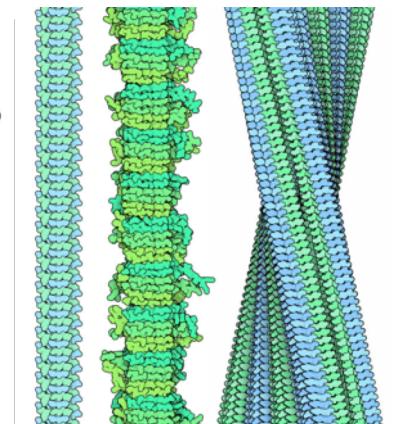
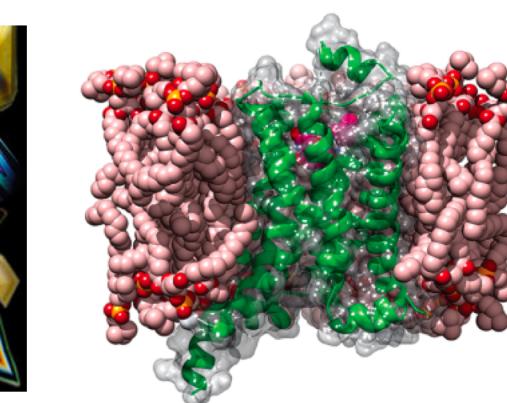
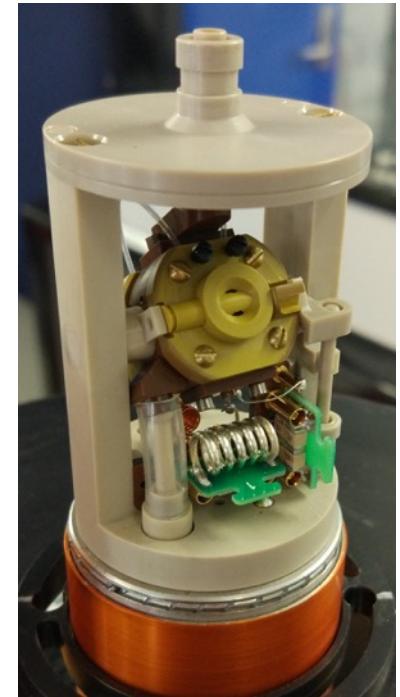
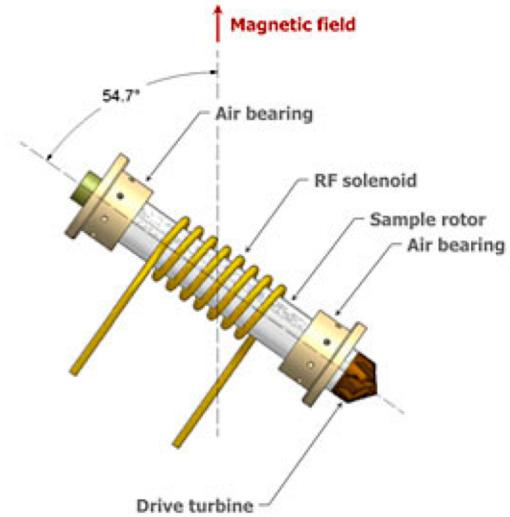


Solid state NMR

CHEM 3013 HPO

An exciting time to study NMR

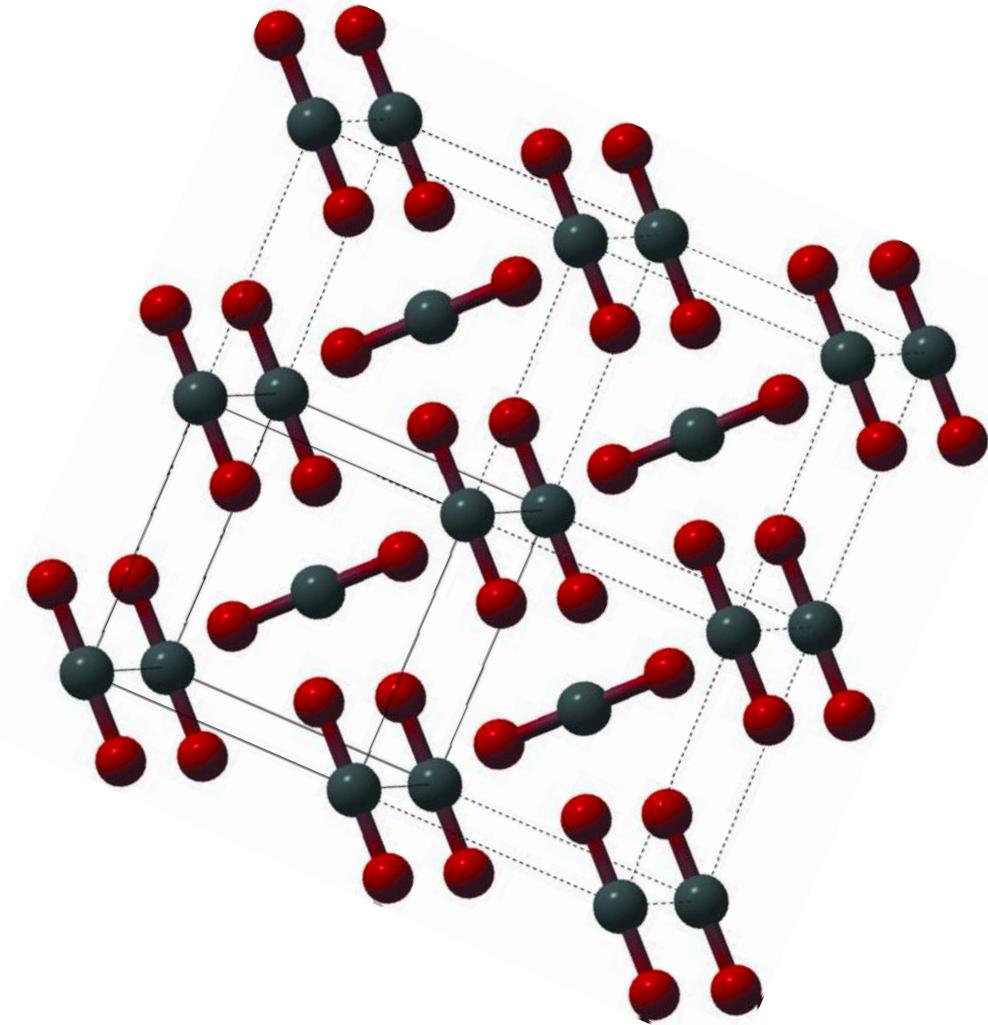
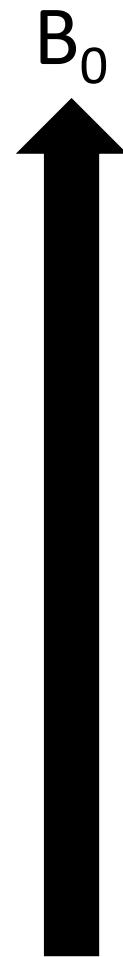
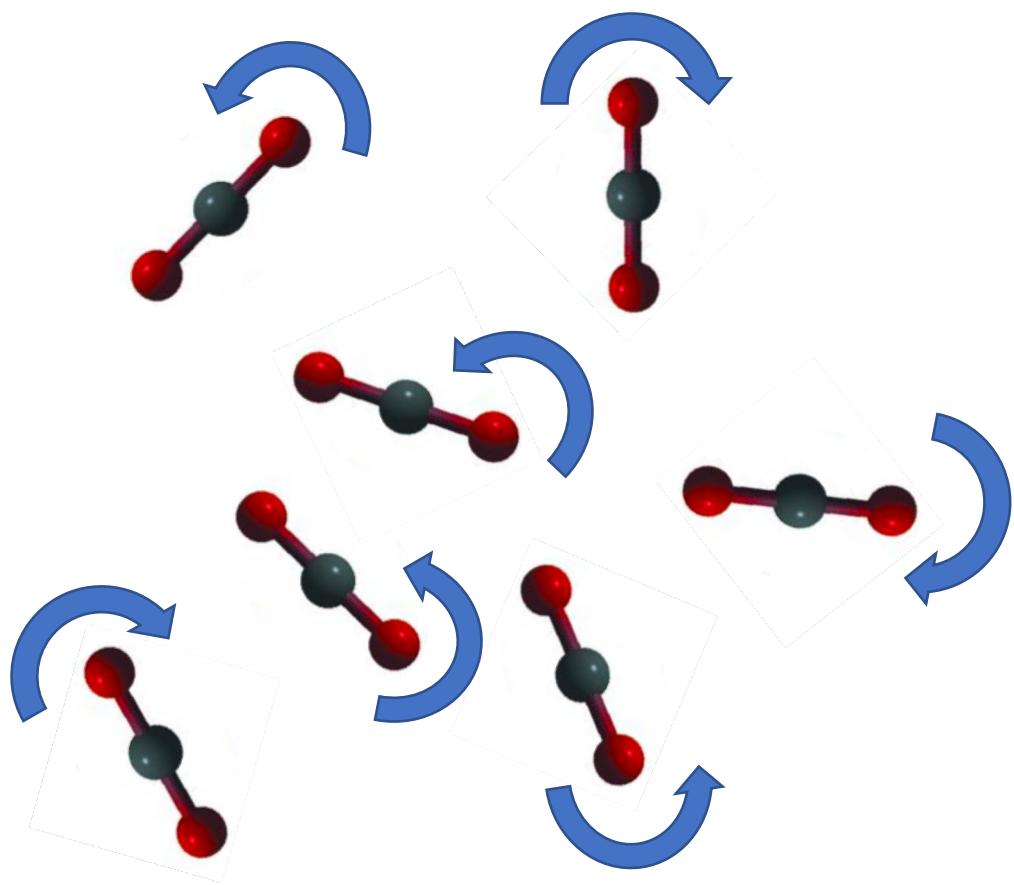
- Solid state NMR is complicated.
- That complexity give spectra rich in structural information (not available in solution NMR)
- Very recent advances solid state technology allow study of macromolecular solids.



