About this part of the module: ***Topics to be covered.***

1. "^{1}H –Nuclear Magnetic Resonance (NMR) and ^{13}C-NMR spectroscopy;
2. Introduction, the nature of NMR absorption, chemical shifts and factors affecting them, information obtained from NMR spectra, more complex spin-spin splitting patterns, application of ^{1}H-NMR spectroscopy;
3. ^{13}C-NMR spectroscopy: introduction and characteristics, DEPT ^{13}C- NMR spectroscopy.

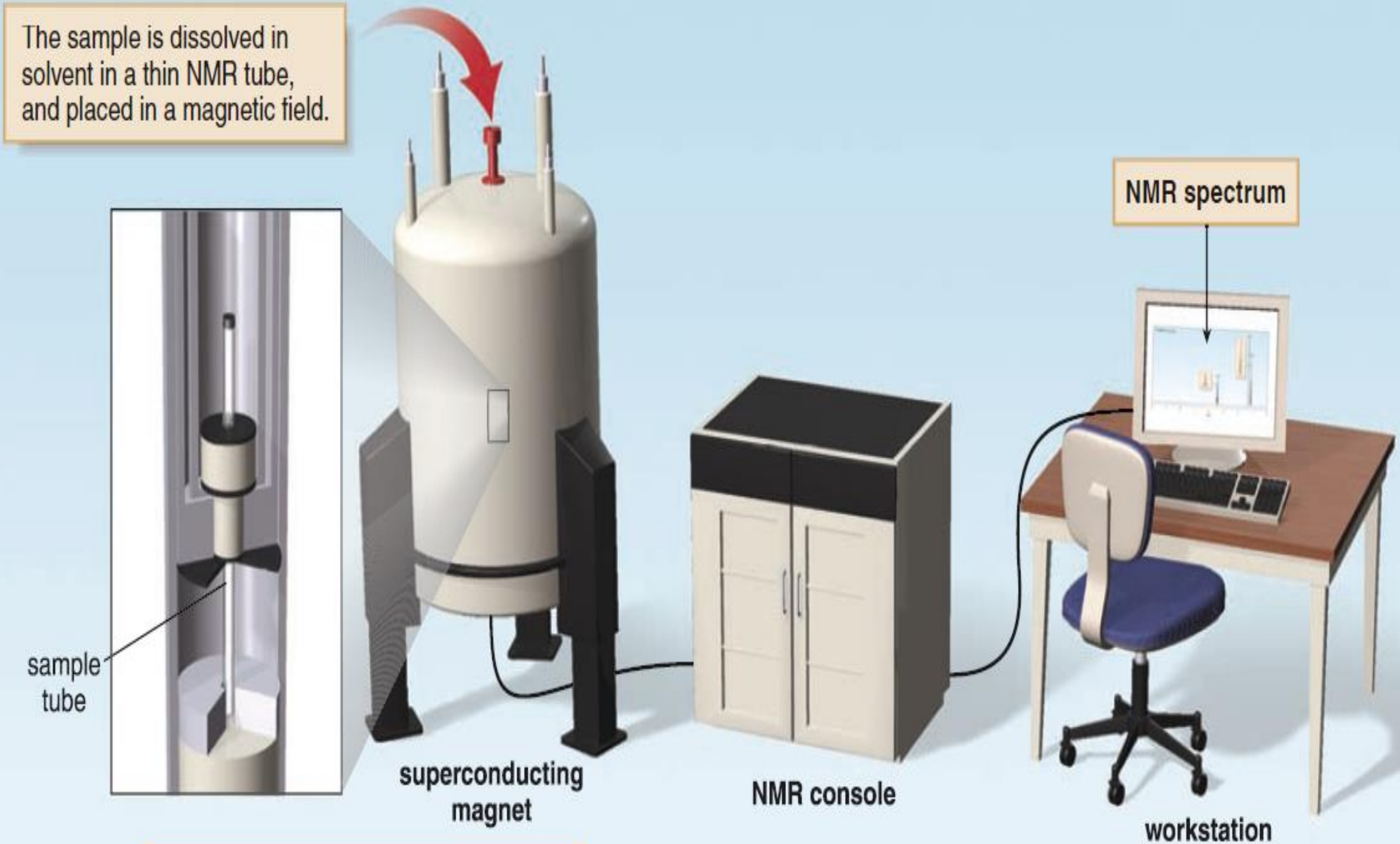
Lecture Contents:

1. ***Introduction to NMR,***
2. ***The nature of NMR absorption,***
3. ***Chemical shifts and factors affecting them,***
4. ***Information obtained from NMR spectra,***
5. ***More complex spin-spin splitting patterns,***
6. ***Application of ^{1}H-NMR spectroscopy;***
7. ***Solving selected problems.***
8. ***introduction to ^{13}C-NMR spectroscopy.***
9. ***Characteristics of ^{13}C- NMR spectroscopy.***
10. ***DEPT (45, 90, and 135) ^{13}C- NMR spectroscopy.***

