SPIN DYNAMICS

Basics of
Nuclear Magnetic
Resonance

Malcolm H. Levitt

Wiley

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Introduction

In December 1945, Purcell, Torrey and Pound detected weak radio-frequency signals generated by the nuclei of atoms in ordinary matter (in fact, about 1 kg of paraffin wax). Almost simultaneously, Bloch, Hansen and Packard independently performed a different experiment in which they observed radio signals from the atomic nuclei in water. These two experiments were the birth of the field we now know as Nuclear Magnetic Resonance (NMR).

Before then, physicists knew a lot about atomic nuclei, but only through experiments on exotic states of matter, such as found in particle beams, or through energetic collisions in accelerators. How amazing to detect atomic nuclei using nothing more sophisticated than a few army surplus electronic components, a rather strong magnet, and a block of wax!

In his Nobel prize address, Purcell was moved to a poetic description of his feeling of wonder (quoted on the inside cover **?**). He went on to describe how **?** "in the winter of our first experiments. . . looking on snow with new eyes. There the snow lay around my doorstep – great heaps of protons quietly precessing in the Earths magnetic field. To see the world for a moment as something rich and strange is the private reward of many a discovery."

In the years since then, NMR has become an incredible physical tool for investigating matter. Its range is staggering, encompassing such diverse areas as brains, bones, cells, ceramics, inorganic chemistry, chocolate, liquid crystals, laser-polarized gases, protein folding, surfaces, superconductors, zeolites, blood flow, quantum geometric phases, drug development, polymers, natural products, electrophoresis, geology, liquid crystals, colloids, catalysis, food processing, metals, gyroscopic navigation, cement, paint, wood, quantum exchange, phase transitions, ionic conductors, membranes, plants, micelles, grains, antiferromagnets, soil, quantum dots, explosives detection,

coal, quantum computing, cement, rubber, glasses, oil wells and antarctic ice.

Two brief examples may suffice here to show the range and power of NMR.

The first example is taken from *functional NMR imaging*. As explained in section 11.3, it is possible to use the radio-frequency signals from the nuclei to build up a detailed picture of the three-dimensional structure of an object. The grey picture in Fig.0.1 shows this method applied to a human head, revealing the lobes of the brain inside the skull. The red and yellow flashes superimposed on the picture reveal *differences* in the NMR signals when the subject is performing some mental task – in this case, processing the memory of a face which has just been removed from view. NMR can map out such mental processes because the brain activity changes slightly the local oxygenation and flow of the blood, which affects the precession of the protons in that region of the brain.

Fig.0.1

The second example illustrates the determination of biomolecular structures by NMR. Fig.0.2 shows the structure of a protein molecule in solution, determined by a combination of multidimensional NMR techniques, including the COSY and NOESY experiments described in chapter 13 and chapter 16 of this book. The structure is colour-coded to reveal the mobility of different parts of the molecule, as determined by NMR relaxation experiments.

Fig.0.2

In this book, I want to provide the basic theoretical and conceptual equipment for understanding these amazing experiments. At the same time, I want to reinforce Purcell's beautiful vision – the heaps of snow, concealing innumerable nuclear magnets, in constant precessional motion. The years since 1945 have shown us that Purcell was right. *Matter really is like that.* My aim in this book is to communicate the rigorous theory of NMR, which is necessary for *really* understanding NMR experiments, but without losing sight of Purcell's heaps of precessing protons.
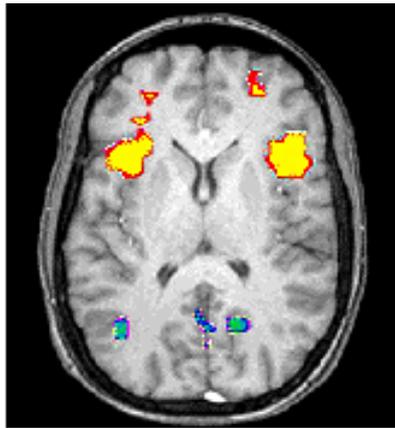
Fig.0.1 A functional NMR image. The gray image is a cross-section through the head of a person (the person may be thought of as lying down on his/her back, head towards you). The gray scale image shows the lobes of the brain. The yellow and red patches show activation of the prefrontal cortex after a face is removed from view, detected as small differences in the NMR signals. The blue patches denote diminished activation of these regions of the brain, under the same task. Figure from S. M. Courtney, L. G. Underleider, K. Keil and J. V. Haxby, *Nature* **386**, 608-611 (1997). Reproduced by permission of Macmillan Publishers **?**.