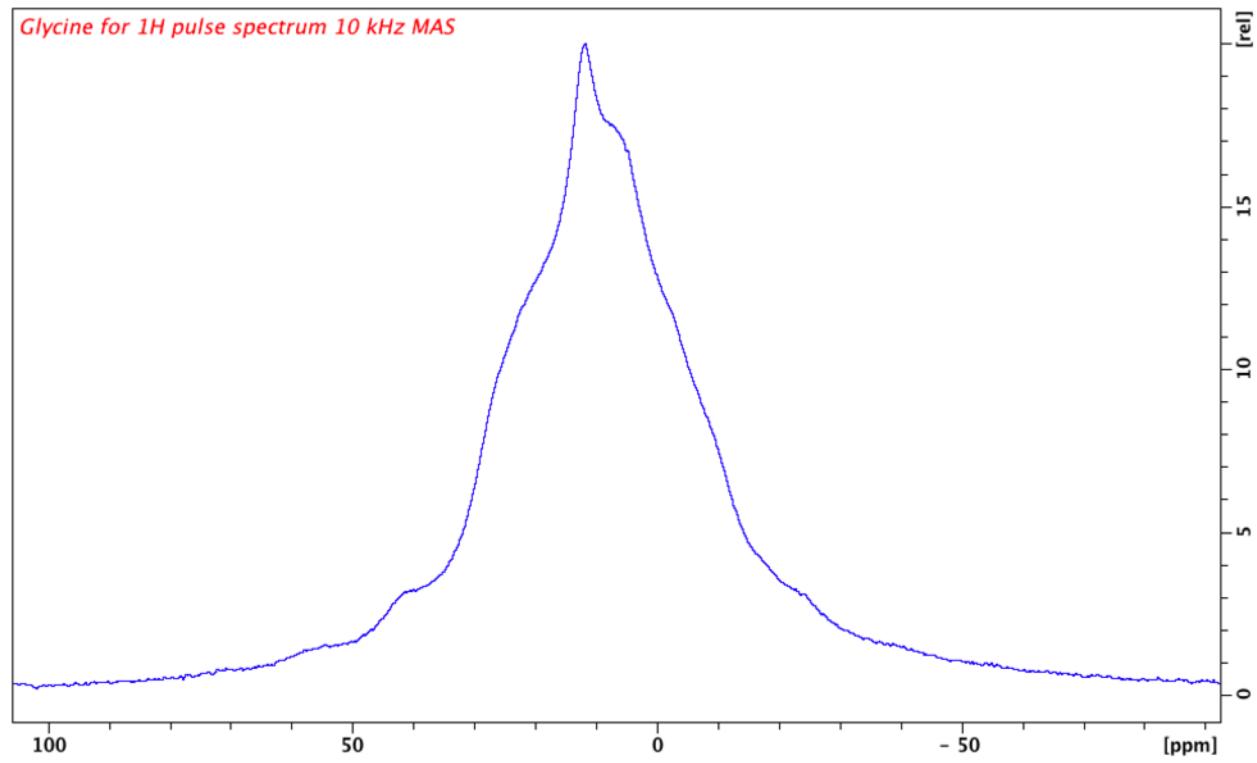
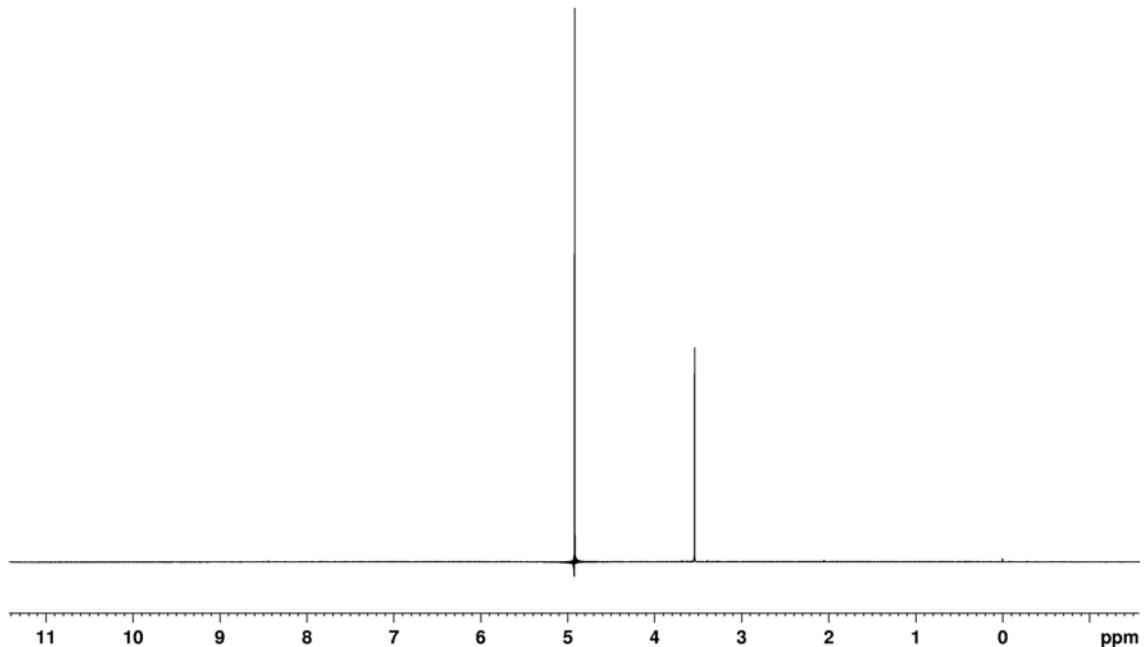
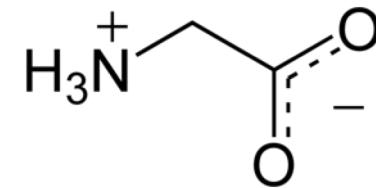
Overview

- Lecture 1: Anisotropic spin interactions
- Lecture 2: Solids spectra and magic angle spinning
- Lecture 3: NMR experiments for biosolids
- Practical:
 - Tuning the magic angle with quadrupolar ^{79}Br
 - Shimming with silicone rubber
 - Compensating frictional heating
 - Cross-polarisation with a microcrystalline protein sample

