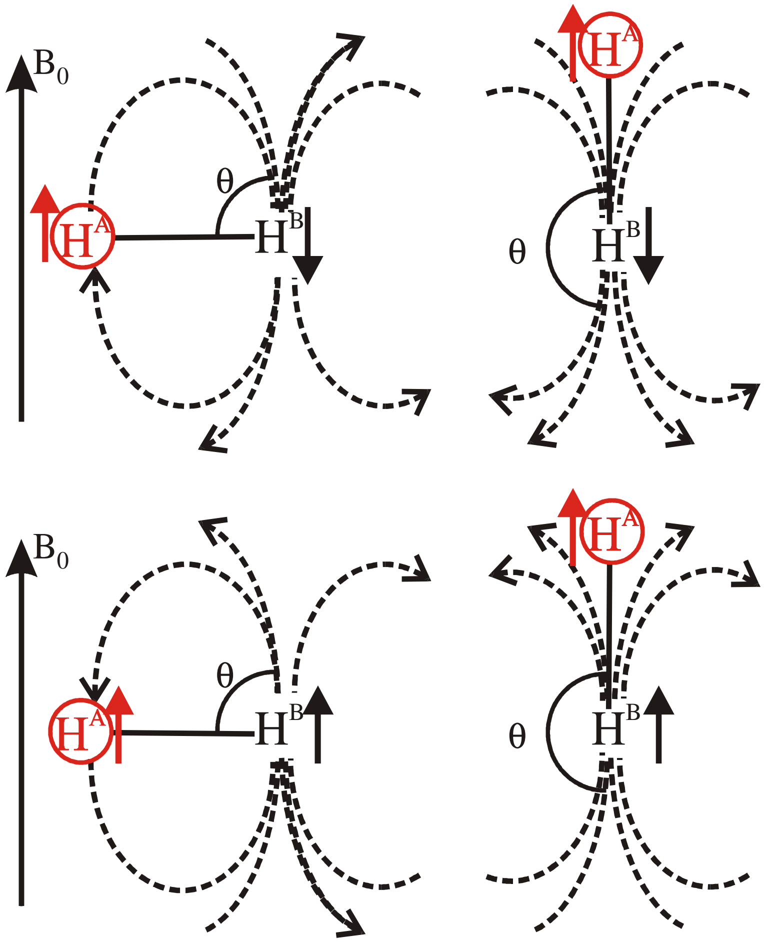
Lecture notes Part 4: Spin-Spin Coupling

F. Holger Försterling October 4, 2011

So far, spins were regarded spins isolated from each other. However, the magnetic moment of nuclear spins also have effect on neighboring spins:

1 Direct (through space) spin-spin coupling:

The energy of spin A will depend on the orientation of B relative to A. The interaction will depend on the distance A-B and the angle of the vector A-B relative to the field:



$\theta = 90^o$ $\theta = 180^o$

Figure 4.1: Dipolar coupling of the spin of **H^A** with a second spin H^B. **Left:** H-H vector ⊥ to B_0: parallel spin orientation of H^B is higher in energy. **Right:** H-H vector ∥ to B_0: parallel orientation of spin H^B is lower in energy

$$\nu^A = \nu_0^A \pm \frac{3}{4}\gamma_A\gamma_B \frac{h}{4\pi^2}\frac{3\cos^2\theta - 1}{r_{AB}^3} = \nu_0 \pm \frac{3}{2}D_{AB} \quad \textbf{(4.1)}$$

D_{AB} is called the dipolar coupling constant and depends on the nature of the nuclei, the distance between them and the angle between the dipolar field and the internuclear vector.
The above figure is very similar to the one shown for induced shielding through remote groups. The difference is that the magnitude of the induced shielding fields depends on the external magnetic field and the orientation of the bond, whereas dipolar coupling is independent of the field.

In solution: Fast **isotropic** tumbling of the molecule will average over all orientations and result in an average coupling $D_{ave} = 0$. Dipolar couplings are not directly observable in isotropic solution, but are important for T_1, T_2 relaxation and NOE. Broad lines in ^{1}H NMR spectra of larger proteins arise from short T_2 due to insufficient averaging of dipolar coupling.
In **anisotropic** solutions (liquid crystals) the averaging will not be complete, and a reduced residual dipolar coupling can be observed in solution.
Solid state: Dipolar couplings are the main reason why proton NMR of solid materials is very challenging.

