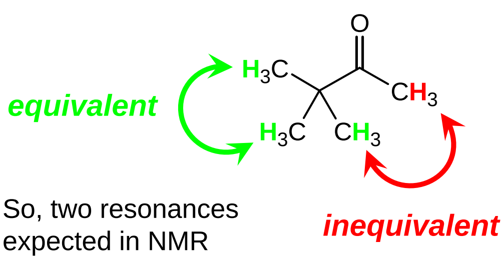
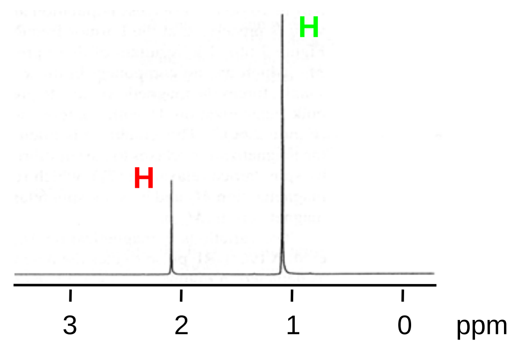
Chemical Shift: Equivalence

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

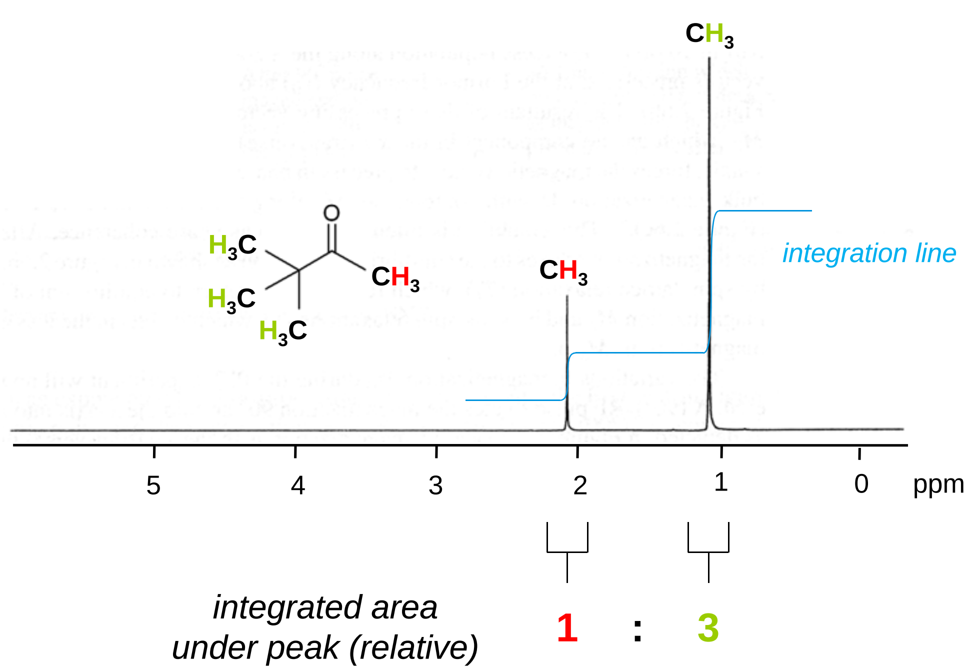
A good way to tell: Looking at two nuclei, would replacing one of them with another atom—say, F—yield the same molecule as replacing the other? (Or its enantiomer?) If so, the two nuclei are equivalent.



So, two resonances expected in NMR spectrum.

