TRANSIENT TECHNIQUES IN NMR OF SOLIDS

An Introduction to Theory and Practice

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PREFACE

Nuclear magnetic resonance (NMR) is truly a remarkable phenomenon. *Remarkable* can imply different things to different people. From the point of view of a physicist, spin dynamics is an elegant example of the use of time-dependent quantum mechanics, and NMR absorption of energy is a prototype for spectroscopic transitions. From the point of view of the practicing chemist and materials scientist, NMR spectroscopy is an invaluable tool for the identification of chemical species and structures.

Had NMR spectroscopic techniques commercially available in the early 1960s been the only result of investigations of this phenomenon, it would have had a major impact on the course of chemical analysis. The study of liquids and solutions for chemical shifts and couplings of protons had produced a rapid means of identifying chemical species nondestructively. The study of dynamical properties also could be addressed by study of temperature dependence of the spectra or of the saturation of the resonance by high-power irradiation.

Even at that time, however, studies of the spin dynamics had already begun to indicate that there were many interesting facets of the NMR phenomenon left to exploit. For example, the Fourier-transform relationship of the free-induction decay and the absorption spectrum had been shown and the basis of the cross-polarization experiment was being investigated. A number of chemists had begun to study the spin–lattice relaxation times of species by pulse NMR techniques by utilizing methods that were not familiar at that time to the typical chemist but that are now commonly employed in NMR analysis.

The principal characteristic of the NMR technique that makes it so useful for chemical analysis of liquids and solutions is the high resolution that allows one to observe very small interactions such as the chemical shift and the spin–spin coupling. These weak interactions are quite sensitive to the local environment of the spin and therefore may be used as a diagnostic for the environment. The connectivity of chemical structure is often mimicked closely in the NMR connectivity of the spectrum, and quantitative information is relatively easy to obtain.

Nuclear magnetic resonance spectra of solids exhibit such resolution

only in special cases. The primary (although not the exclusive) reason for the lack of resolution in the spectrum of a typical solid is the presence of the dipole–dipole interaction, which dominates the NMR spectroscopy of solids that have been of interest to chemists. One solution (no pun intended) to the problem of obtaining chemical-shift information about such solids is to dissolve them and to study them in solution. However, if the solid is insoluble or otherwise intractable or if the analysis involves questions about the properties of the substance *in the solid state,* then there arises a need for techniques to study the weaker interactions in the presence of the dipole–dipole interaction or other overwhelming interactions. This volume describes the means devised by a number of very clever spectroscopists to achieve this goal.

Understanding, like *remarkable,* can imply different things to different people. We have tried to speak to the graduate student who earnestly wishes to learn about NMR spectroscopy of the solid state. A knowledge of quantum mechanics such as one might get in a junior-level physical chemistry course is presumed. Since many graduate students in chemistry characteristically have not been exposed to physics beyond the level of a survey course, very little prior knowledge of the basic theory of electromagnetism is assumed. The reader who is already familiar with NMR of the solid state may thus find that our explanations are long and circuitous. We have strived to provide a background sufficient to allow the student to understand the results at hand. We have also intended this volume as an introduction to concepts of time-dependent quantum mechanics as they apply to NMR spectroscopy of the solid state. As such, we have chosen to discuss certain topics that represent broad applications of this theory to the NMR of solids. Certain other topics, e.g., two-dimensional NMR techniques and multiquantum studies, have been given little exposition here. This choice certainly does not represent any bias on the parts of the authors about the relevance of these techniques to NMR spectroscopy of the solid state.

In the sense that we have provided information for the reader that may help to ease the introduction into this subject, we hope we have contributed to a bridging of the gap of understanding that often frustrates the new student of this field when he encounters the literature, the more advanced books, or a recalcitrant spectrometer. It is our hope that after having read this volume, the student will continue studies of more advanced works but that this work will serve as a reference on some of the machinations that NMR spectroscopists use to explain their experiments on solids.

