

Nuclear Magnetic Resonance Spectroscopy



Features:

- Used to identify products of reactions
- Also gives information about chemical environment, connectivity and bonding of nuclei

Requirements:

- Pure or mostly pure sample of material (not useful for analyzing mixtures)
- > 1 mg material

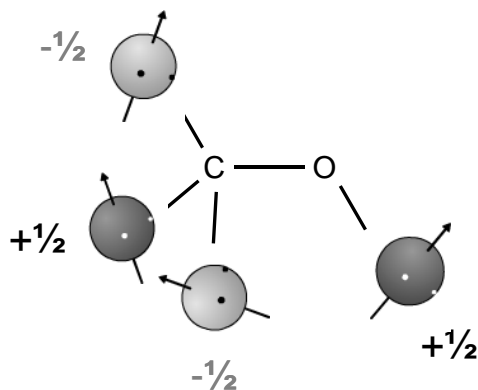
Nuclear Magnetic Resonance Spectroscopy Depends on Nuclear Spin

<u>Nucleus</u>	<u>Spins</u>	<u>Isotope Abundance</u>		<i>spin</i>
^1H	$\pm\frac{1}{2}$	99.9%		$+\frac{1}{2}$
^{12}C	0	98.9%		
^{13}C	$\pm\frac{1}{2}$	1.1%		
^{19}F	$\pm\frac{1}{2}$	100%		$-\frac{1}{2}$
^{31}P	$\pm\frac{1}{2}$	100%		

We'll be talking about spectroscopy of ^1H
(and later ^{13}C).

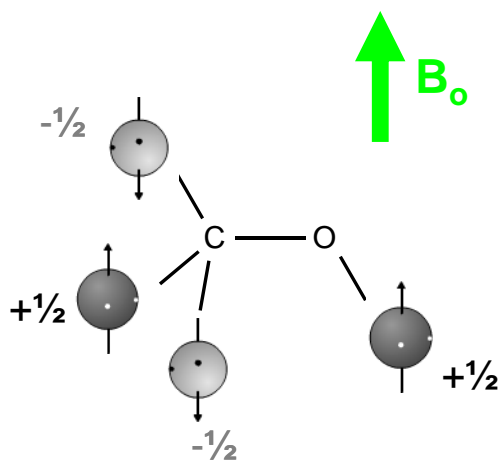
Each ^1H Nucleus Has Its Own Spin

We'll consider ^1H nuclei in CH_3OH as an example.



In the absence of an applied field, nuclei are randomly oriented.

Nuclear Spins Are Aligned By An Applied Magnetic Field

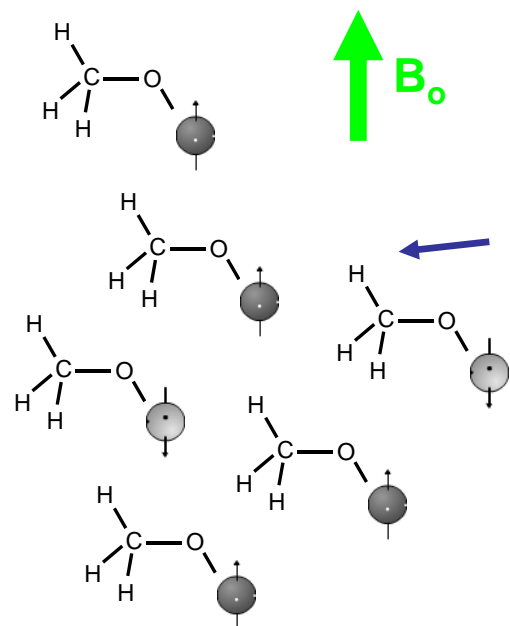


In the absence of an applied field, nuclei are randomly oriented.

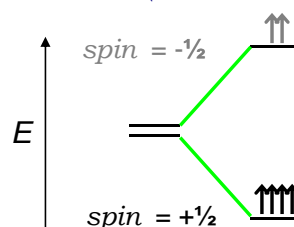
In the presence of an applied field B_0 , nuclei are oriented by the field.

+ spins align with the field,
- spins align against the field.

