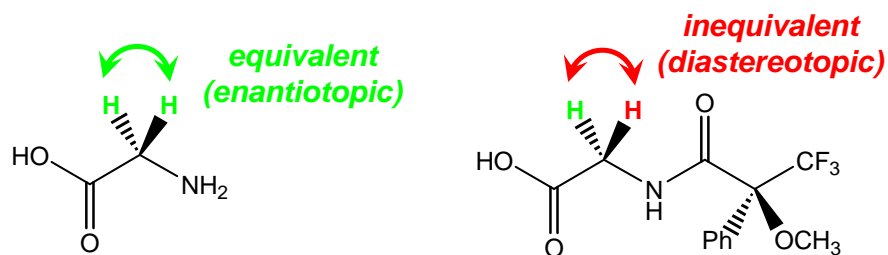


# Chemical Shift: Equivalence

NMR distinguishes diastereotopic protons, but not enantiotopic ones.



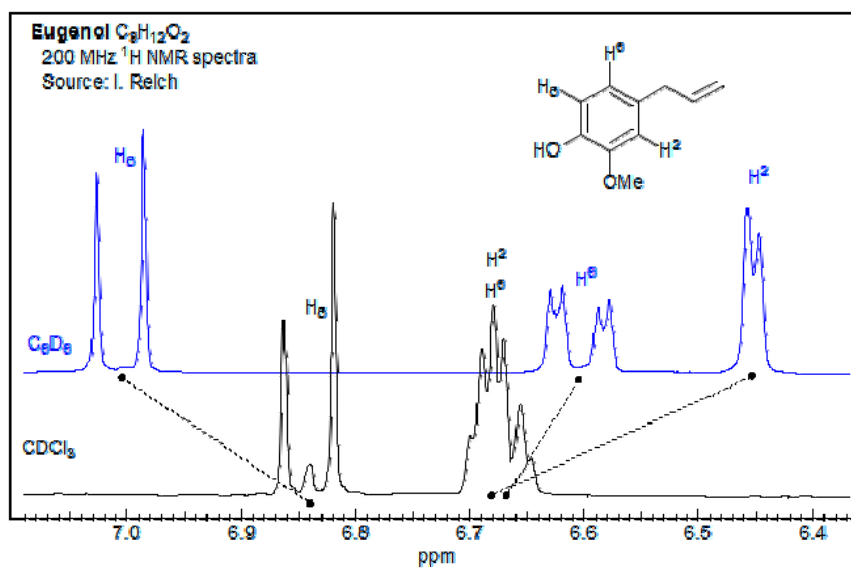
Replacing each H with an X yields two enantiomers that can't be distinguished by NMR.

Replacing each H with an X yields two diastereomers that can be distinguished by NMR.

*Note:* Just because protons are inequivalent, doesn't mean they exhibit different chemical shifts.

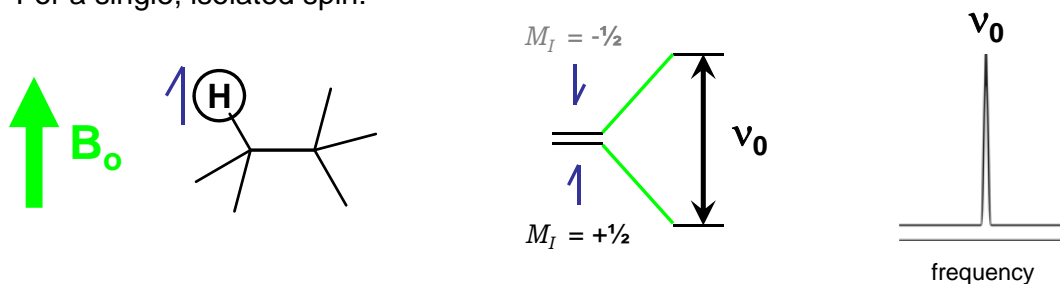
## Solvent Effects on Chemical Shift

Changing NMR solvent (or switching to mixed solvents) can separate overlapping NMR resonances.

