The chemical shift

- The local magnetic field is the field felt by a particular nucleus.
- The applied field B induces currents in the electrons surrounding the nucleus give rise to a shielding. The shielding constant is s.
- The local magnetic field is reduced by shielding by a factor 1 - σ.

$$B_{loc} = B + \delta B = (1 - \sigma)B$$

- The chemical shift is the difference between the resonance frequency of a nucleus and that of a standard.

Chemical shifts are reported on the δ-scale

- The Larmor frequency of a shielded nucleus is:

$$\nu_L = \frac{\gamma B_{loc}}{2\pi}$$

- Chemical shifts are reported on the d-scale.

$$\delta = \frac{\nu - \nu^0}{\nu^0} \times 10^6$$

- The resonance frequency of the standard is ν_0.

Origin of shielding constants

- The shielding constant is the sum of three contributions

$$\sigma = \sigma(local) + \sigma(molecule) + \sigma(solvent)$$

- The local contribution is due to electrons on the atom that contains the nucleus.
- The molecular contribution is from the rest of the molecule.
- The solvent contribution is from surrounding solvent molecules.

The local contribution

- The local contribution is a sum of both diamagnetic σ_d and paramagnetic σ_p parts.
- The diamagnetic part arises from circulation of the electrons in response to B.
- The Lamb formula gives the magnitude of σ_d,

$$\sigma_d = \frac{e^2\mu_0}{3m_e}\int_0^\infty \rho(r)rdr$$

where ρ is the electron probability density $|\Psi^2|$.

σ_d is inversely proportional to the Bohr radius.

The magnetic moment of a current loop $\propto a_o^2$.

The magnetic field generated at the nucleus $\propto 1/a_o^3$.

The molecular contribution

- The applied magnetic field generates currents in neighboring groups proportional to the magnetic susceptibility χ of a group.
- The induced magnetic moment gives rise to a magnetic field that is inversely proportional to the cube of the distance from the nucleus.