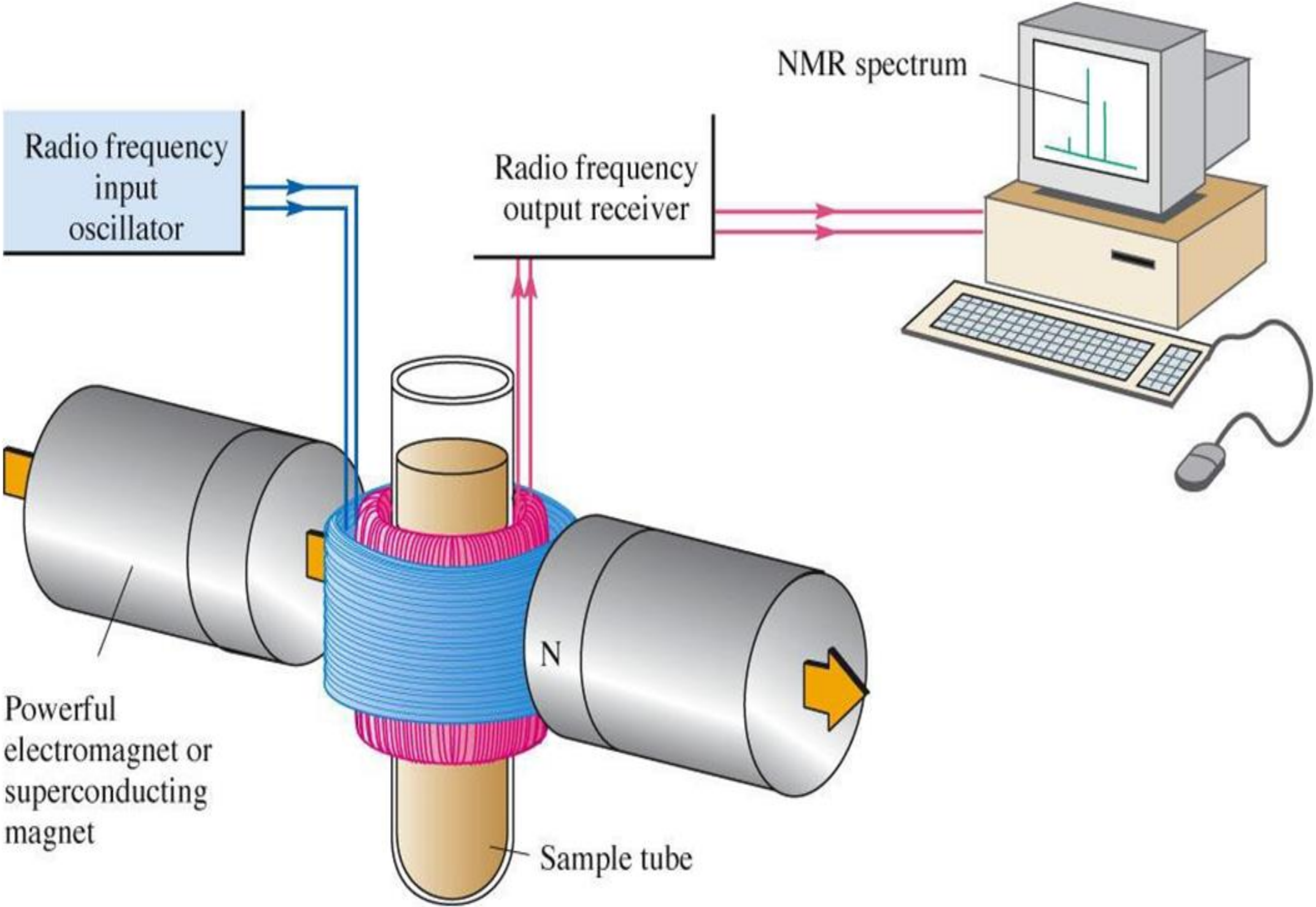
Introduction

Nuclear magnetic resonance spectroscopy is a powerful analytical technique used to characterize organic molecules by identifying carbon-hydrogen frameworks within molecules.

The sample is dissolved in solvent in a thin NMR tube, and placed in a magnetic field.



In the NMR probe, the sample is rotated in a magnetic field and irradiated with a short pulse of RF radiation.


Radio frequency input oscillator
Radio frequency output receiver
NMR spectrum
N
Powerful electromagnet or superconducting magnet
Sample tube

An NMR spectrometer:

- ✓ The sample is dissolved in a solvent, usually $CDCl_3$ (deuterochloroform), and placed in a magnetic field.
- ✓ A radiofrequency generator then irradiates the sample with a short pulse of radiation, causing resonance.
- ✓ When the nuclei fall back to their lower energy state, the detector measures the energy released, and a spectrum is recorded.
- ✓ The superconducting magnets in modern NMR spectrometers have coils that are cooled in liquid helium and conduct electricity with essentially no resistance.

An Introduction to NMR Spectroscopy

Two common types of NMR spectroscopy are used to characterize organic structure:

1. ***^{1}H NMR*** *is used to determine the type and number of H atoms in a molecule;*
2. ***^{13}C NMR*** *is used to determine the type of carbon atoms in the molecule.*

Natural Abundance:

- ^{1}H 99.9%
- ^{13}C 1.1%
- ^{12}C 98.9% (not NMR active)

Only nuclei that contain odd mass numbers (such as ^{1}H, ^{13}C, ^{19}F and ^{31}P) or odd atomic numbers (such as ^{2}H and ^{14}N) give rise to NMR signals.

The source of energy in NMR is radio waves which have long wavelengths, and thus low energy and frequency.

