Chapter III:
Nuclear magnetic resonance (NMR)

III.1. Reminder: atomic structure

III.1.1. Atom — what is it?

An **atom** is the smallest unit of a chemical element that retains its properties. It is made up of **two regions:**

- **Nucleus** (in the center): contains **protons** (+) and **neutrons** (neutral).
- **Electron cloud** (around the nucleus): contains **electrons** (−) distributed in **orbitals.**

Nuclear notation: ${}^{A}_{Z}X$

- ✓ Z: number of protons (atomic number),
- ✓ A: mass number A=Z+N (N = number of neutrons),
- ✓ X: chemical symbol.

- **Electron:**

- ✓ **Charge:** $-e$ where $e = 1.602\ 176\ 634\times10^{-19}$ C.
- ✓ **Mass:** $m_e \approx 9.109\times10^{-31}$ kg ≈ 0.0005486 u.
- ✓ **Role:** determines chemistry (bonds), conductivity, etc.
- ✓ **Nature: quantum** particle — described by a **wave function** ψ; the probability of presence is $|\psi|^2$.
- ✓ **Spin:** intrinsic spin s=1/2 → two states $m_s=+1/2$ or $-1/2$ (↑/↓).

- **Proton**

- ✓ **Charge:** +e (same magnitude as the electron, opposite sign).
- ✓ **Mass:** $m_p \approx 1.6726\times10^{-27}$ kg ≈1.0073 u.
- ✓ **Role:** determines the chemical identity (Z). In the nucleus, participates in the nuclear magnetic moment (nuclear spin).

- **Neutron**

- ✓ **Charge:** 0 (neutral).
- ✓ **Mass:** $m_n \approx 1.6749\times10^{-27}$ kg ≈1.0087 u (slightly heavier than the proton).

- ✓ **Role:** stabilizes the nucleus; variation in the number of neutrons gives **isotopes** (e.g., ^{12}C vs ^{13}C).

• Loads and weight (mass)

- ✓ **Charge of an ion** = (#protons−# electrons) × e
- ✓ **Atomic mass (≈ A)** : expressed in **atomic mass unit** (u): 1 u = 1.660539×10^{-27} kg.
- ✓ **Mass number** $A = Z + N$
- ✓ **Isotopes:** same Z but different N; natural abundance explains the sensitivity in NMR.

• Atomic orbitals

- ✓ **Old image (Bohr):** electrons on circular "orbits" **Modern image (quantum mechanics): orbitals** = regions of space where the probability of finding the electron is high.
- ✓ **Types of orbitals (value of *l*)** :
  - $L = 0 \rightarrow$ **s:** spherical (1 lobe)
  - $L = 1 \rightarrow$ **p** : 3 orbitals (lobes, oriented x, y, z)
  - $L = 2 \rightarrow$ **d:** four-lobed shapes (more complex)
  - $L = 3 \rightarrow$ **f**

- **Number of orbitals per (spatial) layer** = $n^{2.}$
- **Maximum electrons per shell** = $2n^{2}$ (because each orbital accepts 2 electrons with opposite spins).

• Spin

- ✓ Spin is an **intrinsic quantum angular momentum (fundamental** property, not a classical rotation).
- ✓ **For electrons:** s=1/2 → two projections $m_s=+1/2$m or $m_s=-1/2$.
- ✓ **For the nucleus:** we speak of **nuclear spin I** (value dependent on composition Z, N; ex: $^{1}H \rightarrow I=1/2$, $^{12}C \rightarrow I=0$).
- ✓ **Consequences:**
  - Existence of a **magnetic moment** → interaction with magnetic field (NMR, ESR).
  - **Pauli exclusion principle:** two electrons in the same orbital must have opposite spins.
  - **Spectroscopic effects:** separation of levels (Zeeman effect), spin-spin couplings, etc.

• Quantum numbers (the 4 numbers for an electron)

Each electron in an atom is described by a **set of quantum numbers** (n, l, m_l, m_s):

- ✓ **Principal number n**
  - ✓ n = 1, 2, 3, ...
  - ✓ Indicates the **main energy** and size of the orbit (layer).
- ✓ **Azimuth (or angular) number l**
  - ✓ l = 0,1,… ,n−1
  - ✓ Determine the **shape** of the orbital (s,p , d,f).
- ✓ **Magnetic number m_l**
  - ✓ $m_l = -l, -l+1, \dots, +l$
  - ✓ Indicates **the** spatial orientation of the orbital.
- ✓ **Spin number m_s**
  - ✓ ms=+1/2 or −1/2- for the electron.
  - ✓ Spin orientation (↑ or ↓).

III.1.2. How (practical procedures)

(a) How to determine if a nucleus is detectable by NMR?

- Check the **nuclear spin I:**
  - ✓ If Z and N are **even** → I=0 → **no signal** (ex: ^{12}C).
  - ✓ If I≠0→ possible signal (ex: ^{13}C: I=1/2, but low abundance).

How do you calculate the number of spin orientations?

For a spin I (nucleus) or s (particle), the number of magnetic states is 2I+1.

Ex: I=1/2 ⇒ 2(1/2)+ 1= 2 states.

(b) Spin number (or spin quantum number)

The **spin quantum number,** denoted **s,** characterizes this property. Each type of particle has a **fixed spin number:**

Particle	Number of spin(s)	Particle type
Electron	½	Fermion
Proton	½	Fermion
Neutron	½	Fermion
Photon	1	Boson
Alpha particle (^{4}He)	0	Boson

- **Fermions:** These are the **particles that constitute matter** (everything that has mass) . **spin is half-integer:** 1/2, 3/2, 5/2, ...

Examples:

- ✓ **Electron (e^-)** → spin = 1/2
- ✓ **Proton (p^+)** → spin = 1/2
- ✓ **Neutron (n^0)** → spin = 1/2
- ✓ **Quarks** (which make up protons and neutrons)

- **Bosons:** These are the **particles that transmit the forces** of nature. **Their spin is an integer:** 0, 1, 2, ...

Examples:

- ✓ **Photon (γ)** → carries the electromagnetic force (spin = 1)
- ✓ **Gluon (g)** → carries the strong force (spin = 1)
- ✓ **W^+ , W^- and Z^0 bosons** → weak force
- ✓ **Graviton (hypothetical)** → gravitation (spin = 2)
- ✓ **Higgs boson (H)** → gives mass to particles (spin = 0)

(c) Possible values of the spin projection:

For each particle, the projection of the spin onto an axis (often the **z- axis)** is given by:

$m_s = -s, -s+1, ..., +s$

This means that there are **2s + 1 possible** spin orientations.

Examples:

Particle	**s**	**Possible values of m_s**	**Number of orientations**
Electron	½	+½ or −½	2
Proton	½	+½ or −½	2
Photon	1	+1, 0, −1	3
Spin 0 particle	0	0	1

Physical interpretation

- For an **electron,** the spin can be:
  - +½ → we say “spin up” (↑)
  - −½ → we say “spin down” (↓)

These two spin orientations play a crucial role in:

- the **electronic structure of atoms,**
- the **Pauli exclusion principle,**
- and the **magnetic properties** of substances.

Concrete examples

1. **Hydrogen atom (H):**
   - ✓ The electron has a spin of ½, as does the proton.
   - ✓ The two spins can be **parallel** or **antiparallel,** which creates two different energy states (→ basis of the phenomenon of **nuclear magnetic resonance,** NMR).

III.1.3. Total spin state of two electrons:

- ✓ If the two spins are opposite (↑↓), the total spin is **0** (singlet state).
- ✓ **If the spins are parallel (↑↑), the total spin is 1 (triplet state).**

(a) Context: Nuclear spin and NMR

Resonance **(NMR)** detects **nuclei that possess a magnetic moment,** that is, a **non-zero nuclear spin ($I \neq 0$)** .

