

Nuclear magnetic resonance spectroscopy (N.M.R)

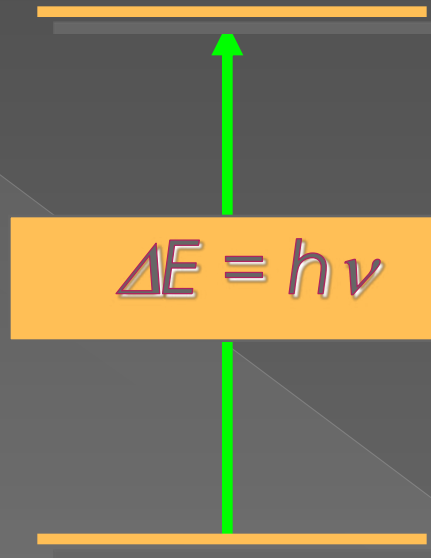
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Nuclear Magnetic Resonance Spectroscopy:

It is commonly referred to as NMR, and is a technique which exploits the magnetic properties of certain nuclei to study physical, chemical, and biological properties of matter. The most interesting isotope ^{12}C has nuclear spin 0 and does NOT exhibit magnetic resonance. The same goes for ^{16}O and ^{32}S (the naturally occurring isotopes). Fortunately, the most abundant isotope ^1H has $I = \frac{1}{2}$ and so it does exhibit magnetic resonance. And also ^{13}C , ^{19}F , ^{31}P and ^{15}N exhibit nuclear magnetic resonance. Thus the wide applications of N.M.R. are based on ^1H and ^{13}C .

Nuclear Magnetic Resonance Spectroscopy

- Nuclear magnetic resonance (NMR) spectroscopy is based on the measurement of absorption of electromagnetic radiation in the radio-frequency region of roughly 4 to 900 MHz.
- Nuclei of atoms rather than outer electrons are involved in the absorption process.
- In order to cause nuclei to develop the energy states required for absorption to occur, it is necessary to place the analyte in an intense magnetic field.
- Nuclear magnetic resonance spectroscopy is one of the most powerful tools for elucidating the structure of chemical species.



Electromagnetic radiation is absorbed when the energy of photon corresponds to difference in energy between two states.

What Kind of States?

electronic

UV-Vis

vibrational

infrared

rotational

microwave

nuclear spin

radiofrequency

NMR is concerned with change in the direction of spin orientation as the result of the absorption of radiofrequency radiation.

The two nuclei that are most useful to organic chemists are:

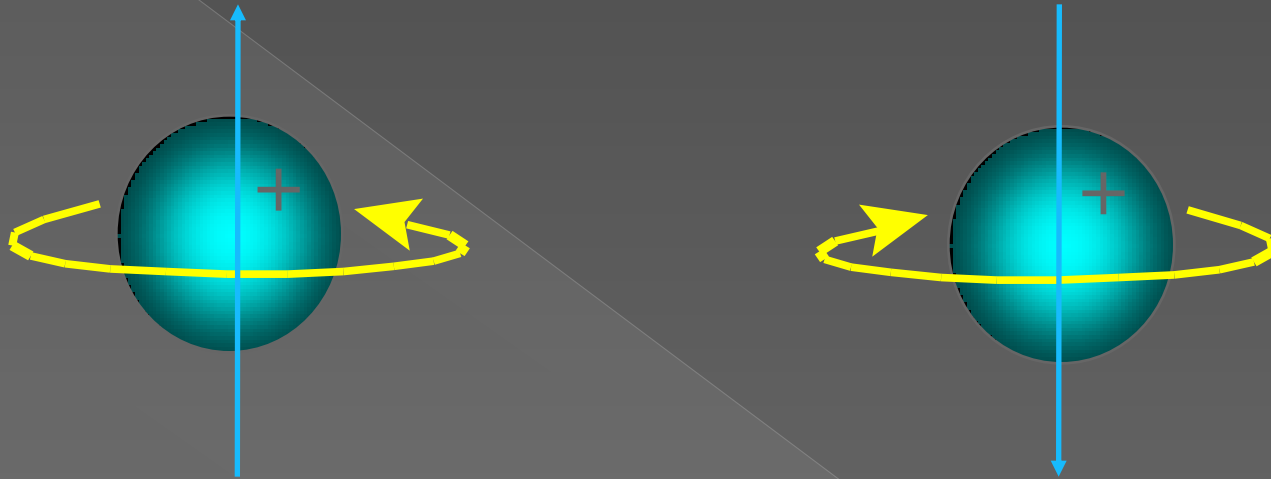
^1H and ^{13}C

both have spin = $\pm 1/2$

^1H is 99% at natural abundance

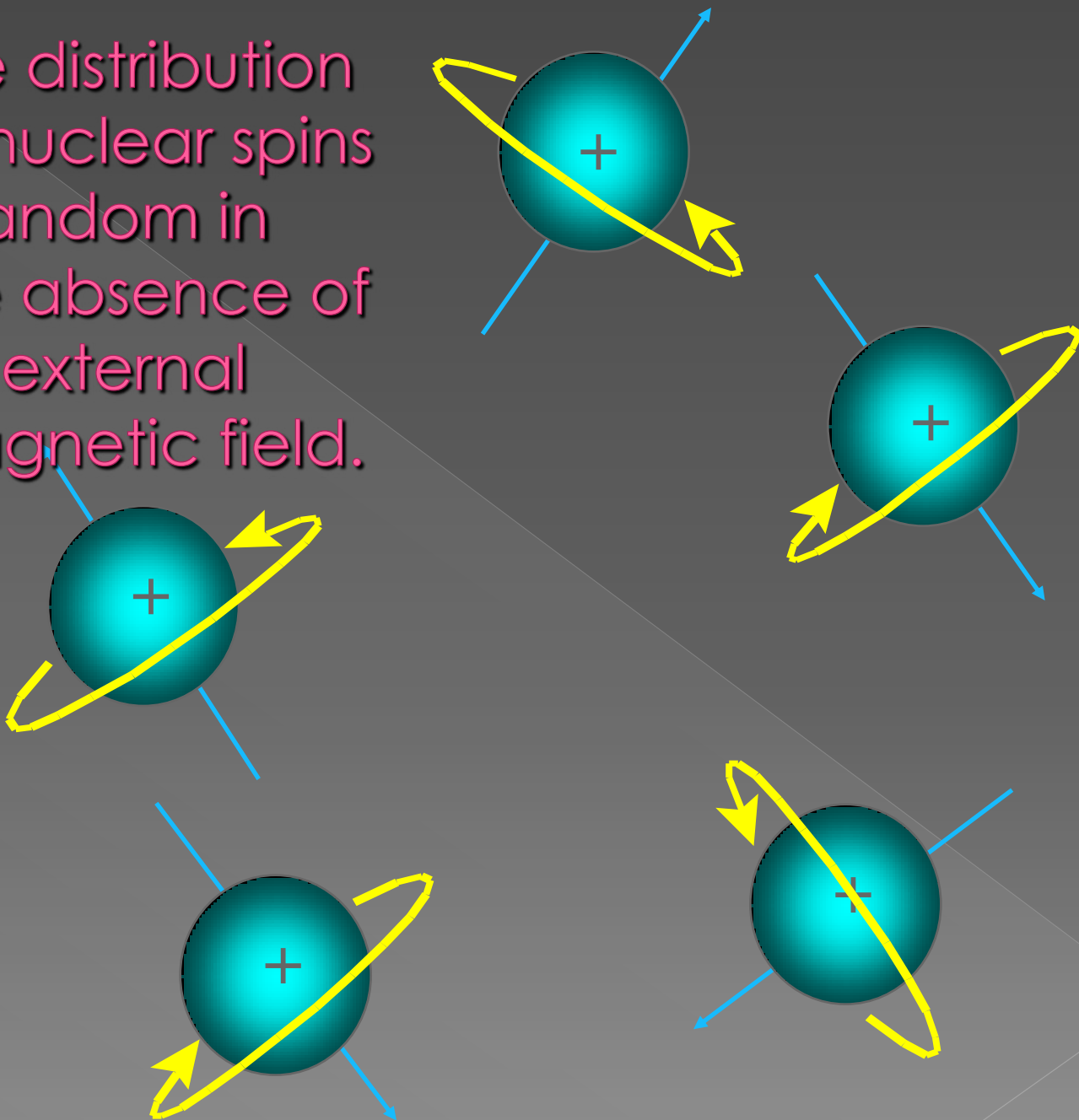
^{13}C is 1.1% at natural abundance

Nuclear Spin

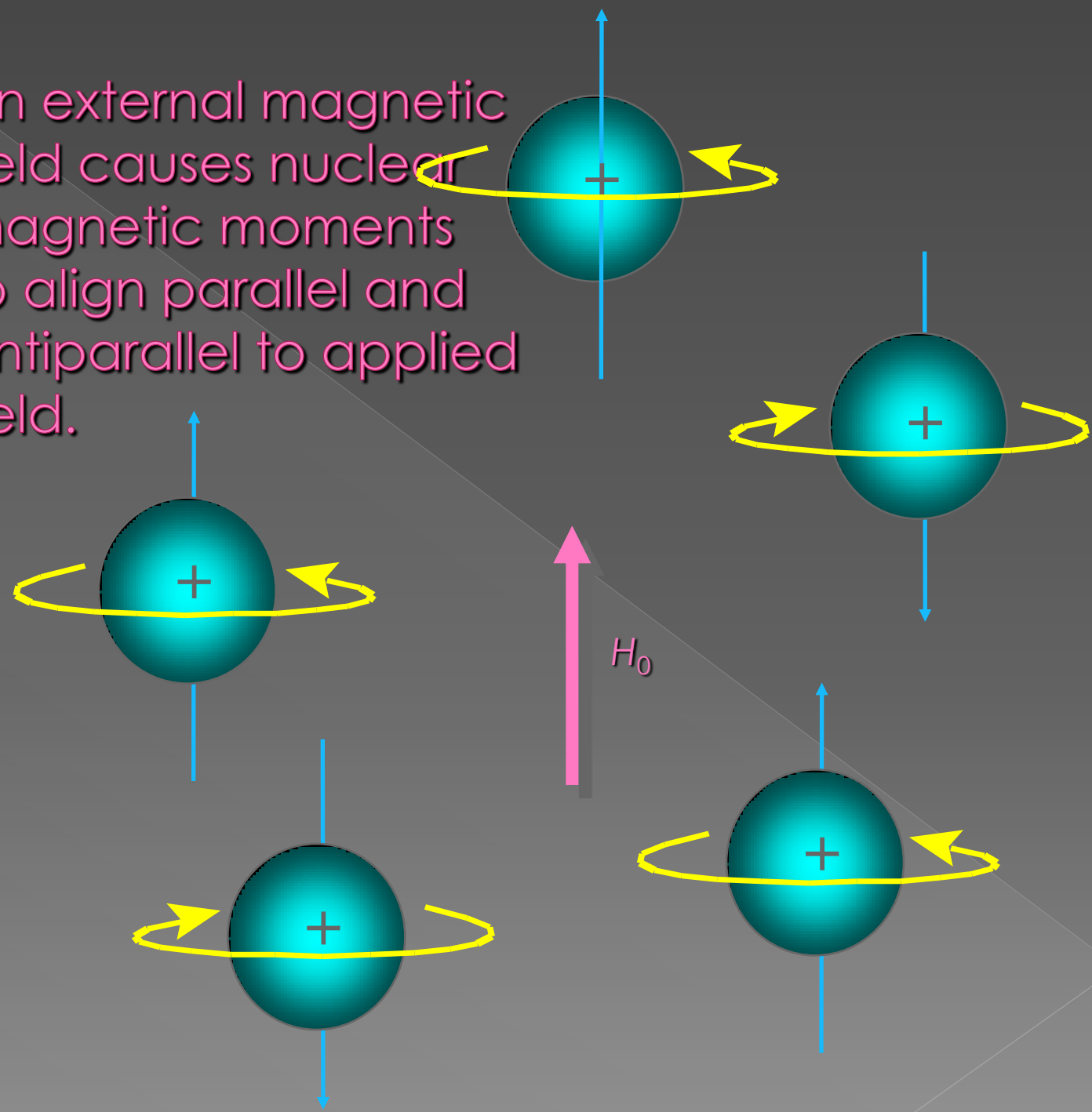


A spinning charge, such as the nucleus of ^1H or ^{13}C , generates a **magnetic field**. The **magnetic field** generated by a nucleus of spin $+1/2$ is opposite in direction from that generated by a nucleus of spin $-1/2$.