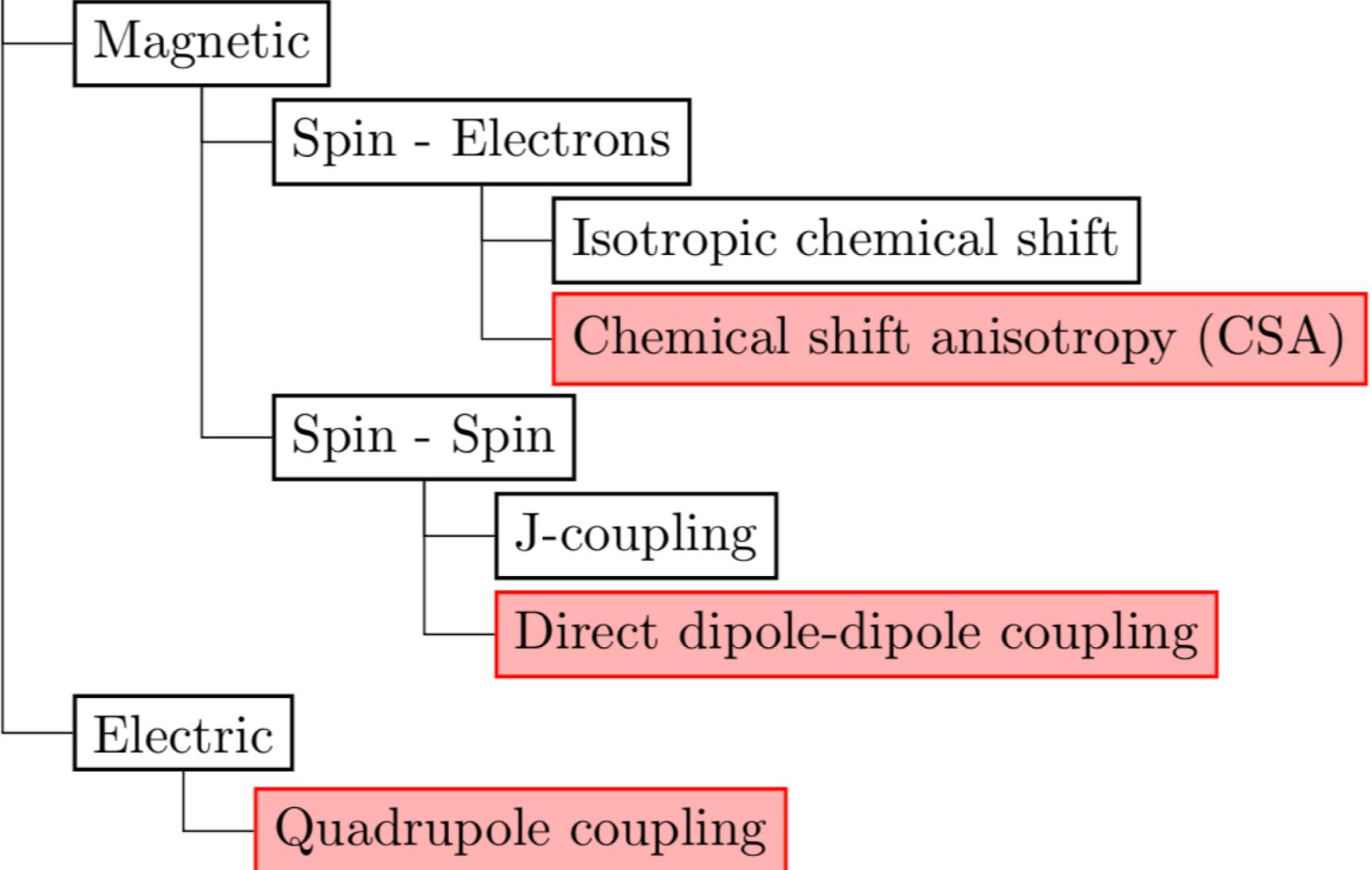
Liquid vs. Solid state NMR



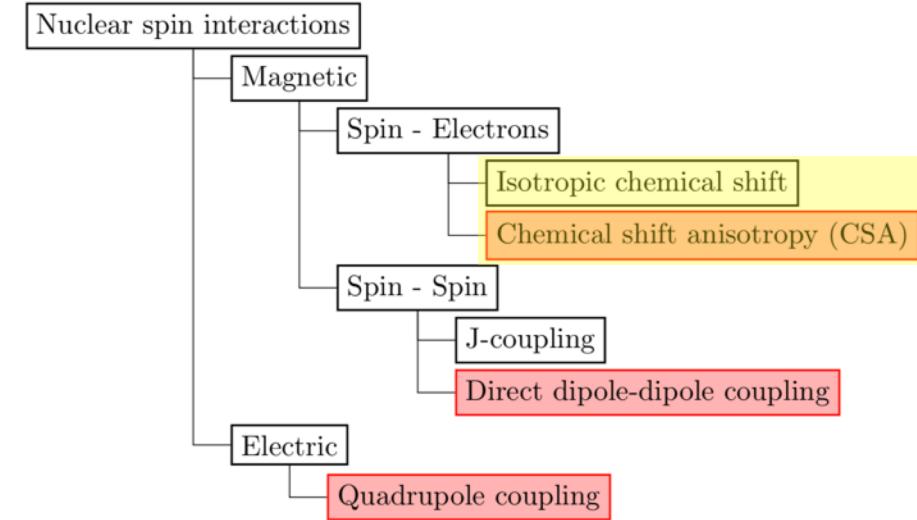
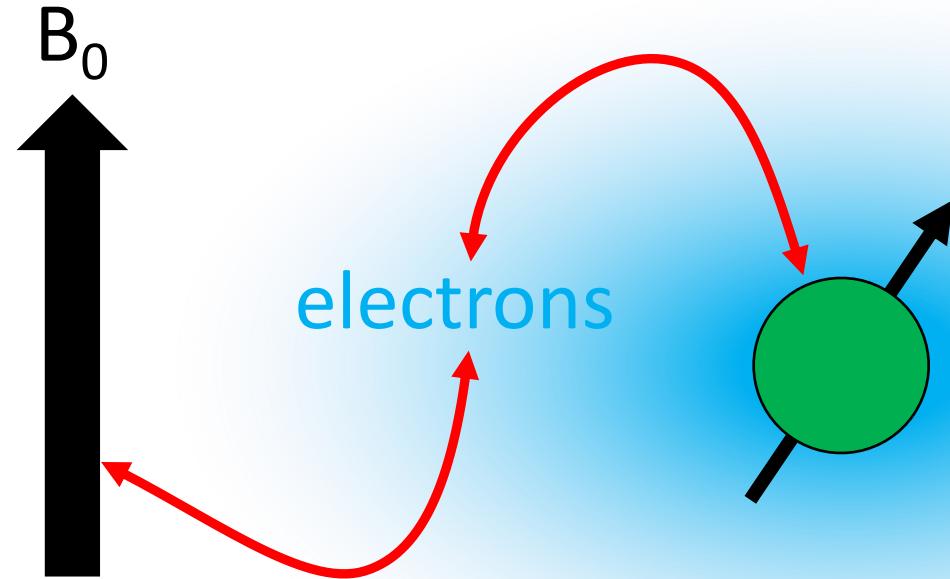
Liquid vs. Solid state NMR



Nuclear spin interactions

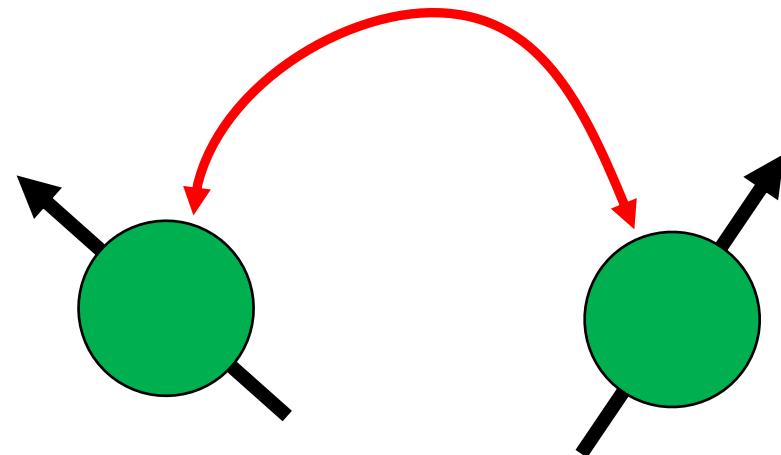
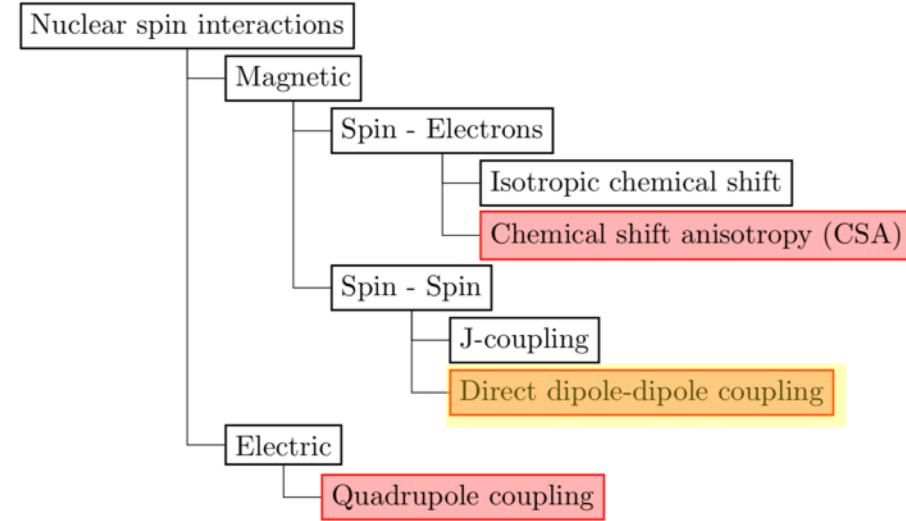


Chemical shift



Chemical shift is an indirect magnetic interaction between **nuclear spin** and the **external magnetic field** via the **electrons**

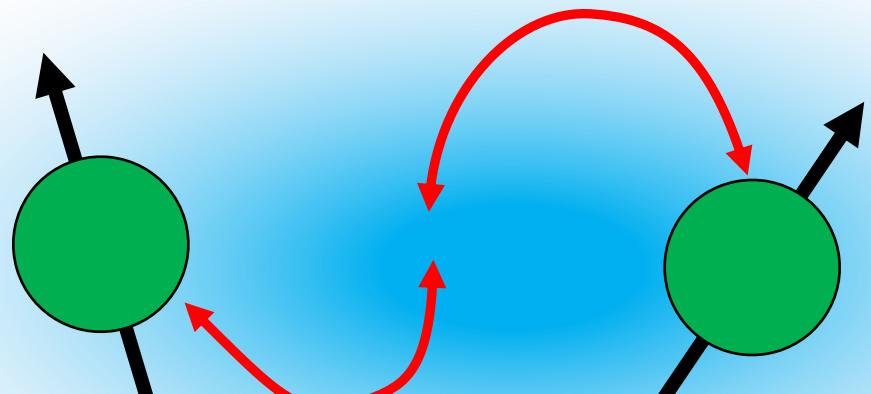
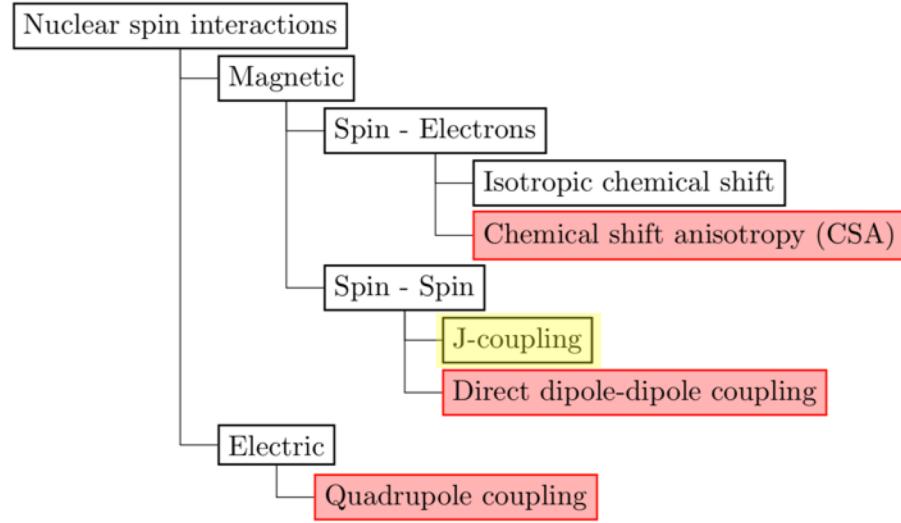
Direct dipole-dipole coupling



Two **nuclear spins** interact directly by their magnetic dipolar fields

Up to 20 kHz!

