Introduction to Solid-State NMR Spectroscopy

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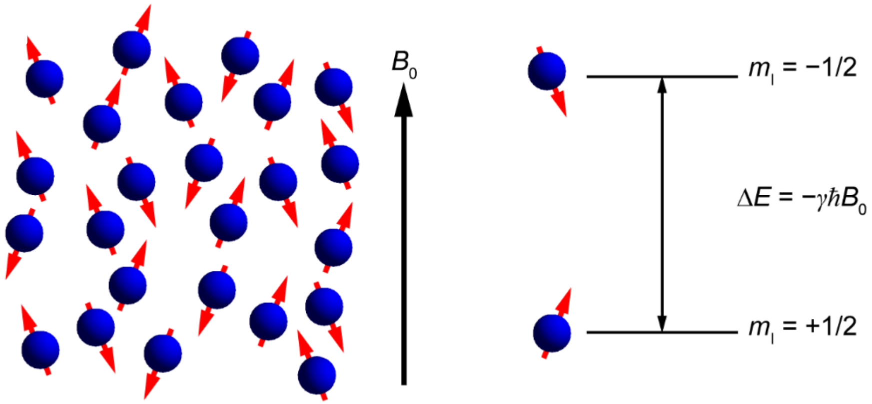
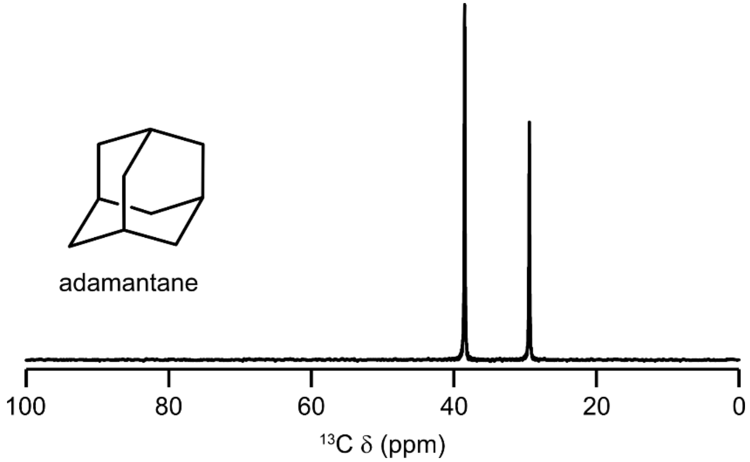
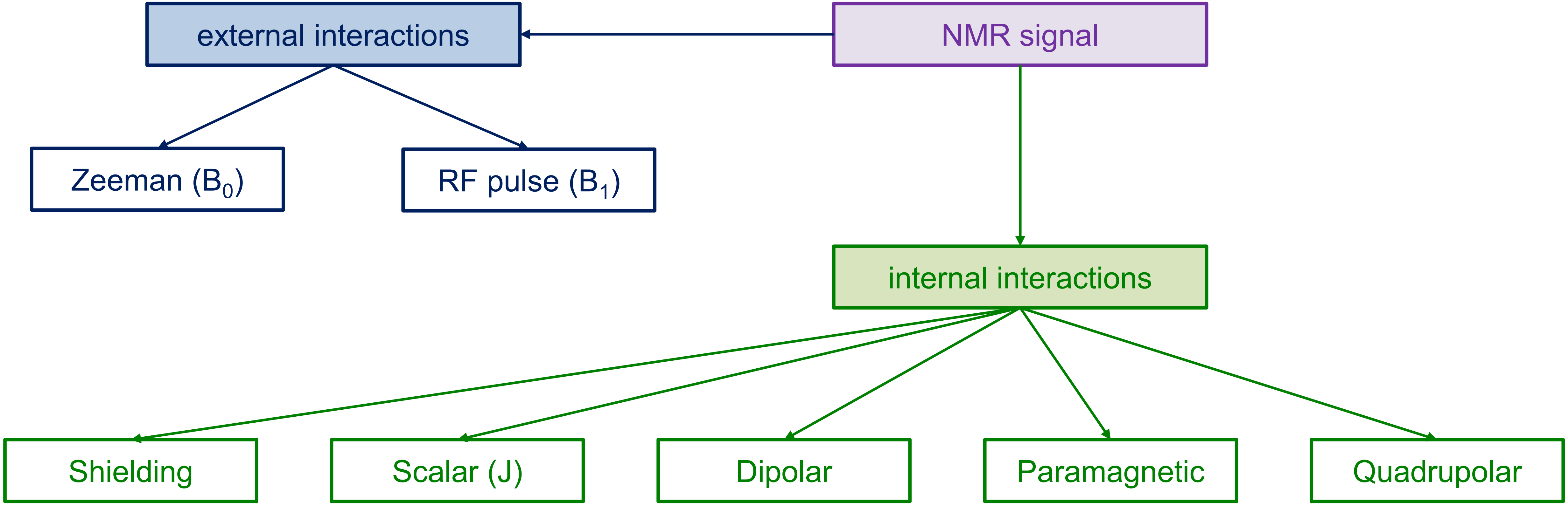
Quick Recap

- NMR looks at nuclei – in theory this gives us a signal at the Larmor frequency (interaction between nucleus and external magnetic field)
- Signals are moved from the Larmor frequency by interactions between nuclei and local magnetic fields
  - interaction with other nuclei: scalar (J) coupling
  - interaction with filled MOs: chemical shift
  - other things to consider like paramagnetic and relativistic shifts in some cases
- All of this is true in liquids and solids





Interactions in NMR



NMR signal

external interactions

Zeeman (B_0)

RF pulse (B_1)

internal interactions

Shielding

Scalar (J)

Dipolar

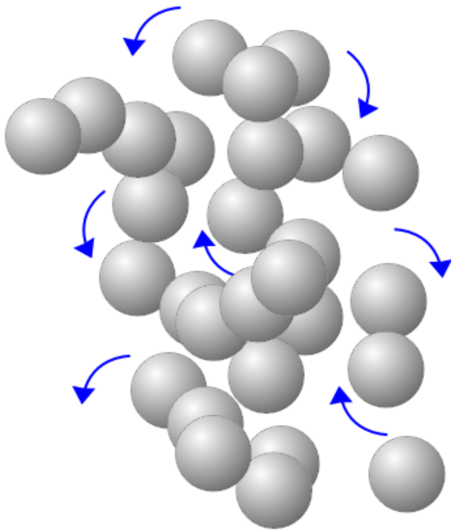
Paramagnetic

Quadrupolar

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

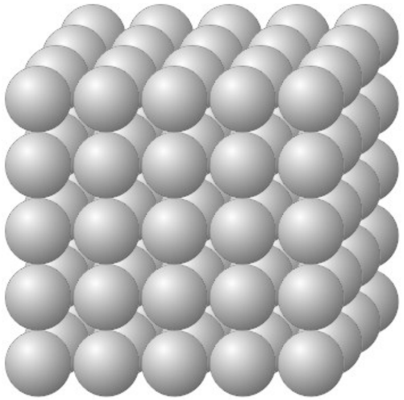
Solids vs Liquids/Solutions

Liquids



- Rapid isotropic tumbling
- On the "NMR timescale" a molecule will sample all possible orientations many times
- NMR interactions averaged to their isotropic values

Solids



- Limited/no motion
- NMR spectrum looks at a frozen snapshot of crystallite orientations
- Full anisotropic interactions must be considered

Anisotropic Interactions

- The word anisotropy can be broken down to three Greek roots

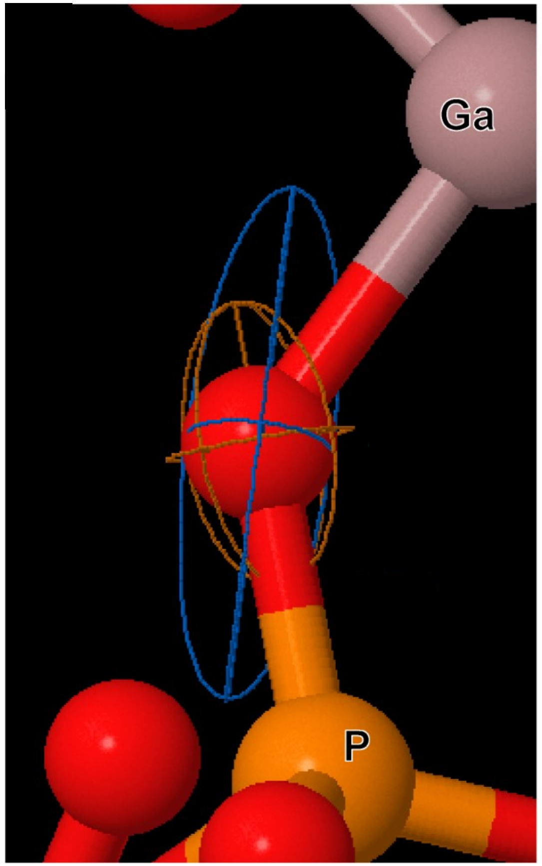
  an (not) + *iso* (the same) + *tropos* (related to direction)

  = not the same in all directions

- When we describe a chemical shift in solution we report δ in ppm
  - this is the isotropic part of the chemical shift, δ_{iso}

- When we describe a chemical shift in a solid, we need to use three numbers, corresponding to the magnitude of the interaction along the three principal axes, δ_{11}, δ_{22} and δ_{33}

- Since these are the same interaction, $\delta_{iso} = (\delta_{11}+\delta_{22}+\delta_{33})/3$



Anisotropic Interactions

- In addition to δ_{iso} we must consider the size of the anisotropy and its asymmetry (deviation from axial symmetry)

- Various conventions exist but here we'll order the components as

$$|\delta_{33} - \delta_{iso}| \geq |\delta_{11} - \delta_{iso}| \geq |\delta_{22} - \delta_{iso}|$$

- The magnitude is given by the anisotropy parameter

$$\Delta\delta = \delta_{33} - \delta_{iso}$$

- The asymmetry is given by

$$\eta = (\delta_{22} - \delta_{11})/\Delta\delta \qquad\qquad 0 < \eta < 1$$

Anisotropic Interactions

- In the PAS frame of the interaction, the interaction for each crystallite looks the same
- We have to rotate from the PAS to the lab frame

$$\sigma^{\mathrm{PAS}} = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix} \xrightarrow{\text{rotate frame of reference}} \sigma^{\mathrm{lab}} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}$$

- You'll notice I've swapped from δ to σ (magnetic shielding) – these are related by $\delta = \sigma_{\mathrm{ref}} - \sigma$, which we get round experimentally by referencing our spectrum to a standard.
- Working with σ for the next slide makes the maths a lot cleaner!

