CHEM40111/CHEM40121

Molecular magnetism

7 Magnetic resonance imaging

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Course Overview

1 Fundamentals • Motivation • Origins of magnetism • Bulk magnetism	**5 Single-molecule magnets I** • Single-molecule magnets • Electrostatic model
2 Quantum mechanics of magnetism • Zeeman effect • Statistical mechanics • Magnetisation • Magnetic susceptibility	**6 Single-molecule magnets II** • Measuring magnetic relaxation • Relaxation mechanisms • Latest research
3 Magnetic coupling • Exchange Hamiltonian • Experimental measurements • Vector coupling	**7 Magnetic resonance imaging** • Paramagnetic NMR • Magnetic resonance imaging • Latest research
4 Magnetic anisotropy • Zero-field splitting • Impact on properties • Lanthanides • Spin-orbit coupling	**8 Quantum information processing** • Quantum information • DiVincenzo criteria • Latest research • ***Question time***

Intended learning outcomes

1. Explain the origin of magnetism arising from electrons in atoms and molecules using formal quantum-mechanical terms

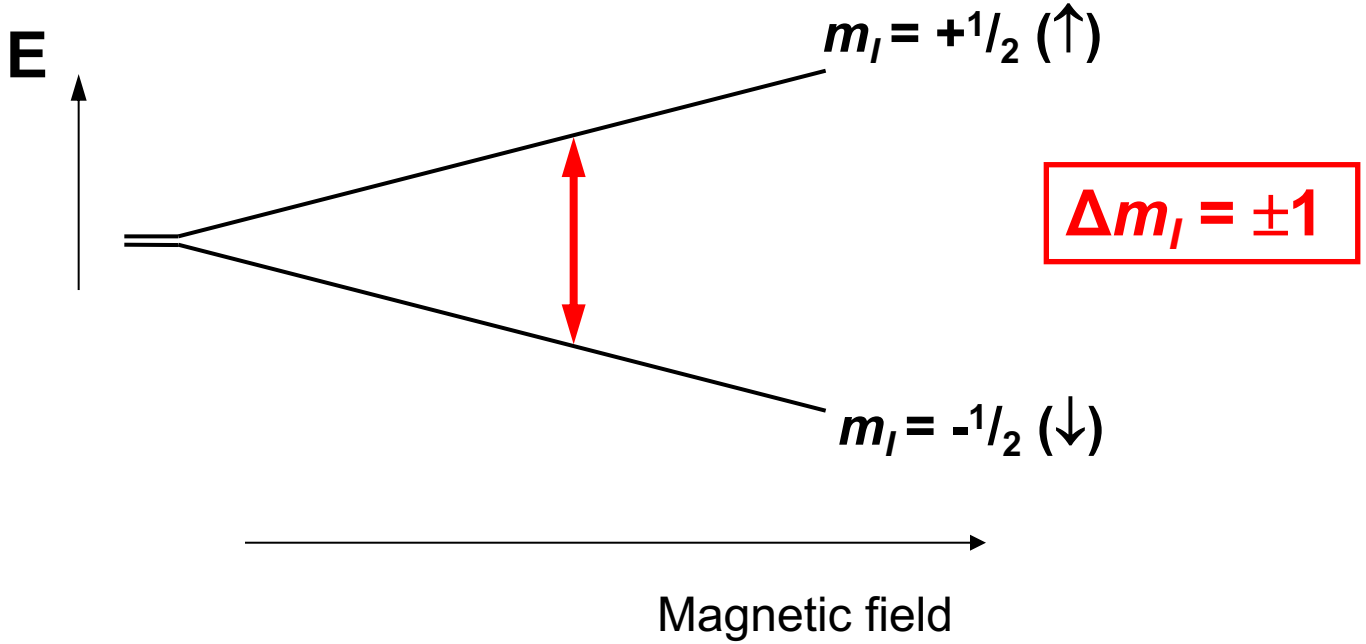
2. Compare and contrast the electronic structure of metal ions in molecules and their magnetic properties, for metals across the periodic table

3. Select and apply appropriate models and methods to calculate molecular magnetic properties such as magnetisation, magnetic susceptibility and paramagnetic NMR shift

4. Deconstruct topical examples of molecular magnetism including single-molecule magnetism, molecular quantum information processing and MRI contrast agents

Reminder: NMR

- Nuclear spin states are split in a magnetic field
  - This is ***exactly*** the same Zeeman effect as for electrons!
  - Just that nuclear magnetism is ***a lot*** smaller!



- Apply radio waves at the right energy and the nuclear spin can flip

Reminder: NMR

- The operating frequency of an NMR spectrometer (400 MHz, 600 MHz, etc.) is roughly the frequency needed to flip ^{1}H nuclei for a given field
  - Higher frequency, bigger magnet!

- But all ^{1}H nuclei are not the same in a molecule, so require slightly different frequencies
  - NMR applies a pulse of that is say 600 MHz ± 0.03 MHz to catch all of them

- The spectrum is simply "what frequency flips each proton"?

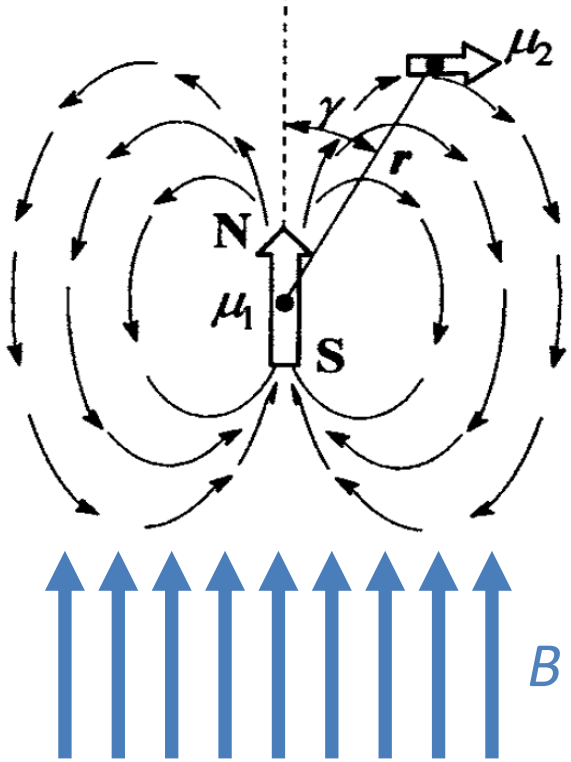
Paramagnetic NMR

- Most of the NMR you will have done is on diamagnetic molecules

- Anyone who has tried NMR on something paramagnetic usually doesn't say nice things…

- Any ideas why?

