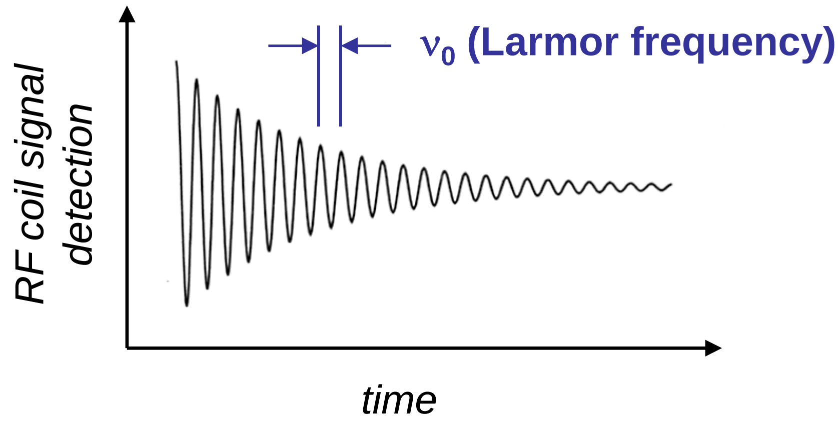
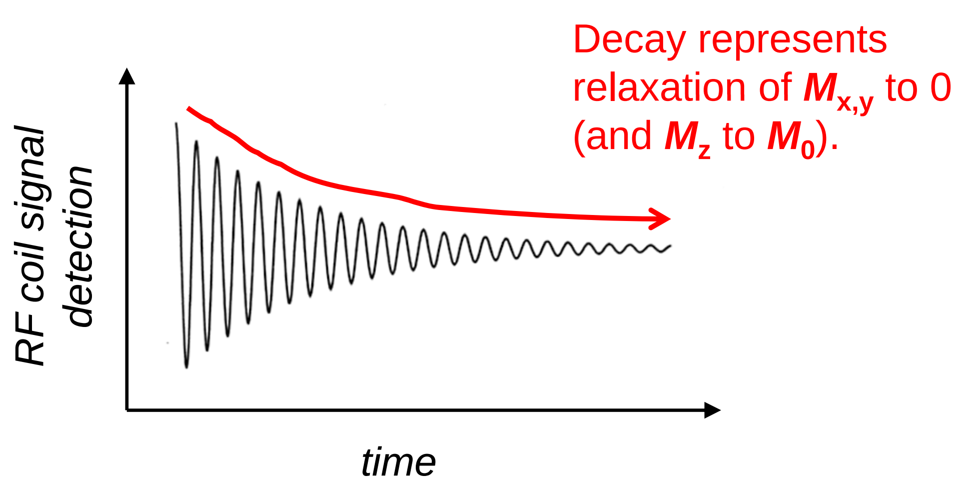
The Free Induction Decay



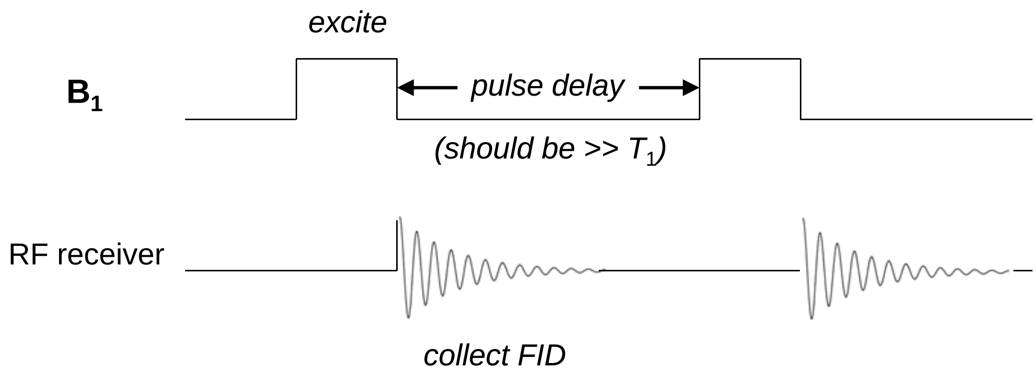
(Actually, observed periodicity is difference between ν_0 and reference frequency ν_{ref}.)