Anisotropic Interactions

- Interactions in NMR are of the form H_A = **I.A.X**
  - **I** is a spin operator
  - **A** is the interaction tensor
  - **X** is another spin, magnetic field, *etc*.

$$H_{CS} = \begin{pmatrix} I_x & I_y & I_z \end{pmatrix} \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix}$$

- This looks hideous but simplifies to $H_{CS} = I_x \sigma_{xx} \gamma B_0 + I_y \sigma_{yy} \gamma B_0 + I_z \sigma_{zz} \gamma B_0$
- In the secular approximation this simplifies even further to $H_{CS} = I_z \sigma_{zz} \gamma B_0$

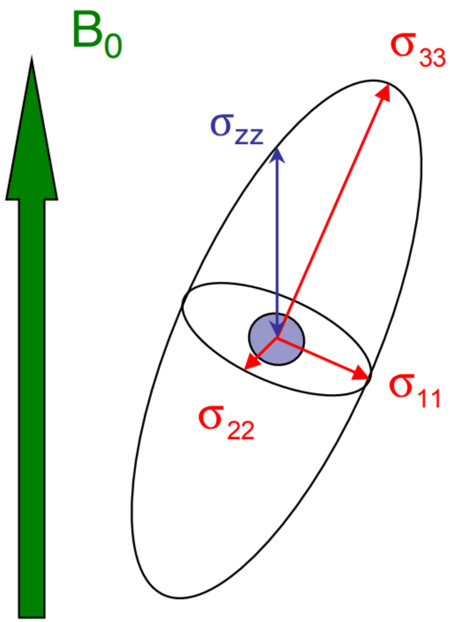
Anisotropic Interactions

- For any given crystallite, the amount of shielding along the magnetic z axis (σ_{zz}) is given by

$$\sigma_{zz} = \sigma_{iso} + \frac{\Delta\delta}{2}\left[\left(3\cos^2\theta - 1\right) + \eta\left(\sin^2\theta\cos 2\phi\right)\right]$$

isotropic anisotropic

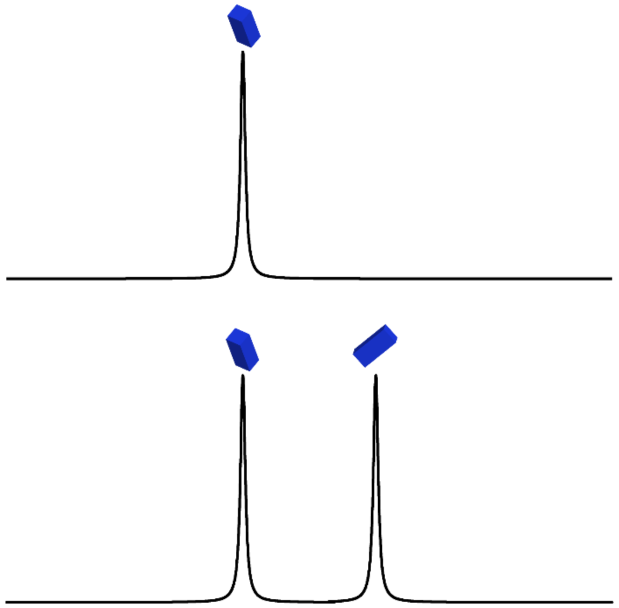
- Each crystallite orientation will give a different peak position *for nuclei in the same environment*



Anisotropic Interactions

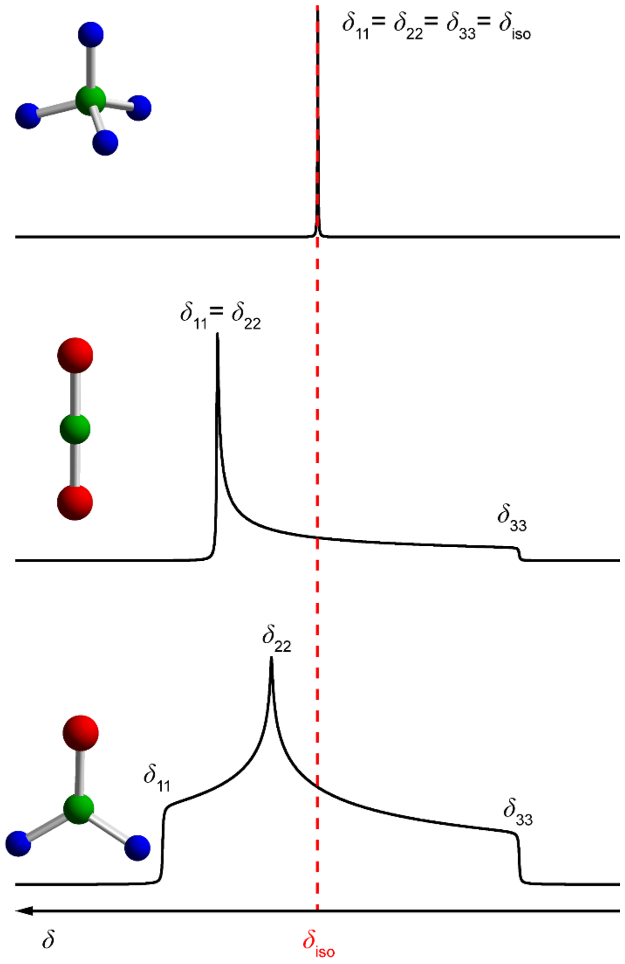
- Each crystallite orientation will give a different peak position *for nuclei in the same environment*

- In a powder, the statistical distribution of crystallites, combined with singularities at δ_{11}, δ_{22} and δ_{33} leads to typical powder pattern lineshapes



Anisotropic Interactions

- Each crystallite orientation will give a different peak position *for nuclei in the same environment*
- In a powder, the statistical distribution of crystallites, combined with singularities at δ_{11}, δ_{22} and δ_{33} leads to typical powder pattern lineshapes
- These lineshapes can provide information on point symmetry at the nucleus
  - Axial symmetry: $\eta = 0$
  - Spherical symmetry (T_d and above) : $\Delta\delta = 0$
- Problematic when there are more than ~2 lineshapes in a spectrum since lines tend to overlap



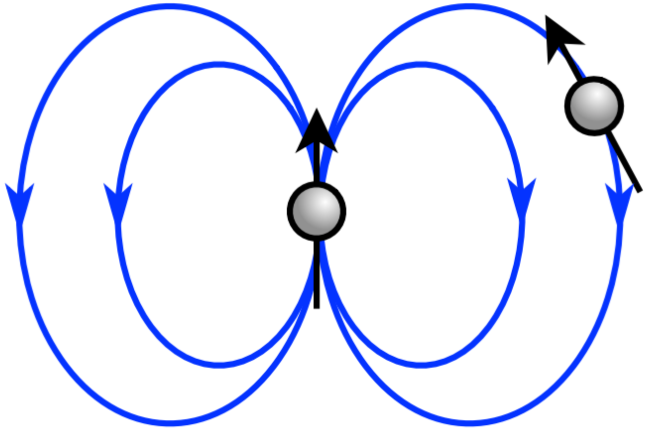
The Dipolar Interaction

- “NMR active nuclei act like tiny magnets”...

- Dipolar interaction between two spins, **I** and **S**

$$H_D = \begin{pmatrix} I_x & I_y & I_z \end{pmatrix} \begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{pmatrix} \begin{pmatrix} S_x \\ S_y \\ S_z \end{pmatrix}$$

- Unlike σ, which comes from molecular orbitals of arbitrary shape, **D** comes from a direct interaction between two point dipoles
  - $\eta_D = 0$
  - $D_{iso} = 0$



The Dipolar Interaction

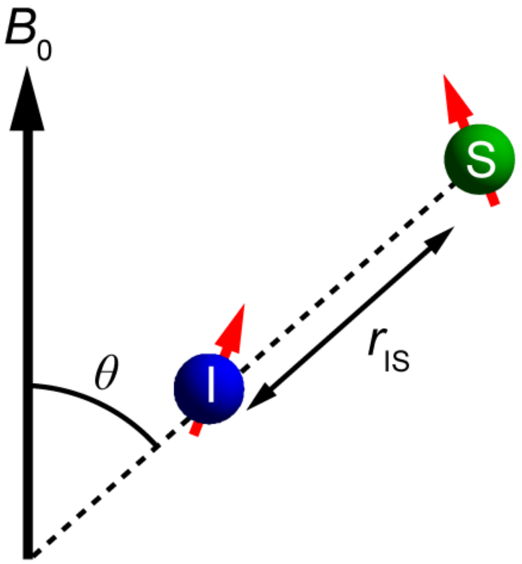
- For heteronuclear coupling (**I** ≠ **S**)

$$H_D = -\frac{\mu}{4\pi}\frac{\gamma_I\gamma_S\hbar}{r_{IS}^3}\left[2I_zS_z\right]\frac{1}{2}\left(3\cos^2\theta-1\right)$$

- For homonuclear coupling (**I** = **S**)

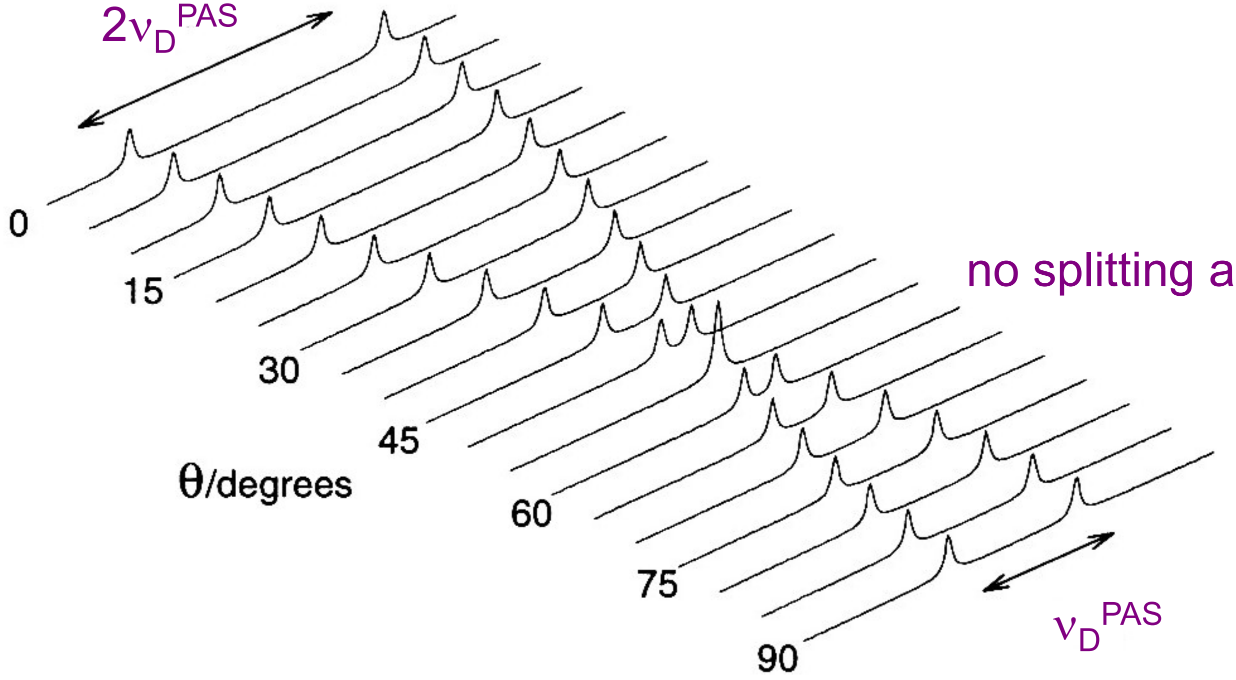
$$H_D = -\frac{\mu}{4\pi}\frac{\gamma_I\gamma_S\hbar}{r_{IS}^3}\left[3I_zS_z-\mathbf{I}\cdot\mathbf{S}\right]\frac{1}{2}\left(3\cos^2\theta-1\right)$$

- The dipolar coupling constant, ν_D depends only on the spin pair (γ_I, γ_S) and the internuclear distance