  - Putting a little magnet ***right next to*** the nucleus!



Paramagnetic NMR

- The paramagnetic ion has two effects:

1. The local magnetic field is different, thus the resonance frequency changes
   - the proton is ***shifted*** in the spectrum, sometimes dramatically!

2. The relaxation rate of the nuclear spin changes
   - this is the same relaxation rate as for SMMs, but for nuclei
   - this can make the peaks very broad

Paramagnetic NMR

- The total chemical shift is therefore:

$$\delta = \delta_{dia} + \delta_{para}$$

- δ_{para} has two parts:

$$\delta_{para} = \delta_{contact} + \delta_{pseudo-contact}$$

Due to the "contact" of spin density with the nucleus.

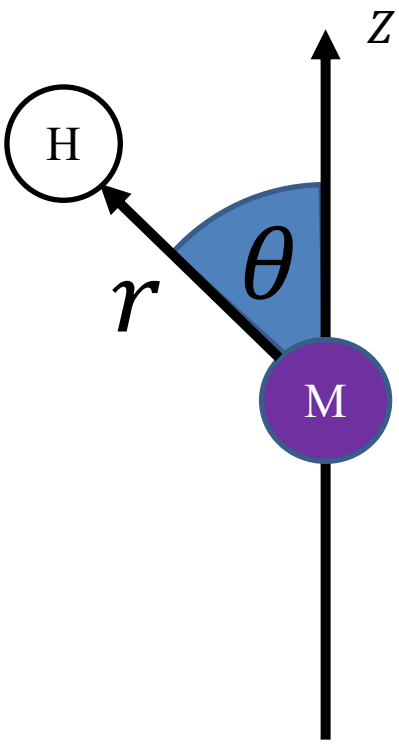
Generally small

Due to dipolar or through-space magnetic field.

Often dominant

Paramagnetic NMR

- If the pseudo-contact term dominates, it can be calculated:



$$\delta_{PCS} = \frac{\chi_z - \chi_{av}}{2N_A} \frac{3\cos^2\theta - 1}{r^3}$$

- Magnetic susceptibility can be anisotropic:

$$\chi_{av} = \frac{\chi_x + \chi_y + \chi_z}{3}$$

[1] I. Bertini, *Prog. Nucl. Magn. Reson. Spectrosc.*, 2002, **40**, 249.

Paramagnetic NMR

- If the pseudo-contact term dominates, it can be calculated:

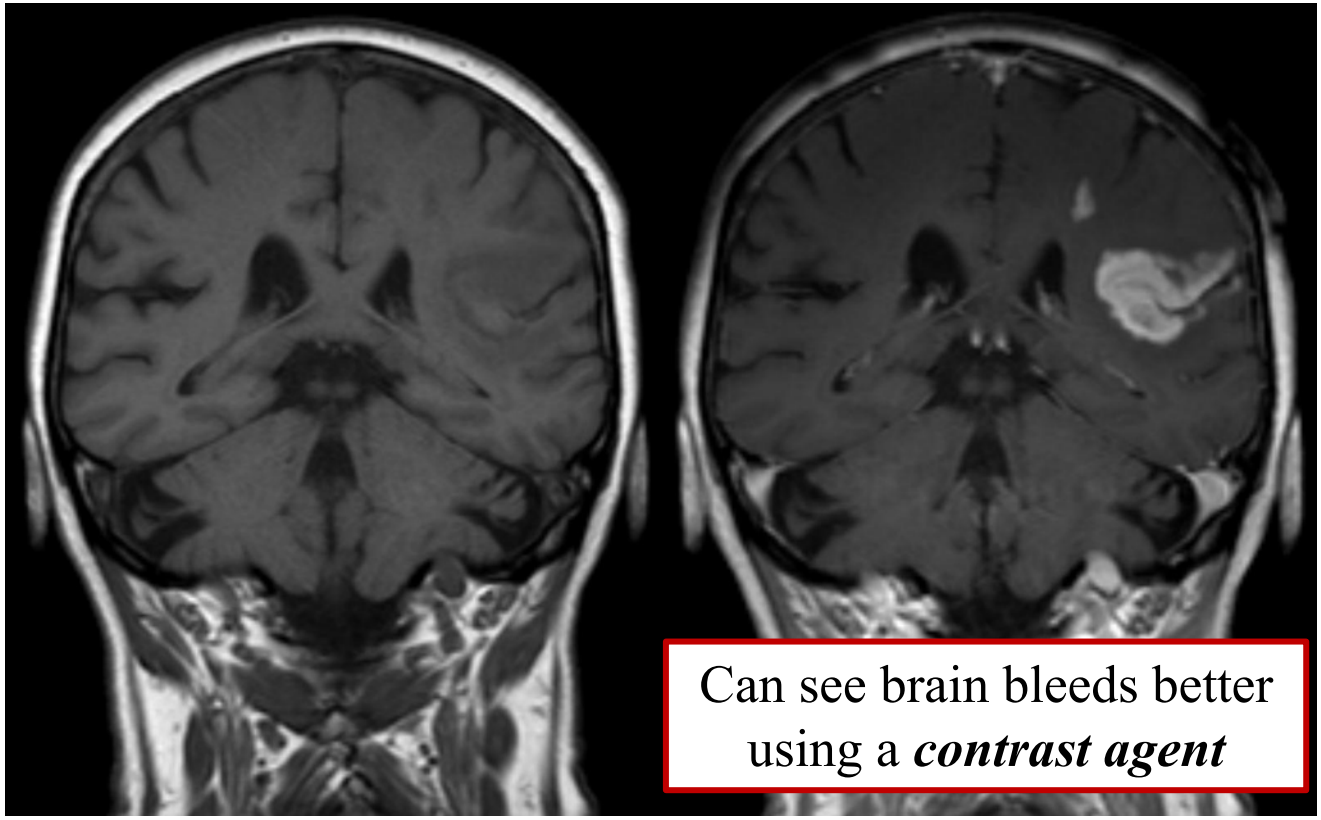
$$\delta_{PCS} = \frac{\chi_z - \chi_{av}}{2N_A} \frac{3\cos^2\theta - 1}{r^3}$$

