

The Principles of
NUCLEAR
MAGNETISM

A. ABRAGAM

J3.832
A158

THE PRINCIPLES OF NUCLEAR MAGNETISM

BY

A. ABRAGAM

PROFESSEUR AU COLLÈGE DE FRANCE
CHEF DE DÉPARTEMENT AU
COMMISSARIAT À L'ÉNERGIE ATOMIQUE

502365

OXFORD
AT THE CLARENDON PRESS

1961



Oxford University Press, Amen House, London E.C.4

GLASGOW NEW YORK TORONTO MELBOURNE WELLINGTON

BOMBAY CALCUTTA MADRAS KARACHI KUALA LUMPUR

CAPE TOWN IBADAN NAIROBI ACCRA

© *Oxford University Press 1961*

PRINTED IN GREAT BRITAIN

PREFACE

People have now-a-days got a strange opinion that everything should be taught by lectures. Now, I cannot see that lectures can do so much good as reading the books from which the lectures are taken.

DR. JOHNSON (1766)

SINCE the first successful detection of nuclear resonance signals late in 1945, nuclear magnetism has developed at a pace which after fifteen years still shows no sign of slackening. Besides its first and obvious application to the measurement of nuclear moments, it has become a major tool in the study of the finer properties of matter in bulk. Structure of molecules, reaction rates and chemical equilibria, chemical bonding, crystal structures, internal motions in solids and liquids, electronic densities in metals, alloys, and semiconductors, internal fields in ferromagnetic and antiferromagnetic substances, density of states in superconductors, properties of quantum liquids, are some of the topics where nuclear magnetism has so far provided specific and detailed information.

Detailed studies of nuclear relaxation processes combined with electron spin resonance have led to original methods of nuclear alignment which may in the near future open up new experimental possibilities to nuclear physicists as well as to the specialists of very low temperatures.

On a more fundamental level, systems of nuclear spins provide examples of problems in statistical mechanics and in the theory of irreversible processes that are sufficiently simple to allow a clean and unambiguous solution both theoretically and experimentally, but are still sufficiently complex to be far from trivial. Thus the hitherto purely academic concept of negative temperature has found its full physical significance in nuclear magnetism. Thus also the trend toward thermal equilibrium of a system (the spin system) coupled to a thermal bath (the lattice) can be investigated, theoretically and experimentally, more fully than is usually possible in other fields of physics.

One of the more remarkable features of nuclear magnetism and, at least for the author of this book, the most deeply satisfying, is the very close connexion between theory and experiment that leaves little room for a theory that could not be tested by a suitable experiment or for an experiment that does not admit of a well-defined theoretical interpretation; this perhaps to a greater extent than in any other branch of modern physics.

Such at any rate was the view that has presided over the writing of this book. It is an attempt to provide an account of the principles and methods of nuclear magnetism that would be acceptable to the theorist and of use to the experimentalist; a wish often expressed, seldom fulfilled, that stands a better chance, it is hoped, in a field where theorist and experimentalist as often as not are the same person.

On the contents of this book the following comments can be made.

The experimental methods are discussed very briefly and in very general terms. The lack of space and the lack of competence of the author have precluded any detailed description of the experimental techniques currently in use. One can only hope that the definite need for a monograph dealing with these problems will be satisfied in the future.

There are no tables of important constants such as nuclear moments, quadrupole couplings, chemical shifts, relaxation times, and spin-spin couplings. The amount of labour involved in the compiling of such data, the space requirements, and also the danger of rapid obsolescence have led to the conclusion that their presentation in review articles in a form comparable to that currently used for electron resonance data is much more suitable. For the same reason it did not seem possible nor indeed desirable to include an extensive bibliography of the published work in the field of nuclear magnetism, which at the time of writing contains well over 2,000 titles and is continually increasing.

The selection of the references included in this book was made on the following basis. The viewpoint adopted is that in a book, in contrast to an article, no references need be given for credit and that it is the privilege and indeed the role of the author to blend together the contributions of the various workers in the field and to modify them as he sees fit, for the benefit of the reader. In fairness to all concerned it should therefore be made perfectly clear that the references given in each case are not necessarily considered by the author as the most original or the most important contributions in the field but rather as convenient sources of information to supplement that given in the book. To give one example among many, the important work of Kubo and Tomita, which has influenced the author very strongly, is not quoted because it was felt that the gist of its contents was dealt with in sufficient detail to make further reference to the original paper less useful for the reader than that to some other, perhaps less important, work. Under such circumstances it was clear that a name index would serve no useful purpose and it has accordingly been omitted.