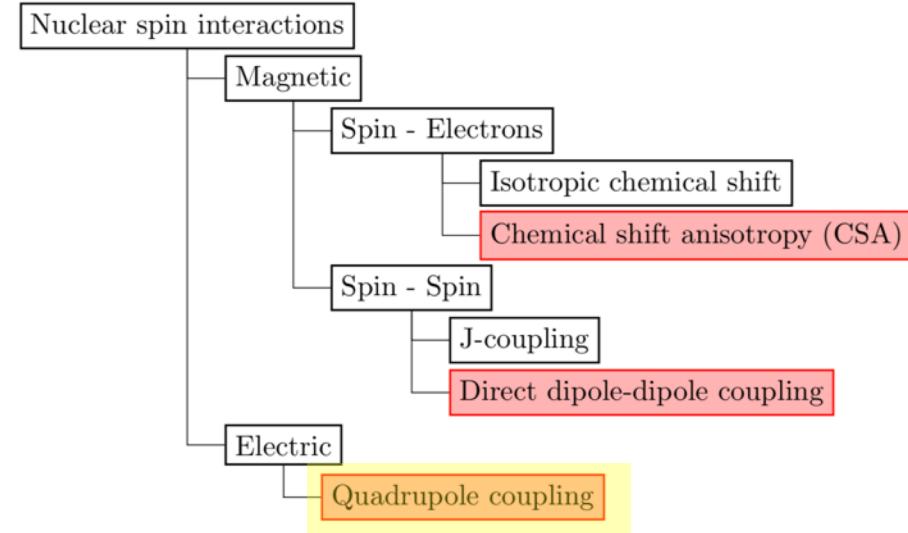
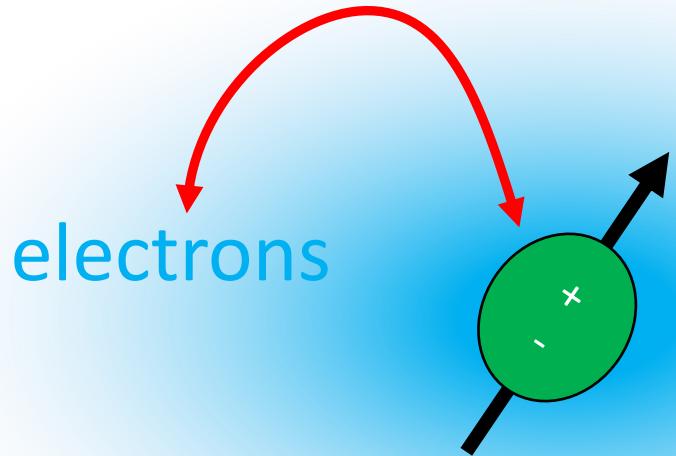
J-coupling



~ 50 Hz

Also called indirect dipole-dipole coupling, J-coupling is an indirect magnetic interaction between **nuclear spins** via the **electrons**

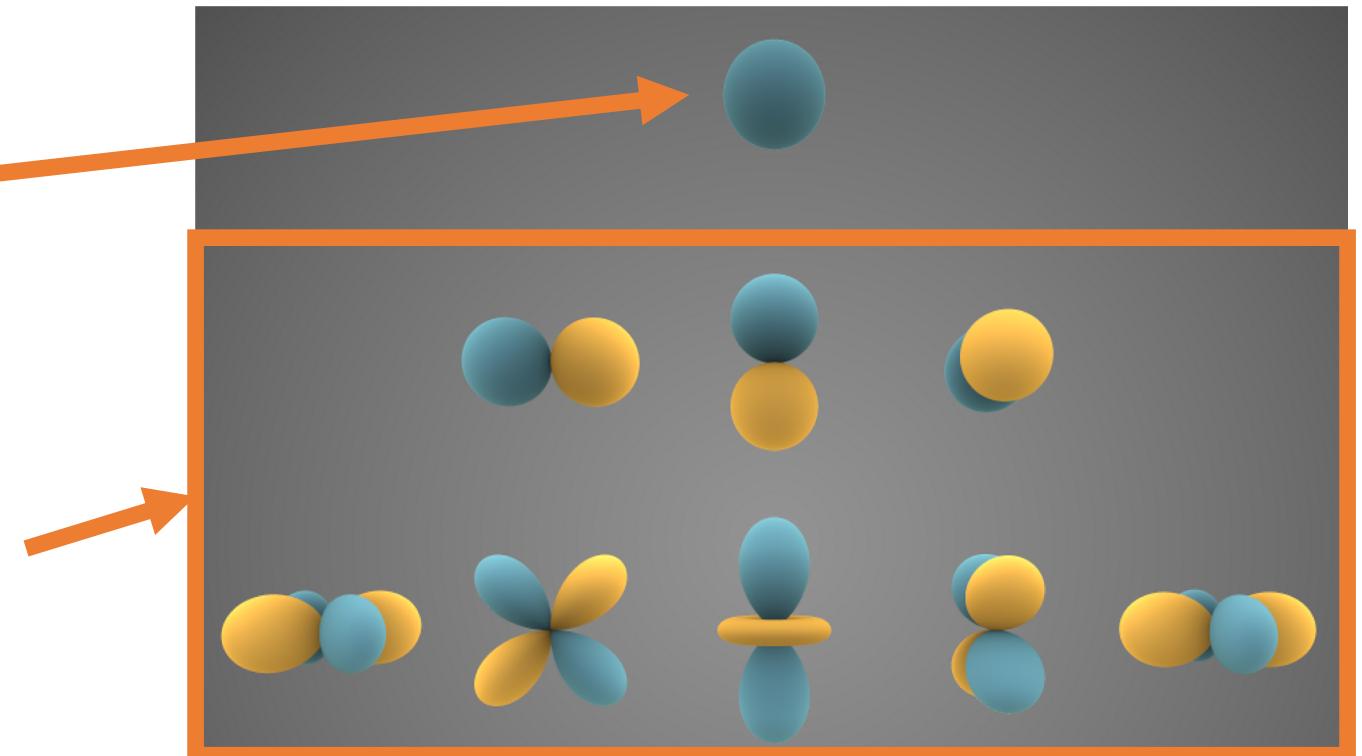
Quadrupole coupling



Quadrupole coupling is an electric interaction of the non-spherical charge density of a **nucleus** with the **electrons**. This only applies for $\text{spin} > 1/2$

Anisotropic interactions

- Isotropic: The magnitude is constant over all orientations
- Anisotropic: The magnitude varies with orientation of the molecule with respect to the external magnetic field.

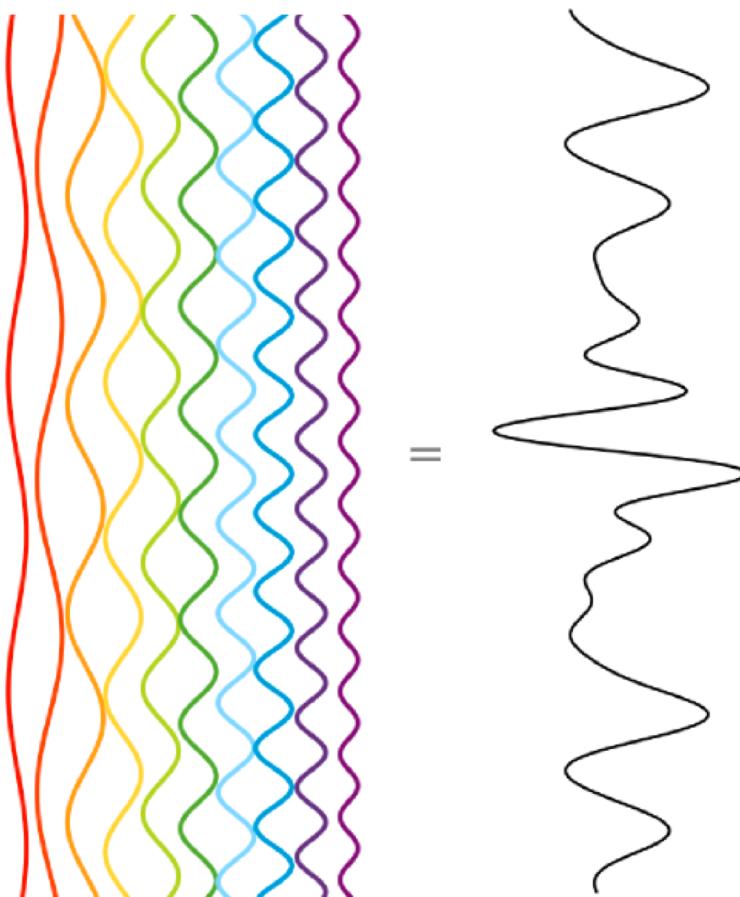


Spherical harmonics (same as molecular orbital theory)

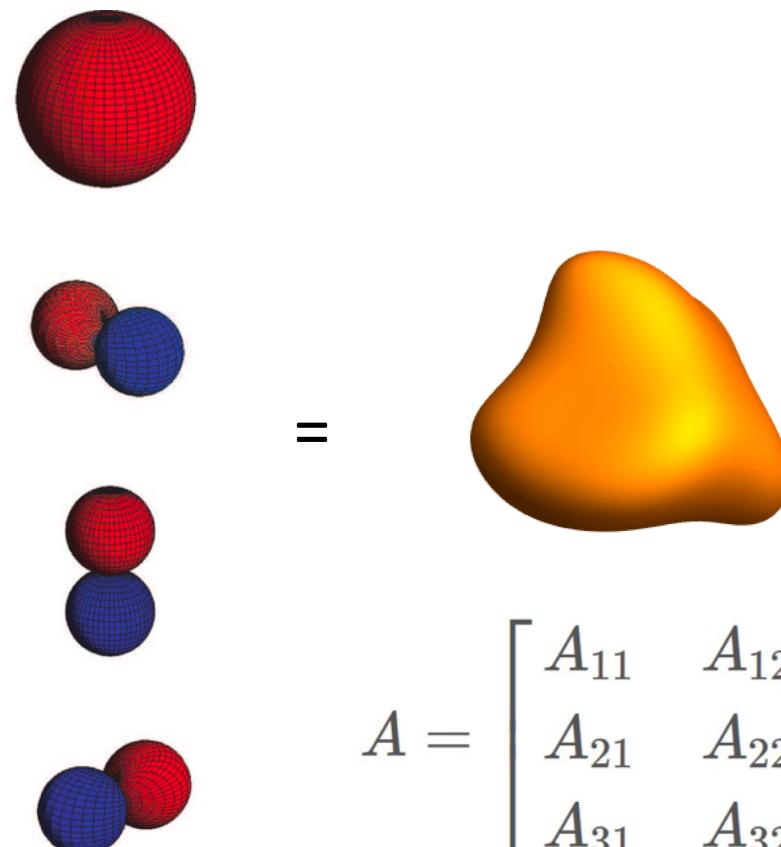
A tensor basis for spatial functions

Fourier decomposition

this sums to...



