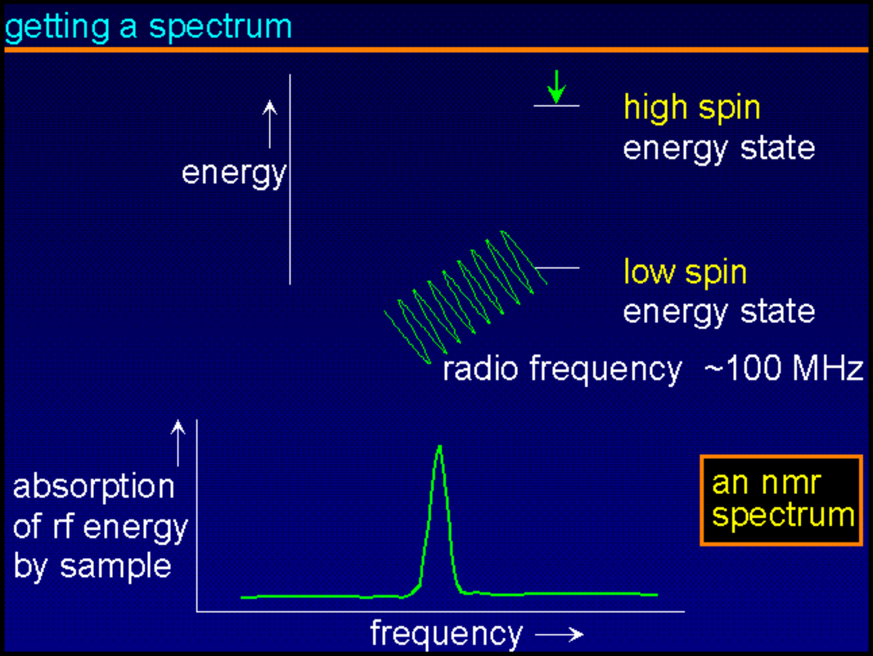
why certain nuclei give signals

some nuclei have magnetic moments
and behave like magnets

these nuclei have a non-zero spin quantum number

i.e. $I \geq ½$ e.g. ^{1}H, ^{13}C have nuclear spin

magnetic moment represented by vector ↑


getting a spectrum
high spin
energy state
energy
low spin
energy state
radio frequency ~100 MHz
absorption
of rf energy
by sample
an nmr
spectrum
frequency

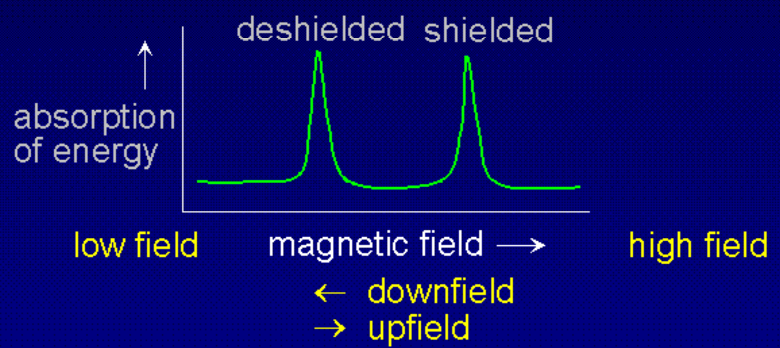
information obtainable from a ^1H nmr spectrum

- number of signals
  gives the number of different types of protons
- positions of signals
  gives chemical environment of each type of proton
- intensities of signals
  gives the ratio of how many protons of each type
- multiplicity of signals
  gives number of neighbouring protons for each type
- D_2O exchangeability of signals
  gives protons attached to heteroatoms

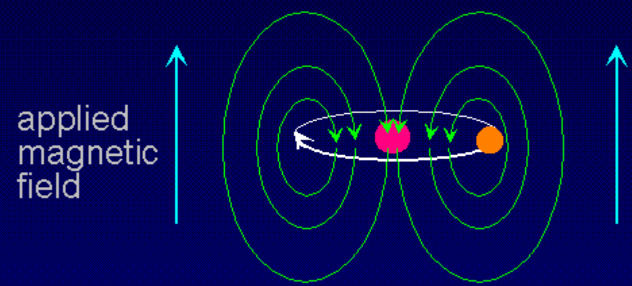
why different protons resonate at different frequencies

at a given radio frequency all protons absorb at the same effective magnetic field strength but they absorb at different applied magnetic field strengths

this is because they have different amounts of shielding



why different protons resonate at different frequencies



fields are opposed at nucleus
i.e. electrons cause shielding

electron withdrawal causes deshielding

CH_3F 4.3 δ, CH_3Cl 3.1 δ, CH_3Br 2.6 δ, CH_3I 2.2 δ

CH_3O- 3.3 δ, $CH_3N<$ 2.3 δ, $CH_3C<$ 0.9 δ

why different protons resonate at different frequencies

electron withdrawal causes deshielding and
conversely electron donation causes shielding

