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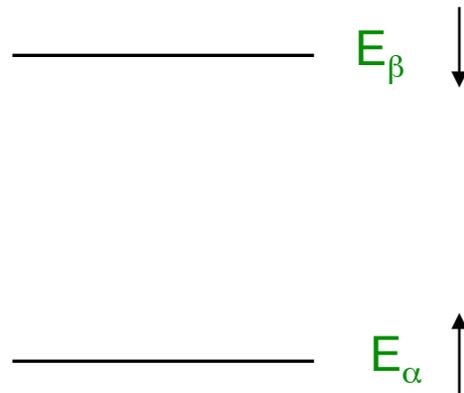
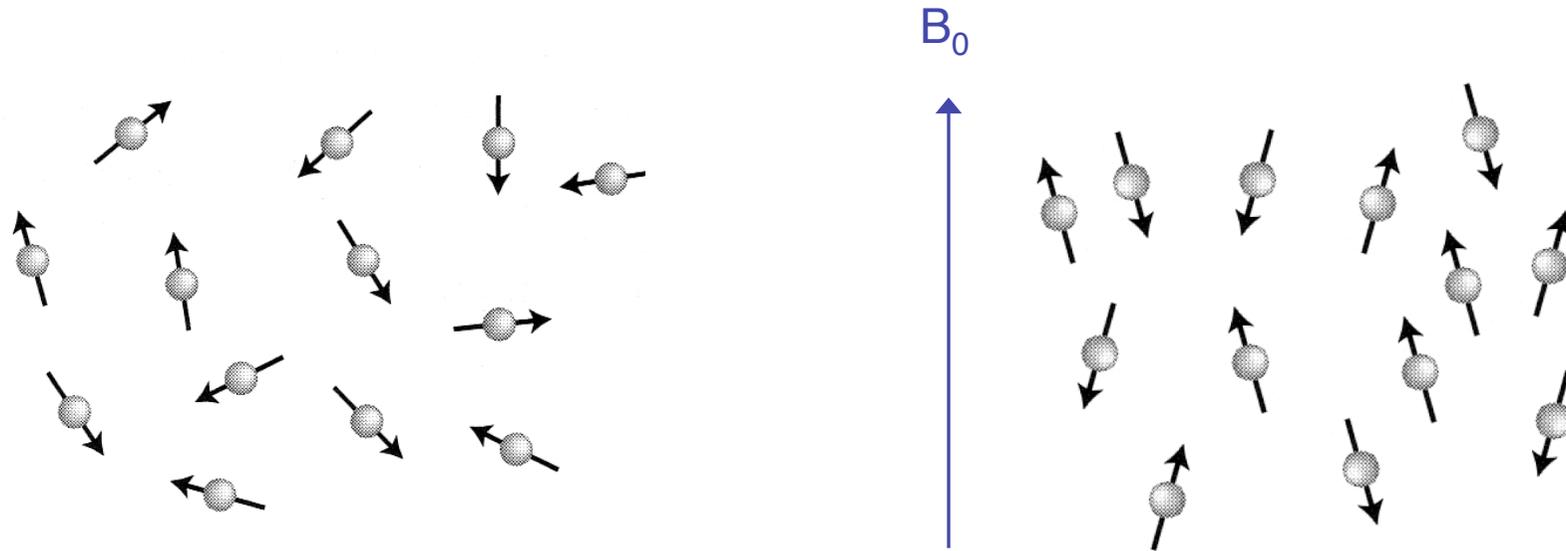
# The Power of Solid-State NMR

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# Origin of NMR



$$\begin{aligned}\Delta E &= E_\beta - E_\alpha \\ &= 2 \times 10^{-25} \text{ J}\end{aligned}$$

radiofrequency radiation

# Spin

- Nuclei possess an intrinsic angular momentum known as spin
- Quantized in units of  $\hbar$
- $I$  is the spin quantum number
- $I$  has  $2I + 1$  projections onto an arbitrary axis
- $m_I$  is the magnetic spin quantum number

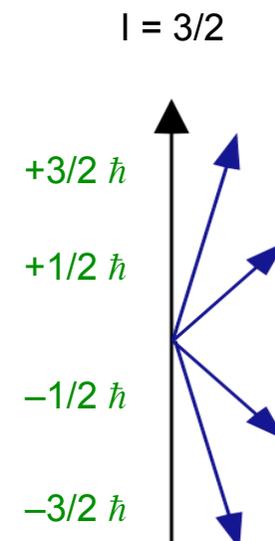
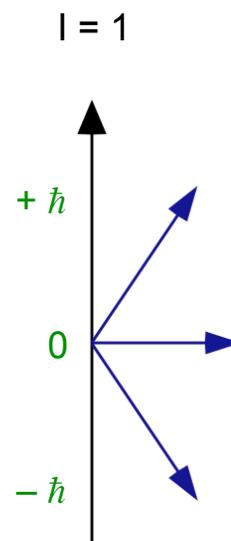
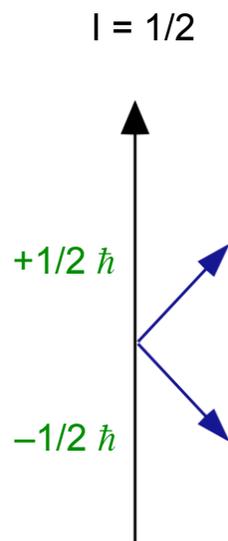
$I$

$$|I| = \hbar (I(I + 1))^{1/2}$$

$$0, 1/2, 1, 3/2, 2, \dots$$

$$I_z = m_I \hbar$$

$$-I, (-I + 1), \dots, (I - 1), I$$

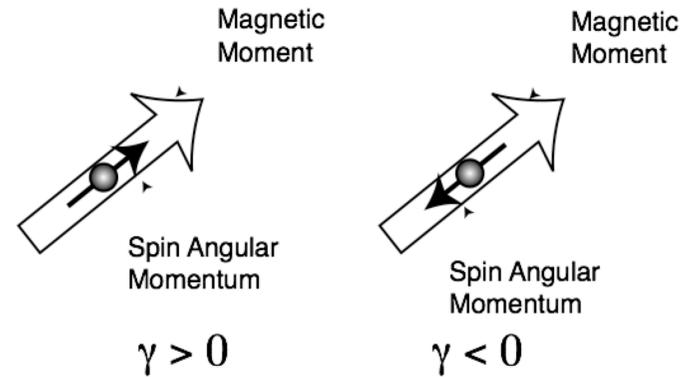


# Zeeman interaction

- The circulating charge creates a magnetic dipole moment

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

- $\gamma$  is the gyromagnetic ratio of the nucleus



- In the absence of a magnetic field all  $2I + 1$  orientations have the same energy
- The application of a strong magnetic field ( $B_0$ ) defines the axis of quantization (usually assumed to be z)
- This Zeeman interaction lifts the degeneracy

$$\begin{aligned} E &= -\mu_z B_0 \\ &= -\gamma m_l \hbar B_0 \end{aligned}$$

- Selection rule

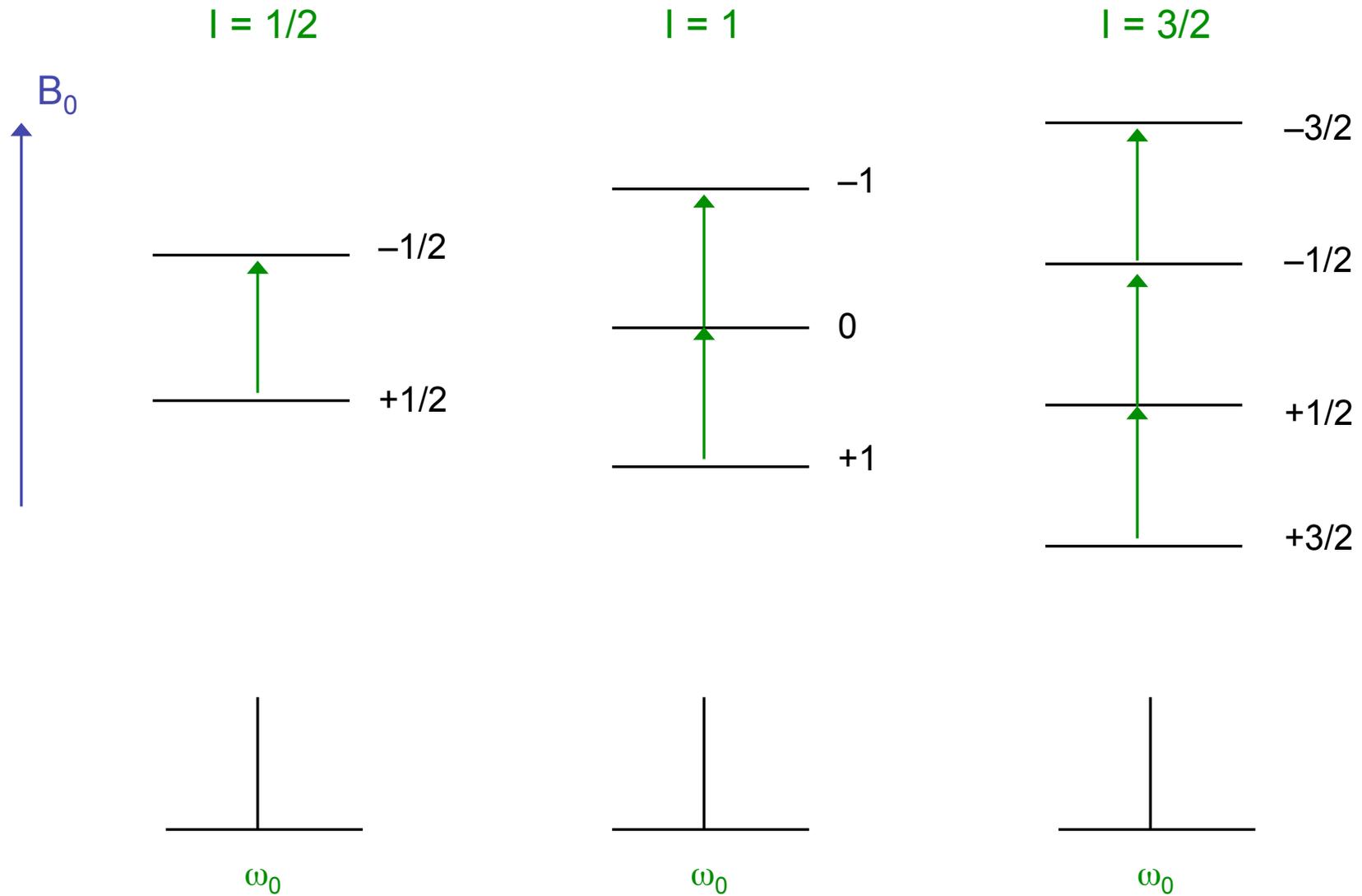
$$\Delta m_l = \pm 1$$

$$\Delta E = -\gamma \hbar B_0$$

- Larmor frequency

$$\omega_0 = \Delta E / \hbar = -\gamma B_0$$

# Zeeman interaction



# Larmor frequencies

Nucleus	I	$\gamma / 10^7 \text{ T}^{-1} \text{ rad s}^{-1}$	$\nu_0 / \text{MHz (9.4 T)}$
<sup>1</sup> H	1/2	26.75	400.0
<sup>2</sup> H	1	4.11	61.4
<sup>7</sup> Li	3/2	10.40	155.5
<sup>11</sup> B	3/2	8.58	128.4
<sup>13</sup> C	1/2	6.73	100.6
<sup>14</sup> N	1	1.93	28.9
<sup>15</sup> N	1/2	-2.71	40.5
<sup>17</sup> O	5/2	-3.63	54.3
<sup>19</sup> F	1/2	25.18	376.5
<sup>23</sup> Na	3/2	7.08	105.8
<sup>25</sup> Mg	5/2	-1.63	24.4
<sup>27</sup> Al	5/2	6.97	104.2
<sup>29</sup> Si	1/2	-5.32	79.6
<sup>31</sup> P	1/2	10.84	162.1
<sup>45</sup> Sc	7/2	6.51	97.2
<sup>59</sup> Co	7/2	6.33	94.9
<sup>87</sup> Rb	3/2	8.79	130.9
<sup>89</sup> Y	1/2	-1.32	19.6
<sup>93</sup> Nb	9/2	6.56	97.9