2 Indirect (scalar) Spin-spin coupling:

Spin-spin interactions are also mediated by electrons:

2.1 General Considerations

Consider a P-H bond: (^{1}H-^{31}P): One electron will be closer to H, the other closer to P, but always with anti-parallel orientation of spin (Pauli principle)
The nucleus will prefer to be *anti parallel* to the nearby electron spin (note that e^- has *negative* charge and the magnetic moment will be aligned parallel); thus the anti parallel orientation of ^{1}H and ^{31}P spins will be lower in energy than the parallel arrangement. The energy difference is denoted by the scalar coupling constant J_{HP}.
If more than two electrons are involved in the transmition of the interaction, then either orientation of nuclear spins can be lower in energy, depending on the circumstances.

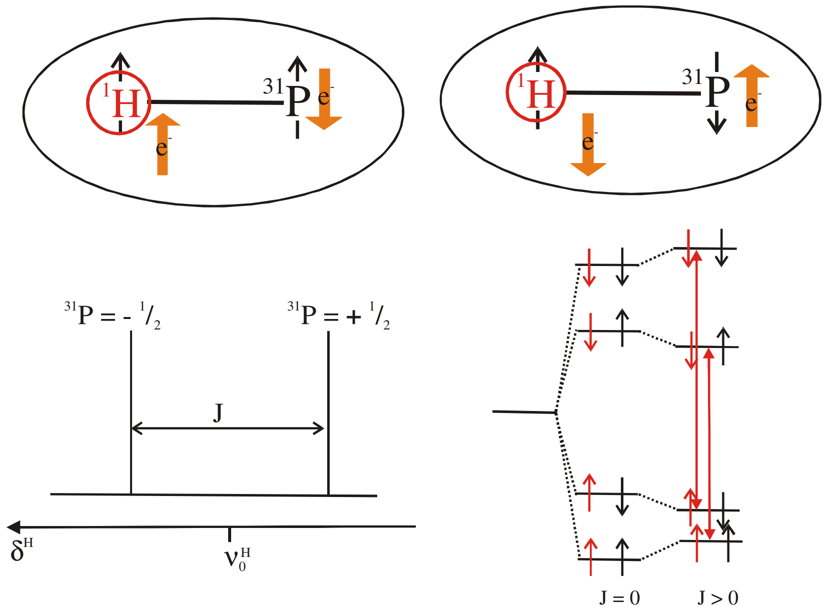


Figure 4.2: Scalar coupling through one bond (all $\gamma_N > 0$). Antiparallel orientation of nuclei is lower in energy => **J > 0**

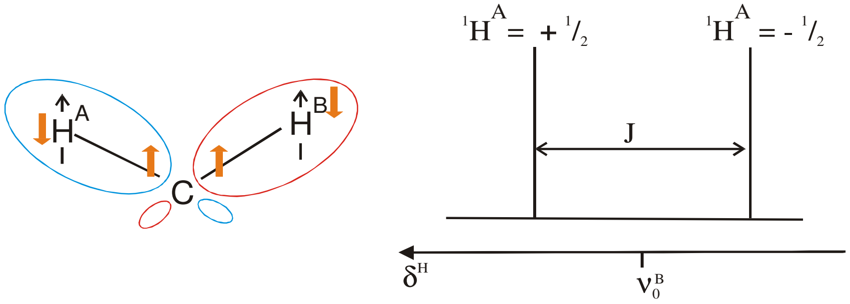


Figure 4.3: Scalar coupling through two bonds: electrons in neighboring orbitals tend to approach each other with equal spin (Hunds rule). Parallel orientation of nuclear spins lower in energy => **J < 0**

This interaction does **NOT** average to zero in solution, as it mainly depends on electron density ***at*** the nucleus (contact interaction). It therefore does **NOT** depend on the orientation of the A-B vector to the field (hence the name scalar coupling). The coupling depends on electron density in s-orbitals as only s-orbitals have a finite electron density at the nucleus.

