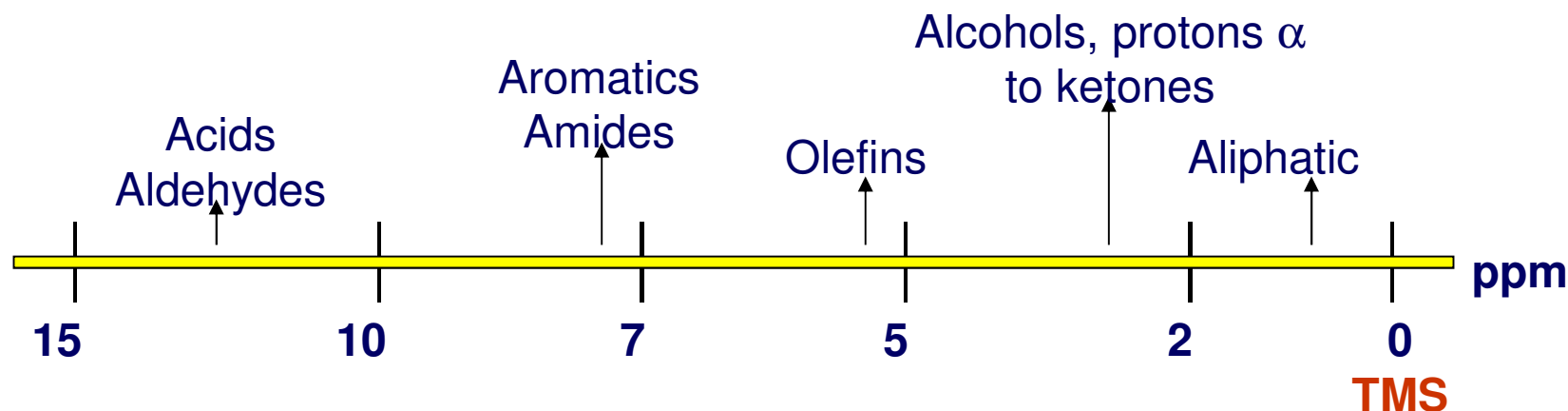## Interpretation of ¹H spectra

• 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:

• 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:

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

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:

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

• 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^{l}, 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^{l} 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, ^{1}H and ^{13}C, we can see that since ^{1}H 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 [1]H…)

Inductive contributions to σ^{dia}

• As we said, an isolated ${}^1H$ atom has a perfectly symmetrical distribution of its **1s** electrons around it.

$$\boxed{H\ (\textit{1s})}$$

• Now, when we add, say, a -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:

$$H\ (\textit{1s})\quad C\ (\textit{sp}^3)$$

• 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:

$$\sigma\ (HF) < \sigma\ (HCl) < \sigma\ (HBr) < \sigma\ (HI)$$

Mesomeric effects - EWGs and EDGs

• Now lets 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, lets 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 ^{1}H will diminish:

5.29

6.11   6.52
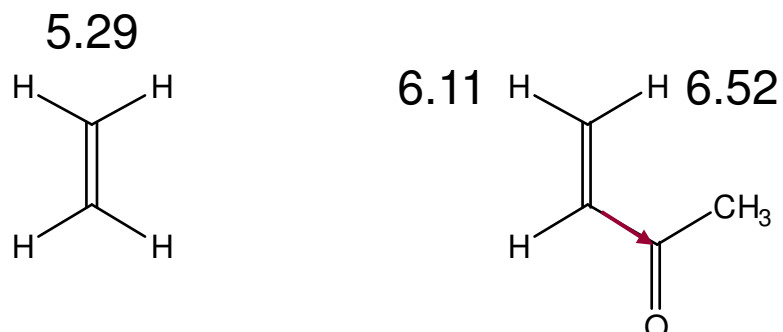
• If on the other hand we consider methylvinylether, the situation is reversed: The methoxy groups (an **EDG**), will donate electrons to the double bond, which will increase the electron density around the ^{1}H and therefore increase the shielding:

5.29

3.74   3.93
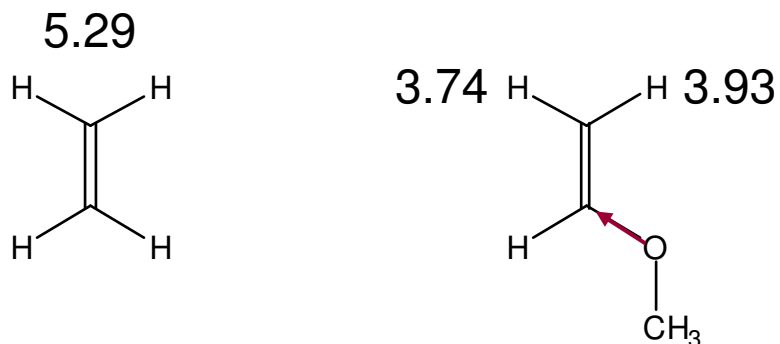
Mesomeric effects (continued)

• A similar reasoning can be used when we analyze the chemical shifts of ^{1}Hs 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 chamical shift):
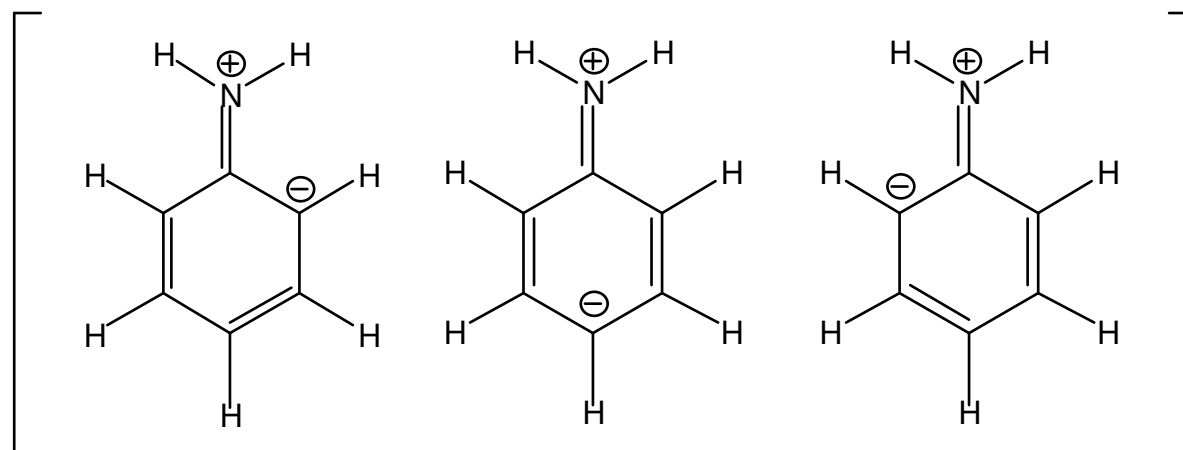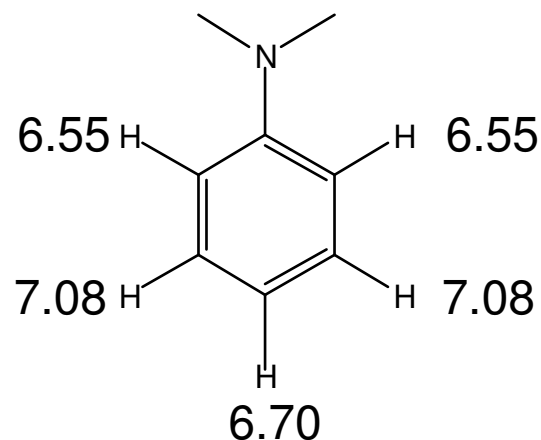
Anisotropic effects

• 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_o), there will be an induced magnetic moment which will also be anisotropic.