# Population differences

- For  $^1\text{H}$  in a 9.4 T field at 298 K

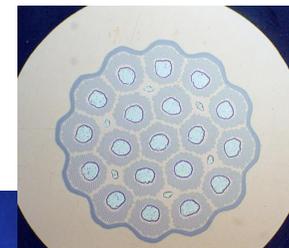
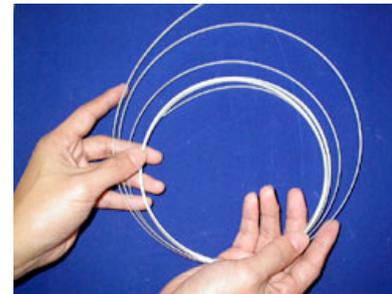
$$\Delta E = 2.65 \times 10^{-25} \text{ J}$$

$$\begin{aligned} n_{\text{upper}}/n_{\text{lower}} &= \exp(-\Delta E / kT) \\ &= 0.999935 \end{aligned}$$

- Populations differences in NMR are very small – sensitivity is always a concern
- Sensitivity is helped by higher magnetic field strengths and higher  $\gamma$  nuclei

- Need to generate a strong magnetic field ( $\sim 2$  to 28 T)
- Use a superconducting wire ( $\sim 100$  km for 850 MHz)

NbTi	10 K	15 T	$\sim \text{£}10 / \text{m}$
Nb <sub>3</sub> Sn	18.3 K	30 T	$\sim \text{£}50 / \text{m}$



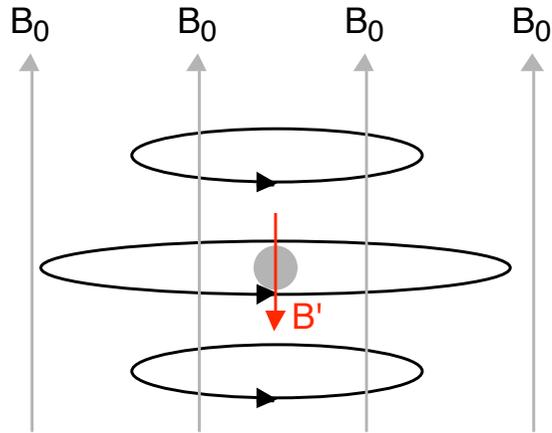
# Superconducting magnets



600 MHz 14.1 T  
~£800,000

400 MHz 9.4 T  
~£300,000

# Chemical shift



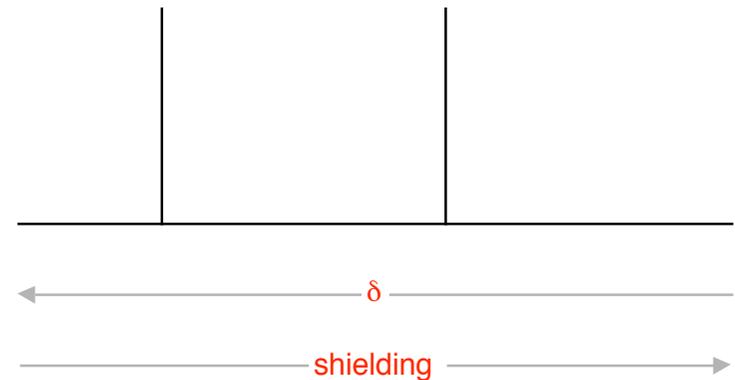
- The magnetic field a nucleus sees,  $B$ , is usually not equal to  $B_0$
- In an atom, the surrounding electrons generate a small magnetic field which opposes  $B_0$
- The nucleus is “shielded” from  $B_0$ , with

$$B = B_0 - B' = B_0 (1 - \sigma)$$

$$|\omega| = \gamma B_0 (1 - \sigma)$$

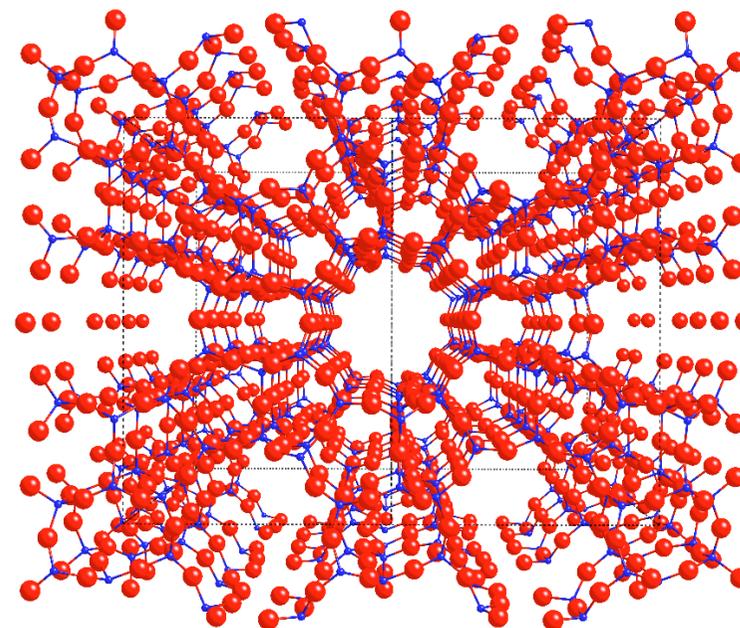
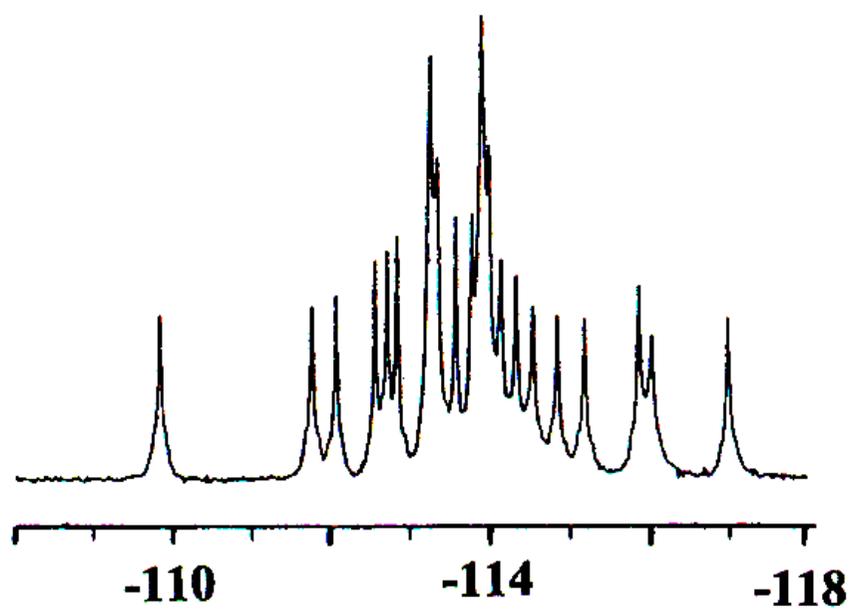
- In molecules the motion of the electrons is more complicated and depends on the bonded atoms and local neighbouring groups of atoms
- Can augment or oppose the field
- This “chemical shift” defines the local environment
- Defined (ppm) relative to a reference

$$\delta = 10^6 (\nu - \nu_{\text{ref}}) / \nu_{\text{ref}}$$



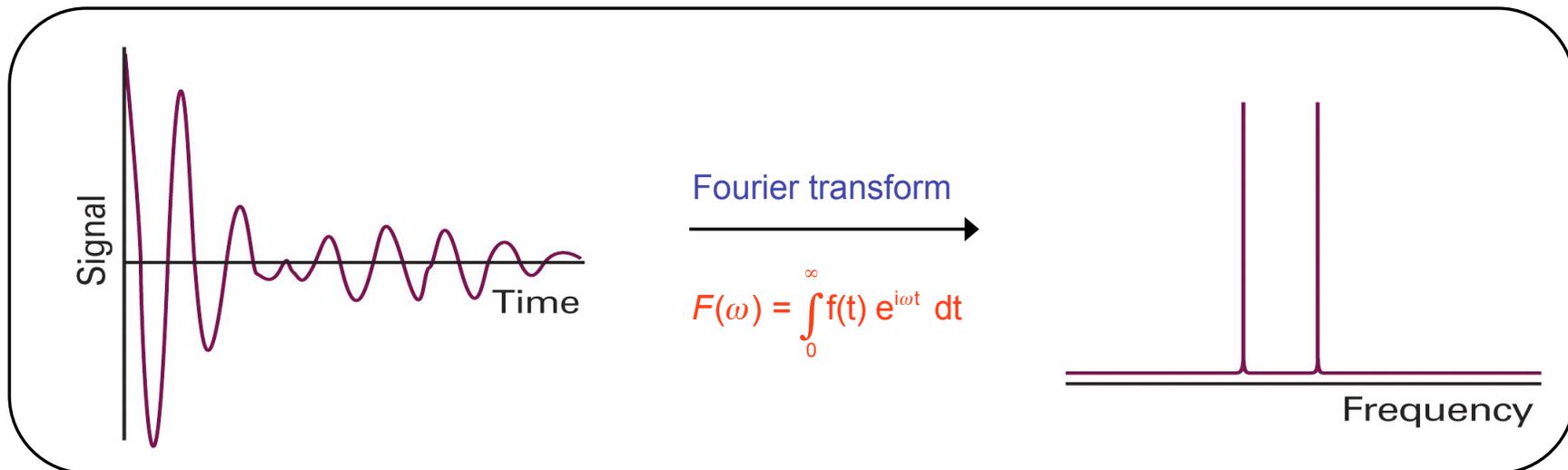
# Chemical shift

$^{29}\text{Si}$  NMR spectrum of zeolite ZSM-5  
(28 different Si species)