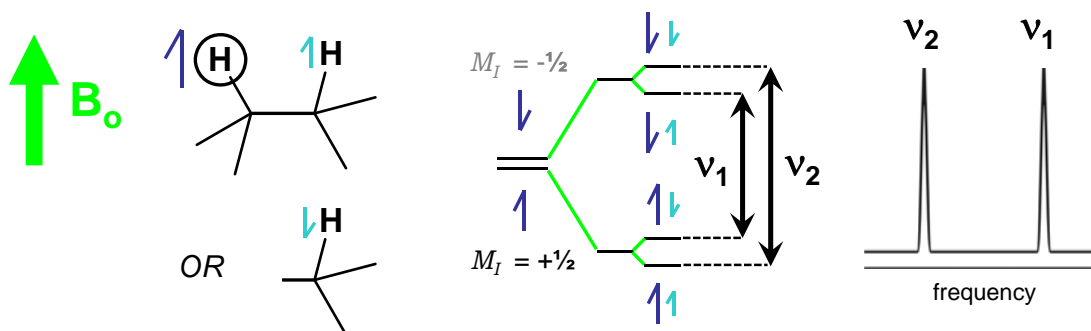


# Spin-Spin Coupling

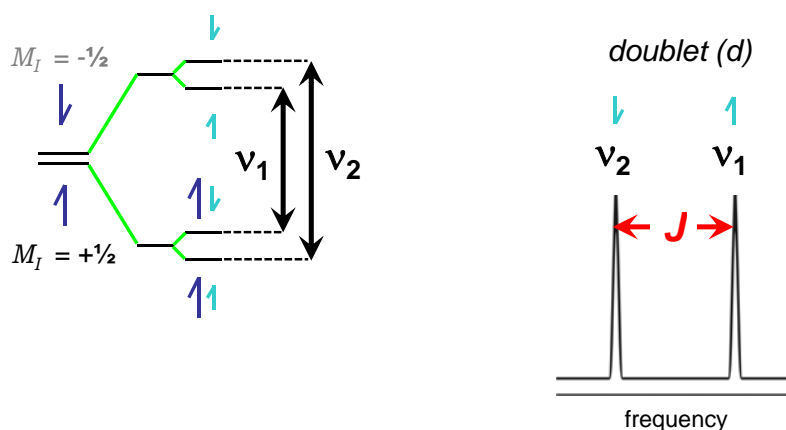
For a single, isolated spin:



In the presence of a nearby spin:



## Spin-Spin Coupling: Simple Splitting



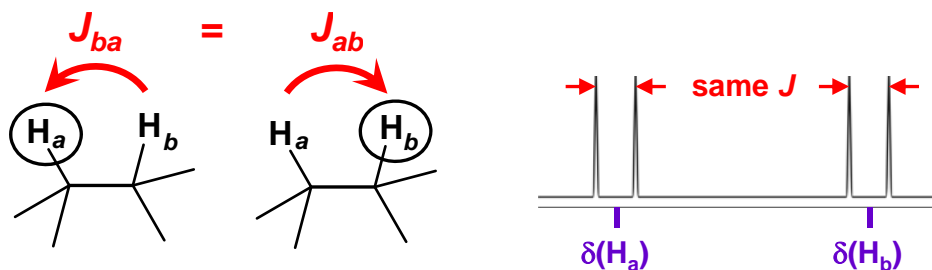
Sum of integrated intensity is equal to that of unsplit peak.  
(So here, each peak has  $\frac{1}{2}$  of integral.)

