

NMR

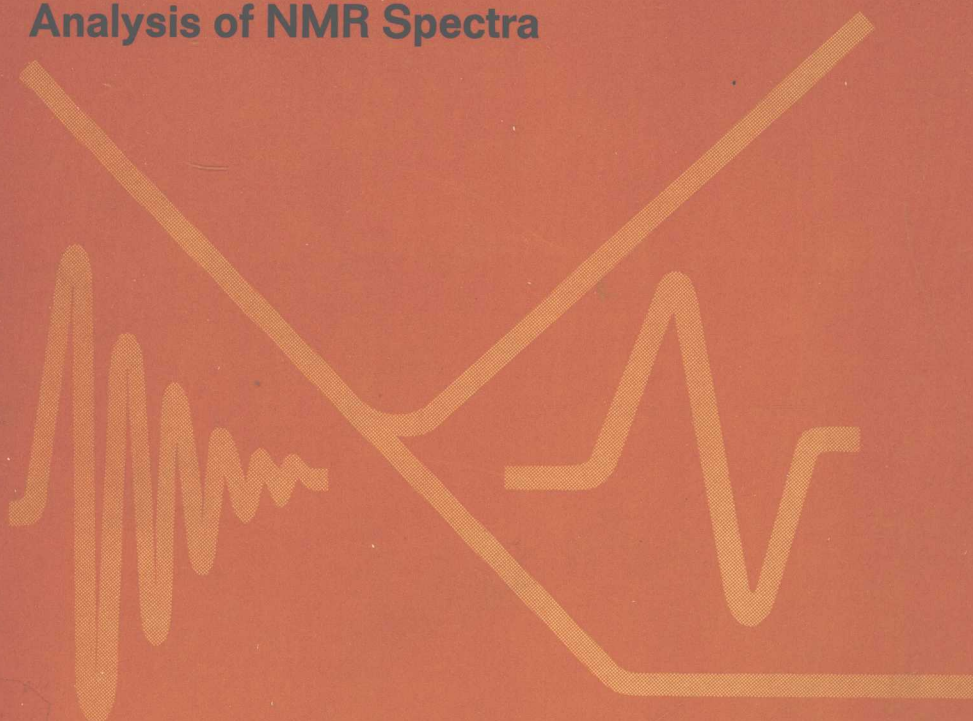
Basic Principles and Progress Grundlagen und Fortschritte

Editors: P. Diehl E. Fluck R. Kosfeld

Volume 5

R.A. Hoffmann · S. Forsén · B. Gestblom

Analysis of NMR Spectra



Springer-Verlag New York · Heidelberg · Berlin

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With 63 Figures



Y078577

Springer-Verlag New York · Heidelberg · Berlin 1971

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ISBN 0-387-05427-8 Springer-Verlag New York · Heidelberg · Berlin
ISBN 3-540-05427-8 Springer-Verlag Berlin · Heidelberg · New York

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Preface

Nuclear magnetic resonance spectroscopy, which has evolved only within the last 20 years, has become one of the very important tools in chemistry and physics. The literature on its theory and application has grown immensely and a comprehensive and adequate treatment of all branches by one author, or even by several, becomes increasingly difficult.

This series is planned to present articles written by experts working in various fields of nuclear magnetic resonance spectroscopy, and will contain review articles as well as progress reports and original work. Its main aim, however, is to fill a gap, existing in literature, by publishing articles written by specialists, which take the reader from the introductory stage to the latest development in the field.

The editors are grateful to the authors for the time and effort spent in writing the articles, and for their invaluable cooperation.

The Editors

Analysis of NMR Spectra

A Guide for Chemists

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Fig. 1. Classical model of the nucleus as a rotating charged sphere.

The angular momentum of a nucleus is quantized, its magnitude being characterized by the nuclear spin quantum number I , which takes on integral or half integral values and is a characteristic number of the nucleus concerned. The magnetic moment of a given nucleus is a vector quantity directed perpendicular to the plane of the current loop and directed along the direction in which a right hand screw would move if turned in the sense of circulation of the current. The loop's magnetic moment is a vector of the current in the loop and the area enclosed by the current.