To conclude, one may ask what category of readers I had in mind in writing this book. This is a difficult question which may be answered in part by saying what kind of book I would have liked to have written. What I had in mind was to attempt for nuclear magnetism what Van Vleck has done for the theory of electric and magnetic susceptibilities in a book which thirty years after its publication is still *the* book on the subject. A *demi-succès* in this undertaking would be good enough.

It is not possible to acknowledge in detail my great indebtedness for illuminating discussions and constructive criticism to so many friends and colleagues and especially to the members of our group at Saclay and to our visitors from abroad. I would like, however, to thank particularly 'the long legg'd spinner', my good friend Ionel Solomon who has patiently coached me in the mysteries of the lock-in detector and who has kindly prepared some beautiful photographs with the express purpose of illustrating this book.

The planning of the book and the writing of many chapters have benefited from the help and advice of Professor R. V. Pound more than I can say. Although I must take full responsibility for the entire book, those familiar with his work will have no difficulty in discerning his influence. Let him be assured of my deep gratitude.

I am very grateful to many colleagues and to the editors of the following journals for permission to reproduce a number of figures from these journals: *Acta Metallurgica*—*Comptes Rendus de l'Academie des Sciences*—*Journal of the Physical Society of Japan*—*Molecular Physics*—*Nature*—*Physica*—*Physical Review*—*Physical Review Letters*—*Proceedings of the Physical Society*—*Proceedings of the Royal Society*—*Science*—*The Journal of Chemical Physics*—*The Physics and Chemistry of Solids*. My special thanks go to those authors who kindly took the trouble of sending original photographs.

I am greatly indebted to Madame Houzé and Madame Gugenberger for their help with the preparation of the manuscript and to Madame Gugenberger for her competent handling of the proof. Mr. Timothy Hall has kindly prepared the subject index.

A. A.

Saclay

October 1960

PLATES

THE following figures appear as plates at the places shown:

FIGS. III, 2-III, 10	<i>between pages 64 and 65</i>
FIG. III, 11	<i>facing page 76</i>
III, 15	85
III, 18	96
III, 19	97
VII, 10	245
VIII, 6 and 7	338
VIII, 8	339
VIII, 10	341
IX, 1a	378
IX, 4 and 5	396
XI, 2	483
XI, 7	496
XI, 8 and 9	497
XII, 1	522

CONTENTS

I. GENERAL INTRODUCTION	1
A. Nuclear paramagnetism	1
B. Special features of radio-frequency spectroscopy	3
C. The phenomenon of resonance; 'resonant' and 'non-resonant' methods	4
(a) Beam measurements of atomic, molecular, and nuclear magnetic moments	5
(b) Measurement of the magnetic moment of the neutron	6
(c) The fine structure of the hydrogen atom	7
(d) The fine structure of positronium	8
(e) The magnetic moment of the μ -meson	9
(f) Resonance detected by optical means	10
(g) Perturbed angular correlations	11
D. Nuclear magnetic resonance	13
(a) The principle	13
(b) Various extensions and generalizations	15
REFERENCES	17
II. MOTION OF FREE SPINS	19
A. Classical treatment	19
B. Quantum mechanical treatment	22
C. Quantum mechanical description of a statistical ensemble of free spins. Density matrix	24
D. Relation with the perturbation method	27
E. Transient effects	32
(a) Free precession	32
(b) Spin echoes	33
(c) The adiabatic theorem, adiabatic passage	34
F. The general problem of two levels coupled by an r.f. field. The fictitious spin $\frac{1}{2}$	36
REFERENCES	38
III. MACROSCOPIC ASPECTS OF NUCLEAR MAGNETISM	39
I. INTRODUCTION	39
A. Static susceptibility	39
B. Resonant absorption of r.f. energy	40
II. THE PHENOMENOLOGICAL EQUATIONS OF BLOCH	44
A. Steady-state solutions--saturation	45
B. Steady-state solutions in an inhomogeneous field	49
C. Modified Bloch equations in low fields	53