- This is ***very*** useful:
  - If you know χ and δ_{PCS} (can be measured independently), then you can calculate the relative position of the proton (θ and r)
  - Structural determination of molecules in solution!
  - Protein conformations and dynamics!

  - Units: $\chi \rightarrow cm^3\ mol^{-1}$ $\quad r \rightarrow m$ $\quad \delta_{PCS} \rightarrow ppm$

MRI

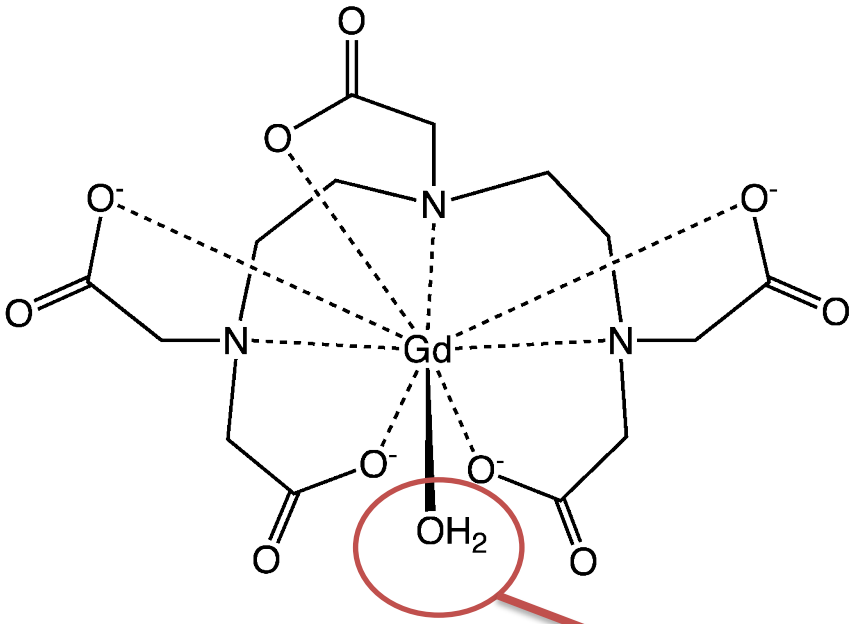
- Aside from the paramagnetic shift, is the change in relaxation rates useful?
  - Yes! MRI scans are whole-body 3D NMR spectra

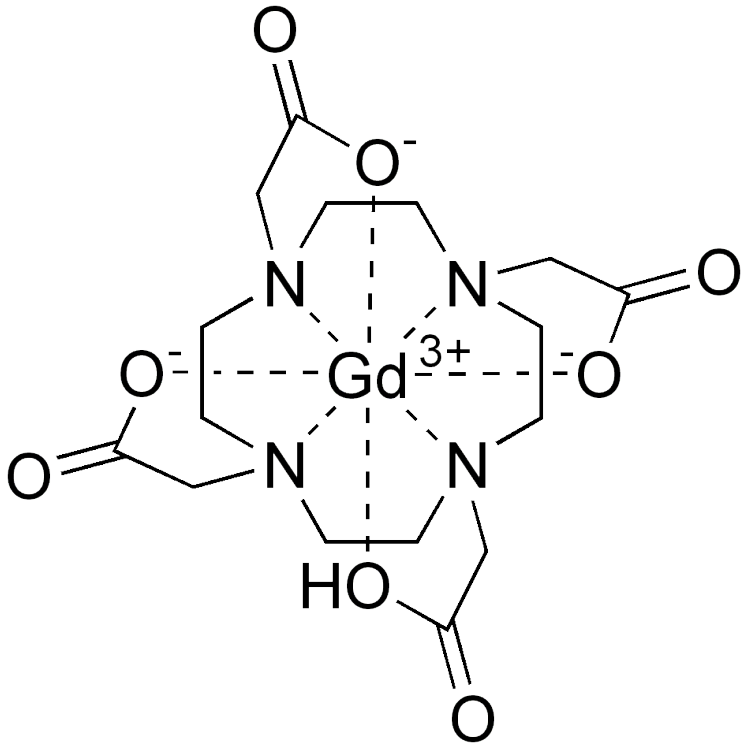


- Shades are not actually the shifts, but are the relaxation rates

MRI

- Some common clinical MRI contrast agents:





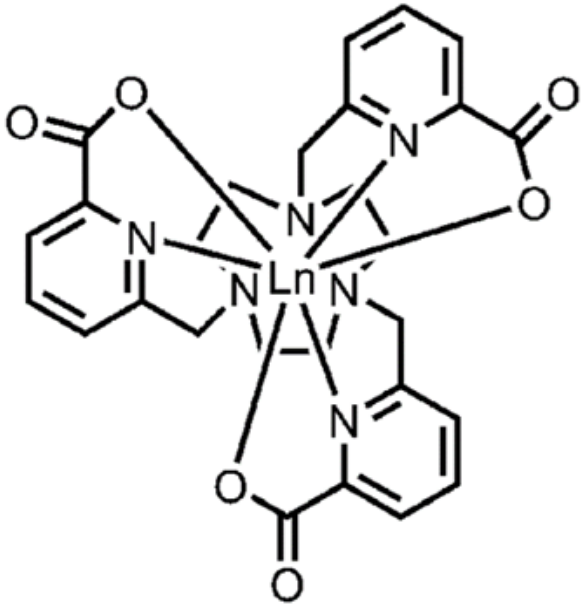
Magnevist (Bayer)

