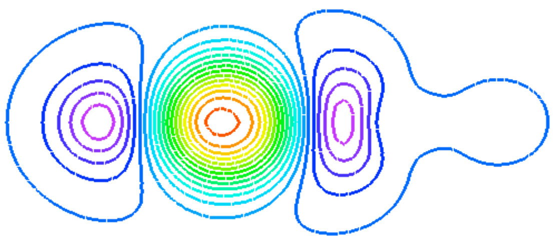
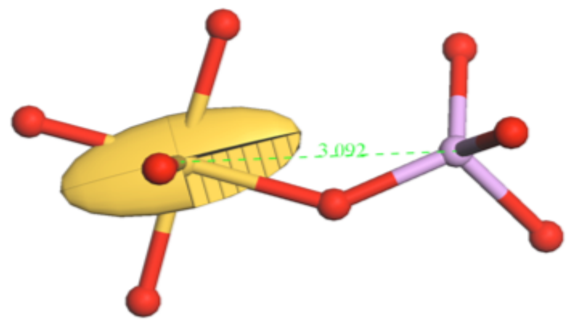
THE UNIVERSITY of York

Solid-state Nuclear Magnetic Resonance (NMR)



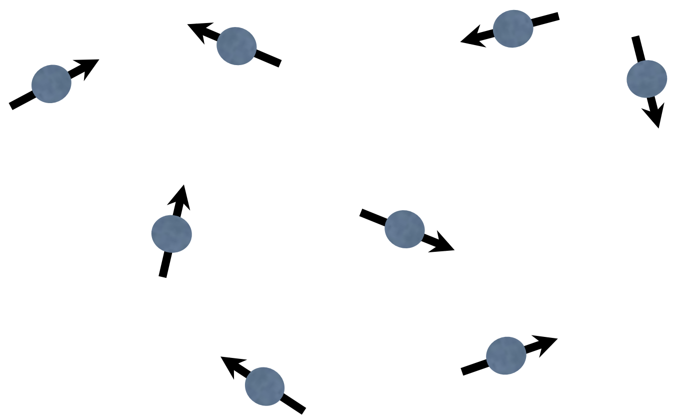


Phil Hasnip
Condensed Matter Dynamics Group
Department of Physics,
University of York, U.K.
http://www-users.york.ac.uk/~pjh503

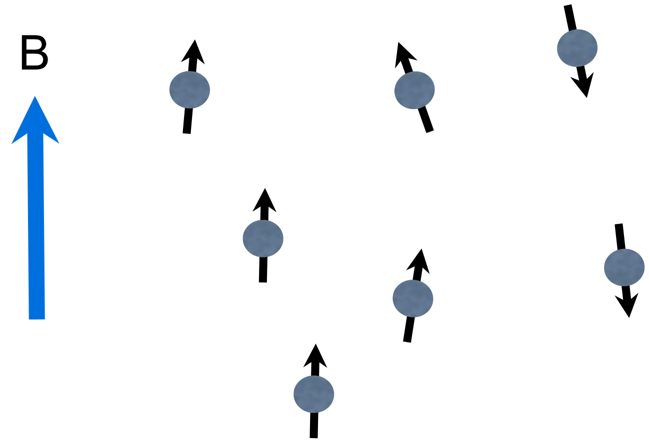
Many slides courtesy of Jonathan Yates (University of Oxford)

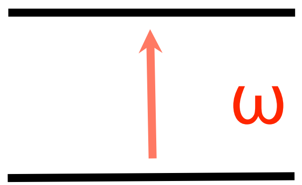
Nuclear Magnetic Resonance

Zero Field



Applied Field





$\omega = \gamma\ B$

magnetogyric ratio

fundamental nuclear constant

NMR signal is proportional to population difference

For ^{1}H in 9.4T at 298K

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

$n_{upper}/n_{lower} \quad = \exp(-\Delta E / kT)$

$= 0.999935$

Sensitivity is an issue! Need Large γ and/or B

Common Isotopes

Isotope	Spin	γ $10^7\ T^{-1}\ rad\ s^{-1}$	Freq MHz @ 9.4T	Abundance %
^{1}H	1/2	26.75	400	100
^{13}C	1/2	6.73	100.6	1.1
^{29}Si	1/2	-5.32	79.6	4.7
^{31}P	1/2	-10.84	162.1	100

Common Isotopes

Isotope	Spin	γ 10^7 T^{-1} rad s^{-1}	Freq MHz @ 9.4T	Abundance %
^{1}H	1/2	26.75	400	100
^{13}C	1/2	6.73	100.6	1.1
^{29}Si	1/2	-5.32	79.6	4.7
^{31}P	1/2	-10.84	162.1	100
^{17}O	5/2	-3.63	54.1	0.04
^{49}Ti	7/2	-1.51	22.6	5.41

THE UNIVERSITY of York

Solid-State NMR Spectrometers

600 MHz 14.1 T
~£800,000

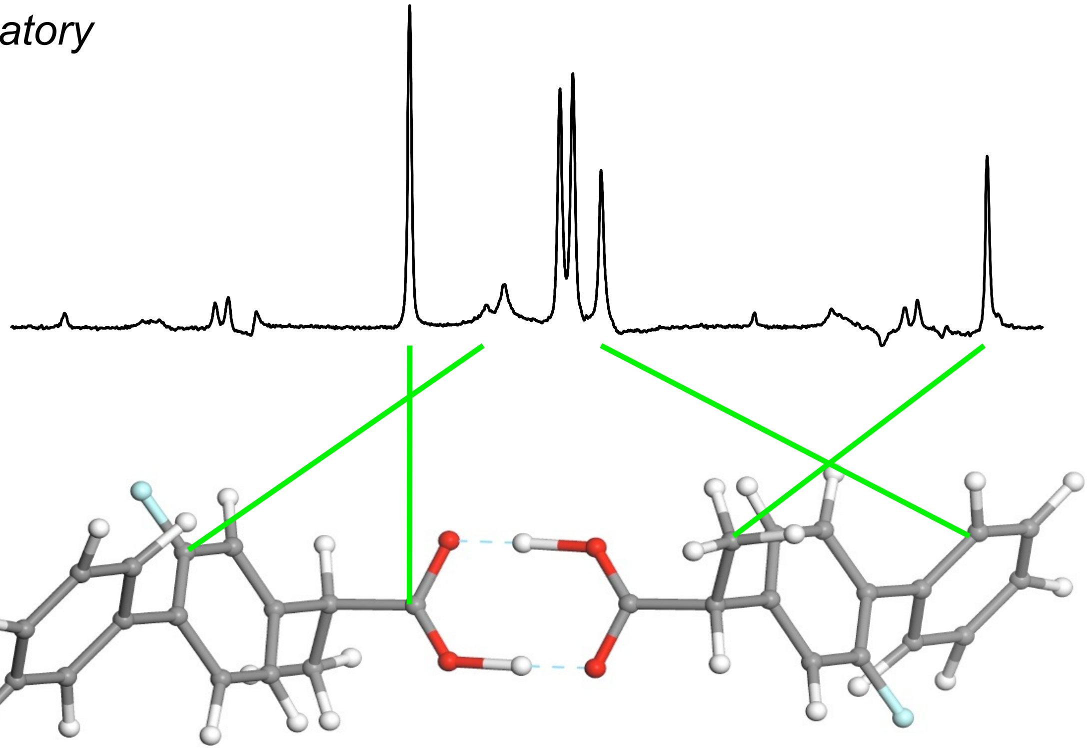
400 MHz 9.4 T
~£300,000

Image courtesy Sharon Ashbrook (St Andrews)

Magnetic Shielding

Flurbiprofen

non-steroidal anti-inflammatory



Each distinct C atom experiences a different magnetic field and resonates at a unique frequency.

Measure the change wrt a standard (for ^{13}C this is liquid tetramethylsilane)

Magnetic Shielding

The local field a nucleus feels is not quite the same as the applied field (B_0). The local field is influenced by the positions of neigbouring atoms and the electronic structure of the material. Hence ***NMR is a sensitive probe of atomic-level structure and dynamics.***

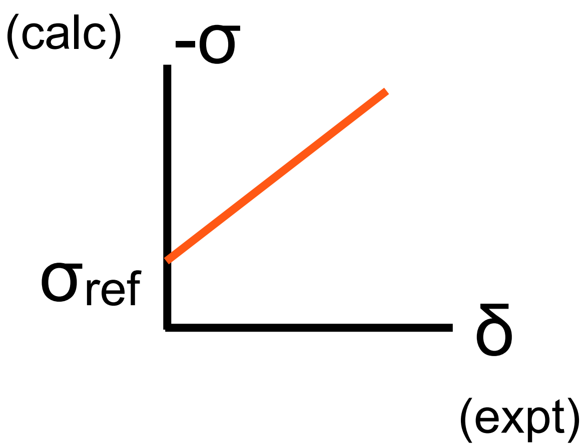
Larmor frequency $\omega = \gamma B$

σ magnetic shielding

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

δ chemical shift

$$\delta = \sigma_{ref} - \sigma$$



σ_{ref} is the shielding of a nucleus in a "standard" material. For ^{13}C this is liquid tetramethylsilane.