I. Principles of NMR Spectroscopy

I.1. The Magnetic Resonance Phenomenon

a) Nuclear Moments

Nuclear magnetic resonance is possible because a number of nuclei possess intrinsic magnetic moments. The existence of an intrinsic magnetic moment is intimately related to the angular momentum properties of the nucleus.

Classically, this relationship may be understood by considering the nucleus as a small but finite rotating charged sphere or ellipsoid, the rotation of which produces a set of infinitesimal current loops whose magnetic fields cooperatively produce a resulting magnetic dipole field (Fig. 1)¹. The only stable nuclei that possess angular momentum are found to be nuclei with odd mass numbers and the stable even mass isotopes ^2H , ^6Li , ^{10}B and ^{14}N . Another electromagnetic property of the nuclei which is of some relevance in magnetic resonance applications is the nuclear quadrupole moment which is a measure of the deviations of the nuclear charge distribution from a spherical symmetry.

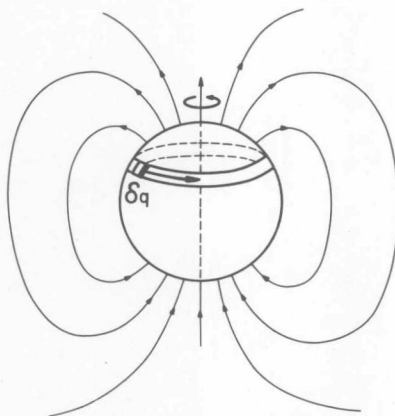


Fig. 1. Classical model of the nucleus as a rotating charged sphere

The angular momentum of a nucleus is quantized, its magnitude being characterized by the nuclear spin quantum number I , which may take on integer or half integer values and is a characteristic number of the isotope considered.

¹ The magnetic moment of a plane current loop is a vector quantity directed perpendicularly to the plane of the current loop and oriented along the direction in which a right hand screw would move if turned in the sense of circulation of the current in the loop. Its magnitude equals the product of the current in the loop and the area enclosed by the current.

The isotopes most commonly employed in magnetic resonance to date, *viz.* ^1H , ^{13}C , ^{19}F and ^{31}P all have $I = 1/2$. Such nuclei with $I = 1/2$ cannot possess a nuclear quadrupole moment and this is usually an advantage in high resolution applications where quadrupole interactions tend to produce unwanted line broadening. Among nuclei with I greater than $1/2$ one may mention ^2H , ^{14}N and ^{10}B as particularly important for NMR applications. Some physical properties of isotopes important in NMR applications are listed in Table 1.

Table 1. *Physical properties of some common nuclei*

Isotope	Spin quantum number I	Relative abundance in nature (%)	Gyromagnetic ratio γ^a	NMR resonance frequency in MHz at a magnetic field of 10 kilogauss
^1H	1/2	99.98	26.7519	42.5759
$^2\text{H}(\text{D})$	1	0.016	4.106	6.53566
^{11}B	3/2	81.17	8.853	13.660
^{12}C	0	98.89	—	—
^{13}C	1/2	1.11	6.726	10.705
^{14}N	1	99.64	1.933	3.076
^{15}N	1/2	0.36	— 2.711 ^b	4.315
^{16}O	0	99.76	—	—
^{17}O	5/2	0.037	— 3.627 ^b	5.772
^{19}F	1/2	100	25.167	40.055
^{27}Al	5/2	100	6.971	11.094
^{31}P	1/2	100	10.829	17.236
^{32}S	0	95.06	—	—
^{33}S	3/2	0.74	2.052	3.266
^{35}Cl	3/2	75.4	2.621	4.172
^{37}Cl	3/2	24.6	2.182	3.472
^{119}Sn	1/2	8.68	— 9.971 ^b	15.87
^{199}Hg	1/2	16.92	4.783	7.60

^a In units of $10^3 \text{ rad (Gauss)}^{-1} (\text{sec})^{-1}$.

