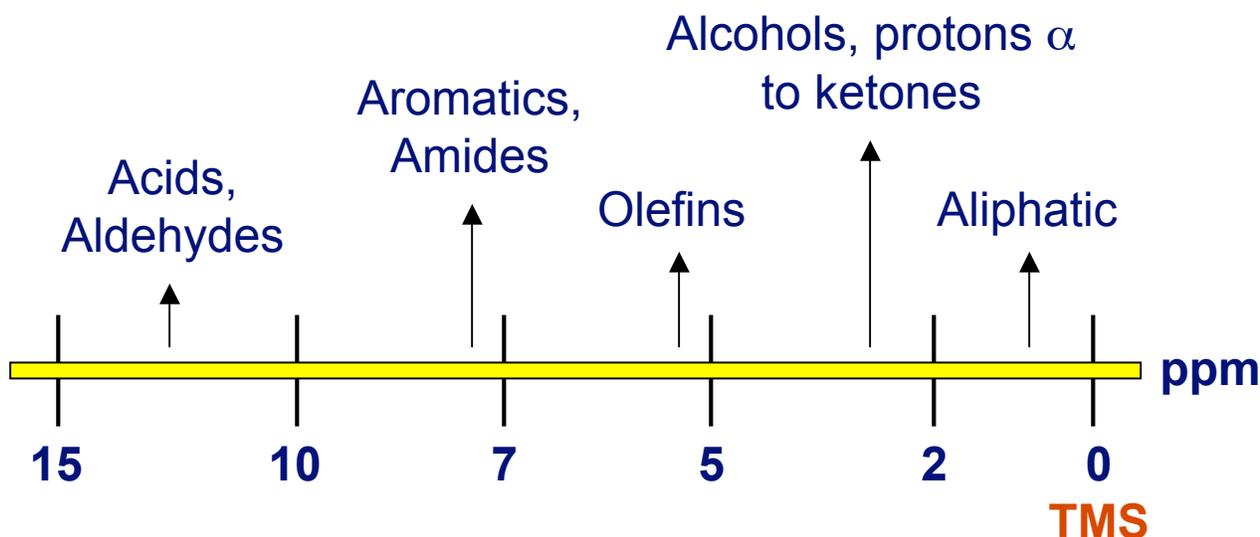


Interpretation of ^1H spectra

- So far we have talked about different NMR techniques and pulse sequences, but we haven't focused seriously on how to analyze the data that we obtain from these experiments.
- Now we will do this, starting from the very bottom. The first thing that we will discuss are ^1H spectra. As we saw before, the chemical shift range for ^1H is pretty small, from 15 to 0 ppm in most cases, although we can get peaks above 20 and below -5 ppm in some cases:



- As we said before, the chemical shifts of different nuclei in a molecule arise due to differences in the local magnetic field or **shielding** (σ) felt by the nuclei in different spots of the molecule:

$$B_{\text{eff}} = B_o - B_{\text{loc}} \quad \text{---} \quad B_{\text{eff}} = B_o(1 - \sigma)$$

Origins of σ (B_{loc})

- The shielding of different nuclei depends on the electron density in its surroundings. We can dissect the contributions to the total shielding:

$$\sigma = \sigma^{dia} + \sigma^{para} + \sigma^{loc}$$

- The term σ^{dia} is the diamagnetic contribution, which arises from the magnetic field opposing B_o from the electrons immediately surrounding the nucleus (**s** orbitals).
- σ^{para} is the paramagnetic term, and is generated by electrons in **p** orbitals (as well as bonds...). It is in favor of B_o .
- The third term, σ^{loc} , is due to neighboring groups, and it can add or subtract from B_o , depending on the nature of the group and its spatial orientation. σ^{loc} is the term that actually makes nuclei with similar characteristics in a molecule have different shieldings (and therefore chemical shifts).
- If we now consider our main players, 1H and ^{13}C , we can see that since 1H have only a **1s** orbital, σ^{dia} will dominate, while for ^{13}C (and other heavier atoms) σ^{para} will dominate because we have more **p** electron shells that can become occupied (lower energy than **p** orbitals in 1H ...)

Origins of σ (continued)

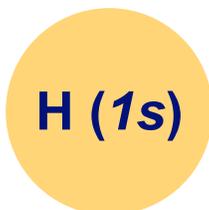
- As we said, what determines the shielding is the electron density, which for an isolated ^1H (which is perfectly spherical), is calculated with the **Lamb formula**:

$$\sigma = \frac{\mu_0 e^2}{3 m_e} \int_0^\infty r \rho(r) dr$$

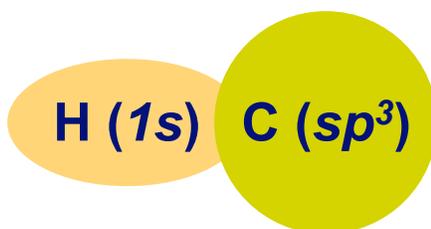
- We could use the same formula to calculate any chemical shift and forget about the dissection into different terms, but the problem is that in a molecule the equation for $\rho(r)$ is very complicated: We have to consider **s**, **p**, **d**, hybrid orbitals (i.e., **spⁿ**), and we also have to consider molecular orbitals.
- This is the realm of quantum mechanical chemical shift calculations, far more than what we want to know.
- However, most of the effects can be qualitatively described by using σ^{dia} and σ^{loc} for protons (remember that σ^{para} has little contributions in ^1H).
- We will start with effects (or contributions) to σ^{dia} . These are known as **inductive and mesomeric effects**, and as we will see, their origin lies in the how the electron density around the ^1H is affected by different species attached to it.

Inductive contributions to σ^{dia}

- As we said, an isolated ^1H atom has a perfectly symmetrical distribution of its **1s** electrons around it. If we use the Lamb formula, we get a value of 17.8 ppm for σ^{dia} :



- Now, when we add, say, a $-\text{CH}_3$ to it (and get methane), the electron cloud on the ^1H (on any of the 4) will become deformed, because the **electronegativity** (**E**) of the carbon will pull the **1s** electron of the ^1H towards it:



- Since we lower the electron density around the nucleus, it will become **deshielded**, and therefore it will move towards lower fields (higher chemical shift).
- For example, if we consider hydrogen halides, we'll see that the more electronegative the halide is, the drop in shielding constants is inversely proportional to the **E** of the halide:



Inductive effects (continued)

- The inductive effect on the shielding of the ^1H is not limited to groups bonded directly to it. We have to remember that the electron density around the ^1H depends on the molecular orbitals of the whole molecule (i.e., the bonds).
- The effects of electronegativity are 'transmitted' through molecular orbitals (bonds): If we have a very electronegative atom bound to a carbon, protons bonded to that carbon will have their $1s$ electrons pulled away more than if we did not have the electronegative group. So, for the methane series we have:

	H-CH₃	H-CH₂I	H-CH₂Br	H-CH₂Cl	H-CH₂F
<i>E</i>	2.1	2.5	2.8	3.0	4.0
δ	0.23	1.98	2.45	2.84	4.13

- A similar correlation to the one we did with electronegativity can be done in the methane series with the polarity (or polarization) of the C-X bond.
- The group creating the inductive effect does not need to be exclusively an halogen (or a single atom). We can consider the effects of chemical groups as a whole, such as **-NO₂**, **-OH**, **-SH**, **-NH₂**, etc.

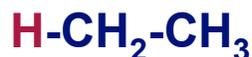
Inductive effects (...)

- Furthermore, we don't need a particularly electronegative atom. If we lengthen the carbon chain, the shielding will also increase.
- To demonstrate this, let's look at the chemical shift of different protons in saturated linear hydrocarbons:

0.23



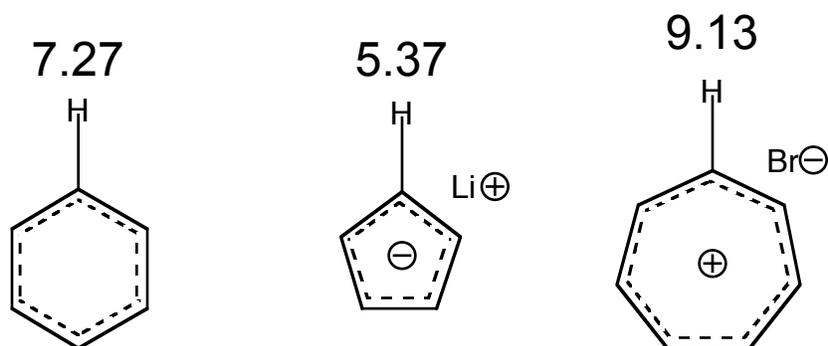
0.80



0.91



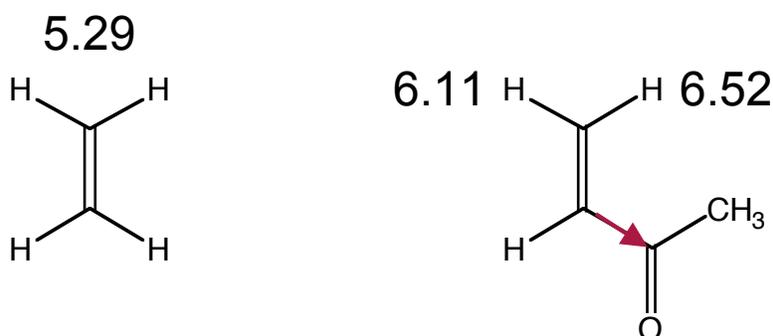
- Another factor affecting the electron density around the proton and therefore its shielding are partial charges on the carbon atom. This is clearly seen if we compare certain aromatic ions to benzene:



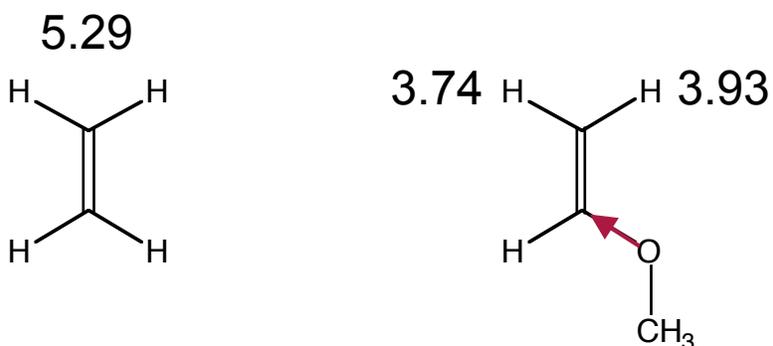
- Note that we have the same number of π electrons in these systems (the $4n + 2$ rule is satisfied...). The charge on the carbon of tropylium ion is positive, so it 'sucks' more the ^1H 's 1s electrons, and gives us less shielding. The reverse happens for the cyclopentadienyl ion...

