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JÜLICH
FORSCHUNGSZENTRUM

MR Fundamentals

26 October 2010

Nuclear Spin

Nuclear Spin

- Nuclear magnetic resonance is observed in atoms with odd number of protons and/or neutrons (possess spin angular momentum)
- Spin angular momentum **S** is an intrinsic vector property of elementary particles

$$\mathbf{S} = \hbar \mathbf{I}$$

I = spin operator

- Associated with **S** is a magnetic dipole moment **μ**

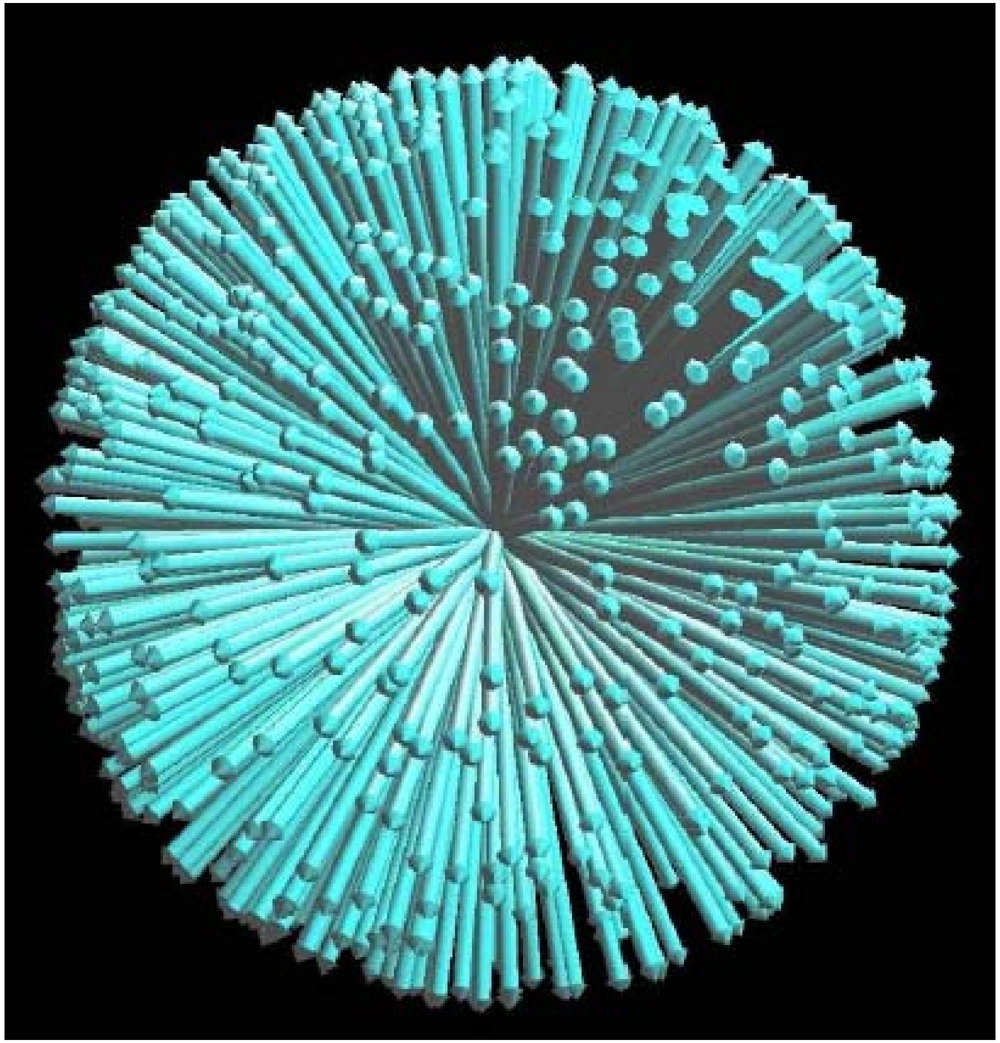
$$\boldsymbol{\mu} = \gamma \mathbf{S} = \gamma \hbar \mathbf{I}$$

γ = gyromagnetic ratio

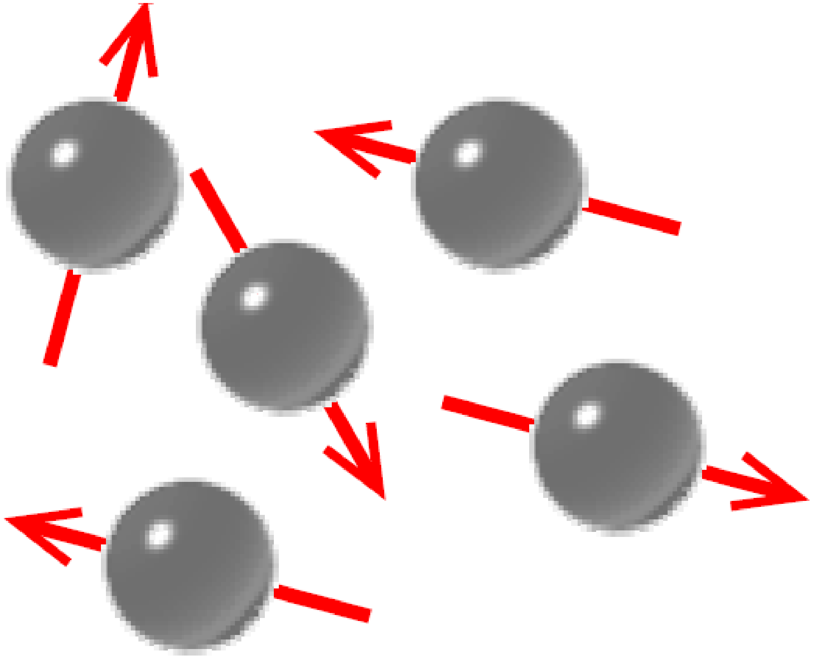
- Classical picture: charged sphere spinning about its axis like a planet

Spin Dynamics
Classical Description

Spins at $B_0 = 0$

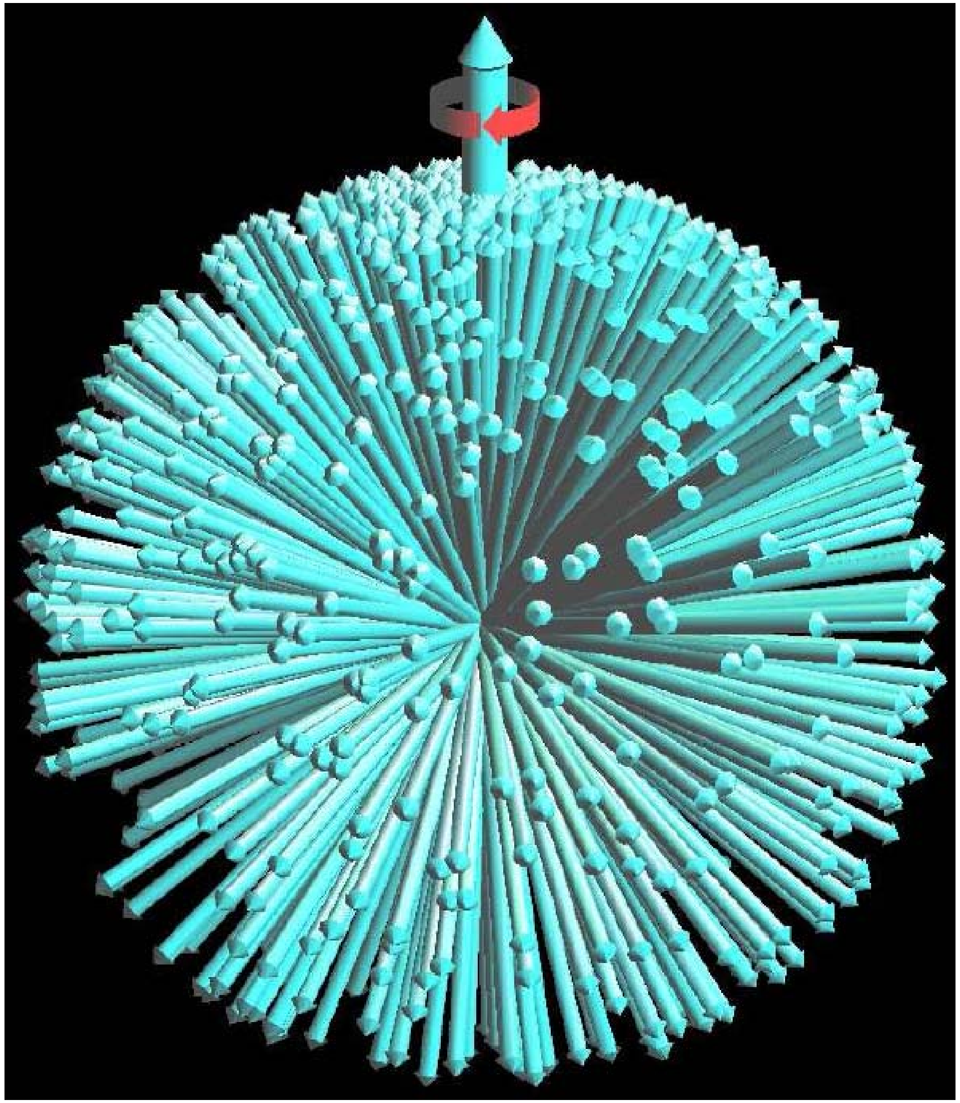


Hanson 2008



- Spins have random orientation
- Vectorsum over spins is zero
- No net magnetisation