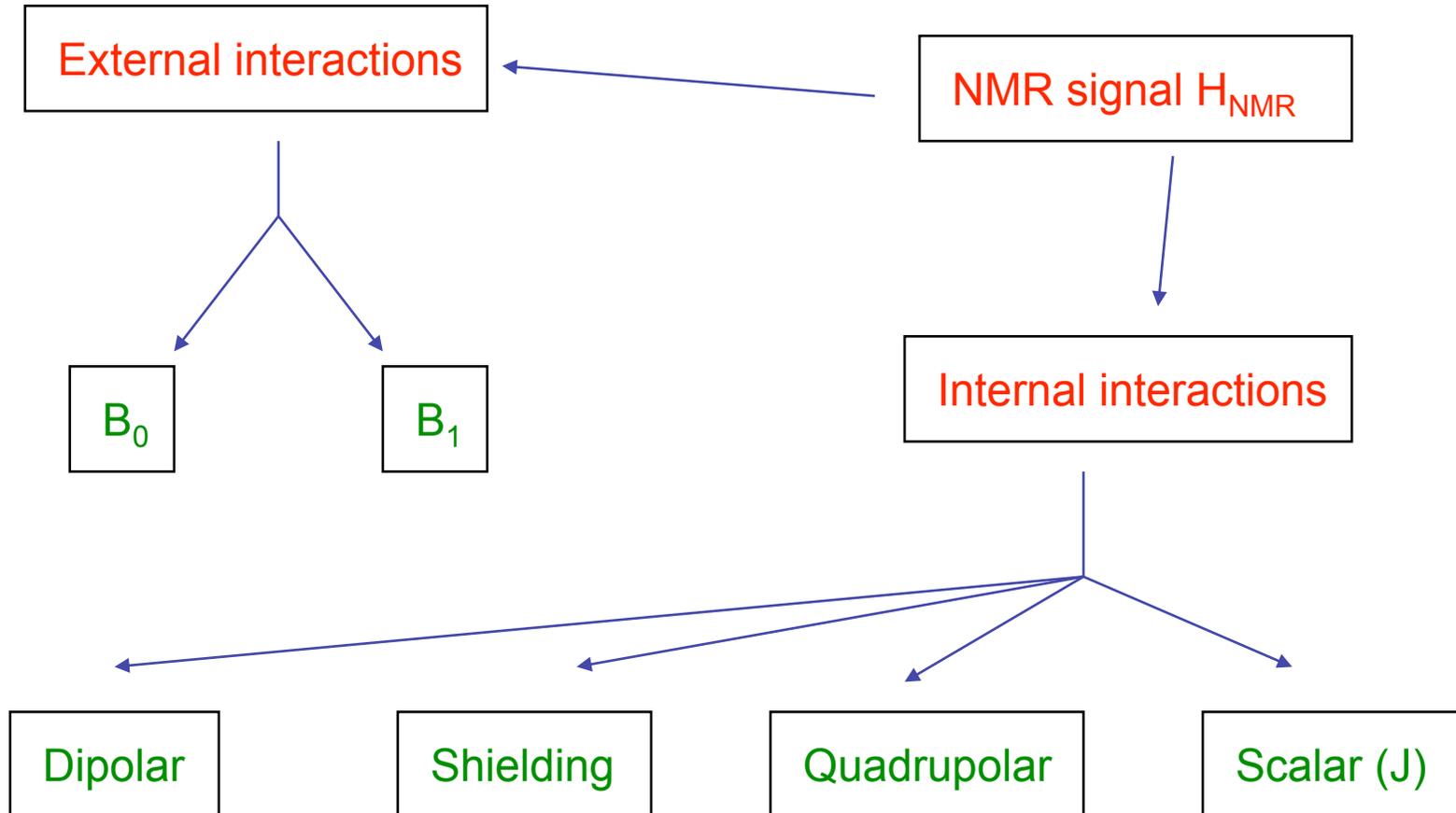


# Pulsed NMR

- Early NMR spectra were acquired by a continuous wave (CW) technique, sweeping the frequency of the rf field and bringing each signal into resonance **sequentially**
- For good resolution the sweep must be slow
- Modern spectrometers employ pulsed NMR where a short burst of intense radiofrequency radiation is applied which excites all resonances **simultaneously**
- After the pulse the response from the spins is measured
- Able to repeat the experiment more quickly and improve sensitivity (S/N increases by  $\sqrt{N}$  for N repetitions)

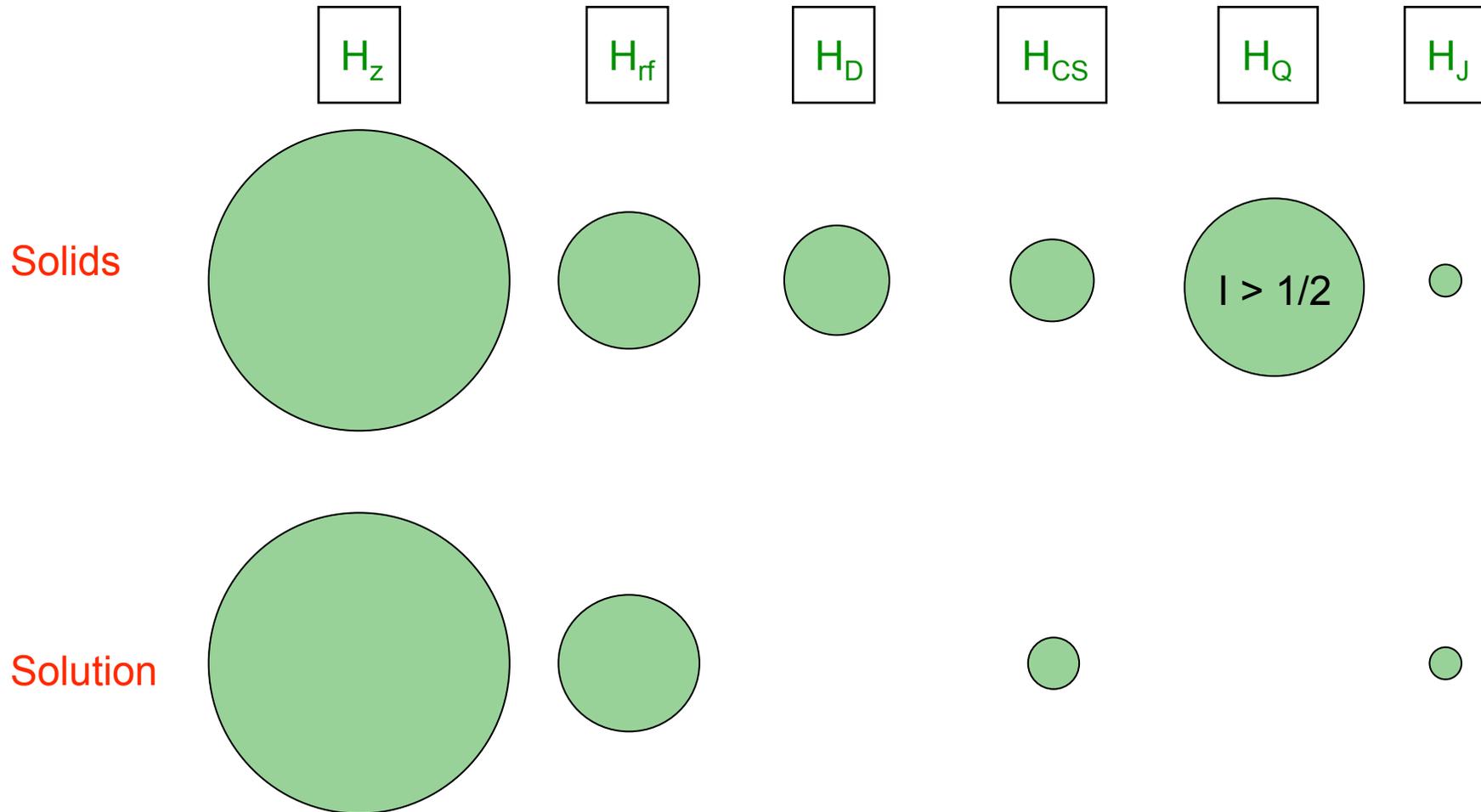


# Interactions in NMR



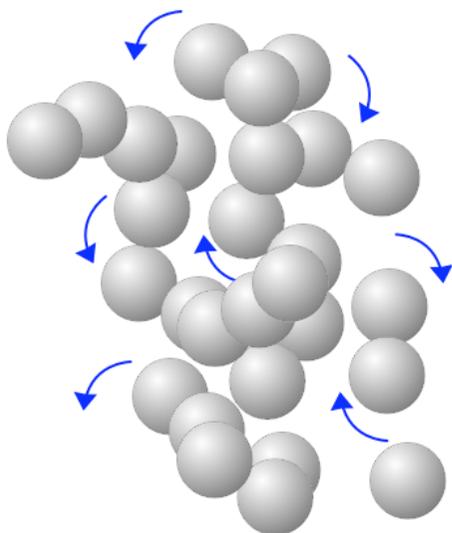
$$H_{\text{NMR}} = H_Z + H_{\text{rf}} + H_D + H_{\text{CS}} + H_Q + H_J$$

# Interactions in NMR

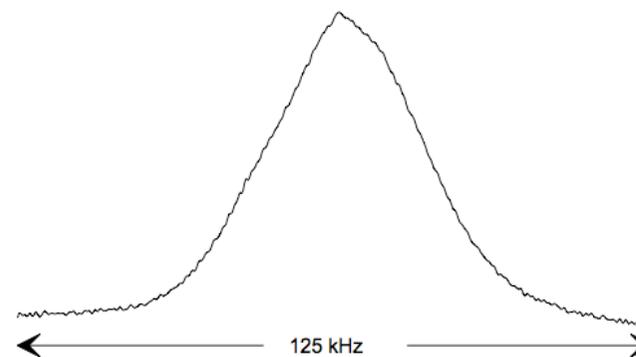
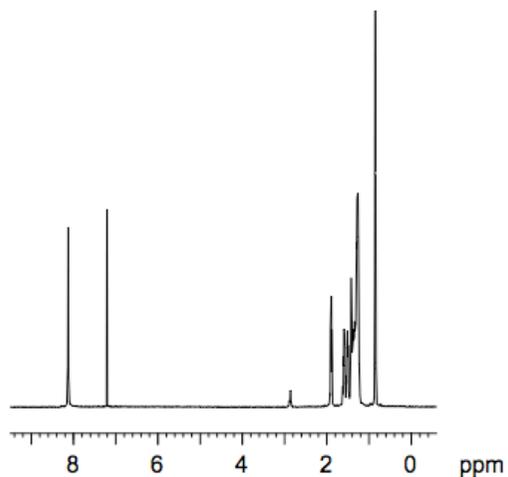
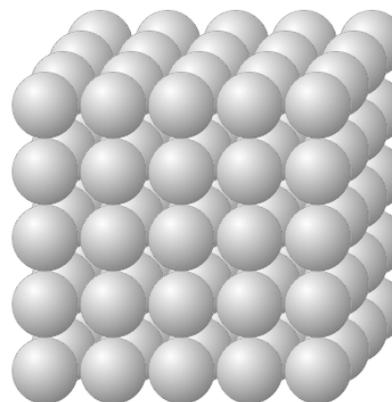


# Averaging of interactions

Liquids



Solids



# Solid-state NMR

- Most of the interactions in NMR can be described in the following form

$$H_{\text{int}} = \mathbf{I} \cdot \mathbf{R} \cdot \mathbf{X}$$
$$= \begin{pmatrix} I_x & I_y & I_z \end{pmatrix} \begin{pmatrix} R_{xx} & R_{xy} & R_{xz} \\ R_{yx} & R_{yy} & R_{yz} \\ R_{zx} & R_{yz} & R_{zz} \end{pmatrix} \begin{pmatrix} X_x \\ X_y \\ X_z \end{pmatrix}$$

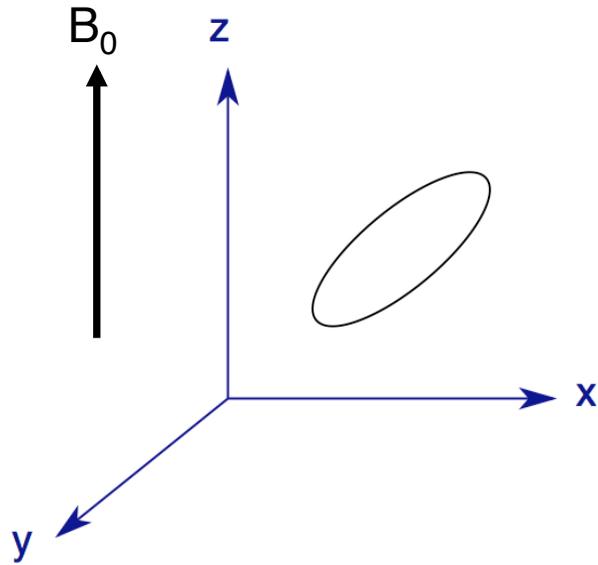
spin angular momentum operator

second-rank tensor defining the interaction

second spin operator or magnetic field

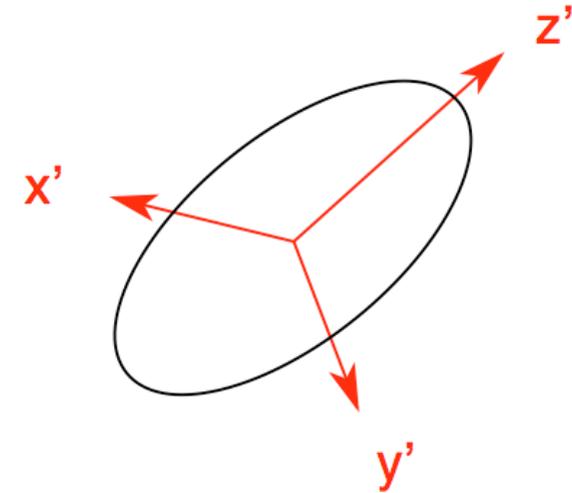
- We can often make a “secular approximation”, owing to the presence of strong external magnetic fields, which simplifies the Hamiltonian by only retaining components parallel to the z axis

# Solid-state NMR



laboratory frame

Rotation  
 $\longleftrightarrow$



crystal frame  
 principal axis system (PAS)

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

Rotation  
 $\longleftrightarrow$

$$\begin{pmatrix} R_{x'x'} & 0 & 0 \\ 0 & R_{y'y'} & 0 \\ 0 & 0 & R_{z'z'} \end{pmatrix}$$