ACKNOWLEDGMENTS

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MAGNETIC MOMENTS,
MAGNETIC FIELDS,
AND A CLASSICAL PICTURE
OF RESONANT ABSORPTION

I. Introduction

The resonant absorption and emission of energy by a system irradiated by light is a fascinating subject. The use of this technique provides an enormous amount of useful information to the chemist whose chief interest is in the determination of the composition, geometry, and reactive characteristics of materials in which he is interested. Although this utilitarian aspect may be the impetus for many practical uses of spectroscopy, the study of the processes underlying these resonant transitions is equally important. It is through the careful study of the details of these processes that more powerful techniques are uncovered, and these allow an even more intimate detailing of molecular behavior, as well as providing means of studying such behavior in realms once thought out of reach. A good example of such developments is the topic of this book—the development of pulse techniques in nuclear magnetic resonance. The novel techniques in NMR that spark so much enthusiasm and whose genesis is no more than a decade old at the time of writing (1981) is the outgrowth of the efforts of a number of investigators who returned to the basic theory describing in detail the interaction of quantum-mechanical systems with resonant radiation. The result of their careful, creative work, together with the happy coupling of theory with experiment, led to results that indicated a still more powerful role for the use of NMR in solving chemical problems in fields as diverse as those of genetics, polymer structure, and heterogeneous catalysis.

In order to understand the fundamentals of the technique used to solve such a broad range of chemical problems, we have recourse to at least two views of the basic mechanism involved, the absorption of resonant radiation by an ensemble of nuclei with magnetic moments. The first is a classical view in which one talks about this ensemble of spins as if it were a single mag-

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net and inquires into how this magnet behaves in an external field (or in fields supplied by other neighboring magnets). The second is a quantum-mechanical view in which the main focus is on a description of how the states of the system are changed in the presence of strong resonant radiation. Both ways of thinking about the nuclear magnetic resonance phenomenon are useful in helping to visualize the effect, and both are developed in this volume.

In this chapter, we focus upon a classical description of magnetic resonance. To this end, we derive the classical equations of motion of a magnetic moment in a field, the classical picture of resonance with a radio-frequency field, and the relations describing relaxation processes by which equilibrium in a magnetic field is established after a resonant perturbation. The result to be immediately obtained is that a magnetic moment [which can be thought of as a circulating charge characterized by a magnetogyric ratio (*vide infra*) γ in a static field **B**] precesses about the field with precession frequency

$$\omega \ (\text{rad sec}^{-1}) = -\gamma \ (\text{rad sec}^{-1} \ G^{-1}) \ \mathbf{B} \ (G) \tag{1.1}$$

This motion is a solution of the equation

$$d\mathbf{M}/dt = \gamma \mathbf{M} \times \mathbf{B} \tag{1.2}$$

The use of (1.2), together with an assumption about the linearity of the differential equations governing relaxation of the x, y, and z components of the spin after an excitation, leads to the Bloch equations and the concept of longitudinal and transverse relaxation, with time constants T_1 and T_2, respectively. It also is seen that solutions of these differential equations describe exactly, in some cases, the observed NMR signal that is the response of a spin system to a resonant radio-frequency excitation.

In addition to discussing the effects of magnetic fields upon classical moments, this chapter deals with the production of radio-frequency fields that are used to act upon the moments and with the spatial distribution of these fields in the circuits used to produce them. The intent of this volume is to provide a source of information on both the theory and the practice of pulse techniques in NMR. Relations that have practical application in the design of circuits for production of resonant radio-frequency pulses are developed and order of magnitude calculations for use in such applications are illustrated.

II. The Relation between Magnetic Moment and Angular Momentum

A concept fundamental to an understanding of the phenomenon of magnetic resonance is that circulating charges give rise both to magnetic moments and to magnetic fields that can be used to probe the environment of
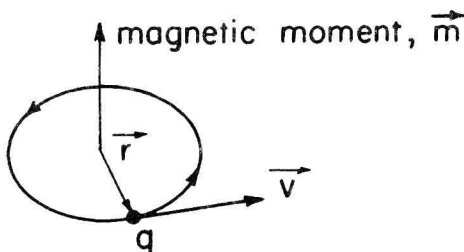
FIG. 1.1. The magnetic moment produced by a current loop (Arrows indicate vectors in the figures; boldface indicates vectors in the text.)

these moments in matter. In classical mechanics, one learns that equations of motion are obtained from Newton's second law, which deals with the relation between force and a change in linear momentum. Similarly, in discussing the classical equations of motion of magnetic moments in external (or internal) fields, one finds that he is dealing with the relation between torque and a change in *angular* momentum. To start the classical discussion of the magnetic resonance experiment, therefore, it is instructive to investigate the relation between the angular momentum of a circulating charge and its magnetic moment. Consider a charge q moving clockwise[†] on a circle of radius r with velocity $\mathbf{V}$, as illustrated in Fig. 1.1. A moving charge is a current, and a current moving in a circle produces a simply describable magnetic field, the development of which is given in Appendix 1. The spatial description of this field, at distances large compared to r, is similar to that of the electric field produced by an *electric dipole*. In fact, when the extent of the electric dipole is small compared to the distance between the center of the dipole and the point at which the field is measured, the spatial distributions of the fields due to a circulating charge and an electric dipole are identical. A charge whose region of circulation is small compared to the distance at which the field is measured is called a *magnetic dipole* with dipole moment $\mathbf{m}$ having absolute value

