1995-1997

Nuclear Magnetic Resonance Spectroscopy

- The physical basis of NMR spectroscopy. Main NMR parameters.

- Chemical shifts.

- Spin-spin coupling.

- Pulse Fourier Transform NMR. The rotating frame of reference.

- Spin-lattice and spin-spin relaxation.

- Experimental aspects. Double resonance. Polarization transfer.

- The nuclear Overhauser effect.

- Two-dimensional NMR.

- Molecular dynamics studies by NMR spectroscopy.

- Solid-state NMR spectroscopy.

Reference Books

General introduction

H. Friebolin,"Basic One- and Two-Dimensional NMR Spectroscopy", VCH, 1993.

R. J. Abraham, J. Fisher and P. Loftus, "Introduction to NMR Spectroscopy", Wiley 1988.

Experimental aspects

A. E. Derome, "Modern NMR Techniques for Chemical Research", Pergamon Press, 1987.

J. K. M. Sanders and B. K. Hunter, "Modern NMR Spectroscopy: a guide for chemists", Oxford University Press, 1993.

R. W. King and K. R. Williams, *J. Chem. Ed.*, 66, A213 (1989); *ibid*, 66, A243 (1989); *ibid*, 67, A93 (1990); *ibid*, 67, A125 (1990).

Spectral interpretation (^{1}H and ^{13}C NMR)

D. H. Williams and I. Fleming, "Spectroscopic Methods in Organic Chemistry", McGraw-Hill, 1989.

H. Günther, "NMR Spectroscopy: Basic Principles, Concepts, and Applications in Chemistry", Wiley, 1995.

R. M. Silverstein, G. C. Bassler and T. C. Morrill, "Spectrometric Identification of Organic Compounds", Wiley, 1991.

Multinuclear NMR

J. Mason (ed.), "Multinuclear NMR", Plenum Press, 1987.

R.K. Harris, B.E. Mann, "NMR and the Periodic Table", Academic Press, 1978.

Physicochemical approach

R. K. Harris, "Nuclear Magnetic Resonance Spectroscopy", Longman, 1986.

D. Shaw, "Fourier Transform NMR Spectroscopy", Elsevier, 1984

T.C. Farrar, E.D. Becker, "Pulse and Fourier Transform NMR", Acad. Press, 1971

J.W. Hennel, J. Klinowski, "Fundamentals of NMR",Longman, 1993

The physical basis of NMR spectroscopy. Main NMR parameters.

Nuclear properties

Any given nucleus can be characterized by its <u>mass, charge and nuclear angular momentum</u>. The magnitude of the nuclear angular momentum P is given by
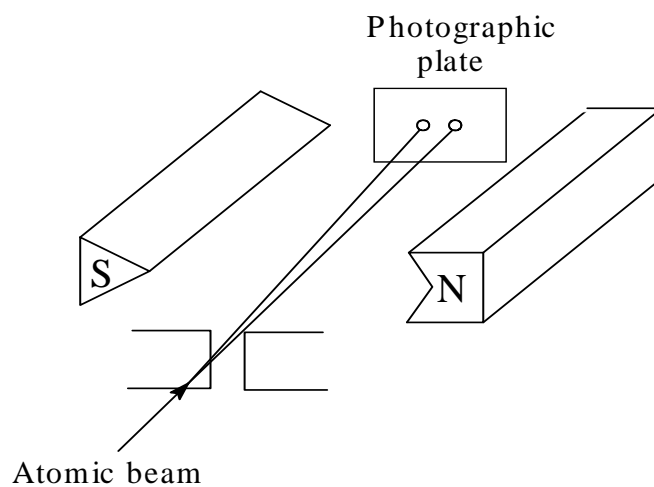
$$P = \hbar \, (I \, (I + 1))^{1/2}$$

where $\hbar = h/2\pi$, h is Planck's constant and I is the angular momentum quantum number (nuclear spin).

Angular momentum is a vector quantity and has associated with it a magnetic moment:

$$\mu = \gamma \, P$$

where γ is the gyromagnetic ratio of the nucleus in question, which is an intrinsic nuclear property.

