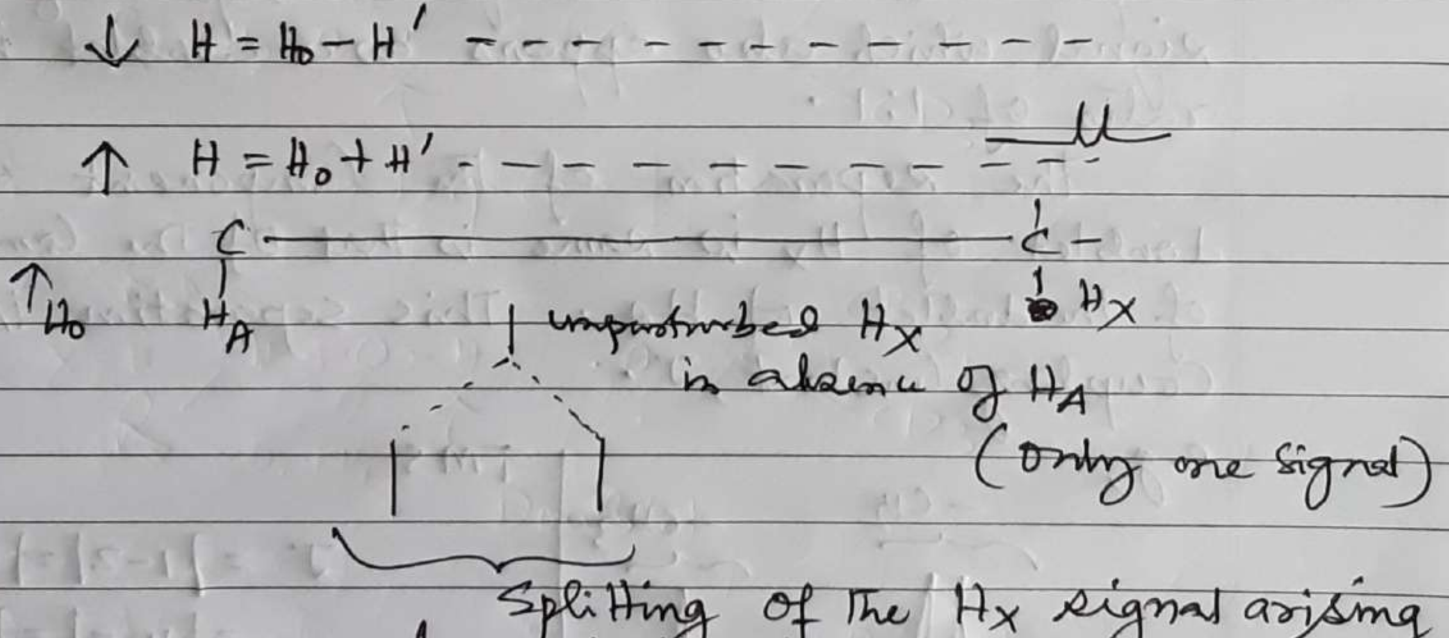
Explanation for the multiplicity of the signal of a proton or protons by an adjacent non-equivalent protons or groups of protons

i) Multiplicity of the signals of proton or protons by an adjacent non-equivalent protons.

The local magnetic fields created by the instantaneous spin arrangement — Results in the split of the signal H_x



Splitting of the H_x signal arising from spin spin interaction of H_A.