# Chemical shift anisotropy

- The shielding of the nucleus is anisotropic (orientationally dependent)
- Although averaged in liquids to an isotropic value, in solids, the chemical shift anisotropy (CSA) becomes important

$$H_{CS} = \mathbf{I} \cdot \boldsymbol{\sigma} \cdot \boldsymbol{\gamma} \mathbf{B}_0$$

secular approximation

$$H_{CS} = \gamma B_0 \sigma_{zz} I_z$$

Principal axis system (PAS)

$$\boldsymbol{\sigma} = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}$$

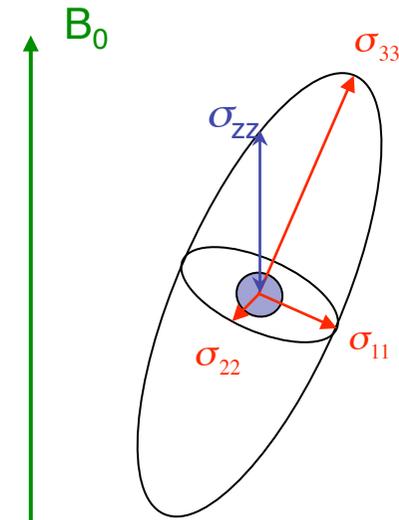
$$\sigma_{iso} = (1/3) (\sigma_{11} + \sigma_{22} + \sigma_{33})$$

$$\Delta\sigma_{CS} = (\sigma_{33} - \sigma_{iso})$$

$$\eta_{CS} = (\sigma_{11} - \sigma_{22}) / (\sigma_{33} - \sigma_{iso}) \quad 0 < \eta_{CS} < 1$$

Alternative convention

$$\Delta\sigma_{CS}' = \sigma_{33} - (\sigma_{22} + \sigma_{11}) / 2 = 3 \Delta\sigma_{CS} / 2$$

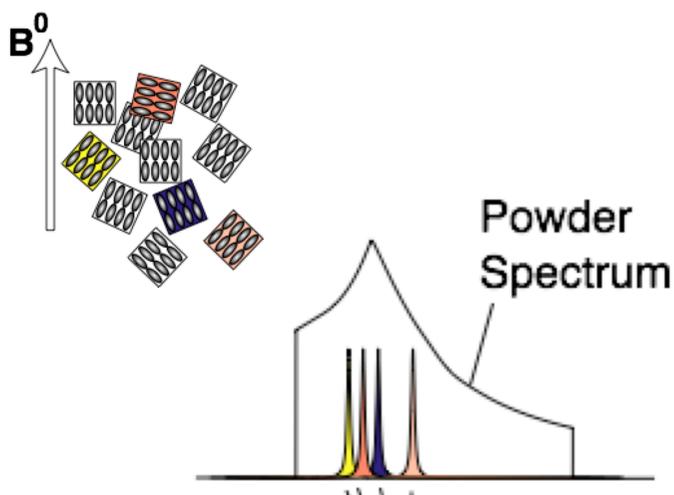
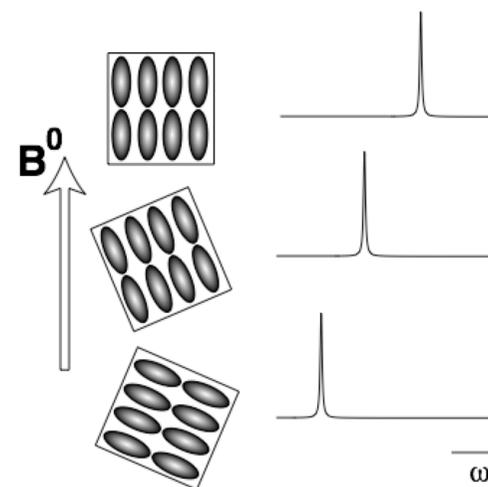


# Chemical shift anisotropy

- We rotate to convert between the PAS and lab frame, which reveals the angular dependence of the shielding

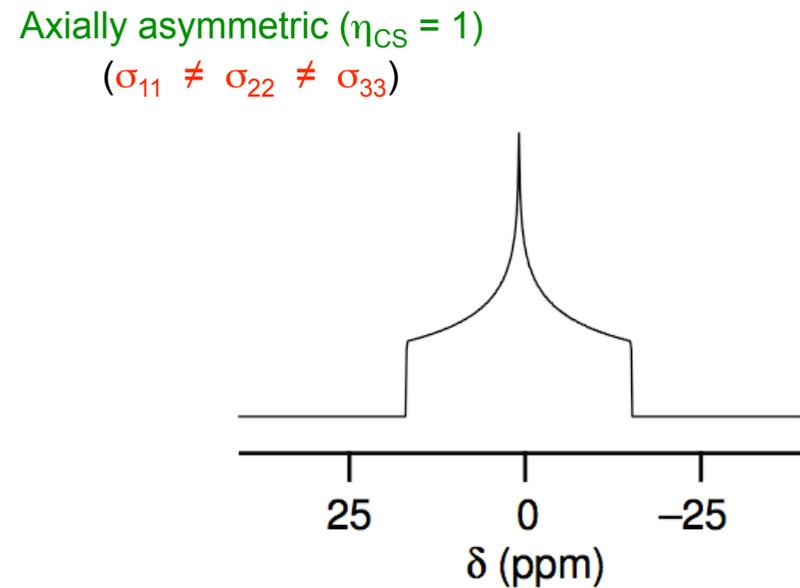
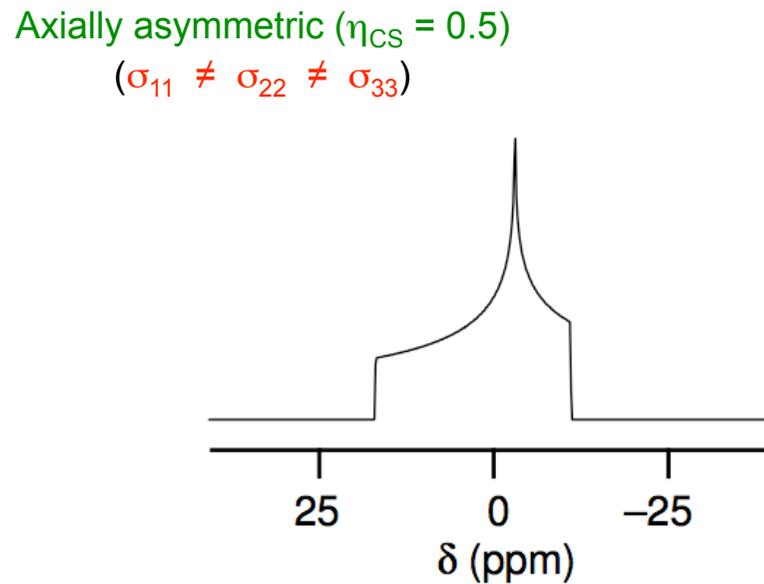
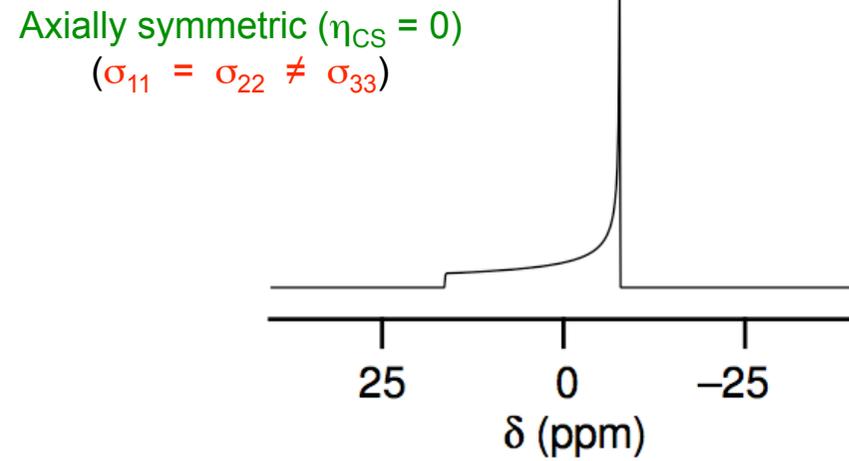
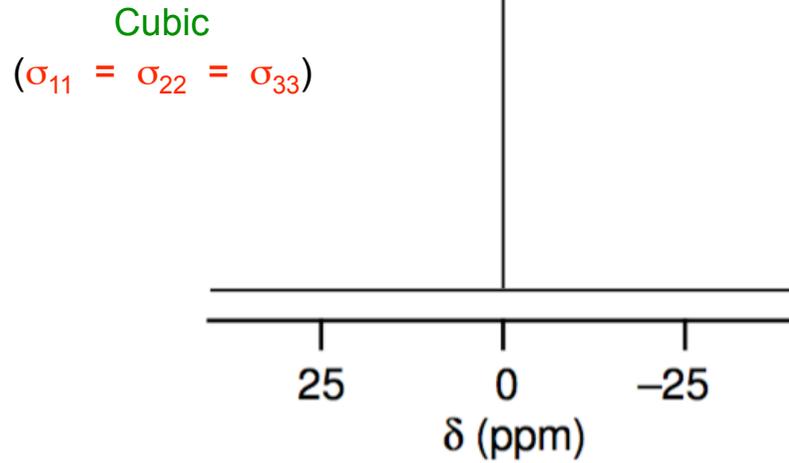
$$\sigma_{zz} = \sigma_{iso} + (\Delta\sigma_{CS}/2) [(3 \cos^2\theta_i - 1) + \eta_{CS}(\sin^2\theta \cos 2\phi)]$$

- In a single crystal all molecules have the same orientation with respect to  $B_0$
- Different single crystals will have a different orientation with respect to  $B_0$  and so a different chemical shift

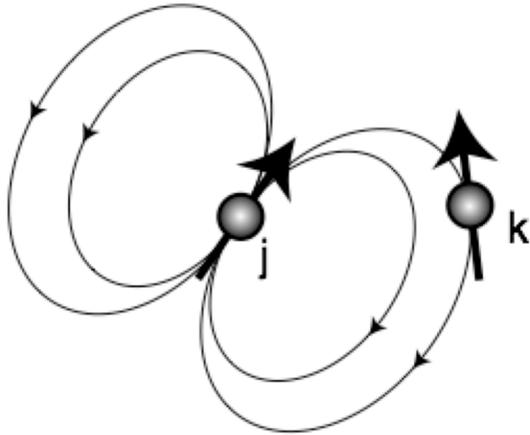


- Powder samples are composed of millions of single crystals all with different orientations
- This results in a broad powder-pattern lineshape with characteristic features
- Typical magnitude  $10^2$ - $10^5$  Hz

# Chemical shift anisotropy



# Dipolar interactions



- The nuclear magnetic dipole moments possess small localized fields which interact with the dipole moments of nearby nuclei
- This **dipolar** interaction is a through-space interaction
- It is averaged to zero in rapidly tumbling liquids

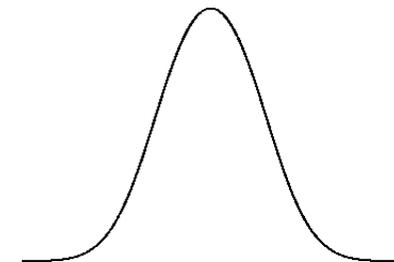
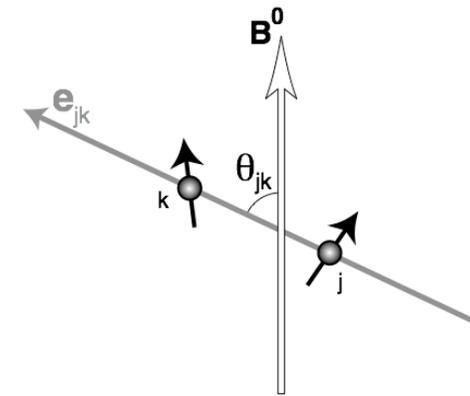
- The dipolar interaction between two spins k and j is given by

$$\omega_D = \omega_D^{\text{PAS}} (3 \cos^2 \theta_{jk} - 1) / 2$$

where  $\omega_D^{\text{PAS}}$  is the dipolar coupling constant

$$\omega_D^{\text{PAS}} = -(\mu_0/4\pi) (\gamma_k \gamma_j \hbar / r_{jk}^3)$$

- For  $^1\text{H} / ^{13}\text{C}$  separated by 100 pm  $\approx$  30 kHz
- In solids many atoms at many different distances and at many angles leads to substantial broadening