Fig.0.2 Backbone structure of a protein molecule in solution (residues 55-206 of the HIV-1 Nef protein), as determined by NMR. The structure is colour-encoded to display the mobilities of different parts of the molecule, as revealed by ^{1}H-^{15}N NOE values (see chapter 16). Blue = least mobile; Red = most mobile. The N-terminal tail that anchors the protein to the membrane is disordered and not shown. Figure from S. Grzesiek, A. Bax, J. Hu, J. Kaufman, I. Palmer, S. J. Stahl, N. Tjandra, and P. T. Wingfield, *Protein Science*, **6**, 1248-1263 (1997). Thanks to Ad Bax for supplying this figure.

Part 1 – Nuclear Magnetism

Chapter 1. Matter

Chapter 2. Magnetism

Chapter 3. NMR Spectroscopy

1. Chapter 1 – Matter

1.1 Properties of Nuclei

1.2 Spin

1.3 Atomic and Molecular Structure

1.4 States of Matter

1. Matter

1.1 Properties of 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. The thermal properties of materials are also strongly influenced by the mass of the atomic nuclei.

The *electric charge* of atomic nuclei is important because 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 less obvious. The magnetism of a nucleus means that the nucleus 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 *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, for example 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. 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. Nuclear magnetic resonance 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:
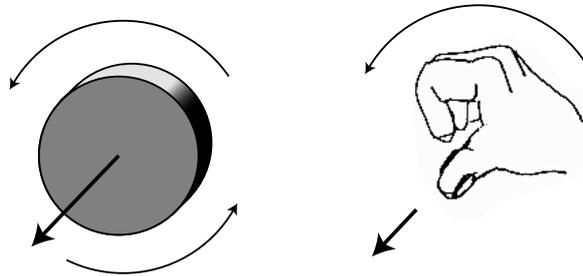
1.2.2 Quantum Angular Momentum

In quantum mechanics, angular momentum is *quantized.* Consider, for example, a diatomic molecule:
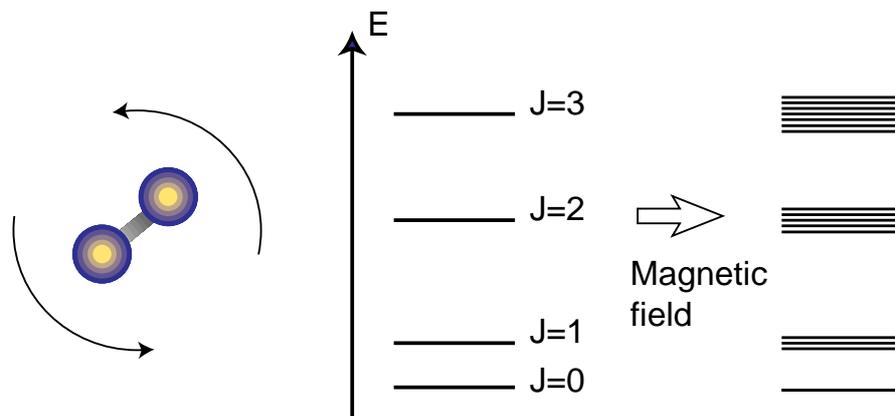
As described in many texts (see *further reading*), and discussed further in chapter 6, a rotating diatomic molecule possesses a set of stable rotational states, in which the total angular momentum L_{tot} has one of the values

$$L_{tot} = [J(J+1)]^{1/2}\hbar \; , \qquad\qquad [1.1]$$

where J takes *integer* values $J = 0, 1, 2 \ldots$ and $\hbar \cong 1.054 \times 10^{-34}$ J s is Planck's constant divided by 2π. 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

$$E_J = BJ(J+1) , \qquad\qquad [1.2]$$

where B is called the rotational constant for the molecule. B is small for a heavy molecule, and 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 rotational 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 $M_J = -J, -J+1 \ldots +J$, 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 chapter 6 and chapter 9.