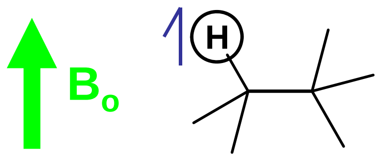


Integrated Area Under Peaks Corresponds to Number of Equivalent Protons



Spin-Spin Coupling

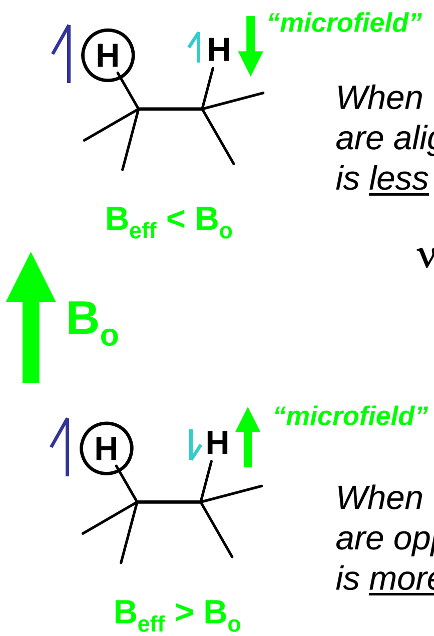
For a single, isolated proton:



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"



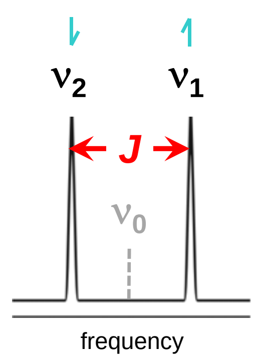
When "coupled" spins are aligned, field felt is <u>less</u> than usual;

$$\nu_1 < \nu_0$$

When "coupled" spins are opposed, field felt is <u>more</u> than usual;

$$\nu_2 > \nu_0$$

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

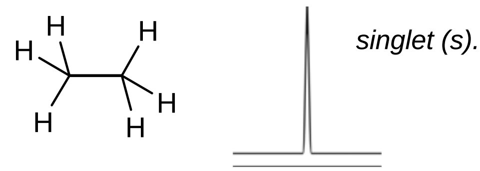


coupling constant

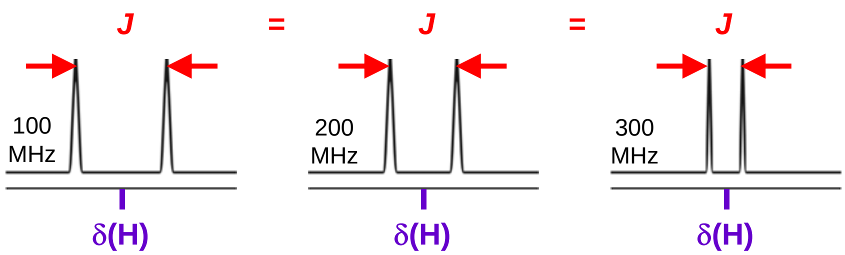
$$J = \nu_2 - \nu_1$$

Characteristics of Splitting

- Coupling is only observed between <u>inequivalent</u> protons.



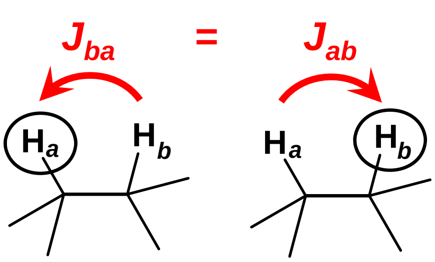
- δ is expressed in **ppm** (because frequency **ratio** Hz/MHz doesn't vary from spectrometer to spectrometer).
- ***J*** is expressed in **Hz** (because frequency **difference** in Hz doesn't vary, so ratio Hz/MHz does).

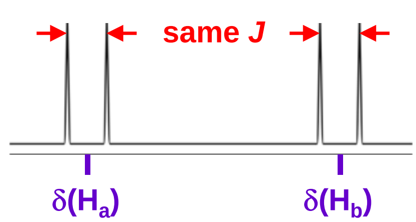


J (Hz) = $\Delta\delta$ (ppm) x ν_0 (MHz)

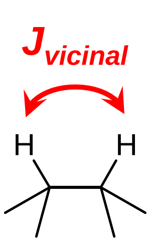
A Little More About *J*

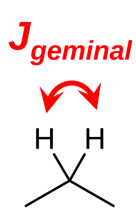
- Coupling constant ***J*** is same in both directions for a coupled pair.



