

Spin-Spin Coupling

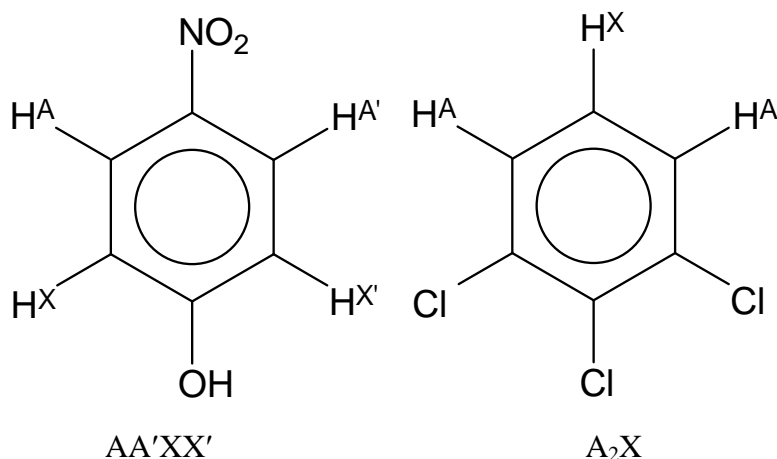
Indirect spin-spin coupling (indirect dipole-dipole interaction, J -coupling) - a magnetic interaction between individual nuclear spins transmitted by the bonding electrons through which the nuclear spins are indirectly connected.

Chemically and magnetically equivalent nuclei

Magnetically equivalent nuclei possess the same resonance frequency and only one characteristic spin-spin interaction with the nuclei of a neighbouring group.

The spin-spin coupling between magnetically equivalent nuclei does not appear in the spectrum.

Nuclei with the same resonance frequency are called chemically equivalent or isochronous. Chemically equivalent nuclei will not be magnetically equivalent if they have different couplings to other nuclei in the molecule.



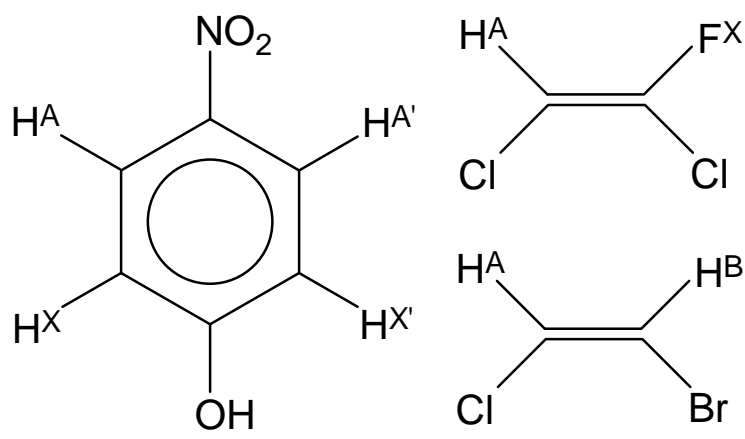
Magnetic equivalence causes great simplification in the resulting NMR spectra, but those cases where nuclei are chemically equivalent but not magnetically equivalent give complicated spectra in which second-order effects are prevalent.

Notation for spin systems

A spin system includes nuclei between which spin-spin interaction exists and defines the number and type of magnetic nuclei and the relationship between them. Each nucleus (spin $\frac{1}{2}$) is assigned a capital letter of the Roman alphabet:

- if the chemical shift difference between a pair of nuclei is much greater than the coupling constant between them, they are assigned letters well apart in the alphabet (AX, AA'XX', etc.)

- if a chemical shift difference is of the order of or less than the corresponding coupling constant, adjacent letters of the alphabet are used for the two nuclei involved (AB, AA'BB', etc.)



Interpretation of multiplet structures

-CH₂-CH₃, energy level diagram:

CH ₂	m _T	CH ₃	m _T
αα	+1	ααα	+3/2
αβ βα	0	ααβ αβα βαα	+1/2
ββ	-1	αββ βαβ ββα	-1/2
		βββ	-3/2
↓		↓	
1:2:1 (CH ₃)		1:3:3:1 (CH ₂)	

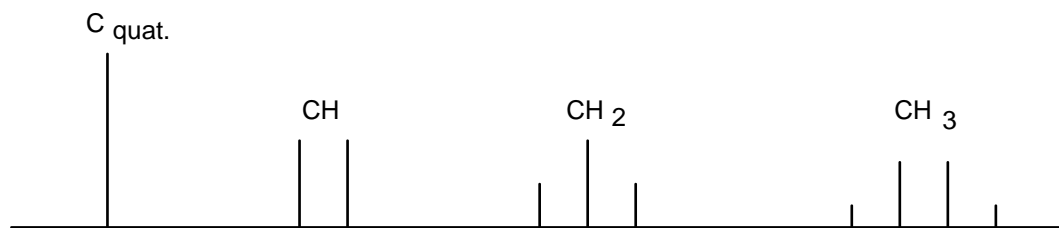
First-order rules ($\Delta\nu / J \gg 1$)

- For nuclei with $I=1/2$ the multiplicity of the splitting equals $n+1$, where n is the number of nuclei in the neighbouring group (for $I > 1/2 \Rightarrow 2nI+1$)

