Experiment and Modelling in Structural NMR

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DFT calculations
of NMR parameters

[04002]

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Prediction of NMR parameters in the solid-state

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NMR parameters

Chemical Shift

Quadrupolar coupling (EFG)

spin-spin coupling (J-coupling)

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Magnetic Shielding

Spin Hamiltonian $H = -\frac{1}{2\pi} \sum_K \gamma_K \mathbf{I}_K (1 - \sigma_K) \mathbf{B}_{\text{ext}}$

$\nwarrow$ Bare $\nearrow$ Dressed

Electronic Response

Induced Current $\mathbf{j}(\mathbf{r})$ Spin Polarisation $\mathbf{m}(\mathbf{r})$
 both cause induced magnetic field at nucleus

Induced Field $H = \frac{1}{h} \mu_K \cdot \mathbf{B}_{\text{in}}(\mathbf{R}_K)$

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

Magnetic Shielding $\sigma_K = -\frac{\mathbf{B}_{\text{in}}(\mathbf{R}_K)}{\mathbf{B}_{\text{ext}}}$

spin contribution averages to zero in a diamagnetic insulator

Orbital Current induced by B-field in Porphyrin ring

¹³C NMR

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 ¹³C this is liquid tetramethylsilane)

$$\delta_{\text{iso}} = \frac{(\omega - \omega_{\text{ref}}) \times 10^6}{\omega_{\text{ref}}}$$

chemical shift
(ppm)

$$\delta_{\text{iso}} = \sigma_{\text{ref}} - \sigma_{\text{iso}}$$

magnetic shielding
(from calc)

current to shift

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

Biot-Savart

$$\mathbf{B}_{\text{in}}(\mathbf{r}) = \frac{1}{c} \int d^3r' \mathbf{j}(\mathbf{r}') \times \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3}$$

Obtain current within perturbation theory (linear response)

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

$$\mathbf{B}_{\text{in}} = -\sigma \mathbf{B}_0$$

note: σ is a rank 2 tensor

Approaches to Compute NMR parameters

Local Orbitals (eg Gaussians)

NMR properties since ~1960s
 Good for finite systems
How to terminate a cluster?
 Expand wavefunctions as Gaussian orbitals
Difficult to systematically converge basis set

Solid-state code (typically planewave basis)

First theory ~2001
 Fourier expansion of wavefunction
 Periodic boundary conditions
 Systematic basis set convergence
difficulties with describing properties near nucleus....

Atomic states

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Periodic Calculations

To simulate periodic systems planewaves are a convenient choice: however describing the tightly bound core states, and oscillatory part of the valence states close to the nucleus are prohibitively expensive. We must approximate...

Frozen Core Approximation

- “Core” electrons taken from free atom fixed during calculation

Pseudopotential Approximation

- Valence electrons experience weak effective potential in the core region

Note: Typically these two approximations are used together. But this does not have to be the case. Some codes can employ ‘self-consistent’ pseudopotentials which allow the core states to ‘relax’ to their specific environment.

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Pseudopotentials

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GIPAW

Overcoming the previous approximations

Frozen Core Approximation

- Contribution of “core” electrons to shielding is not chemically sensitive
1s states in Carbon contribute ~200ppm in diamond, benzene, proteins
ie core states contribute to shielding - but not shift.

Pseudopotential Approximation

- Use PAW method to fix-up valence wavefunction in the core region

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Projector Augmented Waves

$$|\Psi\rangle = \mathcal{T}|\tilde{\Psi}\rangle$$

pseudo

all-electron

$$\mathcal{T} = \mathbf{1} + \sum_{\mathbf{R},n} [|\phi_{\mathbf{R},n}\rangle - |\tilde{\phi}_{\mathbf{R},n}\rangle] \langle \tilde{p}_{\mathbf{R},n}|$$

GIPAW

Gauge-Including Projector Augmented Waves
Modification of PAW by Pickard and Mauri for systems in an external magnetic field - plays a role similar to GIAO in quantum chemistry techniques

GIPAW

A theory for solid-state NMR

GIPAW vs Gaussian
test on small molecules
n.b. v. big Gaussian basis sets

JRY, C. Pickard, F. Mauri PRB 76, 024401 (2007)

Convergence of shielding with #planewaves

J-Resolved Solid-State NMR

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

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

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J-Coupling

Electron-mediated interaction of nuclear spins

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

No J-coupling

with J-coupling

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.