In other words: A nucleus **must have nuclear spin** to be **visible in NMR.** If it has **I = 0,** it **gives no signal.**

(b) Definition of nuclear spin (I)

spin **(I)** depends on:

- of the **number of protons (Z),**
- of the **number of neutrons (N),**
- and how **they combine** in the nucleus.

The general rules are:

Number of protons (Z)	Number of neutrons (N)	Nuclear spin (I)	Example
Peer	Peer	I = 0	^{12}C, ^{16}O
Peer	Odd	I = integer	^{2}H (I=1)
Odd	Peer	I = half-integer	^{1}H (I=½)
Odd	Odd	I = integer	^{14}N (I=1)

Analysis of the given examples

Hydrogen (^{1}H)

- A = 1, Z = 1 → N = 0

- Odd number of protons (1), even number of neutrons (0): Therefore, **nuclear spin I = ½ : Very abundant (99.98%)** → easily detected by NMR: **Conclusion: ^{1}H gives a strong signal in NMR.**

Fluorine (^{19}F)

- A = 19, Z = 9 → N = 10
- Odd Z, even N: **I = ½: Isotopic abundance = 100%: Conclusion: ^{19}F gives a strong and sensitive signal in NMR.**

Carbon-13 (^{13}C)

- A = 13, Z = 6 → N = 7
- Z even, N odd
  I = ½ : But **low isotopic abundance (1.1%): Conclusion: ^{13}C gives a weak signal in NMR** (sensitive instruments or isotopic enrichment are needed).

Carbon-12 (^{12}C)

- A = 12, Z = 6 → N = 6
- Z even, N even
  I = 0 : **No nuclear magnetic moment: Conclusion: ^{12}C gives no signal in NMR.**

(c) The rules for determining nuclear spin I

Number of protons (Z)	Number of neutrons (N)	Core type	Nuclear Spin III	Example
Peer	**Peer**	Even-even nucleus	**I = 0**	^{12}C, ^{16}O, ^{4}He
Peer	**Odd**	Even-odd core	**I = integer (1, 2, …)**	^{2}H (I = 1)
Odd	**Peer**	Odd-even nucleus	**I = half-integer (½, 3/2, …)**	^{1}H (I = ½), ^{19}F (I = ½)
Odd	**Odd**	Odd-odd nucleus	**I = integer or half-integer** (more complex, depends on the coupling)	^{14}N (I = 1), ^{2}H (I = 1)

(d) Spin: a fundamental quantum property

Spin is an **intrinsic (proper) property** of every particle (like mass or charge). It is a **form of quantum angular momentum,** that is, an internal rotation **on a microscopic scale.**

This **is not an actual rotation** like a spinning top, but a **quantum property** that behaves *as if* the particle were spinning on its own axis.

Summary:

Spin: an intrinsic quantum property

Spin **is** not an actual mechanical rotation like a spinning top, but an **internal property** of each particle, much like its charge or mass. It is a **quantity of angular momentum** specific to the particle.

It can be represented by a number called **the spin quantum number:**

$$s=\frac{1}{2},1,\frac{3}{2},......................$$

Each type of particle has a fixed spin **value.**

- The **electron:** $s=\frac{1}{2}$
- The **proton:** $s=\frac{1}{2}$
- The **neutron:** $s=\frac{1}{2}$
- The **photon:** $s=\frac{1}{2}$

(e) **The spin of the electron:** The electron is an **elementary particle,** meaning it has no known internal structure. However, it possesses: A **charge,** a **mass,** and an **intrinsic angular momentum** called **spin.**

This spin can take **two directions:**

$s_m=+\frac{1}{2}$ Or $s_m=-\frac{1}{2}$

It is often said:

- **spin up** (↑) for $s=+\frac{1}{2}$
- **spin down** (↓) for $s=-\frac{1}{2}$

This spin gives rise to a **magnetic moment** , meaning the electron acts like **a tiny magnet** . This principle is the basis of:

- resonance **(NMR)**
- spectroscopy **(ESR)**

(f) The spin of the atomic nucleus:

The **nucleus** is made up of **protons and neutrons,** each with a spin of $\frac{1}{2}$

The **total spin of the nucleus** comes from the **vector sum** of the spins of its nucleons (protons and neutrons).

Example:

- If the nucleus contains **only one proton** (like hydrogen ^{1}H), then: $I = \frac{1}{2}$
- If the nucleus contains several nucleons, their spins can:
  - add up → total non-zero nuclear spin
  - or cancel each other **out** (opposite spins) → zero nuclear spin

Example:

Core	Total Spin I	Remarks
^{1}**H**	1/2	A single proton
^{12}**C**	0	Pairs of protons and neutrons → spins cancel each other out
^{13}**C**	1/2	An unpaired neutron
^{14}**N**	1	Spins do not cancel each other out completely

Definition of nucleons: Nucleons are the **particles that make up the atomic nucleus.** They are located at the **center of the atom** and include:

- protons **(p)**
- neutrons **(n)**

Composition of the electron: The **electron** is an **elementary particle,** meaning that it **is not composed of any other** known particles (according to current physics). It is a **lepton,** one of the fundamental families of matter.

Composition of the proton: The **proton** is **not elementary;** it is made up of **three smaller particles** called **quarks (two** *up* quarks and one *down* quark). This combination results in a **total charge of +1.** The quarks are held together by **gluons,** which ensure the cohesion of the proton through the **strong force** (nuclear force).

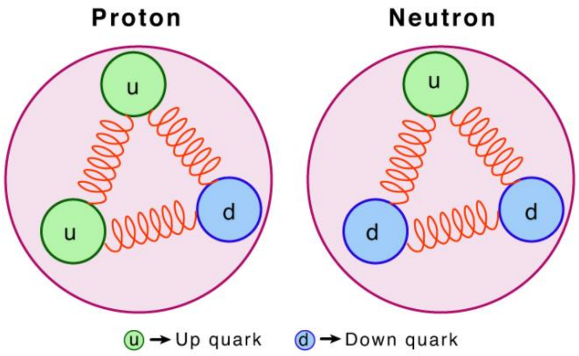


Fig III.1. Shematization of quarks

Composition of the neutron: The **neutron** is very similar to the proton, but **electrically neutral.** It is also made up of **three quarks:**

(1 *up quark and 2 down* quarks), That's why it is **neutral** (total charge = 0).

General summary

Particle	Kind	Composition	Charge	Location	Spin
Electron	Elementary (lepton)	None (indivisible)	-1	Around the core	1/2
Proton	Compound	2 up quarks + 1 down quark	+1	In the core	1/2
Neutron	Compound	1 up quark + 2 down quarks	0	In the core	1/2
Nucleons	Together	Protons + Neutrons	—	Core	—

III.2. Introduction:

Nuclear magnetic resonance (NMR) is a spectroscopic technique used to identify the structure of compounds (liquid or solid), characterize their atomic arrangement, and obtain information about the environment (nature of nearby neighbors) of atomic nuclei. This powerful and highly effective analytical method is used in both structural and quantitative analysis. The NMR phenomenon involves the selective absorption of energy by nuclei possessing a magnetic moment, placed in a magnetic field and irradiated by an electromagnetic wave. NMR has become an indispensable and unparalleled tool and is applicable to elements with a non-zero nuclear spin number.

NMR is applicable to elements possessing a non-zero nuclear spin number. $^{A}_{Z}X$ Any nuclide has a non-zero spin number I if the numbers Z (number of protons) and A (mass number) *are not both even.*

- **Historical Background:**

The first NMR experiments were conducted at the end of 1945 by two American teams. The first results were published in the first months of 1946 by Edward M. Purcell and Felix Bloch. Their work earned them the Nobel Prize in Physics jointly in 1952. It was only at the beginning of the 1970s that the NMR method took off thanks to the work of the Swiss physicist Richard R. Ernst (Nobel Prize in Chemistry in 1991).