Mesomeric effects - EWGs and EDGs

- Now let's look at what happens when we have an olefinic or aromatic proton and we have a substituent that can have different **mesomeric effects** (+M or -M).
- For example, let's consider ethene and **EWGs** or **EDGs** as substituents. If we consider methylvinylketone, the chemical shifts of the olefinic protons will move downfield considerably, because since the ketone (an **EWG**) is taking electrons away from the double bond, the electron density around the ^1H will diminish:

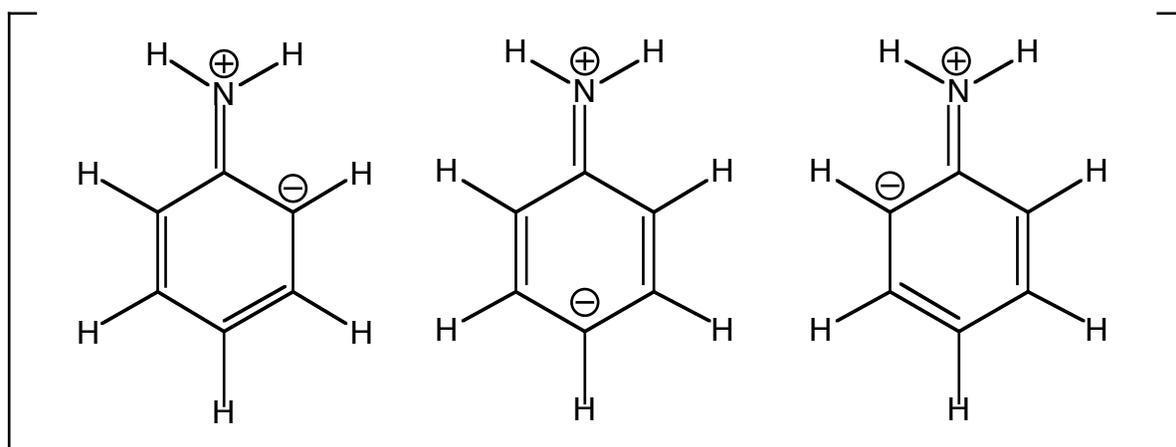
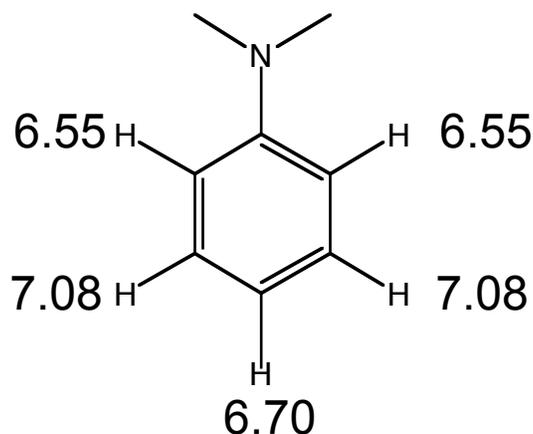


- If on the other hand we consider methylvinylether, the situation is reversed: The methoxy groups (an **EDG**), will donate electrons to the double bond, which will increase the electron density around the ^1H and therefore increase the shielding:



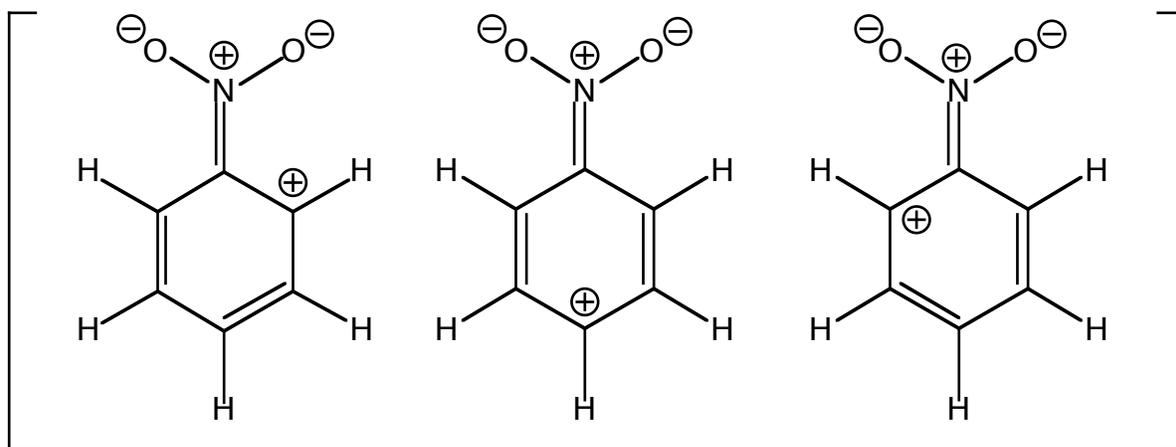
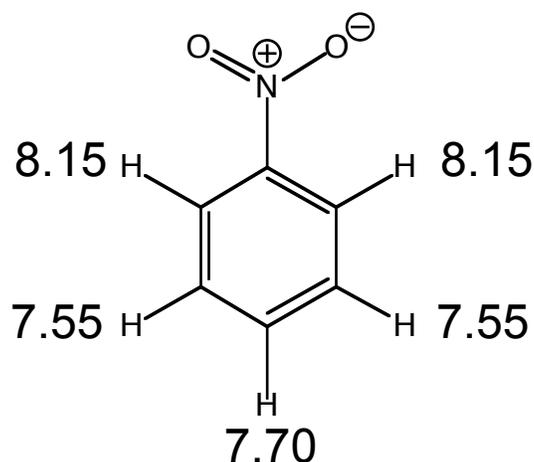
Mesomeric effects (continued)

- A similar reasoning can be used when we analyze the chemical shifts of ^1H s on substituted aromatic systems.
- For example, in aniline we have an **EDG**, which has a **+M** effect. Since we'll have more electron density in the ring, all protons will be more shielded than the respective protons in benzene (7.24 ppm).
- Furthermore, if we draw resonant structures we can see that the **ortho** and **para** positions will have a larger electron density. Therefore, protons attached to the **ortho** or **para** carbons will be more shielded (lower chemical shift):



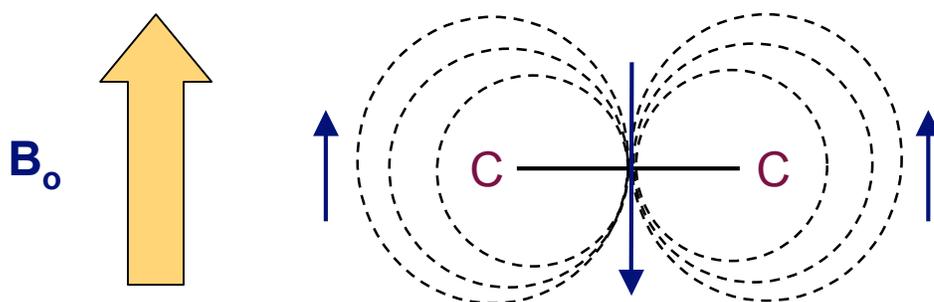
Mesomeric effects (...)

- On the other hand, nitrobenzene, which has an **EWG**, has a **-M** effect. All centers will have a lower electron density, but the ortho and para positions will have a particularly lowered electron density.
- All protons in nitrobenzene will be more deshielded than benzene. In particular, the effect at the *ortho* and *para* positions will be the largest.



Factors affecting σ^{loc} . Anisotropic effects

- Any chemical bond is inherently anisotropic, i.e., it has a direction in space, and depending from which way we look at it, it will be different.
- When we subject the bonds (electron density) to an external magnetic field (B_0), there will be an induced magnetic moment which will also be anisotropic.
- Therefore, the magnetic environment of ^1H s around these groups will be anisotropic (σ^{loc}). This means, depending where the ^1H s are with respect to the group giving rise to the induced magnetic dipole, the effective magnetic field felt by the proton will vary.
- If we consider a single C-C bond, which has cylindrical symmetry, and think of the induced magnetic dipole to be centered right in the middle of the bond, it will look like this:



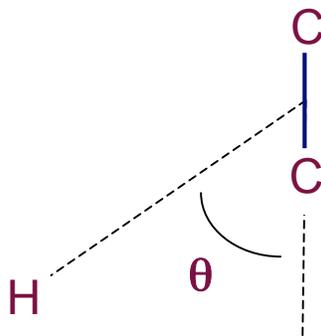
- What we see is that things on the ends of the bond will feel an increased magnetic field, while things sitting above or below will feel a slightly decreased effective field.

Anisotropic effects (continued)

- In order to calculate the magnitude of the induced dipole, we need to know its magnetic susceptibility, χ . We have two of them, one parallel to the bond, χ_{\parallel} , and one perpendicular, χ_{\perp} . The magnitude of the magnetic dipole can then be calculated using the **McConnell** equation:

$$\sigma = \frac{1}{3r^3 4\pi} (\chi_{\parallel} - \chi_{\perp}) \cdot (1 - 3\cos^2\theta)$$

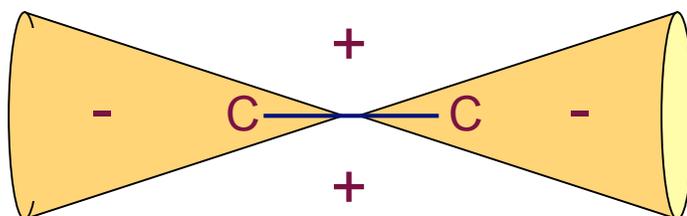
- Here r is the distance from the center of the bond to the ^1H under study, and θ is the angle formed by the vector connecting them and the bond direction:



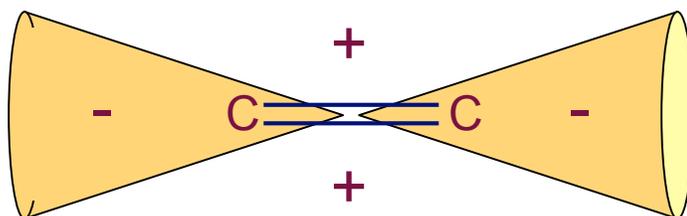
- The formula is an approximation, but it is pretty general, and we can apply it not only to single bonds, but to double and triple bonds, as well as to carbonyl groups, and as a crude approximation, to aromatic systems.

