GIPAW: A solid-state theory for NMR

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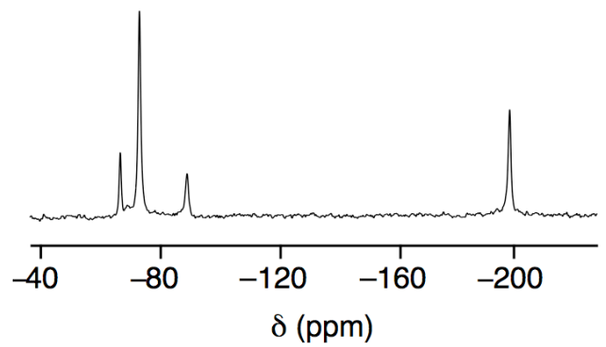
NMR parameters

we will focus on non-metallic, diamagnetic materials

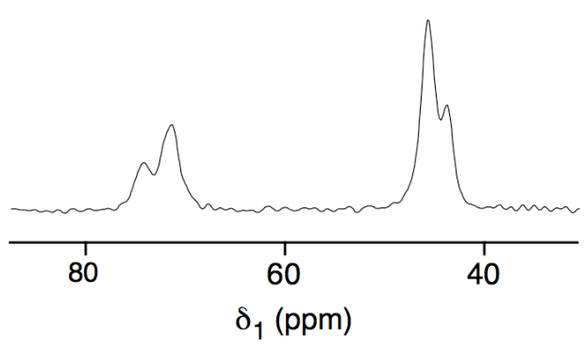
Chemical Shift

Small changes in precession frequency of nucleus
sharp peaks



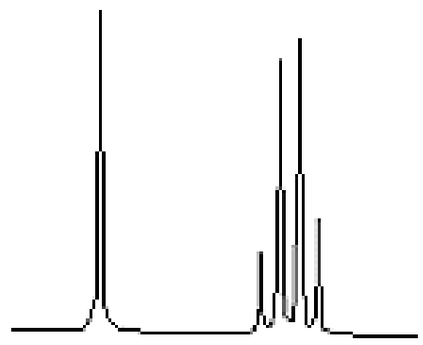
Quadrupolar coupling (EFG)

nuclei spin>1/2 interact with local electric field gradients
Characteristic broad peaks

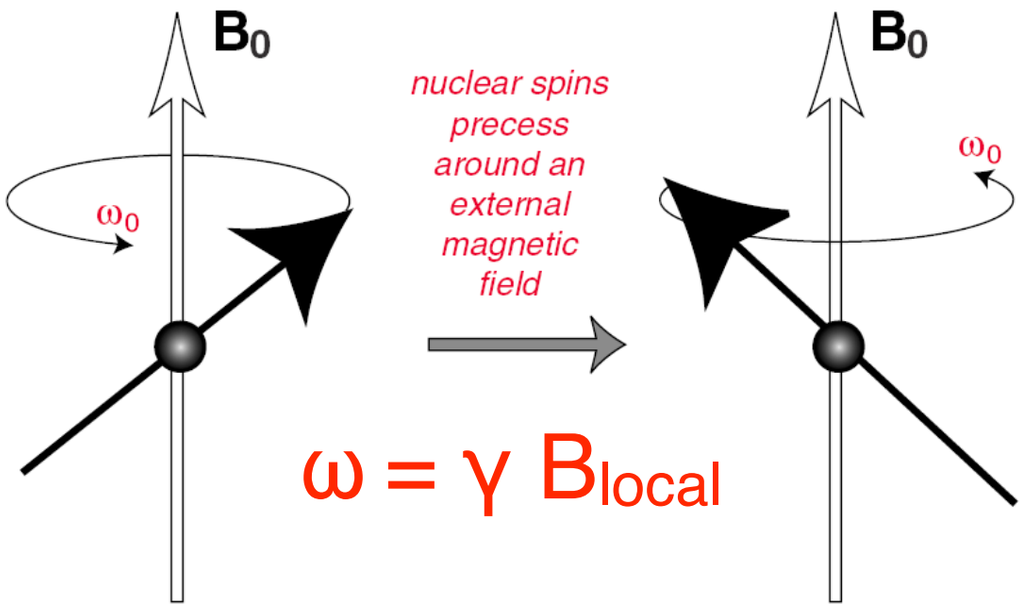


spin-spin coupling (eg J-coupling)