Today, NMR technology has become an invaluable tool in the medical diagnosis of tissues. The examinations performed are MRI scans, or Magnetic Resonance Imaging, an acronym used to "mask" the word "nuclear" for the general public… This presentation of NMR is brief and necessarily incomplete. We will simply say that NMR is indeed the physics experiment that revolutionized chemical analysis.

III.3. General principles of NMR:

III. 3.1. Definition: Nuclear magnetic resonance (NMR) is a spectroscopic technique that allows us to detect atomic nuclei and tells us **what type of nuclear nucleus they are. In their environment,** these nuclei are found inside a molecule.

III.3.2. Nuclear Spin: A nucleus is observable by NMR if it exhibits magnetic properties characterized by the existence of a non-zero spin I. Spin was introduced to account for the fine structure of the hydrogen spectrum. Even in the absence of external perturbations, one or more transitions with very close energy levels are observed, whereas the theory, which only considers the quantum numbers n, l, and m, predicts only a single transition energy.

- n: principal quantum number.
- l: azimuthal quantum number (such that $l < n-1$ or $l = n-1$).
- m: magnetic quantum number (such as $-l < m < l$ or $m = l$ or $m = -l$).

Values	Quantum number	Meaning
n (1, 2, …)	Main	Designate the shells K, L, M, N…
L **(0, 1, …, n−1)**	Azimuth (or angular) momentum)	Defines the subshells s, p, d…
m_l (−l, …, 0, …, +l)	Magnetic	Defines the angular orientation of the orbital
m_s (−1/2, +1/2)	Spin magnetic	Defines the "spin state"

The nucleus of a hydrogen atom consists of a single proton. Its spin I (called nuclear spin) is equal to that of the proton, I = 1/2, which corresponds to two values of the magnetic spin number $ms = \pm 1/2$. For atoms heavier than hydrogen, the nuclear spin I can have a value that is a multiple of 1/2 or can be zero (the case of nuclei for which A and Z are even).

III.3.3. Magnetic spin quantum states:

For a particle or nucleus placed in a magnetic field, the spin states are quantized, meaning they can only take on a specific number of values defined by a spin magnetic quantum number ms. The possible values of the spin magnetic quantum number of a particle or nucleus with spin equal to I are:

- ms = -I, -I+1,... 0, ..., I-1, I.
- The number of distinct stationary states is therefore equal to 2 ×I+1.

III.3.4. General Definition

Nuclear Magnetic Resonance (NMR) is a **physical analysis method** used to study:

- Molecular **structure,**
- **Environment of atomic nuclei,**
- **Molecular dynamics.**

It is based on the **behavior of atomic nuclei placed in an** intense magnetic field and subjected to a radio frequency (RF) wave.

III.4. Fundamental Principle

Some **atomic nuclei** (such as ^{1}H , ^{13}C , ^{19}F , ^{31}P , etc.) possess a **magnetic moment** because they have a **nuclear spin ≠ 0.**

This means they behave like **small magnets.**

When these nuclei are placed in an **external magnetic field** B_0, each small nuclear magnet **aligns itself** either:

- **in the direction of the field** (low energy state),
- **or in the opposite direction** (high energy state).

Spins are said to be **oriented parallel or antiparallel** to the magnetic field.

Magnetic properties of the atomic nucleus:

For a given nucleus with a non-zero spin I, there are 2I+1 different orientations of the angular momentum or magnetic dipole in a static magnetic field.

$$N_{n-Zeeman}=2\times I+1$$

- $N_{n-Zeeman}$ Zeeman level number

- Separation between Zeeman levels

1. What is the Zeeman effect?

The **Zeeman effect** describes the **separation of energy levels of a system (atom, ion or nucleus)** when it is placed in an **external magnetic field B_0.**

In other words:

Without a magnetic field, all spin orientations have **the same energy.** But when a magnetic field is applied, these orientations **differentiate:** some become more stable (lower energy), others more unstable (higher energy).

This **separation of energy levels is** what is called **the Zeeman effect.**

III.4.1. Physical origin:

A nucleus or an electron possessing a **magnetic moment** $\vec{\mu}$ acts like a **small magnet.**

In other words, an isolated nucleus whose spin number is not zero behaves like a small magnet with magnetic moment m (J × $T^{-1)}$ such that:

$$\vec{\mu}=\gamma.\vec{I}$$

This nuclear magnetic moment m is represented by a vector collinear with I, in the same direction or opposite direction, depending on the sign of g which is **called the magnetogyric ratio** (it is also referred to as the **gyromagnetic constant**).

If we subject a nucleus with non-zero spin, which we imagine as a kind of microscopic magnetic needle, to a magnetic induction field B_0 making an arbitrary angle u with the spin vector, a torque appears between B_0 and μ that modifies the potential energy E of the nucleus. Let **μ be the z- value.** The projection of m onto the Oz axis, directed in the direction of B 0 , will give:

$$E=\vec{\mu}.\vec{B}_0$$

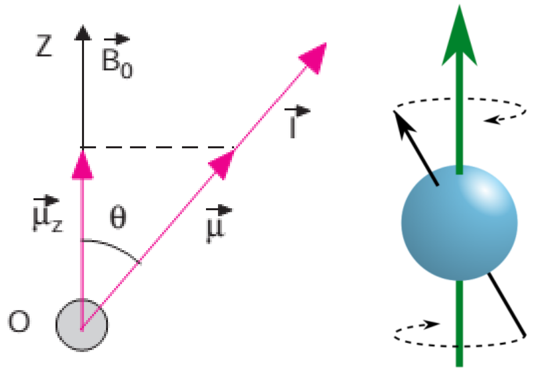


Fig.III.2: Energy diagram of a nuclear spin.

$E=-\mu.B_0$, either $E=-\mu\cos(\theta).B_0$ or $E=-\mu_z.B_0$

According to the rules of quantum mechanics, m z for a nucleus, the potential energy E can only take 2I + 1 values. It follows that in the magnetic field B_0, the potential energy E can also only take 2I + 1 values. The same is true for the angle u. The quantization of m z is a consequence of the allowed values for the projection m of the spin vector onto Oz (m is the magnetic spin number). These are given (in natural units h / 2p) by the terms of the following sequence:

$m = -I, -I + 1, \ldots, I + 1, I$

We arrive at the general expression for the 2I + 1 allowed values of energy:

$$\mathbf{E = - g \cdot m \cdot B_0}$$

In the case where I = 1/2, the two possible values of E (in joules) correspond to m = +1/2 and m = −1/2.

$$E_1\,(\text{or}\,E_\alpha) = -\gamma\frac{1}{2}\frac{h}{2\pi}.B_0 \qquad \text{And} \qquad E_2\,(\text{or}\,E_\beta) = +\gamma\frac{1}{2}\frac{h}{2\pi}.B_0$$

This appearance of several energy levels is reminiscent of the Zeeman effect, which concerns the separation of electronic levels, also in a magnetic field, hence the term sometimes encountered in NMR, of nuclear Zeeman separation.

Quantizing the projection of the spin vector onto the Oz axis nevertheless allows it to sweep the surface of a right circular cone whose angle, between the axis and the apothem, can be calculated, knowing the norms of m and m_z; this precession movement, around an axis parallel to that of the magnetic field, is characterized by its frequency which increases with the intensity of the field.

To get a concrete idea of nuclear spin, we often compare it, on our scale, to the motion of a spinning top rotating around its axis, which, at any given instant, makes an angle θ with respect to the direction of gravity (the Earth's gravitational field). The top describes a gyroscopic motion around this direction, resulting from the combination of its rotation around its axis and the restoring torque due to the gravity vector. Friction slows the rotation, so the angle u increases continuously. For a nucleus in a vacuum, unlike the spinning top principle, the angle remains fixed over time, regardless of the value of the applied field, because the magnitudes of the magnetic moment vector and its projection are quantized. Thus, for a nucleus whose spin number is I = 1/2, we calculate that the allowed angles of I with respect to Oz are approximately 55° and 125°, taking into account the norms of the spin vector on the one hand ($\sqrt{I(I+1)}$), and of its projection (I) on the other.