Spins in a Static Field



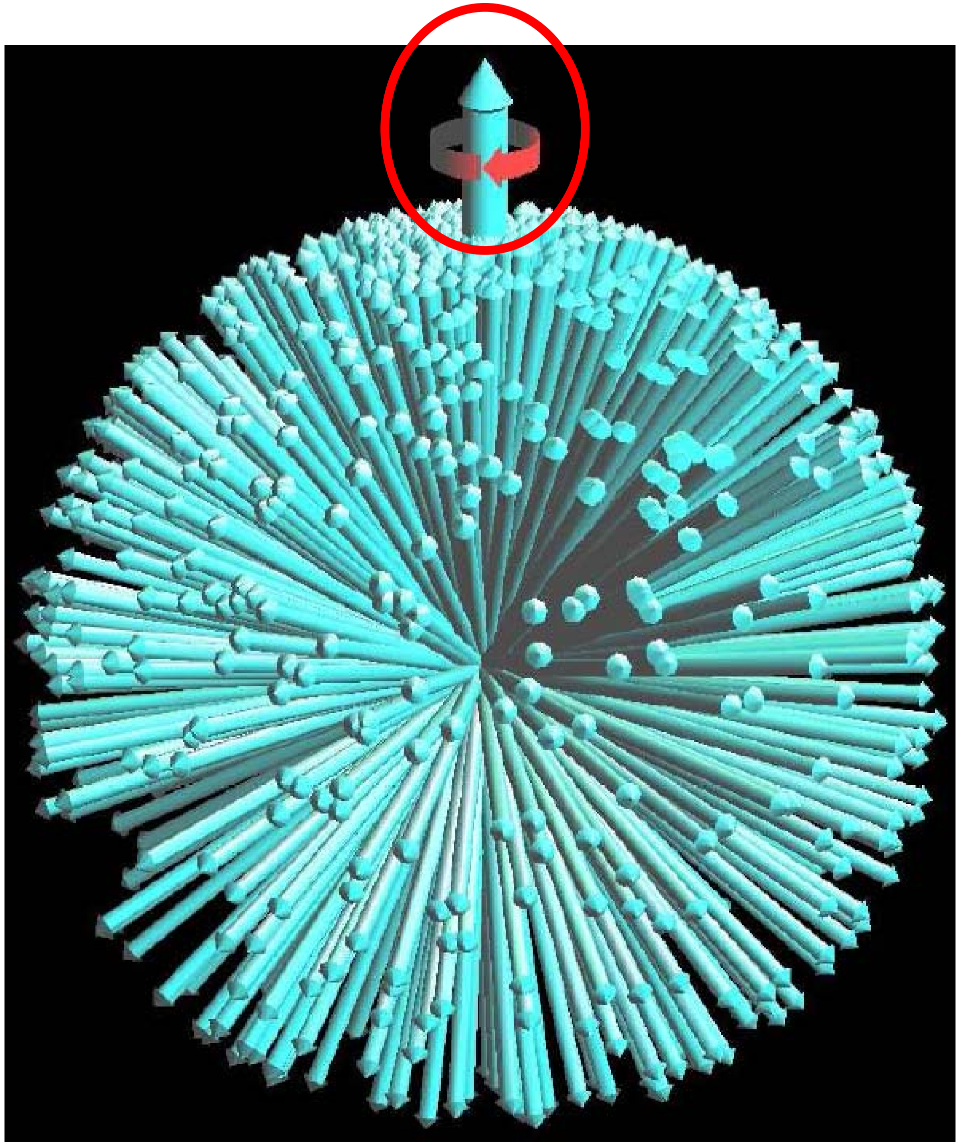
Hanson 2008

- Instantaneous precession of spins around axis of external field at the Larmor frequency

$$\omega_0 = \gamma B_0$$

- Spin distribution skews slightly towards magnetic north pole through relaxation
- $\rightarrow$ net magnetisation along direction of magnetic field is formed

Equilibrium Magnetisation



Hanson 2008

- How large is the equilibrium magnetisation?
- Energy dependent on angle, θ, between field and magnetic moment μ: $E(\theta) = -\mu B_0 \cos\theta$
- Proton magnetic moment: $\mu = \frac{\sqrt{3}}{4\hbar\gamma}$
- Angular spin distribution:

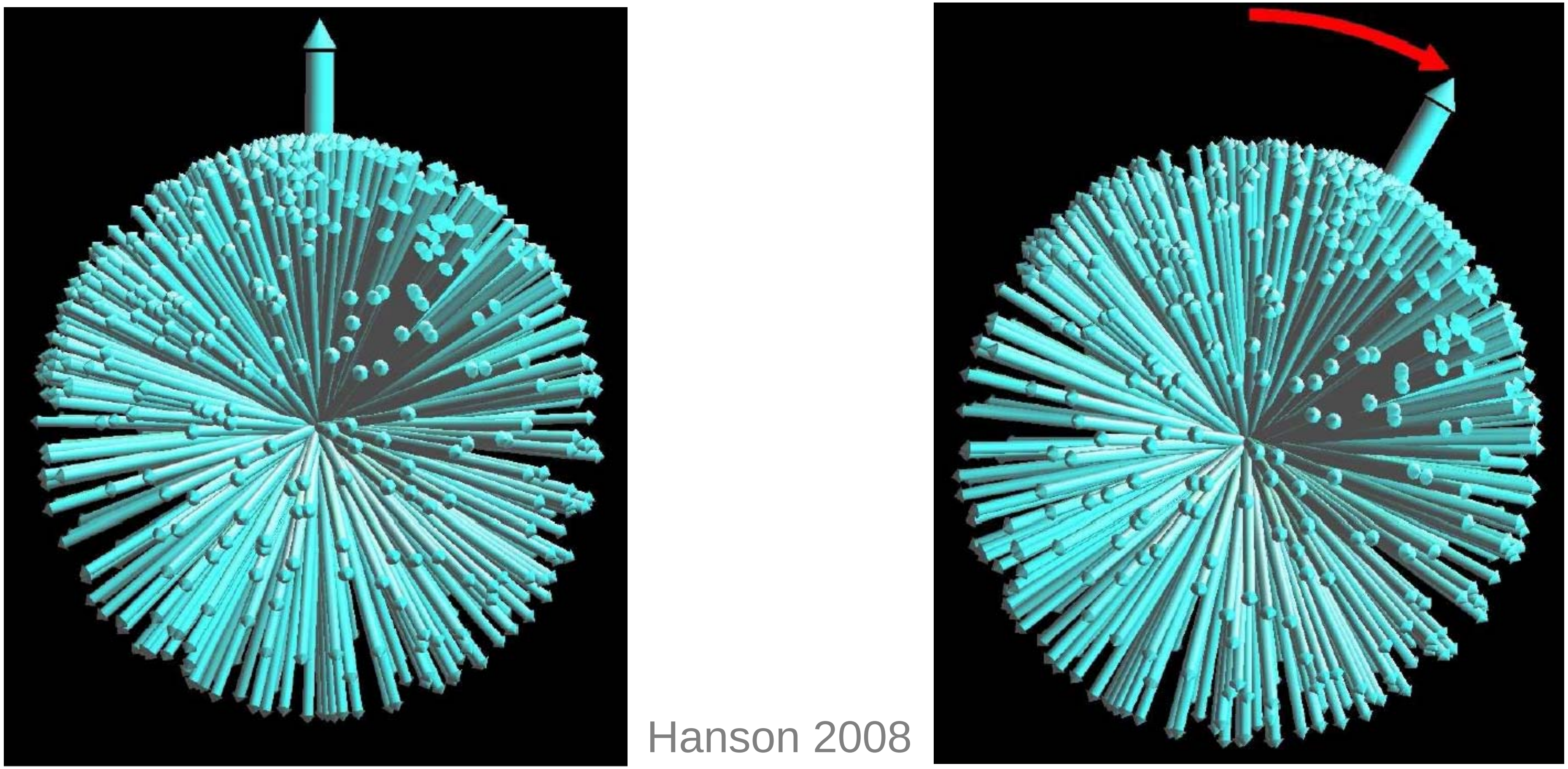
$$P(\theta) = \frac{e^{\frac{-E(\theta)}{kT}}}{\int_0^{\pi} e^{\frac{-E(\theta)}{kT}} \sin(\theta)d\theta}$$

- Z-component of magnetisation

$$\langle \mu_z \rangle = \int_0^{pi} P(\theta)(\mu cos\theta)\sin\theta d\theta$$

$$\boxed{\langle \mu_z \rangle = \mu \frac{\int_{-1}^{1} e^{\frac{\mu B_0 u}{kT}} u du}{\int_{-1}^{1} e^{\frac{\mu B_0 u}{kT}} du} \approx \frac{\hbar^2\gamma^2 B_0}{4kT}}$$

Interaction with a Radio Frequency Field



Hanson 2008

- A homogeneous magnetic field $\mathbf{B}_1$ in the transverse direction rotating at the Larmor frequency is applied
- The $\mathbf{B}_1$ field induces torque on the magnetisation
- Leads to coherent (no spin position change *relative* to one another) rotation of the spin distribution
- Net magnetisation is rotated into the transverse plane

Bloch Equation Without Relaxation

- The magnetic field causes a torque, ***T***, on a magnetic moment, ***μ***.