# J coupling

- Indirect coupling between nuclear spin mediated by the bonding electrons
- Termed J/scalar/spin-spin/indirect dipolar coupling
- “Spectral manifestation of a chemical bond”

$$H_J = 2\pi \mathbf{I}_J \cdot \mathbf{J} \cdot \mathbf{I}_K$$

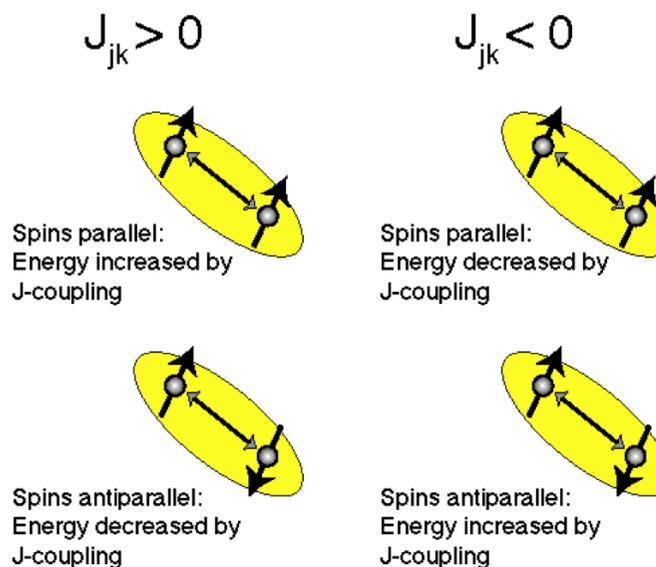
## Principal axis system (PAS)

Isotropic J coupling

$$J_{\text{iso}} = (1/3) (J_{xx} + J_{yy} + J_{zz})$$

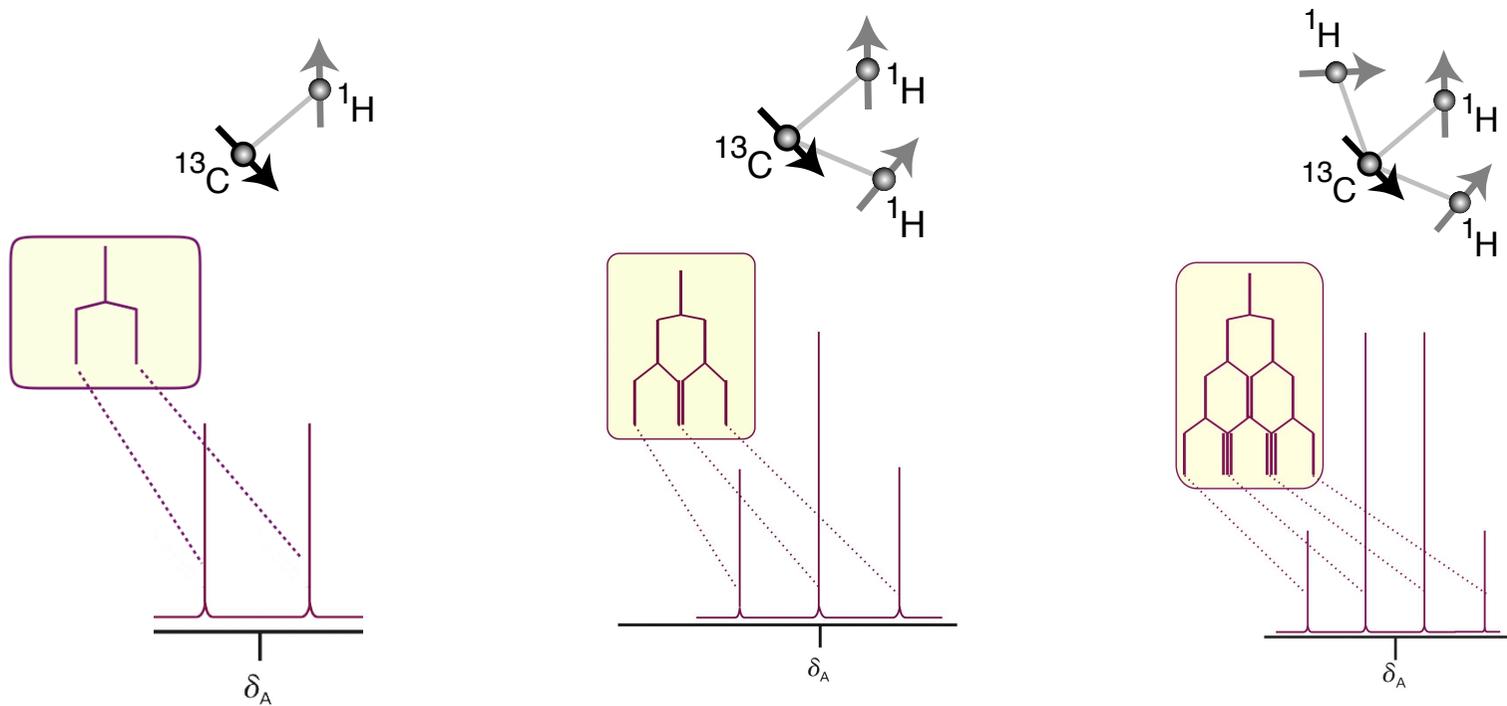
Anisotropic J coupling often small and difficult to distinguish from dipolar coupling

- The sign of J indicates whether the spin-spin contribution lowers or raises the energy of the system
- Typically observed for 1-3 bond interactions and typical magnitudes 1-1000 Hz (e.g.,  $^1\text{H}/^{13}\text{C} \sim 135$  Hz)



# J coupling

- In solution-state NMR spectra many resonances exhibit complicated splitting patterns, resulting from scalar or J coupling
- The multiplet patterns depend upon the number of nuclei to which a spin is coupled



- For solids, the J coupling is usually much smaller than many other interactions and so multiplet structures are rarely resolved
- The coupling can still be used for the transfer of magnetization

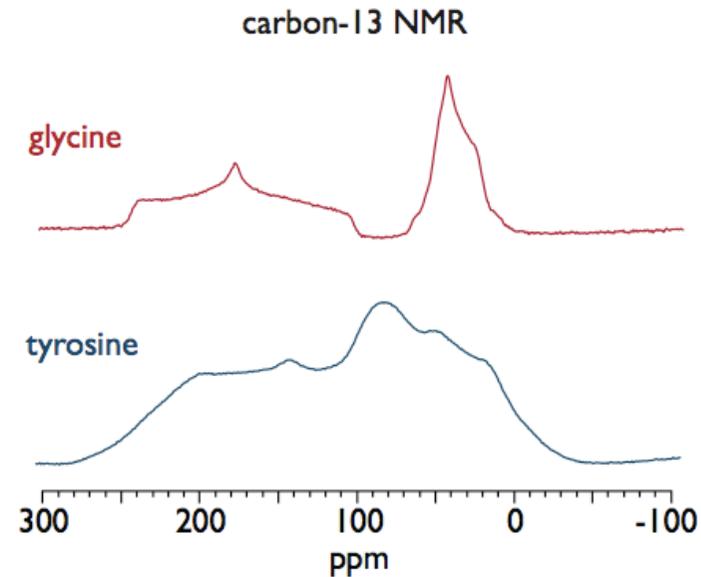
# Solid-state NMR challenges

## Resolution

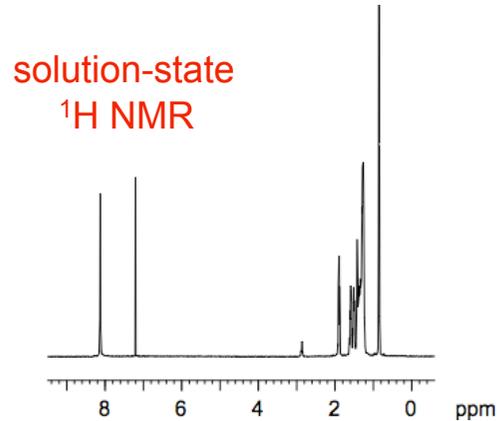
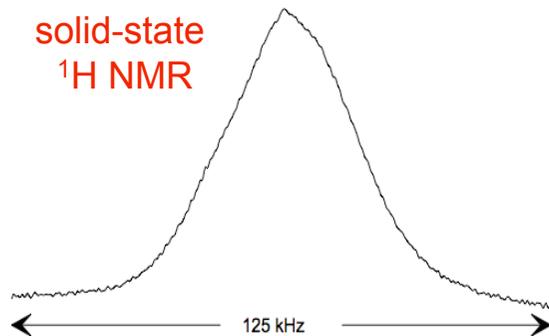
- Anisotropic interactions result in powder lineshapes
- Lineshapes from inequivalent sites overlap
- Multiple interactions result in broad featureless lineshapes

## Sensitivity

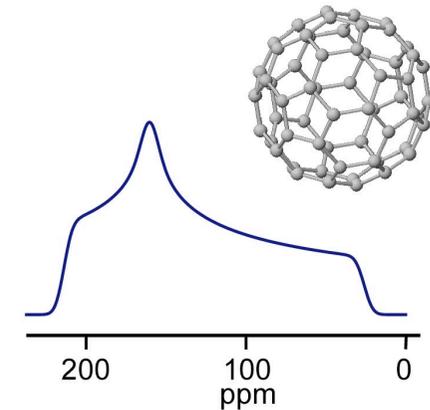
- NMR is inherently insensitive
- Many useful nuclei have low natural abundance ( $^{13}\text{C}$ ,  $^{15}\text{N}$ )
- Inefficient relaxation results in long experiment times



# Motion in NMR

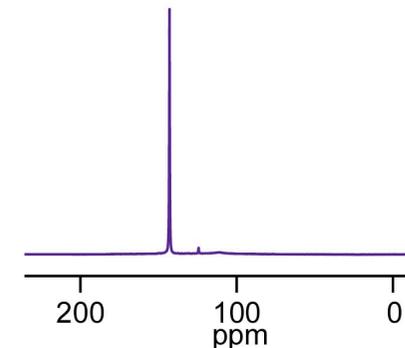


fullerene - carbon-13 NMR  
low temperature



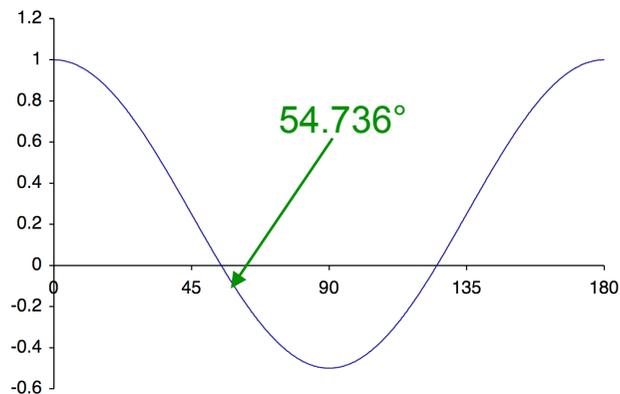
- All internal Hamiltonians have two distinct parts
- A **spatial part** which contains the variation of the interaction with orientation with respect to the  $B_0$  field
- A **spin part** which (in the secular approximation) contains angular momentum terms which are parallel to the  $B_0$  field
- To improve resolution we have to average either in “sample space” or in “spin space”

room temperature  
tumbles isotropically



# Magic-angle spinning (MAS)

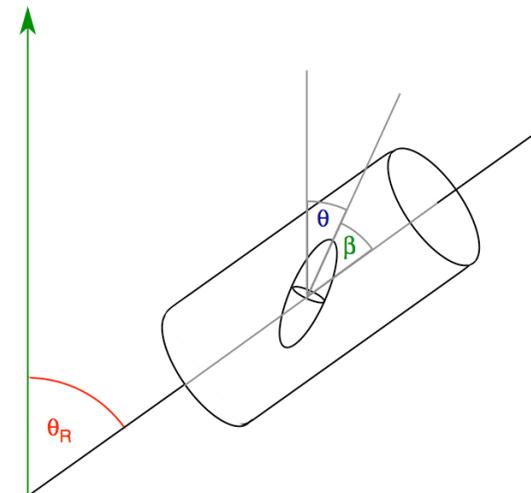
- Magic-angle spinning (MAS) mimics the tumbling motion in solution by rotation of the sample around an axis inclined at an angle  $\theta_R$  to the external magnetic field
- Introduced by Raymond Andrew in 1958