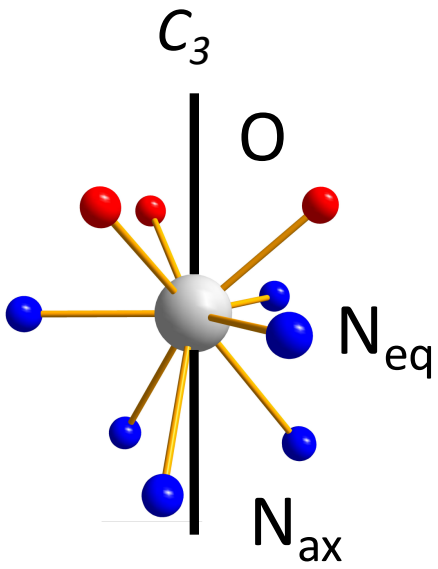
This water molecule is easily replaced – these are the protons MRI measures

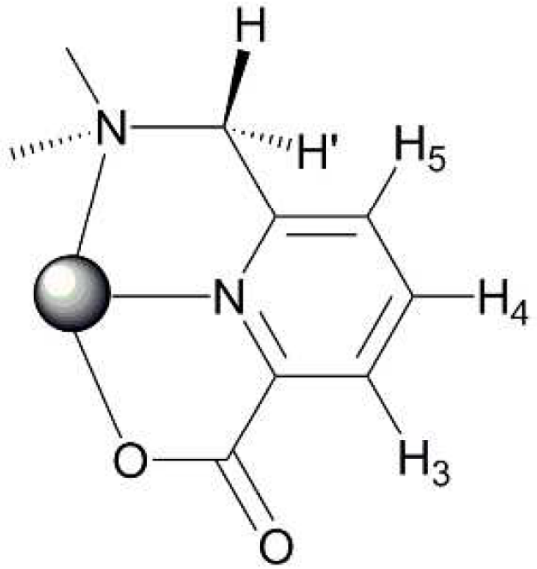
Dotarem (Guerbet)

What's new in MRI contrast

- Collaboration with Prof. David Parker (Durham):







$[LnL^1]$

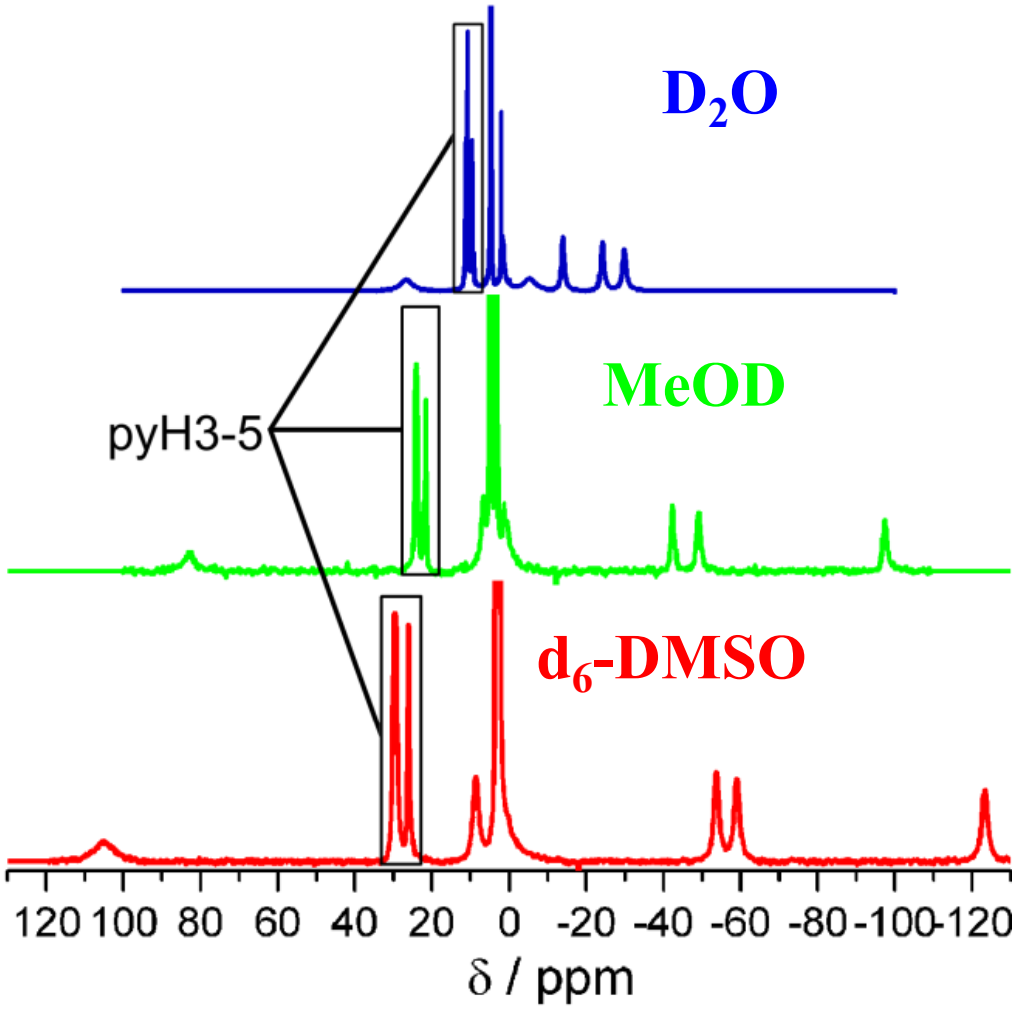
L^1 = 1,4,7-tris[(6-carboxypyridin-2-yl)methyl]-1,4,7-tacn

Ln = Tb^{III}, Dy^{III}, Ho^{III}, Er^{III}, Tm^{III}, Yb^{III}

[1] M. Vonci *et al.*, *J. Am. Chem. Soc.*, 2017, **139**, 14166.