$$\vec{T} = \vec{\mu} \times \vec{B}$$

- The torque is the 1st derivative of the angular momentum, ***I***, with respect to time.

$$\vec{T} = \frac{d\vec{I}}{dt} = \frac{1}{\gamma}\frac{d\vec{\mu}}{dt}$$

- Ensemble averaging from the microscopic magnetic moments to the macroscopic magnetisation:

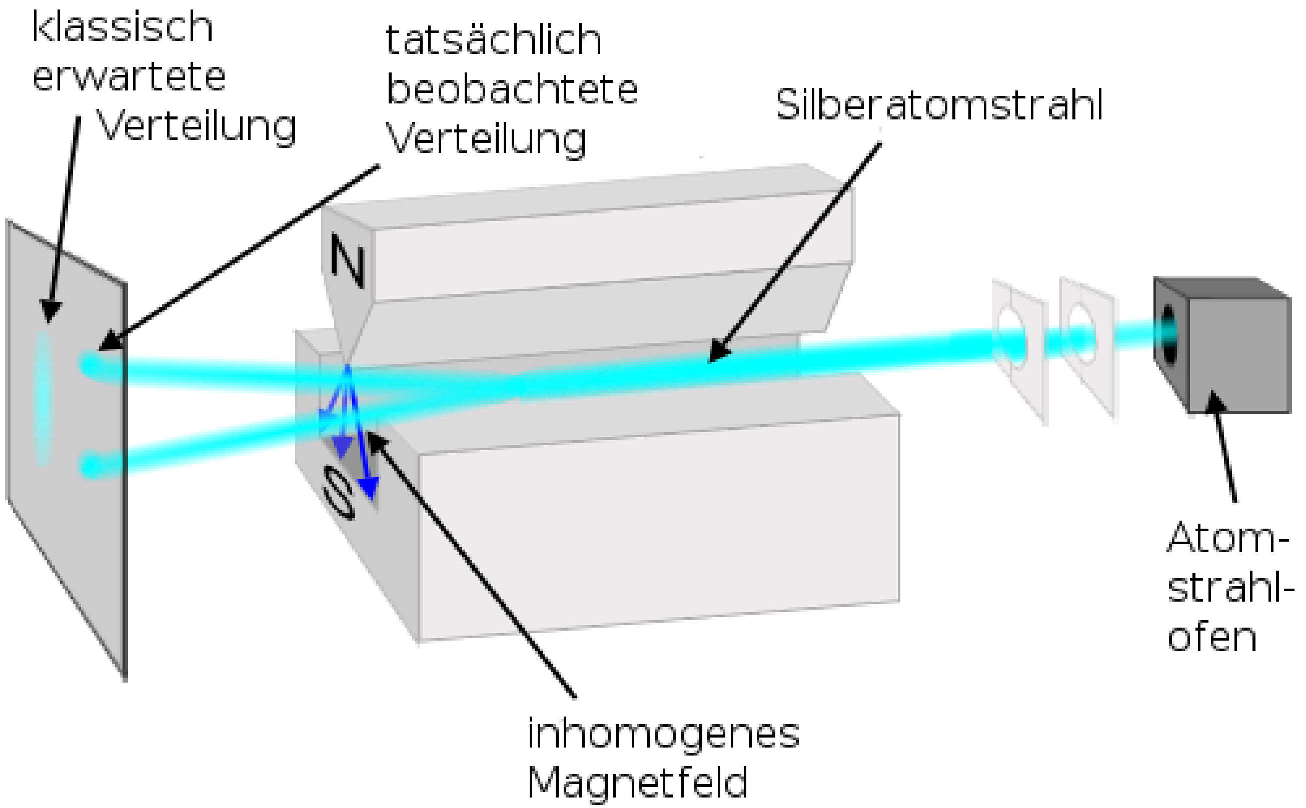
$$\boxed{\frac{d\vec{M}}{dt} = \vec{M} \times \gamma \vec{B} = \vec{\omega} \times \vec{M}}$$

Equation of motion* solved by precessional motion with frequency $\omega=-\gamma \mathbf{B}$. (clockwise).

* "Bloch-Equation without relaxation"

Spin Dynamics
Quantum Mechanics

Zeeman Effect – Stern Gerlach Experiment



http://de.wikipedia.org/w/index.php?title=Datei:Stern-Gerlach_Experiment_de.png

Classical prediction

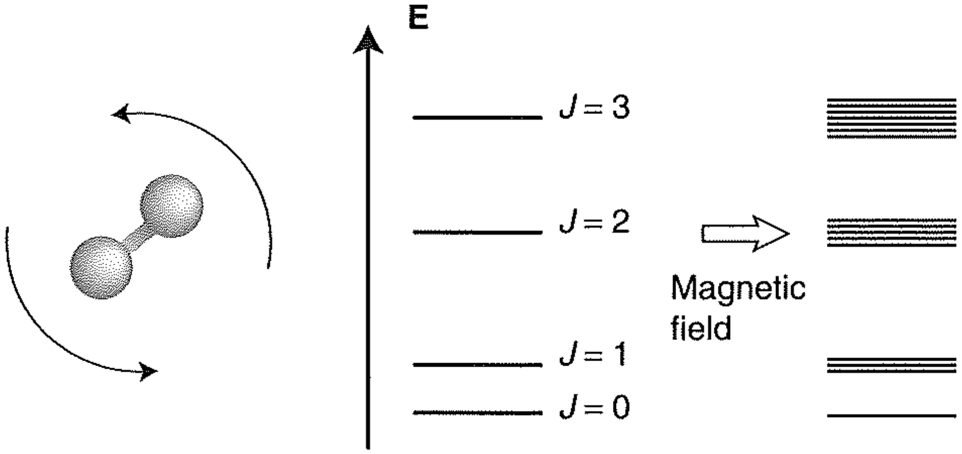
$$\mathbf{F} = \nabla\,(\boldsymbol{\mu}\cdot\mathbf{B}_{ges}) = \begin{pmatrix} 0 \\ 0 \\ \mu_z \cdot \dfrac{\partial B}{\partial z} \end{pmatrix}$$

Observed: two discrete levels

$$J_z = \pm\frac{1}{2}\hbar$$

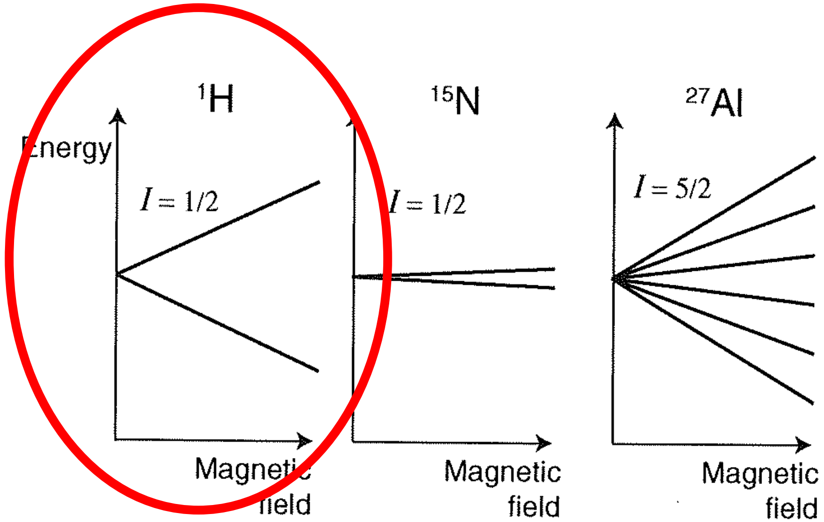
Zeeman Effect

- In absence of field: degenerate states (multiple quantum states with identical energy)
- External magnetic field breaks degeneracy (each sublevel at different energy)



Atomic level

“*Spin dynamics*”, Levitt, p. 6 & 14



Nuclear Zeeman effect

Zeeman Effect

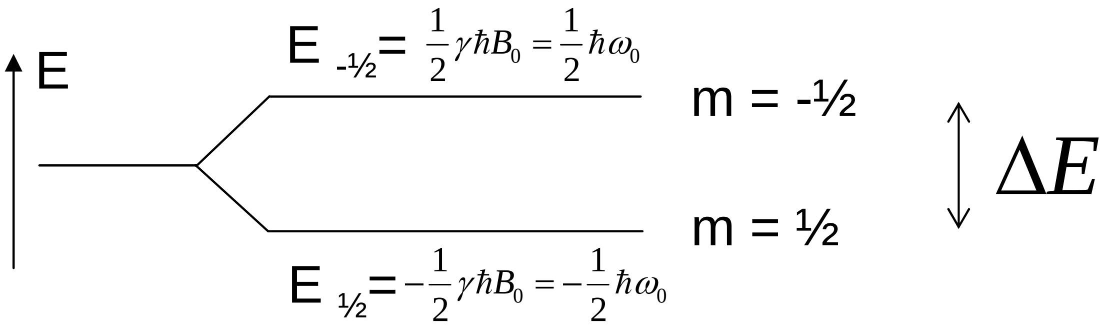
$$H = \boxed{-\boldsymbol{\mu}\cdot\mathbf{B}} = -\gamma\hbar B_0 I_z$$