- When  $\theta = 54.736^\circ$  (the “magic angle”) the magnitude of interactions which depend upon  $(3\cos^2\theta - 1)$  is zero
- To remove the broadening in a powdered sample all the crystallites would have to have this orientation **simultaneously**

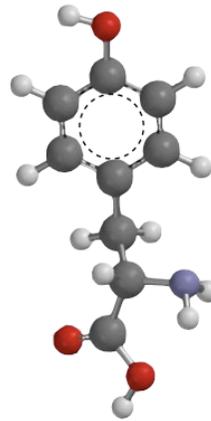
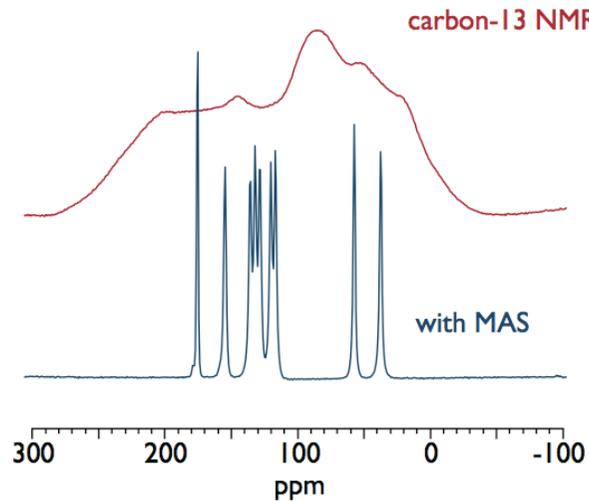
- MAS involves rotation of the sample around an angle of  $\theta_R = 54.736^\circ$  to the magnetic field
- If spinning is sufficiently rapid the “average” orientation of all crystallites is  $54.736^\circ$
- Anisotropic interactions are then averaged to zero but isotropic terms are retained

$$\langle 3 \cos^2\theta - 1 \rangle \propto (3 \cos^2\theta_R - 1) (3 \cos^2\beta - 1)$$

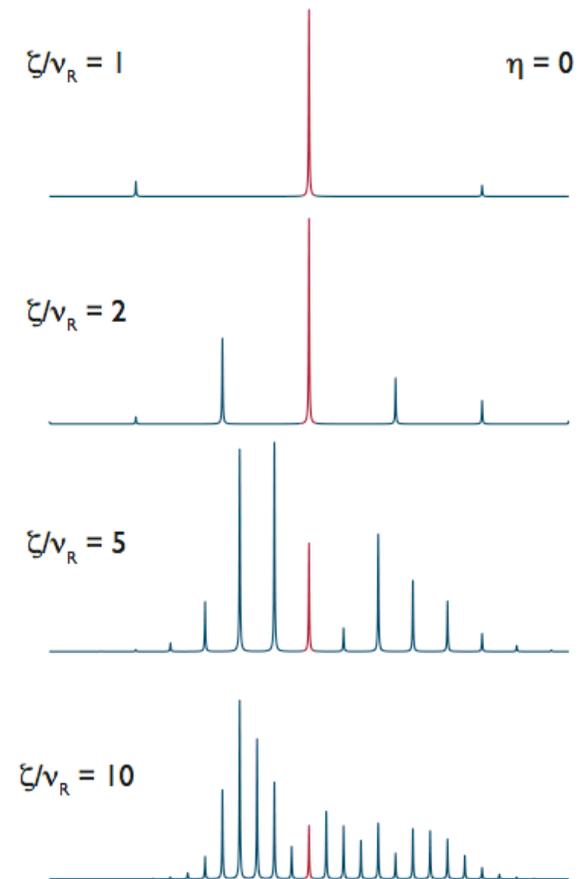


# Magic-angle spinning (MAS)

- MAS improves both the resolution and sensitivity of the spectrum

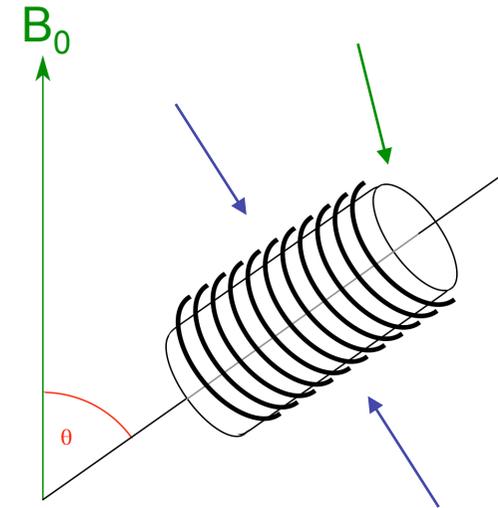


Simulated MAS sideband patterns



- If spinning is not sufficiently rapid the averaging is not complete
- At slower rates the lineshape breaks up into spinning sidebands (separated by the  $\omega_R$ )

# Practical implementation



Diameter / mm	Rate / kHz	Sample volume / $\mu\text{l}$
14	5	1000-3000
7	7	300-500
4	15	50-90
2.5	35	~11
1.3	70	~2

1. Bearing gas reduces friction
2. Drive gas rotates turbines



# Summary: I = 1/2 NMR

- NMR spectra are affected by **CSA**, **dipolar** and **scalar** couplings

- **MAS**            *removes CSA ( $\Delta_{CSA}$ ,  $\eta_{CS}$ )*  
                      *retains  $\delta_{iso}$*

*removes heteronuclear dipolar couplings*

*removes homonuclear dipolar couplings (fast MAS)*

*removes  $J_{aniso}$*

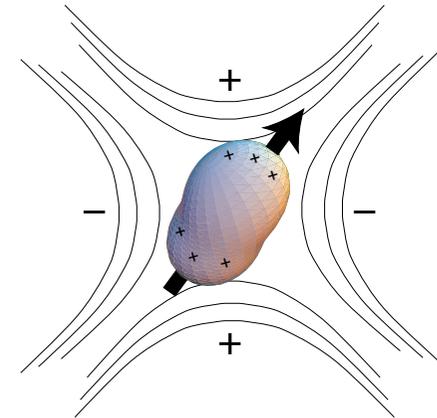
*retains  $J_{iso}$*

- **Decoupling**    *removes heteronuclear dipolar couplings*  
                      *removes homonuclear dipolar couplings*

*removes  $J_{aniso}$  and  $J_{iso}$*

# Quadrupolar nuclei

- Over 75% of nuclides in the Periodic Table have  $I > 1/2$  ( $^2\text{H}$ ,  $^6/7\text{Li}$ ,  $^{11}\text{B}$ ,  $^{14}\text{N}$ ,  $^{17}\text{O}$ ,  $^{23}\text{Na}$ ,  $^{25}\text{Mg}$ ,  $^{27}\text{Al}$ ,  $^{35}\text{Cl}$ ,  $^{39}\text{K}$ ,  $^{45}\text{Sc}$ ,  $^{51}\text{V}$ ,  $^{59}\text{Co}$ ,  $^{71}\text{Ga}$ ,  $^{87}\text{Rb}$ ,  $^{93}\text{Nb}$ , ...)
- Spectra broadened by interaction between the nuclear electric quadrupole moment ( $eQ$ ) and the electric field gradient (EFG)
- Broadening can be very large (often  $\sim\text{MHz}$ )



$$H_Q = \frac{eQ}{2I(2I-1)\hbar} I \cdot V \cdot I$$

Principal axis system (PAS)

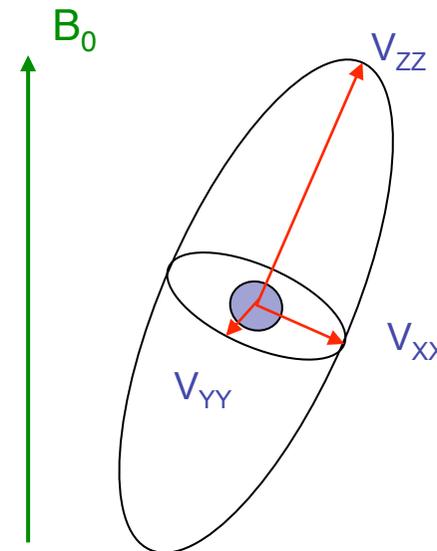
$$\begin{pmatrix} V_{xx} & 0 & 0 \\ 0 & V_{yy} & 0 \\ 0 & 0 & V_{zz} \end{pmatrix}$$

$$C_Q = eQV_{zz} / h$$

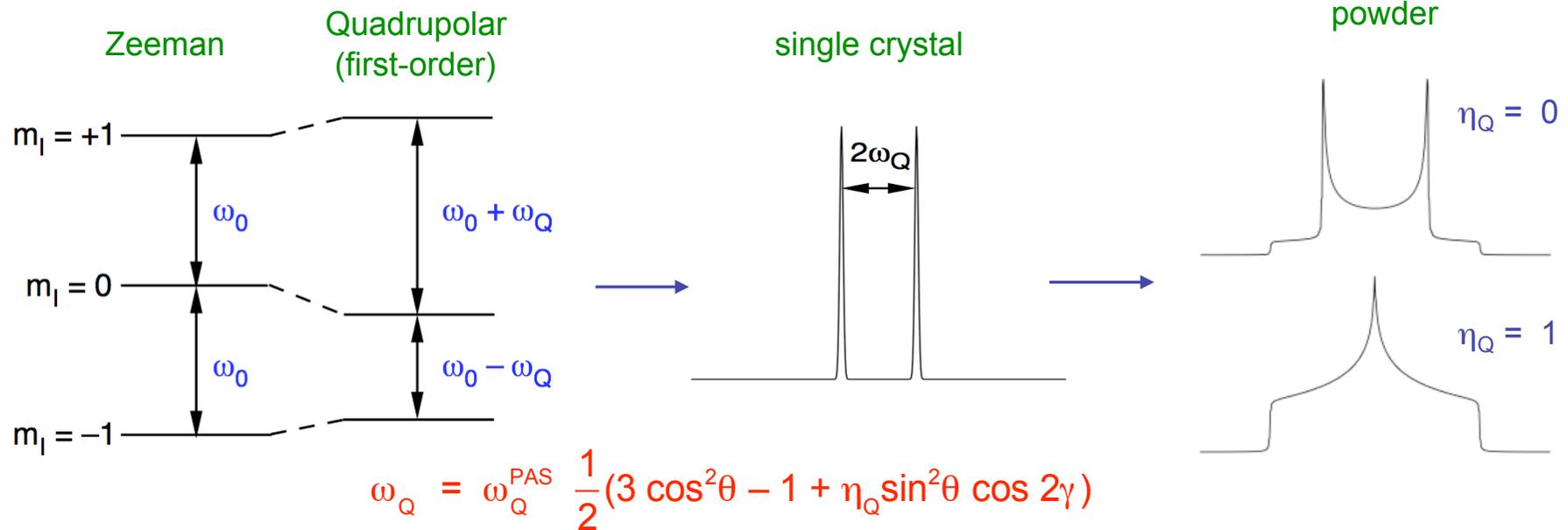
$$\eta_Q = (V_{xx} - V_{yy}) / V_{zz} \quad 0 < \eta_Q < 1$$