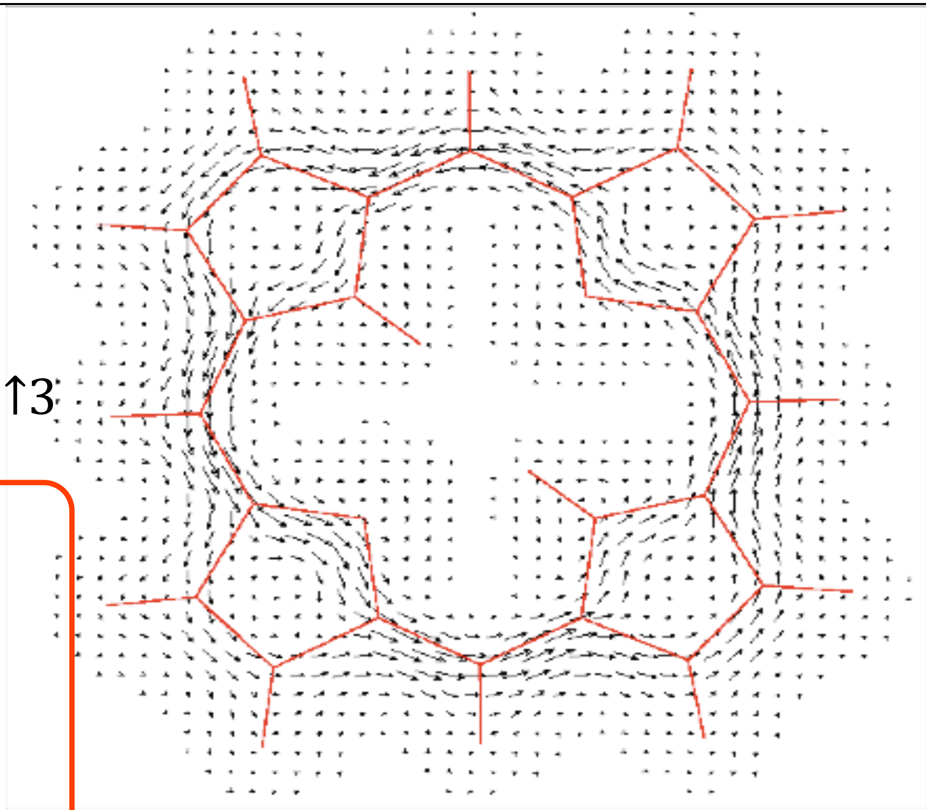
THE UNIVERSITY of York

Induced Current

To compute the chemical shifts we just need to calculate the current induced by the external magnetic field

Biot-Savart: induced magnetic field is

$$B_{in}(r) = \frac{1}{c}\int d^3r' \, j(r') \times \frac{r-r'}{|r-r'|^3}$$



Obtain current within perturbation theory (linear response)

$$O = O^{(0)} + O^{(1)} + \mathcal{O}(\mathbf{B}^2)$$

spin contribution averages to zero in a diamagnetic insulator

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

$$B_{in} = -\sigma\, B_0$$

note: σ is a rank 2 tensor

First-principles NMR

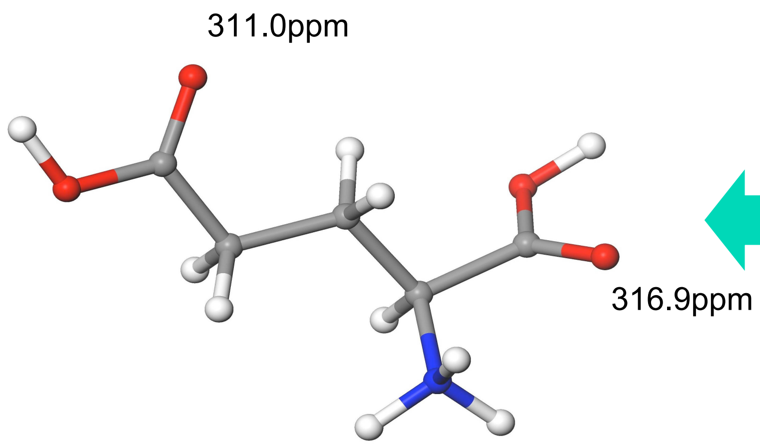
Crystal Structure

X-ray, Neutron diffraction
Cambridge Structural Database

```
C1 -0.602 -0.537 6.384
C2  0.135  0.622 5.689
H1  0.257  0.361 4.639
...
```