interaction energy of the nucleus

- Eigenvalues are give by

$$E = -\gamma\hbar B_0 m \qquad \text{with} \qquad m = I, I-1, \ldots, -I$$

- For Protons I= 1/2 , thus two energy levels



E

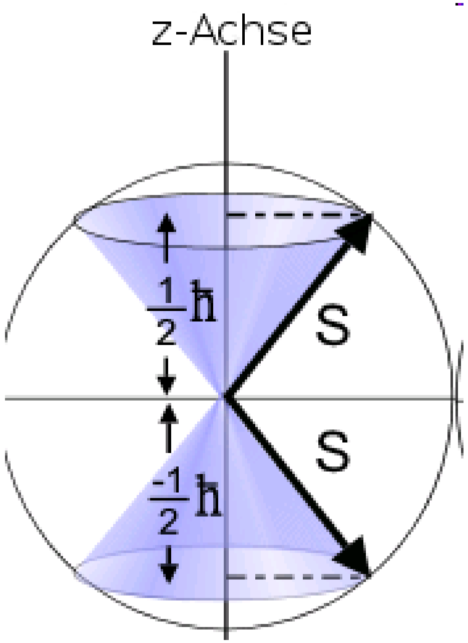
$E_{-1/2} = \frac{1}{2}\gamma\hbar B_0 = \frac{1}{2}\hbar\omega_0$

m = -½

m = ½

ΔE

$E_{1/2} = -\frac{1}{2}\gamma\hbar B_0 = -\frac{1}{2}\hbar\omega_0$



Wikipedia

Equilibrium Magnetisation

- Reminder: using the density operator ρ the expectation value <A> of an operator A can be expressed as

$$\langle A \rangle = Tr(\rho A)$$

- Diagonal elements $P_\uparrow, P_\downarrow$ of the density operator express the relative spin populations
- In equilibrium they are given by the Boltzmann distribution

$$P_\uparrow = \frac{e^{\frac{-E_\uparrow}{kT}}}{e^{\frac{-E_\uparrow}{kT}} + e^{\frac{-E_\downarrow}{kT}}} = \frac{e^{\frac{\hbar\gamma B_0}{2kT}}}{e^{\frac{\hbar\gamma B_0}{2kT}} + e^{\frac{-\hbar\gamma B_0}{2kT}}} \qquad P_\downarrow = \frac{e^{\frac{E_\uparrow}{kT}}}{e^{\frac{-E_\uparrow}{kT}} + e^{\frac{-E_\downarrow}{kT}}} = \frac{e^{-\frac{\hbar\gamma B_0}{2kT}}}{e^{\frac{\hbar\gamma B_0}{2kT}} + e^{\frac{-\hbar\gamma B_0}{2kT}}}$$

- The net longitudinal magnetisation is the observable population difference between Zeeman eigenstates given by

$$\boxed{\langle \mu_z \rangle = \frac{\hbar\gamma}{2}\left(P_\uparrow - P_\downarrow\right) \approx \frac{\hbar^2\gamma^2 B_0}{4kT}}$$

Equation of Motion of the Expectation Value

- In QM coherent evolution can be described using the density operator ρ and the Liouville equation

$$\frac{\partial\rho}{\partial t}=\frac{1}{i\hbar}\left[H,\rho\right]$$

- For the spin-1/2 system we get the following density matrix

$$\rho=\begin{pmatrix}\left|c_\uparrow\right|^2 & c_\uparrow c_\downarrow^* \\ c_\uparrow^* c_\downarrow & \left|c_\downarrow\right|^2\end{pmatrix}$$

- Expectation value $\langle\mu_x\rangle$ of the spins x component is given by

$$\langle\mu_x\rangle=Trace(\mu_x\rho)=\frac{\hbar\gamma}{2}(\rho_{\downarrow\uparrow}+\rho_{\uparrow\downarrow})$$

Equation of Motion of the Expectation Value

- Liouville equation gives us

$$\frac{\partial\langle\mu_x\rangle}{\partial t}=\frac{\hbar\gamma}{2i}\left(i\frac{\partial\rho_{\downarrow\uparrow}}{\partial t}+i\frac{\partial\rho_{\uparrow\downarrow}}{\partial t}\right)=\frac{\gamma}{2i}\left([H,\rho]_{\downarrow\uparrow}+[H,\rho]_{\uparrow\downarrow}\right)$$

$$=\frac{\gamma}{2i}((H_{\downarrow\uparrow}-H_{\uparrow\downarrow})(\rho_{\downarrow\downarrow}-\rho_{\uparrow\uparrow})+(\rho_{\downarrow\uparrow}-\rho_{\uparrow\downarrow})(H_{\downarrow\downarrow}-H_{\uparrow\uparrow}))$$

- Remember we have the dipolar Hamiltonian $H=-\boldsymbol{\mu}\cdot\mathbf{B}$

$$\frac{\partial\langle\mu_x\rangle}{\partial t}=\hbar\gamma^2\left(\frac{-B_y(\rho_{\uparrow\uparrow}-\rho_{\downarrow\downarrow})}{2}+\frac{B_z(\rho_{\downarrow\uparrow}-\rho_{\uparrow\downarrow})}{2i}\right)=-\gamma B_y\langle\mu_z\rangle+\gamma B_z\langle\mu_y\rangle$$

Equation of Motion of the Expectation Value

- Cyclic permutation gives us all three components

$$\frac{\partial\langle\mu_x\rangle}{\partial t} = -\gamma B_y\langle\mu_z\rangle + \gamma B_z\langle\mu_y\rangle$$

$$\frac{\partial\langle\mu_y\rangle}{\partial t} = -\gamma B_z\langle\mu_x\rangle + \gamma B_x\langle\mu_z\rangle$$

$$\frac{\partial\langle\mu_z\rangle}{\partial t} = -\gamma B_x\langle\mu_y\rangle + \gamma B_y\langle\mu_x\rangle$$

$$\boxed{\frac{\partial\boldsymbol{\mu}}{\partial t} = \gamma\langle\boldsymbol{\mu}\rangle\times\mathbf{B}}$$

- This is remarkably similar to the classical Bloch equation without relaxation

$$\frac{d\mathbf{M}}{dt} = \gamma\boldsymbol{\mu}\times\mathbf{B}$$

Equation of Motion of the Expectation Value

- For large populations of non interacting spins QM and classical mechanics give identical results

- Magnetic resonance is a good example of the correspondence principle

- Quantum effects are visible when individual spins are considered or spin-spin interactions occur

Relaxation

Relaxation

- Following an excitation pulse the magnetisation returns to its equilibrium state

- The longitudinal magnetisation regains its equilibrium value M_0

- The transverse magnetisation (the measurable magnetisation component) returns to zero

Stirnberg

Longitudinal Relaxation

- Upon perturbation the longitudinal magnetisation returns to equilibrium by exchanging energy with the surrounding tissue (lattice)
- Time evolution is given by

$$\frac{dM_z}{dt} = -\frac{M_z - M_0}{T_1}$$

M_0 = longitudinal equilibrium magnetisation

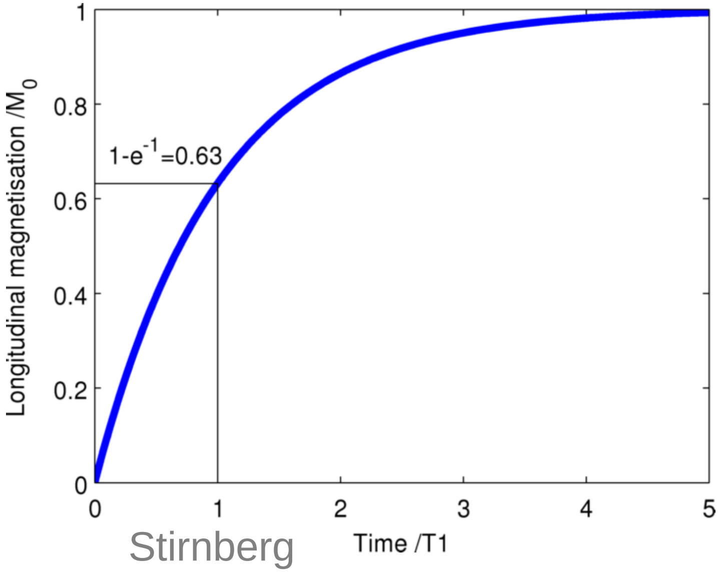
T_1 = spin-lattice relaxation time constant