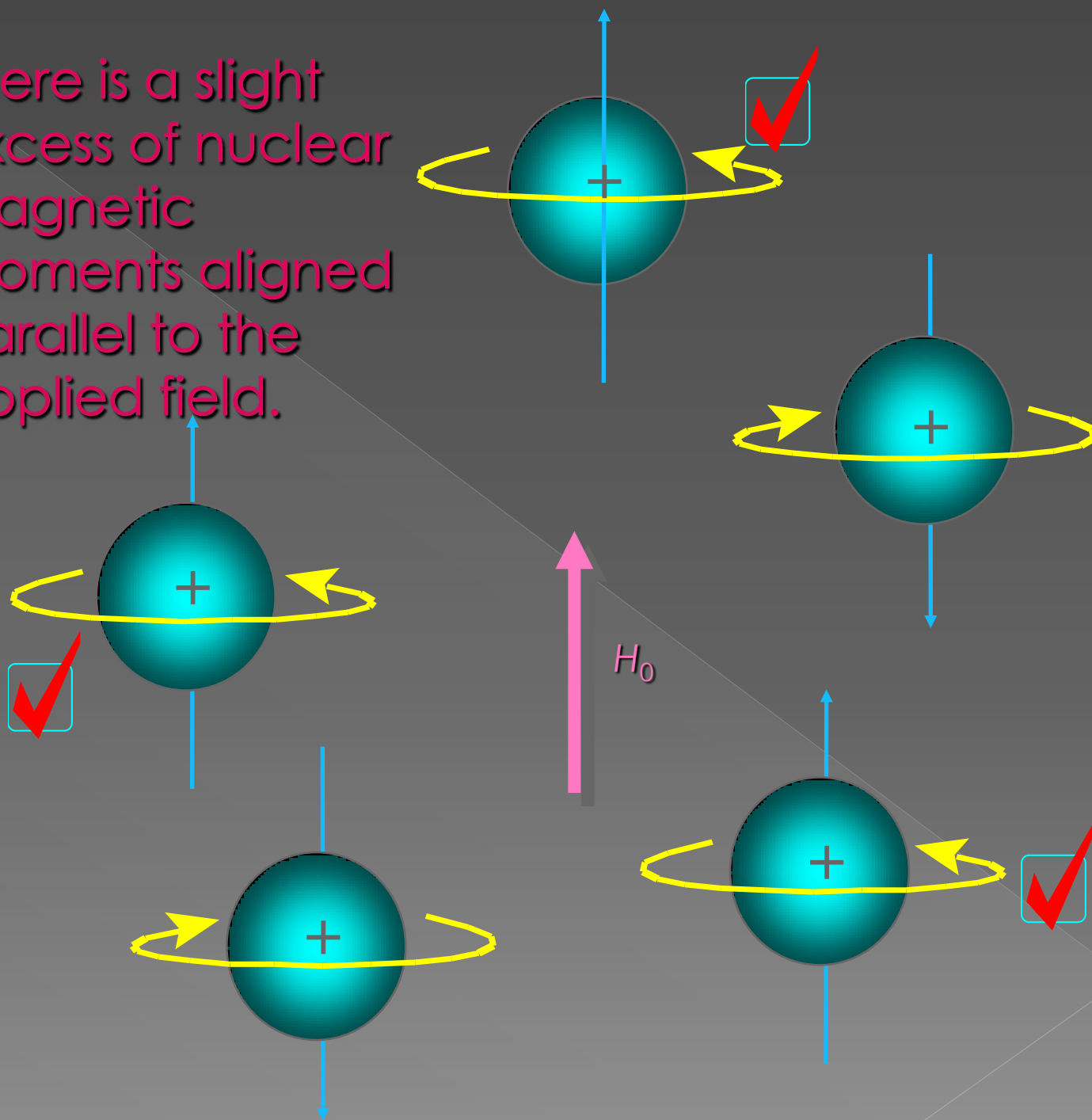
The distribution of nuclear spins is random in the absence of an external magnetic field.



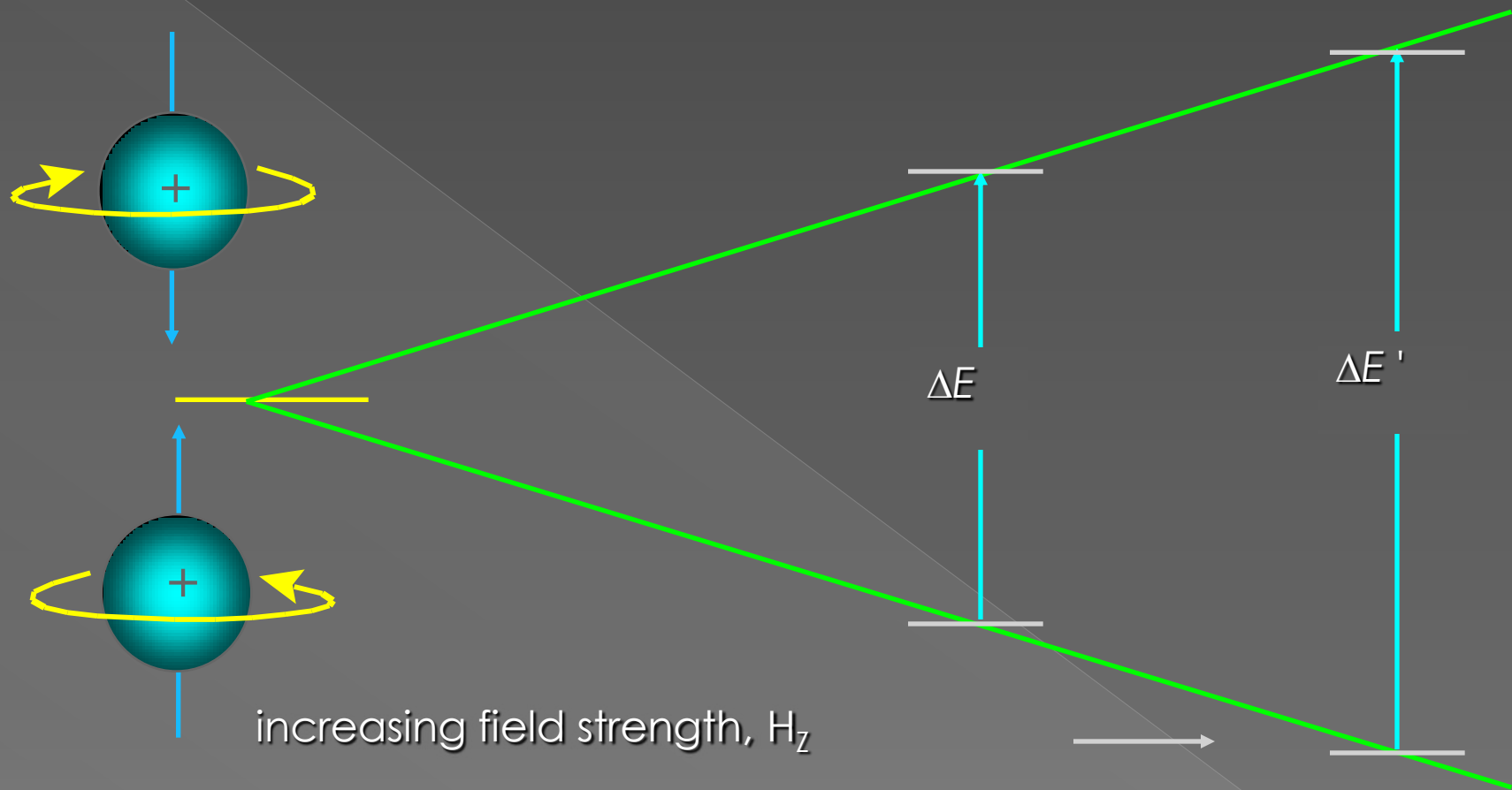
An external magnetic field causes nuclear magnetic moments to align parallel and antiparallel to applied field.



There is a slight excess of nuclear magnetic moments aligned parallel to the applied field.