The Free Induction Decay

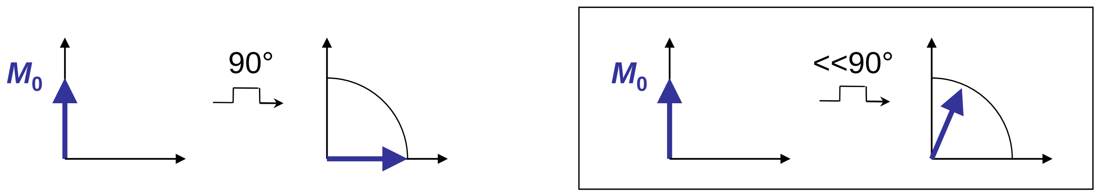


Two mechanisms for signal decay:
1. Spin flipping that restores $\boldsymbol{M}_0$. (timescale T_1)
2. Decoherence of magnetization due to $\mathbf{B}_0$ inhomogeneity. (timescale T_2) Affected by sample prep.

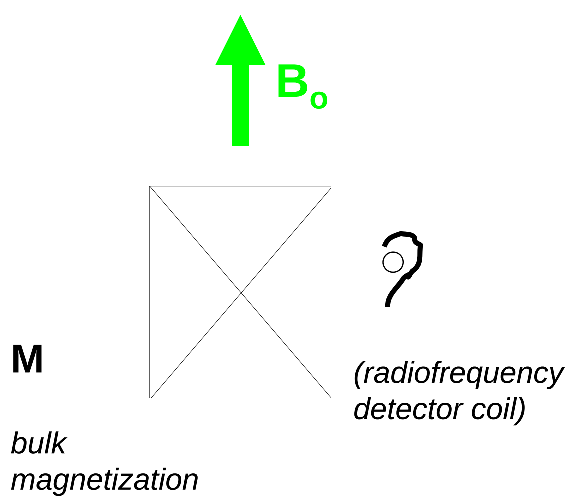
The Typical Pulsed NMR Experiment

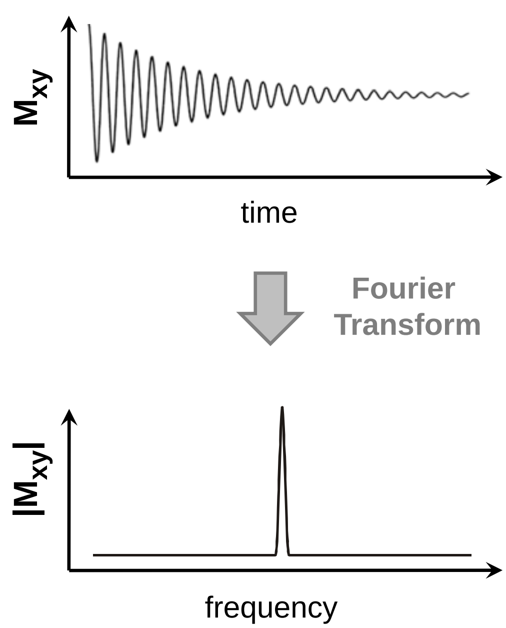


Excitation pulse strength usually expressed in degrees:

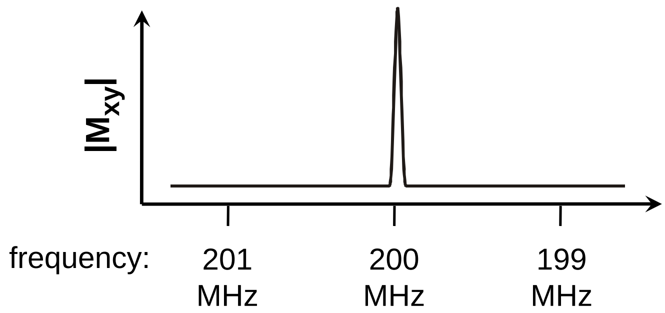


An NMR Spectrometer "Listens" to Frequency of Nuclear Precession



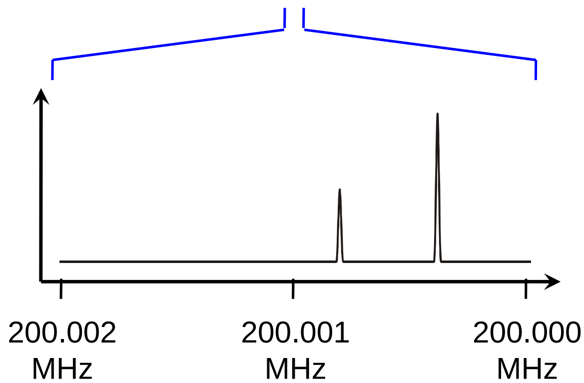


An NMR Spectrum



No surprise: NMR spectrum of CH_3OH shows the presence of ^1H nuclei at Larmor frequency.

