Physical Chemistry - Magnetic Shielding, Chemical Shift, Nuclear Coupling, Multiplet splitting, limitations of continuous pulse NMR and Pulse NMR

Magnetic Shielding
- The exact resonance frequency of a nucleus is a function of the static magnetic field seen by the nucleus - small changes make measurable change in resonance frequency.
- Such small changes occur as a result of local magnetic fields produced by nearby circulation e- - resonance frequency of a nucleus is changed slightly by local arrangement of e- in the molecule (the 'environment' of a particular nucleus).
- Addition of magnetic field produced by electrons $\zeta B$ is proportional to and opposite to applied field: $\zeta B = -\sigma B$: where $\sigma$ is shielding constant (usually positive, but can be negative) and $B$ is magnetic field at nucleus (discussed in previous notes).

The total local field is:
$$\text{ Bloc } = B + \zeta B = (1 - \sigma) B$$
and resonance frequency, which depends on local magnetic field, becomes:
$$\nu = \frac{\nu - \nu_0}{2\pi} = (1 - \sigma) B$$

Chemical Shift
- Because the shielding varies with position in a molecule, the same nuclei e.g. 1H in different parts of the molecule will all resonate at slightly different frequencies. Shifted from an agreed 'standard' frequency $\nu_0$. The difference $\nu - \nu_0$ depends on the standard frequency (or value of B).
- If $\zeta > 0$ resonance frequency is higher than standard and nucleus is said to be deshielded.

However, $\zeta = \frac{\nu - \nu_0}{\nu_0} \times 106$ (ppm)
- Represents a chemical shift that is independent of field, and so will apply to the same nucleus in a molecule in any NMR machine.
- If $\nu > 0$ resonance frequency is higher than standard and nucleus is deshielded.
- Thus we can use NMR spectroscopy to identify protons and other nuclei in a sample in different chemical environments or different parts of a molecule, to obtain quantitative information to help identify.
1) Must use a solvent free of nucleus of interest e.g. D$_2$O
2) Proton standard is commonly tetramethylsilane (TMS) - 12 protons in identical environments.

Nuclear Coupling
- There is an interaction between nuclei in a molecule, which affects energy levels of all other nuclei. However, in liquid samples the effect is negatively small at distances greater than 2 bonds.
- Without detailing energy considerations, we can generalise the fact that:
A group of $P$ equivalent nuclei split a neighbouring group into $P+1$ lines, with intensities given by the $P$th line of Pascal’s triangle.

### Multiplet splitting

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<td>$P$</td>
<td>4</td>
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- This provides structural information, helping to assign spectral lines to particular proton groups
- The observed spacing of the multiplet lines is called coupling constant, $J$. It is independent of the field or measurement frequency and so is quoted in Hz, not ppm.