The angle of **54.74** °, used in some NMR experiments, is called the " **magic angle** ". For this particular value of spin, it corresponds to the angle that the diagonal of a cube makes with its six adjacent edges.

Without a magnetic field With magnetic field

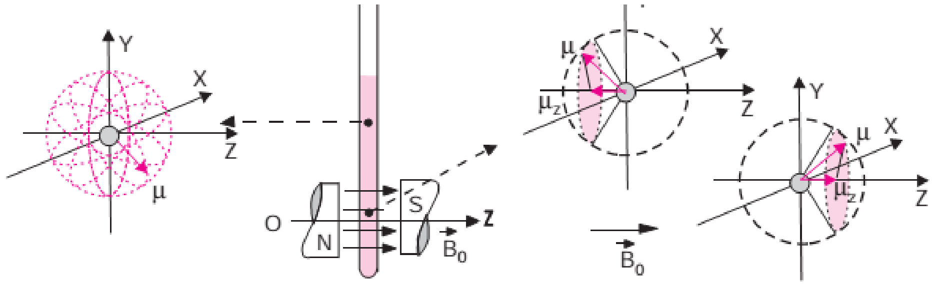
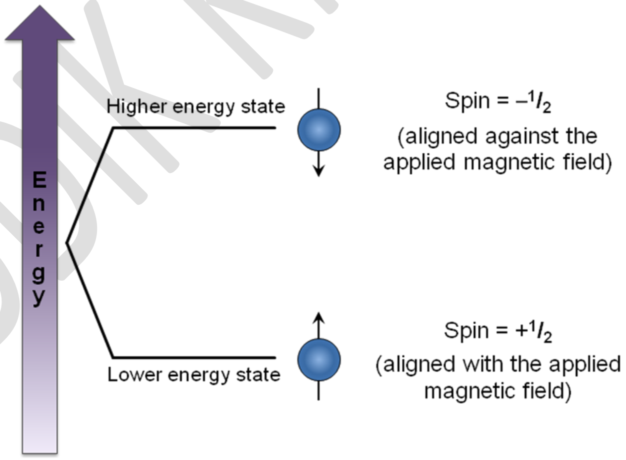


Fig. III.3: Effect of a magnetic field on a nucleus with spin number ½ present in a compound in solution

III.5. BLOCH'S THEORY FOR A NUCLEUS WHICH I = ½

At our macroscopic scale, the smallest quantity of a molecular compound is made up of a considerable number of individual molecules. We are therefore always dealing with such a gigantic collection of nuclei that NMR signals reflect statistical behavior, as in optical spectroscopy. Consider a set of identical nuclei with a spin number of I = 1/2. In the absence of an external field, the orientations of the individual spin vectors are random and constantly changing. From an energetic point of view, these nuclei form a single population, in a so-called degenerate state (Fig. III.4). When these nuclei are placed in the powerful external magnetic induction field B_0 (Oz orientation), an interaction arises between each small nuclear magnetic vector and this field. Two groups of nuclei thus appear, whose energies correspond to E_1 or E_2 , defined previously according to the direction of the projection of their spin vector onto the Oz axis.



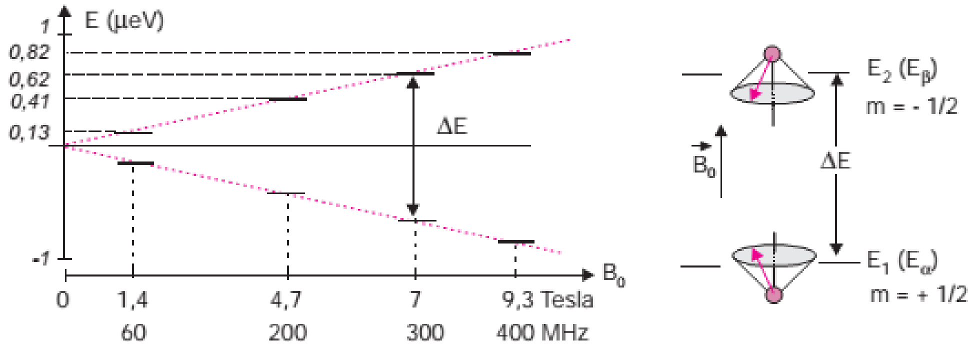


Fig. III.4: Representation of the splitting between the energy levels of a nucleus with spin number 1/2 placed in a magnetic field

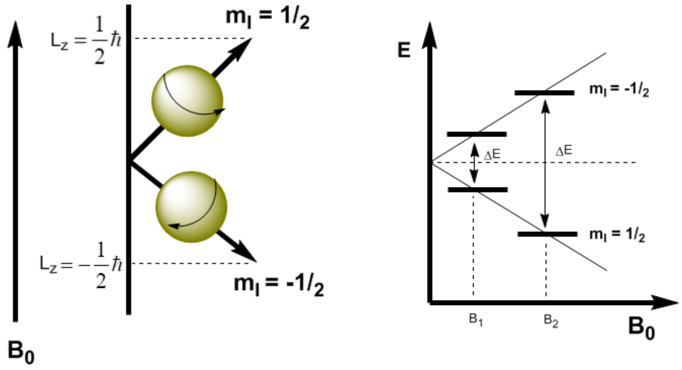


Fig. III.5: Representation of the splitting between the new energies of a nucleus of spin number I = ½ placed in a magnetic field.

The difference ΔE between the two states is:

$$\Delta E = E_2 - E_1 = \gamma \frac{h}{2\pi} B_0$$

ΔE : is proportional to the field B_0. Thus, for the proton, if B 0 = 1.4 T, the energy difference has a very small value: 3.95×10^{-26} J, or 2.47×10^{-7} Ev.

As for the ratio $\frac{E_2 - E_1}{B_0}$, it depends only on g, that is to say on the nucleus studied (Table **15.1)**. The population, which includes the nuclei located in the energy state E2, is slightly less numerous than in the slightly more stable state E1.

Expression **15.5** allows us to calculate the ratio of the two populations (Boltzmann distribution equilibrium).

$$R = \frac{N_2}{N_1} = \exp\left(-\frac{\Delta E}{kT}\right)$$

(For ^1H, we find R = 0.999964 *if* $T = 300$ K and $B_0 = 5.3\ T$ with $k = 1.38 \times 10^{-23}$ $J \cdot K^{-1} \cdot atm^{-1}$)

When this nucleus is placed in a **magnetic field B₀** , it undergoes a **magnetic interaction:**

$$E = \vec{\mu} . \vec{B_0}$$

Depending on the orientation of $\vec{\mu}$ relative to $\vec{B_0}$, the energy changes. But in quantum mechanics, this orientation cannot be continuous: it is **quantized** according to the spin number I.

