

# **Part 1**

## **Nuclear Magnetism**

- 1 Matter**
- 2 Magnetism**
- 3 NMR Spectroscopy**



# 1 Matter

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## 1.1 Atoms and Nuclei

Matter is made of *atoms*. Atoms are made up of electrons and *nuclei*. Each atomic nucleus has four important physical properties: *mass*, *electric charge*, *magnetism* and *spin*.

The *mass* of bulk matter is largely due to the mass of the nuclei. A large number of other physical properties, such as heat capacity and viscosity, are strongly dependent on the nuclear mass.

The *electric charge* of atomic nuclei is supremely important. Atoms and molecules are bound together by strong electrostatic interactions between the positively charged nuclei and the negatively charged electrons. The chemical properties of each element are determined by the electric charge on the atomic nuclei.

The other two properties, nuclear magnetism and nuclear spin, are much less evident. The magnetism of a nucleus implies that it interacts with magnetic fields, like a small bar magnet. However, nuclear magnetism is very weak and is of little consequence for atomic or molecular structure. The bulk magnetism of some materials, such as iron, is due to the electrons, not to the nuclei.

The *spin* of the nucleus is even less tangible. The spin of a nucleus indicates that, very loosely speaking, the atomic nucleus behaves as if it is spinning around, rotating in space like a tiny planet.

Nuclear magnetism and nuclear spin have almost no effect on the normal chemical and physical behaviour of substances. Nevertheless, these two properties provide scientists with a wonderful tool for spying on the microscopic and internal structure of objects without disturbing them.

Magnetic nuclei interact with magnetic fields. These magnetic fields may come from the molecular environment, e.g. the surrounding electrons, or from other nuclear spins in the same molecule. Magnetic fields may also originate from sources outside the sample, such as an external apparatus. This book tells a small part of a long, complicated, and rather unlikely story: How the extremely weak magnetic interactions of atomic nuclei with the molecular environment on one hand, and with the spectrometer apparatus on the other hand, give access to detailed molecular information which is inaccessible by any other current method.

## 1.2 Spin

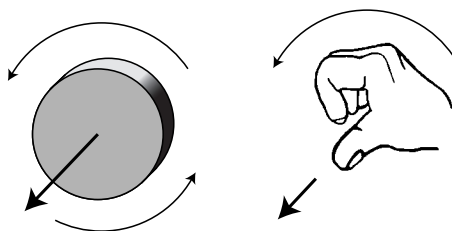
The concept of spin is difficult. It was forced upon scientists by the experimental evidence.<sup>1</sup> Spin is a highly abstract concept, which may never be entirely 'grasped' beyond knowing how to manipulate the quantum mechanical equations.

Nevertheless, it is worth trying. NMR involves detailed manipulations of nuclear spins. The field has developed to a high level of sophistication, in part because of the possibility of thinking 'physically' and 'geometrically' about spins without being entirely wrong. Geometrical arguments can never tell the whole truth, because the human mind is probably incapable of grasping the entire content of quantum mechanics.

Nevertheless, it is possible to acquire a feel for spin beyond a purely technical proficiency in the equations. In this book, I will try to communicate how I think one should think about nuclear spins, as well as presenting the technical mathematics.

### 1.2.1 Classical angular momentum

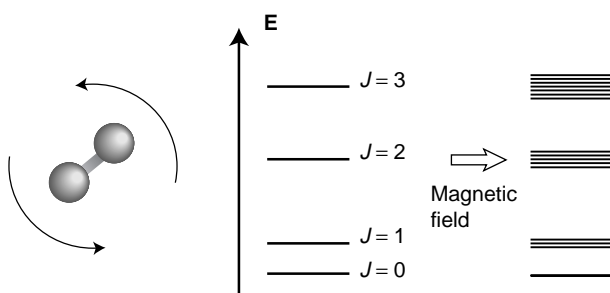
A rotating object possesses a quantity called *angular momentum*. This may be visualized as a vector pointing along the axis about which the object rotates; your right hand may be used to figure out which way the arrow points. If your thumb points along the rotation axis, then the right-hand fingers ‘wrap around’ in the direction of the rotation:



**Figure 1.1**  
Macroscopic angular momentum.

### 1.2.2 Quantum angular momentum

In quantum mechanics, angular momentum is *quantized*. Consider, for example, a diatomic molecule:



**Figure 1.2**  
A rotating molecule, its energy levels, and the Zeeman effect.

As described in many texts (see *Further Reading*), and discussed further in Chapter 7, a rotating diatomic molecule possesses a set of stable rotational states, in which the total angular momentum  $L_{\text{tot}}$  has one of the values<sup>2</sup>

$$L_{\text{tot}} = [J(J + 1)]^{1/2} \hbar \quad (1.1)$$

where  $J$  takes *integer* values  $J = 0, 1, 2 \dots$  and  $\hbar \cong 1.054 \times 10^{-34} \text{ J s}$  is Planck's constant divided by  $2\pi$ . This equation implies the *quantization of total angular momentum*.

The rotational energy of a molecule is proportional to the square of the total angular momentum, so the energy is also quantized. For a rigid molecule, the energies of the stable rotational states are

$$E_J = BJ(J + 1) \quad (1.2)$$

where  $B$  is called the rotational constant for the molecule.  $B$  is small for a heavy molecule and is large for a light one.

The molecule may be in a stable state with zero total angular momentum, or with total angular momentum  $\sqrt{2}\hbar$ , or with total angular momentum  $\sqrt{6}\hbar$ , etc. The actual rotational state of a molecule depends on its history and its environment.

The total angular momentum of the molecule determines how fast it is rotating, but conveys no information on the axis of the rotation.

More detail about the rotation of the molecule is given by specifying a second quantum number,  $M_J$ . This quantum number  $M_J$  takes one of the  $2J + 1$  integer values  $M_J = -J, -J + 1 \dots + J$ , and says something about the direction of the rotation. The quantum number  $M_J$  is sometimes referred to as the *azimuthal quantum number*. The physical significance of  $M_J$  is examined more closely in Chapters 7 and 10.

In the absence of an external field, each of the  $2J + 1$  states with the same value of  $J$  but different values of  $M_J$  are *degenerate*, meaning that they have the same energy.

The application of a magnetic field breaks the degeneracy, causing each of the  $(2J + 1)$  sublevels to have a slightly different energy. This is called the *Zeeman effect*. The energy separation between the  $M_J$  sublevels in a magnetic field is called the *Zeeman splitting*.

The basic features of this phenomenon are displayed by any physical system that is able to rotate. Whatever the system is, there is always the same structure of  $(2J + 1)$ -fold degenerate energy levels. The stable physical states of a rotating quantum system are always specified by a quantum number  $J$  for the total angular momentum and an azimuthal quantum number  $M_J$  that carries information on the direction of the rotation. The total angular momentum is always given by  $[J(J + 1)]^{1/2}\hbar$ , and the azimuthal quantum number  $M_J$  always takes one of the values  $M_J = -J, -J + 1 \dots + J$ . The degeneracy of the  $M_J$  sublevels may be broken by applying an electric or magnetic field.

### 1.2.3 Spin angular momentum

*Spin* is also a form of angular momentum. However, it is not produced by a rotation of the particle, but is an *intrinsic* property of the particle itself.

The total angular momentum of particles with spin takes values of the form  $[S(S + 1)]^{1/2}\hbar$  (the symbol  $S$  is used instead of  $J$  to mark a distinction between spin angular momentum and rotational angular momentum). Particles with spin  $S$  have  $(2S + 1)$  sublevels, which are degenerate in the absence of external fields, but which may have a different energy if a magnetic or electric field is applied.

Each elementary particle has a particular value for the spin quantum number  $S$ . For some particles,  $S$  is given by an integer, i.e. one of 0, 1, 2, ... For other particles,  $S$  is given by a half integer, i.e. one of 1/2, 3/2, 5/2, ...

Particles with integer spin are called *bosons*. Particles with half-integer spin are called *fermions*.

The spin of an elementary particle, such as an electron, is *intrinsic* and is independent of its history. Elementary particles simply *have* spin; molecules *acquire* rotational angular momentum by energetic collisions. At the absolute zero of the temperature scale, all rotational motion ceases ( $J = 0$ ). A particle such as an electron, on the other hand, always has spin, even at absolute zero.

Half-integer spin posed severe problems for the physicists of the 1920s and 1930s. It may be shown that half-integer spin cannot arise from 'something rotating', and, at that time, no other way of producing angular momentum could be imagined. The concept of half-integer spin was resisted until the pressure of experimental evidence became overwhelming. One of the greatest triumphs of theoretical physics was Dirac's derivation of electron spin-1/2 from relativistic quantum mechanics. Nowadays, spin is a central concept in our theoretical understanding of the world.

A particle like an electron may, therefore, have two kinds of angular momentum: (i) A 'conventional' angular momentum arising from its *motion*. For example, an electron in an atom may have *orbital angular momentum* due to its circulating motion around the nucleus. Such motion is associated with an *integer*

angular momentum quantum number and behaves just like the angular momentum of a rotating molecule. (ii) 'Intrinsic' or *spin angular momentum*, which arises from nothing, being simply a feature of the electron's 'nature', and which is always the same, namely  $\text{spin} = 1/2$ .

There is no such concept as the rotation of the electron around its own axis; there is only spin.

The concept of intrinsic angular momentum is very difficult to grasp. Why should this be so? Why is the intrinsic angular momentum of a particle more difficult to understand than intrinsic mass and intrinsic electric charge?

The level of difficulty of a concept tends to be inversely proportional to its familiarity in the macroscopic world. The concept of intrinsic mass is relatively easy to accept because mass has familiar everyday manifestations. This is because the mass of two particles is the sum of the masses of the individual particles. The mass of a book is therefore the sum of the masses of all the electrons, quarks, etc. of which the book is composed (minus a relativistic correction – but let's forget about that!). So the concept of mass 'makes it' to the macroscopic world. We can 'feel' mass and can imagine that fundamental particles 'have a mass'.

Electric charge is a little more difficult, because there are negative and positive charges, and in almost all cases they cancel out for macroscopic objects. However, by performing simple experiments, like rubbing a balloon on a woolly jumper, it is possible to separate some of the charges and achieve obvious macroscopic effects, such as sticking a balloon to the ceiling. Through such experiences it is possible to get a feel for charge, and become comfortable with the idea that fundamental particles 'have a charge'.

Similarly, magnetism acquires familiarity through the existence of ferromagnetic objects that possess macroscopic magnetism.

Spin is more difficult, because there is no such thing as macroscopic spin. Matter is built up in such a way that the spins of the different particles cancel out in any large object. Spin doesn't 'make it' to the macroscopic world.<sup>2</sup>

This is not to say that spin is unimportant. In fact electron spin has a very profound effect on the everyday world, because the stability of molecules and their chemical behaviour rely on it (as will be discussed shortly, in the context of the Pauli principle). However, this effect is not *obviously* a consequence of electron spin, and there are no large objects that have angular momentum 'by themselves', without rotating.<sup>3</sup>

Probably no-one really understands spin on a level above the technical mathematical rules. Fortunately it doesn't matter so much. We know the rules for spin and that's enough to be able to exploit the phenomenon.

### 1.2.4 Combining angular momenta

Consider a system with two parts, each one being a source of angular momentum, with quantum numbers  $J_1$  and  $J_2$ . The angular momenta may be due to rotational motion or to spin. The total angular momentum of the entire system is given by  $[J_3(J_3 + 1)]^{1/2}\hbar$ , where  $J_3$  takes one of the following possible values:

$$J_3 = \begin{cases} |J_1 - J_2| \\ |J_1 - J_2| + 1 \\ \vdots \\ |J_1 + J_2| \end{cases} \quad (1.3)$$

Expressed in words, this means that the complete system has a total angular momentum quantum number given either by the sum of the two individual angular momentum quantum numbers, or by the difference in the two individual angular momentum quantum numbers, or any of the values in between, in integer steps.

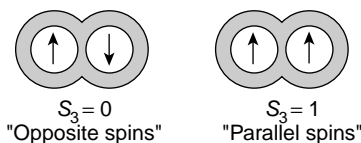
In general, each of the possible total angular momentum states has a different energy. In many cases that state itself behaves like a new object with angular momentum quantum number  $J_3$ .

An important example of this combination rule involves two particles of spin-1/2, i.e.  $S_1 = S_2 = 1/2$ . In this case, we have  $|S_1 - S_2| = 0$  and  $|S_1 + S_2| = 1$ . There are, therefore, only two possibilities for the total

angular momentum quantum number, namely  $S_3 = 0$  and  $S_3 = 1$ . In the state  $S_3 = 0$ , the spins of the two particles cancel each out. This idea is often expressed by saying that the spins are ‘antiparallel’ in the  $S_3 = 0$  state:

**Figure 1.3**

The combination of two spins-1/2 leads to a singlet state with spin  $S = 0$  and a triplet state with spin  $S = 1$ .



In the ‘parallel’ spin state  $S_3 = 1$ , on the other hand, the spins of the two particles reinforce each other. In general, the  $S_3 = 0$  and  $S_3 = 1$  states have different energy. Note that it is not possible to make a general statement as to which state has the *lowest* energy; this depends on the details of the interactions in the system.

The  $S_3 = 1$  energy level has three substates, with azimuthal quantum number  $M_S = \{-1, 0, 1\}$ . If the environment is isotropic (the same in all directions of space), the three substates have the same energy. States with total angular momentum  $S_3 = 1$  are often called *triplet states*, to stress this threefold degeneracy. The degeneracy of the  $S_3 = 1$  level may be broken by applying an external field (magnetic or electric).

The  $S_3 = 0$  level, on the other hand, is not degenerate. The only state in this level has quantum number  $M_S = 0$ . States with total angular momentum  $S_3 = 0$  are often called *singlet states*.

### 1.2.5 The Pauli Principle

The spin of particles has profound consequences. The *Pauli principle*<sup>4</sup> states

two fermions may not have identical quantum states.

Since the electron is a fermion, this has major consequences for atomic and molecular structure. For example, the periodic system, the stability of the chemical bond, and the conductivity of metals may all be explained by allowing electrons to fill up available quantum states, at each stage pairing up electrons with opposite spin before proceeding to the next level. This is called the *Aufbau principle* of matter, and is explained in standard textbooks on atomic and molecular structure (see *Further Reading*).

The everyday fact that one’s body does not collapse spontaneously into a black hole, therefore, depends on the spin-1/2 of the electron.

## 1.3 Nuclei

The next sections discuss briefly how the energy level structures of molecules, atoms, nuclei, and even the elementary particles within the nuclei, fit into the angular momentum hierarchy of nature, according to the rule given in Equation 1.3.

### 1.3.1 The fundamental particles

According to modern physics, everything in the universe is made up of three types of particle: *leptons*, *quarks* and *force particles*.

*Leptons* are low-mass particles. Six varieties of lepton have currently been identified, but only one is familiar to non-specialists. This is the *electron*, a lepton with electric charge  $-e$  and spin-1/2. The unit of electric charge  $e$  is defined as *minus* the electron charge and is equal to  $1.602 \times 10^{-19}$  C.

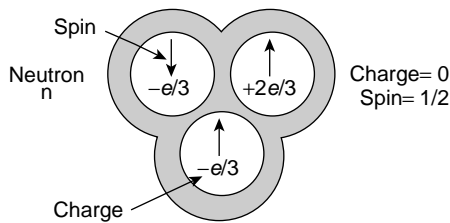
*Quarks* are relatively heavy particles. At the time of writing (2007), it is believed that there are six ‘flavours’ of quarks in nature, all of which have spin- $1/2$ . Three of the quarks have electric charge  $+2e/3$ . The other three quarks have electric charge  $-e/3$ . Apart from their charge, the quarks are distinguished by additional quantum numbers called ‘strangeness’, ‘charm’, ‘top’ and ‘bottom’, but there is no need to discuss these topics here. It is speculated that quarks are themselves built up of extended objects, which have received the dull name ‘superstrings’.

*Force particles* are responsible for mediating the action of the different particles on each other. The most important force particle is the *photon*, which is the particle manifestation of the electromagnetic field. Light, which consists of electromagnetic waves, can be viewed as a stream of photons. The photon has no mass and no electric charge, and has spin = 1. There are also force particles called *gluons* and *vector bosons*. Gluons are manifestations of the so-called *strong nuclear force*, which holds the atomic nucleus and its constituent particles together. Vector bosons are manifestations of the *weak nuclear force*, which is responsible for radioactive  $\beta$ -decay.

### 1.3.2 Neutrons and protons

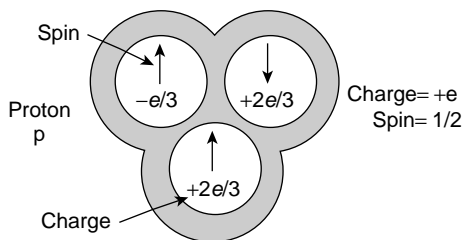
The *neutron* and the *proton* both consist of three quarks, stuck together by gluons.<sup>4</sup>

The *neutron* is composed of three quarks: two with charge  $-e/3$  and one with charge  $+2e/3$ . Therefore, the total electric charge of the neutron is zero; hence its name. The neutron has spin- $1/2$ . The neutron spin is due to combinations of quark spins.<sup>5</sup> For example, if two of the quark spins are antiparallel, we get an  $S = 0$  state. Addition of the third quark spin gives a total neutron spin  $S = 1/2$ :



**Figure 1.4**  
A neutron.

The *proton* is also composed of three quarks, but this time two of the quarks have charge  $+2e/3$  and the other one has charge  $-e/3$ . Therefore, the total electric charge of the proton is  $+e$ . Just as for the neutron, an antiparallel spin configuration for two of the quarks gives rise to a net spin- $1/2$  state for the proton:<sup>4</sup>



**Figure 1.5**  
A proton.

What happens if the quark spins inside the neutron and proton have different configurations? For example, if the three quark spins were all parallel, the total spin would be  $3/2$ . Such particles do in fact exist, but they are only known in high-energy physics experiments (for example, the spin- $3/2$  state of the proton is known as the  $\Delta^+$  particle). High-spin neutrons and protons have enormously higher energies than ordinary neutrons and protons. Under ordinary circumstances, these exotic states may be ignored. The



**Table 1.1** Some properties of the most important elementary particles.

Particle	Rest mass/kg	Charge	Spin
e	$9.109 \times 10^{-31}$	$-e$	1/2
n	$1.675 \times 10^{-26}$	0	1/2
p	$1.673 \times 10^{-26}$	$+e$	1/2
photon	0	0	1

neutron and proton may, therefore, be treated as distinct and independent particles, both with well-defined spin-1/2.

We also ignore the numerous other particles formed by combinations of different sets of quarks. From now on, the only particles to be considered are the electron, the neutron, the proton and the photon, whose relevant properties are summarized in Table 1.1.

### 1.3.3 Isotopes

The atomic nucleus consists of neutrons and protons.<sup>6</sup> Neutrons and protons are known collectively as *nucleons*.

An atomic nucleus is specified by three numbers: the *atomic number*, the *mass number*, and the *spin quantum number*.

The *atomic number*  $Z$  specifies the number of protons inside the nucleus. The electric charge of the nucleus is  $Ze$ . The electric charge of the nucleus determines the chemical properties of the atom of which the nucleus is a part. The atomic number is traditionally denoted by a chemical symbol, for example H for  $Z = 1$ , He for  $Z = 2$ , C for  $Z = 6$ , N for  $Z = 7$ , O for  $Z = 8$ , etc. The periodic table of the elements lists the atomic nuclei in order of increasing atomic number.

The *mass number* specifies the number of nucleons in the nucleus, i.e. the total number of protons and neutrons. Nuclei with the same atomic number but different mass numbers are called *isotopes*. Most isotopes in existence are *stable*, meaning that the nucleus in question has no measurable tendency to explode or disintegrate. Several isotopes are *unstable*, or *radioactive*, meaning that the nucleus tends to disintegrate spontaneously, ejecting energetic particles, which are often dangerous. NMR is mainly concerned with stable isotopes. Stable nuclei are usually formed from approximately equal numbers of protons and neutrons.

Some common examples of stable isotopes are:

$$\begin{aligned} {}^1\text{H} &= \text{p} & {}^{12}\text{C} &= 6\text{p} + 6\text{n} \\ {}^2\text{H} &= \text{p} + \text{n} & {}^{13}\text{C} &= 6\text{p} + 7\text{n} \end{aligned}$$

and so on.

Some examples of unstable (radioactive) isotopes are:

$$\begin{aligned} {}^3\text{H} &= \text{p} + 2\text{n} \\ {}^{14}\text{C} &= 6\text{p} + 8\text{n} \end{aligned}$$

Lighter atomic nuclei were formed by the primal condensation of nucleons as the heat of the big bang dissipated. Heavier nuclei (beyond and including iron) were synthesized later by nuclear fusion processes inside stars. These complex nuclear processes led to a mix of isotopes with varying *isotopic distributions*. These distributions are almost uniform over the surface of the Earth. For example,  $\sim 98.9\%$  of carbon nuclei

**Table 1.2** A selection of nuclear isotopes and their properties. A complete listing of nuclear spins, gyromagnetic ratios and Larmor frequencies (omitting the sign) may be found on the website [www.webelements.com](http://www.webelements.com).

