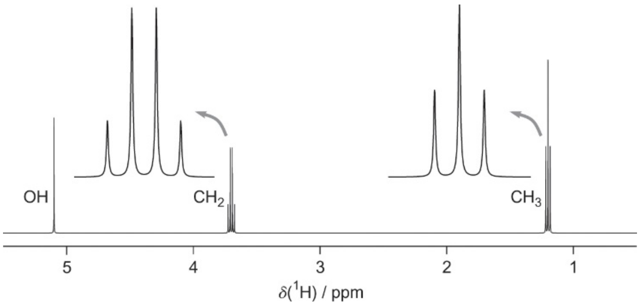
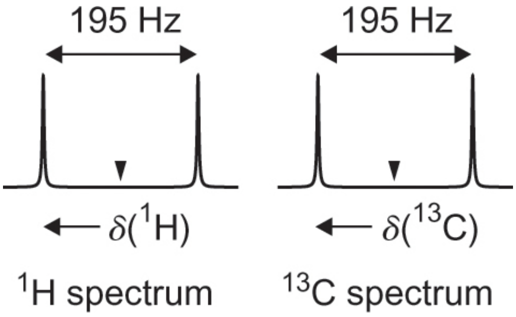
Lecture 3: Spin-spin coupling – *Ralph W. Adams*

The origin of J

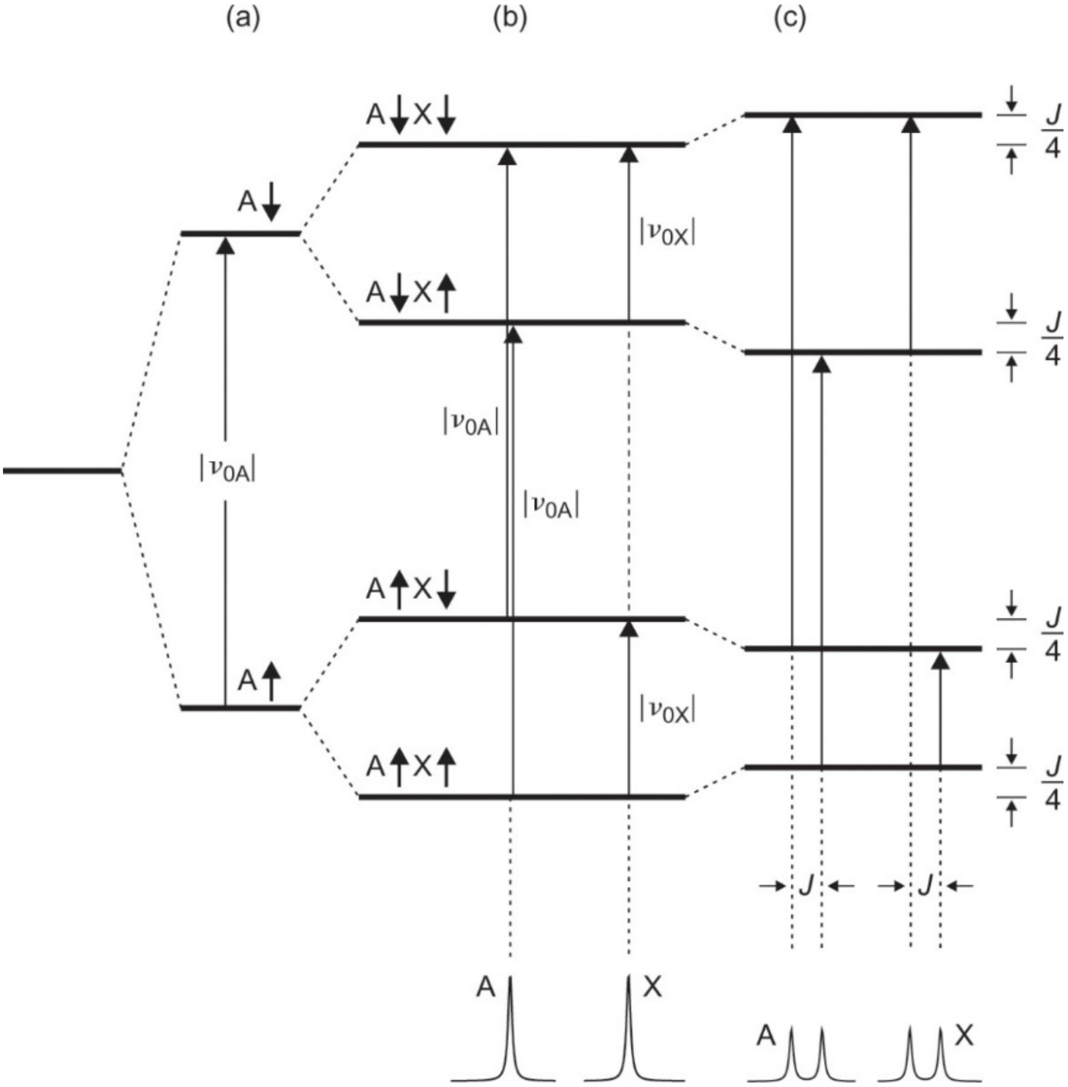
J was first used to designate spin-spin or scalar coupling in a 1951 paper by Erwin Hahn: *Phys. Rev.* 84, 1246.