Calculate forces
refine structure

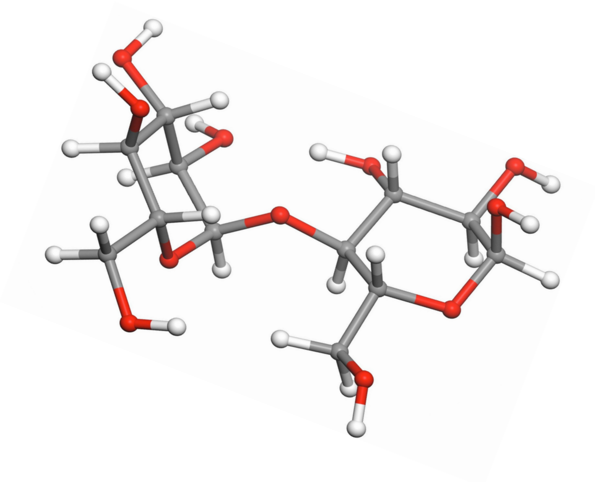
Calculate chemical
shifts



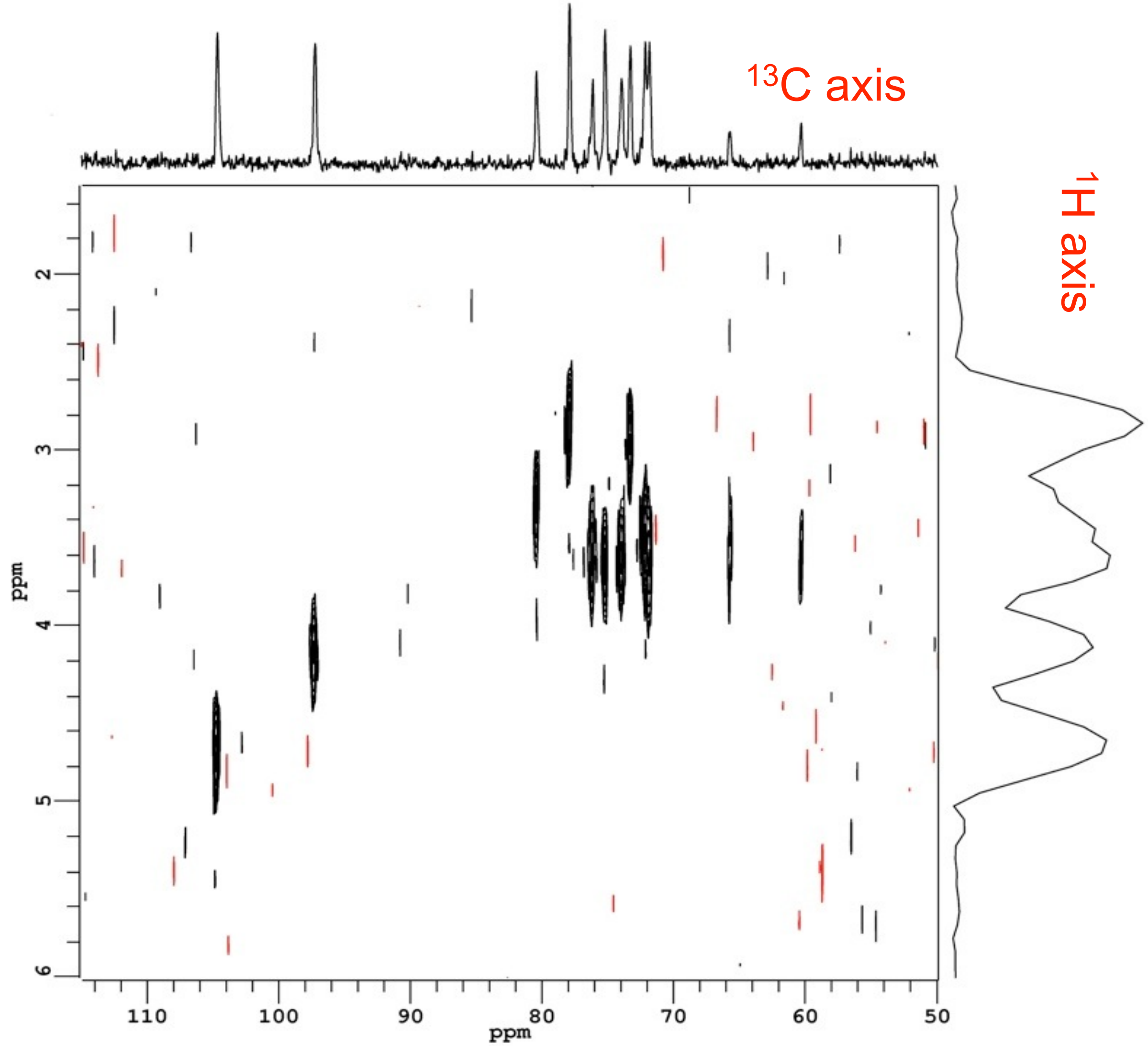
Examples

Maltose

sugar used in brewing



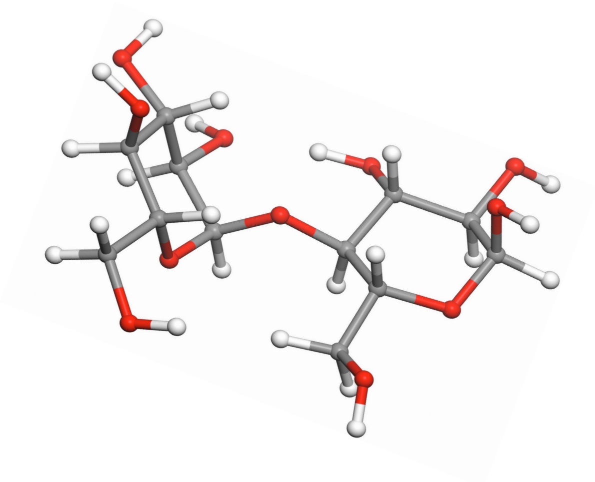
MAS-J-HMQC



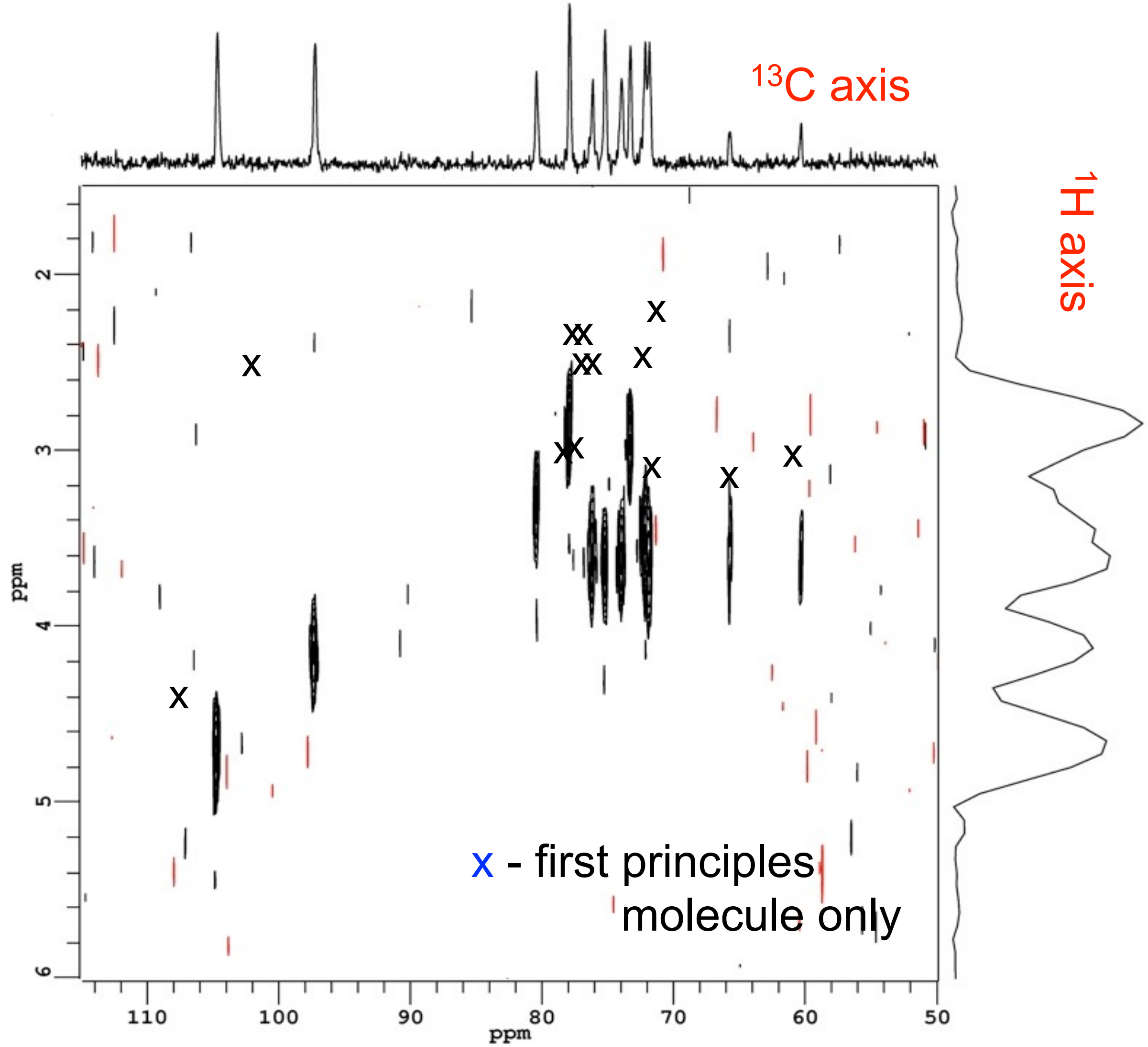
Examples

Maltose

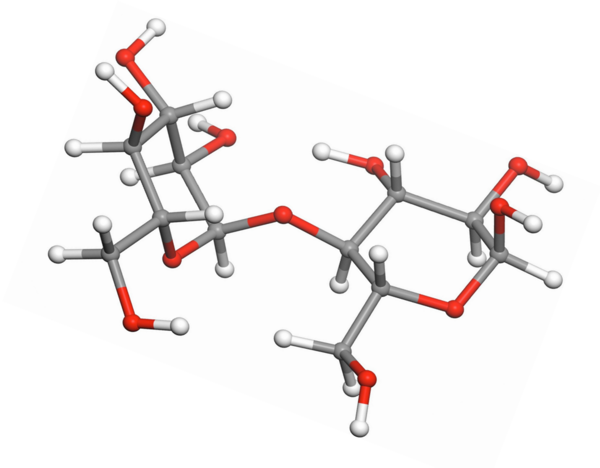
sugar used in brewing

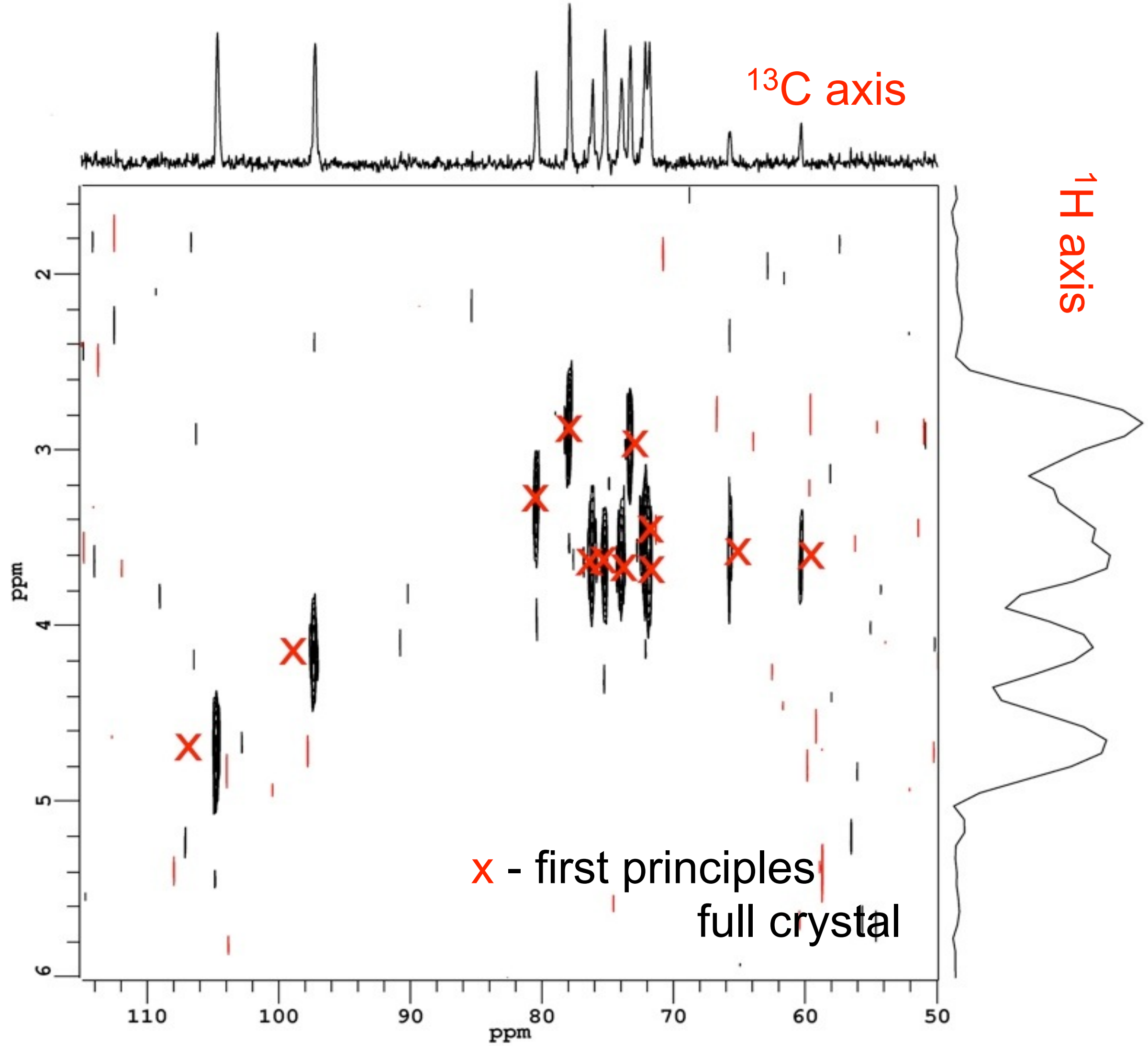


MAS-J-HMQC



Examples





Molecule to solid variation due to intermolecular interactions (weak hydrogen bonds)

J. Am. Chem. Soc. 127 10216 (2005)

Magnetic Fields - an aside

Can create a magnetic field in two ways:

1. Intrinsic spin of electrons (i.e. a magnetisation density)
2. Charge of electrons (moving charge gives magnetic field)

Induced Field