The Stern-Gerlach Experiment

The electron itself, independently whether or not it moves around an orbit, has its own angular momentum, known as electron spin and associated intrinsic magnetic moment:

$$\mu = \gamma P, \qquad \gamma = g \, \frac{-e}{2m_e}, \; g \approx 2 \text{ (Landé factor)}$$

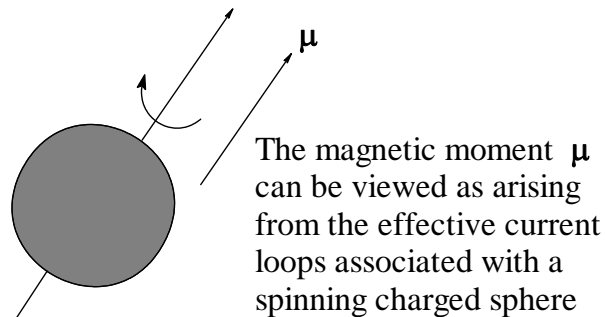The nuclear gyromagnetic ratio: $\qquad \gamma = g_n \, \frac{-e}{2m_p}, \qquad g_n \approx 1$

Since $m_p / m_e = 1836$, the nuclear magnetic moment should be *ca.* 2000 times smaller than the magnetic moment of the electron.

When either N_p or N_n is odd number non-zero total spin results. The spin I of the nucleus is either integral or half-integral: 0, 1/2, 1, 3/2, 2, 5/2, ... A high value of gyromagnetic ratio provides a relatively high sensitivity.

Nucleus	N_p	N_n	Spin	$\gamma / 10^7$ rad T^{-1} s^{-1}
^{1}H	1	0	1/2	26.7519
^{2}H	1	1	1	4.1066
^{3}H	1	2	1/2	28.5350
^{12}C	6	6	0	-
^{13}C	6	7	1/2	6.7283
^{16}O	8	8	0	-
^{17}O	8	9	5/2	-3.6280

Classical model

The nucleus is assumed to be spherical, rotates about an axis.

The magnetic moment μ can be viewed as arising from the effective current loops associated with a spinning charged sphere
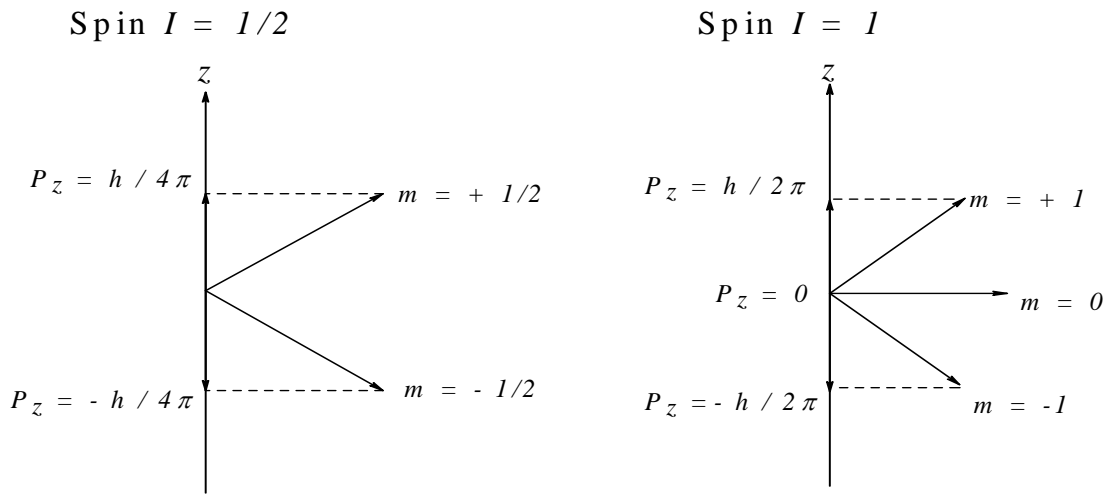
Nuclei in a static magnetic field