Isotope	Ground-state spin	Natural abundance/%	Gyromagnetic ratio $\gamma/10^6 \text{ rad s}^{-1} \text{ T}^{-1}$	NMR frequency at 11.74 T $(\omega^0/2\pi)/\text{MHz}$
$^1\text{H}$	1/2	~100	267.522	–500.000
$^2\text{H}$	1	0.015	41.066	–76.753
$^3\text{H}$	1/2	0	285.349	–533.320
$^{10}\text{B}$	3	19.9	28.747	–53.718
$^{11}\text{B}$	3/2	80.1	85.847	–160.420
$^{13}\text{C}$	1/2	1.1	67.283	–125.725
$^{14}\text{N}$	1	99.6	19.338	–36.132
$^{15}\text{N}$	1/2	0.37	–27.126	+50.684
$^{17}\text{O}$	5/2	0.04	–36.281	+67.782
$^{19}\text{F}$	1/2	~100	251.815	–470.470
$^{23}\text{Na}$	3/2	~100	70.808	–132.259
$^{27}\text{Al}$	5/2	~100	69.763	–130.285
$^{29}\text{Si}$	1/2	4.7	–53.190	+99.336
$^{31}\text{P}$	1/2	~100	108.394	–202.606
$^{35}\text{Cl}$	3/2	75.77	10.610	–48.990
$^{37}\text{Cl}$	3/2	24.23	8.832	–40.779
$^{63}\text{Cu}$	3/2	69.17	71.118	–132.577
$^{65}\text{Cu}$	3/2	30.83	76.044	–142.018
$^{107}\text{Ag}$	1/2	51.84	–10.889	+20.239
$^{109}\text{Ag}$	1/2	48.16	–12.518	+23.268
$^{129}\text{Xe}$	1/2	24.4	–74.521	+139.045
$^{207}\text{Pb}$	1/2	22.1	55.805	–104.603
$^{12}\text{C}$	0	98.9		
$^{16}\text{O}$	0	~100		

have six neutrons ( $^{12}\text{C}$ ), and ~1.1% have seven neutrons ( $^{13}\text{C}$ ). The small local variations in nuclear isotopic distributions are useful for locating the origin and the age of objects. Some natural isotopic abundances are shown in Table 1.2.

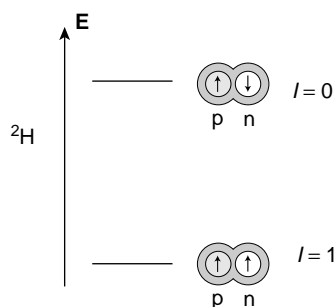
## 1.4 Nuclear Spin

### 1.4.1 Nuclear spin states

Most atomic nuclei possess spin. The nuclear spin quantum number is conventionally denoted  $I$ .

The nucleus of the main isotope of hydrogen,  $^1\text{H}$ , contains a single proton and has  $I = 1/2$ . The spins of other nuclei are formed by combining together the spins of the protons and the neutrons according to the usual rule (Equation 1.3).

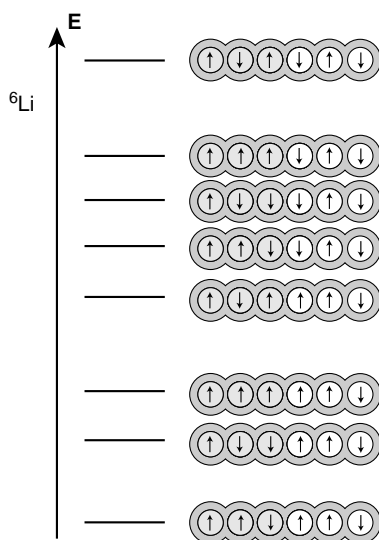
Consider, for example, the  $^2\text{H}$  nucleus, which contains one proton and one neutron. The proton and neutron spins may be combined in a parallel configuration, leading to a nuclear spin  $I = 1$ , or in an antiparallel configuration, leading to a nuclear spin  $I = 0$ :

**Figure 1.6**

Energy levels of a  $^2\text{H}$  nucleus.

These two nuclear spin states have a large energy difference of  $\sim 10^{11} \text{ kJ mol}^{-1}$ . This greatly exceeds the energies available to ordinary chemical reactions or usual electromagnetic fields (for comparison, the available thermal energy at room temperature is around  $\sim 2.5 \text{ kJ mol}^{-1}$ ). The nuclear excited states may, therefore, be ignored, except in exotic circumstances.<sup>7</sup> The value of  $I$  in the lowest energy nuclear state is called the *ground state nuclear spin*. For deuterium (symbol D or  $^2\text{H}$ ), the ground state nuclear spin is  $I = 1$ .

For higher mass nuclei, the ground state is one of a large number of possible spin configurations of the protons and neutrons:

**Figure 1.7**

Energy levels of a  $^6\text{Li}$  nucleus, showing the ground state spin  $I = 1$ .

In general, there are no simple rules for which of the many possible states is the ground state. For our purposes, the ground state nuclear spin is best regarded as an empirical property of each isotope.

Nevertheless, one property may be stated with certainty: from Equation 1.3, isotopes with even mass numbers have integer spin and isotopes with odd mass numbers have half-integer spin.

Two further guidelines apply to isotopes with even mass numbers:

1. If the numbers of protons and neutrons are both even, the ground state nuclear spin is given by  $I = 0$ . Some examples are: the nucleus  $^{12}\text{C}$ , which contains six protons and six neutrons; the nucleus  $^{16}\text{O}$ , which contains eight protons and eight neutrons; and the nucleus  $^{56}\text{Fe}$ , which has 26 protons and 30 neutrons. All of these have a ground state spin  $I = 0$ .

2. If the numbers of protons and neutrons are both odd, the ground state nuclear spin is an integer larger than zero. Some examples are the nuclei  $^2\text{H}$  (1p + 1n, ground state spin  $I = 1$ ),  $^{10}\text{B}$  (5p + 5n, ground state spin  $I = 3$ ),  $^{14}\text{N}$  (7p + 7n, ground state spin  $I = 1$ ) and  $^{40}\text{K}$  (19p + 21n, ground state spin  $I = 4$ ).

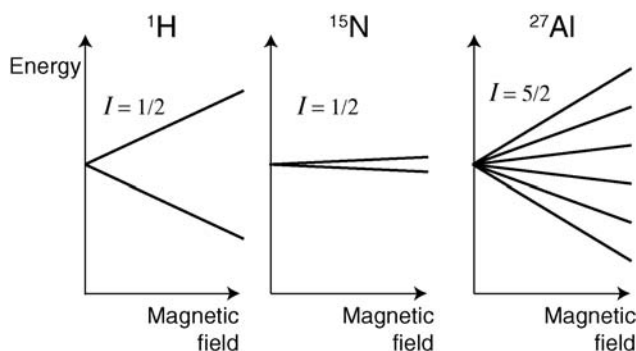
These rules may be understood using models of nuclear structure, a subject that will not be discussed further here.

From now on, the ground state nuclear spin is simply called the 'nuclear spin', for the sake of simplicity. Table 1.2 shows some of the nuclear isotopes of importance in NMR, together with their natural abundances. An overview of all nuclear spins is given in the inside cover as Plates A, B and C.

### 1.4.2 Nuclear Zeeman splitting

A nuclear state with spin  $I$  is  $(2I + 1)$ -fold degenerate. If a magnetic field is applied, the degeneracy is broken, just as in the case of ordinary angular momentum (see Figure 1.2). The splitting between the nuclear spin levels is called the *nuclear Zeeman splitting*. NMR is the spectroscopy of the nuclear Zeeman sublevels.

Figure 1.8 sketches the nuclear Zeeman levels of a  $^1\text{H}$  nucleus, a  $^{15}\text{N}$  nucleus, and a  $^{27}\text{Al}$  nucleus as a function of the applied magnetic field. The  $^1\text{H}$  and  $^{15}\text{N}$  nuclei are both spin-1/2, and so the nuclear ground state splits into two sublevels in the applied magnetic field (since  $2 \times (1/2) + 1 = 2$ ). The  $^{27}\text{Al}$  nucleus is spin-5/2 and, hence, the nuclear ground state splits into six levels in the applied magnetic field (since  $2 \times (5/2) + 1 = 6$ ).



**Figure 1.8**  
Nuclear Zeeman sublevels of the  $^1\text{H}$ ,  $^{15}\text{N}$  and  $^{27}\text{Al}$  nuclear ground states.

The Zeeman splitting of a proton nucleus is about 10 times larger than the Zeeman splitting of a  $^{15}\text{N}$  nucleus, in the same magnetic field. This is because a proton is about 10 times more magnetic than a  $^{15}\text{N}$  nucleus. This will be discussed in Chapter 2.

The Zeeman splitting *within* the nuclear ground state must not be confused with the enormously larger splitting between the nuclear ground state and the nuclear excited states. The Zeeman splittings are far smaller than thermal energies and are the subject of NMR spectroscopy. The splitting between the nuclear excited state and the nuclear ground state is so large that the nuclear excited states may be completely ignored in ordinary chemistry and spectroscopy.<sup>6</sup>

### 1.4.3 Zero-spin nuclei

A minority of nuclear isotopes have zero nuclear spin in the ground state and display no nuclear Zeeman effect. By a quirk of fate, organic substances contain many of these spinless isotopes. The most common isotopes of carbon, oxygen and sulfur, namely  $^{12}\text{C}$ ,  $^{16}\text{O}$  and  $^{32}\text{S}$ , all have zero nuclear spin and are NMR silent.

### 1.4.4 Spin-1/2 nuclei

Nuclei with spin  $I = 1/2$  are of major importance in NMR. As discussed in Chapter 8, such nuclei are spherical in shape and have convenient magnetic properties. Plate A shows the distribution of spin-1/2 nuclei in the periodic table of the elements. They are mainly scattered around the right-hand side of the periodic table.

Most chemical elements have no spin-1/2 isotope. The alkali and alkaline earth metals possess no spin-1/2 isotopes at all. In contrast, spin-1/2 isotopes are well represented in organic materials. The most common isotopes of hydrogen and phosphorus have spin-1/2 ( $^1\text{H}$  and  $^{31}\text{P}$ ), and carbon and nitrogen possess the rare spin-1/2 isotopes  $^{13}\text{C}$  and  $^{15}\text{N}$ . The abundant fluorine isotope  $^{19}\text{F}$  is also of importance.

Spin-1/2 isotopes are well represented in the precious and heavy metals, and the noble gases contain a possess two spin-1/2 isotopes, namely  $^3\text{He}$  and  $^{129}\text{Xe}$ .

### 1.4.5 Quadrupolar nuclei with integer spin

Nuclei with spin  $I > 1/2$  are known as 'quadrupolar nuclei', for reasons discussed in Chapter 8. The NMR of such nuclei is a rich but relatively difficult field, which is increasing in popularity, especially in the context of solid-state NMR.

Quadrupolar nuclei with integer values of  $I$  are uncommon. Plate B shows their distribution in the periodic table. By far the most abundant nucleus of this type is  $^{14}\text{N}$ , which occurs in almost 100% natural abundance. Deuterium ( $^2\text{H}$ ) is of great importance despite its low natural abundance, since it is relatively easy to separate from  $^1\text{H}$  by physical methods and to prepare  $^2\text{H}$ -enriched substances.

The nuclear spins  $I = 3, 4, 5, 6$  and  $7$  are represented by only one isotope each, some of which are obscure. There are no nuclei at all with ground state spin  $I = 2$ . The  $I = 7$  isotope  $^{176}\text{Lu}$  has the highest nuclear spin in the entire periodic table.

### 1.4.6 Quadrupolar nuclei with half-integer spin

Quadrupolar nuclei with  $I = 3/2, 5/2, 7/2$  or  $9/2$  are common (see Plate C). They are well represented throughout the entire periodic table, but are particularly prominent for the alkali metals, the boron-to-thallium group, and the halogens. There is a striking alternation across many parts of the periodic table, with every other element possessing an abundant isotope with a half-integer quadrupolar nucleus. I do not know the reason for this alternation, which must reflect some feature of nuclear structure and energetics.

The importance of the isotopes is not necessarily reflected by their abundance. For example, the isotope  $^{17}\text{O}$  has a very low natural abundance but is, nevertheless, of great importance since it is the only stable oxygen isotope with nuclear spin.

## 1.5 Atomic and Molecular Structure

### 1.5.1 Atoms

The atomic nucleus has a positive electric charge  $+Ze$ . An *atom* is composed of a nucleus surrounded by  $Z$  electrons, each with charge  $-e$ . For example, an atom of  $^4\text{He}$  consists of a nucleus, containing two neutrons and two protons, surrounded by a cloud of two electrons. The simplest atom is hydrogen, which contains a nucleus of one proton and a single orbiting electron.

An atom is electrically charged if the total charge on the nucleus does not balance out exactly the charge on the electron cloud. Such species are called *ions*. For example, a nucleus containing 11 protons and 12 neutrons, surrounded by a cloud of 10 electrons, is called a  $^{23}\text{Na}^+$  ion. A nucleus containing 17 protons and 18 neutrons, surrounded by a cloud of 18 electrons, is called a  $^{35}\text{Cl}^-$  ion.

Atomic structure does not really concern us here, but it is worth seeing how the angular momentum of the atom works out (see *Further Reading* for a more detailed discussion). There are three sources of angular momentum in a hydrogen atom: the electron spin, the proton spin, and the electron orbital angular momentum, which is associated with the motion of the electron around the nucleus. The orbital angular momentum of the electron is characterized by a quantum number, usually called  $l$ . Since this type of angular momentum is associated with motion, the quantum number  $l$  is an integer. Quantum states with zero electron orbital angular momentum are called *s-orbitals*. Quantum states with electron orbital angular momentum  $l = 1$  are called *p-orbitals*, and so on. In addition, the energy levels of the H atom display *fine structure*, which is due to the coupling of the electron orbital angular momentum to the *electron spin*. Even closer observation of the energy levels reveals *hyperfine structure*, which is due to the participation of the *proton spin*.

Atoms containing more than one electron have many more possibilities, because each electron is a source of orbital angular momentum as well as spin angular momentum. In such systems, the *Pauli principle* comes into play. Electrons may only occupy identical orbital states if their spins are antiparallel. In practice this means that the lowest energy states in an atom usually have small values of total electron spin.

## 1.5.2 Molecules

An electron cloud containing more than one nucleus is called a *molecule*. For example, a molecule of water ( $^1\text{H}_2^{16}\text{O}$ ) consists of a cloud of 10 electrons surrounding three nuclei: one with eight protons and eight neutrons (the oxygen nucleus), and two consisting of a single proton (the hydrogen nuclei).

In a molecule, the quantum mechanical motion of the electrons constrains the nuclei to a particular geometric configuration. In the case of the water molecule, the three nuclei are geometrically stable only when the three nuclei form a triangular configuration with an H–O–H angle of around  $105^\circ$ .

A typical molecule contains many potential sources of angular momentum: the motion of the electrons around the nuclei, the motion of the nuclear framework around the centre of mass of the molecule, in some cases the rotation of internal molecular groups, the electron spins, and the nuclear spins. However, because of the Pauli principle, and the quantum rules for chemical bonding, the electron orbital angular momenta and the electron spin angular momenta almost always cancel out in the lowest energy state of a chemically stable molecule (there are a few exceptions, such as  $\text{O}_2$ , which has total electron spin  $S = 1$  in the ground state, and NO, which has finite orbital angular momentum in the ground state). In most cases, the only sources of angular momentum in the molecular ground state are the molecular rotation and the nuclear spins.

The motion of the nuclear framework can very often be treated ‘classically’: the molecule is treated as an ordinary object rotating in space. Inside this rotating molecule are trapped the nuclear spins. This ignores the quantum nature of the molecular motion. Nevertheless, it almost always gives reasonable answers, and we will use it from now on.

Molecules differing only in the mass numbers of the nuclei are called *isotopomers*. Isotopomers usually have almost identical chemical and physical properties, since these are determined almost completely by the charges on the nuclei and the number of surrounding electrons. All substances are mixtures of isotopomers, even when chemically pure. For example, pure water is composed mainly of the predominant isotopomer  $^1\text{H}_2^{16}\text{O}$ , but there are also small amounts of the minor isotopomers  $^1\text{H}^2\text{H}^{17}\text{O}$ ,  $^1\text{H}_2^{17}\text{O}$ , etc. The relative abundance of the isotopomers is governed by the natural statistical distributions of the various isotopes.

There are slight differences in the chemical and physical properties of isotopomers, due to the different nuclear masses. Molecules with different nuclear masses have different vibrational energy levels, altering slightly the rates of certain chemical reactions. Physical properties, such as diffusive mobilities, are also influenced by the molecular mass. This allows isotopomers to be separated by techniques such as gas chromatography. For example, it is possible to separate  $^{13}\text{CO}$  molecules from the abundant  $^{12}\text{CO}$  isotopomers by passing the gas through very long chromatographic columns. The  $^{13}\text{C}$ -labelled carbon monoxide is used as a starting material for total organic synthesis of other  $^{13}\text{C}$ -labelled substances. Many modern NMR experiments use isotopically enriched substances prepared in this way.

NMR is unusual in that different isotopomers behave completely differently. In many cases, one isotopomer gives a large signal while another isotopomer gives none, even though the substances are physically and chemically almost indistinguishable. NMR achieves this distinction because it is based upon the nuclear spin, rather than the nuclear mass.

The mass of a molecule is roughly equal to the sum of the nuclei in the molecule. In the biological sciences, it is popular to specify molecular masses in units of daltons (abbreviation Da). A  $^{12}\text{C}$  atom has a mass of exactly 12 Da. A medium-sized protein molecule has a molecular mass of around  $30 \times 10^3 \text{ Da} = 30 \text{ kDa}$  (30 kilodaltons). Outside the biological sciences, molecular masses are usually specified in units of grams per mole ( $\text{g mol}^{-1}$ ).

## 1.6 States of Matter

The states of matter are assembled from the basic building blocks of atoms, molecules and ions. We will now review the special features of the different material states, since the motions of the molecules in these states have a large effect on NMR experiments.

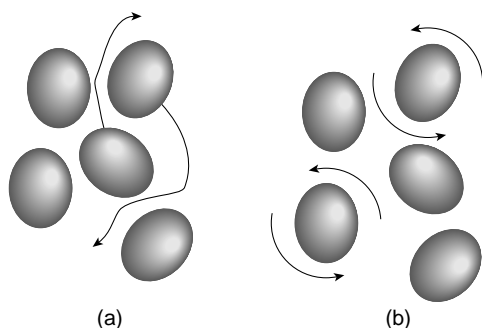
Traditionally, the material states are classified in terms of their bulk mechanical properties (i.e. hard or soft, rigid or flowing). These bulk mechanical properties often reflect the mobility of the constituent molecules or atoms.

### 1.6.1 Gases

*Gases* are defined as low-density material phases that fill the volume of any container to which they are confined, independent of its shape. Gases are characterized by very high mobility of the molecules or atoms. It is possible to perform NMR experiments on gases, although this is not done very often.<sup>8</sup>

### 1.6.2 Liquids

*Liquids* are relatively dense material phases characterized by their flow under shear forces. There is high molecular mobility in liquid phases. This molecular mobility has two aspects: translation mobility and rotational mobility (Figure 1.9). *Translation molecular mobility* means that the molecules or atoms slide past each other rather freely and wander over appreciable distances in a relatively short time. For example, a water molecule at room temperature typically wanders over a distance of  $\sim 7 \mu\text{m}$  over a time interval of 10 ms. *Rotational molecular mobility* means that the individual molecules rotate around their own centres of gravity in a more or less random fashion. For example, a medium-sized protein molecule in water solution typically rotates through an angle of around 1 rad after a time of around 10 ns. Both of these types of mobility are very important for NMR, because they tend to average out many of the nuclear spin interactions, simplifying the behaviour of the nuclear spins.

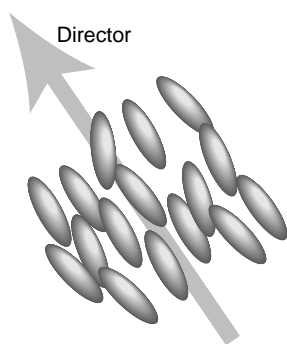
**Figure 1.9**

In a liquid, molecules have both translation mobility (a) and rotational mobility (b). If the liquid is isotropic, the mobilities are the same in all directions.

A further distinction must be made between *isotropic* and *anisotropic* liquid phases.

In isotropic liquids, the translation and rotational mobilities of the molecules are the same in all directions. This is true, for example, in ordinary water or for molecules dissolved at low concentration in common solvents. As discussed in Chapter 8, the molecular motion in an isotropic liquid effectively removes many of the nuclear spin interactions, leading to rather simple NMR spectra.