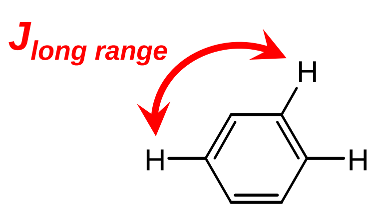


- Coupling is most often vicinal (on adjacent C's). But there are other types.



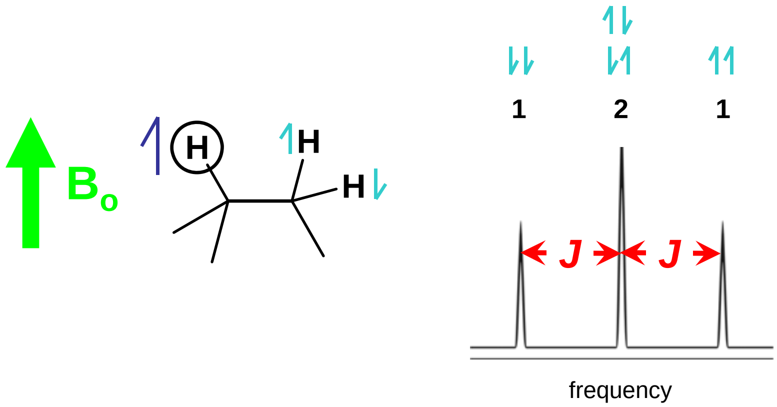


(only if protons are inequivalent)



(in this class, do not worry about this type)

Splitting By Multiple Adjacent Protons



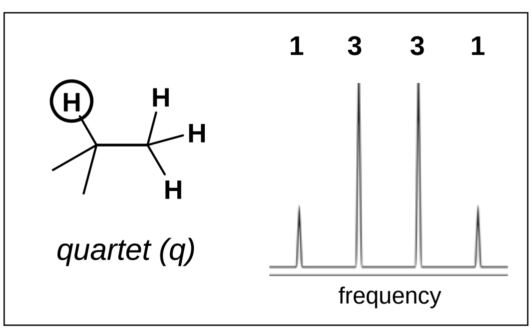
triplet (t).

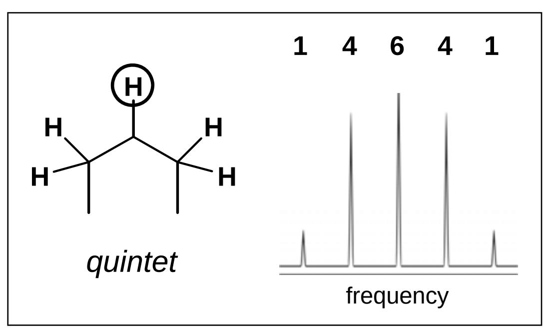
"N + 1" rule:

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:

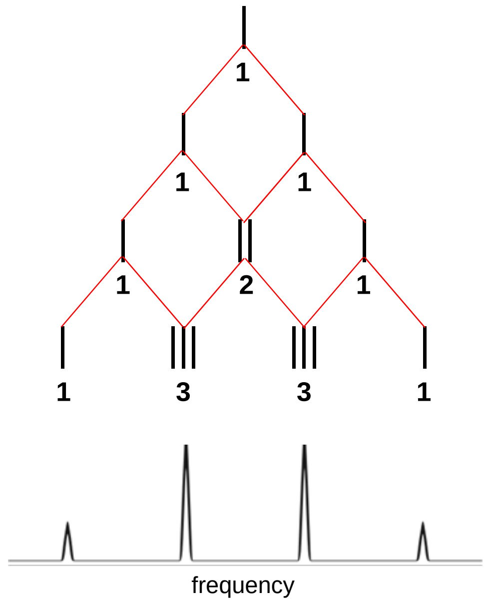
For simple splitting (all J's are equal),
# of peaks = # of interacting nuclei (N) + 1