3 Splitting patterns caused by scalar couplings

Often, many different couplings are present for a nucleus. We need to understand splitting patterns and relate them to the number of neighbored spins

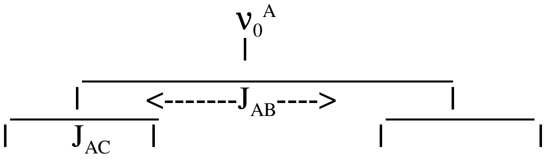
3.1 First Order splittings:

If the chemical shift difference is large compared to the coupling constant J ($\Delta\Omega \gg J$) the splitting can be analyzed by first order rules. Each coupling partner will split the spectral line into two lines of equal intensity, with the separation measured in Hz equal the coupling constant J.

3.1.1 Multiple coupling partners:

If a nucleus is coupled to several different nuclei, the coupling patterns will superimpose:

CH_B-CH_A-CH_C: H_A coupled to H_B and H_C, lets assume $J_{AB} > J_{AC}$

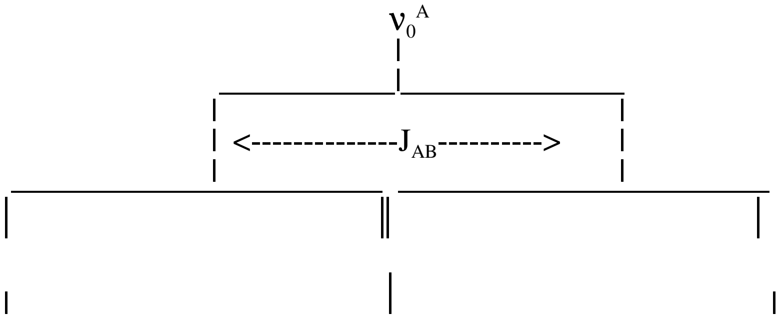


doublet of doublets

in general up to 2^n lines are possible if all coupling different

3.1.2 Coupling to a group of equivalent spins:

special case $J_{AB} = J_{AC}$: same as CH_2 group



Note that this is just a special case of multiple coupling partners. All first order coupling couplings patterns can be regarded as a a superposition of individual doublets.

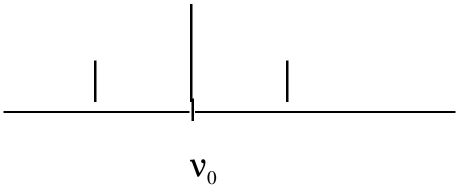
The intensities resulting from coupling to a group of equivalent spins are governed by basic statistics:

Example CH-CH_2 group: proton coupled to two equivalent nuclei:

The two nuclei allow four combinations of their spin states, two of which are equivalent:

spin states	total spin of CH_2 group	Intensity of line ~ number of equivalent combinations of spin states
(+ ½ + ½)	+1	1
(+ ½ ; - ½) (-½ ; + ½)	0	2
(-½ ; - ½)	-1	1

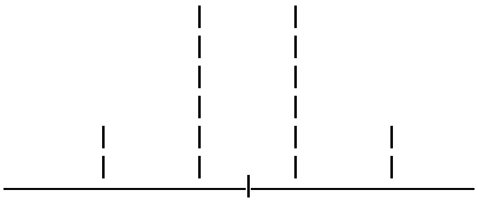
1 :2:1 triplet:



Example CH-CH_3 group: proton coupled to three equivalent nuclei

spin states(+½≡+; - ½≡-)	total spin group	Intensity of line ~ number of equivalent combinations of spin states
(+ + +)	$+{}^{3}/_{2}$	1
(+ - -)(- + +)(- - +)	+ ½	3
(+ - -)(- + -)(- - +)	- ½	3
(- - -)	$-{}^{3}/_{2}$	1

1:3:3:1 quartet:



In general, for a spin with a group of *n* neighbored spins *I*:

Splitting into 2 *n* *I* + 1

```
n
0      1
1     1 1
2    1 2 1
3   1 3 3 1
     . . . . .
```

for *I* = ½ intensities are given by Pascals Triangle (statistics)

Note that for I ≠ ½ intensities will be different (see multiplets of deuterated solvents in ^1H and ^{13}C spectra)

ν_0

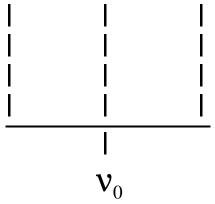
Exercise: Sketch the ^{31}P spectrum of PF_6