• Therefore, the magnetic environment of ^{1}Hs around these groups will be anisotropic. This means, depending were the ^{1}Hs 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:


B_o
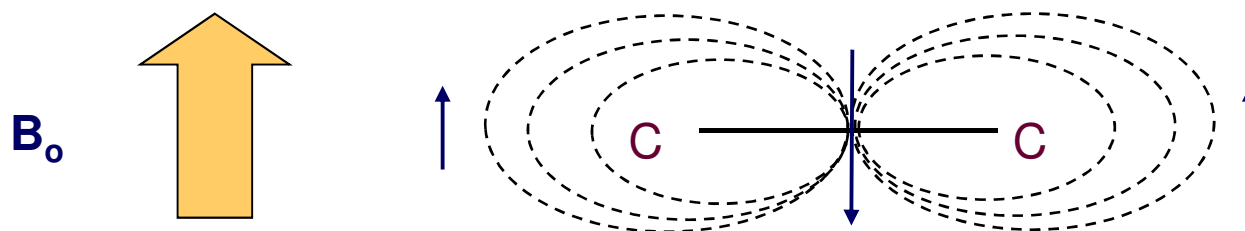
• What we see is that things on the ends of the bond will feel an increased magnetic field, while things sitting above or below will feel a slightly decreased effective field.
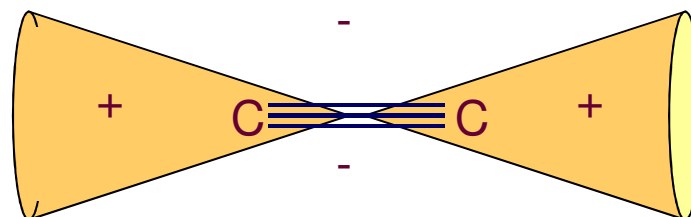
Anisotropic effects (…)

• We 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:
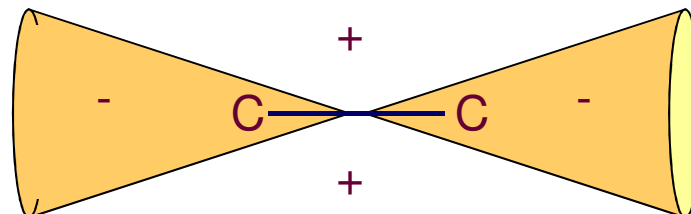

• For double bonds (C=O, C=C), the situation is similar:
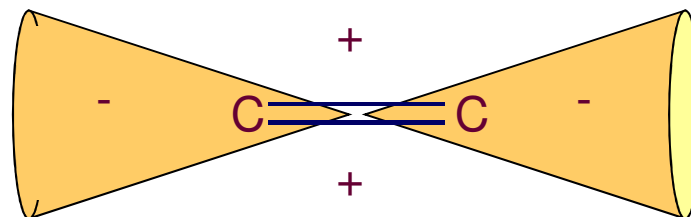
• For triple bonds, the induced magnetic dipole is such that the values of $\chi_{||}$ and $\chi_{\perp}$ are reversed:

Ring current effects

• One of the most pronounced effects arising from induced magnetic moments in a chemical group are due to aromatic rings.