Anomalous behaviour of [DyL^1]

- Dy(III) complex shows an unexpected solvent dependence:

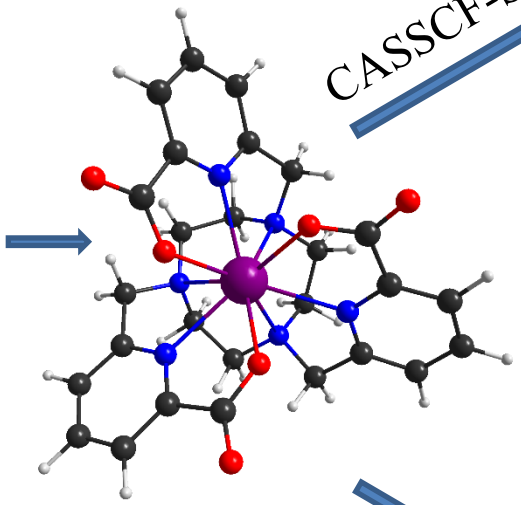


[1] M. Vonci *et al.*, *J. Am. Chem. Soc.*, 2017, **139**, 14166.

Calculation of δ_{PCS}

Solution structure model

Geometry optimisation (DFT + solvent continuum)



CASSCF-SO

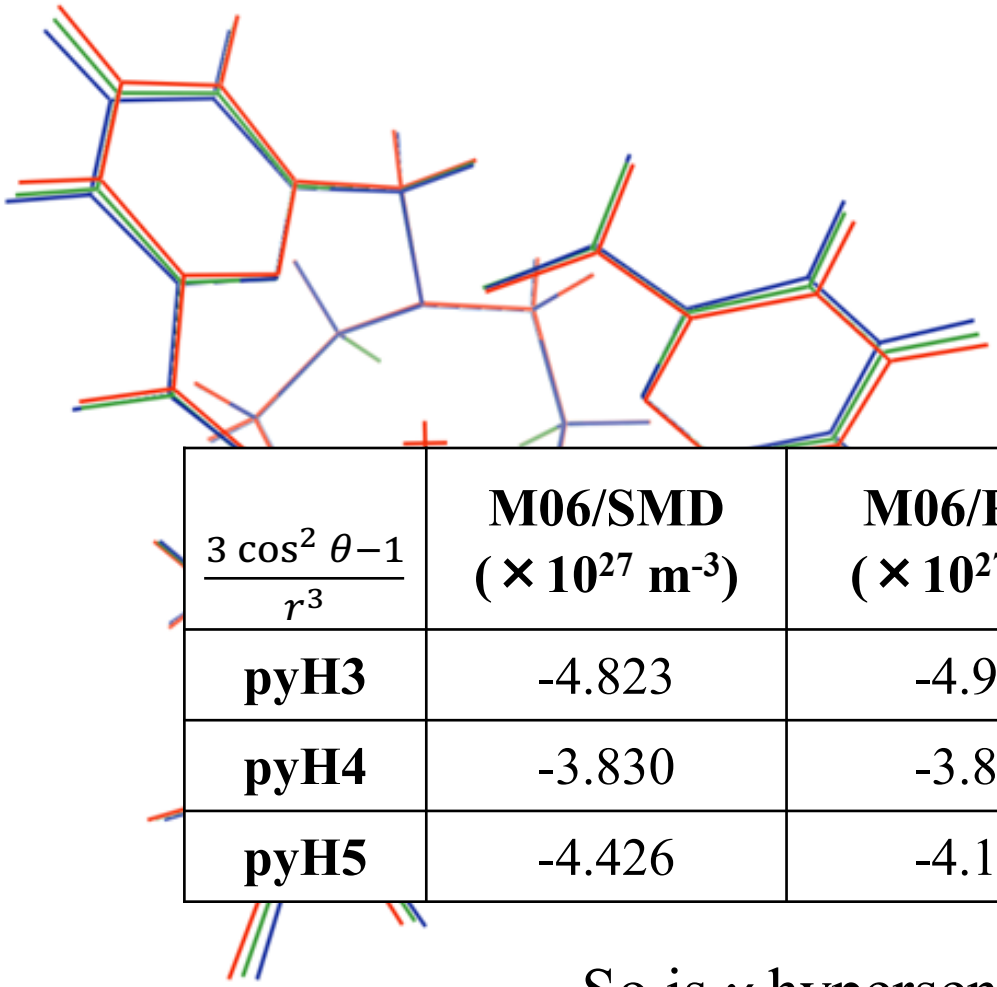
$$\chi_z - \chi_{av}$$

$$\delta_{PCS} = \frac{\chi_z - \chi_{av}}{2N_A} \frac{3\cos^2\theta - 1}{r^3}$$

δ_{PCS}	Experimental (ppm)	M06/SMD (ppm)	M06/PCM (ppm)	BP86/SMD (ppm)
pyH3	**2.9**	**-19.3**	**7.8**	**-33.3**
pyH4	**2.4**	**-15.3**	**6.0**	**-24.8**
pyH5	**1.7**	**-17.7**	**6.6**	**-25.4**

[1] M. Vonci *et al.*, *J. Am. Chem. Soc.*, 2017, **139**, 14166; [2] O. A. Blackburn, *et al.*, *Angew. Chem. Int. Ed.*, 2015, **54**, 10783.

