First-Order NMR Analysis

Conditions:

1. The frequency difference (Δν, Hz) between resonances of nuclei or sets of nuclei must be much larger than the spin-spin coupling (J, Hz). First-order rules work well for so-called "weakly coupled" spin systems, where (Δν / J)>7. Where (Δν / J)<3, the spin system is said to be “strongly coupled” and will not obey first-order rules. In cases where 3<(Δν / J)<7, significant second-order distortions will be observed.

2. Coupling must involve sets of nuclei that are magnetically equivalent, not just chemical shift equivalent (isochronous). Nuclei in a set are magnetically equivalent if they are both isochronous and equally coupled with each other separate nucleus in the spin system.

Rules:

1. A nucleus or group of magnetically equivalent nuclei coupled to a set of n nuclei with spin I will have its resonance split into 2nI+1 lines. For the common case of I=1/2, n+1 lines result. Multiplets are designated according to the number of lines: 1 = singlet (s), 2 = doublet (d), 3 = triplet (t), 4 = quartet (q), 5 = pentet (p)...

2. The relative intensities of the 2nI+1 lines can be determined from the number of ways each spin state may be formed. For the case of I=1/2, the relative intensities are given by the binomial coefficients of (a+b)n, (Pascal’s triangle): d (1:1), t (1:2:1), q (1:3:3:1), p (1:4:6:4:1), etc.

3. The 2nI+1 lines of a first-order multiplet are equally spaced; the frequency separation (Hz) between adjacent lines is equal to the spin-spin coupling constant, J. The magnitude of J is a molecular property, independent of field strength. The width of the first-order multiplet (between outer lines) is given by \( \sum nJ \).

4. Coupling between nuclei within a magnetically equivalent set does not affect the spectrum, i.e. no splitting is observed.

5. When two or more first-order couplings are present, a repetitive procedure can be used to predict the appearance of a multiplet. For example, the resonance of a nucleus coupled to a set of n protons, and also to a set of n’ protons, will be split into a maximum of (n+1)(n’+1) lines and a minimum of n+n’+1 lines. The latter case results if the two coupling constants, J and J’, are equal. The width of the first order multiplet is given by \( \sum nJ + \sum n’J’ \).