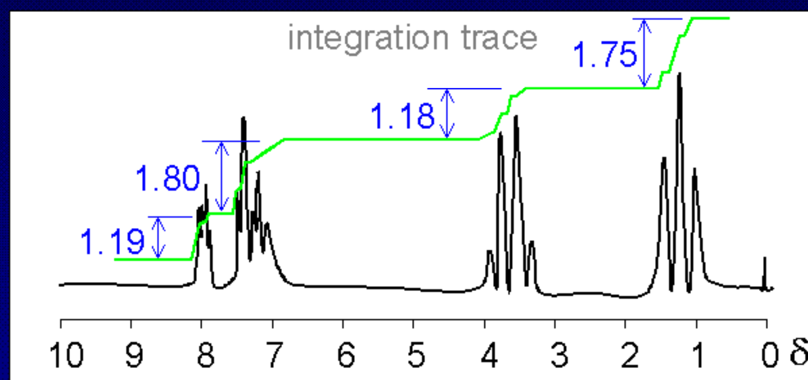
TMS (tetramethylsilane), $(CH_3)_4Si$ is used as the reference compound for both ^{1}H and ^{13}C nmr

- silicon is electropositive (electron donator)
  H and C upfield of most other compounds
- TMS is inert, volatile, organic-solvent soluble

number of protons present

the ratio of the number of protons is related to the area of each signal

the area is usually measured by integration of the spectrum

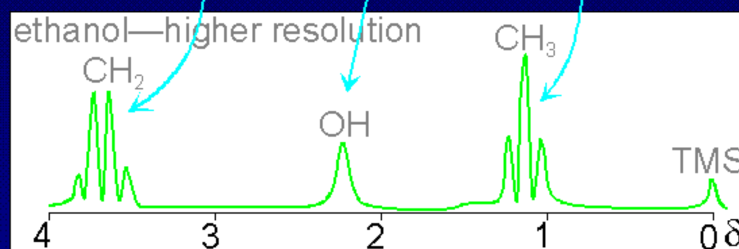


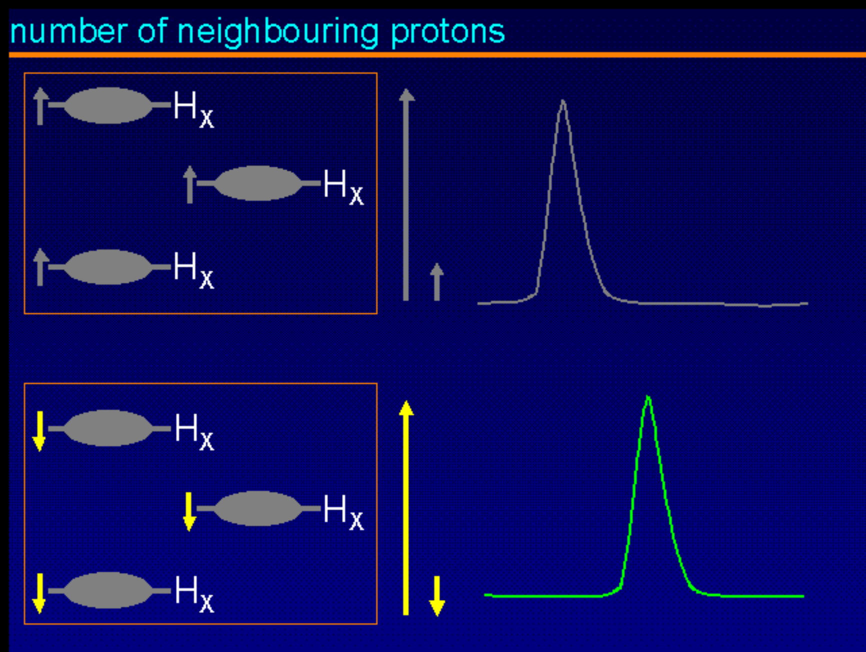
number of neighbouring protons

measure the signal's multiplicity and use the n+1 rule

the signals are split into **multiplets**

quartet singlet triplet





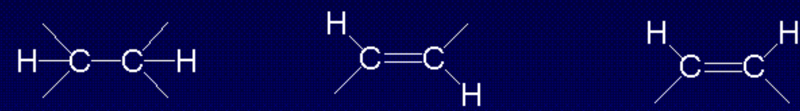
number of neighbouring protons
Hx
Hx
Hx
Hx
Hx
Hx

number of neighbouring protons

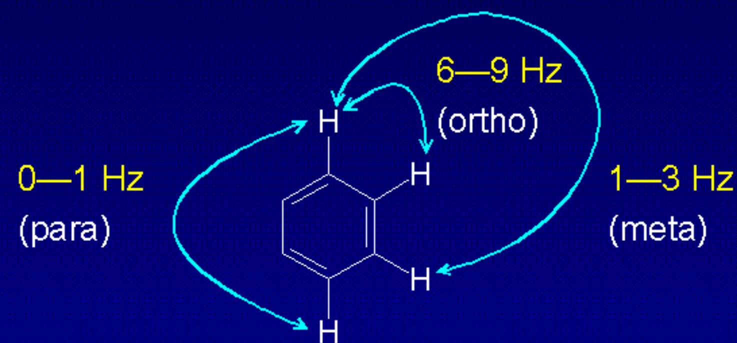
n+1 rule
a set of n equivalent neighbouring protons will split a signal into n+1 peaks

neighbours	no. of peaks	name
0	1	singlet
1	2	doublet
2	3	triplet
3	4	quartet
4	5	quintet
..	..	..

coupling constants, J—examples



0—10 Hz (vicinal) | 13—18 Hz (trans) | 7—12 Hz (cis)



protons attached to heteroatoms

- usually exchange rapidly amongst themselves (cf. hydrogen bonding)
- no coupling with neighbours is observed
- variable chemical shift
- averaging of chemical shifts if multiple types
- exchange with D_2O occurs

$$ROH + D_2O \text{ (excess)} \rightleftharpoons ROD + HOD/D_2O$$

information obtainable from a ^{1}H nmr spectrum