Solid-state NMR

Solutions and liquids - rapid isotropic molecular motion causes averaging of many interactions which are orientation dependent (anisotropic interactions). Motional averaging causes considerable loss of information.

Solids - molecules are generally held rather rigidly and anisotropic interactions are not averaged to zero.

Solid-state NMR spectroscopy is particularly useful as a structural method when:

(i) the sample is amorphous, inhomogeneous, without long range order, or only very small crystallites are available (diffraction techniques are not applicable);

(ii) the sample is insoluble, or decomposes in solution (solution NMR techniques cannot be used);

(iii) it is the structure of the solid itself that is the subject of interest.

Types of anisotropic interactions:

$$H_{NMR} = H_{external} + H_{internal} = (H_Z + H_{RF}) + (H_S + H_D + H_J + H_Q)$$

The external factors are Zeeman (H_Z) and radiofrequency (H_{RF}) terms, representing interaction with B_0 and B_1 fields.

The internal terms represent the shielding (H_S), dipolar (H_D), indirect coupling (H_J) and quadrupolar (H_Q) interactions. In solution state all these terms are reduced to their isotropic averages:

$$H_S \Rightarrow \sigma_{\mathrm{iso}}; \qquad H_D \Rightarrow 0; \qquad H_J \Rightarrow J_{\mathrm{iso}}; \qquad H_Q \Rightarrow 0$$

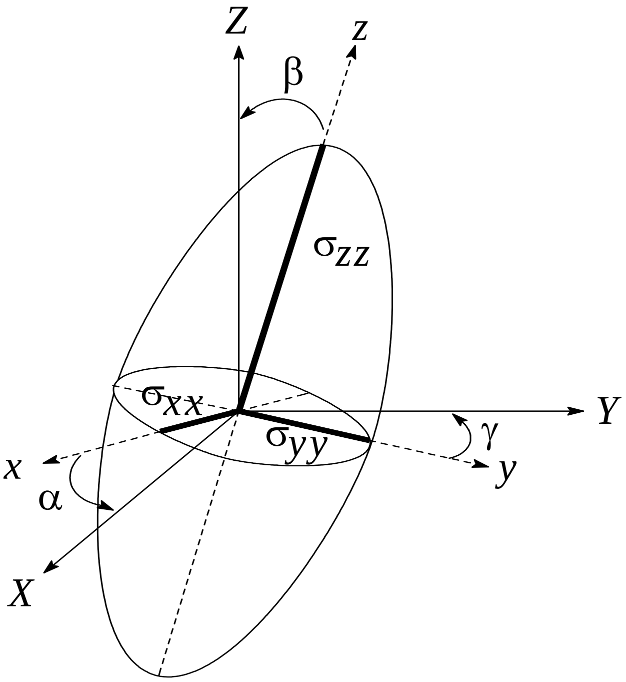
The internal terms are all tensor quantities. A tensor is a property which links two vectors: the shielding tensor, σ, links the magnetic field arising from shielding to the applied magnetic field.

$$B_S = - \sigma B_0$$

Since vectors have three components each, any tensor T may be represented by a 3 × 3 matrix with 9 components. However, it is possible to choose axes (forming principal axes system, PAS) in which T is diagonal:

$$T^{LAB} = \begin{pmatrix} T_{XX} & T_{XY} & T_{XZ} \\ T_{YX} & T_{YY} & T_{YZ} \\ T_{ZX} & T_{ZY} & T_{ZZ} \end{pmatrix} \qquad T^{PAS} = \begin{pmatrix} T_{xx} & 0 & 0 \\ 0 & T_{yy} & 0 \\ 0 & 0 & T_{zz} \end{pmatrix}$$

The shielding tensor, σ, represented by an ellipsoid (second rank surface) in the laboratory system (X,Y,Z) and the principal axes system (x,y,z) [the Euler angles α, β, γ define the orientation of PAS relative to the laboratory frame]:



A usual convention for choosing PAS: $|T_{zz} - T_{iso}| \geq |T_{yy} - T_{iso}| \geq |T_{xx} - T_{iso}|$

The transformation of a tensor from the laboratory frame to the PAS is carried out by a process of rotation involving Euler angles.