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 which 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 which 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 $M_J = -J, -J+1 \ldots + J$. 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 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 a whole 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 1920's and 1930's. 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 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 which 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.

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 which have angular momentum "by themselves", without rotating.

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 possible values:

$$J_3 = \text{one of} \begin{cases} |J_1 - J_2| \\ |J_1 - J_2| + 1 \\ \vdots \\ |J_1 + J_2| \end{cases} \qquad [1.3]$$

Expressed in words, this means that the complete system has a total angular momentum quantum number given by either the sum of the two individual angular momentum quantum numbers, or the difference in the two individual angular moment 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. $S_1 = S_2 = \frac{1}{2}$. 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:

$S_3 = 0$
"opposite spins"

$S_3 = 1$
"parallel spins"
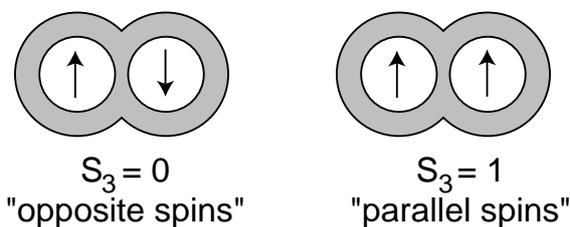
In the "parallel" spin state $S_3 = 1$, on the other hand, the spins of the two particles reinforce each other. In general, the $S_3 = 0$ and $S_3 = 1$ states have different energy. Note that it is not possible to make a general statement as to which state has the *lowest* energy – this depends on the 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 three-fold 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*[1] 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   Atomic and Molecular Structure

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 Eq.[1.3].

1.3.1   The Fundamental Particles

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

Leptons are low-mass particles. 6 varieties of lepton have been currently identified, but only one is familiar to nonspecialists. 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 1.602×10^{-19} C.

Quarks are relatively heavy particles. At the time of writing (2000), it is believed that there are 6 varieties 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. There are recent speculations that quarks may themselves be 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 β-decay.

1.3.2 Neutrons and Protons

The *neutron* and the *proton* both consist of three quarks, stuck together by gluons[2].

The *neutron* is composed of three quarks, two with charge $-e/3$, and one with charge $+2e/3$. The total electric charge of the neutron is therefore 0, hence its name. The neutron has spin-1/2. The neutron spin is due to combinations of quark spins[2]. For example, if two of the quark spins are antiparallel, we get a $S = 0$ state. Addition of the third quark spin gives a total neutron spin $S = \frac{1}{2}$:
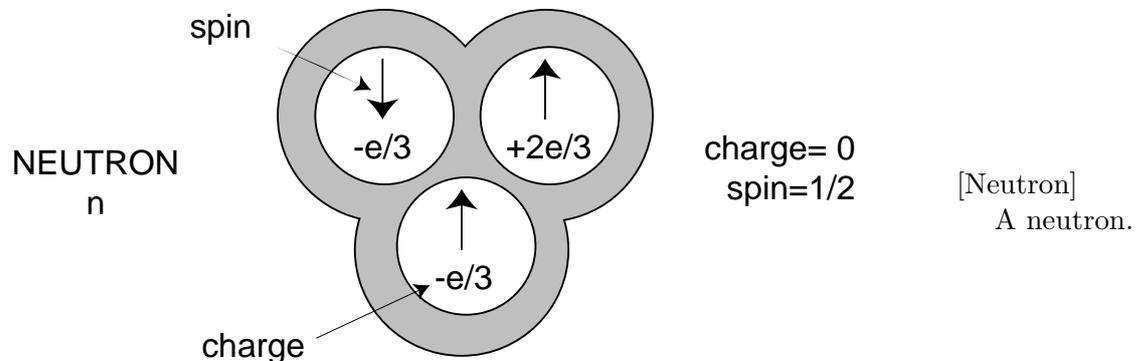
[Neutron]
A neutron.