$$P_Q = C_Q (1 + \eta_Q^2/3)^{1/2}$$

$$\omega_Q^{\text{PAS}} = 3 C_Q / 4I(2I-1) \quad (\text{or } 3 C_Q / 2I(2I-1))$$



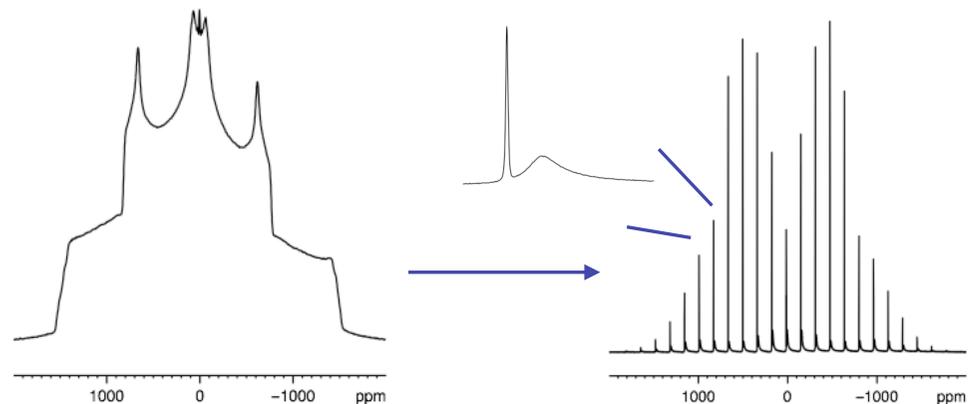
# Spin I = 1



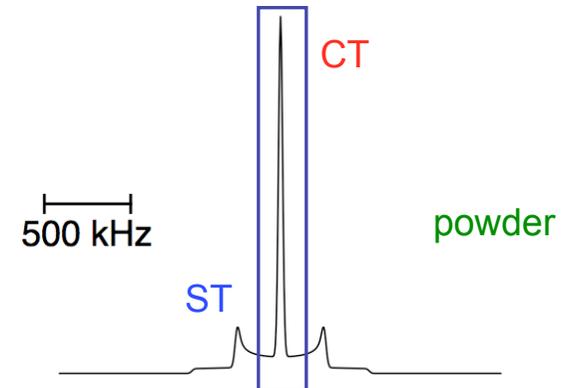
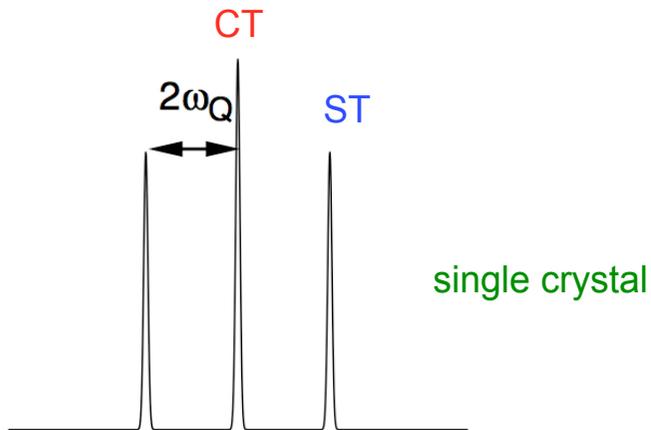
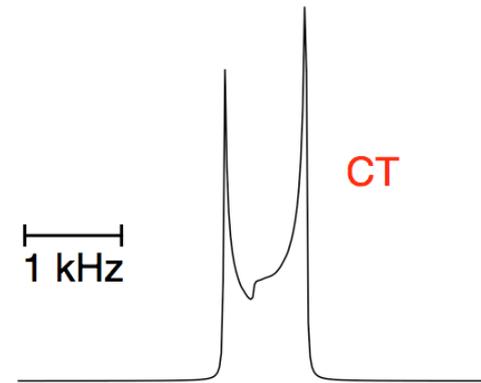
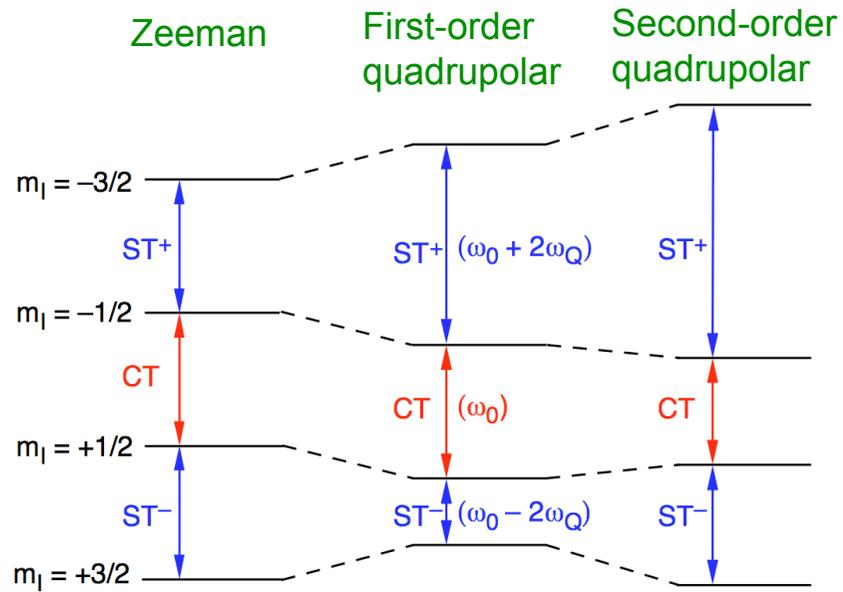
## MAS

- MAS is able to remove the quadrupolar interaction to first order
- Range of spinning sidebands often observed

## $^2\text{H}$ NMR of oxalic acid



# Spin $I = 3/2$



# MAS

$$\omega = \frac{(\omega_Q^{\text{PAS}})^2}{\omega_0} \left[ A + B D_{00}^2(\theta) + C D_{00}^4(\theta) \right]$$

Constant depending upon  $C_Q$ ,  $I$  and  $\omega_0$

Isotropic

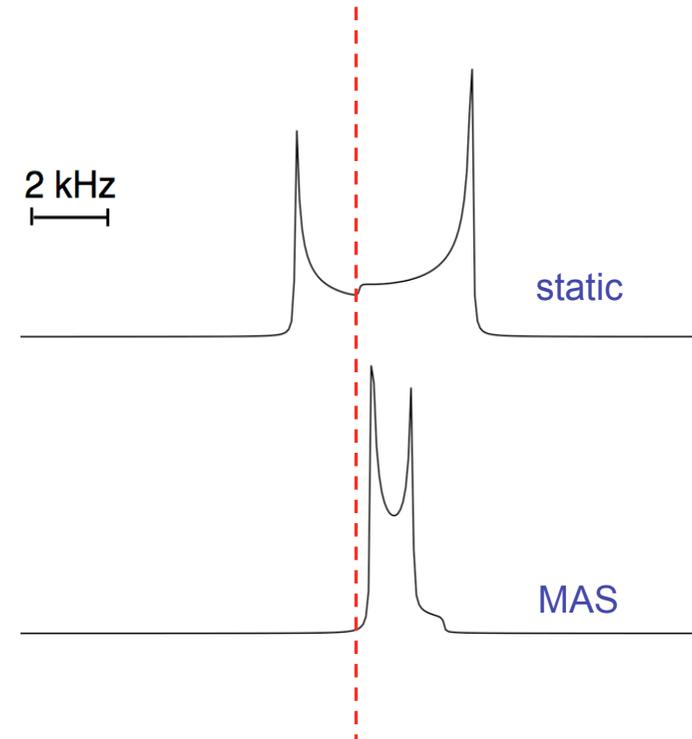
Second-rank anisotropic

Fourth-rank anisotropic

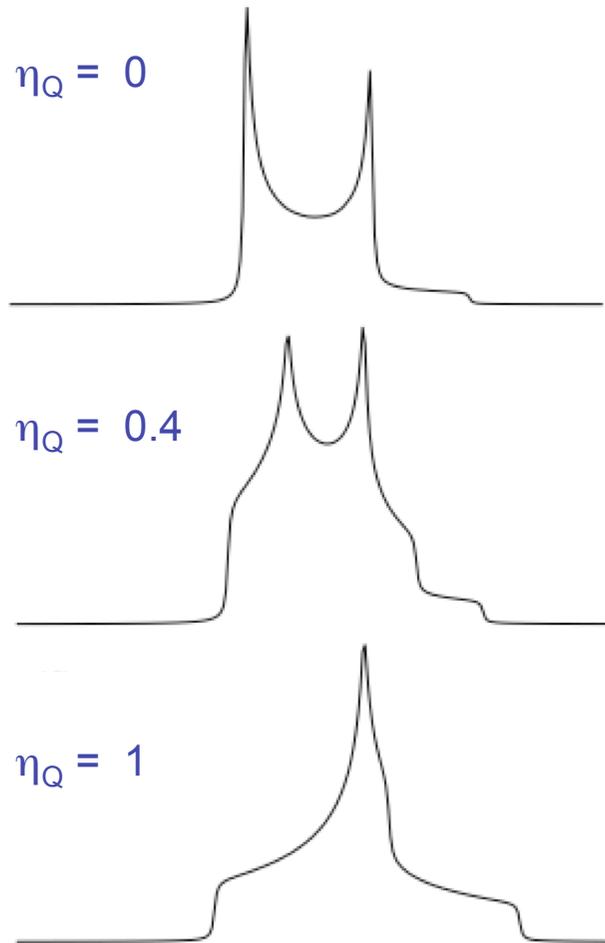
$$D_{00}^2(\theta) \propto 3 \cos^2 \theta - 1$$

$$D_{00}^4(\theta) \propto 35 \cos^4 \theta - 30 \cos^2 \theta + 3$$

- Lineshape is significantly narrowed by MAS
- Fourth-rank anisotropic quadrupolar broadening remains
- Resonance is shifted from chemical shift by isotropic quadrupolar shift

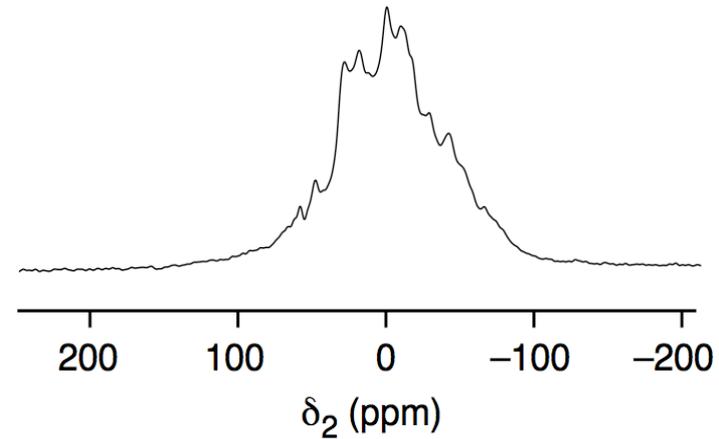


# MAS lineshapes



$^{17}\text{O}$  NMR of  $\text{MgSiO}_3$

9.4 T MAS



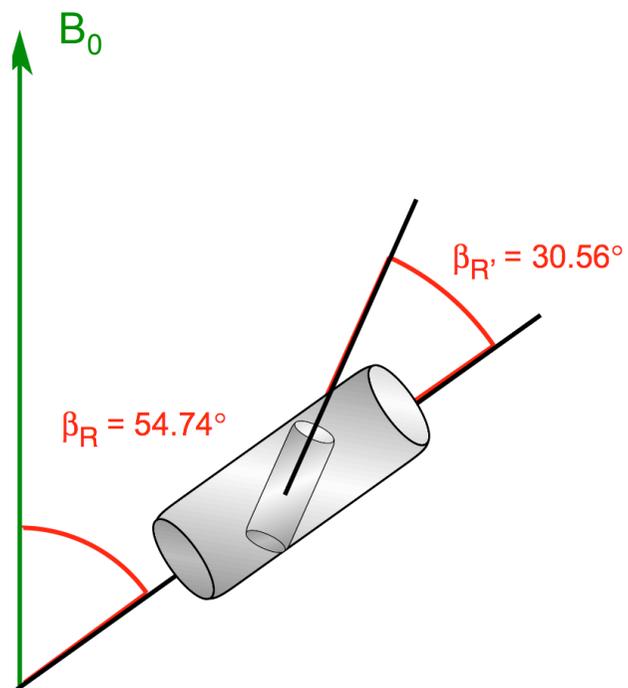
How many oxygen species are present?

What are their quadrupolar and chemical shift parameters?