The <u>isotropic average</u>: $T_{iso} = 1/3 \, \mathrm{Tr} \, (T^{PAS}) = 1/3 \, (T_{xx}+T_{yy}+T_{zz})$

The <u>anisotropy</u>: $\Delta T = T_{zz} - 0.5(T_{xx} + T_{yy})$

For axially symmetric tensors:

$$T_{xx} = T_{yy} = T_{\perp} \qquad T_{zz} = T_{//} \qquad \Delta T = T_{//} - T_{\perp}$$

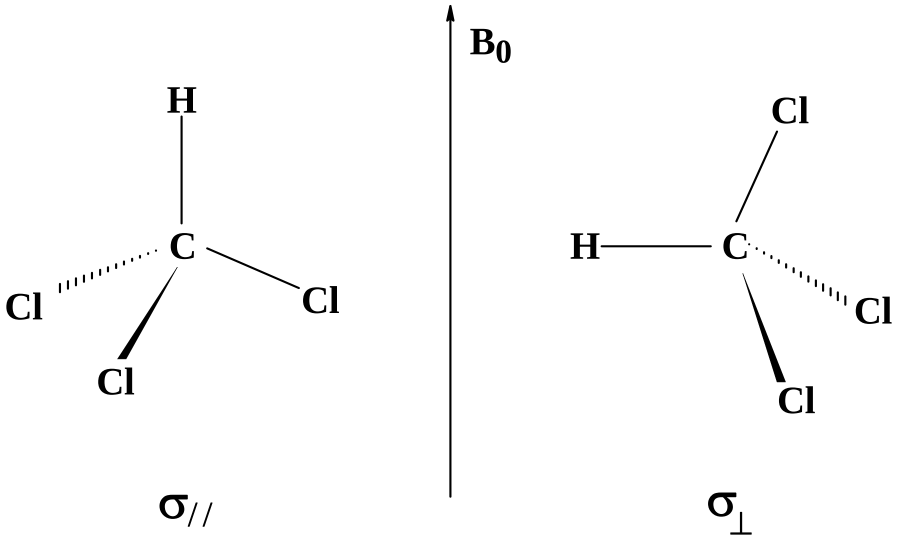
The <u>asymmetry</u>: $\eta = 3 \, (T_{xx} - T_{yy}) \, / \, 2 \, \Delta T$

To first order all four interactions have the orientation dependence of the form $(3 \cos^2\theta - 1)$, where θ represents the angle between B_0 and a local molecule-fixed direction. An angle of

54.7° to the magnetic field (which is the solution to $3\cos^2\theta - 1 = 0$) is a special angle and is known as the “magic-angle”.

Chemical shift anisotropy (CSA)