^b The angular momentum vector and the vector of the magnetic dipole are antiparallel.

b) Magnetic Spin States and Energy Levels

When a magnetic dipole is placed in an external magnetic field (H_0) it interacts with the field through a torque tending to align the dipole with the field just as a compass needle tends to orient itself in the earth's magnetic field. The potential energy of a dipole when placed in an external field becomes lowest when the dipole is aligned along the field and highest when the dipole is opposed to the field. A nucleus of spin quantum number I when placed in an external magnetic field H_0 can under stationary conditions only take up $2I + 1$ different inclinations of the angular momentum vector with respect to that field, each inclination being characterized by its own magnetic quantum number m . Every one of these stationary states corresponds to a definite energy level and the magnetic resonance signal may be viewed as arising from transitions between these energy levels induced by interactions with a radiation field.

The potential energy of a magnetic moment, μ , in an external magnetic field H_0 is given simply by the scalar product:

$$E = -\mu \cdot H_0. \quad (1)$$

The magnetic moment vector, μ , is parallel with the spin angular momentum vector, $I\hbar$, and is given by

$$\mu = \gamma I\hbar \quad (2)$$

where the constant of proportionality, γ , is called the gyromagnetic ratio of the nucleus and \hbar stands for Planck's constant divided by 2π and is an entity of the dimension of an angular momentum.

At this point it becomes convenient to introduce a frame of reference. The Cartesian coordinate systems employed in NMR are always chosen so as to have their $x-y$ plane perpendicular to the magnetic field H_0 . We shall use such a coordinate system, with x and y axes fixed in relationship to the spectrometer probe ("the laboratory frame") and oriented so as to bring the H_0 field along the *negative* z direction. Inserting Eq. (2) into Eq. (1), we obtain in this frame of reference the energy expression:

$$E = +\gamma\hbar H_0 I_z \quad (3)$$

where I_z is the z component of the dimensionless vector I . (Note that Eq. (3) would have retained the minus sign of Eq. (1) if the positive z direction had been chosen along H_0 .)

The component I_z assumes a definite value m in a stationary state of the system (I_z is a "constant of the motion") and Eq. (3) may be rewritten in terms of the *magnetic quantum number* m :

$$E = \gamma\hbar H_0 m. \quad (4)$$

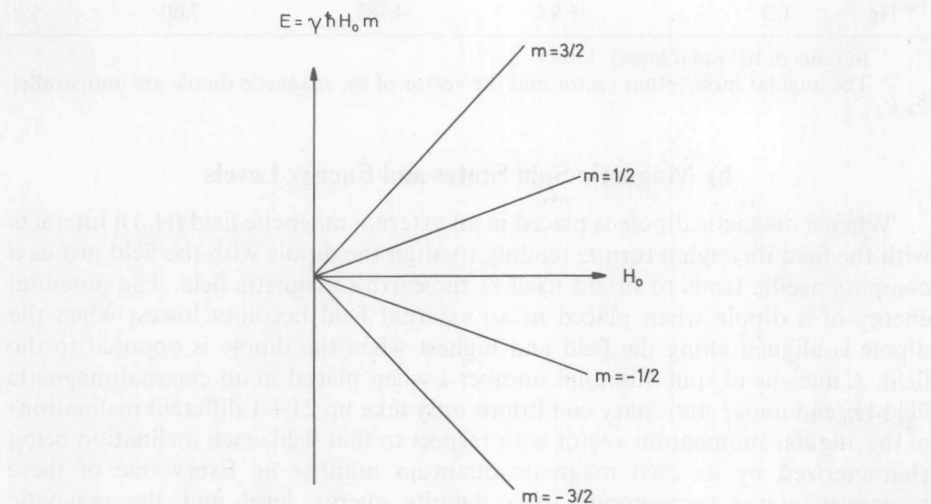


Fig. 2. The spin energy of a nucleus as a function of the magnetic field H_0 . The nucleus has the spin quantum number $I = 3/2$

The magnetic quantum number m of Eq. (4) can assume any one of the $2I + 1$ values

$$\begin{aligned} m &= I \\ m &= I - 1 \\ &\vdots \\ m &= -I. \end{aligned}$$

For example, if $I = 1/2$, m can assume the values of $+1/2$ or $-1/2$, and if $I = 1$ the possible values of m become $+1$, 0 and -1 . It follows that the energy of a magnetic nucleus under the influence of the magnetic field H_0 may assume any one of $2I + 1$ equidistant values, each energy level being characterized by its magnetic quantum number m (Fig. 2).