Effect on NMR spectra





Nuclear spin-spin coupling causes NMR lines to split into a number of components with characteristic intensities. The coupling between spins is mutual, as shown for ^{13}C-labelled-formate and the lines are arranged symmetrically around the chemical shift.



The resonance is split because the magnetic moment of nucleus causes a small local magnetic field.

The local magnetic field can be arranged depending on the nuclear spin quantum number, for spins-1/2 it has two orientations – one which adds to the main field and one which opposes it.

The interactions of a pair of spins-1/2 nuclei can be shown on an energy-level diagram.

The interactions include:
a) spin A with B_0
b) spin B with B_0
c) spin A with spin B via spin-spin coupling

Figures are from *Nuclear Magnetic Resonance (2nd Ed.)* by *P.J. Hore*

Equivalence

Equivalent nuclei are those in identical environments, with identical chemical shifts.

Examples include:
^{1}H nuclei in CH_4
^{19}F nuclei in CF_3COOH

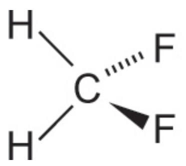
By convention spins with well separated chemical shifts are labelled alphabetically by letters that are far apart.
e.g. AX: $^1H^{13}CO_2^-$

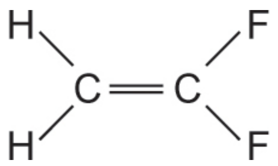
More specifically …

Chemically equivalent nuclei are those in identical environments, with identical chemical shifts.

Magnetically equivalent nuclei are those that are chemically equivalent *and* have identical couplings to the other nuclei in the spin system.

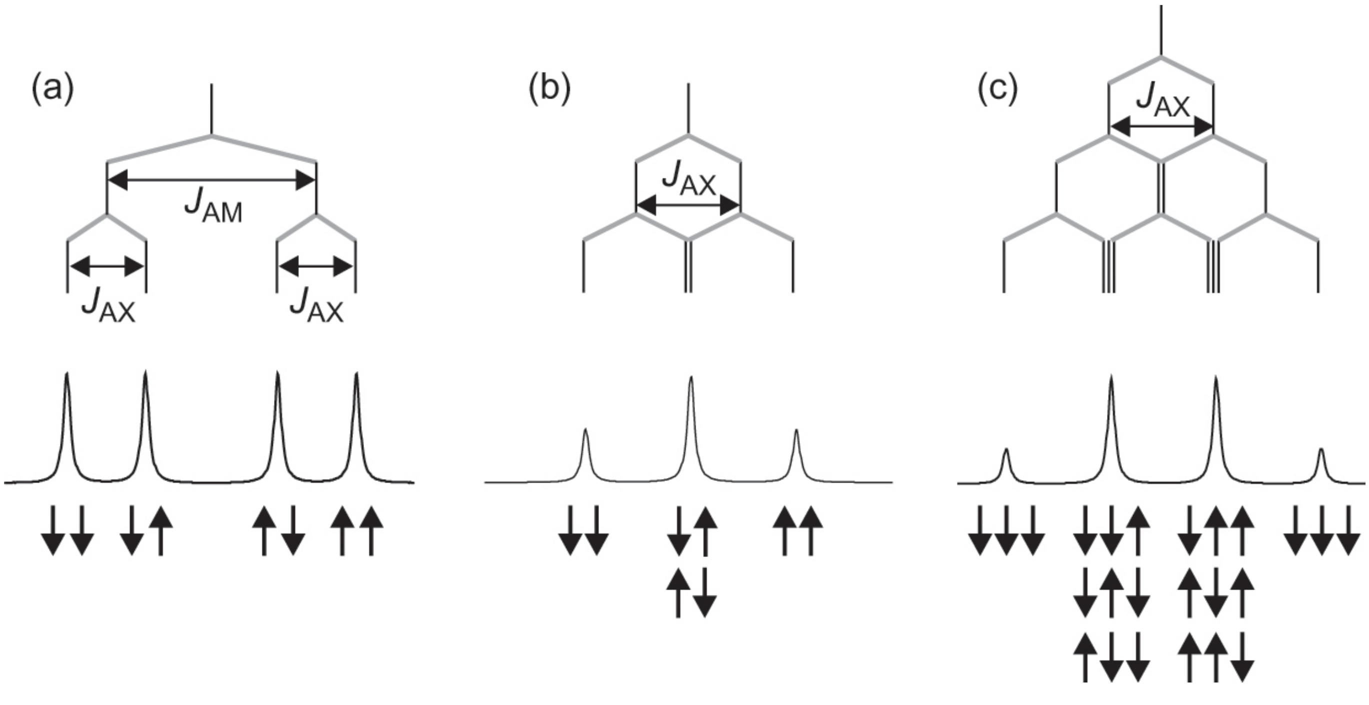
Spin-spin interactions within a group of magnetically equivalent spins do not produce multiplet splittings.