$$m = iA/c \qquad (1.3)$$

where A is the area of the current loop and c the speed of light. The period of rotation of such a particle is

$$t = \text{circumference/speed} = 2\pi r/V \qquad (1.4)$$

[†] Throughout this text, the term *clockwise* will be taken to mean clockwise when viewed in the direction that a right-hand screw would proceed forward when turned right, i.e., when viewed from below to above the plane of Fig. 1.1. Note that when viewed from above the plane, the circulation appears to be counterclockwise.

For a circulating charge q, this gives an equivalent current of

$$i = q/t = qV/2\pi r \tag{1.5}$$

The magnitude of this magnetic moment is then

$$m = (q/2\mu c)/(\mu V r) \tag{1.6}$$

where μ is the charge's mass. The second term in parentheses is the magnitude of the angular momentum of the circulating particle L. Both the magnetic moment and the angular momentum are vectors. The angular momentum is perpendicular to both the radius vector and the velocity. (See Appendix 1.) For the special case of this model

$$\mathbf{m} = (q/2\mu c)\mathbf{L} \tag{1.7}$$

that is, the magnetic moment is proportional to the angular momentum of the particle.

A circulating particle is not a good representation of a very small nucleus. However, the magnetic interactions of nuclei can be quantified in terms of a magnetic moment that is proportional to the angular momentum of the particle

$$\mathbf{m} = \gamma\mathbf{L} \tag{1.8}$$

where γ is the magnetogyric ratio of the particle.

While this result was derived for the model of an orbiting charged particle, one might similarly derive an expression for a rotating charge distribution in a more general sense; that is, one would find for a charge distribution that the magnetic moment is proportional to the rotational angular momentum of the distribution.

III. The Force on, and the Resulting Motion of, a Dipole in a Magnetic Field†

Consider the magnetic dipole's motion in a magnetic field (produced by current loops of one type or another). The fundamental force law for a charge traveling in a magnetic field is

$$\mathbf{F} = q(\mathbf{V}/c) \times \mathbf{B} \tag{1.9}$$

A current loop can be considered to be composed of a number of small segments, each of which has a force exerted on it. If the current is I, then for a small element $d\mathbf{r}_1$

$$q\,d\mathbf{V} = I\,d\mathbf{r}_1$$

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† See Bleaney and Bleaney [1].

where $\mathbf{r}_1$ is a vector along the loop. The differential force on that part of the loop is (for a constant field)

$$dF = (I/c)\,d\mathbf{r}_1 \times \mathbf{B} \qquad (1.9a)$$

When integrated over the whole loop, the total *force* is

$$\oint d\mathbf{F} = \frac{I}{c}\oint d\mathbf{r}_1 \times \mathbf{B} \qquad (1.10)$$

Since $\mathbf{B}$ is uniform across the loop, the integral on the right-hand side is zero. There is therefore no net force on a magnetic moment in a magnetic field. This result may be surprising, but one must remember that, in a uniform magnetic field, the center of mass of a dipole never experiences a translational motion. Infinitesimal forces, however, do exist for small segments of the loop $d\mathbf{r}_1$ and $d\mathbf{r}_2$. It follows from (1.10) that the net forces from various segments must cancel each other exactly, and thus, the combination of two forces on opposite segments causes rotation of the current loop, as indicated in Fig. 1.2.

This action of equal but oppositely directed forces is a *torque* τ and is defined as

$$d\tau = \mathbf{r}_1 \times d\mathbf{F} \qquad (1.11)$$

Replacing $d\mathbf{F}$ as in (1.9a) gives

$$d\tau = (I/2c)\mathbf{r} \times d\mathbf{r}_1 \times \mathbf{B} \qquad (1.12)$$
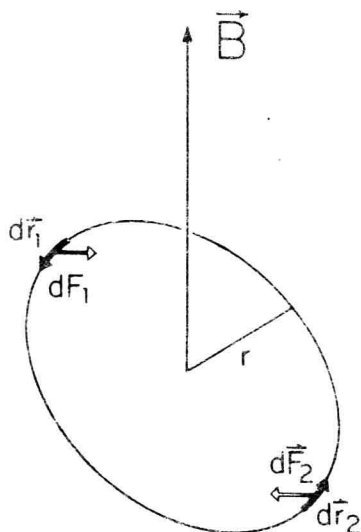
FIG. 1.2. The forces acting on a current loop in a magnetic field $\mathbf{B}$.