When low-energy radio waves interact with a molecule, they can change the nuclear spins of some elements, including ^{1}H and ^{13}C.

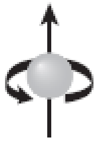
Theory of NMR phenomena

When a charged particle such as a proton spins on its axis, it creates a magnetic field. Thus, the nucleus can be considered to be a tiny bar magnet.

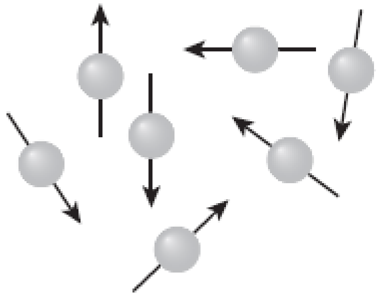
(a)Normally the nuclear magnetic fields are randomly oriented

(b)When placed in an external magnetic field (**B_o**), the nuclear magnetic field can either be aligned with the external magnetic or oppose the external magnetic field:

A spinning proton creates a magnetic field.

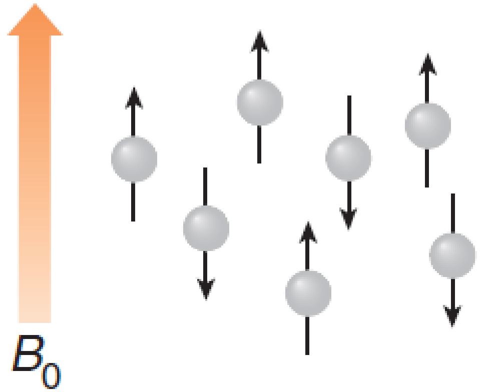


With no external magnetic field...



The nuclear magnets are randomly oriented.

In a magnetic field...