Multiplets

For weakly coupled spins, where the difference in $\Delta\nu = \nu_A - \nu_X$ for the spins is much larger than J_{AX}, multiplet intensities can be calculated based on binomial distributions.



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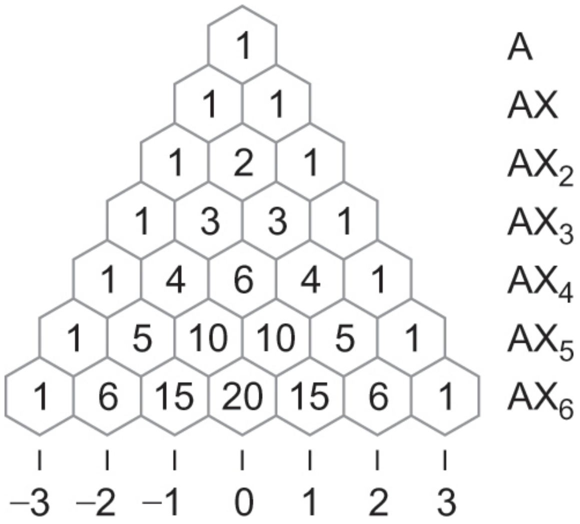
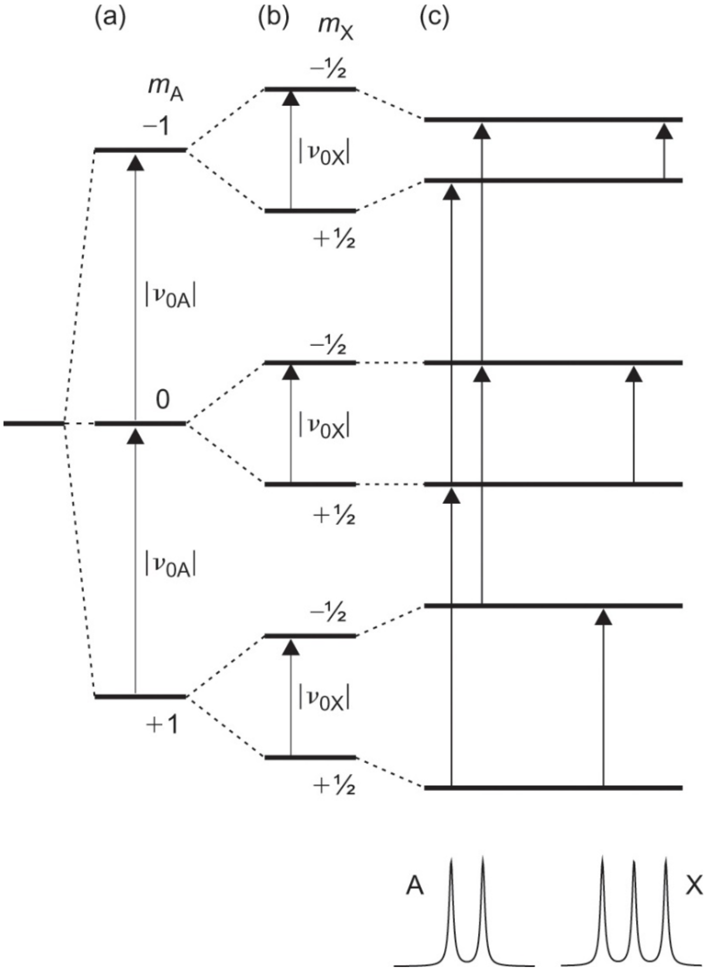