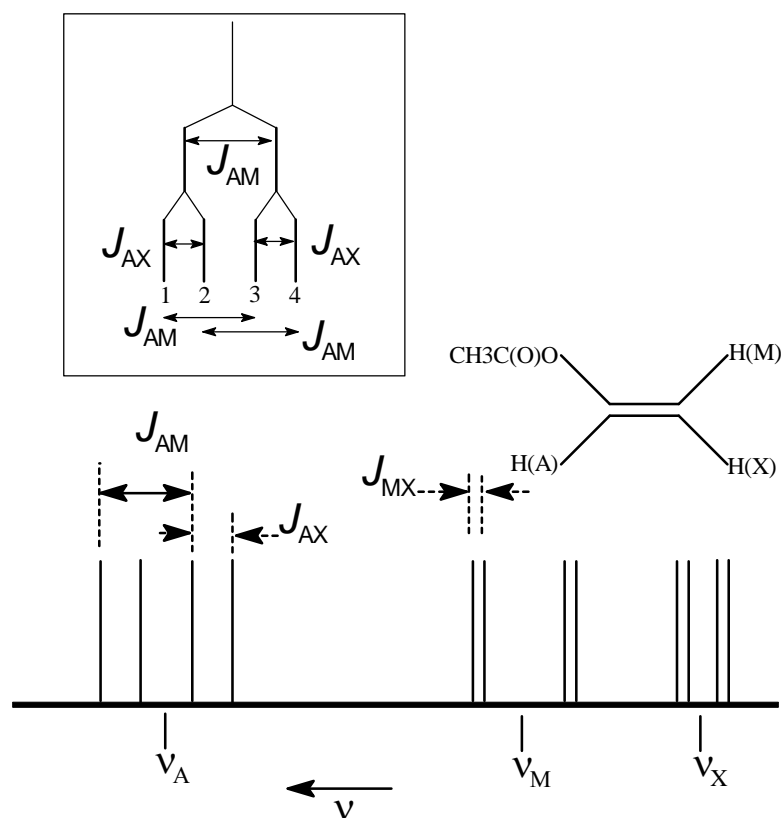
Pascal triangle:

n=0			1								
n=1			1		1						
n=2			1		2		1				
n=3			1		3		3		1		
n=4		1		4		6		4		1	
n=5	1		5		10		10		5		1

^{13}C multiplets due to coupling to ^1H :



- The pattern of lines for a given nucleus may be explained by the method of successive splittings. Consider spin system AMX, assuming $J_{AM} > J_{AX}$. The pattern of A lines may be predicted by considering a splitting by M, and then a further splitting of each of the resulting pair of lines by X. The final pattern includes 4 lines (doublet of doublets). Altogether the spectrum consists of 12 lines (4A, 4M and 4X). Each part of the spectrum is symmetrical about its mid-point, and the mid-point corresponds to the chemical shift frequency of the nucleus concerned.



In principle, for a spin system consisting of n inequivalent spin-1/2 nuclei, each nucleus gives rise to 2^{n-1} lines. The total number of lines is therefore $n 2^{n-1}$.

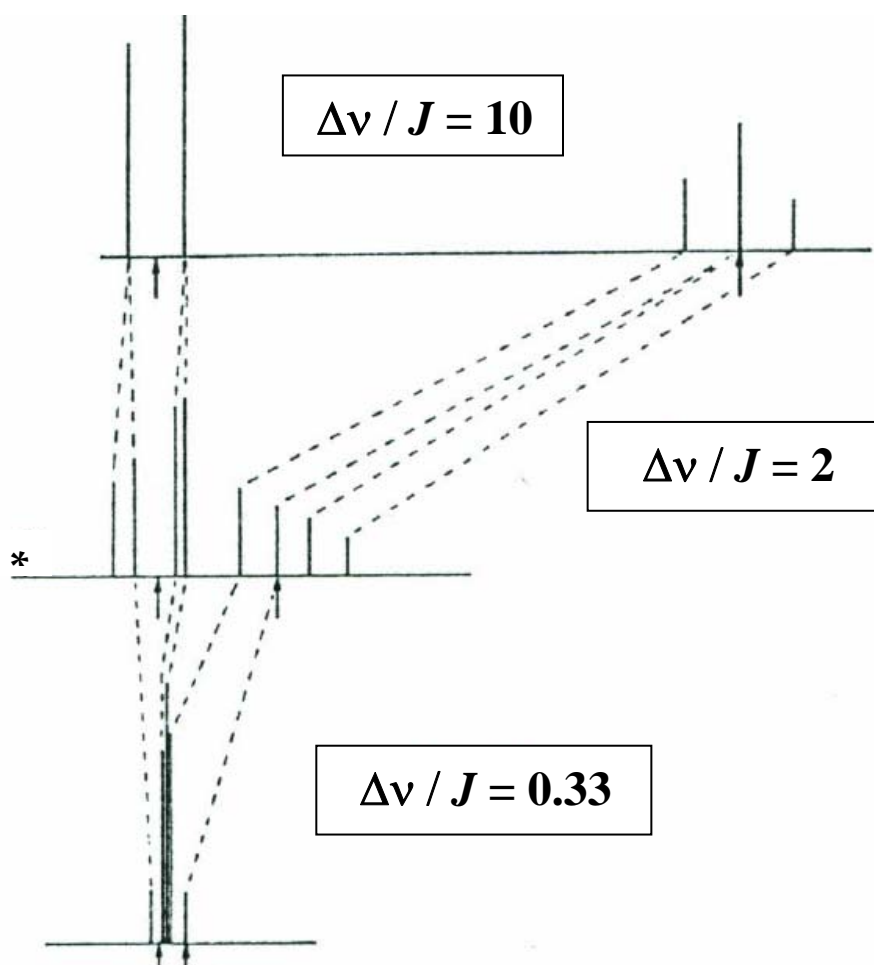
- The splitting patterns are independent of the signs of the coupling constants.
- The magnitude of J -coupling between nuclear spins in general decreases as the number of bonds between the coupled nuclei increases.