Separation of energy levels

Under the influence of the magnetic field B_{0}, an **energy separation** occurs between these two spin orientations.

$$\Delta E = h.\upsilon = \gamma \bar{h} B_0$$

- h = Planck constant,
- ν = resonance frequency,
- γ = gyromagnetic ratio of the nucleus,
- $\bar{h} = h/2\pi$

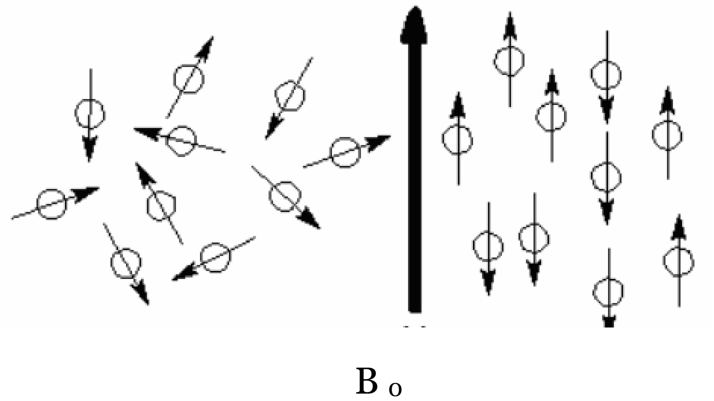
In other references we find:

$$\Delta E = h.\upsilon = \frac{\mu B_0}{I} \qquad \text{and} \qquad \mu = \frac{\gamma.I.h}{2\pi}$$

- μ : nuclear magnetic moment
- γ : gyromagnetic ratio of the nucleus
- For the proton: $\gamma = 2.675221 \times 10^{8}$ rad. $S^{-1}.T^{-1}$

III.6. Interaction between nuclear spin and the magnetic field:

In the absence of an external magnetic field, the magnetic moments of the nuclei are randomly oriented, leading to a global cancellation of their magnetic effect. Conversely, when a static magnetic field B_0 is applied, these magnetic moments interact with the field and tend to align with its direction. This interaction causes the spins to be distributed into different energy states; the basis of the phenomenon observed in nuclear magnetic resonance (NMR).



Random orientation
Without a magnetic field

In the presence of the magnetic field

Fig. III. 5: Interaction between nuclear spin and the magnetic field

Summary:

The α and β states in NMR

When a nucleus (like the proton ^1H) has a spin of ½, it behaves like a tiny magnet.
When this nucleus is placed in an external magnetic field B_0, its magnetic moment can orient itself in two different ways:

State	Orientation relative to B_0	Energy
State α (alpha)	Parallel to field B_0	Low energy
State β (beta)	Antiparallel to the field B_0	High energy

radio frequency (RF) wave is applied at the Larmor frequency:

- The nucleus in the α (low) **state can absorb a quantum of energy** and switch to the **β** (high) state.
- When it **returns** to the α state, it **re-emits** this energy → this is what we **detect** in NMR.

III.7. Larmor's Law:

From an analytical perspective, if we can measure the energy difference separating the two populations in a magnetic field B_0 (in the case where $I = 1/2$), we can identify the corresponding nucleus based on its gyromagnetic constant **γ.** To evaluate this energy difference, we will, as in optical spectroscopy, create the conditions for transitioning from one energy level to the other, that is, induce a resonance signal. Practically, we irradiate the nuclei placed in the magnetic field with a source of electromagnetic radiation of variable frequency whose propagation direction is perpendicular to the external field.

Absorption will occur if: $h\upsilon = E_2 - E_1$

Fundamental resonance relation: $\upsilon = \frac{\gamma}{2\pi} B_0$

This very important and general expression **is called the Larmor relation.** It relates the magnetic field in which the nuclei considered are bathed and the frequency of the electromagnetic radiation which causes the resonance condition (**Table.III.1**).

The radio frequency, which causes the exchange between the two levels, is also the **so-called Larmor precession frequency** at which the spin vector rotates around the average Oz direction. Larmor, an Irish physicist whose work predates that concerning NMR, showed, through independent reasoning, that v, the angular frequency or rotational frequency of the spin vector around Oz has the value:

$\varpi = \gamma B_0$

As before $\varpi = 2\pi\upsilon$, we find the relationship demonstrated in the case of NMR. These two approaches are different: one leads to the frequency of the quantum that separates the two levels, and the other to the mechanical precession frequency. These two frequencies have the same value.

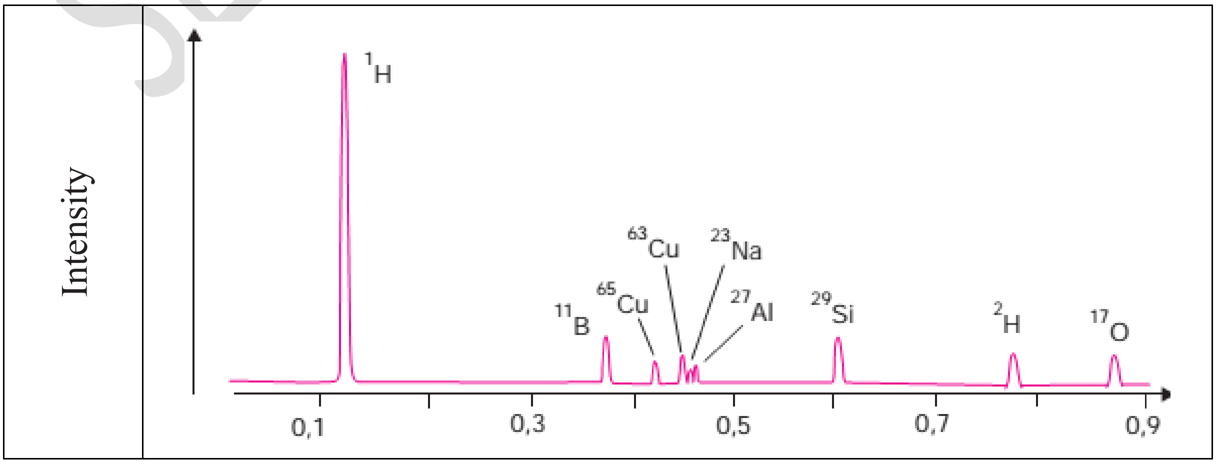
Table.III.1: γ values of the most studied nuclei in R MN

Core	γ (rad. $s^{-1.}$ T^{-1})	Sensitivity
1 hour	2.6752×10^8	1
19F	2.5181×10^8	0.83
31P	1.084×10^8	6.6×10^{-2}
13C	0.6283×10^8	1.8×10^{-4}

The Larmor frequency of a nucleus increases with B_0. It lies in the shortwave range and varies, if the field strength is 1 tesla, from 42.5774 MHz for the hydrogen nucleus (proton) to 0.7292 MHz for gold (Table.III.2). Instruments are designated by the frequency at which protons resonate, even if they are designed to study other nuclei.

Table.III.5: values, MHz For B_0= 1T

N	^{1}H	^{19}F	^{31}P	^{13}C	^{15}N
υ	42.58	40.06	17.24	9.71	4.32



Magnetic field (T)

Fig.III.6: NMR spectrum of a water sample placed in a borosilicate glass container,
observed at a frequency of 5 MHz (the field is expressed in Tesla; Varian document).
There are no commercial devices of this type, as NMR is a method reserved for more in-depth examinations than for determining the elemental composition of samples.

Based on this principle, experimental multi-core devices were initially constructed, enabling field scanning over a wide range while maintaining a fixed radio frequency. This allowed for the qualitative and global identification of the most easily detectable elements of the sample under study by their characteristic resonance frequencies.

III.8. Resonance:

If we send a **radio wave** (RF frequency) whose energy corresponds exactly to the difference between the two levels ($\Delta E = h\nu$), then the nucleus **absorbs** this energy and **changes its spin state.**

The term **RF (Radio Frequency)** refers to an **electromagnetic wave** with a frequency between approximately **3 kHz and 300 GHz.** This is the same range used for **radio, television, and telecommunications;** in **NMR, a small part of this range** is used (often a few tens to hundreds of MHz).

This is what is called **nuclear magnetic resonance.**

Resonance condition: $\upsilon=\frac{\gamma B_0}{2\pi}$

Return to equilibrium and signal emission

After excitation by the RF wave:

- The nuclei return to their initial equilibrium state.
- Upon returning to their base state, they **release the absorbed energy** in the form of a measurable **electrical signal.**

This signal, called **the resonance signal** or **FID (Free Induction Decay),** is then analyzed (via a **Fourier transform)** to give the **NMR spectrum.**

NMR Spectrum: The **NMR spectrum** shows:

- peaks **at characteristic** frequencies,
- corresponding to **the chemical environment** of each nucleus.

These shifts are expressed in **ppm (parts per million)** and called **chemical shifts** (δ).

Each **type of atom (e.g., hydrogen, carbon)** produces a different spectrum:

- **^{1}H NMR** : analyzes hydrogens.
- **^{13}C NMR** : analyzes carbons.