If a nucleus is placed in a static magnetic field B_0, the direction of its angular momentum P is determined by quantum number m:
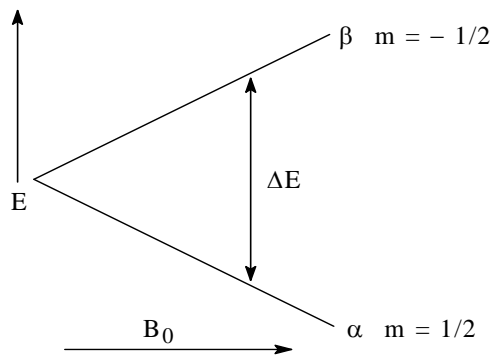
$$P_z = \hbar\, m$$

$| m | \leq I$, the allowed values of m are *I, I-1, I-2...-I*. There will be *(2I+1)* different values of m, corresponding to *(2I+1)* different directions of *P* relative to *B_0*.

$$\mathrm{Spin}\ I\ =\ 1/2 \qquad\qquad \mathrm{Spin}\ I\ =\ 1$$

$$\mu_z = \gamma\, P_z = \gamma\, \hbar\, m$$

$$E = -\, \boldsymbol{\mu}\cdot\mathbf{B_0} = -\, \mu_z\, B_0 = -\gamma\, \hbar\, m\, B_0$$

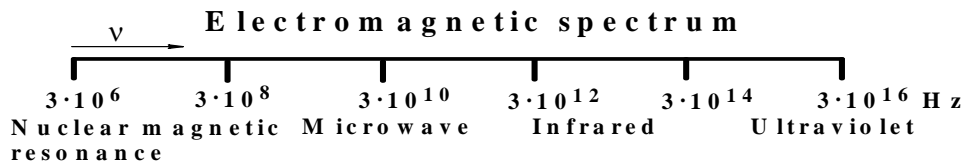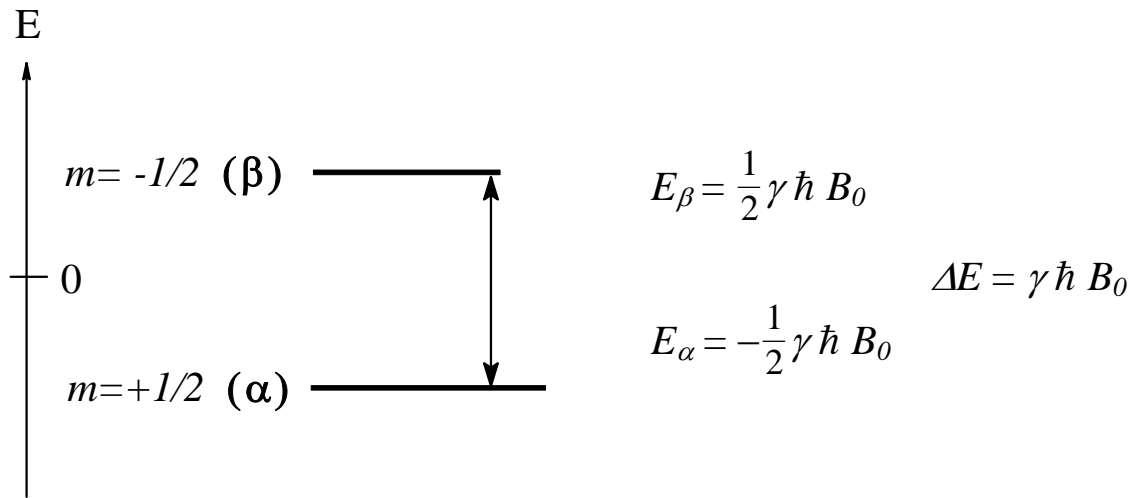There are *(2I+1)* energy states (*the nuclear Zeeman levels*).

For the proton with $I = 1/2$, there are two possible Zeeman levels corresponding to $m=+1/2$ (μ_z is parallel to the field direction, state α) and $m=-1/2$ (μ_z is antiparallel to the field direction, state β).