Energy Differences Between Nuclear Spin States



no energy difference in absence of magnetic field

proportional to strength of external magnetic field

Some important relationships in NMR

The frequency of absorbed electromagnetic radiation is proportional to

the energy difference between two nuclear spin states which is proportional to

the applied magnetic field

Some important relationships in NMR

The frequency (ν) of absorbed electromagnetic radiation is proportional to

Units

Hz (s^{-1})

the energy difference (ΔE) between two nuclear spin states which is proportional to

kJ/mol
(kcal/mol)

the applied magnetic field (H_0)

tesla (T)

Some important relationships in NMR

The frequency of absorbed electromagnetic radiation is different for different elements, and for different isotopes of the same element.

For a field strength of $H_0 = 4.7 \text{ T}$:

^1H absorbs radiation having a frequency of 200 MHz ($200 \times 10^6 \text{ s}^{-1}$)

^{13}C absorbs radiation having a frequency of 50.4 MHz ($50.4 \times 10^6 \text{ s}^{-1}$)

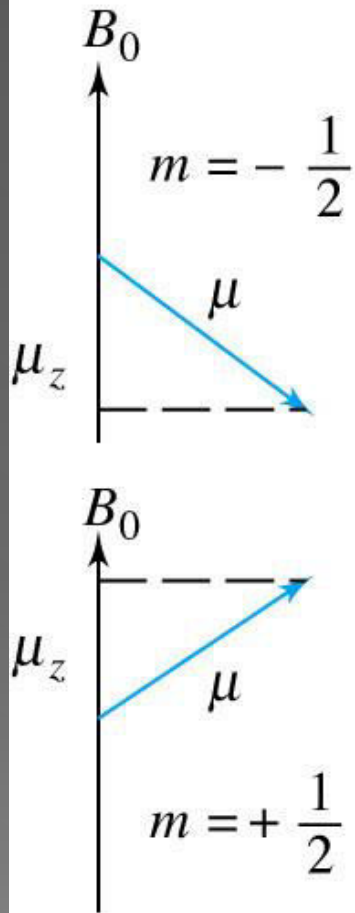
Compare to 10^{15} s^{-1} for electrons; 10^{13} s^{-1} for vibrations

Some important relationships in NMR

The frequency of absorbed electromagnetic radiation for a particular nucleus (such as ^1H or ^{13}C) depends on the **molecular** environment of the nucleus (the electronic environment).

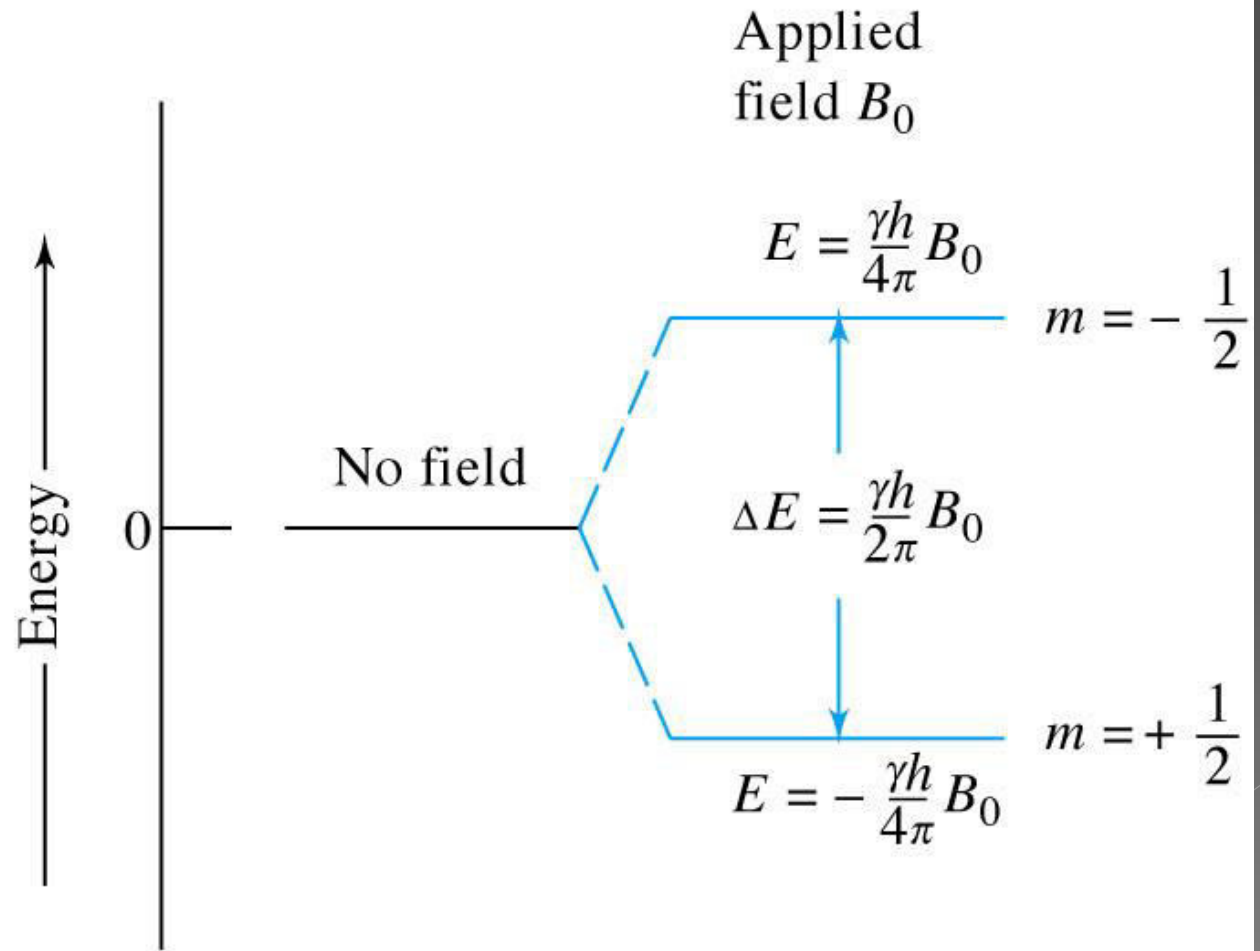
This is why NMR is such a useful tool for structure determination. The signals of different protons and carbon atoms in a molecule show different signals, just like different functional groups show different signals in the IR.