$$\mathbf{B}^{(1)}_{\text{in}}(\mathbf{R}_{\text{K}}) = \frac{\mu_0}{4\pi}\int \mathbf{m}^{(1)}(\mathbf{r}) \cdot \left[\frac{3\mathbf{r}_{\text{K}}\mathbf{r}_{\text{K}} - |\mathbf{r}_{\text{K}}|^2}{|\mathbf{r}_{\text{K}}|^5}\right] \mathrm{d}^3\mathbf{r} + \frac{\mu_0}{4\pi}\frac{8\pi}{3}\int \mathbf{m}^{(1)}(\mathbf{r})\delta(\mathbf{r}_{\text{K}})\,\mathrm{d}^3\mathbf{r}$$

$$+ \frac{\mu_0}{4\pi}\int \mathbf{j}^{(1)}(\mathbf{r}) \times \frac{\mathbf{r}_{\text{K}}}{|\mathbf{r}_{\text{K}}|^3}\,\mathrm{d}^3\mathbf{r}.$$

Spin Dipolar

Fermi Contact

Orbital

Spin Hamiltonian

$$H_{eff} = -\sum_{\mathrm{K}} \gamma_{\mathrm{K}} \mathbf{I}_{\mathrm{K}} (1 + \sigma_{\mathrm{K}}) \mathbf{B}_{\mathrm{ext}} + \sum_{\mathrm{K<L}} \mathbf{I}_{\mathrm{K}} (\mathbf{D}_{\mathrm{KL}} + \mathbf{J}_{\mathrm{KL}}) \mathbf{I}_{\mathrm{L}}$$

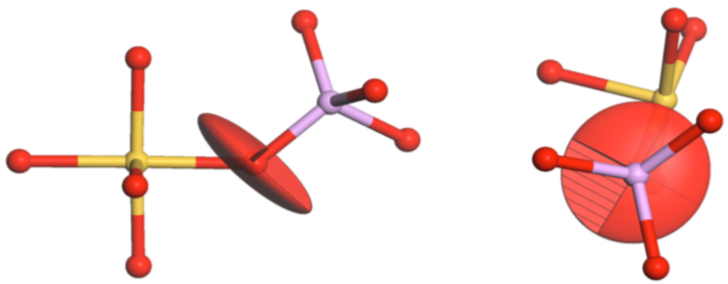
NMR experiments aim to control nuclear spins (I) and external field (B) to measure NMR interaction tensors