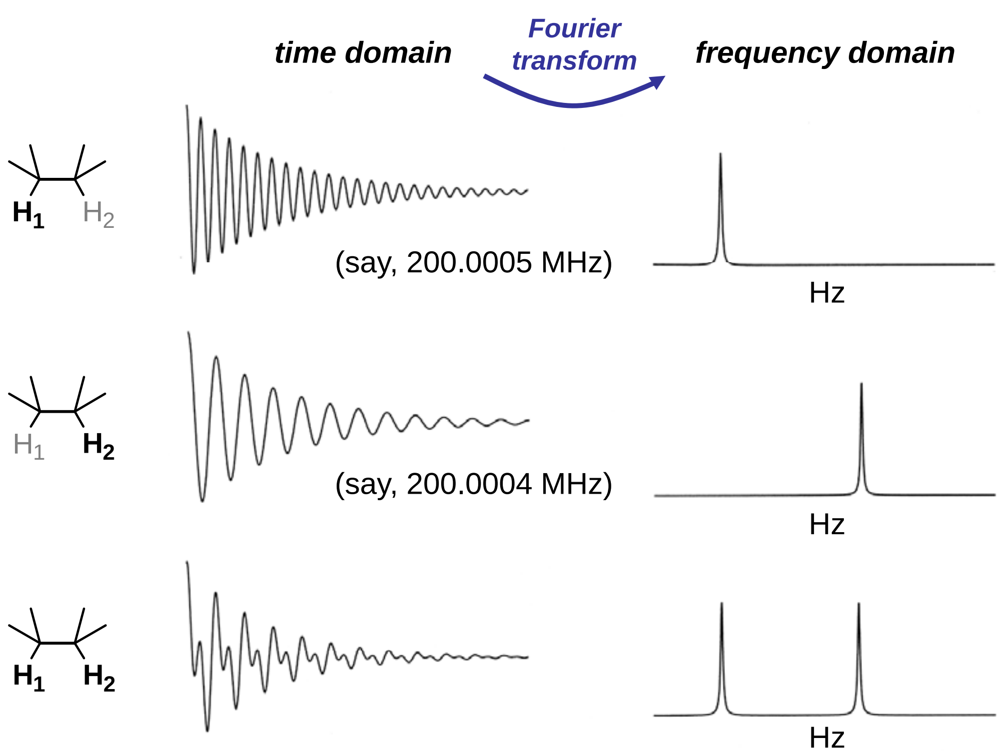
but what if we look closer??



Not all ^1H nuclei wobble at the exact same frequency;

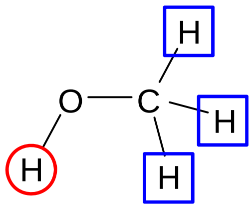
Differences in frequency reflect differences in magnetic environment.

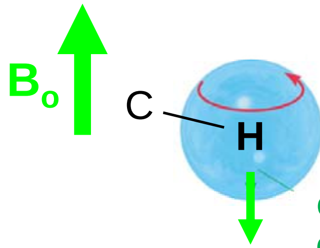
Multiple Nuclei and the Fourier Transform



“Shielding” Influences Proton Frequency

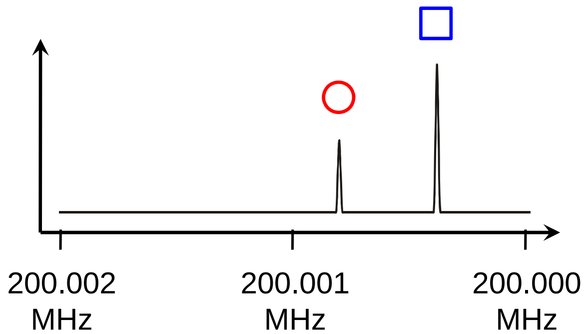
NMR spectrum of CH_3OH:



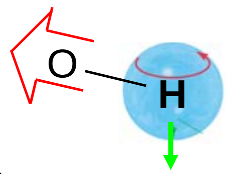


Magnetic field induces circulation of e⁻ cloud.

Circulation generates an *opposing* magnetic field.