Magnetic moments

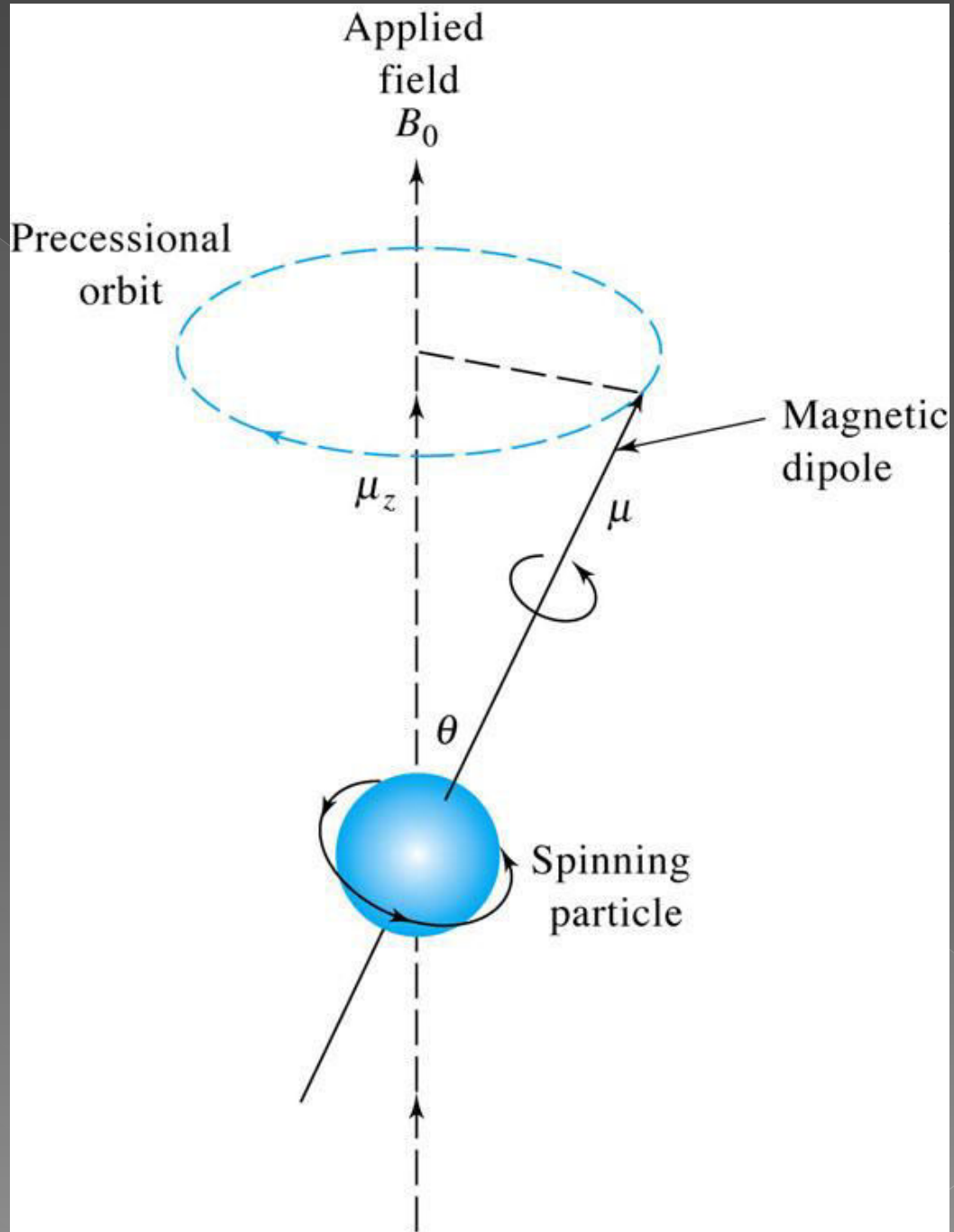


(a)

Energies



(b)



Nuclear Magnetic Resonance Spectroscopy:

- NMR is a physical phenomenon in which nuclei of a given substance under magnetic field absorb and re-emit electromagnetic radiation. This energy is at a particular resonance frequency which depends on the strength of the magnetic field and magnetic properties of the isotope of the atoms.
- As nuclei with an odd mass or odd atomic number have nuclear spin (in a similar fashion to the spin of electrons), the spins of nuclei are sufficiently different that NMR experiments can be sensitive for only one particular isotope of one particular element.
- The rules for determining the net spin of a nucleus are as follows:
 - 1. If both the number of neutrons and the number of protons are even, then the nucleus has NO spin.
 - 2. If the number of neutrons plus the number of protons is odd, then the nucleus has a half-integer spin (i.e. $1/2$, $3/2$, $5/2$)
 - 3. If the number of neutrons and the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3)
- Note that the overall spin is important. Quantum mechanics shares that a nucleus of spin ' I ' has $2I+1$ possible orientations, i.e., a nucleus with spin $1/2$ will have 2 possible orientations. These orientations are of equal energy in the absence of external magnetic field, but the energy levels split once magnetic field is applied.

Nuclear Magnetic Resonance Spectroscopy:

- The energy separation between the different nuclear spin states lies in the microwave spectral region and hence NMR transitions are excited by frequencies about 10^8 Hz and can be varied by applying a magnetic field.
- The nucleus has a positive charge and is spinning, resulting in a small magnetic field. As a result, the nucleus possesses a magnetic moment, which is proportional to its spin, I .

$$\mu = \frac{gIh}{2\pi}$$

- The constant g is gyromagnetic ratio. The energy of a particular energy level is defined as

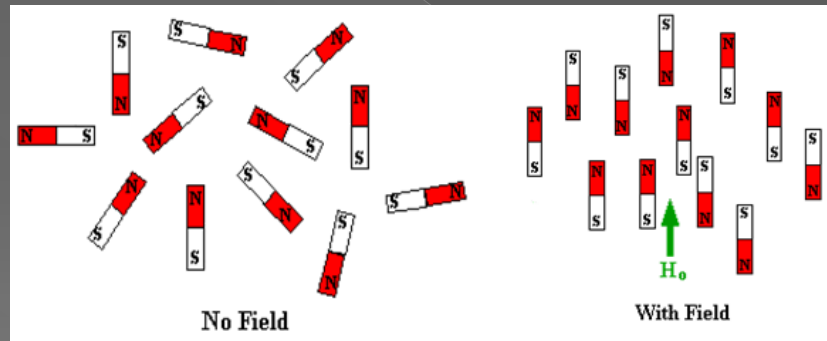
$$E = \frac{gh}{2\pi} mB$$

- where B is the strength of the magnetic field of the nucleus.
- Therefore, the difference in energy levels can be obtained in the form of

