

1 Introduction

The phenomenon of nuclear magnetic resonance (NMR) is based on magnetic properties of nuclei and therefore they are included here.

1.1 Magnetic properties of nuclei

All nuclei carry a charge and in some nuclei this charge spins on the nuclear axis generating a magnetic field along the axis. These nuclei behave as tiny bar magnets. The magnetic properties of a nucleus can be specified in terms of the nuclear spin quantum number I ($I = 0, 1/2, 1, 3/2, 2, 5/2, \dots, 7$) and the magnetic moment μ of the nucleus. The magnetic moment of the nucleus is proportional to the nuclear angular momentum (nuclear spin) and is expressed by:

$$\mu = \gamma \mathbf{p} , \quad (1)$$

with

$$|\mathbf{p}| = [I(I+1)]^{1/2} \hbar . \quad (2)$$

where $\hbar = h/(2\pi)$ and γ is a proportionality constant known as gyromagnetic or magnetogyric ratio (differing for each nucleus and essentially measures the strength of nuclear magnets). h is Planck's constant ($h = 6.626075 \cdot 10^{-34} \text{ J s}$).

The magnetic moment μ can be also expressed in terms of the nuclear magneton μ_N by:

$$\mu = g_N \mu_N \mathbf{p} , \quad (3)$$

where g_N is known as the nuclear g -factor (which is determined experimentally). μ_N is defined as $\mu_N = e \hbar / (2 m_p) = 5.0507866 \cdot 10^{-27} \text{ J T}^{-1}$ (e = electronic charge, m_p = mass of the proton).

Each proton and neutron has its own spin and spin number. I is the resultant of these spins. If the sum of protons and neutrons (i.e. mass number) is odd, I is half-integer ($I = 1/2, 3/2, 5/2, \dots$), if both protons and neutrons are even-numbered, I is zero ($I = 0$ denotes no spin) and if the sum is even, I is integer ($I = 1, 2, 3, 4 \dots$). The magnetic properties of some NMR nuclei are summarized in Table 1. Nuclei with $I > 0$ may be called magnetic as they develop the magnetic fields along the axis of spins and give rise to the phenomenon of nuclear magnetic resonance. Such nuclei do not simply possess magnetic dipoles, but rather possess electric quadrupoles (it measures the electric charge distribution within a nucleus when it possesses non-spherical symmetry) and interact with both, magnetic and electric gradients. The relative importance of the two effects is related to their magnetic moments and electric quadrupole moments.

1.2 Spinning nuclei in magnetic fields

A spinning nucleus generates a magnetic moment and when placed in an uniform magnetic field with the magnetic flux density \mathbf{B} it tends to align itself with the field. Unless the axis of the nuclear magneton is oriented exactly parallel or antiparallel to the magnetic field, a certain force is exerted by the applied field. Because the nucleus is spinning, the effect is that its rotational axis draws out a circle perpendicular to the external field (Fig. 1). This motion is called precession. The precessional angular velocity of a spinning top is known as Larmor frequency ω which is proportional to the applied magnetic flux density \mathbf{B} of the magnetic field and can be expressed by:

$$\omega = \gamma |\mathbf{B}|. \quad (4)$$

Table 1: Magnetic properties of NMR nuclei.

