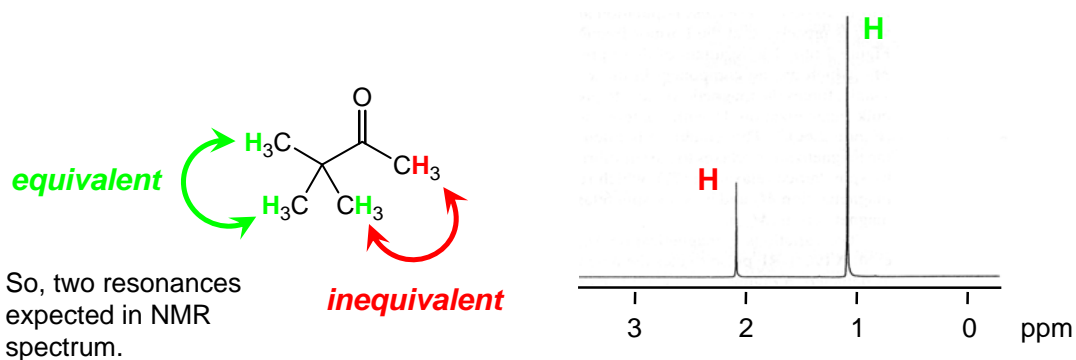


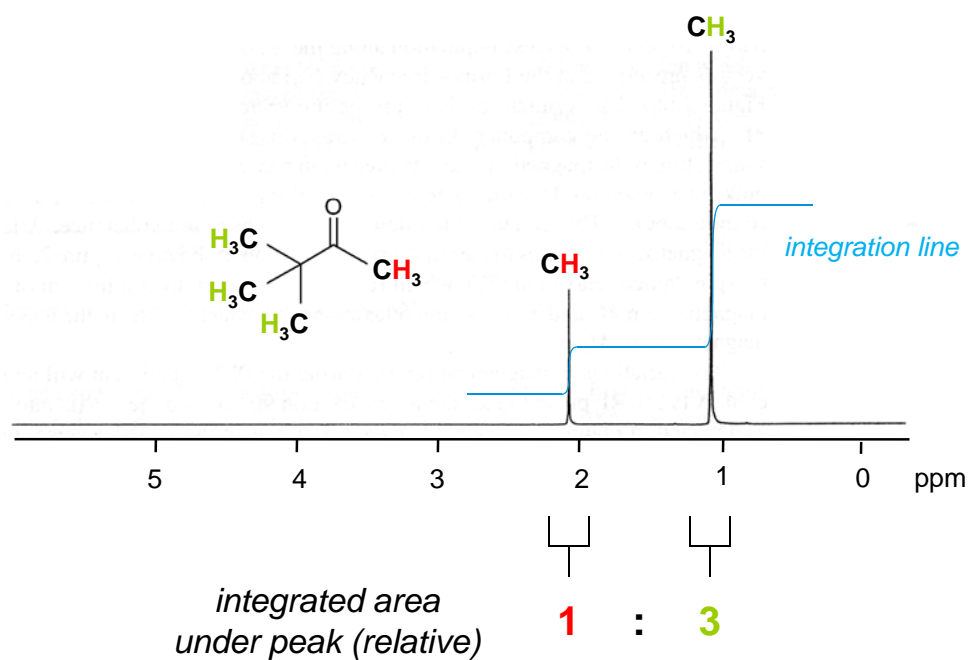
## Chemical Shift: Equivalence

Nuclei are **equivalent** if they experience identical chemical environments. Equivalent nuclei have the same chemical shift (and appear as one resonance).

*A good way to tell:* Looking at two nuclei, would replacing one of them with another atom—say, F—yield the same molecule as replacing the other? (Or its enantiomer?) If so, the two nuclei are equivalent.

