CHE-2F4Y
NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Course outline

1. Basic principles

2. Chemical shifts

3. Spin-spin coupling

4. Chemical exchange

5. Fundamentals of pulsed NMR

6. Nuclear spin relaxation

Nuclear Magnetic Resonance

Originally demonstrated in 1946
- Groups of Purcell and Bloch.

The Nobel prize in 1995 was won by R Ernst for his contributions to the development of NMR.

The Nobel prize in 2002 was won by K Wüthrich for his work in protein structure determination by NMR.

NMR is *the* method for analysing synthetic reactions

Idea of magnetic energy levels
- Pauli in 1924 to explain the atomic hyperfine structure

Magnetic Resonance Imaging (MRI)
2005 Nobel Prize for
Physiology and Medicine

Professors Lauterbur and Mansfield

Fundamentals

Quantisation of angular momentum.

Nucleus has spin
- spin angular momentum
  - **- Nuclear**

Total angular momentum ***P*** can only have discrete values.

$$P = \hbar\sqrt{I(I+1)}$$

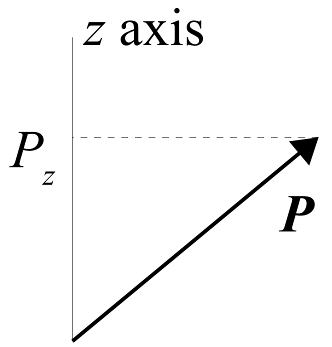
I, spin quantum number
- allowed angular momentum

$\hbar$ is $h/2\pi$

h is Planck's constant = 1.0544 x 10^{-34} Js

Energy is also quantised.

Angular momentum is a vector property.
- must state its direction as well as the magnitude.
- define the projection of the vector onto a *z* axis



Quantise in the z direction

- magnetic quantum number, m_I.

$$P_z = \hbar m_I$$

Allowed values for m_I

$I, I-1, I-2, \ldots\ldots -I$

In total $2I + 1$

Examples

$I = 4$

Allowed m_I = +4, +3, +2, +1, 0, -1, -2, -3, -4

I can also be half integral, for example I = 3/2.

Same conditions apply to m_I

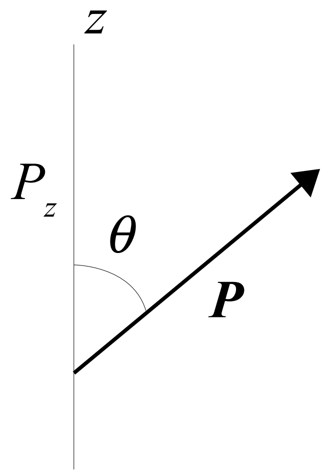
m_I = +3/2, +1/2, -1/2, -3/2.

Most useful nucleus for NMR, the proton, ^1H which has I = 1/2

so m_I = +1/2, -1/2.

If $m_I = 1/2$

Magnitude of the angular momentum P is $\frac{\sqrt{3}}{2}\hbar$



$$\cos\theta = \frac{m_I}{\sqrt{I(I+1)}} = \frac{1}{\sqrt{3}}$$

$$\theta = 54.7^o$$

Degenerate in the absence of a magnetic field

Notice

- direction of the angular momentum vector is only defined in the z axis.
- any direction allowed in the x and y axes.
- in an ensemble with many spins the average value of the x and y components of the angular momentum will be zero.

Nuclear spin

What determines the spin of a given nucleus?

Both the proton and the neutron have spin I=1/2.

1. Odd mass number: Half integral spin
   e.g. ^{1}H, ^{13}C, ^{15}N, I=1/2
   and ^{23}Na, I=3/2

2. Even mass number/
   even charge number: Zero spin
   e.g. ^{12}C, ^{16}O

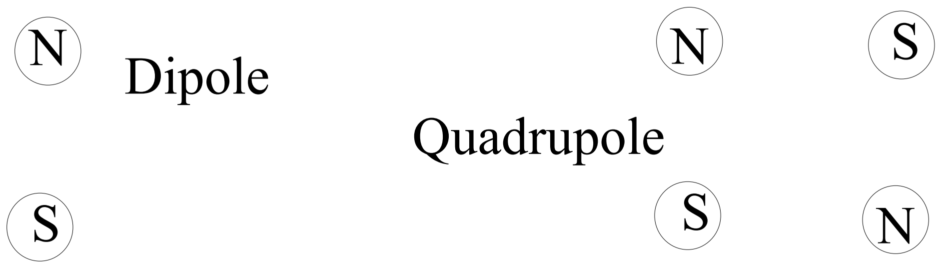
3. Even mass number/
   odd charge number: Integral spin
   e.g ^{2}H, ^{14}N

Consequence
Common nuclei no NMR properties

^{12}C is 99% abundant and ^{16}O is 99.9%.

Quadrupolar nuclei

I >1/2 possess a quadrupole moment



Nuclear magnetic states associated with quadrupolar nuclei tend to have shorter lifetimes

- broader lines
- "no" scalar coupling : Not observable indirectly

Consequently they are not readily studied and for most purposes can be regarded as non-magnetic

Emphasis in these lectures will be on spin-1/2 nuclei.

Magnetic moment

A nucleus possess a charge and is “spinning” it will “generate” a magnetic field.

- **Magnetic**

This is expressed by:

$$\boldsymbol{\mu} = k\,\boldsymbol{P}$$

k is a collection of fundamental constants

$$k = \frac{g_N \mu_N}{\hbar} \quad \text{with} \quad \mu_N = \frac{eh}{4\pi m_p}$$

$\mu_N = 5.05 \times 10^{-27}\ JT^{-1}$

μ_N is the nuclear magneton
g_N is the nuclear g-factor

Notation common to both nuclear and electron spin resonance. But usually in NMR the magnetogyric ratio, γ, is used.

So $k = \gamma$

(UNITS rad $T^{-1}s^{-1}$ with the applied field B in Tesla)

Total magnetic moment

$$\boldsymbol{\mu} = \gamma \boldsymbol{P}$$

since

$$P = \hbar \sqrt{I(I+1)}$$

$$\mu = \gamma \hbar \sqrt{I(I+1)}$$

In the case of the projection onto the *z* axis

$$\mu_z = \gamma \hbar m_I$$