The selection rule: *$\Delta m = \pm 1$*

$$\Delta E = \gamma\, \hbar\, B_0$$

$$\Delta E = h\, \nu \qquad \Rightarrow \qquad \nu_0 = (\gamma / 2\pi)\, B_0$$

B_0 1.41-17.6 T $\Rightarrow \nu_0(^1\mathrm{H})$ 60-750 MHz

E

$m = -1/2$ (β) ————————

0

$m = +1/2$ (α) ————————

$$E_\beta = \frac{1}{2}\gamma\hbar B_0$$

$$\Delta E = \gamma\hbar B_0$$

$$E_\alpha = -\frac{1}{2}\gamma\hbar B_0$$

Electromagnetic spectrum

ν →

| $3\cdot10^6$ | $3\cdot10^8$ | $3\cdot10^{10}$ | $3\cdot10^{12}$ | $3\cdot10^{14}$ | $3\cdot10^{16}$ Hz |

Nuclear magnetic resonance   **Microwave**   **Infrared**   **Ultraviolet**

Classical description of NMR experiment. Larmor precession.

In terms of classical description of the NMR experiment the direction of **μ** is rotating on the surface of a cone with its axis along **B$_0$**. Such a motion is referred as *Larmor precession*.

B$_0$

ω_0
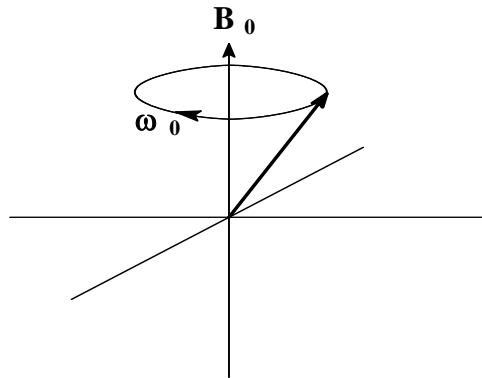
The induced angular velocity is given by

$$\omega_0 = -\gamma B_0$$

$\omega_0 = 2\pi\nu_0$ [with ν_0 (ν_L) referred as Larmor frequency]

Populations of energy levels. The intensity of the NMR line.

For nuclei with spin $I=1/2$, the ratio of the number of nuclei in the upper energy level β to the number of nuclei in the lower energy level α is determined by Boltzmann's equation in high-temperature approximation:

$$N_\beta / N_\alpha = exp\,(-\Delta E / kT) \approx 1 - \Delta E / kT = 1 - \gamma \hbar B_0 / kT$$

where k is the Boltzmann constant and T is the absolute temperature in K. At $T=293$ K, $B_0=1$ T, $\gamma = 26.75 \times 10^7$ T^{-1}s^{-1} (^{1}H) $\Rightarrow N_\beta/N_\alpha = 0.999993$, there are 1000007 spins at level α for 1000000 spins at level β.

For the sample consisting of identical molecules, each with one magnetic nucleus of spin 1/2, the equilibrium population difference between the two states α and β is

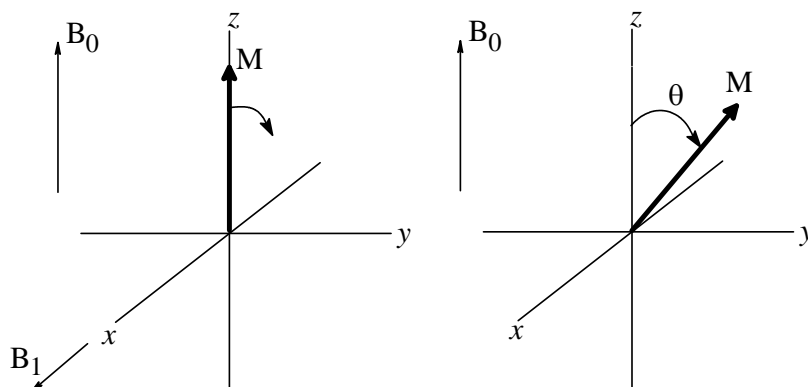$$\Delta n = N_\alpha - N_\beta = N\,\Delta E / 2kT$$