III. TRANSIENT METHODS IN NUCLEAR MAGNETISM	57
A. The method of the spin echoes	58
(d) Spin diffusion	59
(b) Coherent and incoherent pulses	62
B. Free precession	63
(a) Free precession in the earth's field	64
C. Adiabatic passage	65
Applications of the fast-passage methods	66
(a) Measurement of the relaxation time T_1	66
(b) Measurement of T_2 in liquids	67
(c) Other applications of adiabatic fast passage	68
D. The method of transient nutation	68
IV. DETECTION METHODS	71
A. General	71
B. Detection of steady-state nuclear signals	75
(a) Q-meter detection	75
(b) Bridge and crossed coils methods	76
(c) Marginal oscillator	77
(d) Audio-modulation, narrow band amplification, phase sensitive detection, signal-to-noise ratio	78
(1) Lock-in detection and signal-to-noise ratio	79
(2) Signal-to-noise ratio	82
(e) Transient effects in steady-state detection	85
C. Transient methods of detection	86
(a) Adiabatic fast passage	86
(b) Pulse methods, coherent and incoherent pulses	87
D. Negative absorption—masers	89
APPENDIX. Proof of the Kramers-Krönig relations	93
REFERENCES	96
IV. DIPOLAR LINE WIDTH IN A RIGID LATTICE	97
I. INTRODUCTION	97
A. The local field	97
B. General theory of magnetic absorption	98
II. BROADENING BY LIKE SPINS	103
A. Dipole-dipole interaction	103
B. Definition of the moments	106
C. Principle of the calculation of moments	108
D. Calculation of the second and fourth moments	111
E. Relationship between the line shape and the free precession signal	114
F. A comparison between theory and experiment	115
III. DIPOLAR BROADENING BY UNLIKE SPINS	122

IV. DIPOLAR BROADENING IN MAGNETICALLY DILUTED SUBSTANCES	125
A. The method of moments	125
B. The statistical theory	126
V. MODIFICATIONS IN THE DIPOLAR BROADENING CAUSED BY THE EXISTENCE OF QUADRUPOLE COUPLINGS	128
REFERENCES	132
V. SPIN TEMPERATURE	133
A. Non-interacting spins	133
B. Interacting spins in high field	136
C. Interacting spins in low fields	144
D. Zeeman system with more than one spin species	150
E. Dynamics of thermal spin-spin processes	154
REFERENCES	158
VI. ELECTRON-NUCLEUS INTERACTIONS	159
I. ELECTROSTATIC COUPLINGS	159
A. The Hamiltonian	159
B. Ionic crystals	166
C. Molecular crystals	169
II. MAGNETIC INTERACTIONS	170
A. The coupling Hamiltonian	170
B. The effect of electron-nucleus coupling in diamagnetic substances	173
(a) General	173
(b) Calculation of the chemical shift	175
(c) Indirect interaction between nuclear spins in diamagnetic substances	183
(1) The orbital coupling	184
(2) The Heitler-London approximation	186
(3) The method of molecular orbitals	190
C. The effect of electron-nucleus coupling in paramagnetic substances	191
(a) Non-metals	191
(1) Nature of the coupling	191
(2) Observability of nuclear resonance	193
(b) Metals	199
(1) The frequency shift in metals	199
(2) The indirect interactions in metals	206
D. Nuclear resonance in antiferromagnetic and ferromagnetic substances	210
REFERENCES	214