c) The Magnetic Resonance Condition

The selection rule governing the possible transitions in an NMR experiment is

$$\Delta m = \pm 1 \quad (5)$$

and the Bohr frequency condition $h\nu = \Delta E$ gives the magnetic resonance equation

$$h\nu = \gamma \hbar H_0. \quad (6)$$

The magnitude of the level separations is such that the frequency ν of the radiation field quanta (photons) $h\nu$ falls in the radiofrequency region of the electromagnetic spectrum when the applied field H_0 is of a magnitude conveniently generated in the laboratory. In this region the source of radiation will be a radio frequency coil fed by a radio frequency transmitter and this coil is so oriented that it produces an oscillating magnetic field H_1 polarized perpendicular to the steady field H_0 .

d) The Larmor Precession

In radiofrequency spectroscopy the radiation field in the sample volume is almost perfectly coherent, both temporally and spatially. Before the advent of lasers, spectroscopy with such completely coherent radiation sources was virtually unknown in the optical domain and the traditional mode of presenting the elementary theory of spectra does not lend itself well to description of coherence phenomena. In order to take these into account in NMR spectroscopy, one therefore has recourse to a classical model of the nucleus as a spinning charged top. When a spinning top experiences a torque tending to turn over the spinning axis, the resulting motion becomes a precessional motion, the spin axis moving along the surface of a circular cone. A mechanical analogue of a spinning magnetic nucleus is a heavy symmetrical top placed on horizontal support. Under the torque produced by the opposing forces of the gravitational pull at the center of gravity and the upward reaction force from the support, the spinning top does not turn over but precesses around the vertical field lines of

gravity (Fig. 3). The precessional frequency, ν , of a spin magnetic moment $\mu = \gamma I \hbar$ in an external magnetic field H_0 is given by the Larmor equation

$$\nu = \gamma H_0 / 2\pi \quad (7)$$

which classical equation is exactly equivalent to the quantum mechanical relation Eq. (6). A radiofrequency field oscillating in a plane perpendicular to H_0 at a frequency given by Eq. (7) will be in resonance with the precessional motion of the spinning nuclei, thus making possible an energy exchange between the spin system and the radiofrequency field.

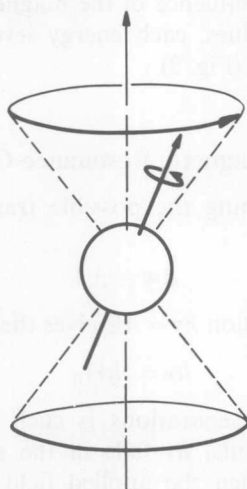


Fig. 3. Precession of a spinning top around the vertical field lines

e) Experimental Aspects

The occurrence of a magnetic resonance may be detected either as a change in impedance of a single coil probe, the energy dissipation corresponding to the magnetic resonance absorption being experienced as an extra resistive contribution to the coil impedance, or in a two-coil probe as an induced voltage in the receiver coil produced by the precessing magnetic moment of the ensemble of nuclei in the sample.

In order to scan the spectrum one may vary the radiofrequency of the transmitter at a given polarizing magnetic field H_0 so as to fulfill the resonance condition (Eqs. (6) or (7)). This *frequency sweep* method has many advantages over the traditional *field sweep* method in which one varies the H_0 field so as to bring the energy level separation into resonance with a constant radiofrequency. It will be noted that this latter method of scanning a spectrum by slowly varying the level separations so as to bring them into resonance with a monochromatic radiation source cannot be realized in optical molecular spectroscopy where the energy level separations are intrinsic molecular properties not under experimental control.

I.2. Chemical Shifts

a) The Screening Constant σ

The resonance conditions, Eqs. (6) and (7), were derived by considering only the interaction between nuclear magnetic moments and the magnetic field H_0 of the laboratory magnet. They are easily generalized, however, to include the screening effect of the electrons in the molecule. In an actual sample, the externally applied magnetic field H_0 induces currents in the electron clouds of the molecules, and these currents in turn produce their own secondary magnetic fields at the sites of the magnetic nuclei, thus shifting the resonance away from that of a bare nucleus (the *chemical shift*). This induced secondary field is proportional in magnitude to the externally applied H_0 field and in *isotropic* environments its direction is of necessity along the H_0 field.