We aim to calculate NMR tensors via the quantum mechanics of electrons

Spectral simulation via nuclear spin dynamics codes

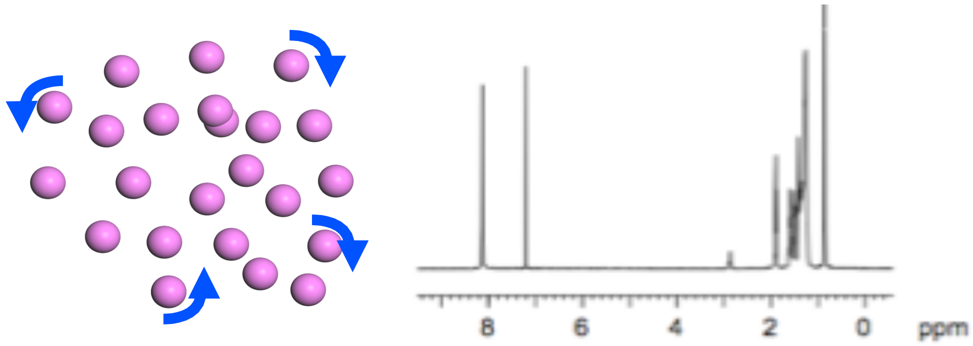
All are tensor properties

$^{1}J_{PO}$

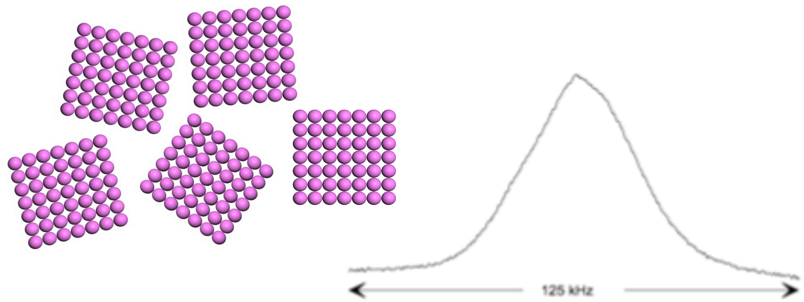


Magic Angle Spinning

Liquid

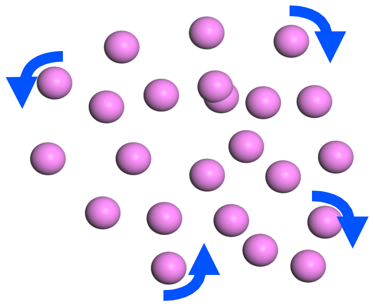


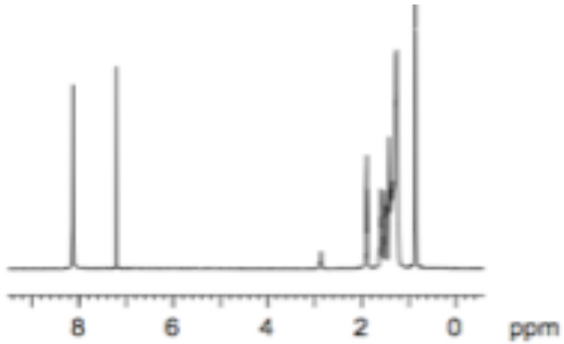
Powdered Solid

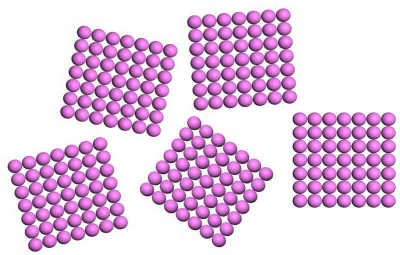


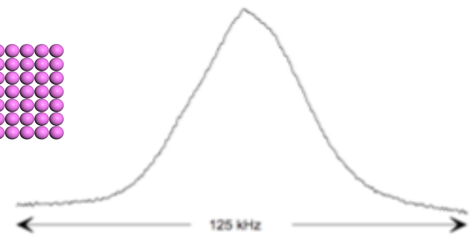
Magic Angle Spinning

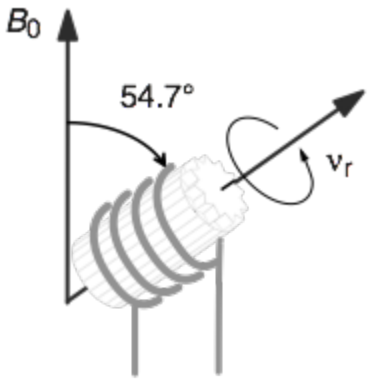
Liquid	Powdered Solid



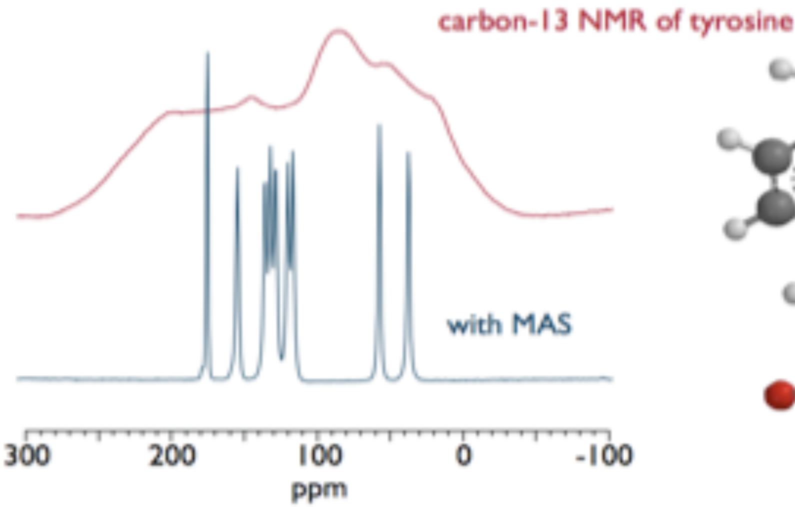


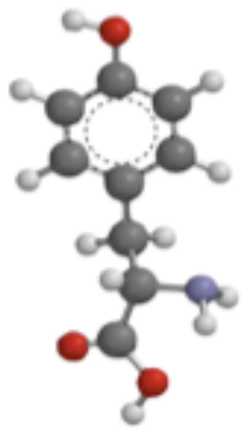






Anisotropic interactions have first order term proportional to ($3\cos^2\theta - 1$)





NMR Interactions

Chemical Shift

orbital currents create magnetic field

Direct Dipolar Coupling

magnetic field created by neighbouring nuclei

n.b. function of atom positions only i.e. not directly an electronic property

Quadrupolar coupling

nuclei with I>1/2 interact with gradient of electric field (non-spherical charge density)

spin-spin coupling (J-coupling)

magnetic field induced by neighbouring nuclei but mediated via valence electrons

Simulation of Observed Spectra

In general not a simple function of NMR interaction tensors. Need to consider experimental conditions (which NMR experiment). Several sophisticated codes to handle this e.g. SIMPSON, Spinevolution (virtual spectrometers)

Magnetic Shielding

Effective Hamiltonian

$$H = -\frac{1}{2\pi}\sum_{K}\gamma_K \mathbf{I}_K(\mathbf{1}-\boldsymbol{\sigma}_K)\mathbf{B}_{\text{ext}}$$

Bare   Dressed

Magnetic Shielding

$$\boldsymbol{\sigma}_K = \frac{\partial^2 E}{\partial \boldsymbol{\mu}_K \partial \boldsymbol{B}_{\text{ext}}}$$

Electronic Response

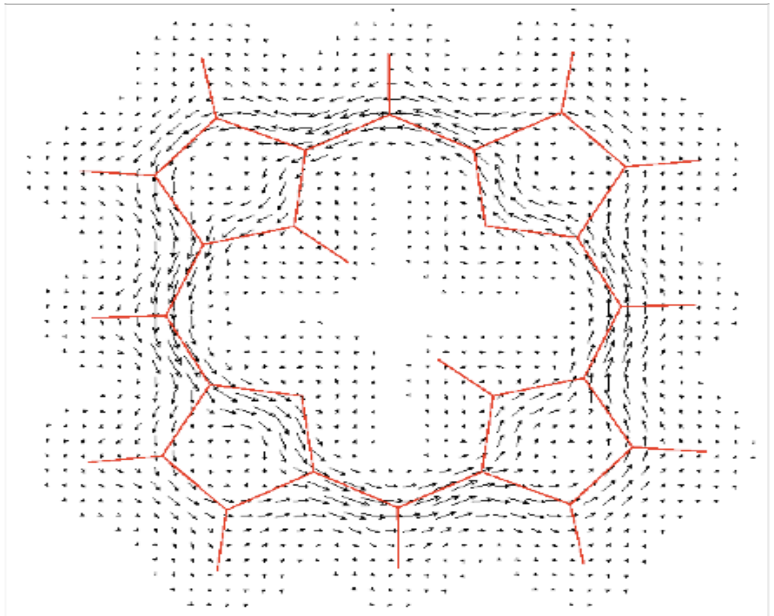
Induced Current $\mathbf{j}$(r)   Spin Polarisation $\mathbf{m}$(r)

both cause induced magnetic field at nucleus

Induced Field

$$\mathbf{B}_{\text{in}}(\mathbf{R}_K) = \frac{\mu_0}{4\pi}\int \mathbf{j}^{(1)}(\mathbf{r}) \times \frac{\mathbf{r}_K}{|\mathbf{r}_K|^3}\,\mathrm{d}^3\mathbf{r}.$$

$$\boldsymbol{\sigma}_K = -\frac{\mathbf{B}_{\text{in}}(\mathbf{R}_K)}{\mathbf{B}_{\text{ext}}}$$

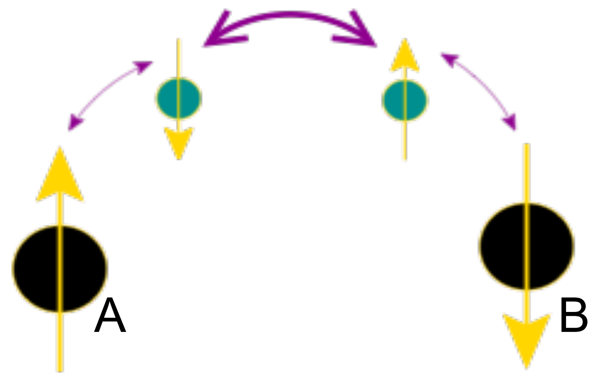


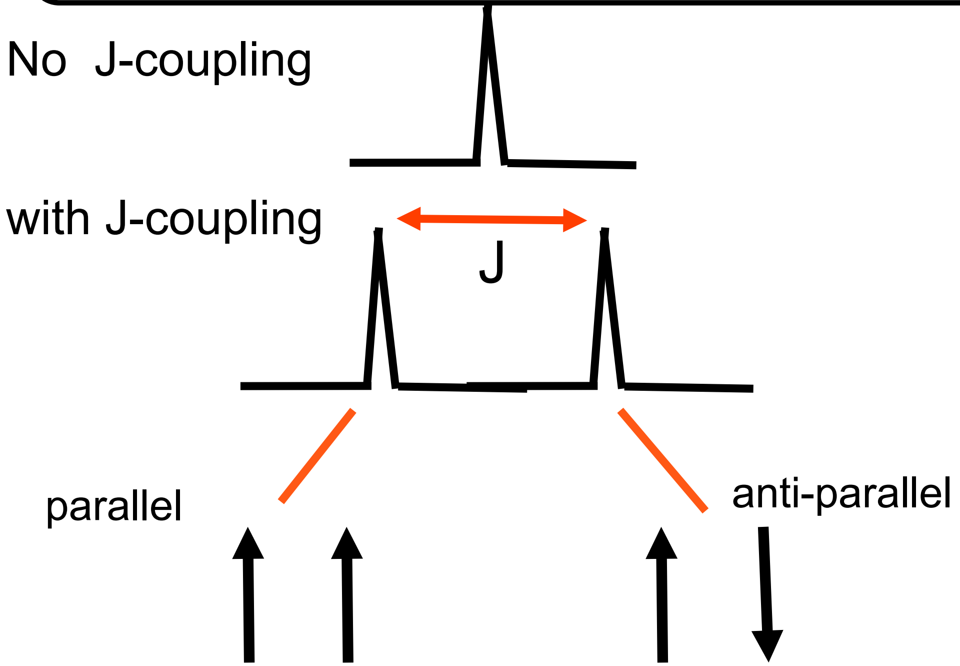
spin contribution averages to zero in a diamagnetic insulator

J-coupling

Electron-mediated interaction of nuclear spins

Nucleus A causes a magnetic field at nucleus B (and vice versa)





In solids J is rarely revealed in splitting of peaks in 1D spectra (anisotropic interactions broaden peaks)

Increasing use of techniques, eg those using spin-echo modulation, to measure J in solids.