VII. FINE STRUCTURE OF RESONANCE LINES— QUADRUPOLE EFFECTS	216
I. FINE STRUCTURE CAUSED BY DIPOLAR COUPLING	216
A. Rigid lattice	216
(a) Two identical spins (two protons) I^1 and I^2	216
(b) Systems of more than two spins	222
B. Nuclear resonance in solid hydrogen	223
(a) Introduction. System of two interacting protons	223
(b) Solid hydrogen	225
(c) <i>Ortho</i> - and <i>para</i> -hydrogen	226
(d) Crystalline potential	227
(e) Magnetic resonance in a strong field	228
(f) Magnetic resonance in zero field	231
(g) Magnetic resonance in HD and D ₂	231
II. ENERGY LEVELS OF NUCLEAR SPINS IN THE PRESENCE OF QUADRUPOLE INTERACTIONS	232
A. High magnetic fields	233
(a) Energy levels in single crystals	233
(b) Imperfect cubic crystals	237
(1) Powder pattern	237
(2) First-order broadening in imperfect crystals	237
(3) Transient methods, multiple echoes	241
(4) Second-order quadrupole broadening in imperfect crystals	246
B. Low magnetic fields	249
(a) Zero field spectra	249
(1) Integer spins	250
(2) Half-integer spins	251
(b) Zeeman splittings of quadrupole levels	253
(1) Integer spins	253
(2) Half-integer spins	254
(c) Transient methods	257
(1) Transient magnetization in zero field	257
(2) Transient magnetization in a small magnetic field H_0	260
APPENDIX. Sign of the quadrupole coupling	261
REFERENCES	263
VIII. THERMAL RELAXATION IN LIQUIDS AND GASES	264
I. INTRODUCTION	264
A. Coupling of the nuclear spins with the radiation field	264
B. Coupling of the spin system with the lattice	267
II. RELAXATION IN LIQUIDS AND GASES	268
A. General	268
B. Definitions	270

C. Motion of a system subject to a perturbation which is a random function of time	272
(a) Transition probability	272
(b) The master equation for populations	274
(c) The master equation for the density matrix	276
(d) The master equation in operator form	278
(e) Macroscopic differential equations	280
(f) Summary of the notation introduced in this section	281
(g) Justification of the four assumptions leading to the generalized master equation	282
D. Quantum mechanical formulation of the problem	283
E. Relaxation by dipolar coupling	289
(a) Like spins	290
(b) Unlike spins	294
(c) Correlation functions resulting from random molecular rotation or translation	297
(1) Rotation	298
(2) Translation	300
F. Other mechanisms of relaxation in liquids	305
(a) General	305
(b) (1) Scalar spin-spin coupling	306
(2) Scalar relaxation of the first kind	308
(3) Scalar relaxation of the second kind	309
(c) Quadrupole relaxation in liquids through molecular reorientation	313
(d) Relaxation through anisotropic chemical shift combined with molecular reorientation	315
G. Nuclear relaxation in gases	316
(a) The H_2 molecule—diatomic molecules	316
(b) Relaxation in monatomic gases	322
III. COMPARISON BETWEEN THEORY AND EXPERIMENT	323
A. Dipolar coupling between like spins	324
(a) Short correlation times, relative values of T_1	324
(b) Absolute values of T_1	326
(c) Long correlation times	327
B. Coupling between unlike spins	328
(a) Single irradiation methods	328
(b) Double irradiation methods	333
(1) The HF molecule	333
(2) Coupling between a nuclear spin and an electronic spin	338
C. Electric quadrupole relaxation in liquids	346
D. Nuclear relaxation in gases	349
(a) Nuclear relaxation in hydrogen gas	349

(b) Nuclear relaxation in liquid hydrogen	350
(c) Relaxation in monatomic gases	352
REFERENCES	353

IX. THERMAL RELAXATION AND DYNAMIC POLARIZATION IN SOLIDS	354
I. CONDUCTION ELECTRONS AND SPIN-LATTICE RELAXATION IN METALS	355
A. An elementary calculation of the relaxation time	356
B. Nuclear relaxation time and spin temperature	359
C. Dynamic nuclear polarization in metals (the Overhauser effect)	364
(a) Fermi statistics and non-equilibrium electron spin distribution	364
(b) Dynamic polarization	367
(c) Coupled equations for nuclear and electron spin polarization	368
D. Comparison with experiment	370
(a) Measurements of T_1	370
(b) Dynamic polarization experiments	373
(c) Dynamic nuclear polarization in metals at the temperatures of liquid helium	375
II. NUCLEAR RELAXATION CAUSED BY FIXED PARAMAGNETIC IMPURITIES	378
A. Theory	379
B. Comparison with experiment	386
III. MAGNETIC RELAXATION AND DYNAMIC POLARIZATION IN SEMICONDUCTORS AND INSULATORS	389
A. Relaxation by conduction electrons in semiconductors	389
B. Dynamic polarization by fixed paramagnetic impurities—solid state effect	392
IV. RELAXATION BY THERMAL VIBRATIONS IN A CRYSTAL-LINE LATTICE	401
A. Lattice vibrations and phonons	402
B. Transition probabilities induced by the spin-phonon coupling	404
C. Magnetic and quadrupole relaxation by spin-phonon coupling	409
(a) Magnetic relaxation	409
(b) Quadrupole relaxation	411
D. Ultrasonic experiments	417
(a) Quadrupole transitions	419
(b) Magnetic transitions	421
REFERENCES	423