where N is the total number of nuclei in the sample.
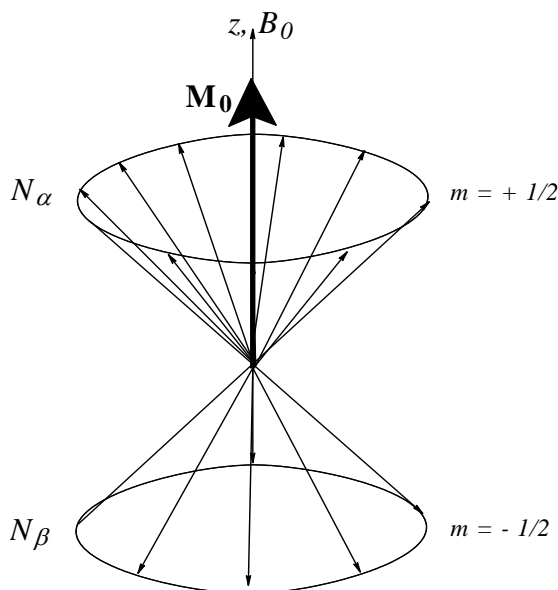
$$M_0 = N_\alpha \mu_{z\alpha} + N_\beta \mu_{z\beta} = \Delta n\,\mu_{z\alpha} = (1/2)\,\gamma\,\hbar\,\Delta n = (1/4)N(\gamma\hbar)^2 B_0 / kT = C\,(B_0 / T)$$

The total magnetization is stationary and aligned along the z axis.

The observed signal height, *S*, is given by:

$$S \propto \gamma^4 B_0^2 N B_1^2 g(\nu) / T$$

where *g(ν)* is a signal shape factor (Lorentzian or Gaussian type function) to account for the fact that there is some transition probability at frequencies differing slightly from exact resonance frequency.

The implications of the above relationship are the following:

(i) the dependence of *S* on γ^4 $\Rightarrow$ those nuclei resonating at high frequencies will have relatively intense signals (^{1}H, ^{19}F);

(ii) the dependence of *S* on B_0 $\Rightarrow$ high-field work is desirable;

(iii) the inverse proportionality of *S* and *T* $\Rightarrow$ low-temperature measurements may provide higher sensitivity.

Main NMR parameters

Anisotropic interactions giving rise to severe broadening of lines in solids are effectively averaged to zero in liquid samples and, therefore, it is possible to observe hyperfine structure in NMR spectra: chemical shift and spin-spin coupling.

The presence of electrons in the molecules makes itself felt in chemical shielding. Putting the sample in the strong, constant external field B_0 induces electronic currents, that, in turn, produce an induced magnetic field B′, which modifies local magnetic field B_{loc} at the site of the nucleus. B′ is proportional to B_0; the chemical shielding parameter is defined by:

$$B_{loc} = (1 - \sigma) B_0$$

The absorption frequency of the nucleus is

$$\nu = (\gamma / 2\pi) \, B_{loc} = (\gamma / 2\pi) \, B_0 \, (1 - \sigma) = \nu_0 \, (1 - \sigma)$$

It is convenient to define a reference frequency, typically that of TMS: $\nu_{ref} = \nu_0 \, (1 - \sigma_{ref})$,

so that we can define a chemical shift δ: $\delta = 10^6 \, (\nu - \nu_{ref}) / \nu_0$

δ (in parts per million, ppm) is independent of B_0.

Consider a simple case of two environments labeled A and X characterized by ν_A and ν_X:

$$\nu_A = \gamma \, B_0 \, (1 - \sigma_A) \qquad\qquad \nu_X = \gamma \, B_0 \, (1 - \sigma_X)$$

The energy of interaction with an external magnetic field is:

$$E(m_A \, m_X) = - h \, \nu_A \, m_A - h \, \nu_X \, m_X$$

X: $\Delta m_X = \pm 1$ A: $\Delta m_A = \pm 1$

        $\Delta m_A = 0$ $\Delta m_X = 0$

This means that there are two transitions in the NMR spectrum at frequencies ν_A and ν_X.

There may also be an interaction between the nuclei themselves arising from an indirect coupling through the electron spins called the *spin-spin interaction*:

$$E(m_A \, m_X) = - h \, \nu_A \, m_A - h \, \nu_X \, m_X + h \, J_{AX} \, m_A \, m_X$$

The presence of *J* coupling causes a further splitting in the energy level system, since the last term is positive or negative depending on the values of m_A and m_X. *J* is field independent and is always expressed in Hz.

Two-spin system

Single-spin system

$J_{AX} = 0$ $J_{AX} \neq 0$