



NMR Interactions



Outlook



- Introduction
- Theoretical background
- Zeeman interaction
- Chemical shift
- Dipolar coupling
- J-coupling
- Quadrupolar interaction
- Paramagnetic interaction



Introduction



- There are six important NMR interaction for nuclei

$$\hat{H}_N = \hat{H}_Z + \hat{H}_Q + \hat{H}_D + \hat{H}_g + \hat{H}_{CS} + \hat{H}_J$$

	Characterisation	Range
\hat{H}_Z	Zeeman interaction – interaction of magnetic field with nuclear spin	100 MHz
\hat{H}_Q	Quadrupolar interaction	1-10 MHz
\hat{H}_D	Dipolar interaction – homo- and heteronuclear interaction	50 kHz
\hat{H}_g	Paramagnetic interaction	50 kHz
\hat{H}_{CS}	Chemical shift – influenced by chemical environment	20 kHz
\hat{H}_J	J – coupling	100 Hz



Introduction



- Analogue the Hamiltonians for the electrons

$$\hat{H}_E = \hat{H}_{EZ} + \hat{H}_{ZFS} + \hat{H}_{HF} + \hat{H}_{NZ} + \hat{H}_{NQ} + \hat{H}_{ee}$$

	Characterization	Range
\hat{H}_{EZ}	Zeeman interaction – for electrons	10 GHz
\hat{H}_{ZFS}	Zero field splitting	0-300 GHz
\hat{H}_{HF}	Hyperfine Structure electron/nucleus interaction	1-100 MHz
\hat{H}_{NZ}	Zeeman interaction – for nuclei	1-10 MHz
\hat{H}_{NQ}	Quadrupolar interaction	0.1-10 MHz
\hat{H}_{ee}	Electron-electron interaction (weak)	0-30 MHz (dipol/dipol) 0-1 GHz (Heisenberg exchange)



Theoretical background



- The wave function describes a system completely
- For special information you need an operator which acts on the wave function

$$\frac{d}{dx} \exp(Ax) = A \exp(Ax)$$

operator eigen- constant/ same function
 function eigenvalue

- Eigenvalue represents the measured observable property, for example the energy
- Operator which acts on the wave function to give the energy as eigenvalue, is called Hamiltonian

$$\hat{H}\Psi = E\Psi$$



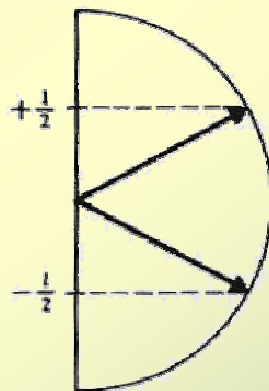
Zeeman interaction



- Zeeman interaction is the interaction between spin and magnetic field B_0
- The corresponding Hamiltonian for the interaction is:

$$\hat{H}_{1\text{spin}} = -\gamma B_0 \hat{I}_z$$

- \hat{I}_z is the angular momentum operator which represents the z component of the angular momentum



Zeeman interaction



- Energy for transition:

$$\hat{H}_{1\text{spin}} \Psi_m = -\gamma B_0 [\hat{I}_z \Psi_m]$$

$$\hat{H}_{1\text{spin}} \Psi_m = -\gamma B_0 [m\hbar \Psi_m]$$

$$\hat{H}_{1\text{spin}} \Psi_m = -m\hbar\gamma B_0 \Psi_m$$

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

- For spin 1/2 nucleus

$$E_{\pm 1/2} = \pm 1/2 \hbar \gamma B_0$$

$$\Delta E = E_{1/2} - E_{-1/2} = \hbar \gamma B_0$$

$$\Delta E = h\nu_0$$

Larmor frequency:

$$\nu_0 = \gamma B_0 / 2\pi$$



Chemical shift



- Also the electrons around a nucleus interact with the applied magnetic field and a new magnetic field is created
- The total field at the nuclear is different to the applied magnetic field

$$\hat{H}_{CS} = \gamma \mathbf{I} \sigma \mathbf{B}_0$$

$$\mathbf{B}_{nuc} = \mathbf{B}_0 + \mathbf{B}_{ind} = \mathbf{B}_0 - \sigma \mathbf{B}_0 = (1 - \sigma) \mathbf{B}_0$$