There are also *anisotropic liquids* (also called *liquid crystals*), in which the molecules adopt a non-isotropic spatial configuration. In some cases the molecules are arranged in layers, in other cases like coins stacked up on top of each other, and in still other cases the molecules adopt a sort of loose helical structure. Despite these loose spatial configurations, the molecules are still very mobile and the substance flows under shear forces, which distinguishes a liquid crystal from a solid. An everyday example of a liquid crystal is a soap film, in which the soap molecules are arranged in layers. As far as NMR is concerned, anisotropic liquids behave very differently from isotropic liquids because the translation and rotational mobilities of the molecules depend on the direction (Figure 1.10). Consider, for example, a case in which the molecules are shaped like long rods and all the rods are, on average, aligned along a particular direction in space (called the *director* in liquid-crystal science). It is easier for the molecules to spin around an axis that is parallel with the director than around an axis that is perpendicular to the director. In the former case they have a better chance of completing a full rotation without hitting a neighbouring molecule, as opposed to the latter case, where collisions are almost inevitable. This motional anisotropy leads to incomplete averaging of the nuclear spin interactions and, hence, more complicated NMR spectra. Nevertheless, the NMR spectra of liquid crystals, and of molecules dissolved in liquid crystals, can be very informative. One way in which anisotropic liquids are used to enhance the study of biological molecules is sketched in Section 16.4.

**Figure 1.10**

In an anisotropic liquid, the molecular mobilities depend on the direction in space.



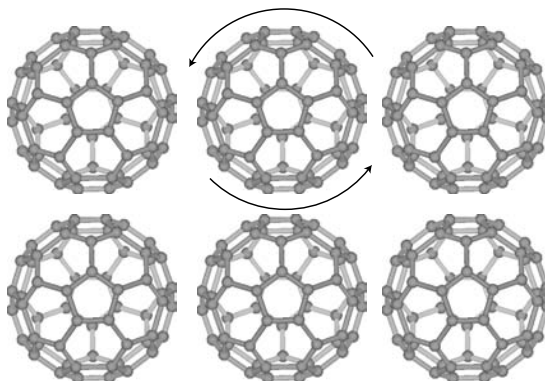
### 1.6.3 Solids

*Solids* are high-density material phases that resist shear forces without flowing. Solid materials have an enormous variety of atomic structures. For example, there are *molecular solids*, which are composed of distinct molecules held together by rather weak intermolecular forces, and *non-molecular solids*, in which the atomic nuclei are gripped in an extended electron cloud network, which may extend to the boundaries of the material. There are *crystals*, in which the nuclei are arranged on a repeating lattice, as well as *glasses* and *amorphous solids*, in which long-range repeating patterns are difficult to identify.

The distinction between 'solid' and 'liquid' is not always unambiguous. The behaviour of matter under shear forces depends strongly on the time-scale involved. For example, an ordinary liquid resists deformations and appears as a hard solid on a time-scale of microseconds – as may be tested by diving stomach first into a swimming pool. On the other hand, hard solids, such as rocks, may behave as liquids under long time-scales.<sup>9</sup>

There is a great variety of electronic behaviour in solids. The majority of materials are *electrical insulators*, with very restricted electron mobility. However, in some cases the electron mobility is high, even though the atomic nuclei are more or less fixed in place. Such substances are *metals*. In special circumstances, the electrons may pair up to form bosons that form macroscopic coherent quantum waves. This happens in *superconductors*.

The motion of atoms and molecules is usually greatly restricted in solids. It is this feature that distinguishes solids from liquids on the molecular level. Nevertheless, there can be substantial local motion. For example, some molecular solids display considerable rotational motion of the molecules around their own lattice positions. This often happens for solids composed of near-spherical molecules, e.g. the football-like fullerene molecule  $C_{60}$ . At room temperature, the  $C_{60}$  'footballs' rotate randomly and isotropically around their own centres in the solid:



**Figure 1.11**

Rotation of  $C_{60}$  molecules in a solid.

Even in molecules that do not jump or rotate as entire units, there are often local groups which have considerable local mobility. For example, methyl groups  $-CH_3$  usually rotate rapidly at room temperature, even in rigid solids. Often, solids display a variety of phases at different temperatures and pressures, with different modes of atomic or molecular mobility.

Generally speaking, the NMR spectra of solids are generally broader and more complex than in liquids. Nevertheless, there has been much recent technical progress in the NMR of solids. The development of experimental techniques has made it possible to obtain solid-state NMR spectra with a resolution approaching that obtained in isotropic liquids in many cases. This is very useful, because there are many substances which cannot, or should not, be dissolved or melted.

## Notes

1. Electron spin was first postulated by the Dutch graduate students Uhlenbeck and Goudsmidt in 1925. Their supervisor stated that they could risk publication since they didn't yet have a reputation to destroy. The influential physicist Pauli initially poured scorn on the idea but later became one of its chief proponents.
2. Throughout this book, a box drawn around an equation indicates that it is important in its own right.
3. Some large objects do in fact 'have angular momentum "by themselves", without rotating', although the consequences are subtle and require fine experimental observations. For example, the *Einstein-de Haas effect* shows that the act of magnetizing a substance imparts angular momentum to it (for example, an object suspended by a fine thread starts rotating slowly as it is magnetized). A magnetized substance, like a lump of iron, does have angular momentum, without rotating! There is even a converse phenomenon called the Barnett effect: rotating an object magnetizes it! See E. T. Jaynes, *Rev. Mod. Phys.* 34, 143 (1962).
4. This is a simplified version of the Pauli principle. The full version is as follows:
 

The quantum mechanical state of a system containing two identical bosons is invariant under exchange of the two bosons. The quantum mechanical state of a system containing two identical fermions changes sign under exchange of the two fermions.

The theorem that two fermions may not occupy the same state follows as a consequence of the full principle. As a matter of fact, the 'Pauli principle' was first given for fermions by Heisenberg, and for bosons by Bose. It is a little mysterious why the principle has become attached to the name of Pauli.
5. The discussion of neutron spin, proton spin, and nuclear spin given in this chapter is oversimplified. In fact, it is known that the orbital motions of the quarks and gluons also contribute to the spin of the proton and neutron (see, e.g., S. D. Bass, *Science* 315, 1672-1673 (2007)). I deliberately give a naive picture of neutron and proton spin here, because the details are not so important anyway for NMR and because it does make a good story.
6. The neutrons and protons are bound together by an interchange of particles known as mesons. Each meson is made up of two quarks.
7. In *Mössbauer spectroscopy*, transitions between the nuclear energy levels are excited using energetic  $\gamma$ -rays.
8. There are some interesting applications of NMR in gases, although the low density of matter in a gas leads to relatively weak NMR signals. For example, NMR of gaseous  $^{129}\text{Xe}$  is used to make images of cavities inside hollow objects, including lungs. In this case, a special technique called *optical pumping* is used to prepare  $^{129}\text{Xe}$  gas with a very high nuclear spin polarization, so as to enhance the NMR signals. See, for example, B. M. Goodson, *J. Magn. Reson.* 155, 157-216 (2002). Some conventional gas-phase NMR spectra, obtained without the help of optical pumping, are shown in Figure 19.21.
9. The first edition of this book propagated the urban myth that old glass windows are thicker at the bottom because the glass creeps slowly under gravity. This is not true. The thickening at the bottom is simply due to the manufacturing process. Thanks to the copy editor for pointing this out.

## Further Reading

- For the fundamentals of quantum mechanics and atomic structure, see J. J. Sakurai, *Modern Quantum Mechanics*, Addison-Wesley, 1994, and C. Cohen-Tannoudji, B. Diu, F. Laloë, *Quantum Mechanics* Wiley, London, 1977.
- For atomic structure and orbitals, see P. W. Atkins, *Molecular Quantum Mechanics*, Oxford University Press, Oxford, 1983.
- For the constituents of matter, see F. Close, 'The quark structure of matter' in *The New Physics*, P. Davies, (ed.), Cambridge University Press, Cambridge, 1989.

## Exercises

- 1.1 Which of the following statements *must* be correct, which *might possibly* be correct, and which *cannot* be correct?
- (i) The nucleus  $^{89}\text{Y}$  (atomic number = 39) has a ground state spin  $I = 1/2$ .
  - (ii) The nucleus  $^{90}\text{Zr}$  (atomic number = 40) has a ground state spin  $I = 1$ .
  - (iii) The nucleus  $^{91}\text{Zr}$  (atomic number = 40) has a ground state spin  $I = 1/2$ .
  - (iv) The nucleus  $^{92}\text{Mo}$  (atomic number = 42) has a ground state spin  $I = 0$ .
  - (v) The nucleus  $^{138}\text{La}$  (atomic number = 57) has a ground state spin  $I = 0$ .
- 1.2 If a particle with spin  $S = 5/2$  couples to a particle with spin  $S = 3/2$ , what are the possible values for the spin of the resulting particle?



# 2 Magnetism

## 2.1 The Electromagnetic Field

It is possible to use either a classical or a quantum description of the electromagnetic field.

In the quantum description, the field appears as a collection of photons. This description is accurate, but is difficult to use.

In the classical description, one associates two vectors, **E** and **B**, with every point of space. The field **E** is called the *electric field*, and interacts with *electric charges*. The field **B** is called the *magnetic field*, and interacts with *magnetic moments*<sup>1</sup>.

In NMR, the discrepancy between the classical and quantum field descriptions is negligible, and the simpler classical formalism is preferable.

The magnitude of **B** is specified in units of tesla (symbol T). The older unit of gauss (symbol G) is also sometimes used. The conversion is as follows:  $1\text{ G} = 10^{-4}\text{ T}$ . The natural magnetic field at the surface of the Earth is  $\sim 50\text{ }\mu\text{T}$ . NMR spectrometers currently operate with magnetic fields between around 4 T and 20 T.

The behaviour of the fields **E** and **B** in time and space is governed by the *Maxwell equations*. As shown in standard texts (see *Further Reading*), these equations predict many effects, including the propagation of fields **E** and **B** in empty space.  $\gamma$ -rays, X-rays, light rays, infrared radiation, microwaves, and radio waves are all electromagnetic waves, distinguished only by frequency. A table of typical frequencies and free-space wavelengths for electromagnetic waves is given in Table 2.1.

**Table 2.1** Typical frequencies and wavelengths of electromagnetic waves.

Type of Wave	Typical frequency /Hz	Typical wavelength
Radio	$\sim 10^8$	$\sim 3\text{ m}$
Microwave	$\sim 10^{10}$	$\sim 3\text{ cm}$
Infrared	$\sim 3 \times 10^{13}$	$\sim 10\text{ }\mu\text{m}$
Ultraviolet	$\sim 3 \times 10^{16}$	$\sim 10\text{ nm}$
X-ray	$\sim 3 \times 10^{18}$	$\sim 0.1\text{ nm}$
$\gamma$ ray	$\sim 3 \times 10^{20}$	$\sim 1\text{ pm}$

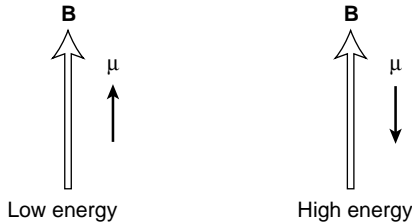
## 2.2 Macroscopic Magnetism

All substances are *magnetic*, meaning that they have the capability of interacting with magnetic fields.

This interaction is usually expressed in terms of a magnetic moment  $\mu$ . The magnetic energy of a small object depends on the interaction between its magnetic moment and the **B** field:

$$E_{\text{mag}} = -\boldsymbol{\mu} \cdot \mathbf{B} \quad (2.1)$$

The dot product indicates that the magnetic energy depends on the relative direction of the vectors  $\mathbf{B}$  and  $\boldsymbol{\mu}$ . The negative sign indicates that the magnetic energy is lowest if the magnetic moment  $\boldsymbol{\mu}$  is parallel to the  $\mathbf{B}$  field:



**Figure 2.1**  
Magnetic energy.

In general, Equation 2.1 should be integrated over the volume of the object.

In some substances, the magnetic moment is *permanent*, as for a bar magnet or a compass needle. In the majority of substances, on the other hand, the magnetism is *induced*, meaning that the magnetic moment appears only when an external magnetic field is present.

An object that is free to move tends to align along an external magnetic field so as to minimize the magnetic energy. This is the principle of the compass needle, which has a permanent magnetic moment  $\boldsymbol{\mu}$ . The compass needle swings around to bring the magnetic moment  $\boldsymbol{\mu}$  parallel to the Earth's field  $\mathbf{B}$ .

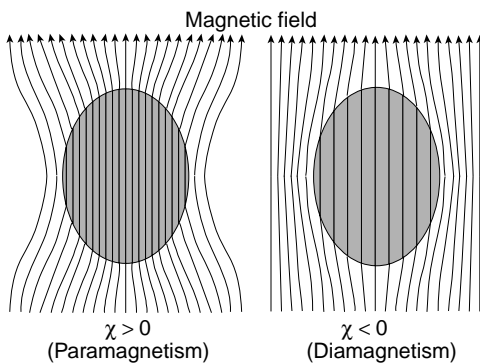
Most objects display *induced* magnetism and only possess a magnetic moment in the presence of an applied magnetic field. Such induced magnetic moments typically take some time to build up. The equilibrium value of the induced magnetic moment is often proportional to the applied magnetic field  $\mathbf{B}$ , and has the same direction. In SI units, this relationship is written<sup>2</sup> as follows:

$$\mu_{\text{induced}} = \mu_0^{-1} V \chi \mathbf{B} \quad (2.2)$$

where  $\mu_0 = 4\pi \times 10^{-7} \text{ H m}^{-1}$  is an awkward constant, called the *magnetic constant* or *vacuum permeability*.  $V$  is the volume of the object. The dimensionless number  $\chi$  is called the *magnetic susceptibility* of the material. It expresses how readily the material develops a magnetic moment on exposure to an external magnetic field.  $\chi$  may have either sign. Materials with a positive value of  $\chi$  are called *paramagnetic*. Most materials have a negative value of  $\chi$ , and are called *diamagnetic*. For example, pure water has a magnetic susceptibility  $\chi = -9.05 \times 10^{-6}$ .

The susceptibility of an object determines how an applied magnetic field is distorted. Objects with a positive susceptibility ( $\chi > 0$ ) tend to pull the magnetic field into the material. Objects with negative susceptibility ( $\chi < 0$ ) tend to push the magnetic field out of the material.

Paramagnetic susceptibilities tend to be larger in magnitude than diamagnetic susceptibilities (as hinted in Figure 2.2).



**Figure 2.2**  
An object distorts the magnetic field according to its magnetic susceptibility. The effect is greatly exaggerated in the diagrams shown here.

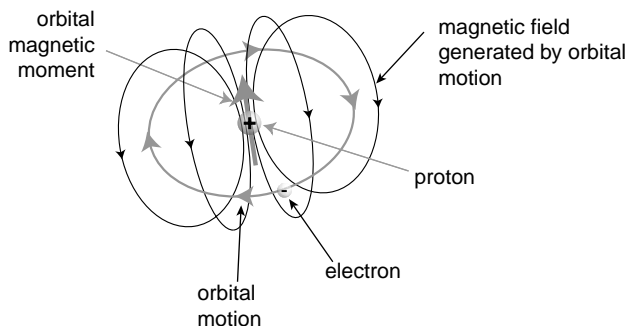
## 2.3 Microscopic Magnetism

Where does magnetism come from?

There are three sources: (i) the circulation of electric currents, (ii) the magnetic moments of the electrons, and (iii) the magnetic moments of the atomic nuclei. The electronic contributions (i) and (ii) are almost always many orders of magnitude larger than the nuclear contribution (iii).

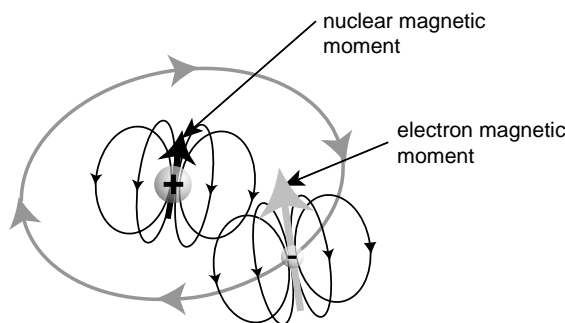
Generally speaking, the circulation of electric currents contributes a negative value to the susceptibility, whereas electron and nuclear magnetic moments contribute a positive value. In diamagnetic substances, contribution (i) is greater than contributions (ii) and (iii).

Effect (i) may be understood from elementary physics: If an electric current is made to flow in a loop, then a magnetic field is generated. In most materials, the circulating electric currents exist on a molecular distance scale and are confined to the atoms or molecules themselves. Consider, for example, a hydrogen atom. If the electron is in a  $p$ -orbital, it circulates around the proton, building a small ‘current loop’ that generates a magnetic field:



**Figure 2.3**  
Orbital magnetism of the electron in a hydrogen atom.

Effects (ii) and (iii) are more difficult to understand. The electrons and nuclei both possess *intrinsic magnetism*, which is not due to a circulating current. The fundamental particles simply ‘have’ a magnetic moment, just like they simply ‘have’ spin angular momentum. Electrons and nuclei have a permanent magnetism.



**Figure 2.4**  
Electron and proton spin magnetism in a hydrogen atom.

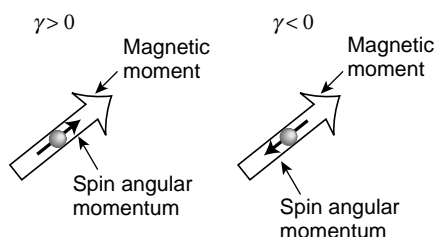
Spin and magnetism are very closely linked. A very fundamental symmetry theorem<sup>3</sup> requires that the spin angular momentum and the magnetic moment are proportional to each other:

$$\hat{\boldsymbol{\mu}} = \gamma \hat{\mathbf{S}} \quad (2.3)$$

The ‘hats’ above these symbols indicate that they are quantum mechanical operators, as described in Chapter 7.

For atomic nuclei, the proportionality constant  $\gamma$  is called the *gyromagnetic ratio* (also called the *magnetogyric ratio*). The gyromagnetic ratio is normally specified in units of  $\text{rad s}^{-1} \text{T}^{-1}$ , for reasons discussed in Section 2.4.

The gyromagnetic ratio may have either sign. For particles with a positive value of  $\gamma$  (including most atomic nuclei), the magnetic moment is parallel to the angular momentum. For particles with a negative value of  $\gamma$  (including the electron and a few atomic nuclei), the magnetic moment is opposite in direction to the angular momentum:



**Figure 2.5**  
The gyromagnetic ratio  $\gamma$ .

The magnetic moment of the electron, like the spin of the electron, was derived by Dirac in his synthesis of quantum mechanics and relativity. The value for the electron's magnetic moment, predicted by quantum electrodynamical theory, is in agreement with the experimental result to the astonishing accuracy of 11 significant figures. The magnetic moments of the quarks, nucleons, and nuclei are not yet understood on this level of detail.

As discussed in Section 1.4.1, atomic nuclei have a ground state spin that derives from the spins and the orbital motions of the constituent particles. Similarly, the nuclear magnetic moment derives from the quark magnetic moments and the currents of charged particles inside the nucleus. The gyromagnetic ratios of some common atomic nuclei are shown in Table 1.2.

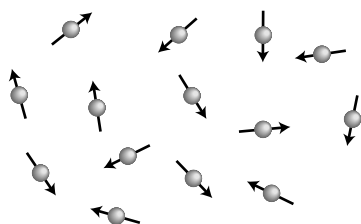
In diamagnetic materials, the pairing of the electron spins cancels out the electron magnetism, to a good approximation. The strong magnetism of paramagnetic and ferromagnetic materials is due to the presence of unpaired electron spins.

We return to the subject of macroscopic magnetism after considering the *dynamic* behaviour of nuclear spins in a magnetic field.

## 2.4 Spin Precession

The angular momentum of a rotating object is a vector. The direction of the vector indicates the axis of the rotational motion. The angular momentum vector may point in any possible direction in space.

The angular momentum of a particle with spin is also a vector, and may also point in any possible direction in space. In this book, the direction of the spin angular momentum is called the *spin polarization axis*. In general, particles with spin, such as proton nuclei, have spin polarization axes pointing in all possible directions:



**Figure 2.6**  
Randomly directed spin polarizations.

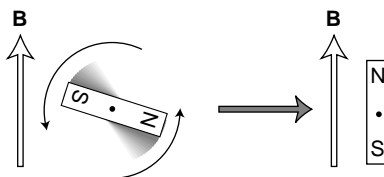


Elementary discussions of NMR often claim that, according to quantum mechanics, only certain directions of spin angular momentum are 'allowed'. For example, it is often stated that spin-1/2 particles may only be polarized either 'up' or 'down'. This is incorrect. In Chapter 10, I discuss what quantum mechanics *does* say about the behaviour of the spin angular momenta.

The magnetic moment of a nucleus points either in the same direction to the spin polarization (for nuclei with  $\gamma > 0$ ), or in the opposite direction to the spin polarization (for nuclei with  $\gamma < 0$ ). For a sample in equilibrium in the absence of a magnetic field, the distribution of magnetic moments is completely *isotropic*, i.e. all possible directions are equally represented.

Now suppose that a magnetic field is suddenly applied to the sample. What happens to the spin magnetic moments?