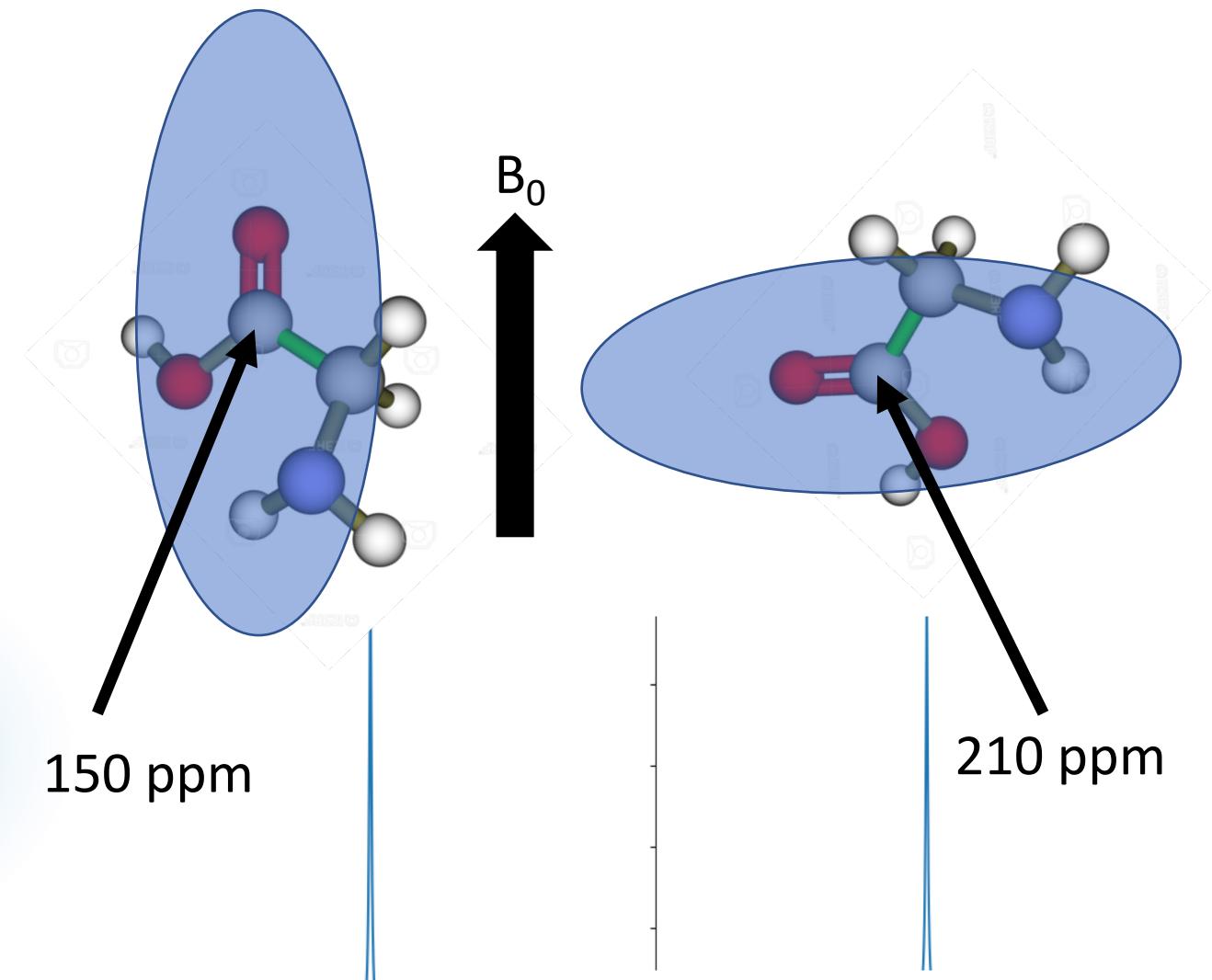
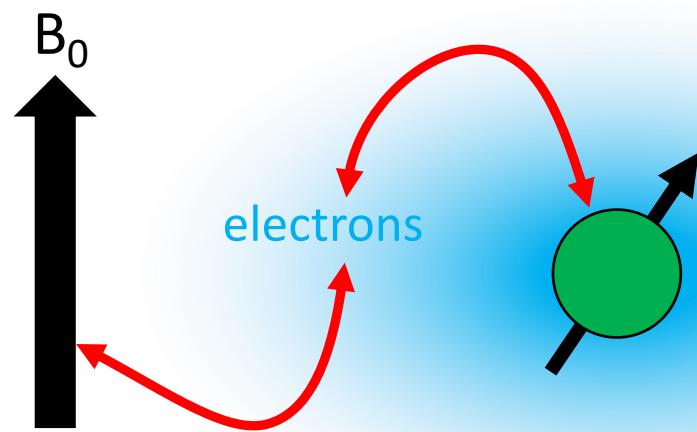
Spherical harmonic
decomposition



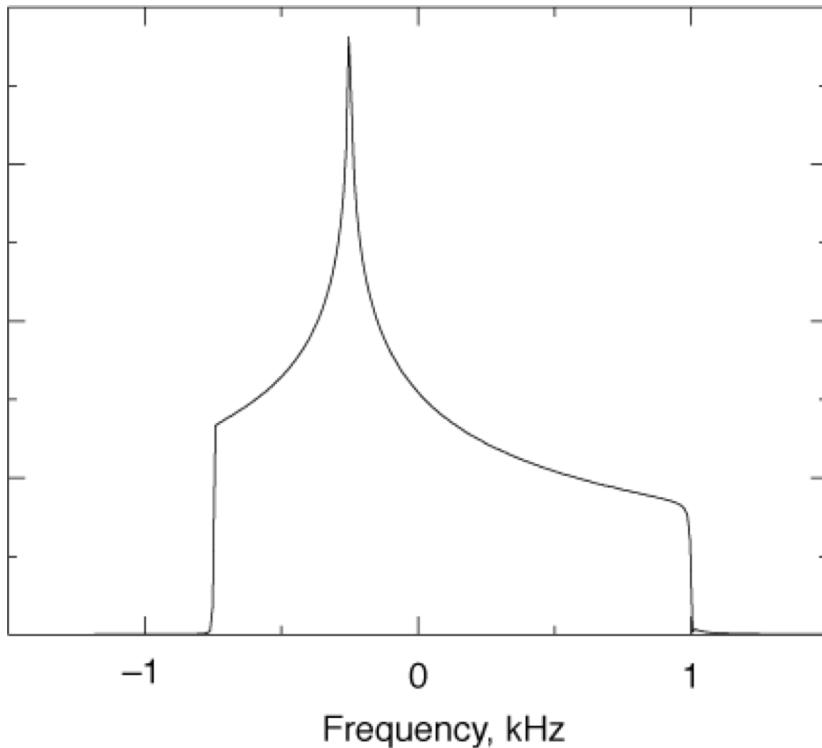
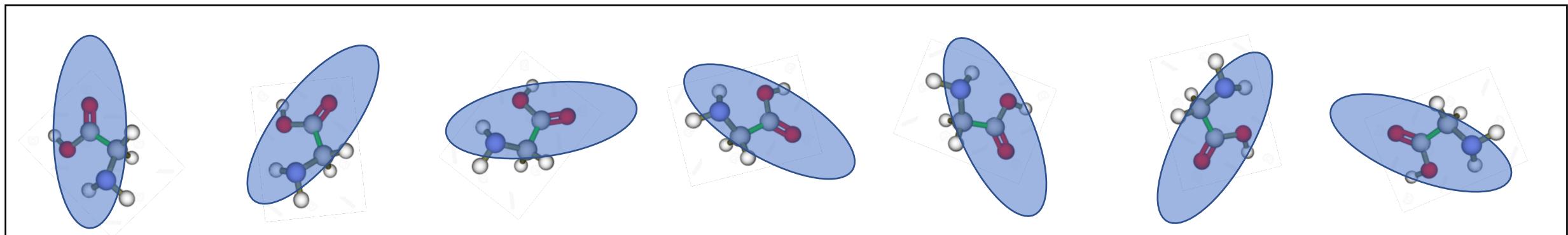
$$A = \begin{bmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{bmatrix}$$

Chemical shift anisotropy (CSA)

- Chemical shift depends on the orientation of the molecular orbitals with respect to the external magnetic field B_0