The Dipolar Interaction

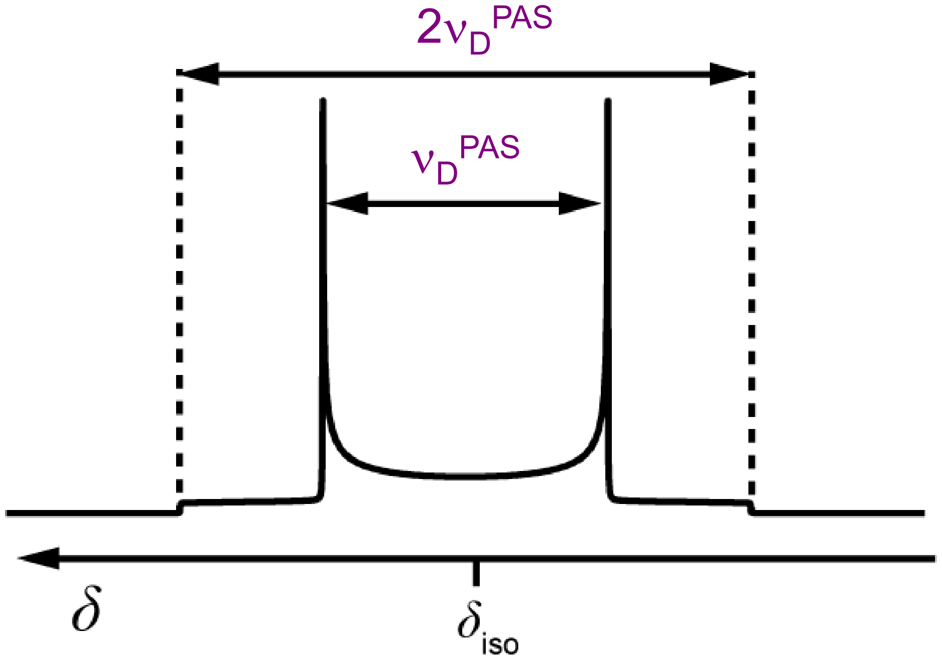
- The dipolar interaction leads to a *splitting* rather than a shift



no splitting at 54.736°

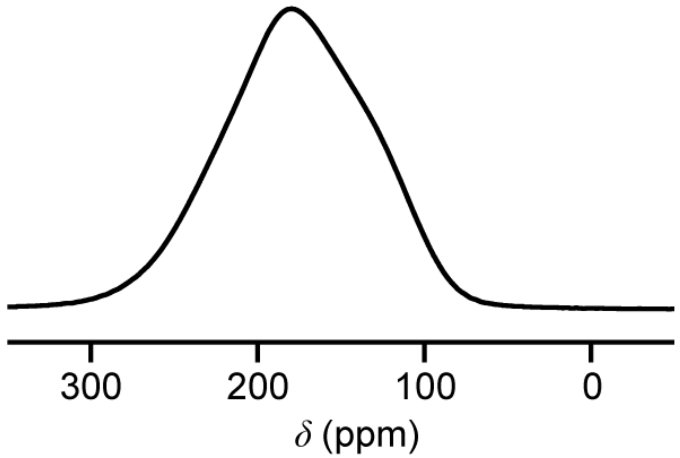
The Dipolar Interaction

- The powder pattern lineshape is a Pake doublet



The Dipolar Interaction

- The reality is that you very rarely see an isolated spin pair!
- Consider your favourite molecule and how many internal C-^{1}H distances it contains...
- Now imagine that molecule packed into a solid with millions of other molecules, all containing more ^{1}H...
- The result is a Gaussian-like broadening of the Pake doublet



^{13}C NMR spectrum of solid gly
99% enriched on the carboxylate

The Scalar Coupling

- The **J** tensor is like **D** but the interaction is mediated by electrons in arbitrarily shaped MOs

- This leads to an isotropic splitting (which we see in solution) and an anisotropic broadening analogous to the dipolar interaction

- We tend to ignore J in solids because it’s tiny ($^1J_{CH} \approx 130$ Hz) compared to D (D_{CH} ~30 kHz for a 1 Å separation)

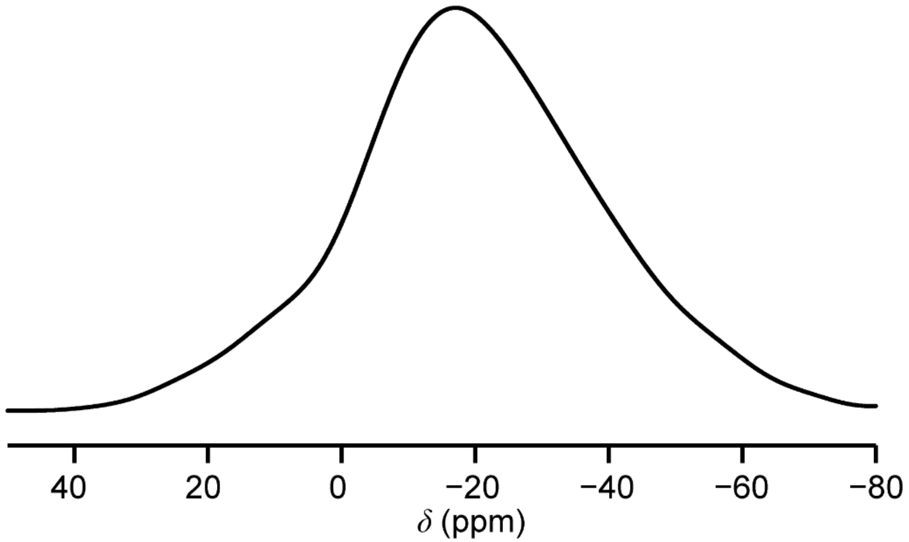
- Just because we can’t see it doesn’t mean it doesn’t exist, and we can still use it in magnetisation transfer experiments

Summary So Far

- In solids we expect resonances to be shifted, split and broadened by a variety of interactions
- Chemical shift – information about atoms within a few bonds
- Chemical shift anisotropy – information about 3D arrangement of nearby atoms
- Dipolar coupling – information about atoms that are close in space
- J coupling – information about atoms within a few bonds

Summary So Far

- So when a solid-state NMR spectrum looks like this...



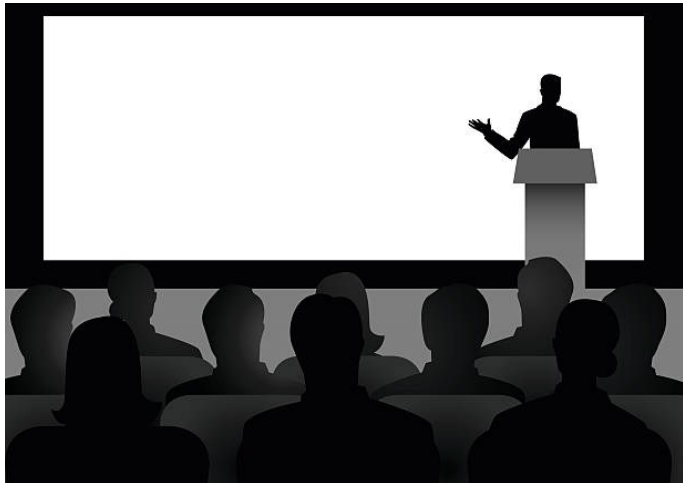
^{31}P NMR spectrum of aluminophosphate AlPO-34 containing three P sites

- It's because there's too much information!

High-Resolution Solid-State NMR

- So how come solution-state NMR is so much more useful when there's so much less information in the spectra?

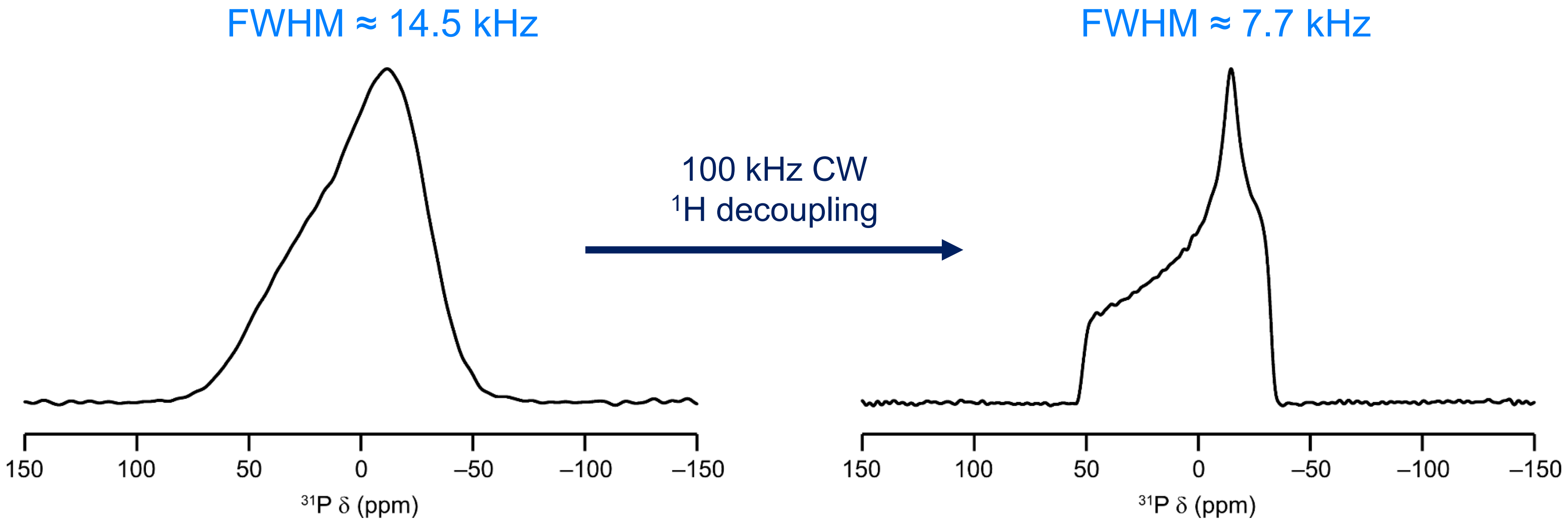
vs.



- For solid-state NMR spectroscopy to be informative, we need to *remove* some information

Decoupling

- We can get rid of spin-spin couplings using decoupling, which works exactly the same as in solution (but is generally much higher power for solids)
- Decoupling the ^{1}H-^{31}P spin-spin interactions in $(NH_4)_2HPO_4$ narrows the line and allows us to see the classic CSA-broadened lineshape



Beyond Static

- The internal interaction Hamiltonians all have two distinct parts
- A spatial part (how the interaction varies with orientation with respect to B_0)
- A spin part (angular momentum terms parallel to B_0)

$$H_{CS} = \sigma_{iso} + \frac{\Delta\delta}{2}\left[\left(3\cos^2\theta - 1\right) + \eta\left(\sin^2\theta\cos 2\phi\right)\right] I_z \gamma B_0$$

$$H_D = -\frac{\mu}{4\pi}\frac{\gamma_I \gamma_S \hbar}{r_{IS}^3}\left[2I_z S_z\right]\frac{1}{2}\left(3\cos^2\theta - 1\right)$$

- Decoupling averages interactions in “spin space” but needs two interacting spins
  - you could decouple I_z from B_0 by removing the sample from the magnet...
- How can we average in real space?