$$\Delta E = \frac{gh}{2\pi} B$$

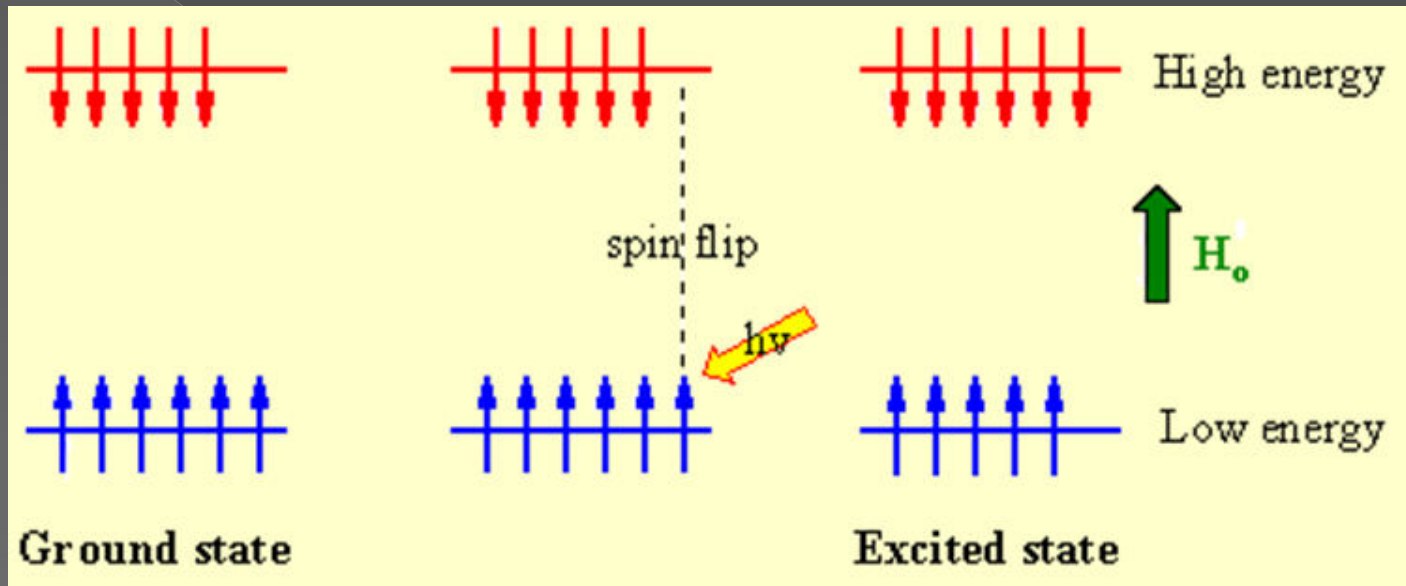
- This equation suggests that if the magnetic field is increased, then the difference in the energy also increases.

- **Nuclear Magnetic Resonance Spectroscopy:**
- Since a nucleus is a charged particle in motion, it will develop a magnetic field. For instance, ^1H and ^{13}C have nuclear spins of $\frac{1}{2}$. Hence, they would behave in a similar fashion to a simple, tiny bar magnet.
- As shown in Figure 1, in the absence of magnetic fields, these are oriented randomly. On the other hand, the application of external magnetic field lines up them parallel to the applied field, but either spin aligned or spin opposed.



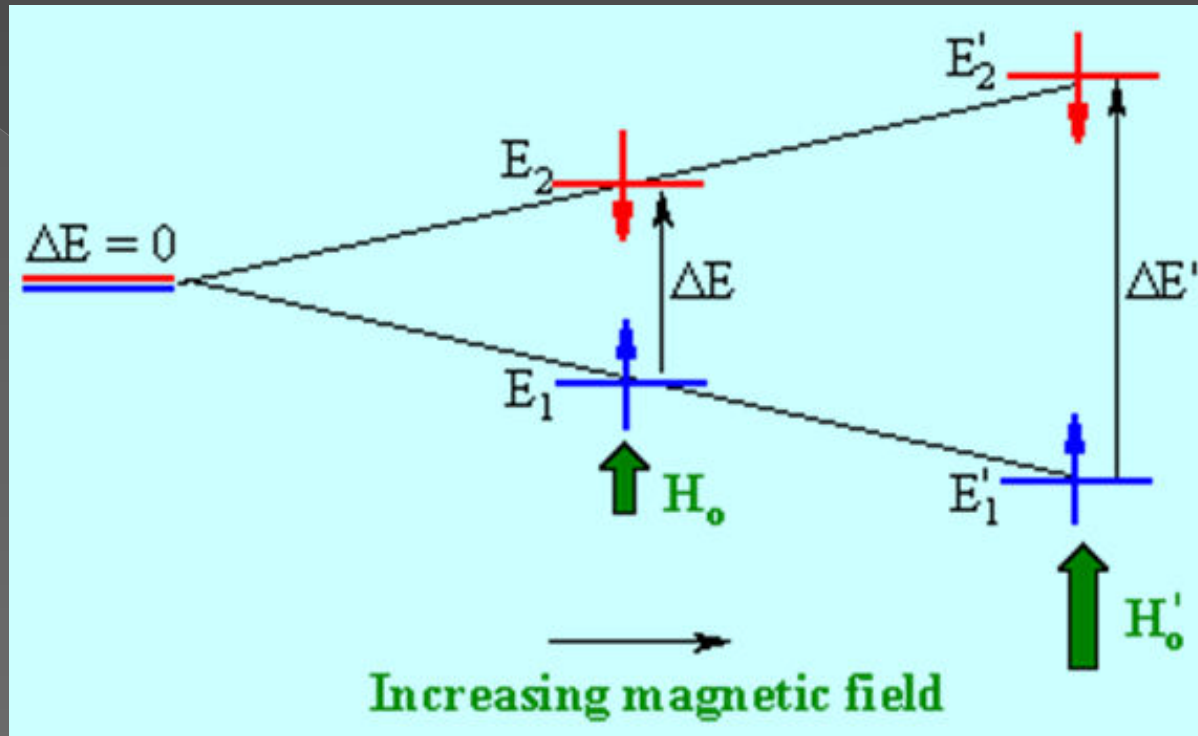
- Figure 1: Schematic representation of nuclear spins or in the form of tiny magnets under zero and finite magnitude of external applied fields.
- As displayed in Figure 35.02, the highly populated state is the lower energy spin aligned situation.

Nuclear Magnetic Resonance Spectroscopy:



- Figure 02: Schematic arrangements of spins in ground and excited states.
- Upon radiating with microwaves, the alignment of nuclear spins from the low energy aligned state is flipped to the higher energy spin opposed state, resulting in an excited state. As derived earlier, the energy required for making this transition depends on the magnitude of the applied magnetic field, as demonstrated in Figure 35.03.
- The two spin states have same energy when the external field is zero, but as the field increases so does the separation of energies of the spin states and therefore so does the frequency required to cause the spin-flip. At a field equal to H_0 , the formula for the energy difference is given.

Nuclear Magnetic Resonance Spectroscopy:



- Figure 03: Schematic drawing of variation in energy required for flipping the spins with increasing applied magnetic fields.
- Typically, one needs strong magnetic field in the range between 1 to 20 Tesla.

Nuclear Magnetic Resonance Spectroscopy:

- The basic arrangement of NMR spectrometer is shown in Figure 4. The sample is positioned in the applied magnetic field using electromagnet and microwaves are used in the radio frequency input circuit to excite the sample and to induce transitions between different nuclear spin states. This induces a radio signal in the output circuit, which generates an output signal.

