



# **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 nucleusnucleus interaction hard to observe in solids....



36

# **Magnetic Shielding**



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** 

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Orbital Current induced by B-field in Porphyrin ring



## <sup>13</sup>C NMR



## current to shift



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. Some codes can employ 'self-consistent' pseudopotentials which allow the core states to 'relax' to their specific environment.

## **Pseudopotentials**





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

## **Projector Augmented Waves**



## 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

$$\mathbf{j}^{(1)}(\mathbf{r}') = 2\sum_{o} \left[ \langle \bar{\Psi}_{o}^{(1)} | \bar{\mathbf{J}}^{(0)}(\mathbf{r}') | \bar{\Psi}_{o}^{(0)} \rangle + \langle \bar{\Psi}_{o}^{(0)} | \bar{\mathbf{J}}^{(0)}(\mathbf{r}') | \bar{\Psi}_{o}^{(1)} \rangle + \langle \bar{\Psi}_{o}^{(0)} | \bar{\mathbf{J}}^{(1)}(\mathbf{r}') | \bar{\Psi}_{o}^{(0)} \rangle \right]$$

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

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

Symmetric gauge:

$$\mathbf{A}(\mathbf{r}) = \mathbf{\tilde{1}}/2\mathbf{B} \times \mathbf{r}$$

$$\mathbf{j}^{(1)}(\mathbf{r}') = 4\sum_{o} \operatorname{Re}\left[\langle \Psi_{o}^{(0)} | \mathbf{J}^{\mathrm{p}}(\mathbf{r}') \mathcal{G}(\varepsilon_{o}^{(0)})\mathbf{r} \times \mathbf{p} | \Psi_{o}^{(0)} \rangle \cdot \mathbf{B}\right] - \frac{1}{2c} \rho(\mathbf{r}') \mathbf{B} \times \mathbf{r}'$$

#### Paramagnetic

Diamagnetic

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## Induced Current pt 2

$$\mathbf{j}^{(1)}(\mathbf{r}') = 4\sum_{o} \operatorname{Re}\left[\langle \Psi_{o}^{(0)} | \mathbf{J}^{\mathrm{p}}(\mathbf{r}') \mathcal{G}(\varepsilon_{o}^{(0)})\mathbf{r} \times \mathbf{p} | \Psi_{o}^{(0)} \rangle \cdot \mathbf{B}\right] - \frac{1}{2c} \rho(\mathbf{r}') \mathbf{B} \times \mathbf{r}'$$

using a "sum rule"

$$\mathbf{j}^{(1)}(\mathbf{r}') = 4\sum_{o} \operatorname{Re}\left[ \langle \Psi_{o}^{(0)} | \mathbf{J}^{\mathrm{p}}(\mathbf{r}') \mathcal{G}(\varepsilon_{o}^{(0)})(\mathbf{r} - \mathbf{r}') \times \mathbf{p} | \Psi_{o}^{(0)} \rangle \cdot \mathbf{B} \right]$$

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

~ substitution

$$(\mathbf{r} - \mathbf{r}') = \lim_{q \mapsto 0} \frac{1}{2q} \sum_{\alpha = x, y, z} \left[ e^{\imath q \mathbf{u}_{\alpha} \cdot (\mathbf{r} - \mathbf{r}')} - e^{-\imath q \mathbf{u}_{\alpha} \cdot (\mathbf{r} - \mathbf{r}')} \right]$$

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## Induced Current pt 3

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

$$\mathbf{S}(\mathbf{r}',q) = \frac{2}{cN_{\mathbf{k}}} \sum_{i=x,y,z} \sum_{o,\mathbf{k}} \operatorname{Re}\left[\frac{1}{i} \langle u_{o,\mathbf{k}}^{(0)} | \mathbf{J}_{\mathbf{k},\mathbf{k}+\mathbf{q}_{i}}^{\mathbf{p}}(\mathbf{r}') \mathcal{G}_{\mathbf{k}+\mathbf{q}_{i}}(\varepsilon_{o,\mathbf{k}}) \mathbf{B} \times \hat{\mathbf{u}}_{i} \cdot (\mathbf{p}+\mathbf{k}) | \bar{u}_{o,\mathbf{k}}^{(0)} \rangle\right]$$

can work with cell periodic functions price is calculation at k±q

### typical q=0.01 bohr<sup>-1</sup>

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## **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....







36

## **Electric Field Gradient**

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

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

Eigenvalues

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

Quadrupolar Coupling

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

Asymmetry

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

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

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<sup>17</sup>O MAS Glutamic Acid . HCl

## Output

======================================					
=== 0	1 Coordinates	1.641	1.522	5.785 A	
тот	'AL Shielding Ter	nsor			
	218.18 13.40 -25.92	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	357 –25 972 –7 205 216	.7690 .2419 .3180	
0 0 0 0 0	<ol> <li>Eigenvalue</li> <li>Eigenvector</li> <li>Eigenvalue</li> <li>Eigenvector</li> <li>Eigenvalue</li> <li>Eigenvalue</li> <li>Eigenvector</li> </ol>	sigma_xx sigma_xx sigma_yy sigma_yy sigma_zz sigma_zz	185.6127 0.5250 193.8979 0.4702 246.6904 -0.7094	(ppm) -0.8103 (ppm) 0.5310 (ppm) -0.2477	0.2603 0.7049 0.6598
0 0 0	<pre>1 Isotropic: 1 Anisotropy: 1 Asymmetry:</pre>	208.733 56.935 0.2183	7 (ppm) 1 (ppm) 3		

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**





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 1 and 1 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

Induced Spin density: C<sub>2</sub>H<sub>2</sub>



# Computing J for solids

J. Chem. Phys. 127, 204107 (2007)



A single calculation give the coupling between one (perturbing) atoms 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





Christian Bonhomme (Paris) Franck Fayon (Orleans) Christel Gervais (Paris)



n.b. to aid comparison with expt this is IJI

### <sup>1</sup>J<sub>PO</sub>



# **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 J. Chem. Phys. 131, 101101 (2009)

# 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 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

#### 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) <u>doi:10.1002/9780470034590.emrstm1009</u>

#### Applications to molecular crystals

Computations 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. 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