Integrating around the whole loop

$$\tau = \left(\frac{I}{2c} \oint \mathbf{r} \times d\mathbf{r} \right) \times \mathbf{B} \tag{1.13}$$

The term in parentheses is the magnetic moment **m** for the dipole. [See (A1.21).]

Hence,

$$\tau = \mathbf{m} \times \mathbf{B} \tag{1.14}$$

We know from classical mechanics that *torque* is the time derivative of the *angular momentum*

$$\tau = \partial \mathbf{L}/\partial t \tag{1.15}$$

Therefore, the equations combine to yield the equation of motion

$$\partial \mathbf{L}/\partial t = \mathbf{m} \times \mathbf{B} \tag{1.16}$$

Using the relation (1.8) one arrives at the classical equation of magnetic resonance

$$\partial \mathbf{m}/\partial t = \gamma \mathbf{m} \times \mathbf{B} \tag{1.17}$$

This equation may be solved as follows: with **B**, defined along the z axis,

$$\mathbf{m} \times \mathbf{B} = \mathbf{i} m_y B - \mathbf{j} m_x B \tag{1.18}$$

Equation (1.17) is really three equations:

$$dm_x/dt = \gamma m_y B \tag{1.19}$$

$$dm_y/dt = -\gamma m_x B \tag{1.20}$$

$$dm_z/dt = 0 \tag{1.21}$$

Equation (1.21) shows that m_z is not coupled to the other components and has the integral result

$$m_z(t) = m_z(0) \tag{1.22}$$

that is, m_z is time independent; m_x and m_y given in (1.19) and (1.20), however, are coupled. The definition

$$m_\pm = m_x \pm i m_y$$

gives

$$dm_\pm/dt = dm_x/dt \pm i\, dm_y/dt = \mp i m_\pm(\gamma B) \tag{1.23}$$

The solutions of (1.23) are

$$m_\pm(t) = m_\pm(0) e^{\mp i\gamma B t} \tag{1.24}$$

which yield

$$m_x(t) = m_x(0)\cos \gamma Bt + m_y(0)\sin \gamma Bt \qquad (1.25a)$$

$$m_y(t) = -m_x(0)\sin \gamma Bt + m_y(0)\cos \gamma Bt \qquad (1.25b)$$

In a constant field, therefore, the component of the magnetic moment along the field is time independent, whereas those perpendicular to the field oscillate in such a way that the magnitude of the transverse component also remains constant:

$$m_x^2(t) + m_y^2(t) = m_x^2(0) + m_y^2(0)$$

The preceding equations have been solved under the assumption that **B** is static. However, as long as the nonrelativistic limit is considered, **B** may be chosen to be time dependent as well. The solutions may not be so simple, but Eq. (1.17) is certainly valid in the classical limit as long as **B** is spatially uniform over the extent of the dipole. For nuclei, this is always true.

The preceding results suggest a picture in which the magnetic moment **m** is rotating about **B** with rotation frequency $\omega = -\gamma B$ rad sec^{-1}. This angular precession frequency is known as the Larmor frequency. The physical situation is illustrated in Fig. 1.3.

The resonance frequencies of NMR active nuclei are supplied in Table 1.1, at a static field in which protons would resonate at 100 MHz. Also supplied are the values of the spin quantum numbers, the natural abundances, and the relative and absolute sensitivities of detection of these nuclei by NMR at
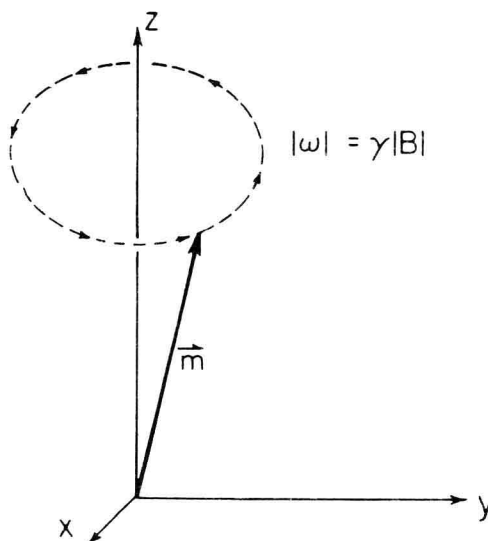

FIG. 1.3. The Larmor precession of a magnetic moment.