Anisotropic effects (...)

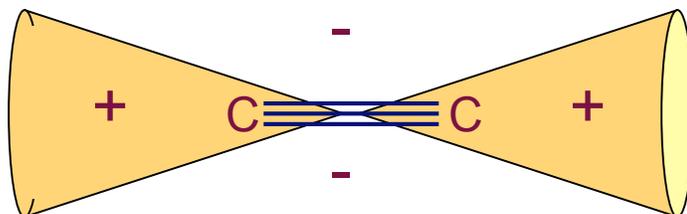
- The most useful thing arising from the equation is that if we plot it, we will get two cones spanning from the center of the bond: Inside the cone, we will be deshielded, on the sides, we'll be shielded. At an angle of 54.7° , the effect is zero:



- For double bonds (C=O, C=C), the situation is similar:

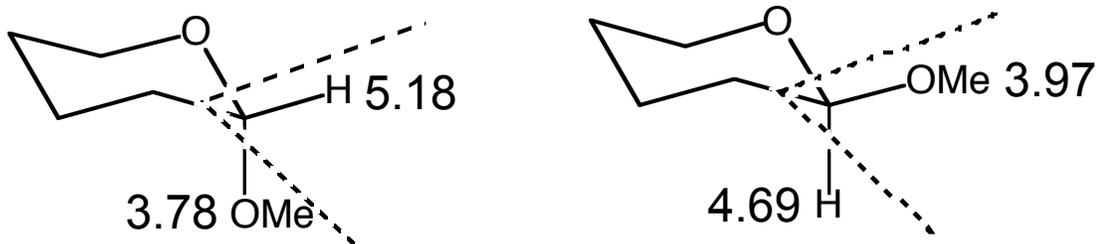


- For triple bonds, the induced magnetic dipole is such that the values of $\chi_{||}$ and χ_{\perp} are reversed:

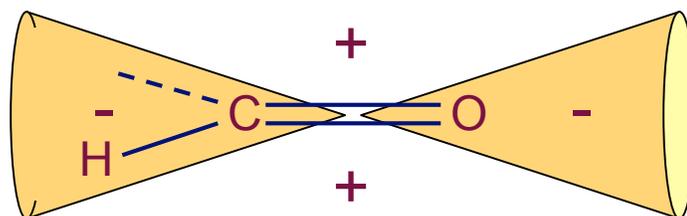


Anisotropic effects (...)

- So, let's look at some examples. In methoxygalactose, we can use this to see which one is α and which one is β .

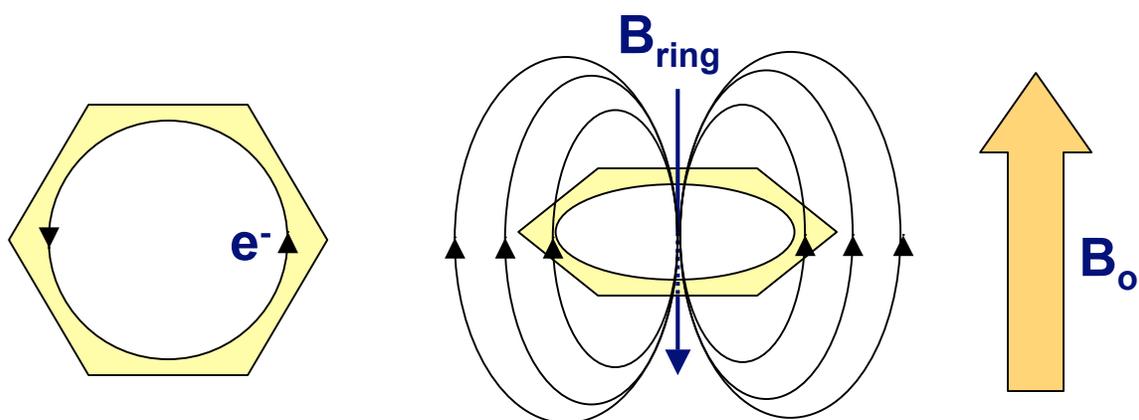


- In the α -isomer, the anomeric ^1H is in the deshielding area of the cone, while in the β -isomer, it sits in the shielding zone.
- Another typical example are aldehydes. The aldehydic proton is very deshielded for two reasons. First, the proton is attached to a carbon with a double bond to an oxygen - It is very electropositive, which therefore draws a lot of the electron density away from the proton, deshielding it.
- Second, the proton is stuck in the deshielding area of the cone of the carbonyl group, which makes it even more deshielded:



Ring current effects

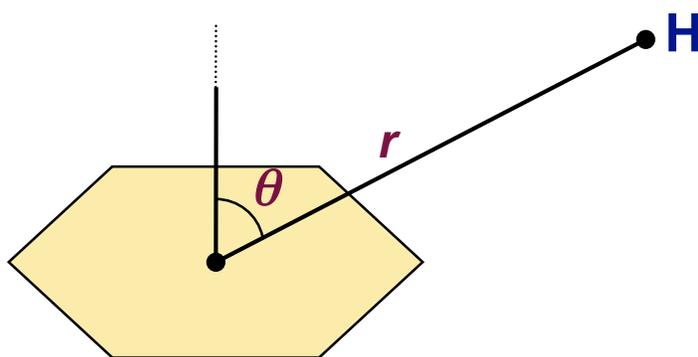
- One of the most pronounced effects arising from induced magnetic moments on ^1H 's are due to aromatic rings.
- The induced magnetic dipole created by an aromatic ring is the easiest to understand. If we consider the ring current of the ring, it will generate a magnetic field perpendicular to the plane of the ring, that will be against the external magnetic field:



- As we see, the field lines through the ring are against of the external magnetic field (the induced magnetic moment will oppose the effect of \mathbf{B}_0), but the 'return' lines, which go on the outside of the ring, are in favor of it.
- Therefore, we can safely assume that protons sitting on the plane of the ring and thereabouts will be deshielded, while those lying on top or below the ring will be shielded (i.e., higher fields and therefore lower chemical shifts).

Ring current effects (continued)

- As we had for simpler systems (single, double, and triple bonds), we can also estimate the degree of shielding as a function of the position of our nuclei around the ring.
- There are several formulas with different degrees of precision, but even the simplest ones give us a pretty decent estimate. The simplest one is the **Popple point-dipole** model:



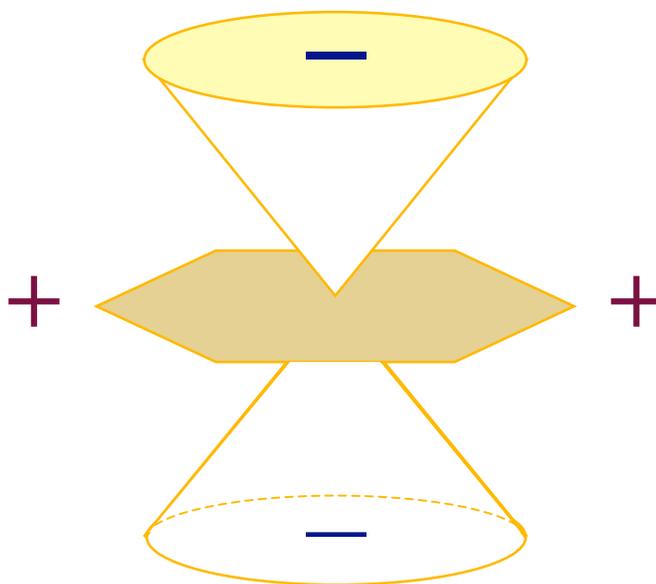
$$\delta_{rc} = C_{popple} * i_{rc} \cdot r^3 \cdot (1 - 3 \cdot \cos^2\theta)$$

- Here C_{popple} is a proportionality constant, which can be determined by calculations or, most commonly, by parametrizing against experimental data. i_{rc} is the intensity factor of the ring current, and depends on the type of aromatic ring. It is **1.00** for benzene.

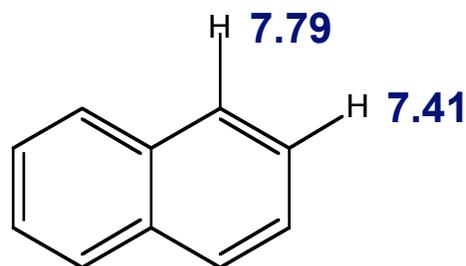
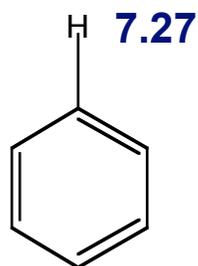
Ring current effects (...)

- As was the case for single, double, and triple bonds, we can plot the shielding as a function of the position in space of the ^1H under study. It will also be cone-shaped, with shielding regions (-, lower chemical shift), and deshielding regions (+, higher chemical shift):

- Protons on the sides of the aromatic ring will feel a higher local field (higher ppm's), while those on top or bottom will feel a lower local field (lower ppm's).



- This is the reason why aromatic protons poking outwards from an aromatic ring have chemical shifts in the 6 to 9 ppm's:



Shoolery chemical shift rules for ^1H

- As we have seen, most of the different effects on ^1H chemical shifts have been tabulated in one way or another.
- Furthermore, we also saw that most of the effects are **additive**, meaning that if we can estimate the different effects on the chemical shift of a certain ^1H from different groups and bonds, we can in principle estimate its chemical shift by adding all the effects together.
- There are several empirical rules, derived mostly by **Shoolery** in the late 50s/early 60s.
- In order to use them, we first have to identify the type of proton we have, such as aliphatic CH_3 , CH_2 , CH , olefinic CH_2 or CH , aromatic, α or β to a ketone or alcohol, belonging to an α,β -unsaturated system, etc. They will have a base value.
- Then we look up the contributions from different groups attached to carbons in the surroundings of our system, and add them up to obtain the estimated chemical shift.

$$\delta H = \delta H_{\text{base}} + \sum \text{contributions}$$

- We'll analyze several cases to see how they work...