Beyond Static

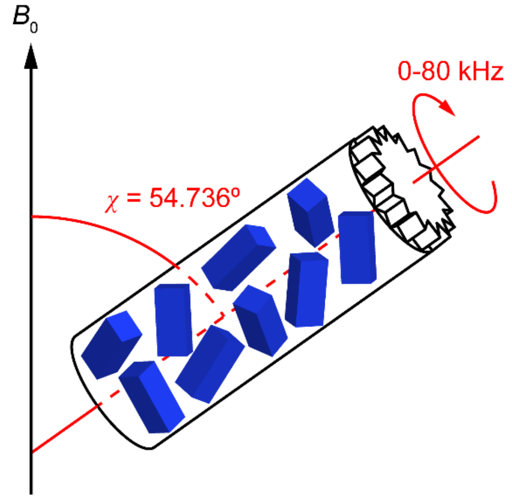
- Orientation dependence of many interactions is proportional to

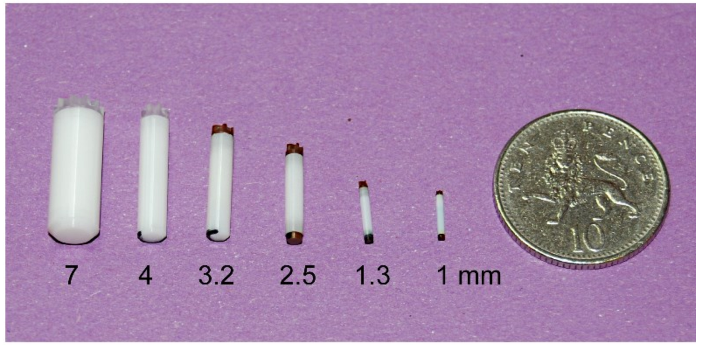
  $(3\cos^2\theta - 1)/2$

- This is zero at the "magic" angle of 54.736°

- Can't align every single one of millions of crystallites in a powder at this angle, but we can instead rotate the whole sample rapidly about an axis inclined at the magic angle

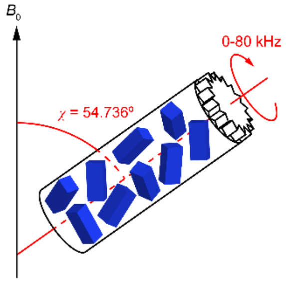
- This approach is called Magic Angle Spinning
  - If the rotation rate is fast enough, the crystallites appear to have an average orientation of 54.736°



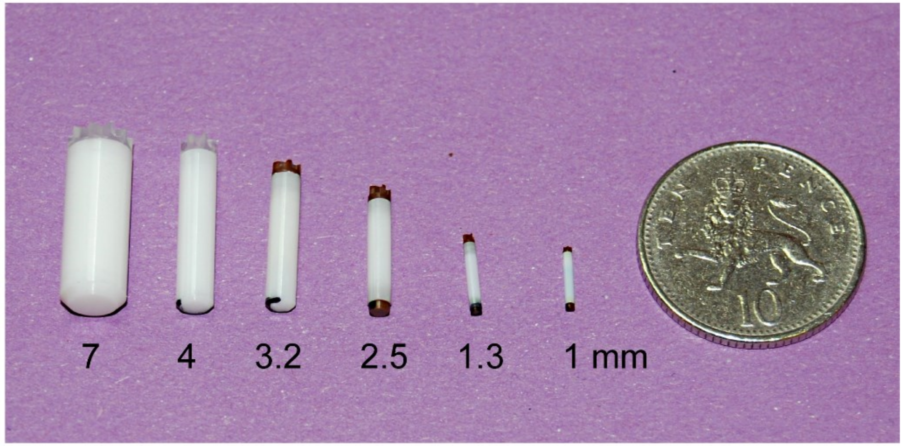


Beyond Static

- Nowadays achievable MAS rates can reach all the way up to >100 kHz
- The trade off between cost, availability, sample volume, frictional heating and sensitivity means that top speed isn't always the best choice

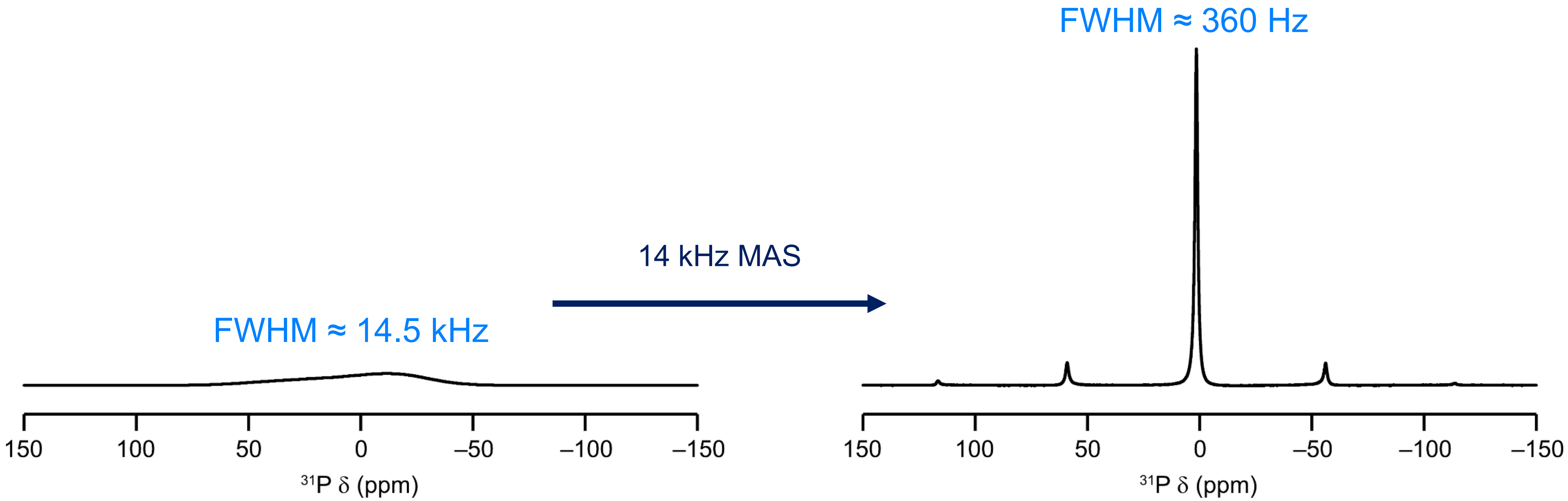


diameter / mm	top MAS rate / kHz	sample mass / mg
7	7	500
4	15	130
3.2	22	80
1.9	42	25
1.3	67	5
1	80	2
0.7	111	~1



The Magic of MAS

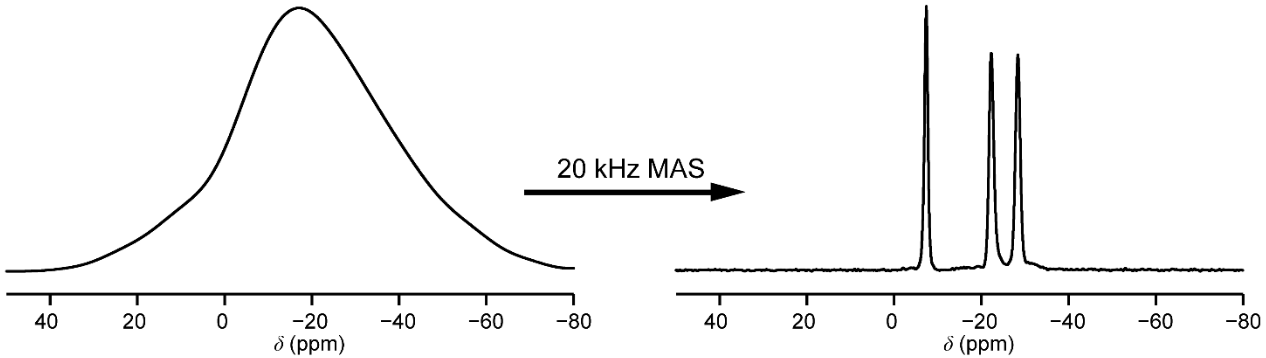
- Going back to our sample of $(NH_4)_2HPO_4$, MAS allows us to remove the CSA and the dipolar broadening, and increases the peak-height-to-noise sensitivity dramatically



The Magic of MAS

- MAS is essential when more than one signal is present

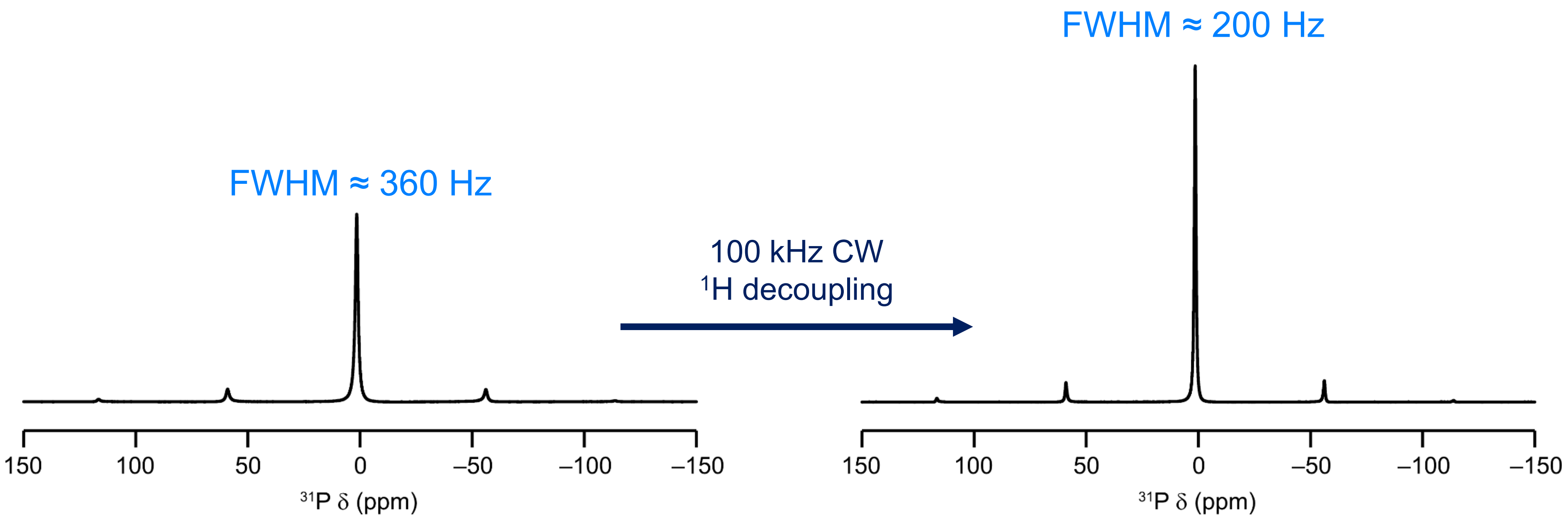
- Three sites clearly resolved in AlPO-34 with MAS



- Is a linewidth of hundreds of Hz really the best we can do for solids though?