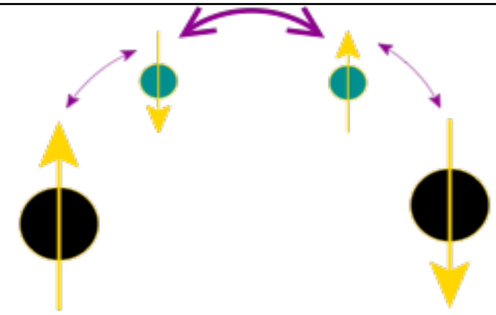
Spin-Spin (J) coupling

Effective Hamiltonian

$$H = \sum_{\mathrm{K<L}} \mathbf{I}_{\mathrm{K}}(\mathbf{D}_{\mathrm{KL}} + \mathbf{J}_{\mathrm{KL}})\mathbf{I}_{\mathrm{L}}$$

Bare

Dressed



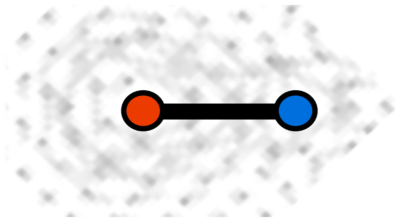
Indirect Coupling

$$\mathbf{J}_{\mathrm{KL}} = \frac{\hbar\gamma_{\mathrm{K}}\gamma_{\mathrm{L}}}{2\pi}\frac{\partial^2 E}{\partial\boldsymbol{\mu}_{\mathrm{K}}\partial\boldsymbol{\mu}_{\mathrm{L}}}$$

(note E here omits the nuclear-nuclear magnetic interaction)

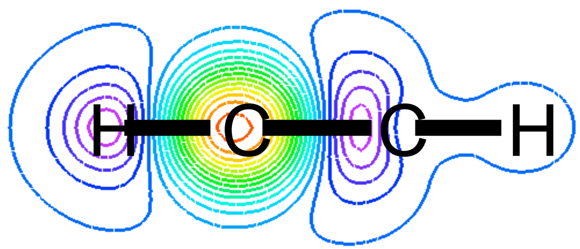
$$\mathbf{B}^{(1)}_{\mathrm{in}}(\mathbf{R}_{\mathrm{K}}) = \frac{2\pi}{\hbar\gamma_{\mathrm{K}}\gamma_{\mathrm{L}}}\mathbf{J}_{\mathrm{KL}}\cdot\boldsymbol{\mu}_{\mathrm{L}}$$

Orbital Magnetic dipole induces orbital motion of electrons



Orbital Current

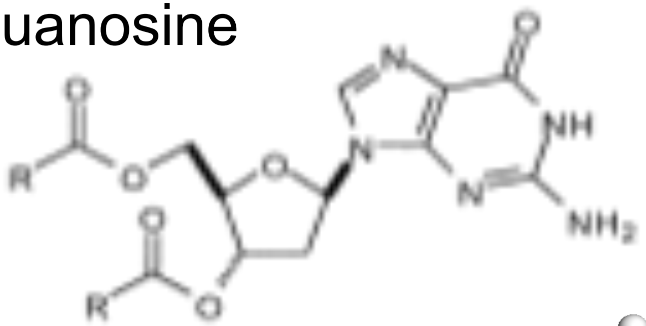
Spin Magnetic dipole induces spin densitv



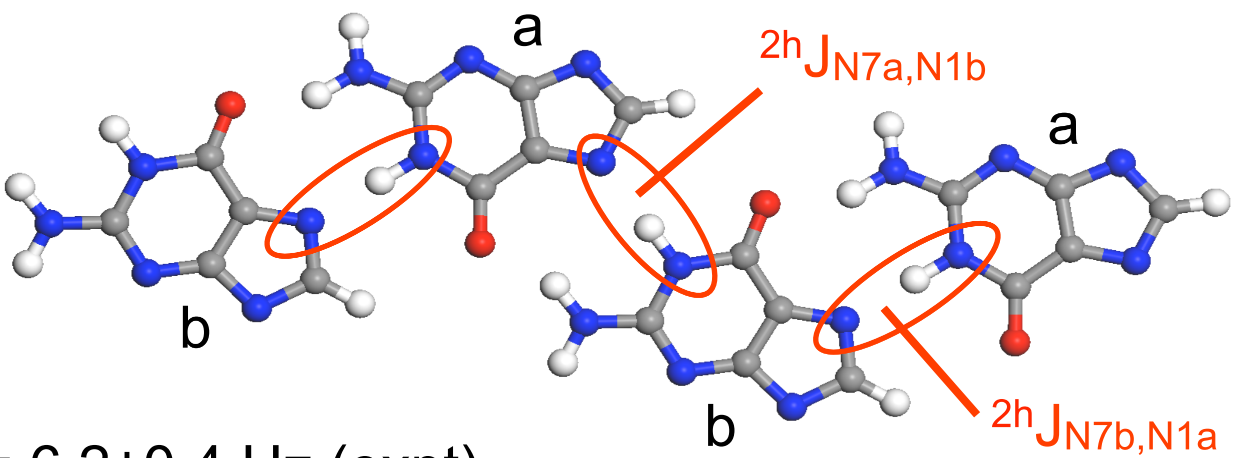
Induced Spin density

J-coupling

Guanosine



self-assembles into ribbons
molecular electronics (FET)



$^{2h}J_{N7b,N1a}$ = 6.2±0.4 Hz (expt)
6.5 Hz (calc)

$^{2h}J_{N7a,N1b}$ = 7.4±0.4 Hz (expt)
7.7 Hz (calc)

J. Am. Chem. Soc. **130**, 12663 (2008)

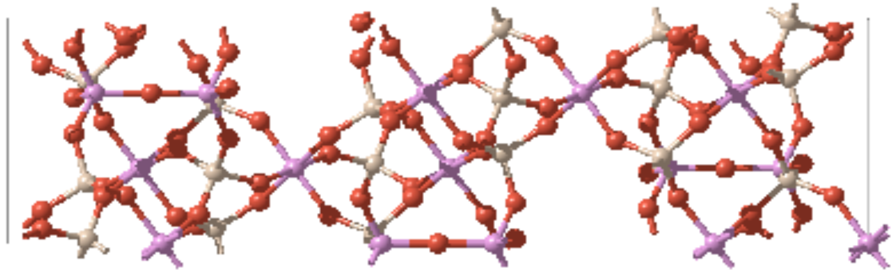
THE UNIVERSITY of York

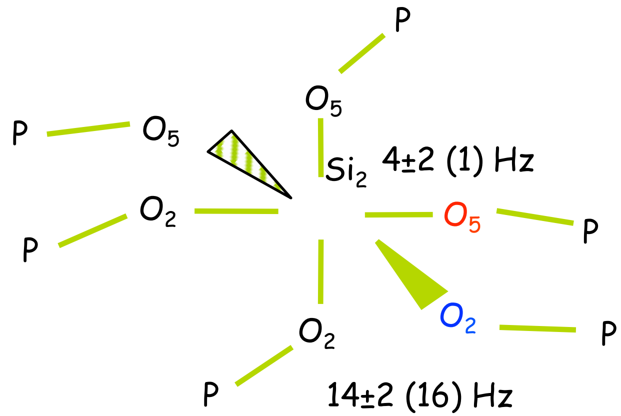
Silicophophates

Christian Bonhomme *(Paris)*

$Si_5O(PO_4)_6$

$^2J_{SiP}$	Expt	Theory
Si_1–O_5–P	15±2 Hz	17 Hz
Si_2–O_2–P	14±2 Hz	16 Hz
Si_3–O_5–P	12±2 Hz	14 Hz
Si_2–O_2–P	4±2 Hz	1 Hz





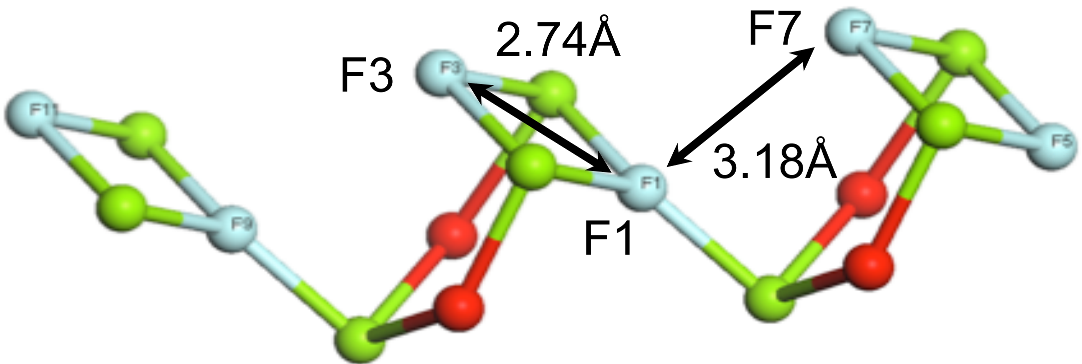
Expt: Inorg. Chem. 46, 1379 (2007)
Calc: J. Chem. Phys. 127, 204107 (2007)