Shoolery rules (continued)

- **Aliphatic compounds.** There are two approaches to the calculation of additive effects on the ^1H chemical shifts.
- The first one is very simple. We just use two 'skeletons' with two base values, $\text{R}_1\text{-CH}_2\text{-R}_2$ or $\text{R}_1\text{-CH}(\text{R}_2)\text{-R}_3$, and add the effects from the R_1 , R_2 , or R_3 groups:

$$\frac{\text{R}_1\text{-CH}_2\text{-R}_2}{\delta = 1.25 + \text{R}_1 + \text{R}_2}$$

$$\frac{\text{R}_1\text{-CH}(\text{R}_2)\text{-R}_3}{\delta = 1.50 + \text{R}_1 + \text{R}_2 + \text{R}_3}$$

Substituent	δ
Alkyl	0.0
-C=C-	0.8
-C \equiv C-	0.9
-C ₆ H ₅	1.3
-CO-R	1.3
-OH	1.7
-O-R	1.5
-O-CO-R	2.7
-NH ₂	1.0
-Br	1.9
-Cl	2.0

- So CH_2Br_2 would be $\delta = 1.25 + 1.9 + 1.9 = 5.05$ ppm, which compares pretty well with the experimental value of 4.94 ppm.

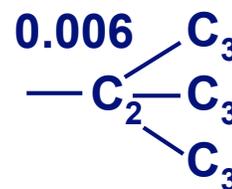
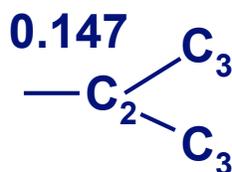
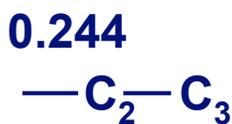
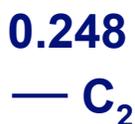
Shoolery rules (...)

- The second method is pretty more general. We start with methane (δ_{base} of 0.23 ppm), and then we add substituent effects directly.

$$\delta = \delta_{\text{base}} + \sum S(\delta)$$

CH₃-	0.47
Cl-	2.53
RO-	2.36
RC(=O)O-	3.13

- Now, if instead of methane we have a longer carbon chain, δ_{base} is 0.933 ppm and we have to consider how many carbons it has, and each carbon will have an increment we will need to add to the base value:



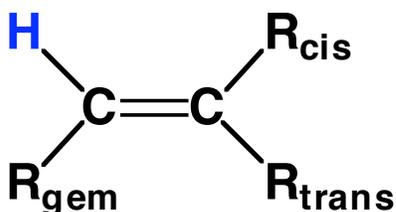
- Furthermore, if the carbons of these chains are substituted, we have to add increments according to their position in the carbon chain.

	C₁	C₂	C₃
HO-	2.47	0.048	0.235
Br-	1.995	0.363	0.023
Cl-	2.170	0.254	0.177
=O	-	1.021	0.004

- It is a lot more more general (and some say more accurate).

Shoolery rules (...)

- **Olefines.** For alkenes we change the tables for the base values, but we also have to consider the stereochemistry of the substituent (*cis*, *trans*, or *gem*):



$$\delta = 5.25 + R_{\text{gem}} + R_{\text{trans}} + R_{\text{cis}}$$

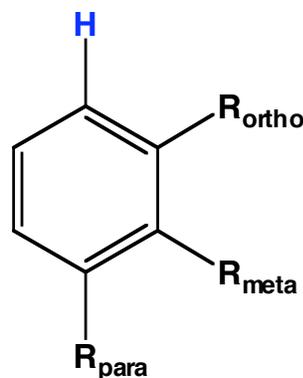
Substituent	δ_{gem}	δ_{cis}	δ_{trans}
H-	0.0	0.0	0.0
Alkyl-	0.45	-0.22	-0.28
-OR	1.21	-0.60	-1.00
-COOH	0.80	0.98	0.32
-Ar	1.38	0.36	-0.07
-C=C-	1.24	0.02	-0.05
-OH	1.22	-1.07	-1.21
-Cl	1.08	-0.40	-1.02

- So for cinnamic acid (*trans* Ph-CH^a=CH^b-COOH), we get that $\delta\text{H}^a = 5.25 + 1.38 + 0 + 0.98 = 7.61$, and $\delta\text{H}^b = 5.25 + 0.80 + 0 + 0.36 = 6.41$, pretty close to the reported values of 7.82 and 6.47 ppm.

Shoolery rules (...)

- **Aromatics.** Finally, the Shoolery rules allow us to calculate the approximate chemical shifts in aromatic compounds. Again, we have a different base value of 7.27 (benzene...).

$$\delta = 7.27 + R_{\text{ortho}} + R_{\text{meta}} + R_{\text{para}}$$



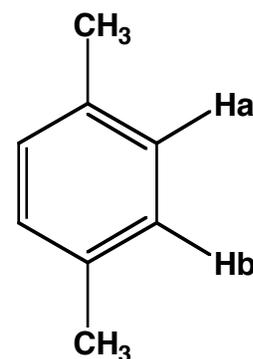
Substituent	δ_{ortho}	δ_{meta}	δ_{para}
-H	0.0	0.0	0.0
-CH ₃	-0.17	-0.09	-0.18
-NO ₂	0.95	0.17	0.33
-COOH	0.80	0.14	0.20
-OCH ₃	-0.43	-0.09	-0.37
-Cl	0.02	-0.06	-0.04
-F	-0.30	-0.02	-0.22
-NH ₂	-0.75	-0.24	-0.63
-C ₆ H ₅	0.18	0.00	0.08
-SCH ₃	-0.03	0.00	0.00

Shoolery rules (...)

- For *p*-Xylene:

$$\delta H_a = 7.27 - 0.17 - 0.09 = 7.00 \text{ (6.97)}$$

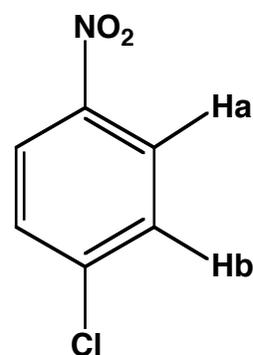
$$\delta H_b = \delta H_a$$



- For 1-Chloro-4-nitrobenzene

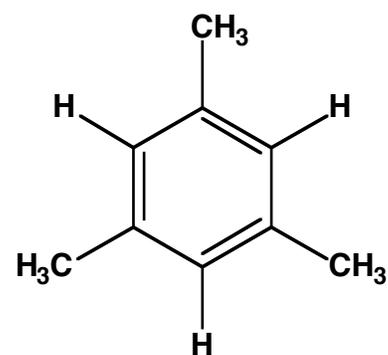
$$\delta H_a = 7.27 + 0.95 - 0.06 = 8.16 \text{ (8.17)}$$

$$\delta H_b = 7.27 + 0.02 + 0.17 = 7.46 \text{ (7.52)}$$



- For mesitylene

$$\delta H = 7.27 - 2 * 0.17 - 0.18 = 6.75 \text{ (6.78)}$$

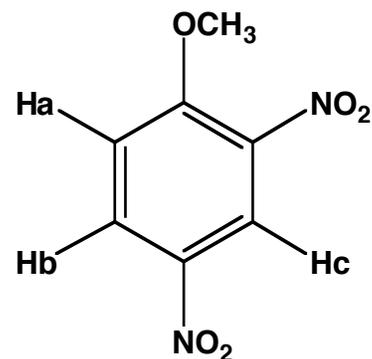


- For 2,4-dinitro-1-methoxybenzene

$$\delta H_a = 7.27 - 0.43 + 2 * 0.17 = 7.18 \text{ (7.28)}$$

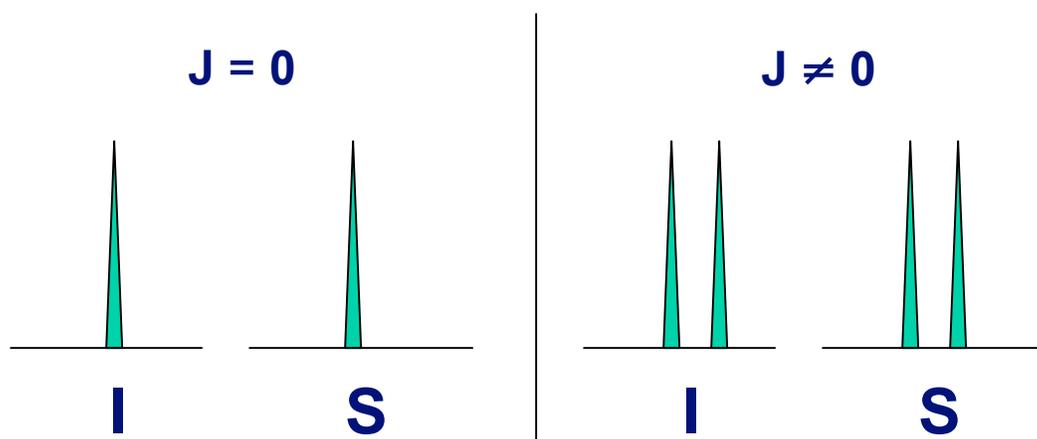
$$\delta H_b = 7.27 + 0.95 + 0.33 - 0.09 = 8.46 \text{ (8.47)}$$

