

**TRANSIENT
TECHNIQUES
IN NMR OF SOLIDS**
**An Introduction
to Theory and Practice**

B.C.Gerstein and C.R.Dybowski

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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 multi-quantum 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.

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As with all projects of this magnitude, there are many people who contribute to the final result by offering suggestions, by proofreading, and by doing legwork for the authors. In our case, we have had the good fortune to have been associated with a warm, encouraging group of such persons: Professor Thomas Apple, Dr. Jo-Anne Bonesteel, Dr. Anita J. Brandolini, Mr. Charles Fry, Dr. Mary Kaiser, Mr. Taka Sogabe, and Professor Toshihiko Taki as well as the many students and friends in the NMR community who have helped us in many ways to improve this effort. We also acknowledge the tremendous debt we owe to the late Professor Robert W. Vaughan, whose enthusiasm for the subject of NMR spectroscopy of the solid state and whose unending quest for the deeper meaning in each new experiment not only produced many new avenues of experimentation, but also engendered in those who knew him such a fascination with the subject that two of them might write a volume such as this one.

CONTENTS

PREFACE	ix
ACKNOWLEDGMENTS	xi

Chapter 1 **Magnetic Moments, Magnetic Fields, and a Classical Picture of Resonant Absorption**

I.	Introduction	1
II.	The Relation between Magnetic Moment and Angular Momentum	2
III.	The Force, on, and the Resulting Motion of, a Dipole in a Magnetic Field	4
IV.	Macroscopic Moments	11
V.	The Bloch Equations: Relaxation	12
VI.	The Rotating Frame	16
VII.	The Pulse NMR Experiment: Pulse and Fourier-Transform NMR	21
VIII.	Relaxation in the Rotating Frame: $T_{1\rho}$	30
IX.	The Magnetic Field of a Solenoid	31
X.	The Production of Radio-Frequency Fields: A Brief Introduction to Alternating-Current Circuit Theory	35
	Problems	39
	References	41

Chapter 2 **Quantum Mechanics of Spin States, the Density Matrix, Interaction Frames, and the Polarization Vector**

I.	Introduction	42
II.	Dirac's Picture of Quantum Mechanics	42
III.	Observables: Physical Interpretation	44
IV.	Angular Momentum Operators and Eigenstates	46
V.	Spin- $\frac{1}{2}$	49
VI.	The Schrödinger Equation for Spin- $\frac{1}{2}$ with a Zeeman Interaction	51
VII.	The Single-Particle Probability Operator	53
VIII.	The Spin- $\frac{1}{2}$ Problem with an Arbitrary Hamiltonian: The Density Operator	54
IX.	The Equilibrium Density Matrix for Spin- $\frac{1}{2}$	57
X.	The Total Density Operator	59
XI.	Time Evolution of the Density Operator: Methods of Solution of the Liouville-von Neumann Equation	61

XII.	Exponential Operators	65
XIII.	Interaction Frames: The $\pi/2$ Pulse Described Quantum Mechanically for Spin- $\frac{1}{2}$	69
XIV.	The Calculation of T_1	79
XV.	The Polarization Vector and Spin- $\frac{1}{2}$: A Quantum Analog of the Magnetization Vector	85
XVI.	The Equation of Motion of the Vector P : The Quantum Analog of the Bloch Equation	87
XVII.	Macroscopic Thermodynamics and the Density Operator	88
	Problems	89
	References	90

Chapter 3 **Internal Hamiltonians and Their Spectra**

I.	Introduction	91
II.	The Zeeman Interaction	92
III.	The Direct Dipole–Dipole Interaction	94
IV.	The Chemical Shift	103
V.	Indirect Nuclear–Nuclear Interactions	119
VI.	The Quadrupolar Interaction	121
VII.	T_1 for Randomly Modulated Hamiltonians	132
VIII.	Concluding Remarks	135
	Problems	135
	References	136

Chapter 4 **Exponential Approximations for Evolution Operators: The BCH Formula, the Magnus Expansion, and the Dyson Expression**

I.	Introduction	137
II.	The Baker–Campbell–Hausdorff Formula, the Magnus Expansion, and the Dyson Expression	138
III.	Interaction Frames Revisited: Examples of the Use of the Magnus Expansion and the Dyson Expression	151
IV.	Secular Perturbations	160
	Problems	163
	References	163

Chapter 5 **Homonuclear Pulse NMR Experiments**

I.	Introduction	164
II.	Multiple-Pulse NMR and the Average Hamiltonian	166
III.	The Symmetry of \mathcal{H}_{int} in the Frame of the Radio Frequency	171

IV.	Treatment of Nonideal RF Perturbations	175
V.	Sample Calculations	182
VI.	The Effect of Motion upon Removal of Dipolar Interactions by Multiple-Pulse Techniques	207
VII.	Second Averaging	209
VIII.	Combined Rotation and Multiple-Pulse Spectroscopy: Addition of Magic-Angle Spinning	213
IX.	Tuning the Spectrometer for Multiple-Pulse Experiments	215
X.	Experimental Considerations	221
	Problems	223
	References	226