X. THEORY OF LINE WIDTH IN THE PRESENCE OF MOTION OF THE SPINS	424
I. INTRODUCTION	424

CONTENTS

xv

II. THE ADIABATIC CASE	427
A. General theory	427
B. Exchange narrowing	435
C. Brownian motion narrowing	439
III. THE NON-ADIABATIC LINE WIDTH	441
A. Line width and transverse relaxation time	441
B. General case	442
IV. DESTRUCTION OF FINE STRUCTURES THROUGH MOTION	447
V. INFLUENCE OF INTERNAL MOTIONS IN SOLIDS ON THE WIDTH AND RELAXATION PROPERTIES OF ZEEMAN RESONANCE LINES	451
A. Rotational motions	451
B. Translational diffusion in solids	458
VI. INFLUENCE OF INTERNAL MOTIONS IN SOLIDS ON THE WIDTH AND RELAXATION OF QUADRUPOLE RESONANCE LINES	467
A. Torsion oscillations	468
(a) The spin Hamiltonian	468
(b) The line width	470
(c) Relaxation time	472
(d) The spectral densities	473
B. Hindered rotations	474
(a) Fast motion	474
(b) Slow motion	477
REFERENCES	479
XI. MULTIPLY STRUCTURE OF RESONANCE LINES IN LIQUIDS	480
I. ENERGY LEVELS OBSERVED BY CONTINUOUS WAVE METHODS	480
A. $J \ll \delta$	482
B. J and δ comparable for two spins $\frac{1}{2}$	484
C. J and δ comparable, for two groups G and G' of p equivalent spins i and p' equivalent spins i' , respectively	488
D. Perturbation method	489
E. Isochronous non-equivalent spins	491
II. MULTIPLY SPECTRA OBSERVED BY TRANSIENT METHODS	495
A. The method of free precession	495
B. The method of spin echoes	497
III. LINE WIDTH PROBLEMS IN MULTIPLY SPECTRA	501
A. Effects of quadrupole relaxation and chemical exchange	501
B. Effects of magnetic relaxation	506
REFERENCES	510

XII. THE EFFECTS OF STRONG RADIO-FREQUENCY FIELDS	511
I. STRONG RADIO-FREQUENCY FIELDS IN LIQUIDS	511
A. 'Non-viscous liquids'	511
B. 'Viscous liquids'	517
C. Bloch equations for a 'simple' line	522
D. Decoupling of spins through 'stirring' by a radio-frequency field	527
(a) Introduction	527
(b) The intermediate pattern (elementary theory)	530
(c) The intermediate pattern (detailed theory)	533
II. STRONG RADIO-FREQUENCY FIELDS IN SOLIDS	539
A. Introduction	539
B. Spin temperature in the rotating frame, reversible fast passage	545
C. Spin temperature in the rotating frame, steady-state solutions	555
D. Spin-lattice relaxation in the rotating frame	560
(a) Relaxation for a single spin species	560
(b) Relaxation in the presence of two spin species	562
E. Double irradiation methods	566
(a) Rotary saturation	566
(1) Rotary saturation in liquids	566
(2) Rotary saturation in solids	569
(b) Line narrowing by double frequency irradiation	570
(c) Transient methods of double irradiation	578
REFERENCES	580
INDEX OF NUCLEAR SPECIES	583
SUBJECT INDEX	591

GENERAL INTRODUCTION

... pale, deluding beams.

PURCELL (*Dido and Aeneas*)

A. Nuclear paramagnetism

THE subject matter of this book is the magnetic behaviour of assemblies of large numbers of atomic nuclei.