Isotope	Natural abundance %	Spin quantum number I	Magnetogyric ratio γ [$10^7 \text{ T}^{-1} \text{ s}^{-1}$]	Magnetic moment μ/μ_N	Quadrupole moment Q [fm^2]
^1n		1/2		-1.913042	
$^1\text{H}_1$	99.9844	1/2	26.752	2.7928474	
$^2\text{H}_1$	0.156	1	4.107	0.85738	0.2860
$^3\text{H}_1$	–	1/2	28.5335	2.9788	
$^3\text{He}_2$	0.000137	1/2		-2.127624	
$^7\text{Li}_3$	92.5	3/2		3.256424	4.01
$^{10}\text{B}_5$	18.83	3	2.8747	1.8006	8.459
$^{11}\text{B}_5$	81.17	3/2	8.5827	2.6880	4.059
$^{13}\text{C}_6$	1.108	1/2	6.728	0.70216	
$^{14}\text{N}_7$	99.635	1	1.9324	0.40357	2.02
$^{15}\text{N}_7$	0.365	1/2	-2.7126	-0.28304	
$^{17}\text{O}_8$	0.037	5/2	-3.628	-1.8930	-2.558
$^{19}\text{F}_9$	100.00	1/2	25.179	2.6273	
$^{23}\text{Na}_{11}$	100	3/2		2.217520	10.89
$^{29}\text{Si}_{14}$	4.70	1/2	-5.319	-0.55477	
$^{31}\text{P}_{15}$	100.00	1/2	10.840	1.1305	
$^{33}\text{S}_{16}$	0.74	3/2	2.054	0.64274	-6.78
$^{35}\text{Cl}_{17}$	75.40	3/2	2.627	0.82089	-8.165
$^{37}\text{Cl}_{17}$	24.60	3/2	2.184	0.68329	-6.435
$^{51}\text{V}_{23}$	99.750	7/2		5.1487	-5.2
$^{57}\text{Fe}_{26}$	2.1	1/2		0.090623	
$^{59}\text{Co}_{27}$	100	7/2		4.627	40.4
$^{73}\text{Ge}_{32}$	7.73	9/2		-0.8794677	-6.73
$^{75}\text{As}_{33}$	100	3/2		1.43947	31.4
$^{77}\text{Se}_{34}$	7.58	1/2	5.101	0.535042	
$^{79}\text{Br}_{35}$	50.54	3/2	6.7256	2.0991	29.3
$^{81}\text{Br}_{35}$	49.46	3/2	7.2245	2.2626	27.0
$^{89}\text{Y}_{39}$	100	1/2		-0.137415	
$^{95}\text{Mo}_{42}$	15.92	5/2		-0.9142	2.2
$^{113}\text{Cd}_{48}$	12.22	1/2		-0.62230	
$^{117}\text{Sn}_{50}$	7.61	1/2	-9.589	-1.00104	
$^{119}\text{Sn}_{50}$	8.58	1/2	-10.0318	-1.04728	
$^{123}\text{Te}_{52}$	0.908	1/2		-0.7369478	
$^{125}\text{Te}_{52}$	7.139	1/2		-0.8885051	-0.79
$^{127}\text{I}_{53}$	100.00	5/2	5.33521	2.7937	-0.789
$^{183}\text{W}_{74}$	14.40	1/2	–	0.11778	
$^{207}\text{Pb}_{82}$	22.6	1/2	5.56264	0.58219	

With $\omega/(2\pi) = \nu$ and therefore $2\pi\nu = \gamma|\mathbf{B}|$ the precessional frequency ν can be expressed by:

$$\nu = \gamma |\mathbf{B}| / (2\pi). \quad (5)$$

The Larmor frequency is such that a projection of the angular momentum on the direction of \mathbf{B} always assumes whole multiple of \hbar and therefore, not all possible precession “cones” occur, only some selected ones. The number of the possible alignments is $2I+1$ for spin I in the direction of magnetic field. These $2I+1$ orientations are quantized in the direction of magnetic field and the absorbable component m_I of the spin I can be expressed by the following equations for half-integer and integer spins, respectively:

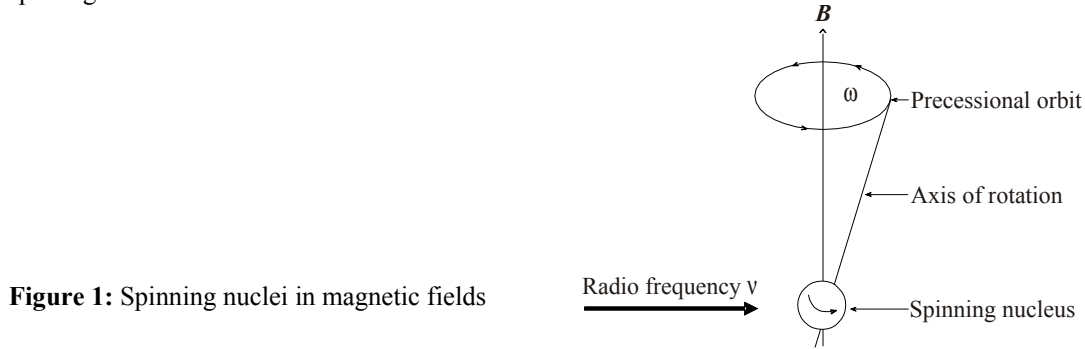
$$m_I = I, I-1, I-2, \dots, 1/2, -1/2, \dots, -(I-2), -(I-1), -I, \quad (6)$$

$$m_I = I, I-1, I-2, \dots, 1, 0, -1, \dots, -(I-2), -(I-1), -I. \quad (7)$$

In each case there are $2I+1$ values of the magnetic quantum number m_I . Each orientation is associated with a different energy level E and can be expressed by:

$$E = -\mu \mathbf{B} \text{ or } E = -\gamma \hbar |\mathbf{B}| m_I = -\hbar \omega m_I \quad (8).$$

This type of splitting of energy levels in magnetic fields for a nucleus ($I > 0$) is called nuclear Zeeman splitting.