Let us Consider the splitting of H_x signal by H_A. The spin states of H_A may be either parallel or antiparallel with the external magnetic field. Accordingly there will be two local fields

$H = H_0 + H'$

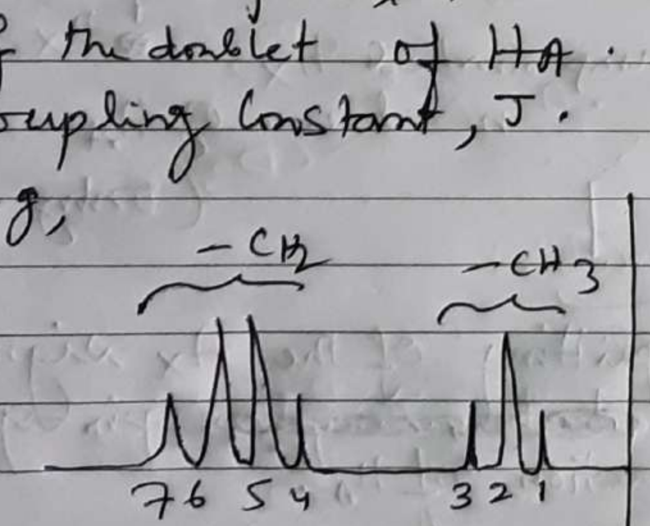
$H = H_0 - H'$

The magnetic effects of two spin arrangement of H_A is transmitted to the bonded electrons of H_x. Thus H_A Can either increase the net magnetic field of H_x or decrease it. Thus the two spin orientation of H_A creates two different magnetic fields around H_X. Therefore H_X comes to resonance and gives rise to a doublet.

Since the probability of existance of each of the two spin arrangement of H_A is equal. It follows that the intensities of the two transition will be in the ratio of 1:1 ~~intensity of the Component of the~~ The same explanation holds true for the splitting of H_A-signal which also appears as a doublet in the ratio of 1:1.

The separation of the Component of the doublet of H_X is same is that of the Component of the doublet of H_A. This separation is called Coupling Constant, J.

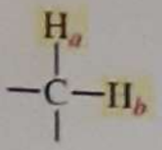
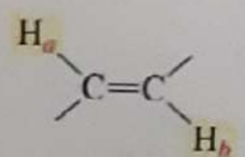
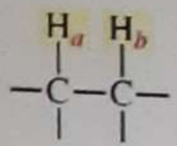
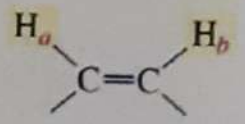
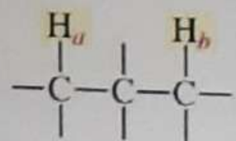
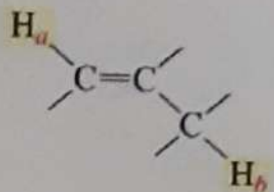
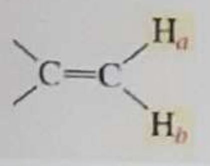
e.g.,



$$J = |1-2| = |2-3|$$
$$= |4-5| = |5-6|$$
$$= |6-7|$$

Since this is a process of spin-spin interaction of two protons which is transmitted through the bonded electron it is called electron coupled spin-spin interaction.

Coupling Constants

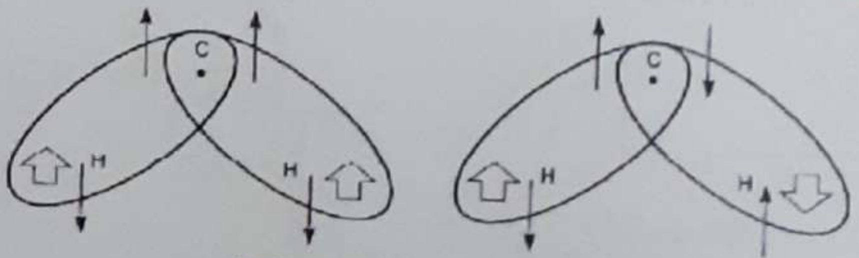
Structure	Approximate value of J_{ab} (Hz)	Structure	Approximate value of J_{ab} (Hz)
	12		15 (trans)
	7		10 (cis)
	0		1 (long-range coupling)
	2 (geminal coupling)		