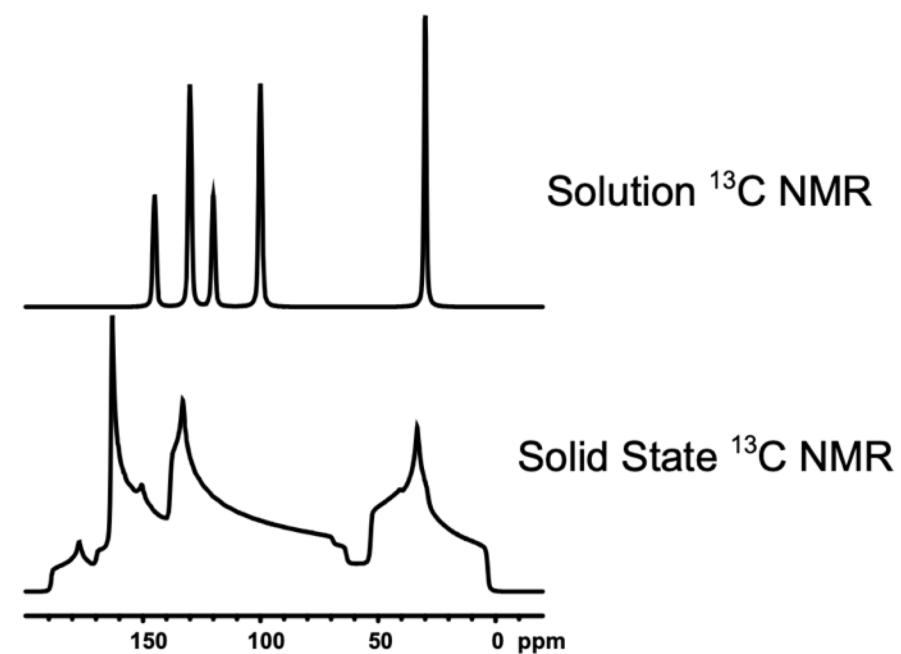


Chemical shift in an unordered ensemble

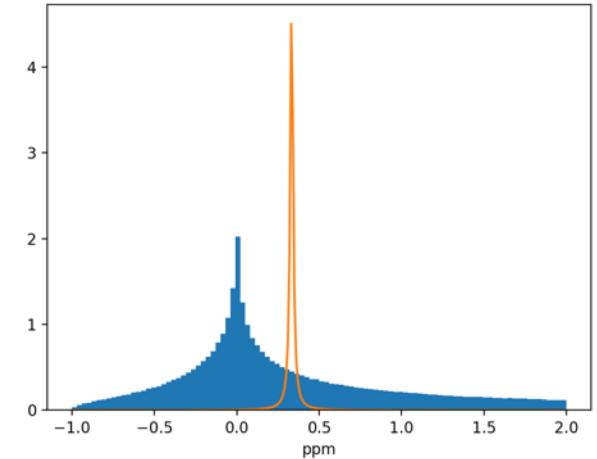
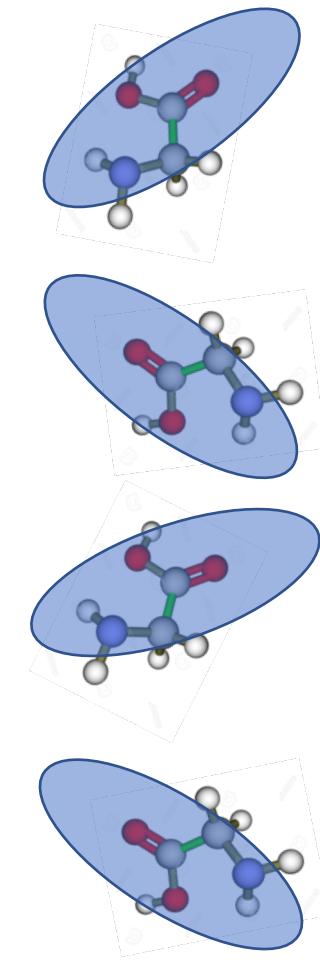
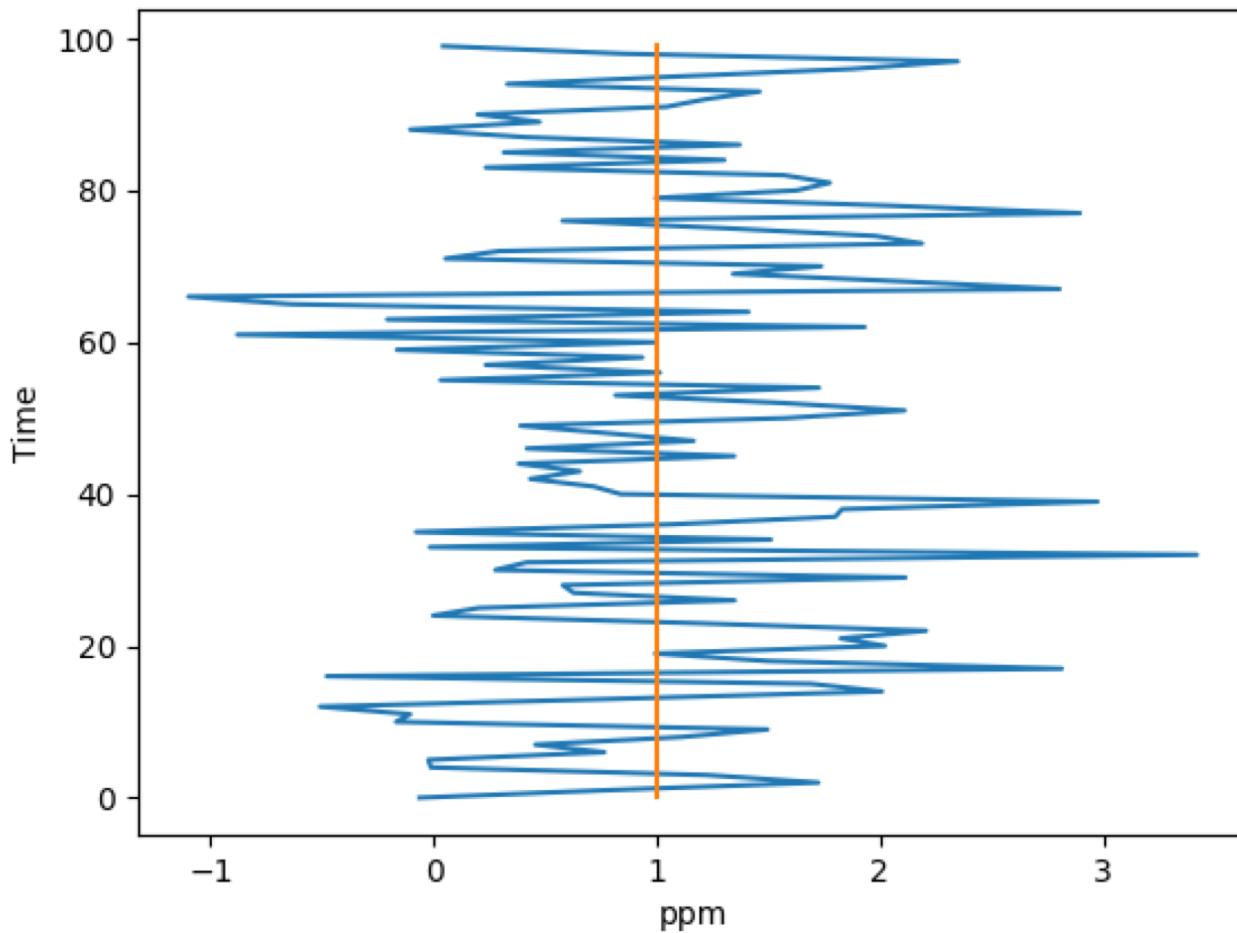


“Powder pattern”

This is like a histogram for the chemical shift of uniformly distributed molecular orientations over a sample.



CSA not visible in solution NMR



Like fast-exchange, all chemical shifts are averaged on the time-scale of rotational tumbling.

A tensor description of CSA

$$i\hbar \frac{\partial |\psi\rangle}{\partial t} = \hat{H} |\psi\rangle$$



$$\hat{H}_{\text{CS}} = \hat{\vec{L}} \cdot \vec{\sigma} \cdot \vec{B}_0$$



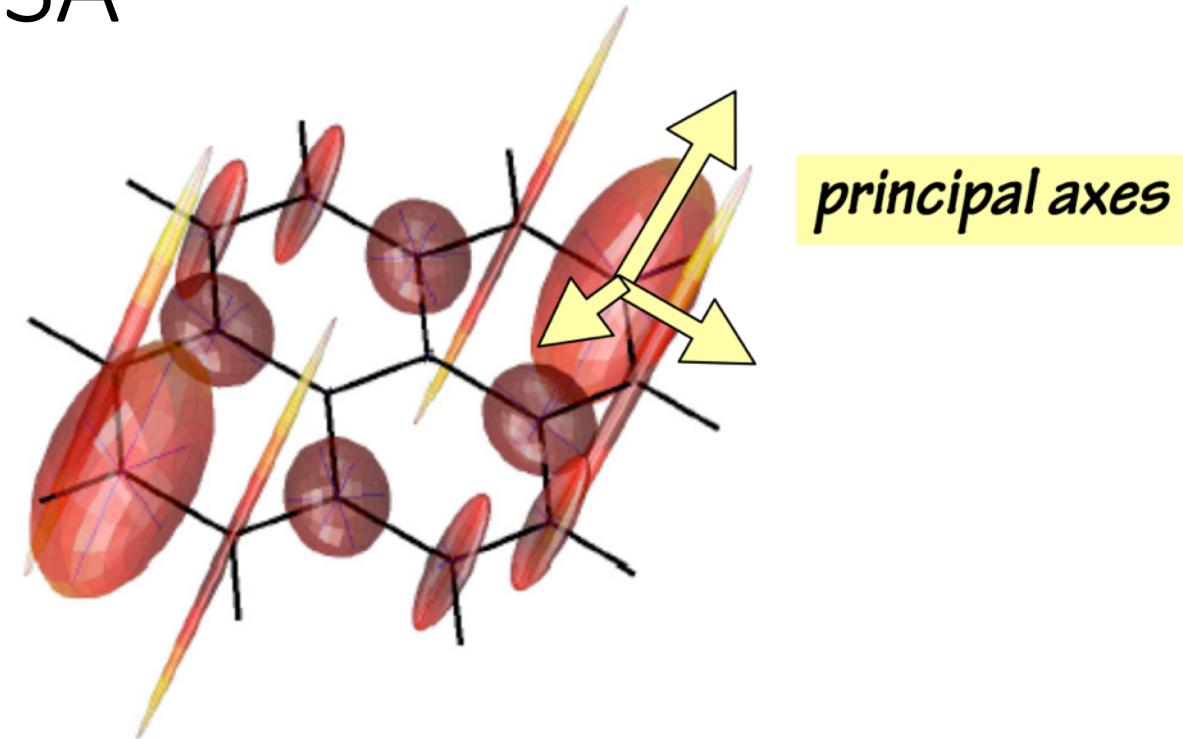
?