What NMR allows us to obtain

- **Number of signals** → number of different chemical environments.
- **Position (δ)** → chemical nature (groups, bonds, etc.).
- **Multiplicity (spin-spin coupling)** → number of neighboring atoms.
- **Area under the peak** → proportion of atoms in each environment

III.9. Equipment:

An **NMR spectrometer** includes:

1. A **superconducting magnet** (creates B0B_0B0)
2. A **radio frequency (RF) wave generator**
3. A **probe** where the sample is placed
4. A **computer** to detect and transform the signal (FFT)

III.7. The principle of obtaining the spectrum by NMR:

NMR instruments allow the application of a very intense magnetic field. Instruments with frequencies from 300 to 600 MHz are commonly used for chemical analysis (Fig.III.7). Obtaining such intense magnetic fields is currently achieved through the use of solenoids made of superconducting materials maintained at the temperature of liquid helium, i.e., -269 °C (4 K). An electromagnetic excitation, around the frequency ν_0, is generated within the instrument. Its frequency range is sufficiently broad to excite all the nuclei of the chemical species being studied. After excitation, the nuclei return to their initial state following a relaxation time specific to each. The energy released during this return generates a small current in a secondary circuit. This is the signal that is detected. The signal, with intensity I as a function of time, is analyzed by Fourier transform and translated into a frequency spectrum.

Therefore: An NMR apparatus consists of a powerful magnet to generate a static magnetic field (B_0), a radio frequency (RF) transceiver to excite the nuclei, a sample coil where the sample is placed, a computer to process the signals and generate the spectrum, and a cooling method to maintain the superconducting magnet. This assembly allows for the analysis of molecular structure by observing how atomic nuclei interact with the magnetic field and radio waves.

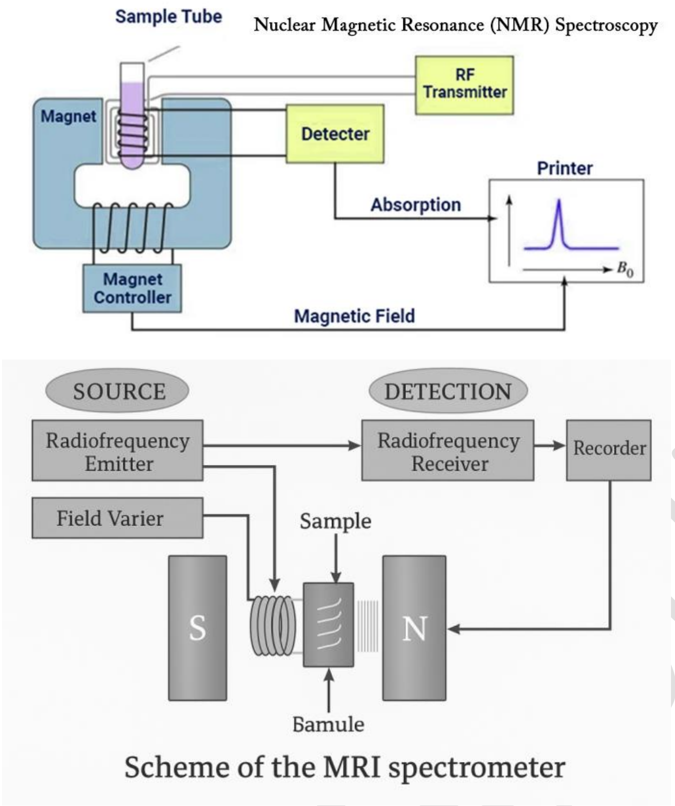


Fig. III.7. Schematic of the MNR spectroscopy

III. 8. Hydrogen NMR (^{1}H NMR):

III.8.1. Chemical shift:

When a molecule is placed in a magnetic field B_0, the internal electrons will **shield** the nucleus from the external field applied to it; the local field will be:

$$E_{\text{Effective}} = B_0(1-\sigma) = B_0 + B_1$$

The resonance condition is: $\upsilon = \frac{\gamma B_0}{2\pi}$

(σ) is the screening constant; it can be positive or negative depending on whether the induced field is opposite or in the same direction as the applied field. The chemical shift is defined as the ratio of the nuclear electrical screening to the applied field; the field is a function of the nucleus and its environment.

The signal the reference used in NMR is TMS: tetramethyl silane $Si(CH_3)_4$.

This internal standard is added to the samples to allow for the identification of other peaks. Since the chemical shift is proportional to the applied magnetic field, it is measured as a function of the TMS by constructing ppm (parts per million). This represents the relative difference between the frequency in question and a reference frequency.

$$\delta = \frac{\upsilon_{\text{sample}} - \upsilon_{\text{TMS}}}{\upsilon_{\text{spectrosomtrie}}} \times 10^6$$

TMS has several advantages:

- It has 12 equivalent protons and gives a single signal;
- The signal is intense (12H), a small amount is used.
- Inert and volatile.

This peak constitutes the origin of the measurement scale: $\delta_{TMS} = 0$ ppm

III.10.2. Definition of chemical shift (δ):

The **chemical shift δ** represents **the position of an NMR signal** on the x-axis of the spectrum. It indicates **the chemical environment in which** a nucleus (often a proton or a carbon) is found.

In other words, δ **measures the effect of the electronic environment** around the nucleus on its **resonance frequency.**

III.9. Physical Principle

When a nucleus (for example a proton ^1H) is placed in an **external magnetic field** B_0, it should resonate at a given $\upsilon_0 = \frac{\gamma B_0}{2\pi}$ **Larmor frequency:**

But in a real molecule, the **electrons around the nucleus** create a **local magnetic field opposite** to B_0. This phenomenon is called **electron screening** (or **shielding effect)**.

Result:

$$B_{eff} = B_0(1-\sigma)$$

where σ: is the **screening factor.**

Thus, according to the electron density around the nucleus:

- If the nucleus is **strongly surrounded by electrons → more "protected" → resonates at a lower frequency** (peak to the left, low δ).
- If the nucleus is **sparsely surrounded by electrons → less protected → resonates at a higher frequency** (peak to the right, large δ).

III.9.1. Mathematical Definition:

The chemical shift δ is defined relative to a **standard reference: TMS** (tetramethylsilane *, Si $(CH_3)_4$),* whose signal is set at **0 ppm.**

$$\delta = \frac{\upsilon_{sample} - \upsilon_{TMS}}{\upsilon_{spectrosomtrie}} \times 10^6$$

- υ_{sample} : frequency of the observed signal
- υ_{sample} : frequency of TMS (reference to 0 ppm)

- $\upsilon_{spectrosomtrie}$: frequency of the applied magnetic field (in MHz)
- The factor 10^6 converts to **ppm** (parts *per million).*

III.11.2. Chemical Interpretation:

δ (ppm)	Proton type	Example
0 – 2	Saturated protons (CH_3 , CH_2)	$CH_3-CH_2-CH_3$
2 – 4	Protons near electronegative atoms (O, Cl, N)	CH_2-Cl, CH_2-O-CH_3
4.5 – 6.5	Vinyl protons (C=C–H)	$CH{=}CH_2$
6-8	Aromatic protons	C_6H_6
9-12	Acid protons (COOH, CHO)	CH_3COOH, HCHO

- **In summary**

Element	Meaning
δ (ppm)	Position of the signal on the spectrum
Unit	ppm (parts *per million*)
Reference	TMS at 0 ppm
Cause of the displacement	Electron density around the nucleus
Low δ	Highly shielded nucleus (electron-rich environment)
Fort δ	Deshielded nucleus (electron-poor environment)