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



Magnetic Shielding



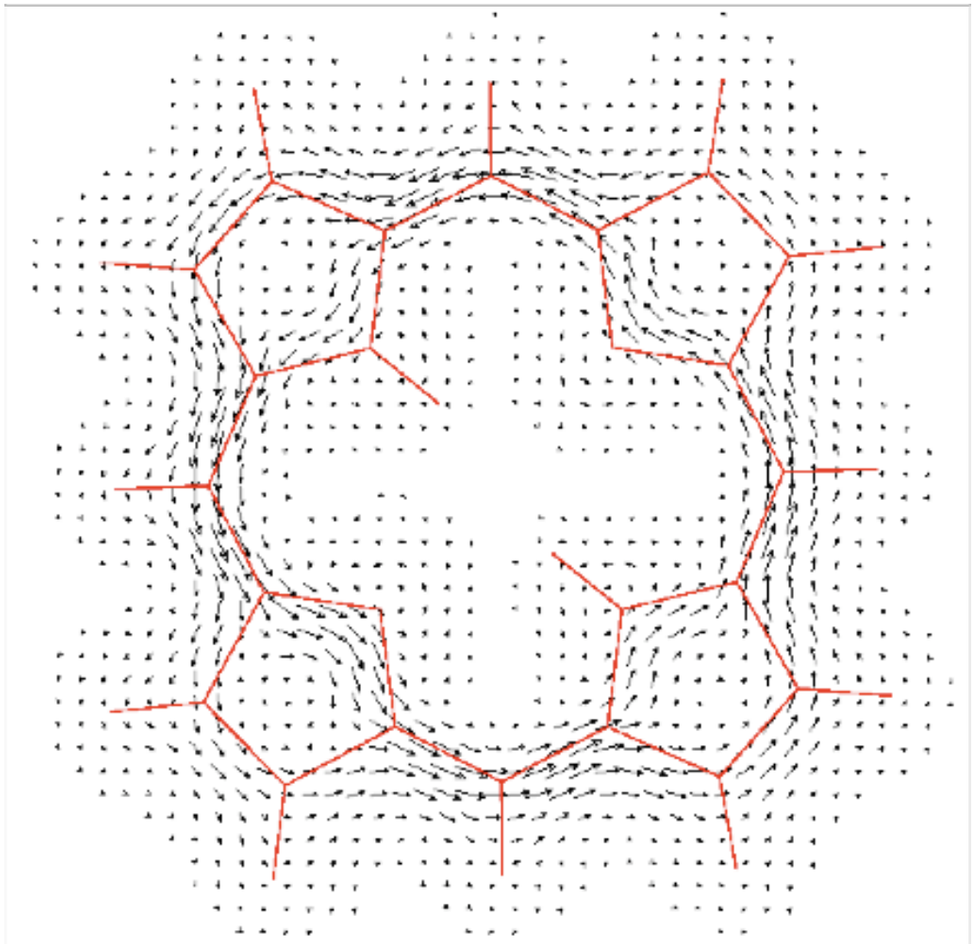
$$\omega = \gamma B_{local}$$

$$B_{local} = B_0 + B_{induced}$$

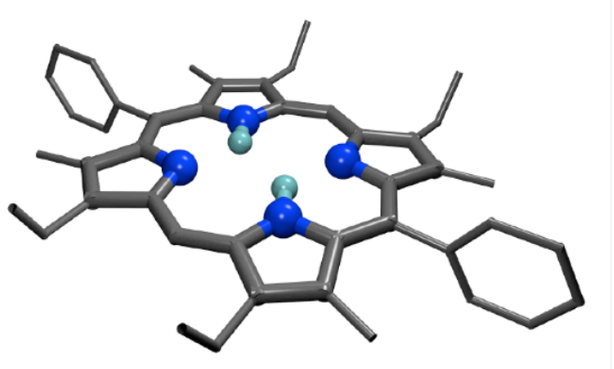
$$B_{induced} = -\sigma B_0$$

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**



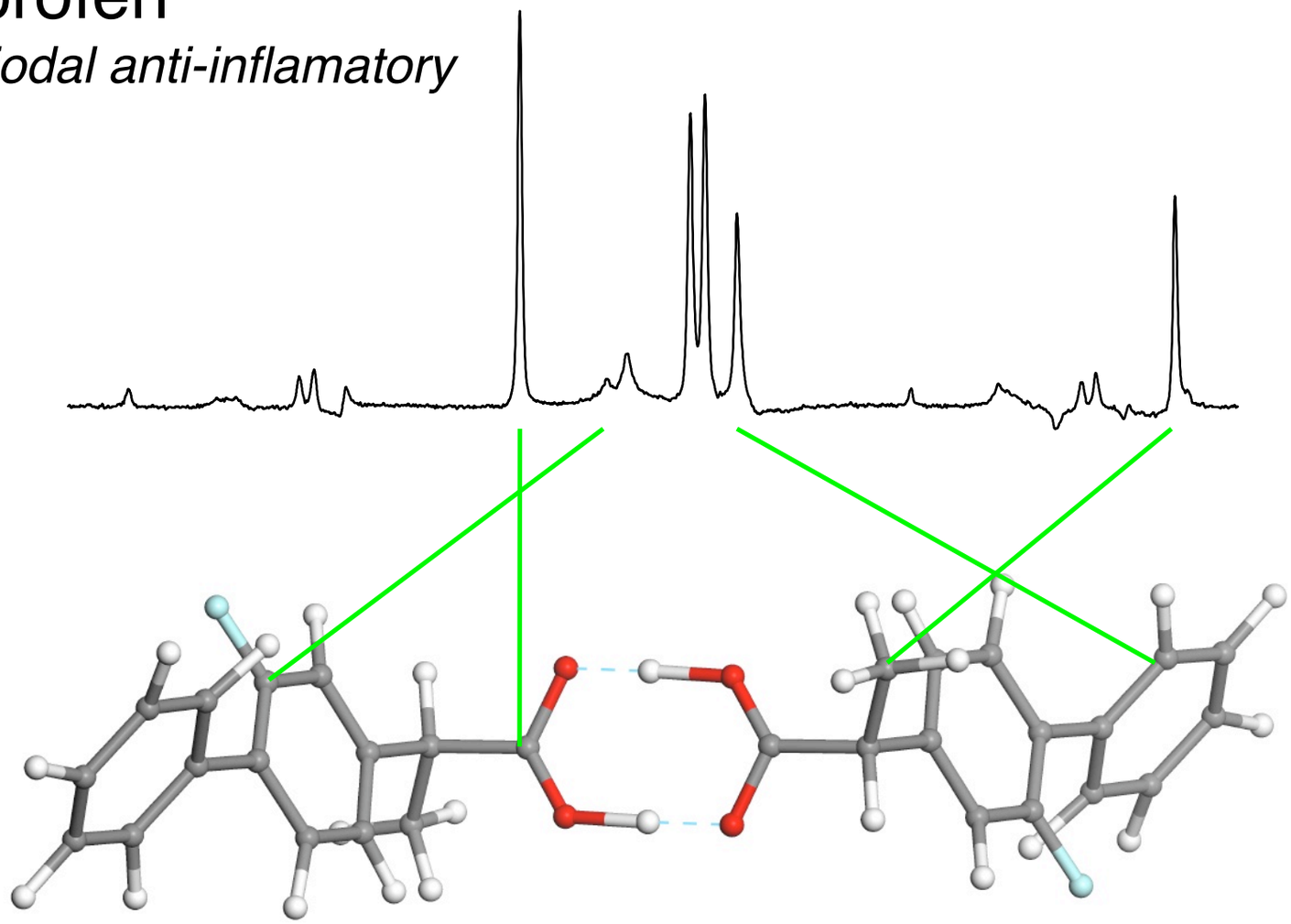
Orbital Current induced by B-field in Porphyrin ring



^{13}C NMR

Flurbiprofen

non-steriodal anti-inflamatory



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

chemical shift (ppm)

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

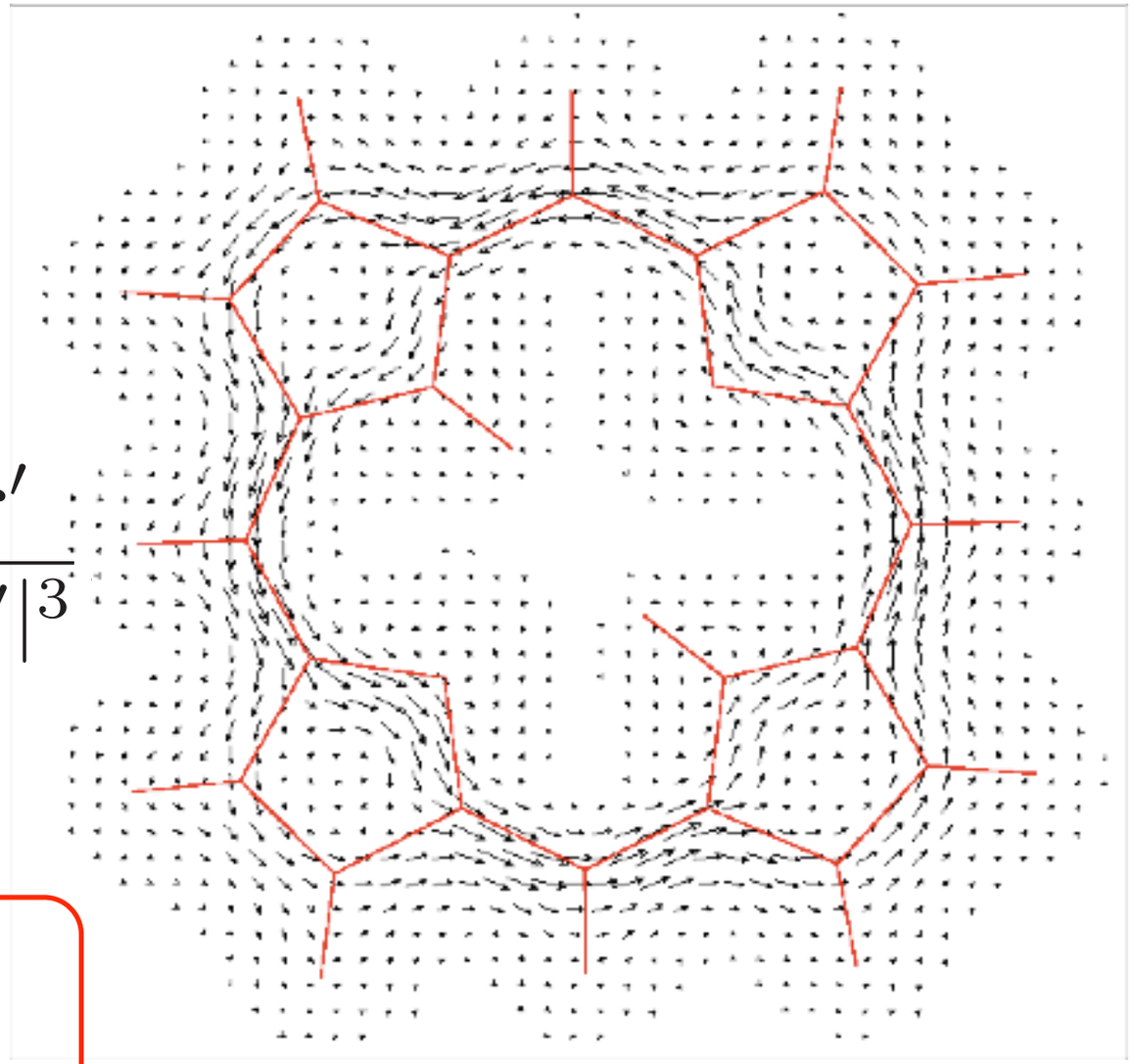
magnetic shielding (from calc)

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)

current to shift

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



Biot-Savart

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

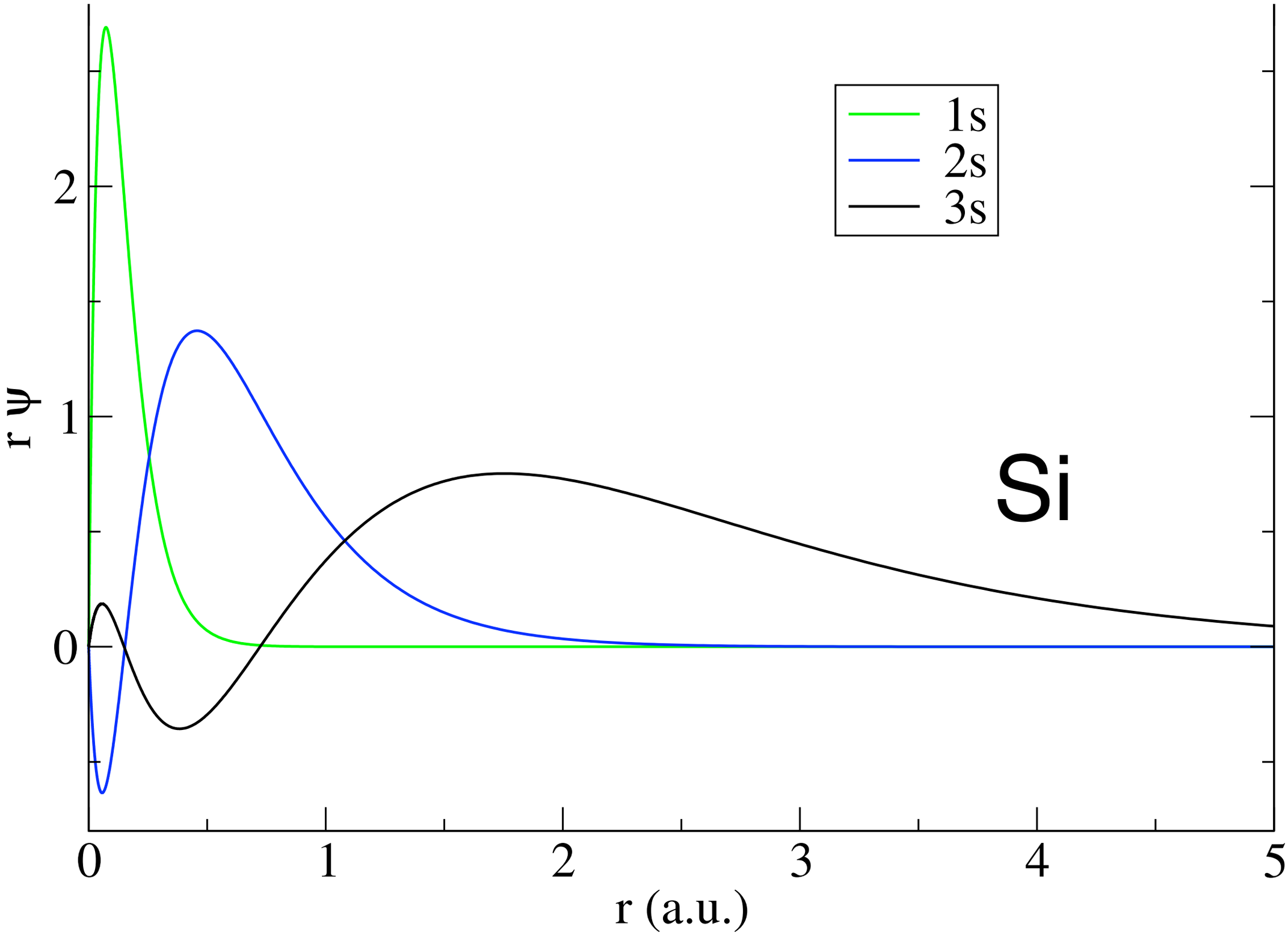
Obtain current within perturbation theory (linear response)