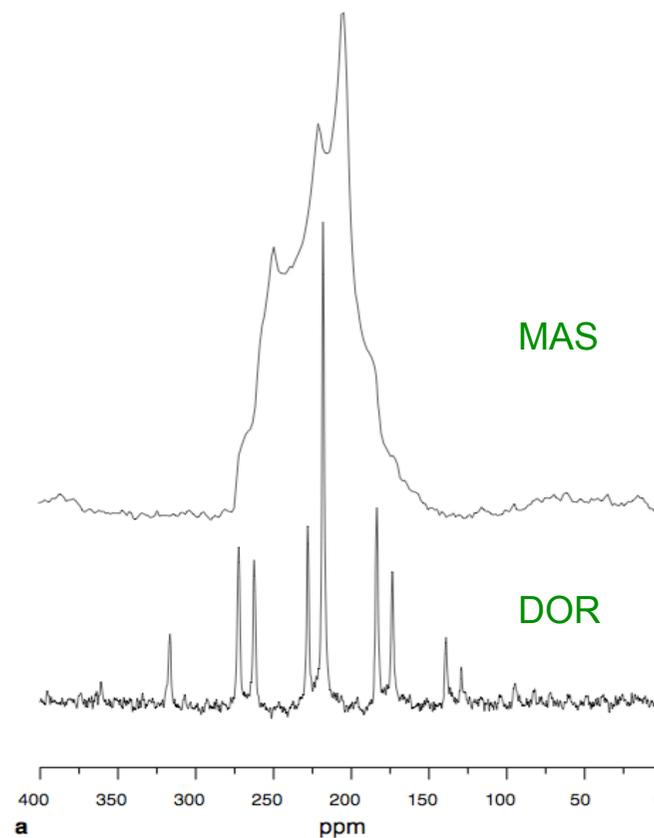
Can we remove the quadrupolar broadening completely and improve resolution?

# High-resolution: DOR

- Double rotation: rotation around two angles simultaneously
- Technically very complex and requires an expensive specialist probe
- Slow MAS rates ( $\sim 2$  kHz) of the outer rotor can be a problem, producing many spinning sidebands

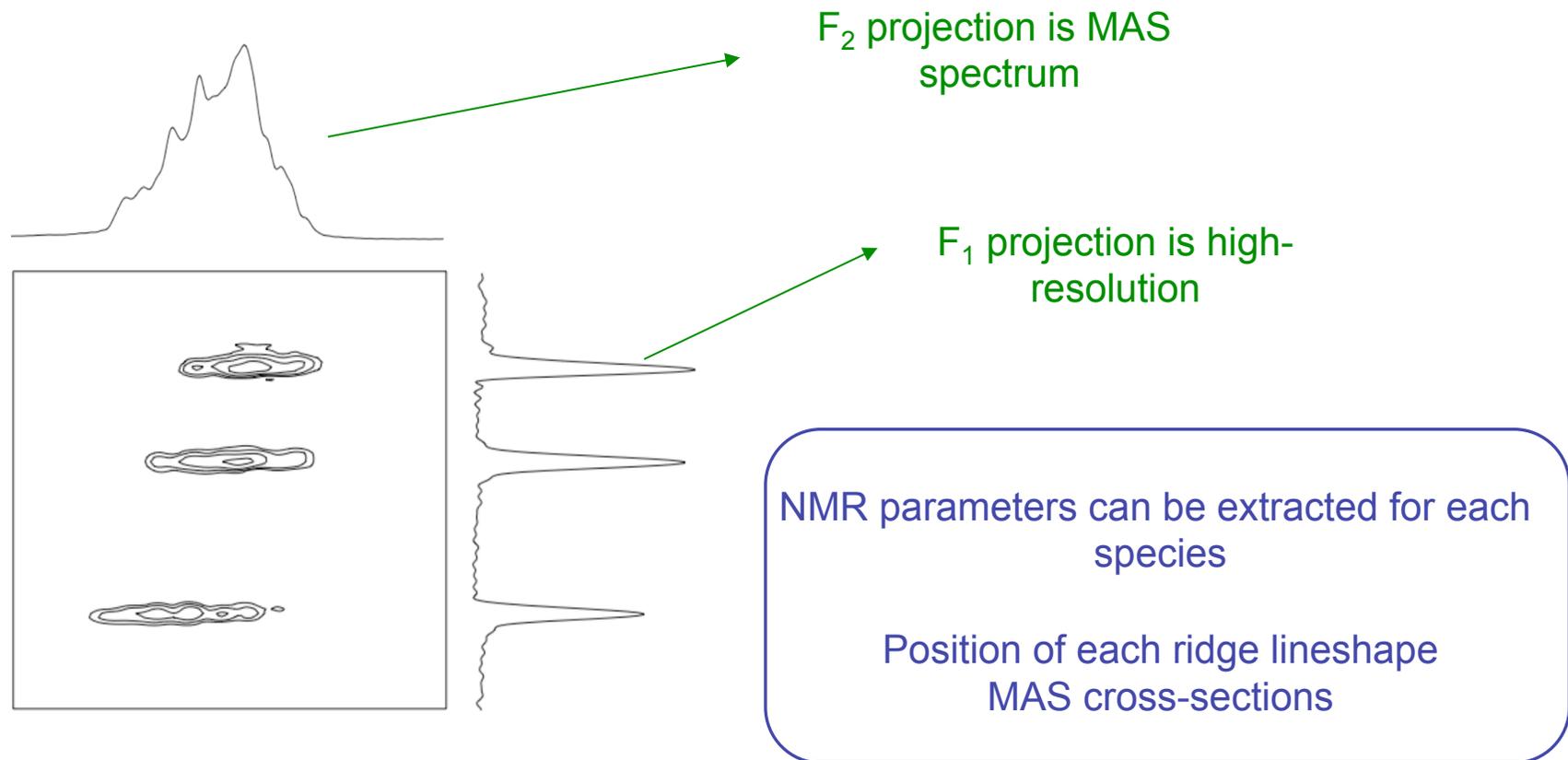


$^{17}\text{O}$  NMR of alanine



# High-resolution: MQMAS

- Multiple-quantum MAS (**MQMAS**) is a two-dimensional MAS experiment which allows the acquisition of high-resolution spectra for half-integer quadrupolar nuclei
- Removes completely the second-order quadrupolar broadening and requires only conventional MAS hardware, although sensitivity can be reduced



# Summary: $I > 1/2$ NMR

- NMR spectra are affected by CSA, dipolar, scalar and quadrupolar couplings
- **Integer spin** *MAS removes first-order quadrupolar broadening  
Lines can be too broad to observe if  $C_Q$  is large*
- **Half-integer spin** *MAS can remove first-order broadening in ST  
CT unaffected by first-order broadening  
MAS unable to remove second-order broadening of CT  
DOR/MQMAS/STMAS removes all quadrupolar broadening*
- Do we always use MAS?

*If  $C_Q$  is very large MAS cannot easily be used*

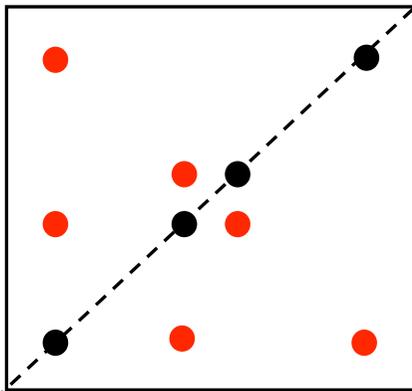
*Acquire wideline spectra on static samples*

*Provides information on quadrupolar interaction (and CSA if  $B_0$  is large)*

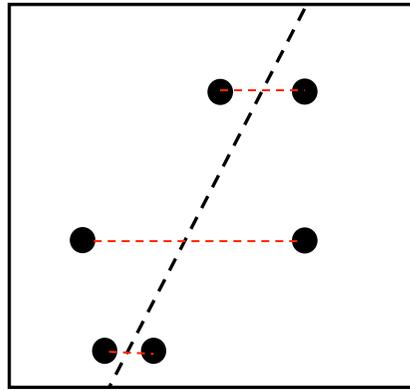
*Limited to materials with relatively few distinct species*

# Advanced approaches

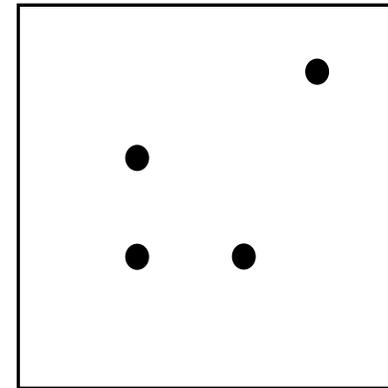
- NMR parameters provide information on structure and symmetry but much of this information is removed in the quest for higher resolution
- **Recoupling** *Reintroduction of interactions into NMR spectra in a controlled manner*  
*Measurement of dipolar couplings and distances*  
*Measurement of CSA parameters*
- **2D NMR** *Separation of different interactions in different dimensions*  
*Magnetization transfer by dipolar coupling giving through-space connectivity*  
*Magnetization transfer by J coupling giving through-bond connectivity*



Homonuclear: COSY like



Homonuclear: DQ experiments



Heteronuclear

# Summary: NMR parameters

CSA	<i>coordination numbers, coordinating atoms, symmetry</i>
Dipolar coupling	<i>spatial proximity, distances, angles, disorder</i>
J coupling	<i>chemical bonding, H bonding distances, torsion angles</i>
Quadrupolar	<i>coordination numbers, symmetry, distortions, covalency</i>

Chemical shielding  $\delta_{\text{iso}}, \Delta_{\text{CSA}}, \eta_{\text{CS}}, (\alpha, \beta, \gamma)$

J coupling  $J_{\text{iso}}, (J_{\text{aniso}})$

Quadrupolar coupling  $C_{\text{Q}}, \eta_{\text{Q}}, (\alpha', \beta', \gamma')$

# Choice of nucleus

Larmor frequency

*Nuclei with low  $\gamma$  and low  $\omega_0$  have poor sensitivity  
( $^{89}\text{Y}$  is  $\times 10000$  less sensitive than  $^1\text{H}$ )*

Abundance

*Problematic if low (e.g.,  $^{17}\text{O}$  (0.037%),  $^{13}\text{C}$  (1%),  $^{29}\text{Si}$  (4.9%))*

Chemical shift range

*Larger the range more possibility for resolution  
(e.g.,  $^{31}\text{P}$  500 ppm,  $^1\text{H}$  10 ppm)*

Chemical abundance

*Presence of the element in a range of systems (e.g., O, C)*

Relaxation times

*Long relaxation times slow acquisition (e.g.,  $^{89}\text{Y}$  10000 s,  $^1\text{H}$  5 s)*

Large CSA

*Can be difficult to acquire (many overlapping sidebands), but  
can provide extra information (e.g.,  $^{119}\text{Sn}$ ,  $^{207}\text{Pb}$ )*

Strong dipolar interactions

*Can be problematic if homonuclear and high  $\gamma$  (e.g.,  $^1\text{H}$ ,  $^{19}\text{F}$ )*

Quadrupolar interactions

*Require much more complex experimental techniques  
(e.g.,  $^{27}\text{Al}$ ,  $^{23}\text{Na}$ ,  $^{59}\text{Co}$ ,  $^{45}\text{Sc}$ ,  $^{25}\text{Mg}$ ,  $^{93}\text{Nb}$ ,  $^{17}\text{O}$ ,  $^{51}\text{V}$ ,  $^6\text{Li}$ ,  $^{14}\text{N}$ ,  $^2\text{H}$ ...)*

Paramagnetism

*Can often cause problems in NMR - often best avoided!*

# Summary of interactions

$H_n$	Interaction	Size	Liquids	Solids	Comments
$H_Z$	Zeeman	$10^7-10^9$	Yes	Yes	Interaction with main field
$H_{rf}$	RF	$10^3-10^5$	Yes	Yes	Interaction with rf
$H_{CS}$	shielding	$10^2-10^5$	Isotropic	Anisotropic	Alteration of magnetic field by local electrons
$H_J$	J	$1-10^3$	Isotropic	Anisotropic	Through-bond spin-spin magnetic coupling
$H_D$	dipolar	$10^3-10^5$	0	Anisotropic	Through-space magnetic spin-spin coupling
$H_Q$	quadrupolar	$10^3-10^7$	0	Anisotropic	Interaction of nuclear quadrupole moment with EFG