Two-Bond Coupling

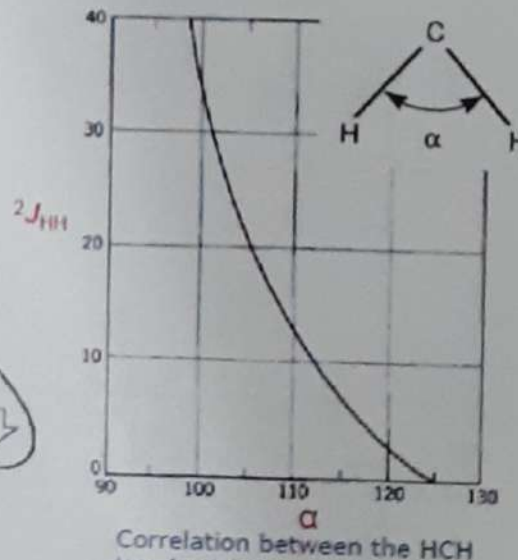
Two-Bond Coupling constants (^2J)

→ geminal coupling constant

→ invoke nuclear-electronic spin coupling as a means of transmitting spin information from one nucleus to the other

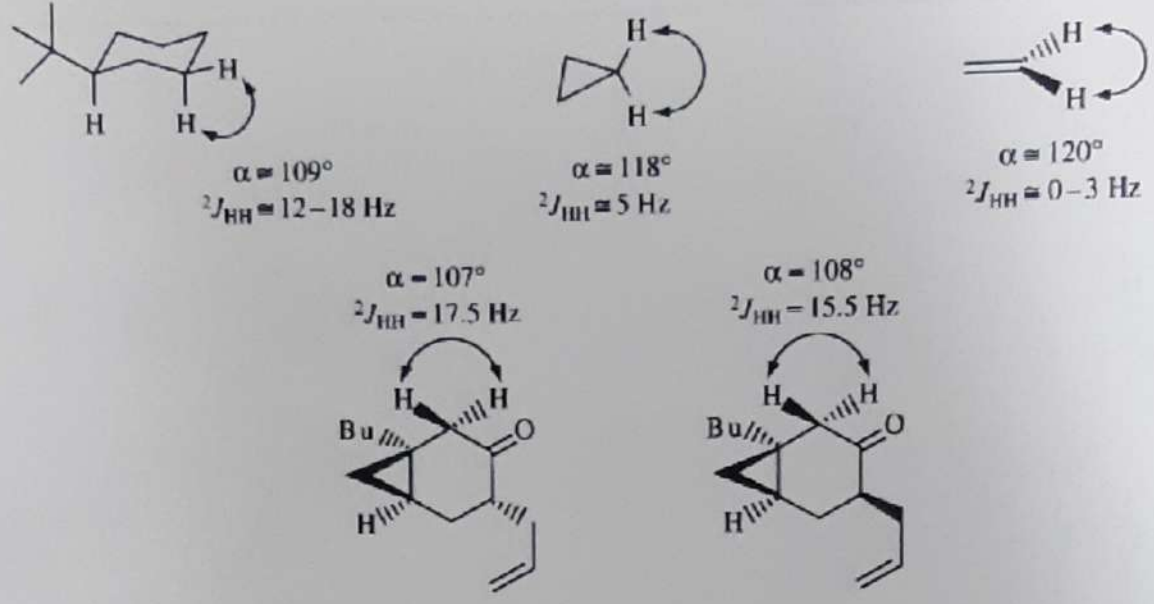


Mechanisms of geminal coupling



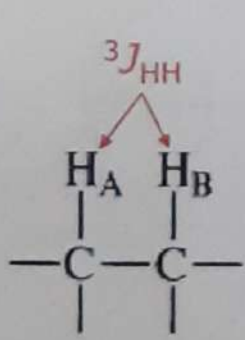
Correlation between the HCH bond angle (α) and approximate value of $^2J_{HH}$