The *proton* is also composed of three quarks, but this time two of the quarks have charge $+2e/3$, while the other one has charge $-e/3$. The total electric charge of the proton is therefore $+e$. 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[2]:

PROTON
p

spin

-e/3   +2e/3

+2e/3

charge

charge= +e
spin=1/2
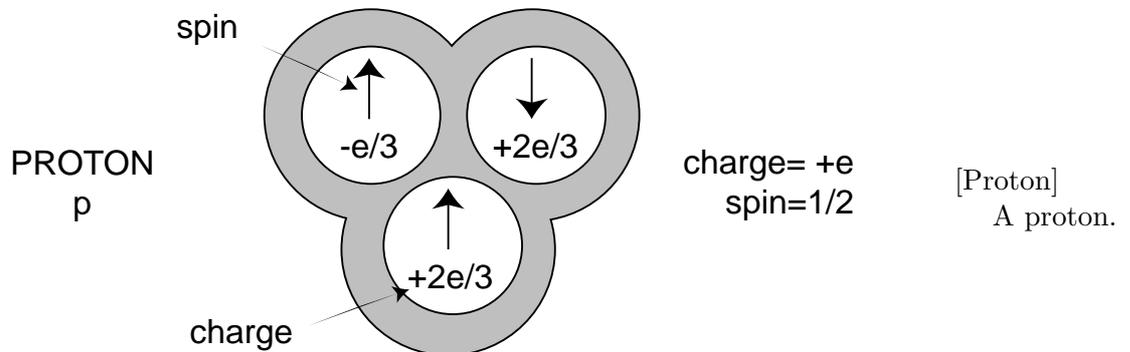
[Proton]
A proton.

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 Δ^+ 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 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.

Table 1.1

1.3.3 The Atomic Nucleus

The atomic nucleus consists of neutrons and protons[3]. 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

particle	rest mass/kg	charge	spin
e	9.109×10^{-30}	$-e$	1/2
n	1.675×10^{-26}	0	1/2
p	1.673×10^{-26}	$+e$	1/2
photon	0	0	1

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

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:

$$^1\text{H} = p$$

$$^2\text{H} = p + n$$

$$^{12}\text{C} = 6p + 6n$$

$$^{13}\text{C} = 6p + 7n \ ,$$

and so on.

Some examples of unstable (radioactive) isotopes are:

$$^3\text{H} = p + 2n$$

$$^{14}\text{C} = 6p + 8n \ .$$

Isotopes occur in nature with varying *isotopic distributions*. These distributions are almost uniform over the surface of the earth. For example, $\sim 98.9\%$ of carbon nuclei have six neutrons (^{12}C), while $\sim 1.1\%$ have seven neutrons (^{13}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.

Table 1.2

Most atomic nuclei also possess spin. The nuclear spin quantum number is conventionally denoted I. The nucleus of the main isotope of hydrogen, ^1H, contains a single proton and has $I = \frac{1}{2}$. The spins of other nuclei are formed by combining together the spins of the protons and the neutrons according to the usual rule (Eq.[1.3]).