- σ is a second rank tensor

$$\sigma = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}$$

- This tensor relates the direction and the magnitude B_{nuc} at the nucleus to an external uniform magnetic field B_0



Chemical shift



- A matrix can be decomposed into a symmetrical and a antisymmetrical part

$$\sigma = \sigma^{\text{symmetric}} + \sigma^{\text{antisymmetric}} = (\sigma + \sigma^T)/2 + (\sigma - \sigma^T)/2$$

- The symmetric tensor can be decomposed again in an isotropic and a traceless symmetric tensor

$$\sigma = \sigma^{\text{iso}} + \sigma^{\text{sym}} + \sigma^{\text{anti}}$$

- It is possible to diagonalize σ^{sym} to give its principal values and principal axes \longrightarrow transfers the Cartesian coordinate to principal axis system of σ^{sym}



Chemical shift

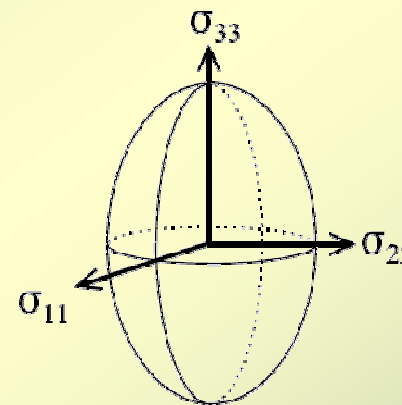


$$\sigma^{pa} = \sigma^{iso} + \sigma^{sym} + \sigma^{anti}$$

$$\sigma^{iso} = \sigma^{av} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\sigma^{sym} = \delta \begin{pmatrix} -\frac{1}{2}(1+\eta) & 0 & 0 \\ 0 & -\frac{1}{2}(1-\eta) & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\sigma^{anti} = \begin{pmatrix} 0 & \sigma_{12} & \sigma_{13} \\ -\sigma_{12} & 0 & \sigma_{23} \\ -\sigma_{13} & -\sigma_{23} & 0 \end{pmatrix}$$



$$\sigma^{av} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$$

$$\Delta\sigma = \sigma_{33} - (\sigma_{11} + \sigma_{22})/2$$

$$\delta = \sigma_{33} - \sigma_{av} = (2/3) \Delta\sigma$$

$$\eta = (\sigma_{22} - \sigma_{11}) / (\sigma_{33} - \sigma_{av})$$

$$= (\sigma_{22} - \sigma_{11})\delta$$

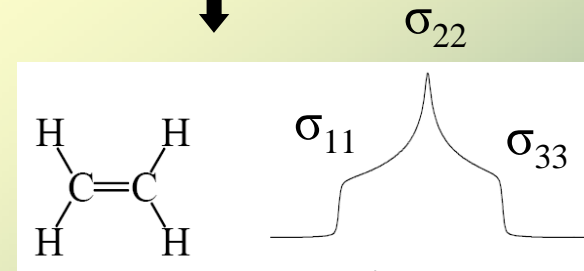
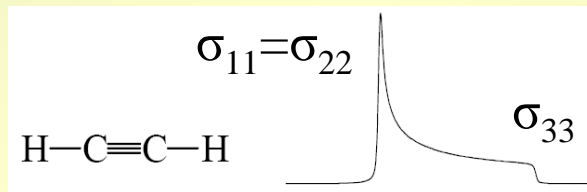
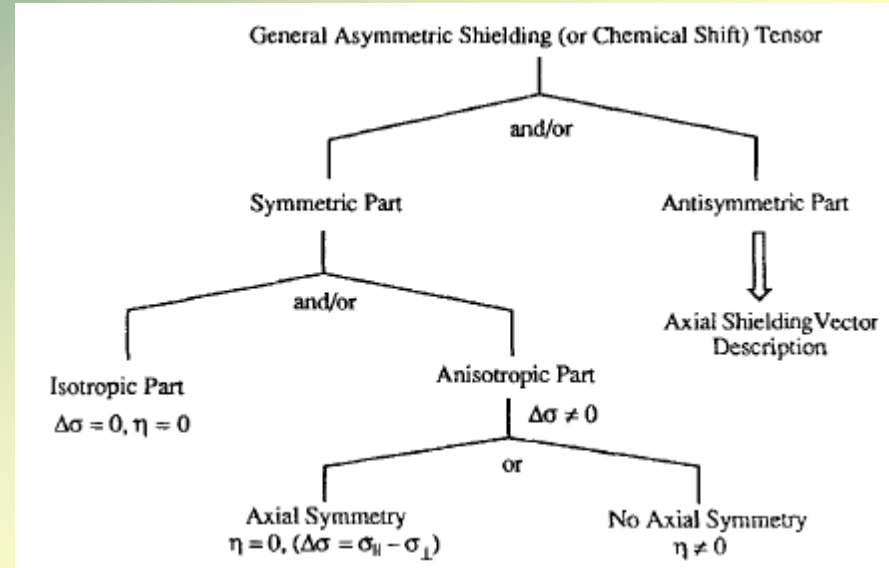
$$= (\sigma_{22} - \sigma_{11}) / [(2/3)\Delta\sigma]$$