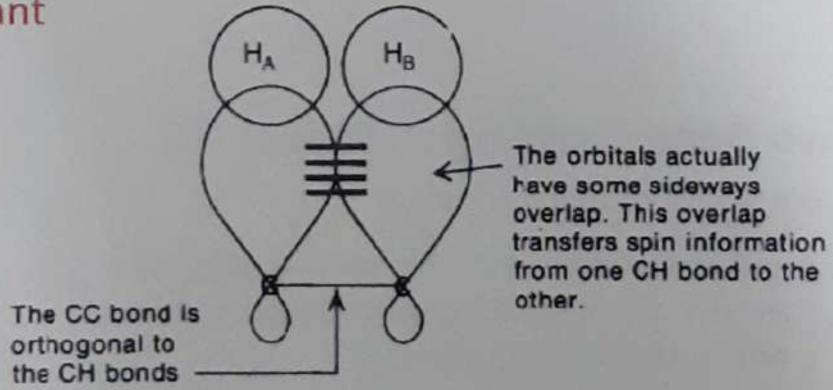
Two-Bond Coupling

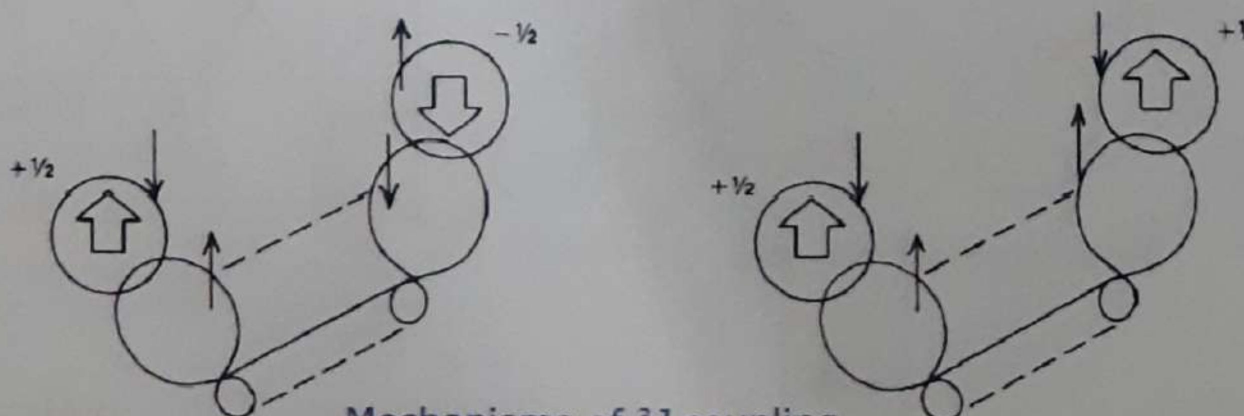


Three-Bond Coupling

→ vicinal coupling constant

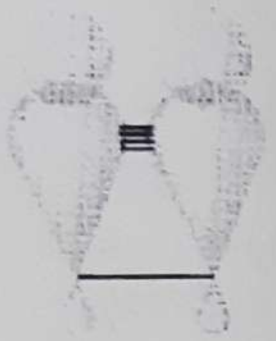






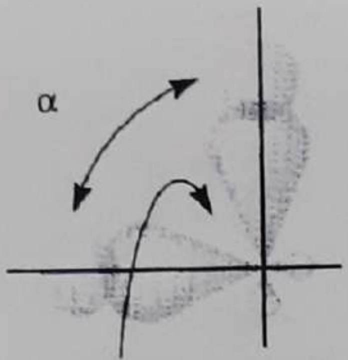
Mechanisms of ^3J coupling

α = 0° (side view)



Maximum overlap

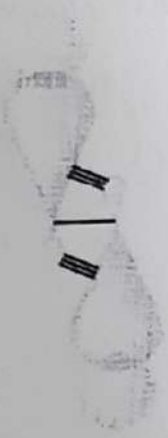
α = 90° (end view)