Role of Calculations of J

Design and optimisation of NMR experiments
Interpretation of experiment

Through-space J-coupling

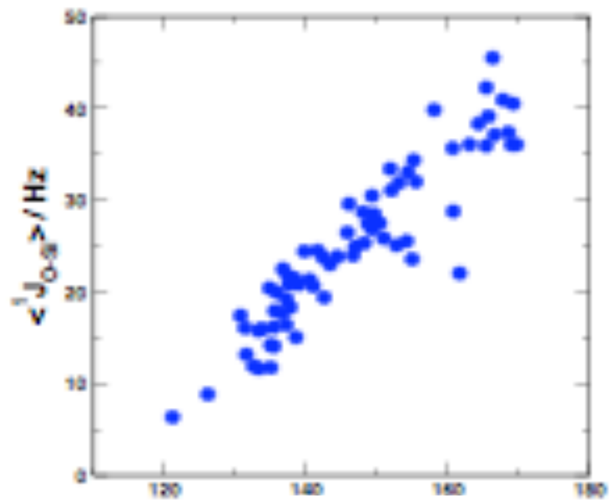
$^{1i}J_{FF}$	Expt	Calc
F1-F3:	18 Hz	12.5 Hz
F1-F7:	2.6 Hz	3.6 Hz



fluorine-substituted deuterated hydrous magnesium silicate

J. Am. Chem. Soc. 132 15651 (2010

Distributions of J in amorphous solids



Si-O-Si (deg)

silica glass

THE UNIVERSITY of York

Electric Field Gradients

Function of the charge density - ie ground-state property. Also computed by all-electron codes such as Wien2k, Crystal

$$V_{\boldsymbol{\alpha\beta}}(\mathrm{r}) = \int d^3 \mathrm{r}' \, \boldsymbol{n}(\mathrm{r}) / |\mathrm{r}-\mathrm{r}'|^3 \left[\delta_{\alpha\beta} - 3(\mathrm{r}_\alpha - \mathrm{r}'_\alpha)(\mathrm{r}_\beta - \mathrm{r}'_\beta) / |\mathrm{r}-\mathrm{r}'|^2 \right]$$

charge density

Eigenvalues

$$V_{\mathrm{xx}}, V_{\mathrm{yy}}, V_{\mathrm{zz}} \qquad |V_{\mathrm{zz}}| > |V_{\mathrm{yy}}| > |V_{\mathrm{xx}}|$$

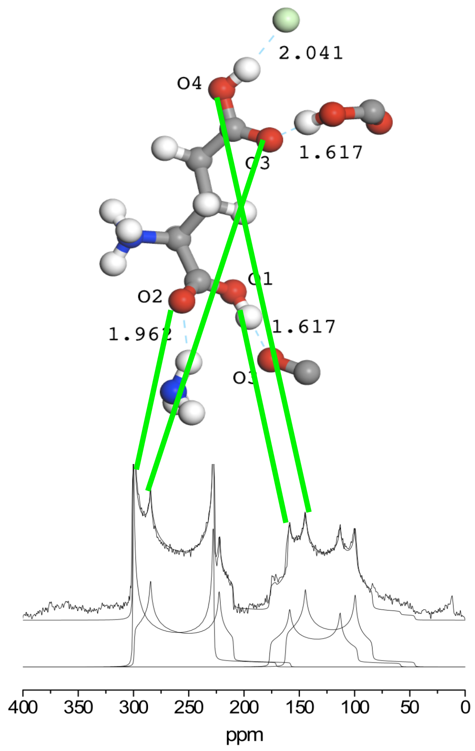
Quadrupolar Coupling

$$C_Q = \frac{eQV_{\mathrm{zz}}}{h}$$

Asymmetry

$$\eta_Q = \frac{V_{\mathrm{xx}} - V_{\mathrm{yy}}}{V_{\mathrm{zz}}}$$

Note: The quadrupolar moment, Q, is a nuclear property. Most recent values given in "*Year-2008 Standard Values of Nuclear Quadrupole Moments*": P. Pyykkö, Mol. Phys. 106, 1965-1974 (2008)
But note Q appears as a simple scaling factor



^{17}O MAS Glutamic Acid . HCl

Practical Details

*.param file

```
task          : magres
magres_task   : shielding
                efg
                nmr
                jcoupling
```

chemical shift/shielding

electric field gradient

both

Must use on-the-fly pseudopotentials

Highly sensitive to geometry – particularly important to optimise H positions; many structures are obtained from XRD, and H is nearly invisible to X-rays!

CONVERGE!

(basis cut-off & k-points)

*.castep file

```
==========================================================================
|                  Chemical Shielding Tensor                             |
|------------------------------------------------------------------------|
|     Nucleus                           Shielding tensor                 |
|   Species    Ion               Iso(ppm)   Aniso(ppm)  Asym            |
|     H         1                 23.81        5.27      0.40           |
|     H         2                 24.75       -3.35      0.85           |
|     H         3                 27.30       -5.79      0.90           |
|     O         5                -43.73      504.95      0.47           |
|     O         6                -63.53      620.75      0.53           |
|     O         7                -43.73      504.95      0.47           |
|     O         8                -63.53      620.75      0.53           |
==========================================================================
```

Anisotropy

$$\sigma_{\mathrm{aniso}} = \sigma_{\mathrm{zz}} - 1/2(\sigma_{\mathrm{xx}} - \sigma_{\mathrm{yy}})$$

Asymmetry

$$\eta = 3(\sigma_{\mathrm{yy}} - \sigma_{\mathrm{xx}})/2\sigma_{\mathrm{aniso}}$$

THE UNIVERSITY of York

*.magres file

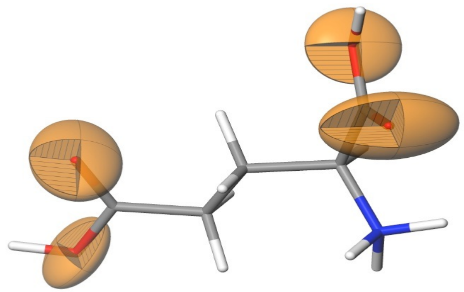
```
============
Atom: O    1
============
O     1 Coordinates      1.641     1.522     5.785    A

TOTAL Shielding Tensor

             218.1858     12.1357    -25.7690
              13.4699    191.6972     -7.2419
             -25.9178     -6.5205    216.3180

O     1 Eigenvalue  sigma_xx     185.6127 (ppm)
O     1 Eigenvector sigma_xx       0.5250      -0.8103      0.2603
O     1 Eigenvalue  sigma_yy     193.8979 (ppm)
O     1 Eigenvector sigma_yy       0.4702       0.5310      0.7049
O     1 Eigenvalue  sigma_zz     246.6904 (ppm)
O     1 Eigenvector sigma_zz      -0.7094      -0.2477

O     1 Isotropic:      208.7337 (ppm)
O     1 Anisotropy:      56.9351 (ppm)
O     1 Asymmetry:        0.2183
```

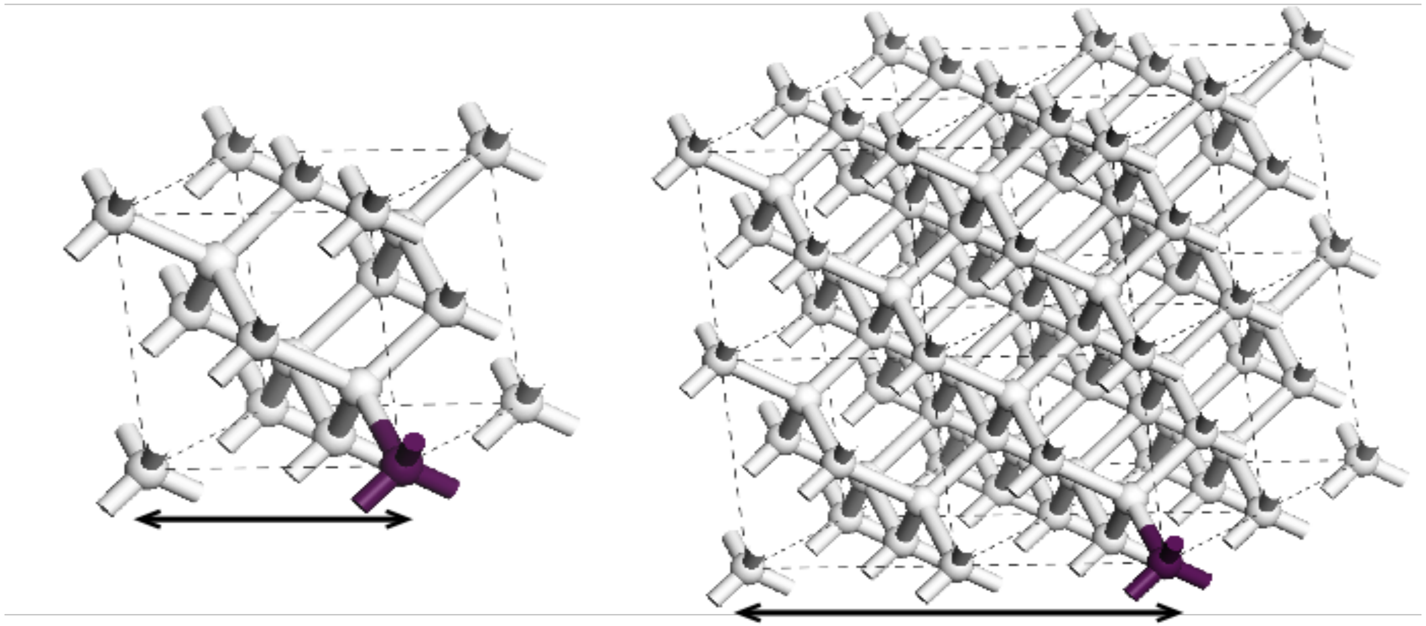


Note: shielding tensor has a symmetric and an antisymmetric component.
Typical NMR experiments are only sensitive to the symmetric part.
Therefore we only diagonalise the symmetric part of the shielding tensor

J-coupling

A single calculation gives the coupling between one (perturbing) atom and all others. Might need several calculations to get all of the couplings of interest.