Second-order (or strong coupling) effects

Chemical shift difference	$\Delta\nu$ ($\nu_0 \delta$)
Spin-spin coupling constant	J
Zero-order spectrum (no coupling)	$\Delta\nu / J \Rightarrow +\infty$
First-order spectrum ("weak" coupling)	$\Delta\nu / J \gg 1$
Second-order spectrum ("strong" coupling)	$\Delta\nu / J \approx 1$

When $\Delta\nu / J \approx 1$, the effects due to J -coupling and chemical shift have similar energies. This leads to alterations in relative line intensities and in line positions. The intensity of the lines nearest to the multiplet of the neighbouring group is greatly enhanced while that of other lines decreases ("roof" effect). Generally, more lines are observed in the second-order spectrum than one would expect for the corresponding first-order spectrum.

The perturbation of the spectra from the first-order appearance is a function of the ratio $\Delta\nu / J = \nu_0 \delta / J$ and at a high enough frequency many second-order spectra approach their first-order limit.



A combination line (*) corresponds to a combined transition of several spins such that

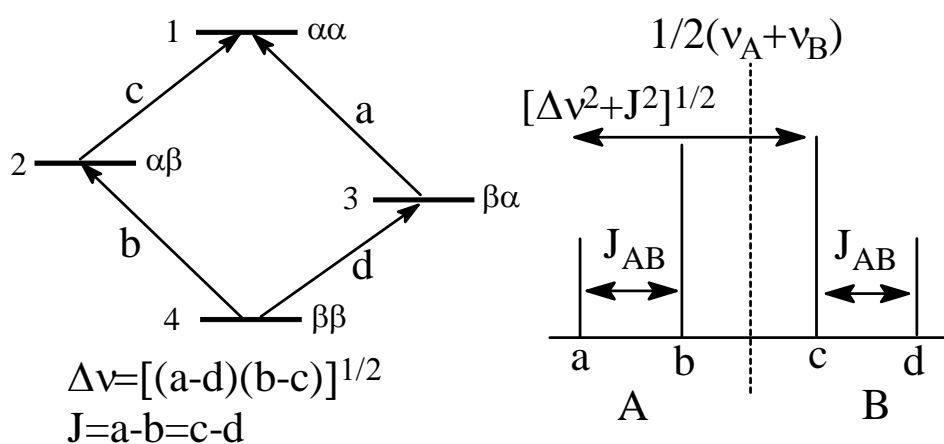
$$\Delta \sum m = 1, \text{ e.g. } -++ \Rightarrow +-- (\beta\alpha\alpha \Rightarrow \alpha\beta\beta)$$

Strong coupling: AB spin system

Two states ($\alpha\beta$, $\beta\alpha$) have the same total spin and the quantum-mechanical equations can only be solved for two linear combinations of $\alpha\beta$ and $\beta\alpha$ (*mixing of the states*):

State	Wavefunction	Energy level / Hz
1	$\alpha\alpha$	$1/2 (v_A+v_B)+1/4 J$
2	$C_1(\alpha\beta)+C_2(\beta\alpha)$	$1/2 (\Delta v^2+J^2)^{1/2}-1/4 J$
3	$-C_2(\alpha\beta)+C_1(\beta\alpha)$	$-1/2 (\Delta v^2+J^2)^{1/2}-1/4 J$
4	$\beta\beta$	$-1/2 (v_A+v_B)+1/4 J$

$\Delta v = |v_A - v_B|$. The transition energies are the differences between 4 pairs of energy states: 3-4, 2-4, 1-3 and 1-2, each transition involving a mixed energy level.



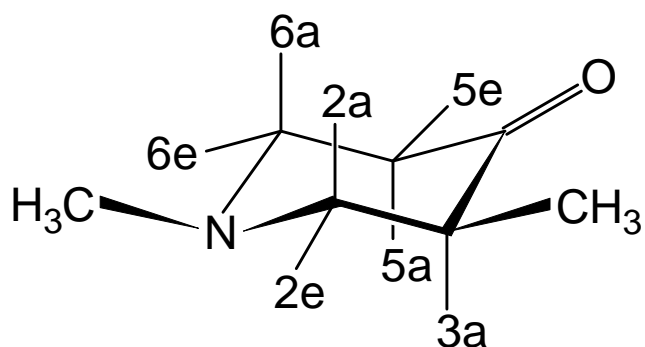
COMPUTER ANALYSIS

For the more complicated spin systems without symmetry or with a large number of nuclei in general no explicit equations can be derived for the NMR parameters. In these cases for a full analysis of a second-order multiplet it is necessary to apply computational techniques (e.g., LAOCOON).

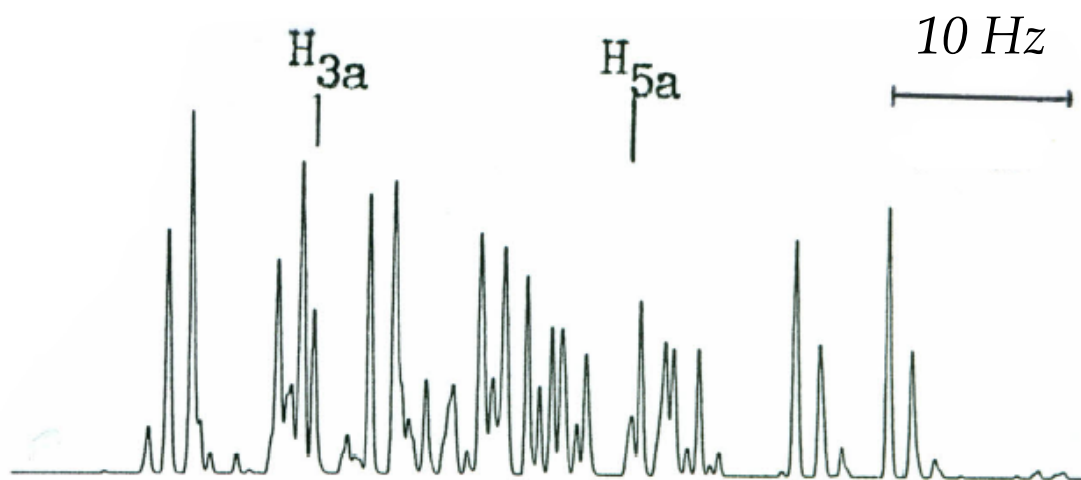
The analysis starts with the calculation of a trial spectrum with a set of estimated starting parameters [chemical shifts, ν_i , and spin-spin coupling constants, J_{ij} (including the sign of the J -coupling)] followed by the very important step of assigning the lines of the experimental spectrum to the lines of the simulated spectrum. Then an iterative fitting is performed to optimize the agreement between calculated and experimental spectrum. Note that for the iterative fitting procedure used the best set of parameters is the one that leads to the minimum value of the following sum:

$$\sum_{i=1}^k (f_{\text{exp}} - f_{\text{calc}})_i^2$$

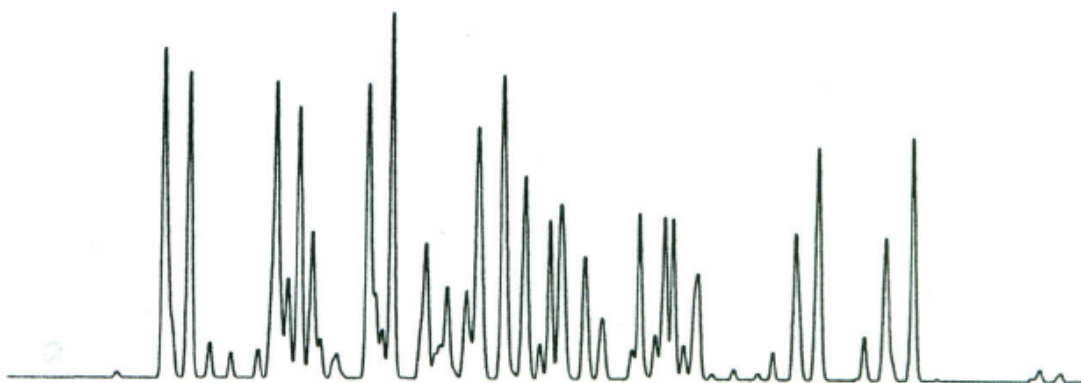
where k is the number of measured lines and $(f_{\text{exp}} - f_{\text{calc}})$ is the frequency difference between the observed and calculated transitions for the i th line.



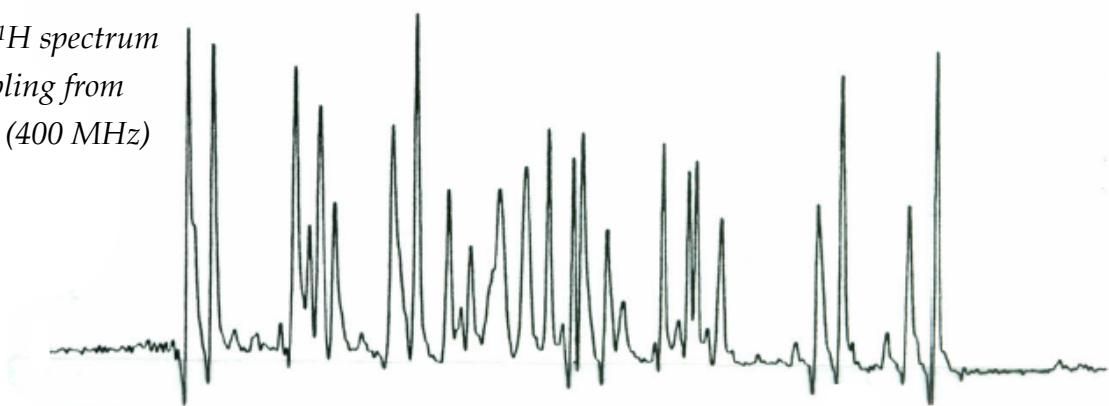
Calculated
spectrum
with ${}^4J_{3a5a} < 0$



Calculated
spectrum with
 ${}^4J_{3a5a} > 0$



Experimental ${}^1\text{H}$ spectrum
with decoupling from
3-Me protons (400 MHz)



Factors affecting spin-spin coupling

Spin-spin coupling over one bond	$1J$
Geminal spin-spin coupling	$2J$
Vicinal spin-spin coupling	$3J$
Long-range spin-spin coupling	$nJ, n \geq 4$

Spin-spin coupling constants are not easy to predict theoretically, and depend on a number of factors:

- (i) the hybridization of the atoms involved in the coupling;
- (ii) the bond angles;
- (iii) the dihedral angles;
- (iv) the C - C bond length;
- (v) substituent effects (electronegativity, neighbouring π -bond and lone pair effects);

1J -coupling between ^1H and ^2H

$$|{}^1J_{\text{DH}}| = 42.94 \text{ Hz} \quad {}^1J_{\text{HH}} / {}^1J_{\text{DH}} = \gamma_{\text{H}} / \gamma_{\text{D}} = 6.514 \quad |{}^1J_{\text{HH}}| = 280 \text{ Hz}$$
$$\{ {}^1J_{\text{NX}} / {}^1J_{\text{N'X}} = \gamma_{\text{N}} / \gamma_{\text{N'}} \}$$

1J -coupling between ^{13}C and ^1H

The hybridization dependence: ${}^1J_{\text{CH}} = 500 s(i)$

$s(i) = 0.25$	sp^3 carbon	${}^1J_{\text{CH}} = 125 \text{ Hz}$
$s(i) = 0.33$	sp^2 carbon	${}^1J_{\text{CH}} = 165 \text{ Hz}$
$s(i) = 0.50$	sp carbon	${}^1J_{\text{CH}} = 250 \text{ Hz}$