- **Illustrative example:**

Let 's **take CH_3Cl** and **CH_3 - CH_3:**

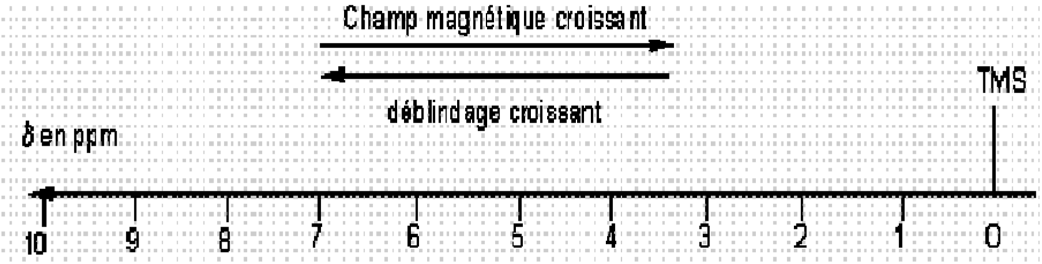
- In **CH_3 - CH_3,** the protons are very shielded → signal around **0.9 ppm.**
- In **CH_3Cl, chlorine** attracts electrons → less protected protons → signal towards **3.0 ppm.**

III.10. Armored and unarmored cores:

When a nucleus is placed in an external magnetic field, the electrons surrounding it begin to move and generate a **local magnetic field.** This local field can interact with the applied field in two ways:

a) **If the electron field opposes the external field,** it reduces its effect at the nucleus. The **nucleus is then said to be shielded.** In this case, a stronger external magnetic field is required to achieve resonance. On the NMR spectrum, the corresponding signal appears **shifted to the right** (towards the strong fields).

b) **If the electron field is added to the external field,** it reinforces the effect of the applied field. The **nucleus is then deshielded,** and resonance occurs at weaker fields. The signal therefore appears **towards the left of the spectrum** (see Figure 4.3).



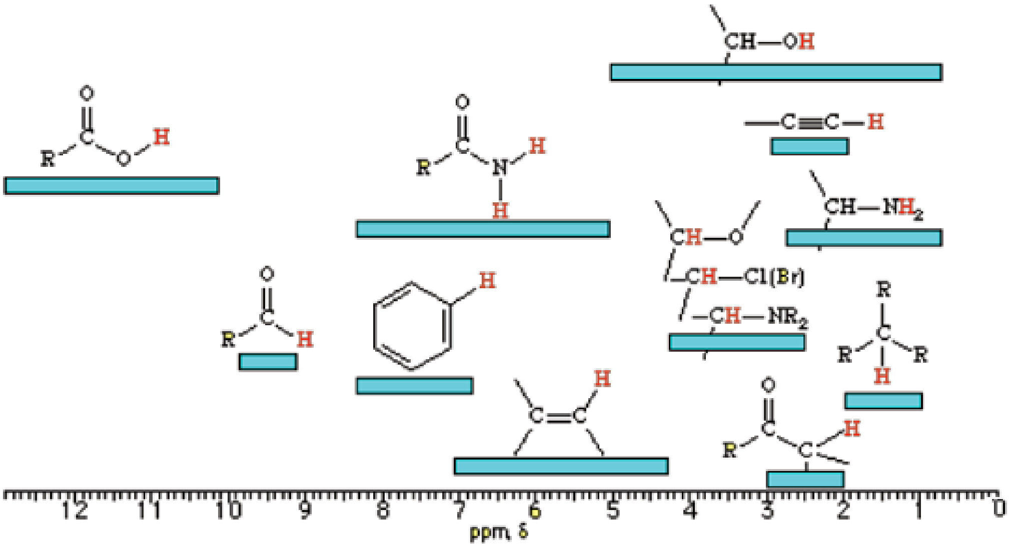


Fig. **III.8.** Typical chemical shift of ^{1}H NMR.

III.11. Factors influencing δ:

(a) **Electronic effects:** An electron-withdrawing effect Deshields protons, the signal shifts towards large wavelengths. An electron-donating effect shields protons, the signal shifts towards small wavelengths.

Example: RC H$_2$-R δ (1.2 - 1.4 ppm) R: alkyl donor group.

RC H$_2$-X δ (3.1 - 3.7 ppm) X: attractor halogen

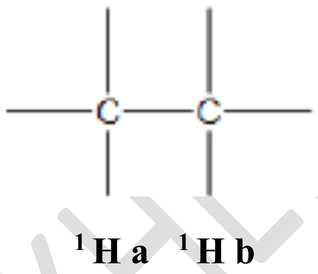
Hydrogen bonding: Hydrogens involved in H bonds resonate over a wide range of δ (OH between 0.5 and 7.7 ppm).

III. 11.1. Hyperfine Structure:

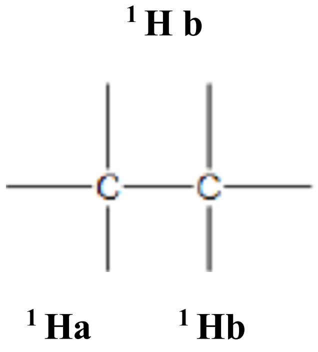
NMR spectra generally contain more signals than there are nuclei with different chemical shifts. This is because the external magnetic field surrounding all the atoms of the compound under study causes an orientation of all the spins of its nuclei, and the orientation of a nucleus is transmitted, from an energetic point of view, to neighboring nuclei via the bonding electrons of that atom. This *coupling between nuclei weakens very rapidly with distance. Homonuclear* couplings (between nuclei of the same type), or *heteronuclear nuclei* (between nuclei of different types) results in small signal shifts. This hyperfine structure of the spectrum provides additional information about the compound being examined. Homonuclear coupling between protons is very common, and the presence of 13C, 31P, and 19F also leads to heteronuclear coupling with protons.

III.11.2. Spin-spin coupling:

^{1}H**a** nucleus has other ^{1}H nuclei in its vicinity, it is subjected not only to the magnetic field of the device, but also to small fields induced by neighboring ^{1}H nuclei. Consider the case where **^{1}H has** a non-equivalent neighbor **^{1}Hb**:

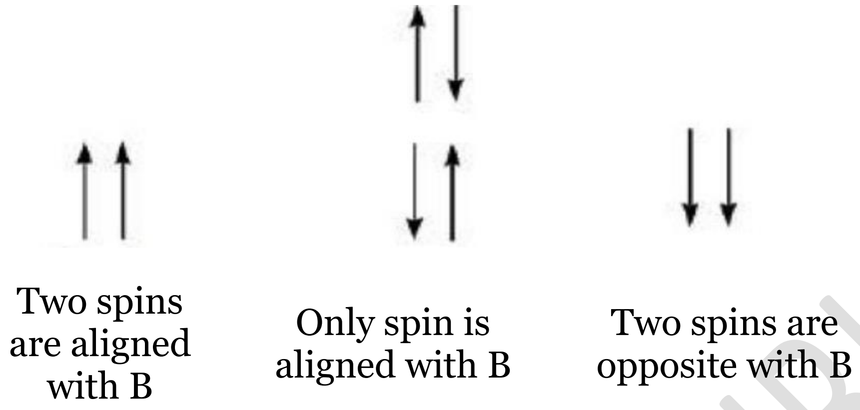


The proton **^{1}H a** is affected by the local magnetic field induced by **^{1}H$_b$** due to its two orientations. The proton 1Ha experiences the magnetic field **$B_0 \pm B_1$: its signal will be split into two equal peaks, called a doublet. Let us** consider the case where **^{1}H$_a$** has two equivalent neighbors **^{1}H$_b$**:



The two nuclei **^{1}Hb** can present the following three orientations:

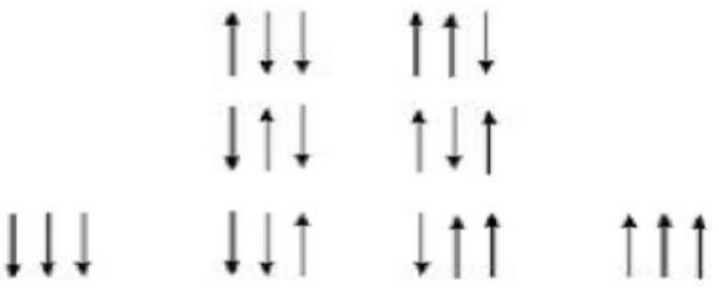
Spin states



In this case, the ^{1}**H signal** will be split into three intensity peaks 1/2/1: **it is a triplet.**

Consider the case where ^{1}**H$_a$** has three equivalent neighbors ^{1}**H $_b$:** In this case, the two nuclei ^{1}**H$_b$** can have the following orientations:

Spin states



Intensity: 1/3/3/1

The Ha signal will be split into four peaks of intensity 1/3/3/1: it is a quadruplet.