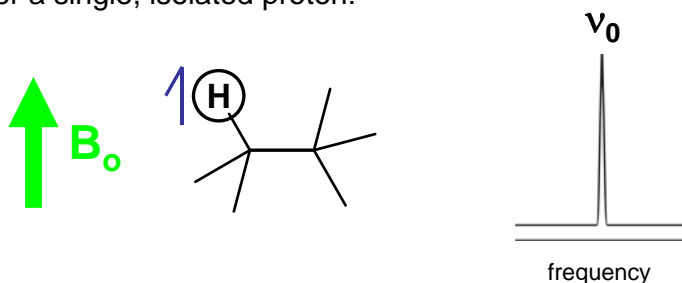


## Integrated Area Under Peaks Corresponds to Number of Equivalent Protons



# Spin-Spin Coupling

For a single, isolated proton:

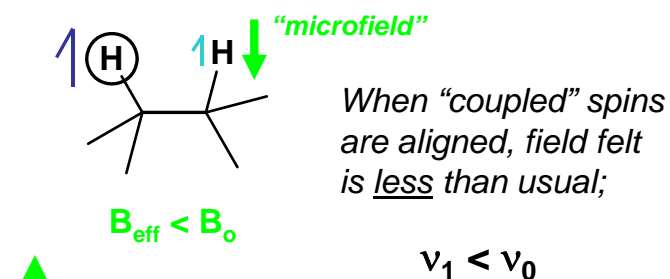


Just one peak, corresponding to one frequency.

Field felt by a proton is affected by spin of adjacent proton:

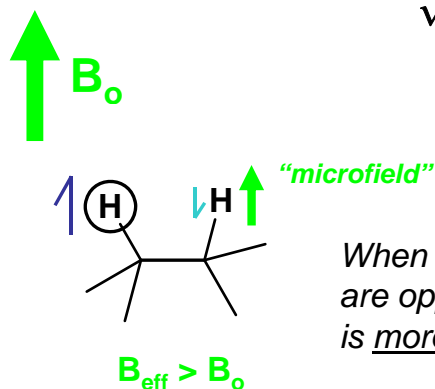


## Spin-Spin Coupling Leads to Peak "Splitting"



When "coupled" spins are aligned, field felt is less than usual;

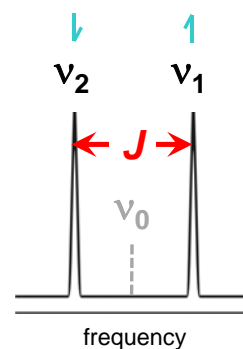
$$\nu_1 < \nu_0$$



When "coupled" spins are opposed, field felt is more than usual;

$$\nu_2 > \nu_0$$

So, a proton with one adjacent proton will produce a **doublet** ("d").

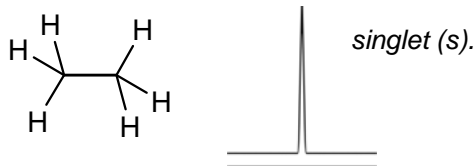


**coupling constant**

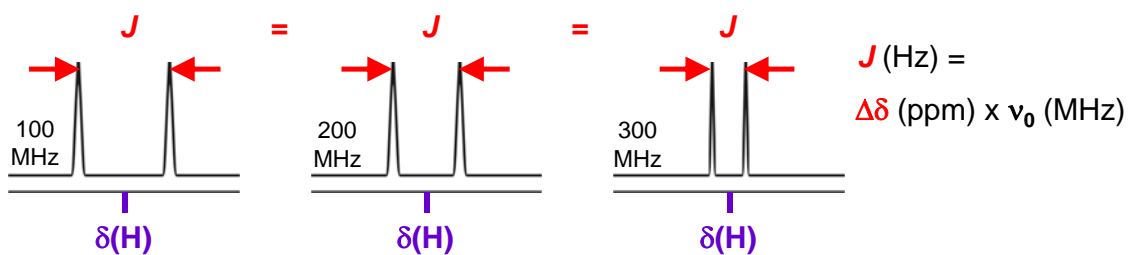
$$J = \nu_2 - \nu_1$$

# Characteristics of Splitting

- Coupling is only observed between inequivalent protons.

