5.1: Nuclear Magnetic Resonance (NMR) - Intrinsic Spins

Proton Nuclear Magnetic Resonance (^1H NMR) Spectroscopy is a powerful method used in the determination of the structure of unknown compounds. Many useful properties can be extracted from NMR techniques and only a few are discussed here:

For example, from organic chemistry, we learned that ^1H NMR spectrum gives:

- the # of different types of hydrogens present in the molecule
- the relative #'s of the different types of hydrogens
- the electronic environment of the different types of hydrogens
- the number of hydrogen "neighbor" a hydrogen has

Many types of information can be obtained from an NMR spectrum. Much like using infrared spectroscopy (IR) to identify functional groups, analysis of a NMR spectrum provides information on the number and type of chemical entities in a molecule. However, NMR provides much more information than IR. The impact of NMR spectroscopy on the natural sciences has been substantial. It can, among other things, be used to study mixtures of analytes, to understand dynamic effects such as change in temperature and reaction mechanisms, and is an invaluable tool in understanding protein and nucleic acid structure and function. It can be applied to a wide variety of samples, both in the solution and the solid state.

Spins

The concept of spin is regularly addressed in subatomic particle physics. However, to most people spin seems like an abstract concept. This is due to the fact there is no macroscopic equivalent of what spin is. However, for those people who have taken an introduction to chemistry course have seen the concept of spin in electrons. Electrons are subatomic particles which have spin intrinsic to them.

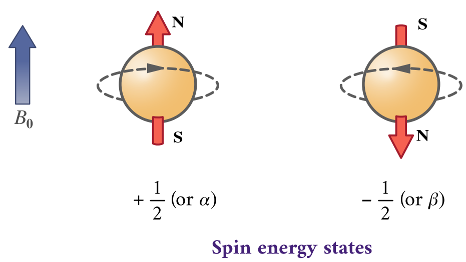

Figure 5.1.1: "Spinning" electrons. (CC BY-SA-ND; Reusch)

The nucleus is not much different. Spin is just another form of angular momentum. The nucleus consists of protons and neutrons and neutrons and protons are comprised of subatomic particles known as quarks and gluons. The neutron has 2 quarks with a -e/3 charge and one quark with a +2e/3 charge resulting in a total charge of 0. The proton however, has 2 quarks with +2e/3 charge and only one quark with a -e/3 charge giving it a net positive charge. Both protons and neutrons are spin=1/2.

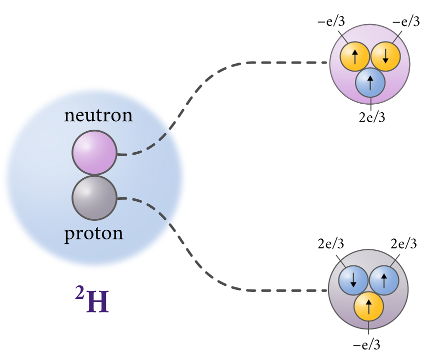

Figure 5.1.2: The atomic nucleus (black) of ^2H. The proton (green) and neutron (red) are composed of quarks (purple and teal) which have a charge and spin (arrow).

For any system consisting of n multiple parts, each with an angular momentum the total angular momentum can be described by J where

$$J = |J_1 + J_2 + ... + J_n|, |J_1 + J_2 + ... + J_n| - 1, ... |J_1 - J_2 - ... - J_n|$$

Here are some examples using the isotopes of hydrogen

- ${}^{1}H$ = 1 proton so J=1/2
- ${}^{2}H$= 1 proton and 1 neutron so $J = 1$ or 0.

For larger nuclei, it is not immediately evident what the spin should be as there are a multitude of possible values. For the remainder of the discussion we will attribute the spin of the nucleus, I, to be an intrinsic value. There are some rules that the nuclei do follow with respect to nuclear spin. They are summarized in the table below.

Table 1. General rules for determination of nuclear spin quantum numbers

Mass Number	Number of Protons	Number of Neutrons	Spin (I)	Example
Even	Even	Even	0	${}^{16}O$
	Odd	Odd	Integer (1,2,...)	${}^{2}H$
Odd	Even	Odd	Half-Integer (1/2, 3/2,...)	${}^{13}C$
	Odd	Even	Half-Integer (1/2, 3/2,...)	${}^{15}N$

General Rule

Nuclei with even Z and even A have $I = 0$. Confirm with the examples above.

The interaction of with an external magnetic field, $\vec{H}$ (or $\overrightarrow{B_0}$) comprises the spectroscopy we call **NMR**. Most nuclei of greatest interest in NMR have I=1/2, for example, ${}^{1}H$, ${}^{13}C$, ${}^{19}F$, ${}^{31}P$. However, many nuclei are non-magnetic, I=0 and cannot be studied by NMR: ${}^{4}He$, ${}^{12}O$, ${}^{32}S$, ${}^{12}C$. NMR can only be performed on isotopes whose natural abundance is high enough to be detected. Some of the nuclei routinely used in NMR are listed below.

Nuclei	Unpaired Protons	Unpaired Neutrons	Net Spin
${}^{1}H$	1	0	1/2
${}^{2}H$	1	1	1
${}^{31}P$	1	0	1/2
${}^{23}Na$	1	2	3/2
${}^{14}N$	1	1	1
${}^{13}C$	0	1	1/2
${}^{19}F$	1	0	1/2

$\vec{J}$ is the angular momentum of the nucleus and has dimensions of $\hbar$. For convenience, let's define a vector $\vec{I}$ that is parallel to $\vec{J}$, but is dimensionless:

$$\vec{J} = \hbar \vec{I}$$

The magnetic moment is also proportional to $\vec{J}$ and is collinear. We can introduce the proportionality constant, γ (also called the **magnetogyric ratio** or **gyromagnetic ratio**)

$$\vec{\mu}_N = \gamma \vec{J} = \gamma \hbar \vec{I}$$

For most nuclei, γ is positive, so $\overrightarrow{\mu_N}$ and are $\vec{I}$ parallel. But for some (^{15}N and ^{17}O), is negative, so and are *antiparallel* for these nuclei.

Nucleus	γ (10^6 rad.s^{-1}.T^{-1})	$\gamma/2\pi$ (MHz.T^{-1})
^{1}H	267.513	42.576
^{2}H	41.065	6.536
^{3}He	-203.789	-32.434
^{7}Li	103.962	16.546
^{13}C	67.262	10.705
^{14}N	19.331	3.077
^{15}N	-27.116	-4.316
^{17}O	-36.264	-5.772
^{19}F	251.662	40.053
^{23}Na	70.761	11.262
^{31}P	108.291	17.235
^{129}Xe	-73.997	-11.777

By the way

For electron gyromagnetic ratio is much, much bigger (addressed with EPR - electron paramagnetic resonance)

$$\gamma_{\mathrm{e}} = -1.760859770(44) \times 10^{11} \mathrm{rad s}^{-1}\ \mathrm{T}^{-1}$$

Bulk Magnetization

The net or bulk magnetization of the sample is given by M and is the sum of each individual magnetic vector, or

$$\vec{M} = \sum \vec{\mu}_i$$

since these magnetic moments are vectors and are randomly aligned, the bulk magnetization arising from the nucleus is zero in the absence of an external magnetic field. There may be unpaired electrons which give rise to paramagnetic, anti ferromagnetic, or ferromagnetic properties. However, if an external magnetic field is applied, the nuclei will align either with or against the field and result in a non-zero bulk magnetization.