1.3 Theory of nuclear resonance

The basis of nuclear magnetic resonance is to induce transitions between the nuclear Zeeman energy levels. Such transitions are affected by placing an alternating field \mathbf{H}_a perpendicular to the applied field \mathbf{H} in such a way that frequency can be altered conveniently. Selection rules permit such transitions between energy levels 2 and 1 that $m_{I,2} - m_{I,1} = \Delta m_I = \pm 1$ i.e. $\Delta m_I = +1$ when energy is absorbed (transition is from lower to higher energy level) and $\Delta m_I = -1$ when energy is emitted (transition from higher to lower energy level). The transitions from E_2 to E_1 energy levels can be expressed by:

$$\Delta E = E_2 - E_1 = \gamma \hbar |\mathbf{B}| m_{I,2} - \gamma \hbar |\mathbf{B}| m_{I,1} = \gamma \hbar |\mathbf{B}| (m_{I,2} - m_{I,1}) \quad (9)$$

According to selection rules of quantum mechanics, $m_{I,2} - m_{I,1} = \pm 1$ depending on whether energy is absorbed or emitted, Eq. (9) is reduced:

$$\Delta E = \pm \gamma \hbar |\mathbf{B}| \quad (10)$$

When the frequency of electromagnetic radiation necessary to induce a transition from one nuclear spin state to another is exactly equal to the precessional frequency of spinning nucleus, they are in resonance and the phenomenon of resonance occurs. Thus nuclear resonance (absorption or emission of energy) occurs when a magnetic nucleus ($I > 0$) is placed in a uniform magnetic field H and subjected to electromagnetic radiation of appropriate frequency matching to the precessional frequency of spinning. Under these conditions the frequency of electromagnetic radiation causing resonance can be expressed by:

$$\Delta E = h \nu = \gamma \hbar |\mathbf{B}| \text{ or } \nu = \gamma |\mathbf{B}| / (2 \pi). \quad (11)$$

Eq. (11) also exhibits that the precessional frequency ν is $\gamma |\mathbf{B}| / (2 \pi)$.

Eq. (11) correlating electromagnetic frequency causing nuclear resonance with magnetic field strength is the basis of NMR spectroscopy and from this equation the electro-radiation frequency causing the resonance for various field strengths can be calculated. Precessional frequencies for some nuclei at various magnetic field strengths are summarized in Table 2.

1.4 Chemical shift

The fundamental NMR Equation (11), $\nu = \gamma |\mathbf{B}| / (2 \pi)$, exhibits that a single peak should be obtained from the interaction of radiofrequency energy and the magnetic field on a nucleus as γ is characteristic for a nucleus. However, the nucleus is shielded by an electron cloud whose density varies with the environment. This variation gives rise to different absorption positions. Under the influence of the applied magnetic field electrons circulate and generate their own magnetic field opposing the applied field and cause a shielding effect. The magnitude of the induced field is proportional to the magnetic field. The effective magnetic field \mathbf{B}_{eff} experienced by the nucleus is changed by this small local field $\sigma \mathbf{B}$ (due to electronic circulation), such that $\mathbf{B}_{\text{eff}} = \mathbf{B} - \sigma \mathbf{B}$ with σ = shielding constant. This shielding effect influences the resonance condition:

$$\nu = [\gamma |\mathbf{B}| / (2 \pi)](1 - \sigma) \quad (12)$$

A nucleus in different environments is shielded by the circulation of surrounding electrons to different extents. Different values of $\sigma \mathbf{B}$, each depending on the magnitude of the applied \mathbf{B} field are obtained for the nucleus. Because the strength of the applied magnetic field cannot be determined to the required degree of accuracy, the absolute position of absorptions cannot be obtained directly from the instrument. However, the relative position of absorption can readily be obtained with an accuracy of ± 1 Hz or lower. The separation of resonance frequencies of a nucleus in different structural environments from an arbitrarily chosen standard is termed as chemical shift. A plot of the chemical shifts (frequencies of absorption peaks) versus the intensities of absorption peaks (which for some nuclei may by integration provide the number of nuclei) constitutes a NMR spectrum. The chemical shift is symbolized by δ (delta) and is measured in ppm (parts per million) according to:

$$\delta \text{ (in ppm)} = [(\nu_s - \nu_r) / \nu_r] \cdot 10^6 \quad (13)$$

where ν_s and ν_r are the resonance frequencies in Hz of the sample s and the reference substance r , respectively, at constant field $B = B_r = B_s$. Since field and frequency are linearly related, Equation (13) can be transformed to:

$$\delta \text{ (in ppm)} = [(B_s - B_r) / B_r] \cdot 10^6 \quad (14)$$

where B_s and B_r refer to the fields at resonance for the sample s and the reference substance r , respectively, at constant frequency $\nu = \nu_r = \nu_s$. The chemical shift in Hz is directly proportional to the applied field B and therefore to the applied frequency. It is dependent on diamagnetic shielding induced by the applied field. It is the ratio of the necessary change in field to the reference field or the necessary change in frequency to the reference frequency and hence a dimensionless number. To spread out chemical shifts i.e. to increase separation of resonance signals, a high magnetic field is applied which constitutes high resolution NMR spectroscopy. In the 1950s and 1960s, chemical shifts were also expressed in an alternative scale, τ , which is related to δ :

$$\tau = 10.00 - \delta \quad (15)$$

but this convention has been abandoned.

High values of chemical shifts (δ in ppm) correspond to high-frequency shifts (“downfield”) due to a deshielding of the nucleus; and low values correspond to low-frequency shifts (“upfield”) due to shielding.

Table 2: Precessional frequencies ν as a function of the magnetic flux density B

	ν [MHz]						
B [T]	2.35	4.70	7.05	9.40	11.74	14.09	21.14
Nucleus							
$^1\text{H}_1$	100.0	200.0	300.0	400.0	500.0	600.0	900.0
$^2\text{H}_1$	15.3	30.7	46.1	61.4	76.8	92.1	138.2
$^3\text{H}_1$	106.7	213.3	320.0	426.7	533.3	640.0	960.0
$^3\text{He}_2$	76.2	152.4	228.5	304.7	380.9	457.1	685.6
$^7\text{Li}_3$	38.9	77.7	116.6	155.5	194.3	233.2	349.8
$^{10}\text{B}_5$	10.5	21.5	32.2	43.0	53.7	64.5	96.7
$^{11}\text{B}_5$	32.0	64.2	96.3	128.3	160.4	192.5	288.8
$^{13}\text{C}_6$	25.1	50.3	75.4	100.6	125.7	150.9	226.3
$^{14}\text{N}_7$	7.2	14.4	21.7	28.9	36.1	43.3	65.0
$^{15}\text{N}_7$	10.1	20.3	30.4	40.5	50.7	60.8	91.2
$^{17}\text{O}_8$	13.6	27.1	40.7	54.2	67.8	81.3	122.0
$^{19}\text{F}_9$	94.1	188.2	282.2	376.3	470.4	564.5	846.7
$^{23}\text{Na}_{11}$	26.5	52.9	79.4	105.8	132.3	158.7	238.1
$^{29}\text{Si}_{14}$	19.5	39.7	59.6	79.5	99.3	119.2	17.8
$^{31}\text{P}_{15}$	40.5	81.0	121.4	161.9	202.4	242.9	364.3
$^{33}\text{S}_{16}$	7.6	15.3	23.0	30.7	38.	4.6	6.9
$^{35}\text{Cl}_{17}$	9.6	19.6	29.4	39.2	49.0	58.8	88.2
$^{37}\text{Cl}_{17}$	8.2	16.3	24.5	32.6	40.8	48.9	73.4
$^{51}\text{V}_{23}$	9.6	52.6	78.9	105.2	131.4	157.7	236.6
$^{57}\text{Fe}_{26}$	3.2	6.5	9.7	12.9	16.2	19.4	29.1
$^{59}\text{Co}_{27}$	23.6	47.2	70.8	94.5	118.1	141.7	212.5
$^{73}\text{Ge}_{32}$	3.5	7.0	10.5	14.0	17.4	20.9	31.4
$^{75}\text{As}_{33}$	17.1	34.3	51.4	68.5	85.6	102.8	154.1
$^{77}\text{Se}_{34}$	19.1	38.1	57.2	76.3	95.3	114.4	171.6
$^{79}\text{Br}_{35}$	24.5	50.1	75.2	100.2	125.3	150.3	225.5
$^{81}\text{Br}_{35}$	26.5	54.0	81.0	108.0	135.0	162.0	243.1
$^{89}\text{Y}_{39}$	4.9	9.8	14.7	19.6	24.5	29.4	44.1
$^{95}\text{Mo}_{42}$	6.5	13.0	19.5	26.1	32.6	39.1	58.6
$^{113}\text{Cd}_{48}$	22.2	44.4	66.5	88.7	110.9	133.1	119.6
$^{117}\text{Sn}_{50}$	35.6	71.3	106.9	142.5	178.1	213.8	320.6
$^{119}\text{Sn}_{50}$	37.3	74.5	111.8	149.1	186.4	223.6	335.5
$^{123}\text{Te}_{52}$	26.2	52.4	78.6	104.8	131.0	157.2	235.9
$^{125}\text{Te}_{52}$	31.6	63.2	94.8	126.4	158.0	189.6	284.4
$^{127}\text{I}_{53}$	20.0	40.0	60.0	80.0	100.0	120.0	180.1
$^{129}\text{Xe}_{54}$	27.7	55.3	83.0	110.6	138.3	166.0	248.9
$^{183}\text{W}_{74}$	4.1	8.3	12.5	16.6	20.8	25.0	37.4
$^{187}\text{Os}_{76}$	2.3	4.6	6.9	9.2	11.5	13.8	20.7
$^{195}\text{Pt}_{78}$	21.5	43.0	64.5	86.0	107.5	129.0	193.5
$^{199}\text{Hg}_{80}$	17.8	35.7	53.5	71.3	89.1	107.0	160.4
$^{205}\text{Tl}_{81}$	57.7	115.4	173.1	230.8	288.5	346.2	519.4
$^{207}\text{Pb}_{82}$	X	41.8	62.8	83.7	104.6	125.5	188.3