Thus the effective magnetic field H at the nucleus is given by

$$H = H_0 - \sigma H_0 \quad (8)$$

where σ is a dimensionless constant, called the (isotropic) *screening constant* of the nucleus in the environment considered.

Isotropic surroundings are effectively produced in fluid media (liquids, solutions and gases) and these are also the media where high-resolution NMR is normally employed (cf. Section II.2, Example 1). For hydrogen nuclei in diamagnetic samples the screening constant σ varies over a range of some 10 to 20 ppm. Screening constants of heavier nuclei tend to be a few orders of magnitude larger because of the greater ease of inducing currents in their electron clouds. Insofar as the sizes of the currents induced in a charge distribution

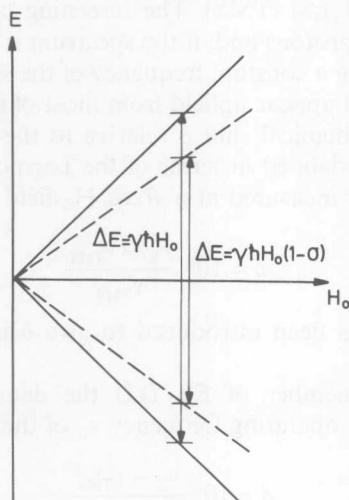


Fig. 4. The spin energy of a nucleus ($I = 1/2$) as a function of the magnetic field H_0 . The full lines show the energy levels of the bare nucleus, while the broken lines show the energy levels when the chemical shift (screening constant σ) is taken into account. The screening effect has been exaggerated in the figure

depend on the amount of charge present, one may expect a simple correlation between screening constants (chemical shifts) and charge densities, but this correlation must not be taken for granted.

The magnetic energy of a screened nucleus in an externally applied field H_0 is obtained by a slight generalization of Eq. (4) and is given by

$$E = \gamma \hbar H_0 (1 - \sigma) m \quad (9)$$

with the H_0 of Eq. (4) replaced by the effective magnetic field H of Eq. (8). The energy expression (9) when combined with the selection rule of Eq. (5) and the Bohr frequency condition $h\nu = \Delta E$ yields the resonance condition

$$\nu = \frac{\gamma}{2\pi} H_0 (1 - \sigma) \quad (10)$$

for a nucleus of gyromagnetic ratio γ in an environment described by a screening constant σ and subject to an applied magnetic field H_0 .

The frequency ν defined by Eq. (10) will henceforth be called the *Larmor frequency* of the nucleus in question, whether or not additional interactions displace (or split) the resonance frequency away from that given by Eq. (10).

The effect of a chemical shift on the energy levels and the transition frequency of a nucleus is illustrated in Fig. 4.

b) Chemical Shift Scales (σ and τ)

Since the resonance frequency of the bare nucleus is seldom known, screening constants and chemical shifts are usually related to some standard reference. In proton magnetic resonance spectroscopy the generally accepted standard reference is tetramethylsilane $(\text{CH}_3)_4\text{Si}$ (TMS). The screening constant of TMS is larger than that of most other protons and, if the spectrum is recorded by sweeping the magnetic field while using a constant frequency of the stimulating radiofrequency field, the TMS signal will appear upfield from most of the other absorption lines.

Quantitatively, the chemical shift δ relative to the reference (TMS) of some proton X in a sample is defined in terms of the Larmor frequencies ν_X and ν_{TMS} as given by Eq. (10) and measured at a *fixed* H_0 field. Thus δ is defined by the expression

$$\delta = 10^6 \frac{\nu_X - \nu_{\text{TMS}}}{\nu_{\text{TMS}}} \quad (11)$$

where the factor 10^6 has been introduced to give δ in the convenient units of parts per million (ppm).

In the right-hand member of Eq. (11) the denominator ν_{TMS} is usually replaced by the nominal operating frequency ν_0 of the spectrometer to yield the simple equation,

$$\delta = 10^6 \frac{\nu_X - \nu_{\text{TMS}}}{\nu_0} \quad (12)$$

The difference $(\nu_X - \nu_{\text{TMS}})$ can be read off directly on a precalibrated recorder chart or obtained more accurately by modulation side-band techniques so that the δ values of Eq. (12) are easily evaluated.