$$\delta H_c = 7.27 + 2 * 0.95 - 0.09 = 9.08 \text{ (8.72)}$$



Spin-spin coupling analysis

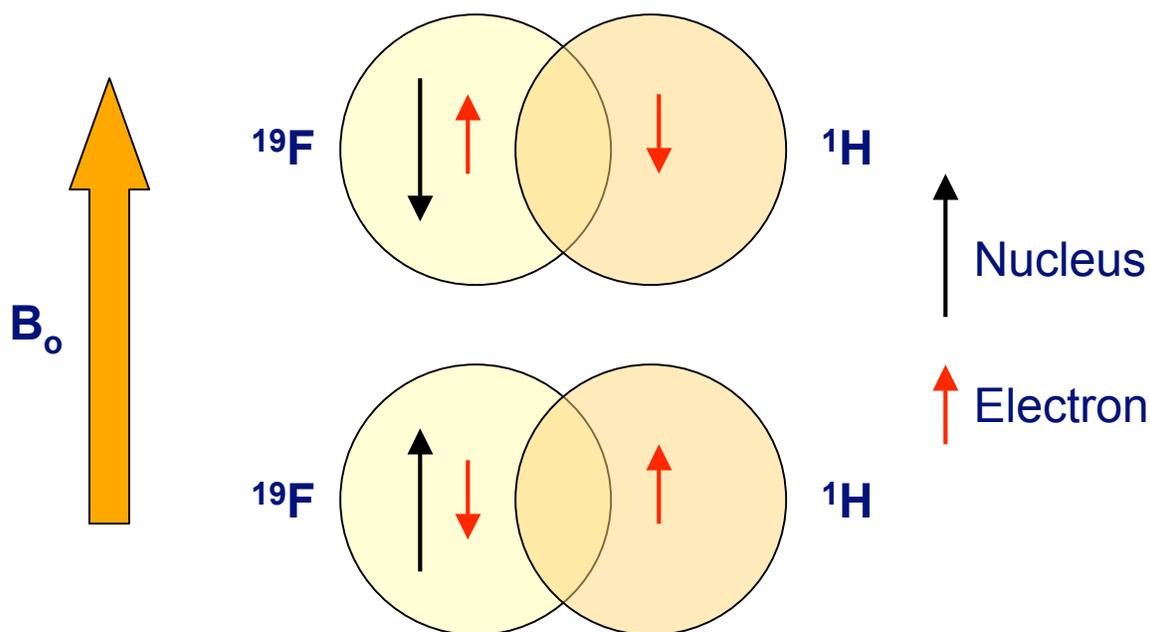
- The last parameter that we will discuss concerning the interpretation of NMR spectra is the ^1H spin-spin coupling. Couplings are perhaps the most important parameter in NMR, as they allow us to elucidate chemical structure.
- Scalar spin-spin coupling shows up as a splitting, or fine structure, in our spectrum. It will occur between two magnetically active nuclei that are connected through chemical bonds. We can see it for two atoms directly bonded, or for atoms that 'see' one another across several bonds.



- A splitting of a signal means that we have more energies involved in the transition of a certain nuclei. So why do we have more energies?
- The reason is the bonding electrons and their magnetic moments. The magnetic moment of the nuclei produces a small **polarization** (orientation...) of the bonding electron, and this is transmitted by overlapping orbitals to the other nuclei.

Spin-spin coupling (continued)

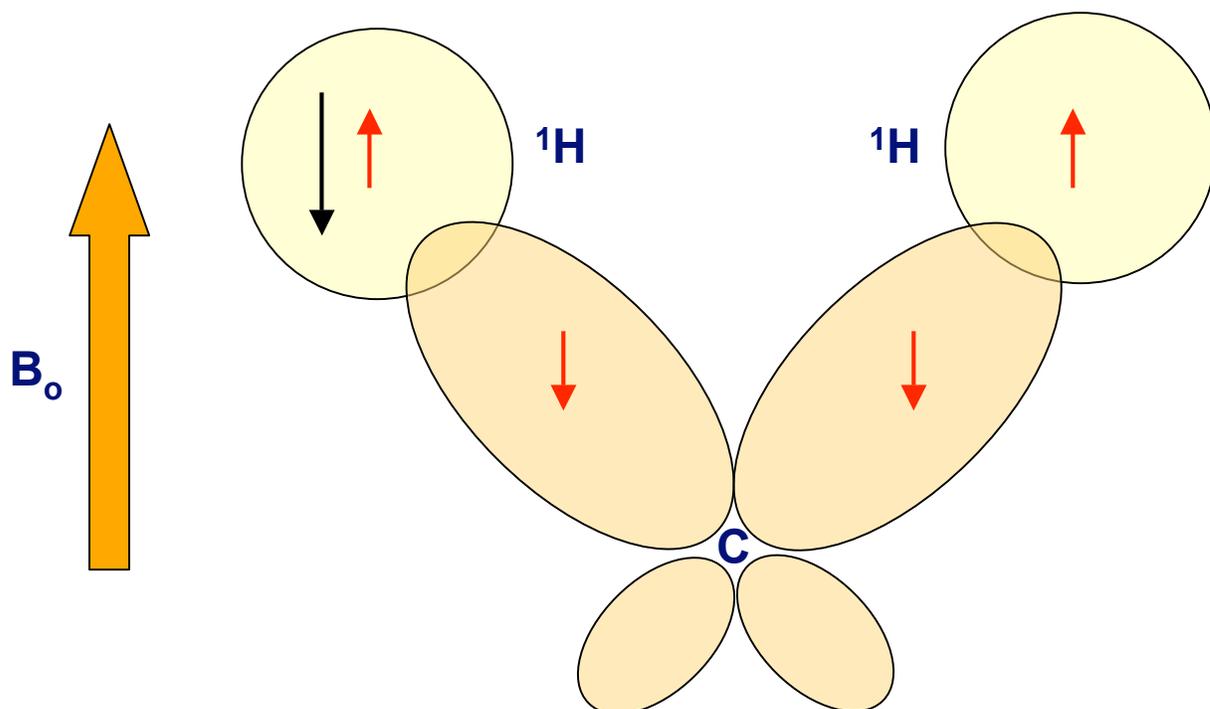
- We can explain this better by looking at HF:



- The nuclear magnetic moment of ^{19}F polarizes the F bonding electron (up), which, since we are following quantum mechanics rules, makes the other electron point down (the electron spins have to be antiparallel).
- Now, since we have different states for the ^1H electrons depending on the state of the ^{19}F nucleus, we will have slightly different energies for the ^1H nuclear magnetic moment (remember that the **1s** electron of the ^1H generates an induced field...).
- This difference in energies for the ^1H results in a splitting of the ^1H resonance line.

Spin-spin coupling (...)

- We can do a similar analysis for a CH₂ group:

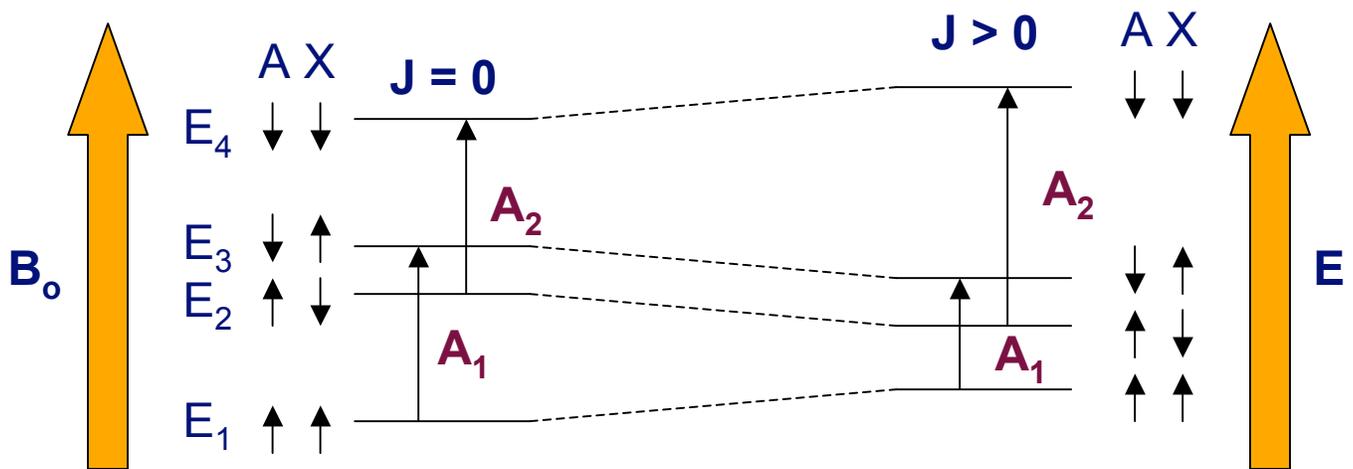


- The only difference here is that the C bonds are hybrid bonds (*sp*³), and therefore the **Pauli principle** and **Hundi's rules** predict that the two electrons will be parallel.
- Irrespective of this, the state of one of the ¹H nuclei is transmitted along the bonds to the other ¹H, and we get a splitting (a doublet in this case...). The energy of the interactions between two spins **A** and **B** can be found by the relationship:

$$E = J_{AB} * I_A * I_B$$

Spin-spin coupling (...)

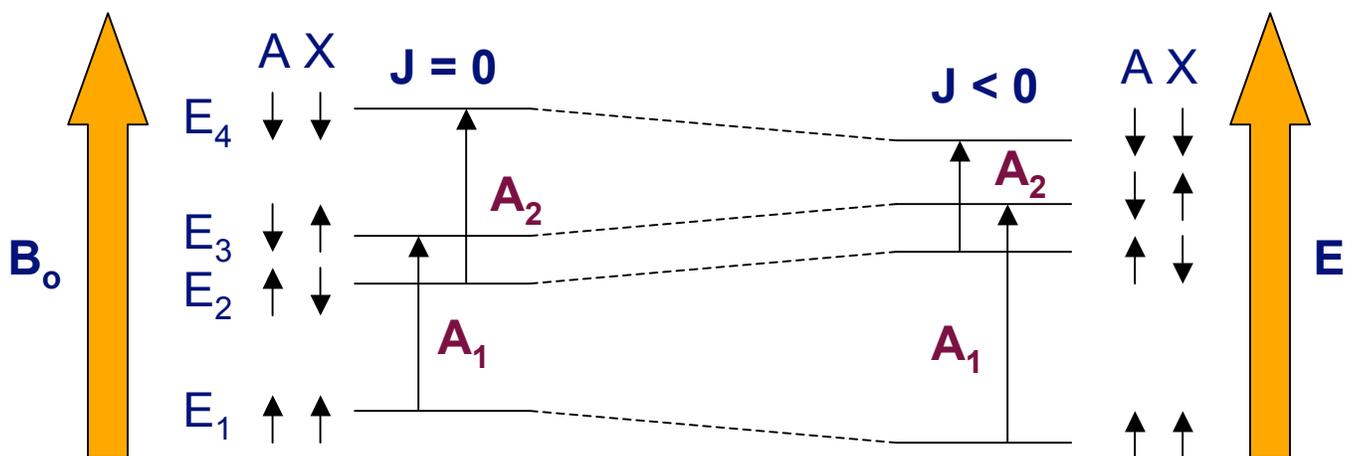
- I_A and I_B are the nuclear spin vectors, and are proportional to μ_A and μ_B , the magnetic moments of the two nuclei. J_{AB} is the **scalar coupling constant**. So we see a very important feature of couplings. It does not matter if we have a 60, a 400, or an 800 MHz magnet, **the coupling constants are always the same!!!**
- Lets do a more detailed analysis in term of the energies. Lets think a two energy level system, and the transitions for nuclei **A**. When we have no coupling ($J = 0$), the energy involved in either transition (A_1 or A_2) is equal (no spin-spin interaction).



