GIPAW: A solid-state theory for NMR

Jonathan Yates

jonathan.yates@materials.ox.ac.uk

Materials Modelling Laboratory, Oxford Materials
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....
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.
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)
To compute the chemical shifts we just need to calculate the current induced by the external magnetic field.

**Biot-Savart**

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

Obtain current within perturbation theory (linear response)

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

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

note: \(\sigma\) is a rank 2 tensor.
Atomic states

![Graph showing atomic states for Si]

- Green line with label 1s
- Blue line with label 2s
- Black line with label 3s

$r \psi$ vs. $r$ (a.u.)
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.
Pseudopotentials

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

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

pseudo \hspace{2cm} all-electron

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

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)
Induced Current

Current given by perturbation theory

\[ j^{(1)}(r') = 2 \sum_o \left[ \langle \Psi_o^{(1)} | \mathbf{J}^{(0)}(r') | \Psi_o^{(0)} \rangle + \langle \Psi_o^{(0)} | \mathbf{J}^{(0)}(r') | \Psi_o^{(1)} \rangle + \langle \Psi_o^{(0)} | \mathbf{J}^{(1)}(r') | \Psi_o^{(0)} \rangle \right] \]

\[ \mathbf{J}(r') = \frac{1}{c} \mathbf{A}(r') |r'\rangle \langle r'| - \frac{\mathbf{p}|r'\rangle \langle r'| + |r'\rangle \langle r'| \mathbf{p}}{2} \]

\[ |\Psi_o^{(1)}\rangle = \sum_e \frac{|\Psi_e^{(0)}\rangle \langle \Psi_e^{(0)}|}{\varepsilon - \varepsilon_e} H^{(1)} |\Psi_o^{(0)}\rangle = \mathcal{G}(\varepsilon_o^{(0)}) H^{(1)} |\Psi_o^{(0)}\rangle \]

Symmetric gauge:  \[ \mathbf{A}(r) = \frac{1}{\lambda_s} 2 \mathbf{B} \times r \]

\[ j^{(1)}(r') = 4 \sum_o \text{Re} \left[ \langle \Psi_o^{(0)} | \mathbf{J}^p(r') \mathcal{G}(\varepsilon_o^{(0)}) r \times \mathbf{p} |\Psi_o^{(0)}\rangle \cdot \mathbf{B} \right] - \frac{1}{2c} \rho(r') \mathbf{B} \times r' \]

Paramagnetic  Diamagnetic
Induced Current pt 2

\[ j^{(1)}(r') = 4 \sum_o \text{Re} \left[ \langle \Psi^{(0)}_o | J^p(r') G(\varepsilon^{(0)}_o) r \times p | \Psi^{(0)}_o \rangle \cdot B \right] - \frac{1}{2c} \rho(r') B \times r' \]

using a “sum rule”

\[ j^{(1)}(r') = 4 \sum_o \text{Re} \left[ \langle \Psi^{(0)}_o | J^p(r') G(\varepsilon^{(0)}_o) (r - r') \times p | \Psi^{(0)}_o \rangle \cdot B \right] \]

formally use periodic field \( B = \sin(q \cdot r) \hat{q}. \)

\sim \text{substitution}

\[ (r - r') = \lim_{q \to 0} \frac{1}{2q} \sum_{\alpha=x,y,z} \left[ e^{iqu_\alpha \cdot (r-r')} - e^{-iqu_\alpha \cdot (r-r')} \right] \]
Induced Current pt 3

\[ j^{(1)}(r') = \lim_{q \to 0} \frac{1}{2q} [S(r', q) - S(r', -q)] \]

\[ S(r', q) = \frac{2}{cN_k} \sum_{i=x,y,z} \sum_{o,k} \text{Re} \left[ \frac{1}{i} \langle u_o^i, k | J^p_{k,k+q_i}(r') G_{k+q_i} (\varepsilon_{o,k}) B \times \hat{u}_i \cdot (p + k) | \bar{u}_o^{(0)} \rangle \right] \]

can work with cell periodic functions
price is calculation at \( k \pm q \)

typical \( q = 0.01 \) bohr\(^{-1}\)
NMR parameters

Chemical Shift

orbital currents

Quadrupolar coupling (EFG)

nuclei I>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

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

**Eigenvalues**

\[ V_{xx}, V_{yy}, V_{zz} \quad |V_{zz}| > |V_{yy}| > |V_{xx}| \]

**Quadrupolar Coupling**

\[ C_Q = \frac{eQV_{zz}}{\hbar} \]

**Asymmetry**

\[ \eta_Q = \frac{V_{xx} - V_{yy}}{V_{zz}} \]

But note Q appears as a simple scaling factor
Output

 Atom: O 1

TOTAL Shielding Tensor

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>218.1858</td>
<td>12.1357</td>
<td>-25.7690</td>
<td></td>
</tr>
<tr>
<td>13.4699</td>
<td>191.6972</td>
<td>-7.2419</td>
<td></td>
</tr>
<tr>
<td>-25.9178</td>
<td>-6.5205</td>
<td>216.3180</td>
<td></td>
</tr>
</tbody>
</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.
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

parallel

anti-parallel

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.
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**
Computing J for solids


### Measured J is a product of nuclear constants and an electronic term

\[
J_{AB} = \gamma_A \gamma_B K_{AB}
\]

- \(J_{\text{X-^6Li}} = 10\text{Hz}\)
- \(J_{\text{X-^7Li}} = 26\text{Hz}\)

A single calculation gives J from perturbing site to all others in system.

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 in uracil (Hz)**

- Single Calculation gives J from perturbing site to all others in system.

---

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.
$^{2}J_{POP}$

Expt $^{2}J_{P-O-P}$ (Hz)

Calc $^{2}J_{P-O-P}$ (Hz)

Polyphosphate

Pyrophosphate

n.b. to aid comparison with expt this is $|J|$
$^{1}J_{PO}$

![Graph showing $^{1}J_{PO}$ vs. $r_{PO}$ (Ang) for different compounds.](image)

- **$\alpha$-Ca$_2$P$_2$O$_7$**
  - $J_{P1-O}$: 96Hz (Expt) 105Hz (Calc)
  - $J_{P2-O}$: 92Hz (Expt) 102Hz (Calc)

  *Average P-O couplings*

  **Expt F. Fayon (Orleans)**

  *aniso 50Hz (BO) to 110Hz (NBO)*

*Note: The graph and data are based on the provided image and text.*
Other Approaches

**CPMD - Daniel Sebastiani**
Transform Bloch states to localised Wannier orbitals to overcome position operator problem
No pseudopotential correction (limited to H and first row)

**CP2K - GPAW (confusing name!!)**
All-electron mixed gaussian and planewaves. Gamma point only? large cells
THE JOURNAL OF CHEMICAL PHYSICS 131, 014106 (2009)

**Converse Approach**
Compute shielding as finite difference of orbital magnetisation wrt nuclear moment
Uses GIPAW for pseudopotential augmentation
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)

Computation of Magnetic Resonance Parameters for Crystalline Systems: Principles
Jonathan R. Yates, Chris J. Pickard

Applications to molecular crystals

Computation 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

www.gipaw.net