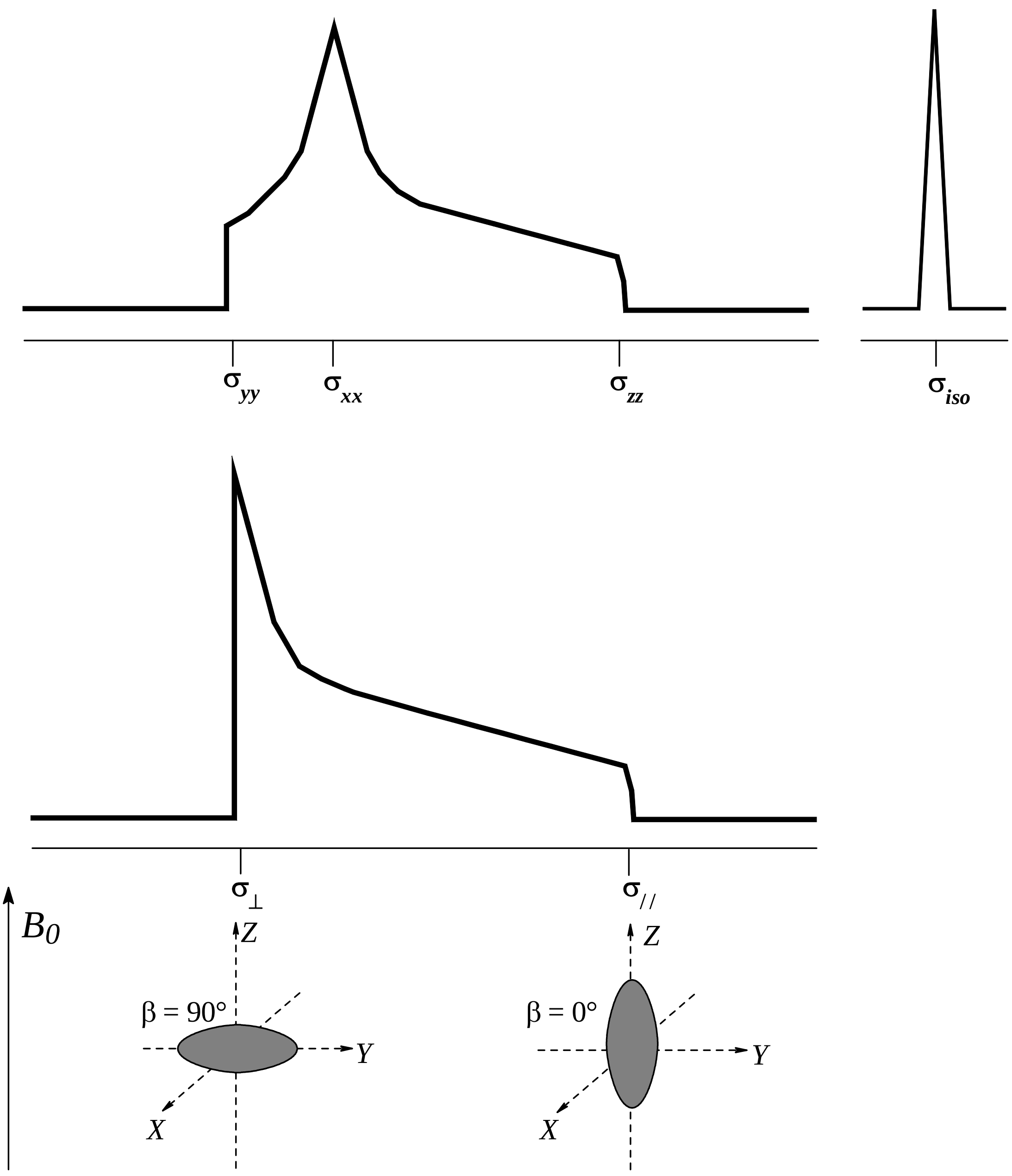
When a molecule is placed in a magnetic field, the nuclei are shielded by the electrons. In general, the electrons are not spherically distributed. When a magnetic field is applied along different directions, different amounts of electron current around the field direction (and, therefore, different amounts of shielding) are expected. Shielding is therefore anisotropic and is characterized by a tensor σ.



In the case of axial symmetry, the effective shielding in the direction of B_0 is:

$$\sigma_{ZZ} = \underset{\text{isotropic average}}{1/3(\sigma_{//} + \sigma_\perp)} \quad + \quad \underset{\text{anisotropy}}{1/3(3\cos^2\theta - 1)(\sigma_{//} - \sigma_\perp)}$$

The lineshape due to the CSA changes when the molecules reorient, since the molecular motion changes the orientation of the shielding tensor with respect to the field (B_0). The lineshape expected for a particular motional symmetry at a particular frequency of the motion can be simulated and compared with experiment.



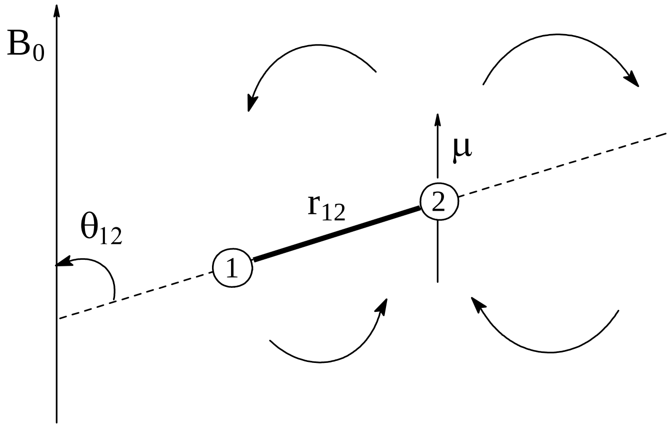
Dipolar interactions

(1) are independent of the magnetic field strength, B_0;

(2) have a short range, being proportional to r_{ij}^{-3};

(3) vanish for $\cos^2\theta_{\mathrm{ij}} = 1/3$.