3.1.3 Coupling to nuclei with I > ½ :

important to understand spectra of deuterated solvents

^{13}C spectrum of $CDCl_3$ (one coupling partner of I=1):

m_I	intensity
+1	1
0	1
-1	1



^{13}C spectrum of DMSO-d_6 (CD_3-SO-CD_3) (three coupling partners with I=1)

m_I	I_{tot}	Intensity
(+1 +1 +1)	+3	1
(+1 +1 0)(+1 0 +1)(0 +1 +1)	+2	3
(+1 +1 -1)(+1 -1 +1)(-1 +1 +1)(0 0 +1)(0 +1 0)(+1 0 0)	+1	6
(0 0 0)(+1 -1 0)(+1 0 -1)(0 +1 -1)(-1 +1 0)(-1 0 +1)(0 -1 +1)	0	7
(-1-+1+1)(-1 +1 -1)(+1 -1 -1)(0 0 -1)(0 -1 0)(-1 0 0)	-1	6
(-1 -1 0)(-1 0 -1)(0 -1 -1)	-2	3
(-1 -1 -1)	-3	1

Note that proton signals of deuterated solvents arise from partially protonated isotopomers. The proton spectrum of deuterated DMSO will be that of CD_3-SO-C**H**D_2, so there will be **two** coupling partners with I = 1.

Exercise: Sketch the ^{19}F spectrum of BF_4^- and SbF_6^-

3.2 Deviation from first order rules

3.2.1 Equivalent spins: In the case of equivalent nuclei ($\Delta\Omega_{AB} = 0$, $J_{AB} \neq 0$) , no splitting of lines is observed from coupling between the equivalent spins. The coupling is still present, but it is not observed in the spectrum.

3.2.2 Higher order spectra: If the difference in chemical shift is similar to magnitude of coupling, higher order effects are observed. One can intuitively understand that there has to be an intermediate regime between two equivalent and two very

different spins.

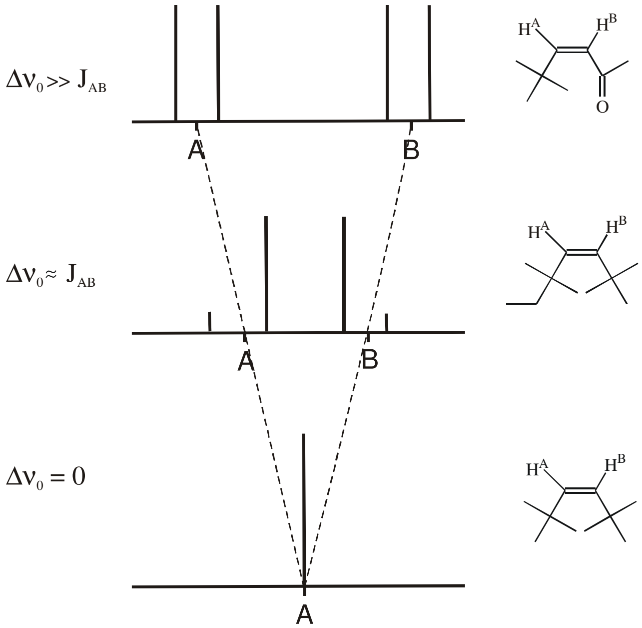


Figure 4.4: Spectra of two coupled protons with very different (top), similar (middle) and identical (bottom) shifts.