A tensor description of CSA

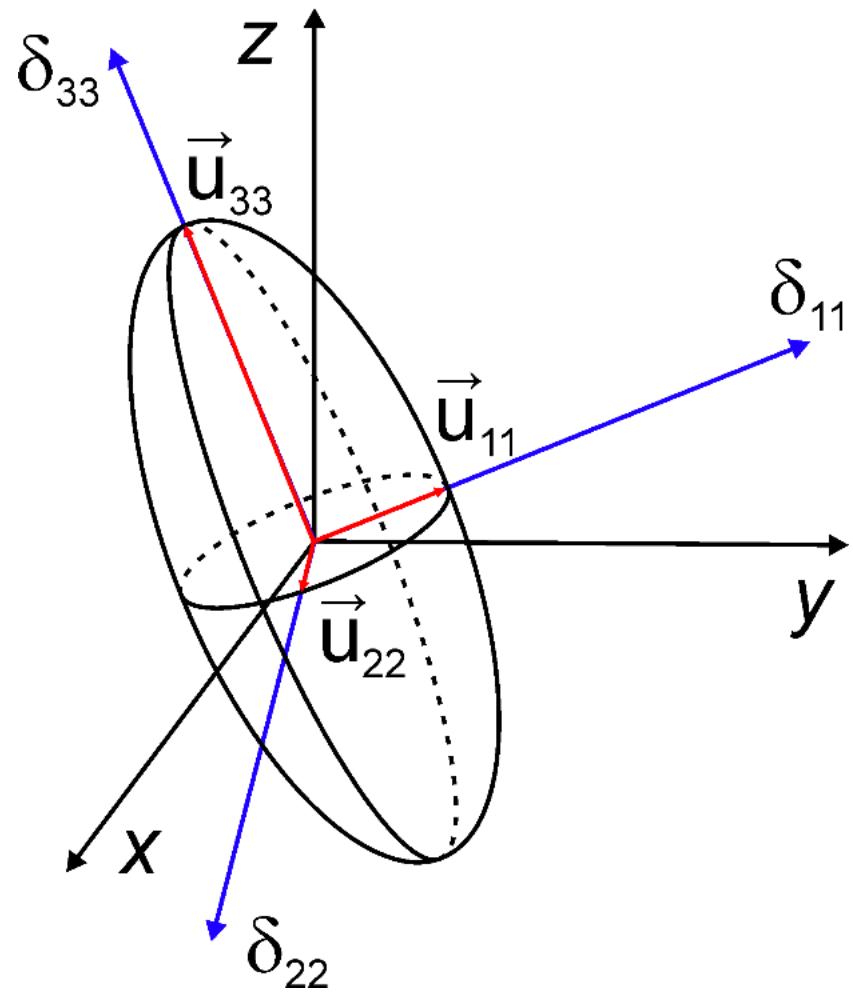
$$\hat{H}_{\text{CS}} = \hat{\vec{L}} \cdot \vec{\sigma} \cdot \vec{B}_0$$

$$\vec{\sigma} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{xy} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{xz} & \sigma_{yz} & \sigma_{zz} \end{bmatrix}$$

$$= R \begin{bmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{bmatrix} \cdot R^{-1}$$

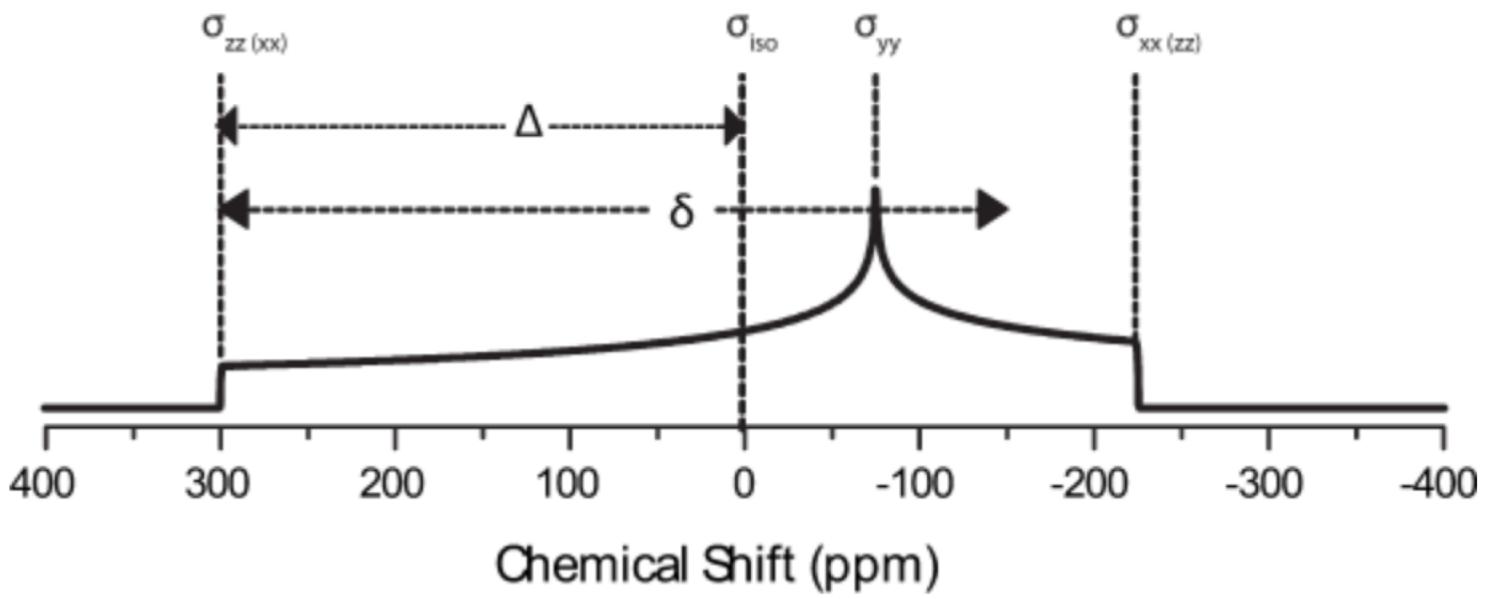


A tensor description of CSA

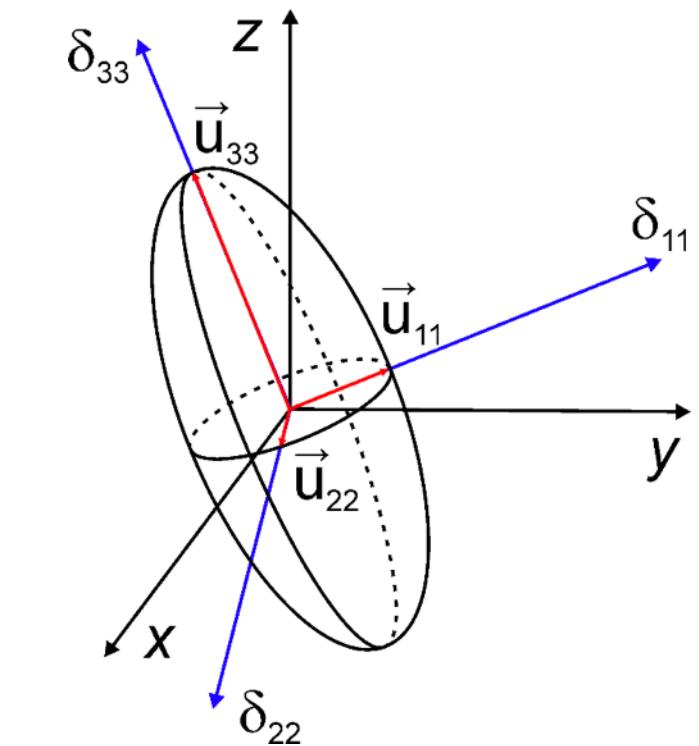


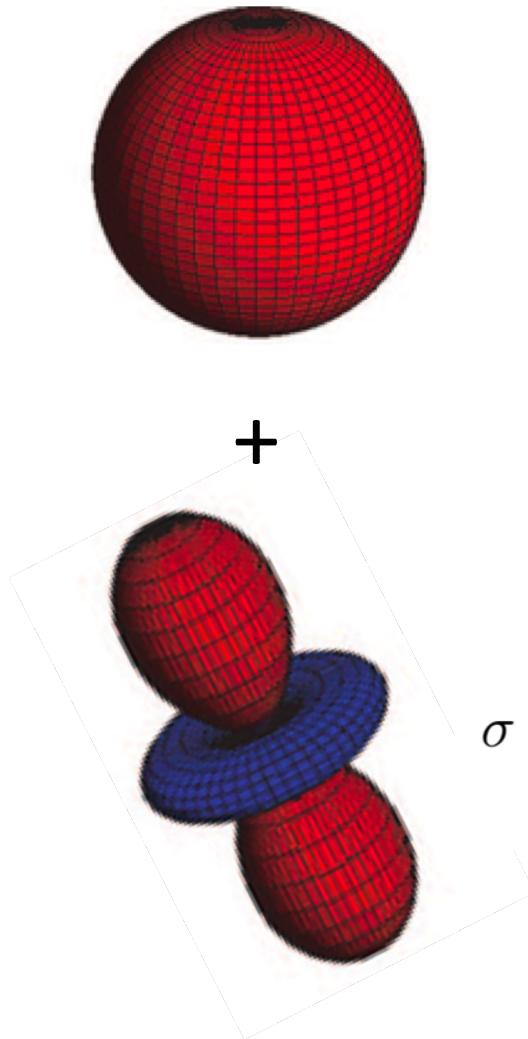
$$\sigma = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{xy} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{xz} & \sigma_{yz} & \sigma_{zz} \end{bmatrix}$$

$$= R \begin{bmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{bmatrix} . R^{-1}$$