A compass needle rotates so as to bring the magnetic moment parallel to the field, minimizing the magnetic energy:



**Figure 2.7**

Motion of a compass in a magnetic field.

However, a nuclear spin is not a compass needle.<sup>4</sup> The actual response of the spin polarization is to move *around* the field. The magnetic moment of the spin moves on a cone, keeping a constant angle between the spin magnetic moment and the field. This motion is called *precession*.

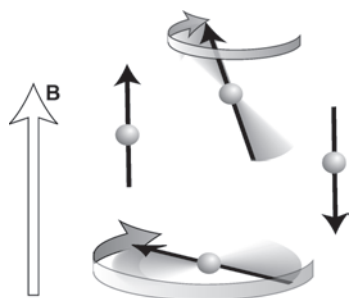


**Figure 2.8**

Spin precession.

The spin polarization axis goes around and around on the same precession cone, always keeping the same angle between the spin axis and the field.

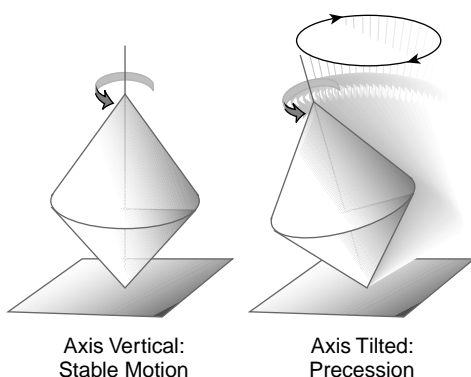
The angle of the cone depends only on the initial spin polarization. If the spin is initially polarized exactly along or against the field, then it simply stays there, corresponding to precession on a cone of zero angle. If the spin is initially polarized exactly perpendicular to the field, then the spin polarization moves on a flat disk. For the majority of spins, the angle is intermediate between these extremes:

**Figure 2.9**

The angle of the precession cone depends on the initial direction of the spin.

Spins behave in this way because they possess *angular momentum* as well as a magnetic moment. The presence of angular momentum sharply changes the dynamical properties of the magnetic moment.

Spin precession has many parallels in classical physics. Consider for example, a child's spinning top:

**Figure 2.10**

Precessional motion of a spinning top.

If the top is set spinning with its axis exactly vertical, it has a stable motion. However, if its axis is slightly skew, then the gravitational pull on the top plus the reaction of the ground on the top's tip combine to produce a torque that 'tries' to pull the top to the ground. Nevertheless, if the top is spinning fast enough, the top does not fall over immediately. Instead, the spinning axis executes a precessional motion, going around in a circle. The term 'precession' is used in classical physics to describe such phenomena.

A similar effect may be observed while riding a bicycle. By leaning slightly to one side, one produces a gravitational torque on the bicycle that might be expected to pull the bicycle immediately to the ground. However, since the wheels have angular momentum, the effect produced is instead to rotate the axis of the wheels so that the bicycle turns a corner. Motorcyclists exploit this effect by hanging off their vehicles on one side when rounding a corner at speed.

A full treatment of such classical examples is very complicated, since they also involve friction, internal degrees of freedom, and additional sources of angular momentum. It is possible to fall off a bicycle by leaning too far, and a skewed top eventually does fall over. For nuclear spins, on the other hand, there are essentially no complications. Precessing spins in a magnetic field offer extremely clean dynamics, free from complicating factors.

## 2.5 Larmor Frequency

A quantum description of spin precession is given in Chapter 10. This treatment shows that the frequency of precession  $\omega^0$  is equal to

$$\omega^0 = -\gamma B^0 \quad (2.4)$$

where  $B^0$  is the magnetic field at the site of the particle and  $\gamma$  is the gyromagnetic ratio. For nuclear spins,  $\omega^0$  is called the nuclear *Larmor frequency*. The Larmor frequency is proportional to the magnetic field.

There are two common ways of specifying the frequency of an oscillation. The most familiar way is to write a frequency in *cycles per second*, or hertz (which is the same thing). For example, a Larmor frequency of 200 MHz implies that the nuclear spin completes 200 million revolutions around its precession cone every second.

The second way of specifying a frequency is in units of radians per second. This is called an *angular frequency*, and is given by the frequency in hertz multiplied by a factor of  $2\pi$ . A Larmor frequency of 200 MHz corresponds to an angular frequency of  $400 \times 10^6 \pi \text{ rad s}^{-1}$ .

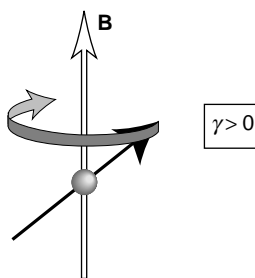
In general, the two frequency units may always be converted into each other through the relationships:

$$\begin{aligned} \text{frequency in units of rad s}^{-1} &= 2\pi \times (\text{frequency in units of Hz}) \\ \text{frequency in units of Hz} &= (\text{frequency in units of rad s}^{-1})/2\pi \end{aligned} \quad (2.5)$$

Although angular frequencies appear to be awkward, they make the equations simpler. In this book, the symbol  $\omega$  always implies an angular frequency in units of radians per second. A frequency in hertz is usually written as  $\omega/2\pi$ , i.e. the angular frequency divided by  $2\pi$ .

Equation 2.4 defines the Larmor frequency in radians per second. The Larmor frequency in hertz is given by  $-\gamma B^0/2\pi$ .

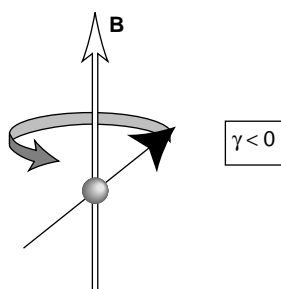
The Larmor frequency has a defined sign. The sign indicates the *sense* of the spin precession around the applied field.<sup>5</sup> Most nuclei have positive  $\gamma$ , in which case the Larmor frequency is *negative*. This means that the precession is in the *clockwise* direction, as seen when looking ‘upstream’ with respect to the direction of the magnetic field (i.e. standing at the top of Figure 2.11 and looking down):



**Figure 2.11**

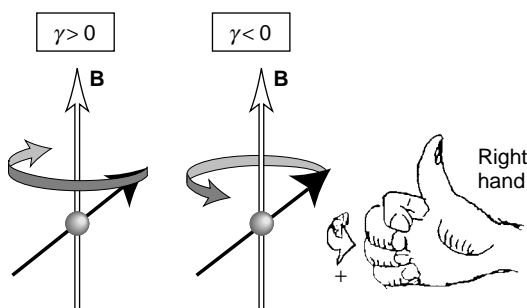
Negative precession for nuclei with positive gyromagnetic ratio.

A few nuclei, such as  $^{15}\text{N}$  and  $^{29}\text{Si}$ , and also the electron, have negative values of  $\gamma$ , in which case the Larmor frequency is *positive*. This indicates precession in the *anticlockwise* direction, as seen when looking ‘upstream’ with respect to the direction of the magnetic field:

**Figure 2.12**

Positive precession for nuclei with negative gyromagnetic ratio.

The sense of positive and negative precessions may be obtained using one's right hand: if the thumb points along the magnetic field, the fingers wrap around in the direction of positive precession:

**Figure 2.13**

Using one's right hand to determine the sense of precession.

The Larmor frequencies of some common nuclear isotopes in a typical NMR field of  $B^0 = 11.74 \text{ T}$  are given in Table 1.2.

## 2.6 Spin–Lattice Relaxation: Nuclear Paramagnetism

Consider again the  $^1\text{H}$  nuclei in a sample of water. In the absence of an external magnetic field, the spin polarizations are uniformly distributed, pointing in all possible directions in space. The *total* magnetic moment of the sample is very close to zero, since approximately the same number of spins point towards a given direction as against it.

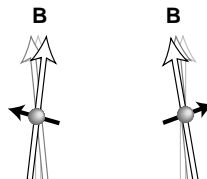
If a magnetic field is suddenly turned on, all proton spins begin executing Larmor precession around the field. For the sake of concreteness, suppose that the external field is  $11.74 \text{ T}$ . The proton Larmor frequency is  $\omega^0/2\pi \cong -500 \text{ MHz}$ . Each proton spin completes 500 million full cycles of precession every second, moving always in the negative sense (clockwise looking 'upstream' with respect to the magnetic field).

This precessional motion is essentially invisible. It does nothing to change the total magnetic moment of the sample. An *isotropic* distribution of spin polarizations makes no contribution to the magnetism of the material.

However, the proton spins are not alone: the water molecules, which carry the protons, undergo constant vigorous motion. The orientation of each molecule in space changes constantly, and the relative positions of the molecules interchange all the time. How does this affect the motion of the nuclear spins?

Remarkably, the answer is almost not at all. To a very good approximation, each nuclear spin is oblivious of its immediate environment. As the molecule rotates, the nuclear spin polarizations continue to point in the same direction in space. If a magnetic field is present, the spin polarization vectors steadily precess around the magnetic field, independent of the fact that they are transported in molecules undergoing violent rotations and collisions. One is reminded of a ship's gyroscopic compass, which keeps calm even in a rough sea.

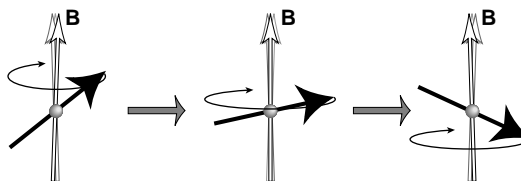
However, on a closer look, one finds that the violent molecular surroundings do slightly influence the nuclear magnets. Each molecule is full of magnetic particles: the electrons and nuclei are all sources of magnetic fields. These fields are small, and they fluctuate rapidly because of the thermal motion of the environment. At any given moment, the spin precesses about a field that is the sum of the external field, which is static, and a very small microscopic field, which varies in time, and which may have any possible direction in space. The total magnetic field seen by each spin, therefore, has a slightly fluctuating magnitude, and also a slightly fluctuating *direction*. At any given time, the local magnetic field experienced by any one nuclear spin is slightly different, both in magnitude and direction, to that of its neighbour:



**Figure 2.14**  
Microscopic fields.

These variations are very small: for protons in a sample of water in a 11.74 T field, the local magnetic field at the nuclei fluctuates in direction by only around  $10^{-4}$  degrees. Nevertheless, these tiny fluctuations are very important, because in the long term they allow the isotropy of the nuclear spin polarization to be broken and, hence, a macroscopic nuclear magnetic moment to develop. Without the fluctuating molecular fields, nuclear magnetism would be unobservable.

What happens is quite complicated. The small fluctuating fields from the thermal environment cause a gradual breakdown of the constant-angle ‘cone precession’ of the nuclear spins. For each spin, the angle between the spin magnetic moment and the external field varies slightly. Over a long time, the magnetic moment of each nuclear spin wanders around, moving between different ‘precession cones’, and eventually sampling the entire range of possible orientations:

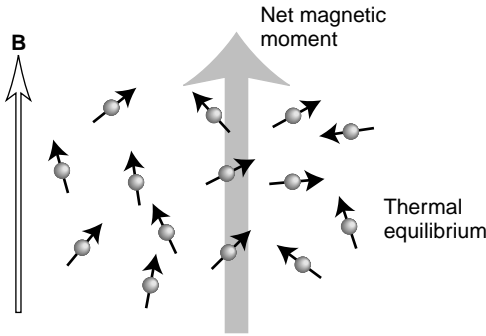


**Figure 2.15**  
Precession in a  
fluctuating field.

The ‘precessional’ and ‘wandering’ motions have very different time-scales. For nuclear spins, the time-scale of the precessional motion is set by the inverse of the Larmor frequency, i.e. a few nanoseconds. The time-scale for the ‘wandering motion’ under the random molecular fields, on the other hand, is often as long as seconds. In typical cases, a nuclear spin executes many millions of precession circuits before deviating appreciably from its cone of constant angle with respect to the external field.

The important thing is that this wandering motion is *not* completely isotropic. Since the environment has a finite temperature, it is slightly more probable that the nuclear spin is driven towards an orientation with low magnetic energy than towards an orientation with high magnetic energy. The thermal wandering motion is therefore slightly biased towards spin orientations with magnetic moments parallel to the magnetic field.

The biased wandering motion leads eventually to a stable *anisotropic* distribution of nuclear spin polarizations, called *thermal equilibrium*. Although this thermal equilibrium distribution is *stable*, it is not *static* on a microscopic scale. The individual spin magnetic moments still execute continuously their precessing and wandering motion. However, the net *distribution* of spin orientations, with magnetic moments along the field slightly more probable than orientations with magnetic moments opposed to the field, is independent of time. The following figure greatly exaggerates the anisotropy, for the sake of clarity:



**Figure 2.16**  
Thermal equilibrium.

At realistic field strengths, the anisotropy of the polarization distribution at thermal equilibrium is directly proportional to the ratio of the magnetic and thermal energies. The difference in magnetic energy between a single proton polarized along the field and one polarized opposite to the field is  $\hbar\gamma B^0 = 3.3 \times 10^{-25} \text{ J}$  in a field of  $B^0 = 11.74 \text{ T}$ . The available thermal energy at room temperature is  $k_B T = 4.1 \times 10^{-21} \text{ J}$ , which is four orders of magnitude larger. For nuclear spins, there is only a very slight bias in the spin polarization distribution at thermal equilibrium.

The anisotropy of the magnetization distribution in thermal equilibrium means that the entire sample acquires a small net magnetic moment along the field, i.e. a *longitudinal* magnetic moment. This is the microscopic mechanism of *nuclear paramagnetism*. For protons in water, the nuclear contribution to the magnetic susceptibility may be calculated to be

$$\chi_{\text{nuc}} = \frac{\mu_0 \hbar^2 \gamma^2 c}{4k_B T}$$

where  $c$  is the number of protons per unit volume. This evaluates to

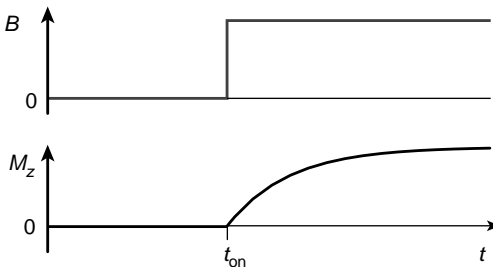
$$\chi_{\text{nuc}} = +4.04 \times 10^{-9}$$

This is about three orders of magnitude smaller than the observed diamagnetism of water, which is due to the electrons rather than to the nuclei (see Section 2.2).

If the external magnetic field is suddenly turned on (or if the sample is rapidly brought into the field) the macroscopic nuclear magnetization is initially zero but gradually grows due to the biased wandering of the spin polarizations, as discussed above. The build-up curve is usually approximately exponential. Suppose that  $t_{\text{on}}$  is defined as the moment when the external magnetic field is applied, and the direction of the field is defined to be the  $z$ -axis. The build-up of longitudinal magnetization has the form

$$M_z^{\text{nuc}}(t) = M_{\text{eq}}^{\text{nuc}} (1 - \exp\{-(t - t_{\text{on}})/T_1\}) \quad (2.6)$$

for times  $t \geq t_{\text{on}}$ :



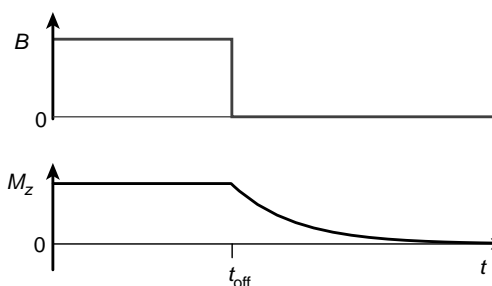
**Figure 2.17**  
The build-up of longitudinal spin magnetization, after the magnetic field is turned on.

The exponential time constant for the process  $T_1$  is known as either the *spin-lattice relaxation time constant* or the *longitudinal relaxation time constant*. The use of the term ‘lattice’ derives from the early days of NMR, when theoretical effort concentrated on the treatment of NMR in solids and when thermal equilibration was explained in terms of the interactions between the nuclear spins and the crystal lattice. By extension, the term is now used, misleadingly, even for NMR in liquids and gases, which lack a ‘lattice’. The term ‘longitudinal’ simply indicates that the magnetization builds up in the same direction as the applied magnetic field.

The term ‘relaxation’ is widely used in the physical sciences to indicate the re-establishment of thermal equilibrium after some perturbation is applied. In the case under discussion, thermal equilibrium is first established in the absence of a field, so that all nuclear spin orientations are equally likely. When a magnetic field is applied, this situation no longer corresponds to equilibrium, and the system ‘relaxes’ to the new equilibrium state, in which the spin polarizations are distributed anisotropically. If the magnetic field is suddenly switched off at a later time  $t_{\text{off}}$  (where  $t_{\text{on}} - t_{\text{off}} \gg T_1$ ), the nuclear spin magnetization relaxes back to zero again, following the law

$$M_z^{\text{nuc}}(t) = M_{\text{eq}}^{\text{nuc}} \exp\{-(t - t_{\text{off}})/T_1\}$$

for times  $t \geq t_{\text{off}}$ :



**Figure 2.18**

The decay of longitudinal spin magnetization, after the magnetic field is turned off.

The relaxation time constant  $T_1$  depends on the nuclear isotope and the sample, including parameters such as temperature and viscosity, if the sample is a liquid. Typically, the value of  $T_1$  is in the range milliseconds to seconds, although  $T_1$  may be as long as days or even months in exceptional cases. The principles of nuclear spin relaxation are discussed in Chapter 20.

## 2.7 Transverse Magnetization and Transverse Relaxation

The longitudinal nuclear spin magnetization, described above, is almost undetectable. It is about four orders of magnitude less than the typical diamagnetism of the sample, associated with the electrons. Experimental study of the longitudinal nuclear magnetization is impractical.<sup>6</sup>

NMR spectroscopy takes a different approach. Instead of measuring the nuclear spin magnetization *along* the field, the magnetization *perpendicular* to the field is measured.

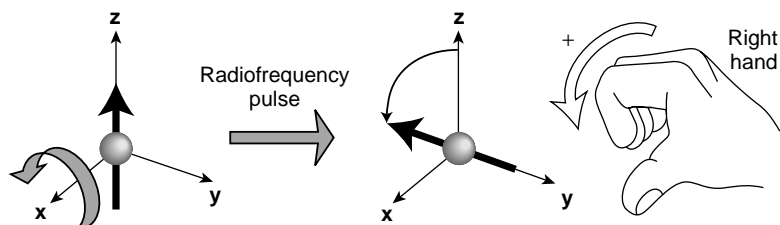
Suppose that the spin system is allowed to reach thermal equilibrium in a large magnetic field. The macroscopic nuclear magnetization has an equilibrium value  $M_{\text{eq}}^{\text{nuc}}$  along the direction of the external field (the  $z$ -axis, by convention).

As described above, this equilibrium situation corresponds, on a microscopic level, to a large number of nuclear spin magnets, all precessing around the magnetic field at the same frequency  $\omega^0$ . The overwhelming majority of nuclear magnets are polarized at an angle to the field and execute precessional motion on wide-angle cones. Nevertheless, there is no *net* magnetization perpendicular to the field, because,

on average, the magnetization distribution in thermal equilibrium is cylindrically symmetrical around the  $z$ -axis.

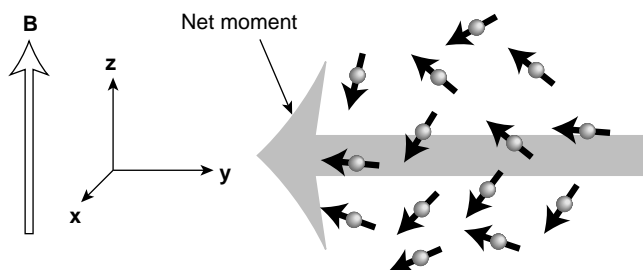
Now suppose that the polarization of every single spin is suddenly rotated by  $\pi/2$  radians around the  $x$ -axis, by some external agency. We will see in Chapter 10 that this is achieved by applying an *r.f. pulse* – an oscillating magnetic field, of appropriate frequency and duration. For the time being, however, we ignore the mechanism and discuss the consequences.

If a spin polarization is initially along the  $z$ -axis and is rotated by  $\pi/2$  about the  $x$ -axis, then the result is a spin polarization along the  $-y$ -axis:



**Figure 2.19**  
Rotation of a spin  
around the  $x$ -axis.

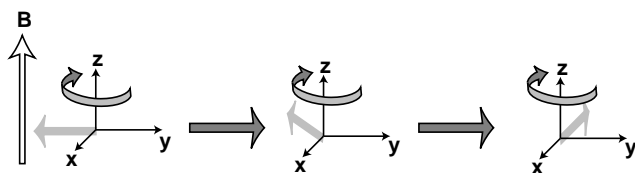
Since the pulse rotates the polarization of every single spin in the sample by the same angle, the pulse also rotates the entire nuclear magnetization distribution of the sample. The net spin polarization along the  $z$ -axis is therefore transferred into a net spin polarization along the  $-y$ -axis, i.e. along an axis perpendicular to the magnetic field. If we were to look 'down' the magnetic field, immediately after the pulse is switched off, we would see slightly more spins polarized along the  $-y$ -axis than along the  $y$ -axis.<sup>7</sup>



**Figure 2.20**  
Polarization  
distribution after a  
pulse.

This net magnetic moment perpendicular to the magnetic field is called *transverse magnetization*.