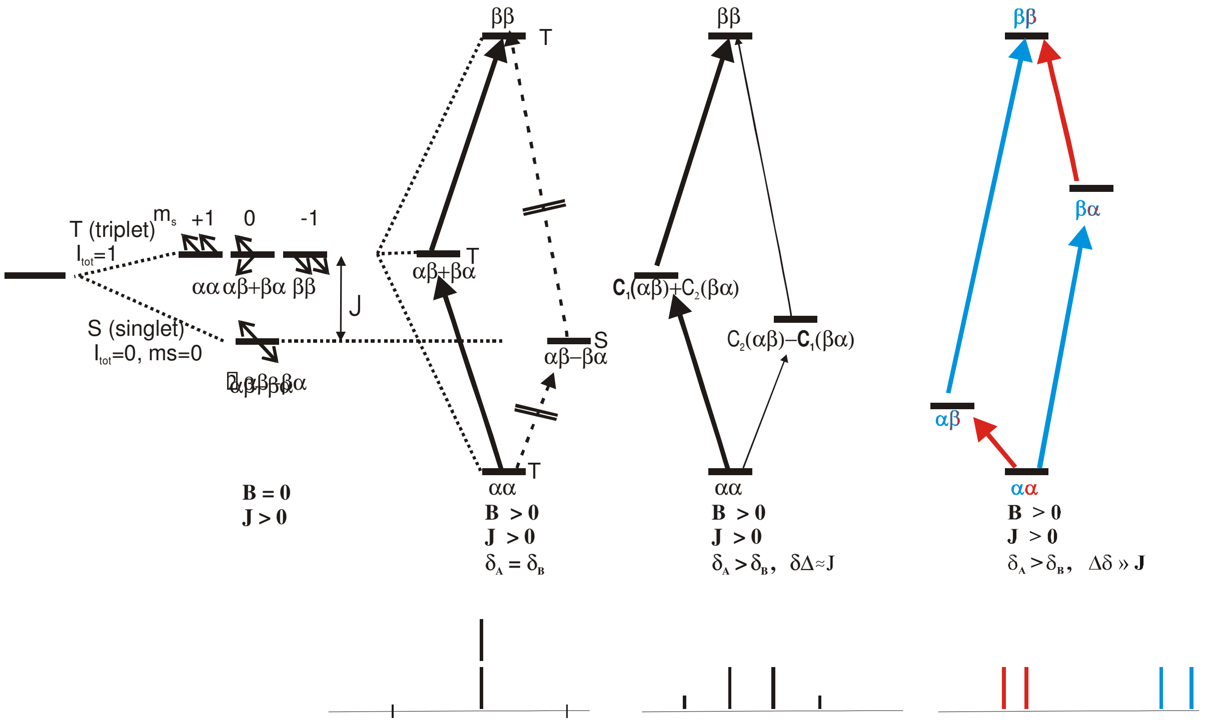
As $\Delta\nu_0$ is measured in Hz and thus depends on the magnetic field B_0 for the same ppm separation, a higher order spectrum $\Delta\nu_0 \approx J_{AB}$ can transform into a first order spectrum ($\Delta\nu_0 \gg J_{AB}$) when using a stronger magnet

3.2.3 Quantum mechanical explanation:

Consider a symmetric system of two spin ½ nuclei (simplest case: H_2 molecule). In the absence of an magnetic field, spin-spin coupling will split the energy levels into a singlet state with combined spin 0 and a degenerate triplet state with combined spin 1.

Application of a magnetic field will leave the singlet state unchanged, but split the triplet into three levels according with $I_z = +1$, 0 and -1. As transitions between singlet and triplet states are forbidden, only transitions within the triplet state will be observed, which for symmetry reasons are equal in frequency. Hence a single peak is observed in the spectrum.

If the two spins are non equivalent, the separation of singlet and triplet state no longer holds, as precession of the spins will interconvert Singlet and Triplet/I_Z=0 states. Hence the Singlet to Triplet transitions will become allowed. For small shift separations, the S-T transitions are weak, and give rise weak “satelite” signals.



Something to think about:

For dihydrogen, the interconversion of Singlet and Triplet state is so slow, that the two forms are considered as two isomers, *para*- and *ortho*-hydrogen. At room temperature, the equilibrium ratio is 25/75 para/ortho, but at 77 K it is 52/48, and at 20 K 99.8/0.2. What ratios would be expected using the H-H coupling constant listed below, and how can we explain the discepancy ?

4 Magnitude of coupling constants

4.1 General considerations

J does **NOT** depend on field B_0 and is thus measured in units of Hz.

Its magnitude is proportional to the γ values of the involved nuclei. Therefore, C-D couplings in deuterated solvents are scaled compared to the ones in the equivalent protonated compound.

$$J_{CD} = \frac{\gamma_D}{\gamma_H} J_{CH} \quad \textbf{(4.2)}$$

The magnitude of measured J couplings can range from a fraction of a Hz to several thousand Hz in case of some heavy metals.

4.2 Couplings through one bond

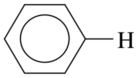
4.2.1 $^1J_{HH}$:

Dihydrogen H-H 276 Hz ~> How would one measure this ?

for dihydrogen complexes M-(η^2-H_2) somewhat lower values are observed (220 - 140 Hz). Measuring $^1J_{HH}$ (if possible) is then a good way to distinguish dihydrogen complexes (η^2-H_2)M from dihydride complexes H_2M.