Calculation of δ_{PCS}



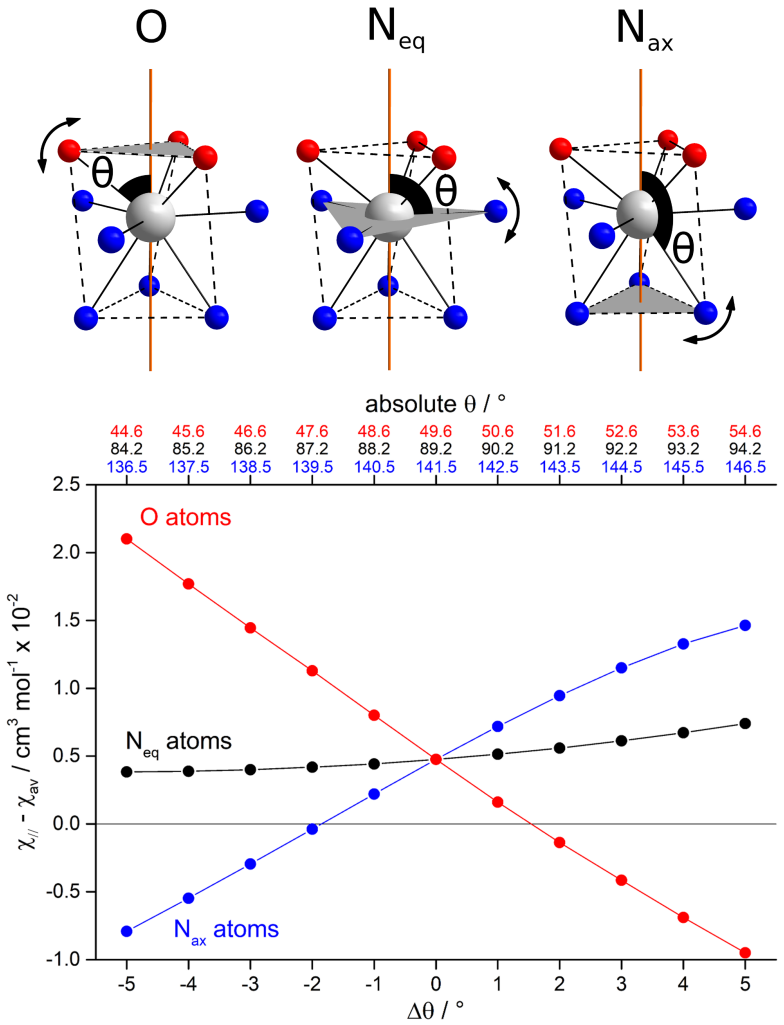
- M06/SMD
- M06/PCM
- BP86/SMD

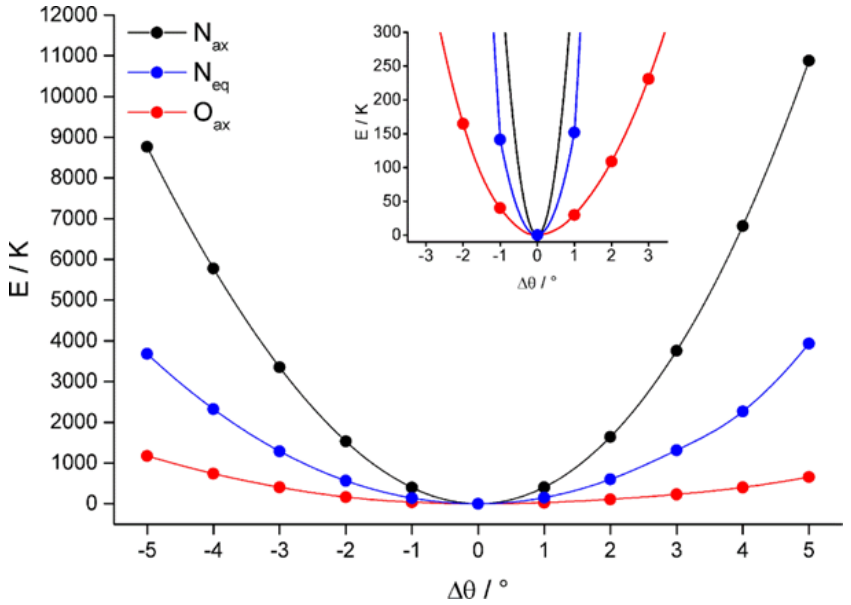
$\frac{3\cos^2\theta-1}{r^3}$	**M06/SMD ($\times 10^{27}$ m^{-3})**	**M06/PCM ($\times 10^{27}$ m^{-3})**	**BP86/SMD ($\times 10^{27}$ m^{-3})**	**RSD**
pyH3	-4.823	-4.945	-4.925	1%
pyH4	-3.830	-3.808	-3.666	2%
pyH5	-4.426	-4.173	-3.750	8%

So is χ hypersensitive to the structure?

[1] M. Vonci *et al.*, *J. Am. Chem. Soc.*, 2017, **139**, 14166.

