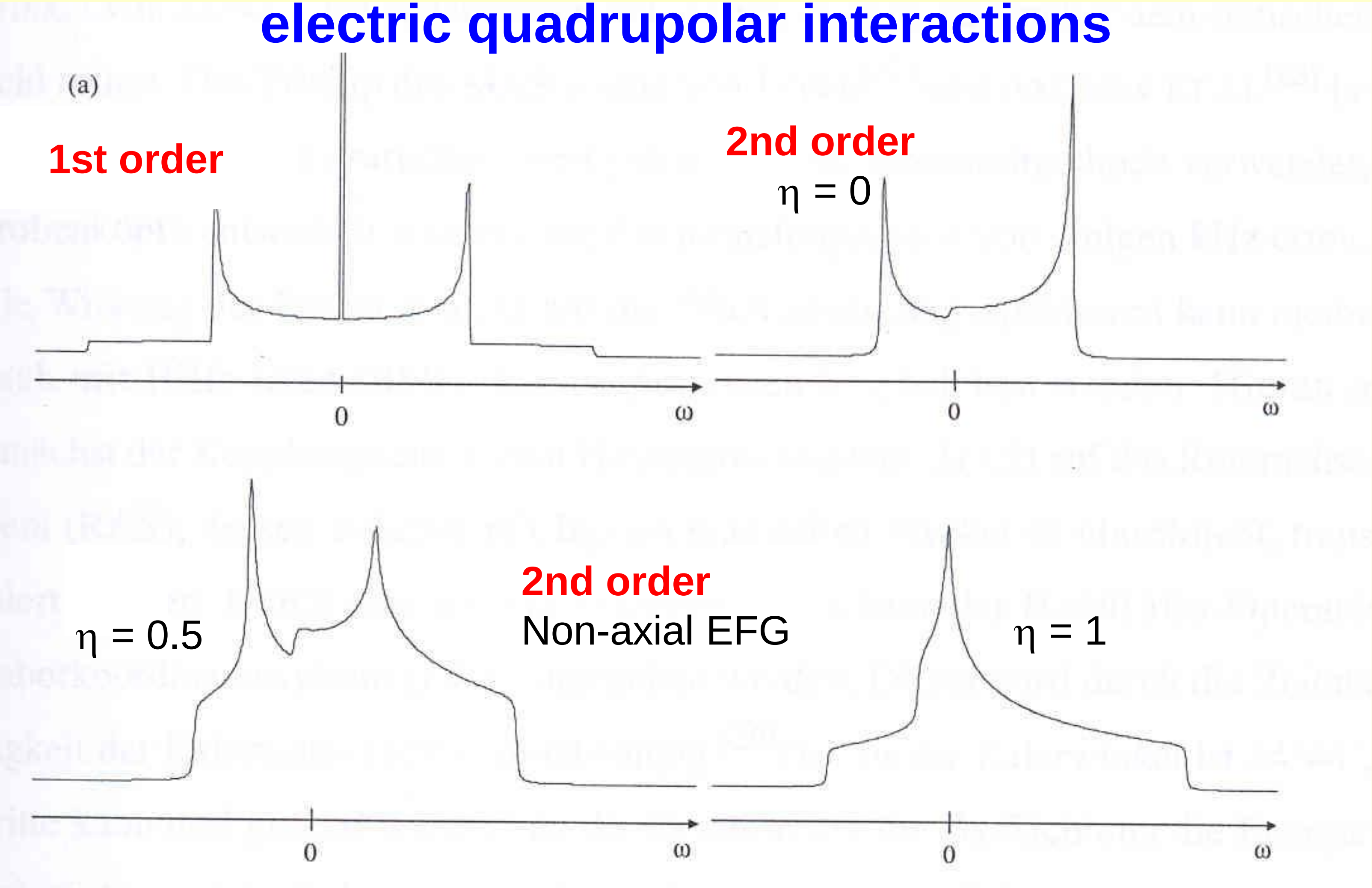


Stronger Quadrupole Coupling:

Second-order perturbation theory



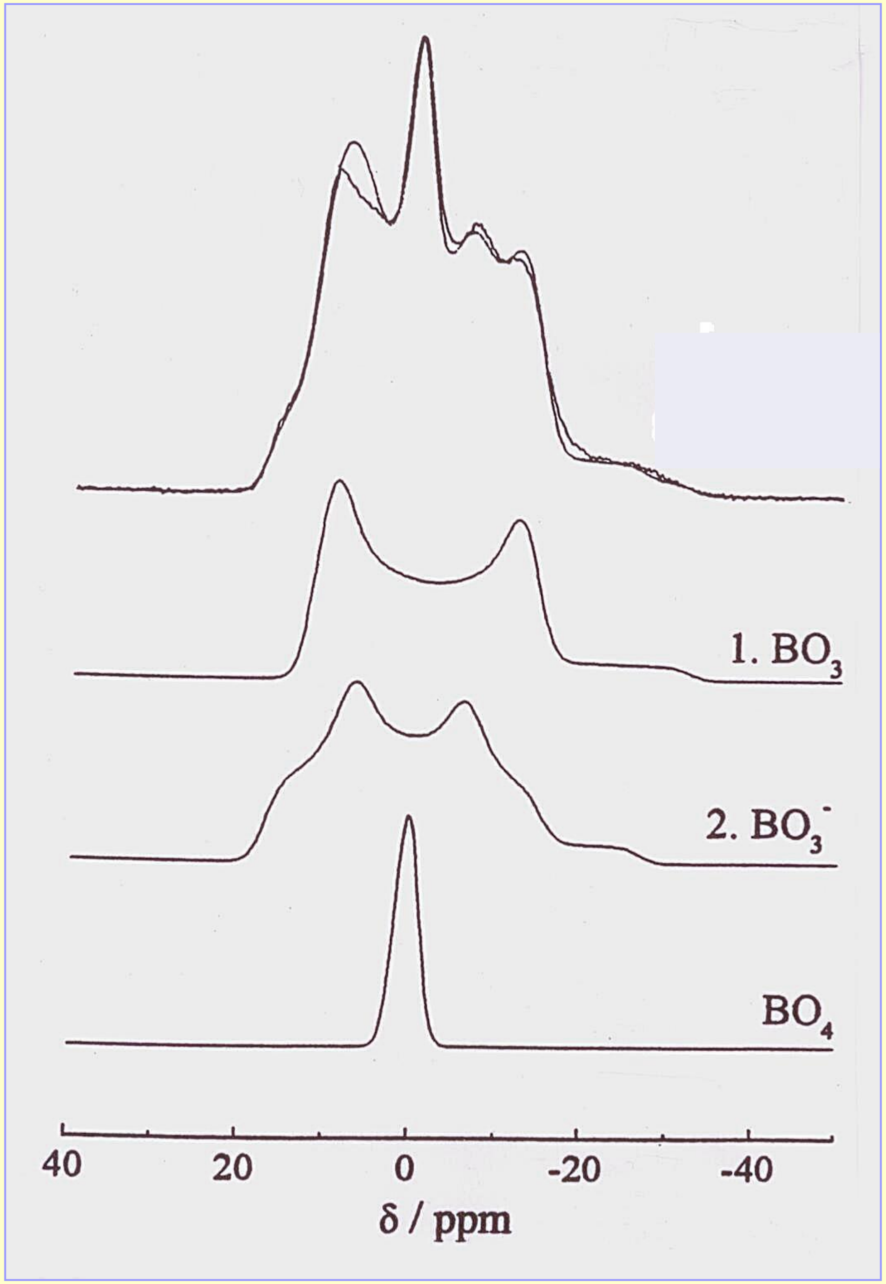
Anisotropic lineshape broadening caused by electric quadrupolar interactions



C_Q: maximum component.
$\eta = (q_{xx}-q_{yy})/q_{zz}$: asym. Parameter.