4.2.2 $^1J_{CH}$:

Depends on s-orbital contribution to the bond. In hydrocarbons one finds J = 500 Hz · %s where %s = 0.25 for sp^3, 0.33 for sp^2 and 0.5 for sp-orbitals:

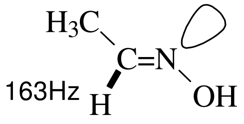
R-CH_3	**=CRH,** 	**≡C-H**
≈125 Hz	**140-160 Hz**	**250 Hz**

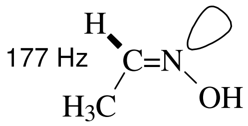
Substituents have an inductive effect (EN substituents cause an increase in J_{CH}):

CH_3-Li	CH_3-H	CH_3-Cl	CH_2Cl_2	$CHCl_3$	$CHCF_3$
98	125	150	178	205	239

H_2C=CHX	X =	H	-CHO	CN	Cl	F
		156.4	162.3	178	195	200

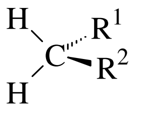
Effect of nitrogen lone pair in imines and similar compounds: $^1J_{CH}$ (trans) < $^1J_{CH}$ (cis) with respect to the lone pair)



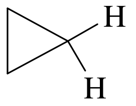


4.3 Coupling through two bonds

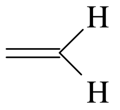
$^2J_{HH}$: depends on hybridization of the connecting C-atom, with couplings across an *sp^3* center large, but near zero across an *sp^2* center. Similar considerations apply to $^2J_{CH}$ couplings.



-10 - -16 Hz



- 4 - +2 Hz

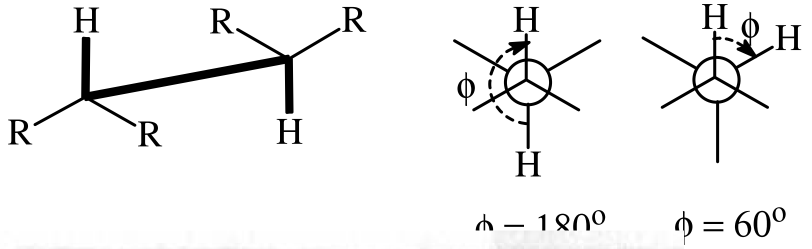


-3 - +2 Hz

4.4 Coupling through three bonds

$^3J_{HH}$: The most important one in structure determination

Depends on dihedral angle ϕ:



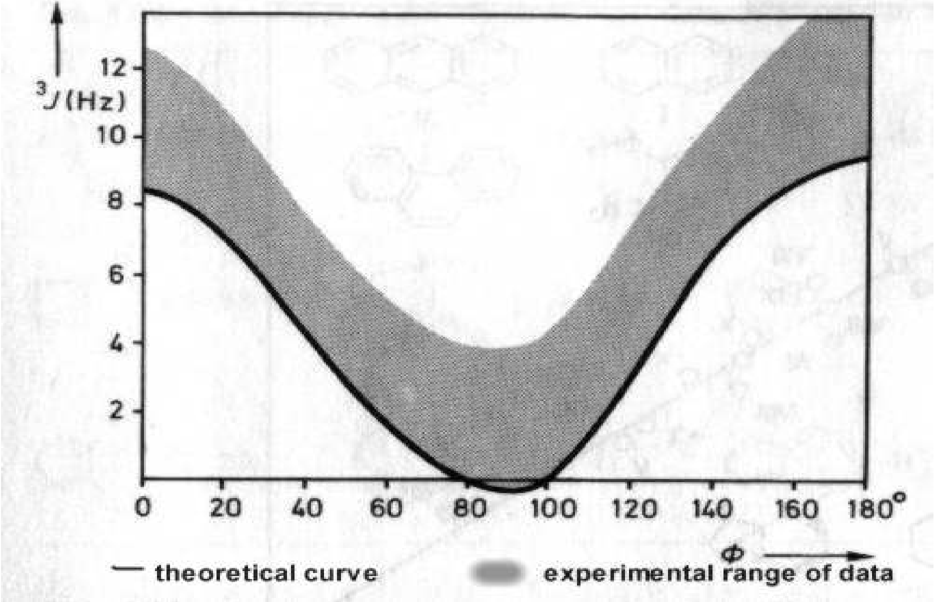


Figure 4.5: $^3J = A + B\cos(\phi) + C\cos^2(\phi)$ (Karplus equation)

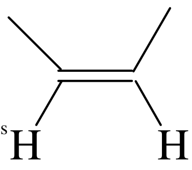
	A	B	C
calculated for HC-CH fragment	-0.28	-0.5	9.8
empirical to fit experimental data	2	-1	10

often specific parameters A, B and C are determined for a class of compounds to better fit account for other influences on coupling constant (bond order, substituent effects ...)