It should be pointed out at this stage that the definition of Eq. (11) gives a unique chemical shift value for a given proton in a given sample, whereas the rather loose definition of Eq. (12) does not, but to the three or four significant figures usually quoted for chemical shifts this difference is unobservable.

By introduction of the definitions of Eq. (10) for ν_X and ν_{TMS} in Eq. (11), we find that δ is related to the screening constants σ_X and σ_{TMS} through the equation

$$\delta = 10^6 \frac{\sigma_{TMS} - \sigma_X}{1 - \sigma_{TMS}} \quad (13)$$

and since σ_{TMS} is only of the order of 10^{-5} , it follows that δ is practically equal to the difference in screening constants ($\sigma_{TMS} - \sigma_X$) as expressed in ppm.

The definition of Eq. (11) is directly applicable to a frequency sweep spectrum. If the spectrum is instead recorded by sweeping the magnetic field at a constant spectrometer frequency ν_0 , the resonant values of the magnetic field, *viz.* H_0 for the sample and $(H_0 + \Delta H_0)$ for the TMS reference, are related by the equations

$$\nu_0 = \frac{\gamma}{2\pi} H_0 (1 - \sigma_X) = \frac{\gamma}{2\pi} (H_0 + \Delta H_0) (1 - \sigma_{TMS}). \quad (14)$$

From the last two members of Eq. (14) one can derive the expression

$$\frac{\Delta H_0}{H_0} = \frac{\sigma_{TMS} - \sigma_X}{1 - \sigma_{TMS}} \quad (15)$$

and it follows from Eqs. (13) and (15), that δ may be defined as

$$\delta = 10^6 \frac{\Delta H_0}{H_0}. \quad (16)$$

In actual practice, the magnetic fields H_0 and ΔH_0 are never measured directly, and the δ values quoted by experimentalists are always those defined by Eq. (12) with $(\nu_X - \nu_{TMS})$ obtained by precalibration or by modulation side-band techniques. In terms of the sweep variable then, the quantity $(\nu_X - \nu_{TMS})$ represents *either* the difference between the frequencies used to excite the sample and reference resonances at a fixed H_0 field, *or* the frequency equivalent $\Delta\nu$, given by

$$\Delta\nu = \Delta H_0 \gamma / 2\pi \quad (17)$$

of the difference ΔH_0 between the magnetic fields $(H_0 + \Delta H_0)$ and H_0 used to excite the reference and sample resonances at a fixed spectrometer frequency ν_0 .

In proton magnetic resonance the sweep variable (H_0 or ν_0) normally varies by less than 10 or 20 ppm over the high-resolution spectrum. If one abstains from double-irradiation experiments, one then obtains field-sweep spectra that are indistinguishable from the corresponding frequency-sweep spectra as long as relative accuracies of 10^{-5} are not attainable. It will be noted, however, that the correspondence requires opposite directions of the two sweeps. Thus a positive δ requires according to Eqs. (14)–(16) that the X-resonance is *downfield* from TMS and, according to Eq. (12), that the sample resonance frequency ν_X

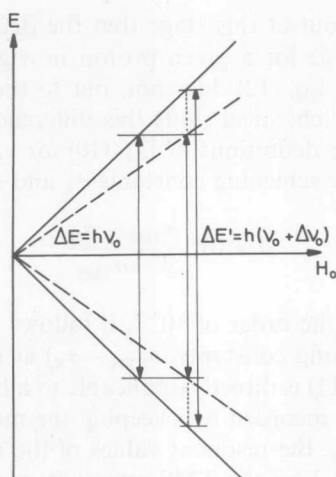


Fig. 5. Energy levels and transitions of two nuclei ($I = 1/2$) which are chemically shifted relative to each other. It is seen that at constant field H_0 the more screened nucleus will be observed at a lower radiofrequency than that of the less screened nucleus. If the radiofrequency is fixed, i.e. $\Delta E = h\nu_0$ is constant, the more screened nucleus will be observed at a higher H_0 field than the less screened nucleus

will be *higher* than that of TMS when compared at a given H_0 field. This inversion of relative magnitudes is illustrated graphically in Fig. 5.