Chapter 6 **Heteronuclear Pulse Experiments**

I.	Introduction	227
II.	Pulse Decoupling	229
III.	Continuous-Wave Decoupling	234
IV.	Signal Enhancement by Cross-Polarization	240
V.	Magic-Angle Spinning	255
VI.	Transient Dipole-Dipole Oscillations	267
VII.	Effect of Coupling of Quadrupolar Nuclei to Spin- $\frac{1}{2}$ Nuclei	271
VIII.	Concluding Remarks	273
	Problems	274
	References	275

Appendix 1 **The Field of a Current Loop: A Classical Model** 277

Appendix 2 **Units and Physical Constants** 282

Appendix 3 **Vectors, Tensors, and Transformations** 286

BIBLIOGRAPHY 289

INDEX 291

CHAPTER 1

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-

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 \mathbf{B}] precesses about the field with precession frequency

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

This motion is a solution of the equation

$$d\mathbf{M}/dt = \gamma \mathbf{M} \times \mathbf{B} \quad (1.2)$$

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

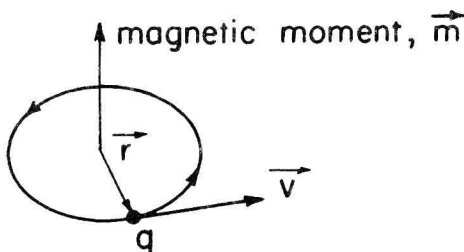


FIG. 1.1. The magnetic moment produced by a current loop (Arrows indicate vectors in the figures; boldface indicates vectors in the text.)

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 \vec{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 \vec{m} having absolute value

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

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

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

[†] 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

$$i = q/t = qV/2\pi r \quad (1.5)$$

The magnitude of this magnetic moment is then

$$m = (q/2\mu c)/(\mu Vr) \quad (1.6)$$

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

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

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

$$\mathbf{m} = \gamma\mathbf{L} \quad (1.8)$$

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

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

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 $d\mathbf{r}_1$

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

† 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)

$$d\mathbf{F} = (I/c) d\mathbf{r}_1 \times \mathbf{B} \quad (1.9a)$$

When integrated over the whole loop, the total force is

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

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

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

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

$$d\tau = (I/2c) \mathbf{r} \times d\mathbf{r}_1 \times \mathbf{B} \quad (1.12)$$

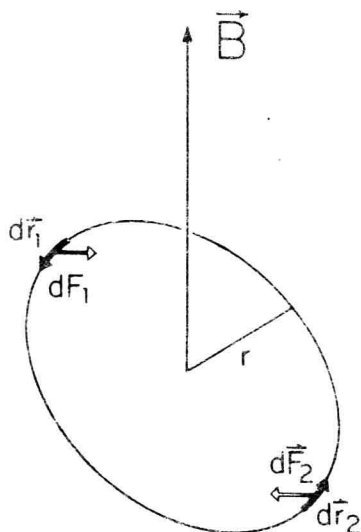


FIG. 1.2. The forces acting on a current loop in a magnetic field \mathbf{B} .

Integrating around the whole loop

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

The term in parentheses is the magnetic moment \mathbf{m} for the dipole. [See (A1.21).]

Hence,

$$\boldsymbol{\tau} = \mathbf{m} \times \mathbf{B} \quad (1.14)$$

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

$$\boldsymbol{\tau} = \partial \mathbf{L} / \partial t \quad (1.15)$$

Therefore, the equations combine to yield the equation of motion

$$\partial \mathbf{L} / \partial t = \mathbf{m} \times \mathbf{B} \quad (1.16)$$

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

$$\partial \mathbf{m} / \partial t = \gamma \mathbf{m} \times \mathbf{B} \quad (1.17)$$

This equation may be solved as follows: with \mathbf{B} , defined along the z axis,

$$\mathbf{m} \times \mathbf{B} = i m_y B - j m_x B \quad (1.18)$$

Equation (1.17) is really three equations:

$$dm_x/dt = \gamma m_y B \quad (1.19)$$

$$dm_y/dt = -\gamma m_x B \quad (1.20)$$

$$dm_z/dt = 0 \quad (1.21)$$

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

$$m_z(t) = m_z(0) \quad (1.22)$$

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

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

The solutions of (1.23) are

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

which yield

$$m_x(t) = m_x(0) \cos \gamma B t + m_y(0) \sin \gamma B t \quad (1.25a)$$

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

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 \mathbf{B} is static. However, as long as the nonrelativistic limit is considered, \mathbf{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 \mathbf{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 \mathbf{m} is rotating about \mathbf{B} with rotation frequency $\omega = -\gamma \mathbf{B}$ 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

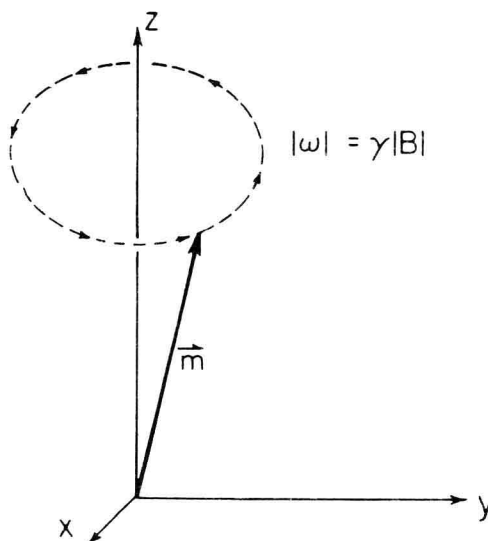


FIG. 1.3. The Larmor precession of a magnetic moment.