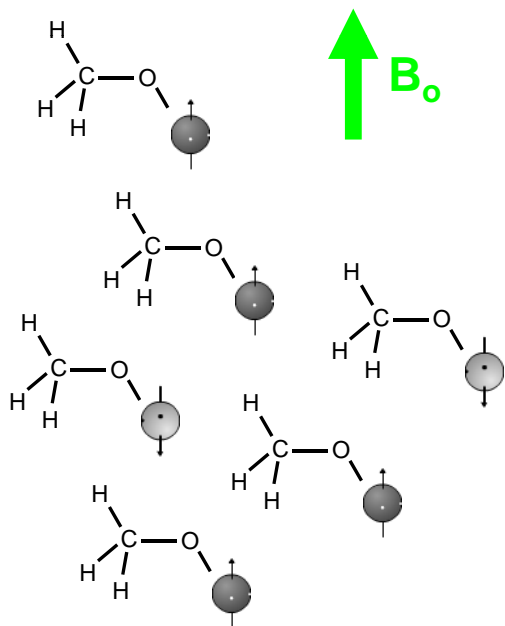
Overall, Applied Field Leads to Bulk Spin Magnetization



Being aligned with field is more stable than against field.
So, more spins align with the field.



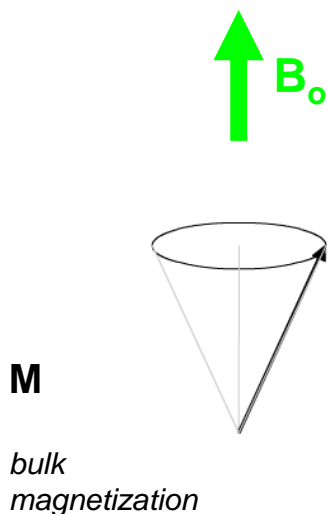
Overall, Applied Field Leads to Bulk Spin Magnetization



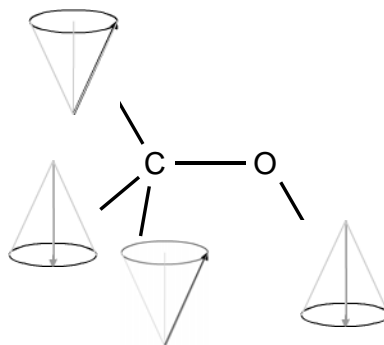
Being aligned with field is more stable than against field.
So, more spins align with the field, and sum of spins also aligns with the field.

= **M**
bulk magnetization

Spins, And Overall Spin, Precess (Wobble) in Applied Magnetic Field

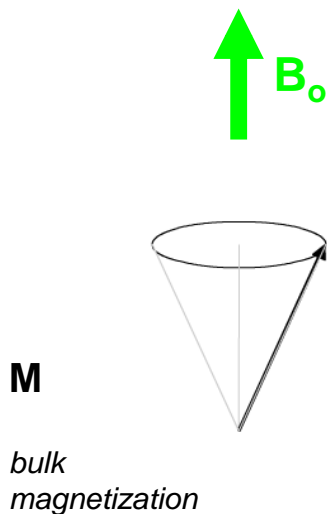


Again, using CH₃OH as an example,



All nuclei wobble at a characteristic frequency.

Spins, And Overall Spin, Precess (Wobble) in Applied Magnetic Field



Nuclei precess at the **Larmor frequency.**

$$\nu_o = \frac{\gamma B_o}{2\pi}$$

B_o	4.73 T	9.46 T	11.75 T
ν_o (¹H)	200 MHz	400 MHz	500 MHz
ν_o (¹³C)	50 MHz	75 MHz	125 MHz

(Precession is fast.)

Big Fields Means Big Magnets



Interior of a 4.73 T magnet (on display in NMR Facility, Smith Hall)