anisotropy
parameter

asymmetry
parameter



Chemical shift



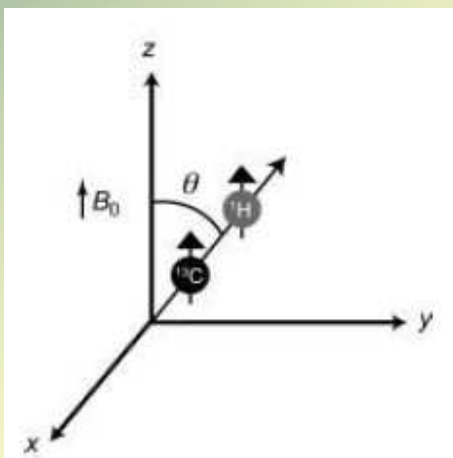
Dipolar Coupling



- The dipolar coupling is based on the interaction of small local fields of the nuclear magnetic moments of different nuclear

$$\hat{H}_D = \sum \mathbf{I}_i \mathbf{D} \mathbf{I}_j$$

- It is possible to write the Hamiltonian in a different way, separated for heteronuclear and homonuclear case



$$\hat{H}_{IS} = -d(3\cos^2\Theta - 1)I_Z S_Z \quad d = \left(\frac{\mu_0}{4\pi} \right) \frac{\hbar \gamma_I \gamma_S}{r_{IS}^3}$$

$$\hat{H}_{II} = -d/2 (3\cos^2\Theta - 1) (2I_{1Z} I_{2Z} - 1/2 (I_1^+ I_2^- + I_1^- I_2^+))$$

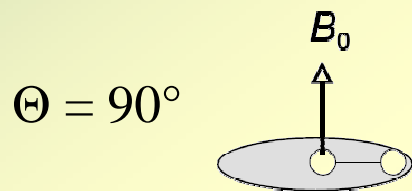
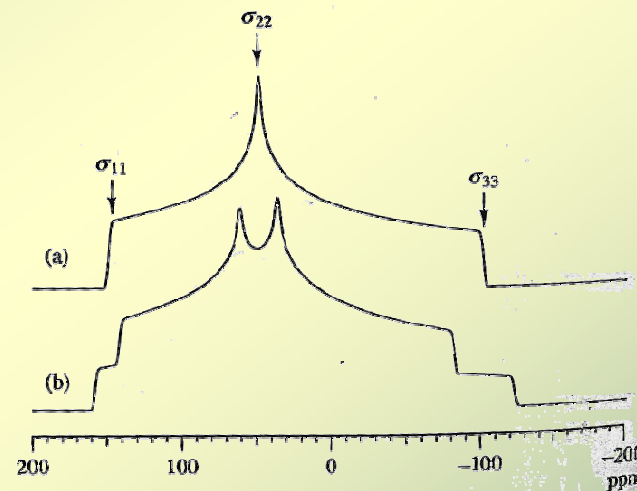
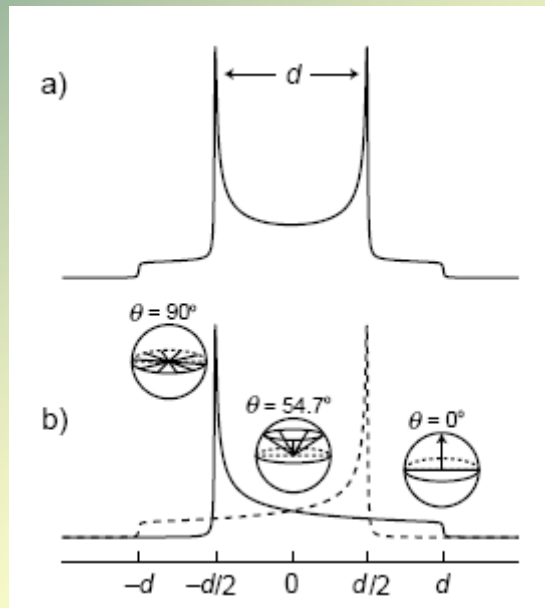
- Keep in mind:
 - the strength of the coupling depends on γ
 - it is inversely proportional to the distance
 - the orientation is important