The amplitude of the coupling, or the number of hertz by which the signal is split, is called the coupling constant, symbolized by J. This constant is affected by the spatial arrangement of the atoms. Thus, the coupling of two hydrogens in *cis* will be different from that of two hydrogens in *trans,* for example.

III.11.3. Equivalent Protons:

Equivalent protons are protons that are **in the same chemical environment.**
In other words, they are **surrounded by the same atoms** and **undergo the same electronic influences.**

• **Consequence:** Since they experience the same local magnetic field, they resonate **at the same chemical shift** on the NMR spectrum. They therefore give **one and the same signal.**

Example:

In the **methane molecule (CH_4),** the four protons are equivalent because they are all bonded to the same carbon atom in an identical environment. → Result:
a single peak is observed on the proton NMR spectrum.

CH_3 –CH_3 (ethane) → 1 single signal

The two **CH_3 groups** are **equivalent** due to the symmetry of the molecule.
→ All protons have the same electronic environment. **Result:** a **single signal** on the spectrum.

CH_3 –O–CH_2 –CH_2 –O–CH_3 (dimethoxymethane) → 2 signals

- The protons of the **CH_3 (methyl) groups** are equivalent to each other.
- The protons of the **CH_2 (methylene) groups** are also equivalent to each other, but **different** from those of the CH_3 groups.
  Result: 2 types of protons → **2 signals.**

CH_3 –CH_2 –CH_2 –Cl (1 -chloropropane) → 3 signals

- **The** protons of the **terminal CH_3** have a different environment than those of the **CH_2.**
- The two **CH_2 groups** are not equivalent:
  - The one **near Cl** is influenced by the electronegative (unshielded) atom.
  - The one **near the CH_3** is more heavily armored.
    Result: 3 types of protons → **3 signals.**

III.11.4. Integration:

The relative intensity of a signal corresponds to the relative abundance of the nucleus that causes it. By measuring the area under a peak and comparing it to other peaks, it is possible to estimate the number of protons corresponding to each peak (Fig.III.9). NMR spectrometers are equipped with an electronic integrator that plots an integration curve above each peak. The heights of these integration curves are proportional to the areas under the peaks.

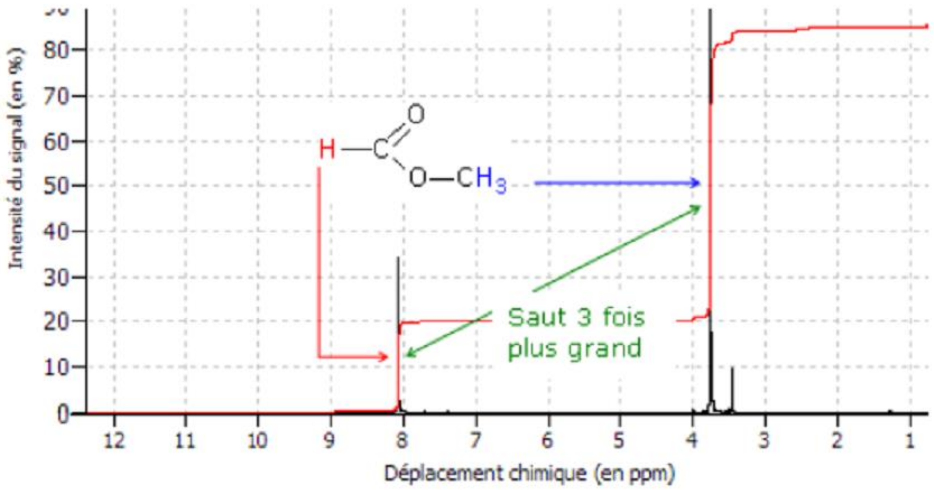


Fig.III.9: NMR spectrum of methyl formate.

To calculate the number of hydrogen atoms corresponding to each peak, we can use the following formula:

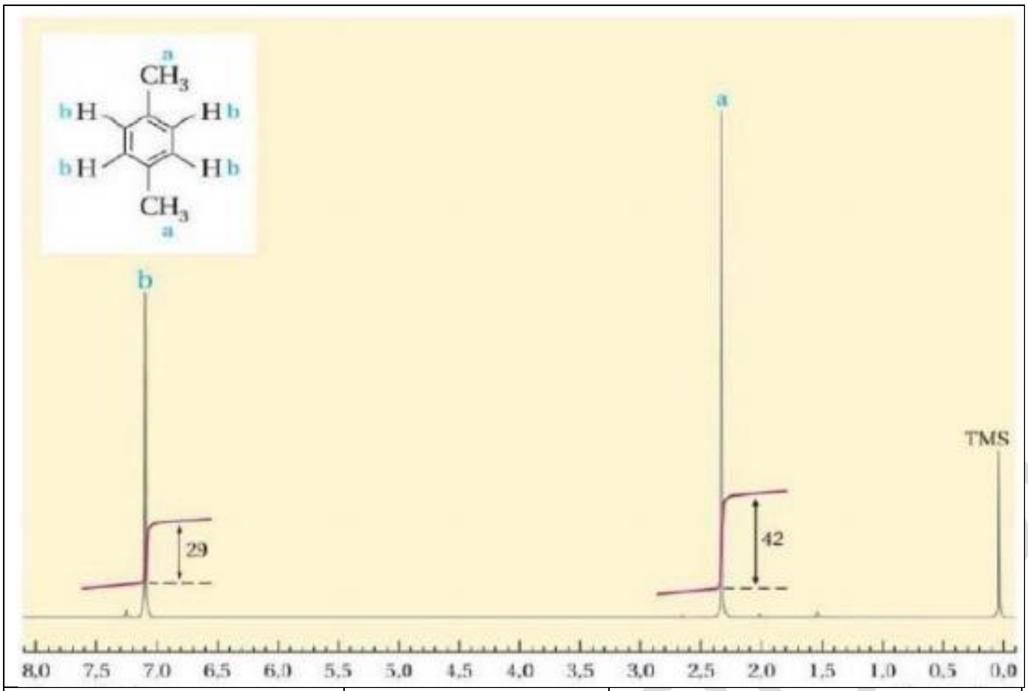
$$\text{Number of hydrogens} = \frac{(\text{Value of the peak integration}) \times \sum(\text{hydrogens})}{\sum \text{of the integrations}}$$

Example:

p-xylene.

Peak (a): Number of H= 42×10/71= 6H Peak

(b): Number of H=29×10/71= 4H



Weak field	d (ppm)	High field

III.11.5. Signal multiplicity rule:

When a nucleus ^{1}**H** has ^{n1}**H** neighbors, its signal will be split into n+1 peaks (Table 5.1).

Table 5.1: Pascal's triangle.

Number of neighboring H, N	**Number of peaks, N+1**	**Multiplet name (abbreviation)**	**Peak area ratio**
0	1	Singlet(s)	1
1	2	Doublet (d)	1:1
2	3	Triplet (t)	1:2:1
3	4	Quadruplet (q)	1:3:3:1
4	5	Quintuplet (quin)	1:4:6:4:1
5	6	Sextuplet (sex)	1:5:10:10:5:1
6	7	Septuplet (seven)	1:6:15:20:15:6:1