**coupling constant**

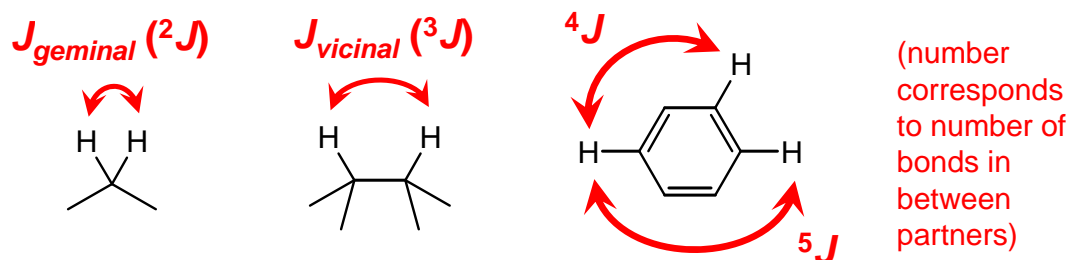
$$J = \nu_2 - \nu_1$$

## A Little Bit About $J$

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

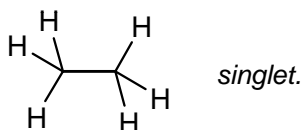


- Coupling is most often vicinal, but also occasionally geminal, long-range.

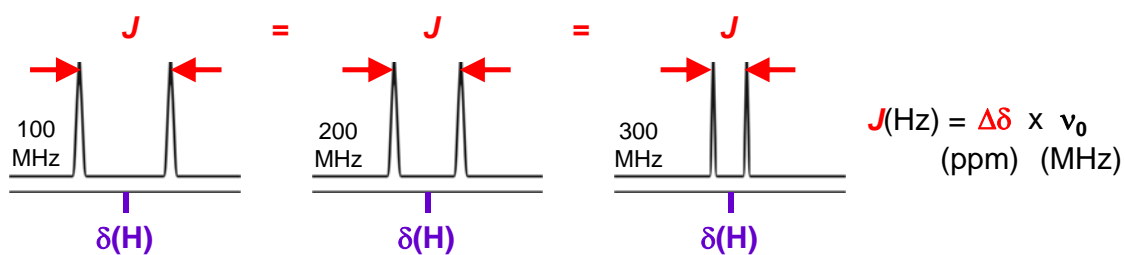


## A Little Bit About $J$

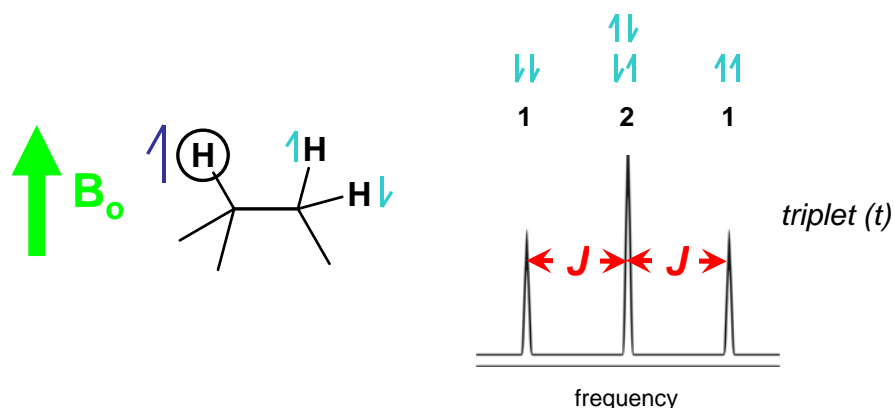
- Coupling is only observed between magnetically inequivalent protons.



- $\delta$  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).



## Spin-Spin Coupling: Simple Splitting

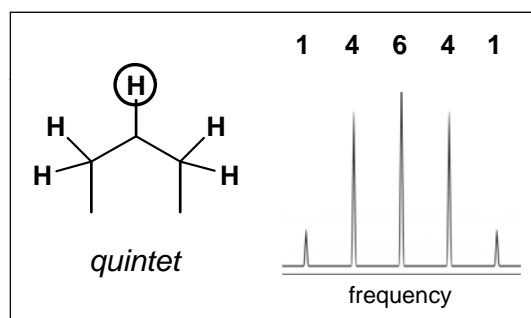
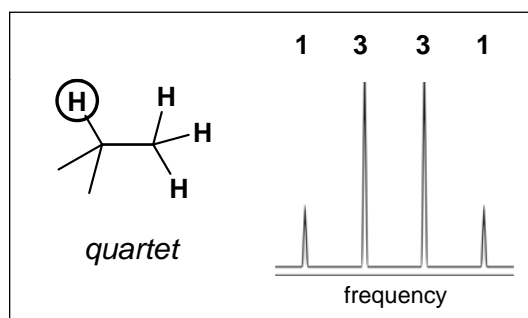