- Solution:

$$M_z = M_0 + (M_z(0) - M_0)e^{\frac{-t}{T_1}}$$

- Assuming a 90° excitation pulse at t=0; $M_z(0)=0$:

$$M_z = M_0\left(1 - e^{\frac{-t}{T_1}}\right)$$



Stirnberg

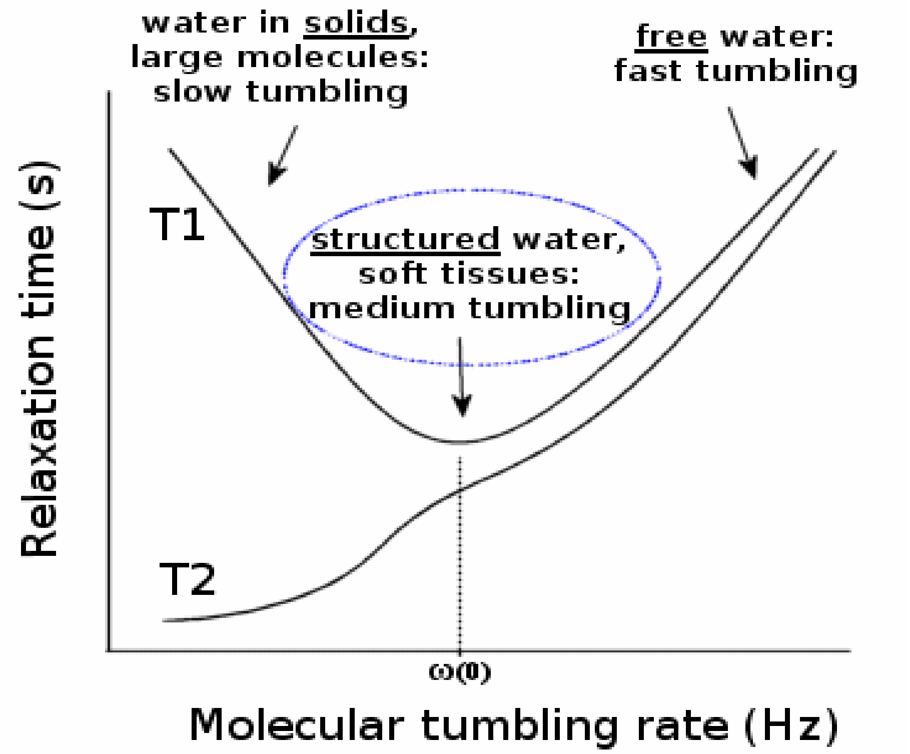
Longitudinal Relaxation

- Energy exchange with surrounding tissue (mostly water and fat) requires interaction at or near resonance condition
- Energy transfer via oscillating field resulting from movement of the spins molecule (molecular tumbling)
- Possible motions: rotation, vibration and translation

With respect to T_1 three states of water are of interest:

- Free water; unbound
- „structured“ water; bound to macromolecule with single bond (retains rotational freedom)
- „bound“ water; bound to macromolecule with two bonds

BPP Theory (Bloembergen *et al.* 1948)



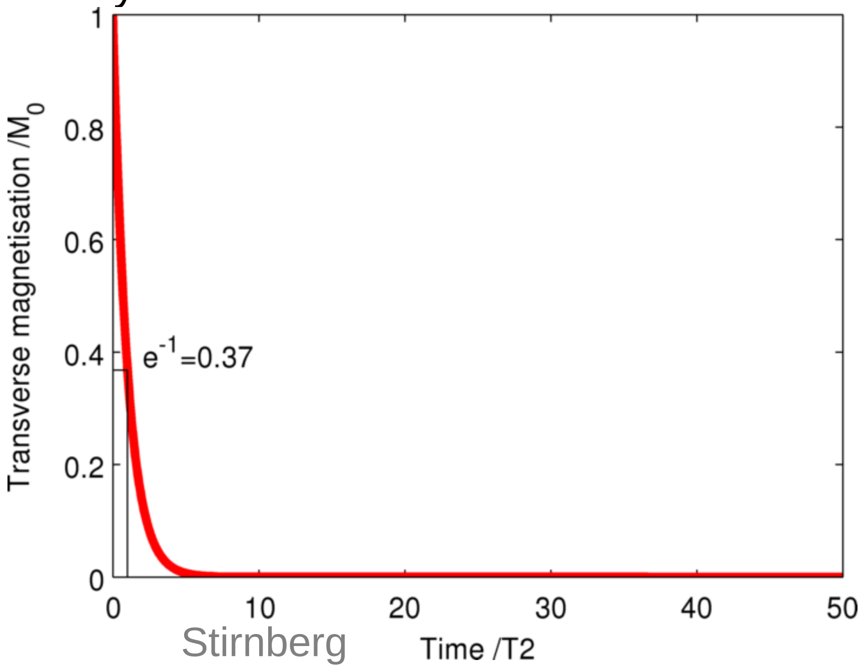
http://www.revisemri.com/images/tumbling.gif

Transverse Relaxation

- Transient and random local field fluctuations occur on atomic level through spin-spin interactions
- Leads to *irreversible* loss of phase coherence between the spins
- The time evolution of the transverse magnetisation is described by $$\frac{dM_{xy}}{dt} = -\frac{M_{xy}}{T_2}$$
- Assuming a 90° pulse at t=0 and $M_{xy}(0)=M_0$ the solution is

T_2 = spin-spin relaxation time constant

$$M_{xy} = M_o e^{\frac{-t}{T_2}}$$

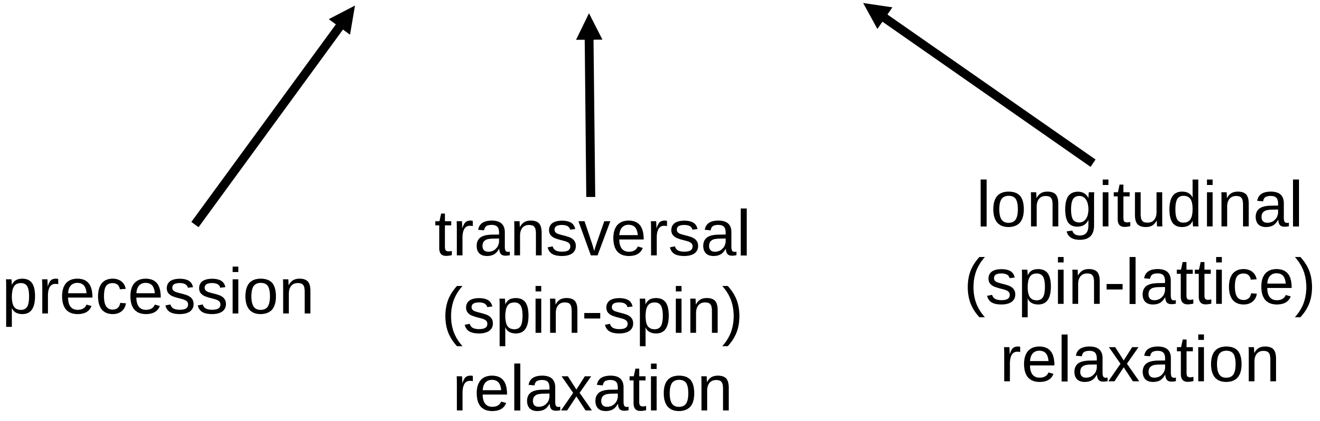


Stirnberg

Bloch Equation with Relaxation

- Adding the relaxation terms to our equation of motion we arrive at the phenomenological Bloch equation which completely describes our spin system

$$\boxed{\frac{d\mathbf{M}}{dt} = \mathbf{M} \times \gamma \mathbf{B} - \frac{M_x \mathbf{i}}{T_2} - \frac{(M_z - M_0)\mathbf{k}}{T_1}}$$



precession

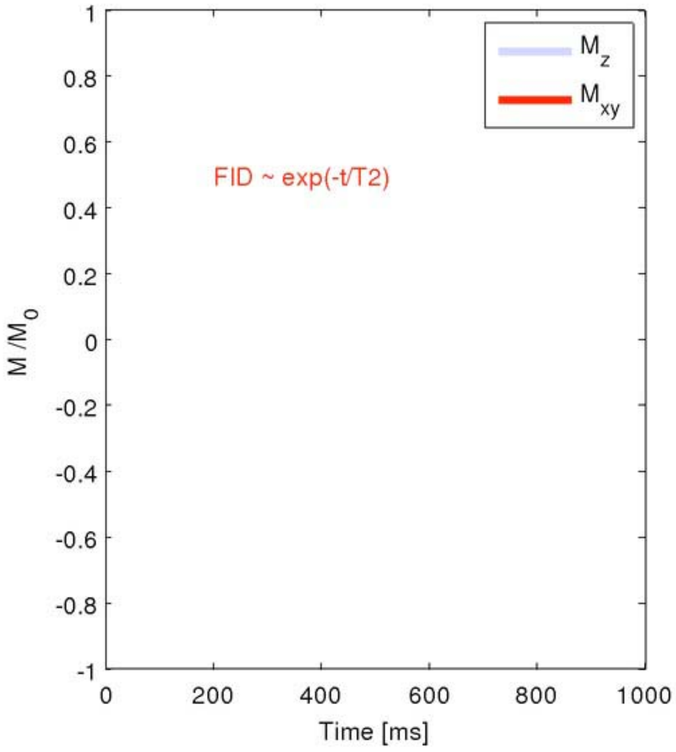
transversal
(spin-spin)
relaxation

longitudinal
(spin-lattice)
relaxation

γ = gyromagnetic ratio
T_1 = spin-lattice relaxation time
T_2 = spin-spin relaxation time
M_0 = equilibrium magnetisation
$\mathbf{i}, \mathbf{j}, \mathbf{k}$ = unit vectors in x,y,z