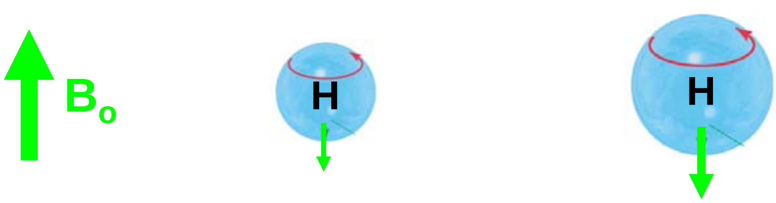


So, magnetic field and frequency are *lower* than one might expect.

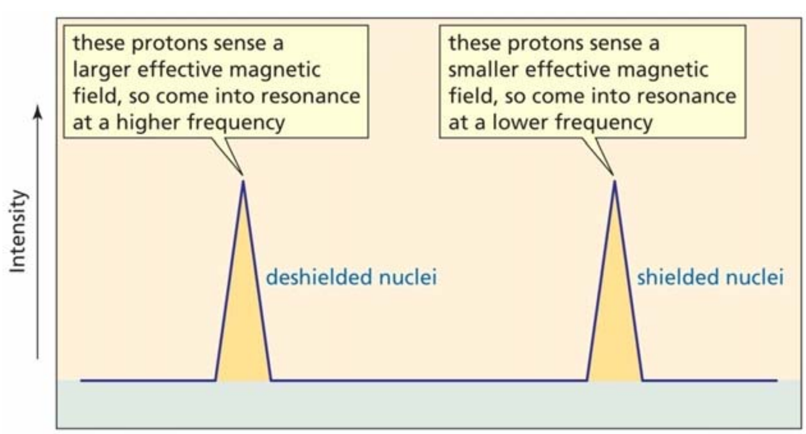


Electron-withdrawing oxygen means
- Smaller e^- cloud on H
- Less opposing magnetic field
- **Higher frequency**

“Shielding” Influences Proton Frequency



Electron cloud “shields” ^{1}H nucleus.



“downfield”: ← frequency ← ***“upfield”:***

Lower magnetic field strength would be required to achieve the same frequency.

Higher magnetic field strength would be required to counteract shielding electrons and achieve the same frequency.

Chemical Shift:
A Proportional Horizontal Axis

Problem: Differences in frequency depend on spectrometer field strength, vary from instrument to instrument.

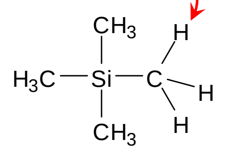
Solution: Define an absolute scale independent of spectrometer frequency, called "chemical shift".

$$\text{chemical shift, ppm } \delta = \frac{\text{shift downfield from TMS (in Hz)}}{\text{spectrometer frequency (in MHz)}}$$

← frequency

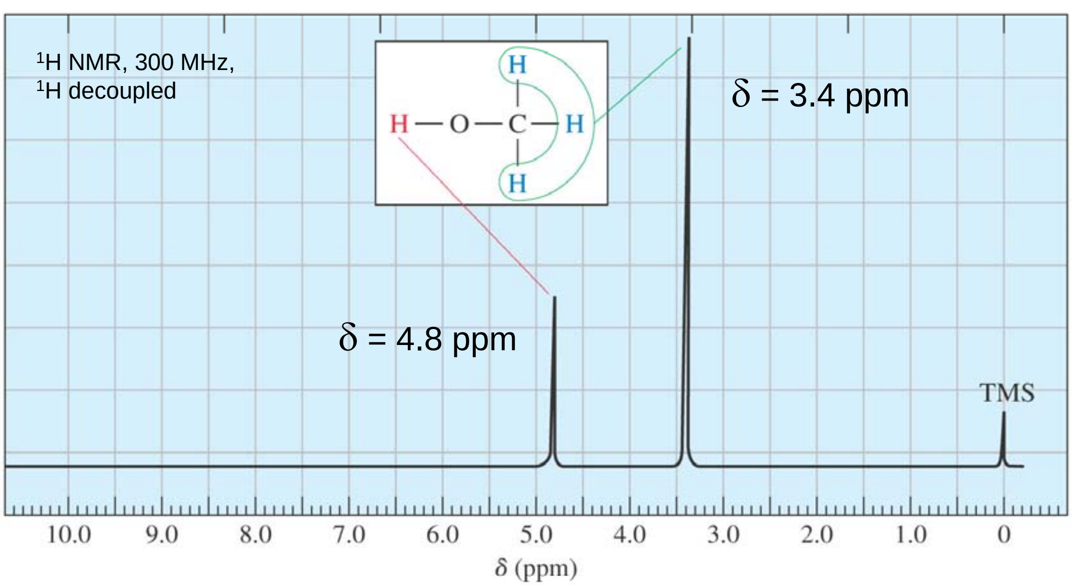
200.002	200.001	200.000	MHz
2000	1000	0	Hz (*diff.*)
10	5	0	ppm

Frequency defined as δ = 0 ppm



tetramethylsilane (TMS)

Chemical Shift:
A Proportional Horizontal Axis



CH_3OH protons have these chemical shifts (ppm values), regardless of instrument they are measured on.