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Electron's view of J-coupling

Orbital

Dipole induces orbital motion of electrons (due to electron charge)
This creates a localised magnetic field
similar mechanism to NMR shielding

Spin

Dipole induces spin density (relative displacement of $\uparrow$ and $\downarrow$ electrons)
This creates induced field via:
Fermi-Contact ('s' like density at nucleus)
Spin-dipolar (non-spherical distribution of spin)
similar mechanism to EPR-hyperfine & Knight-shift

Total J = Orbital + Spin

DNA bases

(Warwick)

Guanosine

self-assembles into ribbons
molecular electronics (FET)

$2hJ_{N7b,N1a} = 6.2 \pm 0.4$ Hz (expt)
6.5 Hz (calc)

$2hJ_{N7a,N1b} = 7.4 \pm 0.4$ Hz (expt)
7.7 Hz (calc)

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

Predictions

$2hJ_{O6a,N2b} = 5.7$ Hz

$1J_{O6a,C1a} = 22.0$ Hz

Guanosine

Coupling	Calc (Hz)	Expt (Hz)
${}^2hJ_{N_{1a}-N_{7b}}$	6.5	6.2 ± 0.4
${}^2hJ_{N_{1b}-N_{7a}}$	7.7	7.4 ± 0.4
${}^2J_{N_{2a}-N_{3a}}$	5.4	6.6 ± 0.7^i
${}^2J_{N_{2b}-N_{3b}}$	5.7	
${}^2J_{N_{3a}-N_{9a}}$	4.4	4.3 ± 0.2^i
${}^2J_{N_{3b}-N_{9b}}$	4.2	
${}^2J_{N_{1a}-N_{2a}}$	2.4	DQ intensity
${}^2J_{N_{1b}-N_{2b}}$	2.3	DQ intensity
${}^2J_{N_{1a}-N_{3a}}$	-1.1	-
${}^2J_{N_{1b}-N_{3b}}$	-1.1	-
${}^2J_{N_{7a}-N_{9a}}$	-1.2	-
${}^2J_{N_{7a}-N_{9b}}$	-1.3	-

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Electric Field Gradient

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

$$\text{EFG} \quad V_{\alpha\beta}(\mathbf{r}) = \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} \left[\delta_{\alpha\beta} - 3 \frac{(r_\alpha - r'_\alpha)(r_\beta - r'_\beta)}{|\mathbf{r} - \mathbf{r}'|^2} \right]$$

Eigenvalues

$$V_{xx}, V_{yy}, V_{zz} \quad |V_{zz}| > |V_{yy}| > |V_{xx}|$$

Quadrupolar Coupling

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

Asymmetry

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

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

¹⁷O MAS Glutamic Acid . HCl

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NMR parameters - solid-state electronic structure

Quadrupolar coupling (EFG)

Ground state property - charge density

Health Warning!
diamagnetic insulators

Chemical Shift (magnetic shielding)

Response property - change in local B field due to screening currents

spin-spin coupling (J-coupling)

Response property:

screening current + spin polarisation

Solid-state theory 2007 - development version of CASTEP

$^1J_{PO}$
All are tensor properties

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Output

```
=====
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      0.6598

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

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Comparing Theory and Experiment

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 - spectra are recorded at finite T.

How to account for that in (static) calculations?

Accuracy

How good are our present (approximate) density functionals?

Static 'Disorder'

Temperature

MLF peptide ^{13}C rms error

Static relaxed structure	4.2ppm	2 pm
ab-initio MD	3.3ppm	
classical MD	3.0ppm	5 μm

Ab-initio MD

Captures large (20ppm) fluctuations on fs timescale

Classical MD

Samples rotameric states

half of sites have errors <1ppm - limitations of PBE

J. Am. Chem. Soc. **132**, 3993 (2010)

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Maltose

Steven Brown (Warwick)

CH

J. Am. Chem. Soc. 127 10216-10220 (2005)

OH

Phys. Chem. Chem. Phys., 12, 6970 (2010)

Compare Calculation with experiment

C-H max error 0.3ppm (mean 0.1ppm)

O-H max error 0.6ppm (mean 0.4ppm)

Why are there larger errors for hydroxyl protons?

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Effect of Temperature (expt)

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Density Functional Theory

Most solid-state studies of NMR parameters use PBE functional (1996)

- Typically 'good' agreement with experiment ~1-4% of shift range.
- Systematic errors
- Much larger systematic error for ^{19}F (several authors)
- Major failure for localised orbitals eg Ca.

John Griffin *J. Am. Chem. Soc.* 132 15651 (2010)

What are the prospects for improvement?

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Density Functional Theory

Local Density Functions

Exchange-Correlation potential depends on charge-density (& gradient) at that point

Non-local Functionals

Exchange-Correlation potential depends all points in space

- eg B3LYP, PBE0, screened exchange (sX)
- very expensive in planewaves
- implemented for ground-state properties in most periodic codes
- speed-ups in development

Dispersion forces

Extreme non-locality!

Required for correct potential energy surface of molecular crystals

DFT+D functionals (various flavours) appearing in codes

Getting more information

A more in depth introduction to the theory (email JRY for a copy)

Computations of Magnetic Resonance Parameters for Crystalline Systems: Principles

Jonathan R. Yates, Chris J. Pickard

Encyclopedia of Magnetic Resonance (2008) [doi:10.1002/9780470034590.emrstm1009](https://doi.org/10.1002/9780470034590.emrstm1009)

Review of J-Coupling

Prediction of NMR J-coupling in solids with the planewave pseudopotential approach

Jonathan R. Yates

Magn. Reson. Chem 48, S23 (2010)

Recent Review of GIPAW

First principles calculation of Solid-State NMR parameters

Jonathan R Yates, Chris J Pickard, Davide Ceresoli

Psik Highlight 102 (2010) - <http://www.psi-k.org>

www.gipaw.net

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)