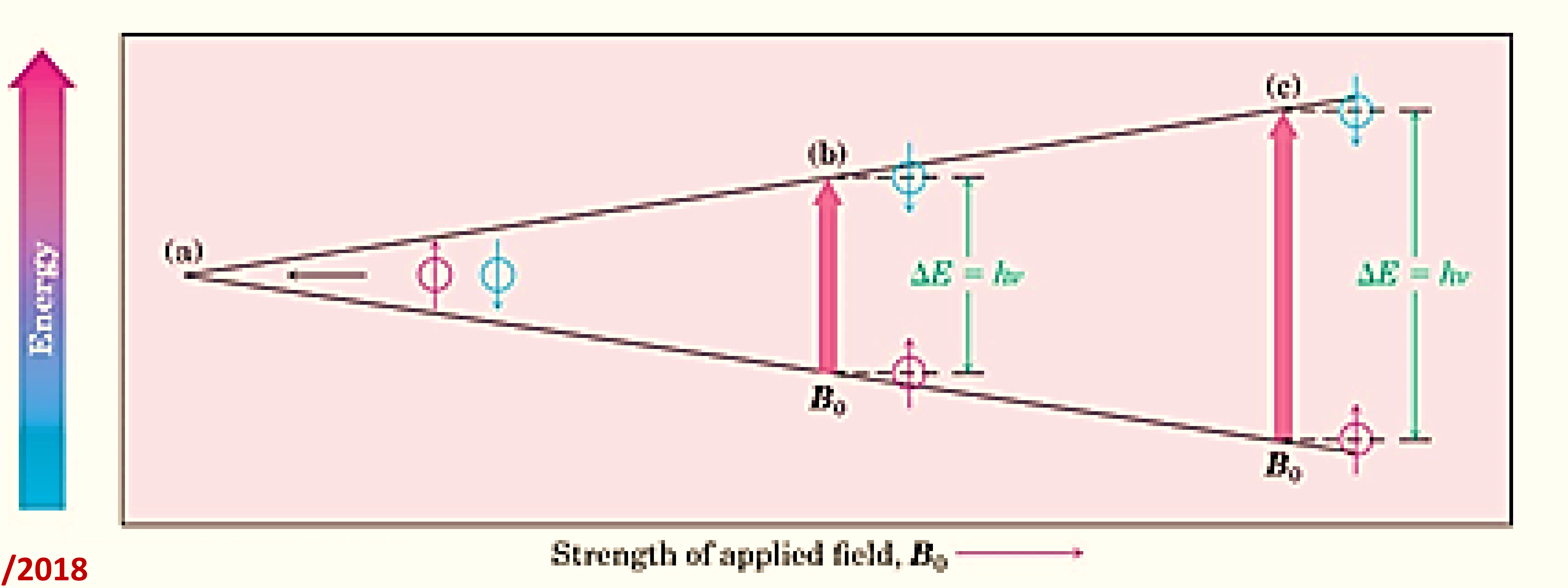


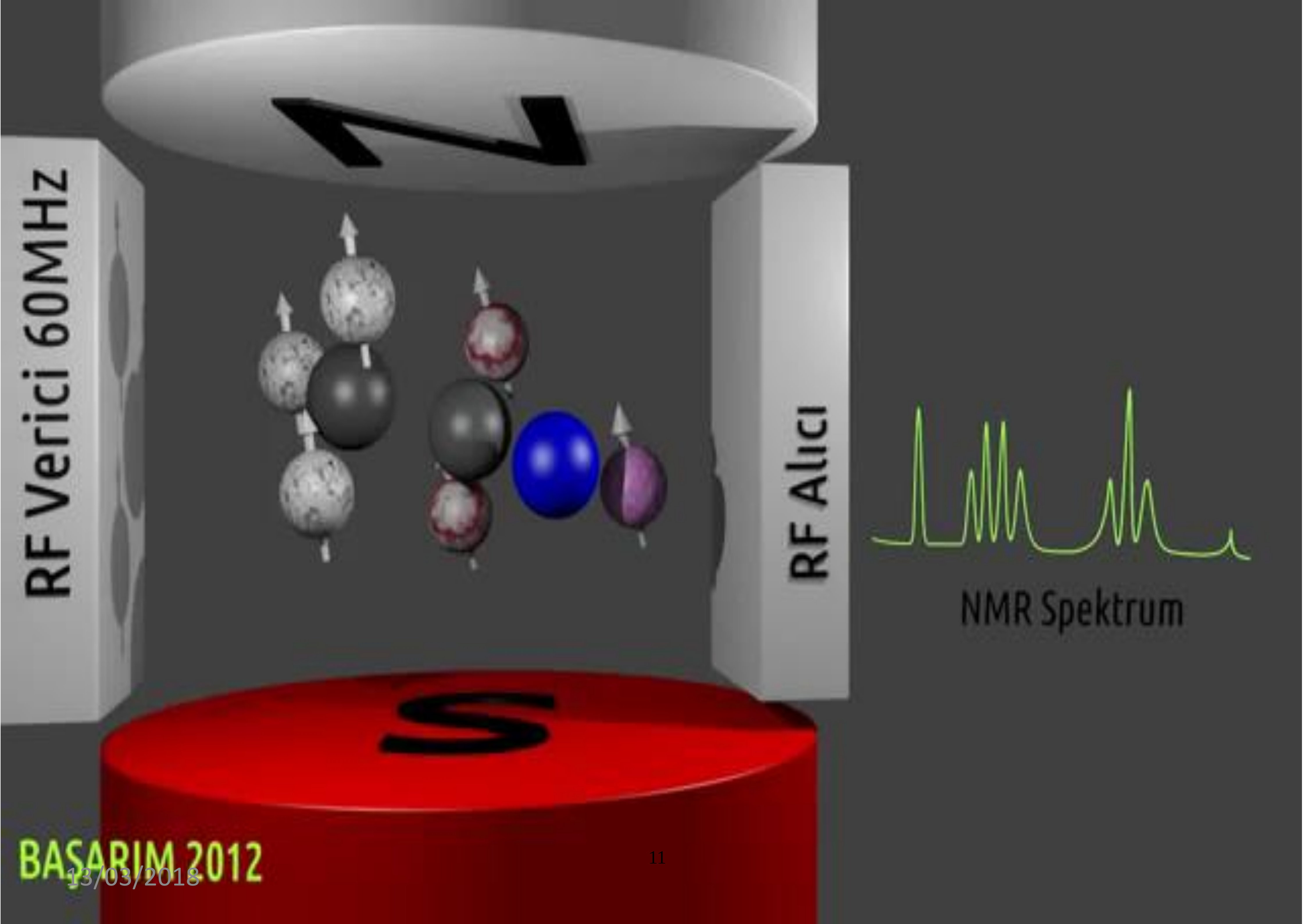
The nuclear magnets are oriented **with or against B_0.**

More nuclei are oriented with the applied field because this arrangement is lower in energy.

The energy difference between these two states is very small (<0.1 cal). Energy difference between aligned and opposed to the external magnetic field (B_o) is generally small and is dependent upon B_o

Applied EM radiation (radio waves) causes the nuclei to absorb energy and thus the spin flips and the nuclei are said to be in ***resonance*** with B_o




