Introduction to Nuclear Magnetic Resonance

Chapter 1

Atomic structure and magnetic properties of the materials

Atomic structure

Introduction

Our theory about the atom has changed over time as innovative studies are done, figure 1. Even though no one has ever seen an atom up close we are still able to make new discoveries – just like we have made new discoveries about dinosaurs.

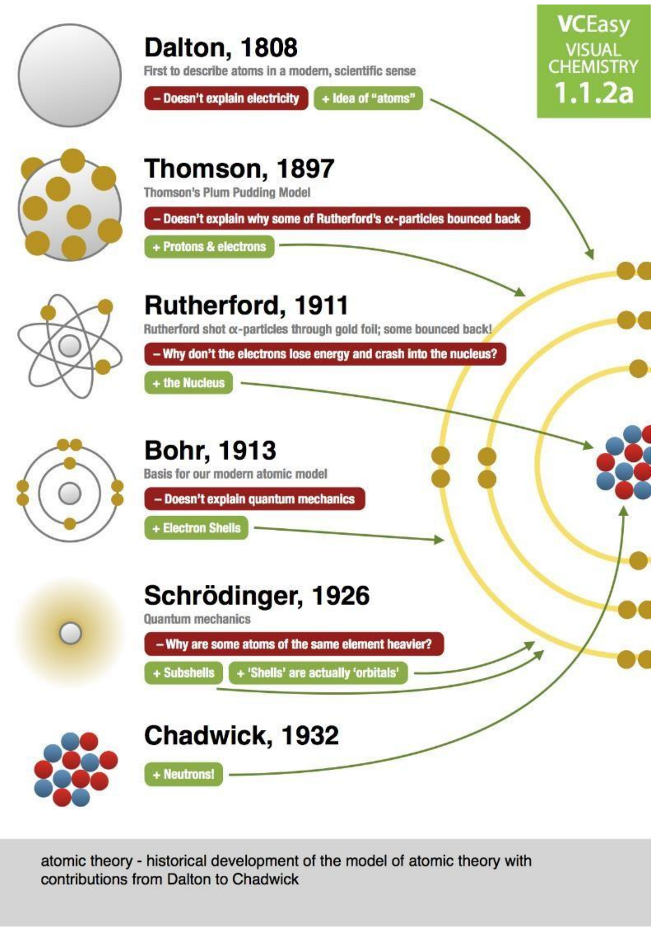


Figure 1 The development of atomic theory

The Greek word "Atomos" means not able to be divided or "indivisible."

Democritus

Democritus, figure 2, was an ancient Greek philosopher who lived from 460 - 370 B.C. His first observation about cutting matter in half was:

- There was a limit to how far you could divide matter.
- You would eventually end up with a piece of matter that could not be cut.

He concluded that:

- Atoms are small hard particles.
- Made of a single material that's formed into different shapes and sizes.
- They are always moving.
- They form varied materials by joining together.

Figure 2 Democritus

Aristotle

Aristotle, figure 3, was an incredibly famous Greek philosopher who believed that matter could be divided into smaller and smaller pieces forever. He held an extraordinarily strong influence on widely held belief and his views on this were accepted for two thousand years.

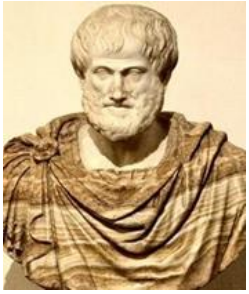


Figure 3 Aristotle

What is an Atom?

An atom is the smallest particle that an element can be divided and still be that element. For example, the smallest particle of carbon is a single atom of carbon. If you divide it is no longer carbon anymore.

John Dalton 1776-1844

Two thousand years later a British chemist and schoolteacher, John Dalton, brings back Democritus's idea of the atom, figure 4. He performed many experiments to study how elements join together to form new substances. He found that they combine in specific ratios, and he supposed it was because the elements are made of atoms, figure 5.

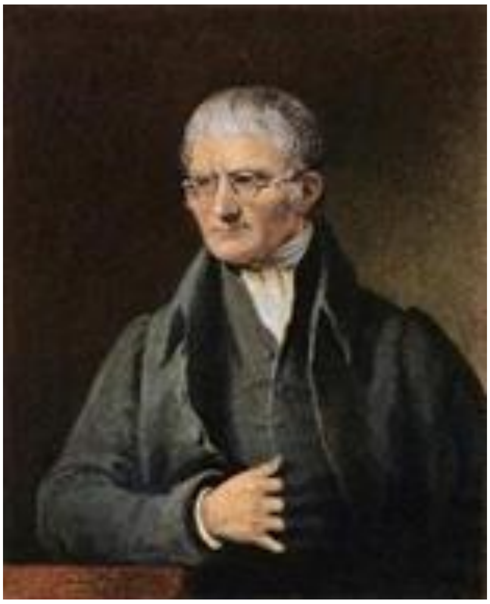


Figure 4 John Dalton

What 3 new ideas did John Dalton propose about the atom?

- All substances are made up of atoms which are small particles that cannot be created, divided, or destroyed.
- Atoms of the same element are exactly alike, and atoms of different elements are different.
- Atoms join with other atoms to form different substances.

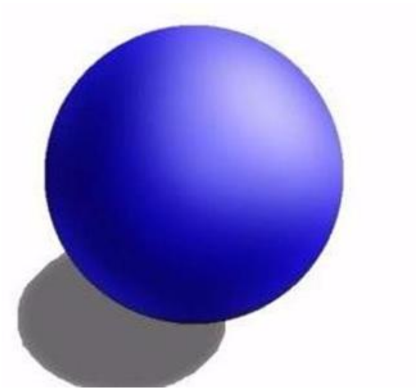


Figure 5 Dalton atomic model

J.J. Thomson 1856-1940

J.J. Thomson discovered that atoms are made of smaller negatively charged particles called electrons. Thomson's discovery was the result of doing experiments with "cathode ray tubes". Stream of electrons is attracted to positively charged plate here.

The Plum Pudding Model

Thomson, figure 6, did not know how the electrons in an atom were arranged. He believed they were mixed throughout an atom. He proposed that the atom was a sphere of positively charged material. Spread throughout the atom were the negatively charged electrons similar to plums in a pudding or chocolate chips in ice cream.

Figure 6 J.J. Thomson

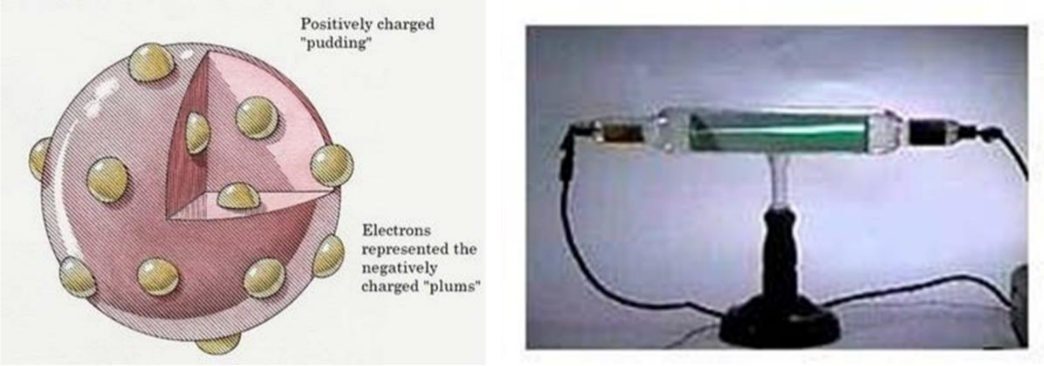


Figure 7 (a) The Plum Pudding Model and (b) Thomson cathode ray tube

Ernest Rutherford (1871 - 1937)

Awarded the Nobel Prize in Chemistry for his discovery of alpha particles, positively charged particles emitted from radioactive elements. Was a student of J.J. Thomson but disagreed with the "Plum Pudding Model". Devised an experiment to investigate the structure of positive and negative charges in the atom, figure 8.

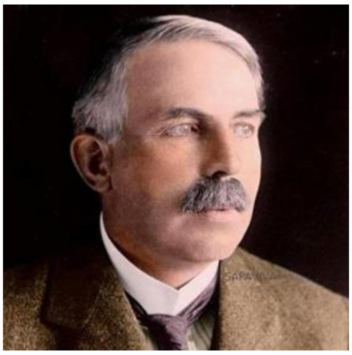
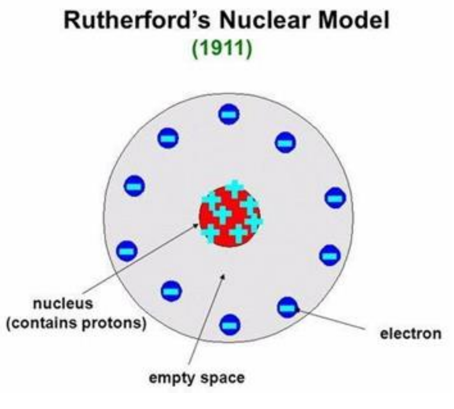


Figure 8 Ernest Rutherford



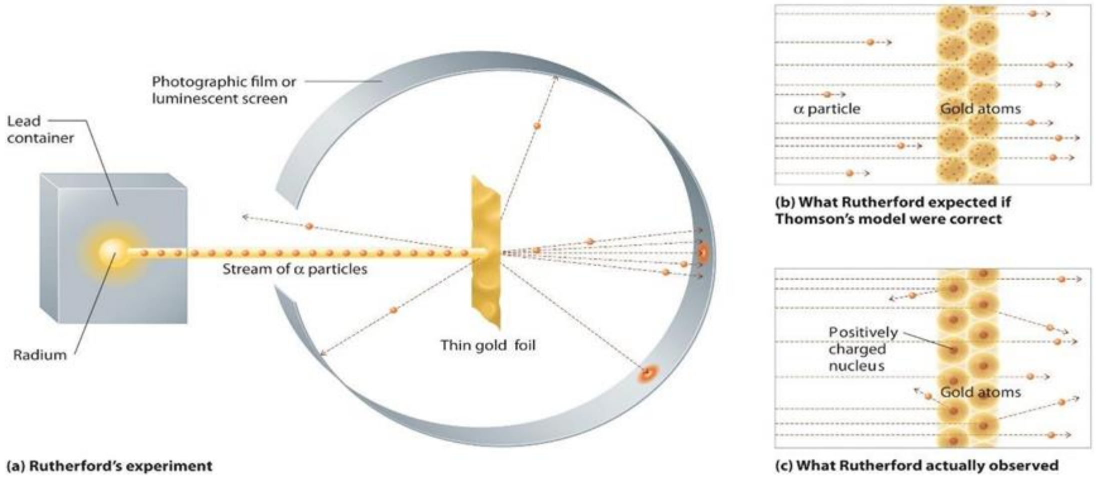


Figure 9 (a) Rutherford atomic model and (b) Gold foil experiment

What did most of the particles shot at the gold foil do?

- Most of the particles traveled straight through the gold foil

What was the surprising behavior of a few of the particles?

- A few of the particles were deflected and some even bounced back

Rutherford's Revised Atomic Theory (1911)

Result: Most of the positively charged particles went straight through the gold foil.

Atomic Theory: Most of the matter of the atom is found in a very small part of the atom. This is called the nucleus of the atom. It is very tiny and extremely dense.

Result: Some of the positively charged particles were deflected or even bounced back.

Atomic Theory: Like charges repel so the nucleus must have a positive charge. If electrons have a negative charge, they could not be in a positively charged nucleus. Electrons must surround the nucleus at a distance.

Result: The diameter of the nucleus is 100,000 times smaller than the diameter of the entire gold atom.

.Atomic Theory: Atoms are mostly empty space with a tiny, massive nucleus at the center.

The Bohr Model of the Atom

Bohr, figure 10, proposed that electrons move in paths at certain distances around the nucleus. Electrons can jump from a path on one level to a path on another level, figure 11.

Figure 10 Bohr

The Modern Theory of the Atom

Electrons travel in regions called “electron clouds”. You cannot predict exactly where an electron will be found.

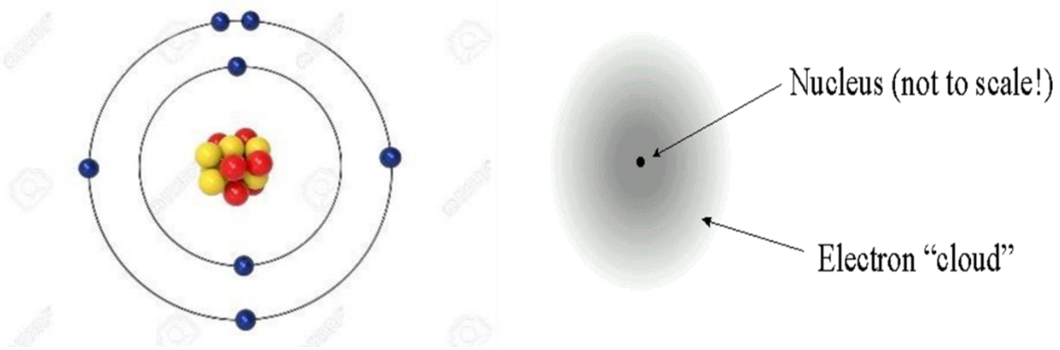


Figure 11 (a) Bohr Model of the Atom and (b) Modern Theory of the Atom

Energy Levels

The energy that an electron has is based on its location around the nucleus. (Electrons that are closer to the nucleus have less energy than those that are farther away from the nucleus), figure 12.

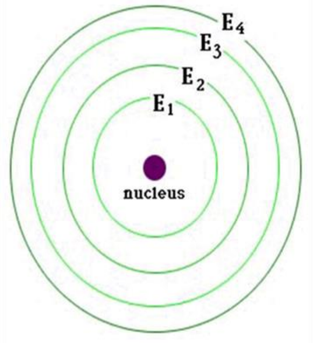


Figure 12 Diagram of energy level

<u>How can bookshelves help you understand the movement of electrons?</u>

- Each shelf represents an energy level
- Each book represents an electron
- You can move a book to a higher or lower shelf with the correct amount of energy.
- A book cannot be between shelves
- (An electron can move by gaining or losing energy but can never be between energy levels), figure 13.

Figure 13 comparison between energy level with bookshelves

Electron Density

Based on Heisenberg uncertainty principle and Schrodinger wave equation. Gives the probability that an electron will be found in a particular region of an atom. Regions of high electron density represent a high probability of locating the electron.

Atomic Orbital

- Way to distinguish Bohr's model from the current quantum mechanical model.
- Probability of locating the electron in 3D space around the nucleus.
- Has a characteristic energy, figure 14.

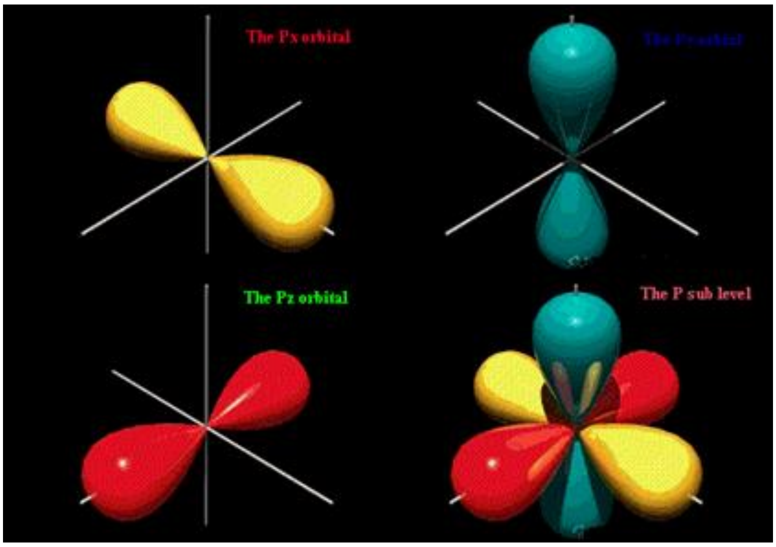


Figure 14 Atomic orbitals

Quantum numbers

Quantum numbers used to describe atomic orbitals and to label electrons that reside in them

- Principle quantum number (n)
- Angular momentum quantum number
- Magnetic quantum number
- Electron spin quantum number

Principal Quantum Number n:

It gives information about size and energy distance of e- from the nucleus n = 1, 2, 3, 4, … as n increases orbitals become larger e- is further from the nucleus, figures (15, 16 and 17).

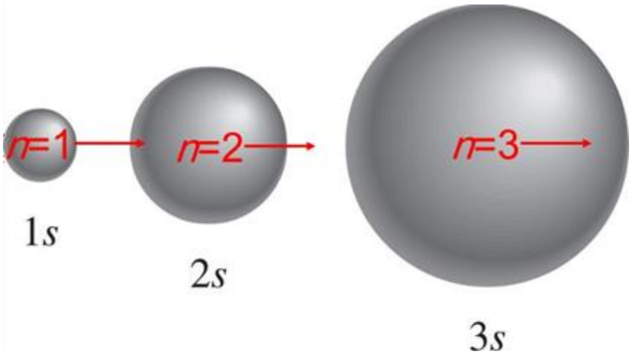


Figure 15 Principal Quantum Number n

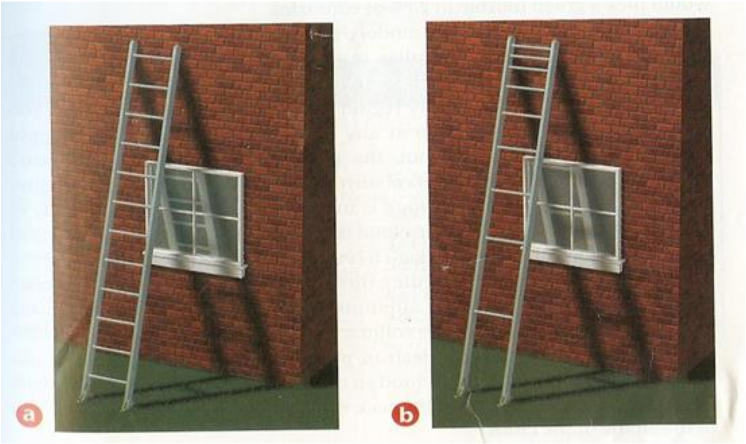
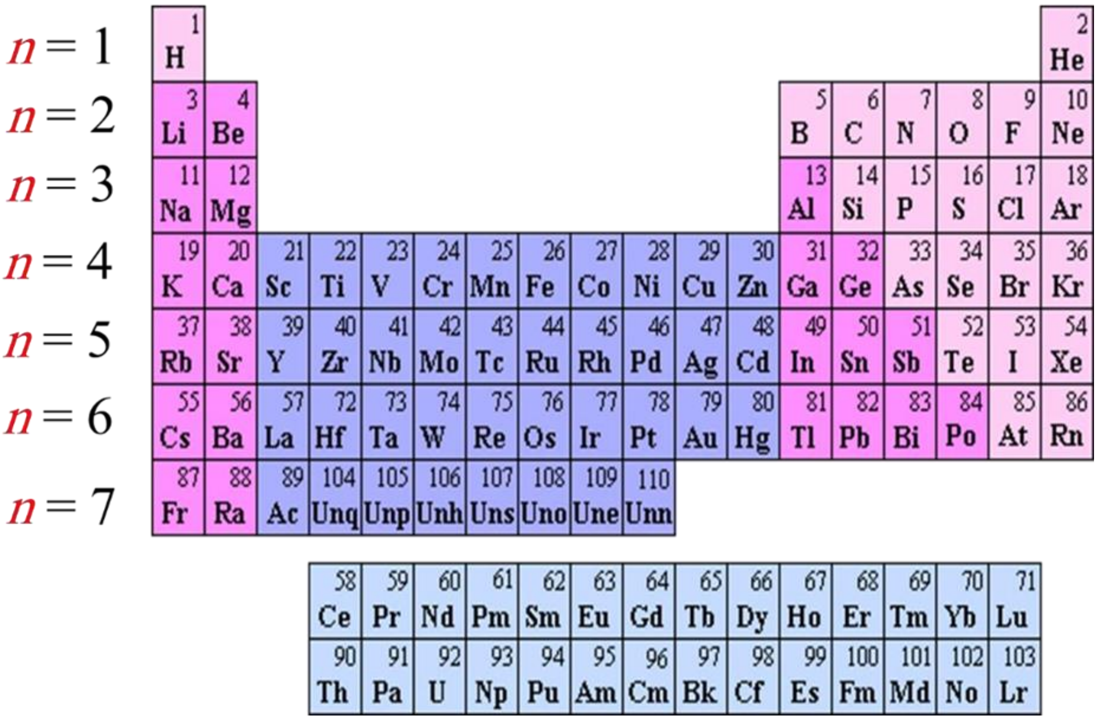


Figure 16 (a) Energy levels are like rungs of a ladder.

You cannot be in between a rung and (b) Energy levels in an atom's electron are unequally spaced. The higher energy levels are closer together.



$n = 1$	1 H																	2 He
$n = 2$	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
$n = 3$	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
$n = 4$	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
$n = 5$	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
$n = 6$	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
$n = 7$	87 Fr	88 Ra	89 Ac	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	110 Unn								
				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Figure 17 Principal Quantum Number n in the periodic table

Angular Momentum Quantum Number

Shape of the "volume" of space that the e- occupies , From 0 to (n-1), figure 18.

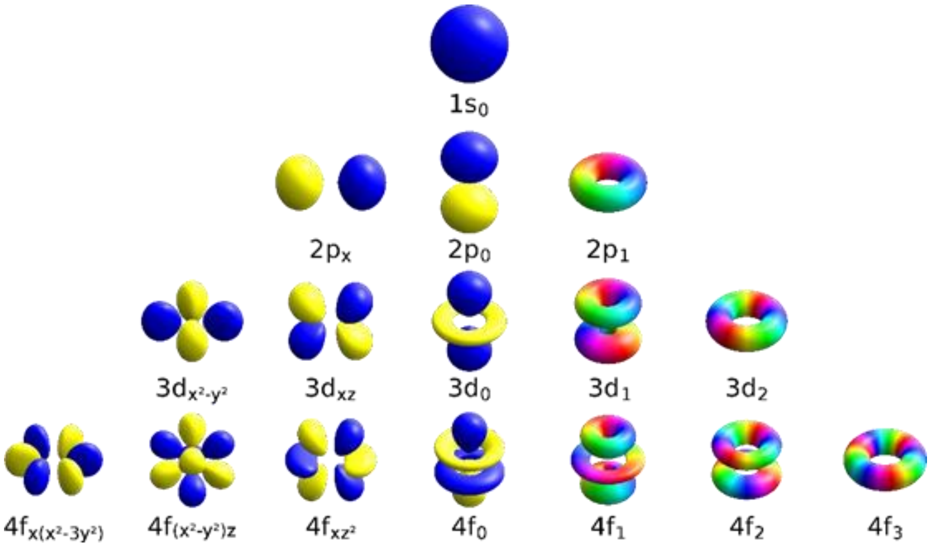


Figure 18 Different shapes of atomic orbitals with different Angular Momentum Quantum Number

Magnetic Quantum Number

Describes the orientation of the orbitals in space. All orientations are identical in energy. Its value from –l,0,l, figure 19 and 20.

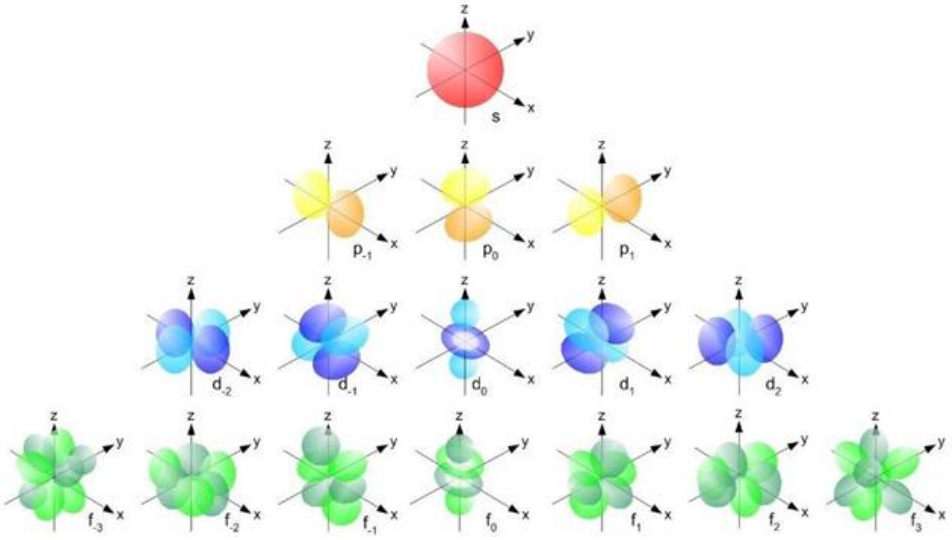
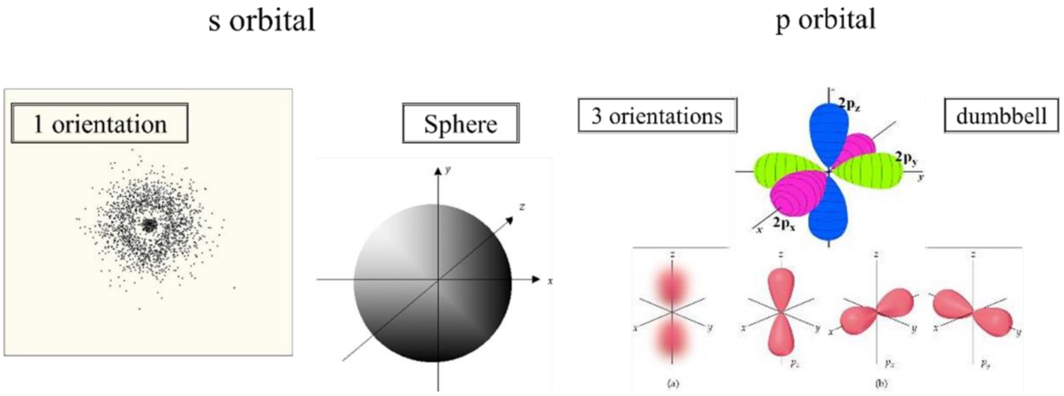
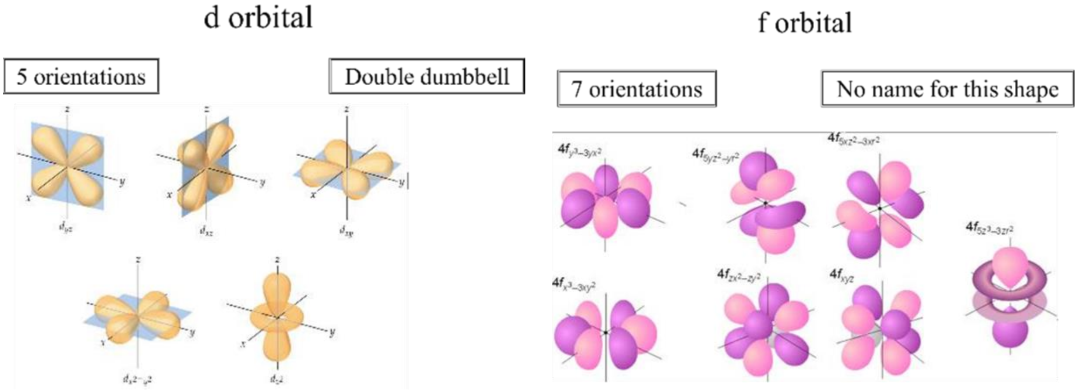


Figure 19 Magnetic Quantum Number and orientations of atomic orbitals


s orbital

p orbital


d orbital

f orbital

Figure 20 atomic orbitals shapes and orientations

Electron Spin Quantum Number

Electrons are thought to be spinning on their own axes-clockwise, or counterclockwise. The up and down arrows denote the direction of the spin.

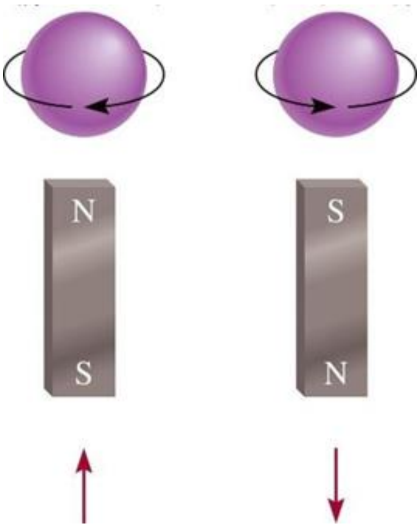


Figure 21 Electron Spin Quantum Number

Summary

Table 1 Summery of atomic numbers

Orbital	shape	# of orientations	Total # of electrons
s	sphere	1	2
p	dumbbell	3	6
d	double dumbell	5	10
f	no name	7	14

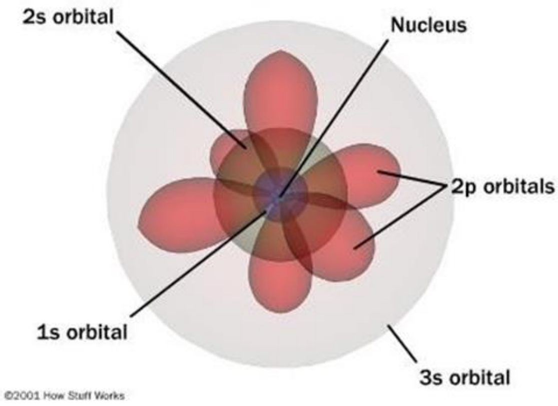


Figure 22 Summery of atomic numbers

Energy of Orbitals

Depends on principle and angular momentum quantum numbers

Shielding Effect

- Why is the 2s orbital lower in energy than the 2p?
- “shielding” reduces the electrostatic attraction, figure 23.
- Energy difference also depends on orbital shape.

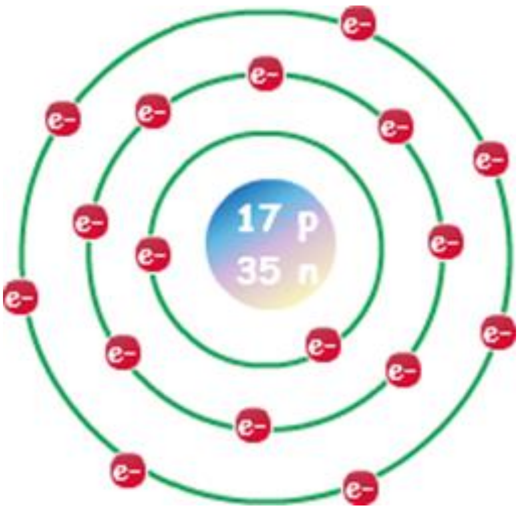
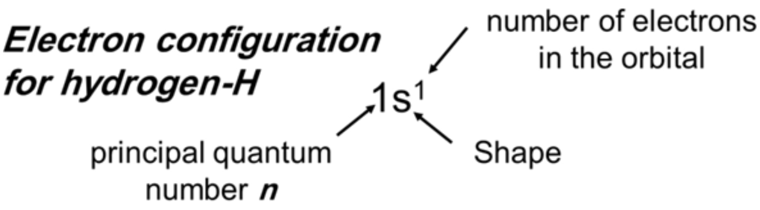
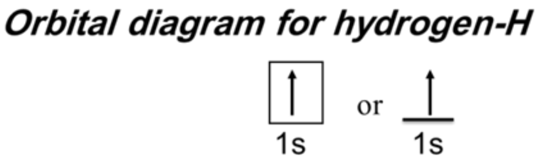


Figure 23 Shielding Effect

Electron Configuration vs Orbital diagram





Aufbau Principle

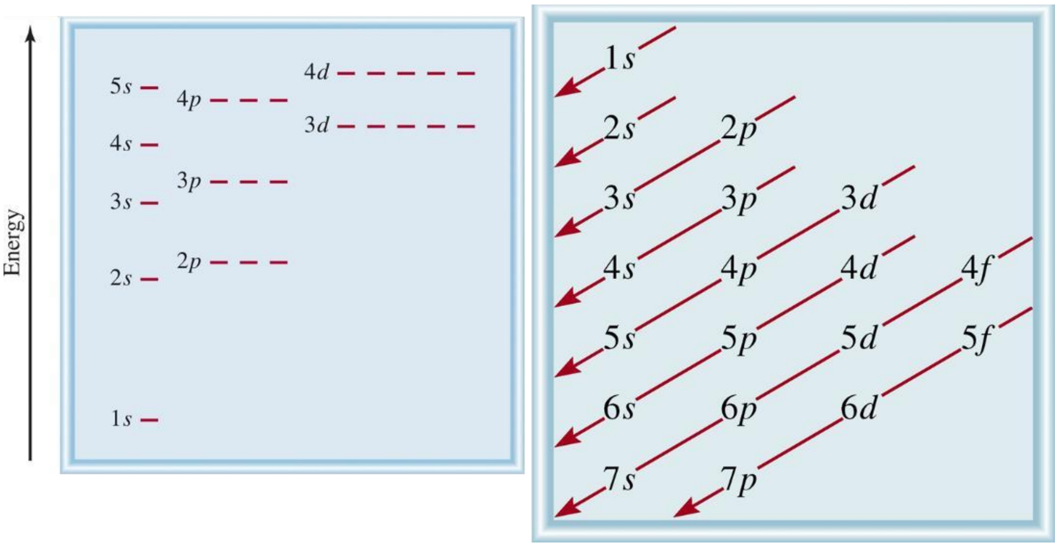
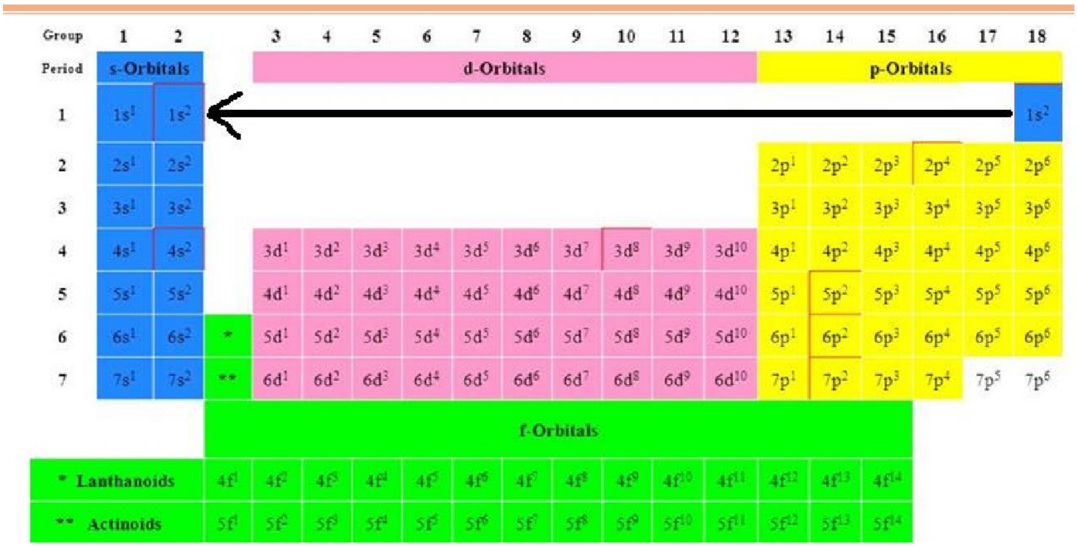


Figure 24 Electron configuration according to Aufbau Principle



Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period	s-Orbitals			d-Orbitals										p-Orbitals					
1	$1s^1$	$1s^2$																	$1s^2$
2	$2s^1$	$2s^2$												$2p^1$	$2p^2$	$2p^3$	$2p^4$	$2p^5$	$2p^6$
3	$3s^1$	$3s^2$												$3p^1$	$3p^2$	$3p^3$	$3p^4$	$3p^5$	$3p^6$
4	$4s^1$	$4s^2$		$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$	$4p^1$	$4p^2$	$4p^3$	$4p^4$	$4p^5$	$4p^6$
5	$5s^1$	$5s^2$		$4d^1$	$4d^2$	$4d^3$	$4d^4$	$4d^5$	$4d^6$	$4d^7$	$4d^8$	$4d^9$	$4d^{10}$	$5p^1$	$5p^2$	$5p^3$	$5p^4$	$5p^5$	$5p^6$
6	$6s^1$	$6s^2$	*	$5d^1$	$5d^2$	$5d^3$	$5d^4$	$5d^5$	$5d^6$	$5d^7$	$5d^8$	$5d^9$	$5d^{10}$	$6p^1$	$6p^2$	$6p^3$	$6p^4$	$6p^5$	$6p^6$
7	$7s^1$	$7s^2$	**	$6d^1$	$6d^2$	$6d^3$	$6d^4$	$6d^5$	$6d^6$	$6d^7$	$6d^8$	$6d^9$	$6d^{10}$	$7p^1$	$7p^2$	$7p^3$	$7p^4$	$7p^5$	$7p^6$
			f-Orbitals																
* Lanthanoids			$4f^1$	$4f^2$	$4f^3$	$4f^4$	$4f^5$	$4f^6$	$4f^7$	$4f^8$	$4f^9$	$4f^{10}$	$4f^{11}$	$4f^{12}$	$4f^{13}$	$4f^{14}$			
** Actinoids			$5f^1$	$5f^2$	$5f^3$	$5f^4$	$5f^5$	$5f^6$	$5f^7$	$5f^8$	$5f^9$	$5f^{10}$	$5f^{11}$	$5f^{12}$	$5f^{13}$	$5f^{14}$			

Figure 25 Orbitals in the Periodic Table

Pauli Exclusion Principle

- No two electrons can have the same 4 quantum numbers
- Only two electrons may occupy the same atomic orbital, and these electrons must have opposite spins
- Electrons that have opposite spins are said to be paired

Hund's Rule

- ❖ The most stable arrangement of electrons in an orbital is the one with the greatest number of parallel spins
- ❖ e- will occupy singly before filling with opposite spins, figure 26.

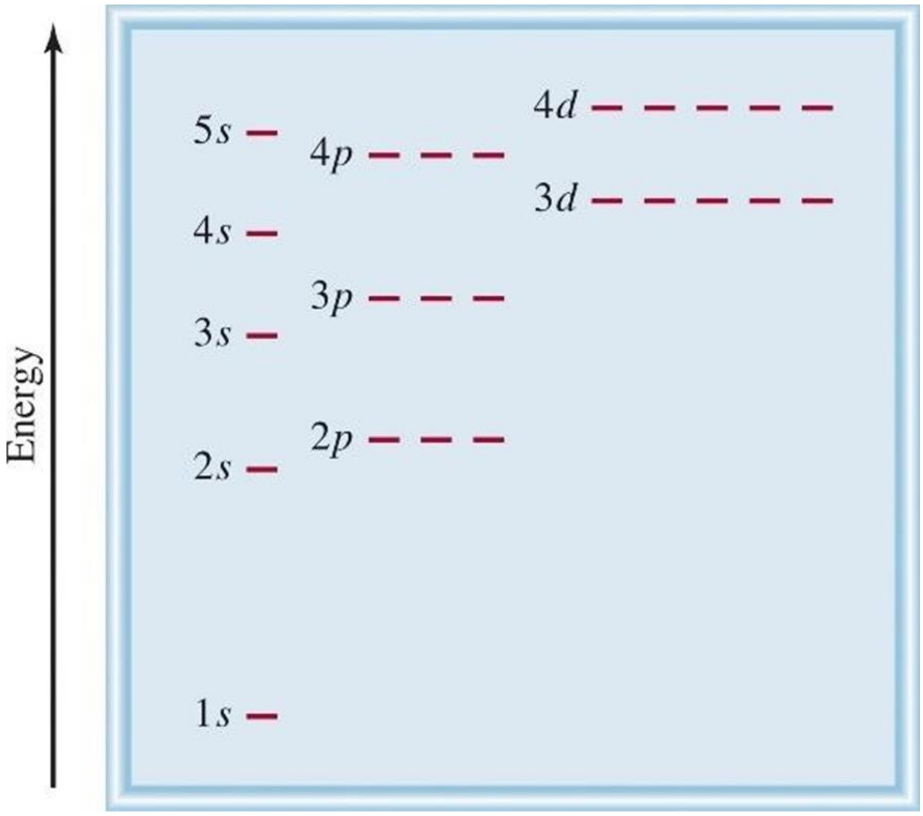
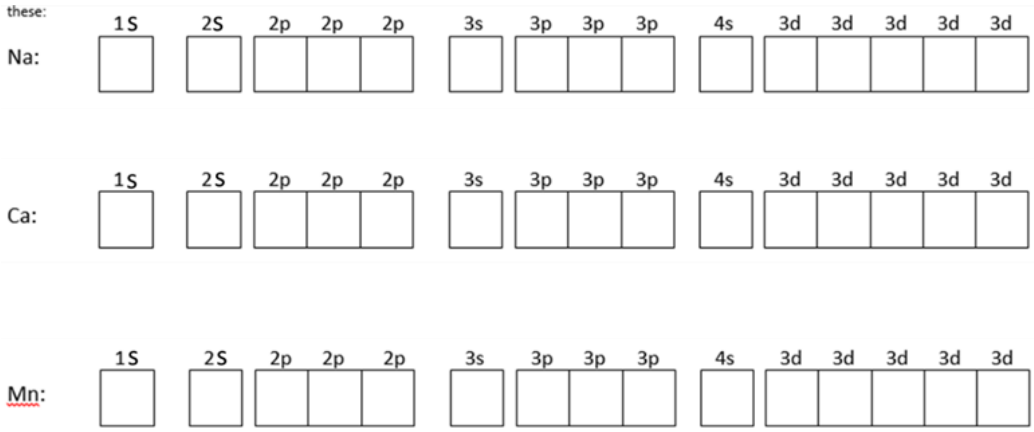


Figure 26 Electron configuration according to Hund's Rule

Practice: Fill in the condensed orbital diagram, and write the electron configuration for the following atoms:


these:

	1S	2S	2p	2p	2p	3s	3p	3p	3p	4s	3d	3d	3d	3d	3d
Na:	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
Ca:	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
Mn:	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

Valence Electrons

- Electrons in the outermost s and p orbitals (highest n shell)
- These electrons participate in chemical reactions.

Example of Exceptions to the Rules

Copper and chromium are exceptions to the Aufbau principle. These are not the only two exceptions.

Element	Should be	Actually is
Copper	$1s^22s^22p^63s^23p^63d^44s^2$	$1s^22s^22p^63s^23p^63d^54s^1$
Chromium	$1s^22s^22p^63s^23p^63d^94s^2$	$1s^22s^22p^63s^23p^63d^{10}4s^1$

Some configurations violate the Aufbau Principle because half-filled sublevels are not as stable as filled sublevels, but they are more stable than other configurations.

Noble Gas Configuration

What is the electron configuration for Ne?

Ne: --

What is the electron configuration for Mg?

Mg: --

What do both electron configurations have in common?

Practice Write the noble gas electron configuration for the following atoms:

Na:

Mn:

Co:

Sn:

History of Magnetism

The history of permanent magnetism dates back over many centuries. The earliest observations of magnetism can be traced back to the Greek philosopher Thales in the 6th Century B.C. However, it was not until 1600 that the modern understanding of magnetism began.

Table 2 History of Magnetism

1600	Dr. William Gilbert published the first systematic experiments on magnetism in "De Magnate".
1819	Oersted accidentally made the connection between magnetism and electricity discovering that a current carrying wire deflected a compass needle.
1825	Sturgeon invented the electromagnet.
1880	Warburg produced the first hysteresis loop for iron.
1895	The Curie law was proposed.
1905	Langevin first explained the theory of diamagnetism and paramagnetism.
1906	Weiss proposed ferromagnetic theory.
1920	The physics of magnetism was developed with theories involving electron spins and exchange interactions, the beginnings of quantum mechanics.

The progress of permanent magnetic materials proceeds in a series of steps. Each material is developed and improved before being supplanted by a new one. This trend is shown in figure 27a which shows the development of permanent magnet materials throughout the 20th century. The graph shows the improvement in maximum energy product of the materials, which is used as a figure of merit, as it is a measure of the ability of magnets to do work per unit volume of material. The reduction in size of magnets is illustrated more vividly in figure 27b.

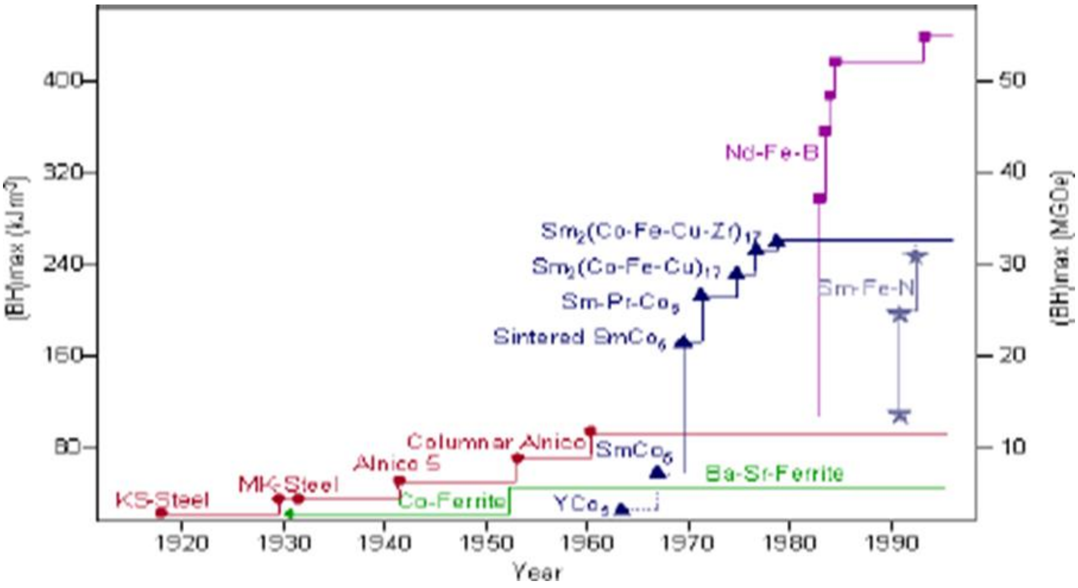


Figure 27 (a): The development of permanent magnets in the 20th Century. BHmax has improved exponentially, doubling every 12 years.

Figure 28 (b): Brass bound lodestone, ferrite block and NdFeB magnet: each store the same magnetic energy (~0.4J) & contain ~70% iron by weight, yet the mass has decreased a thousand-fold.

Origin of Magnetism

Almost everyone is familiar with what a magnetic material can do but very few know how a magnet works. To understand this phenomenon, one must first grasp the complex connection that exists between magnetism and electricity. A simple electromagnet can be produced by wrapping copper wire into the form of a coil and connecting the wire to a battery. A magnetic field is created in the coil, but it remains there only while electricity flows through the wire. An ordinary bar magnet does not have an obvious connection with electricity so how does it work? The field created by the magnet is associated with the motions and interactions of its electrons, the minute charged particles which orbit the nucleus of each atom. Electricity is the movement of electrons, whether in a wire or in an atom, so each atom represents a tiny permanent magnet in its own right. The circulating electron produces its own orbital magnetic moment, measured in Bohr magnetons (μB), and there is also a spin magnetic moment associated with it due to the electron itself spinning, like the earth, on its own axis (illustrated in figure 29). In most materials there is resultant magnetic moment, due to the electrons being grouped in pairs causing the magnetic moment to be cancelled by its neighbor.

In certain magnetic materials the magnetic moments of a large proportion of the electrons align, producing a unified magnetic field. The field produced in the material (or by an electromagnet) has a direction of flow and any magnet will experience a force trying to align it with an externally applied field, just like a compass needle. These forces are used to drive electric motors, produce sounds in a speaker system, control the voice coil in a CD player, etc... The interactions between magnetism and electricity are therefore an essential aspect of many devices we use every day.

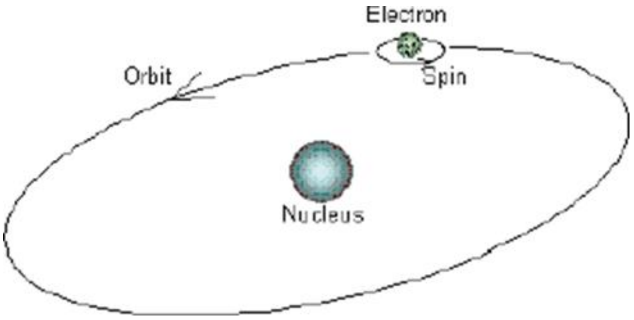


Figure 29 The orbit of a spinning electron about the nucleus of an atom.

Magnetic Units & Terminology

In the study of magnetism there are two systems of units currently in use: the mks (meters-kilograms-seconds) system, which has been adopted as the S.I. units and the cgs (centimeters-grams-seconds) system, which is also known as the Gaussian system. The cgs system is used by many magnets experts due to the numerical equivalence of the magnetic induction (B) and the applied field (H).

Magnetic quantities

When a field is applied to a material it responds by producing a magnetic field, the magnetization (M)

- Magnetization (M): is a measure of the magnetic moment per unit volume of material but can also be expressed per unit mass.
- The magnetic induction (B), which is the total flux of magnetic field lines through a unit cross sectional area of the material, considering both lines of force from the applied field and from the magnetization of the material. B, H and M are related by equation 1a in S.I. units and by equation 1b in cgs units.

$$B = \mu_o (H + M)$$

$$B = H + 4\pi M$$

In equation 1a, the constant μo is the permeability of free space ($4\pi \times 10^{-7}$ Hm^{-1}), which is the ratio of B/H measured in a vacuum. In cgs units the permeability of free space is unity and so does not appear in equation 1b. The units of B, H and M for both S.I. and cgs systems are given in table 3. Note that in the cgs system 4πM is usually quoted as it has units of Gauss and is numerically equivalent to B and H.

- The magnetic susceptibility (χ) is a parameter that demonstrates the type of magnetic material and the strength of that type of magnetic effect.

$$\chi = \frac{M}{H}$$

Sometimes the mass susceptibility (χ_m) is quoted, and this has the units of m3kg-1 and can be calculated by dividing the susceptibility of the material by the density.

- The permeability (μ) is a parameter that demonstrates the type of magnetic material and the strength of that type of magnetic, this is defined in equation 3 (the same for S.I. and cgs units).

$$\mu = \frac{B}{H}$$

In the S.I. system of units, the permeability is related to the susceptibility, as shown in equation 4 and can also be broken down into μ_o and the relative permeability (μr), as shown in equation 5.

$$\mu_r = \chi + 1$$

$$\mu = \mu_o \, \mu_r$$

- The magnetic polarization (J), also referred to as the intensity of magnetization (I). This value is effectively the magnetization of a sample expressed in Tesla and can be calculated as shown in equation 6.

$$J = \mu_o \, M$$

Table 3 The relationship between some magnetic parameters in cgs and S.I. units. (Where: G = Gauss, Oe = Oersted, T = Tesla)

Quantity	Gaussian (cgs units)	S.I. Units	Conversion factor (cgs to S.I.)
Magnetic Induction (B)	G	T	10^{-4}
Applied Field (H)	Oe	Am^{-1}	$10^3 / 4\pi$
Magnetization (M)	emu cm^{-3}	Am-1	10^3
Magnetization (4πM)	G	-	-
Magnetic Polarization (J)	-	T	-
Specific Magnetization (s)	emu g^{-1}	$JT^{-1}kg^{-1}$	1
Permeability (μ)	Dimensionless	H m-1	$4\pi \cdot 10^{-7}$
Relative Permeability (μr)	-	Dimensionless	-
Susceptibility (χ)	emu cm^{-3} Oe^{-1}	Dimensionless	4 π
Maximum Energy Product (BHmax)	M G Oe	k J m^{-3}	$10^2 / 4\pi$

Classification of Magnetic Materials

All materials can be classified in terms of their magnetic behavior falling into one of five categories depending on their bulk magnetic susceptibility. The two most common types of magnetism are diamagnetism and paramagnetism, which account for the magnetic properties of most of the periodic table of elements at room temperature (see figure 30).

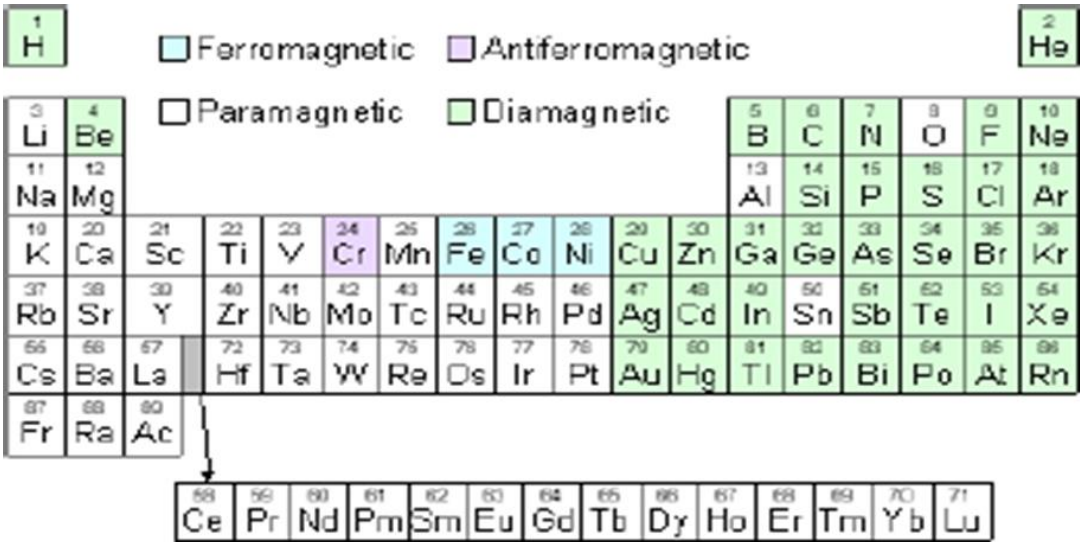
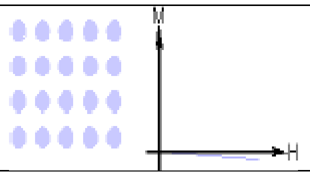
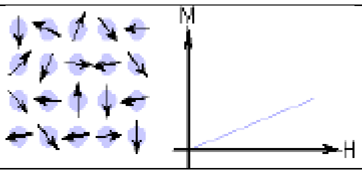
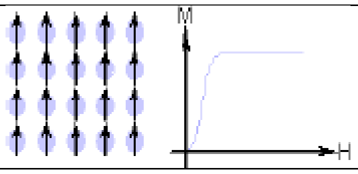
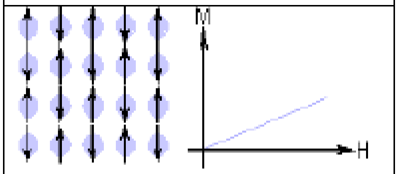
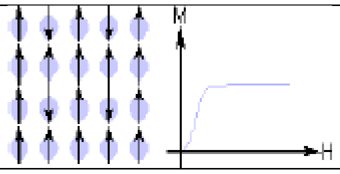


Figure 30 A periodic table showing the type of magnetic behavior of each element at room temperature.

Table 4 Summary of different types of magnetic behavior

Type of Magnetism	Susceptibility	Atomic / Magnetic Behavior	Example/Susceptibility
Diamagnetism	Small & negative	Atoms have no magnetic moment 	Au/-2.74x10^{-6} Cu/-0.77x10^{-6}
Paramagnetism	Small & positive	Atoms have randomly oriented magnetic moments 	β-Sn/0.19x10^{-6} Pt/21.04x10^{-6} Mn/66.1x10^{-6}
Ferromagnetism	Large & positive, function of applied field, microstructure dependent	Atoms have parallel aligned magnetic moments 	Fe/~100,000
Antiferromagnetizm	Small & positive	Atoms have mixed parallel and anti- parallel aligned magnetic moments 	Cr/3.6x10^{-6}
Ferrimagnetism	Large & positive, function of applied field, microstructure dependent	Atoms have anti- parallel aligned magnetic moments 	Ba ferrite/~3

Diamagnetism

Diamagnetic metals have a very weak and negative susceptibility to magnetic fields. Diamagnetic materials are slightly repelled by a magnetic field and the material does not retain the magnetic properties when the external field is removed. Diamagnetic materials are solids with all paired electron resulting in no permanent net magnetic moment per atom. Diamagnetic properties arise from the realignment of the electron orbits under the influence of an external magnetic field. Most elements in the periodic table, including copper, silver, and gold, are diamagnetic.

Paramagnetism

There are several theories of paramagnetism, which are valid for specific types of material. The Langevin model, which is true for materials with non-interacting localized electrons, states that each atom has a magnetic moment which is randomly oriented as a result of thermal agitation. The application of a magnetic field creates a slight alignment of these moments and hence a low magnetization in the same direction as the applied field. As the temperature increases, then the thermal agitation will increase, and it will become harder to align the atomic magnetic moments and hence the susceptibility will decrease. This behavior is known as the Curie law and is shown below in Equ.7, where C is a material constant called the Curie constant.

$$\chi = \frac{C}{T}$$

Materials which obey this law are materials in which the magnetic moments are localized at the atomic or ionic sites and where there is no interaction between neighboring magnetic moments. The hydrated salts of the transition metals, e.g. $CuSO4\cdot5H2O$, are examples of this type of behavior as the transition metal ions, which have a magnetic moment, are surrounded by a number of non-magnetic ions / atoms, which prevent interaction between neighboring magnetic moments. In fact, the Curie law is a special case of the more general Curie-Weiss law (equ.8), which incorporates a temperature constant (θ) and derives from Weiss theory, proposed for ferromagnetic materials, which incorporates the interaction between magnetic moments:

$$\chi = \frac{C}{T - \theta}$$

In this equation θ can either be positive, negative or zero. Clearly when θ = 0 then the Curie-Weiss law equates to the Curie law.

- When θ is non-zero then there is an interaction between neighboring magnetic moments and the material is only paramagnetic above a certain transition temperature.
- If θ is positive then the material is ferromagnetic below the transition temperature and the value of θ corresponds to the transition temperature (Curie temperature, TC).
- If θ is negative then the material is antiferromagnetic below the transition temperature (Néel temperature, TN), however the value of θ does not relate to TN. It is important to note that this equation is only valid when the material is in a paramagnetic state. It is also not valid for many metals as the electrons contributing to the magnetic moment are not localized. However, the law does apply to some metals, e.g. the rare earths, where the 4f electrons, that create the magnetic moment, are closely bound.

The Pauli model of paramagnetism is true for materials where the electrons are free and interact to form a conduction band this is valid for most paramagnetic metals. In this model the conduction electrons are considered essentially to be free and under an applied field an imbalance between electrons with opposite spin is set up leading to a low. magnetization in the same direction as the applied field. The susceptibility is independent of temperature, although the electronic band structure may be affected, which will then have an effect on the susceptibility.

Ferromagnetism

Ferromagnetism is only possible when atoms are arranged in a lattice and the atomic magnetic moments can interact to align parallel to each other. This effect is explained in classical theory by the presence of a molecular field within the ferromagnetic material, which was first postulated by Weiss in 1907. This field is sufficient to magnetize the material to saturation. In quantum mechanics, the Heisenberg model of ferromagnetism describes the parallel alignment of magnetic moments in terms of an exchange interaction between neighboring moments.

Weiss postulated the presence of magnetic domains within the material, which are regions where the atomic magnetic moments are aligned. The movement of these domains determines how the material responds to a magnetic field and as a consequence the susceptible is a function of applied magnetic field. Therefore, ferromagnetic materials are usually compared in terms of saturation magnetization (magnetization when all domains are aligned) rather than susceptibility.

In the periodic table of elements only Fe, Co and Ni are ferromagnetic at and above room temperature. As ferromagnetic materials are heated then the thermal agitation of the atoms means that the degree of alignment of the atomic magnetic moments decreases and hence the saturation magnetization also decreases. Eventually the thermal agitation becomes so great that the material becomes paramagnetic; the temperature of this transition is the Curie temperature, TC (Fe: TC =770°C, Co: TC =1131°C and Ni: TC =358°C). Above TC then the susceptibility varies according to the Curie-Weiss law.

Antiferromagnetism

In the periodic table the only element exhibiting antiferromagnetism at room temperature is chromium. Antiferromagnetic materials are remarkably similar to ferromagnetic materials but the exchange interaction between neighboring atoms leads to the anti-parallel alignment of the atomic magnetic moments. Therefore, the magnetic field cancels out and the material appears to behave in the same way as a paramagnetic material. Like ferromagnetic materials these materials become paramagnetic above a transition temperature, known as the Néel temperature, TN. (Cr: TN=37ºC).

Ferrimagnetism

Ferrimagnetism is only observed in compounds, which have more complex crystal structures than pure elements. Within these materials the exchange interactions lead to parallel alignment of atoms in some of the crystal sites and anti-parallel alignment of others. The material breaks down into magnetic domains, just like a ferromagnetic material and the magnetic behavior is also very similar, although ferrimagnetic materials usually have lower saturation magnetizations. For example in Barium ferrite (BaO.6Fe2O3) the unit cell contains 64 ions of which the barium and oxygen ions have no magnetic moment, 16 Fe3+ ions have moments aligned parallel and 8 Fe3+ aligned anti-parallel giving a net magnetization parallel to the applied field, but with a relatively low magnitude as only ⅛ of the ions contribute to the magnetization of the material.

Intrinsic Properties of Magnetic Materials

The intrinsic properties of a magnetic material are those properties that are characteristic of the material and are unaffected by the microstructure (e.g. grain size, crystal orientation of grains). These properties include the Curie temperature, the saturation magnetization and the magneto crystalline anisotropy.

Saturation Magnetization

The saturation magnetization (MS) is a measure of the maximum amount of field that can be generated by a material. It will depend on the strength of the dipole moments on the atoms that make up the material and how densely they are packed together. The atomic dipole moment will be affected by the nature of the atom and the overall electronic structure within the compound. The packing density of the atomic moments will be determined by the crystal structure (i.e., the spacing of the moments) and the presence of any non-magnetic elements within the structure.

For ferromagnetic materials, at finite temperatures, MS will also depend on how well these moments are aligned, as thermal vibration of the atoms causes misalignment of the moments and a reduction in MS. For ferrimagnetic materials not all of the moments align parallel, even at zero Kelvin and hence MS will depend on the relative alignment of the moments as well as the temperature. The saturation magnetization is also referred to as the spontaneous magnetization, although this term is usually used to describe the magnetization within a single magnetic domain. Table 3 gives some examples of the saturation polarization and Curie temperature of materials commonly used in magnetic applications.

Table 5 The saturation polarization (JS) and Curie temperature (TC) of a range of magnetic materials.

Material	Magnetic Structure	MS at 298K (T)	TC (ºC)
Fe	Ferro	2.15	770
Co	Ferro	1.76	1131
Ni	Ferro	0.60	358
$Nd_2Fe_{14}B$	Ferro	1.59	312
$SmCo_5$	Ferro	1.14	720
Sm2Co17	Ferro	1.25	820
$BaO.6Fe_2O_3$	Ferri	0.48	450
$SrO.6Fe_2O_3$	Ferri	0.48	450
Fe 3wt% Si	Ferro	2.00	740
Fe 4wt% Si	Ferro	1.97	690
Fe 35wt% Co	Ferro	2.45	970
Fe 78wt% Ni	Ferro	0.70	580
Fe 50wt% Ni	Ferro	1.55	500
$MnO.Fe_2O_3$	Ferri	0.51	300

Magnetic Anisotropy

In a crystalline magnetic material, the magnetic properties will vary depending on the crystallographic direction in which the magnetic dipoles are aligned. Figure 31 demonstrates this effect for a single crystal of cobalt. The hexagonal crystal structure of Co can be magnetized easily in the direction (i.e. along the c-axis) but has hard directions of magnetization in the [110] type directions, which lie in the basal plane (90° from the easy direction). A measure of the magneto crystalline anisotropy in the easy direction of magnetization is the anisotropy field, Ha (illustrated in figure 30), which is the field required to rotate all the moments by 90° as one unit in a saturated single crystal. The anisotropy is caused by a coupling of the electron orbitals to the lattice, and in the easy direction of magnetization this coupling is such that these orbitals are in the lowest energy state. The easy direction of magnetization for a permanent magnet, based on ferrite or the rare earth alloys, must be uniaxial, however, it is also possible to have materials with multiple easy axes or where the easy direction can lie anywhere on a certain plane or on the surface of a cone. The fact that a permanent magnet has uniaxial anisotropy means that it is difficult to demagnetize as it is resistant to rotation of the direction of magnetization.

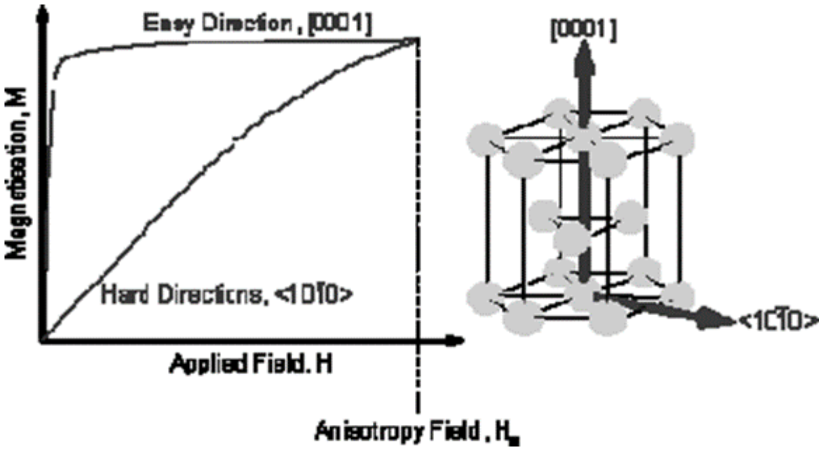


Figure 31 The magneto crystalline anisotropy of cobalt.

Magnetic Domains

In order to explain the fact that ferromagnetic materials with spontaneous magnetization could exist in the demagnetized state Weiss proposed the concept of magnetic domains. Weiss built on earlier work carried out by Ampère, Weber and Ewing suggesting their existence. The findings of this work revealed that within domain large numbers of atomic moments are aligned typically 1012-1018, over a much larger volume than was previously suspected. The magnetization within the domain is saturated and will always lie in the easy direction of magnetization when there is no externally applied field. The direction of the domain alignment across a large volume of material is more or less random and hence the magnetization of a specimen can be zero. Magnetic domains exist in order to reduce the energy of the system. A uniformly magnetized specimen as shown in figure 32(a) has a large magnetostatics energy associated with it. This is the result of the presence of magnetic free poles at the surface of the specimen generating a demagnetizing field, Hd. From the convention adopted for the definition of the magnetic moment for a magnetic dipole the magnetization within the specimen points from the South Pole to the North Pole, while the direction of the magnetic field points from north to south. Therefore, the demagnetizing field is in opposition to the magnetization of the specimen. The magnitude of Hd is dependent on the geometry and magnetization of the specimen. In general, if the sample has a high length to diameter ratio (and is magnetized in the long axis) then the demagnetizing field and the magnetostatics energy will be low. The breakup of the magnetization into two domains as illustrated in figure 32(b) reduces the magnetostatics energy by half. In fact, if the magnet breaks down into N domains, then the magnetostatics energy is reduced by a factor of 1/N, hence figure 32(c) has a quarter of the magnetostatic .

energy of figure 32(a). Figure 32(d) shows a closure domain structure where the magnetostatics energy is zero, however, this is only possible for materials that do not have a strong uniaxial anisotropy, and the neighboring domains do not have to be at 180º to each other.

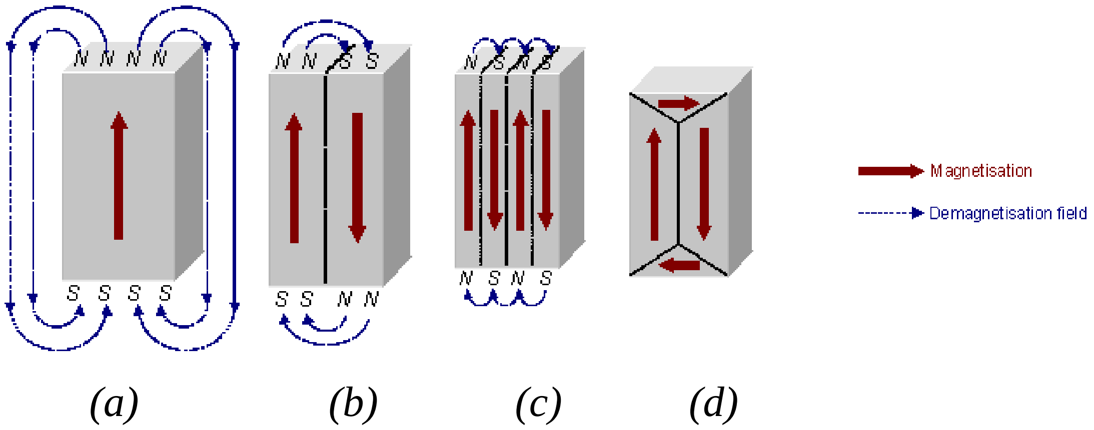


Figure 32 Schematic illustration of the breakup of magnetization into domains (a) single domain, (b) two domains, (c) four domains and (d) closure domains.

The introduction of a domain raises the overall energy of the system, therefore the division into domains only continues while the reduction in magnetostatics energy is greater than the energy required to form the domain wall. The energy associated a domain wall is proportional to its area. The schematic representation of the domain wall, shown in figure 33, illustrates that the dipole moments of the atoms within the wall are not pointing in the easy direction of magnetization and hence are in a higher energy state. In addition, the atomic dipoles within the wall are not at 180º to each other and so the exchange energy is also raised within the wall. Therefore, the domain wall energy is an intrinsic property of a material depending on the degree of magneto crystalline anisotropy and the strength of the exchange interaction between neighboring atoms. The thickness of the wall will also vary in relation to these parameters, as a strong magneto crystalline anisotropy will favor a narrow wall, whereas a strong exchange interaction will favor a wider wall.

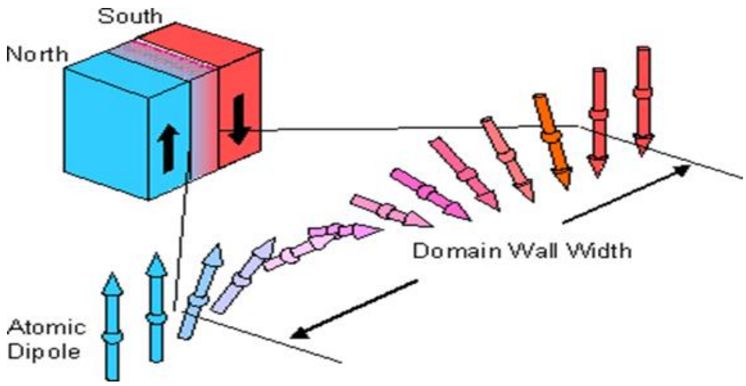


Figure 33 Schematic representation of a 180º domain wall.

A minimum energy can therefore be achieved with a specific number of domains within a specimen. This number of domains will depend on the size and shape of the sample (which will affect the magnetostatics energy) and the intrinsic magnetic properties of the material (which will affect the magnetostatics energy and the domain wall energy).

The Hysteresis Loop and Magnetic Properties

A great deal of information can be learned about the magnetic properties of a material by studying its hysteresis loop. A hysteresis loop shows the relationship between the induced magnetic flux density (B) and the magnetizing force (H). It is often referred to as the B-H loop. An example hysteresis loop is shown below.

The loop is generated by measuring the magnetic flux of a ferromagnetic material while the magnetizing force is changed. A ferromagnetic material that has never been previously magnetized or has been thoroughly demagnetized will follow the dashed line as H is increased. As the line demonstrates, the greater the amount of current applied (H+), the stronger the magnetic field in the component (B+). At point "a" almost all of the magnetic domains are aligned and an additional increase in the magnetizing force will produce very little increase in magnetic flux. The material has reached the point of magnetic saturation. When H is reduced to zero, the curve will move from point "a" to point "b." At this point, it can be seen that some magnetic flux remains in the material even though the magnetizing force is zero. This is referred to as the point of retentivity on the graph and indicates the remanence or level of residual magnetism in the material. (Some of the magnetic domains remain aligned but some have lost their alignment.) As the magnetizing force is reversed, the curve moves to point "c", where the flux has been reduced to zero. This is called the point of coercivity on the curve. (The reversed magnetizing force has flipped enough of the domains so that the net flux within the material is zero.) The force required to remove the residual magnetism from the material is called the coercive force or coercivity of the material. As the magnetizing force is increased in the negative direction, the material will again become magnetically saturated but in the opposite direction (point "d"). Reducing H to zero brings the curve to point "e." It will have a level of residual magnetism equal to that achieved in the other direction. Increasing H back in the positive direction will return B to zero.

Notice that the curve did not return to the origin of the graph because some force is required to remove the residual magnetism. The curve will take a different path from point "f" back to the saturation point where it with complete the loop. From the hysteresis loop, a number of primary magnetic properties of a material can be determined.

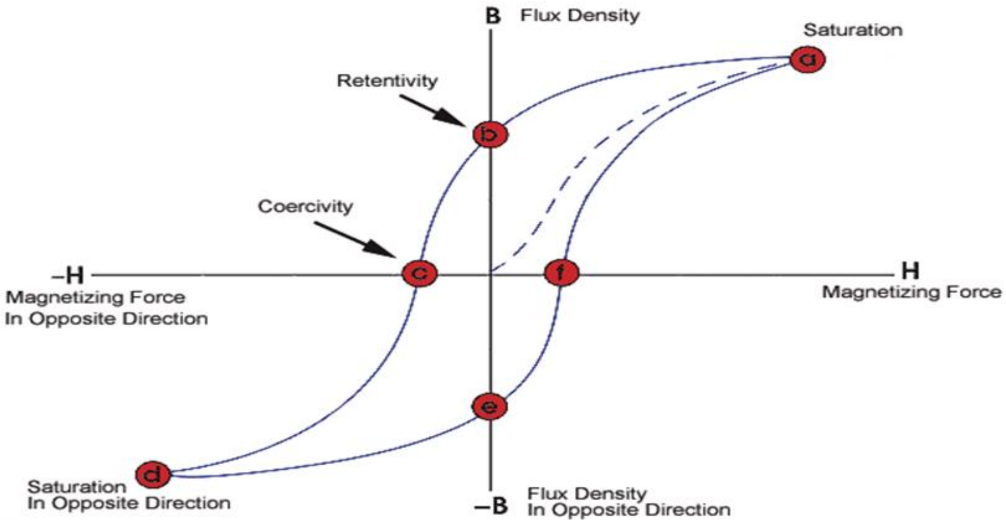


Figure 34 A typical hysteresis loop for a ferro- or ferri- magnetic material

1. **Retentivity** - A measure of the residual flux density corresponding to the saturation induction of a magnetic material. In other words, it is a material's ability to retain a certain amount of residual magnetic field when the magnetizing force is removed after achieving saturation. (The value of B at point b on the hysteresis curve).
2. **Residual Magnetism or Residual Flux** - The magnetic flux density that remains in a material when the magnetizing force is zero. Note that residual magnetism and retentivity are the same when the material has been magnetized to the saturation point. However, the level of residual magnetism may be lower than the retentivity value when the magnetizing force did not reach the saturation level.
3. **Coercive Force** - The amount of reverse magnetic field which must be applied to a magnetic material to make the magnetic flux return to zero. (The value of H at point c on the hysteresis curve.)
4. **Permeability, m** - A property of a material that describes the ease with which a magnetic flux is established in the component.
5. **Reluctance** - Is the opposition that a ferromagnetic material shows to the establishment of a magnetic field. Reluctance is analogous to the resistance in an electrical circuit.

Chapter 2

Nuclear magnetic resonance

Introduction

Nuclear magnetic resonance, or NMR as it is abbreviated by scientists, is a phenomenon, which occurs when the nuclei of certain atoms are immersed in a static magnetic field and exposed to a second oscillating magnetic field. Some nuclei experience this phenomenon, and others do not, dependent upon whether they possess a property called spin, figure 35.

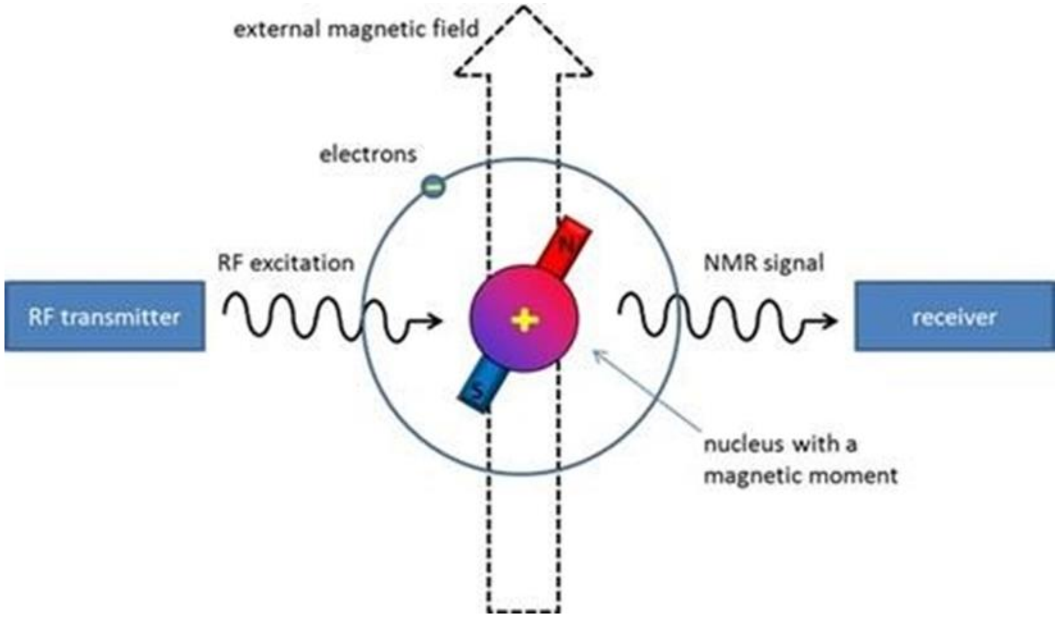
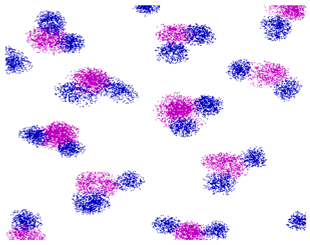


Figure 35 Mechanism of NMR

Now first let us review some basis concepts to understand the physics of NMR.

- Most of the matter you can examine with NMR is composed of molecules.
- Molecules are composed of atoms. Here are a few water molecules.



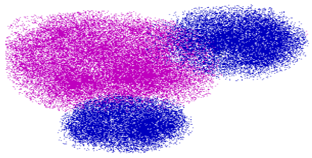


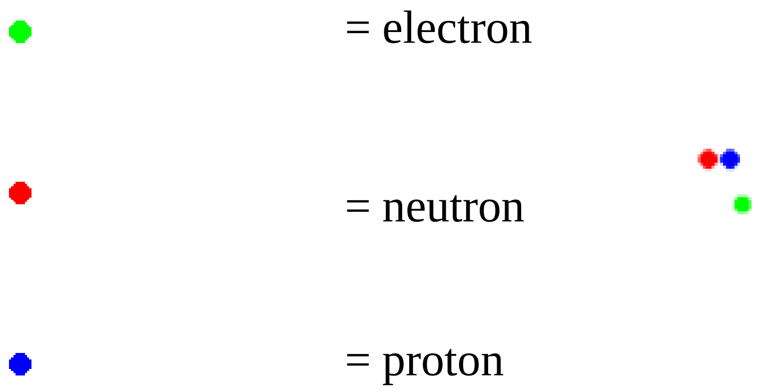
Figure 36 Orientation of water molecules

Each water molecule has one oxygen and two hydrogen atoms, figure 37. If we zoom into one of the hydrogens past the electron cloud, we see a nucleus composed of a single proton. The proton possesses a property called spin which:

1. Can be thought of as a small magnetic field,
2. Will cause the nucleus to produce an NMR signal.

Spin

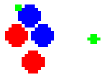
Spin is a fundamental property of nature like electrical charge or mass. Spin comes in multiples of 1/2 and can be + or -. Protons, electrons, and neutrons possess spin. Individual unpaired electrons, protons, and neutrons each possesses a spin of 1/2. In the deuterium atom (^{2}H), with one unpaired electron, one unpaired proton, and one unpaired neutron, the total electronic spin = 1/2 and the total nuclear spin = 1.



Two or more particles with spins having opposite signs can pair up to eliminate the observable manifestations of spin. An example is helium. In nuclear magnetic resonance, it is unpaired nuclear spins that are of importance.

🟢 =electron

🔴 =neutron



🔵 = proton

Properties of Spin

When placed in a magnetic field of strength B, a particle with ν a net spin can absorb a photon, of frequency ν. The frequency depends on the gyromagnetic ratio, γ of the particle.

$$\nu = \gamma B$$

For hydrogen, $\gamma = 42.58$ MHz / T

Nuclei with Spin

The shell model for the nucleus tells us that nucleons, just like electrons, fill orbitals. When the number of protons or neutrons equals 2, 8, 20, 28, 50, 82, and 126, orbitals are filled. Because nucleons have spin, just like electrons do, their spin can pair up when the orbitals are being filled and cancel out. Almost every element in the periodic table has an isotope with a non-zero nuclear spin. NMR can only be performed on isotopes whose natural abundance is high enough to be detected. Some of the nuclei routinely used in NMR are listed in table 6.

Table 6 Main nuclei in NMR

Nuclei	Unpaired Protons	Unpaired Neutrons	Net Spin	γ (MHz/T)
^1H	1	0	1/2	42.58

^{2}H	1	1	1	6.54
^{31}P	1	0	1/2	17.25
^{23}Na	1	2	3/2	11.27
^{14}N	1	1	1	3.08
^{13}C	0	1	1/2	10.71
^{19}F	1	0	1/2	40.08

Energy Levels

To understand how particles with spin behave in a magnetic field, consider a proton. This proton has the property called spin. Think of the spin of this proton as a magnetic moment vector, causing the proton to behave like a tiny magnet with a north and south pole. When the proton is placed in an external magnetic field, the spin vector of the particle aligns itself with the external field, just like a magnet would. There is a low energy configuration or state where the poles are aligned N- S-N-S and a high energy state N-N-S-S, figure 37.

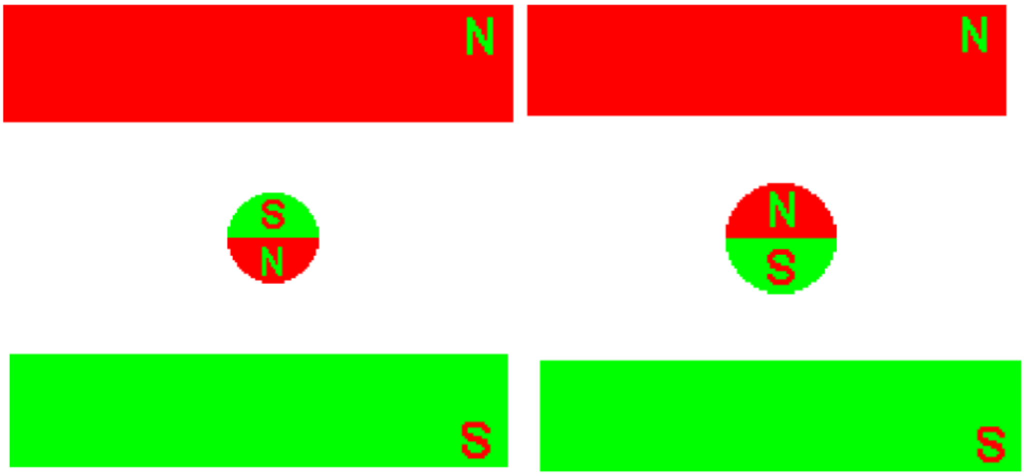


Figure 37 Alignment of proton in the external magnetic field

Transitions

This particle can undergo a transition between the two energy states by the absorption of a photon, figure 38. A particle in the lower energy state absorbs a photon and ends up in the upper energy state. The energy of this photon must exactly match the energy difference between the two states. The energy, E, of a photon is related to its frequency, ν, by Planck's constant (h = 6.626x10-34 J s).

$$E = h \nu$$

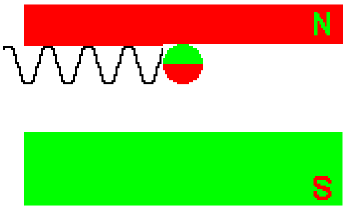


Figure 38 Transition between the two energy states

In NMR and MRI, the quantity ν is called the resonance frequency and the Larmor frequency.

Energy Level Diagrams

The energy of the two spin states can be represented by an energy level diagram, figure 39. We have seen that $= \gamma B$ and $E = h$, therefore the energy of the photon needed to cause a transition between the two spin states is

$$E = h\,\gamma B$$

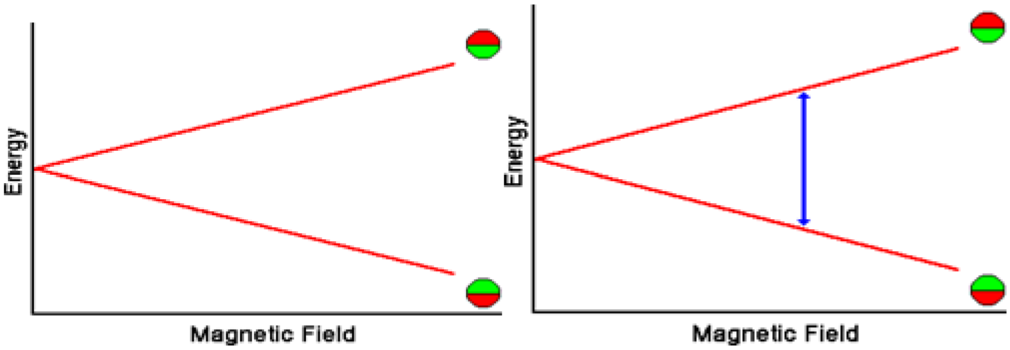


Figure 39 Energy level diagram

When the energy of the photon matches the energy difference between the two spin states an absorption of energy occurs. In the NMR experiment, the frequency of the photon is in the radio frequency (RF) range. In NMR spectroscopy, is between 60 and 800 MHz for hydrogen nuclei. In clinical MRI, ν is typically between 15 and 80 MHz for hydrogen imaging.

CW NMR Experiment

The simplest NMR experiment is the continuous wave (CW) experiment. There are two ways of performing this experiment. In the first, a constant frequency, which is continuously on, probes the energy levels while the magnetic field is varied. The energy of this frequency is represented by the blue line in the energy level diagram.

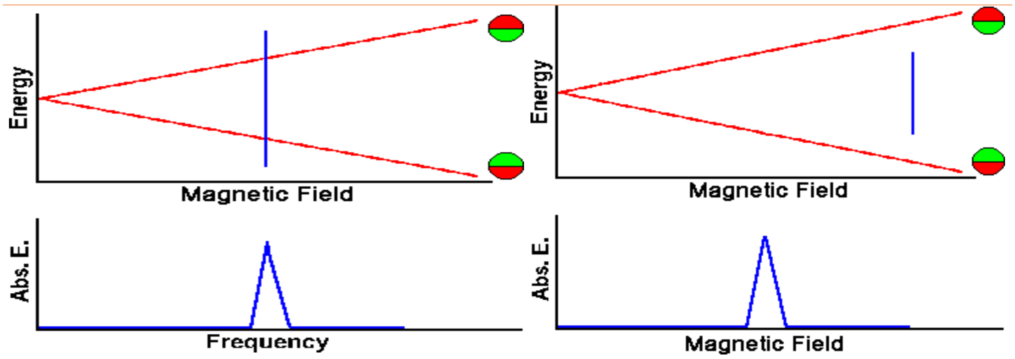


Figure 40 CW NMR Experiment (a) with constant frequency and (B) with constant magnetic field

The CW experiment can also be performed with a constant magnetic field and a frequency which is varied. The magnitude of the constant magnetic field is represented by the position of the vertical blue line in the energy level diagram.

Boltzmann Statistics

When a group of spins is placed in a magnetic field, each spin aligns in one of the two possible orientations, figure 41. At room temperature, the number of spins in the lower energy level, N+, slightly outnumbers the number in the upper level, N-. Boltzmann statistics tells us that:

$$N^{-}/N^{+} = e^{-E/KT}$$

E is the energy difference between the spin states; k is Boltzmann's constant, 1.3805×10^{-23} J/Kelvin; and T is the temperature in Kelvin. As the temperature decreases, so does the ratio N^{-}/N^{+}. As the temperatureincreases, the ratio approaches one.

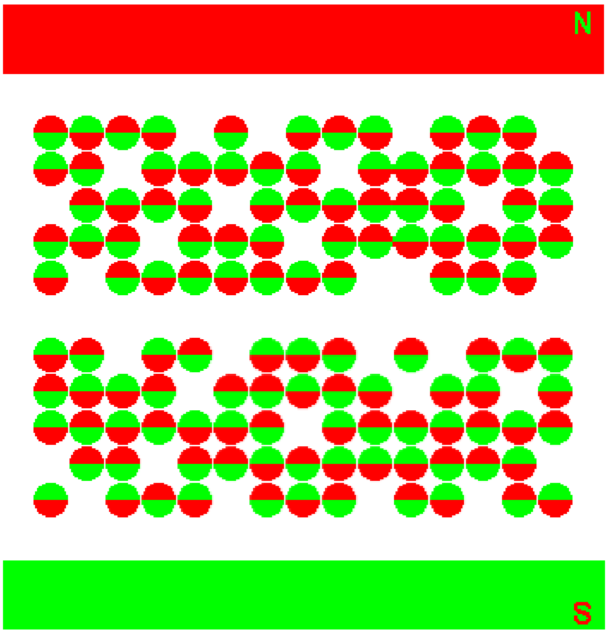


Figure 41 Group of spins is placed in a magnetic field

The signal in NMR spectroscopy results from the difference between the energy absorbed by the spins which make a transition from the lower energy state to the higher energy state, and the energy emitted by the spins which simultaneously make a transition from the higher energy state to the lower energy state. The signal is thus proportional to the population difference between the states. NMR is a rather sensitive spectroscopy since it is capable of detecting these exceedingly small population differences. It is the resonance, or exchange of energy at a specific frequency between the spins and the spectrometer, which gives NMR its sensitivity.

Spin Packets

It is cumbersome to describe NMR on a microscopic scale. A macroscopic picture is more convenient. The first step in developing the macroscopic picture is to define the spin packet. A spin packet is a group of spins experiencing the same magnetic field strength. In this example, the spins within each grid section represent a spin packet, figure 42.

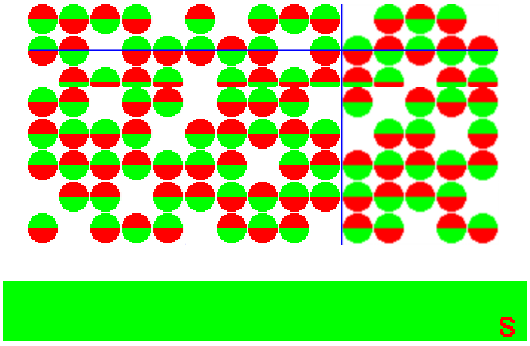


Figure 42 A spin packet

At any instant in time, the magnetic field due to the spins in each spin packet can be represented by a magnetization vector, figure 43.

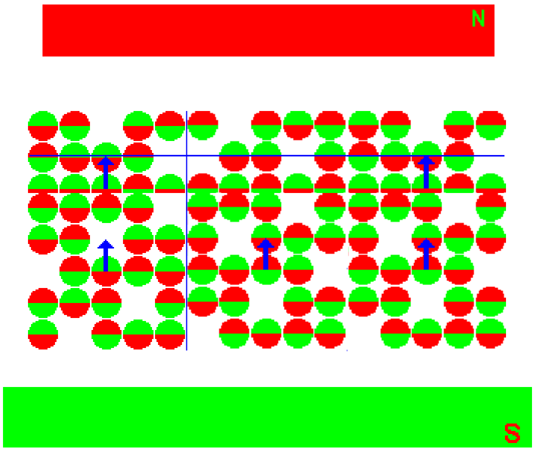


Figure 43 Magnetization vector in spin packet

The size of each vector is proportional to (N+ - N-). The vector sum of the magnetization vectors from all of the spin packets is the net magnetization. In order to describe pulsed NMR is necessary from here on to talk in terms of the net magnetization, figure 44.

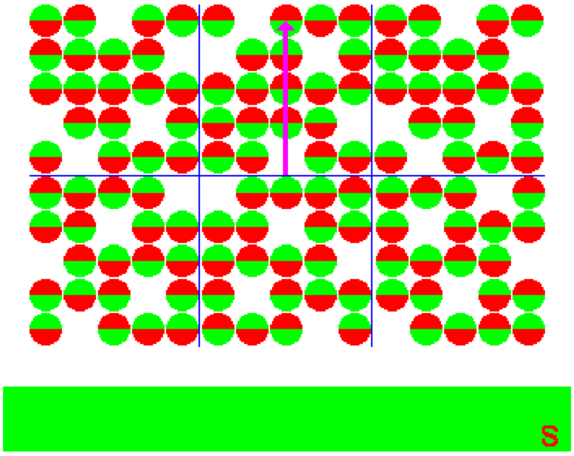


Figure 44 net magnetization

Adapting the conventional NMR coordinate system, the external magnetic field and the net magnetization vector at equilibrium are both along the Z axis.

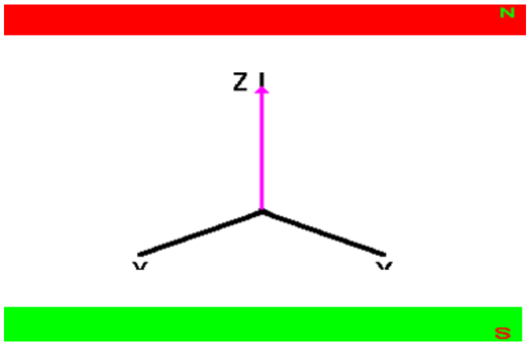


Figure 45 Net magnetization vector at equilibrium

The magnetization of nuclei

A proton has a spin, and thus the electrical charge of the proton also moves. A moving electrical charge is an electrical current, and this is accompanied by a magnetic field. Thus, the proton has its own magnetic field, and it can be seen as a little bar magnet, figure 46.

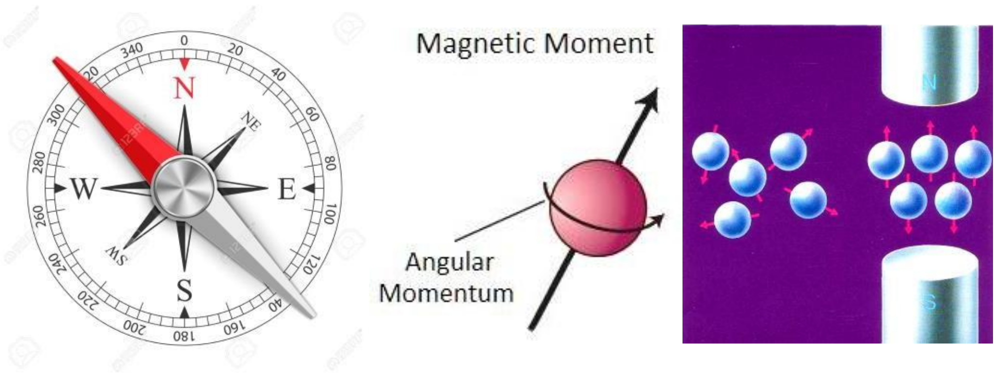


Figure 46 Proton as a little magnet

What happens to the protons when we put them into an external magnetic field?

The protons - being little magnets - align themselves in the external magnetic field like a compass needle in the magnetic field of the earth. However , there is a significant difference. For the compass needle there is only one way to align itself with the magnetic field.

For the protons however, there are two:

The protons may align with their South and North poles in the direction of the external field, parallel to it. Or they may point exactly in the complete opposite direction, anti-parallel, figure 47.

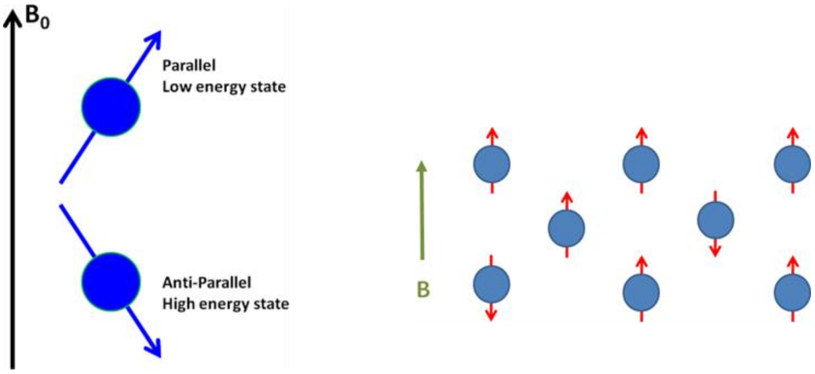


Figure 47 Alignment of proton in the external magnetic field

These types of alignment are on different energy levels . To explain this; a man can align himself parallel to the magnetic field of the earth i.e., walk on his feet, or he can align himself anti-parallel, in the opposite direction. Both states are on different energy levels, i.e., need different amounts of energy . Walking on one's feet is undoubtedly less exhausting , takes less energy than walking on one's hands.

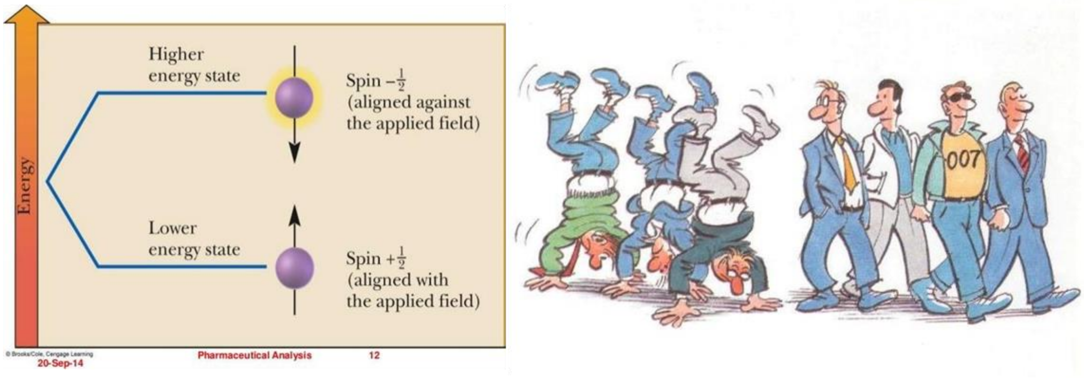


Figure 48 Possible energy states of excited proton in the external magnetic field

Naturally, the preferred state of alignment is the one that needs less energy. So more protons are on the lower energy level, parallel to the external magnetic field (walk on their feet). The difference in number is, however, very small and depends on the strength of the applied magnetic field. To get a rough idea: for about 10 million protons "walking on their hands", there are about 10 000 007 "walking on their feet" (the difference "007" is probably easy to remember). It may be obvious at this point already, that for NMR the mobile protons are important.

Let us take a closer look at these protons

We will see that the protons do not just lay there, aligned parallel or anti-parallel to the magnetic field lines. Instead, they move around in a certain way. The type of movement is called precession, figure 49.

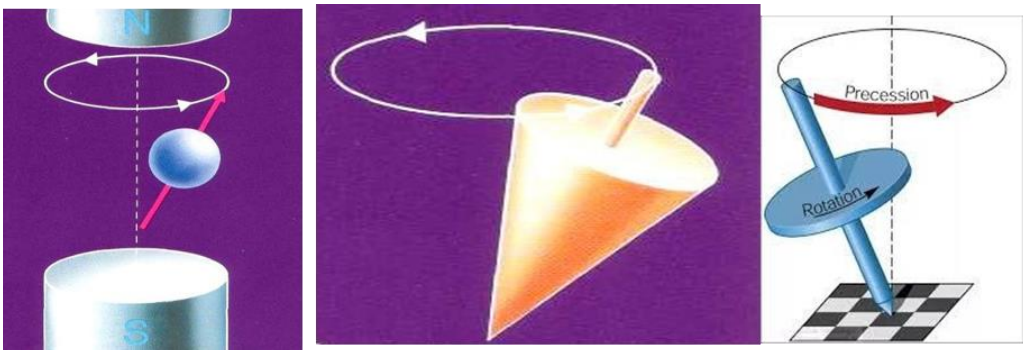


Figure 49 Precession of proton

What type of movement is "precession"?

Just imagine a spinning top.

When you hit it, it starts to "wobble" or tumble around. It does not, however, fall over. During this precession, the axis of the spinning top circles forming a cone shape. It is hard to draw such a processing proton, as this is an amazingly fast movement as we will see below. It is important to know how fast the protons process. This speed can be measured as precession frequency, that is, how many times the protons process per second. This precession frequency is not constant. It depends upon the strength of the magnetic field, in which the protons are placed. The stronger the magnetic field, the faster the precession rate and the higher the precession frequency.

- It is possible and necessary to precisely calculate this frequency. This is done by using an equation called Larmor equation:

$$\omega_0 = \gamma B_0$$

- ω_0 is the precession frequency (in Hz or MHz),
- B0 is the strength of the external magnetic field, which is given in Tesla (T)
- γ is the so-called gyromagnetic ratio.

The equation states that the precession frequency becomes higher when the magnetic field strength increases. The exact relationship is determined by the gyro-magnetic ratio This gyro-magnetic ratio is different for varied materials (e.g., the value for protons is (42.5 MHz/T).

Time to take a break however, let us briefly review, what we have read up to now:

- Protons have a positive electrical charge, which is constantly moving, because the protons possess a spin.
- This moving electrical charge is nothing more than an electrical current, and the latter always induces a magnetic field.
- every proton has its little magnetic field and can thus be seen as a little bar magnet.
- When we put an atom in a magnet, the protons, being little magnets, align with the external magnetic field. They do this in two ways: parallel and anti-parallel.
- The state that needs less energy is preferred, and so there are a few more protons "walking on their feet" than "on their hands".
- The protons process along the field lines of the magnetic field, just like a spinning top that processes along the field lines of the magnetic field of earth.
- The precession frequency can be calculated by the Larmor equation and is higher in stronger magnetic fields.

Introducing the coordinate system

To make communication (and drawing of illustrations) easier, let us start using a coordinate system like we know from school. As you see, the z- axis runs in the direction of the magnetic field lines, and thus can represent them. So, we can stop drawing the external magnet in all other illustrations, figure 50.

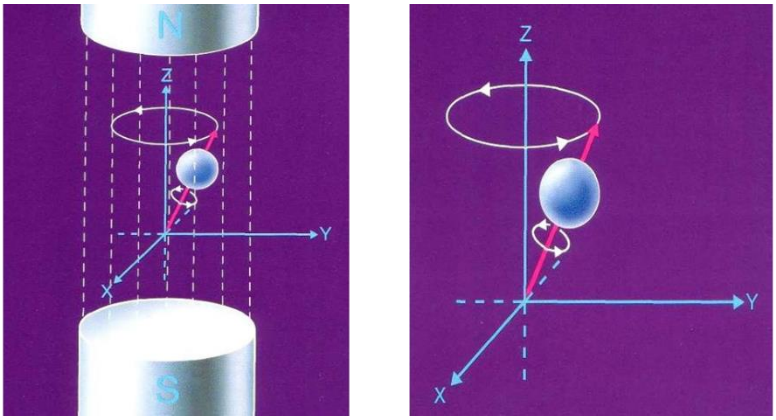


Figure 50 Introducing the coordinate system; the z-axis runs in the direction of the magnetic field lines

There we have 9 protons pointing up, processing parallel to the external magnetic field lines, and 5 protons pointing down, processing anti- parallel to the external magnetic field.

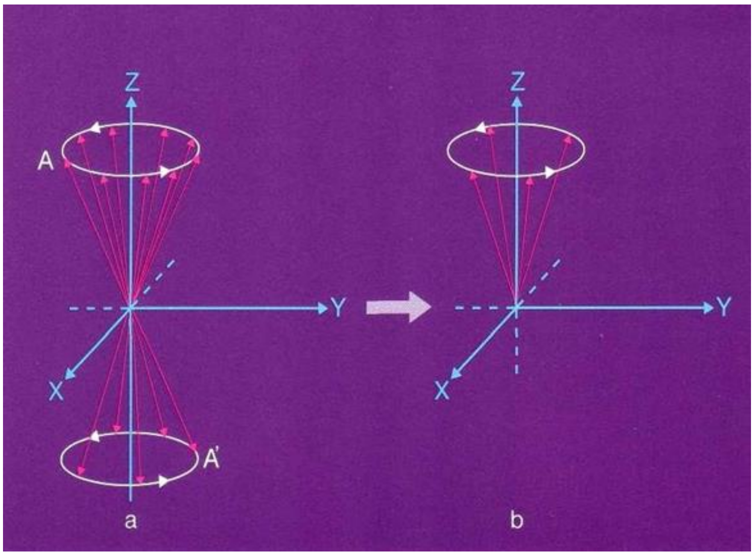


Figure 51 Introducing the coordinate system; proton align parallel and antiparallel to the external magnetic field

The result is especially important; the magnetic forces in the opposing directions cancel each other out, like two persons pulling at the opposite ends of a rope. Finally, for every proton pointing down, there is one pointing up, cancelling its magnetic effects. But as we have read: there-are more protons pointing up than down, and the magnetic forces of these protons are not cancelled by others. So we are left – in effect - with some protons (4 in our example) pointing up. However, not only magnetic forces pointing up and down can cancel or neutralize each other. As the protons that are left pointing up, process, there may be one pointing to the right, when there is another one pointing to the left; or for one pointing to the front, there is one pointing backwards, and so on (the corresponding protons are marked A and A', B and B' for example), figure 52.

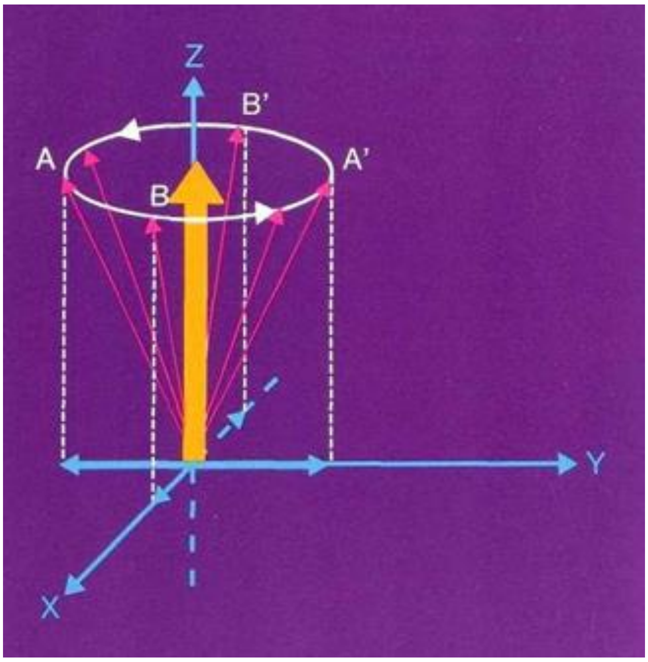


Figure 52 Introducing the coordinate system; Ney magnetic vector in the direction of the external magnetic field (the arrow on the z-axis)

This means that the opposing magnetic forces of the remaining protons cancel each other out in these directions. This is true for all but one direction, the direction of the z-axis, along the external magnetic field. In this direction, the single vectors, the single magnetic forces add up, like people pulling on the same end of a rope. What we end up with in effect is a magnetic vector in the direction of the external magnetic field (the arrow on the z-axis); and this vector is a sum vector made up by adding the magnetic vectors of the protons pointing upwards, figure 53.

To illustrate this:

Imagine that you are standing on a boat, floating down a river. You have a water hose in your hand and squirt water into the river. For somebody who is watching you from the shore, it is impossible to tell how much water you pour out (this shall be how much new magnetization is added in the old direction).

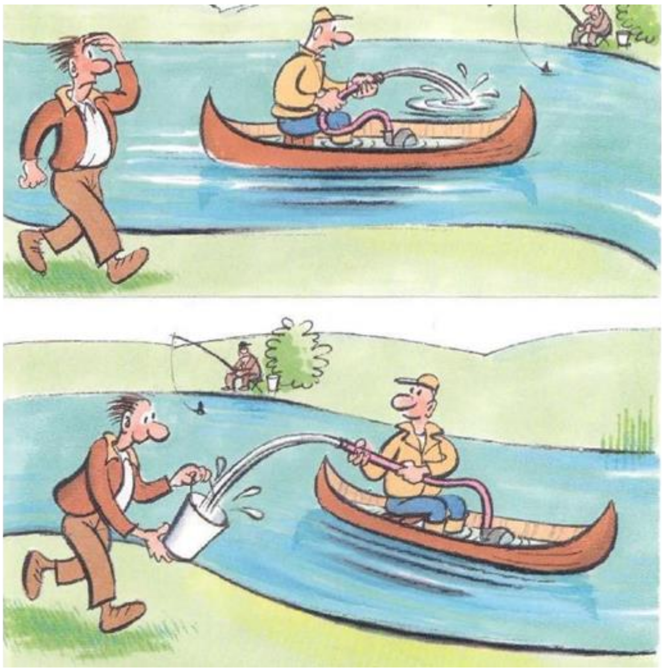


Figure 53 Simulation of how much new magnetization is added in the old direction of the external magnetic field

However, when you point the water hose to the shore, change the direction of the new magnetic field, then the water may perhaps be directly picked up and measured by an impartial observer on the shore, figure 54.

What we should learn from this is:

- magnetization along or, better, longitudinal to the external magnetic field cannot be measured directly.
- For this we need a magnetization which is not longitudinal, but transversal to the external magnetic field.

Time to take a break . . .

but before you walk off, just read the brief summary. And when you come back, start out with the summary again.

- Protons have a positive charge and possess a spin. Due to this, they have a magnetic field and can be seen as little bar magnets.
- When we put them into a strong external magnetic field, they align with it, some parallel (pointing up), some anti-parallel (pointing down).
- The protons do not just lay there, but process around the magnetic field lines. And the stronger the magnetic field, the higher the precession frequency, a relationship that is mathematically described in the Larmor equation.
- Anti-parallel and parallel protons can cancel each other's forces out.

But as there are more parallel protons on the lower energy level ("pointing up"), we are left with some protons, the magnetic forces of which are not cancelled. All of these protons pointing up, add up their forces in the direction of the external magnetic field. And so, when we put the atom in the NMR magnet, it has his own magnetic field, which is longitudinal to the external field of the NMR machine's magnet. Because it is longitudinal however, it cannot be measured directly.

The role of RF pulses

What happens after we put the atoms into the magnet? We send in a radio wave.

The term radio wave is used to describe an electromagnetic wave, which is in the frequency range of the waves which you receive in your radio. What we actually send into the atoms is not a wave of long duration, but a short burst of some electromagnetic wave, which is called a radio frequency (RF) pulse. The purpose of this RF pulse is to disturb the protons, which are peacefully processing in alignment with the external magnetic field. Not every RF pulse disturbs the alignment of the protons. For this, we need a special RF pulse, one that can exchange energy with the protons.

But when can an RF pulse exchange energy with the protons?

For this it must have the same frequency; the same "speed" as the protons. Just imagine that you are driving down a racetrack in your car, and someone in the lane next to you wants to hand you a couple of sandwiches, i.e., exchange energy with you, figure 54.

- Energy transfer is possible when both cars have the same speed, move around the racetrack with the same frequency
- With differences in speed/ frequency less or no energy transfer is possible.

Figure 54 Simulation of how RF exchange energy with the protons

What speed, or better, what frequency did the protons have?

They had their precession frequency which can be calculated by the Larmor equation. So, the Larmor equation gives us the necessary frequency of the RF pulse to send in. Only when the RF pulse and the protons have the same frequency, can protons pick up some energy from the radio wave, a phenomenon called resonance (this is where the "resonance" in magnetic resonance comes from). The term resonance can be illustrated by the use of tuning forks. Imagine that you are in a room with different kinds of tuning forks, tuned e.g. to a, e, and d. Somebody enters the room with a tuning fork with "a"-frequency, that was struck to emit sound. From all the tuning forks in the room, all ofa sudden, the other "a" forks, and only those, pick up energy, start to vibrate and to emit sound, they show a phenomenon called resonance.

What happens with the protons when they are exposed to this RF-pulse?

Some of them pick up energy and go from a lower to a higher energy level. Some, which were walking on their feet, start walking on their hands. And this has some effect on the atom's magnetization.

- Let us assume that from the net sum of 6 protons pointing up, after the RF pulse is sent in 2 points down.
- The result is that these 2 protons cancel out the magnetic forces of the same number of protons, which point up.
- In effect, then, the magnetization in longitudinal direction decreases from 6 to 2, figure 55.

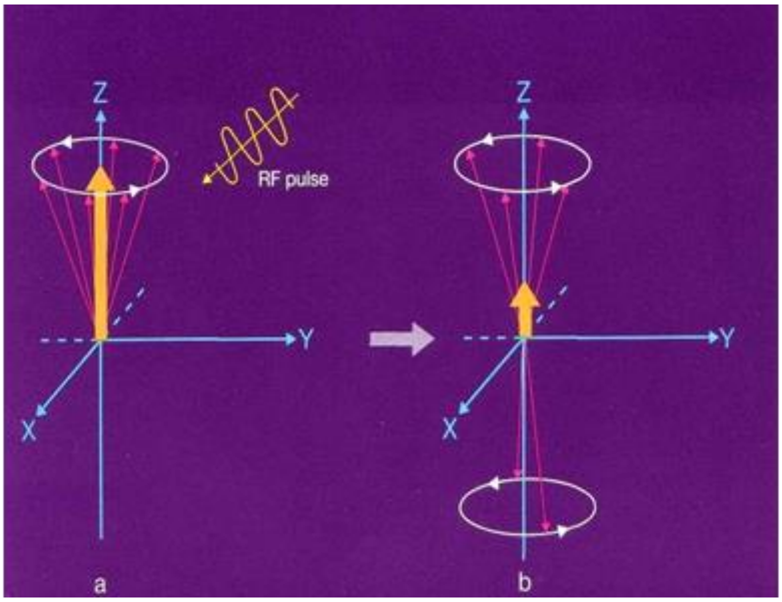


Figure 55 Decrease of longitudinal magnetization due to RF excitation

But something else happens.

Do you remember what drawings of radio waves look like?

They resemble a whip, and the RF pulse also has a whip-like action: it gets the processing protons in synch and this has another important effect, figure 56.

Figure 56 Simulation of RF excitation of protons.

When the protons randomly point left/right, back/forth and so on, they also cancel their magnetic forces in these directions. Due to the RF pulse, the protons do not point in random directions anymore, but move in step, in synch - they are "in phase", figure 57.

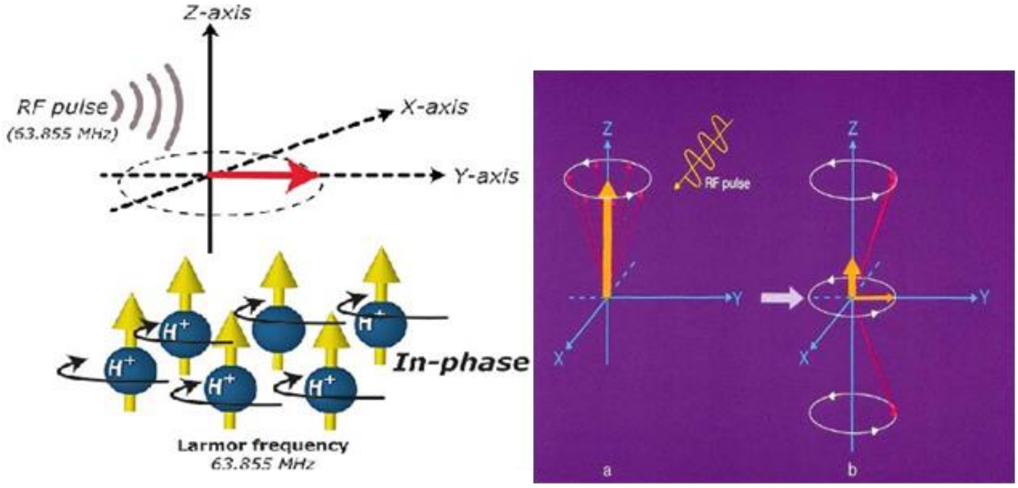


Figure 57 RF pulse make proton presses in phase to generate the transvers magnetization

- They now point in the same direction at the same time, and thus their magnetic vectors add up in this direction.
- This results in a magnetic vector pointing to the side to which the processing protons point, and this is in a transverse direction.

- This is why it is called transversal magnetization.

So - what were the new things that we have learned?

- When we put the atoms in the NMR machine, the protons line up parallel or anti-parallel to the machines magnetic field.
- A magnetic field in the atoms, longitudinal to the external field results.
- Sending in an RF pulse that has the same frequency as the precession frequency of the protons causes two effects:
- Some protons pick up energy, start to walk on their hands, and thus decrease the amount of longitudinal magnetization.
- The protons get in synch, start to process in phase. Their vectors now also add up in a direction transverse to the external magnetic field, and thus a transversal magnetization is established.

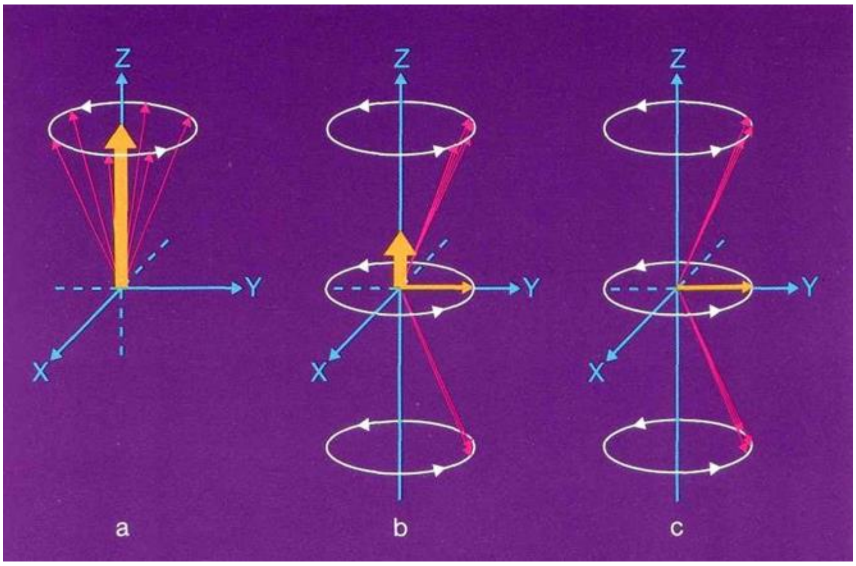


Figure 58 Summery of the effect of RF pulses on the net magnetization of protons

In summary: The RF pulse causes longitudinal magnetization to decrease, and establishes a new transversal magnetization

But . . . How can we take our NMR signal?

For this we have to know where in the medium the signal came from.

How can we know that?

- The trick is really quite simple: we do not put the atoms into a magnetic field which has the same strength all over the section of the medium, which we want to examine.
- Instead, we take a magnetic field, which has a different strength at each point of the atoms cross section.

What does this do?

- We heard that the precession frequency of a proton depends on the strength of the magnetic field.
- If this strength is different from point to point in the atoms, then protons in different places process with different frequencies.
- And as they process with different frequencies, the resulting NMR signal from different locations also has a different frequency.
- And by the frequency we can assign a signal to a certain location.

Further details about the NMR signal

- If our protons rotated around in synch, in phase, and nothing would change, then we would get a signal as it is illustrated before this, however, is not what happens.
- As soon as the RF pulse is switched off, the complete system, which was disturbed by the RF pulse, goes back to its original quiet, peaceful state, it relaxes.
- The newly established transverse magnetization starts to disappear (a process called transversal relaxation), and the longitudinal magnetization grows back to its original size (a process called longitudinal relaxation).

Why is that?

- The reason why the longitudinal magnetization grows back to its normal size is easier to explain, so let us start with that.
- The protons that were lifted to a higher energy level by the RF pulse go back to their lower energy level.

- Not all protons do this at the very same time, instead it is a continuous process, as if one proton after the other goes back to its original state. For the sake of simplicity, the protons are shown as being out of phase, which of course they are not in the beginning.
- Why and how they stop processing in phase will be explained a little later.

What happens to the energy which they had picked up from the RF pulse?

- This energy is just handed over to their surroundings, the so-called lattice.
- And this is why this processis not only called longitudinal relaxation, but also spin-lattice-relaxation.

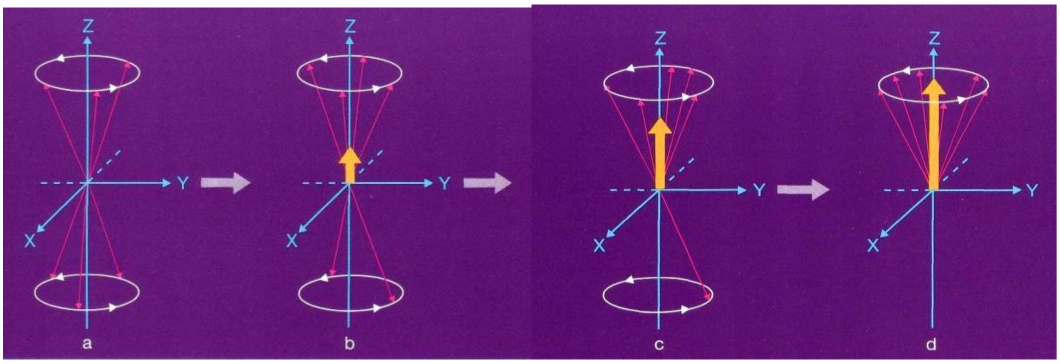


Figure 59 The return of protons to its original state after switching off RF By going back to its original state on their feet, pointing upwards again, these protons no longer cancel out the magnetic vectors of the same number of protons pointing up, as they did before. So, the magnetization in this direction, the longitudinal magnetization increases, and finally goes back to its original value, figure 60. If you plot the time vs. longitudinal magnetization, you get a curve like figure 60, it increases with time. This curve is also called a T1-curve.

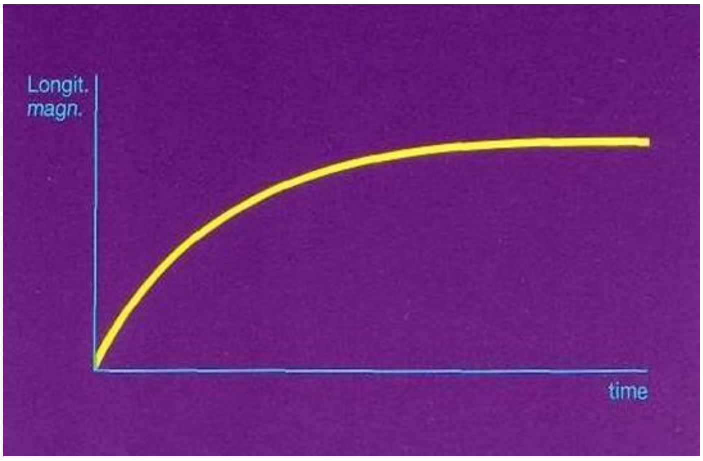


Figure 60 Relaxation time T1 curve

- The time that it takes for the longitudinal magnetization to recover, to go back to its original value, is described by the longitudinal relaxation time, also called T1.
- This actually is not the exact time it takes, but a time constant, describing how fast this process goes.
- Longitudinal relaxation has something to do with exchange of energy, thermal energy, which the protons emit to the surrounding lattice while returning to their lower state of energy.

Enough of the longitudinal magnetization -what happens with the transversal magnetization?

- After the RF pulse is switched off, the protons get out of step, out of phase again, as nobody is telling them to stay in step, figure 61.
- For the sake of simplicity this has been illustrated for a group of protons which all "point up".
- We heard earlier that protons process with a frequency which is determined by the magnetic field strength that they are in.
- All the protons should experience the same magnetic field. This, however, is not the case:
- the field of the NMR magnet, in which the atoms is placed, is not uniform, not totally homogenous, but varies a little, thus causing different precession frequencies.

- Each proton is influenced by the small magnetic fields from neighboring nuclei, which are also not distributed evenly, thus causing different precession frequencies too.
- These internal magnetic field variations are somehow characteristic for the medium.

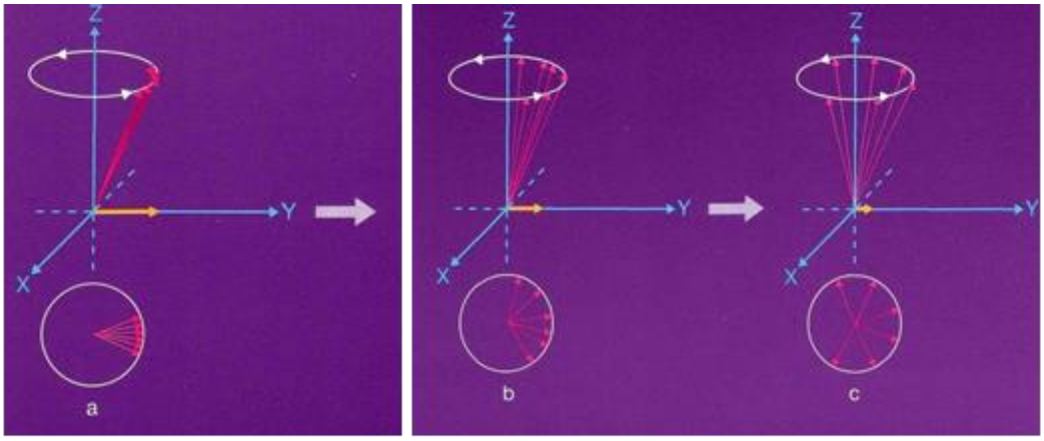


Figure 61 Transversal magnetization after switching off RF

- So, after the RF pulse is switched off, the protons are no longer forced to stay in step; and as they have different precession frequencies, they will be soon out of phase.
- It is interesting to see, how fast the protons get out of phase: just suppose that one proton (p1) is rotating/ processing with a frequency of 10 megahertz, i.e. 10 million revolutions per second.
- Due to inhomogeneities a neighboring proton (p2) is in a magnetic field, which is 1 % stronger; this proton has a precession frequency of 10.1 megahertz, 1 % more.
- In 5 microseconds (0.000005 sec or 5 x 10^{-6}), p1 will have made 50.5 turns/revolutions, while proton p2 will have made only 50.
- So, in this short time span, the protons will be 180° out of phase, cancelling their magnetic moments in the respective plane.

Similar to what we did for the longitudinal magnetization, we can plot transversal magnetization versus time, figure 62. What we get is a curve like in the figure. This curve is going downhill, as transversal magnetization disappears with time. And as you probably expect there is also a time constant, describing how fast transversal magnetization vanishes, goes downhill. This time constant is the transversal relaxation time T2. Another term for transversal relaxation is spin-spin-relaxation, reminding us of the underlying mechanism, a spin-spin interaction.

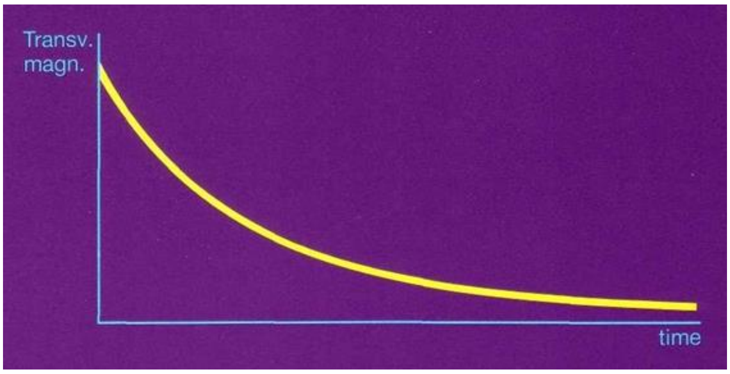


Figure 62 relaxation time T2 curve

How to remember, which one is the T1- and which the T2-curve?

Just put both curves together, and you can see something like a mountain with a ski slope. You first have to go uphill (T1-curve), before you jump down (T2-curve), figure 63.

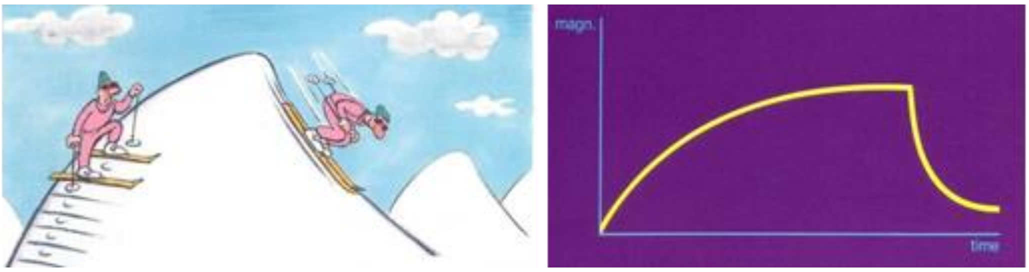


Figure 63 combination of both relaxation times in one graph

So, time to review We have learned that

- Protons are like little magnets in an external magnetic field they align parallel or antiparallel.

- The lower energy state (parallel) is preferred, so a few more protons align this way
- The protons perform a motion that resembles the wobbling of a spinning top, which was hit, this motion is called precession
- The precession frequency is dependent on the strength of the external magnetic field (a relationship which is described by the Larmor equation).
- The stronger the magnetic field, the higher the precession frequency.
- Protons "pointing" in opposite directions cancel each other's magnetic effects in the respective directions.
- As there are more protons aligned parallel to the external field, there is a net magnetic moment aligned with or longitudinal to the external magnetic field.
- A radio frequency pulse that has the same frequency as the processing protons, can cause resonance, transfer energy to the protons. This results in more protons being anti-parallel and thus neutralizing/cancelling more protons in the opposite direction. Consequence: the longitudinal magnetization decreases.
- The RF pulse also causes the protons to precess in synch, in phase.

This results in a new magnetic vector, the transversal magnetization.

- When the RF pulse is switched off:
    - Longitudinal magnetization increases again; this longitudinal relaxation is described by a time constant T1, the longitudinal relaxation time.
    - Transversal magnetization decreases and disappears; this transversal relaxation is described by a time constant T2, the transversal relaxation time.
    - Longitudinal and transversal relaxation are different, independent processes, and that is why we discussed them individually.

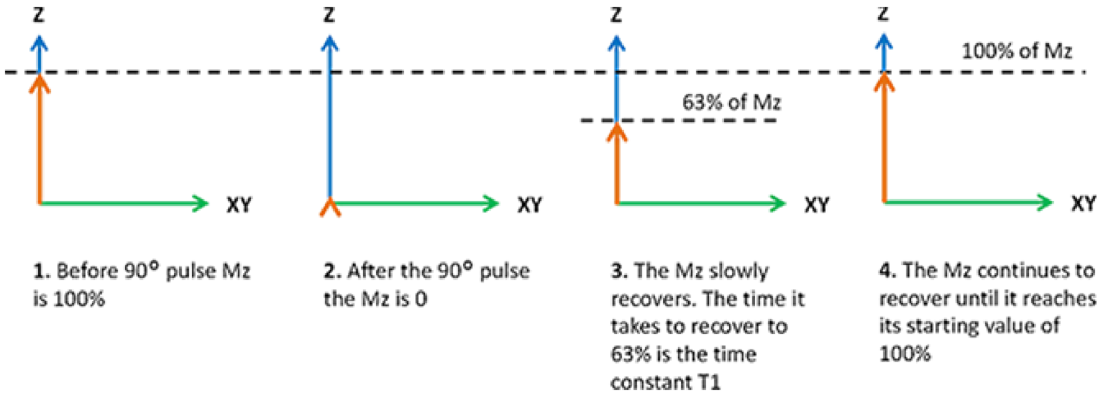
How long is a relaxation time?

Look at our example with the T1- and T2-curves. It is probably easy and logical, that it takes you more time to get to the top of the mountain, than to go back down, to jump off. This means T1 is longer than T2, figure 64.

Figure 64 Simulation of How long is a relaxation time

In biological tissues:

T1 is about 300 to 2000 msec, and T2 is about 30 to 150 msec. It is difficult to pinpoint the end of the longitudinal and transversal relaxation exactly. Thus, T1 and T2 were not defined as the times when relaxation is completed. Instead T1 was defined as the time when about 63% of the original longitudinal magnetization is reached, figure 65.



1. Before 90° pulse Mz is 100%

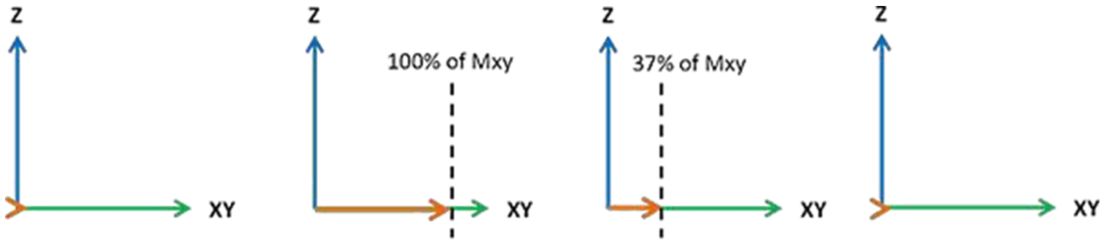
2. After the 90° pulse the Mz is 0

3. The Mz slowly recovers. The time it takes to recover to 63% is the time constant T1

4. The Mz continues to recover until it reaches its starting value of 100%

Figure 65 Illustration of relaxation time T1

T2 is the time when transversal magnetization decreased to 37% of the original value, figure 66. These percentages are derived from mathematical equations (63% = 1-1/e; 37% = 1/e) describing signal intensity, but we do not want to go into more detail here. (However, we should mention that 1/T1 is also called longitudinal relaxation rate, and 1/T2 transversal relaxation rate).



1. Before 90° pulse Mxy is 0%

2. After the 90° pulse the Mxy is 100%

3. The Mxy slowly decays. The time it takes to decay to 37% is the time constant T2

4. The Mxy continues to decay until it reaches its starting value of 0%

Figure 66 Illustration of relaxation time T2

Previously it was believed that measuring the relaxation times, would give tissue characteristic results, and thus enable exact tissue typing. This, however, proved to be wrong, as there is quite some overlap of time ranges; and also, T1 is dependent on the magnetic field strength used for the examination.

What is T1 influenced by?

Actually, T1 depends on tissue composition, structure and surroundings. As we have read, T1-relaxation has something to do with the exchange of thermal energy, which is handed over from the protons to the surroundings, the lattice. The processing protons have a magnetic field, that constantly changes directions, that constantly fluctuates with the Larmor frequency. The lattice also has its own magnetic fields. The protons now want to hand energy over to the lattice to relax .This can be done very effectively, when the fluctuations of the magnetic fields in the lattice occur with a frequency that is near the Larmor frequency.

When the lattice consists of pure liquid/water, it is difficult for the protons to get rid of their energy, as the small water molecules move too rapidly. And as the protons (which are on the higher energy level) cannot hand their energy over to the lattice quickly, they will only slowly go back to their lower energy level, their longitudinal alignment. Thus, it takes a long time for the longitudinal magnetization to show up again, and this means that liquids/water have long T1s.

When the lattice consists of medium-size molecules (most body tissues can be looked at as liquids containing various sized molecules, kind of like a soup), that move and have fluctuating magnetic fields near the Larmor frequency of the processing protons, energy can be transferred much faster, thus T1 is short. This can again be illustrated by our sandwich and race car example: handing over sandwiches (i.e. energy) from one car (proton) to the other (lattice) is easy and efficient, when both move with the same speed. With a difference in speeds, the energy transfer will be less efficient.

Why does fat have a short T1?

The carbon bonds at the ends of the fatty acids have frequencies near the Larmor frequency, thus resulting in effective energy transfer. why is T1 longer in stronger magnetic fields?

It is easy to imagine that in a stronger magnetic field it takes more energy for the protons to align against it. Thus, these protons have more energy to hand down to the lattice, and this takes longer than handing down just a small amount of energy. Even though it may seem logical, this is the wrong explanation.

The correct explanation is:

As we heard in the beginning, the precession frequency depends on magnetic field strength, a relationship described by the Larmor equation. If we have a stronger magnetic field, then the protons process faster. And when they process faster, they have more problems handing down their energy to a lattice with more slowly fluctuating magnetic fields.

What influences T2?

T2-relaxation comes about when protons get out of phase, which - as we already know – has two causes: inhomogeneities of the external magnetic field, and inhomogeneities of the local magnetic fields within the tissues, figure 67. As water molecules move around very fast, their local magnetic fields fluctuate fast, and thus kind of average each other out, so there are no big net differences in internal magnetic fields from place to place. if there are no big differences in magnetic field strength inside of a tissue, the protons stay in step for a long time, and so T2 is longer.

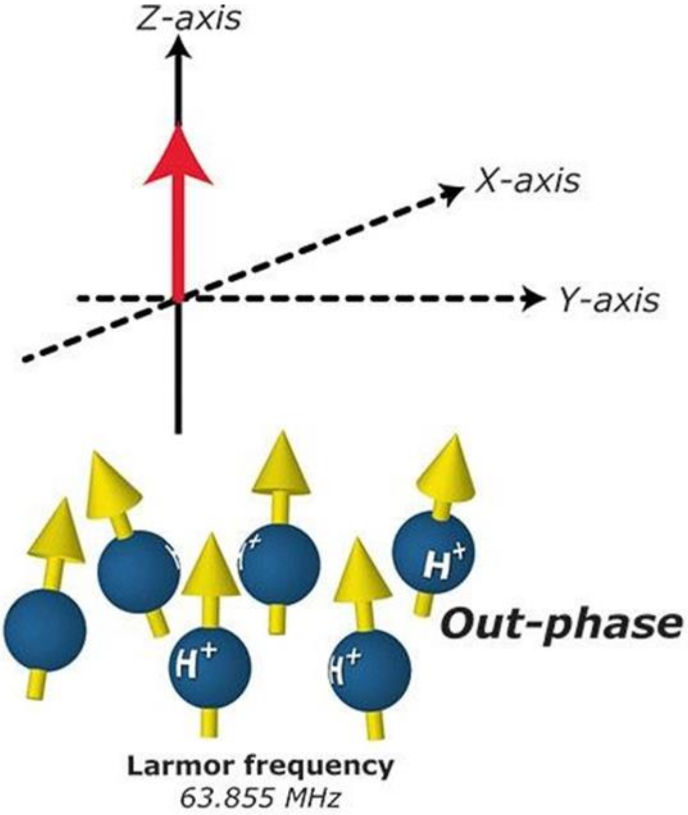


Figure 67 Protons are out of phase after switching of RF pluses

With impure liquids, e.g. those containing some larger molecules, there are bigger variations in the local magnetic fields. The larger molecules do not move around as fast, so their local magnetic fields do not cancel each other out as much. These larger differences in local magnetic fields consequently cause larger differences in precession frequencies, thus protons get out of phase faster, T2 is shorter.

A brief review might be advisable

- T1 is longer than T2.
- T1 varies with the magnetic field strength; it is longer in stronger magnetic fields.
- Water has a long T1, fat has a short T1.
- T2 of water is longer than the T2 of impure liquids containing larger olecules.

Look at figure 68, where you see two protons, processing around the z-axis. I hope that you recall that the z-axis indicates the direction of a magnetic field line. Instead of only these two protons, in reality there may be 12 pointing up and 10 pointing down, or 102 up and 100 down – there shall only be two more protons pointing up. As we know, these are the ones that have a net magnetic effect because their effects are not cancelled out.

Now let us send in an RF pulse, which has just the correct strength and duration, that one of the two protons pick up energy, to go into the higher state of energy.

NMR experiment

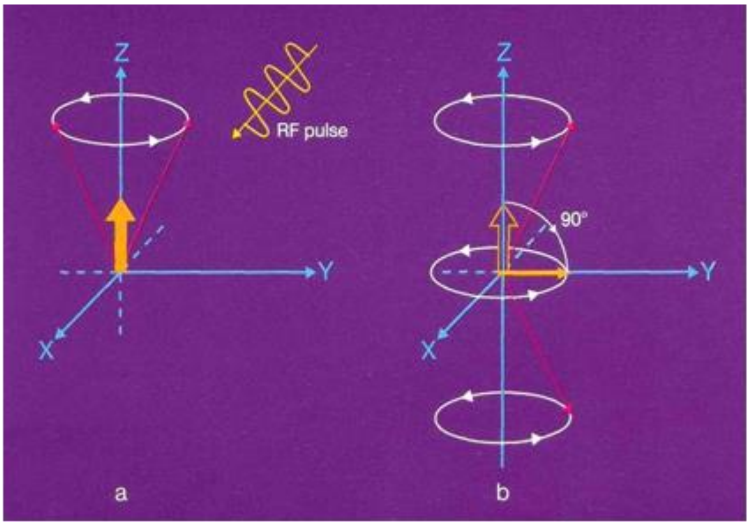


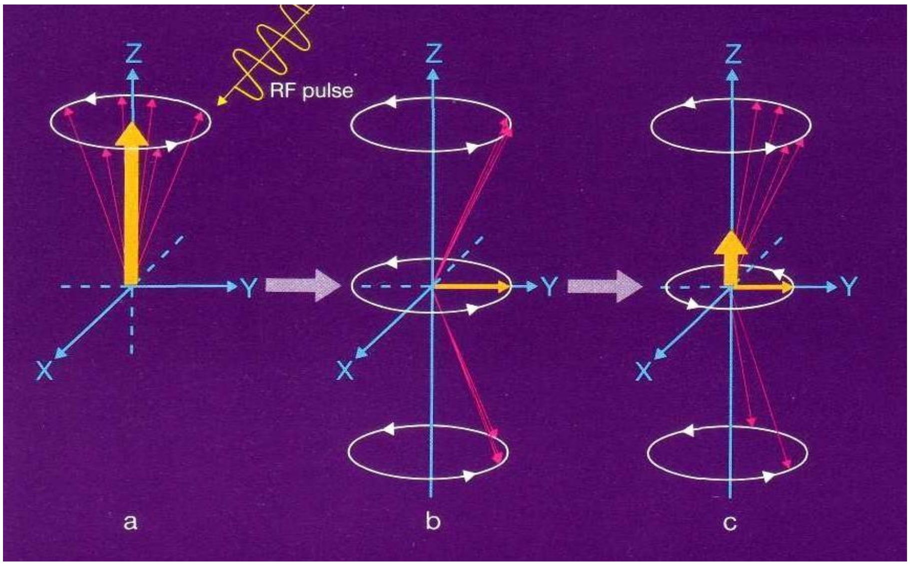
Figure 68 Example of transformation of longitudinal magnetization to transversal magnetization

What will happen?

- The longitudinal magnetization (up to now resulting from two protons pointing up) will decrease, in our example to zero (one pointing up is neutralized by one pointing down).
- But: as both protons are in phase, now there is a transversal magnetization which had not been there before.
- This can be looked at - in effect - that a longitudinal magnetic vector is tilted 90° to the side.
- An RF pulse which "tilts" the magnetization 90° is called a 90° pulse. Naturally, other RF pulses are also possible, and are named accordingly, e.g., 180° pulse.

To really understand this let us look at another example.

- In the figure 69 (a) we have 6 protons pointing up; we send in a RF pulse, which lifts up 3 of them to a higher energy level (b).
- The result: we no longer have a longitudinal, but a transversal magnetization (again having used a 90° pulse).



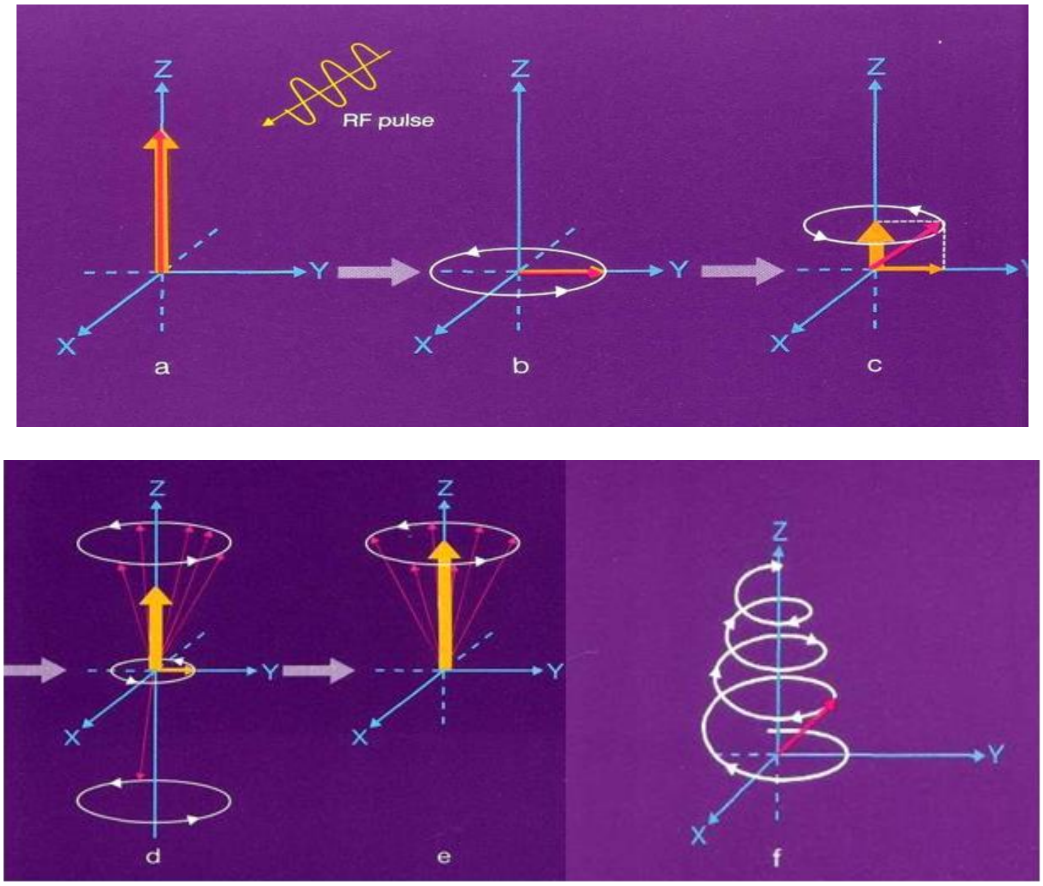


Figure 69 Example of transformation of longitudinal magnetization to transversal magnetization

What happens, when the RF pulse is switched off?

Protons go back to their lower state of energy, and they lose phase coherence. It is important to note that both processes occur simultaneously and independently. For the sake of simplicity, let us look at what happens step by step, and first focus on the longitudinal magnetization: In (c), one proton goes back to the lower energy state; resulting in 4 protons pointing up, and two pointing down. In net effect: we now have a longitudinal magnetization of "2".Then the next proton goes back up; now 5 protons point up, and one down, resulting in a net longitudinal magnetization of "4" (fig.d). After the next proton goes up, longitudinal magnetization equals "6" (fig.e). At the same time, transversal magnetization decreases (fig.c-e).

Why? (You should be able to answer this:)

The processing protons lose phase coherence. In figure b, all protons point in the same direction, but then get increasingly out of phase and thus kind of fan out (figure c-e). In the following fig., only the longitudinal and transversal magnetic vectors are shown at corresponding times as in the previous figure. These magnetic vectors add up to a sum vector. If you have forgotten; vectors represent forces of a certain size and a certain direction. If you add vectors pointing to different directions up, you will produce a direction that is somewhere in between, depending on the amount of force in the original directions. This sum vector is particularly important, as it represents the total magnetic moment of the medium in general, and thus can be used instead of the two single vectors, representing longitudinal and transversal magnetization separately. Our magnetic sum vector during relaxation goes back to a longitudinal direction, in the end equaling the longitudinal magnetization. What we have to remember is that this whole system actually is processing, including the sum magnetic vector/moment. And thus, the sum vector will actually perform an increase motion (figure f).

Hope that you recall that a changing magnetic force/ moment can induce an electrical current, which was the signal that we receive and use in NMR. If we put up an antenna somewhere, we will get a signal, figure 70. This is easy to imagine, if you think of the antenna as a microphone, and the sum magnetic vector as having a bell at its tip. The further the vector goes away from the microphone, the less loud the sound. The frequency of the sound, however, remains the same because the sum vector spins with the processing frequency.

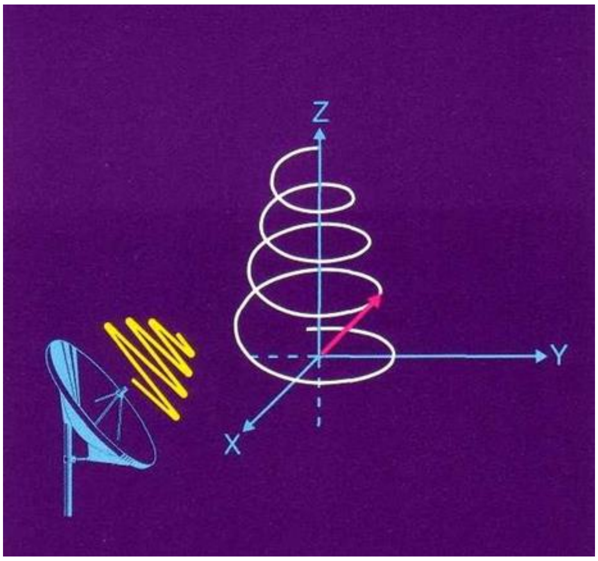


Figure 70 Illustration of Rf signal

This type of signal is called an FID signal, from free induction decay, figure 71. It is easy to imagine, that you get a particularly good strong signal directly after the 90° RF pulse (as the bell comes awfully close to the microphone in our example).

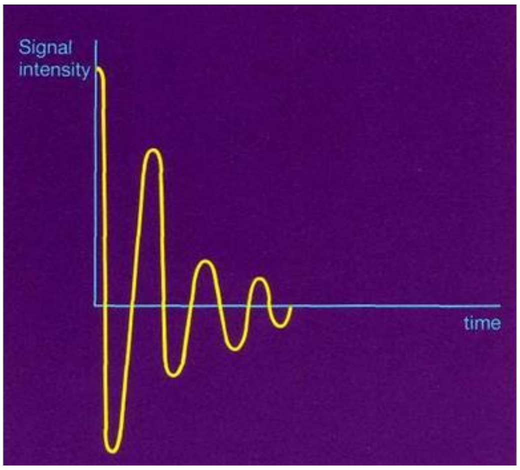


Figure 71 FID signal

By now it should be obvious that the magnetic vectors directly determine the NMR signal and signal intensity by inducing electrical currents in the antenna. Instead of the terms "longitudinal" or "transversal magnetization", we can also use the term "signal or signal intensity“ at the axis of our T1, and T2 curves. This will hopefully become clearer as you continue reading.

Chapter 3

Applications of NMR

Introduction

Today, NMR has become a sophisticated and powerful analytical technology that has found a variety of applications in many disciplines of scientific research, medicine, and various industries. Modern NMR spectroscopy has been emphasizing the application in biomolecular systems and plays a significant role in structural biology. With developments in both methodology and instrumentation in the past two decades, NMR has become one of the most powerful and versatile spectroscopic techniques for the analysis of biomacromolecules, allowing characterization of biomacromolecules and their complexes up to 100 kDa. Together with X-ray crystallography, NMR spectroscopy is one of the two leading technologies for the structure determination of biomacromolecules at atomic resolution. In addition, NMR provides unique and important molecular motional and interaction profiles containing pivotal information on protein function. The information is also critical in drug development. Some of the applications of NMR spectroscopy are listed below:

- Solution structure the only method for atomic-resolution structure determination of biomacromolecules in aqueous solutions under near physiological conditions or membrane mimetic environments.
- Molecular dynamics the most powerful technique for quantifying motional properties of biomacromolecules.
- Protein folding the most powerful tool for determining the residual structures of unfolded proteins and the structures of folding intermediates.
- Ionization state the most powerful tool for determining the chemical properties of functional groups in biomacromolecules, such as the ionization states of ionizable groups at the active sites of enzymes.

- Weak intermolecular interactions Allowing weak functional interactions between macro biomolecules (e.g., those with dissociation constants in the micromolar to millimolar range) to be studied, which is not possible with other technologies.
- Protein hydration A power tool for the detection of interior water and its interaction with biomacromolecules.
- Hydrogen bonding A unique technique for the DIRECT detection of hydrogen bonding interactions.
- Drug screening and design Particularly useful for identifying drug leads and determining the conformations of the compounds bound to enzymes, receptors, and other proteins.
- Metabolite analysis A very powerful technology for metabolite analysis.
- Chemical analysis A matured technique for chemical identification and conformational analysis of chemicals whether synthetic or natural.
- Material science A powerful tool in the research of polymer chemistry and physics.

Nuclear magnetic resonance spectroscopy

Spectroscopy is the study of the interaction of electromagnetic radiation with matter. Nuclear magnetic resonance spectroscopy is the use of the NMR phenomenon to study physical, chemical, and biological properties of matter. As a consequence, NMR spectroscopy finds applications in several areas of science. NMR spectroscopy is routinely used by chemists to study chemical structure using simple one-dimensional techniques. Two-dimensional techniques are used to determine the structure of more complicated molecules. These techniques are replacing x-ray crystallography for the determination of protein structure. Time domain NMR spectroscopic techniques are used to probe molecular dynamics in solutions. Solid state NMR spectroscopy is used to determine the molecular structure of solids. Other scientists have developed NMR methods of measuring diffusion coefficients. The versatility of NMR makes it pervasive in the sciences. Scientists and students are discovering that knowledge of the science and technology of NMR is essential for applying, as well as developing, new applications for it.

Chemical Shift

When an atom is placed in a magnetic field, its electrons circulate about the direction of the applied magnetic field. This circulation causes a small magnetic field at the nucleus which opposes the externally applied field, figure 72.

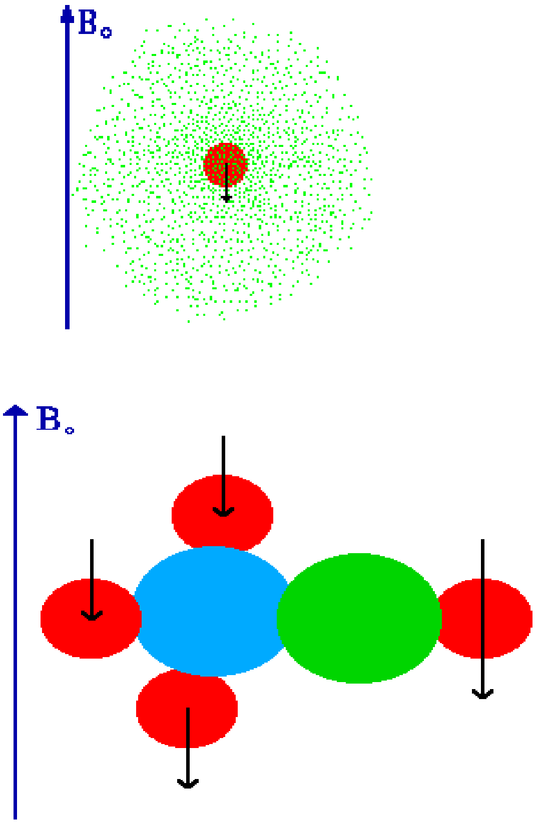


Figure 72 Illustration of chemical shift

The magnetic field at the nucleus (the effective field) is therefore generally less than the applied field by a fraction σ.

$$B = Bo\ (1-◎)$$

In some cases, such as the benzene molecule, the circulation of the electrons in the aromatic orbitals creates π a magnetic field at the hydrogen nuclei which enhances the Bo field. This phenomenon is called de- shielding, figure 73. In this example, the Bo field is applied perpendicular to the plane of the molecule. The ring current is traveling clockwise if you look down at the plane.

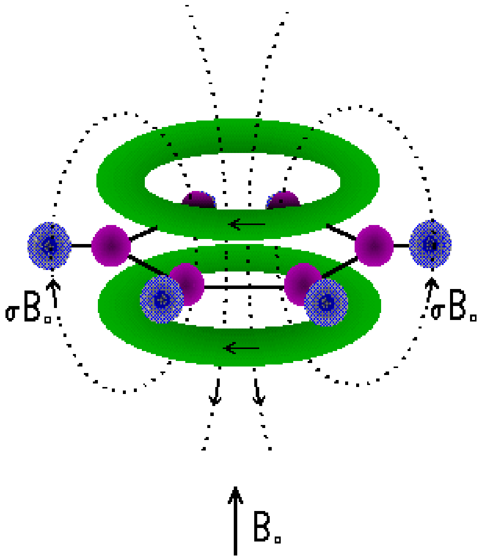


Figure 73 Illustration of de-shielding effect

The electron density around each nucleus in a molecule varies according to the types of nuclei and bonds in the molecule. The opposing field and therefore the effective field at each nucleus will vary. This is called the chemical shift phenomenon. Consider the methanol molecule. The resonance frequency of two types of nuclei in this example differs. This difference will depend on the strength of the magnetic field, Bo, used to perform the NMR spectroscopy. The greater the value of Bo, the greater the frequency difference. This relationship could make it difficult to compare NMR spectra taken on spectrometers operating at different field strengths. The term chemical shift was developed to avoid this problem. The chemical shift of a nucleus is the difference between the resonance frequency of the nucleus and a standard, relative to the standard. This quantity is reported in ppm and given the symbol delta, δ.

$$\delta = (\nu - \nu_{REF}) \text{ x}10^6 / \nu_{REF}$$

In NMR spectroscopy, this standard is often tetramethyl silane, Si(CH3)4, abbreviated TMS. The chemical shift is a very precise metric of the chemical environment around a nucleus. For example, the hydrogen chemical shift of a

CH2 hydrogen next to a Cl will be different than that of a CH3 next to the same Cl. It is therefore difficult to give a detailed list of chemical shifts in a limited space. The animation window displays a chart of selected hydrogen chemical shifts of pure liquids and some gasses, figure 74.

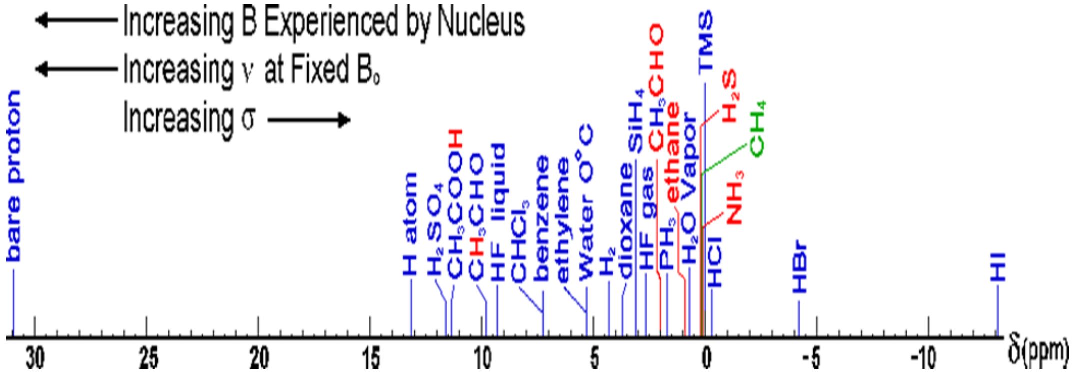


Figure 74 Hydrogen chemical shifts of pure liquids and some gasses

The magnitude of the screening depends on the atom. For example, carbon-13 chemical shifts are much greater than hydrogen-1 chemical shifts. The following tables present a few selected chemical shifts of fluorine-19 containing compounds, carbon-13 containing compounds, nitrogen-14 containing compounds, and phosphorous-31 containing compounds. These shifts are all relative to the bare nucleus. The reader is directed to a more comprehensive list of chemical shifts for use in spectral interpretation.

Table 7 Fluorine-19 Chemical Shifts

Fluorine-19 Environment	**Chemical Shift Range (ppm)**
UF_6	-540
FNO	-269
F_2	-210

bare nucleus	0
$C(CF_3)_4$	284
$CF_3(COOH)$	297
fluorobenzene	333
F-	338
BF_3	345
HF	415

Table 8 Carbon-13 Chemical Shifts

Carbon-13* Environment	**Chemical Shift Range (ppm)**
$(CH_3)_2C*O$	-12
CS2	0
CH_3C*OOH	16
C6H6	65
CHCl CHCl (cis)	71
CH3C*N	73
CCl_4	97
dioxane	126
$C*H_3CN$	196
CHI_3	332

Table 9 Nitrogen-14 Chemical Shifts

Nitrogen-14* Environment	**Chemical Shift Range (ppm)**
NO_2Na	-355
NO_3- (aqueous)	-115
N_2 (liquid)	-101

pyridine	-93
bare nucleus	0
CH_3CN	25
CH_3CONH_2 (aqueous)	152
NH_4+ (aqueous)	245
NH_3 (liquid)	266

Table 10 Phosphorous-31 Chemical Shifts

Phosphorous-31 Environment	Chemical Shift Range (ppm)
PBr_3	-228
$(C_2H_5O)_3$ P	-137
PF_3	-97
85% phosphoric acid	0
PCl_5	80
PH_3	238
P_4	450

Spin-Spin Coupling

Nuclei experiencing the same chemical environment or chemical shift are called equivalent. Those nuclei experiencing different environment or having different chemical shifts are nonequivalent. Nuclei which are close to one another exert an influence on each other's effective magnetic field. This effect shows up in the NMR spectrum when the nuclei are nonequivalent. If the distance between non-equivalent nuclei is less than or equal to three bond lengths, this effect is observable. This effect is called spin-spin coupling or J coupling. Consider the following example, figure 75. There are two nuclei, A and B, three bonds away from one another in a molecule. The spin of each nucleus can be either aligned with the external field such that the fields are N-S-N-S, called spin up, or opposed to the external field such that the fields are N-N-S-S, called spin down. The magnetic field at nucleus A will be either greater than Bo or less than Bo by a constant amount due to the influence of nucleus B.

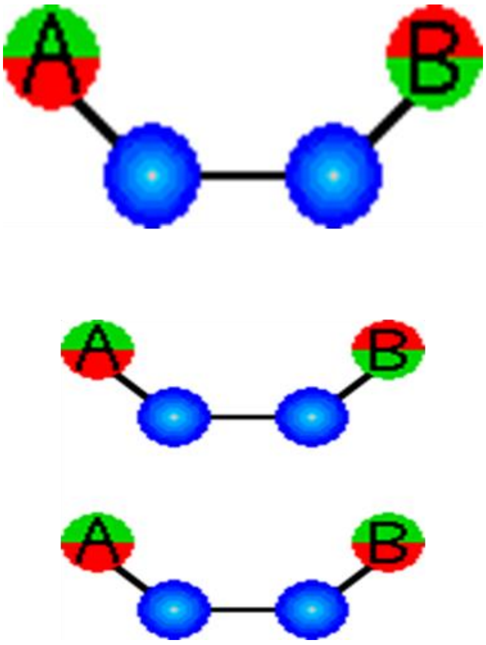


Figure 75 Spin – Spin coupling in two nuclei, A and B, three bonds away from one another in a molecule

There is a total of four possible configurations for the two nuclei in a magnetic field. Arranging these configurations in order of increasing energy gives the following arrangement.

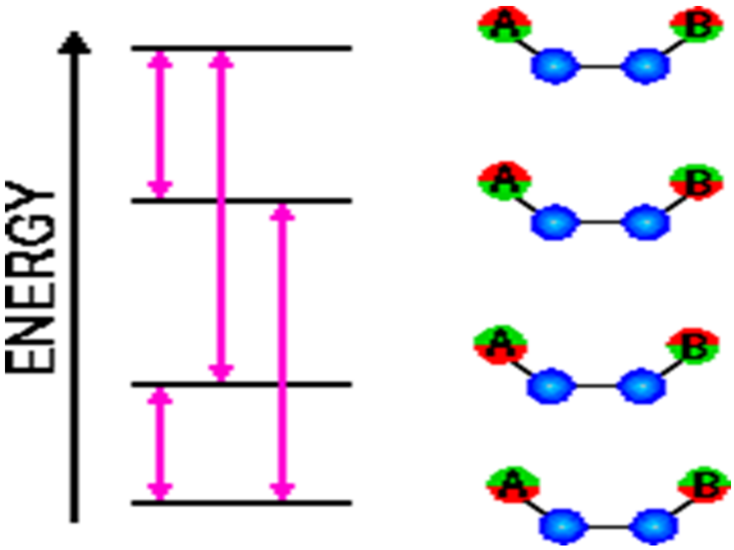


Figure 76 Allowed transition between energy levels for A and B nuclei

The vertical lines in this diagram represent the allowed transitions between energy levels. In NMR, an allowed transition is one where the spin of one nucleus changes from spin up to spin down or spin down to spin up. Absorptions of δenergy where two or more nuclei change spin at the same time δ are not allowed. There are two absorption frequencies for the A nucleus and two for the B nucleus represented by the vertical lines between the energy levels in this diagram. The NMR spectrum for nuclei A and B reflects the splitting observed in the energy level diagram. The A absorption line is split into 2 absorption lines centered on A, and the B absorption line is split into 2 lines centered on B. The distance between two split absorption lines is called the J coupling constant or the spin-spin splitting constant and is a measure of the magnetic interaction between two nuclei.

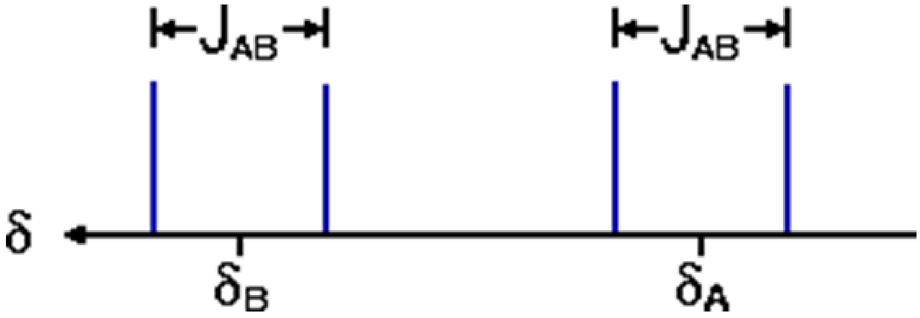


Figure 77 Splitting of absorption lines in nuclei A and B due to Spin – Spin coupling

For the next example, consider a molecule with three spin 1/2 nuclei, one type A and two type B, figure 78. The type B nuclei are both three bonds away from the type A nucleus.

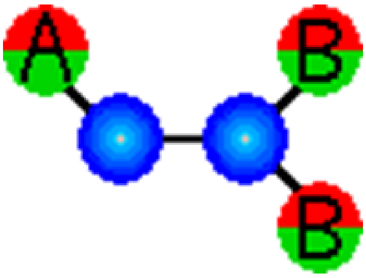


Figure 78 Molecule with three spin 1/2 nuclei, one type A and two type B

The magnetic field at the A nucleus has three possible values due to four possible spin configurations of the two B nuclei, figure 79.

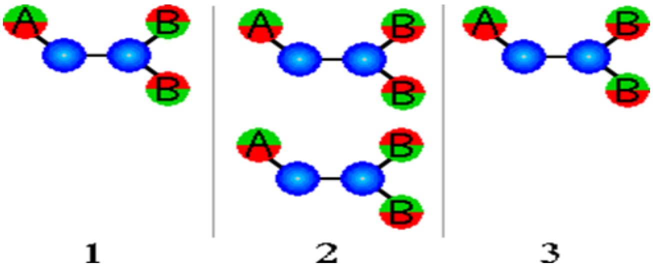


Figure 79 The magnetic field at the A nucleus

The magnetic field at a B nucleus has two possible values, figure 80.

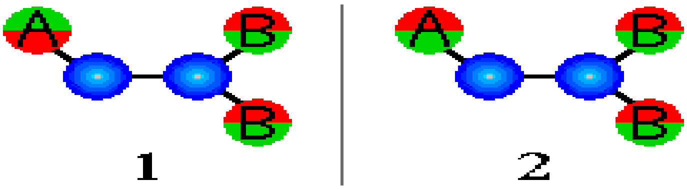


Figure 80 The magnetic field at the B nucleus

The energy level diagram for this molecule has six states or levels because there are two sets of levels with the same energy, figure 81. Energy levels with the same energy are said to be degenerate. The vertical lines represent the allowed transitions or absorptions of energy. Note that there are two lines drawn between some levels because of the degeneracy of those levels.

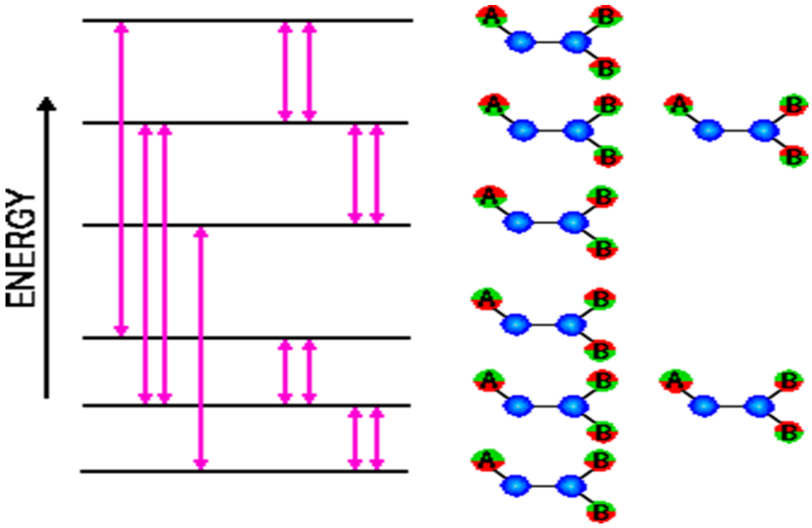


Figure 81 Allowed transition between energy levels for A and B nuclei

The resultant NMR spectrum is depicted in the animation window. Note that the center absorption line of those centered at A δ is twice as high as the either of the outer two. This is because there were twice as many transitions in the energy level diagram for this transition. The peaks at B are taller because there is twice as many B type spins than A type spins, figure 82.

δ

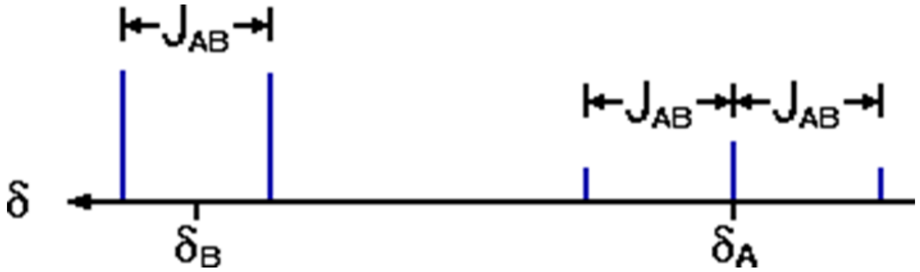


Figure 82 Splitting of absorption lines in nuclei A and B due to Spin – Spin coupling

The complexity of the splitting pattern in a spectrum increases as the number of B nuclei increases. The following table contains a few examples.

Table 11 Examples of absorption line splitting due different atomic configurations.

Configuration	Peak Ratios
A	1
AB	1:1
AB_2	1:2:1
AB_3	1:3:3:1
AB_4	1:4:6:4:1
AB_5	1:5:10:10:5:1
AB_6	1:6:15:20:15:6:1

This series is called Pascal's triangle and can be calculated from the coefficients of the expansion of the equation (x+1) n where n is the number of B nuclei in the above table. When there are two diverse types of nuclei three bonds away there will be two values of J, one for each pair of nuclei. By now you get the idea of the number of possible configurations and the energy level diagram for these configurations, so we can skip to the spectrum. In the following example JAB is greater JBC.

The Time Domain NMR Signal

An NMR sample may contain many different magnetization components, each with its own Larmor frequency. These magnetization components are associated with the nuclear spin configurations joined by an allowed transition line in the energy level diagram. Based on the number of allowed absorptions due to chemical shifts and spin-spin couplings of the different nuclei in a molecule, an NMR spectrum may contain many different frequency lines. In pulsed NMR spectroscopy, signal is detected after these magnetization vectors are rotated into the XY plane. Once a magnetization vector is in the XY plane it rotates about the direction of the Bo field, the +Z axis. As transverse magnetization rotates about the Z axis, it will induce a current in a coil of wire located around the X axis. Plotting current as a function of time gives a sine wave. This wave will, of course, decay with time constant T2* due to dephasing of the spin packets. This signal is called a free induction decay (FID).

The +/- Frequency Convention

Transverse magnetization vectors rotating faster than the rotating frame of reference are said to be rotating at a positive frequency relative to the rotating frame (+ν).Vectors rotating slower than the rotating frame are said to be rotating at a negative frequency relative to the rotating frame (-ν). It is worthwhile noting here that in most NMR spectra, the resonance frequency of a nucleus, as well as the magnetic field experienced by the nucleus and the chemical shift of a nucleus, increase from right to left. The frequency plots used in this hypertext book to describe Fourier transforms will use the more conventional mathematical axis of frequency increasing from left to right.

Nuclear magnetic resonance imaging (MRI)

MRI is a noninvasive cross-sectional imaging modality that does not require any ionizing radiation. For acquiring images, MRI uses the physical principle of magnetic resonance that was first described by Felix Bloch and Edward Purcell in 1946 who then received the Nobel Prize in Physics in 1952 for their discovery. Paul Lauterbur and Peter Mansfield received a Nobel Prize in Medicine in 2003 for their description on how to acquire MR images from the human body. Since then, the field of MRI has grown tremendously and is now an established and advanced imaging modality in radiology that allows to acquire high-resolution anatomical images as well as time- resolved physiological and functional datasets.

Main nuclei imaged in human MRI

In clinical MRI, Hydrogen is the most frequently imaged nucleus due to its great abundance in biological tissues. Other nuclei such as ^{13}C, ^{19}F, ^{31}P, ^{23}Na have a net nuclear spin and can be imaged in MRI. However, they are much less abundant than hydrogen in biological tissues and require adedicated RF chain, tuned to their resonance frequency.

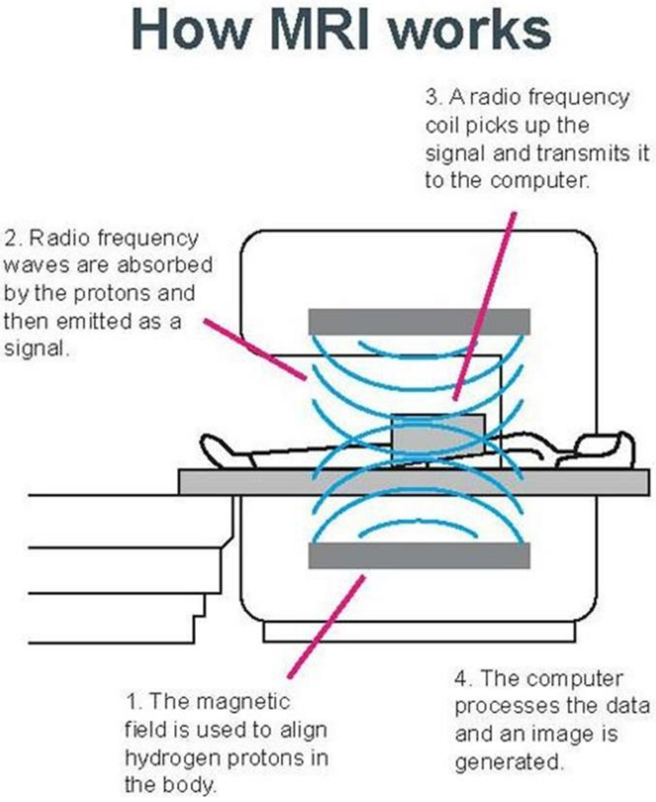


Figure 83 Illustration of how MRI works

MR machine

A patient is placed in the bore of the MRI machine, figure 84. The convention of the axes is shown below. There are several components to an MRI machine, figure 84.

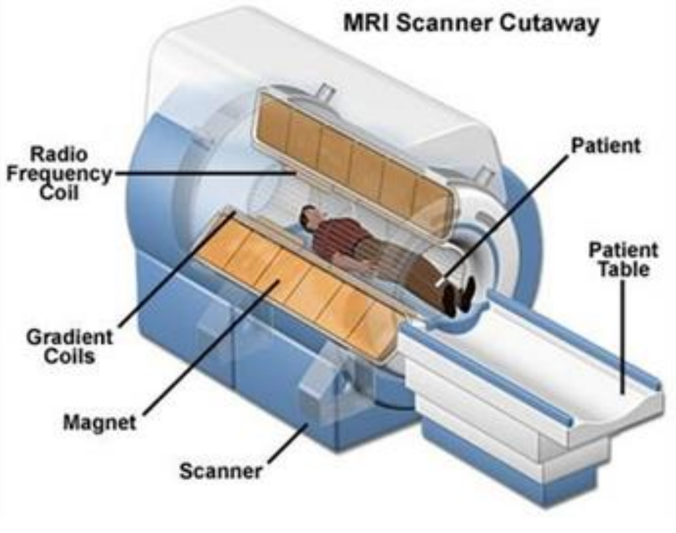


Figure 84 MRI machine

1. Superconducting electromagnet

A superconducting magnet is an electromagnet that is made from superconducting wires that are cooled with liquid helium. For clinical MRI systems, these superconducting wires are most commonly made of an alloy of niobium and titanium (NbTi), figure 85.

<u>The main characteristics of a magnet are:</u>

- Type (superconducting or resistive electromagnets, permanent magnets)
- Strength of the field produced, measured in Tesla (T). In current clinical practice, this varies from 0.2 to 3.0 T. In research, magnets with strengths of 7 T or even 11 T and over are used.
- Homogeneity

Figure 85 Superconducting electromagnet

2. Shim coils

These lie just inside of the outer main magnet and are used to fine-tune the main magnetic field to ensure it is as uniform as possible, figure 86.

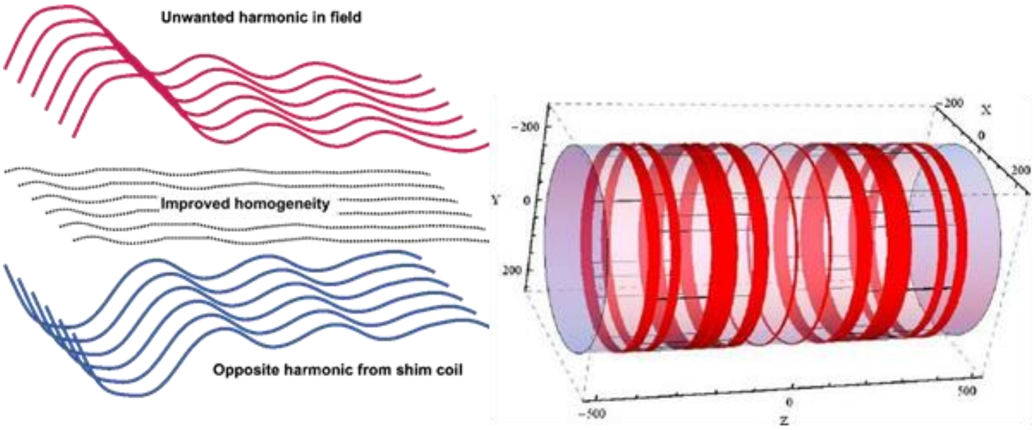


Figure 86 Shim coils

3. Gradient coils

Gradient coils are used to produce deliberate variations in the main magnetic field. There are usually three sets of gradient coils, one for each direction, figure 87. The variation in the magnetic field permits localization of image slices as well as phase encoding and frequency encoding. The set of gradient coils for the z axis are Helmholtz pairs, and for the x and y axis paired saddle coils.

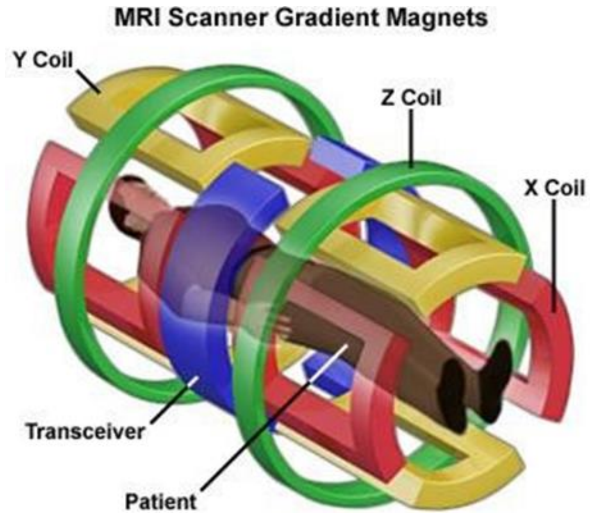


Figure 87 Gradient coils

4. RF (radiofrequency) coils

These coils are tuned to a particular frequency. They produce a magnetic field at right angles (XY plane) to the main magnetic field and also receive the

MR signals being produced. To maximize the signal the coils, have to be placed as close to the part being imaged as possible, figure 88.

There are several types of RF coils:

1. Standard body coil (transmit and receive): permanent part of the scanner. Used to image large parts of the body.
2. Head coil (transmit and receive): incorporated into a helmet and used for head scans.
3. Surface (or local) coils (receive only): these are small coils applied as close to the area being imaged as possible e.g. arm coils, leg, orbits, lumbar spine coils etc.
4. Phased array coils: multiple receiver coils that receive the signals individually but are then combined to improve the signal-to-noise ratio
5. Transmit phased array coils.

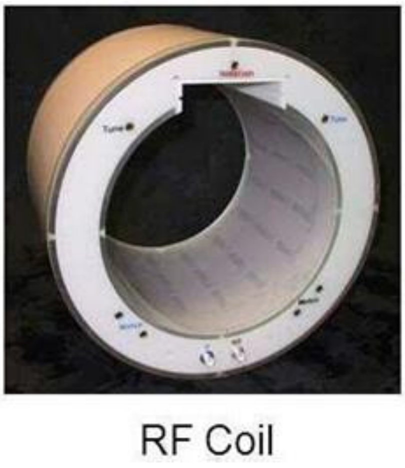


Figure 88 RF coil

Image formation

When the RF pulse is turned off the hydrogen proton slowly return to their natural alignment within a magnetic field and release their excess stored energy, figure 89. This is known as relaxation.

What happens to released energy?

1. Release as heat. OR
2. Exchanged and absorbed by another proton. OR
3. released as radio wave.

Measuring the MR signal:

- The moving proton induces a signal in the RF antenna.
- The signal is picked up by a coil and sent to computer system.
- The computer receives mathematical data , which is converted through the use of a Fourier transform into an MR 3D image.

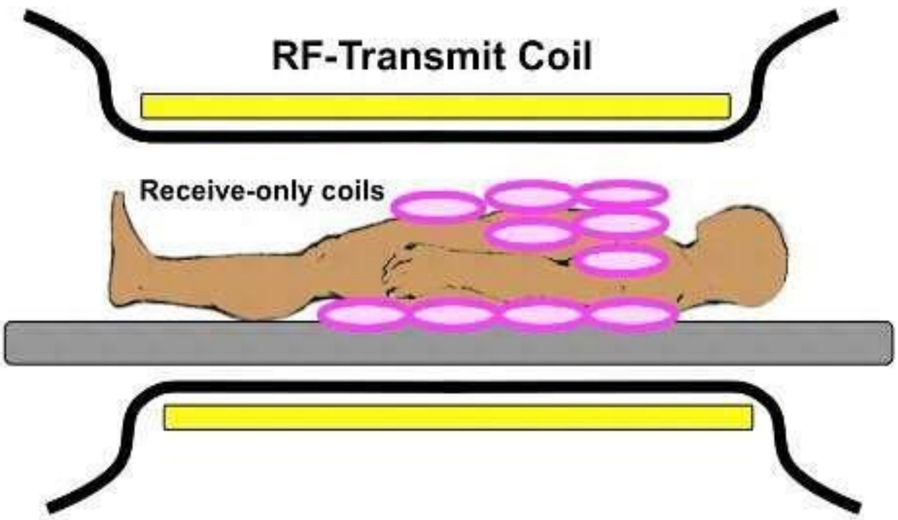


Figure 89 simulation of MRI

MATRIX

- Amount of anatomy covered of a patient is called field of view (FOV).
- FOV is square or rectangle shaped and divided into – matrix (picture element).
- Matrix size is annotated by two fingers.
- No. of frequency sample taken –and – No. of phase encoding performed.

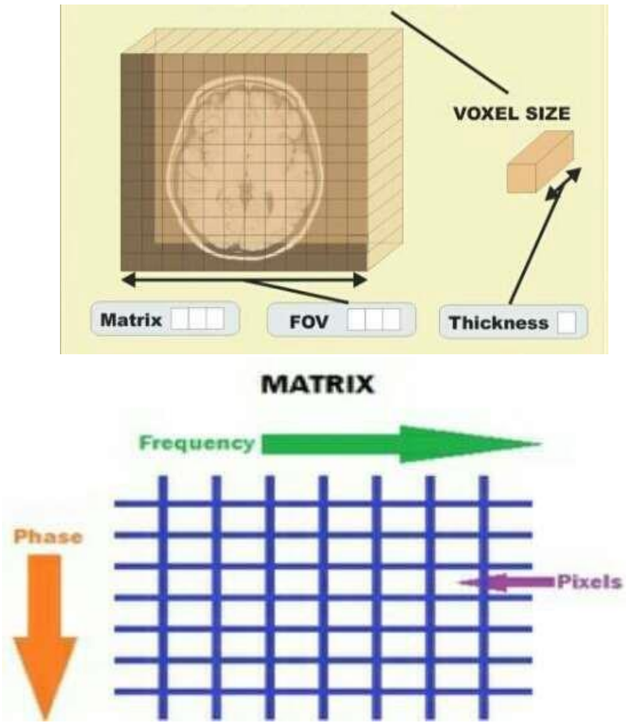


Figure 90 illustration of image construction through MRI matrix

<u>Pixel</u>

Each square of image matrix is called pixel (volume + element) and it is represented by block of tissue called voxel (volume element). pixels do not have a fixed size , their diameter are generally measured in micrometer (microns), figure 91.

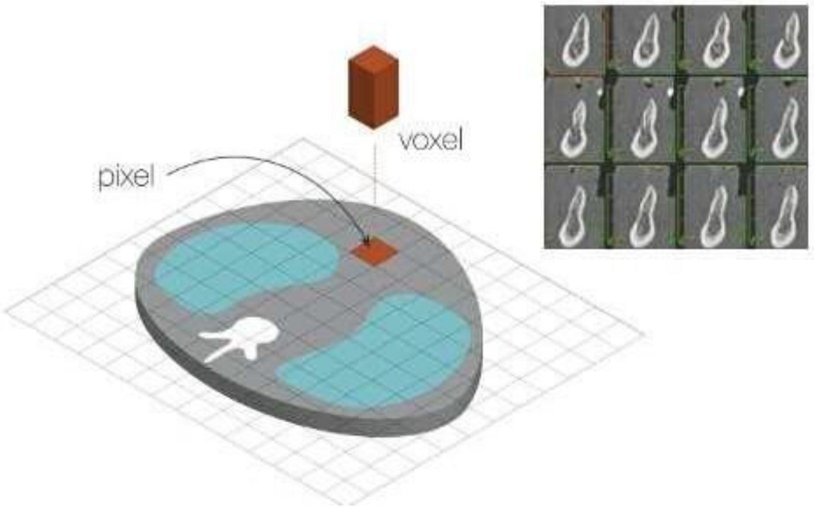


Figure 91 difference between pixel and voxel

Image construction

Localizing and encoding MRI signals

The MRI signal is localized in three dimensions using three separate magnetic field gradients termed:

1. slice-selection gradient
2. phase-encoding gradient (GP)
3. frequency-encoding gradient (GF).

(1) Slice-selection gradient

Slice localization is achieved by using gradient coils to generate a gradient field orientated along a chosen axis. This gradient field alters the strength of B0 in the chosen direction, so that protons within the gradient field have different Larmor frequencies. Typically, the RF pulse is applied as a small range of frequencies (bandwidth) rather than as a single frequency. This excites a slice of a certain thickness. Slice thickness can be altered in two ways:

1. changing the bandwidth of the RF pulse or 2- changing the steepness of the gradient field.

With a given slice selectively excited, the signals arising from each slice element (pixel) within that section need to be spatially encoded. This is achieved using phase- and frequency encoding gradients, figure 92.

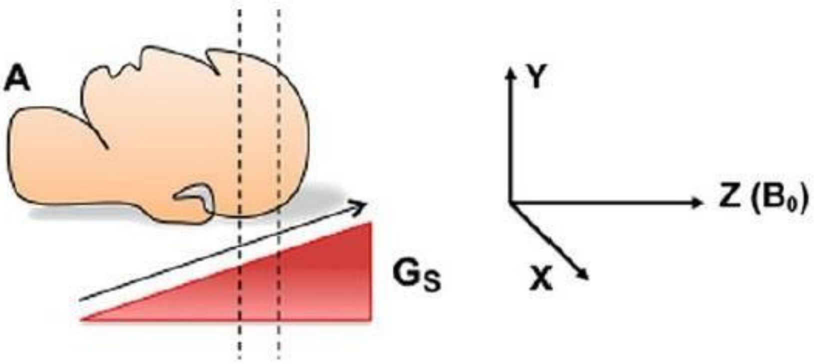


Figure 92 illustration of Slice-selection gradient

(2) Phase-encoding gradient

Following an excitatory RF pulse, the protons process in phase. Applying a new gradient magnetic field will make some of the protons process faster than others depending on their position within the gradient. When the gradient is switched off, all protons will express the same precession frequency and will emit the same signal, but they will no longer be in phase, and this allows the protons to be differentiated. The gradient applied is called the GP and the direction of application is termed the phase- encoding direction. Thus, spin phases will vary linearly over the phase- encode direction, figure 93.

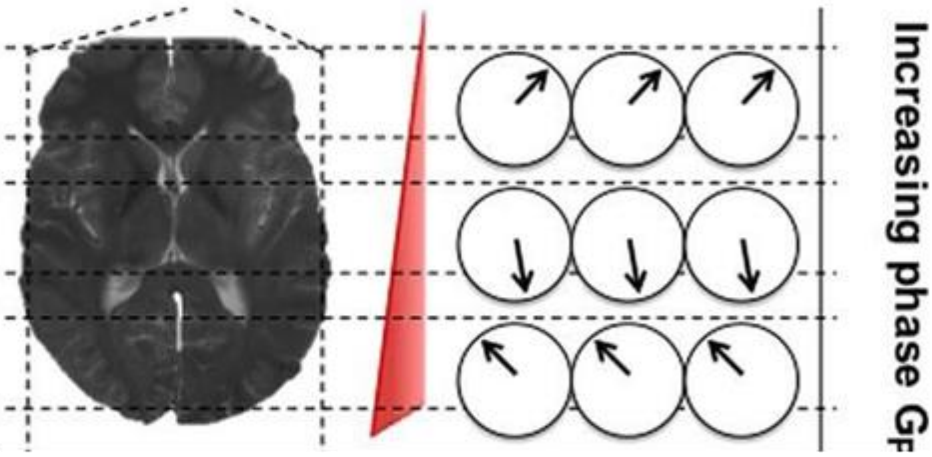


Figure 93 illustration of Phase-encoding gradient

(3)Frequency-encoding gradient

The GF is applied following and perpendicular to the phase-encoding gradient. It causes the protons to rotate at different frequencies according to their relative position along the gradient, permitting differentiation of the signal in a third plane. Two additional gradient pulses are typically used in this three-step process, one immediately after the slice-selection gradient and the other immediately before the GF. These pulses are used to neutralize any de-phasing of the transverse magnetization that may be caused by the imaging gradients and ensures that maximum echo (sampling signal) is achieved. It should be emphasized that RF pulses excite all protons in a slice at the same time and that a single echo signal is recorded from the entire slice forone phase-encoding step. Thus, to acquire sufficient phase-encoding information for a signal to be assigned to each location within the slice, the pulse sequence (comprising slice selection, frequency encoding and phase encoding) is repeated many times. During each repetition, the same slice selection and frequency encoding are performed but the strength of the phase-encoding gradient is increased by equal increments, figure 94. Each repetition of the phase-encoding step generates a signal echo that is digitized and stored in a raw data matrix called 'k-space'. Data points in k-space represent the spatial frequencies content of an MRI. Data in k-space are converted into an image using a mathematical tool called a Fourier transform.

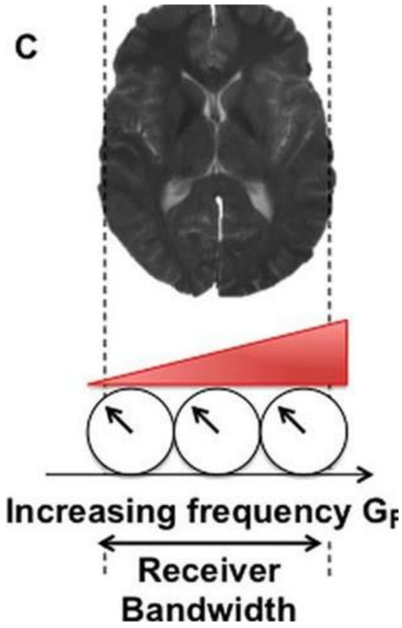


Figure 94 illustration of Frequency-encoding gradient

Effects of T1 and T2 in MRI image

All molecules are in a constant state of random motion. Rates of molecular motion vary for different tissues.

Water molecules in pure water are relatively small and move very quickly, so the protons in them experience field fluctuations at a frequency much higher than the Larmor frequency at 1.5 T. Proteins and other macromolecules are larger and relatively slow-moving, so protons in them experience a field that changes much more slowly than the Larmor frequency at 1.5 T. It turns out that protons in fat have a natural frequency of motion that is close to the Larmor frequency at 1.5 T, and therefore the longitudinal relaxation of fat is fast, and its T1 time is noticeably short. Water molecules that interact with proteins and macromolecules are slowed by their attraction to them, so protein-containing fluids also have short T1 times. Protons in the majority of tissues other than free water are at the slower end of the spectrum, slower than the Larmor frequency, figure 95.

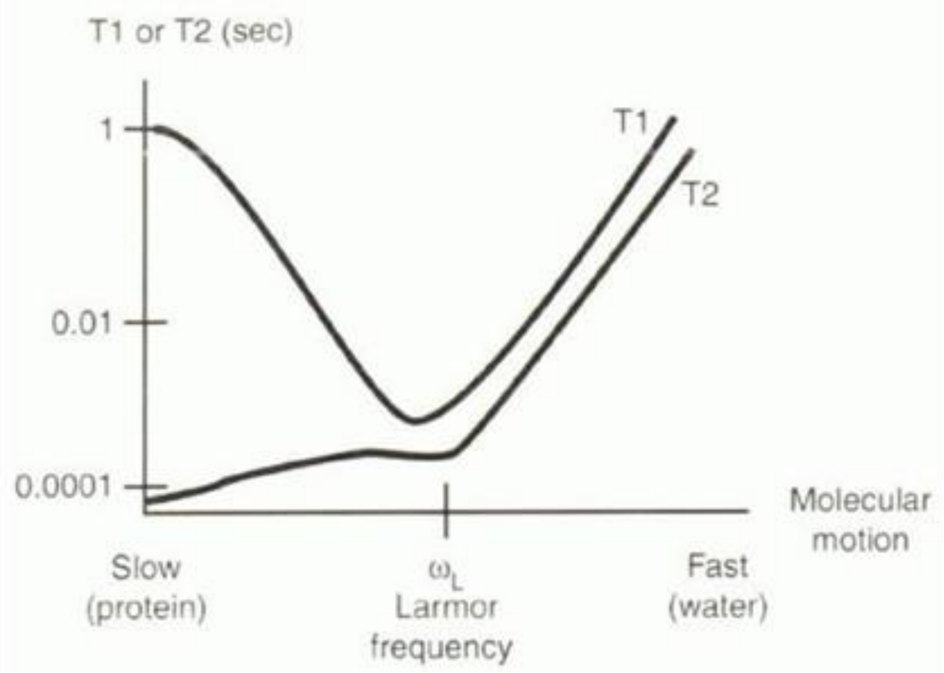


Figure 95 Effects of T1 and T2 in MRI image

Fat and protein: short T1, Long T2.

Water: long T1, long T2.

Bone / calcium / metal: long T1, short T2.

T2* or free induction decay

What has just been described is the exponential curve of transverse decay in the ideal world. However, when we measure it in the real world, we find that the transverse decay is much quicker; the signal reduces to zero faster than expected. This is due to the effect of the local magnetic field inhomogeneities, figure 96.

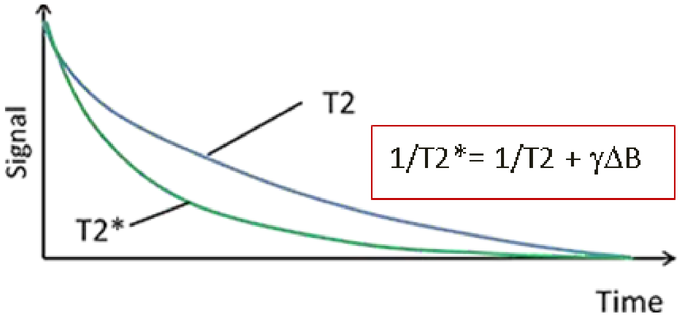


Figure 96 T2* or free induction decay curve

Received Signal: Free Induction Decay (FID)

Once the RF pulse is stopped, the magnetic properties of each nuclei alter the local magnetic field and causes some to process faster and some slower (remember, the processional, or Larmor frequency, is determined by the strength of the magnetic field). Gradually the nuclei lose their coherence, and the net transverse magnetization reduces to zero. The rate it does so is exponential and named the "Free Induction Decay", figure 97.

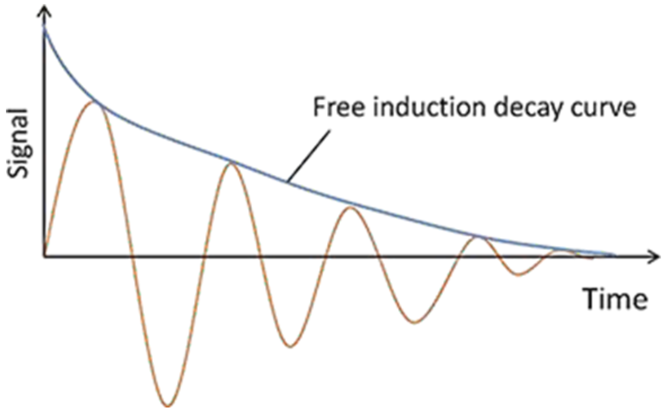


Figure 97 Free Induction Decay curve

Pulse Repetition Time (TR)

Distance between successive RF pulses, figure 98.

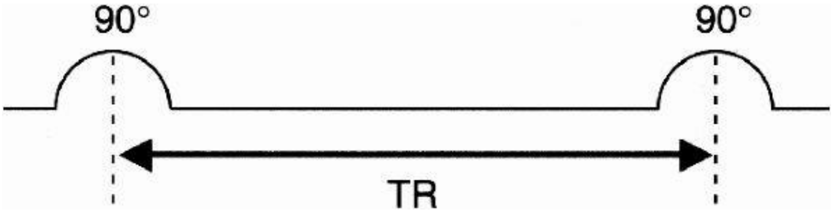
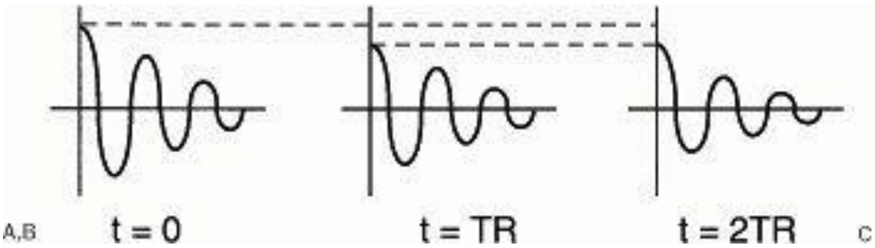


Figure 98 Illustration of Pulse Repetition Time (TR)

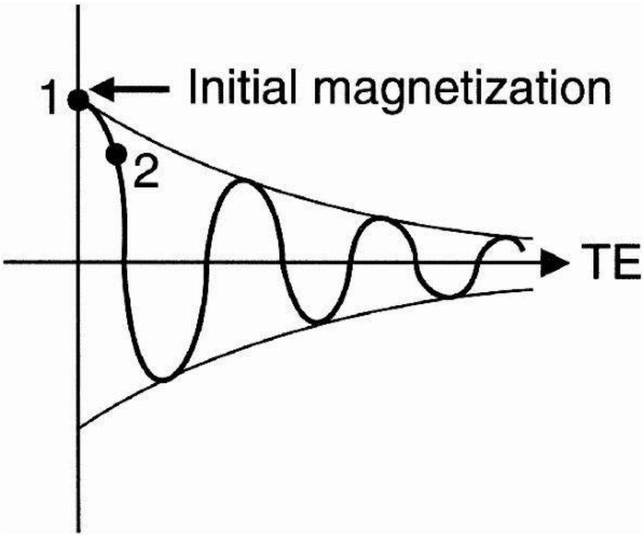


Echo Time or Time to Echo (TE)

Instead of making the measurement immediately after the RF pulse, we wait a brief period of time TE and then make the measurement, figure 99

- Time sampling of FID starts

Figure 99 illustration of Echo Time (TE)



T1, T2 and PD weighted imaging

Unlike imaging using radiation, in which the contrast depends on the different attenuation of the structures being imaged, the contrast in MRI images depends on the magnetic properties and number of hydrogen nuclei in the area being imaged. Different contrasts in the area being imaged can be selected for by running different sequences with different weightings. The main three sequences are:

1. T1-weighted (maximum T1 contrast shown)
2. T2-weighted (maximum T2 contrast shown)
3. Proton density (PD) weighting (density of hydrogen protons shown)

T1-weighted imaging

T1 relaxation is the recovery of the longitudinal magnetization (Mz). The higher the Mz at the time of applying the 90° RF pulse the greater the transverse signal (Mxy). The TR (time to repetition) is what determines the length of time between 90° RF pulses, figure 100:

The longer the TR

↓

The longer the time to the next 90° RF pulse

↓

The more time Mz will have had to recover

↓

The higher the transverse signal when the 90° RF pulse is applied

***** i.e., it is the TR that determines the T1 signal *****

To maximize the contrast between the T1 properties of tissues in the sample being imaged, we need to set the TR so that it occurs at the point in the curve at which there is the greatest difference. As seen on the curve above, this is at a short TR.

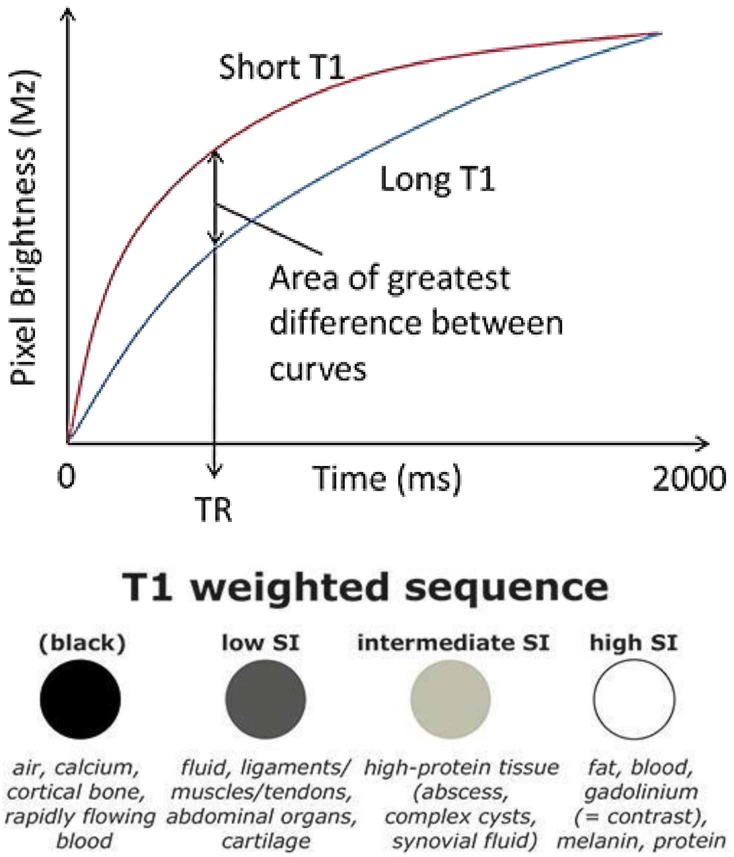


Figure 100 T1-weighted image sequence

T2-Weighted Imaging

T2 decay is the decay of the transverse magnetization (Mxy) after application of the 90° RF pulse.

The longer the time after the 90° RF pulse, the more the Mxy decays and the smaller the transverse signal. As we saw in the spin echo sequence, TE is the "time to echo". If we leave a long TE we give more time for the Mxy (T2 signal) to decay and we get a smaller signal, figure 101.

The longer the TE

↓

The longer the time allowed for Mxy to decay

↓

The smaller the transverse (T2) signal

***** i.e. it is the TE that determines the T2 signal *****

To maximize the T2 contrast a long TE is used, although not too long that the signal is negligible.

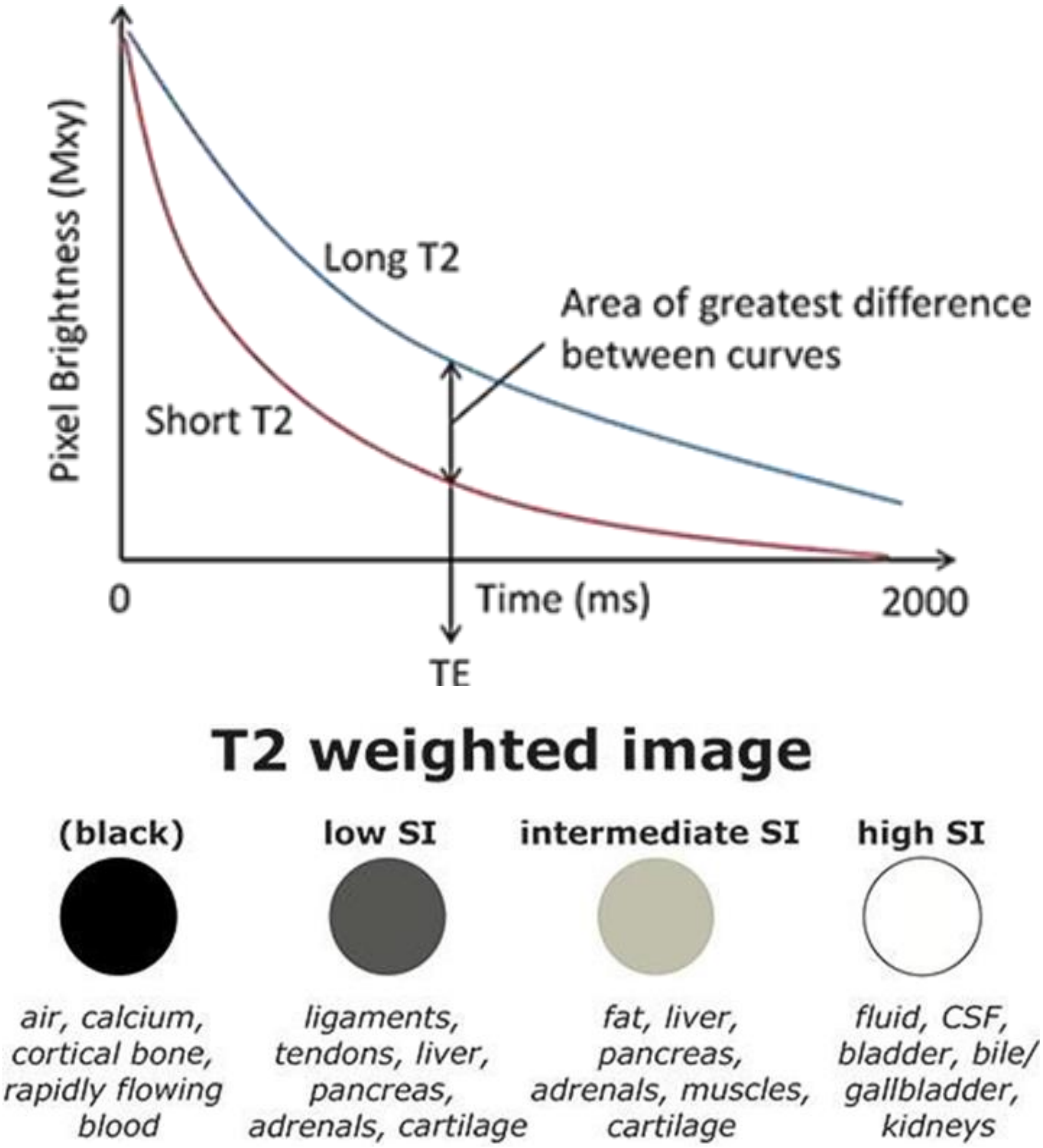


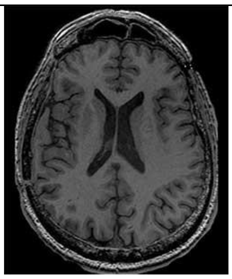
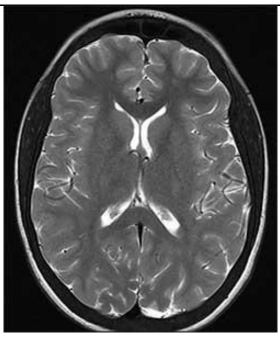
Figure 101 T2-weighted image sequence

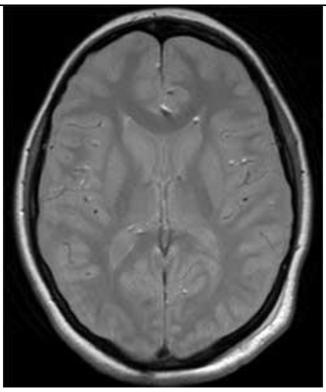
Proton Density Imaging

Unlike T1 and T2 weighted images, proton density (PD) does not display the magnetic characteristics of the hydrogen nuclei but the number of nuclei in the area being imaged. To get a PD weighted image we want to minimize the contribution of both T1 and T2 contrast, figure 102.

- ❖ T1 minimized with a long TR: large signal and small T1 contrast
- ❖ T2 minimized with a short TE: large signal and small T2 contrast

Table 12 Comparison between T1, T2 and Proton Density Imaging

T1	
Image	
Water signal	Water has a long T1. T1-WI uses a short TR so the signal from water is still low, therefore, water appears dark
Fat signal	Fat has a short T1, so even though the TR is short the signal is still high, and fat appears bright
TR	Short. 300-600 ms
TE	Short. 10-30 ms
T2	
Image	
Water signal	T2-WI uses a long TE so the signal from water is high, therefore, water appears bright

Fat signal	Fat has a short T2 so at a long TE the signal is less bright, and it will be darker than water
TR	Long. 2000 ms
TE	Long. 90-140 ms
PD	
Image	
Water signal	A long TR results in a high-water signal, but a short TE means that this is less than the signal of a T2 scan. The signal of water is in the middle
Fat signal	A long TR results in a high fat signal and short TE means this signal is higher than on a T2-WI: fat appears bright
TR	Long. 1000-3000 ms
TE	Short. 15 ms

Other applications of NMR

By studying the peaks of nuclear magnetic resonance spectra, chemists can determine the structure of many compounds. It can be a very selective technique, distinguishing among many atoms within a molecule or collection of molecules of the same type but which differ only in terms of their local chemical environment. NMR spectroscopy is used to unambiguously identify known and novel compounds, and as such, is usually required by scientific journals for identity confirmation of synthesized new compounds.

A chemist can determine the identity of a compound by comparing the observed nuclear precession frequencies to known frequencies. Further structural data can be elucidated by observing spin-spin coupling, a process by which the precession frequency of a nucleus can be influenced by the spin orientation of a chemically bonded nucleus. Spin-spin coupling is easily observed in NMR of hydrogen-1 (1H NMR) since its natural abundance is nearly 100%.

Because the nuclear magnetic resonance timescale is rather slow, compared to other spectroscopic methods, changing the temperature of a T2* experiment can also give information about fast reactions, such as the Cope rearrangement or about structural dynamics, such as ring-flipping in cyclohexane. At low enough temperatures, a distinction can be made between the axial and equatorial hydrogens in cyclohexane.

An example of nuclear magnetic resonance being used in the determination of a structure is that of buckminsterfullerene (often called "buckyballs", composition C60). This now famous form of carbon has 60 carbon atoms forming a sphere. The carbon atoms are all in identical environments and so should see the same internal H field. Unfortunately, buckminsterfullerene contains no hydrogen and so 13C nuclear magnetic resonance has to be used. 13C spectra require longer acquisition times since carbon-13 is not the common isotope of carbon (unlike hydrogen, where 1H is the common isotope). However, in 1990 the spectrum was obtained by R. Taylor and co-workers at the University of Sussex and was found to contain a single peak, confirming the unusual structure of buckminsterfullerene.

Purity determination (w/w NMR)

While NMR is primarily used for structural determination, it can also be used for purity determination, provided that the structure and molecular weight of the compound is known. This technique requires the use of an internal standard of known purity. Typically, this standard will have a high molecular weight to facilitate accurate weighing, but relatively few protons so as to give a clear peak for later integration e.g. 1,2,4,5-tetrachloro-3-nitrobenzene. Accurately weighed portions of the standard and sample are combined and analysed by NMR. Suitable peaks from both compounds are selected and the purity of the sample is determined via the following equation.

$$\mathrm{Purity} = \frac{w_{\mathrm{std}} \times n[\mathrm{H}]_{\mathrm{std}} \times MW_{\mathrm{spl}}}{w_{\mathrm{spl}} \times MW_{\mathrm{std}} \times n[\mathrm{H}]_{\mathrm{spl}}} \times P$$

Where wstd: weight of internal standard, wspl: weight of sample, n[H]std: the integrated area of the peak selected for comparison in the standard, corrected for the number of protons in that functional group, n[H]spl: the integrated area of the peak selected for comparison in the sample, corrected for the number of protons in that functional group, MWstd: molecular weight of standard, MWspl: molecular weight of sample and P: purity of internal standard

.

Non-destructive testing

Nuclear magnetic resonance is extremely useful for analyzing samples non-destructively. Radio-frequency magnetic fields easily penetrate many types of matter and anything that is not highly conductive or inherently ferromagnetic. For example, various expensive biological samples, such as nucleic acids, including RNA and DNA, or proteins, can be studied using nuclear magnetic resonance for weeks or months before using destructive biochemical experiments. This also makes nuclear magnetic resonance an excellent choice for analyzing dangerous samples.

Segmental and molecular motions

In addition to providing static information on molecules by determining their 3D structures, one of the remarkable advantages of NMR over X-ray crystallography is that it can be used to obtain important dynamic information. This is due to the orientation dependence of the chemical- shift, dipole-coupling, or electric-quadrupole-coupling contributions to the instantaneous NMR frequency in an anisotropic molecular environment. When the molecule or segment containing the NMR-observed nucleus changes its orientation relative to the external field, the NMR frequency changes, which can result in changes in one- or two-dimensional spectra or in the relaxation times, depending on the correlation time and amplitude of the motion.

Data acquisition in the petroleum industry

Another use for nuclear magnetic resonance is data acquisition in the petroleum industry for petroleum and natural gas exploration and recovery. Initial research in this domain began in the 1950s, however, the first commercial instruments were not released until the early 1990s. A borehole is drilled into rock and sedimentary strata into which nuclear magnetic resonance logging equipment is lowered. Nuclear magnetic resonance analysis of these boreholes is used to measure rock porosity, estimate permeability from pore size distribution and identify pore fluids (water, oil, and gas). These instruments are typically low field NMR spectrometers.

NMR logging, a subcategory of electromagnetic logging, measures the induced magnet moment of hydrogen nuclei (protons) contained within the fluid-filled pore space of porous media (reservoir rocks). Unlike conventional logging measurements (e.g., acoustic, density, neutron, and resistivity), which respond to both the rock matrix and fluid properties and are strongly dependent on mineralogy, NMR-logging measurements respond to the presence of hydrogen. Because hydrogen atoms primarily occur in pore fluids, NMR effectively responds to the volume, composition, viscosity, and distribution of these fluids, for example oil, gas or water. NMR logs provide information about the quantities of fluids present, the properties of these fluids, and the sizes of the pores containing these fluids. From this information, it is possible to infer or estimate:

- The volume (porosity) and distribution (permeability) of the rock pore space
- Rock composition
- Type and quantity of fluid hydrocarbons
- Hydrocarbon producibility

The basic core and log measurement is the T2 decay, presented as a distribution of T2 amplitudes versus time at each sample depth, typically from 0.3 ms to 3 s. The T2 decay is further processed to give the total pore volume (the total porosity) and pore volumes within different ranges of T2. The most common volumes are the bound fluid and free fluid. A permeability estimate is made using a transform such as the Timur-Coates or SDR permeability transforms. By running the log with different acquisition parameters, direct hydrocarbon typing, and enhanced diffusionare possible.

Flow probes for NMR spectroscopy

Recently, real-time applications of NMR in liquid media have been developed using specifically designed flow probes (flow cell assemblies) which can replace standard tube probes. This has enabled techniques that can incorporate the use of high-performance liquid chromatography (HPLC) or other continuous flow sample introduction devices. These flow probes have used in various online process monitoring such as chemical reactions, environmental pollutant degradation figure 102.

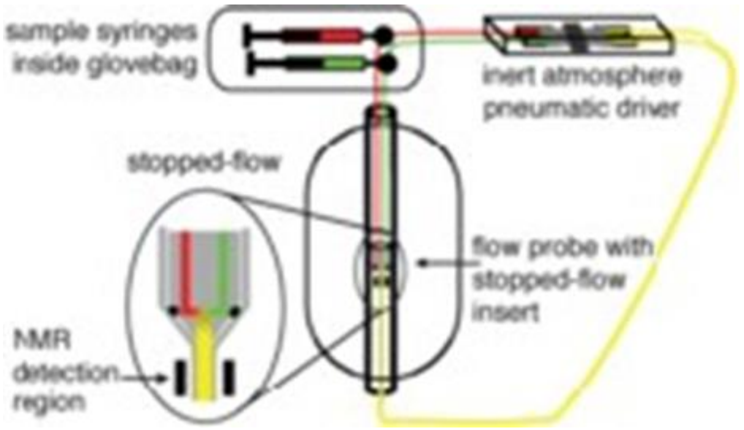


Figure 102 Schematic diagram of a NMR Stopped Flow Probe

Process control

NMR has now entered the arena of real-time process control and process optimization in oil refineries and petrochemical plants. Two different types of NMR analysis are utilized to provide real time analysis of feeds and products in order to control and optimize unit operations. Time-domain NMR (TD-NMR) spectrometers operating at low field (2–20 MHz for 1H) yield free induction decay data that can be used to determine absolute hydrogen content values, rheological information, and component composition. These spectrometers are used in mining, polymer production, cosmetics and food manufacturing as well as coal analysis. High resolution FT-NMR spectrometers operating in the 60 MHz range with shielded permanent magnet systems yield high resolution 1H NMR spectra of refinery and petrochemical streams. The variation observed in these spectra with changing physical and chemical properties is modeled using chemometrics to yield predictions on unknown samples. The prediction results are provided to control systems via analogue or digital outputs from the spectrometer.

Earth's field NMR

In the Earth's magnetic field, NMR frequencies are in the audio frequency range, or the very low frequency and ultra-low frequency bands of the radio frequency spectrum. Earth's field NMR (EFNMR) is typically stimulated by applying a relatively strong dc magnetic field pulse to the sample and, after the end of the pulse, analyzing the resulting low frequency alternating magnetic field that occurs in the Earth's magnetic field due to free induction decay (FID). These effects are exploited in some types of magnetometers, EFNMR spectrometers, and MRI imagers. Their inexpensive portable nature makes these instruments valuable for field use and for teaching the principles of NMR and MRI. An important feature of EFNMR spectrometry compared with high-field NMR is that some aspects of molecular structure can be observed more clearly at low fields and low frequencies, whereas other aspects observable at high fields are not observable at low fields. This is because:

- Electron-mediated heteronuclear J-couplings (spin-spin couplings) are field independent, producing clusters of two or more frequencies separated by several Hz, which are more easily observed in a fundamental resonance of about 2 kHz. "Indeed it appears that enhanced resolution is possible due to the long spin relaxation times and high field homogeneity which prevail in EFNMR."
- Chemical shifts of several ppm are clearly separated in high field NMR spectra but have separations of only a few millihertz at proton EFNMR frequencies, so are usually not resolved.

Zero field NMR

In zero field NMR all magnetic fields are shielded such that magnetic fields below 1 nT (nanotesla) are achieved and the nuclear precession frequencies of all nuclei are close to zero and indistinguishable. Under those circumstances the observed spectra are no-longer dictated by chemical shifts but primarily by J-coupling interactions which are independent of the external magnetic field. Since inductive detection schemes are not sensitive at very low frequencies, on the order of the J- couplings (typically between 0 and 1000 Hz), alternative detection schemes are used. Specifically, sensitive magnetometers turn out to be good detectors for zero field NMR. A zero magnetic field environment does not provide any polarization hence it is the combination of zero field NMR with hyperpolarization schemes that makes zero field NMR attractive.

Quantum computing

NMR quantum computing uses the spin states of nuclei within molecules as qubits. NMR differs from other implementations of quantum computers in that it uses an ensemble of systems, in this case, molecules.

Magnetometers

Various magnetometers use NMR effects to measure magnetic fields, including proton precession magnetometers (PPM) (also known as proton magnetometers), and Over Hauser magnetometers. See also Earth's field NMR.

SNMR

Surface magnetic resonance (or magnetic resonance sounding) is based on the principle of nuclear magnetic resonance (NMR) and measurements can be used to indirectly estimate the water content of saturated and unsaturated zones in the earths subsurface. SNMR is used to estimate aquifer properties, including quantity of water contained in the aquifer, porosity, and hydraulic conductivity.

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