• 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:
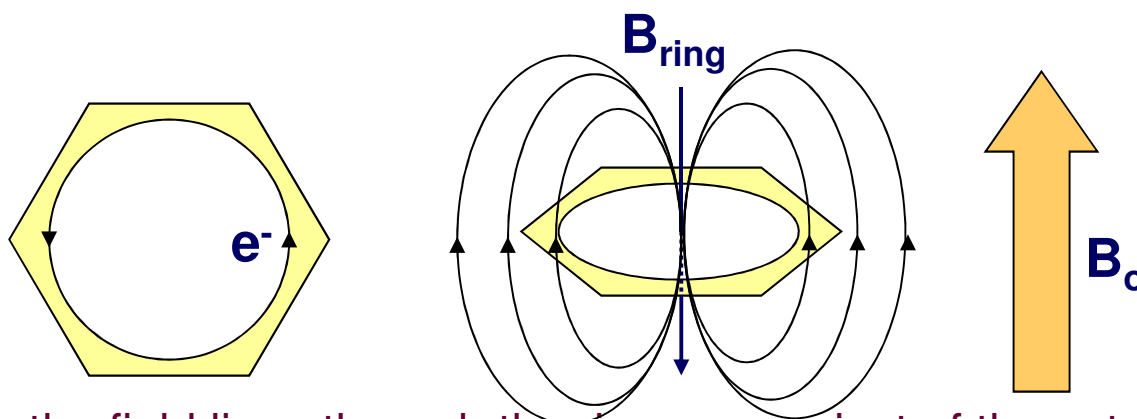

• As we see, the field lines through the ring are against of the external magnetic field (the induced magnetic moment will oppose the effect of B_o), but the 'return' lines, which go on the outside of the ring, are in favor of it.

• 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 (…)

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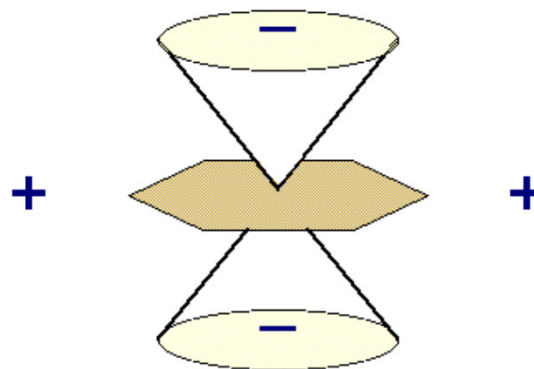

• Protons on the sides of the aromatic ring will feel a higher local magnetic field (higher ppm's), while those on top or bottom will feel a lower local magnetic field (lower ppm's).

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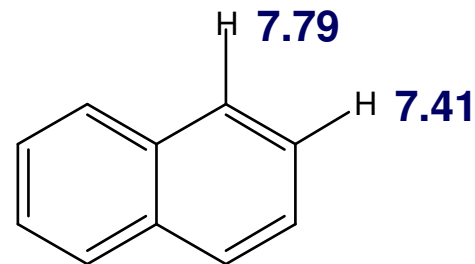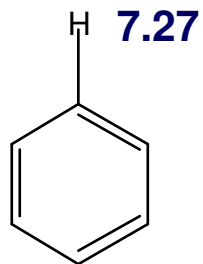
Spin-spin coupling analysis

• The last parameter that we will discuss concerning the interpretation of NMR spectra are ^{1}H spin-spin couplings. 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 connected, or for atoms that 'see' one another across several bonds.

J = 0   **J ≠ 0**

I   S   I   S
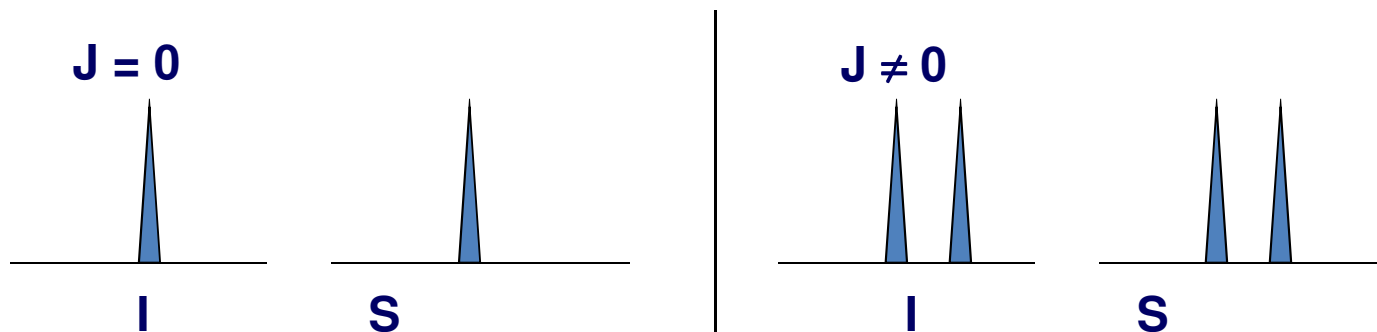
• A splitting of a signal means that we have more energies involved in the transition of a certain nuclei. So why do we have more energies?

