1.4: What is chemical shift and how does it relate to resonance frequency?

If each type of nucleus (e.g. all protons) gave a single resonance frequency, as implied by Equation 3.4, NMR would not be of much use to chemists. The actual nuclear resonance frequency is highly dependent on the local chemical environment. The effective magnetic field, B_{eff}, felt by a nucleus differs from that of the applied magnetic field, B_o, due to shielding by the motion of the electron clouds surrounding the nucleus. The greater the electron density around the nucleus, the larger is this shielding effect. The amount of shielding is expressed as the magnetic shielding constant σ, where $B_{eff} = (1 - \sigma)B_o$. Therefore, the resonance frequency of each nucleus differs depending on the value of B_{eff}.

$$\nu = \frac{\gamma(1-\sigma)B_o}{2\pi} = \frac{\gamma B_{eff}}{2\pi} \tag{1.4.1}$$

The chemical shift of a nucleus reveals much about the structure of a molecule as shielding constants are well correlated with local chemical environment. For example I can know whether a molecule contains a methyl group or an aromatic ring depending on the chemical shifts of the protons in my NMR spectrum.

Early NMR spectrometers were scanning instruments in which the radio frequency was scanned through the proton chemical shift range until a frequency was reached at which energy was absorbed by the sample; this is the resonance condition. Modern instruments irradiate the sample with a broad band, or range, of frequencies and excite all of the protons at the same time.