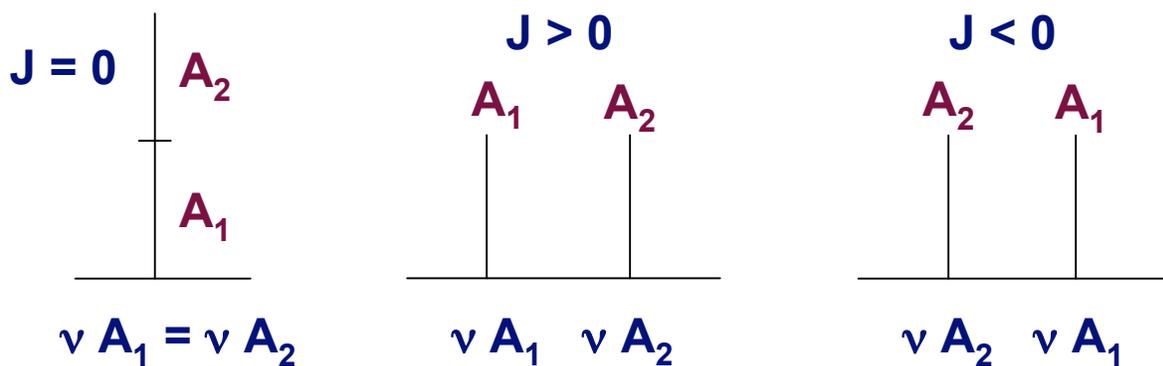
- The relative orientations of the nuclear moments does not matter. We see a single line (two with equal frequency).
- When $J > 0$, the energy levels of the spin system will be either stabilized or destabilized. Depending on the relative orientations of the nuclear moments, the energies for the A_1 and A_2 transition will change giving two different frequencies (two peaks for **A**).

Spin-spin coupling (...)

- We choose $J > 0$ as that related to antiparallel nuclear moments (lower energy). The energy diagram for $J < 0$ would then be:



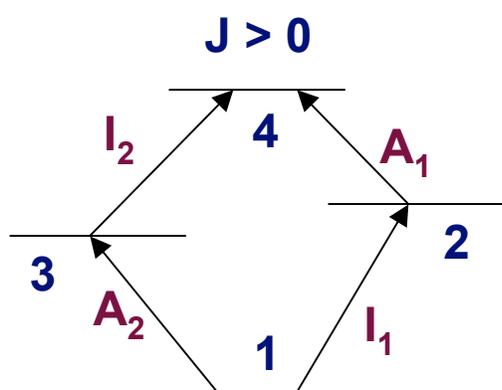
- If we look at it as a stick spectrum for either case we get:



- As mentioned before, the choice of positive or negative J is a definition. However, we see that we won't be able to tell if we have a positive or negative J , because the lines in the spectrum corresponding to the different transitions basically change places. Unless we are interested in studying the energies, this is not important for structure elucidation...

Spin-spin coupling (...)

- We can do a quantitative analysis of the energy values from to gain some more insight on the phenomenon. The base energies of the system are related to the **Larmor** frequencies, and the spin-spin interaction is J_{AX} :



$$E_4 = \frac{1}{2} \nu_A + \frac{1}{2} \nu_B + \frac{1}{4} J_{AX}$$

$$E_3 = \frac{1}{2} \nu_A - \frac{1}{2} \nu_B - \frac{1}{4} J_{AX}$$

$$E_2 = -\frac{1}{2} \nu_A + \frac{1}{2} \nu_B - \frac{1}{4} J_{AX}$$

$$E_1 = -\frac{1}{2} \nu_A - \frac{1}{2} \nu_B + \frac{1}{4} J_{AX}$$

- So if we now consider the transitions that we see in the spectrum, we get:

$$A_1 = E_4 - E_2 = \nu_A - \frac{1}{2} J_{AX}$$

$$A_2 = E_3 - E_1 = \nu_A + \frac{1}{2} J_{AX}$$

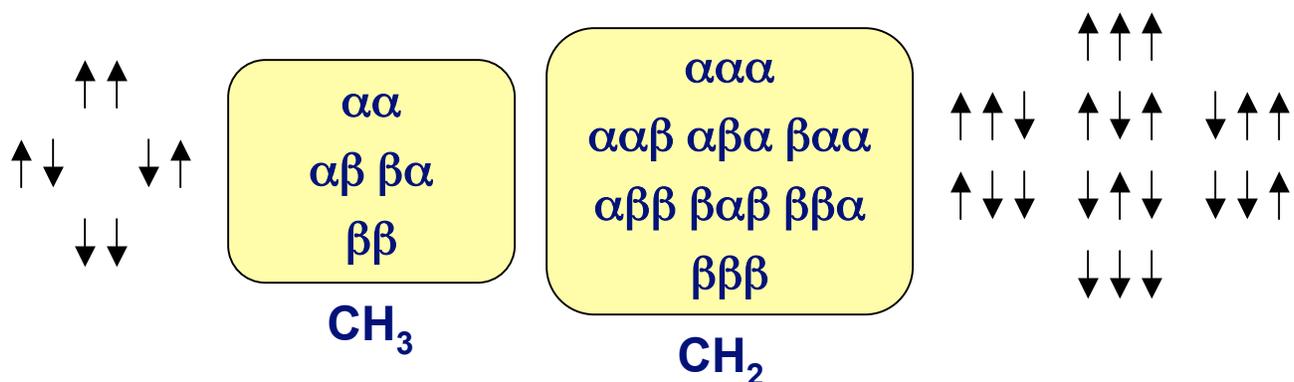
$$I_1 = E_2 - E_1 = \nu_B - \frac{1}{2} J_{AX}$$

$$I_2 = E_4 - E_3 = \nu_B + \frac{1}{2} J_{AX}$$

- This explains the lines in our spectrum quantitatively...

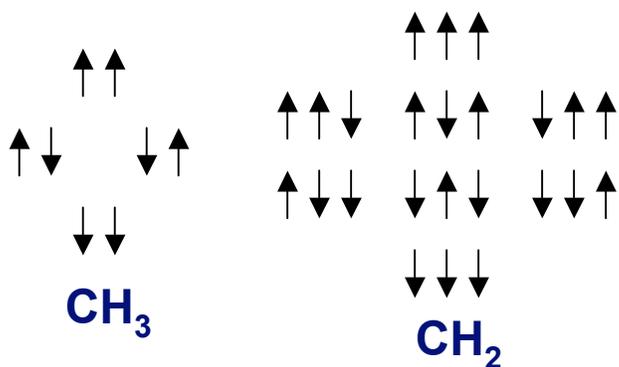
Analysis of 1st order systems

- Now we will focus on the simplest type of coupling we can have, which is one of the limits of a more complex quantum mechanical description.
- Lets say that we have ethylacetate. In this molecule, the resonance of the CH₃ from the ethyl will be ~ 1.5, while that for the CH₂ will be ~ 4.5 ppm. In most spectrometers this means that the difference in chemicals shifts, $\Delta\nu$, will be a lot bigger than the coupling constant **J**, which for this system is ~ 7 Hz. In this case, we say that we have a **first order spin system**.
- If we analyze the system in the same way we did the simple AX system, we will see that each ¹H on the CH₂ will see 4 possible states of the CH₃ ¹Hs, while each ¹H on the CH₃ will see 3 possible states of the CH₂ protons. We have to keep in mind that the two ¹Hs of the CH₂ and the three ¹Hs of the CH₃ are equivalent.
- In order to see this better, we can build a diagram that has the possible states of each ¹H type in EtOAC:

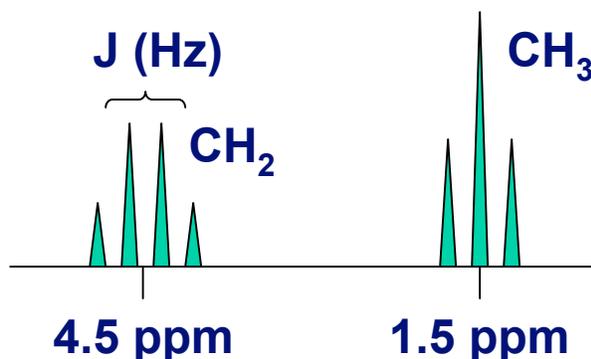


1st order systems (continued)

- If we generalize, we see that if a certain nuclei **A** is coupled to n identical nuclei **X** (of spin $1/2$), **A** will show up as $n + 1$ lines in the spectrum. Therefore, the CH₂ in EtOAc will show up as four lines, or a **quartet**. Analogously, the CH₃ in EtOAc will show up as three lines, or a **triplet**.
- The separation of the lines will be equal to the coupling constant between the two types of nuclei (CH₂'s and CH₃'s in EtOAc, approximately 7 Hz).
- If we consider the diagram of the possible states of each nuclei, we can also see what will be the intensities of the lines:

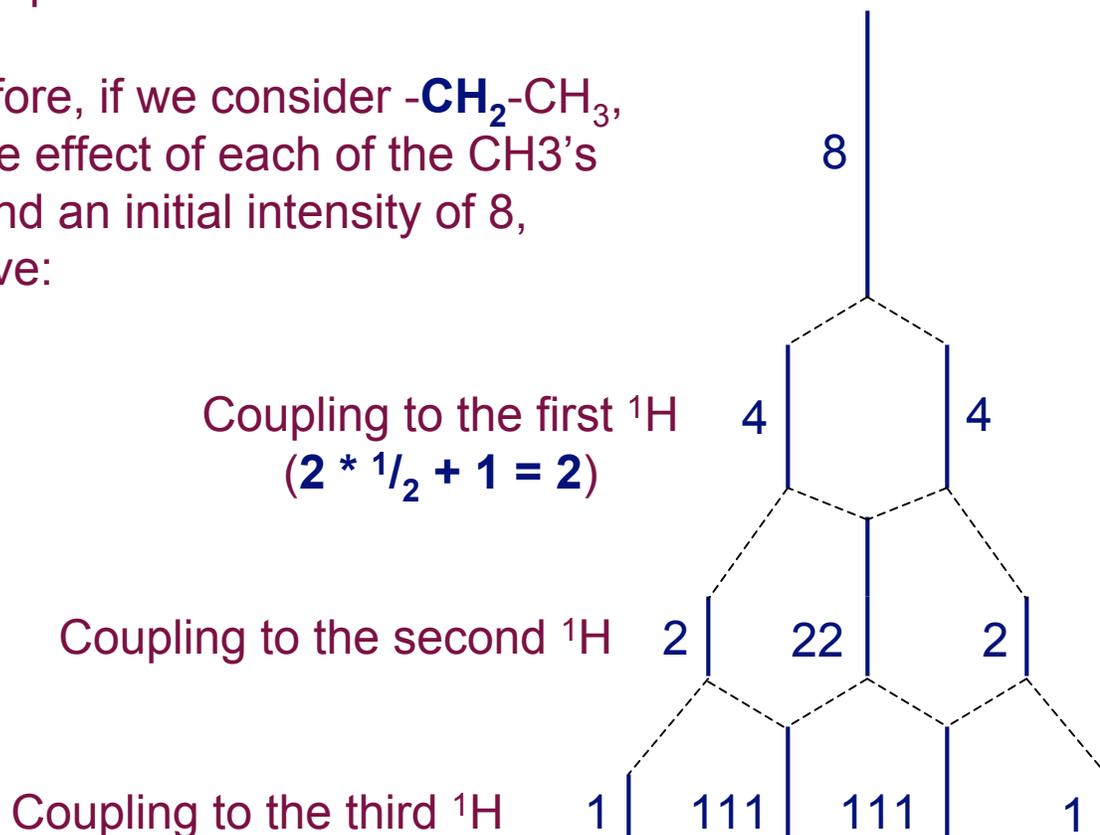


- Since we have the same probability of finding the system in any of the states, and states in the same rows have equal energy, the intensity will have a ratio **1:2:1** for the CH₃, and a ratio of **1:3:3:1** for the CH₂:



1st order systems (...)

- These rules are actually a generalization of a more general rule. The splitting of the resonance of a nuclei **A** by a nuclei **X** with spin number **I** will be **2I + 1**.
- Therefore, if we consider **-CH₂-CH₃**, and the effect of each of the CH₃'s ¹Hs, and an initial intensity of 8, we have:

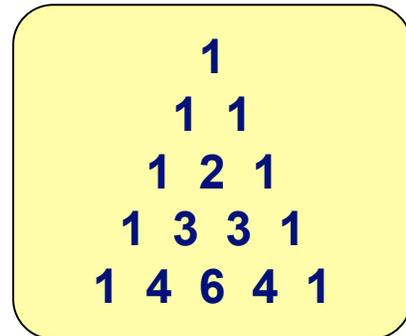


- Since the coupling to each ¹H of the CH₃ is the same, the lines will fall on top of one another.
- In general, the number of lines in these cases will be a binomial expansion, known as the **Pascal Triangle**:

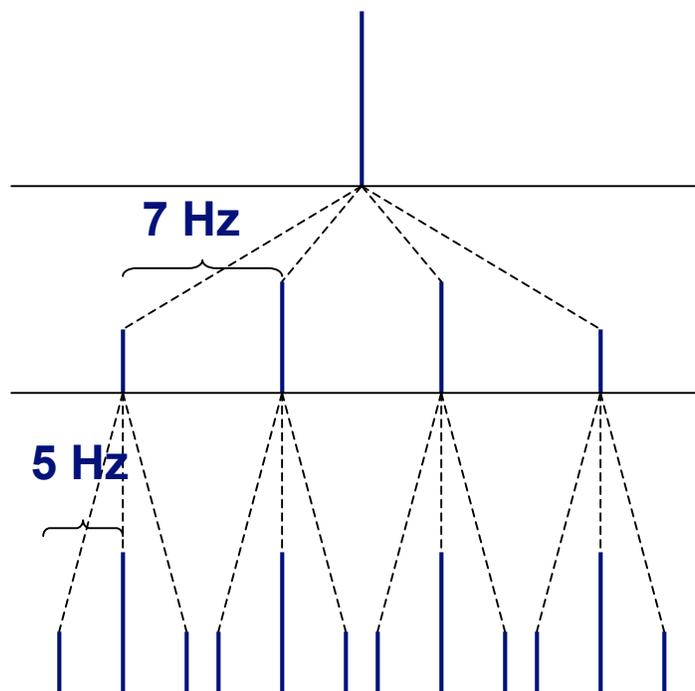
$$1 : n / 1 : n(n - 1) / 2 : n(n - 1)(n - 2) / 6 : \dots$$

1st order systems (...)

- Here **n** is the number of equivalent spins $1/2$ we are coupled to: The results for several **n**'s:



- In a spin system in which we have a certain nuclei coupled to more than one nuclei, all first order, the splitting will be basically an extension of what we saw before.
- Say that we have a CH (**A**) coupled to a CH₃ (**M**) with a J_{AM} of 7 Hz, and to a CH₂ (**X**) with a J_{AX} of 5 Hz. We basically go in steps. First the big coupling, which will give a quartet:



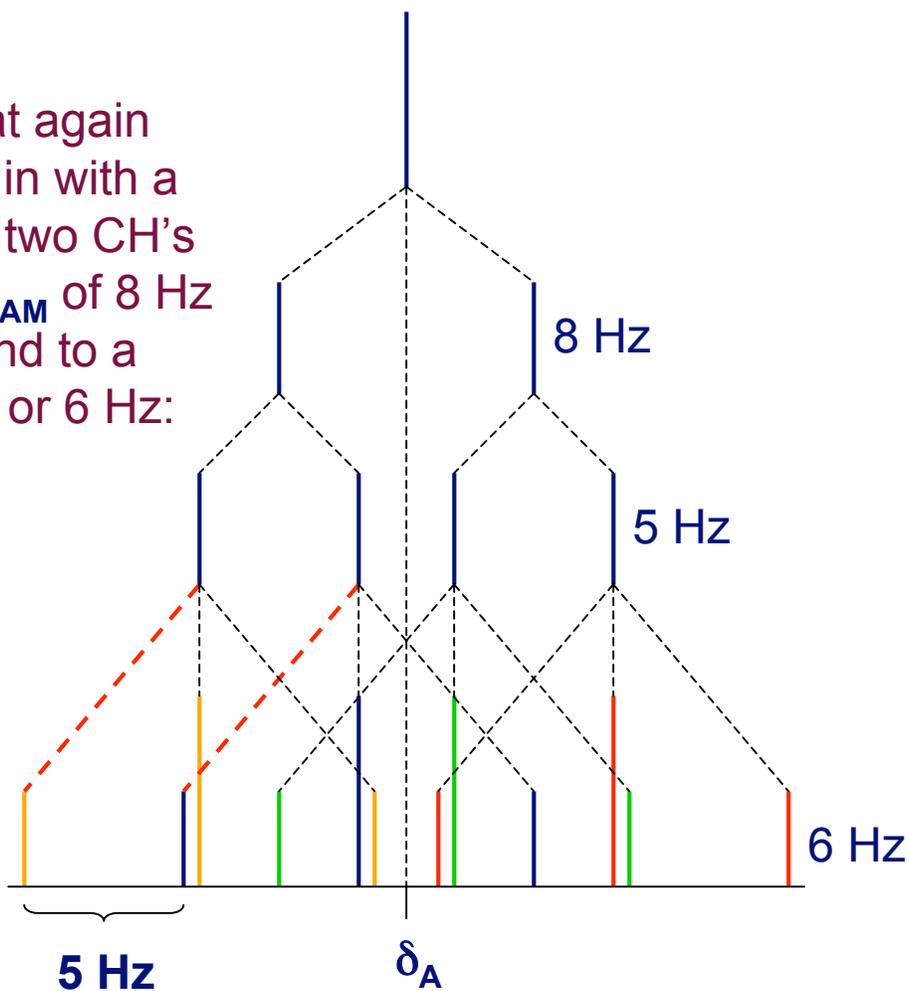
- Then the small coupling, which will split each line in the quartet into a triplet:

- This is called a **triplet of quartets** (big effect is the last...).

1st order systems (...)

- Lets finish our analysis of 1st order system with some pretty simple rules that we can use when we are actually looking at 1D ¹H spectra.

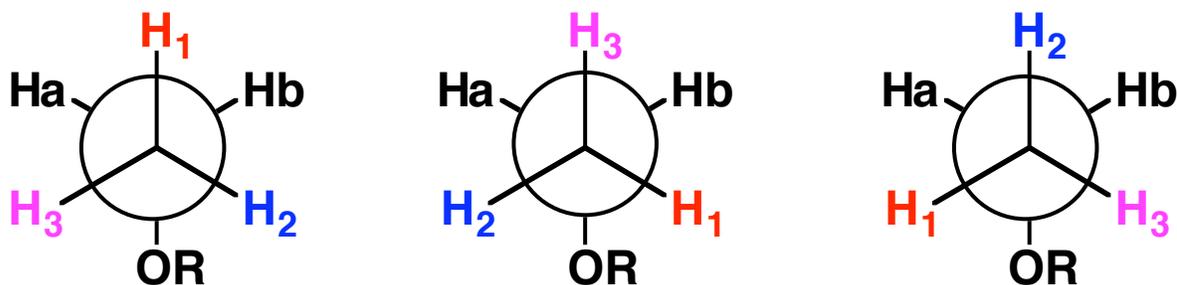
- To do that, say that again we have a system in with a CH (**A**) coupled to two CH's (**M** and **R**) with a J_{AM} of 8 Hz and J_{AR} of 5 Hz, and to a CH₂ (**X**) with a J_{AX} or 6 Hz:



- The first rule is that if we have a clear-cut first order system, the chemical shift of nuclei **A**, δ_A , is always at the center of mass of the multiplet.
- The second one is that no matter how complicated the pattern may end up being, the outermost splitting is always the smallest coupling for nuclei **A**. We can measure it without worrying about picking the wrong peaks from the pattern.