Now suppose that the pulse is turned off and the spins resume their precessional motion. On a microscopic level, this is 'business as usual'. The individual spins precess on their individual cones. On a macroscopic scale, however, a new feature appears. The state immediately after the pulse corresponds to a net polarization *along the  $-y$ -axis*, perpendicular to the main field. Since every single spin precesses, the bulk magnetic moment also precesses. The macroscopic nuclear magnetization rotates in the  $xy$ -plane, perpendicular to the main magnetic field:



**Figure 2.21**  
Precession of the  
transverse  
magnetization.

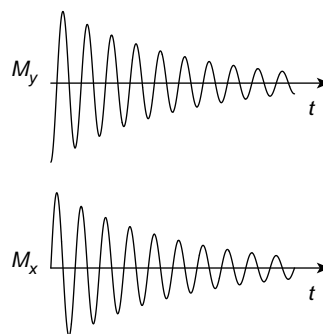


The precession frequency of the transverse magnetic moment is equal to the precession frequency of the individual spins, i.e. the nuclear Larmor frequency (Equation 2.4).

The macroscopic magnetization components at a time  $t$  after the pulse have the form

$$\begin{aligned} M_y^{\text{nuc}} &= -M_{\text{eq}}^{\text{nuc}} \cos(\omega^0 t) \exp\{-t/T_2\} \\ M_x^{\text{nuc}} &= M_{\text{eq}}^{\text{nuc}} \sin(\omega^0 t) \exp\{-t/T_2\} \end{aligned} \quad (2.7)$$

The transverse magnetic moment precesses at the nuclear Larmor frequency  $\omega^0$ , slowly decaying at the same time:



**Figure 2.22**  
Decay and oscillation of  
the transverse  
magnetization.

The transverse magnetization decays slowly because it is impossible to maintain exact synchrony between the precessing nuclear magnets. Since the microscopic magnetic fields fluctuate slightly, the precessing nuclear magnets gradually get out of phase with each other. Imagine a large number of clocks, started at the same instant. For the first few hours or days, the clocks show exactly the same time. However, over a period of weeks, small fluctuations in the timing of the different clocks cause them to lose synchrony, and after a year or so the times shown will be completely random. The clocks will have lost coherence with each other.

This decay process is irreversible. Once the transverse magnetization is gone, it cannot be recovered. The clocks cannot be brought back into phase again without starting the whole experiment all over again. This type of process is called *homogeneous decay* in the jargon of NMR.

The time constant  $T_2$  takes into account the homogeneous decay of the precessing macroscopic nuclear magnetization. This time constant has various names, the most common being *transverse relaxation time constant*, *coherence dephasing time constant*, *coherence decay time constant*, and *spin-spin relaxation time constant*. The last of these is misleading, as it seems to imply that the destruction of transverse magnetization requires interactions between the nuclear spins, which is not the case. All that is required is that different spins experience slightly different magnetic fields, so that they precess at slightly different frequencies. This will always be true in a real sample, independent of whether the spins interact with each other.

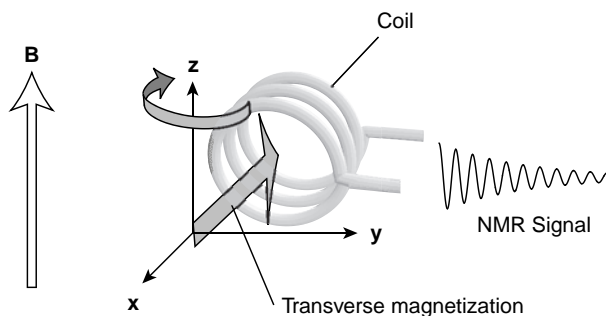
For the NMR of small molecules in liquids,  $T_2$  is typically of the same order of magnitude as  $T_1$ , i.e. several seconds. This implies that the nuclear spins execute several tens of millions of Larmor precession cycles without losing synchrony, which is rather impressive. In other circumstances, such as for large molecules in liquids, or for solids, the transverse relaxation time constant  $T_2$  may be as short as milliseconds.

This picture of transverse spin precession is greatly oversimplified because (i) it assumes that all spins in the sample experience exactly the same magnetic field on the average and (ii) the interactions *between* the nuclear spins are ignored. The true dynamics of nuclear spins are, in reality, considerably more complicated than this. Nevertheless, the conceptual sketch given above is a reasonable first approximation. In certain contexts, such as many NMR imaging experiments, this simple picture is quite adequate.

## 2.8 NMR Signal

The precessing transverse magnetization after an r.f. pulse is very small. Nevertheless, it is detectable, because it oscillates at a very well-defined frequency.

A rotating magnetic moment generates a rotating magnetic field. Through Maxwell's equations, a changing magnetic field is associated with an electric field.<sup>8</sup> If a wire coil is near the sample, then the electric field sets the electrons in the wire in motion, i.e. an oscillating electric current flows in the wire. It is possible to detect this small oscillating current by using a sensitive r.f. detector.



**Figure 2.23**  
The induction of an NMR signal.

Note the geometry of this arrangement: the winding axis of the coil is *perpendicular* to the main magnetic field, in order to detect the precessing *transverse* magnetization.

Essentially the same principle is used in the *bicycle dynamo*, where a rotating magnet, driven by the wheels, generates an electric current that is used to power a lamp.<sup>9</sup>

The oscillating electric current induced by the precessing nuclear transverse magnetization is called the *NMR signal* or *free-induction decay* (FID).

The NMR spectrometer is basically a device capable of: (i) magnetizing the nuclear spins with a large applied magnetic field; (ii) rotating the spin polarizations by r.f. pulses to produce transverse nuclear magnetization; (iii) detecting the small oscillating electric currents induced by the precessing transverse spin magnetization. To some extent, everything else is details.

## 2.9 Electronic Magnetism

Since electronic magnetism is not the subject of this book, this summary is exceedingly brief. As far as NMR is concerned, the main points to note are as follows.

1. In most materials and molecules, the electronic *ground state* has no net electron spin and no net orbital angular momentum. This is a consequence of the Pauli principle, which requires electrons to pair up in stable molecules. Most molecules have an even number of electrons and, therefore, have no magnetic moment in the electronic ground state. However, there are exceptions. For example, molecular oxygen has a triplet ( $S = 1$ ) ground state. Many transition metal compounds have finite electron spin in the ground state. Molecules with an odd number of electrons, such as free radicals, also have finite electron spin in the ground state.
2. The majority of substances have no magnetic moment in the electronic ground state and are weakly *diamagnetic* ( $\chi < 0$ ). The weak diamagnetism of these substances arises from electron orbital currents induced by the applied magnetic field.

3. Substances with magnetic ground states are usually *paramagnetic* ( $\chi > 0$ ). If the electron magnetic moments interact relatively weakly with each other, then it is possible to perform *electron paramagnetic resonance* (EPR) experiments which are closely analogous to NMR experiments (EPR is also called *electron magnetic resonance* (EMR) or *electron spin resonance* (ESR)). There are considerable technical differences between nuclear and electron magnetic resonance, connected with the much larger linewidths, higher frequencies, and shorter time-scales in the EPR case. We will not be concerned further with EPR here.
4. In many magnetic substances, the electron spins on neighbouring magnetic sites interact strongly. This can give rise to strong cooperative effects, such as *ferromagnetism* and *antiferromagnetism*. The direction of spin polarization on one molecular site strongly influences that of its neighbour, which in turn affects its neighbour, and so on. In the end, millions of spins may be aligned mutually by a small external perturbation, in a sort of molecular ‘domino effect’. Cooperative electronic magnetism is often strong enough to be directly tangible. How long would it have taken for humanity to discover the magnetic field if naturally occurring pieces of ferromagnetic iron from meteorites did not exist?

For various reasons, NMR is relatively difficult in paramagnetic and ferromagnetic materials. This book is concerned with nuclear magnetism in diamagnetic materials, in which case the existence of electronic magnetism can be more or less ignored. This is not because it is small; on the contrary, electronic magnetism is typically many orders of magnitude larger than the nuclear magnetism, even in diamagnetic substances. Electronic diamagnetism is unimportant in NMR not because it is small, but because it is time independent. It simply leads to a small change of the bulk magnetic field inside the sample, which is easily taken into account by a rather trivial correction term.

The macroscopic aspects of electronic diamagnetism, therefore, are not very important in NMR. However, there is also a *microscopic* aspect to electronic magnetism that has more important consequences. The distribution of electrons in matter is very inhomogeneous when viewed on a molecular distance scale: most of the electrons are very close to the nuclei or are located in the chemical bonds between the nuclei. Nuclear spins at different sites within the same molecule, therefore, experience slightly different magnetic fields. This important effect is called the *chemical shift*, which is introduced in Chapter 3.

## Notes

1. **B** is also called the *magnetic flux density field* or the *magnetic induction field*. The field **B** is often confused with a different field, conventionally notated **H**, which is introduced for mathematical convenience in certain calculations. **H** may be regarded as the field **B** corrected for the bulk magnetism of the material, and has no ‘fundamental significance’. The **H** field is not used in this book.
2. The relationship shown by Equation 2.2 is not always valid. In anisotropic materials, such as solids and liquid crystals, the induced magnetic moment is not necessarily in the same direction as the applied field. The magnetic properties of anisotropic substances are described by a *susceptibility tensor*, which may be written as a  $3 \times 3$  matrix.
3. The proportionality of the magnetic moment and the spin angular momentum may be deduced from the *Wigner–Eckart theorem* of quantum mechanics (see *Further Reading*).
4. Juan Paniagua has pointed out that the behaviour of a compass needle is not *fundamentally* different from that of a nuclear spin. The magnetism of a compass needle is derived from electron spins and is therefore also associated with an angular momentum. As a consequence, even a compass needle precesses around the magnetic field, at least in principle. The main difference is that the electron spins in a compass needle have very rapid spin–lattice relaxation. As a result, the magnetic energy is rapidly

converted into thermal energy before a significant amount of precession takes place. For a nucleus, on the other hand, the slow relaxation allows many millions of precession circuits to take place before relaxation leads to reorientation.

5. In many NMR experiments, it is not necessary to consider the sign of the precession frequency in order to perform the experiment. This is because one usually interacts with the nuclei with a *linearly polarized* r.f. field, rather than a *rotating* r.f. field (see Section 8.4.2). Despite this, I carefully include the sign of precession throughout this book, for the following reasons: (i) there are some NMR experiments, especially in NMR imaging, where a *rotating* r.f. field is used – in these cases, it is essential to get the sense of rotation correct in order to perform the experiment; (ii) careful consideration of signs is necessary in many experiments in order to interpret the data correctly; (iii) I’m just irrationally obsessed by the issue.
6. It is possible to detect longitudinal nuclear magnetism by using the very sensitive detector known as a superconducting quantum interference device (SQUID); see C. Connor, *Adv. Magn. Opt. Reson.* **15**, 201 (1990).
7. The axes mentioned here refer to the rotating reference frame, as explained in Chapter 10.
8. The relevant Maxwell equation is

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

which links the time derivative of the magnetic field to a ‘circulating’ electric field. In NMR, the circulating electric field drives the electrons around the windings of the coil (see *Further Reading*).

9. In practice, a bicycle dynamo is usually constructed the other way round, with the coil rotating and the magnet fixed.

## Further Reading

- For the relationship of the nuclear magnetic moment to the spin angular momentum, and the Wigner–Eckart theorem, see A. Abragam, *The Principles of Nuclear Magnetism*, Clarendon Press, Oxford, 1961, and E. Merzbacher, *Quantum Mechanics*, 3rd Edition, Wiley, New York, 1998.
- For texts on electromagnetism, see B. I. Bleaney and B. Bleaney, *Electricity and Magnetism*, Oxford University Press, Oxford, 1976, and J. D. Jackson, *Classical Electrodynamics*, Wiley, New York, 1975.

## Exercises

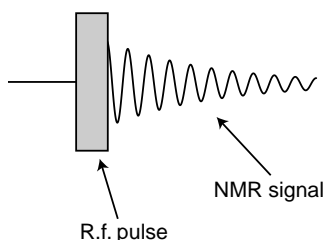
- 2.1 A sample containing magnetic nuclei is left to reach thermal equilibrium in zero magnetic field. A magnetic field is switched on suddenly along the  $z$ -axis. After some time, the direction of the field is instantaneously switched to the  $x$ -axis. Predict the motion of the three components of the nuclear spin magnetization through this sequence of events, and describe the dynamics of the nuclear spins on a microscopic level.

# 3 NMR Spectroscopy

## 3.1 A Simple Pulse Sequence

The magnetic nuclear spins in a sample are detected through their *FID*. As discussed above, the *FID* is induced by (i) allowing them to reach thermal equilibrium in a large magnetic field; (ii) rotating the nuclear spin polarizations by an *r. f. pulse*; and (iii) detecting and amplifying the weak *r. f.* signal that is emitted as the spins resume their precessional motion in the magnetic field.

This basic NMR technique is often depicted by the following icon:



**Figure 3.1**  
A simple pulse sequence.

showing the *r. f.* pulse and the induced *NMR* signal. We will see many such iconic pulse sequence representations in the following pages.

In the chapters below, we investigate the theory behind this process, and the instrumentation that is used to carry it out effectively. Before going into details, let us investigate, on a highly qualitative level, what the *FID* tells us about the nuclear spins and the sample in which they are located.

## 3.2 A Simple Spectrum

As discussed before, the transverse magnetization components after the *r.f.* pulse have the following form:

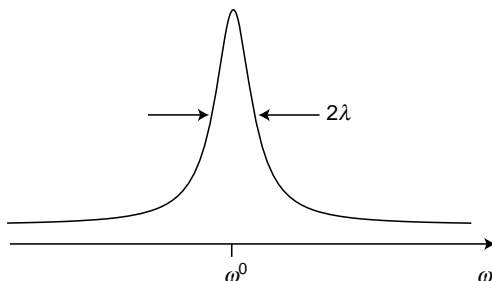
$$\begin{aligned}M_y^{\text{nuc}} &= -M_{\text{eq}}^{\text{nuc}} \cos(\omega^0 t) \exp\{-t/T_2\} \\M_x^{\text{nuc}} &= M_{\text{eq}}^{\text{nuc}} \sin(\omega^0 t) \exp\{-t/T_2\}\end{aligned}\quad (3.1)$$

Both components oscillate at the nuclear Larmor frequency  $\omega^0$  and decay with the time constant  $T_2$ .

Suppose that these two oscillating magnetization components  $M_y^{\text{nuc}}(t)$  and  $M_x^{\text{nuc}}(t)$  are measured as a function of time, converted into digital form, and stored in a computer. In fact, the experiment cannot really

be done this way, for technical reasons.<sup>1</sup> Nevertheless, let us persist with this ‘thought experiment’, for the sake of argument. Later on, the true operation of an NMR spectrometer is discussed.

The signals described in Equation 3.1 contain enough information to determine both the magnitude of the Larmor frequency  $\omega^0$  and the decay time constant  $T_2$ . The larger the Larmor frequency  $\omega^0$ , the faster the magnetization oscillates; and the larger the decay time constant  $T_2$ , the more slowly the signals decay. The computer analyses the oscillations and presents the result as the following curve:



**Figure 3.2**  
A simple spectrum.

The horizontal axis is an angular frequency axis, marked by the symbol  $\omega$ . The centre of the peak is placed at the Larmor frequency of the spins, equal to  $\omega^0$ .

In practice, this analysis is performed by a numerical operation called a *Fourier transform*, which is described fully in Chapter 5.

The above plot is a simple example of an *NMR spectrum*. The Fourier transform generates a function with the following mathematical form:

$$S(\omega) = \frac{\lambda}{\lambda^2 + (\omega - \omega^0)^2} \quad (3.2)$$

The value of  $S$  is at a maximum when the frequency coordinate  $\omega$  is equal to the Larmor frequency  $\omega^0$ , since  $\omega - \omega^0$  vanishes in this case. The value of  $S$  is small when the frequency coordinate  $\omega$  is far from the centre of the peak.

The parameter  $\lambda$  is called the *coherence decay rate constant*, and is equal to the inverse of the transverse relaxation time constant  $T_2$ :

$$\lambda = \frac{1}{T_2} \quad (3.3)$$

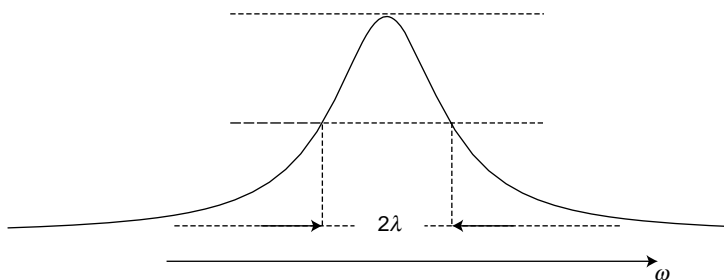
The function in Equation 3.2 is called an *absorption Lorentzian*. It is encountered very often in the theory of NMR.

The frequency axis in the NMR spectrum is labelled with the symbol  $\omega$ . As mentioned in Section 2.5, this book uses the symbol  $\omega$  to indicate an *angular frequency*, measured in units of radians per second. Angular frequency units are most convenient for NMR theory, since the equations have their simplest form in such units.

The Lorentzian peakshape has a finite width. As marked on the diagram, the *peakwidth at half-height*, measured in  $\text{rad s}^{-1}$ , is equal to  $2/T_2 = 2\lambda$ . This is defined in the following way: Determine the maximum peak height, and then draw a horizontal line at half this vertical value:

**Figure 3.3**

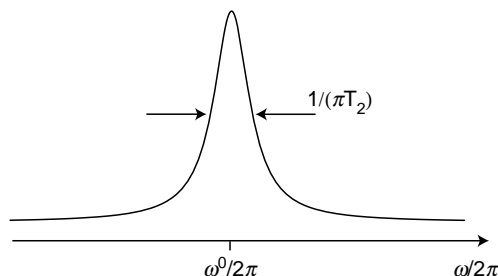
Full width at half-height.



The horizontal line intersects the Lorentzian peak at two points, which are separated by  $2\lambda$  along the horizontal axis.

Since  $\lambda$  is equal to the inverse of the transverse relaxation time constant  $T_2$ , this implies that the peakwidth at half-height is equal to  $2/T_2$ , in units of radians per second.

The same NMR spectrum appears as follows when using a frequency scale of hertz:

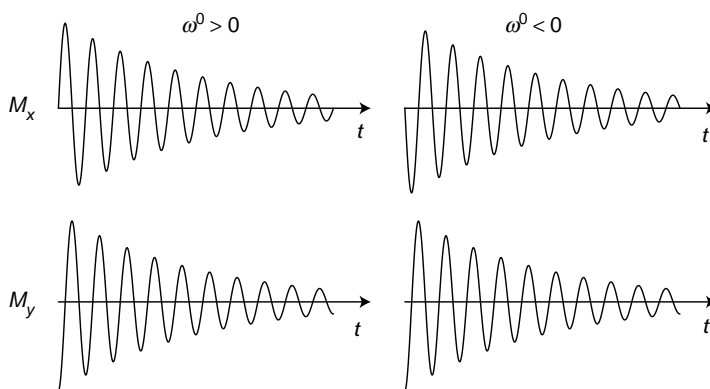
**Figure 3.4**

Frequency scale in hertz.

The peakwidth in units of hertz is given by  $2\lambda/2\pi = \lambda/\pi = 1/(\pi T_2)$ .

Note that a *rapid* decay of the transverse magnetization corresponds to a *broad* spectral peak. A *slow* decay of the transverse magnetization corresponds to a *narrow* spectral peak.

The two transverse magnetization components in Equation 3.1 contain enough information to determine the *sign* of the Larmor frequency  $\omega^0$ , as well as its magnitude. Note the different appearance of the two oscillating components, for Larmor frequencies of the opposite sign:

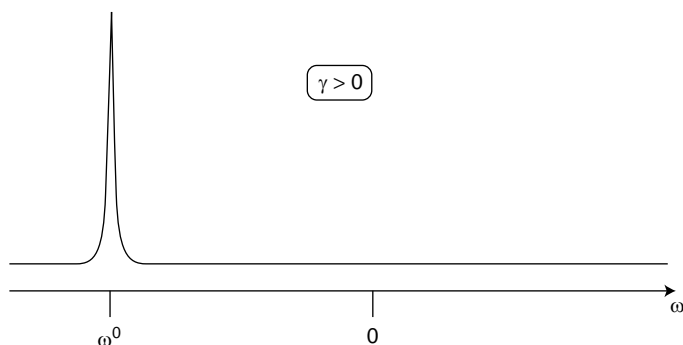
**Figure 3.5**

Transverse magnetization components for opposite signs of  $\omega^0$ .