Hypersensitivity of χ_{ax}

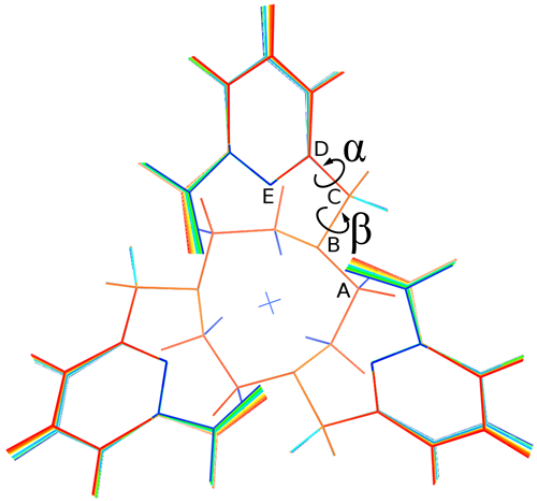


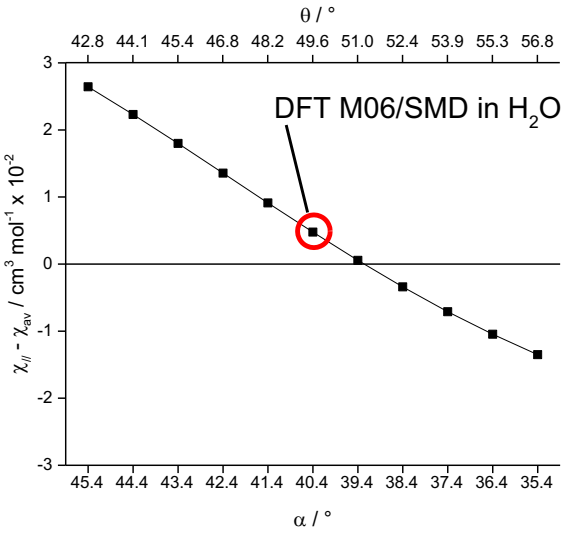


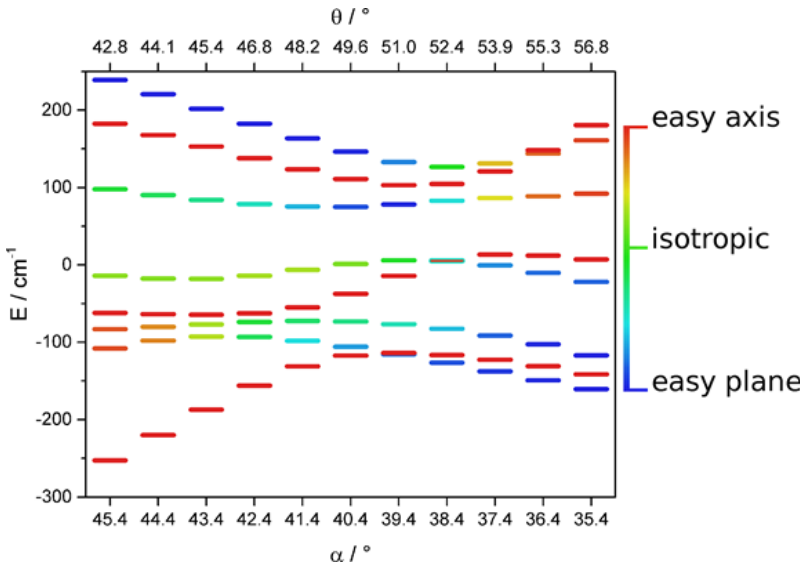
Easy to distort O-atoms

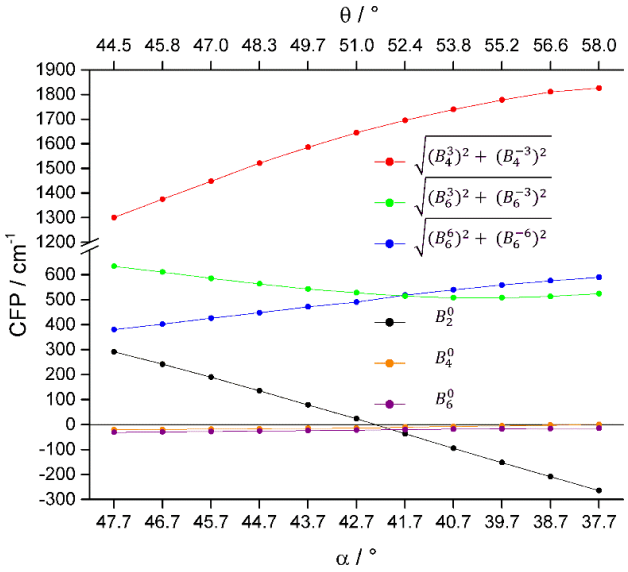
[1] M. Vonci *et al.*, *J. Am. Chem. Soc.*, 2017, **139**, 14166.