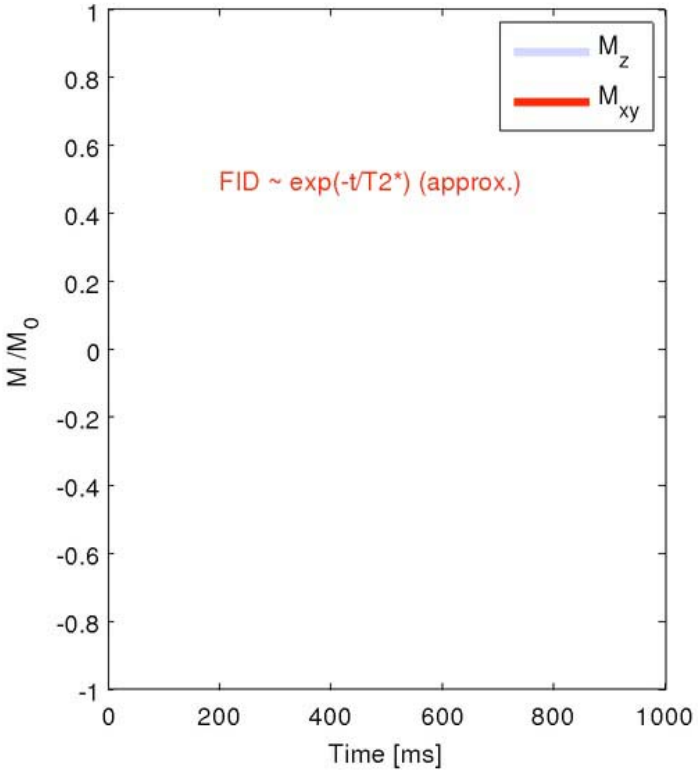
Free Induction Decay (FID)

- A 90° excitation pulse is applied at time t=0
- The received MR signal decays exponentially with the time constant T_2
- At the same time the longitudinal magnetisation (M_z) recovers



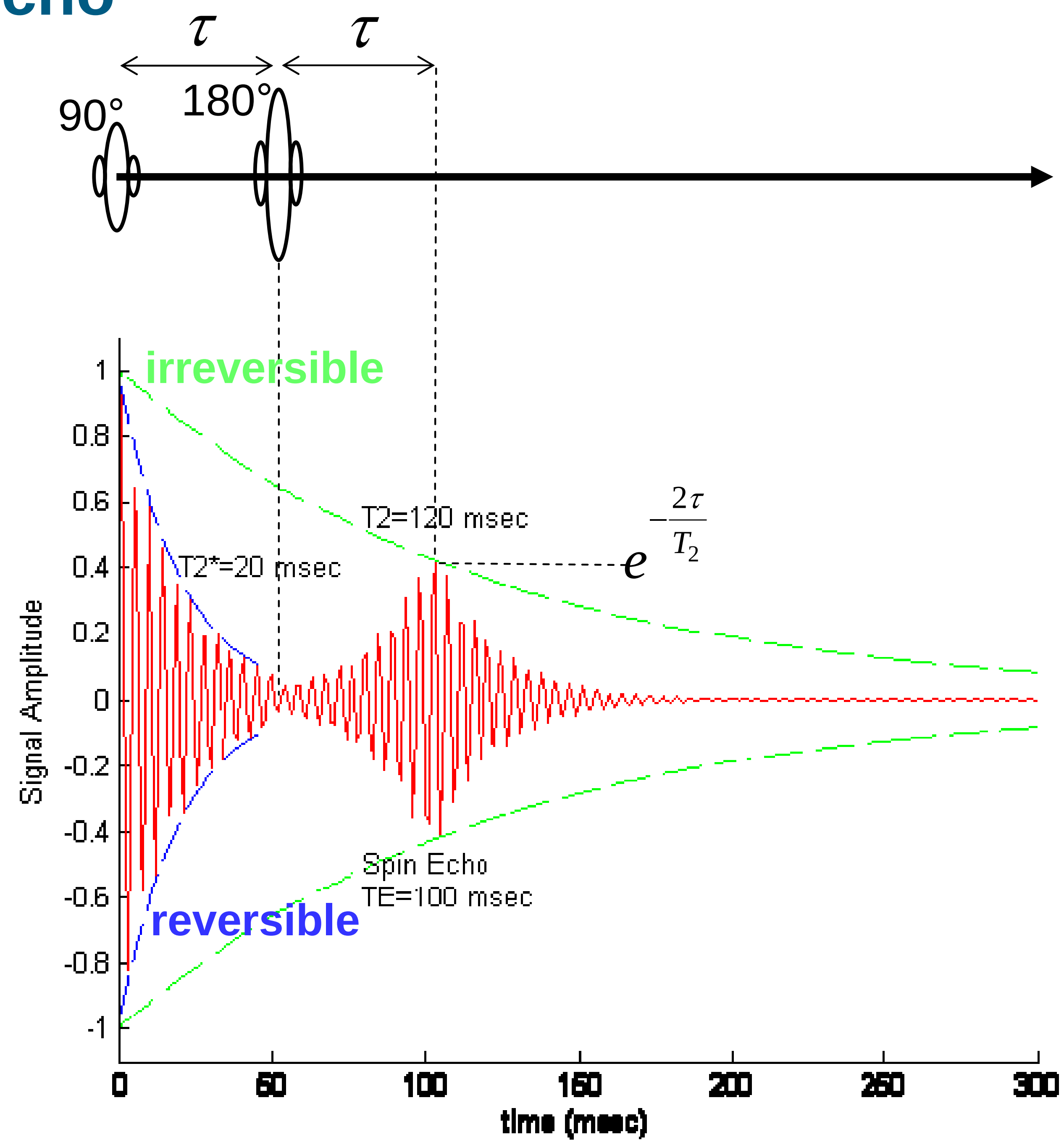
T_2^* Decay

- Spin-spin interaction lead to irreversible loss of phase coherence between the spins (T_2-decay)
- B_0 inhomogeneities and susceptibility effects cause additional shortening with time constant T_2’ (reversible with spin-echo)
- Additional shortening of decay constant to T_2* given by $\frac{1}{T_2^*}=\frac{1}{T_2}+\frac{1}{T_2'}$



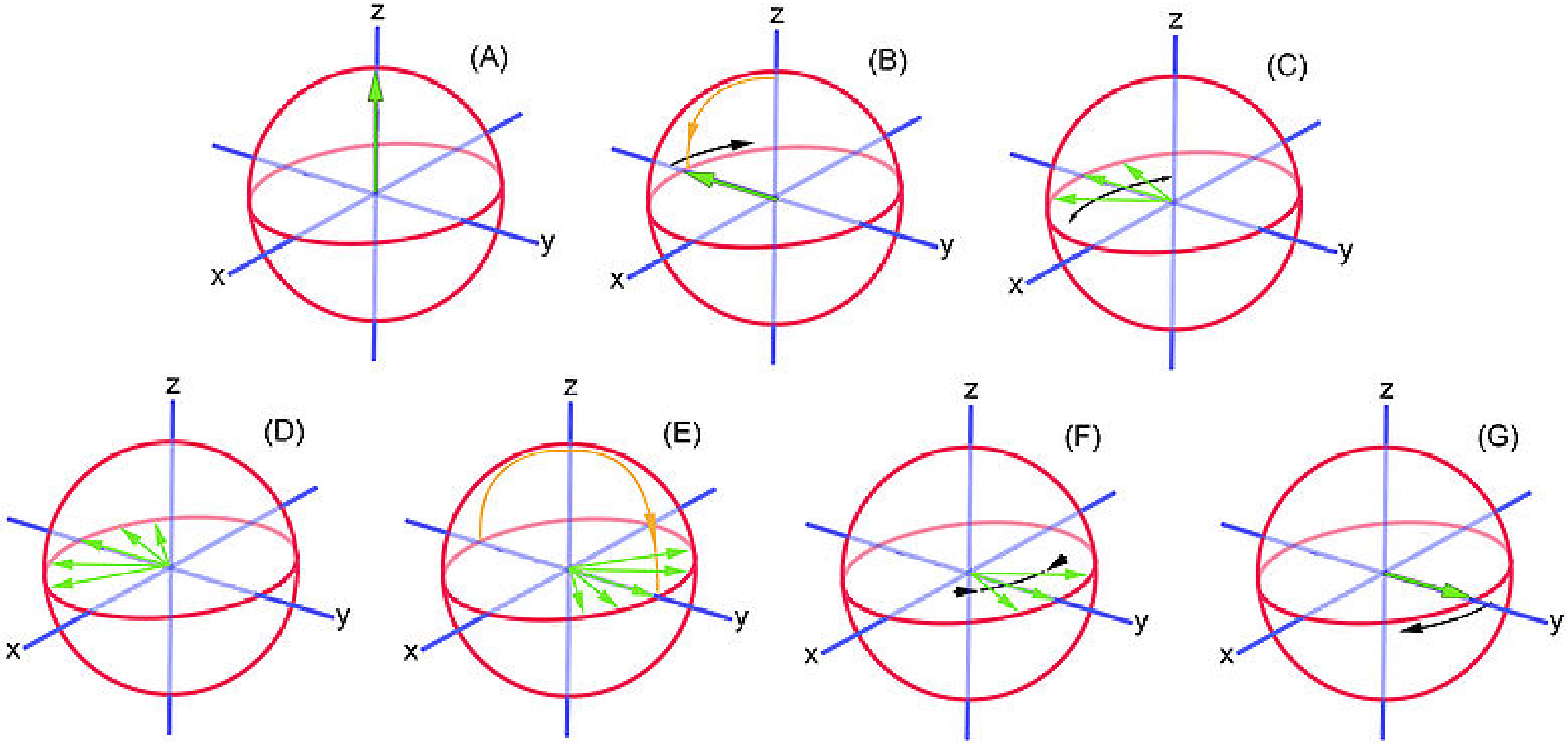
Important Effects

Spin Echo



http://upload.wikimedia.org/wikipedia/commons/7/7a/Spin_Echo.gif

Spin Echo



Equilibrium

90° RF

Dephasing

More Dephasing

180° RF

Rephasing

Echo!