Consider, for example, the ^2H 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 $I = 0$:
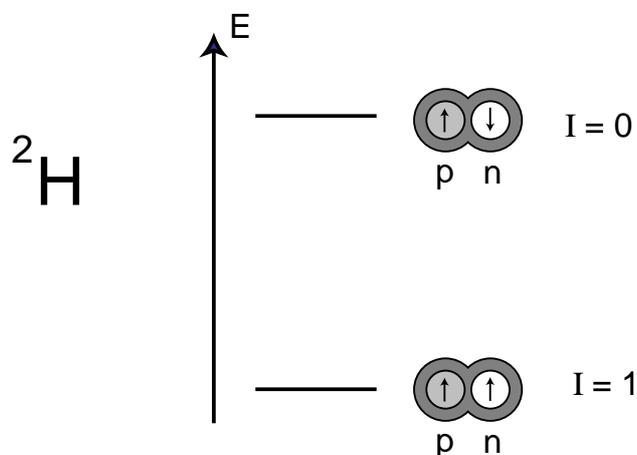
[Htwo]
Energy levels of a ^{2}H nucleus.

These two nuclear spin states have a large energy difference of $\sim 10^{11}\,\mathrm{kJ\,mol^{-1}}$. 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 $\sim 2.5\,\mathrm{kJ\,mol^{-1}}$). The nuclear excited states may therefore be ignored, except in exotic circumstances[4]. The value of I in the lowest energy nuclear state is called the *ground state nuclear spin*. For deuterium (symbol D or ^{2}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:
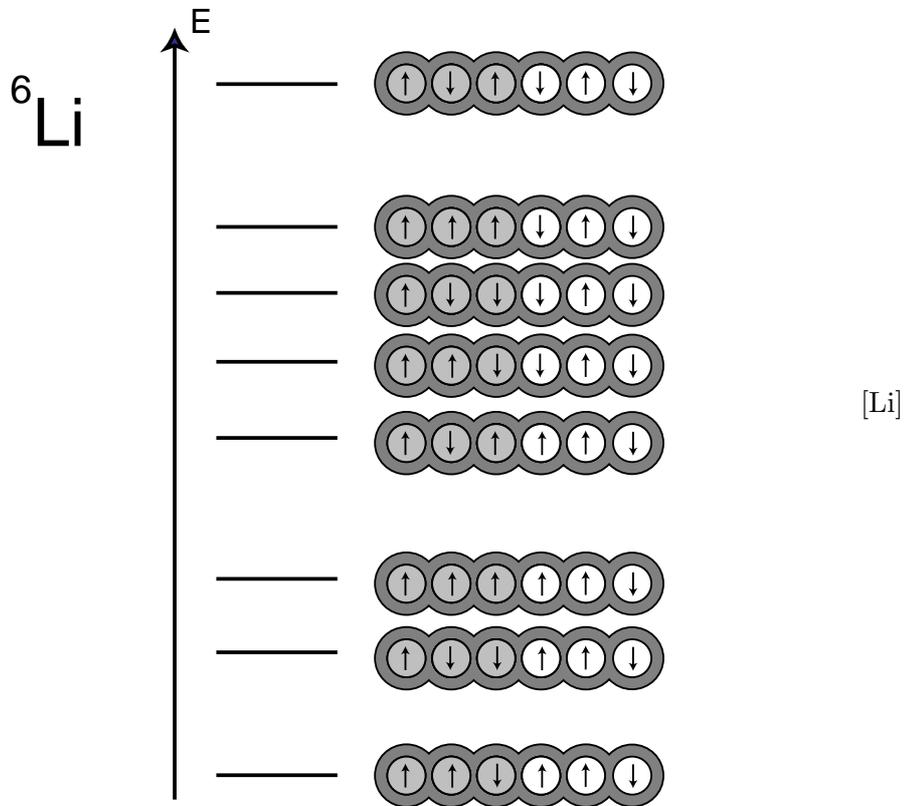
In general, there are no simple rules for which of the many possible states is the ground state. For our purposes, the ground state nuclear spin is best regarded as an empirical property of each isotope.

Nevertheless, one property may be stated with certainty: From Eq.[1.3], isotopes with even mass numbers have integer spin, while 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}C, which contains 6 protons and 6 neutrons, the nucleus ^{16}O which contains 8 protons and 8 neutrons, and the nucleus ^{56}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}H (1 proton + 1 neutron, ground state spin $I = 1$), ^{10}B (5 protons + 5 neutrons, ground state spin $I = 3$), ^{14}N (7 protons + 7 neutrons, ground state spin $I = 1$) and ^{40}K (19 protons + 21 neutrons, ground state spin $I = 4$).