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

$B_{in} = -\sigma B_0$

note: σ 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

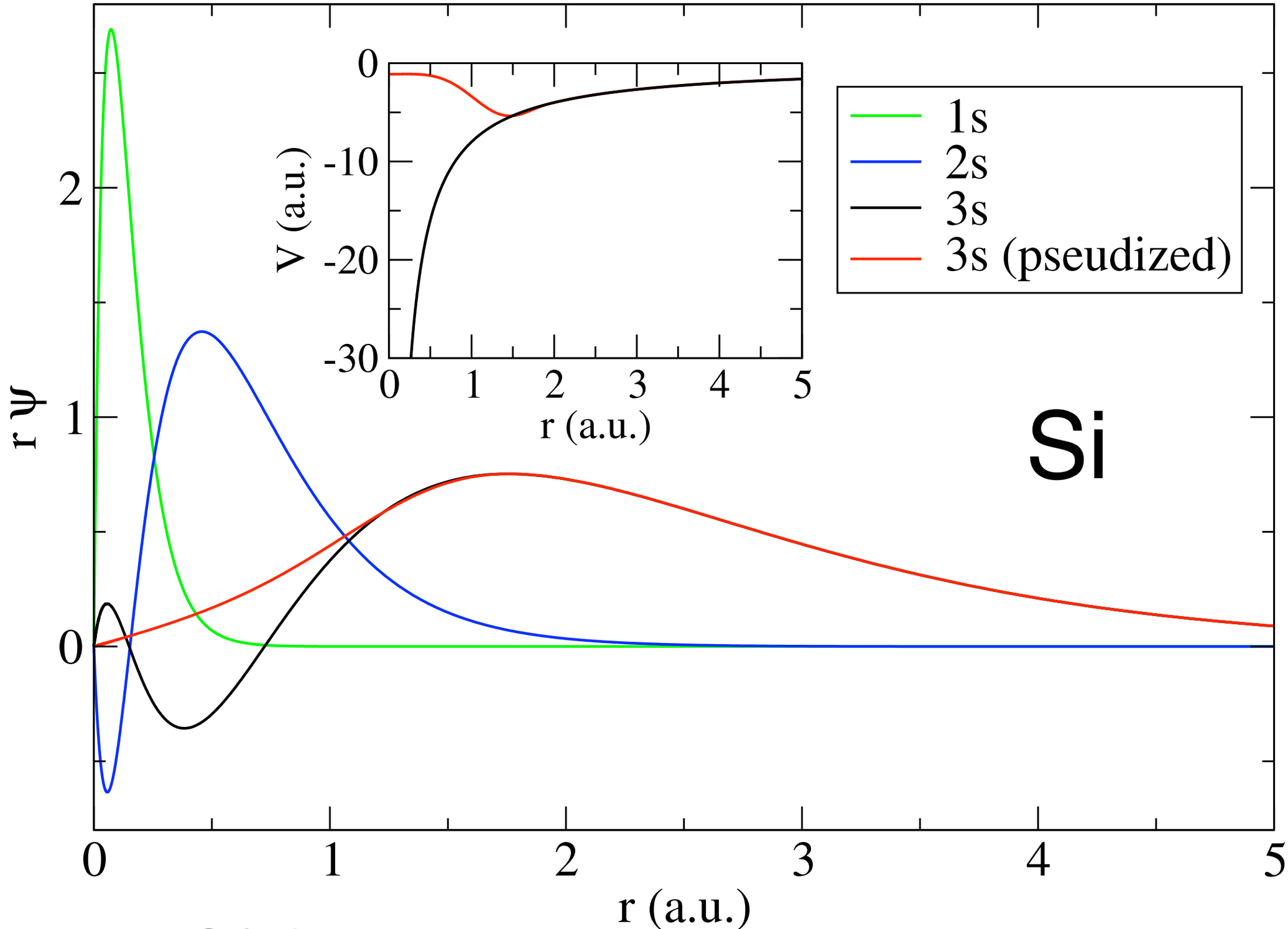
- “Core” electrons taken from free atom fixed during calculation

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



GIPAW

Overcoming the previous approximations

Representation of Position Operator

- r is not a cell periodic function (won't discuss this further)

  $H^{(1)}=(rxp).B$

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

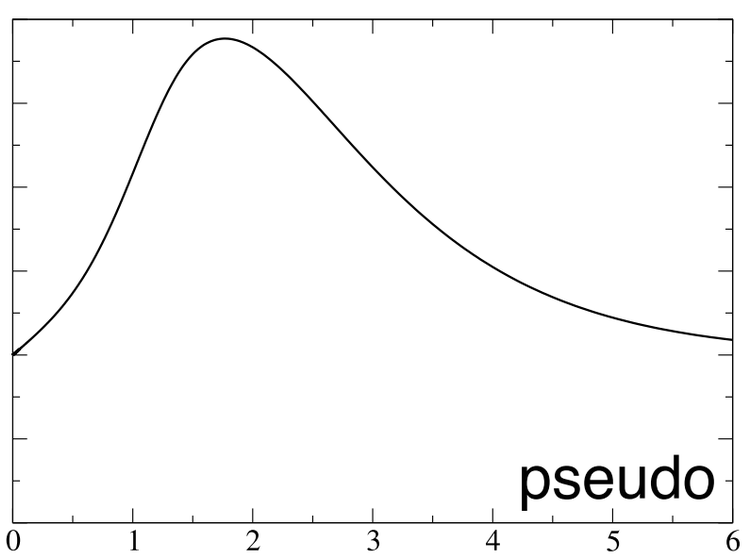
- Use PAW method to fix-up valence wavefunction in the core region

Projector Augmented Waves

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

pseudo all-electron

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



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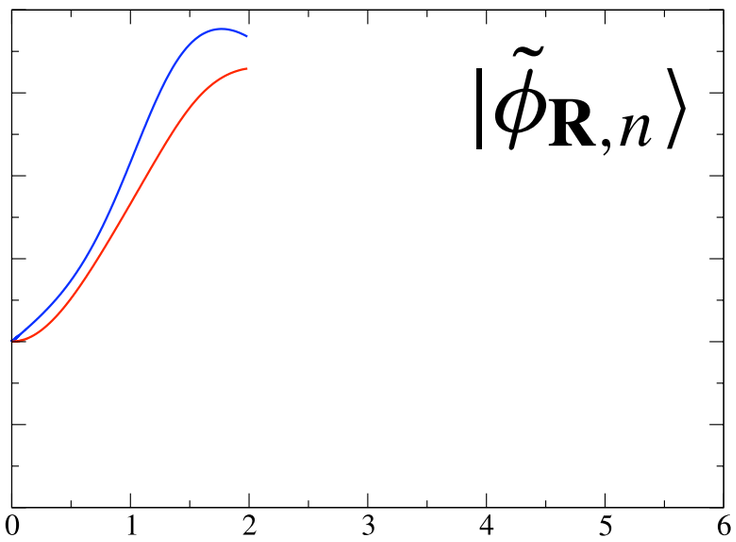