http://en.wikipedia.org/wiki/File:Spin_Echo_Diagram.jpg

Chemical Shift

- Small displacement of the resonance frequency due to shielding by local electronic environment
- Effective field experienced by the nucleus is given by

$$B_{eff} = B_0 - B_{0\sigma} = B_0(1-\sigma)$$

$$\Leftrightarrow \omega_{eff} = \omega_0 - \omega_{0\sigma} = \omega_0(1-\sigma)$$

- Defined relative to reference frequency

$$\delta = \frac{\omega_S - \omega_R}{\omega_R} \times 10^6 = \frac{\sigma_R - \sigma_S}{1-\sigma_R} \times 10^6 \approx (\sigma_R - \sigma_S) \times 10^6$$

σ = environment dependent shielding constant

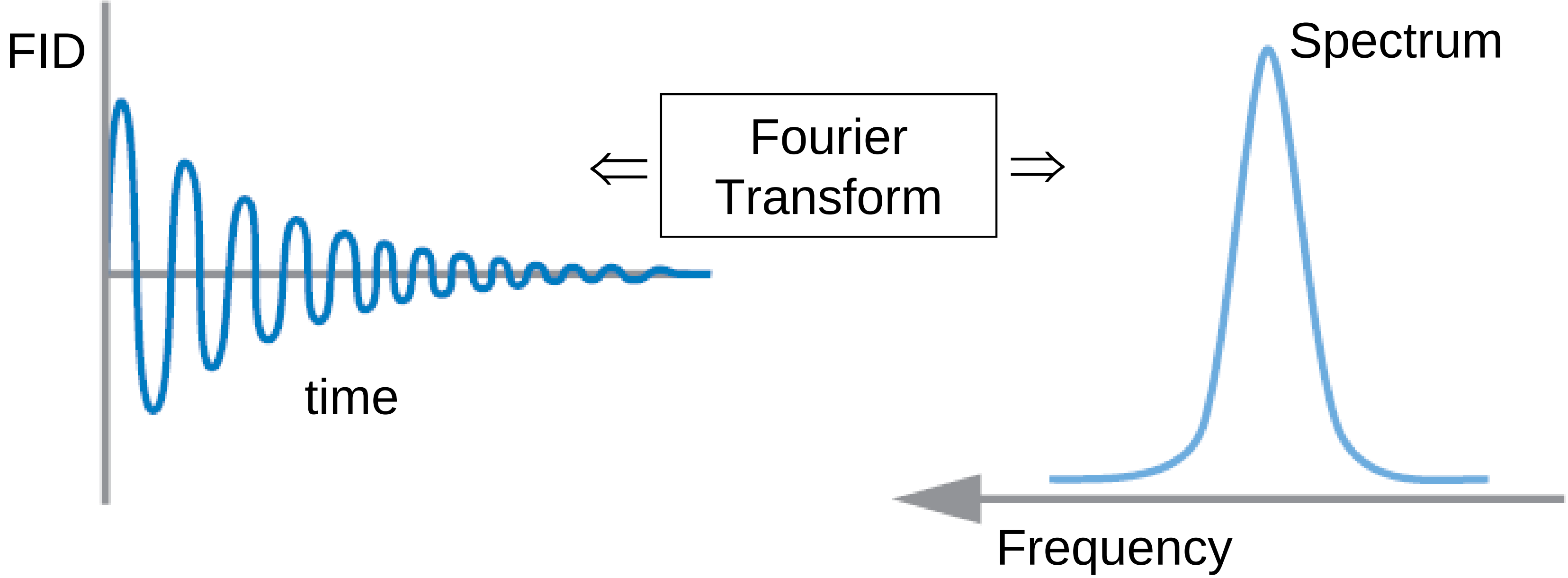
ω_R = reference frequency

ω_S = resonance frequency of sample

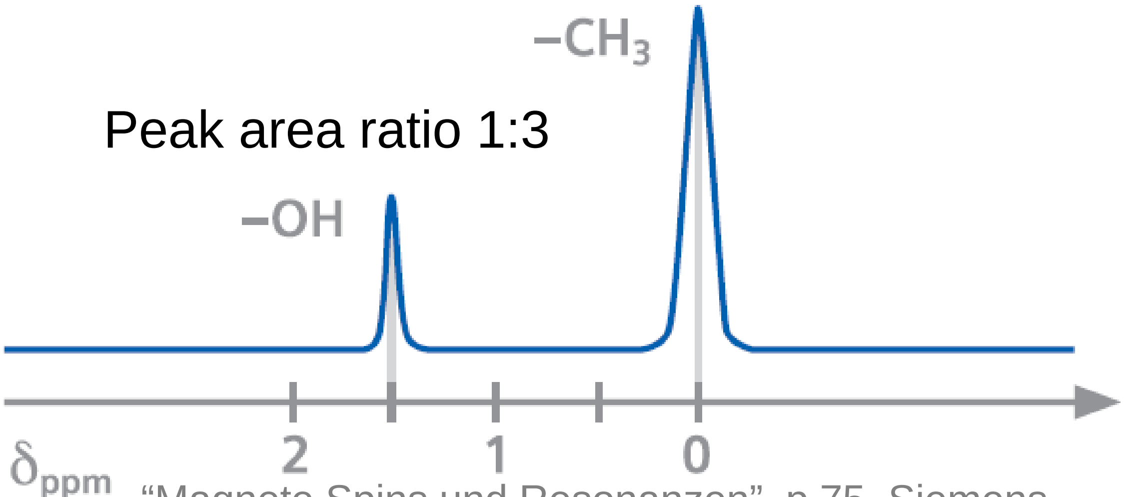
δ = chemical shift in parts per million (ppm)

Chemical Shift

- NMR spectroscopy: acquire FID and Fourier transform



^{1}H spectrum of Methanol (CH_3OH)