Dipolar interaction - the direct influence of neighbouring magnetic dipoles on the magnetic field felt at the nucleus under investigation.



$$B_{loc} \propto \frac{\mu}{r_{12}^3}\left(3\cos^2\theta_{12} - 1\right)$$

For a typical molecular distance $r = 2$ Å $\Rightarrow B_{loc} = 2 \times 10^{-4}$ T (for ^{1}H).

For comparison, a 10 ppm CS range at $B_0 = 2.35$ T corresponds to 2.35×10^{-5} T.

Dipolar powder spectrum

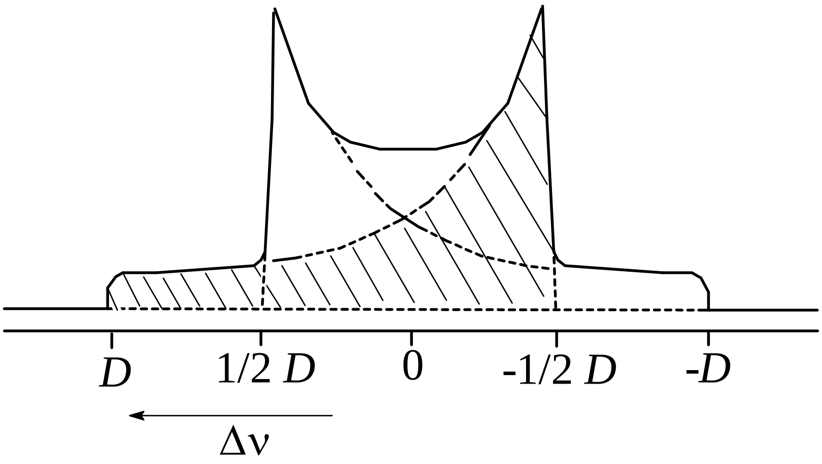
For a single crystal there are two transitions:

$\nu = \nu_L \pm \frac{3}{4} D\,(1 - 3\cos^2\theta)$ homonuclear case

$\nu = \nu_L \pm \frac{1}{2} D\,(1 - 3\cos^2\theta)$ heteronuclear case

For a sample in a microcrystalline or powdered form all orientations are possible at random. A powder pattern (a Pake doublet) is observed.

Dipolar powder pattern for a heteronuclear two-spin system:



Quadrupolar interactions

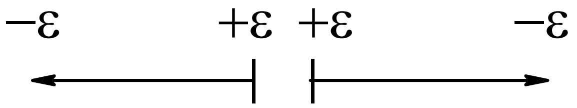
General description of point electric charges:

$$\sum_i \varepsilon_i \ \mathbf{r}_i^n, \qquad n = 1,2,4,8...$$

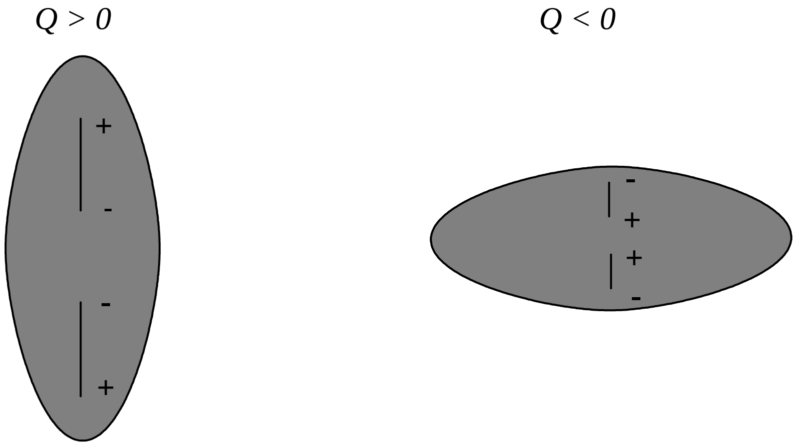
$n = 1$ - electric dipole moment

$n = 2$ - electric quadrupole moment

“back-to-back” arrangement of two dipoles:



Nuclei with spin quantum numbers I greater than 1/2 possess electric quadrupole moments eQ ($Q \sim 10^{-28}\ m^2$)



For ^{2}H: $I = 1,\ Q = 2.8 \times 10^{-31}\ m^2$

Quadrupole moment eQ ⇔ Electric field gradient (EFG) $eq_{zz}(V_{zz}=d^2V/dz^2)$

EFGs exist at nuclei due to asymmetries in the spatial arrangement of the bonding electrons.
In the case of ^{2}H, imperfect mutual cancelation of nuclear and electronic contributions from all the atoms of the molecule gives rise to a weak field gradient around the deuteron with its largest component V_{zz} along the relevant X-^{2}H bond in the principal axis system:

$$V^{LAB} = \begin{pmatrix} V_{XX} & V_{XY} & V_{XZ} \\ V_{YX} & V_{YY} & V_{YZ} \\ V_{ZX} & V_{ZY} & V_{ZZ} \end{pmatrix} \qquad V^{PAS} = \begin{pmatrix} V_{xx} & 0 & 0 \\ 0 & V_{yy} & 0 \\ 0 & 0 & V_{zz} \end{pmatrix} \qquad V_{xx}+V_{yy}+V_{zz}=0$$

$$|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$$

Quadrupole coupling constant (in frequency units):

$$\chi = \frac{e^2 Q q_{zz}}{h}$$

Asymmetry parameter:

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}; \qquad 0 \leq \eta \leq 1$$

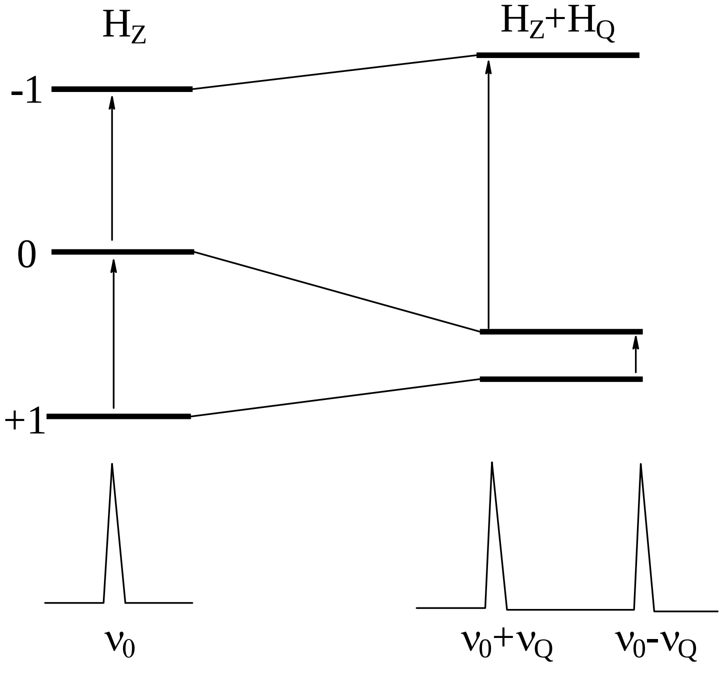
Typical values of χ: ^{2}H 250 kHz; ^{14}N 4 MHz; ^{35}Cl 80 MHz.