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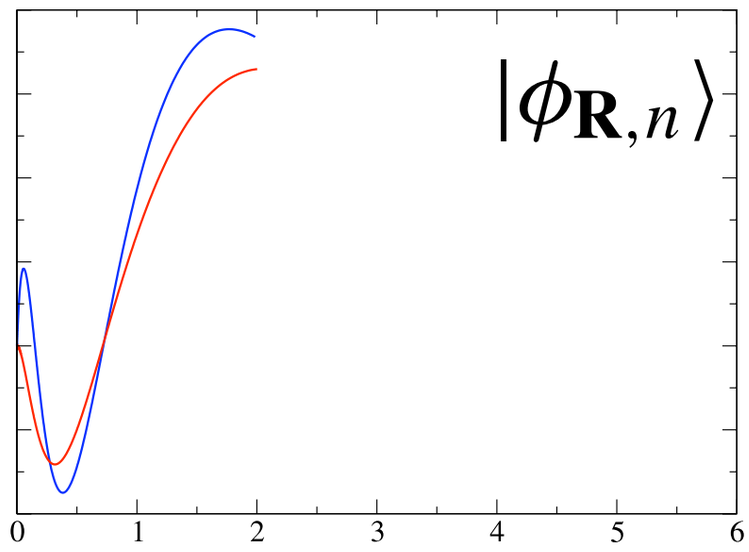

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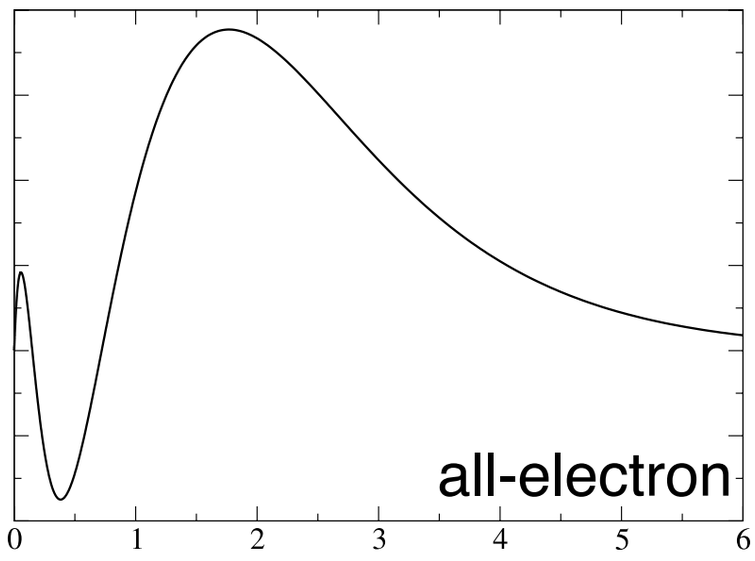


GIPAW

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

NMR - CASTEP code:

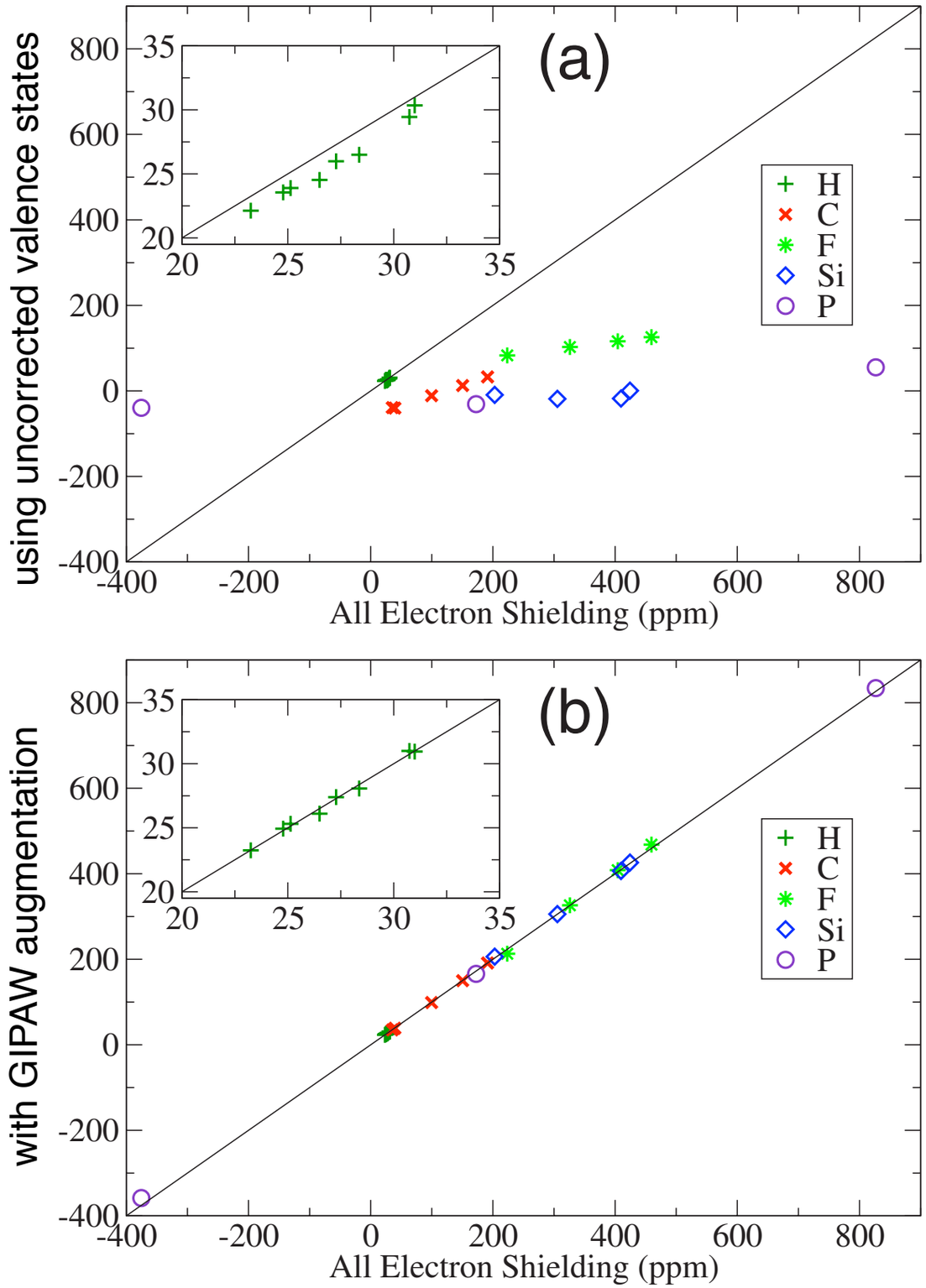
JRY, CJP, F. Mauri (Paris)

NMR-CASTEP vs Gaussian

test on small molecules

n.b. v. big Gaussian basis sets

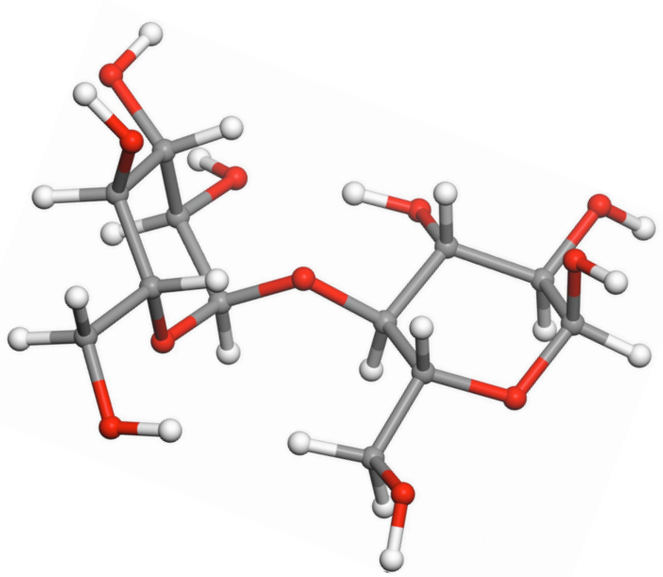
JRY, C. Pickard, F. Mauri PRB 76, 024401 (2007)