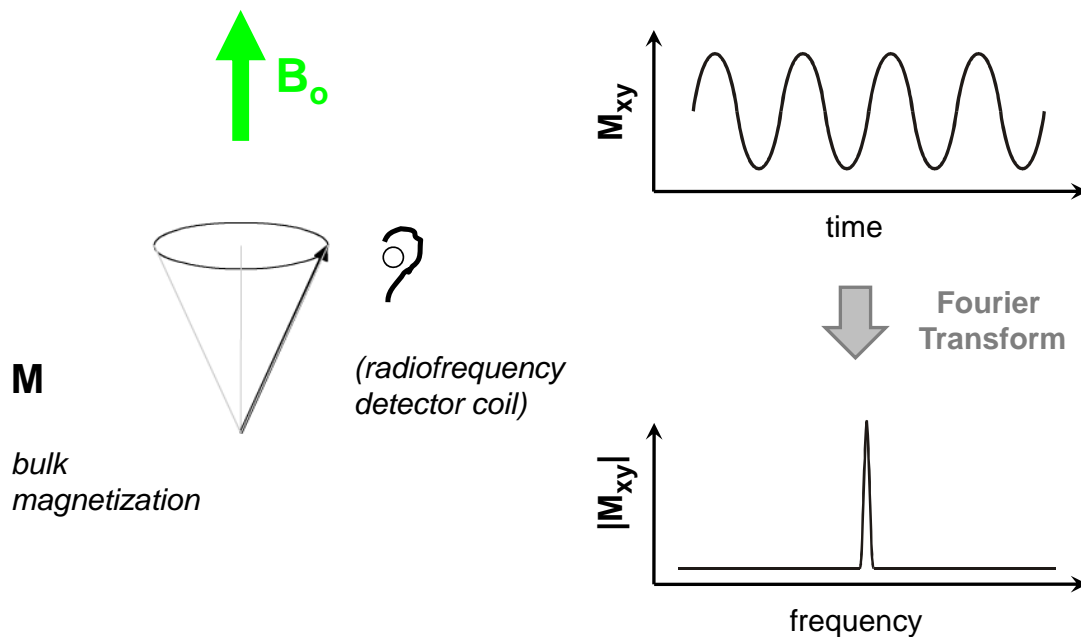


Installation of 16.45 T magnet in Hasselmo Hall.

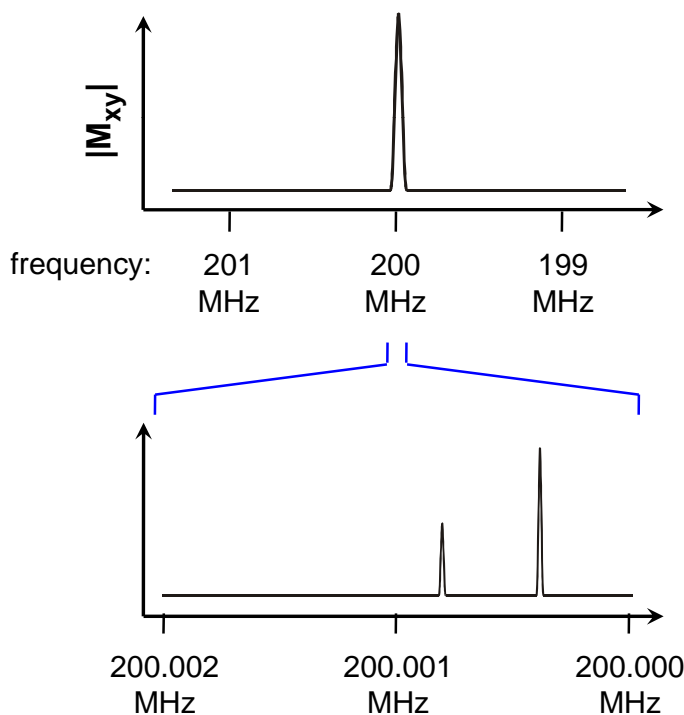
An NMR Facility



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.