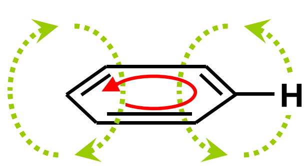
Different Types of Protons Have Characteristic Chemical Shifts

Type of Proton	Approximate δ	Type of Proton	Approximate δ
alkane (—CH_3)	0.9	>C=C<CH_3	1.7
alkane (—CH_2—)	1.3	Ph—H	7.2
alkane (—CH—) (with a third bond)	1.4	Ph—CH_3	2.3
		R—CHO	9–10
—C(=O)—CH_3	2.1	R—COOH	10–12
—C≡C—H	2.5	R—OH	variable, about 2–5
R—CH_2—X (X = halogen, O)	3–4	Ar—OH	variable, about 4–7
		R—NH_2	variable, about 1.5–4
>C=C<H	5–6		

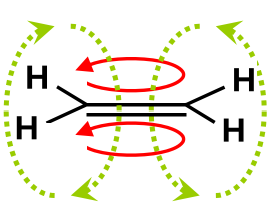
A better resource: http://www.chem.wisc.edu/areas/reich/Handouts/nmr-h/hdata.htm

Chemical Shift: Multiple Bonds and Induced Current

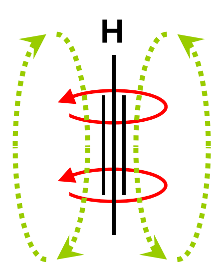
In presence of applied field  B_0 ,



"Ring current" *reinforces* applied B_0 field; **deshields** aromatic protons (δ = 6.5-8.5 ppm).



Induced current is less effective in olefins, still **deshields**, but less (δ = 4-6 ppm).

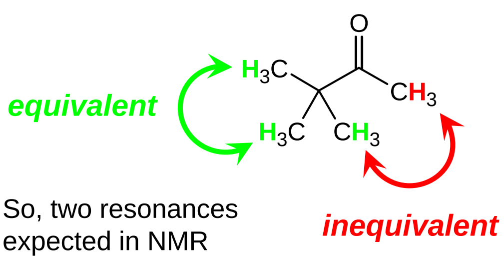


Acetylene protons are **shielded** (δ = 1.5-3 ppm).

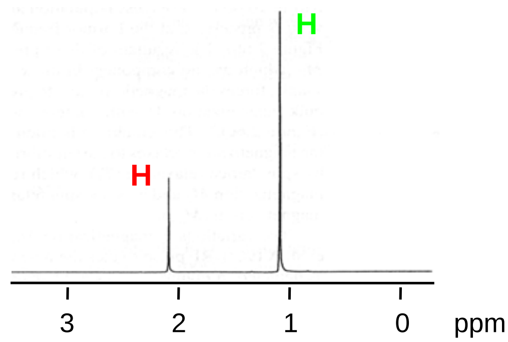
Chemical Equivalence

Nuclei are **chemically 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.

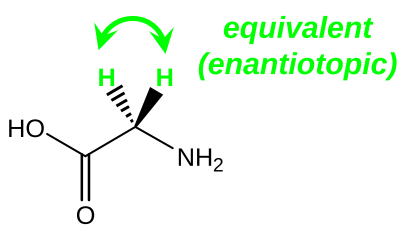


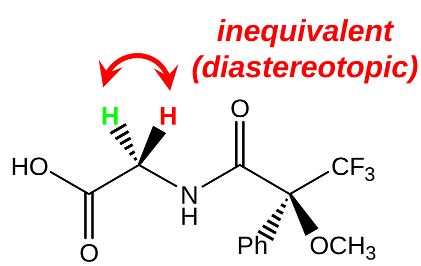
So, two resonances expected in NMR spectrum.



Chemical Shift: Equivalence

Less obvious:





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.

Integrated Area Under Peaks Corresponds to Number of Equivalent Protons