N
RF Verici 60MHz
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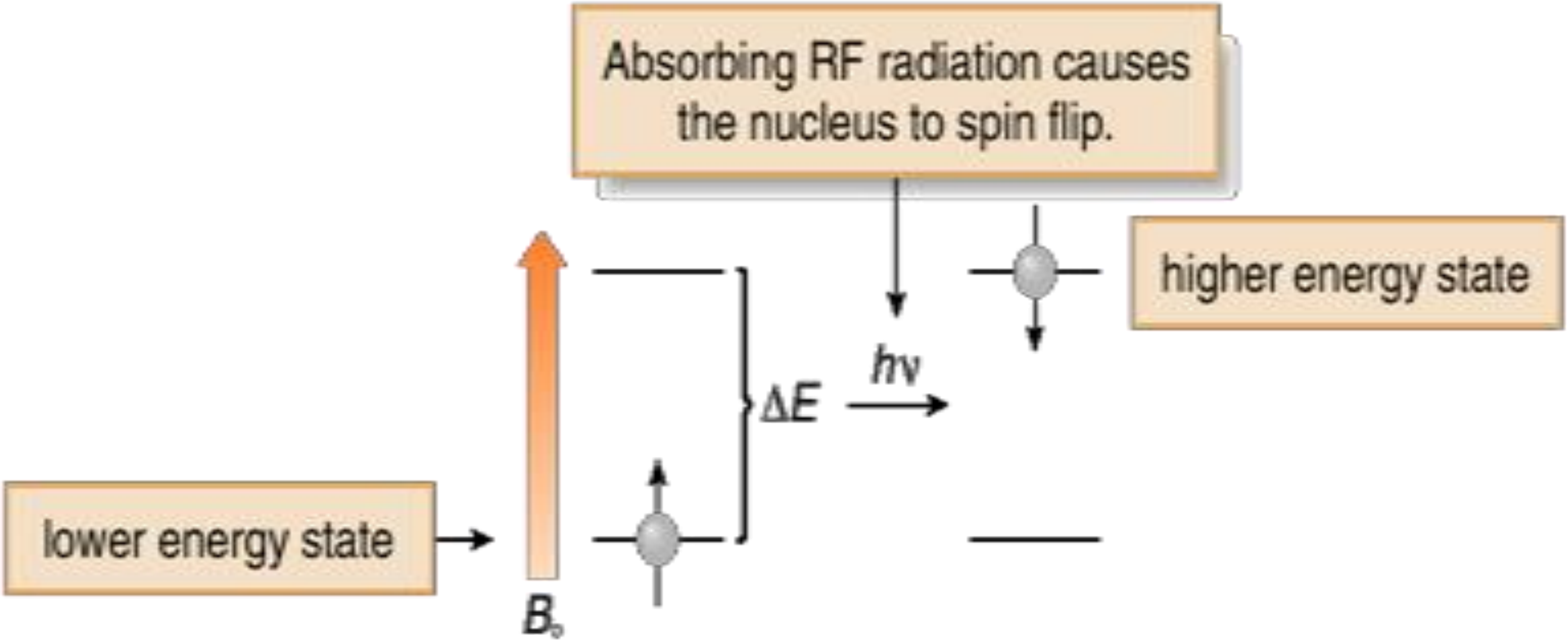
resonance, measured in hertz (Hz), or megahertz (MHz)—(1 MHz = 10^6 Hz).



$$\Delta E = hv$$

The frequency needed for resonance and the applied magnetic field strength are proportionally related:

$$V \alpha B_0$$

The stronger the magnetic field, the larger the energy difference between the two nuclear spin states, and the higher the v needed for resonance.

Difference in energy between the two states is given by:

$\Delta E = \gamma \mathbf{h} B_o / 2\pi$, $\Delta E = \mathbf{h} v$ *Therefore,* $v = \gamma B_o / 2\pi$

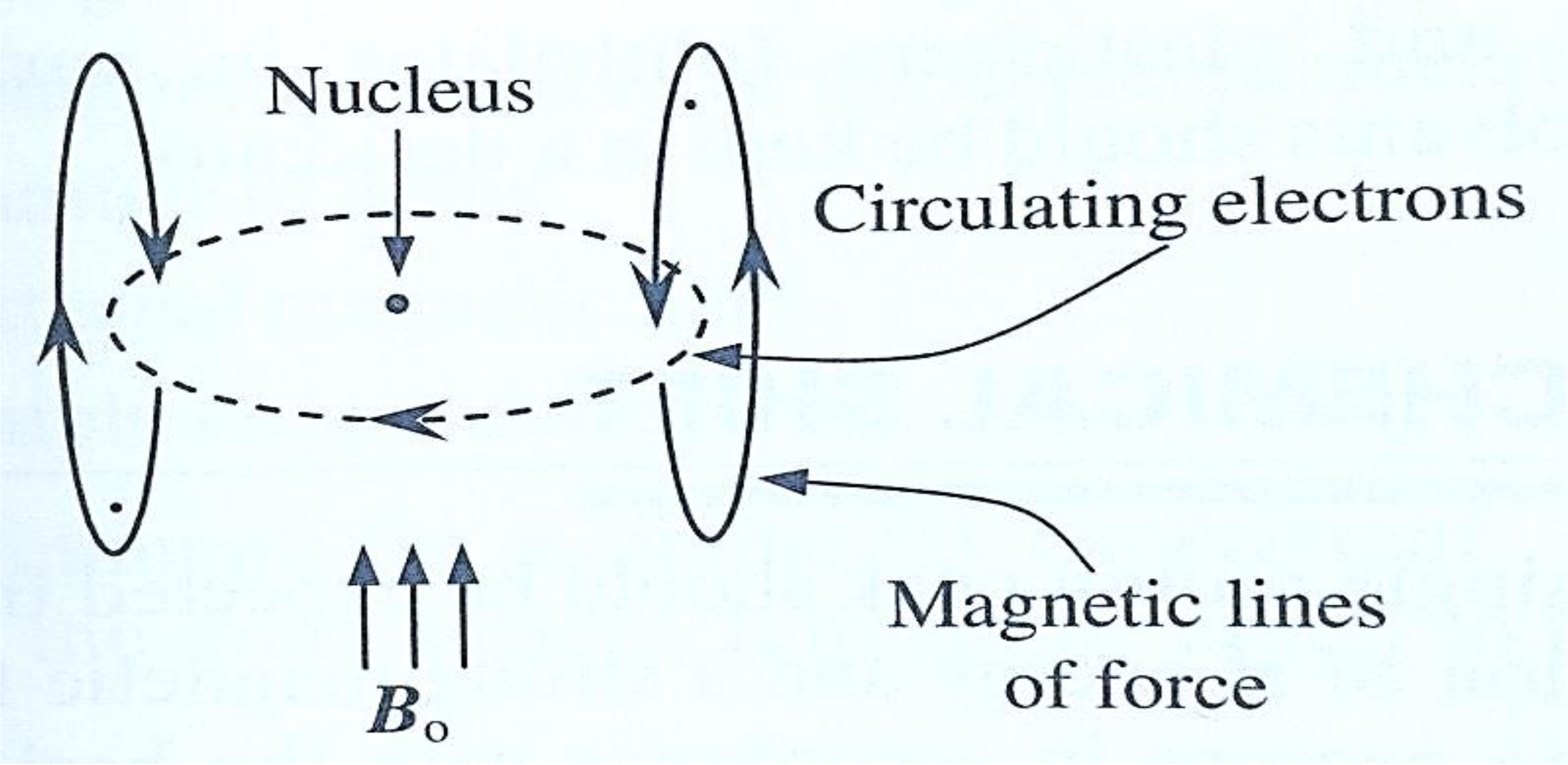
where:

B_o =external magnetic field
h = Planck's constant
γ= gyromagnetic ratio

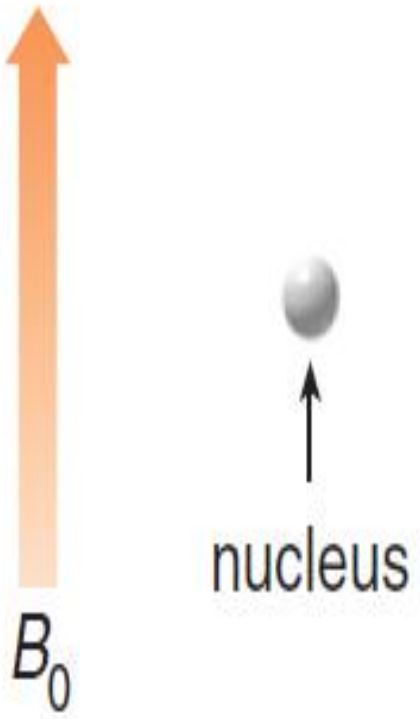
Protons in different environments absorb at slightly different frequencies, so they are distinguishable by NMR.

The frequency at which a particular proton absorbs is determined by its *electronic environment*.

The size of the magnetic field generated by the electrons around a proton determines where it absorbs.

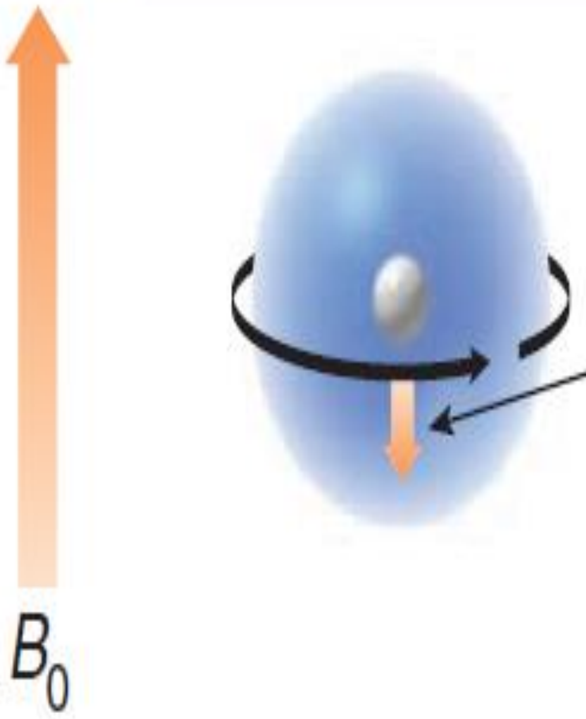


An isolated proton



The nucleus “feels” B_0 only.

A proton surrounded by electron density



magnetic field induced by the electron (opposite to B_0)

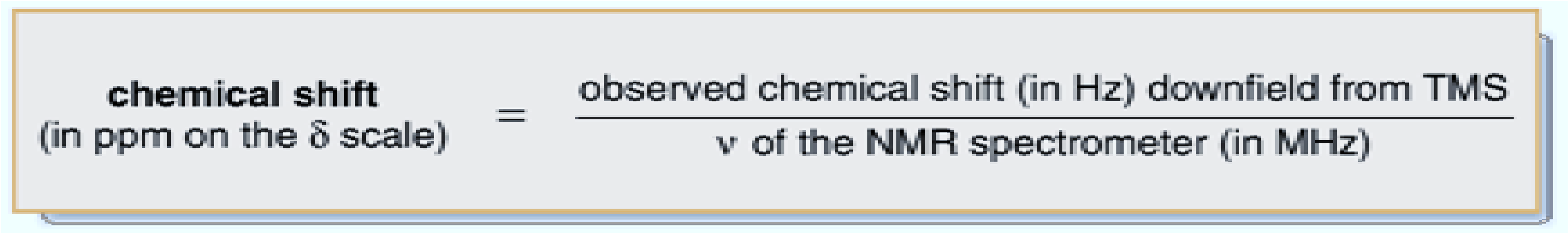
The induced field *decreases* the strength of the magnetic field “felt” by the nucleus.

This nucleus is shielded.

A proton in a molecule is ***shielded*** to a very small extent by its electron cloud, the density of which varies with the chemical environment.

The variation gives rise to differences in ***chemical shift*** positions; this ability to discriminate among the individual absorptions describes high resolution NMR spectrometry.