• 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:
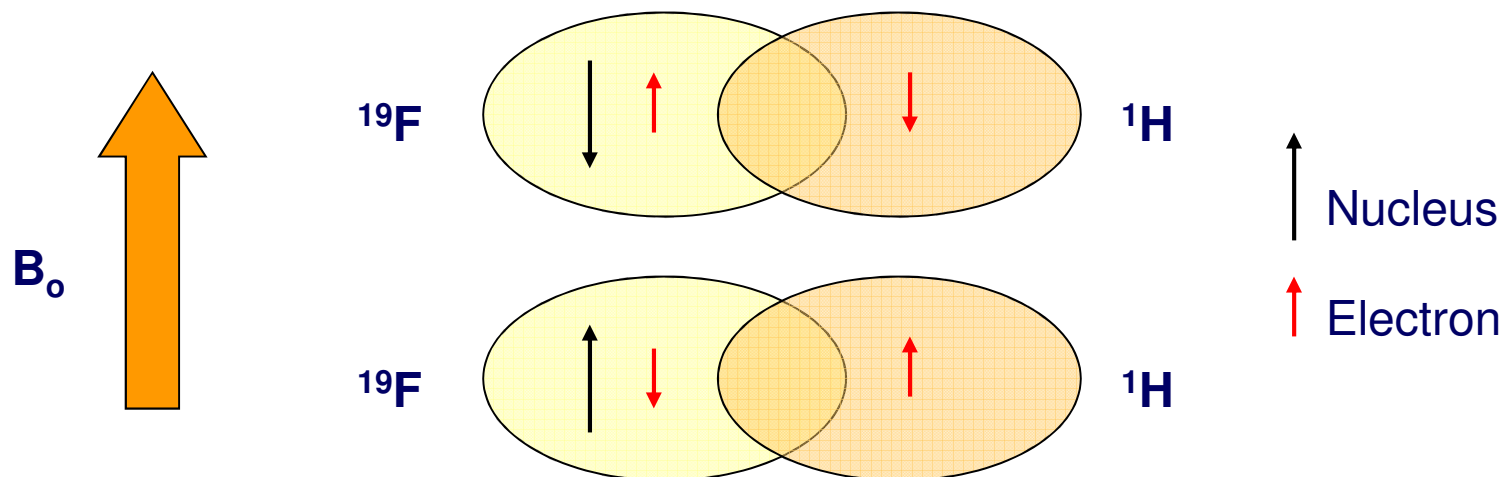
- The nuclear magnetic moment of ^{19}F polarizes the F bonding electron (up), which, since we are following quantum mechanics rules, makes the other electron point down (the electron spins have to be antiparallel).

- Now, the since we have different states for the ^{1}H electrons depending on the state of the ^{19}F nucleus, we will have slightly different energies for the ^{1}H nuclear magnetic moment (remember that the **1s** electron of the ^{1}H generates an induced field…).

- This difference in energies for the ^{1}H result in a splitting of the ^{1}H resonance line.