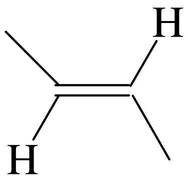
	A	*B*	*C*
$^3J_{H\alpha,HN}$ in proteins	1.9	-1.4	6.4
$^3J_{H\alpha,H\beta}$ in proteins	1.8	-1.6	9.5

- **Always:** $^3J(\phi=0°) < {}^3J(\phi=180°)$

- **in olefins**, $^3J_{cis} < {}^3J_{trans}$

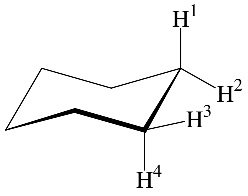


$^3J_{HH}$ = 7-12Hz

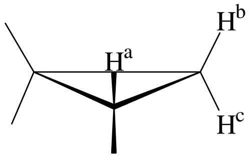


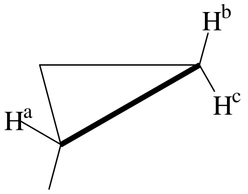
$^3J_{HH}$ = 12 - 18 Hz

- In **cyclohexane** (chair conformation): coupling between two axial protons larger than between equatorial or axial with equatorial protons: $^3J_{a,a} > {}^3J_{a,e} \approx {}^3J_{e,e}$ $^2J_{1,2}$ = -14.5 Hz $^3J_{1,3}$ = 2.2 Hz $^3J_{1,4}$ = 10.6 Hz $^3J_{2,3}$ = 5.6 Hz



- **Cyclopropanes**: $\phi_{trans} \approx 0°$, $\phi_{cis} \approx 135°$=> $^3J_{cis} > {}^3J_{trans}$





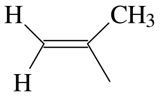
In flexible aliphatic chains fast conformational interconversion occurs (rotation about C-C single bond) => average coupling of 7 - 8 Hz observed

Similar considerations also apply to other couplings over 3 bonds ($^3J_{CH}$, $^3J_{PH}$, $^3J_{cc}$ etc)

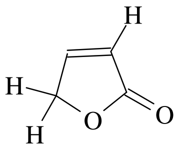
4.5 Long range couplings:

presence of double bonds and/or favored conformations in rings required:

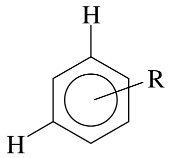
allylic, naphthalene or condensed aromatics, selected ring systems



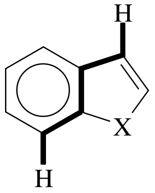
$^4J_{HH}$ = -1 Hz



$^4J_{HH}$ = ()4.1 Hz

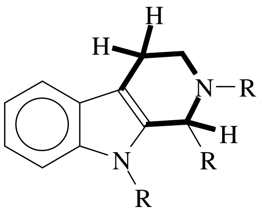


$^4J_{HH}$ = 0.5 - 1.1 Hz



$^5J_{HH}$ = 0.5 - 1 Hz

X = O,S, NH



$^5J_{HH}$ = 2 - 2.5 Hz

5 Extended Vector picture to describe couplings:

Chemical shift can be described be one magnetization vector rotating with angular frequency Ω. The two multiplet lines of a doublet can be described by two vectors rotating in opposite directions at a frequency $2\pi \bullet J/2 = \pi J$ (assuming $\Omega = 0$). One line will be associated with the coupling partner in the α spin state ($\mathbf{I^A_{x,y} I_\alpha^B}$), the other one with the coupling partner in the β state ($\mathbf{I^A_{x,y} I_\beta^B}$). Separation of these vectors into their *x*- and *y*-components yields the corresponding rotation equation for coupling. For a ^{13}C-^1H group $M^C(t=0) = -M_0 \cdot I_y^C$ we obtain an in phase doublet along *y* as the cosine component as and an antiphase doublet along *x* as sine component:

$$M^C = -M_0 I_y^C (I_\alpha^H + I_\beta^H) \cos(\pi J t) + I_x^C (I_\alpha^H - I_\beta^H)\, i \sin(\pi J t)$$

we can use the relations $I_\alpha^H + I_\beta^H = \mathbf{1}$ (normalization) and $I_\alpha^H - I_\beta^H = I_z^H$ (population difference) and obtain

$$\boxed{M = M_0(-I_y^C \cos(\pi Jt) + I_x^C I_z^H \sin(\pi Jt)) \qquad \mathbf{(4.3)}}$$

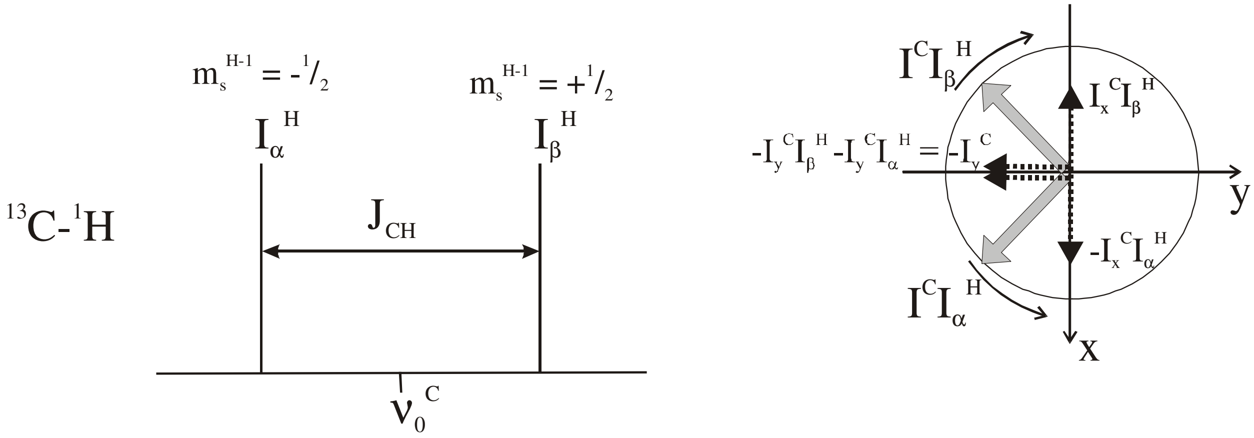


Figure 4.6: Description of a doublet using an extended vector picture. Using the relation $I_x^C I_\beta^H - I_x^C I_\alpha^H = I_x^C(I_\alpha^H - I_\beta^H) = I_x^C I_z^H$ rationalizes the product operator for non observable anti phase magnetization

This describes mathematically a rotation about the $\mathbf{I_z^C I_z^H}$ axis. Such an axis is not easily visualized, but application of the corresponding equation is staightforward. The vector $I_x^C I_z^H$ is the first example of a non-observable quantity, and also the first two spin vector. I a full quantum mechanical treatment these vectors emerge as operators, but in this case we still can picture them as vectors.

5.1 Summary: three basic rotations describe most NMR experiments

Most NMR experiments can be described by a combination of the three basic rotations pulse, chemical shift precession and spin-spin coupling.

Initial state $\xrightarrow{\text{rotation}}$ cos component(initial) + sine component(new, ⊥ to rotation axis and initial state)

5.1.1 Pulses: rotation about x- or y-axis with angular frequency ω_1

Pulse about x- axis: $I_z^A \xrightarrow{\theta x} I_z \cos(\theta t) - i \sin(\theta t)$

5.1.2 chemical shift: rotation about z axis with angular frequency Ω

Precession about z axis: $I_y^A \xrightarrow{\Omega} I_y \cos(\Omega t) - i\, I_x \sin(\Omega t)$

5.1.3 scalar coupling: rotation about $I_z^A I_z^B$ with angular frequency πJ_{AB}

Rotation about $I_z^A I_z^B$: $I_y^A \xrightarrow{\pi J(AB)} I_y^A \cos(\pi J t) - i\, I_x^A I_z^B \sin(\pi J t)$