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

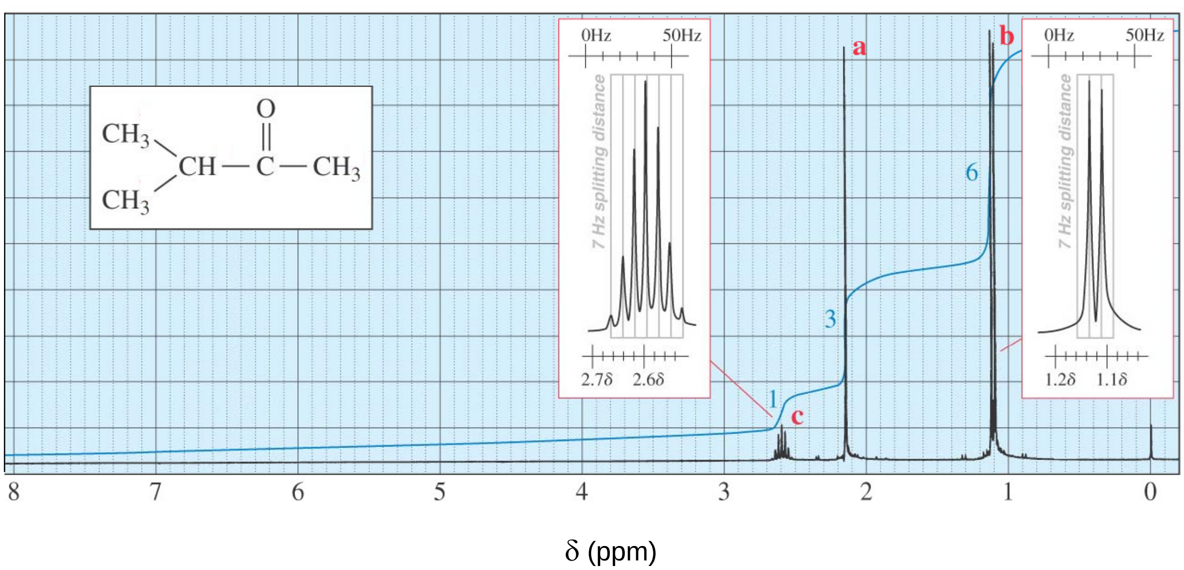
Spin-Spin Coupling: Simple Splitting and Pascal's Triangle

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

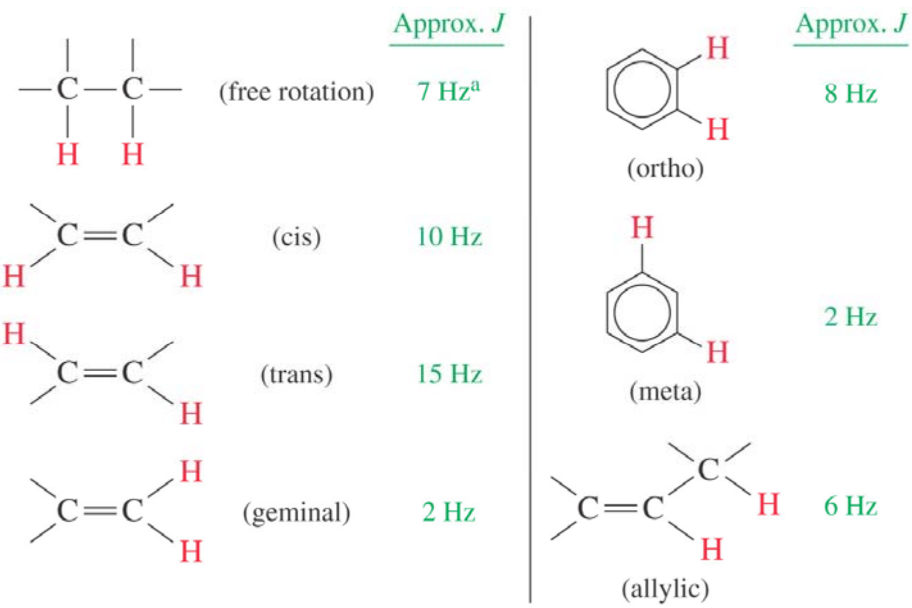
1. Start apex of triangle with a single line, intensity 1.
2. Create next row with one more line. Make outside line intensities 1.
3. Make inside line intensities sum of two lines above.
4. Repeat steps 2 & 3 until you have N + 1 lines.