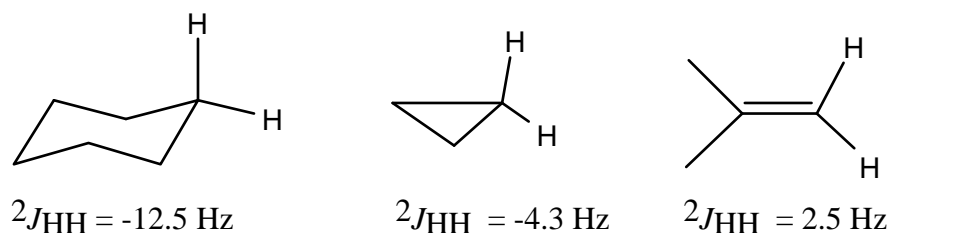
Values are slightly higher (20-30 Hz) if there is an electronegative substituent on the carbon, and/or if the carbon is in a 3- or 4-membered ring. For methane derivatives, CHXYZ , there are additive substituent contributions, ϵ , such that

$${}^1J_{\text{CH}} = {}^1J_0 + \epsilon_{\text{X}} + \epsilon_{\text{Y}} + \epsilon_{\text{Z}}$$

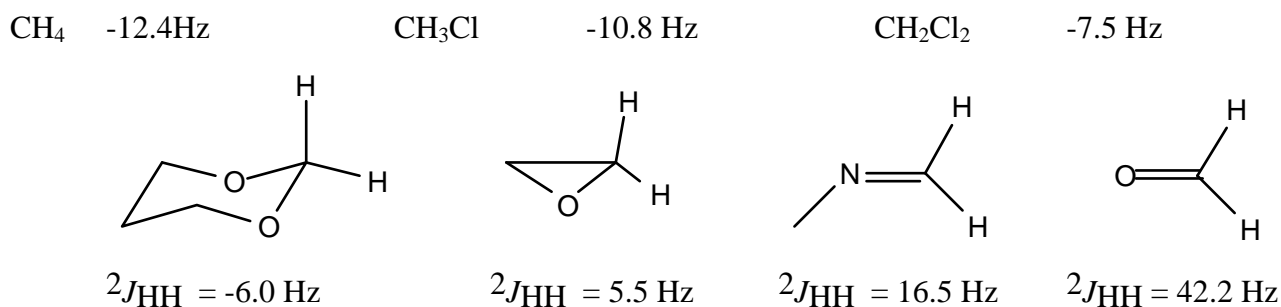
For multiple substitution by highly electronegative groups, extra terms must be introduced to account for pairwise interactions. The parameters ϵ correlate with the electronegativity of the substituent, which affects the s -electron density at the carbon atom.

2J -coupling between ^1H and ^1H

Geminal coupling between protons (with values between -23 and +42 Hz) depend mainly on the H-C-H bond angle, the influence of α and β substituents and the hybridization of the carbon.



These values can be affected by the nature of the α -substituents:

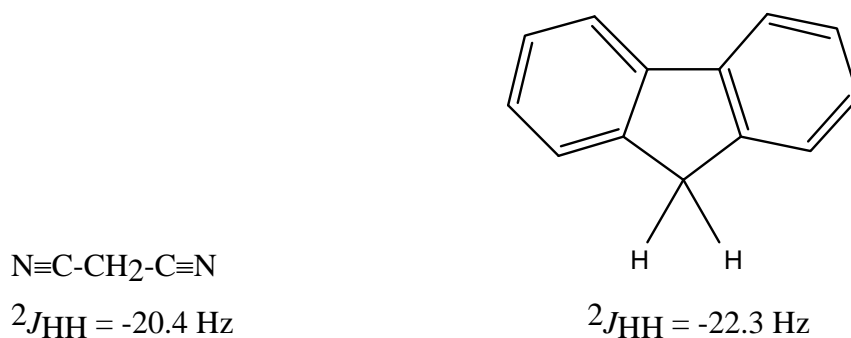


An electronegative β -substituents leads to a negative change in the coupling constant:

$\text{CH}_2=\text{CHX}$

X	Li	H	PR_2	Cl	OCH_3	F
$^2J / \text{Hz}$	+7.1	+2.5	+2.0	-1.4	-2.0	-3.2

The effect of adjacent π -bonds:



The effect of neighbouring π -bonds on the geminal coupling constant is a function of the angle ϕ between the π -orbital and the C - H bond. The largest effect is observed when the neighbouring orbital and the plane of the CH_2 group are parallel.

2J -coupling between ^{13}C and ^1H

Difficult to predict.

Depends on substitution and hybridization, similar to $^2J_{\text{HH}}$.

