GIPAW: A solid-state theory for NMR

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NMR parameters

*we will focus on non-metallic, diamagnetic materials*

**Chemical Shift**
- Small changes in precession frequency of nucleus
- Sharp peaks

**Quadrupolar coupling (EFG)**
- Nuclei spin>1/2 interact with local electric field gradients
- Characteristic broad peaks

**Spin-spin coupling (eg J-coupling)**
- Splitting of resonance due to nucleus-nucleus interaction
- Hard to observe in solids....
Magnetic Shielding

\[ \omega = \gamma B_{\text{local}} \]

\[ B_{\text{local}} = B_0 + B_{\text{induced}} \]

\[ B_{\text{induced}} = -\sigma B_0 \]

The flow of orbital currents induced by the external magnetic field causes a spatial variation in the local magnetic field. This is characterised by the magnetic shielding tensor.
Flurbiprofen

_magnetic shielding (from calc)_

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)

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

\[ \delta_{iso} = \sigma_{ref} - \sigma_{iso} \]
current to shift

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

Biot-Savart

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

Obtain current within perturbation theory (linear response)

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

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

note: $\sigma$ is a rank 2 tensor
Atomic states
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. CASTEP can employ ‘self-consistent’ pseudopotentials which allow the core states to ‘relax’ to their specific environment.
Pseudopotentials

\[ V(\text{a.u.}) \]

\[ r \psi \]

\[ r \text{ (a.u.)} \]

\[ \text{Si} \]

\[ 1s \]

\[ 2s \]

\[ 3s \]

\[ 3s \text{ (pseudized)} \]
GIPAW

Overcoming the previous approximations

Representation of Position Operator
• r is not a cell periodic function (won’t discuss this further)
  \( H^{(1)} = (r\times p).B \)

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
Projector Augmented Waves

\[ |\Psi\rangle = \mathcal{T} |\tilde{\Psi}\rangle \]

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

**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.
NMR - CASTEP code:
JRY, CJP, F. Mauri (Paris)

NMR-CASTEP vs Gaussian
test on small molecules
n.b. v. big Gaussian basis sets
JRY, C. Pickard, F. Mauri PRB 76, 024401 (2007)

GIPAW
A theory for solid-state NMR

![Graphs showing comparison between NMR-CASTEP and Gaussian methods.
(a) Using uncorrected valence states.
(b) With GIPAW augmentation.](image)
Maltose

sugar used in brewing

Cross-peaks when J-coupling between spins: -
C-H “bonds”
Solid-state effects

- $^{13}$C axis
- $^1$H axis

$X$ - first principles
molecule only
Solid-state effects

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

$J. \text{Am. Chem. Soc.}$ 127 10216 (2005)
$J. \text{Am. Chem. Soc.}$ 130 945 (2008)

X - first principles
full crystal
NMR parameters

Chemical Shift

orbital currents

Quadrupolar coupling (EFG)

nuclei $l>1/2$ interact with local electric field gradients
Function of charge density

spin-spin coupling (eg J-coupling)

splitting of resonance due to nucleus-nucleus interaction hard to observe in solids....
Electric Field Gradient

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

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

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. CASTEP uses the most recent IUPAC values as defaults. But you can over-ride these (anhow it is a simple scaling factor)
Calculations

*.param file

task : magres
magres_task : shielding
efg

chemical shift/shielding

electric field gradient

both

Must use on-the-fly pseudopotentials

Highly sensitive to geometry (optimise H X-ray positions)

CONVERGE
(basis cut-off & k-points)
### Chemical Shielding Tensor

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Species</th>
<th>Ion</th>
<th>Iso (ppm)</th>
<th>Aniso (ppm)</th>
<th>Asym</th>
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<td>504.95</td>
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<td>8</td>
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<td>-63.53</td>
<td>620.75</td>
<td>0.53</td>
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</tbody>
</table>

#### Anisotropy

\[
\sigma_{\text{aniso}} = \sigma_{zz} - \frac{1}{2}(\sigma_{xx} - \sigma_{yy})
\]

#### Asymmetry

\[
\eta = \frac{3(\sigma_{yy} - \sigma_{xx})}{2\sigma_{\text{aniso}}}
\]
*.magres File

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

TOTAL Shielding Tensor

<p>| | | |</p>
<table>
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<td>13.4699</td>
<td>191.6972</td>
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<td>-25.9178</td>
<td>-6.5205</td>
<td>216.3180</td>
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</table>

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.
Electron-mediated interaction of nuclear spins

Solution-state NMR

J-coupling splits spectral peaks $J \sim 1\text{-}100$ Hz

No J-coupling

with J-coupling

parallel

anti-parallel
Electron’s perspective: J-coupling

Nucleus A causes a local magnetic field

• The response of the electron’s charge = current
• The response of the electron’s spin = spin density

Both the current and the spin density cause a magnetic field at Nucleus B

Calculations of the J-coupling are new to CASTEP. So new they’re not in the released version! However, there is a tutorial with a pre-release version of the code - this will give you much more information.

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.
## 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*

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<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Species</th>
<th>Ion</th>
<th>FC</th>
<th>SD</th>
<th>PARA</th>
<th>DIA</th>
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<td>0.01</td>
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<td>0.23</td>
<td>0.39</td>
<td>0.01</td>
<td>15.03</td>
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<table>
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<tr>
<th>Bond</th>
<th>Length (A)</th>
<th>1st image</th>
<th>Iso (Hz)</th>
<th>Aniso (Hz)</th>
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<td>15.03</td>
<td>8.39</td>
</tr>
</tbody>
</table>
DNA bases

Guanosine

self-assembles into ribbons

molecular electronics (FET)

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

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


Predictions

\[ 2hJ_{O6a,N2b} = 5.7 \text{ Hz} \]
\[ 1J_{O6a,C1a} = 22.0 \text{ Hz} \]
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

Introduction to solid-state NMR
*Introduction to Solid-State NMR Spectroscopy (Paperback)*
Melinda Duer

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

Recent advances in solid-state NMR spectroscopy of quadrupolar nuclei
Getting more information

GIPAW Theory

A more in depth introduction to the theory (email JRY for a copy)
Comptuations of Magnetic Resonance Parameters for Crystalline Systems: Principles
Jonathan R. Yates, Chris J. Pickard

Applications to molecular crystals
Comptuations of Magnetic Resonance Parameters for Molecular Crystalline Systems: Practise
Robin K. Harris, Paul Hodgkinson, Chris J. Pickard, Jonathan R. Yates, Vadim Zorin
Encyclopedia of Magnetic Resonance (2008)

Original Theory Papers:
All-electron magnetic response with pseudopotentials: NMR chemical shifts,
Chris J. Pickard, and Francesco Mauri.

Calculation of NMR Chemical Shifts for extended systems using Ultrasoft Pseudopotentials

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

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