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

Most nuclear isotopes have non-zero nuclear spin in the ground state. Table 1.2 shows some of the nuclear isotopes of importance in NMR, together with their natural abundances.

From now on, the ground state nuclear spin is simply called the "nuclear spin," for the sake of simplicity.

1.3.4 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}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}Na^{+} ion. A nucleus containing 17 protons and 18 neutrons, surrounded by a cloud of 18 electrons, is called a ^{35}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

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*. The *hyperfine couplings* between electrons and nuclei are encountered again later on in this book (section 15.5.5).

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.

1.3.5 Molecules

An electron cloud containing more than one nucleus is called a *molecule*. For example, a molecule of water (^{1}H$_2$^{16}O) consists of a cloud of 10 electrons surrounding three nuclei: One with 8 protons and 8 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 a H-O-H angle of around 105°.

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 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 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 ${}^1H_2{}^{16}O$, but there are also small amounts of the minor isotopomers ${}^1H{}^2H{}^{16}O$, ${}^2H_2{}^{16}O$, ${}^1H_2{}^{17}O$, 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}CO molecules from the abundant ^{12}CO isotopomers by pressing the gas through very long chromatographic columns. The ^{13}C-labelled carbon monoxide is used as a starting material for total organic synthesis of other ^{13}C-labelled substances. Many modern NMR experiments use isotopically-enriched substances prepared in this way.

Nuclear magnetic resonance 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}C nucleus has a mass of exactly $12\,Da$. A medium-sized protein molecule has a molecular mass of around $30 \times 10^3\,Da = 30\,kDa$ (30 kilodaltons). Outside the biological sciences, molecular masses are usually specified in units of grams per mole ($g\,mol^{-1}$).

1.4   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 nuclear magnetic resonance 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.

1.4.1   Gases

Gases are defined as low-density material phases which 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[5].

1.4.2   Liquids

Liquids are relatively high-density 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 (Fig.1.3). *Translation molecular mobility* means that the molecules or atoms slide past each other rather freely, and wander over appreciable distances in a rather short time. For example, a water molecule at room temperature typically wanders over a distance of $\sim 7\,\mu$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
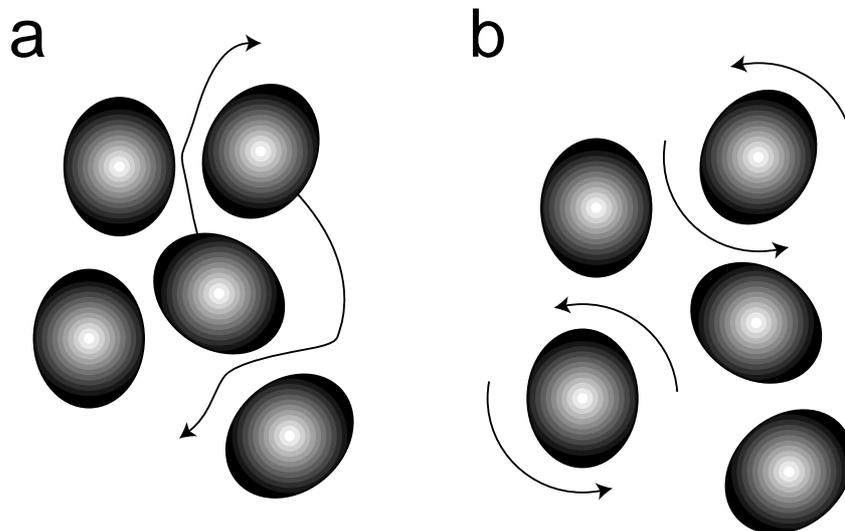
Fig.1.3

Fig.1.3 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 spatial directions.

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.