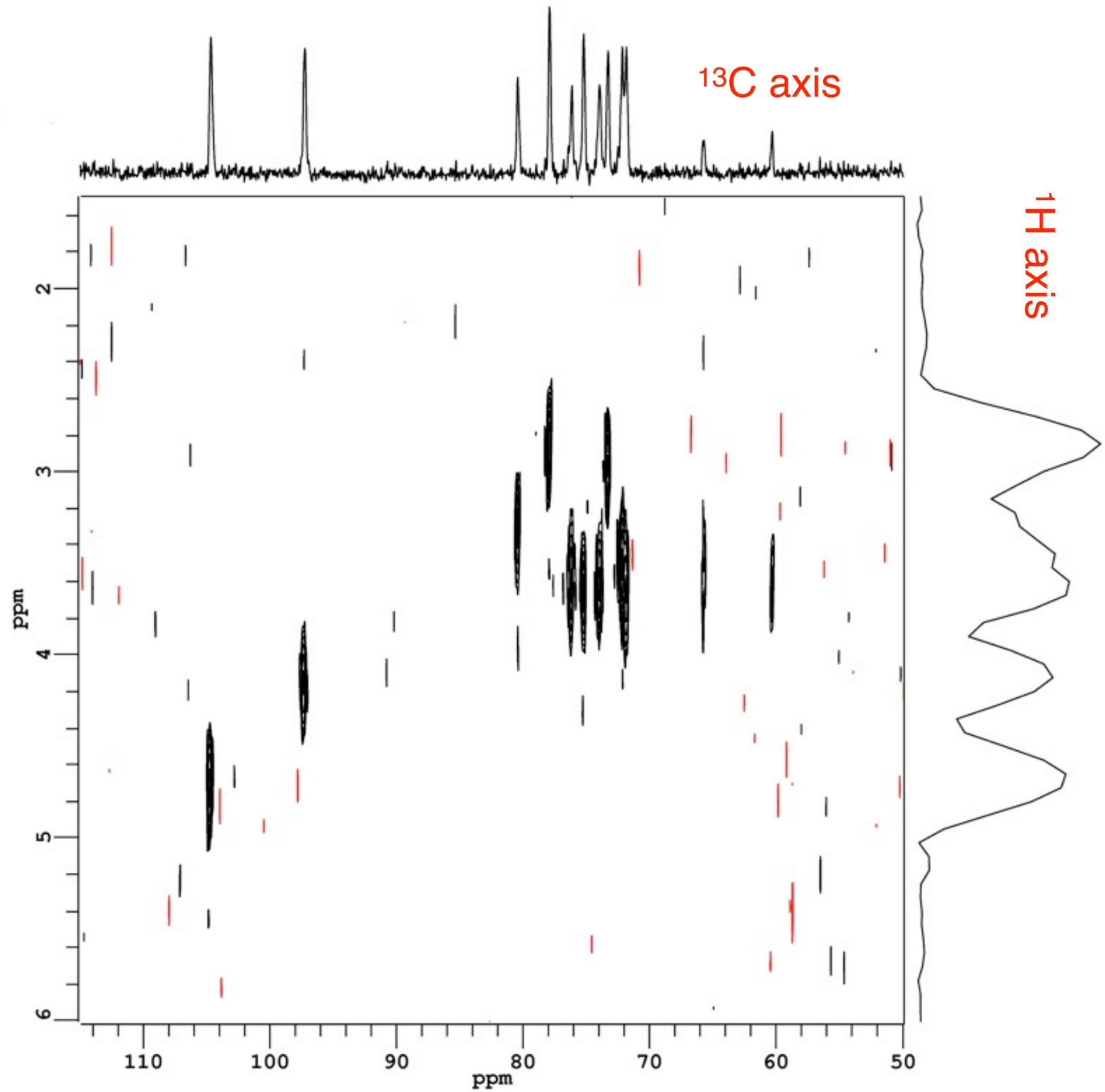
Solid-state effects (Warwick)

Maltose

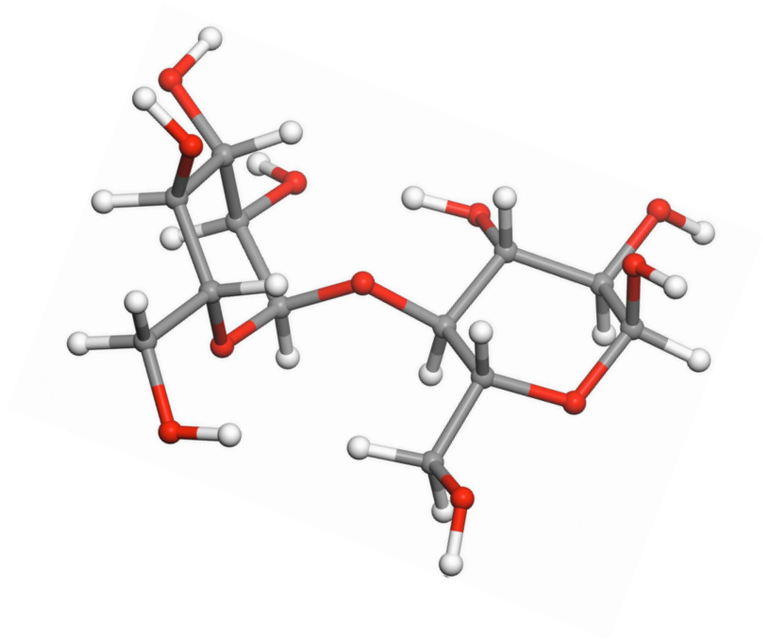
sugar used in brewing

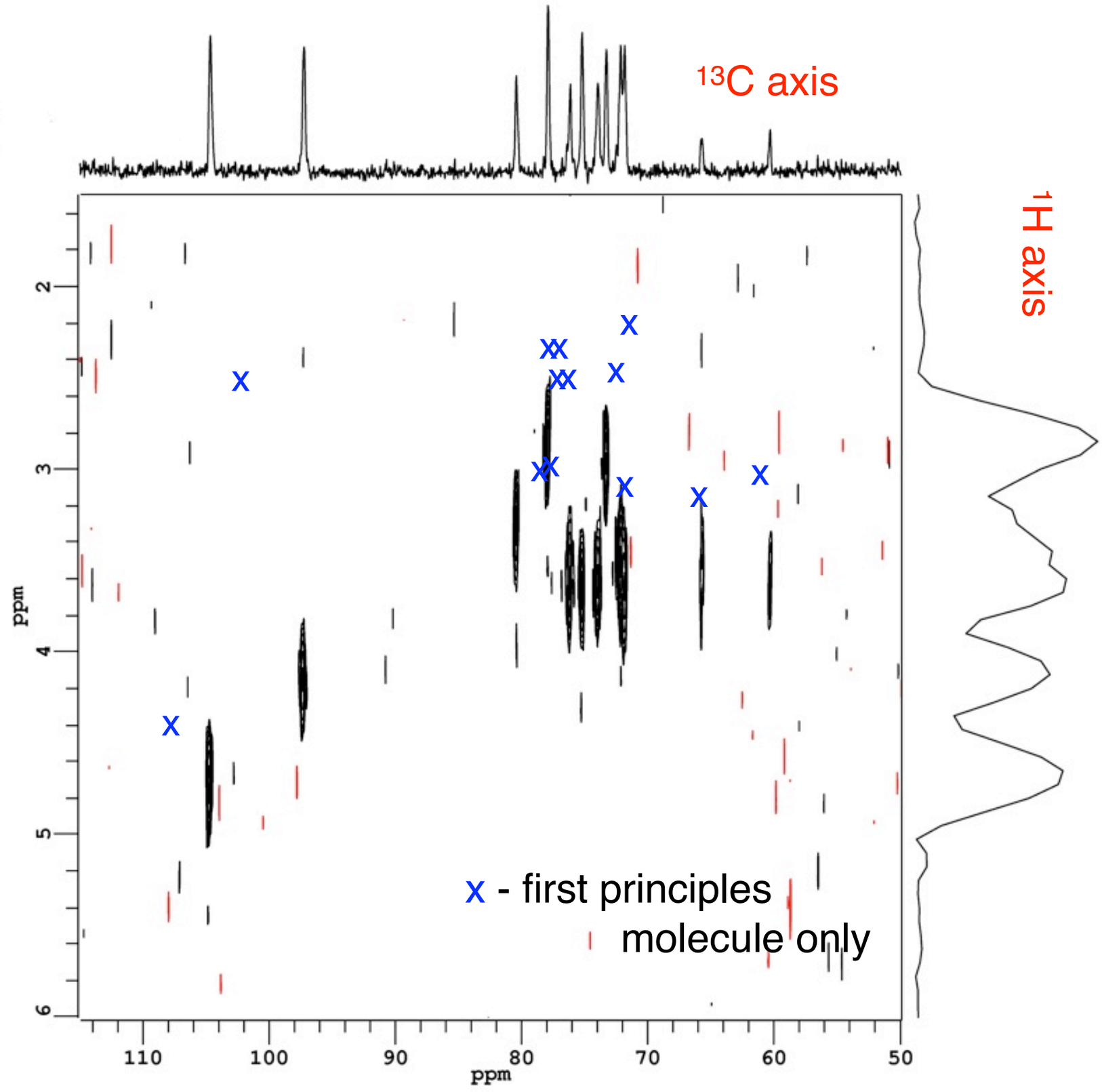


Cross-peaks when J-coupling between spins: -
C-H “bonds”