MAS + Decoupling

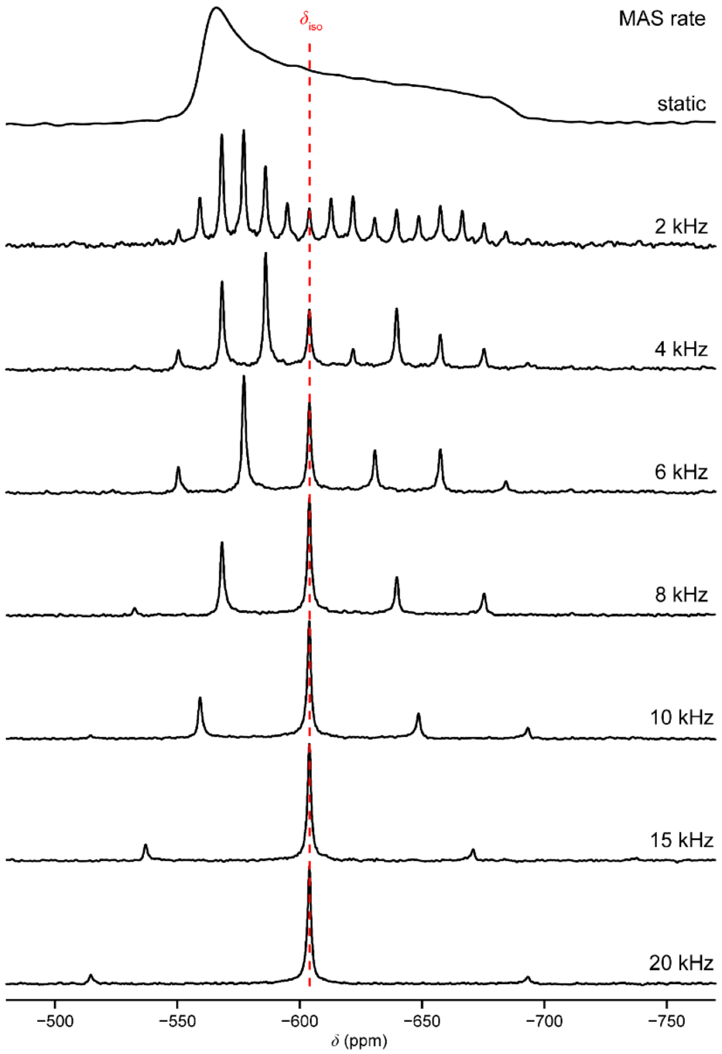
- We can average in spin space at the same time as in real space by combining MAS with decoupling to remove large dipolar couplings and smaller CSAs at moderate MAS rates



- Various inhomogeneities in solids (different magnetic environments in bulk/surface, potential defects, stacking faults, *etc*.) and practical effects (we don’t shim or set the magic angle for every experiment) contribute to residual linewidth

Spinning Sidebands

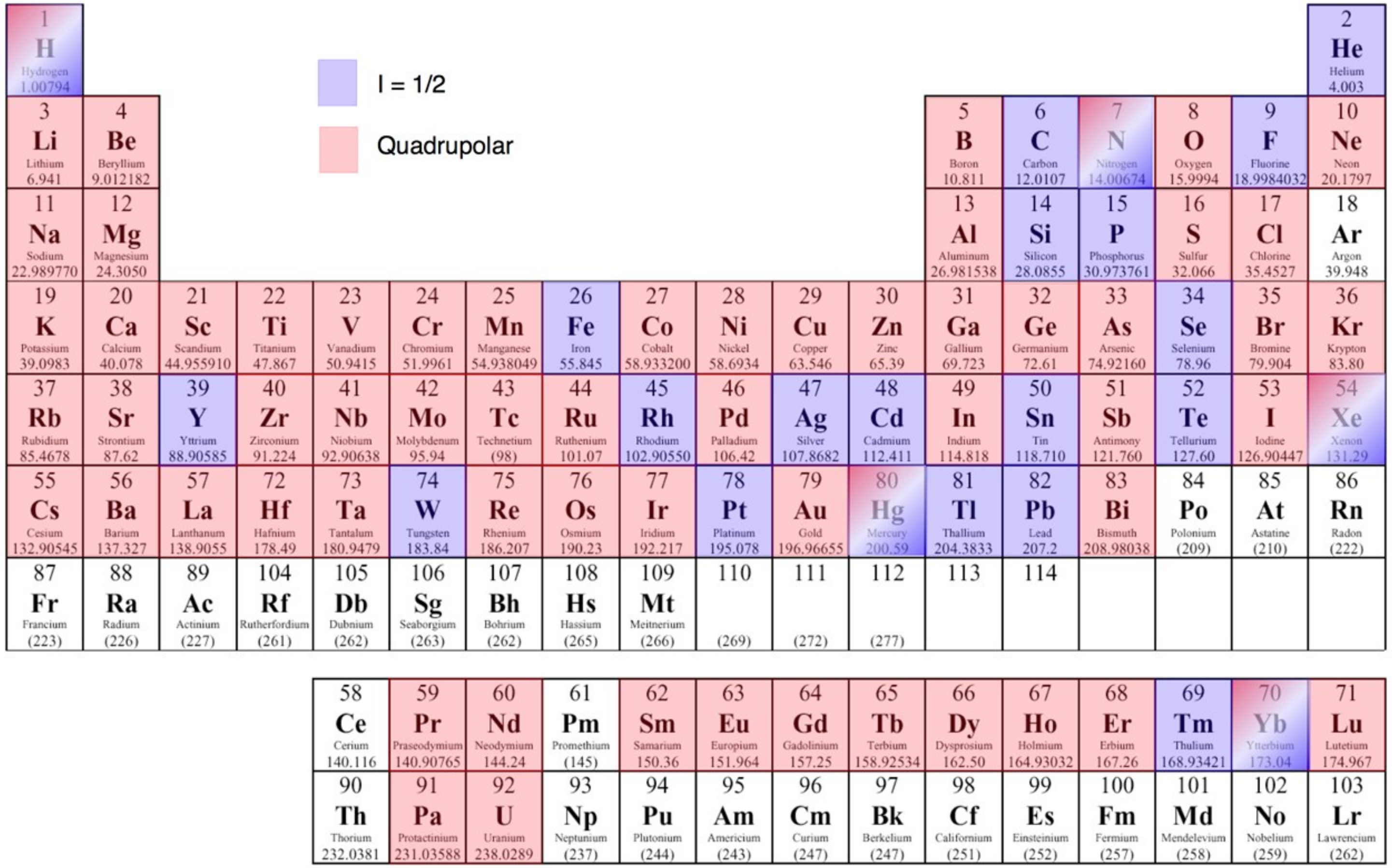
- How fast is “sufficiently fast” MAS?
- Depends what you want to see – usually taken to be
  - MAS rate > magnitude of interaction to average
- At slower MAS rates the spectrum will be separated into a series of spinning sidebands whose position varies with the MAS rate
  - Useful for identifying SSBs
- At very slow rates the intensities of the SSBs map out the static lineshape
  - May be useful for measuring CSAs of multiple sites



^{119}Sn NMR spectra of SnO_2

The Quadrupolar Interaction

- Many nuclei in the periodic table have spin > 1/2



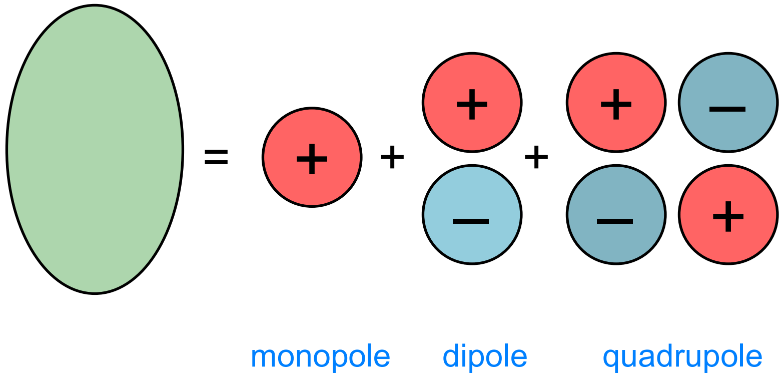
🟦 I = 1/2

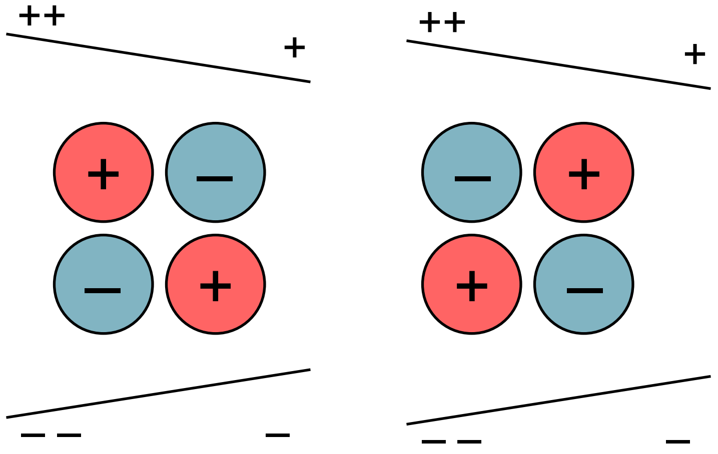
🟥 Quadrupolar

🟥🟦 1 H Hydrogen 1.00794																	🟦 2 He Helium 4.003
🟥 3 Li Lithium 6.941	🟥 4 Be Beryllium 9.012182											🟥 5 B Boron 10.811	🟦 6 C Carbon 12.0107	🟥🟦 7 N Nitrogen 14.00674	🟥 8 O Oxygen 15.9994	🟦 9 F Fluorine 18.9984032	🟥 10 Ne Neon 20.1797
🟥 11 Na Sodium 22.989770	🟥 12 Mg Magnesium 24.3050											🟥 13 Al Aluminum 26.981538	🟦 14 Si Silicon 28.0855	🟦 15 P Phosphorus 30.973761	🟥 16 S Sulfur 32.066	🟥 17 Cl Chlorine 35.4527	18 Ar Argon 39.948
🟥 19 K Potassium 39.0983	🟥 20 Ca Calcium 40.078	🟥 21 Sc Scandium 44.955910	🟥 22 Ti Titanium 47.867	🟥 23 V Vanadium 50.9415	🟥 24 Cr Chromium 51.9961	🟥 25 Mn Manganese 54.938049	🟦 26 Fe Iron 55.845	🟥 27 Co Cobalt 58.933200	🟥 28 Ni Nickel 58.6934	🟥 29 Cu Copper 63.546	🟥 30 Zn Zinc 65.39	🟥 31 Ga Gallium 69.723	🟥 32 Ge Germanium 72.61	🟥 33 As Arsenic 74.92160	🟦 34 Se Selenium 78.96	🟥 35 Br Bromine 79.904	🟥 36 Kr Krypton 83.80
🟥 37 Rb Rubidium 85.4678	🟥 38 Sr Strontium 87.62	🟦 39 Y Yttrium 88.90585	🟥 40 Zr Zirconium 91.224	🟥 41 Nb Niobium 92.90638	🟥 42 Mo Molybdenum 95.94	🟥 43 Tc Technetium (98)	🟥 44 Ru Ruthenium 101.07	🟦 45 Rh Rhodium 102.90550	🟥 46 Pd Palladium 106.42	🟦 47 Ag Silver 107.8682	🟦 48 Cd Cadmium 112.411	🟥 49 In Indium 114.818	🟦 50 Sn Tin 118.710	🟥 51 Sb Antimony 121.760	🟦 52 Te Tellurium 127.60	🟥 53 I Iodine 126.90447	🟥🟦 54 Xe Xenon 131.29
🟥 55 Cs Cesium 132.90545	🟥 56 Ba Barium 137.327	🟥 57 La Lanthanum 138.9055	🟥 72 Hf Hafnium 178.49	🟥 73 Ta Tantalum 180.9479	🟦 74 W Tungsten 183.84	🟥 75 Re Rhenium 186.207	🟥 76 Os Osmium 190.23	🟥 77 Ir Iridium 192.217	🟦 78 Pt Platinum 195.078	🟥 79 Au Gold 196.96655	🟥🟦 80 Hg Mercury 200.59	🟦 81 Tl Thallium 204.3833	🟦 82 Pb Lead 207.2	🟥 83 Bi Bismuth 208.98038	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (262)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114				
				58 Ce Cerium 140.116	🟥 59 Pr Praseodymium 140.90765	🟥 60 Nd Neodymium 144.24	61 Pm Promethium (145)	🟥 62 Sm Samarium 150.36	🟥 63 Eu Europium 151.964	🟥 64 Gd Gadolinium 157.25	🟥 65 Tb Terbium 158.92534	🟥 66 Dy Dysprosium 162.50	🟥 67 Ho Holmium 164.93032	🟥 68 Er Erbium 167.26	🟦 69 Tm Thulium 168.93421	🟥🟦 70 Yb Ytterbium 173.04	🟥 71 Lu Lutetium 174.967
				90 Th Thorium 232.0381	🟥 91 Pa Protactinium 231.03588	🟥 92 U Uranium 238.0289	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