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 molecules dissolved at low concentration in common solvents. As discussed in chapter 7, 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, 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 (Fig.1.4). Consider, for example, a case in which the molecules $\boxed{\text{Fig.1.4}}$ 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 which is parallel with the director, than around an axis which 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 13.4 of this book.

1.4.3 Solids

Solids are high-density material phases which 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,
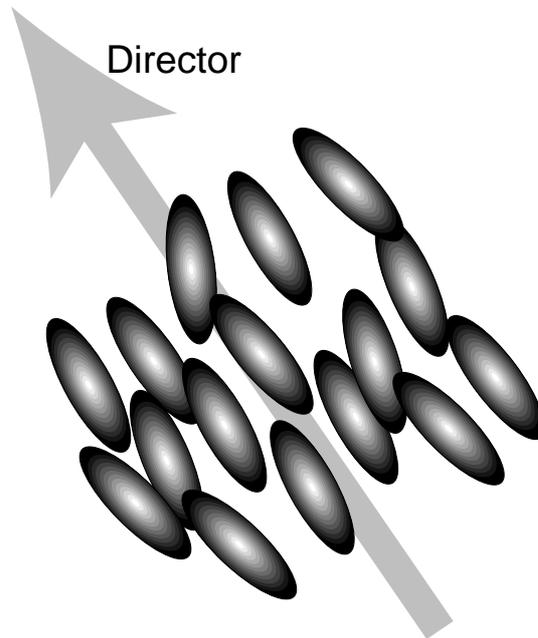
Fig.1.4 In an anisotropic liquid, the molecular mobilities depend on the direction in space.

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 *amorphous solids* and *glasses*, in which long-range repeating patterns cannot be discerned.

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 into a swimming pool stomach-first. On the other hand, a hard solid such as glass may behave as a liquid under long timescales. For example, the windows of old buildings are often thicker at the bottom than at the top:

The glass has flowed under gravity on the timescale of hundreds of years. The geology and geography of our planet have been shaped by the flow of rocks over extremely long periods of time.

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, 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 which 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 which 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, for example 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:
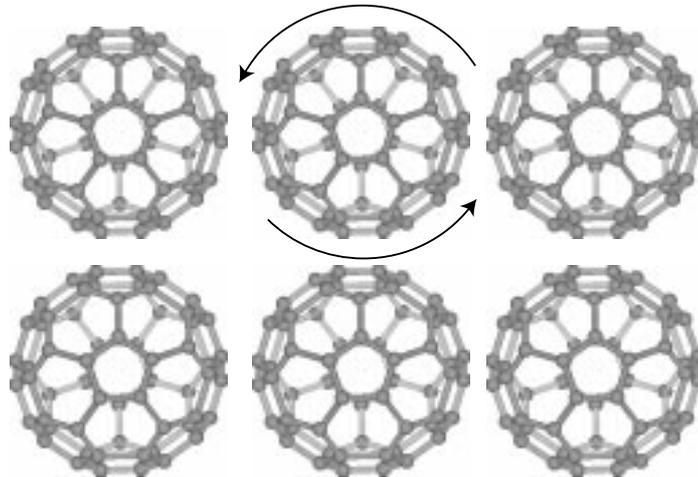
[C60]
Rotation of C_{60} molecules in a solid.

Even in molecules which 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 technique 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 to Chapter 1.

1. 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.

2. The discussion of neutron spin, proton spin, and nuclear spin
    given in this chapter is greatly oversimplified. In fact, it is
    known that the orbital motions of the quarks and gluons also
    contribute heavily to the spin of the proton and neutron. 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.

3. The neutrons and protons are bound together by an interchange
    of particles known as mesons. Each meson is made up of two
    quarks.