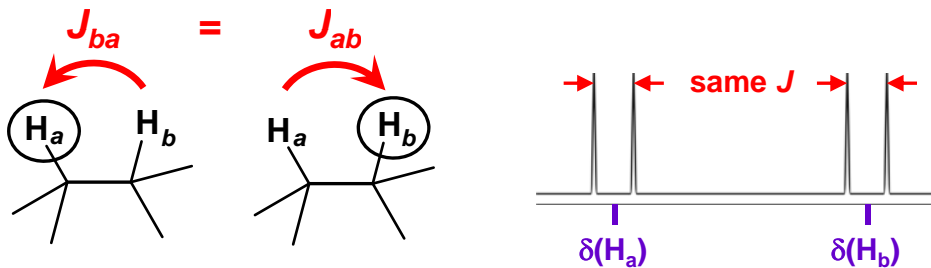


- $\delta$  is expressed in **ppm** (because frequency **ratio** Hz/MHz doesn't vary from spectrometer to spectrometer).
- $J$  is expressed in **Hz** (because frequency **difference** in Hz doesn't vary, so ratio Hz/MHz does).

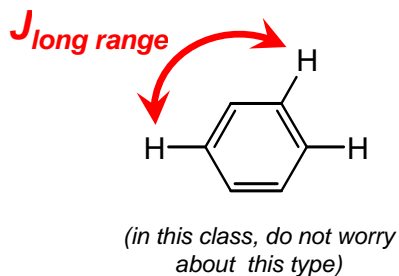
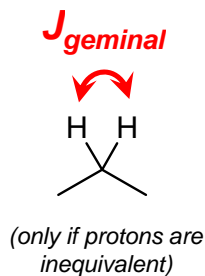
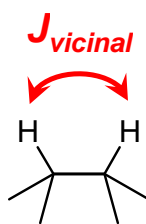


## A Little More About $J$

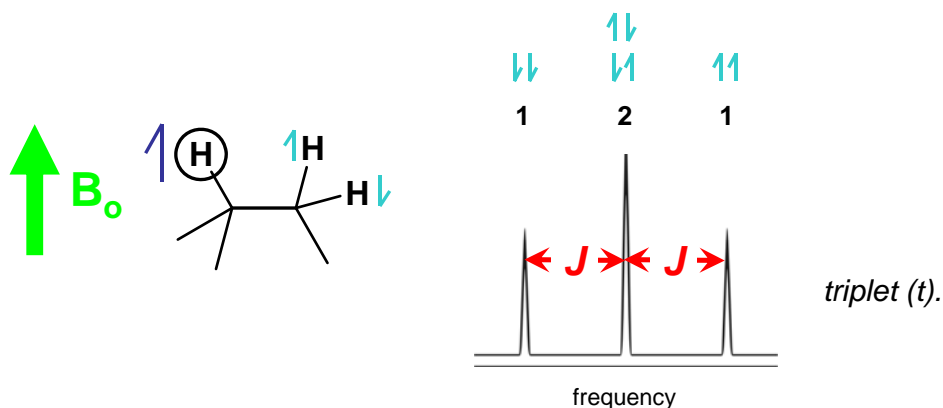
- Coupling constant  $J$  is same in both directions for a coupled pair.



- Coupling is most often vicinal (on adjacent C's). But there are other types.



## Splitting By Multiple Adjacent Protons

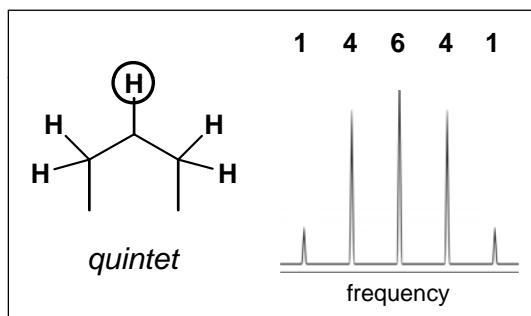
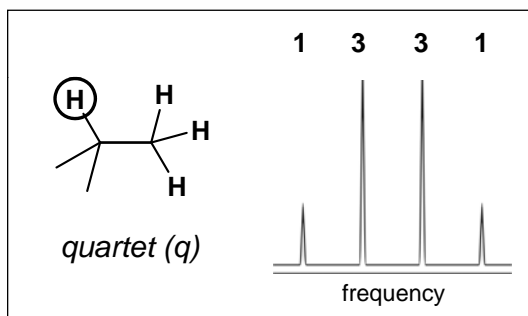


“N + 1” rule:

*For simple splitting (all J's are equal),*  
**# of peaks = # of interacting nuclei (N) + 1**

For H above, # of peaks = 2 + 1 = 3.