The Quadrupolar Interaction

- Nuclei with I > 1/2 have a non-spherical charge distribution at the nucleus giving rise to a nuclear electric quadrupole moment, eQ

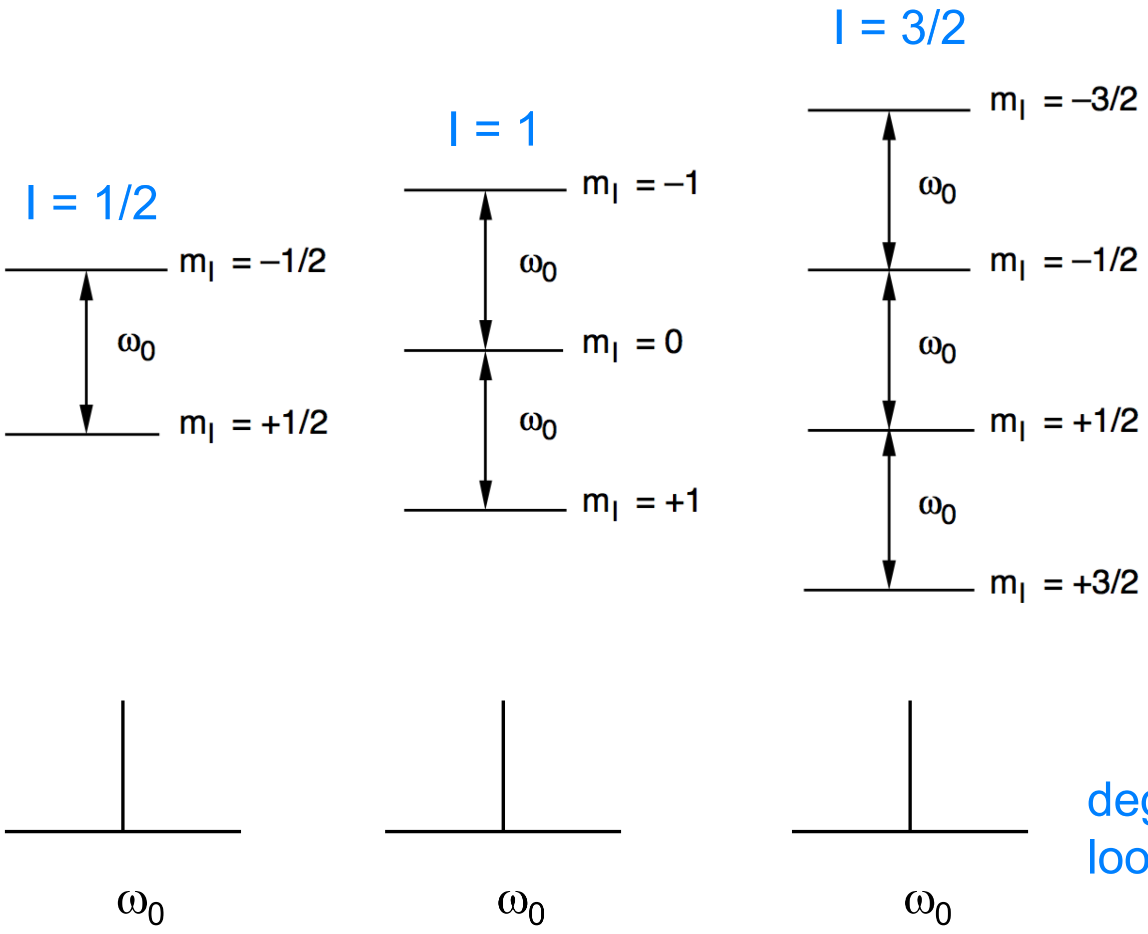




- If an Electric Field Gradient is present at the nucleus (*i.e.* if symmetry is less that spherical) then this will interact with the quadrupole moment

The Quadrupolar Interaction

- Quadrupolar nuclei have multiple Zeeman states



degenerate transitions when we only look at the Zeeman interaction

The Quadrupolar Interaction

- The quadrupolar Hamiltonian involves the spin interacting with itself via the EFG tensor, **V**

$$H_Q = \frac{eQ}{2I(2I-1)\hbar}\mathbf{I}\cdot\mathbf{V}\cdot\mathbf{I} = \frac{eQ}{2I(2I-1)\hbar}\begin{pmatrix} I_x & I_y & I_z \end{pmatrix}\begin{pmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{pmatrix}\begin{pmatrix} I_x \\ I_y \\ I_z \end{pmatrix}$$

- In the PAS, **V** is diagonal
  - $|V_{ZZ}| \geq |V_{XX}| \geq |V_{YY}|$

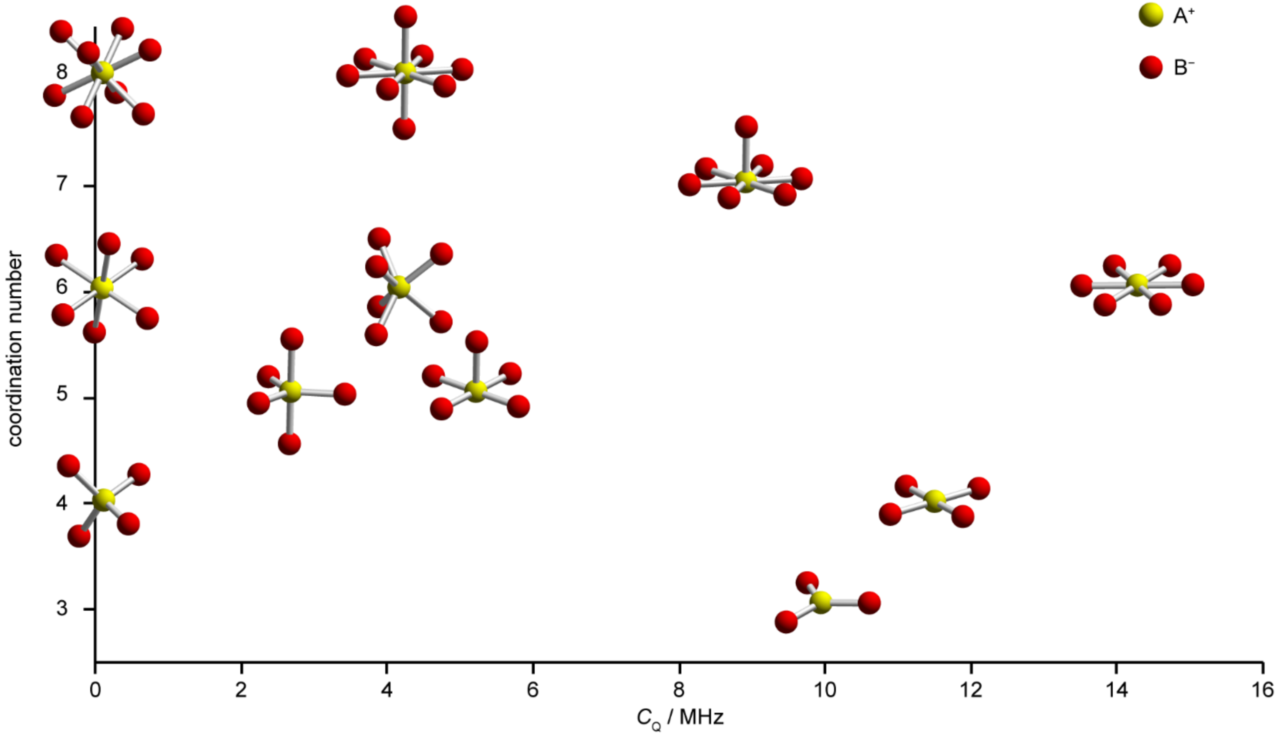
$$\begin{pmatrix} V_{XX} & 0 & 0 \\ 0 & V_{YY} & 0 \\ 0 & 0 & V_{ZZ} \end{pmatrix}$$

- The magnitude of the interation is given by the quadrupolar coupling constant
  - $C_Q = eQV_{ZZ}/h$

- The asymmetry, or “shape” parameter is defined similarly to the CSA
  - $\eta_Q = (V_{YY} - V_{XX})/V_{ZZ}$

The Quadrupolar Interaction

- The EFG is caused by charge distribution (*i.e.*, where atoms, electrons and ions are nearby)
- Large interaction (~MHz scale) so sensitive to long-range effects but usually dominated by the first coordination sphere

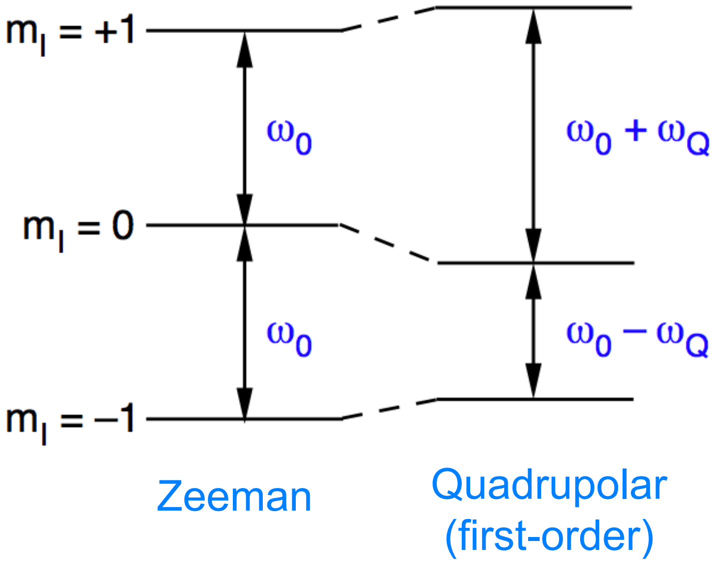


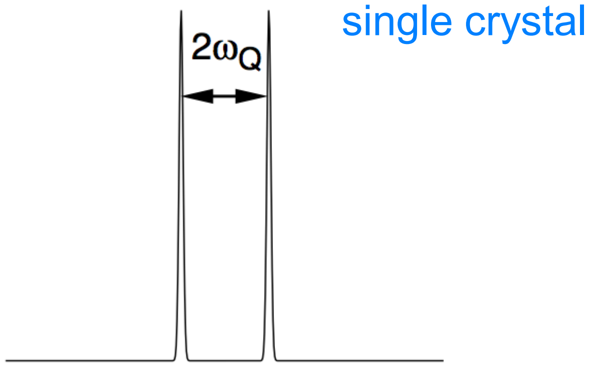
This example uses ^{23}Na and O^{2-}, interactions can be much larger or smaller depending on eQ