Spin-spin coupling (continued)

• We can do a similar analysis for a CH_2 group:
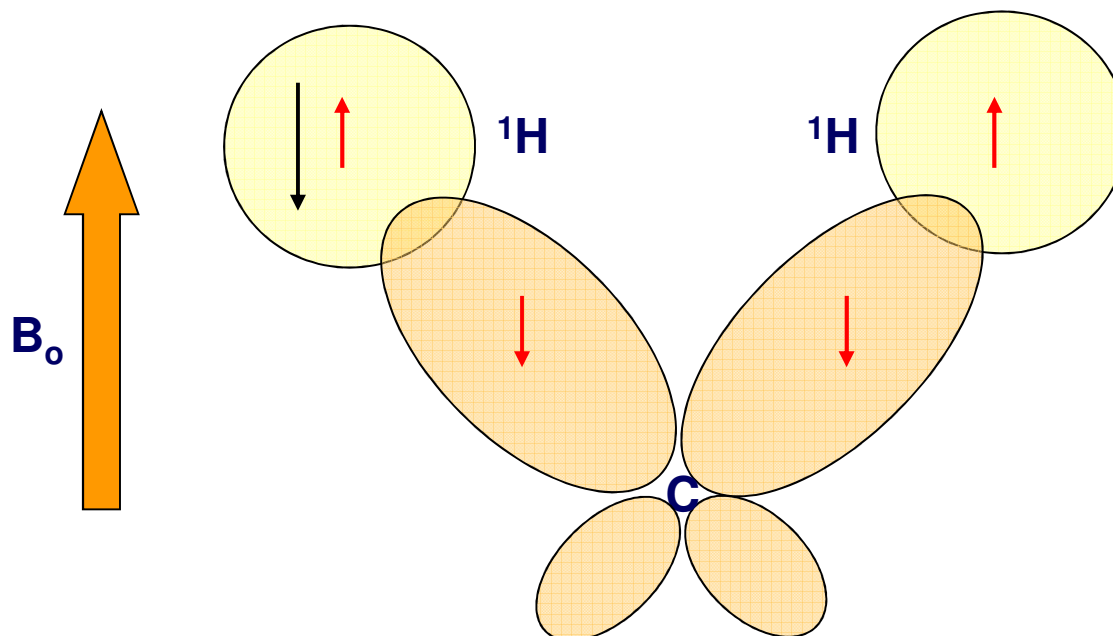
• The only difference here is that the C bonds are hybrid bonds (**sp³**), and therefore the **Pauli principle** and **Hundi's rules** predict that the two electrons will be parallel.

• 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!!!**

• Now 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$_2$**) are the same, because
 we have no spin-spin interaction.
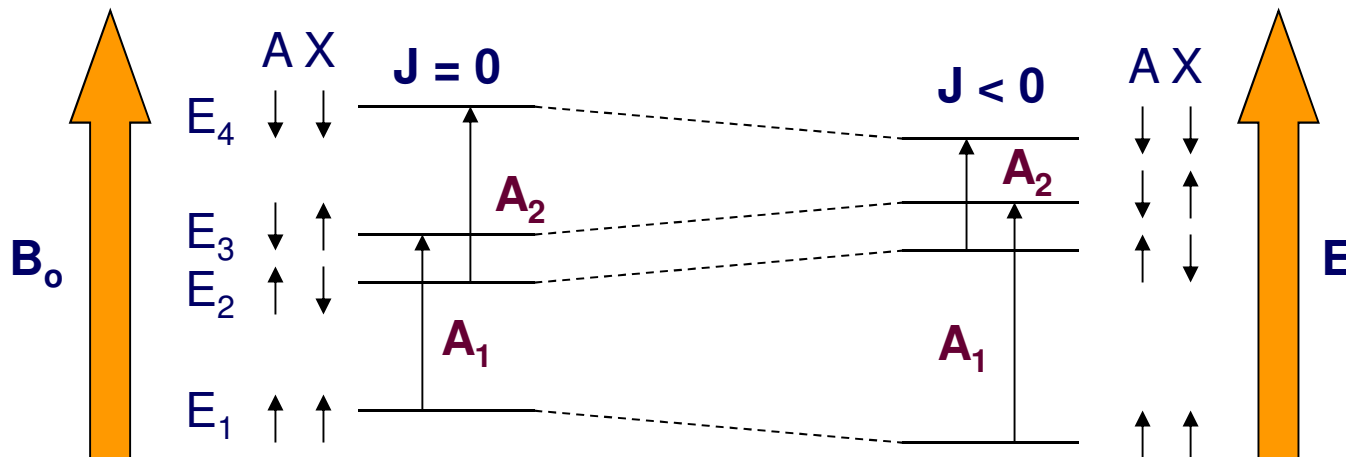
• Therefore, the relative orientations of the nuclear moments does not matter - We see a single line (two with equal frequency). When **J > 0**, the energy levels of the spin system will be either stabilized or destabilized, depending on the
  relative orientations of the nuclear moments, and the energies for the **A$_1$** and **A$_2$** transition change, and we have two different frequencies (two peaks for **A**).