Dipolar Coupling



Pake Pattern:



$\Theta = 0^\circ$



J-Coupling



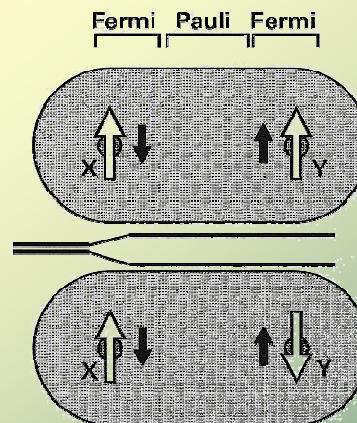
- Unlike the direct dipolar coupling there is also the indirect coupling of the spins via the bonding electrons

$$\hat{H}_J = \hbar \mathbf{I}_1 \mathbf{J} \mathbf{I}_2$$

- The second rank tensor \mathbf{J} can be decomposed in:

$$\mathbf{J} = \mathbf{J}^{\text{iso}} + \mathbf{J}^{\text{sym}} + \mathbf{J}^{\text{anti}}$$

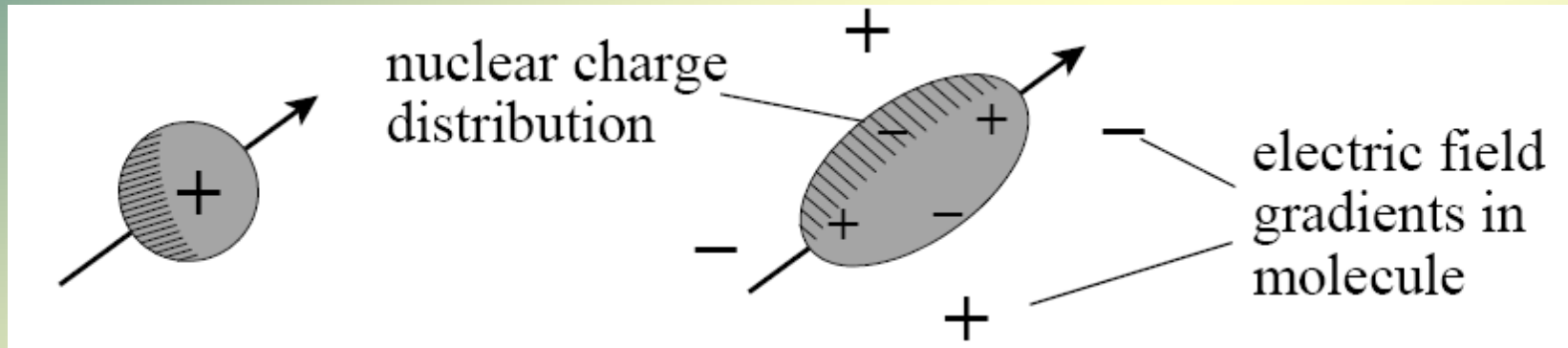
- Again only \mathbf{J}^{iso} and \mathbf{J}^{sym} affect the appearance of an NMR spectrum
- Mechanism of the coupling:



Quadrupolar interaction



- Nuclei with spin $> 1/2$ have a asymmetric distribution of nucleons (non spherical distribution of positive electric charge)