In this book, we will always be faithful to the sign of the Larmor frequency. As described in Section 2.4, the sign of the spin precession is a very real physical property of the nucleus, as real as the mass and the

charge. Since the Larmor frequency is given by  $\omega^0 = -\gamma B^0$ , and the magnetic field  $B^0$  is always positive, the sign of the Larmor frequency is opposite to the sign of the gyromagnetic ratio  $\gamma$ .

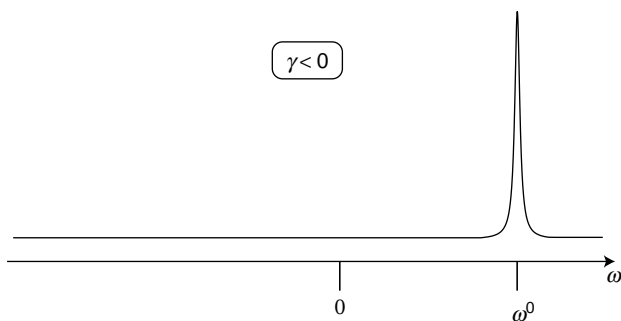
Most nuclear spins have positive  $\gamma$  and, therefore, have negative Larmor frequencies  $\omega^0$ . In the 'NMR thought experiment' described above, the spectral peak for these nuclei would appear at negative frequencies:



**Figure 3.6**  
NMR spectrum for positive  $\gamma$ .

(The width of the peak is greatly exaggerated.)

Some nuclear spins have negative  $\gamma$  and, therefore, have positive Larmor frequencies  $\omega^0$ . In the 'NMR thought experiment', the spectral peak would appear at positive frequencies:

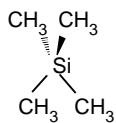


**Figure 3.7**  
NMR spectrum for negative  $\gamma$ .

(The width of the peak is greatly exaggerated again.)

### 3.3 Isotopomeric Spectra

Now consider a real chemical compound and its NMR spectrum in the 'thought experiment'. Suppose that the sample is a tube containing pure liquid tetramethylsilane,  $\text{Si}(\text{CH}_3)_4$  (TMS). The molecular structure of this compound is as follows:



**Figure 3.8**  
Tetramethylsilane  
(TMS).

This sample contains three chemical elements, Si and C, H, with the common isotopes shown in Table 3.1. It follows that the sample is a mixture of four major isotopomers (see Table 3.2).



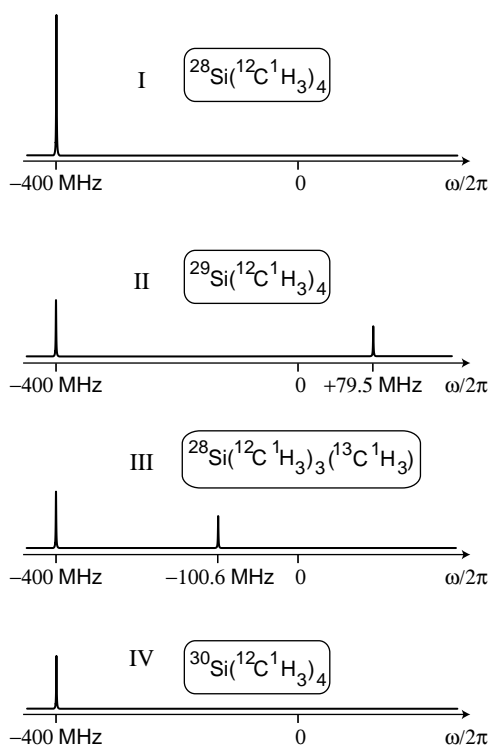
**Table 3.1** Common isotopes in TMS.

Isotope	Spin	Natural abundance/%	$\gamma/10^6 \text{ rad s}^{-1} \text{ T}^{-1}$
$^1\text{H}$	1/2	$\sim 100$	267.5
$^{12}\text{C}$	0	$\sim 98.9$	—
$^{13}\text{C}$	1/2	$\sim 1.1$	67.3
$^{28}\text{Si}$	0	$\sim 92.2$	—
$^{29}\text{Si}$	1/2	$\sim 4.7$	−53.2
$^{30}\text{Si}$	0	$\sim 3.1$	—

The abundances of the different isotopomers are easily calculated using simple statistical arguments. For example, the probability of a Si nucleus having mass number 28 is around 0.953, whereas the probability of a C nucleus having mass numbers 12 or 13 is around 0.989 and 0.011 respectively. The probability of a TMS molecule having one  $^{28}\text{Si}$  nucleus, three  $^{12}\text{C}$  nuclei, and one  $^{13}\text{C}$  nucleus is therefore  $\sim 4 \times 0.922 \times 0.989^3 \times 0.011 \cong 0.0392 = 3.92\%$  (the factor of 4 is needed because it doesn't matter which of the four carbon nuclei is  $^{13}\text{C}$ , so there are four equivalent ways of getting the same isotopomer).

Each isotopomer emits a different NMR signal. Suppose that the magnetic field is 9.3950 T, so that the Larmor frequency of the proton spins is exactly  $\omega^0/2\pi = -400.000 \text{ MHz}$ . In this magnetic field, the Larmor frequency of the  $^{13}\text{C}$  spins is  $\omega^0/2\pi = -100.577 \text{ MHz}$ , and the Larmor frequency of the  $^{29}\text{Si}$  spins is  $\omega^0/2\pi = +79.460 \text{ MHz}$ . The  $^{12}\text{C}$ ,  $^{28}\text{Si}$  and  $^{30}\text{Si}$  isotopes are 'silent', because these nuclei have no spin and are not magnetic.

In the 'thought experiment', we imagine that the complete NMR spectrum, generated by all nuclei at the same time, is detected. (To repeat, this is not actually possible, for technical reasons.) The individual NMR spectra from isotopomers I, II, III and IV would have the following appearance (the peak heights are not to scale):

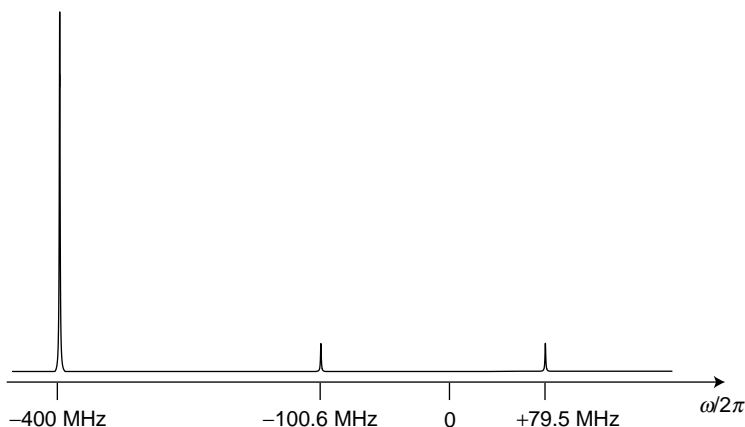


**Figure 3.9**  
Subspectra of TMS  
isotopomers.

**Table 3.2** Major isotopomers in TMS. Rare species containing  $^2\text{H}$  nuclei, more than one  $^{13}\text{C}$  nucleus, or a  $^{13}\text{C}$  nucleus as well as a  $^{29}\text{Si}$  nucleus are neglected.

Isotopomer	Isotopic composition	Natural abundance/%
I	$^{28}\text{Si}(^{12}\text{C}^1\text{H}_3)_4$	$\sim 88.2$
II	$^{29}\text{Si}(^{12}\text{C}^1\text{H}_3)_4$	$\sim 4.5$
III	$^{28}\text{Si}(^{12}\text{C}^1\text{H}_3)_3(^{13}\text{C}^1\text{H}_3)_1$	$\sim 3.9$
IV	$^{30}\text{Si}(^{12}\text{C}^1\text{H}_3)_4$	$\sim 3.0$

The *total* NMR spectrum from the TMS sample is sketched in Figure 3.10.



**Figure 3.10**  
Total TMS spectrum.

These spectra use absolute frequency axes and neglect the spectral fine structure (see Sections 3.7 and 3.8).

Note carefully that the major spectral features are produced from different molecules. The proton peak at  $\omega^0/2\pi = -400.00$  MHz comes mainly from isotopomers I and IV. The  $^{29}\text{Si}$  peak at  $\omega^0/2\pi = +79.460$  MHz, on the other hand, comes mainly from isotopomer II. The  $^{13}\text{C}$  peak at  $\omega^0/2\pi = -100.577$  MHz comes mainly from isotopomer III.

The widths of the spectral peaks are greatly exaggerated in the spectra shown above. In reality, they are extremely narrow. The transverse relaxation time constant  $T_2$  for protons in liquid TMS is around 5 s. This corresponds to a peakwidth-at-half-height of  $1/(\pi T_2) \cong 50$  mHz, which is about 10 orders of magnitude less than the Larmor frequencies themselves. If the spectra were drawn to scale, the width of the NMR peaks would be around the size of a single ink molecule!

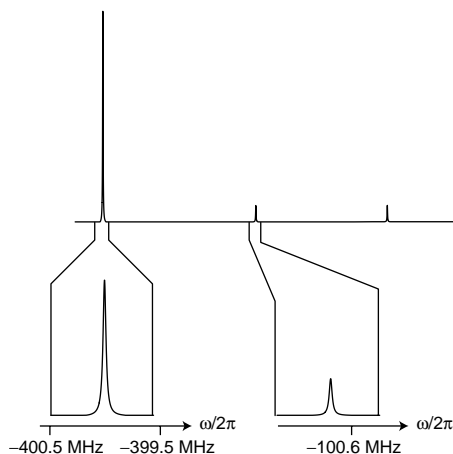
### 3.4 Relative Spectral Frequencies: Case of Positive Gyromagnetic Ratio

In reality, it is not possible to examine the entire NMR spectrum at once. It is only possible to access a small number of narrow frequency ‘bands’ or ‘windows’.

The NMR spectrometer has a set of independent frequency *channels*, each of which may be *tuned* so as to examine a single narrow frequency window. For example, a two-channel spectrometer may be used to examine narrow frequency windows around the  $^1\text{H}$  and  $^{13}\text{C}$  Larmor frequencies. For the TMS spectrum discussed above, the idea is as follows:

**Figure 3.11**

Regions of the TMS spectrum.

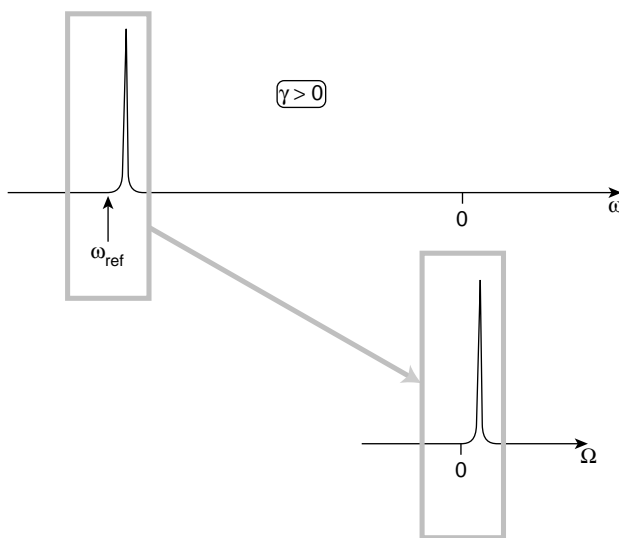


Only the  $^1\text{H}$  and  $^{13}\text{C}$  signals are visible with the spectrometer in this configuration.

In practice, the bandwidth of each 'window' is around 1 MHz or less, which is almost always smaller than the separation between nuclear Larmor frequencies of different isotopes. As a result, each spectrometer channel only detects the NMR signals from a single isotopic species, except in very rare cases. One therefore speaks of the ' $^1\text{H}$  channel', or the ' $^{13}\text{C}$  channel', and so on, when referring to the different frequency windows accessible to a given NMR instrument.

The centre frequency of each 'window' is under operator control. In this book, the centre frequency of a given channel is called the *reference frequency*, and denoted  $\omega_{\text{ref}}$  (in units of radians per second). The sign of the reference frequency is the same as the sign of the nuclear Larmor frequency for the isotope detected in that channel. The reference frequency in units of hertz is written  $\omega_{\text{ref}}/2\pi$ .

The NMR spectrometer always determines *relative* frequencies, produced by subtracting the reference frequency  $\omega_{\text{ref}}$  from the frequency coordinate. This may be thought of as a shift of the spectral window, to bring the reference frequency to the new zero position:

**Figure 3.12**

Constructing a spectrum using a relative frequency scale (case of positive  $\gamma$ ).

In this book, relative frequencies are denoted by the symbol  $\Omega$ :

$$\Omega = \omega - \omega_{\text{ref}} \quad (3.4)$$

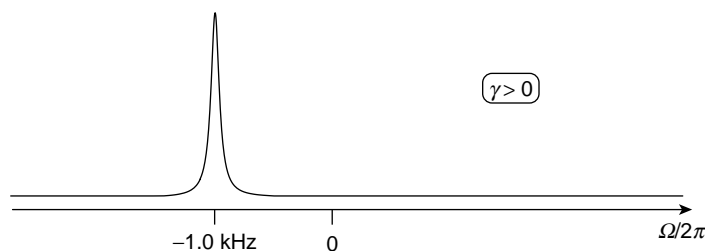
For example, the Larmor frequency  $\omega^0$ , relative to the spectrometer reference frequency  $\omega_{\text{ref}}$ , is defined as

$$\Omega^0 = \omega^0 - \omega_{\text{ref}} \quad (3.5)$$

As usual, the symbol  $\Omega$  indicates an angular frequency in units of radians per second. Frequencies in units of hertz are denoted  $\Omega/2\pi$  and are obtained by dividing the angular frequency by  $2\pi$ .

The relative Larmor frequency  $\Omega^0$  has a sign, indicating whether the absolute Larmor frequency  $\omega^0$  is more negative or more positive than the spectrometer reference frequency  $\omega_{\text{ref}}$ . For example, suppose that the nuclear Larmor frequency for protons is exactly  $\omega^0/2\pi = -400.000\,000$  MHz. If the reference frequency of the spectrometer ‘window’ is set to  $\omega_{\text{ref}}/2\pi = -399.999\,000$  MHz, then the centre of the NMR peak appears at  $\Omega^0/2\pi = -1$  kHz. If the reference frequency of the spectrometer ‘window’ is set to  $\omega_{\text{ref}}/2\pi = -400.001\,000$  MHz, then the centre of the NMR peak appears at  $\Omega^0/2\pi = +1$  kHz.

By convention the NMR spectra of spins with positive  $\gamma$  (the most common case) are plotted with the frequency axis  $\Omega$  increasing from left to right. Signals with *negative* values of  $\Omega^0$  appear on the left-hand side of the spectrum; signals with *positive* values of  $\Omega^0$  appear on the right-hand side of the spectrum. For example, the case with reference frequency  $\omega_{\text{ref}}/2\pi = -399.999\,000$  MHz and Larmor frequency  $\omega^0/2\pi = -400.000\,000$  MHz appears as follows:



**Figure 3.13**  
NMR spectrum using a relative frequency scale (case of positive  $\gamma$ ).

The relative Larmor frequency  $\Omega^0$  is also known as the *resonance offset* or the *Larmor frequency in the rotating frame*. These names are explained in Chapter 10.

⚠ There is confusion about frequency axes in the NMR literature: very often the frequency axis is labelled *as if* positive relative frequencies appeared on the left, and negative relative frequencies appeared on the right.<sup>2</sup> Nevertheless, the sense in which the *spectrum* is plotted (but not necessarily the way the frequency axis is labelled!) *always* conforms to the conventions used in this book.

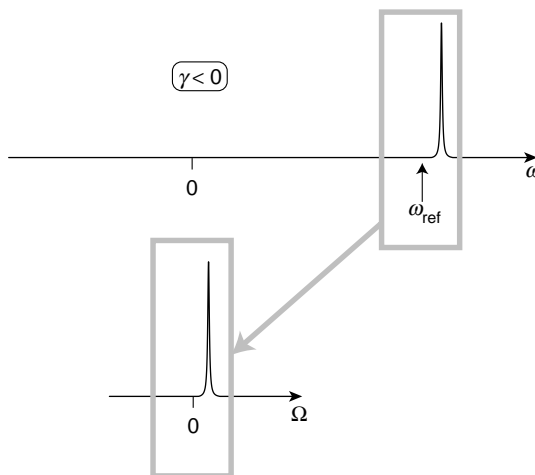
### 3.5 Relative Spectral Frequencies: Case of Negative Gyromagnetic Ratio

Unfortunately, the treatment of the NMR signals from spins with negative  $\gamma$  generates even more confusion.

Spins with negative  $\gamma$  have positive Larmor frequencies  $\omega^0$ . The reference frequency  $\omega_{\text{ref}}$  of the corresponding spectrometer channel is also positive. The spectrometer detects relative frequencies, defined according to

$$\Omega^0 = \omega^0 - \omega_{\text{ref}}$$

One may imagine the spectral window to be shifted by  $-\omega_{\text{ref}}$ , so that it is centred around zero frequency:

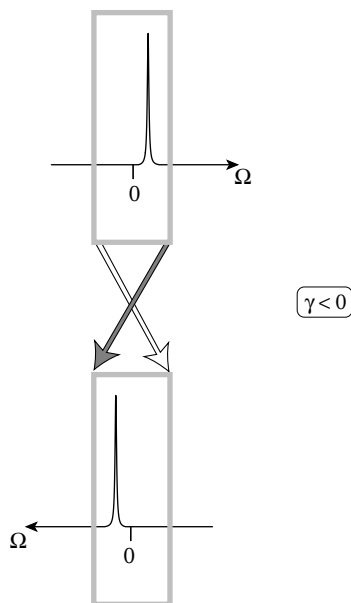


**Figure 3.14**

Constructing a spectrum using a relative frequency scale (case of negative  $\gamma$ ).

For example, suppose that the nuclear Larmor frequency for  $^{29}\text{Si}$  is exactly  $\omega^0/2\pi = +79.460\,000$  MHz. If the reference frequency of the spectrometer ‘window’ is set to  $\omega_{\text{ref}}/2\pi = +79.461\,000$  MHz, then the centre of the NMR peak appears at  $\Omega^0/2\pi = -1$  kHz. If the reference frequency of the spectrometer ‘window’ is set to  $\omega_{\text{ref}}/2\pi = +79.459\,000$  MHz, then the centre of the NMR peak appears at  $\Omega^0/2\pi = +1$  kHz.

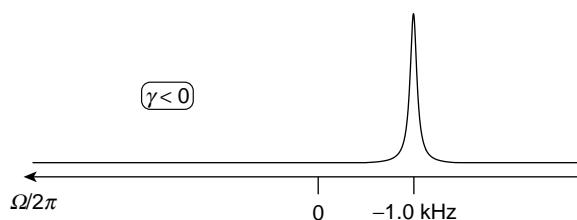
⚠ Now here’s a difficult thing: For technical reasons,<sup>3</sup> the spectra from spins with negative  $\gamma$  are always plotted with the frequency coordinate running ‘backwards’, i.e. with negative relative frequencies on the right and positive relative frequencies on the left! In other words, the spectrum is ‘flipped over’ before it is plotted:



**Figure 3.15**

The conventional reversal of the frequency scale, in the case of negative  $\gamma$ .

For example, the case with reference frequency  $\omega_{\text{ref}}/2\pi = +79.461\,000$  MHz and Larmor frequency  $\omega^0/2\pi = +79.460\,000$  MHz is plotted as follows:

**Figure 3.16**

NMR spectrum using a relative frequency scale (case of negative  $\gamma$ ).

As discussed in Section 3.7, this way of plotting spectra ensures that the chemical shift scale always increases from right to left, which is a universal convention in NMR.

The reader is again advised to ignore the frequency axis *labelling* of NMR spectra in the literature.<sup>2</sup> The way the *spectra themselves* are presented is always consistent with the usage in this book.

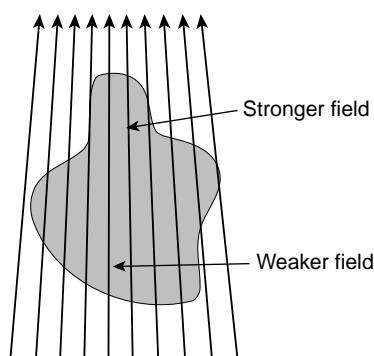
## 3.6 Inhomogeneous Broadening

So far, we have assumed that the magnetic field  $B^0$  is the same in all parts of the sample, i.e. that the magnetic field is perfectly *homogeneous*. In practice, this may not be the case, since

- It is difficult to generate a perfectly homogeneous magnetic field, for technical reasons.
- The sample itself tends to distort the applied magnetic field, because of its magnetic susceptibility.
- In some NMR experiments, spatially dependent magnetic fields are *deliberately* applied, using specially designed additional field coils. This is the case in, for example, NMR imaging experiments.

An inhomogeneous magnetic field may be denoted  $B^0(\mathbf{r})$ , indicating that the value of the magnetic field depends on the position in space, denoted by the vector  $\mathbf{r}$ .