Isotropy and anisotropy

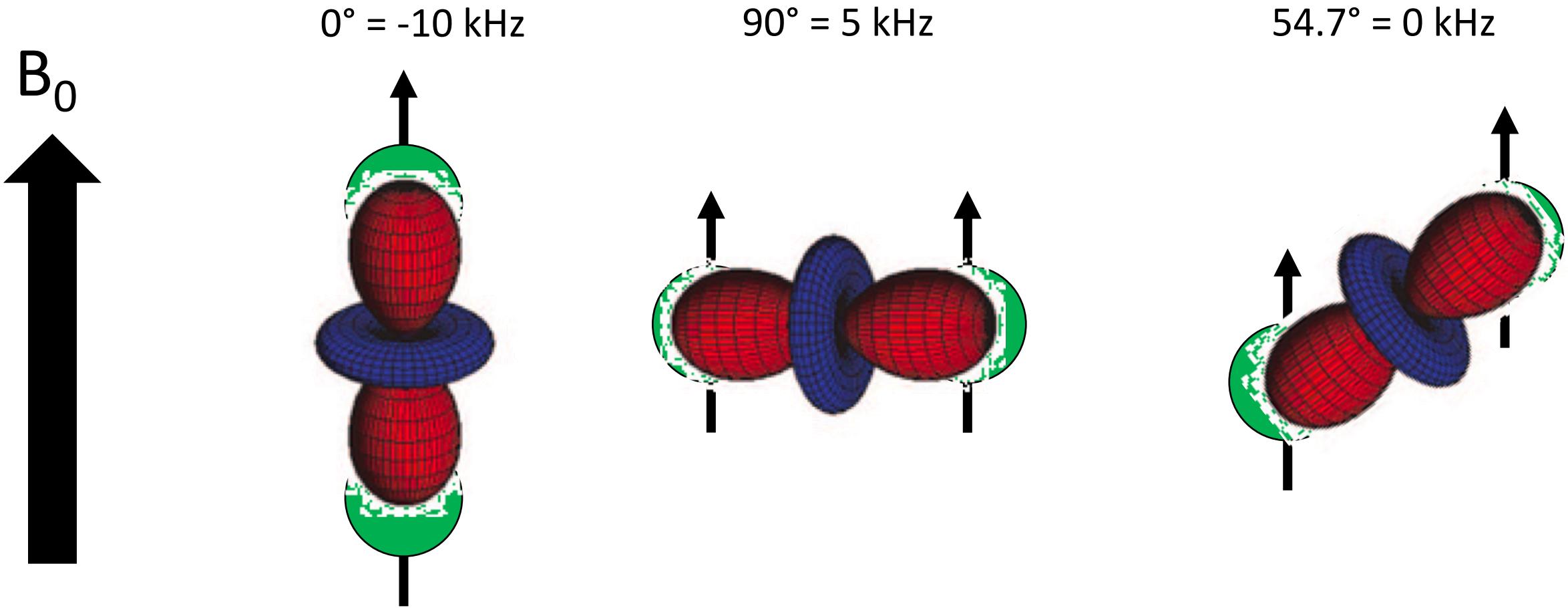

$$= \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{xy} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{xz} & \sigma_{yz} & \sigma_{zz} \end{bmatrix}$$



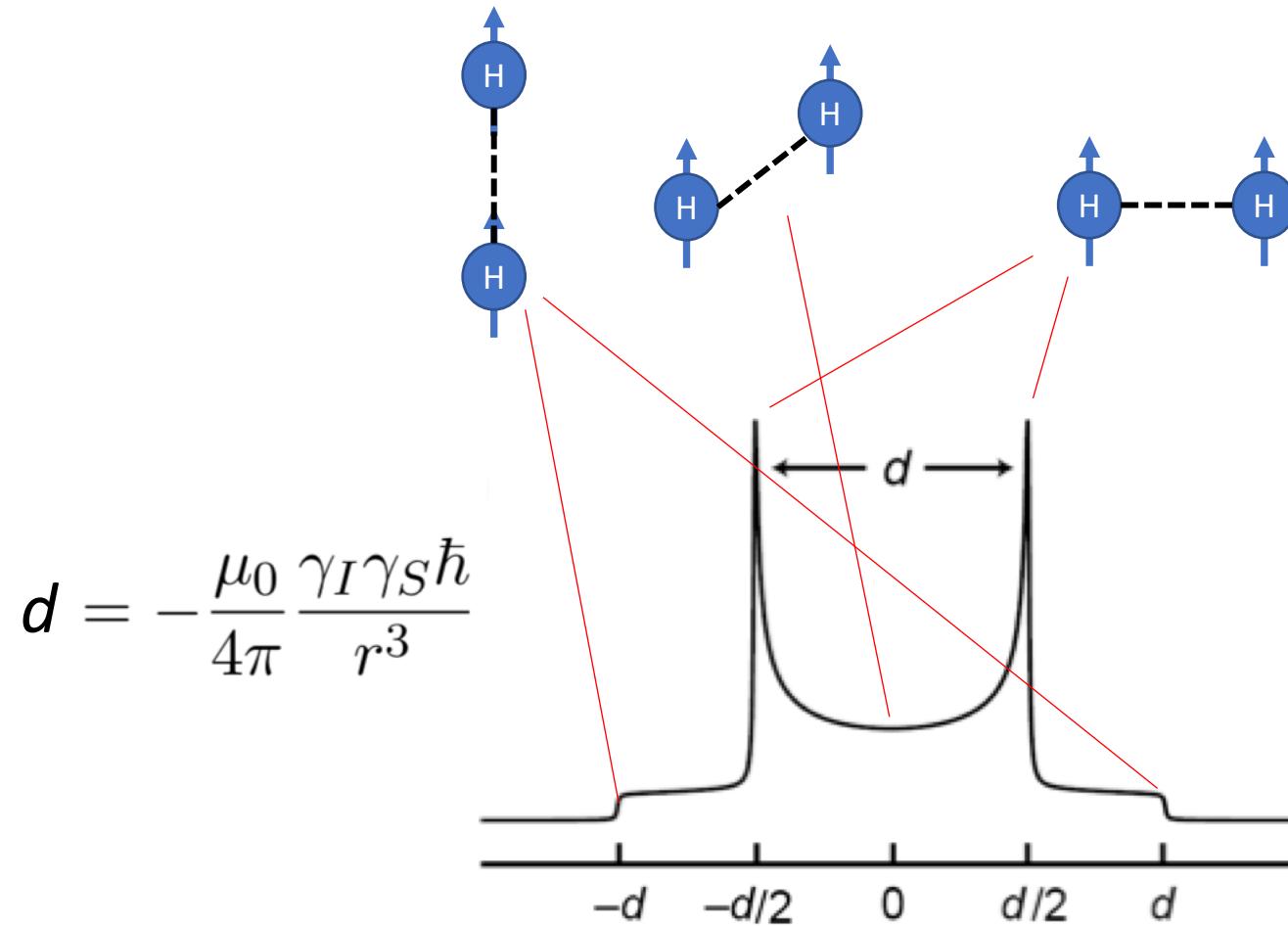
$$\sigma_{\text{iso}} = \frac{1}{3} \text{Tr}[\sigma] = \frac{1}{3} (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$$

$$\sigma = \begin{bmatrix} \sigma_{xx} - \sigma_{\text{iso}} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{xy} & \sigma_{yy} - \sigma_{\text{iso}} & \sigma_{yz} \\ \sigma_{xz} & \sigma_{yz} & \sigma_{zz} - \sigma_{\text{iso}} \end{bmatrix}$$

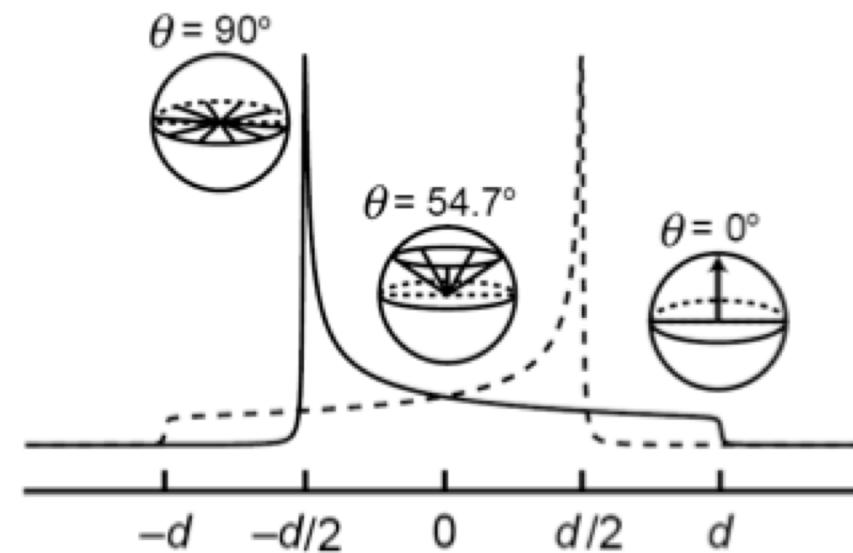
Direct dipole-dipole coupling



Direct dipole-dipole coupling anisotropy



“Pake pattern”
This is like a histogram for the coupling of uniformly distributed bond vector orientations over a sample.



A tensor description of direct dipole-dipole coupling

$$b_{IS} = -\frac{\mu_0}{4\pi} \frac{\gamma_I \gamma_S \hbar}{r^3}$$

$$\begin{aligned}\hat{H}_{DD} &= b_{IS} \left(\frac{3}{r^2} (\hat{\vec{I}} \cdot \hat{\vec{r}}) (\hat{\vec{r}} \cdot \hat{\vec{S}}) - \hat{\vec{I}} \cdot \hat{\vec{S}} \right) \\ &= b_{IS} \hat{\vec{I}} \cdot \mathbf{A} \cdot \hat{\vec{S}}\end{aligned}$$

$$\mathbf{A} = \begin{bmatrix} 3x^2 - r^2 & 3xy & 3xz \\ 3xy & 3y^2 - r^2 & 3yz \\ 3xz & 3xy & 3z^2 - r^2 \end{bmatrix}$$

$$\hat{H}_{DD} = \frac{b_{IS}}{2} (3 \cos^2 \theta_{IS} - 1) \hat{\vec{I}} \cdot \hat{\vec{S}}$$

$$\boxed{\begin{array}{l} Tr[\mathbf{A}] = 0 \\ \int_0^{2\pi} (3 \cos^2 \theta - 1) (\cos \theta) d\theta = 0 \end{array}}$$

Not observed in solution NMR!

Summary

- In solution NMR we see isotropic interactions: chemical shift and j -coupling.
- Anisotropic interactions are observable in solid state NMR: Chemical shift anisotropy, direct DD coupling, quadrupole coupling.
- Anisotropic spin interactions can be described by spherical tensors.
- A tensor has a matrix representation with principle axes.