Notes on NMR Spectroscopy: Basic principles of 1HNMR spectroscopy, number of signals (homotopic, enantiotopic and diastereotopic protons)

Certain nuclei such as 1H, 13C, 19F, and 31P have allowed spin states of +1/2 and –1/2; this property allows them to be studied by NMR.
The essential condition for this is both atomic number and mass number of the element should not be even. When such nuclei are exposed to an external magnetic field, they behave as magnets and align themselves with the external magnetic field. There are two spin states possible, one with the external magnetic field and one against the external magnetic field. The lower and more stable orientation is the one in which the nuclei are aligned with the external magnetic field. When energy in the form of electromagnetic radiation in the radio frequency region is supplied, the nuclei absorb the energy and change their spin state to align themselves against the external magnetic field. When the applied energy is removed, the nuclei go back to their original spin state. This is called nuclear magnetic resonance.

The amount of energy required for this is given by the equation $\nu = \gamma H_o / 2\pi$ where, ν is the frequency of the external electromagnetic radio waves, H_o is the strength of the magnetic field, γ is a constant known as the magnetogyric ratio. It is a constant for a particular type of nuclei. Therefore from the above equation we can see that the frequency of the radio wave required to change the spin state of the nuclei is directly proportional to the strength of the magnetic field which keeps the nuclei aligned with it. The equation condition may be achieved in two ways: either by keeping the frequency of radio waves constant and varying the strength of the magnetic field or by keeping the strength of the magnetic field constant and changing the frequency of the radio waves. From a practical point of view it is more feasible to keep the frequency of the radio waves constant and change the strength of the magnetic field.

If we go to the previous equation, NMR would have been useless since all the protons in a molecule would have absorbed at the same frequency. This is because all the terms in the equation are constants for a particular nucleus, in this case a proton. However what makes NMR interesting and useful is the fact that the nuclei (protons) are not isolated in a molecule. They are surrounded by electrons which are also charged bodies in motion, and therefore generate their own magnetic field. In fact since the charge on an electron in negative, the magnetic field of an electron is opposite to that of a proton. The electrons surrounding a nucleus affect the effective magnetic field sensed by the nucleus.

What makes NMR extremely useful is that all the protons in a molecule are not in the same electronic environment because of differing electronic density. What this essentially means is that the **applied** magnetic field (applied by the instrument) is not the same as the **effective** magnetic field which is the field “felt” by the proton, which depends on its electronic environment. This gives rise to the concept of ‘shielding’ and ‘deshielding’. Protons in electron rich environments are ‘shielded’ from the external magnetic field and require a higher field to resonate. Protons in electron deficient environment are ‘deshielded’ from the external magnetic field and require lesser field to resonate. Shielded protons absorb at higher fields (upfield) and deshielded protons absorb at lower fields (downfield). Since electrons are an essential component of bonds,

what it implies is that **electronically different protons are also chemically different and give peaks at different regions in a spectrum.**
Therefore NMR can differentiate between magnetically different protons and this translates into chemically different protons. Thus the number of signals observed in a NMR spectrum is equal to the number of chemically different protons in the molecule.

Homotopic protons: These are such protons in a molecule which when replaced by the same atom or group give molecules which are identical in all respects.
Enantiotopic protons: These are such protons in a molecule which when replaced by the same atom or group give molecules which are enantiomers.
Diastereotopic protons: These are such protons in a molecule which when replaced by the same atom or group give molecules which are diastereomers of each other.

In NMR spectroscopy: Homotopic protons have the exact same chemical shift. Enantiotopic protons have the same chemical shift in the vast majority of situations. However, if they are placed in a chiral environment (e.g. a chiral solvent) they will have different chemical shifts. Diastereotopic protons have different chemical shifts in all situations