Magnetic and chemical equivalence

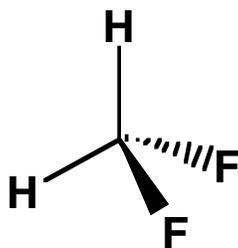
- Before we get deeper into analysis of coupling patterns, let's pay some more attention to naming conventions, as well as to some concepts regarding chemical and magnetic equivalence.
- Our first definition will be that of a **spin system**. We have a spin system when we have a group of n nuclei (with $I = 1/2$) that is characterized by no more than n frequencies (chemical shifts) ν_i and $n(n-1)/2$ couplings J_{ij} . The couplings have to be within nuclei in the spin system.
- We start by defining **magnetic equivalence** by analyzing some examples. Say that we have an ethoxy group (-O-CH₂-CH₃).
- As we saw last time, we can do a very simple first order analysis of this spin system, because we assumed that all CH₂ protons were 'equal,' and all CH₃ protons were 'equal.' Is this true?



- We can easily see that they are chemically equivalent. Additionally, we have free rotation around the bond, which makes their chemical shifts and couplings equal.

Magnetic equivalence (continued)

- Since the ^1H s can change places, they will alternate their chemical shifts (those bonded to the same carbon), and we will see an average.
- The same happens for the **J** couplings. We'll see an average of all the J_{HH} couplings, so in effect, the coupling of any proton in CH_2 to any proton in the CH_3 will be the same.
- If we introduce some notation, and remembering that $\delta(\text{CH}_2)$ is $\gg \delta(\text{CH}_3)$, this would be an **A₂X₃** system: We have 2 magnetically equivalent ^1H s on the CH_2 , and 3 on the CH_3 .
- The $^2J_{\text{HH}}$ coupling (that is, the coupling between two nuclei bound to the same carbon) is zero in this case, because the energies for any of the three (or two) protons is the same.
- Finally, we use **A** to refer to the CH_2 protons, and **X** to refer to the CH_3 protons because they have very different δ s. We usually start with the letter **A** for the most deshielded spin.
- Difluoromethane is another example of an '**AX**' type system:

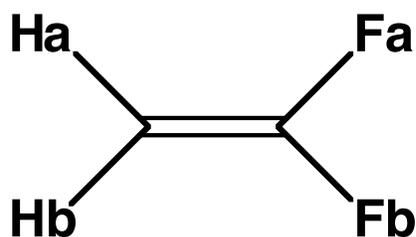


- In this case, ^1H s and ^{19}F s are equal not due to rotation, but to symmetry around the carbon. It's an **A₂X₂** system.

Magnetic equivalence (...)

- For CH_2F_2 , we can also compare the couplings to check that the ^1H s and ^{19}F s are equivalent: $J_{\text{H}_1\text{F}_1} = J_{\text{H}_1\text{F}_2} = J_{\text{H}_2\text{F}_1} = J_{\text{H}_2\text{F}_2}$. All due to their symmetry...

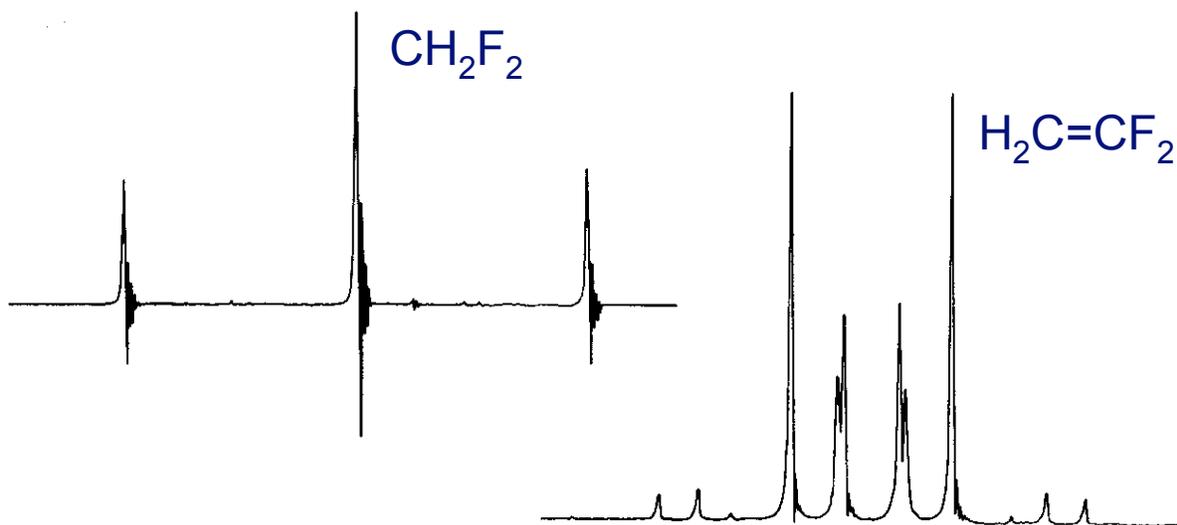
- Now, what about the the ^1H s and ^{19}F s in 1,1-difluoroethene?



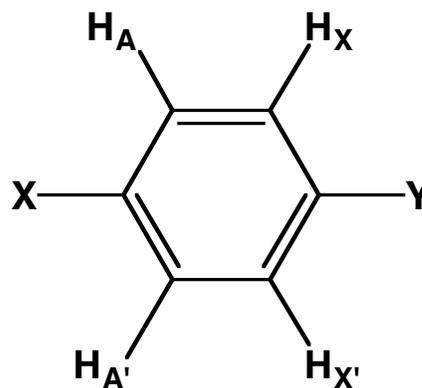
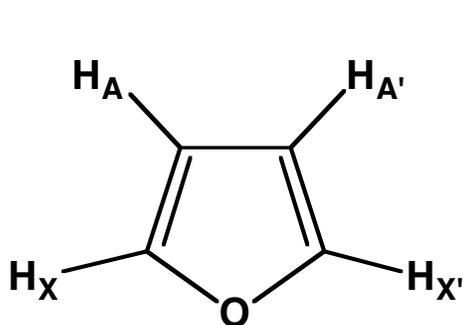
- Here we also have symmetry, but no rotation. The two ^1H s and the two ^{19}F s are chemically equivalent, and we can easily see that $\delta\text{H}_a = \delta\text{H}_b$ and $\delta\text{F}_a = \delta\text{F}_b$.
- However, due to the geometry of this compound, $J_{\text{H}_a\text{F}_a} \neq J_{\text{H}_a\text{F}_b}$. Analogously, $J_{\text{H}_b\text{F}_a} \neq J_{\text{H}_b\text{F}_b}$.
- Furthermore, since the couplings are different, the energy levels for H_a and H_b are different (not degenerate anymore as in CH_3), and we have $J_{\text{H}_a\text{H}_b} \neq 0$.
- If we consider all the possible couplings we have, we have three different couplings for each proton. For H_a , we have $J_{\text{H}_a\text{F}_a}$, $J_{\text{H}_a\text{F}_b}$, and $J_{\text{H}_a\text{H}_b}$. For H_b , we have $J_{\text{H}_b\text{F}_a}$, $J_{\text{H}_b\text{F}_b}$, and $J_{\text{H}_b\text{H}_a}$. This means *more* than the eight possible transitions ($2 \times 2 \times 2$) in the energy diagram, and an equal number of possible lines in the spectrum!

Magnetic equivalence (...)

- These are representative spectra (only the ^1H spectrum is shown) of CH_2F_2 and $\text{F}_2\text{C}=\text{CH}_2$:



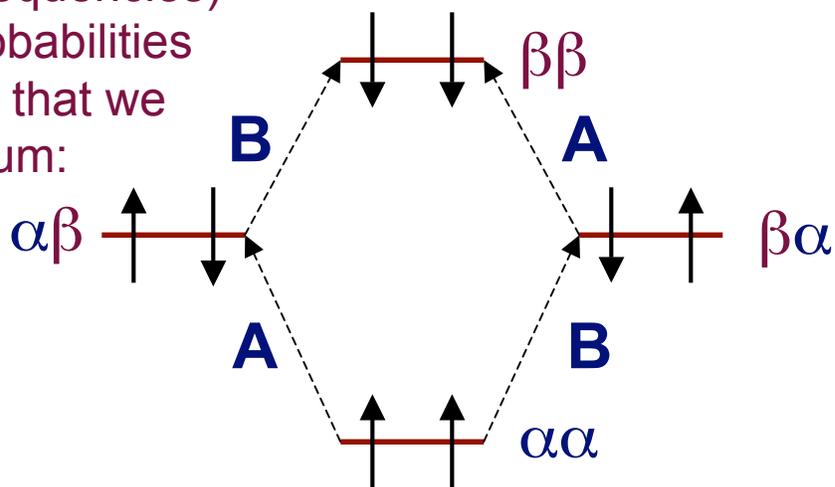
- A system like this is not an A_2X_2 , but an $\text{AA}'\text{XX}'$ system. We have two A nuclei with the same chemical shift but that are not magnetically equivalent. The same goes for the X nuclei.
- The following are other examples of $\text{AA}'\text{XX}'$ systems:



Energy diagrams for 2nd order systems

- From what we've seen, most cases of magnetic non-equivalence give rise to 2nd order systems, because we will have two nuclei with the same chemical environment and the same chemical shift, but with different couplings (**AA'** type...).
- We have analyzed qualitatively how a 2nd order **AB** looks like.

In an **AB** system we have two spins in which $\Delta\delta \sim J_{AB}$. The energy diagram looks a lot like a 1st order **AX** system, but the energies involved (frequencies) and the transition probabilities (intensities) are such that we get a messier spectrum:



- Some examples of AB systems:

