I

Magnetism in Nature

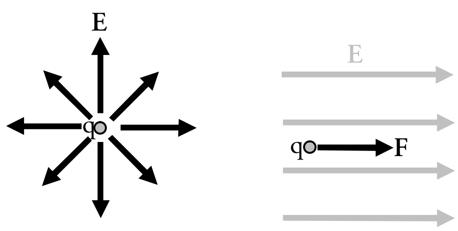
Lecture notes by Assaf Tal

1. Basic Spin Physics

1.1 Magnetism

Before talking about magnetic resonance, we need to recount a few basic facts about magnetism.

Electromagnetism (EM) is the field of study that deals with magnetic (**B**) and electric (**E**) fields, and their interactions with matter. The basic entity that creates electric fields is the electric charge. For example, the electron has a charge, q, and it creates an electric field about it, $\mathbf{E}=\frac{1}{4\pi\varepsilon_0}\frac{q}{r^2}\hat{\mathbf{r}}$, where **r** is a vector extending from the electron to the point of observation. The electric field, in turn, can act on another electron or charged particle by applying a force **F**=q**E**.

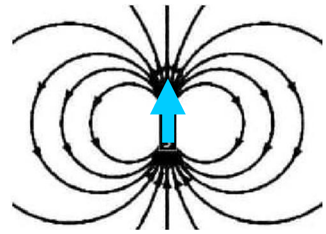


Left: a (stationary) electric charge *q* will create a radial electric field about it. Right: a charge *q* in a constant electric field will experience a force **F**=q**E**.

There is, however, no magnetic charge. The "elementary unit of magnetism" is the **magnetic moment**, also sometimes called the **magnetic dipole**. It is more complicated than charge because it is a vector, meaning it has both magnitude and direction. We will ask ourselves three basic questions:

1. What sort of magnetic fields does a magnetic moment create?
2. Where/how do magnetic moments appear in nature?
3. How does an external magnetic field affect the magnetic moment (apply force/torque, etc)?

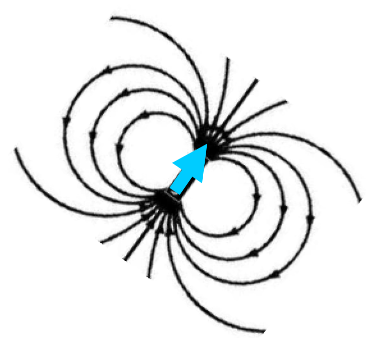
We begin by answering the first question: the magnetic moment creates magnetic field lines (to which **B** is parallel) which resemble in shape of an apple's core:



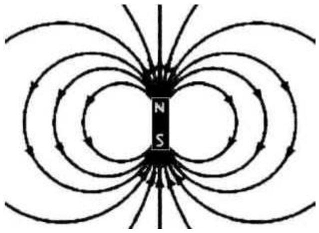
Mathematically, if we have a point magnetic moment **m** at the origin, and if **r** is a vector pointing from the origin to the point of observation, then:

$$\mathrm{B}(\mathbf{r})=\frac{\mu_0}{4\pi}\frac{3(\mathbf{m}\cdot\hat{\mathbf{r}})\hat{\mathbf{r}}-\mathbf{m}}{\mathrm{r}^3}$$

The magnitude of the generated magnetic field **B** is proportional to the size of the magnetic charge. The direction of the magnetic moment determines the direction of the field lines. For example, if we tilt the moment, we tilt the lines with it:

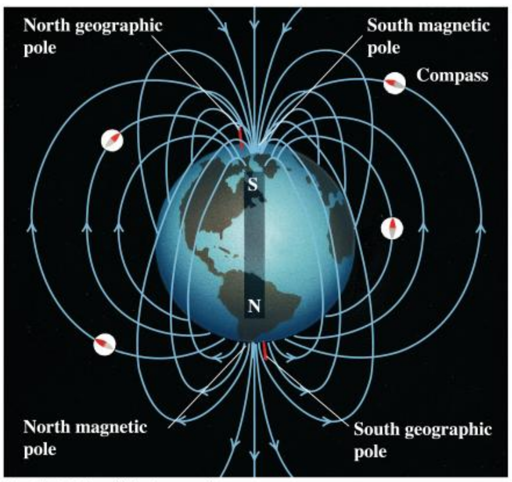


The simplest example of a magnetic moment is the refrigerator magnet. This, however, is not a microscopic moment and its field will often deviate from that of an ideal magnetic dipole. We'll soon meet other, much smaller and weaker magnetic moments, when we discuss the atomic nucleus.



Your refrigerator magnet
has a permanent magnetic moment

Another interesting example is the Earth itself, which behaves as if it had a giant magnetic moment stuck in its core:



If you take a compass, which is nothing more than a magnetized iron needle, having a magnetic moment itself, it will align itself along the earth's magnetic field. This illustrates another point of interest which we'll make use of: magnetic moments tend to align themselves along the magnetic field they are in when in equilibrium, in which they minimize the moment's energy:

$$E = -\mathbf{m} \cdot \mathbf{B} \, .$$

Whether or not they actually align is dependent on competing interactions, such as their thermal energy which tends to randomize them.

The phrase "tend to" is quite sloppy, since, as we'll see, it's the things they do until they align themselves that constitute the heart of MR. Nevertheless, the fact that moments "want" to align themselves to an applied field indicates that:

> The most energetically favorable position (i.e. "minimum energy") for a magnetic moment in an external field is parallel to the field (the most energetically unfavorable position is anti-parallel)

Magnetic moments are measured in units of Joule/Tesla or (equivalently) in Ampere·meter^2 (1 J/T = 1 A·m^2).

1.2 Magnetic Moments in Nature

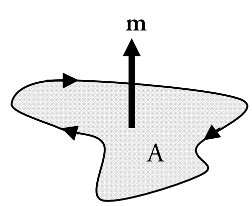
Magnetic moments are divided into two groups: current-induced and intrinsic.

Current-Induced Moments

Basic electromagnetism tells us that a current flowing in a closed loop will give off a magnetic field. The loop can be *macroscopic*, like a wire, or *microscopic*, like an electron orbiting the nucleus. Far away from the current loop the field will look **as if** it were being generated by a magnetic dipole. If the magnetic loop is assumed to be planar, the magnetic dipole will be perpendicular to the loop, and have a magnitude given by

$$m = IA$$

where I is the current in the loop and A is the area enclosed by the loop:



For a general (non-planar) current loop, the expression for **m** is somewhat more complicated, but the principle is the same.

Intrinsic Moments

It also appears that several fundamental particles - the proton and the electron – carry **intrinsic** magnetic moments. That is, they "give off" a magnetic field as if a magnetic dipole were fixed to them, without having any current associated with them.

	Electron	Neutron	Proton
Charge (Coulombs)	-1.6×10^{-19}	0	1.6×10^{-19}
Mass (kg)	9.1×10^{-31}	1.6×10^{-27}	1.6×10^{-27}
Magnetic moment (J/T), $2\pi\gamma S$	9.26×10^{-24}	-0.96×10^{-26}	1.4×10^{-26}
Magnetic moment (μ_B)	-1.0	Irrelevant	Irrelevant
Magnetic moment (μ_N)	Irrelevant	-1.91	2.79
Spin, S (in units of $\hbar$)	1/2	1/2	1/2
Gyromagnetic ratio, γ (Hz/T)	$2.8\cdot10^{10}$	-2.91×10^{7}	4.257×10^{7}

The **Bohr magneton**, μ_B, is just a quantity that makes it easy to talk about electron magnetism. It's not used often in nuclear magnetism, thought:

$$\mu_B = \tfrac{e\hbar}{2m_e} = 9.27\times10^{-24}\,\tfrac{J}{T}\,.$$

A similar quantity, the nuclear magneton, μ_N, is used more often in nuclear magnetism, although we won't be making direct use of it:

$$\mu_N = \tfrac{e\hbar}{2m_p} = 5.05\times10^{-27}\,\tfrac{J}{T}\,.$$

The phenomenon of intrinsic magnetic moments is directly related to another fundamental property of these particles called **spin**, and one speaks of a "nuclear spin" or an "electron spin". This is intrinsic angular momentum possessed by all electrons, protons and neutrons. Semi-classically, we can think of the proton or electron as a rotating ball of charge. The rotating charge can be thought of as loops of current, which give off a magnetic moment. In reality this picture is wrong, and you should always keep in mind spin is an intrinsic, somewhat weird quantum mechanical property; for example, the neutron has no charge and yet has a spin magnetic moment.

The semi-classical picture gets one thing right: the angular momentum and magnetic moment of the spinning sphere are parallel:

$$\mathbf{m} = \gamma\mathbf{S}\,.$$

The constant of proportionality is known as the *gyromagnetic ratio*, and is given in units of

$$[\gamma] = \frac{\text{Coulomb}}{\text{kg}} = \frac{\text{Hz}}{\text{Tesla}}\,.$$

A word of caution about units: some books or tables quote γ in units of rad·MHz/T. For example, $\gamma=2\pi\cdot42.576$ rad·MHz/T for the hydrogen nucleus. Always be mindful of the units being used. Remember that, if we multiply γ by 2π, we will sometimes need to divide another quantity by 2π along the way. A simple example is that of the magnetic moment of the proton:

$$\mathbf{m} = \underbrace{\gamma}_{\substack{42.576\text{ MHz/T}\\(\text{no }2\pi)}} \times \underbrace{\mathbf{S}}_{\substack{=(1/2)\text{h for proton}\\(\text{has }2\pi)}}\,.$$

Equivalently,

$$\mathbf{m} = \underbrace{\gamma}_{\substack{2\pi\cdot42.576\text{ MHz/T}\\(\text{has }2\pi)}} \times \underbrace{\mathbf{S}}_{\substack{(1/2)\hbar\\(\text{no }2\pi)}}\,.$$

In the second form, I moved the 2π factor from h to γ. The end result is the same, but now we must remember to specify the angular momentum in units without radians.

All electrons have an intrinsic magnetic moment, but that is not true for all nuclei, since nuclei are made up of smaller more elementary units (protons and neutrons) which sometimes cancel out. In fact, it is energetically favorable for two magnetic moments to cancel out:

The Nuclear Magnetic Moment

The nucleus is made up of protons and neutrons. Proton and neutron spins tend to pair up anti-parallel due to the Pauli exclusion principle, in a manner similar to that of the electronic model of the atom, where levels fill up from lowest energy and up. This is quite surprising when you consider how strongly coupled the nucleons are, but it works.

This reasoning works fairly well. For example, it predicts that **nuclei with an equal number of protons and neutrons should have 0 nuclear spin**. This works well for ^{12}C, ^{16}O, but not for ^{2}H, as shown by the next table:

Number of protons	Number of neutrons	Spin quantum number	Examples
Even	Even	0	^{12}C, ^{16}O, ^{32}S
Odd	Even	1/2	^{1}H, ^{19}F, ^{31}P
"	"	3/2	^{11}B, ^{35}Cl, ^{79}Br
Even	Odd	1/2	^{13}C
"	"	3/2	^{127}I
"	"	5/2	^{17}O
Odd	Odd	1	^{2}H, ^{14}N

It also predicts nuclei with an "extra" neutron or proton should have spin-½. This works for ^{13}C, ^{1}H, ^{31}P, ^{19}F, but not for ^{17}O. The breakdown of the pairing occurs before some nuclei have asymmetric nuclear charge distributions. These lead in some cases to favorable energy configurations with non-paired nucleons. Nuclei with asymmetric charge distribution are known as **quadrupolar nuclei**, and we'll discuss them later on in the course.

Atomic Magnetism

When one speaks of atomic magnetism one usually refers to magnetism created by the electrons, which is larger and therefore more dominant than the nuclear term. This is a combination of intrinsic electronic magnetism (spin) and induced electronic magnet moments in external fields.

1.3 Field-Moment Interactions

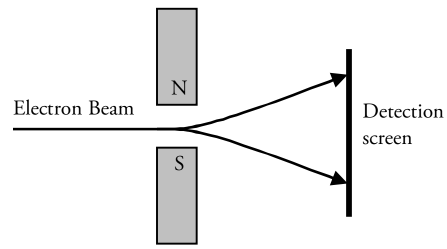
A microscopic (point-like) magnetic moment **m** in a magnetic field **B** will be affected in two ways: it will feel a **torque**,

$$\boldsymbol{\tau}=\mathbf{m}\times\mathbf{B},$$

and will also feel a force:

$$\mathbf{F}=(\mathbf{m}\cdot\nabla)\mathbf{B}=m_x\frac{\partial\mathbf{B}}{\partial x}+m_y\frac{\partial\mathbf{B}}{\partial y}+m_z\frac{\partial\mathbf{B}}{\partial z}.$$

A corollary to this is that a magnetic moment in a spatially constant magnetic field will not feel any force on it (but *will* feel a torque). If you've ever heard of the Stern-Gerlarch experiment conducted in the 1920s, then you already know this at least partially: there, the experimentalists employed a non-uniform magnetic field between two magnetic poles, and fired a beam of electrons through it (actually, it was silver atoms having an unpaired electron, but the effect was the same); electrons having their spin pointing "up" felt a force in one direction, and electrons having their spin pointing "down" felt a force in the opposite direction, effectively splitting the beam into two groups and proving electron spin was quantized:



In the Stern-Gerlach experiment, a nonuniform field between two magnetic poles deflected "up" spins in one direction and "down" spins in the opposite direction with a force $\mathbf{F}=(\mathbf{m}\cdot\nabla)\mathbf{B}$.

In magnetic resonance almost all of the fields we'll encounter will be spatially uniform; even non-spatially uniform ones will have a negligible effect since the force they'll exert will be negligible (both **m** and $\nabla\mathbf{B}$ will be small). However, the torque will turn out to be important, and will lead to an important vectorial equation of motion called the **Bloch Equation**.

To derive the Bloch Equation (BE), we note that for both intrinsic and induced magnetic moments, the moment is proportional to the angular momentum:

$$\mathbf{m}=\gamma\mathbf{L}.$$

Differentiating, and making use of the fact that the derivative of the angular momentum equals the torque,

$$\boxed{\frac{d\mathbf{m}}{dt}=\gamma\frac{d\mathbf{L}}{dt}=\gamma\boldsymbol{\tau}=\gamma\mathbf{m}\times\mathbf{B}}$$

The Bloch Equation

This is, perhaps, one of the most important equations in magnetic resonance, and we will make great use of it in subsequent chapters.

1.4 Larmor Precession

Solving the Bloch Equation (BE) involves solving a set of three first order, linear, coupled, ordinary differential equations. Given **m**(t=0), the BE allows us to calculate **m**(t) for any time t.

Luckily, we can "solve" the BE geometrically without resorting to differential equations. "dot"-ing both sides by **m**,

$$\mathbf{m}\cdot\frac{d\mathbf{m}}{dt}=\gamma\mathbf{m}\cdot\left(\mathbf{m}\times\mathbf{B}\right),$$

and using the identities

$$\frac{1}{2}\frac{dm^2}{dt}=\mathbf{m}\cdot\frac{d\mathbf{m}}{dt}$$
$$\mathbf{A}\cdot\left(\mathbf{B}\times\mathbf{C}\right)=\mathbf{C}\cdot\left(\mathbf{A}\times\mathbf{B}\right)$$

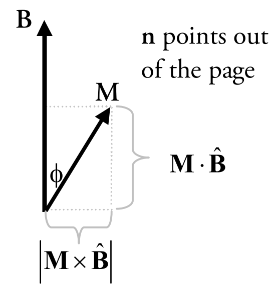
we obtain

$$\frac{d\left(\mathbf{m}^2\right)}{dt}=2\mathbf{m}\cdot\frac{d\mathbf{m}}{dt}=\gamma\mathbf{B}\cdot\left(\mathbf{m}\times\mathbf{m}\right)=0\cdot$$

This means the square of the length of **M** does not change with time; this also means that the size of **M** doesn't change with time. So all that happens to **M**, our magnetic moment, is that it changes its direction, not length. To find out exactly how that direction changes, write $\mathbf{M}=\mathrm{M}\hat{\mathbf{M}}$, where $\hat{\mathbf{M}}$ is a unit vector pointing in the direction of **M**. M, the magnitude of **M**, is constant, so $\dot{\mathbf{M}}=\mathrm{M}\dot{\hat{\mathbf{M}}}$, and:

$$\dot{\mathbf{M}}=\mathrm{M}\dot{\hat{\mathbf{M}}}=\gamma\mathbf{M}\times\mathbf{B}=\gamma\mathrm{MB}\sin\phi\hat{\mathbf{n}}\ .$$

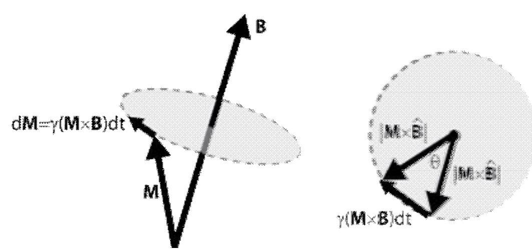
where ϕ is the angle between **M** and **B** and $\hat{\mathbf{n}}$ is a unit vector pointing in the plane perpendicular to both **M** and **B**. Thus, if we assumed **M** and **B** to be contained in this sheet of paper, $\hat{\mathbf{n}}$ would be pointing out of the page according to the right hand rule (i.e., towards you, the reader):



Since the magnitude of **M** is fixed, its tip can only move on a "sphere", the radius of which is |**M**|. Furthermore, the *projection* of **M** on **B** is fixed, because this projection, equal to $\mathbf{M}\cdot\hat{\mathbf{B}}$, is independent of time:

$$\frac{\mathrm{d}\left(\mathbf{M}\cdot\hat{\mathbf{B}}\right)}{\mathrm{dt}}=\frac{\mathrm{d}\mathbf{M}}{\mathrm{dt}}\cdot\hat{\mathbf{B}}+\mathbf{M}\cdot\cancel{\frac{\mathrm{d}\hat{\mathbf{B}}}{\mathrm{dt}}}=\gamma\left(\mathbf{M}\times\mathbf{B}\right)\cdot\hat{\mathbf{B}}\ .$$

The last term on the right is zero because **M**×**B** is perpendicular to **B**, so their dot product is zero. Thus, **M** is actually constrained to move on a circle about **B**, as shown on the figure to the left:



We next argue the angular rate of this precession is *constant*. Looking at the figure to the right, which shows the motion from a "top-down" perspective (looking down at the field vector **B**), we can see the motion of the projection of **M** on the plane perpendicular to **B**. From simple vector algebra, the projection's size is $|\mathbf{M}\times\hat{\mathbf{B}}|$, and, from trigonometry, we have:

$$|\mathbf{M}\times\hat{\mathbf{B}}|\sin\left(\mathrm{d}\theta\right)\approx\gamma\,|\mathbf{M}\times\mathbf{B}|\,\mathrm{dt}\ .$$

Approximating sin(dθ)≈dθ, and dividing by $|\mathbf{M}\times\hat{\mathbf{B}}|$, we obtain:

$$\frac{d\theta}{dt} \approx \gamma B .$$

Our conclusion is, therefore: *the vector* **M** *rotates about an axis defined by* **B**, *with an angular velocity given by* $\omega=\gamma B$. This sort of motion is called a ***precession***. Remember this idea: it will be central to understanding a lot of the subsequent ideas.

As a corollary, if we place a magnetic moment in a strong, constant external magnetic field, $\mathbf{B}_0$, it will precess around it with an angular frequency

$$\omega_L = \gamma B_0 .$$

This frequency is called the ***Larmor frequency***.

1.5 How Spins "Talk"

Magnetic moments create magnetic fields, as pointed out in the introduction, so two spins close-by will affect each other. This is called a dipolar interaction. Thus, different nuclei "talk" to each other, as do the electron and nucleus. In physics, we say they are **coupled** by the dipolar interaction, which is one of the most important and pervasive type of coupling in NMR.

We will encounter other types of coupling as we progress throughout the course. It will turn out that in many cases we can ignore such couplings because they average out, for example due to the thermal motion of the spins or through some other mechanism. This is called **motional narrowing**. Why *narrowing*? When molecules are static the effect of complex coupling to their spin neighbors manifests itself as a broadening of their spectral line. Once the molecules are tumbling fast and the interactions average out, these lines usually become much narrower and their lifetime increases dramatically. For example, typical NMR dipolar linewidths in solids can reach tens of kHz, while in liquid they are as narrow as 1 Hz.

1.6 Some Pitfalls

A few words of caution:

1. It is important to stress that intrinsic magnetic moments live in their own "space". For example, if you take a proton and rotate it in space, the direction of its intrinsic magnetic moment **will not change**. This is very strange, yet true! It's also unlike induced magnetic moments, for which a change in orientation of the current loop **will** change the direction of the induced magnetic moment. The only way to change the orientation of an intrinsic moment is to apply a magnetic field to it.
2. The above expressions for the field created by a magnetic moment assumes it's static. The expression remains true even when the moment changes, as long as we're in the "near field". How near is that? If the moment has some periodic time dependence $\mathbf{m}(t)$ with some frequency ν, then it will have an associated wavelength $\lambda=c/\nu$. The near field approximation holds when our distance is smaller than λ. This will be the case for almost all of our discussions, but it's worth keeping in mind. When we go too far away we need to start worrying about radiation fields, which will be negligible in our discussions. For example, for a typical 11 Tesla NMR spectrometer, $\nu \approx 500$ MHz and consequently $\lambda \approx 0.6$ meters, much larger than the dimensions of the spectrometer or the sample.

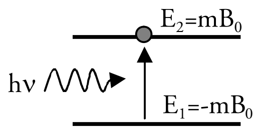
1.7 The Quantum Nature of Spin

Spin is a quantum mechanical entity. Electrons, protons and neutrons have spin S=½, but some nuclei have spin that is 1, 1½, 2, ... For example, the oxygen ^{17}O isotope's nucleus has a spin of S=2½, and deuterium (^2H) has a spin of S=1.

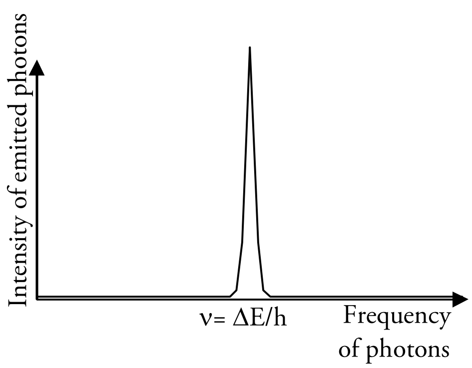
Being quantum mechanical, a spin with magnitude S in a constant magnetic field B_0 can only assume 2S+1 discrete values for its energy, given by:

$$E_n = n\hbar\gamma B_0, \quad n = -S, -S+1, \ldots, S .$$

Since spin is a quantum mechanical property, so is the magnetic moment. You might have heard that "electron/nuclear spin can only be up or down". This seems to go against what the idea of spin precession which in fact only happens when the magnetic moment is *not* aligned with the magnetic field. Furthermore, spectroscopy books abound with drawings such as this, in which external irradiation induces observable transitions between discretized (quantum) levels in an ensemble of, say, spin-½ atoms (we'll always be talking about ensembles):



What the above drawing represents is absorption, in which a photon having an energy that matches the difference in energy levels is absorbed by the system and a transition occurs. After a short amount of time the system will perform *spontaneous emission*. If we measure the emitted energy as a function of the frequency ν of the photons, we will obtain a "dip" when $h\nu=(E_2-E_1)$:



The problem with this picture is that it is incomplete. It only portrays what happens to the system *incoherently*, while a great deal of NMR/EPR phenomena is *coherent*, such as precession. In precession, the magnetization precesses around the external field B_0 and therefore its energy $E=-\mathbf{m}\cdot\mathbf{B}_0$ is constant (just draw the vectors and you'll see the projection of **m** on **B** remains constant). This means there can't be any motion between the energy levels, since that would change the energy of the system. However, if we were to record a signal from a precessing spin we would see oscillations in the signal. Since things can't move around in the energy level diagram, we can't explain any oscillatory motion using it.

The full quantum mechanical description, with Hamiltonians and Schroedinger's time dependent equation, fully accounts for the phenomenon of precession as well as all other phenomena. I therefore suggest that you treat the above picture with the utmost caution. When **is** it applicable? When we deal with *incoherent* phenomena, such as the **thermodynamics** of the spin system.

2. Bulk Magnetism

2.1 Types of Magnetism

A magnetic material is one which interacts with an external magnetic field. Almost all materials in nature are magnetic, although the degree varies tremendously. The source of this magnetism stems from the interaction of the atoms with the external field. The atom has three sources of magnetism:

1. The intrinsic nuclear magnetic moment, resulting from the intrinsic nuclear spin.
2. The intrinsic electron magnetic moment, resulting from the intrinsic electron spin.
3. The magnetic moment induced by the orbital motion of the electrons around the nucleus.

These interact with an external field in several interesting ways, which we will cover next. In general, if we apply an external, constant, magnetic field B_0, we will tend to magnetize most materials.

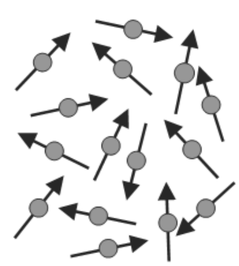
2.2 Paramagnetism

Paramagnetism is the easiest to understand. The energy of a magnetic moment **m** in an external field **B** is

$$E=-\mathbf{m}\cdot\mathbf{B}\,.$$

This means that, if **m** is anti-parallel to **B** the energy is highest and if **m** is parallel to **B** the energy is lowest.

Imagine a collection of non-interacting magnetic moments, free to rotate. In the absence of any external field and at a finite temperature, they will orient themselves in all directions randomly due to thermal fluctuations:

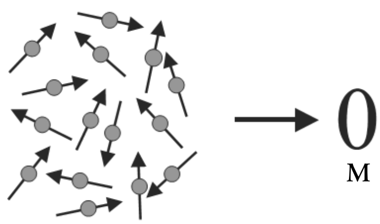


In the above illustration each “dot” is an idealized molecule, and each “arrow” is, say, the nuclear (or electronic) spin magnetic moment.

The bulk magnetization **M** of the volume V is defined as the (vector!) sum over all elements $\mathbf{m}_i$ in the volume:

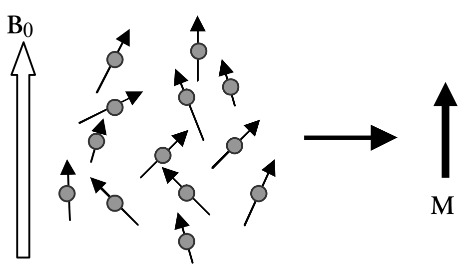
$$\mathbf{M} = \sum_{i=1}^{N} \mathbf{m}_i \ .$$

In the above example, **M=0** because the spins cancel out each other:



The $\mathbf{m}_i$

Upon the application of an external field, the spins tend to align along the field – although thermal motion will prevent them from doing so completely. A “snapshot” of the spins in the presence of an external field might look like this:



The $\mathbf{m}_i$

This is a result of the system trying to minimize the energy of the spins (at thermal equilibrium). This is offset by the spins’ thermal energy, which tends to disorient them. The degree of macroscopic orientation will be determined by the relative size of the magnetic energy ($\mathbf{m}\cdot\mathbf{B}$) and the thermal energy (kT). For nuclear and electronic spins, $\mathbf{m}\cdot\mathbf{B} \ll kT$ so the orientation is small.

Any system that is comprised of permanent magnetic moments will display some degree of paramagnetism. Nuclear paramagnetism is very weak and cannot be observed without using NMR under practical conditions. Electronic paramagnetism only occurs in paramagnetic substances – i.e., those with an unpaired electron. For example: oxygen (O_2), in either gas or liquid form. Electronic paramagnetism is stronger than nuclear paramagnetism simply because $\gamma_e \gg \gamma_n$.

We now calculate the macroscopic magnetic moment per unit volume created by placing N non-interacting nuclei or electrons (with some gyromagnetic ratio γ) in an external, constant field $\mathbf{B}_0$. As noted above, the quantum mechanical picture is valid here and we will use it.

The macroscopic magnetic moment is a statistical concept. The whole of statistical physics rests on the following Boltzmann hypothesis: at thermal equilibrium, the probability of the system being in a state with energy E is:

$$\Pr(E) = \tfrac{1}{Z} e^{-E/kT}$$

where Z is a constant number independent of the energy or kT, given by:

$$Z = e^{-E_1/kT} + \ldots + e^{-E_n/kT} \ ,$$

where the system has N states having energies $E_1, \ldots, E_N$. The probability of being in state i is:

$$\Pr(i) = \tfrac{1}{Z} e^{-E_i/kT}$$

Note that our definition of Z implies that:

$$\Pr(1) + \Pr(2) + \ldots + \Pr(N) = 1$$

or

$$\tfrac{1}{Z} e^{-E_1/kT} + \ldots + \tfrac{1}{Z} e^{-E_N/kT} = 1 \ .$$

This is the only point in our lectures where we’ll use the quantum-mechanical nature of spin. Quantum mechanics tells us a spin S in a field B_0 has 2S+1 energy levels:

$$E_n = n\hbar\gamma B_0, \qquad n = -S, -S+1, \ldots, S \ .$$

We now ask: *what is the average magnetic moment of (one) such spin at thermal equilibrium*? Our previous discussion of paramagnetism implies $\langle m_x \rangle = \langle m_y \rangle = 0$ (where B_0 is taken to point along the z-axis). For the z-component,

$$\langle m_z \rangle = \sum_{n=-S}^{S} m_n \Pr(E_n) = \sum_{n=-S}^{S} \left(-\tfrac{n\gamma\hbar}{Z}\right) \exp\left(-\tfrac{n\hbar\gamma B_0}{kT}\right).$$

If we knew that, then for N non-interacting spins at equilibrium,

$$\mathbf{M} = N < m_z > \hat{\mathbf{z}},$$

which would be our <u>equilibrium magnetic moment</u>. So we really just need to compute $<m_z>$. Our assumption of non-interacting spins is a bit suspect, since the nuclear spins "talk" via dipolar coupling, but one can prove using quantum mechanics this holds even in the presence of dipolar and other interactions.

The expression for $\langle m_z \rangle$ can be simplified considerably if we remember that, for a<<1:

$$e^a \approx 1 + a$$
$$(\text{e.g. } e^{-0.01} \approx 0.99)$$

In our case, at room temperature (homework!),

$$\frac{n\hbar\gamma B_0}{kT} << 1 \qquad (\text{for all } n = -S, \ldots, S),$$

so we can simplify:

$$Z = \sum_{n=-S}^{S} \exp\left(-\tfrac{n\hbar\gamma B_0}{kT}\right) \approx \sum_{n=-S}^{S} \left(1 - \tfrac{n\hbar\gamma B_0}{kT}\right) = (2S+1)$$
$$\langle m_z \rangle \approx \sum_{n=-S}^{S} \tfrac{-n\gamma\hbar}{(2S+1)} \left(1 - \tfrac{n\hbar\gamma B_0}{kT}\right) = \sum_{n=-S}^{S} \tfrac{n\gamma\hbar}{(2S+1)} \tfrac{n\hbar\gamma B_0}{kT}$$

Using the algebraic identity

$$\sum_{n=-S}^{S} n^2 = \tfrac{1}{3} S(S+1)(2S+1)$$

yields:

$$\langle m_z \rangle \approx \sum_{n=-S}^{S} \tfrac{n\gamma\hbar}{(2S+1)} \left(1 - \tfrac{n\hbar\gamma B_0}{kT}\right) = -\tfrac{\gamma^2\hbar^2 S(S+1)}{3kT} B_0.$$

and, for N spins,

$$\boxed{M_0 = \frac{N(\gamma\hbar)^2 S(S+1)}{3kT} B_0}$$

Equilibrium macroscopic magnetic moment

You will show in the homework that, for a 1 cm^3 drop of water, the bulk nuclear magnetic moment of the hydrogen (H) nuclei is:

$$M_0 \approx 3.7 \times 10^{-8} \frac{\text{Joule}}{\text{Tesla}}$$

Note this has units of energy per unit field. You can think of it as the amount of energy you create when you put the water in a field of such and such Tesla. It's quite small!

2.3 <u>Diamagnetism</u>

Diamagnetism is a quantum mechanical phenomenon, in which materials shield themselves from an external magnetic field. The amount of shielding varies: superconductors, which display perfect diamagnetism, completely shield their insides from external fields (known as the **Meissner effect**). Most ordinary materials, however, display much weaker shielding. Water, for example, shields only about 0.001% of the applied magnetic field (10^{-5}).

Although quantum mechanical in nature, a sloppy classical explanation can be given. Faraday's law states that any change in the flux of the magnetic field through a current loop will oppose that current by applying a force that will slow the electrons down. If we think of the electrons orbiting the nuclei in a material as small current loops, we can predict changing the magnetic flux through them by putting them in an external field will cause them to generate magnetization which will oppose the field and reduce it. We will not pursue these notions further here.

2.4 Ferromagnetism

Ferromagnetism arises because of strong couplings between permanent electronic spin magnetic moments. It persists even in the absence of an external magnetic field and is pretty much the only type of magnetism strong enough to be detected in our everyday lives. You're probably most familiar with it from your refrigerator magnets from your favorite pizza delivery.

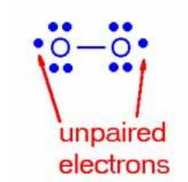
Ferromagnetism is the spontaneous alignment of electron spins in materials on a macroscopic scale. This is "unnatural" in the sense that magnetic moments are at their lowest energy when their are anti-parallel, not parallel. As you know, systems tend to minimize their energies, so we must ask: what trumps the electronic spin coupling energy? The answer is electrostatic energy. In magnetic solids, electron spins are about 2 Å apart, with a dipolar energy of ~ 10^{-4} eV, while electrostatic energy is ~ 0.1 eV, i.e. much much larger. The particular mechanism is, again, quantum mechanical and we will not delve into it. We will not deal with ferromagnetism in this course, nor with its many variations (ferrimagnetism, etc).

2.5 Magnitude of Effects

The general picture you should keep in mind is:

Nuclear diamgnetism
<< Nuclear paramagnetism
<< Electronic diagmagnetism
<< Electronic paramagnetism
<< Electronic ferromagnetism

1. Nuclear diagmagnetism, which occurs when currents are induced in the nuclear charge cloud in an external field, is so small that it is only observed in the most extreme conditions and has no effect in NMR or, indeed, most of physics.
2. Nuclear paramagnetism due to nuclear spin is present in nuclei that have a magnetic moment and gives rise to the NMR phenomena.
3. Electronic diamagnetism is present in all materials.
4. Electronic paramagnetism is only observable in paramagnetic materials that have unpaired electron spins. For example, in O_2, or in free radicals.



The source of O_2 paramagnetism is its two unpaired electrons

5. Ferromagnetism is only present in several special materials such as iron, and then only in bulk.

Q: If nuclear paramagnetism is so weak compared to electronic diamagnetism, how can we observe it?
A: It is the **resonance phenomena** that makes NMR observable. NMR nuclei resonates at very particular ranges of frequencies not inhabited by any other transitions, making them easy (well, not that easy ...) to selectively excite and detect.