Typical values: -6 - -4 Hz

Unusual values: $^2J_{\text{CH}} = 25$ Hz for coupling to aldehyde proton

$^2J_{\text{CH}} = 40\text{-}50$ Hz for coupling to terminal ethynyl groups

3J -coupling between ^1H and ^1H

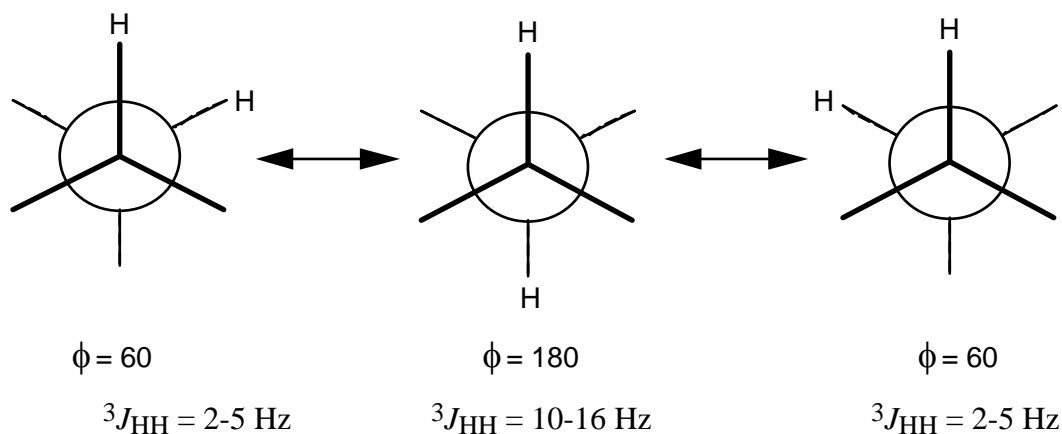
The dihedral angle (ϕ) dependence, the Karplus equation:

$$^3J_{\text{HH}} = A + B \cos \phi + C \cos 2\phi$$

where ϕ is the dihedral angle between the two C–H vectors, and A , B and C are constants with empirical values for hydrocarbons found to be $A = 7$ Hz, $B = -1$ Hz and $C = 5$ Hz.

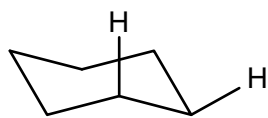
Generally 3J -coupling constants are greatest when $\phi = 180^\circ$ and $\phi = 0^\circ$ ($^3J_{180} > ^3J_0$), and very small when $\phi = 90^\circ$. The Karplus model describes the observed coupling behaviour moderately well, but is valid in the absence of electronegative substituents and of departure from tetrahedral angles at carbon.

n-Alkanes

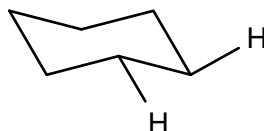


An average $^3J_{\text{HH}}$: $(2 J_{\text{gauche}} + J_{\text{trans}})/3 \sim 7$ Hz.

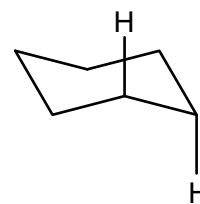
Cycloalkane derivatives.



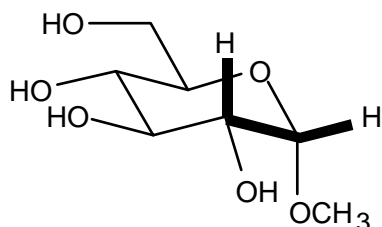
$${}^3J_{ae} = 2-4.5 \text{ Hz}$$



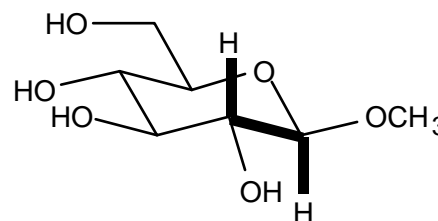
$${}^3J_{ee} = 2-4.5 \text{ Hz}$$



$${}^3J_{aa} = 8-11 \text{ Hz}$$

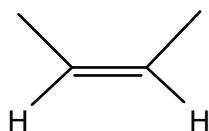


$${}^3J_{HH} = 4.0 \text{ Hz}$$



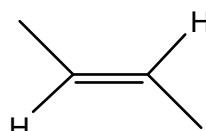
$${}^3J_{HH} = 9.0 \text{ Hz}$$

Ethylene derivatives:



$${}^3J_{cis} = 8-12 \text{ Hz}$$

$$\phi = 0^\circ$$



$${}^3J_{trans} = 14-18 \text{ Hz}$$

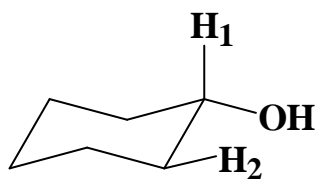
$$\phi = 180^\circ$$

Aromatic compounds: ${}^3J_{ortho}$ is normally 7-9 Hz for benzene, 5-9 Hz for pyridine.

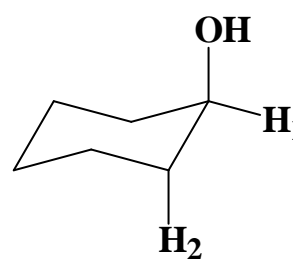
A decrease in 3J is observed when an electronegative substituent is introduced at the H-C-C-H fragment:

	3J		${}^3J_{cis}$	${}^3J_{trans}$
$\text{H}_3\text{C}-\text{CH}_2-\text{Li}$	8.9	$\text{H}_2\text{C}=\text{CH}-\text{Li}$	19.8	23.9
-SiR ₃	8.0	-SiR ₃	14.7	20.4
-CN	7.6	-CH ₃	10.0	16.8
-Cl	7.2	-Cl	7.3	14.4
-OCH ₂ CH ₃	7.0	-F	4.7	12.8
-OR ₂	4.7			