Suppose, for example, that the magnetic field  $B^0$  is stronger at the 'top' of the sample than at the 'bottom'. This situation could be depicted as follows:

**Figure 3.17**

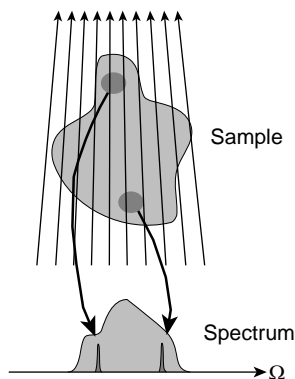
An inhomogeneous magnetic field

where closely spaced 'magnetic flux lines' indicate a stronger field, and more widely spaced 'magnetic flux lines' indicate a weaker field. This diagram is greatly exaggerated – in practice, the magnetic flux density differs only by about one part in a thousand even in NMR imaging experiments.

Suppose that the NMR spectrum is taken of nuclei with positive  $\gamma$ , such as protons. Since, the Larmor frequency  $\omega^0$  is proportional to the magnetic field, the nuclear Larmor frequency is spatially dependent:

$$\omega^0(\mathbf{r}) = -\gamma B^0(\mathbf{r})$$

With the magnetic field configuration indicated above, nuclear spins at the top of the sample have a *more negative* Larmor frequency, and appear on the *left-hand side* of the spectrum. Nuclear spins at the bottom of the sample have a *less negative* Larmor frequency, and appear on the *right-hand side* of the spectrum. The total proton NMR spectrum is a superposition of very many narrow peaks, each one coming from a different place in the sample:

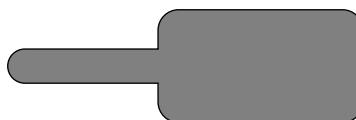


**Figure 3.18**  
An inhomogeneously broadened spectrum.

This effect is called *inhomogeneous broadening*. Since the magnetic field is inhomogeneous, the width of the NMR peak may be much larger than would be predicted by the  $1/(\pi T_2)$  formula.

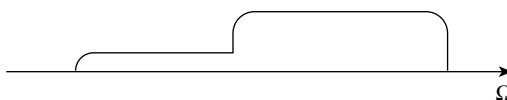
For a long time, inhomogeneous broadening was assumed to be a nuisance, and great efforts were made in order to eliminate it. However, in 1972, Paul Lauterbur and Peter Mansfield realized independently that controlled inhomogeneous broadening can be enormously useful because it causes the NMR spectrum to depend on the *shape* of the sample and the distribution of magnetic spins within it. They received the Nobel Prize for this insight in 2003. The inhomogeneously broadened NMR spectrum is a way of examining the *spatial structure* of an object.

Consider, for example, the following bottle-shaped object, filled with a sample (such as water) containing magnetic nuclear spins (protons, in this case):



**Figure 3.19**  
A bottle.

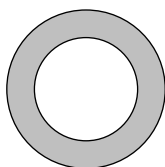
Suppose this sample is placed in a magnetic field that depends on position in the way described before. The top of the sample is in a stronger field than the bottom of the sample. If the magnetic field inhomogeneity is carefully controlled, so that the field varies linearly with respect to vertical position, then the NMR spectrum generated by the bottle-shaped sample has the following appearance:



**Figure 3.20**  
Spectrum of a bottle in a linear field gradient.

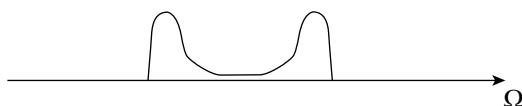
since the total amplitude of the NMR spectrum at a particular frequency depends on the number of spins with just that Larmor frequency. There are fewer spins in the 'neck' than in the 'body', so the height of the spectrum is less on the left than on the right. The 'bottle-shaped' profile of the sample is reproduced (lying down) along the frequency axis of the NMR spectrum.

If the sample had a ring shape:



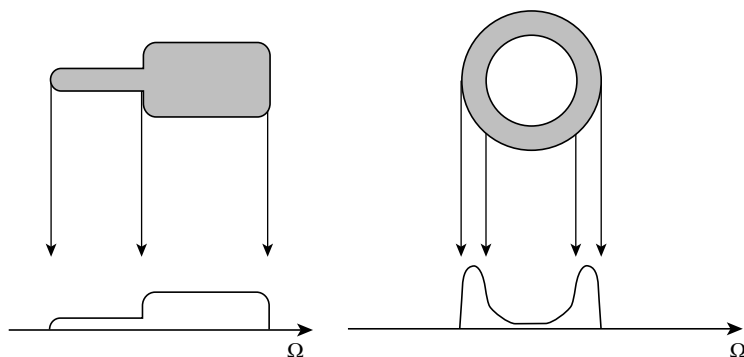
**Figure 3.21**  
A ring.

and the magnetic field was unchanged, then the NMR spectrum would look as follows:



**Figure 3.22**  
Spectrum of a ring in a linear field gradient.

The NMR spectra betray the *spin density distribution* in the sample, *projected* onto the vertical axis:



**Figure 3.23**  
Spatial projections and NMR spectra in a field gradient.

An NMR spectrum taken in the presence of a magnetic field gradient is therefore a strange sort of image of the object, flattened onto one axis. Section 12.6 discusses how the method may be extended to remove this flattening effect, allowing one to build up two- or three-dimensional pictures.

This is *NMR imaging*, a method of immense medical value. NMR imaging allows doctors and surgeons to visualize the interior of the human body, without any invasive surgery or damaging high-energy radiation.

In order to avoid the term 'nuclear', which tends to cause anxiety, NMR imaging is generally known in the medical world as *magnetic resonance imaging* (MRI).

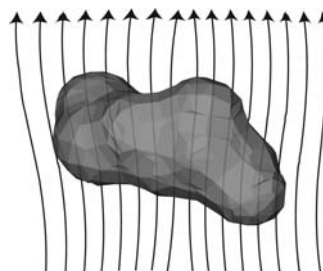
## 3.7 Chemical Shifts

Let us return to the situation in which the magnetic field is perfectly homogeneous, i.e. exactly the same over the entire volume of the sample. In this case, there is no inhomogeneous broadening, so the width of the NMR peaks is equal to the homogeneous peakwidth ( $1/(\pi T_2)$  in units of hertz).



Since the magnetic field is homogeneous, it might be expected that each nuclear isotope would give a single narrow peak, reflecting its Larmor frequency in that magnetic field. For most substances, this turns out to be incorrect. Although the magnetic field may be made very uniform on a *macroscopic* scale, it always has small 'wrinkles' on a *microscopic* scale.

These microscopic magnetic wrinkles are caused by the fact that matter is made up of atoms. Although a sample of water appears to be very homogeneous on a macroscopic distance scale, it is not at all homogeneous when viewed on a molecular distance scale of a nanometre or less. The grainy microscopic environment creates a slight lumpiness in the magnetic field. The size of these small magnetic wrinkles is about the size of a single molecule:



**Figure 3.24**  
Microscopic field  
inhomogeneities.

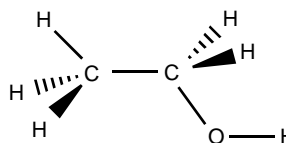
Because of these microscopic wrinkles, the precise Larmor frequency of a given nucleus depends on the atomic environment.

There are two important microscopic effects that influence the Larmor frequency of a given nuclear spin:

- Since electrons are magnetic, the nuclear Larmor frequency depends on the local *electronic* environment. This effect is called the *chemical shift* in diamagnetic materials, the *Knight shift* in metals and superconductors, and the *paramagnetic shift* in paramagnetic substances.
- The Larmor frequency depends on the presence of *other magnetic nuclear spins* in the same molecule, and also the directions of their magnetic moments. This effect is called the *nuclear spin-spin coupling*.

These effects are very useful because they allow the atomic nuclei to behave as microscopic radio transmitters, sending out highly local molecular information encoded as radio waves. The nuclear magnetic signals reveal the electronic and nuclear environment of the observed spins.

Consider, for example, the chemical compound ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ), which is a liquid at room temperature. The molecular structure is as follows:



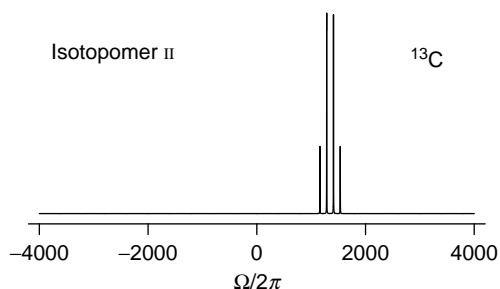
**Figure 3.25**  
Ethanol.

The most common isotopomers are shown in Table 3.3.

**Table 3.3** Major isotopomers in ethanol.

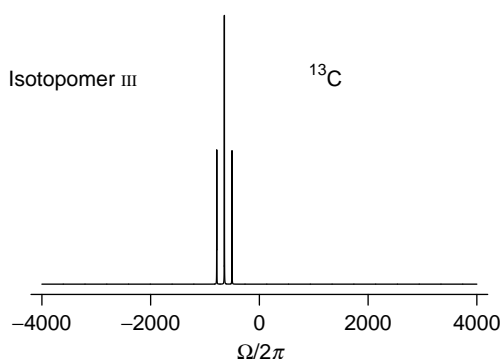
	Isotopomer	Natural abundance/%
I	$^{12}\text{C}^1\text{H}_3^{12}\text{C}^1\text{H}_2^{16}\text{O}^1\text{H}$	$\sim 97.8$
II	$^{13}\text{C}^1\text{H}_3^{12}\text{C}^1\text{H}_2^{16}\text{O}^1\text{H}$	$\sim 1.1$
III	$^{12}\text{C}^1\text{H}_3^{13}\text{C}^1\text{H}_2^{16}\text{O}^1\text{H}$	$\sim 1.1$

The  $^{13}\text{C}$  spectrum of ethanol is generated predominantly by isotopomers of type II and III. If the magnetic field is  $B^0 = 4.70\text{ T}$ , then the subspectrum from isotopomer II has the following form:

**Figure 3.26**

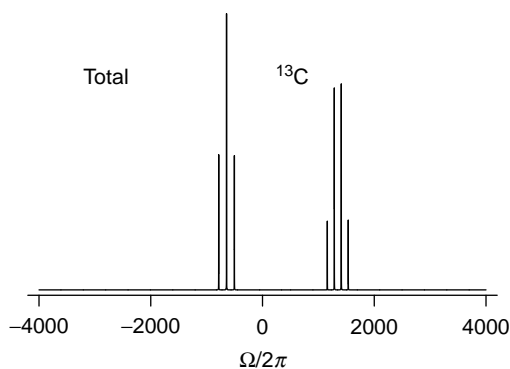
$^{13}\text{C}$  spectrum of ethanol isotopomer II in a field of 4.7 T.

The subspectrum from isotopomer III has the form shown here:

**Figure 3.27**

$^{13}\text{C}$  spectrum of ethanol isotopomer III in a field of 4.7 T.

The total  $^{13}\text{C}$  NMR spectrum is a superposition of these two subspectra, and appears as follows:

**Figure 3.28**

Total  $^{13}\text{C}$  spectrum of ethanol in a field of 4.7 T.

The form of this spectrum is the result of two effects:

- Each  $^{13}\text{C}$  peak is split into a *multiplet*, meaning a group of equally spaced peaks with a symmetrical intensity pattern.
- The multiplet from isotopomer II is shifted with respect to the multiplet from isotopomer III, by 1991 Hz in the positive direction.

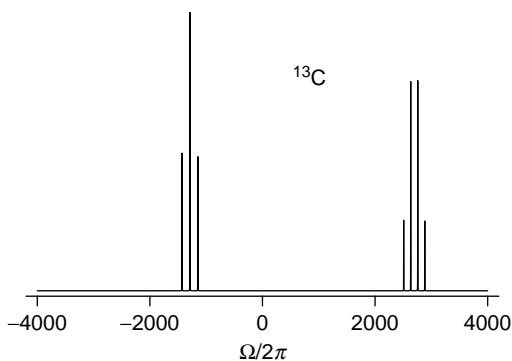
We will consider the multiplet structure later. For the moment, consider the 1991 Hz frequency shift between the  $^{13}\text{C}$  peaks of the two isotopomers.

This shift arises because the electrons in the outer atomic shells, and in the chemical bonds holding the ethanol molecule together, generate small magnetic fields that add to or subtract from the external magnetic field  $B^0$ . In some parts of the molecule the magnetic field is enhanced, in other places it is decreased, compared with the applied external magnetic field. The precession frequency of a given atomic nucleus is proportional to the local value of the magnetic field. As a result, the Larmor frequency depends on the location of the nucleus in the molecule and on details of the electronic structure.

This effect is called the *chemical shift* because the induced field is generated by the valence and bonding electrons, which are also heavily implicated in the chemical properties of the molecule.

The chemical shift (measured in frequency units) is *field dependent*. If the magnetic field is increased, then the chemical shift also increases. To a very good approximation, *the chemical shift, measured in frequency units, is linearly proportional to the applied magnetic field*.

If the external magnetic field is increased to  $B^0 = 9.40\text{ T}$ , then the  $^{13}\text{C}$  NMR spectrum has the following appearance:



**Figure 3.29**  
Total  $^{13}\text{C}$  spectrum of ethanol in a field of 9.40 T.

The multiplet structure is the same, but the frequency difference between the isotopomer II and isotopomer III signals is doubled, and is given by 3983 Hz.

Since the nuclear Larmor frequency and the chemical shift are both proportional to the applied magnetic field, the ratio of these two quantities is fixed. In practical applications, it is convenient to specify chemical shifts in terms of this ratio, since it only depends on the sample, not on the instrument. The field-independent expression for the chemical shift is

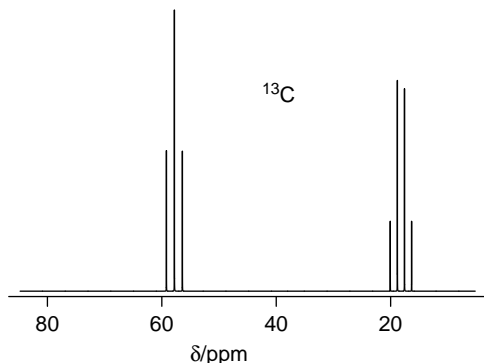
$$\delta = \frac{\omega^0 - \omega_{\text{TMS}}^0}{\omega_{\text{TMS}}^0} \quad (3.6)$$

where  $\omega^0$  is the Larmor frequency of a particular nucleus, in the molecular site of interest, and  $\omega_{\text{TMS}}^0$  is the Larmor frequency of the same isotope in a *reference compound* (TMS) exposed to the same applied field. If the applied field is increased, then both quantities  $\omega^0$  and  $\omega_{\text{TMS}}^0$  increase in the same proportion, so the ratio  $\delta$  remains constant.

The equation assumes that TMS is chosen as the reference compound, which is often the case. By definition, TMS spins have a chemical shift  $\delta = 0$ . TMS is particularly suitable as the chemical shift reference for the  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  chemical shift scales. TMS is chemically rather inert, and gives a sharp strong NMR signal, which is usually at a frequency that is well displaced from other peaks. Often, a small amount of TMS is added to the sample in order to set the reference for the chemical shift  $\delta$  scale.

Chemical shifts  $\delta$  are small numbers. It is common to specify them in terms of parts per million (ppm), where the dimensionless symbol ppm has exactly the same meaning as  $10^{-6}$ .

For ethanol, the  $\text{CH}_2$  site has a  $^{13}\text{C}$  chemical shift of 57.8 ppm, whereas the  $\text{CH}_3$  site has a  $^{13}\text{C}$  chemical shift of 18.2 ppm. The ethanol spectrum may be labelled with a  $\delta$  scale as follows:



**Figure 3.30**

Total  $^{13}\text{C}$  spectrum of ethanol in a field of 4.7 T ( $\delta$  chemical shift scale).

⚠ The chemical shift  $\delta$  scale *always* increases from right to left in plotted spectra. This is a universal convention in NMR.

It is also convenient to associate the reference frequency of the spectrometer with a chemical shift value  $\delta_{\text{ref}}$ , through the following equation:

$$\delta_{\text{ref}} = \frac{\omega_{\text{ref}} - \omega_{\text{TMS}}^0}{\omega_{\text{TMS}}^0} \quad (3.7)$$

The value of  $\delta_{\text{ref}}$  corresponds to the exact centre of the NMR spectrum, on the ppm scale. The spectrum shown above assumes that the spectrometer reference frequency is placed at  $\delta_{\text{ref}} = 45.0$  ppm.

⚠ The Larmor frequency of spins in the reference compound (denoted  $\omega_{\text{TMS}}^0$ ) should not be confused with the spectrometer reference frequency (denoted  $\omega_{\text{ref}}$ ). The frequency  $\omega_{\text{TMS}}^0$  sets the origin of the chemical shift scale, whereas the frequency  $\omega_{\text{ref}}$  determines the position of the centre of the NMR spectrum, and may be freely changed by the operator.

Equations 3.6 and 3.7 may be used to obtain the relative Larmor frequency of a spin with chemical shift  $\delta$ , given the chemical shift at the centre of the spectrum  $\delta_{\text{ref}}$ :

$$\Omega^0 = \omega^0 - \omega_{\text{ref}} = (\delta - \delta_{\text{ref}}) \omega_{\text{TMS}}^0$$

where  $\omega_{\text{TMS}}^0$  is the Larmor frequency of spins in the reference compound.

In practice, the following slightly looser equation may safely be used:

$$\Omega^0 = \omega^0 - \omega_{\text{ref}} \cong (\delta - \delta_{\text{ref}}) \omega^0 \quad (3.8)$$

which ignores the fine distinction between  $\omega^0$  and  $\omega_{\text{TMS}}^0$ . The errors introduced are very small for chemical shifts of normal size.

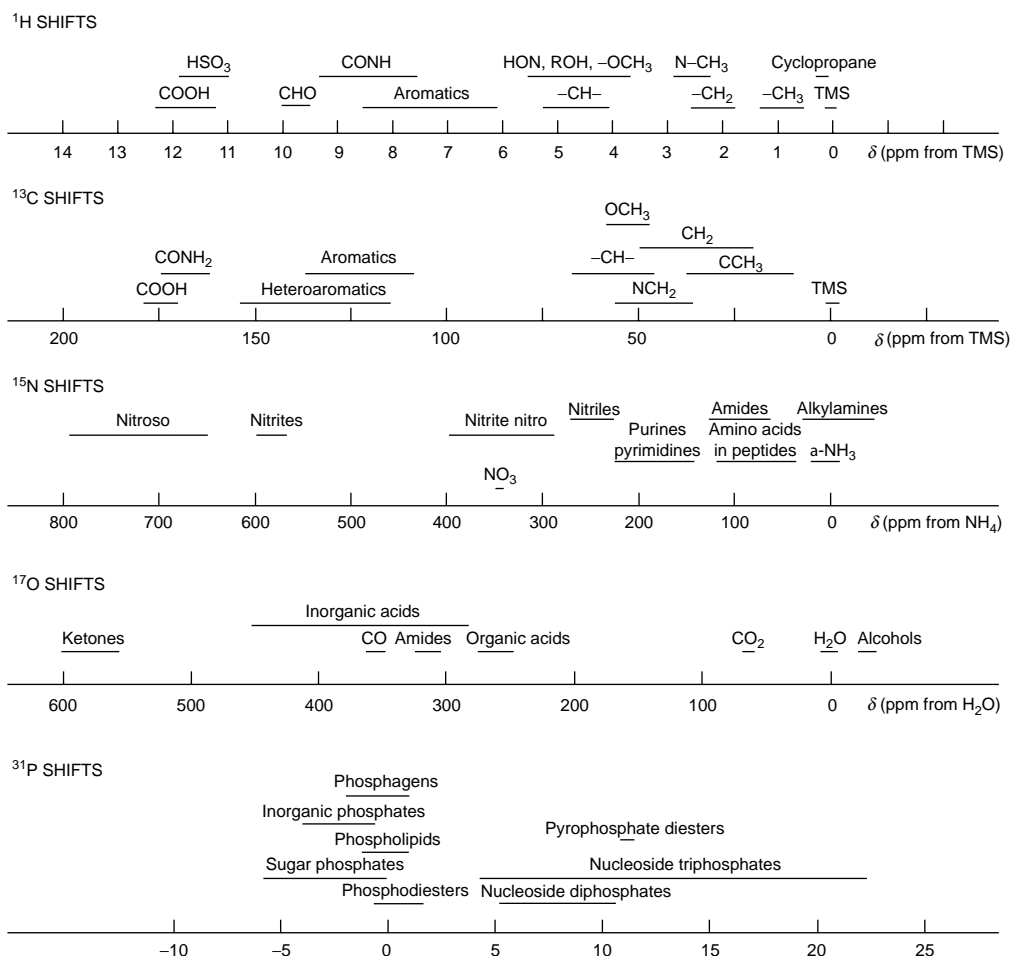
For example, for ethanol, if the  $^{13}\text{C}$  Larmor frequency is  $-50.288\text{ MHz}$  and the spectrometer reference frequency is placed at  $\delta_{\text{ref}} = 45.0\text{ ppm}$ , then the relative  $^{13}\text{C}$  Larmor frequency of the  $\text{CH}_2$  site is

$$\Omega^0/2\pi = (57.8 \times 10^{-6} - 45.0 \times 10^{-6}) \times (-50.288 \times 10^6)\text{ Hz} = -643.6\text{ Hz}$$

and the relative  $^{13}\text{C}$  Larmor frequency of the  $\text{CH}_3$  site is

$$\Omega^0/2\pi = (18.2 \times 10^{-6} - 45.0 \times 10^{-6}) \times (-50.288 \times 10^6)\text{ Hz} = +1347.7\text{ Hz}$$

The chemical shift is an empirical tool of immense use in chemistry. Some typical chemical shifts for different nuclei are given in Figure 3.31. The molecular mechanism of the chemical shift is explored in Section 9.1.