Pascal's triangle shows the binomial coefficients, giving the intensities of the lines in a multiplet for spin A coupled to spin-1/2 X nuclei.

Multiplets with spin ≠ ½



The interaction of a spin-1/2 nucleus with a spin-1 nucleus produces more lines than the interaction of 2 spins-1/2 with each other

The interactions include:
a) spin A (*I*=1) with the magnetic field B_0
b) spin X (*I*=1/2) with the magnetic field B_0
c) spin A with spin X via spin-spin coupling

A binomial doublet is seen for spin A while a 1:1:1 triplet is seen for spin X

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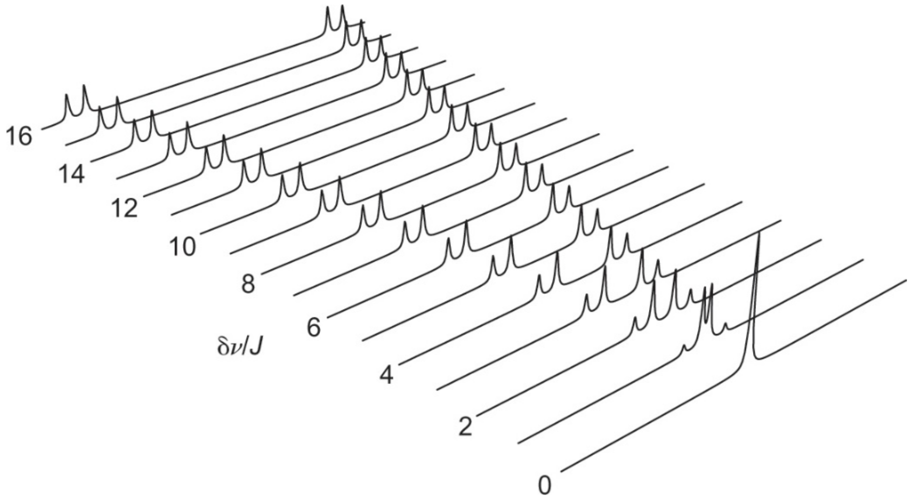
Decoupling

^{13}C nuclei couple to ^{1}H nuclei to produce multiplets – for example $^{13}CH_3$ group give a binomial quartet in the ^{13}C NMR spectrum. There is a significant loss in sensitivity if the magnetisation is divided into the multiplet components so ^{1}H decoupling is used to collapse the couplings between ^{1}H and ^{13}C. Decoupling usually yields singlets in $^{13}C\{^{1}H\}$ spectra. ^{13}C-^{13}C spin-spin coupling produces satellite signals at <1 % intensity so is rarely seen in ^{13}C NMR spectra.

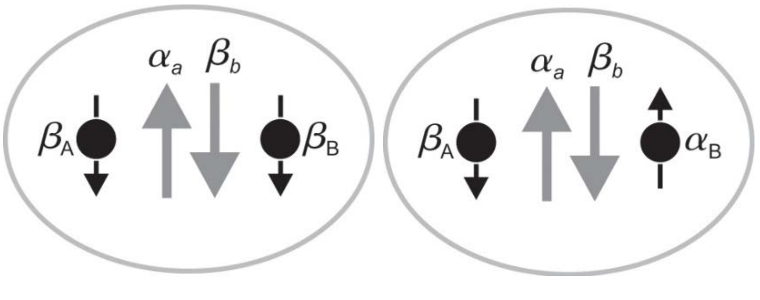
Decoupling is achieved by rapidly interconverting the states of the coupled spin so that it appears averaged.

Strong coupling and equivalence

When $\Delta\nu \gg J_{AX}$ the multiplets in an NMR spectrum appear as binomial multiplets with intensities which can be easily predicted. As $\Delta\nu$ is reduced the spins become more equivalent (until $\Delta\nu = 0$ when they become chemically equivalent). For an AX system (called an AB system when $\Delta\nu$ is small) the effects – roofing where the inner multiplet components increase in intensity and the otter components decrease – of strong coupling are normally easy to recognise but when the number of spins increases computational analysis is usually required.