- These nuclei have a electric quadrupol moment Q which is a property like γ and interacts with the electric field gradients

$$\hat{H}_Q = \hat{H}_1 + \hat{H}_2 \dots$$

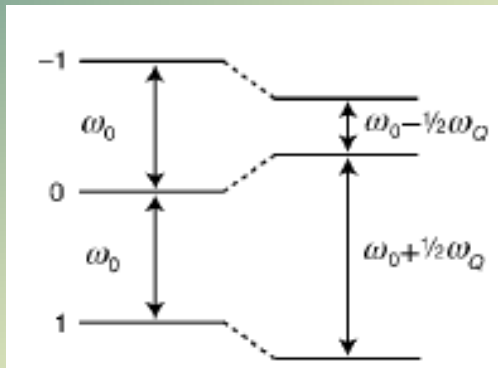
- If the molecule is non symmetric there are changings of the Zeeman interaction



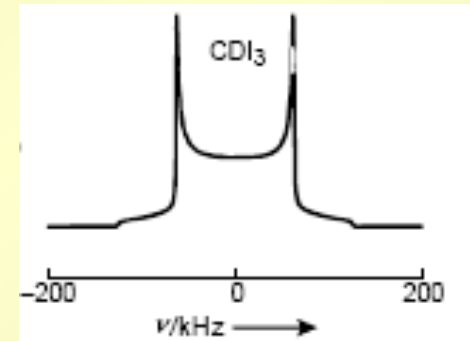
Quadrupolar interaction



- The energy between two states is not equal because of the first order quadrupolar coupling



$$\omega_Q = \frac{3eqeQ}{2I(2I-1)\hbar}$$



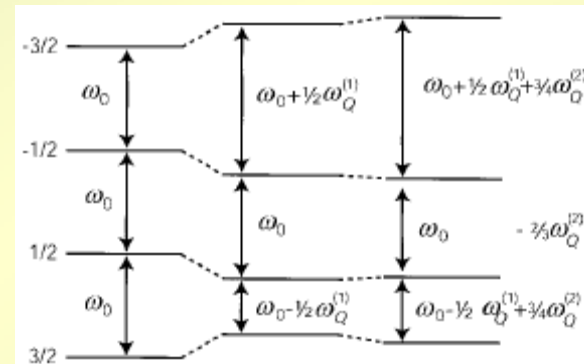
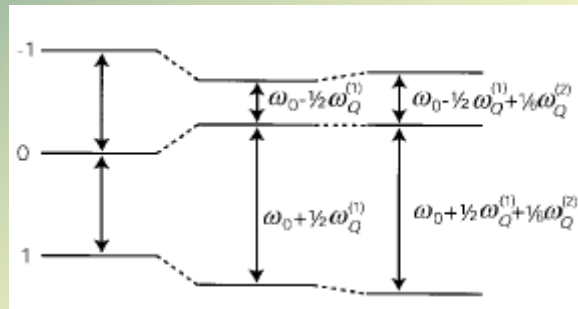
- The relaxation time is short because of quadrupolar coupling
- It is possible to get information of intramolecular mobility and orientation via quadrupolar coupling



Quadrupolar interaction



- The second order quadrupolar coupling is important for nuclei with large ω_Q



$$\omega_Q^{(2)} = \frac{(\omega_Q^{(1)})^2}{2\omega_0}$$

- The second order quadrupolar coupling has a more complex dependence of the orientation

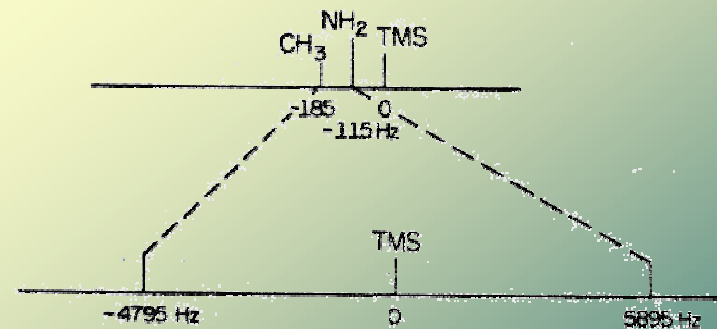


Paramagnetic interaction



- Observable for molecules with unpaired electrons (transition metal, radicals)
- The relaxation time of molecules with unpaired electrons is very short
- The chemical shift is strongly dependent on the temperature
- The range of the chemical is different

	Diamagnetic molecules	Paramagnetic molecules
^1H	0-12 ppm	-500-1500 ppm
^{13}C	0-220 ppm	-2000-1500 ppm





Thank you for your attention