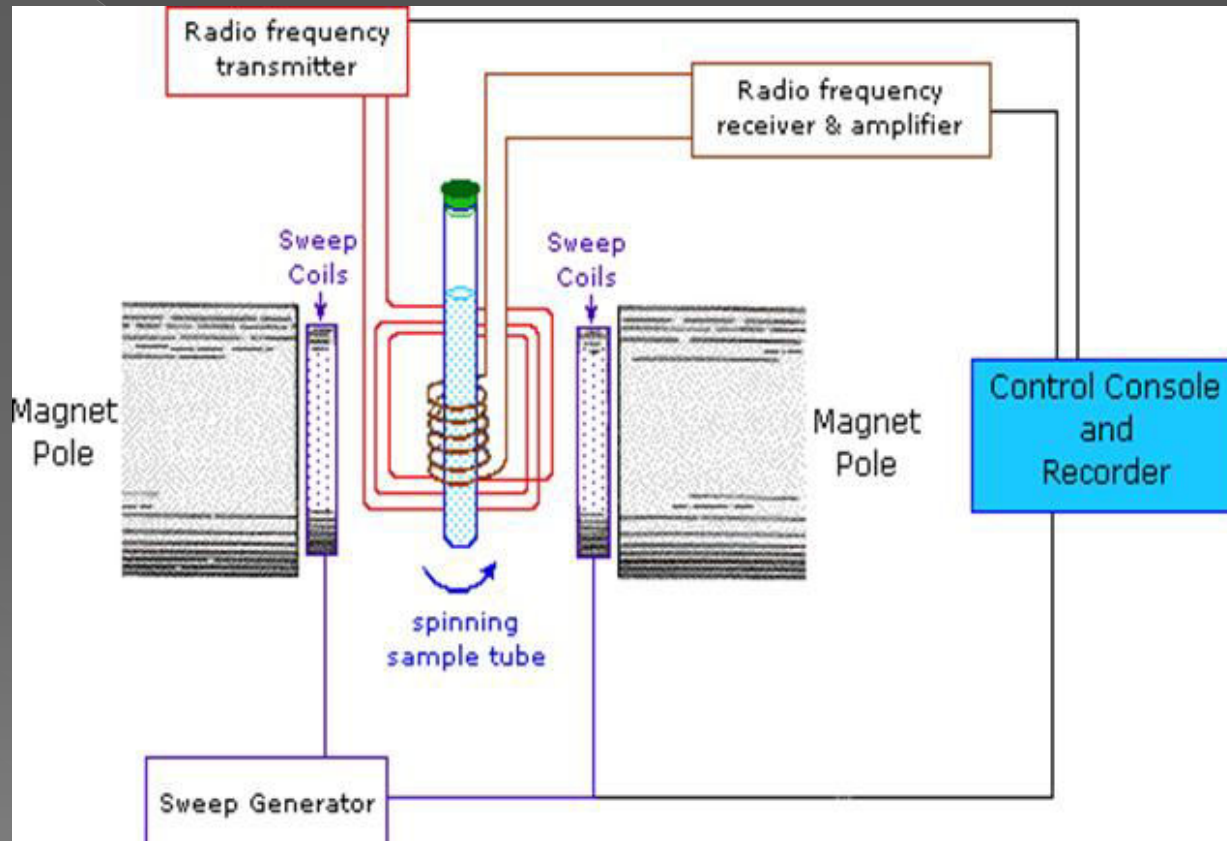
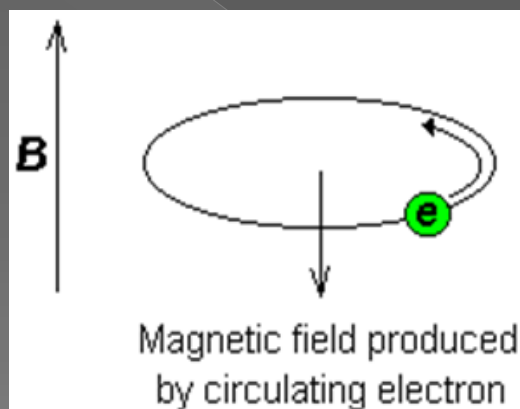


Figure 4: Basic arrangement of NMR Spectrometer.

Nuclear Magnetic Resonance Spectroscopy: Nuclear Shielding:

- The power of NMR is based on the concept of nuclear shielding. The magnetic field at the nucleus is not equal to the applied magnetic field. This is because, every atom is surrounded by electrons, which orbit the nucleus. When charged particles move in a loop, they create a magnetic field. Hence, the field produced by the movement of electron is felt by the nucleus. Therefore, the field experienced by the nucleus is not same as applied field, known as shielding. Therefore, the change in the energy levels requires a different frequency to excite the spin flip. The shielding allows for structural determination of molecules.
- Consider the s-electrons in a molecule as displayed in Figure 5. They have spherical symmetry and circulate in the applied field, producing a magnetic field which opposes the applied field. This means that the applied field strength must be increased in order for the nucleus to absorb at its transition frequency. This up-field shift is also termed diamagnetic shift.



- Figure 5: Schematic of nuclear shielding.
- Similarly, electrons in p-orbitals having no spherical symmetry produce comparatively large magnetic fields at the nucleus giving a low-field shift and termed as a paramagnetic shift.

Nuclear Magnetic Resonance Spectroscopy:

Chemical Shift:

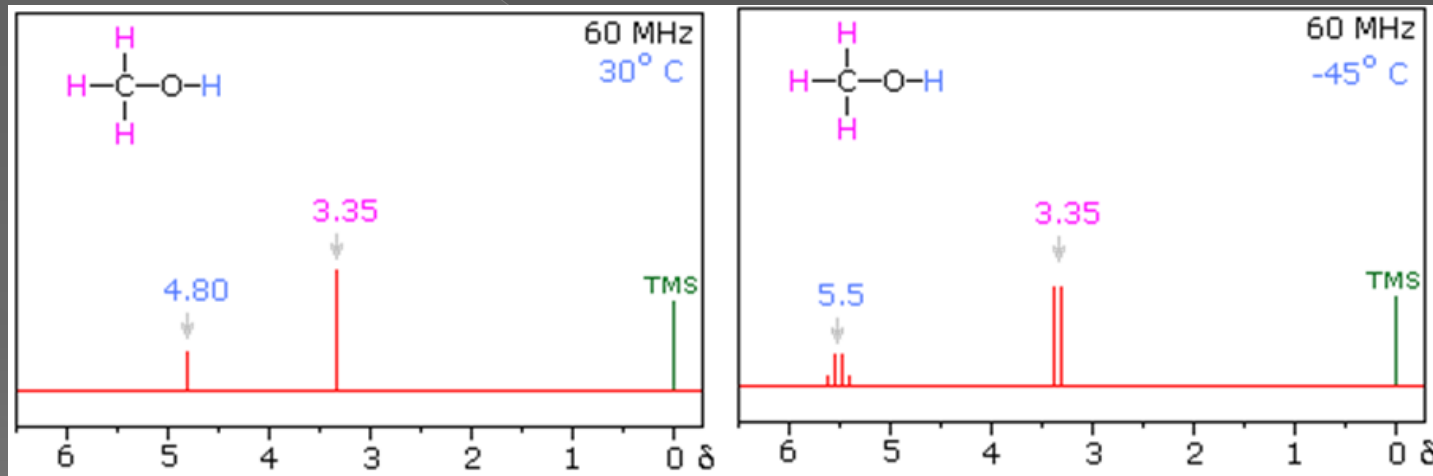
- 1) NMR spectrum is a plot of the ratio of the frequency applied against absorption.
- 2) A signal in the spectrum is referred to as a resonance.
- 3) The frequency of a signal is known as its chemical shift.
- The chemical shift is defined as**

$$\text{chemical shift, } \delta = \frac{\nu_{\text{signal}} - \nu_{\text{reference}}}{\text{spectrometer frequency}} \times 10^6$$