The steric orientation of the substituent X is also of significance:



$${}^3J_{12} = 4.2 \text{ Hz}$$



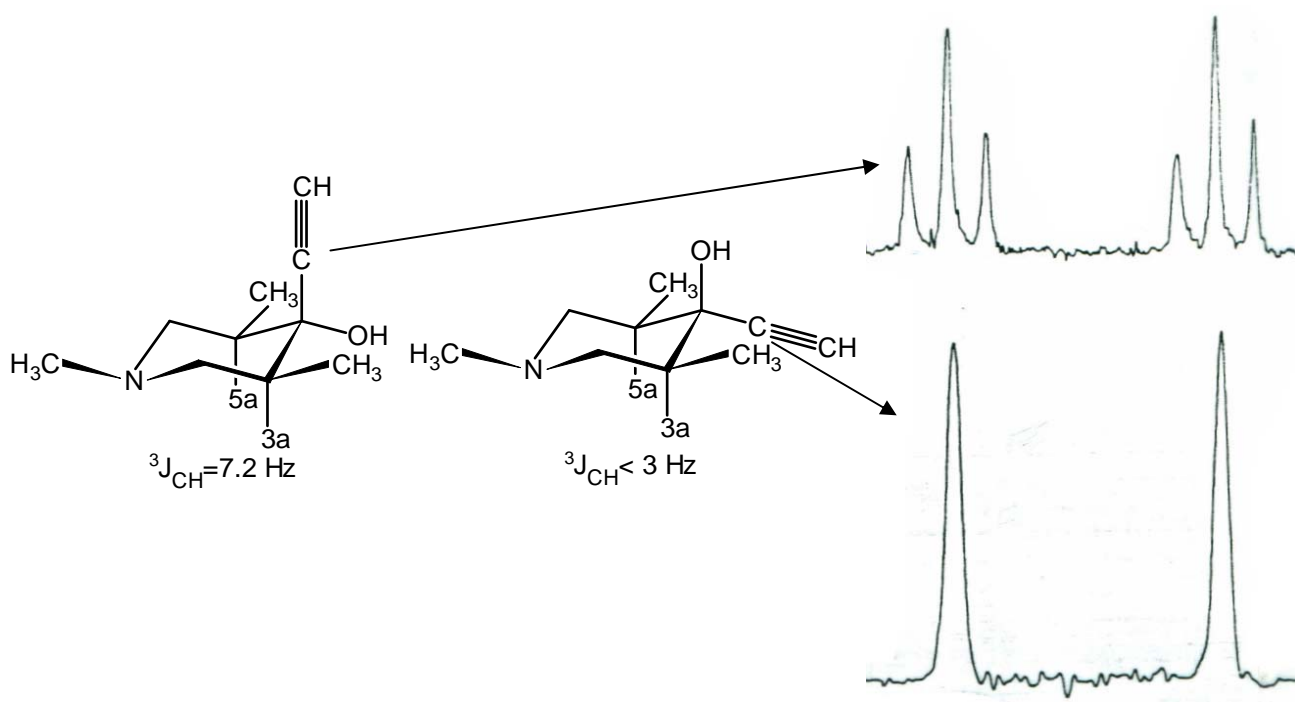
$${}^3J_{12} = 2.7 \text{ Hz}$$

The sign of ${}^3J_{\text{HH}}$ is always positive. Relative signs of other coupling constants are often determined on the assumption that ${}^3J_{\text{HH}} > 0$.

3J -coupling between ${}^{13}\text{C}$ and ${}^1\text{H}$

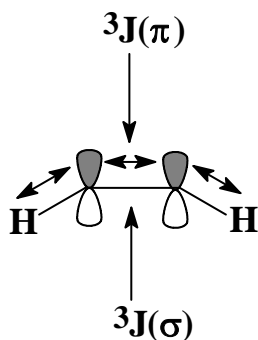
$${}^3J_{\text{CH}} = 3.8 - 0.9 \cos \phi + 3.8 \cos 2\phi$$

Similar Karplus-type equations have been developed for 3J -couplings for other spin pairs: (${}^{13}\text{C}, {}^{13}\text{C}$), (${}^{15}\text{N}, {}^{13}\text{C}$), (${}^{31}\text{P}, {}^{13}\text{C}$), (${}^{15}\text{N}, {}^1\text{H}$).

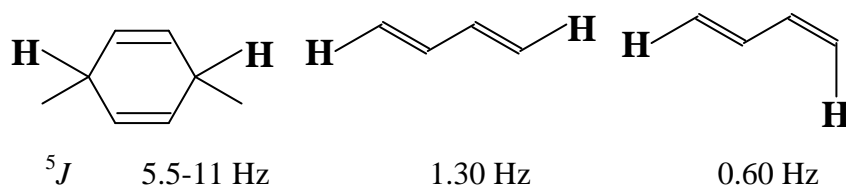


Long-range ${}^1\text{H}$ - ${}^1\text{H}$ coupling

A σ - and π -mechanisms:



The spin-spin interaction is approximated as the sum of two quantities, $J(\sigma)$ and $J(\pi)$, transmitted via σ - and π -electrons. Since the spin-spin interaction via σ -electrons decrease rapidly with an increasing number of bonds, the contribution of π -electrons to long-range coupling becomes important.



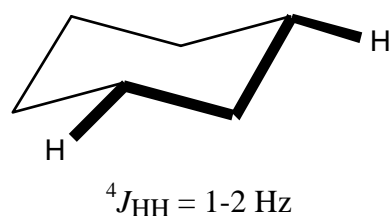
The long-range nature of $J(\pi)$ is well illustrated by the following example:



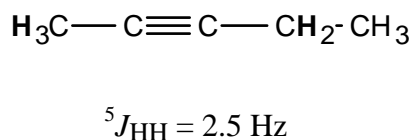
Aromatic compounds: ${}^4J_{\text{meta}} \approx 2 \text{ Hz}$, ${}^5J_{\text{para}} \approx 0.8 \text{ Hz}$.

Saturated systems:

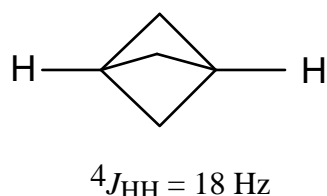
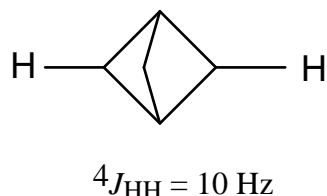
“W-coupling” (zig-zag bond systems)



Through alkynes



$|{}^{4,5,6}J_{\text{HH}}|$ increases rapidly as the number of “coupling paths” increases:



Both negative and positive values of ${}^4J_{\text{HH}}$ have been reported, but the value for the zig-zag relationship (π -effects are absent) is always positive.