Wideline solid-state ^{2}H NMR

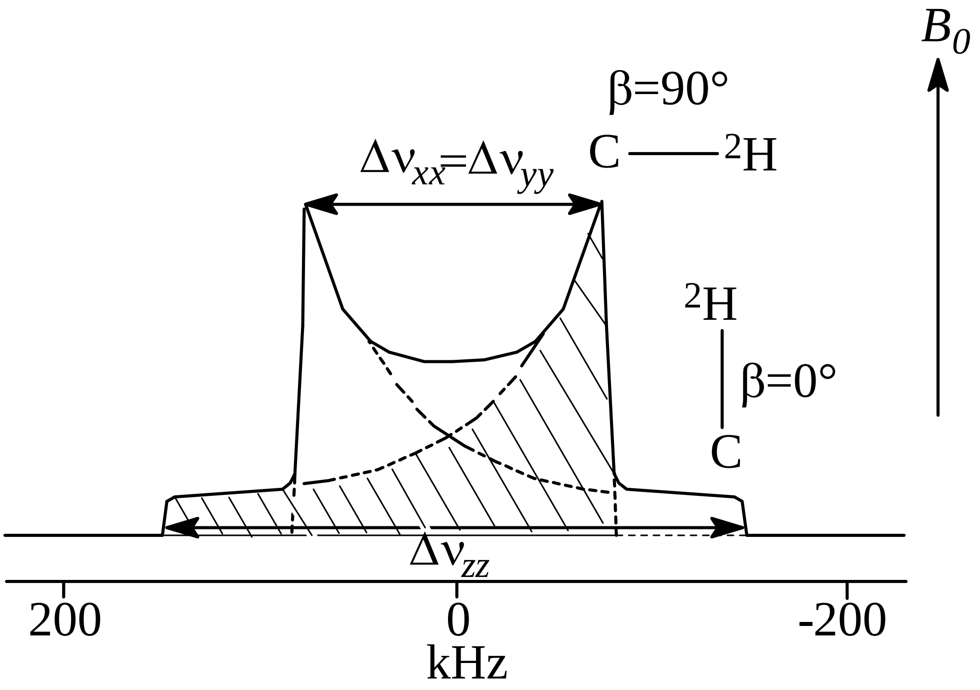
In a 7 T magnet:

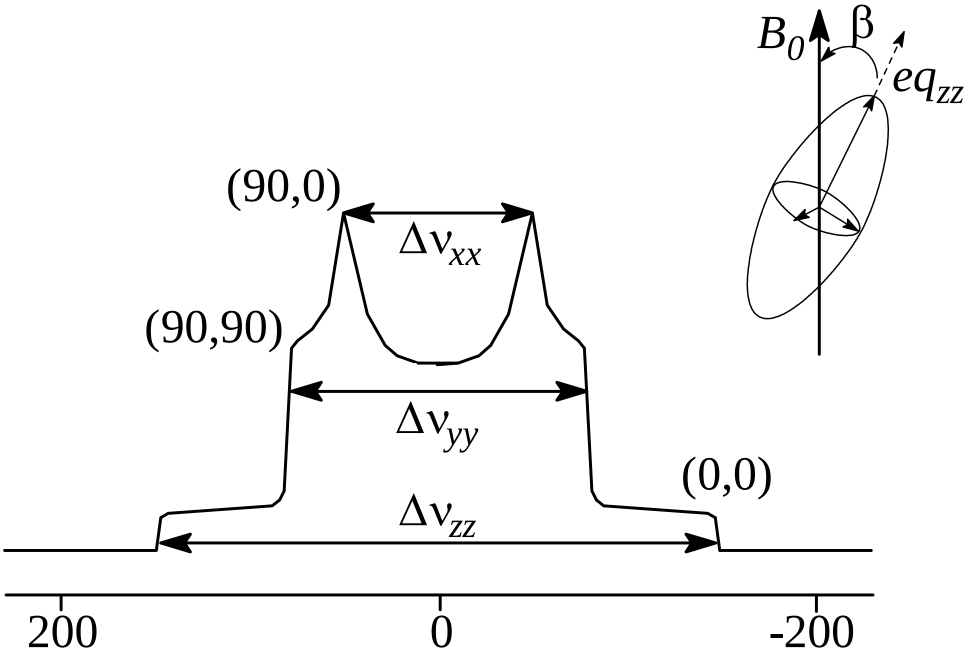
H	=	H_Z	+	H_Q	+	H_D	+	H_{CSA}	+	H_J
		46 MHz		250 kHz		2 kHz		0.5 kHz		0.02 kHz
H	=	H_Z	+	H_Q						

$H_Q << H_Z$ high-field approximation



$$2\nu_Q = \frac{3}{4}\chi\left[\left(3\cos^2\beta - 1\right) + \eta \sin^2\beta \, \cos 2\gamma\right]$$





Next to discontinuities in the lineshape are the corresponding (β,γ) values.

