Practical 5 – NMR

OBJECTIVES:

1. Perform *ab initio* calculations of NMR parameters
2. Examine the convergence of the chemical shieldings for ethanol with planewave cutoff and compare to experiment
3. Compute the chemical shift and electric field gradient for alanine and assign the ^{17}O NMR spectrum
4. Compute the chemical shift and electric field gradient for two silicates and assign the ^{17}O NMR spectrum

Ethanol - CH3CH2OH

The discovery that one could actually see chemical shifts in hydrogen spectra was made in 1951 at Stanford University by Packard, Arnold, Dharmatti (shown in Fig 1). We will try to reproduce this result.

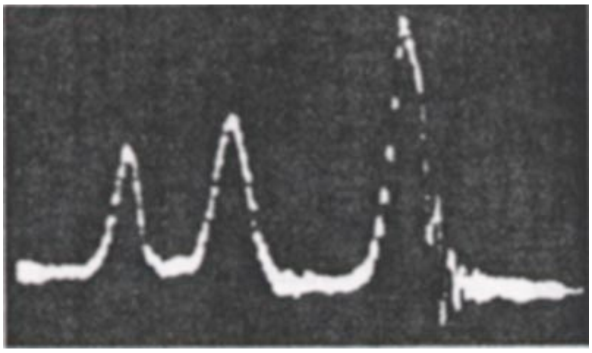

Figure 1: Original ^{1}H NMR spectrum of liquid ethanol

1- Look at the `ethanol.cell` and `ethanol.param` files. Note that the only special keyword is ‘**`task = magres`**’.
2- Run `castep ethanol` and look at the output file. At the end the isotropic chemical shielding, anisotropy, and asymmetry are reported (for now we are only interested in the isotropic value).
3- This information, plus the full tensors is also given in the file `ethanol.magres`
4- Examine the effect of increasing the cutoff energy (say 300 – 700 eV in steps of 100 eV). It always helps to plot a graph of the convergence (e.g. with xmgrace)
5- Find the ‘converged’ hydrogen (or proton in NMR language) shieldings. We will compare them to experiment. The three methyl (CH3) protons undergo fast exchange; they ‘rotate’

faster than the nuclear magnetic moment processes. The magnetic moment will therefore 'see' an average chemical shielding. The same is true of the CH2 protons.

6- Average the CH3 and CH2 chemical shieldings. This will give you 3 unique chemical shieldings.

7- We now need to convert the chemical shieldings σ_{iso} to chemical shifts δ_{iso} on the experimental scale. We use the relation: $\delta_{iso} = \sigma_{ref} - \sigma_{iso}$ where a suitable σ_{ref} for ^{1}H is 30.97ppm.

8- Fig 2 shows a modern high-resolution ^{1}H spectrum for liquid ethanol. (note that the peaks are split due to J-coupling - the interaction of the ^{1}H magnetic moments - but we shall ignore that for now). The three peaks are roughly at 1.2ppm, 2.7ppm and 5ppm. You should find that your computed values agree for two sites. Do you know why the other site has such a large disagreement with experiment?