“N + 1” rule:

*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:

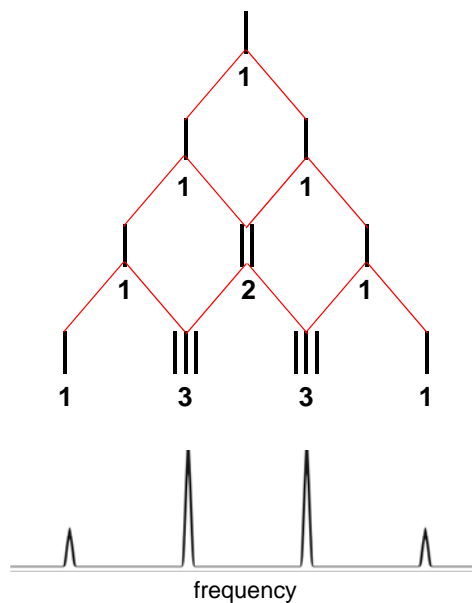
*For simple splitting (all  $J$ 's are equal),*  
**# of peaks = # of interacting nuclei (N) + 1**

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

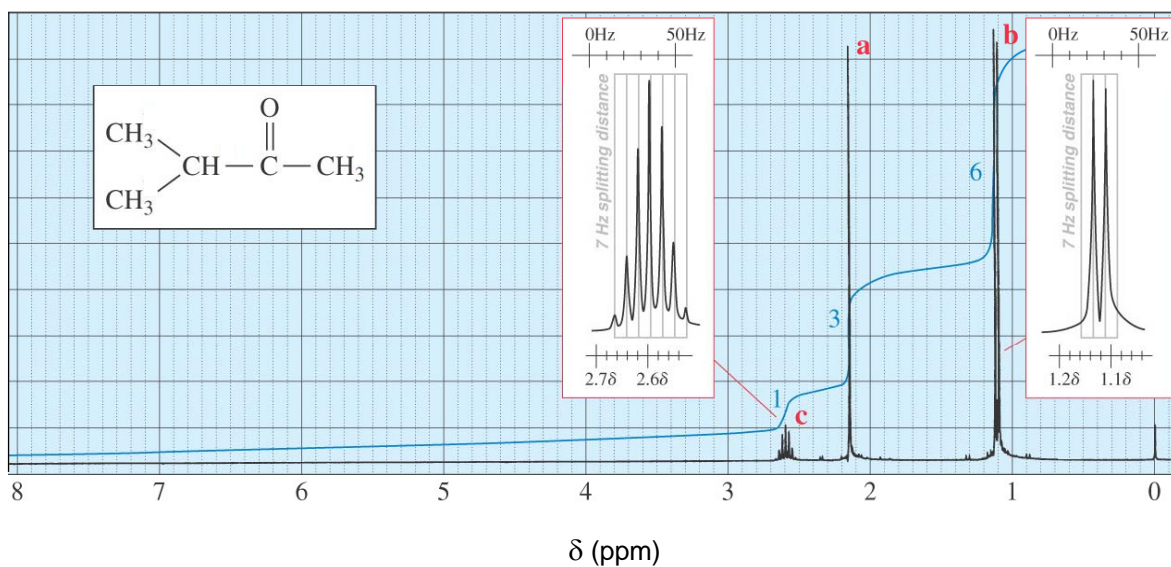
# Spin-Spin Coupling: Simple Splitting and Pascal's Triangle

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