TABLE 1.1
Parameters for Selected NMR Active Nuclei

Isotope	Spin	Natural abundance (%)	Quadrupole moment (10^{-28} m^2)	Sensitivity		NMR frequency (MHz) at a field of 2.3488T
				Relative ^a	Absolute ^b	
¹ H	$\frac{1}{2}$	99.98		1.00	1.00	100.000
² H	1	1.5×10^{-2}	2.73×10^{-3}	9.65×10^{-3}	1.45×10^{-6}	15.351
³ H	$\frac{1}{2}$	0		1.21	0	106.663
³ He	$\frac{1}{2}$	1.3×10^{-4}		0.44	5.75×10^{-7}	76.178
⁶ Li	1	7.42	-8.0×10^{-4}	8.50×10^{-3}	6.31×10^{-4}	14.716
⁷ Li	$\frac{3}{2}$	92.58	4.5×10^{-3}	0.29	0.27	38.863
⁹ Be	$\frac{3}{2}$	100	5.2×10^{-2}	1.39×10^{-2}	1.39×10^{-2}	14.053
¹⁰ B	3	19.58	7.4×10^{-2}	1.99×10^{-2}	3.90×10^{-3}	10.746
¹¹ B	$\frac{3}{2}$	80.42	3.55×10^{-2}	0.17	0.13	32.084
¹³ C	$\frac{1}{2}$	1.08		1.59×10^{-2}	1.76×10^{-4}	25.144
¹⁴ N	1	99.63	1.6×10^{-2}	1.01×10^{-3}	1.01×10^{-3}	7.224
¹⁵ N	$\frac{1}{2}$	0.37		1.04×10^{-3}	3.85×10^{-6}	10.133
¹⁷ O	$\frac{5}{2}$	3.7×10^{-3}	-2.6×10^{-2}	2.9×10^{-2}	1.08×10^{-5}	13.557
¹⁹ F	$\frac{1}{2}$	100	—	0.83	0.83	94.077
²¹ Ne	$\frac{1}{2}$	9.257	9.0×10^{-2}	2.50×10^{-3}	6.43×10^{-6}	7.894
²³ Na	$\frac{3}{2}$	100	0.12	9.25×10^{-2}	9.25×10^{-2}	26.451
²⁵ Mg	$\frac{5}{2}$	10.13	0.22	2.67×10^{-3}	2.71×10^{-4}	6.1195
²⁷ Al	$\frac{5}{2}$	100	0.149	0.21	0.21	26.057
²⁹ Si	$\frac{3}{2}$	4.7		7.84×10^{-3}	3.69×10^{-4}	19.865
³¹ P	$\frac{1}{2}$	100		6.63×10^{-2}	6.63×10^{-2}	40.481
³³ S	$\frac{3}{2}$	0.76	5.5×10^{-2}	2.26×10^{-3}	1.72×10^{-5}	7.670
³⁵ Cl	$\frac{3}{2}$	75.83	8.0×10^{-2}	4.70×10^{-3}	3.55×10^{-3}	9.798
³⁷ Cl	$\frac{3}{2}$	24.49	6.32×10^{-2}	2.71×10^{-3}	6.63×10^{-4}	8.156
³⁹ K	$\frac{3}{2}$	93.1	5.5×10^{-2}	5.08×10^{-4}	4.73×10^{-4}	4.667
⁴¹ K	$\frac{3}{2}$	6.88	6.7×10^{-2}	8.40×10^{-5}	5.78×10^{-6}	2.561
⁴³ Ca	$\frac{7}{2}$	0.145	0.05	6.40×10^{-3}	9.28×10^{-6}	6.728
⁴⁵ Sc	$\frac{7}{2}$	100	0.22	0.30	0.30	24.290
⁴⁷ Ti	$\frac{5}{2}$	7.28	0.29	2.09×10^{-3}	1.52×10^{-4}	5.637
⁴⁹ Ti	$\frac{5}{2}$	5.51	0.24	3.76×10^{-3}	2.07×10^{-4}	5.638
⁵¹ V	$\frac{7}{2}$	0.24	± 0.21	5.55×10^{-2}	1.33×10^{-4}	9.970
⁵¹ V	$\frac{7}{2}$	99.76	-5.2×10^{-2}	0.38	0.38	26.289
⁵³ Cr	$\frac{3}{2}$	9.55	$\pm 3.0 \times 10^{-2}$	9.03×10^{-4}	8.62×10^{-3}	5.652

^a at constant field for equal numbers of nuclei.

^b product of relative sensitivity and natural abundance.

(continued)