Example of Spin-Spin Coupling

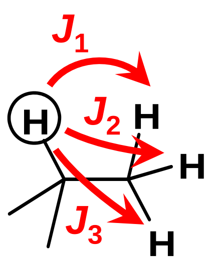


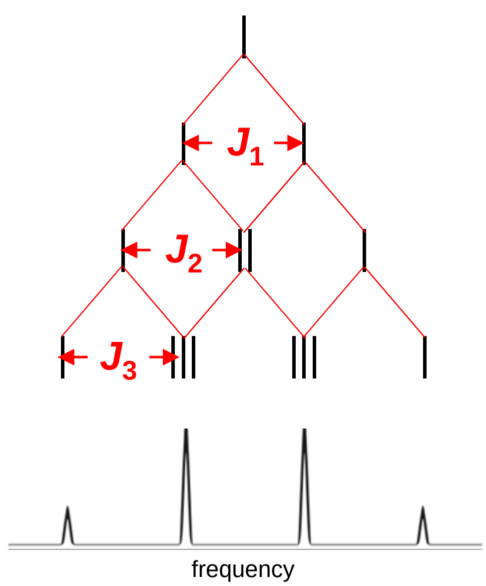
Typical J Values



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.

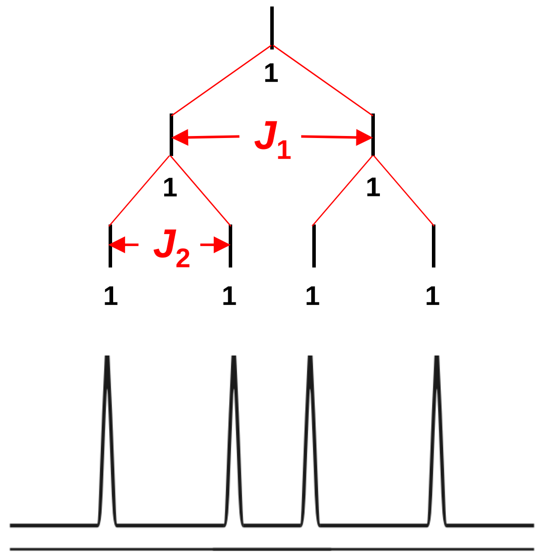




Spin-Spin Coupling: More Complex Splitting

What if coupling constants aren't equal?

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



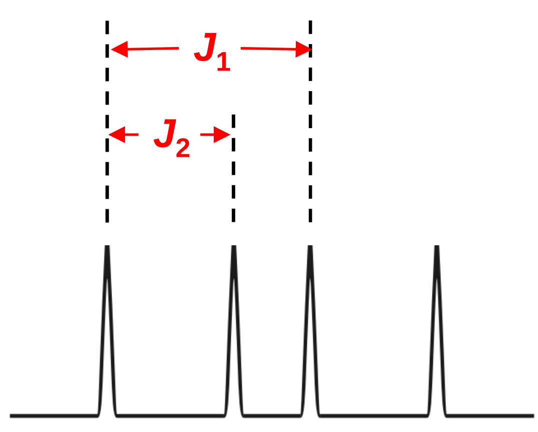
doublet of doublets (dd)

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.



doublet of doublets (dd)