$C_Q \sim \Sigma\, q_{eff}/r^3$
(point charge model)

Example of an application: Electric field gradients in borates



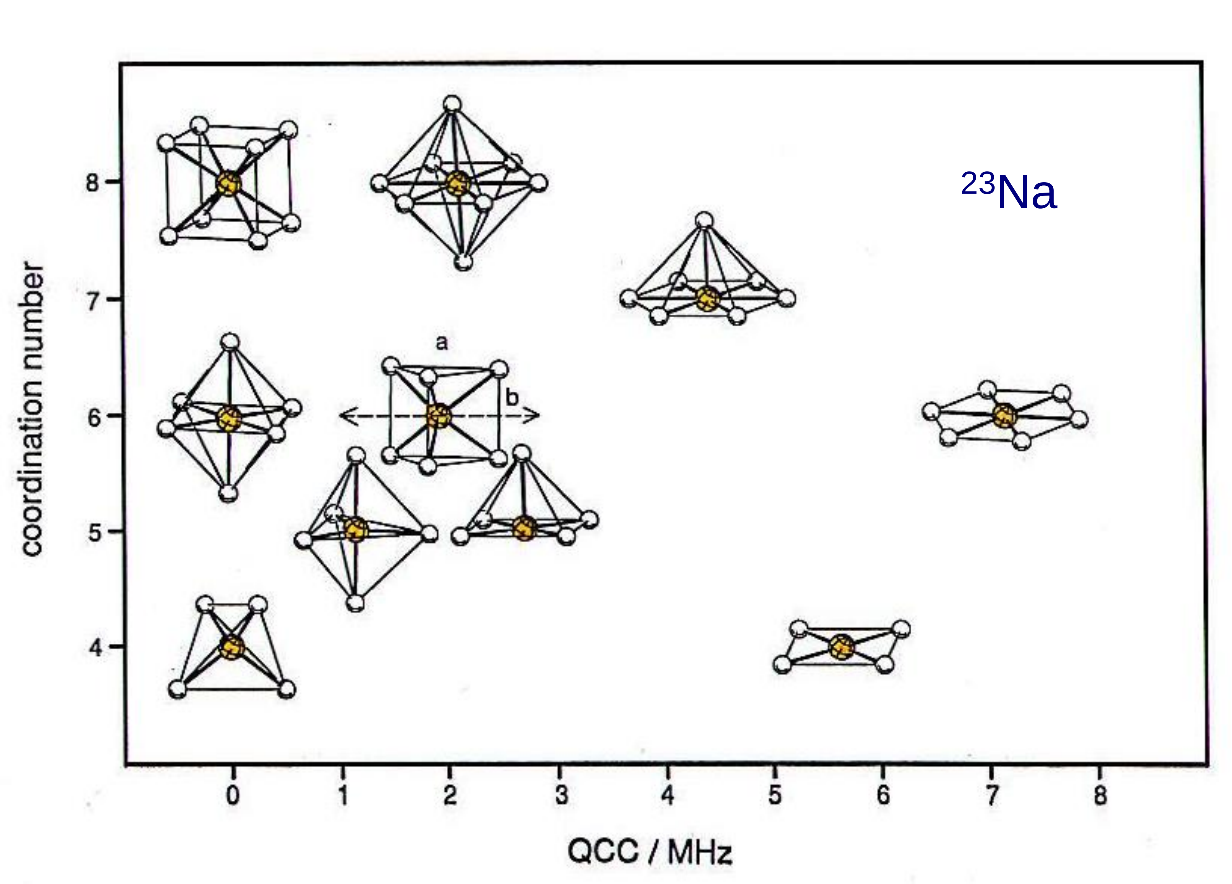
Typical spectrum of a borate glass

Trigonal planar D_{3h}

Three-coord. C_{2v}

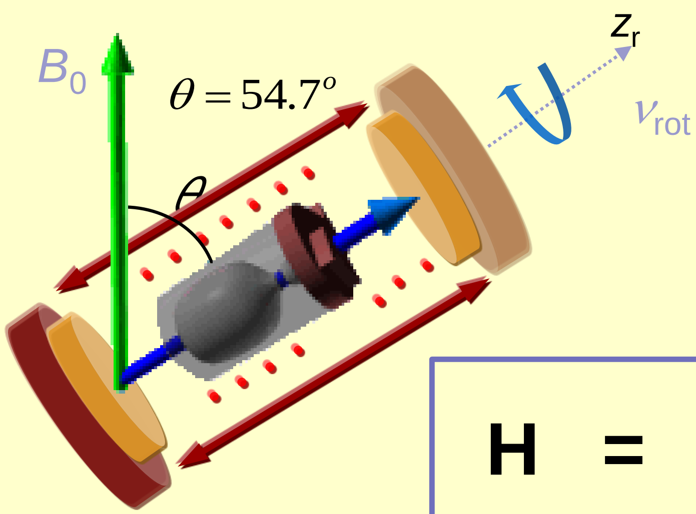
Tetrahedral T_d

^{23}Na Quadrupole Interaction and Na Coordination



H. Koller, G. Engelhardt, A.P.M. Kentgens, J. Sauer,