Perturbing atom breaks periodicity - if the unit cell is small you might need to build a supercell to inhibit the interaction with periodic images



J-coupling

Contributions to J-coupling

Spin: Fermi Contact (FC)   Spin Dipolar (SD)

Charge: Paramagnetic (PARA) and Diamagnetic (DIA) - terms similar to shielding

note: *only total J is observable*

Perturbing atom

```
=====================================================================================
|                               Isotropic J-coupling                                |
|-----------------------------------------------------------------------------------|
|     Nucleus                                 J-coupling values                     |
|  Species    Ion      FC            SD            PARA         DIA        TOT(Hz)  |
|    O         1      25.37         0.31          -5.61         0.10        20.18   |
|**  Si        1       -.-           -.-           -.-           -.-         -.-    |
|    Si       10      12.41        -0.04          0.41          0.01        12.79   |
|    Si       16      17.97         0.07          0.43          0.01        18.48   |
|    Si       30      14.40         0.23          0.39          0.01        15.03   |
             Bond          Length (A)  1st image     Iso(Hz)
Aniso(Hz)

===========================================================================
      Si 001 --  O 001   1.61808     12.06908       20.18       57.86
      Si 001 -- Si 038   3.02674     11.25096       12.90        3.09
      Si 001 -- Si 010   3.03908      7.70290       12.79        3.47
      Si 001 -- Si 016   3.09623      9.83675       18.48        6.54
      Si 001 -- Si 030   3.17013     11.91281       15.03        8.39
```

Practical Things

Some practical things to keep in mind

Structure

NMR is very sensitive to structure!

XRD atom positions are often not sufficient for accurate simulation of NMR parameters.

Dynamics

Atoms move, and spectra are recorded at finite T.

How to account for that in (static) calculations?

Accuracy

How good are our present (approximate) density functionals?

Challenges

Effects of Relativity

scalar relativistic effects easy to treat (relativistic_treatment)
spin-orbit interaction is much harder, but may be needed
(e.g. for shifts on light atoms bonded to heavy atoms)

Localised *d*/*f* Electrons

Local Density Approximation (LDA) not enough, need lower self-interaction error.

Paramagnetic Materials

Magnetic fields from electronic spin

CCP NC

Collaborative Computational Project for NMR Crystallography

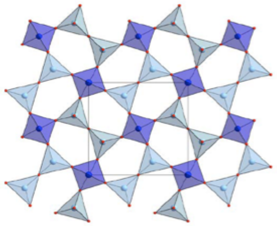
An emerging field, defined as the combined use of experimental solid-state NMR and computation to provide new insight, with atomic resolutions, into structure, disorder and dynamics in the solid state

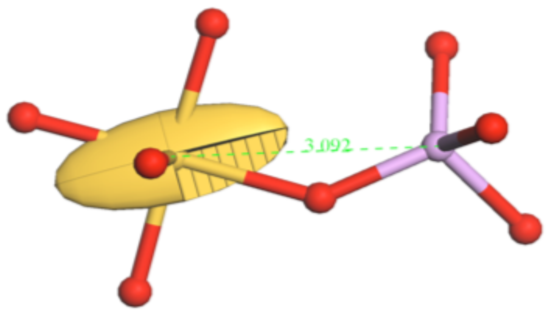
crystal structure ⟷ first-principles ⟷ spin-simulation

crystal structure ⟷ diffraction

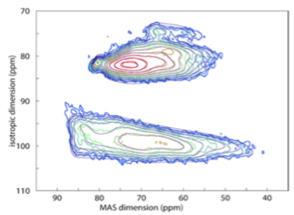
spin-simulation ⟷ NMR spectrum

diffraction





NMR spectrum



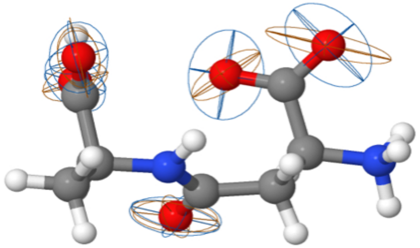
CCP NC

Collaborative Computational Project for NMR Crystallography

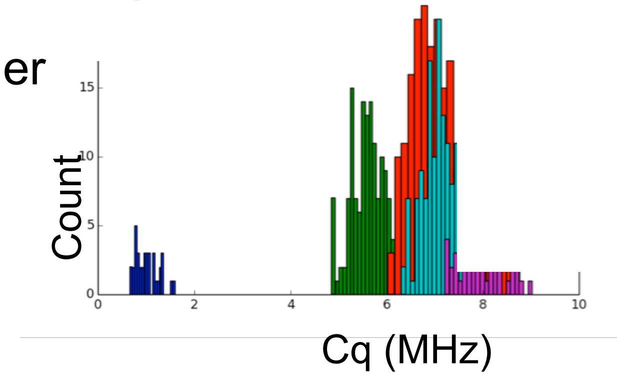
Development of Open-source (free) tools for visualisation and processing of first-principles NMR data

Magres Fileformat - community standard format for first-principles NMR data

MagresView - view NMR tensors - link to spin-dynamics



MagresPython - process NMR parameters - dynamics and disorder



www.ccpnc.ac.uk

Validated pseudopotential library - released with CASTEP 8
MagresDatabase - in development

Getting more information

NMR Books

Good Introduction
Nuclear Magnetic Resonance (Oxford Chemistry Primers)
P. J. Hore

More advanced
Spin Dynamics: Basics of Nuclear Magnetic Resonance
Malcolm H. Levitt

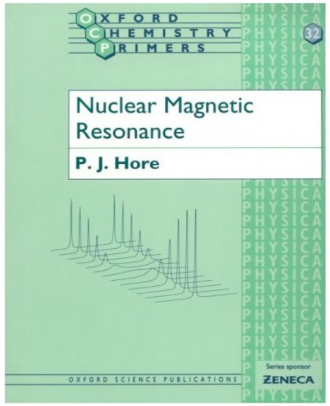
Solid state NMR
Solid-State NMR: Basic Principles and Practice
David Apperley, Robin Harris, Paul Hodgkinson

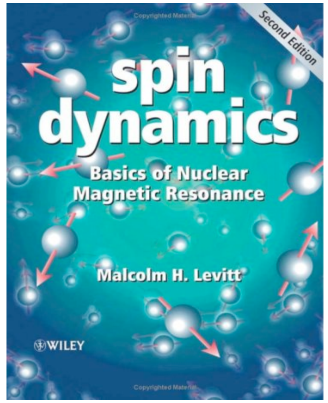
Useful survey of applications
Multinuclear Solid-State Nuclear Magnetic Resonance of Inorganic Materials
Kenneth J.D. MacKenzie, M.E. Smith

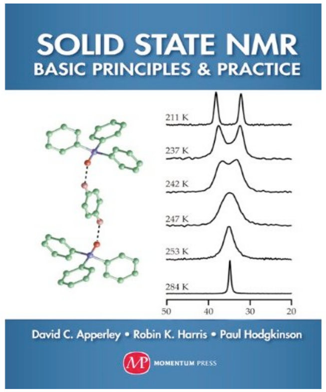
Recent Review Articles

Recent advances in solid-state NMR spectroscopy of spin *I* = 1/2 nuclei
Anne Lesage, *Phys. Chem. Chem. Phys.*, 2009, **11**, 6876

Recent advances in solid-state NMR spectroscopy of quadrupolar nuclei
Sharon E. Ashbrook, *Phys. Chem. Chem. Phys.*, 2009, **11**, 6892







Getting more information

GIPAW Theory

Comprehensive review of applications and theory:
First-Principle Calculation of NMR Parameters Using the GIPAW (Gauge Including Projector Augmented Wave) Method: a Chemist's Point of View
Bonhomme, Gervais, Babonneau, Coelho, Pourpoint, Azais, Ashbrook, Griffin, Yates, Mauri, Pickard,
Chemical Reviews 112 (11), 5733-5779 (2012)

Original Theory Papers:
All-electron magnetic response with pseudopotentials: NMR chemical shifts,
Chris J. Pickard, and Francesco Mauri.
Phys. Rev. B, 63, 245101 (2001)

Calculation of NMR Chemical Shifts for extended systems using Ultrasoft Pseudopotentials
Jonathan R. Yates, Chris J. Pickard, and Francesco Mauri.
Physical Review B 76, 024401 (2007)

A First Principles Theory of Nuclear Magnetic Resonance J-Coupling in solid-state systems
Sian A. Joyce, Jonathan R. Yates, Chris J. Pickard, Francesco Mauri
J. Chem. Phys. 127, 204107 (2007)

www.gipaw.net