1st order systems

• 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 CH_2 in EtOAc will show up as four lines, or a **quartet**. Analogously, the CH_3 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 (CH_2's and CH_3'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:
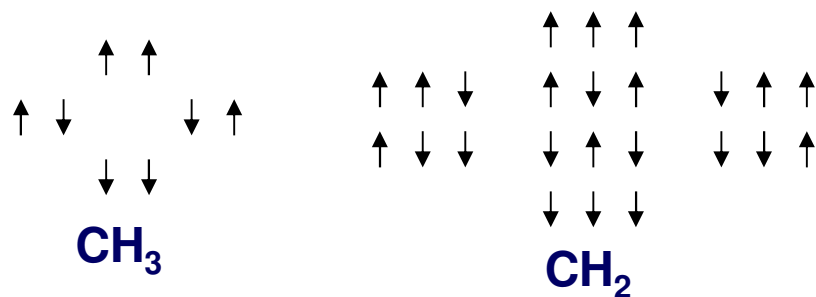
• Since we have the same probability of finding the system in any of the states, and states in the same rows have equal energy, the intensity will have a ratio **1:2:1** for the CH_3, and a ratio of **1:3:3:1** for the CH_2:
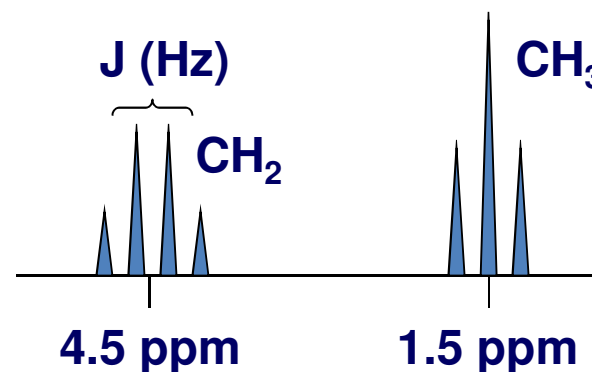
2nd order systems. The AB system

• What we have been describing so far is a spin system in which $\Delta\nu >> J$, and as we said, we are analyzing one of the limiting cases that QM predict.

• As $\Delta\nu$ approaches J, there will be more transitions of similar energy and thus our spectrum will start showing more signals than our simple analysis predicted. Furthermore, the intensities and positions of the lines of the multiplets will be different from what we saw so far.

• Lets say that we have two coupled nuclei, **A** and **B**, and we start decreasing our **B$_o$**. $\Delta\nu$ will get smaller with **J** staying the same. After a while, $\Delta\nu \sim$ **J**. What we see is the following:

• What we did here is to start with an **AX** system (the chemical shifts of **A** and **X** are very different) and finish with an **AB** system, in which $\Delta\nu \sim$ **J**.

$\Delta\nu >> J$

$\Delta\nu = 0$