4. In *Mössbauer spectroscopy*, transitions between the nuclear
    energy levels are excited using energetic γ-rays.

5. 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}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}Xe gas with a very high nuclear spin polarization, so as to enhance the NMR signals. See for example G. Navon, Y.-Q. Song, T. Rööm, S. Appelt, R. E. Taylor and A. Pines, *Science* **271**, 1848 (1996). Some conventional gas-phase NMR spectra, obtained without the help of optical pumping, are shown in Fig.[15.2] .

isotope	ground state spin	natural abundance	magnetogyric ratio $\gamma/\,\mathrm{rad\,s^{-1}\,T^{-1}}$	NMR frequency at 11.7433 T $(\omega^0/2\pi)/\,\mathrm{MHz}$
^{1}H	$\frac{1}{2}$	$\sim 100\%$	267.522×10^6	-500.000
^{2}H	1	0.015%	41.066×10^6	-76.753
^{3}H	$\frac{1}{2}$	0	285.349×10^6	-533.320
^{10}B	3	19.9%	28.747×10^6	-53.718
^{11}B	$\frac{3}{2}$	80.1%	85.847×10^6	-160.420
^{13}C	$\frac{1}{2}$	1.1%	67.283×10^6	-125.725
^{14}N	1	99.6%	19.338×10^6	-36.132
^{15}N	$\frac{1}{2}$	0.37%	-27.126×10^6	$+50.684$
^{17}O	$\frac{5}{2}$	0.04%	-36.281×10^6	$+67.782$
^{19}F	$\frac{1}{2}$	$\sim 100\%$	251.815×10^6	-470.470
^{23}Na	$\frac{3}{2}$	$\sim 100\%$	70.808×10^6	-132.259
^{27}Al	$\frac{5}{2}$	$\sim 100\%$	69.763×10^6	-130.285
^{29}Si	$\frac{1}{2}$	4.7%	-53.190×10^6	$+99.336$
^{31}P	$\frac{1}{2}$	$\sim 100\%$	108.394×10^6	-202.606
^{35}Cl	$\frac{3}{2}$	75.77%	10.610×10^6	-48.990
^{37}Cl	$\frac{3}{2}$	24.23%	8.832×10^6	-40.779
^{63}Cu	$\frac{3}{2}$	69.17%	71.118×10^6	-132.577
^{65}Cu	$\frac{3}{2}$	30.83%	76.044×10^6	-142.018
^{107}Ag	$\frac{1}{2}$	51.84%	-10.889×10^6	$+20.239$
^{109}Ag	$\frac{1}{2}$	48.16%	-12.518×10^6	$+23.268$
^{129}Xe	$\frac{1}{2}$	24.4%	-74.521×10^6	$+139.045$
^{207}Pb	$\frac{1}{2}$	22.1%	55.805×10^6	-104.603
^{12}C	0	98.9%		
^{16}O	0	$\sim 100\%$		

Table 1.2. A selection of nuclear isotopes and their properties.
A complete listing of nuclear spins, magnetogyric ratios and
Larmor frequencies (omitting the sign) may be found on the
web site www.webelements.com.

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 and 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 consituents of matter, see F. Close, "The Quark Structure of Matter" in "The New Physics.", Ed. P. Davies, (Cambridge University Press, Cambridge, 1989).

Exercises for Chapter 1

1.1 Which of the following statements *must* be correct, which *might possibly* be correct, and which *cannot* be correct?

    i. The nucleus ^{89}Y (atomic number $= 39$) has a ground state spin $I = \frac{1}{2}$.

    ii. The nucleus ^{90}Zr (atomic number $= 40$) has a ground state spin $I = 1$.

    iii. The nucleus ^{91}Zr (atomic number $= 40$) has a ground state spin $I = \frac{1}{2}$.

    iv. The nucleus ^{92}Mo (atomic number $= 42$) has a ground state spin $I = 0$.

    v. The nucleus ^{138}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. Chapter 2 – Magnetism

2.1 The Electromagnetic Field

2.2 Macroscopic Magnetism

2.3 Microscopic Magnetism

2.4 Spin Precession

2.5 Larmor Frequency

2.6 Spin-Lattice Relaxation; Nuclear Paramagnetism

2.7 Transverse Magnetization and Transverse Relaxation

2.8 NMR Signal

2.9 Electronic Magnetism