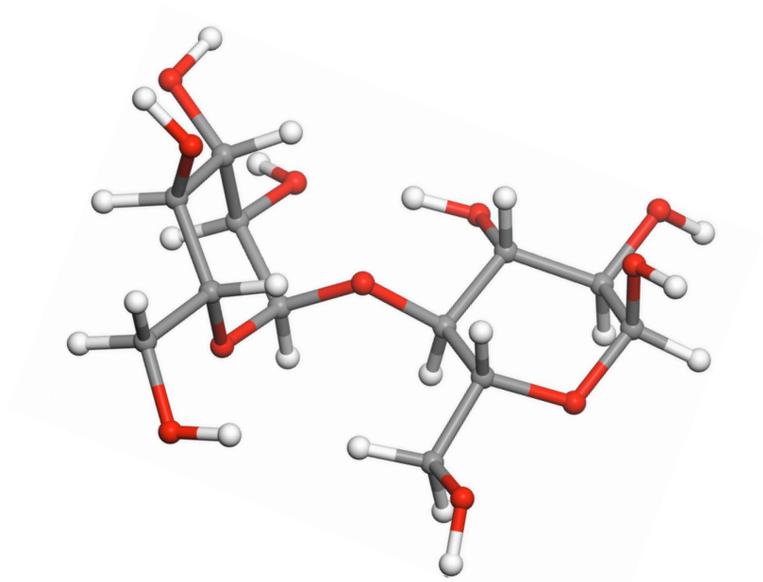


Solid-state effects



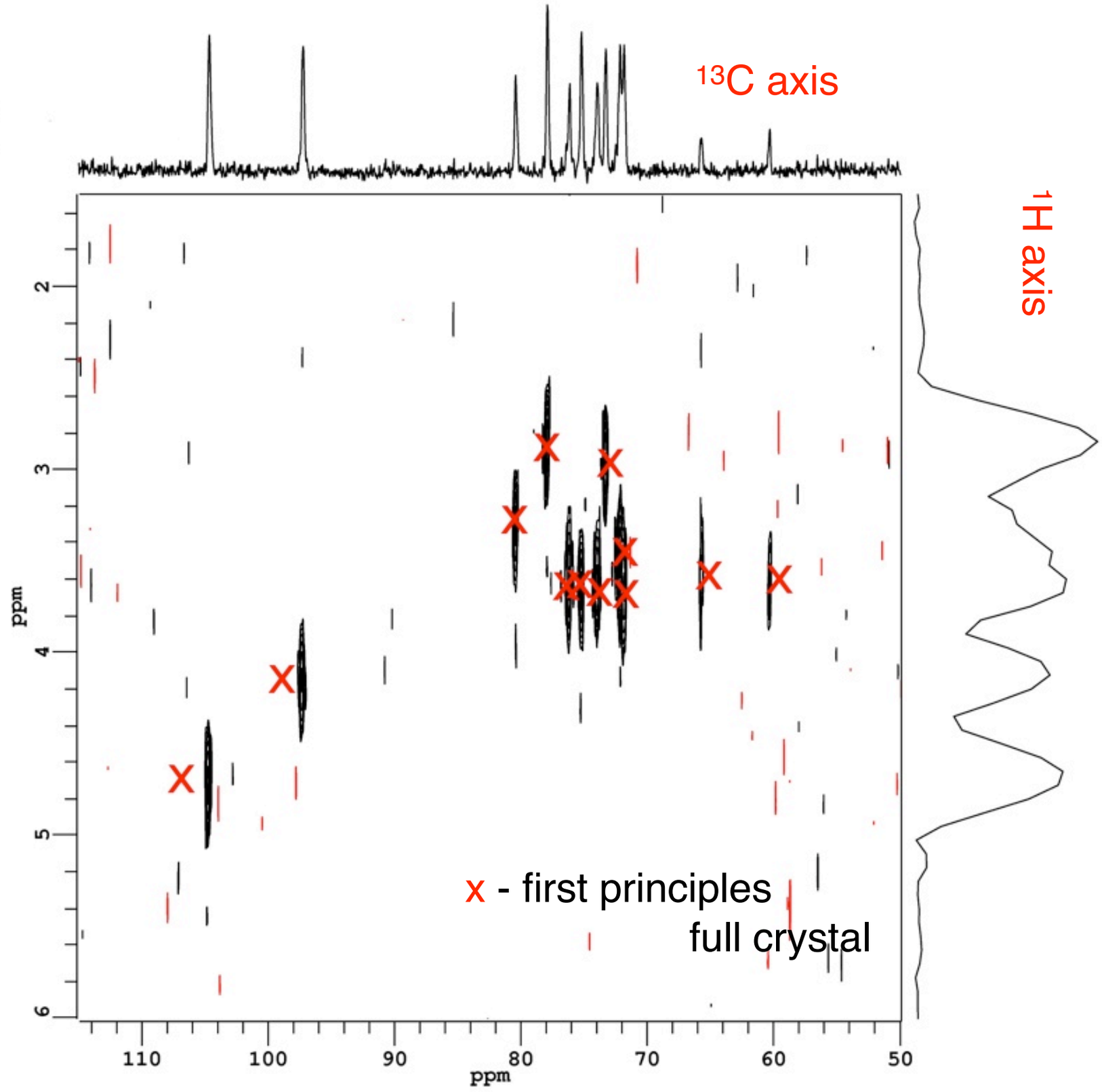


Solid-state effects



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

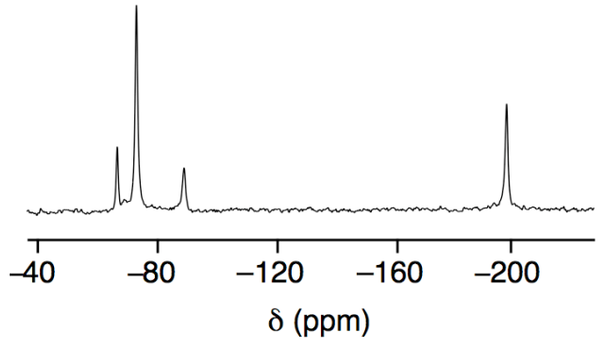
J. Am. Chem. Soc. 127 10216 (2005)
J. Am. Chem. Soc. 130 945 (2008)



NMR parameters

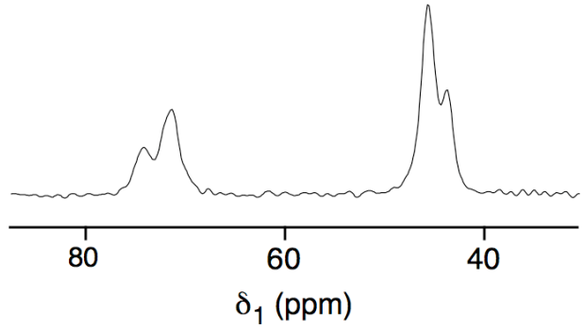
Chemical Shift

orbital currents



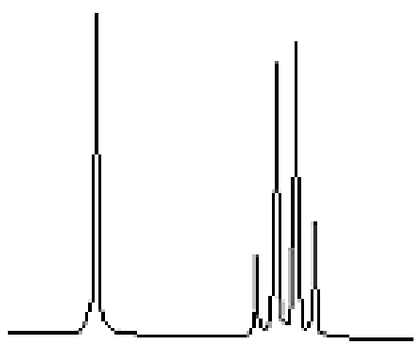
Quadrupolar coupling (EFG)

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

charge density

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

Eigenvalues

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

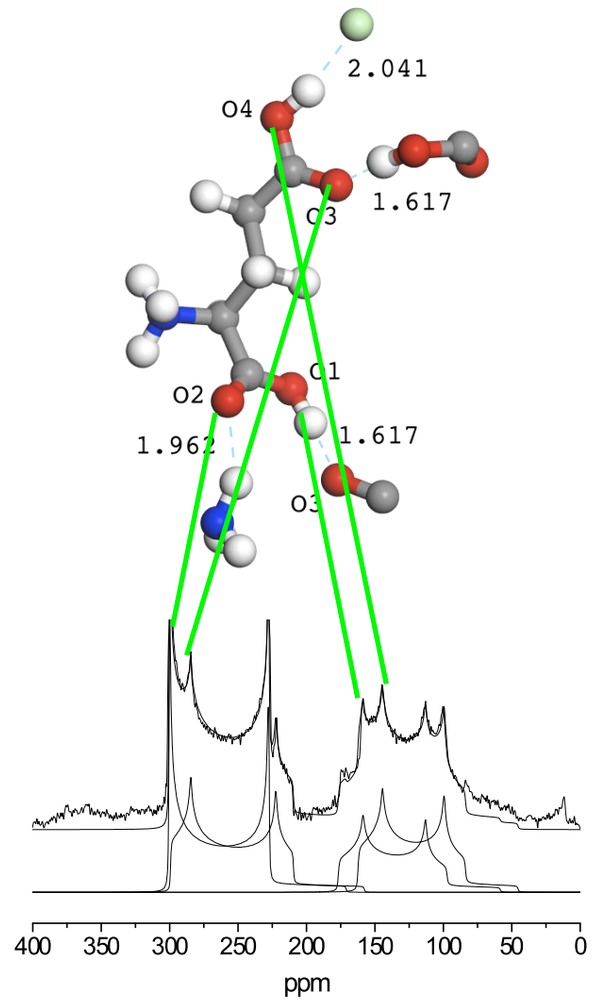
Quadrupolar Coupling

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

Asymmetry

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

Note: The quadrupolar moment, Q, is a nuclear property. CASTEP uses the most recent IUPAC values as defaults. But you can over-ride these (anyhow it is a simple scaling factor)



^{17}O MAS Glutamic Acid . HCl

Calculations

*.param file

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

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)

*.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

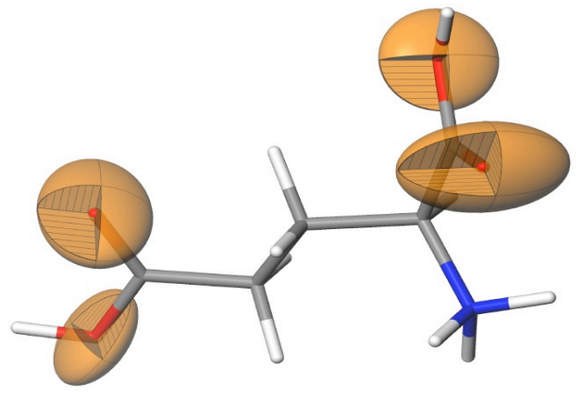
$$\sigma_{\mathrm{aniso}} = \sigma_{\mathrm{zz}} - 1/2(\sigma_{\mathrm{xx}} - \sigma_{\mathrm{yy}})$$