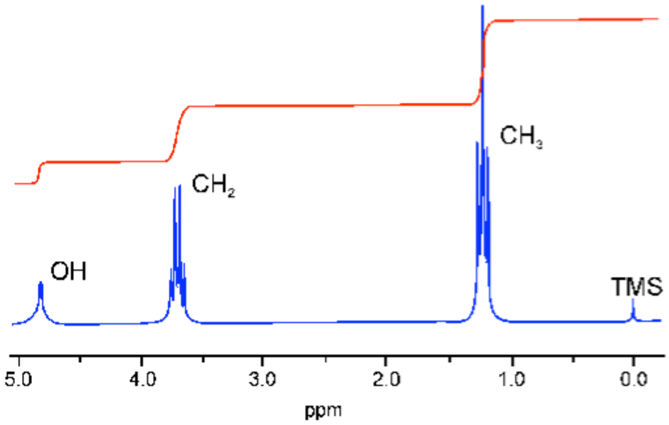

Figure 2: Modern ^{1}H NMR spectrum of liquid ethanol

Comment on Oxygen-17 NMR *Oxygen is a component of many geological materials. Oxygen is also important element in organic and biological molecules since it is often intimately involved in hydrogen bonding. Solid State* ^{17}O *NMR should be a uniquely valuable probe as the chemical shift range of* ^{17}O *covers almost 1000 ppm in organic molecules. Furthermore* ^{17}O *has spin* $I = 5/2$ *and hence a net quadrupole moment. As a consequence of this the solid state NMR spectrum is strongly affected by the electric field gradient at the nucleus.*

Because the isotopic abundance of ^{17}O *is very low (0.037%) and the NMR linewidths due to the electric field gradient relatively large, only limited Solid State NMR data is available. This is particularly true for organic materials. First principles calculations of* ^{17}O *NMR parameters have played a vital role in assigning experimental spectra, and developing empirical rules between NMR parameters and local atomic structure.*

Alanine, a simple amino acid

1- Look at the `alanine.cell` and `alanine.param` files. The geometry for alanine was obtained by neutron diffraction and was downloaded from the Cambridge Crystallographic database `alanine.pdb` – a common structure format.

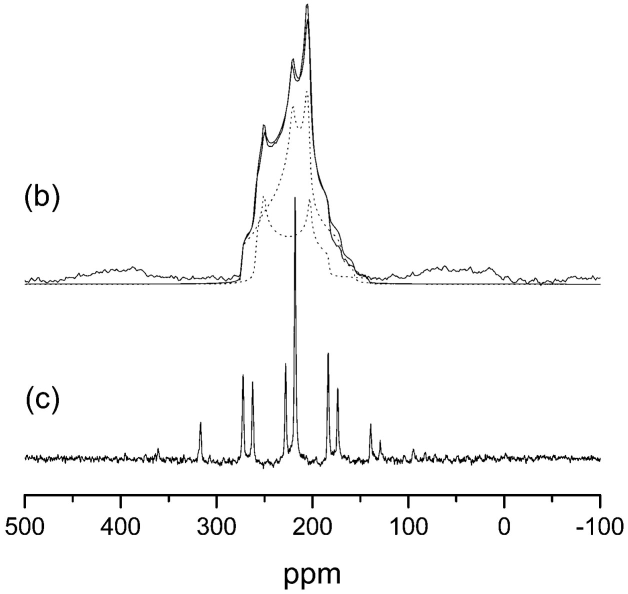

Figure 3: (a) ^{17}O NMR spectrum of l-alanine (b) is from magic angle spinning (c) is from double-orientation rotation

2- Run the example - the calculation is not fully converged. However, if we look at the relative shift between the two sites that is fairly converged.

3- The experimental ^{17}O NMR spectrum shows two peaks (Fig 3 (b)) - they are very broad due to the quadrupolar coupling, and overlap. The experimental parameters are given in Table 1.

4- Assign the two resonances A and B. Do all three computed parameters support this assignment?

Table 1: Experimental 17O NMR parameters for alanine. The two resonance are labelled A and B. Isotropic chemical shift δ, quadrupolar coupling C_Q and EFG asymmetry η_Q

δ(A)-δ (B)(ppm)	23.5
CQ (A) (MHz)	7.86
ηQ (A)	0.28
CQ(A) (MHz)	6.53
ηQ(A)	0.70

Silicates - Quartz and Cristoballite

1- Look at the files for the two different silicates – `quartz.cell` and `crist.cell`

2- The ^{17}O parameters for two silicates are reported in Table 2. From the values you compute can you tell which one (A or B) is quartz? (a suitable σ_{ref} is 265ppm)

Table 2: Experimental ^{17}O NMR parameters for two silicates. Isotropic chemical shift δ, quadrupolar coupling C_Q, and EFG asymmetry η_Q

	δ (ppm)	CQ (MHz)	ηQ
Material A	37.2	5.21	0.13
Material B	40.8	5.19	0.19