The ***chemical shift*** of the x axis gives the position of an NMR signal, measured in **ppm**, according to the following equation:



$$\underset{\text{(in ppm on the } \delta \text{ scale)}}{\textbf{chemical shift}} = \frac{\text{observed chemical shift (in Hz) downfield from TMS}}{\nu \text{ of the NMR spectrometer (in MHz)}}$$

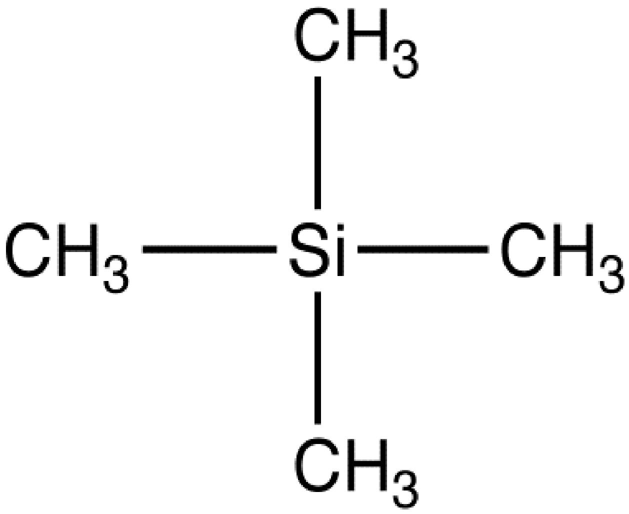
For instance, the proposed chemical shift of particular proton is 4ppm then the observed chemical shift (in Hz) downfield from TMS in 300MHz and 600MHz NMR spectrometry will be 1200Hz and 2400Hz respectively. ***(Hint: utilize the previous formula)***

Modern NMR spectrometers use a constant magnetic field strength B_0, and then a narrow range of frequencies is applied to achieve the resonance of all protons.

The difference in absorption position of particular proton from absorption position of reference proton is called the chemical shift of a particular proton.

The most generally useful reference compound is tetramethylsilane (TMS).

Advantages of TMS:



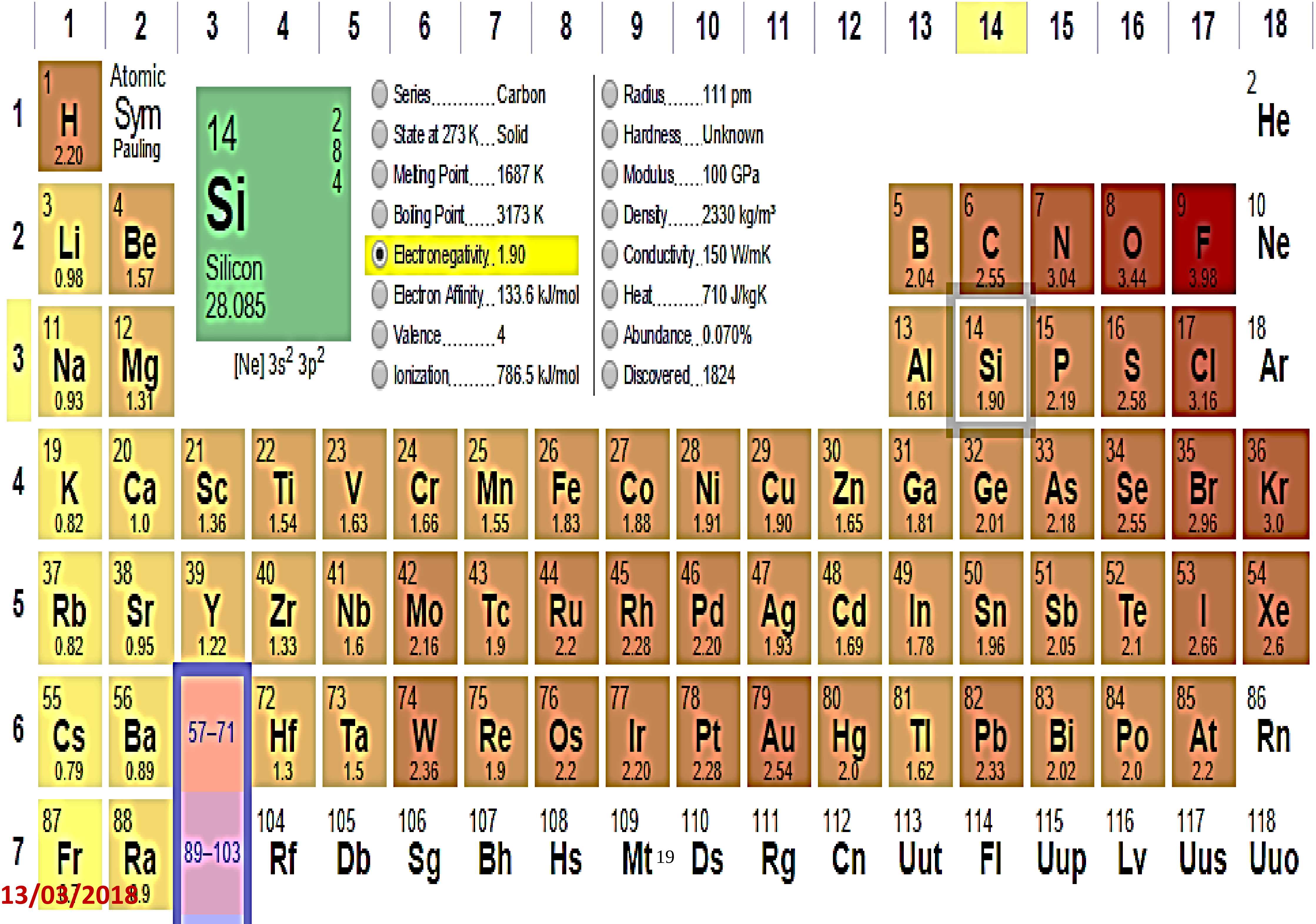
1. *Chemically inert.*
2. *Symmetrical.*
3. *Volatile.*
4. *Soluble in most organic solvents.*
5. *Gives single, intense, and sharp peak.*
6. *Its protons are more* ***shielded*** *than almost all organic protons.*