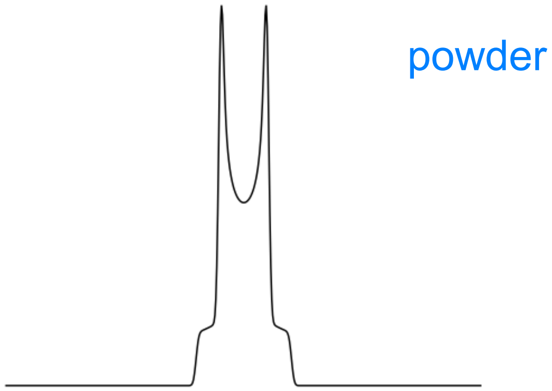
C_Q = 0 for high symmetry

The Quadrupolar Interaction

- For spin I = 1 the quadrupolar interaction lifts the degeneracies of the two transitions







$$\omega_Q = \omega_Q^{PAS} \frac{1}{2}(3\cos^2\theta - 1 + \eta_Q \sin^2\theta \cos 2\gamma) \qquad \omega_Q^{PAS} = 3C_Q / 4I(2I - 1)$$

- Again we have a spin-dependent part and an orientation-dependent part

The Quadrupolar Interaction

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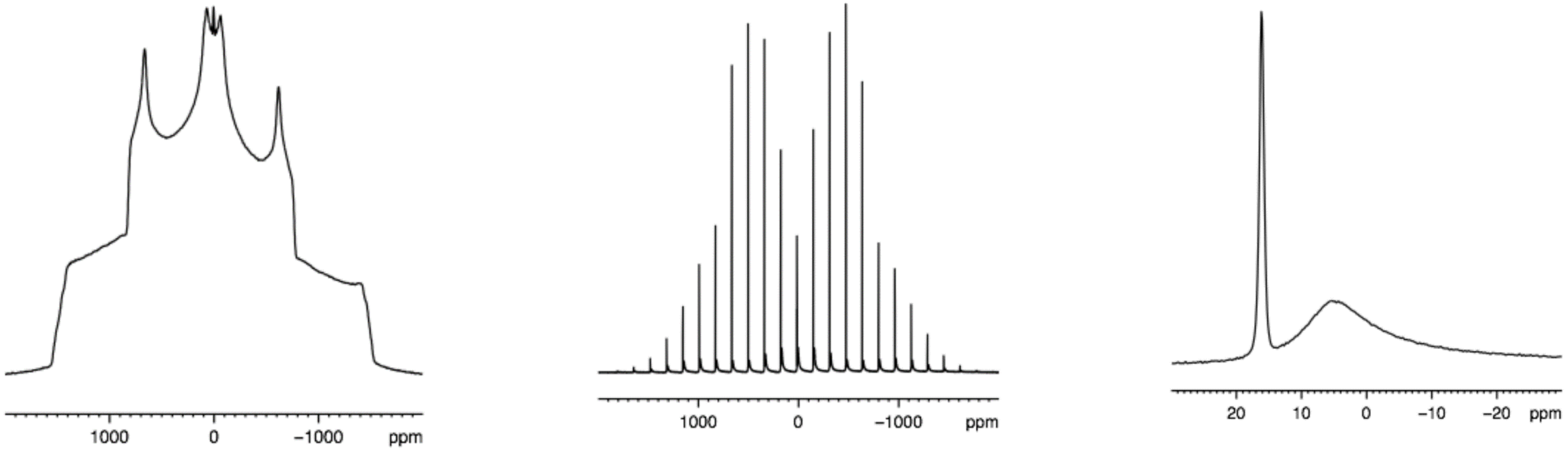
- In theory we can remove this with MAS but in practice C_Q is hundreds of kHz for ^{2}H and ^{6}Li, MHz for ^{14}N, and there aren't any other integer spin quadrupolar nuclei worth looking at*



^{2}H NMR spectra of oxalic acid hydrate $(CO_2D)_2.D_2O$

static

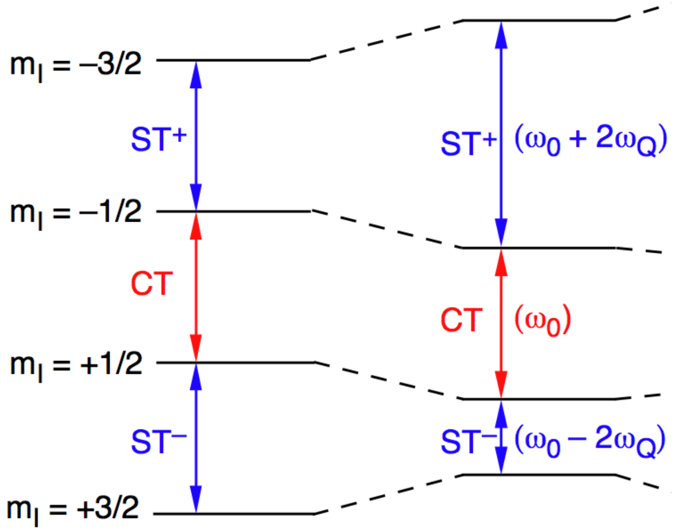
10 kHz MAS

sharp isotropic peaks

*the complete list is I = 1: ^{2}H, ^{6}Li, ^{14}N; I = 3: ^{10}B; I = 5: ^{138}La; I = 6: ^{50}V; I = 7: ^{176}Lu

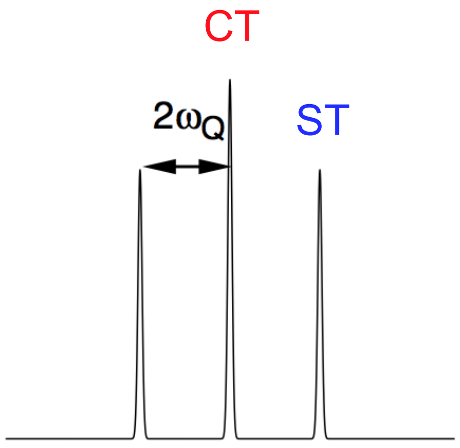
The Quadrupolar Interaction

- For spin I = 3/2 the quadrupolar interaction lifts the degeneracies of the three transitions

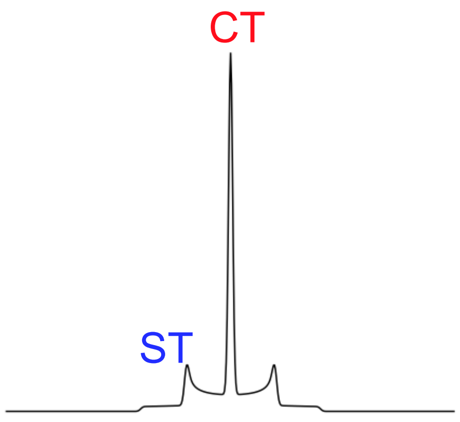


Zeeman

Quadrupolar (first-order)



single crystal

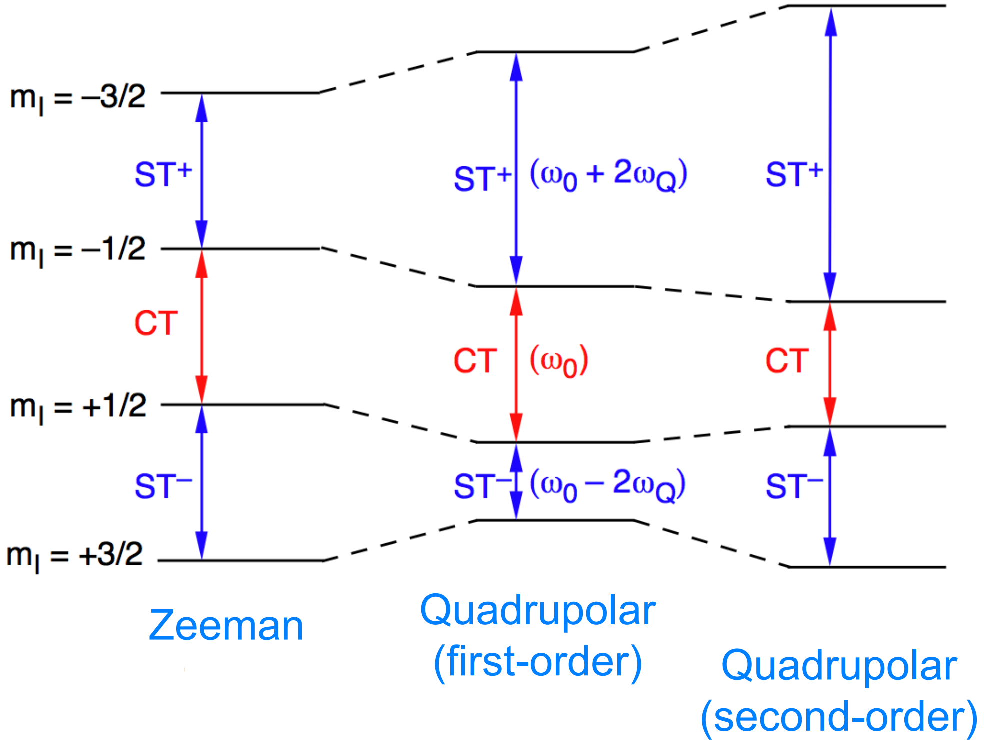


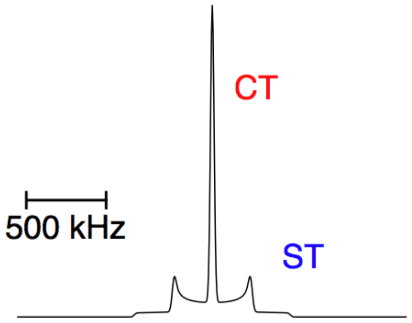
powder

- With a small C_Q the CT remains sharp and the STs are broadened into a Pake doublet

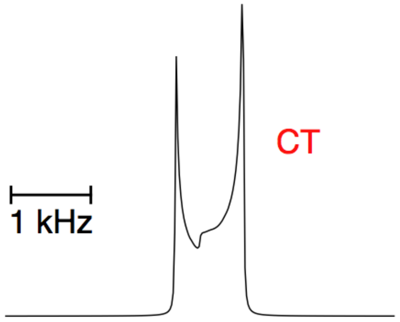
The Quadrupolar Interaction

- For larger C_Q (more than a few hundred kHz) we must consider a second order perturbation





first-order



second order (CT only)

The Quadrupolar Interaction

- The second-order perturbation is

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

- The spin space term is field dependent ($1/B_0$)
- There is now an isotropic quadrupolar shift term
- The second-rank anisotropic term can be removed by MAS
- The fourth rank anisotropic term has more complicated orientation dependence

$$d^2_{00}(\theta) = 1/2\,(3\cos^2\theta - 1)$$

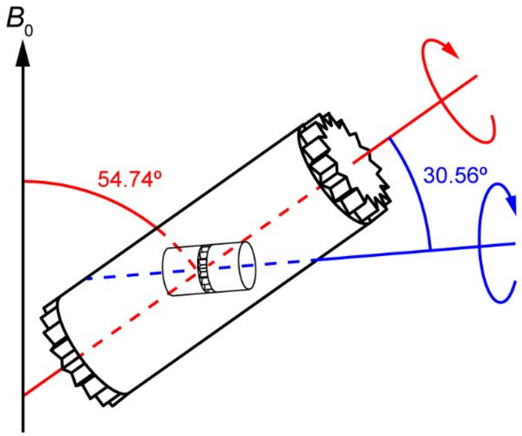
$$d^4_{00}(\theta) = 1/8\,(35\cos^4\theta - 30\cos^2\theta + 3)$$