**Figure 3.31** Typical chemical shift ranges for  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{17}\text{O}$  and  $^{31}\text{P}$  in organic compounds. After O. Jardetzky and G. C. K. Roberts, *NMR in Molecular Biology*, Academic Press, New York, 1981, copyright Academic Press.

⚠ The terms ‘high-field’ and ‘low-field’ are sometimes encountered. ‘High-field’ peaks correspond to small  $\delta$  values, whereas ‘low-field’ peaks correspond to large  $\delta$  values. These terms are of historical origin and are highly misleading.<sup>5</sup> I will avoid the high-field/low-field terminology in this book.

## 3.8 *J*-Coupling Multiplets

Now consider the multiplet structure of the ethanol  $^{13}\text{C}$  spectrum.

The left-hand  $\text{CH}_2$  peak, from isotopomer III, is split into a group of three equally spaced peaks, with relative intensities 1:2:1. A multiplet of this type is called a *triplet*. The right-hand  $\text{CH}_3$  peak, from isotopomer II, is split into a group of four equally spaced peaks, with relative intensities 1:3:3:1. A multiplet of this type is called a *quartet*. The  $^{13}\text{C}$  spectrum of liquid ethanol consists of a triplet on the left of the spectrum (which comes from isotopomer III) and a quartet on the right of the spectrum (which comes from isotopomer II).

Other compounds display different types of multiplet. A group of two peaks, with equal intensities, is called a *doublet*. A group of five equally spaced peaks, with relative intensities 1:4:6:4:1, is called a *quintet*. An isolated peak, which does not belong to a multiplet, is called a *singlet*.

These multiplets arise because the precessing  $^{13}\text{C}$  spins are influenced by the magnetic  $^1\text{H}$  nuclei in the same molecule. One says that the  $^{13}\text{C}$  and  $^1\text{H}$  spins are *coupled*.

As discussed in Chapter 8, there are two different mechanisms of spin–spin coupling. The strongest mechanism is called the *direct dipole–dipole coupling*. This involves the direct influence of each spin on its neighbour through the magnetic fields emanating through space. However, this mechanism is *not* responsible for the multiplet structure in isotropic liquids. As discussed in Section 9.3, the direct dipole–dipole coupling is effectively eliminated by the rapid molecular tumbling.

The mechanism responsible for the multiplet structure in isotropic liquids is called the *J-coupling*, or the *indirect dipole–dipole coupling*. The term ‘indirect’ indicates that the nuclear spins are coupled together with the help of the molecular electrons. Each proton weakly magnetizes the molecular electrons, which generate a magnetic field at the site of the  $^{13}\text{C}$  spins. This transmitted field allows each  $^{13}\text{C}$  spin to sense the presence of the neighbouring protons. The coupling also works the other way round: the  $^{13}\text{C}$  spin also weakly magnetizes the electrons, which generate a field at the location of the  $^1\text{H}$  spins. As discussed in Section 9.4, a part of this indirect dipole–dipole coupling survives in isotropic liquids, and generates the observed multiplet structure.

The *J*-coupling is always specified in hertz. For example, the *J*-coupling between the  $^{13}\text{C}$  and  $^1\text{H}$  spins in the  $\text{CH}_3$  group of ethanol is  $J_{\text{CH}} = 124.9$  Hz. The *J*-coupling between the  $^{13}\text{C}$  and  $^1\text{H}$  spins in the  $\text{CH}_2$  group is  $J_{\text{CH}} = 140.4$  Hz. These numbers correspond to the frequency separation between the multiplet peaks.

Sometimes a superscript prefix is used to specify the number of chemical bonds separating the nuclei involved in the *J*-coupling. The *J*-couplings specified above are written  $^1J_{\text{CH}} = 124.9$  Hz and  $^1J_{\text{CH}} = 140.4$  Hz to indicate that the participating atoms are separated by one chemical bond. There are also *long-range J-couplings* that involve atoms separated by two or more chemical bonds. For example, the *J*-coupling between a  $^{13}\text{C}$  spin located on the  $\text{CH}_2$  group and the three  $\text{CH}_3$  protons of ethanol is  $^2J_{\text{CH}} = -4.6$  Hz.

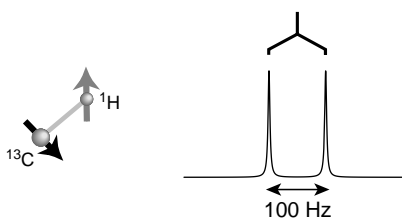
The meaning of the sign of the *J*-coupling is discussed in Section 9.4.

The *J*-splitting phenomenon is explained in Chapters 15 and 17. For the moment, I mention the phenomenological rules for predicting the spectral structure, which work in many cases.

Consider first a simple case in which the molecules contain one  $^{13}\text{C}$  spin and one  $^1\text{H}$ , with a *J*-coupling equal to  $J_{\text{CH}} = 100$  Hz. The spectral peak generated by the  $^{13}\text{C}$  spins is ‘split’ by the neighbouring proton, appearing as a doublet with one peak shifted to positive frequency by 50 Hz and one peak shifted to negative frequency by the same amount:

**Figure 3.32**

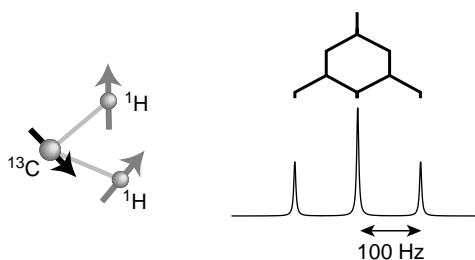
A  $^{13}\text{C}$  doublet, caused by coupling to one proton.



If the  $^{13}\text{C}$  spin is coupled to *two* protons, then the splitting occurs twice, one for each  $^{13}\text{C}$ - $^1\text{H}$   $J$ -coupling. If both couplings are equal to  $J_{\text{CH}} = 100$  Hz, then a triplet pattern is generated:

**Figure 3.33**

A  $^{13}\text{C}$  triplet, caused by coupling to two protons.

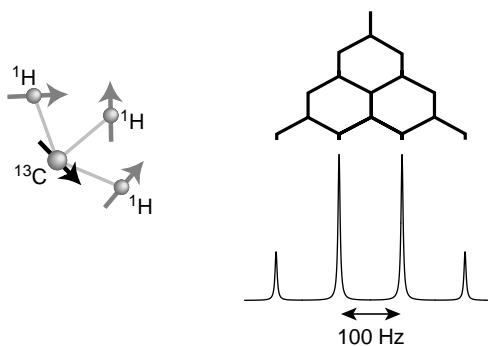


The amplitude ratio of 1:2:1 occurs because there are two ways of generating the inner peaks and only one way of generating the outer ones.

If the  $^{13}\text{C}$  spin is coupled to *three* protons, then the splitting occurs three times. If all three couplings are equal, then a quartet pattern is generated:

**Figure 3.34**

A  $^{13}\text{C}$  quartet, caused by coupling to three protons.



The amplitude ratio of 1:3:3:1 occurs because there are three ways of generating the inner peaks and only one way of generating the outer ones.

In general, if a nuclear spin is coupled to  $n$  equivalent spins-1/2, its peak is split into an  $(n + 1)$ -fold multiplet, where the peak intensities within the multiplet are proportional to the binomial coefficients  ${}_nC_r$ , where  $r = 0, 1 \dots n$ . The binomial coefficients are given by

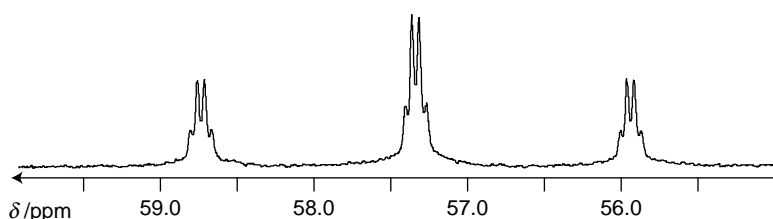
$${}_nC_r = \frac{n!}{(n-r)!r!}$$

For example, the NMR peak of a  $^{13}\text{C}$  that is coupled to six equivalent protons is split into a 1:6:15:20:15:6:1 septet. The intensity ratios may be derived as follows:

$$\begin{aligned} {}_6C_0 &= \frac{6!}{6! \times 0!} = 1 & {}_6C_2 &= \frac{6!}{4! \times 2!} = 15 \\ {}_6C_1 &= \frac{6!}{5! \times 1!} = 6 & {}_6C_3 &= \frac{6!}{3! \times 3!} = 20 \end{aligned}$$

and so on.

Now consider more closely the signals of ethanol isotopomer III, which are split into a triplet because of the one-bond coupling between the  $^{13}\text{C}$  and  $^1\text{H}$  spins in the  $\text{CH}_2$  group. An experimental  $^{13}\text{C}$  spectrum of the  $\text{CH}_2$  region is shown below:

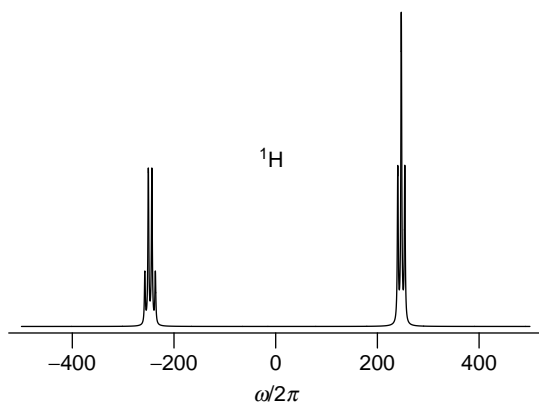


**Figure 3.35**  
Experimental  $^{13}\text{C}$   
spectrum of the  $\text{CH}_2$   
region in ethanol.

This shows an additional quartet *fine structure*. This may be attributed to the two-bond coupling between the  $^{13}\text{C}$  spin in the  $\text{CH}_2$  group and the three  $^1\text{H}$  spins in the  $\text{CH}_3$  group.

In general, the spectral peaks are split again and again, according to the  $J$ -couplings of the corresponding spin with all the other spins in the molecule.

What about the *proton* spectrum of ethanol? This spectrum is generated mainly from the abundant isotopomer I, which does not contain a  $^{13}\text{C}$  spin. At a field of  $B^0 = 4.70\text{ T}$ , and with a spectrometer reference frequency corresponding to  $\delta_{\text{ref}} = 2.4\text{ ppm}$ , the spectrum of this isotopomer appears as follows:



**Figure 3.36**  
 $^1\text{H}$  spectrum of ethanol,  
in a field of 4.7 T.



The peak on the right is centred at  $\delta_j = 1.19$  ppm, and arises from the three protons of the  $\text{CH}_3$  group. This peak is split into a triplet because each of these protons has a  $^3J_{\text{HH}} = 6.9$  Hz coupling with the two protons of the  $\text{CH}_2$  group. The peak on the left is centred at  $\delta_k = 3.66$  ppm, and arises from the two protons of the  $\text{CH}_2$  group. This peak is split into a quartet by the  $^3J_{\text{HH}} = 6.9$  Hz coupling with the three protons of the  $\text{CH}_3$  group.

Note that the relative positions of the triplet and quartet are exchanged relative to the  $^{13}\text{C}$  spectrum.

This spectrum illustrates two additional points.

First, the OH proton was ignored in the above discussion. Under most circumstances, this proton only gives broad signals, and does not split the signals of the other spins in the molecule. This is because of a *chemical exchange* process. The OH proton is labile and hops around rapidly between the ethanol molecules, unless the ethanol is exceptionally pure (the exchange process is catalysed by acid or base). In most circumstances, the chemical exchange is fast enough to remove the  $J$ -coupling to this proton completely. This phenomenon is discussed in Section 19.5.3.

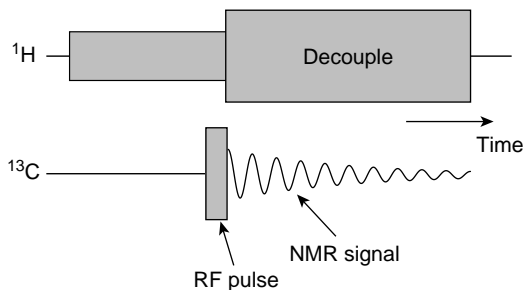
Second, it is possible to predict the  $^1\text{H}$  spectrum without considering the coupling of the two  $\text{CH}_2$  protons *with each other*. In Chapter 17, it is shown that the coupling between the two  $\text{CH}_2$  protons may be ignored because they are *magnetically equivalent*. This means that they have the same chemical shift, as well as the same  $J$ -couplings with other spins in the same molecule. The three  $\text{CH}_3$  protons are also magnetically equivalent, so their mutual coupling may be ignored too. Magnetic equivalence and its consequences are discussed in Section 17.5.

### 3.9 Heteronuclear Decoupling

The  $J$ -coupling structure is very useful for providing qualitative molecular structural information. However, in some cases this splitting structure is undesirable, since

- The  $J$ -splittings distribute the signal intensity over many smaller peaks. This makes it more difficult to detect the NMR signals.
- In complex molecules, the  $J$ -splittings make the spectrum crowded and more difficult to interpret.

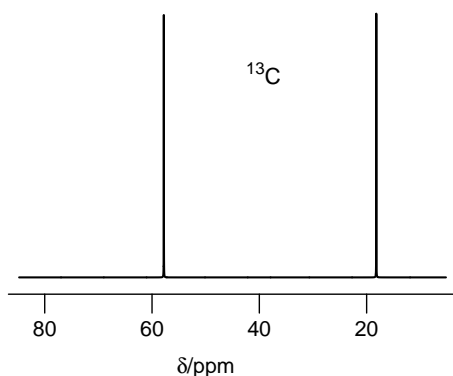
Fortunately, there is a very simple method for eliminating the  $^{13}\text{C} - ^1\text{H}$  splittings from  $^{13}\text{C}$  spectra. One simply acquires the  $^{13}\text{C}$  NMR signal at the same time as applying an r.f. field at the  $^1\text{H}$  Larmor frequency. This is usually denoted as follows:



**Figure 3.37**  
Heteronuclear pulse  
sequence involving  $^1\text{H}$   
decoupling.

If the  $^1\text{H}$  r.f. field is sufficiently strong, and has a frequency sufficiently close to the Larmor frequency of the relevant protons, the  $^{13}\text{C}$  spins behave *as if* the heteronuclear  $J$ -couplings does not exist. The  $^{13}\text{C}$  spectrum is determined by the  $^{13}\text{C}$  chemical shifts alone.

This method is called *heteronuclear decoupling*. In the case of ethanol, the proton-decoupled  $^{13}\text{C}$  spectrum has the following appearance:



**Figure 3.38**  
 $^1\text{H}$ -decoupled  $^{13}\text{C}$   
 spectrum of ethanol.

The right-hand peak comes from isotopomer II; the left-hand peak comes from isotopomer III. Note the disappearance of the multiplet structure.

In practice, the  $^1\text{H}$  decoupling field is usually subjected to a specialized modulation scheme, in order to make the decoupling more effective and to reduce the heating of the sample (see *Further Reading*).

The pulse sequence diagram given above also includes  $^1\text{H}$  irradiation *before* the pulse is applied to the  $^{13}\text{C}$  spins. The purpose of this irradiation is to enhance the  $^{13}\text{C}$  magnetization through a phenomenon called the *nuclear Overhauser effect* (NOE), which is discussed in Section 20.5. The proton irradiation *before* the  $^{13}\text{C}$  pulse has nothing to do with decoupling, but simply causes the  $^{13}\text{C}$  signals to be stronger, in suitable cases.

## Notes

1. The devices used to convert a varying voltage into digital form (analogue-to-digital converters) can only operate accurately enough at relatively low frequencies. In 2007, the maximum operation frequency of these devices is less than most common nuclear Larmor frequencies. However, the continuing advances in high-frequency electronics may soon change this situation.
2. The relative frequency axis used to label NMR spectra in much literature and on most commercial spectrometers corresponds to the coordinate  $|\omega| - |\omega_{\text{ref}}|$ . This is equal to  $-\Omega$  in the case of positive  $\gamma$ , and is equal to  $+\Omega$  in the case of negative  $\gamma$ .
3. NMR spectrometers do not actually process the data from nuclei with negative  $\gamma$  in a special way. The ‘flipping’ effect described in Section 3.5 is an unintentional consequence of ignoring the sign of precession during the excitation process and when the signal is detected. This issue is examined in detail in M. H. Levitt. *J. Magn. Reson.*, **126**, 164–182 (1997).
4. The symbols ppm and % do not represent *units* but *numbers*, i.e.  $5 \text{ ppm} = 5 \times 10^{-6}$  and  $5\% = 0.05$ . Therefore, they behave differently from, for example, a unit such as the kilogram (an equation such as  $1 \text{ kg} = 10^{-3}$  would be completely incorrect). This point is often misunderstood.
5. Before around 1966, most NMR spectra were acquired using a fixed r.f. frequency, while varying the external magnetic field in order to bring different spin sites into resonance. Traditionally, the applied magnetic field was plotted from left to right across the spectrum. Peaks appearing on the left-hand side of the spectrum were called ‘low-field’ peaks, and peaks appearing on the right-hand side were called ‘high-field’ peaks. Nowadays (2007), almost all NMR spectra are acquired in a completely different way,

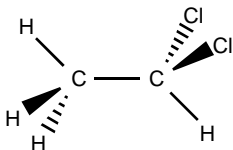
using the pulse-Fourier transform approach at a fixed external magnetic field, which has rendered these terms obsolete and confusing. For example, a 'low-field' spin site actually has a high *local* magnetic field from the molecular environment, so that a relatively low *external* magnetic field is needed in order to bring this site into resonance in a variable-field NMR experiment.

## Further Reading

- For the applications of chemical shifts and *J*-couplings in chemistry, see the many articles in the *Encyclopedia of Nuclear Magnetic Resonance*, D. M. Grant and R. K. Harris (eds), Wiley, 1996, as well as R. K. Harris, *Nuclear Magnetic Resonance Spectroscopy: A Physicochemical View*, Longman, 1986, and J. K. Sanders and B. K. Hunter, *Modern NMR Spectroscopy. A Guide for Chemists*, Oxford University Press, Oxford, 1993.
- For a review of modulation schemes for heteronuclear decoupling, and a summary of the theory, see A. J. Shaka and J. Keeler, *Prog. NMR Spectrosc.* **19**, 47(1987) and R. Freeman, *Spin Choreography. Basic Steps in High Resolution NMR*, Spektrum, Oxford, 1997.

## Exercises

- 3.1 Describe the  $^1\text{H}$  and  $^{13}\text{C}$  spectra of the compound



- 3.2 Assume isotopic abundances of 100% for  $^1\text{H}$  and 1% for  $^{13}\text{C}$ . Assume that the one-bond  $^{13}\text{C}$ - $^1\text{H}$  *J*-couplings are around 135 Hz and the three-bond  $^1\text{H}$ - $^1\text{H}$  *J*-couplings are 7 Hz. Ignore the couplings to the Cl nuclei. How would the  $^{13}\text{C}$  spectrum change if strong r. f. irradiation were applied at the  $^1\text{H}$  Larmor frequency?
- 3.3 A sample of acetone (propan-2-one,  $(\text{CH}_3)_2\text{CO}$ ) is enriched in  $^{13}\text{C}$  so that exactly 40% of the C atoms are  $^{13}\text{C}$  and the other 60% are  $^{12}\text{C}$  (spin  $I = 0$ ). The  $^{13}\text{C}$  atoms are randomly distributed. How many isotopomers are there, and what are their relative proportions? (Ignore the isotopes of hydrogen and oxygen.) Sketch the  $^1\text{H}$ -decoupled  $^{13}\text{C}$  spectrum of each isotopomer, assuming that one-bond  $^{13}\text{C}$ - $^{13}\text{C}$  couplings are 50 Hz. Sketch the  $^1\text{H}$ -decoupled  $^{13}\text{C}$  spectrum of the whole sample.
- 3.4 A compound has two different  $^{13}\text{C}$  sites with chemical shifts equal to 30 ppm and 100 ppm.
- (i) At what magnetic field is the chemical frequency difference equal to 10 kHz?
  - (ii) The relative Larmor frequency of peaks from the two  $^{13}\text{C}$  sites are  $\Omega_1^0/2\pi = +6.0\text{ kHz}$  and  $\Omega_2^0/2\pi = -4.0\text{ kHz}$ . What is the ppm value  $\delta_{\text{ref}}$  of the spectrometer reference frequency?