Peak area ratio 1:3

"Magnete Spins und Resonanzen", p.75, Siemens

Lorentzian line shape G(ω) due to T_2 decay, centered at frequency ω_0

$$G(\omega) = \frac{T_2}{1+(\omega-\omega_0)^2 T_2^2}$$

Chemical Shift

- ^{1}H spectrum of the brain

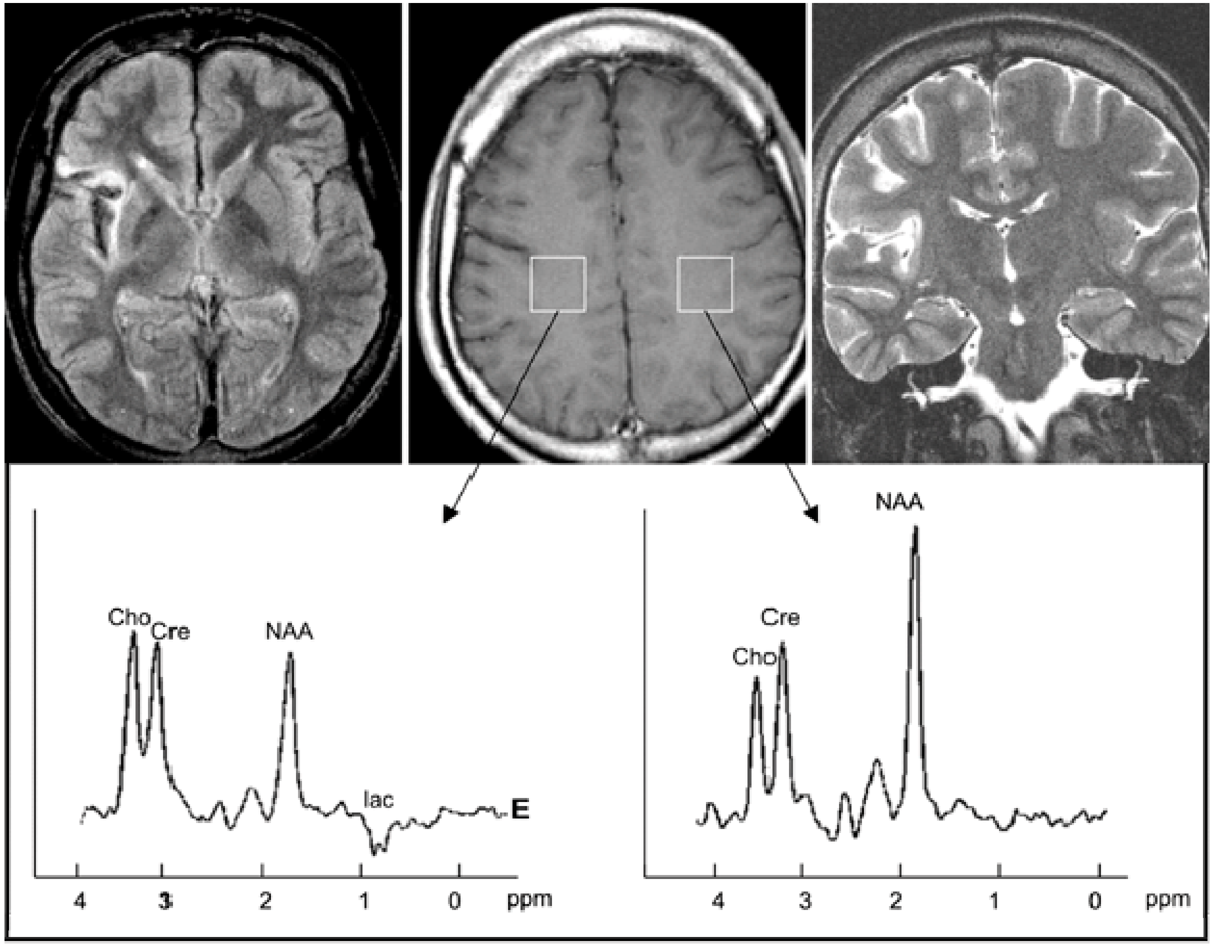
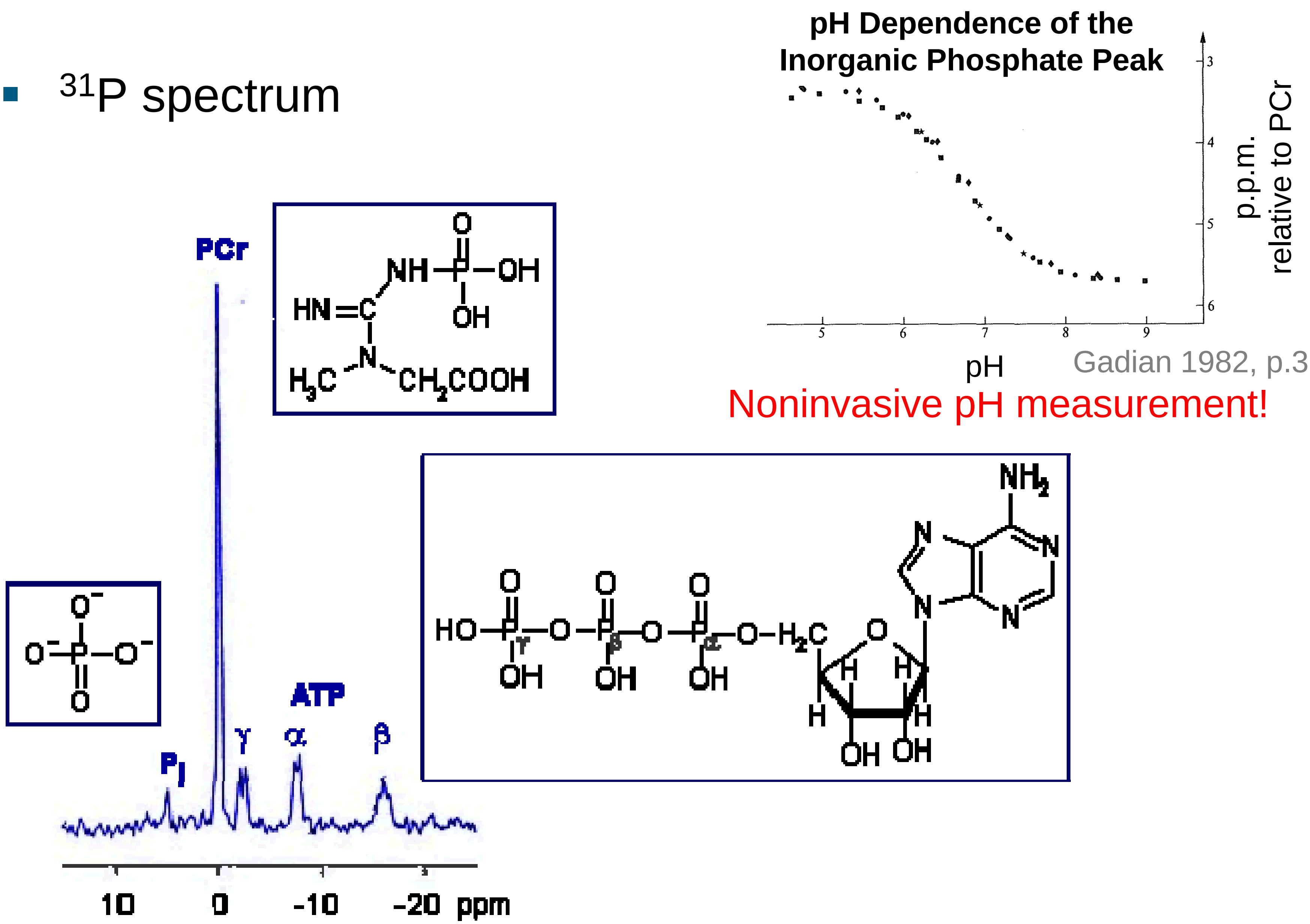


Fig 8. Rasmussen's encephalitis. Right insular hyperintense signal in axial FLAIR (top, left) and coronal T2 (top, right) weighted images with parenchyma retraction, noted by cortical sulci asymmetry. Decreased NAA signal and increased choline (Cho) and lactate (lac) are observed relative to contralateral homologous area (bottom).

Faria *et al*. 2004; doi:10.1590/S0000-282X2004000300010

Chemical Shift

- ^{31}P spectrum



pH Dependence of the Inorganic Phosphate Peak

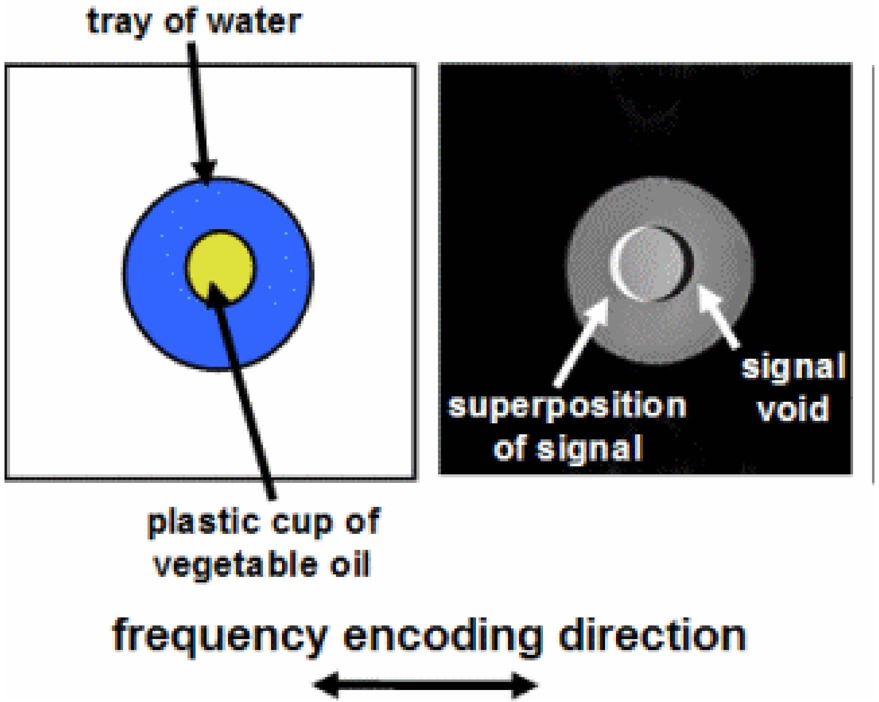
Gadian 1982, p.32

Noninvasive pH measurement!

Friebolin “Ein- und zweidimensionale NMR-Spketroskopie”, p. 358, 1999

Chemical Shift

- Chemical shift artefact in MRI (fat/water)

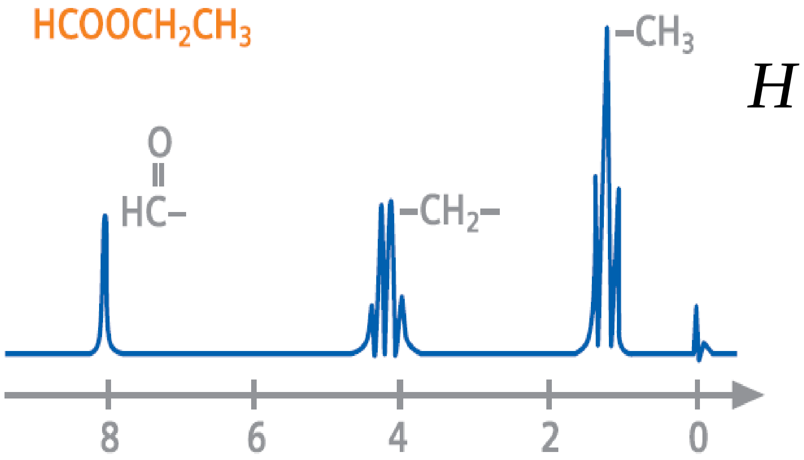


http://www.revisemri.com/images/chemshift.gif

- Frequency is used for spatial encoding in MRI
- Chemical shift changes frequency -> erroneous encoding
- CS good for spectroscopy
- Not so good for imaging -> fat suppression

J-Coupling

- Indirect coupling between two nuclear spins of a molecule through involvement of bonding electrons
- Observable in NMR spectroscopy
- Leads to splitting of lines into multiplets in molecular spectra
- Independent of magnetic field (opposed to chemical shift)
- Quantum effect (not explainable within classical mechanics)
- Coupling between nuclear pins $\mathbf{I}_j$ and $\mathbf{I}_k$ described by 3x3 J-coupling tensor $\mathbf{J}_{jk}$ (reduces to scalar coupling in isotropic liquids)



$$H = 2\pi \mathbf{I}_j \cdot \mathbf{J}_{jk} \cdot \mathbf{I}_k$$

“Magnete Spins und Resonanzen”, p.158, Siemens

Additional References

Textbooks

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