The universally accepted mode of displaying NMR spectra is a left-to-right arrangement in which H_0 in a field sweep spectrum increases from left to right and, consequently, ν in a frequency sweep spectrum decreases from left to right.

The frequency sweep mode of operation is the one which has a counterpart in other fields of spectroscopy and, for this reason, it is the conceptually simpler method. The sense of *increasing* frequency (and hence increasing transition energy) in the frequency-sweep mode corresponds to a *downfield* sweep in the field-sweep mode. In our opinion this represents a very strong argument in favour of a sign convention in which the frequency scale (and the chemical shift) *increases downfield* from TMS. This is the convention used in the definition of δ and is the one recommended for proton magnetic resonance by the American Society for Testing and Materials (ASTM, Manual of February 1966, sponsored by committee E-13) but is contrary to that of the τ -scale, introduced by TIERS [1] and recommended by the Chemical Society of London. The parameter τ is defined as

$$\tau = 10 - \delta. \quad (18)$$

I.3. Spin Coupling Constants

So far we have only considered the interaction between the magnetic moment of a nucleus and a stationary magnetic field H_0 or H , produced by the laboratory magnet and modified by induced electronic currents. In actual spin systems, however, interactions between different nuclear spins in a molecule produce

additional structure in the NMR spectrum. In isotropic fluids this interaction is not caused by direct "through space" interactions of the individual magnetic dipoles because this interaction averages out to zero through the rapid random reorientations of the internuclear axes. There remains, however, a small isotropic interaction between nuclear spins mediated by the electron-nuclear and electron-electron interactions in the molecule. The energy of this interaction is proportional to the scalar product of the two spin vectors involved and may be written

$$E = hJ_{AB} \mathbf{I}(A) \cdot \mathbf{I}(B) \quad (19)$$

where $\mathbf{I}(A)$ and $\mathbf{I}(B)$ are the spin vectors of the coupled nuclei A and B and where the constant J_{AB} has the dimension of frequency and is called the spin-coupling constant between A and B.

Example 1: Spin-spin Splitting in the HD Molecule

The mechanism of spin coupling and its effects on the high-resolution spectrum will now be briefly discussed with reference to spin-spin splitting in the HD NMR spectrum at $H_0 = 14,100$ gauss, taken as an example.

The orienting effect of the magnetic field H_0 in this case is very much larger than that of the spin-spin coupling and both the proton and the deuteron will be individually characterized by their magnetic quantum numbers, m_H and m_D , in a stationary state. Since $I(H) = 1/2$ and $I(D) = 1$, the possible values of m_H are $+1/2$ and $-1/2$, while the possible values of m_D are $+1$, 0 and -1 . The magnetic energy of the spin system is very small compared to its thermal energy and every magnetic quantum state will be occupied with (almost) the same probability (the Boltzmann factors of the different levels are very nearly equal).

Now consider a molecule in which $m_H = -1/2$, i.e. the proton is aligned with the external field H_0 . Because of magnetic interactions between the proton spin and the $1s$ electrons of the molecule, the electron spin when close to the proton becomes slightly polarized and tends to oppose the external field. The spins of the two electrons forming the bond are, however, strongly correlated and a polarization of an electron close to the proton favours an electron density of opposite spin close to the deuteron. The magnetic interaction between this electron spin density around the deuteron and the deuteron magnetic moment in turn results in a spin coupling *contribution* to the total energy of the spin system which is highest when the deuteron and the proton have parallel spins and lowest when their spins are opposed. This state of affairs is described by a positive value of the spin-coupling constant².

The proton magnetic resonance spectrum may be considered to arise from transitions between the $m_H = +1/2$ and $m_H = -1/2$ states of the proton in three different sets of molecules, viz. those having $m_D = +1$, $m_D = 0$ and $m_D = -1$.

² From the foregoing it should be obvious that not only the magnitude but also the sign of the spin-coupling constant is an intrinsic molecular parameter determined by the mechanism of spin polarization transfer in the molecule. Unfortunately, however, the *absolute* signs of spin-coupling constants cannot be determined from high resolution NMR spectra except in very special cases. However, the *relative* signs of different spin couplings in complex spin systems can generally be determined either by a detailed analysis of the spectrum or by double-irradiation techniques.