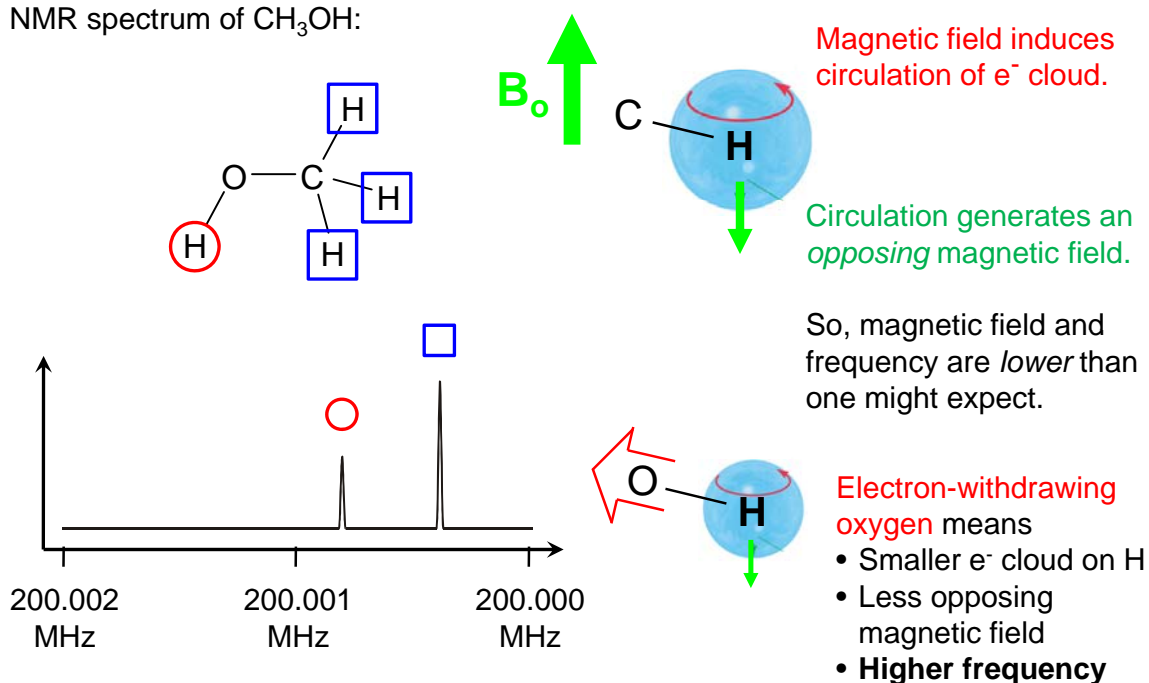
but what if we look closer??

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

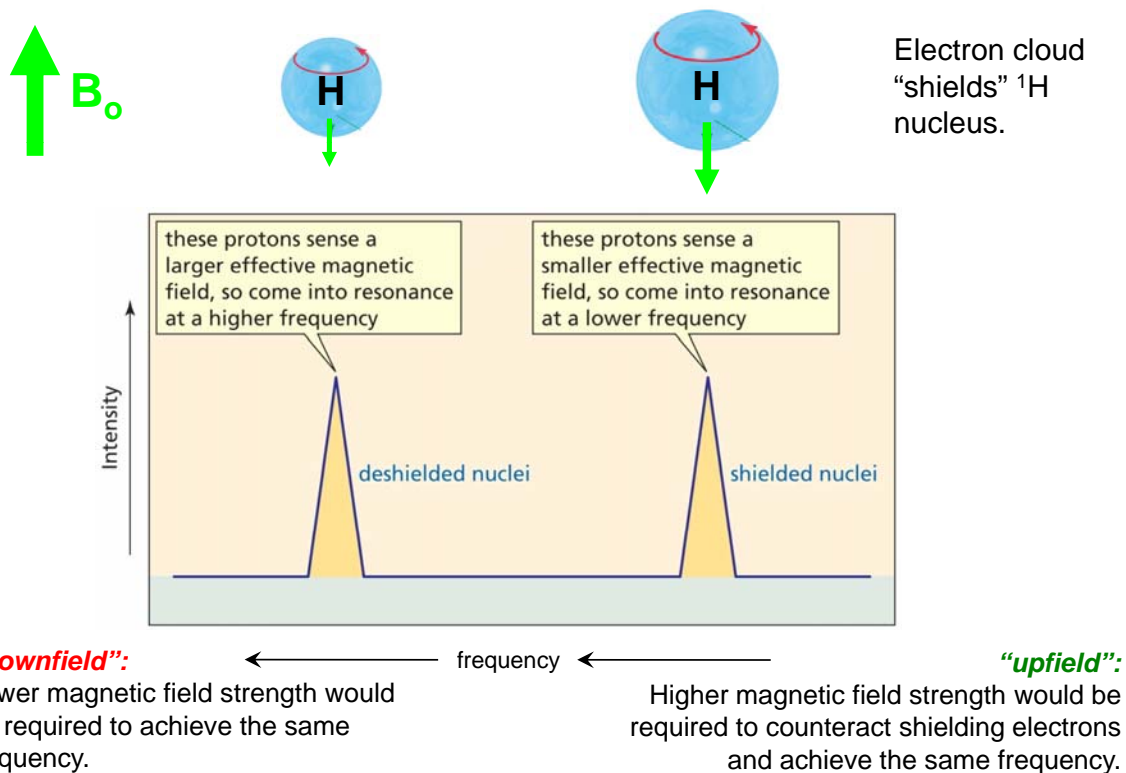
Differences in frequency reflect differences in magnetic environment.