J. Phys. Chem. **98** (1994), 1544-1551

Magic Angle Spinning - MAS



$$H_{aniso} = A \cdot \{\overline{3\cos^2\theta - 1}\}$$

$$H = H_Z + \cancel{H_D} + \underset{iso}{\cancel{H_J}} + \underset{iso}{\cancel{H_{CS}}} + \underset{2nd.}{\cancel{H_Q}}$$

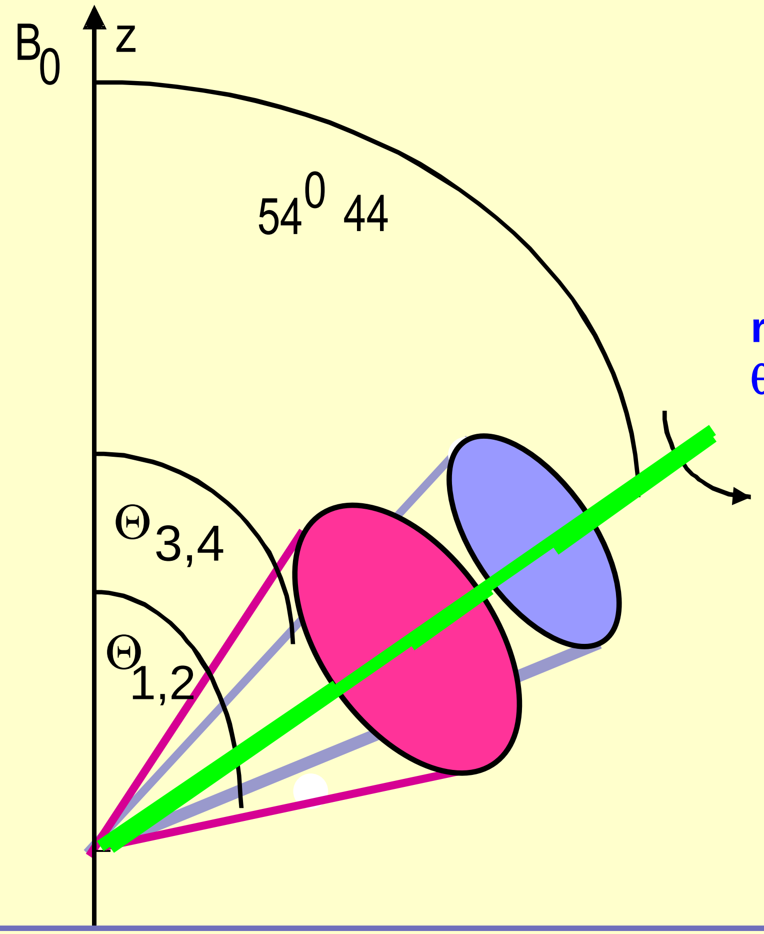
High-resolution spectra, governed by isotropic chemical shifts and J-coupling