H.W:

How can you explain the shielding attribute of the TMS protons?

Hint: **use the electronegativity features of atoms.**

http://www.ptable.com/#Property/Electronegativity (shown in the next slide)



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 2.20	Atomic Sym Pauling																2 He
2	3 Li 0.98	4 Be 1.57											5 B 2.04	6 C 2.55	7 N 3.04	8 O 3.44	9 F 3.98	10 Ne
3	11 Na 0.93	12 Mg 1.31											13 Al 1.61	14 Si 1.90	15 P 2.19	16 S 2.58	17 Cl 3.16	18 Ar
4	19 K 0.82	20 Ca 1.0	21 Sc 1.36	22 Ti 1.54	23 V 1.63	24 Cr 1.66	25 Mn 1.55	26 Fe 1.83	27 Co 1.88	28 Ni 1.91	29 Cu 1.90	30 Zn 1.65	31 Ga 1.81	32 Ge 2.01	33 As 2.18	34 Se 2.55	35 Br 2.96	36 Kr 3.0
5	37 Rb 0.82	38 Sr 0.95	39 Y 1.22	40 Zr 1.33	41 Nb 1.6	42 Mo 2.16	43 Tc 1.9	44 Ru 2.2	45 Rh 2.28	46 Pd 2.20	47 Ag 1.93	48 Cd 1.69	49 In 1.78	50 Sn 1.96	51 Sb 2.05	52 Te 2.1	53 I 2.66	54 Xe 2.6
6	55 Cs 0.79	56 Ba 0.89	57–71	72 Hf 1.3	73 Ta 1.5	74 W 2.36	75 Re 1.9	76 Os 2.2	77 Ir 2.20	78 Pt 2.28	79 Au 2.54	80 Hg 2.0	81 Tl 1.62	82 Pb 2.33	83 Bi 2.02	84 Po 2.0	85 At 2.2	86 Rn
7	87 Fr 0.7	88 Ra 0.9	89–103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

14
2
8
4
Si
Silicon
28.085
[Ne] $3s^2\ 3p^2$

○ Series..........Carbon
○ State at 273 K...Solid
○ Melting Point.....1687 K
○ Boiling Point.....3173 K
● Electronegativity..1.90
○ Electron Affinity...133.6 kJ/mol
○ Valence..........4
○ Ionization........786.5 kJ/mol

○ Radius........111 pm
○ Hardness.....Unknown
○ Modulus......100 GPa
○ Density.......2330 kg/m³
○ Conductivity..150 W/mK
○ Heat..........710 J/kgK
○ Abundance...0.070%
○ Discovered...1824

Thus, the protons in different chemical environments have different chemical shifts.

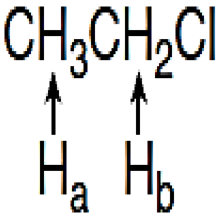
Conversely, the protons in the same chemical environments have the same chemical shifts.

H.W:

Do the following methylene groups have the same or different chemical environments?

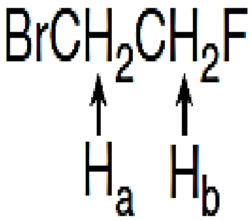
1. $ClCH_2CH_2OH$
2. $ClCH_2CH_2Cl$
3. $CH_3CH_2CH_2OH$
4. $CH_3CH_2CH_2CH_3$

Examples of shielding and de-shielding



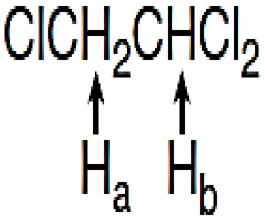
$$\underset{H_a}{\overset{\uparrow}{CH_3}}\underset{H_b}{\overset{\uparrow}{CH_2}}Cl$$

- The H_b protons are **deshielded** because they are closer to the electronegative Cl atom, so they absorb **downfield** from H_a.



$$Br\underset{H_a}{\overset{\uparrow}{CH_2}}\underset{H_b}{\overset{\uparrow}{CH_2}}F$$

- Because F is more electronegative than Br, the H_b protons are more **deshielded** than the H_a protons and absorb farther **downfield.**



$$Cl\underset{H_a}{\overset{\uparrow}{CH_2}}\underset{H_b}{\overset{\uparrow}{CH}}Cl_2$$

- The larger number of electronegative Cl atoms (two versus one) **deshields** H_b more than H_a, so it absorbs **downfield** from H_a.