1.5 Coupling constant

The position of the resonance signal of a nucleus A depends on its electronic and magnetic environment. In addition, it may be affected by neighboring nuclei B if these are magnetic themselves and act through intervening bonds (scalar coupling). For example, in the case of both nuclei A and B possessing $I = 1/2$, nucleus B can either have its magnetic moment aligned parallel to that of nucleus A or opposite; both spin orientations of B are nearly equally populated (Boltzmann distribution). In this way, nucleus B can either increase the net magnetic field experienced by A or decrease it, a consequence of the different energies of the spin interaction. Thereby, the two spin orientations of B give rise to two resonance lines of nucleus A. Their distance, usually given in Hz, is called the coupling constant J . If the antiparallel combination of the spin states of A and B is energetically favored (right-hand resonance of the doublet), the sign of J is positive by definition, whereas $J < 0$ if the parallel combination is favored. Such signs cannot be read easily from NMR signals so that, generally, coupling constants reported in the literature are given as absolute values. Of course, nucleus A has the same effect on B, i.e., the signal of B is a doublet as well with the same frequency distance.

Coupling constants (in Hz) are independent of the external field because they reflect an intramolecular nuclear interaction energy. However, there is a strong dependence of J -values of the number of bonds between the coupling partners. One-bond couplings [$^1J(A,B)$] are the largest, and J -values tend to decrease with the number of intervening bonds: *geminal* [$^2J(A,B)$], *vicinal* [$^3J(A,B)$] and long-range coupling [$^nJ(A,B)$; $n > 3$]. On the other hand, electronegativities of attached atoms or groups and stereochemical influences play a significant role as well.

If a nucleus A has more than one coupling partner, its signal appearance changes in that each partner causes a new duplication. Thereby, multiplets arise from which the number of coupling partners and the coupling constants for each pair can be determined. However, this evaluation procedure is possible only in first-order spin systems where the ratio of the chemical shift difference $\Delta\nu = \nu(A) - \nu(B)$ (in Hz, not in ppm) and the coupling constant $J(A,B)$ is larger than 10. At lower ratios, quantum mechanics effects may obscure line distances and relative intensities within multiplets so that exact chemical shifts and coupling constants can be detected only by calculation and simulation, not by direct evaluation.

1.6 Organization of data

The volume III/35D contains chemical shifts δ (in ppm) and coupling constants J (in Hz) for carbon-13 nuclei. The present subvolume III/35D, Part 2 provides data for aromatic compounds. For each nucleus the arrangement of compounds is based on their gross formulae arranged according to Hill's system: carbon comes first, hydrogen second and then other element in alphabetical order.