Little or no overlap when orbitals are perpendicular

Minimum overlap

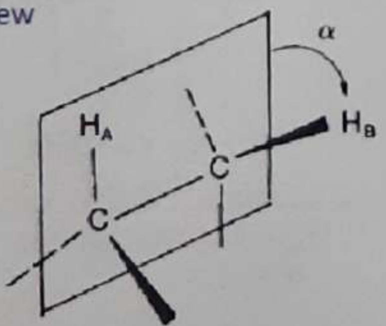
α = 180° (side view)



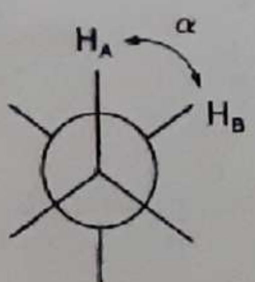
Maximum overlap

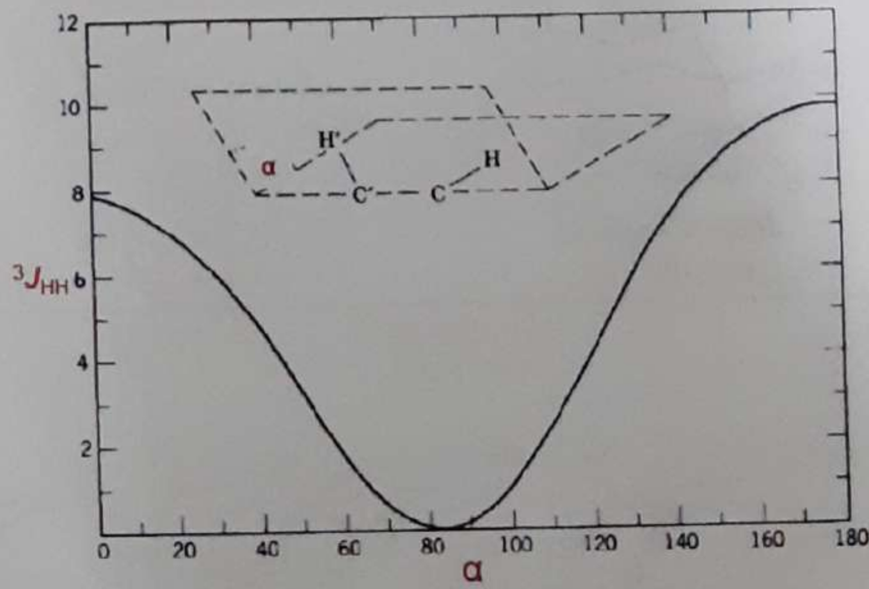
Definition of dihedral angle (α):

(i) Side view



(ii) End view





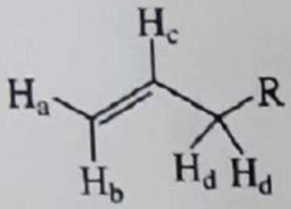
Karplus Correlation between dihedral angle (α) and approximate value of $^3J_{HH}$

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

Long-Range Coupling

→ Long-range couplings are common in allylic systems, aromatic rings & rigid bicyclic systems.

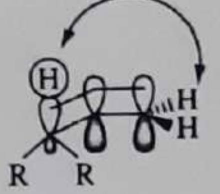
(i) Allylic coupling



$|^4J_{ad}| = 0 - 3$ Hz

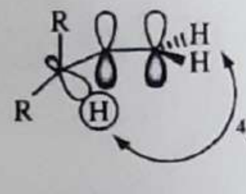
$|^4J_{bd}| = 0 - 3$ Hz

^4J maximum



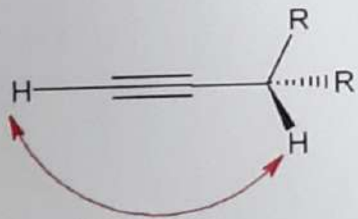
C—H σ orbital parallel to π orbital

C—H σ orbital orthogonal to π orbital



(ii) Propargylic coupling

$^4J = 2$ to 4 Hz



^4J