Mechanism

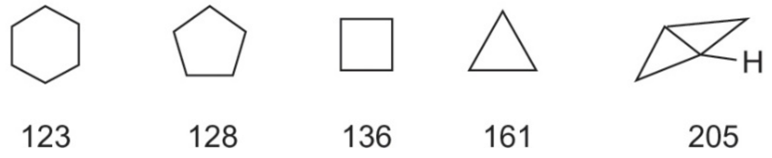


Spin-spin coupling is mediated by the Fermi-contact interaction. This involves the nuclei interacting indirectly with each other via electrons. For H_2, the low energy configuration occurs when the nuclear spins are antiparallel, the high energy configuration occurs when the spins are parallel.

Properties

^{1}J - In most cases the interpretation of the magnitudes of J-coupling constants is tricky. In general 100 Hz < $^{1}J_{CH}$ < 250 Hz. $^{1}J_{CH}$ can be empirically related to the amount of s-character of a C–H bond.

H_3C-CH_3	125	CH_4	125	CH_3Cl	147
$H_2C=CH_2$	157	CH_3OH	141	CH_2Cl_2	177
$HC\equiv CH$	250	CH_3CN	136	$CHCl_3$	208



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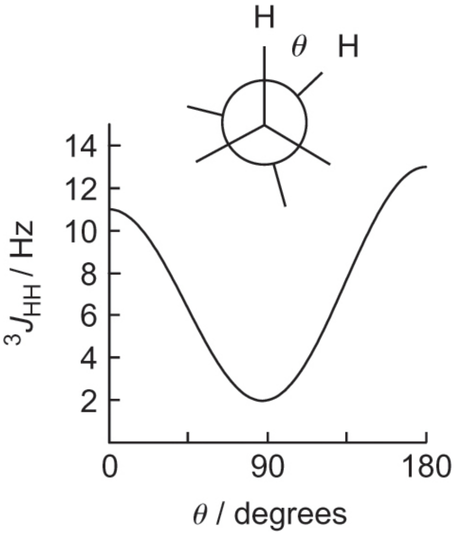
^2J - In general, geminal couplings have $-20 < {}^2J_{HH} < 40$ Hz. $^2J_{HH}$ is affected strongly by substituents and $^2J_{HH}$ for sp^2 CH_2 is normally smaller than for methyl groups.

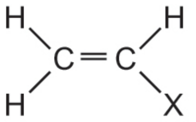
X	$H_2C{=}CHX$	$CH_3{-}X$
H	+2.3	−12.4
Ph	+1.3	−14.5
Cl	−1.3	−10.8
CN	+0.9	−16.9

^3J - Three bond $^3J_{HH}$ couplings are most useful as they vary with the dihedral angle in an H–C–C–H fragment according to the Karplus equation:

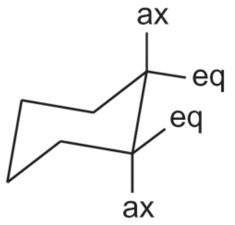
$$^3J = A + B\cos\vartheta + C\cos^2\vartheta$$

Typical values are A = 2 Hz, B = -1, and C = 10 Hz. $^3J_{HH}$ couplings are useful for conformational analysis.





X	cis	trans	$CH_3CH_2{-}X$
H	11.5	19.0	8.0
Ph	10.7	17.5	7.6
Cl	7.4	14.8	7.2
CN	11.8	17.9	7.6



		θ
ax–ax	11.8	180°
ax–eq	3.9	60°
eq–eq	3.9	60°

Long range - When protons are separated by more than 3 bonds coupling constants are general < 1 Hz. Exceptions occur when the coupling is transmitted via zig-zag or 'W' arrangements of bonds and/or through π bonds.

$^5J_{HH} = +2.2$

$H{-}C{\equiv}C{-}C{\equiv}C{-}H$

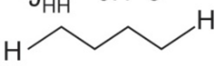
$^7J_{HH} = -1.3$

$H_3C{-}C{\equiv}C{-}C{\equiv}C{-}CH_3$

ortho	7–10
meta	2–3
para	0.1–1

$^4J_{HH}$ 0.1–3

$^5J_{HH}$ 0.1–3



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