Hypersensitivity of χ_{ax}



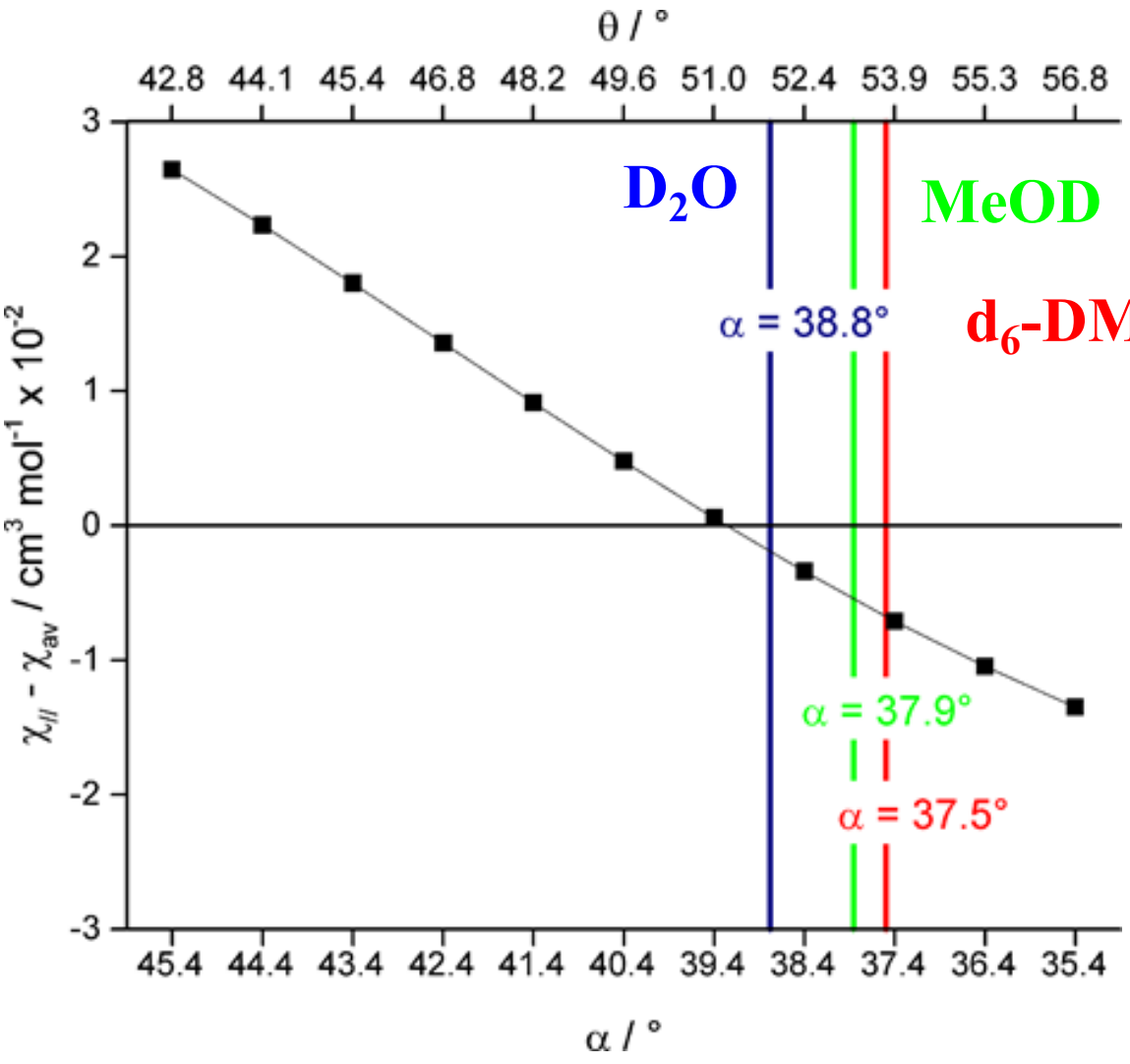




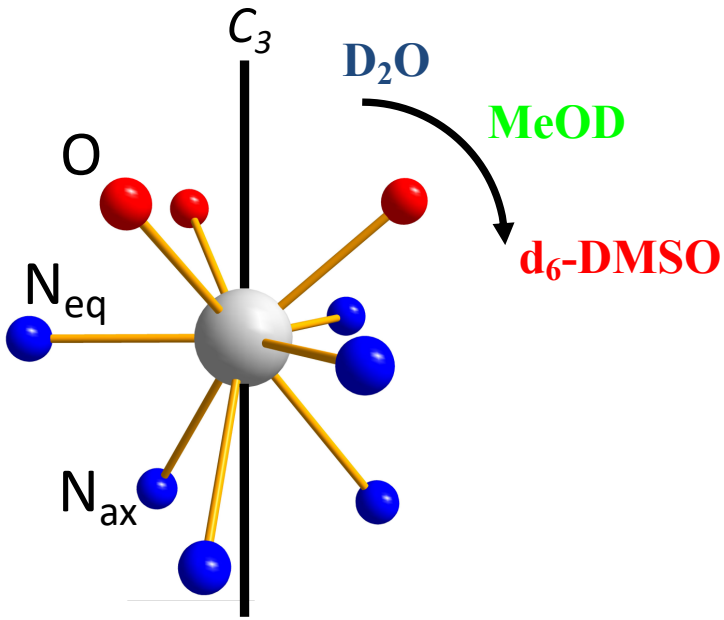


[1] M. Vonci *et al.*, *J. Am. Chem. Soc.*, 2017, **139**, 14166.

Determine solution structure from δ_{PCS}



Change in α < 1.5 ° explains δ_{PCS} solvent dependence!

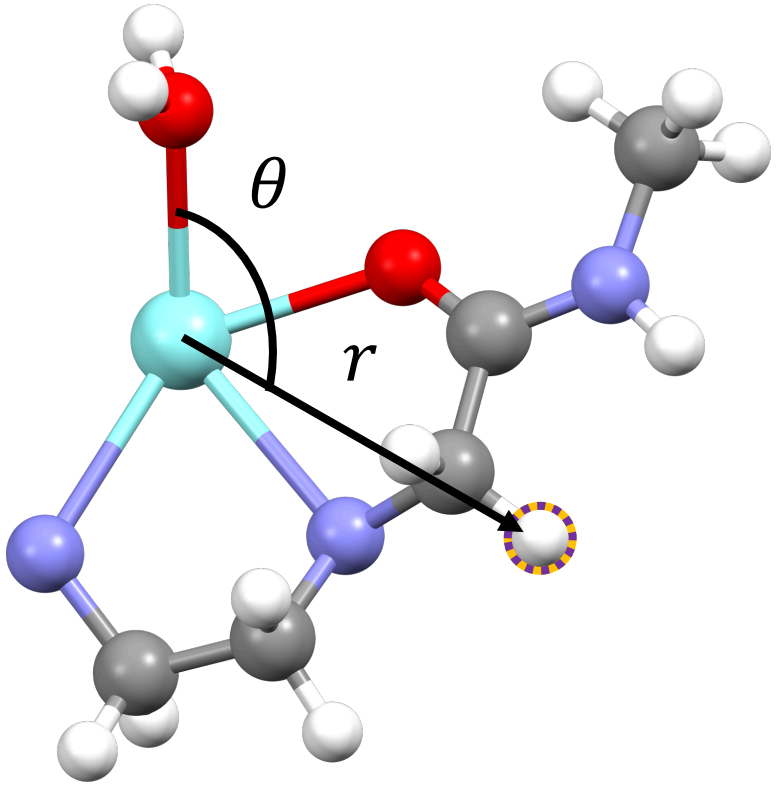


Polarity probes!

[1] M. Vonci *et al.*, *J. Am. Chem. Soc.*, 2017, **139**, 14166.

Problem set:

1. Given the structural coordinates of the labelled proton below from single-crystal X-ray diffraction and its paramagnetic NMR shift, determine the axiality of the magnetic susceptibility of the complex, $\chi_z - \chi_{av}$. Recall that $\delta_{PCS} = \frac{\chi_z - \chi_{av}}{2N_A} \frac{3\cos^2\theta - 1}{r^3}$.



$$\theta = 122°$$
$$r = 3.57 \times 10^{-10}\ m$$
$$\delta_{PCS} = -11.2\ ppm$$