- The shielding of the nucleus allows for chemically inequivalent environments to be determined by Fourier Transforming the NMR signal, which results in a spectrum.
- In general, the spectrum consists of a set of peaks in which each peak corresponds to a distinct chemical environment.
- The area underneath the peak is directly proportional to the number of nuclei in that chemical environment.
- The x-axis of an NMR spectrum is given in parts per million (ppm).

Nuclear Magnetic Resonance Spectroscopy: NMR Spectrum:

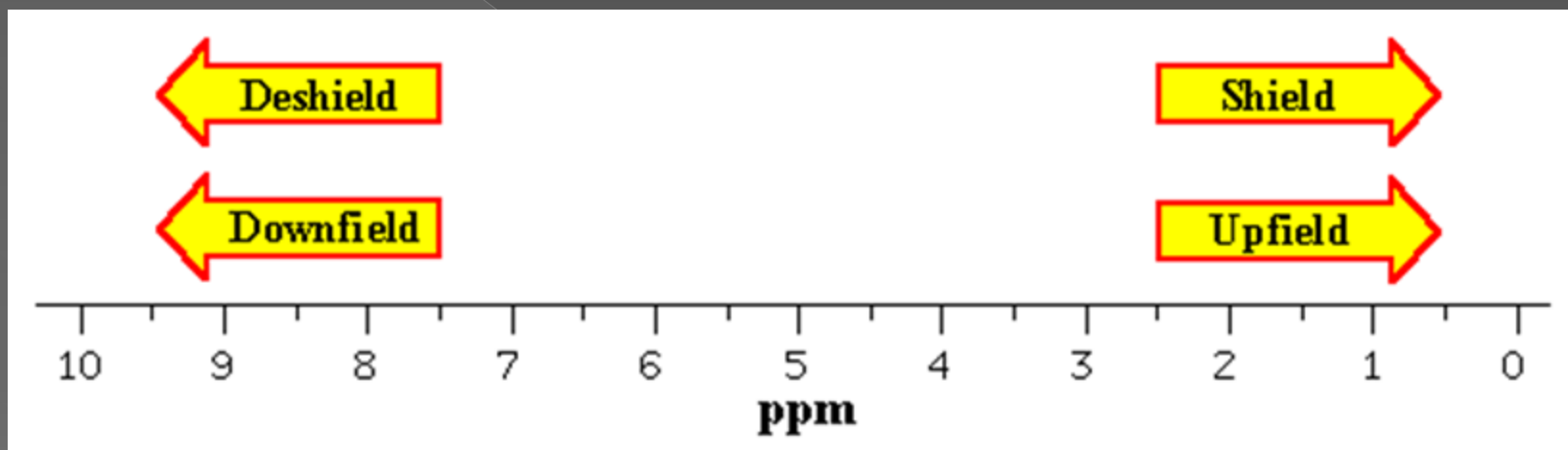
- The 60 MHz proton NMR spectrum of pure methanol as shown in Figure 6 exhibits two signals located at 3.35 and 4.80 ppm. The higher-field methyl signal (magenta) being three times as strong as OH signal (orange) at a lower field.
- Cooling the methanol to -45°C , the larger higher-field signal changes to a doublet ($J = 5.2$ Hz) having the same chemical shift. The smaller signal moves downfield to $\delta 5.5$ ppm and splits into a quartet ($J = 5.2$ Hz). However, the relative intensities of signals remain unchanged.



- Figure 6:: NMR Spectra of pure methanol at 30°C (left) and -45°C [1].
- Ref.[1].
<https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/spectrpy/nmr/nmr2.htm>.

Nuclear Magnetic Resonance Spectroscopy: Chemical Shift:

- It is convenient to describe the relative positions of the resonances in an NMR spectrum. For instance, as shown in Figure 7, a peak at a chemical shift, δ , of 10 ppm is said to be downfield or deshielded with respect to a peak at 5 ppm. Otherwise, the peak at 5 ppm is upfield or shielded with respect to the peak at 10 ppm.



- Figure 7: Schematic representation of de-shielded and shielded in NMR spectrum.
- Taking the example shown in Figure 6, we can conclude that the peak at 4.8 is downfield or deshielded with respect to peak at 3.35 or the peak at 3.35 is upfield or shielded to peak at 4.8 ppm.

Nuclear Magnetic Resonance Spectroscopy: NMR Spectrum:

- Figure 8 displays another NMR spectrum of CH_3Br . Since CH_3Br contains only a single type of hydrogen atom, only a single peak at 2.7 ppm was observed.
- The position is slightly de-shielded due to the presence of the Br.

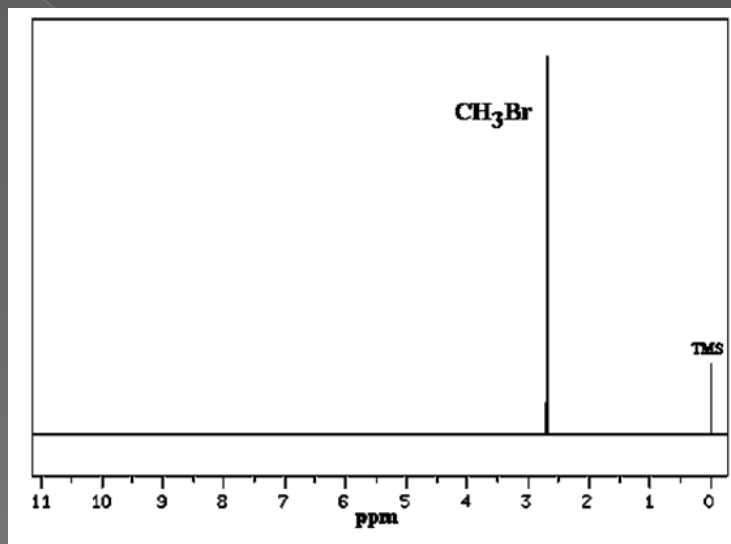


Figure 8: NMR Spectrum of methyl bromide.