

GIPAW – NMR

Exercise 1: molecules

The purpose of this exercise is to learn how to calculate NMR chemical shieldings for several simple molecules. We will compare our results with ^{13}C and ^1H experimental spectra and other theoretical results when available.

Since observed chemical shieldings (σ) are dependent on experimental parameters, chemical shifts (δ) are given with respect to a reference system, which is generally TMS (tetramethyl silane) for C and H. So instead of TMS, we'll use benzene as our reference compound:

$$\delta(\text{benzene}) = \sigma(\text{TMS}) - \sigma(\text{benzene})$$

$$\delta(\text{molecule}) = \sigma(\text{TMS}) - \sigma(\text{molecule})$$

$$= \delta(\text{benzene}) + \sigma(\text{benzene}) - \sigma(\text{molecule})$$

By knowing the experimental $\delta(\text{benzene})$ we can eliminate $\sigma(\text{TMS})$ from previous equations. Theoretical values are shifts can be extracted from sample files for benzene.

For every molecule we examine, we need to run first an scf calculation to get the ground state by using pw.x, then an nmr calculation by gipaw.x. You can find sample input and output files for benzene in **Input File Directory**.

Instructions:

1. Go to **Input File Directory**; view the sample input and output files for benzene. You'll need to adopt these to the molecules you'll study.

I would go ahead and run both of the input files to make sure you get the same data. In c6h6.scf.in, you only have to change the pseudo_dir and outdir. In c6h6.nmr.in, you need to change the tmp_dir and the iverosity (only acceptable values are low or high).

When running the codes:

1. pw.x -in c6h6.scf.in > c6h6.scf.out2
2. gipaw.x -in c6h6.nmr.in > c6h6.nmr.out2

In c6h6.nmr.out2, you are mainly looking at the Total NMR chemical shifts in ppm. There, for each the atoms, you will have a sigma, anisotropy, the tensor elements (σ_{xx} , σ_{yy} , & σ_{zz}). The sigma values for C and H will create the benchmark values in which you will use for all following examples.

Make sure to change *nat* and *ntyp* when necessary. You may need to add pseudopotentials for O and N in the *ATOMIC_SPECIES* list. You can find the pseudopotentials in *pseduo_dir* address and the atomic coordinates in the corresponding XYZ file for each molecule.

2. There are 3 sets of exercises you can follow according to your liking:

- Heterocyclic compounds: Here we'll calculate C and H chemical shifts of the following 4-membered saturated molecules: C₄H₈ (cyclobutane), C₃H₇N (azetidine), C₃H₆O (oxetane). **Calculations for each one of these take approx. 1h**, you can choose to do only one of them.

Experimental values for benzene are (in ppm):

- $\delta(^{13}\text{C}, \text{benzene}) = 128.36$
- $\delta(^1\text{H}, \text{benzene}) = 7.339$

$\sigma(^{13}\text{C}, \text{benzene}) = 40.33$

$\sigma(^1\text{H}, \text{benzene}) = 23.52$

$\delta(\text{molecule}) = \delta(\text{benzene}) + \sigma(\text{benzene}) - \sigma(\text{molecule})$

	C ₄ H ₈ (cyclobutane)	C ₃ H ₇ N (azetidine)	C ₃ H ₆ O (oxetane)
¹³ C shieldings			
Chemical shifts			
Experimental chemical shift	22.86	22.41 48.18	22.9 72.6
¹ H shieldings			
Chemical shifts			
Experimental chemical shift	1.96	3.62 2.33 2.08	2.68 4.70