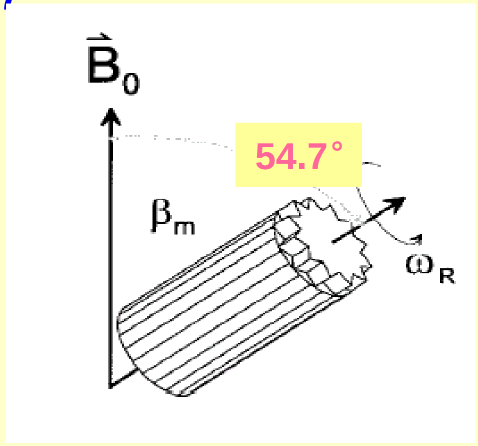
-- connectivities

-- coordination numbers

Magic Angle Spinning

$$\mathcal{H}_{aniso} = A \cdot \overline{\{3\cos^2\theta - 1\}}$$

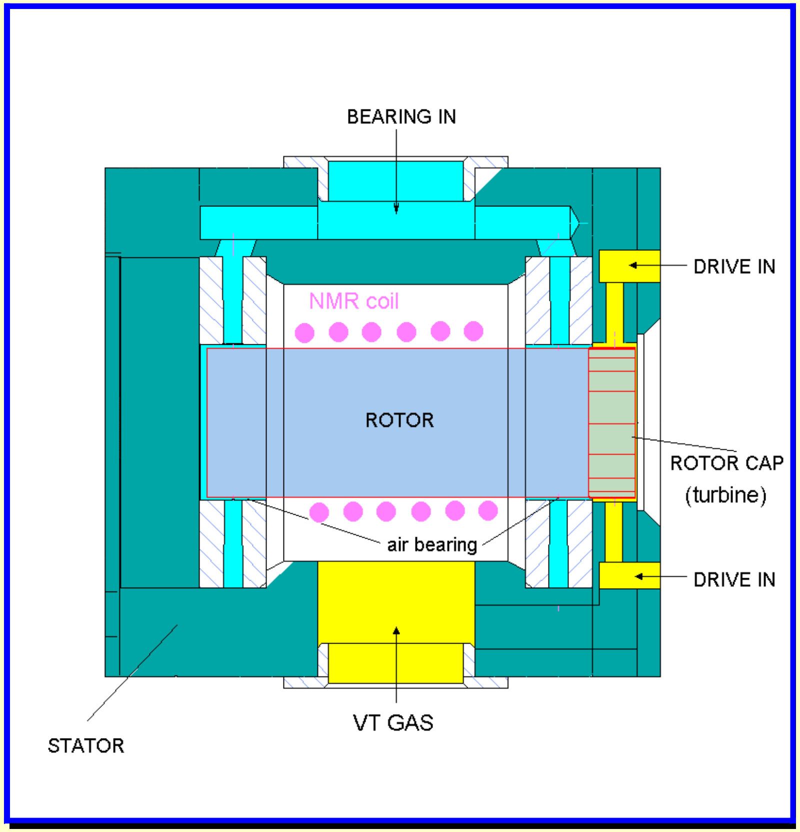


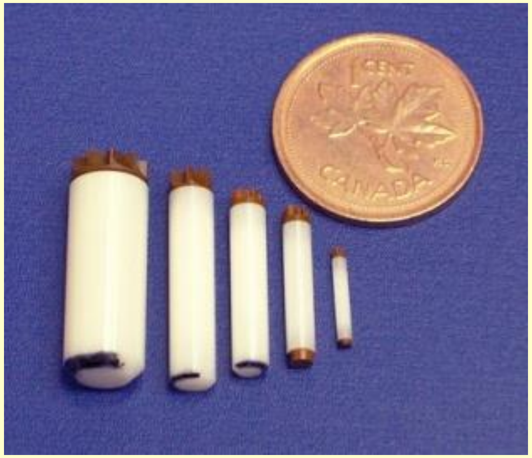


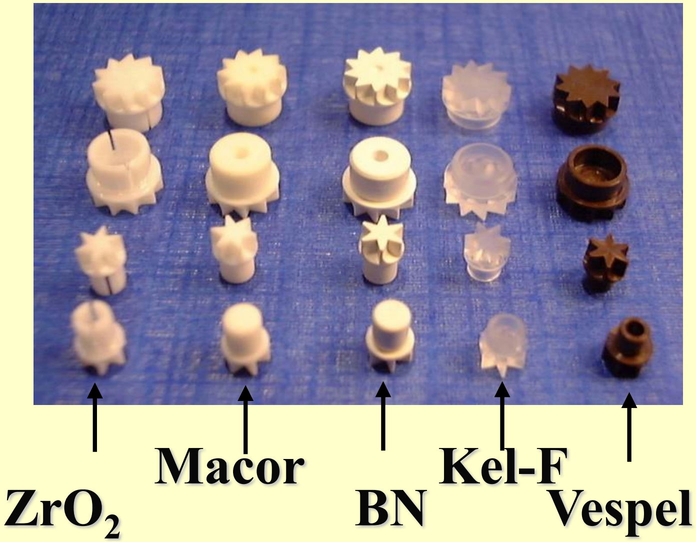
$$H = H_Z + \cancel{H_D} + \cancel{H_J} + \cancel{H_{CS}} + \cancel{H_Q}$$

iso iso 2nd.