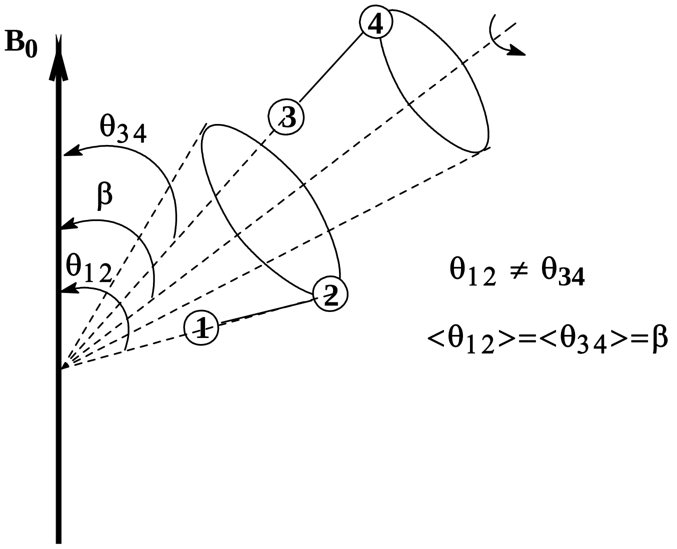
$$\chi = \frac{2}{3}\Delta\nu_{zz} \qquad \eta = \frac{\Delta\nu_{yy} - \Delta\nu_{xx}}{\Delta\nu_{zz}}$$

High-resolution solid-state NMR

Magic-angle spinning (MAS)

Anisotropic interactions have the orientation dependence of the form ($3\cos^2\theta - 1$). Geometric considerations show that macroscopic spinning about the angle β leads to an average function:

$$\langle 3\cos^2\theta - 1\rangle \quad \propto \quad (3\cos^2\beta - 1) \quad \Rightarrow \quad \beta = 54.7°$$



Dipolar decoupling

<u>^{1}H-S spin pair - strong heteronuclear dipolar interactions</u>

While the S spin (e.g., ^{13}C) is detected, the protons are simultaneously subjected to strong on-resonance irradiation. Very high powers ($\gamma B_1/2\pi$ up to 100 kHz) may be required (e.g., for decoupling in the case of rigid CH_2 groups). The method consists of application of a continuous pulse at the ^{1}H resonance frequency in a direction perpendicular to B_0. As a result, ^{1}H spin vectors are directed perpendicular to those of S nuclei and since the dipolar interaction depends on $\mathbf{I}_H \cdot \mathbf{I}_S$, the dipolar interaction is reduced to zero. The usual single-pulse sequence for the S nuclei is then used to measure the FID while pulsing at ^{1}H frequency. Continuous high-power decoupling not only averages the heteronuclear direct dipolar coupling to zero, but also the heteronuclear indirect coupling (J-coupling, $J << D$).

Multipulse decoupling

In the presence of strong (> 25 kHz) homonuclear dipolar interactions, MAS spinning rates ν_R and decoupler amplitudes $\nu_1 = - \gamma B_1 / 2\pi$ are too weak for efficient decoupling. In such cases multipulse techniques can be used, which consist of a cycle of rf pulses repetitively applied to the spin system. Depending on the pulse sequence, these selectively average different interactions. For example, special pulse sequences may be constructed in such a way that at certain points the effect of the dipolar interaction on the nuclear magnetization is zero. If the magnetization is detected only at these points, the effects of dipolar coupling are removed from the spectrum.

Cross polarization

When observing rare nuclei *S* (e.g., ^{13}C, ^{15}N or ^{29}Si), a significant gain in sensitivity can be achieved if magnetization is transferred to the rare spins *S* from abundant spins *I* (usually ^{1}H).

Advantages:

(i) a higher polarization of the *S* spins is achieved

(ii) the experiment can be repeated on a timescale related to *I* spin (proton) relaxation times.

If the magnitudes of both rf fields are matched by the Hartmann-Hahn condition,

$$\gamma_S B_{1S} = \gamma_I B_{1I}$$

each spin species precesses with the same frequency $\nu_1 = - \gamma B_1 / 2\pi$ around the axis of its rf field in its own rotating frame. However, because both rotating frames share the same *z* axis, there will be an oscillation of local *I* and *S* magnetization components along the *z* axis with the same frequency ν_1. By this frequency match, magnetization can be exchanged between both spin species. However, because only the *I* spins were polarized, magnetization is transferred from the *I* spins to the *S* spins.