TABLE 1.1
Parameters for Selected NMR Active Nuclei

Isotope	Spin	Natural abundance (%)	Quadrupole moment (10^{-28} m²)	Sensitivity Relative[a]	Sensitivity Absolute[b]	NMR frequency (MHz) at a field of 2.3488T
¹H	$\frac{1}{2}$	99.98		1.00	1.00	100.000
²H	1	1.5×10^{-2}	2.73×10^{-3}	9.65×10^{-3}	1.45×10^{-6}	15.351
³H	$\frac{1}{2}$	0		1.21	0	106.663
³He	$\frac{1}{2}$	1.3×10^{-4}		0.44	5.75×10^{-7}	76.178
⁶Li	1	7.42	-8.0×10^{-4}	8.50×10^{-3}	6.31×10^{-4}	14.716
⁷Li	$\frac{3}{2}$	92.58	4.5×10^{-2}	0.29	0.27	38.863
⁹Be	$\frac{3}{2}$	100	5.2×10^{-2}	1.39×10^{-2}	1.39×10^{-2}	14.053
¹⁰B	3	19.58	7.4×10^{-2}	1.99×10^{-2}	3.90×10^{-3}	10.746
¹¹B	$\frac{3}{2}$	80.42	3.55×10^{-2}	0.17	0.13	32.084
¹³C	$\frac{1}{2}$	1.108		1.59×10^{-2}	1.76×10^{-4}	25.144
¹⁴N	1	99.63	1.6×10^{-2}	1.01×10^{-3}	1.01×10^{-3}	7.224
¹⁵N	$\frac{1}{2}$	0.37		1.04×10^{-3}	3.85×10^{-6}	10.133
¹⁷O	$\frac{5}{2}$	3.7×10^{-2}	-2.6×10^{-2}	2.9×10^{-2}	1.08×10^{-5}	13.557
¹⁹F	$\frac{1}{2}$	100	--	0.83	0.83	94.077
²¹Ne	$\frac{3}{2}$	0.257	9.0×10^{-2}	2.50×10^{-3}	6.43×10^{-6}	7.894
²³Na	$\frac{3}{2}$	100	0.12	9.25×10^{-2}	9.25×10^{-2}	26.451
²⁵Mg	$\frac{5}{2}$	10.13	0.22	2.67×10^{-3}	2.71×10^{-4}	6.1195
²⁷Al	$\frac{5}{2}$	100	0.149	0.21	0.21	26.057
²⁹Si	$\frac{1}{2}$	4.7		7.84×10^{-3}	3.69×10^{-4}	19.865
³¹P	$\frac{1}{2}$	100		6.63×10^{-2}	6.63×10^{-2}	40.481
³³S	$\frac{3}{2}$	0.76	-5.5×10^{-2}	2.26×10^{-3}	1.72×10^{-5}	7.670
³⁵Cl	$\frac{3}{2}$	75.53	-8.0×10^{-2}	4.70×10^{-3}	3.55×10^{-3}	9.798
³⁷Cl	$\frac{3}{2}$	24.47	-6.32×10^{-2}	2.71×10^{-3}	6.63×10^{-4}	8.156
³⁹K	$\frac{3}{2}$	93.1	5.5×10^{-2}	5.08×10^{-4}	4.73×10^{-4}	4.667
⁴¹K	$\frac{3}{2}$	6.88	6.7×10^{-2}	8.40×10^{-5}	5.78×10^{-6}	2.561
⁴³Ca	$\frac{7}{2}$	0.145	0.05	6.40×10^{-3}	9.28×10^{-6}	6.728
⁴⁵Sc	$\frac{7}{2}$	100	-0.22	0.30	0.30	24.290
⁴⁷Ti	$\frac{5}{2}$	7.28	0.29	2.09×10^{-3}	1.52×10^{-4}	5.637
⁴⁹Ti	$\frac{7}{2}$	5.51	0.24	3.76×10^{-3}	2.07×10^{-4}	5.638
⁵⁰V	6	0.24	±0.21	5.55×10^{-2}	1.33×10^{-4}	9.970
⁵¹V	$\frac{7}{2}$	99.76	-5.2×10^{-2}	0.38	0.38	26.289
⁵³Cr	$\frac{3}{2}$	9.55	$\pm3.0 \times 10^{-2}$	9.03×10^{-4}	8.62×10^{-5}	5.652

[a] at constant field for equal numbers of nuclei.
[b] product of relative sensitivity and natural abundance.