“Shielding” Influences Proton Frequency

NMR spectrum of CH₃OH:



“Shielding” Influences Proton Frequency



Chemical Shift: A Proportional Horizontal Axis

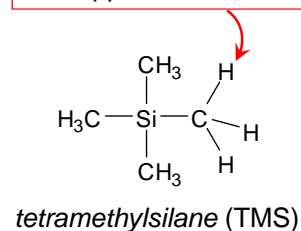
Problem: Differences in frequency depend on spectrometer field strength, vary from instrument to instrument.

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

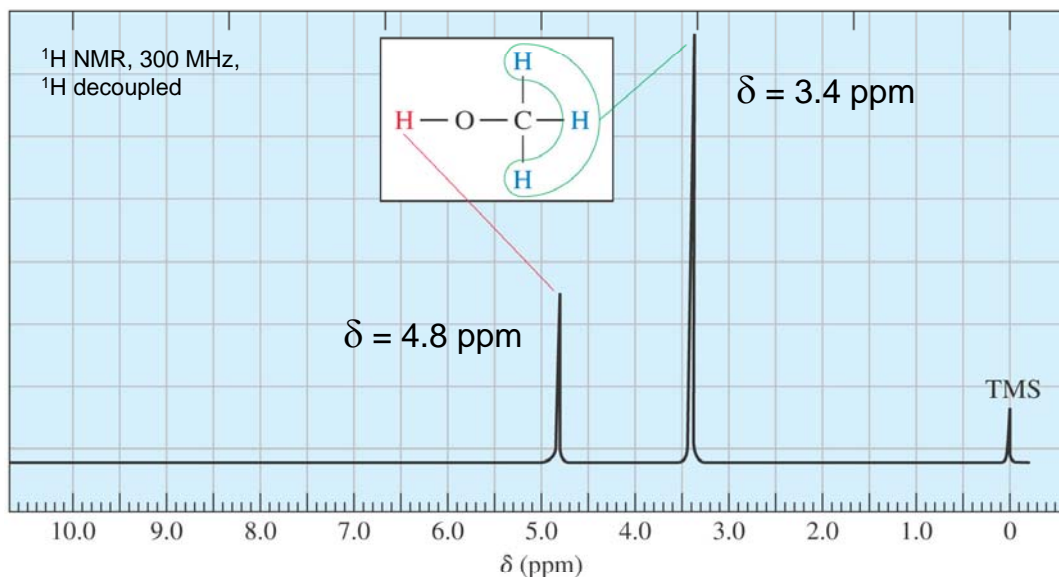
$$\text{chemical shift, ppm } \delta = \frac{\text{shift downfield from TMS (in Hz)}}{\text{spectrometer frequency (in MHz)}}$$

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

Frequency defined as
 $\delta = 0$ ppm



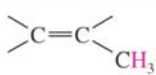
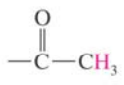
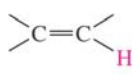
Chemical Shift: A Proportional Horizontal Axis



CH₃OH protons have these chemical shifts (ppm values), regardless of instrument they are measured on.

Different Types of Protons Have Characteristic Chemical Shifts

TABLE 13-3 Typical Values of Chemical Shifts

Type of Proton	Approximate δ	Type of Proton	Approximate δ
alkane ($-\text{CH}_3$)	0.9		1.7
alkane ($-\text{CH}_2-$)	1.3	Ph- H	7.2
alkane ($-\text{CH}-$)	1.4	Ph- CH ₃	2.3
	2.1	R- CHO	9-10
$-\text{C}\equiv\text{C}-\text{H}$	2.5	R- COOH	10-12
R- CH ₂ -X (X = halogen, O)	3-4	R- OH	variable, about 2-5
	5-6	Ar- OH	variable, about 4-7
		R- NH ₂	variable, about 1.5-4

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 ,