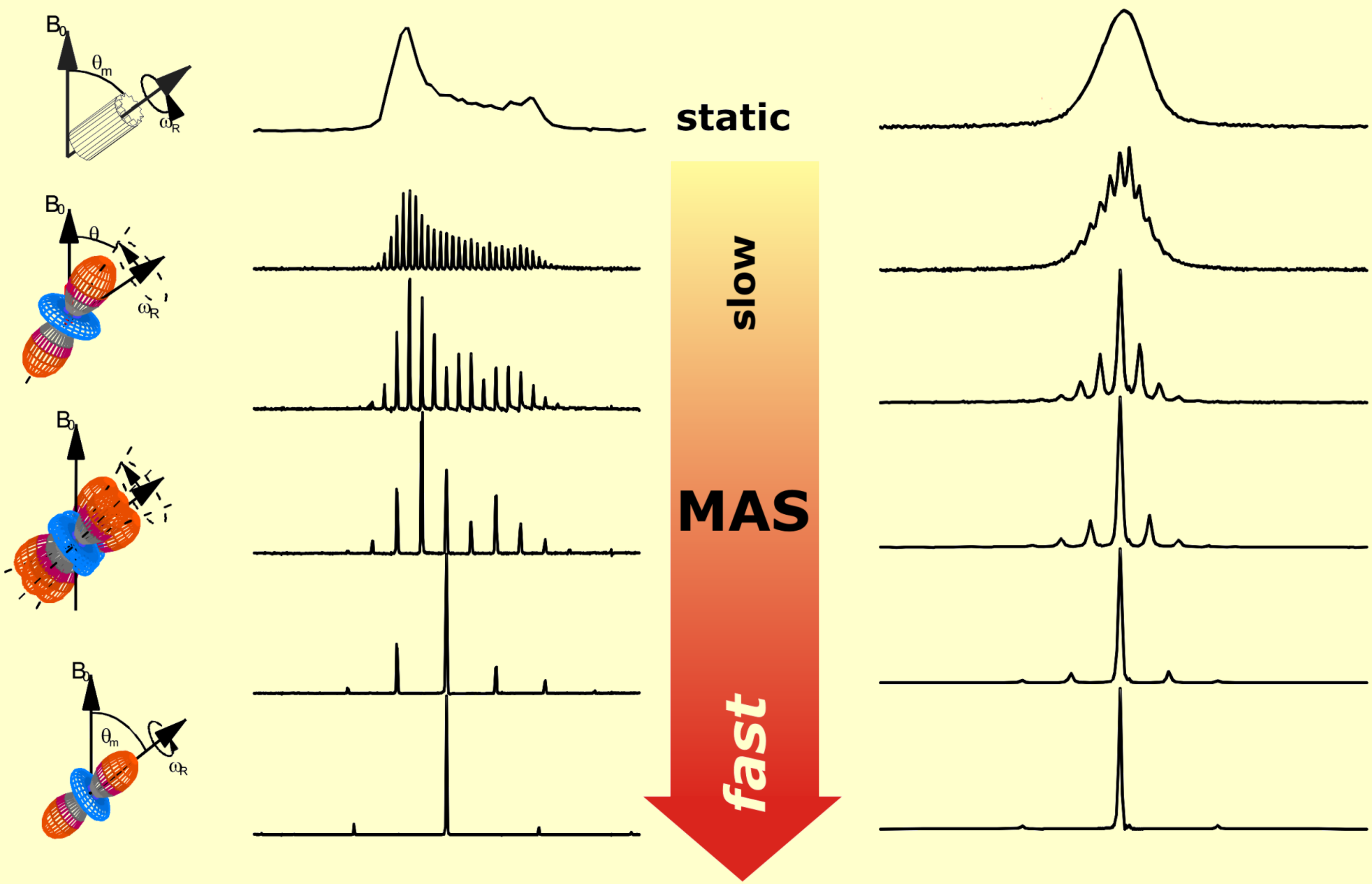
MAS-NMR probe





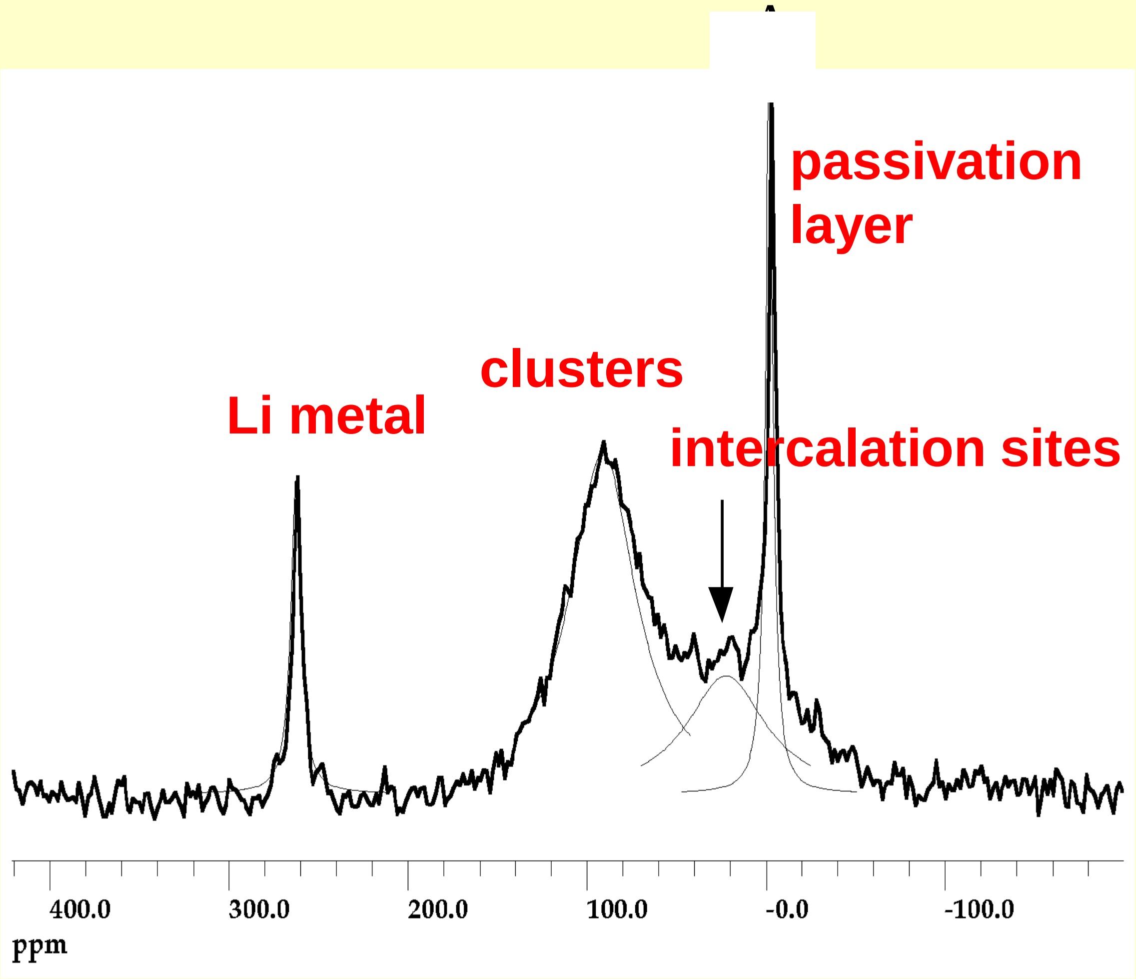


The effect of spinning speed



Lithium inventory in LiC_n electrodes

studied by ^7Li NMR



S. Hayes, H. Eckert et al., J. Phys. Chem. A107, 3866 (2003)

NMR as a Technique in Solid State Sciences

Local Selectivity:	Disorder/Lack of Periodicity
Element Selectivity:	Compositional Complexity Low Scattering Contrast (H; Si/Al)
Interaction Selectivity:	Distance Measurements Connectivity Information Electron Density Information
Uniform Sensitivity:	Quantitative Applications
Dynamic Sensitivity:	Motional Processes on Continuous Timescale (10^{2} to 10^{-9} s)

Low Detection Sensitivity:	10^{17} to 10^{18} spins required
Bulk Method:	poor spatial resolution surfaces/interfaces difficult to study
Magnetic Interference:	transition metals, rare earths: limited