Inorganic compounds.

Coupling to quadrupolar nuclei ($I > 1/2$) is seen comparatively rarely (“self-decoupling”). Exception: NH_4^+ ${}^1J({}^{14}\text{N}, {}^1\text{H})=52.5 \text{ Hz}$

Heteronuclear J -couplings may be substantially larger than J_{HH} or J_{CH} : ${}^1J({}^{205}\text{Tl}, {}^{13}\text{C}) = 2-10 \text{ kHz}$, ${}^3J({}^{205}\text{Tl}, {}^{13}\text{C}) \sim 1 \text{ kHz}$, ${}^1J({}^{119}\text{Sn}, {}^{117}\text{Sn}) = 4.264 \text{ kHz}$, ${}^1J({}^{119}\text{Sn}, {}^1\text{H}) = 1.931 \text{ kHz}$. The value of $|{}^1J({}^{199}\text{Hg}, {}^{199}\text{Hg})|$ in the $[\text{Hg}_3]^{2+}$ ion has been reported to be 139 kHz.

An empirical relationship of coupling constants 1J to hybridization have a wider validity. For PF_5 derivatives $^1J_{\text{PF}}$ is negative and its magnitude is greater for equatorial fluorine atoms than for axial fluorines. This is because equatorial bonds have greater s-character than axial bonds, as is reflected in the fact that the former are shorter than the latter.

For couplings between ^{13}C and a metal with spin in organometallic complexes, the values of J -couplings to some extent still reflect the degree of s character:

$$^1J(^{183}\text{W}, ^{13}\text{C}) = 124.5 \text{ Hz in } [\text{W}(\text{CO})_6] \text{ (sp carbon)}$$

$$^1J(^{183}\text{W}, ^{13}\text{C}) = 43.2 \text{ Hz in } [\text{W}(\text{CH}_3)_6] \text{ (sp}^3 \text{ carbon).}$$

Single bond couplings between ^{31}P and a metal are large, and are dependent on the ligand trans to the phosphorus:

P-Pt-X system, $^1J(^{31}\text{P}-^{195}\text{Pt})$	4226 Hz for X=Cl
	2870 Hz for X=CN
	1794 Hz for X=CH ₃

2J -couplings between ^{31}P nuclei in P-M-P systems depend on the bond angle and the metal involved: $^2J(^{31}\text{P}-^{31}\text{P})$ is small when the bond angle is close to 90° , and far larger when the bond angle is 180° .

Homo- and heteronuclear 3J coupling constants are usually positive, although negative values of $^3J_{\text{FF}}$ are well-known.

Reduced coupling constants: $K = 4 \pi^2 J / h \gamma_A \gamma_B$:

$^1J(^1\text{H}-^{13}\text{C})$	CH ₄	+125 Hz	$^1K = +4.1 (\times 10^{20} \text{ N A}^{-2}\text{m}^{-3})$
$^1J(^1\text{H}-^{29}\text{Si})$	SiH ₄	-202 Hz	$^1K = +8.5$
$^1J(^1\text{H}-^{73}\text{Ge})$	GeH ₄	(-)98 Hz	$^1K = (+)23.3$
$^1J(^1\text{H}-^{119}\text{Sn})$	SnH ₄	-1931 Hz	$^1K = +43.0$

Coupling mechanism between nuclear and electron spins

J -coupling between nuclei and electrons is transmitted via:

- the electron-orbital term - the interaction between the magnetic moments due to nuclear and electron orbital motion;
- the electron-dipole term - the dipolar interaction between the electron and nuclear spins;

- the Fermi contact term - includes the possibility that the electron may be in the same region of space as the nucleus (quantum-mechanically this is possible). The mathematical representation of this term (which is usually dominant) includes the Dirac delta function $\delta(r_{eN})$ [$\delta(r_{eN}) = 1$, if $r_{eN}=0$; $\delta(r_{eN}) = 0$, if $r_{eN}\neq 0$]:

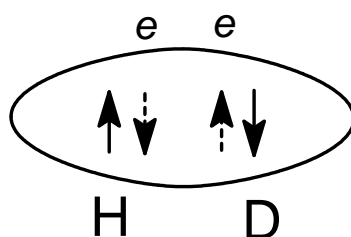
$$E_{eN} \sim \gamma_N \delta(r_{eN}) \mathbf{I}_N \mathbf{S}_e$$

↓ ($\mathbf{I}_N, \mathbf{S}_e$ - nuclear and electron spin vectors)

the contact term stabilizes the anti-parallel orientation of an electron at a nuclear spin (for $\gamma_N > 0$).

For spin-spin interaction between two nuclei N and N': $E_{NN'} \sim \gamma_N \gamma_{N'}$

The Dirac vector model

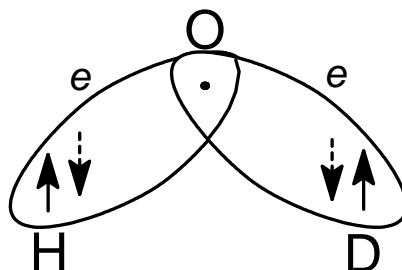


A coupling constant is defined as positive if coupling stabilizes anti-parallel spins:

$$E(m_A m_X) = -h \nu_A m_A - h \nu_X m_X + h J_{AX} m_A m_X$$

↓

$${}^1J_{HD} > 0$$



$${}^2J_{HD} < 0$$

In general, the sign of J should alternate as the number of bonds separating the nuclei increases, although there are exceptions, since this model considers only σ -bonds.