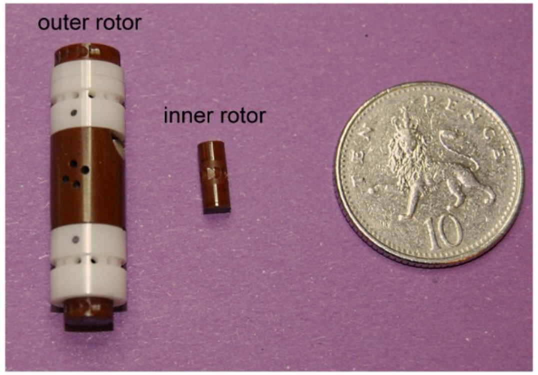
- With MAS the fourth-rank anisotropic term is reduced to about 0.39

High-Resolution Quadrupolar NMR

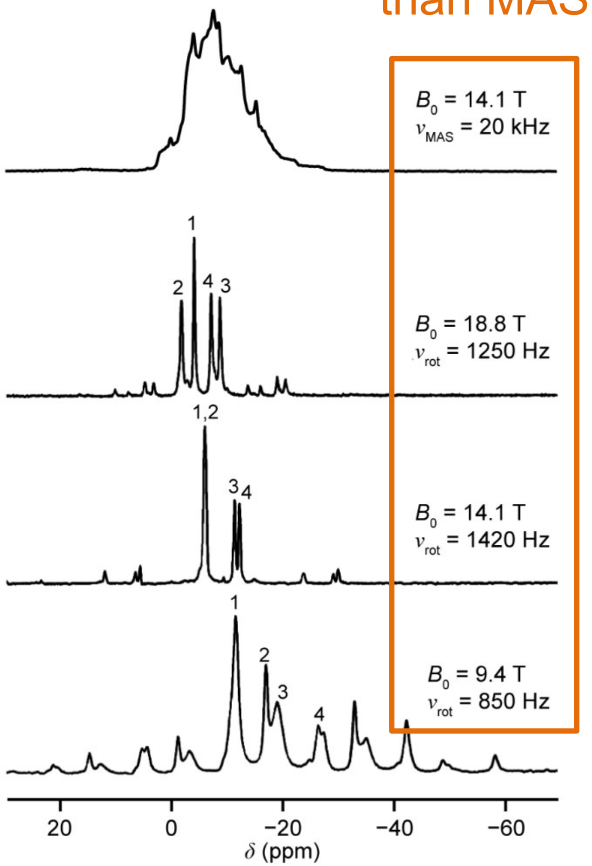
$$\omega = \frac{\left(\omega_Q^{PAS}\right)^2}{\omega_0}\left[A + B\, d^2_{00}(\theta) + C\, d^4_{00}(\theta)\right]$$

- Averaging in real space would require spinning round two angles simultaneously, 54.736° and 30.56° or 70.12°
- This sounds insane but DOuble Rotation NMR was the only answer for many years...
- Used multiple-field data to separate δ_{iso} and δ_Q





much slower rotation rates than MAS



High-Resolution Quadrupolar NMR

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

- Averaging in spin space requires a two-dimensional Multiple Quantum (MQ) MAS or Satellite Transition (ST) MAS experiment

- MQMAS correlates the CT with the symmetric $m_I = n/2 \leftrightarrow m_I = -n/2$ transition (typically $n = 3$). Since $\Delta m_I \neq 1$, this transition is forbidden and the experiment is very insensitive

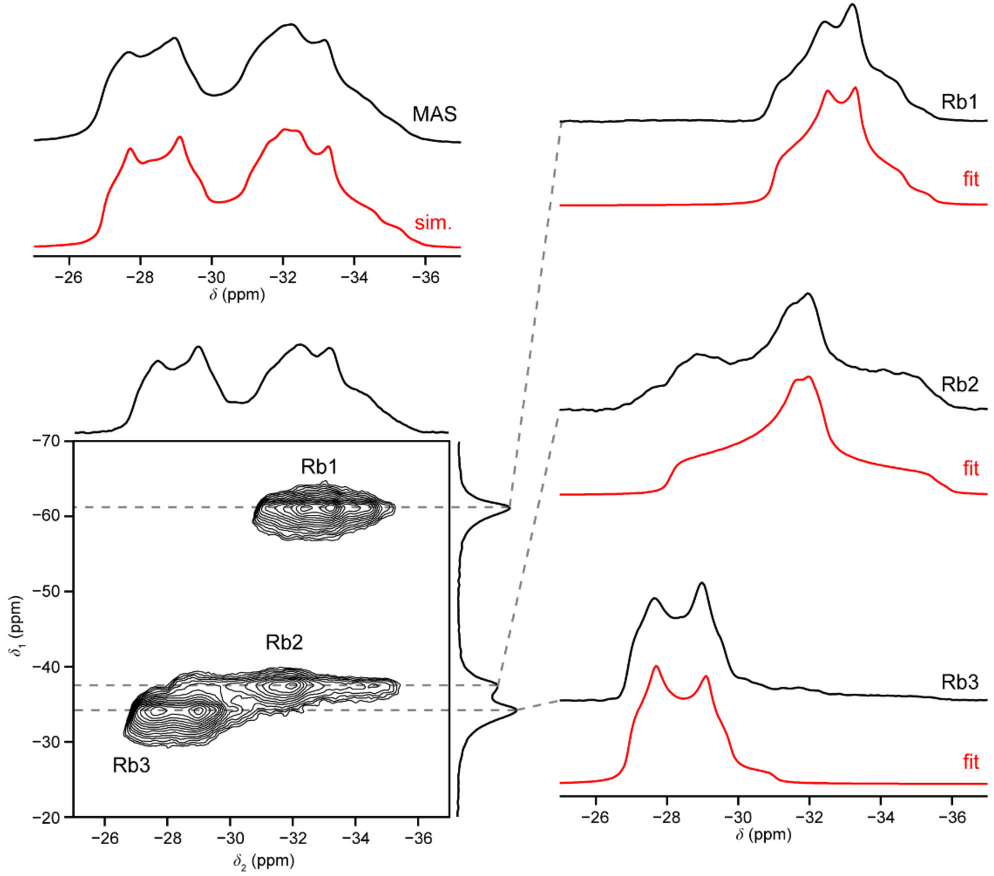
- STMAS correlates the CT with one of the STs $m_I = \pm n/2 \leftrightarrow m_I = \pm(n+1)/2$ (typically $n = 1$). The ST is allowed but very broad so the magic angle must be perfectly set and the spinning must be perfectly stable

High-Resolution Quadrupolar NMR

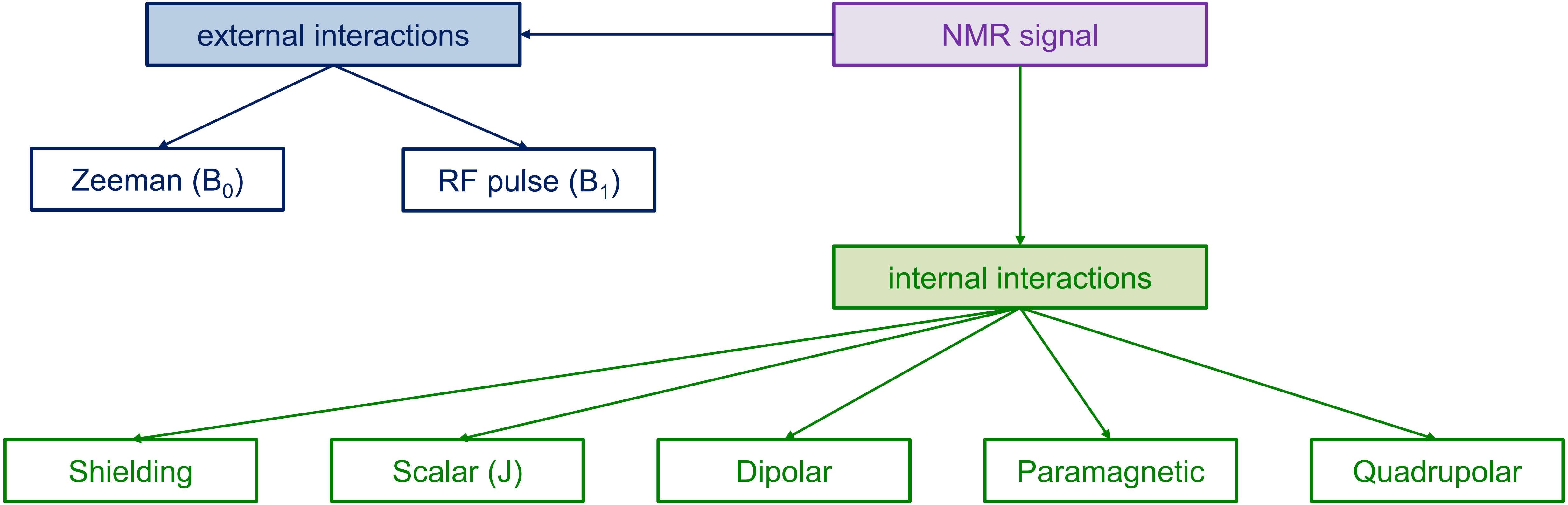
$$\omega = \frac{\left(\omega_Q^{PAS}\right)^2}{\omega_0}\left[A + B\, d^2_{00}(\theta) + C\, d^4_{00}(\theta)\right]$$

- Both experiments exploit the fact that A, B and C are different for different transitions
- After appropriate processing, the 2D spectrum contains ridges parallel to δ_2
- The projection onto δ_1 is the isotropic spectrum
- The ridges are MAS lineshapes for each separate signal

^{87}Rb NMR of RbNO$_3$



Summary: Interactions



external interactions

NMR signal

Zeeman (B_0)

RF pulse (B_1)

internal interactions

Shielding

Scalar (J)

Dipolar

Paramagnetic

Quadrupolar

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

Summary: Interactions

- Interactions in NMR have components in spin space and real space

- Decoupling in spin space works just like in solution
  - removes D and J
  - no effect on chemical shift or quadrupolar interactions

- MAS removes or reduces anisotropic terms with $(3\cos^2\theta - 1)/2$ orientation dependence
  - removes D, J anisotropy, chemical shift anisotropy, 1st order quadrupolar
  - reduces 2nd order quadrupolar
  - leaves isotropic chemical and quadrupolar shifts, J splitting

- Quadrupolar nuclei are more complicated and for truly isotropic spectra you need MQMAS (or STMAS or DOR)

Where can I do Solid-State NMR?

- 300 MHz – Edinburgh (automated sample changer for 4 mm HX probe with X detect only)
- 400 MHz – Heriot Watt (4 mm HRMAS probe)
- 400 MHz – St Andrews (7-1.3 mm probes, low-γ, HFX and HFXY capabilities)
- 600 MHz – St Andrews (4-1.3 mm probes, low-γ, HX, FX and HXY capabilities)
- 800 MHz – SHF lab at Edinburgh (3.2-1.3 mm probes, low-γ, HX, FX and HXY capabilities)
- 850-1200 MHz – NRF at Warwick (7-0.7 mm probes, whole range of specialist capabilities, free access and conference bursaries available if you present results from the NRF)