Asymmetry

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

*.magres File

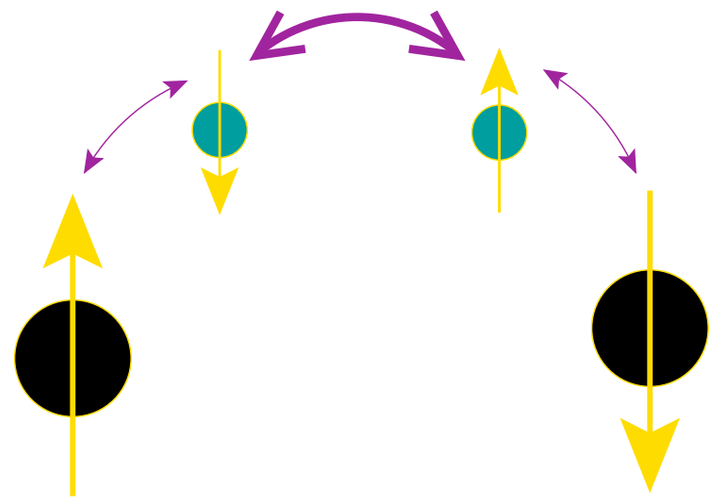
```
============
Atom: O    1
============
O    1 Coordinates      1.641    1.522    5.785   A

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      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

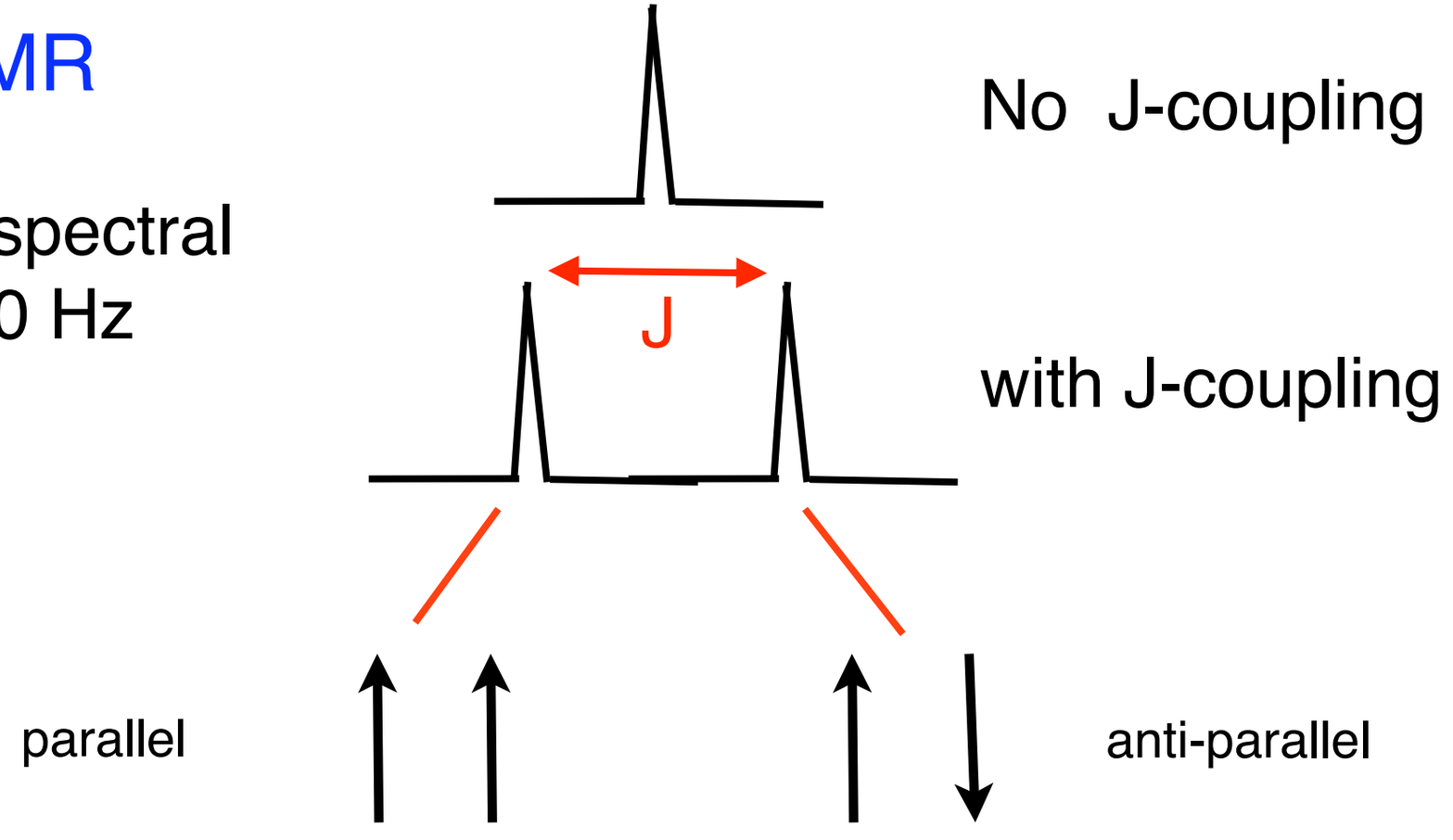
J-Coupling

Electron-mediated interaction of nuclear spins



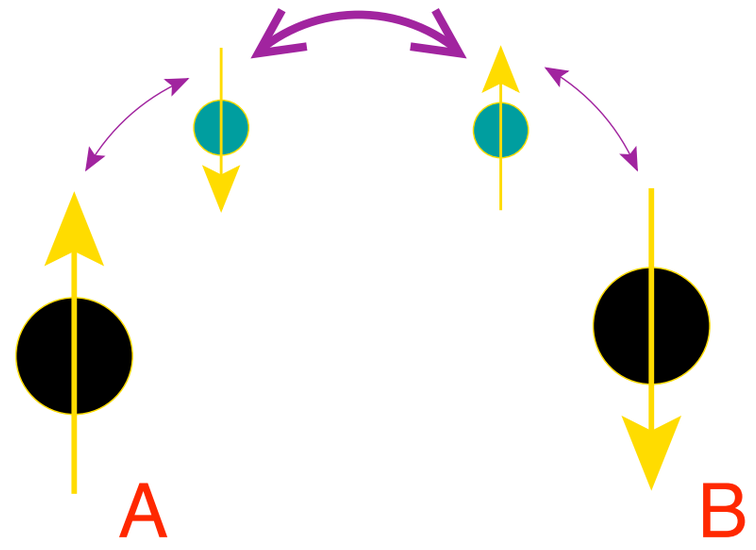
Solution-state NMR

J-coupling splits spectral peaks J ~ 1-100 Hz



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

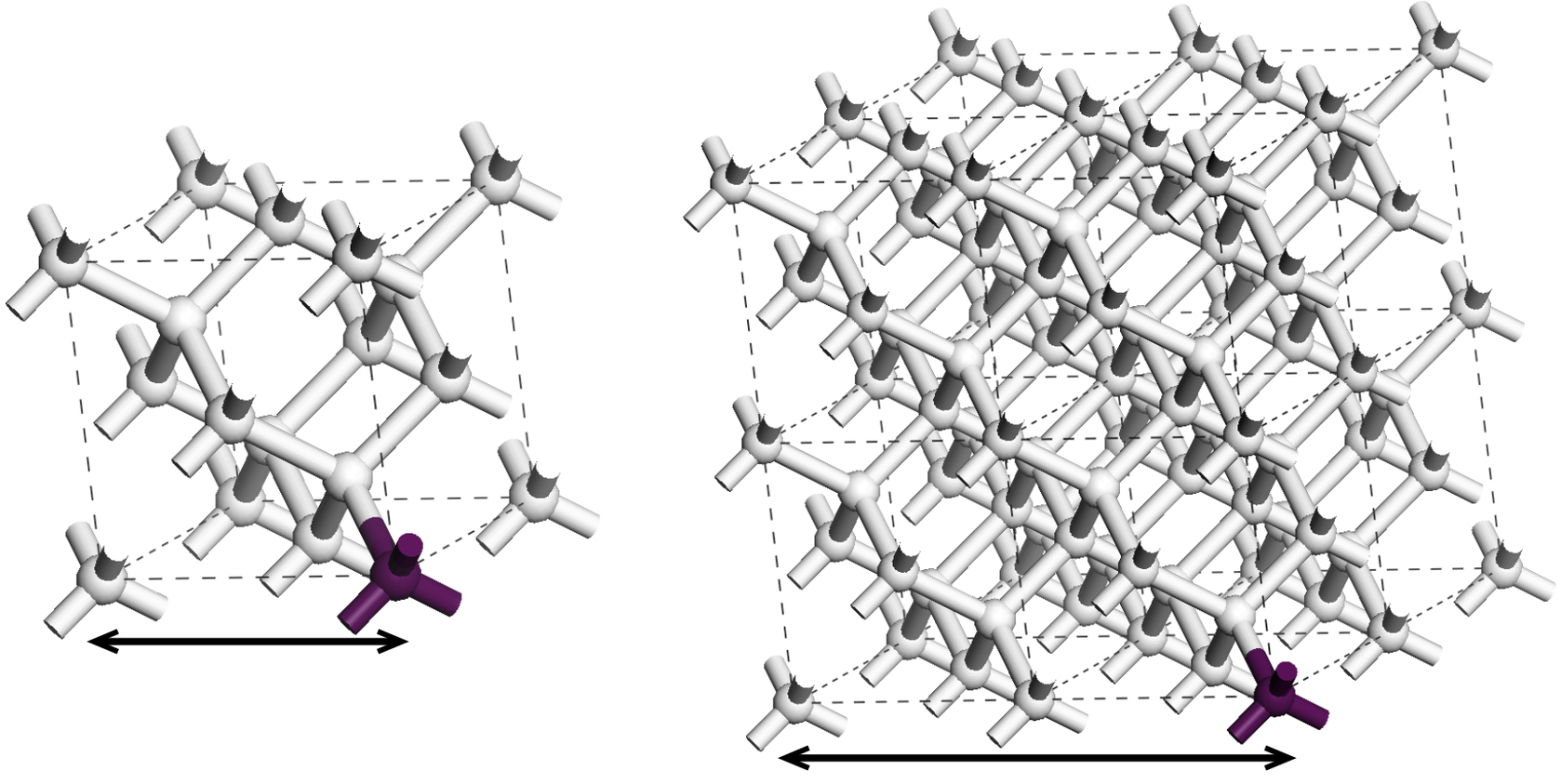
J. Chem. Phys. 127, 204107 (2007)

J-coupling

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 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



J-coupling - *.castep

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*

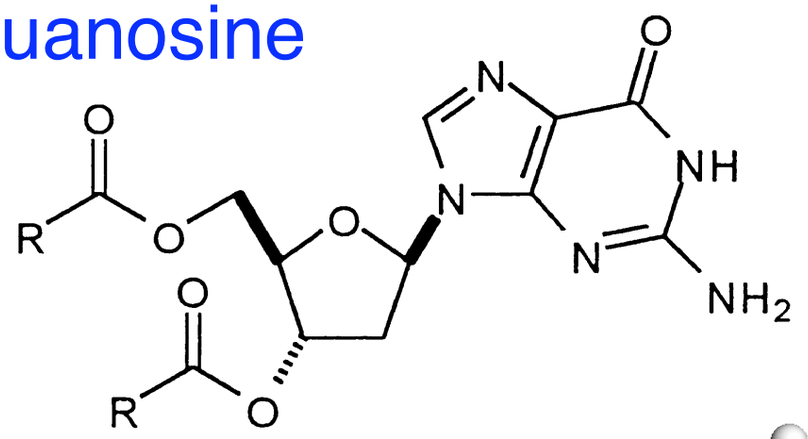
Perturbing atom →

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	-3895.99	-53.73	-171.54	1.86	-4119.41