## Splitting By Multiple Adjacent Protons



“N + 1” rule:

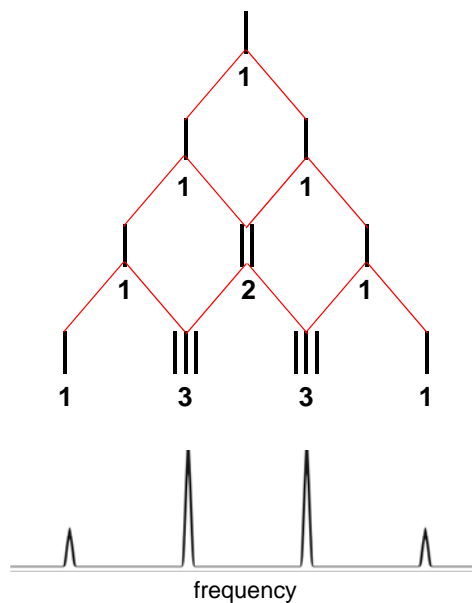
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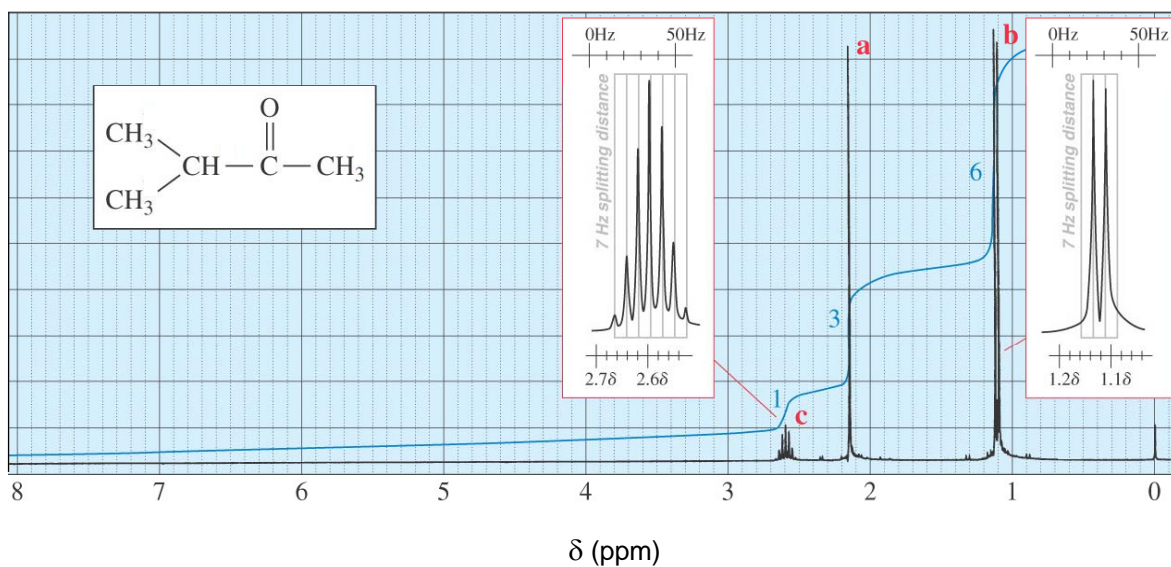
# Spin-Spin Coupling: Simple Splitting and Pascal's Triangle

Splitting patterns for multiple protons (if all  $J$  values are the same) can be evaluated by Pascal's triangle:

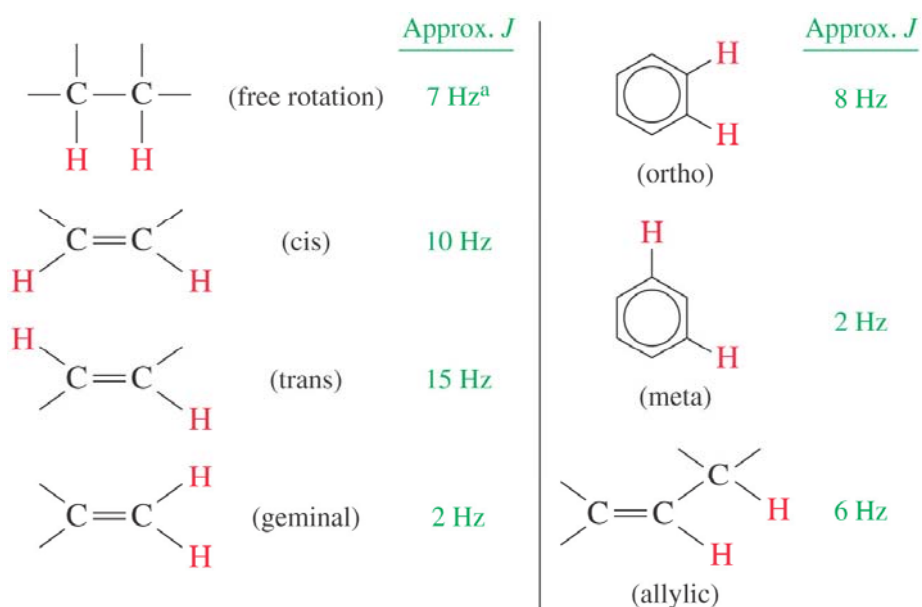
1. Start apex of triangle with a single line, intensity 1.
2. Create next row with one more line. Make outside line intensities 1.
3. Make inside line intensities sum of two lines above.
4. Repeat steps 2 & 3 until you have  $N + 1$  lines.



## Example of Spin-Spin Coupling

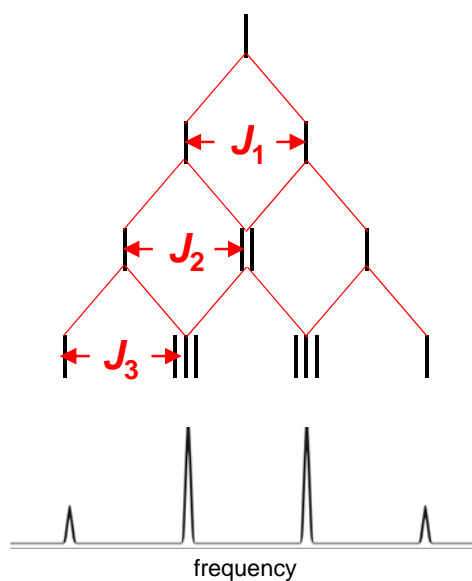
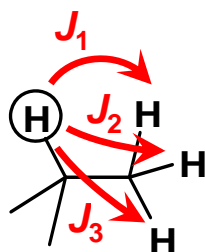


# Typical $J$ Values



## Spin-Spin Coupling: Simple Splitting and Pascal's Triangle

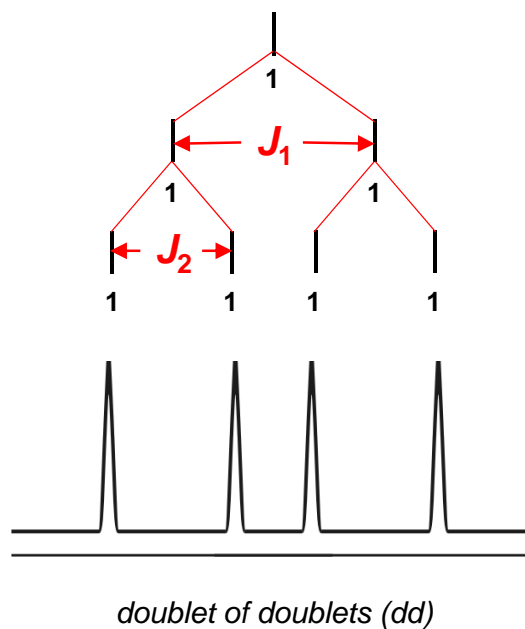
Can think of Pascal's triangle as a way of expressing splitting for multiple coupling constants  $J_1$ ,  $J_2$ ,  $J_3$ , etc., where  $J_1 = J_2 = J_3$ .



## Spin-Spin Coupling: More Complex Splitting

What if coupling constants aren't equal?

Splitting pattern gets more complicated, doesn't follow Pascal's triangle.



## Spin-Spin Coupling: More Complex Splitting

What if coupling constants aren't equal?

Splitting pattern gets more complicated, doesn't follow Pascal's triangle.

For case of doublet of doublets, can measure  $J$ 's directly from spectrum.