We denote their collective macroscopic magnetic properties by the term 'nuclear magnetism' in analogy with the term electronic magnetism for assemblies of electrons.

It is essentially this collective aspect of the problem that distinguishes both theory and experiments in the field of nuclear magnetism proper, from other research in the field of nuclear moments.

Many atomic nuclei in their ground state have a non-zero spin angular momentum $I\hbar$ (integer or half integer in units of \hbar) and a dipolar magnetic moment $\mu = \gamma\hbar I$ collinear with it. With few exceptions, the order of magnitude of these moments is between 10^{-3} and 10^{-4} Bohr magnetons. It is these moments that give rise to nuclear magnetism. Without attempting a detailed parallel between nuclear and electronic magnetism, a few differences can be pointed out. Of the three usual aspects of magnetism, namely ferromagnetism (or antiferromagnetism), diamagnetism, and paramagnetism, only the last is of interest in nuclear magnetism. It will be remembered that ferromagnetism may arise when the temperature, T of the sample, times the Boltzmann constant k (i.e. kT), becomes comparable to the couplings between the spins. The strong exchange coupling of electrostatic origin that gives rise to electronic ferromagnetism is absent in nuclear magnetism, and, because of the smallness of nuclear moments, the magnetic coupling between nuclear spins is such that temperatures of the order of 10^{-7} °K or less would be required for a possible observation of nuclear ferromagnetism (or antiferromagnetism). This makes nuclear ferromagnetism a subject beyond experimental possibilities for the time being (although possibly not for ever). A nuclear analogue of electronic diamagnetism, that is of magnetism arising from the Larmor precession of the electronic charges in an applied magnetic field, is not easy to visualize, but

at least in bulk matter it can reasonably be expected to be entirely negligible.

We are thus left with nuclear paramagnetism. While for electronic paramagnetism there is an appreciable contribution from the orbital motion of the bound electrons, the nuclear paramagnetism of orbital origin is entirely negligible in bulk matter (for reasons that will appear in Chapter VI) and only that due to the nuclear spins will be considered.

The existence of spin paramagnetism, that is, the appearance in a sample containing a large number of elementary spin-moments of a net macroscopic magnetization when placed in a magnetic field H_0 , is due to the fact that different orientations of the spins with respect to the field, described by different values of the quantum number $I_z = m$ of the spin quantized along the field, correspond to different magnetic energies E_m . According to the fundamental Boltzmann law of statistical mechanics, the populations P_m of the energy levels are proportional to $\exp(-E_m/kT) = \exp(\gamma\hbar m H_0/kT)$. The net magnetization of a sample containing N spins will thus be

$$M = N\gamma\hbar \frac{\sum_{m=-I}^I m \exp(\gamma\hbar m H_0/kT)}{\sum_{m=-I}^I \exp(\gamma\hbar m H_0/kT)}. \quad (1)$$

In nuclear magnetism, where the ratio $\gamma\hbar H_0/kT$ is almost always a very small number, it is permissible to make a linear expansion of the Boltzmann exponential, thus obtaining

$$M = \frac{N\gamma^2\hbar^2 H_0}{kT} \frac{\sum_{m=-I}^I m^2}{2I+1} = \frac{N\gamma^2\hbar^2 I(I+1)}{3kT} H_0 = \chi_0 H_0, \quad (2)$$

where χ_0 is the static nuclear susceptibility. The proportionality of χ_0 to $1/T$ is the well-known Curie law.

Since the static nuclear susceptibility is, according to (2), proportional to $\gamma^2\hbar^2 I(I+1)$, that is, to the square of the magnitude of the elementary nuclear moment, it will be smaller than the electronic paramagnetic susceptibility by a factor of the order of 10^{-6} to 10^{-8} . Because of this smallness it is very difficult to observe by the conventional magneto-static methods. To give an example, the static proton susceptibility of a cubic centimetre of water is at room temperature of the order of 3×10^{-10} c.g.s. units. Although a static measurement of nuclear magnetic susceptibility had been made as early as 1937 (1), on solid hydrogen at 2° K (to take advantage of the large factor $1/T$ in (2)), nuclear