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

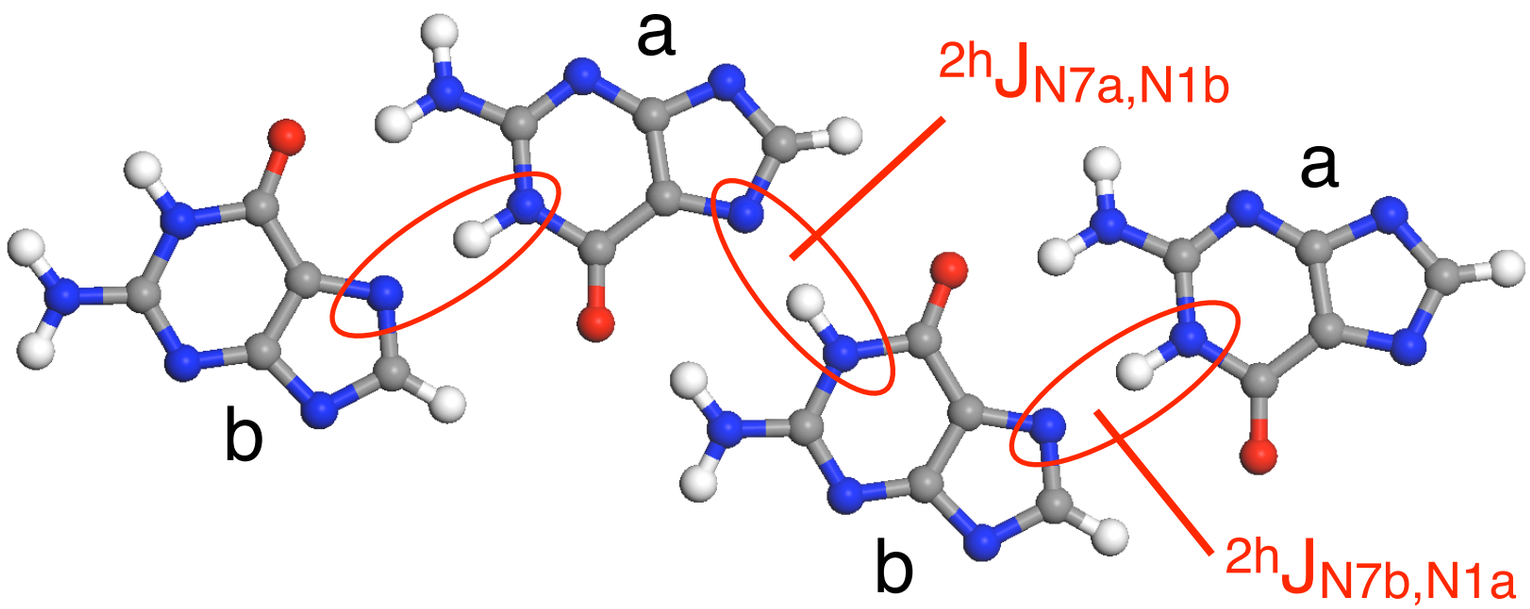
Bond	Length (A)	1st image	Iso(Hz)	Aniso(Hz)
Si 001 -- O 001	1.61808	12.06908	20.18	57.86
Si 001 -- Si 038	3.02674	11.25096	12.90	3.09
Si 001 -- Si 010	3.03908	7.70290	12.79	3.47
Si 001 -- Si 016	3.09623	9.83675	18.48	6.54
Si 001 -- Si 030	3.17013	11.91281	15.03	8.39

DNA bases (Warwick)

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. (2008) doi:10.1021/ja800419m

Predictions

$^{2h}J_{O6a,N2b}$ = 5.7 Hz
$^{1}J_{O6a,C1a}$ = 22.0 Hz

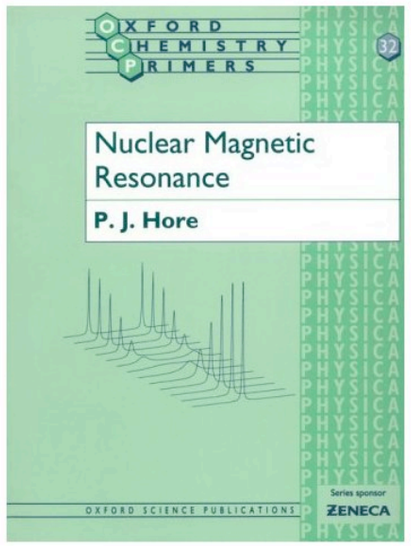
DFT+spectroscopy: Oxford 2009 *Jonathan R. Yates*

Getting more information

NMR Books

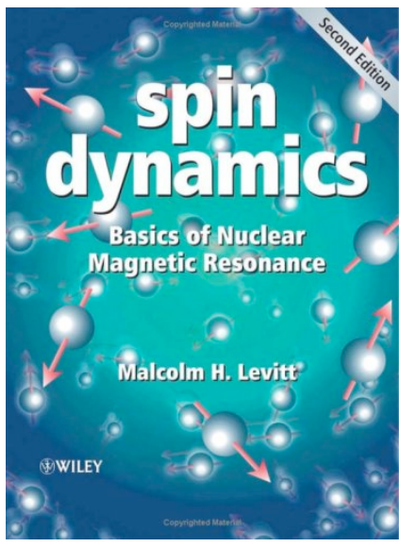
Good Introduction

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



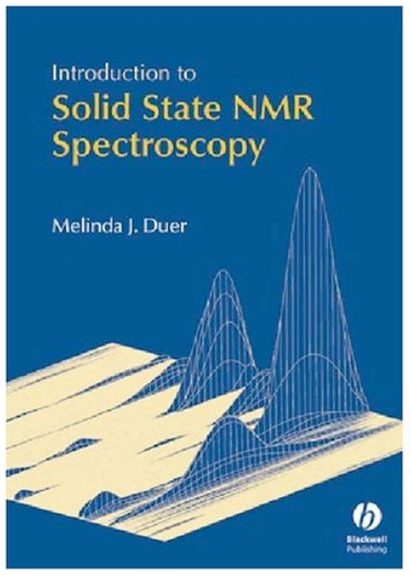
More advanced

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) doi:10.1002/9780470034590.emrstm1009

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
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