

---

# Nuclear Magnetic Resonance Spectroscopy

*A Physicochemical View*

---

Robin K Harris

Department of Chemistry  
University of Durham, England



Longman  
Scientific &  
Technical

---

---

# Nuclear Magnetic Resonance Spectroscopy

*A Physicochemical View*

---

**Robin K Harris**

Department of Chemistry  
University of Durham, England

 Longman  
Scientific &  
Technical

---

**Longman Scientific & Technical,  
Longman Group UK Limited,**  
Longman House, Burnt Mill, Harlow,  
Essex CM20 2JE, England  
*and Associated Companies throughout the world.*

© Robin K. Harris 1983, 1986

All rights reserved; no part of this publication  
may be reproduced, stored in a retrieval system,  
or transmitted in any form or by any means, electronic,  
mechanical, photocopying, recording, or otherwise,  
without the prior written permission of the Publishers.

First published 1983 by Pitman Publishing Limited  
Reprinted as revised paperback edition 1986 by Longman Group UK Limited

**British Library Cataloguing in Publication Data**

Harris, R.K.

Nuclear magnetic resonance spectroscopy:  
a physiochemical view.—Pepr. with  
revisions

1. Nuclear magnetic resonance spectroscopy

I. Title

538'.362 QC762

ISBN 0-582-44653-8

ISBN 0-582-44653-8

Printed in Great Britain at The Bath Press, Avon

# Preface to the revised reprint

Reprinting this book provides an opportunity to correct typographical errors, to carry out some small cosmetic improvements to the presentation and to make a few additional changes. I have attempted, for instance, to clarify the difference between the frequency of the electromagnetic radiation and its strength as indicated by the precession it induces in the magnetization. The symbol  $\omega_1$  is retained for the former and  $\Omega_1 (= \gamma B_1)$  introduced for the latter. New sections have been added to Chapters 6 and 7 in recognition of the growing importance of NMR work on solids and of 2-D NMR techniques. Furthermore, an increased emphasis has been placed on the tensor nature of NMR interactions by minor changes in the text and, more importantly, by the addition of a new Appendix.

It is hoped that these changes are welcomed and that publication in paperback form enables the book to reach a wider readership, particularly among graduate students.

Since the original book was published, I have moved to a different University. I take this opportunity to thank my former colleagues at the University of East Anglia for assisting greatly in my continued chemical education over the past 20 years. I also wish to thank G. A. Morris for helpful discussion of Chapter 7.

University of Durham,  
January 1986

Robin Harris

# Preface

Nuclear magnetic resonance spectroscopy has occupied an important place in the armoury of physical techniques available to the chemist for over 25 years. Indeed, it is arguable that it is the single most important tool for obtaining detailed information on chemical systems at the molecular level. In spite of the high cost of NMR spectrometers no moderately-sized chemical laboratory, whether industrial or academic, can be considered to be properly-equipped without at least one such instrument. No university undergraduate chemistry course is complete without a discussion of the basic principles of NMR. The subject has proved to be remarkable for the number of innovations that have appeared and become established as valuable additions. Thus, in the early 1970s the use of high-resolution techniques based on the Fourier transform (FT) principle profoundly modified the practice of NMR and provided a quantum jump in the amount of information accessible by NMR. The FT mode also ushered in an era in which an increasing number of spectrometer operations are computer-controlled, leading also to the ability both to perform new experiments and to enhance the quality of the results. The past five or six years have seen several additional 'quantum jumps' in NMR, for instance (a) multinuclear studies, (b) very-high-field operation, (c) high-resolution work on solids, (d) 'two-dimensional' operation, and (e) spin imaging. These advances owe much to the ever-increasing variety of pulse sequences which can be implemented.

It is clear that many of these advances must be incorporated into undergraduate and graduate teaching. In 1969 Dr Ruth Lynden-Bell and I wrote a book entitled *Nuclear Magnetic Resonance Spectroscopy* (published by Thomas Nelson & Sons Ltd, but now out of print) which took a physicochemical approach to such teaching. Although very little in that book has become outmoded, the material is now wholly inadequate for a proper view of NMR—the FT technique, for instance, was not mentioned. The aim of the present work is to provide an updated text based on the same philosophy of a physicochemical approach. Material from the earlier book has been incorporated (with modifications), particularly in Chapters 1, 2 and 8, but the total amount of text has roughly doubled, since much has been added. The

new book is intended to cover NMR adequately for students taking Bachelor's and Master's degrees in chemistry, and should also be valuable in Ph.D. work and for people involved in NMR to a greater or lesser extent in industrial and Government laboratories.

It is, perhaps, obvious that considerable difficulty was encountered in deciding which topics to include and which to exclude. The choice is, to some extent, personal, but the policy has been to avoid mention of topics at a trivial level, such as would have been necessary to keep the size of the book within reasonable bounds if all the conceivably relevant areas were to be mentioned. Therefore several topics have been totally omitted. The principal among these are (a) NMR in liquid crystals and liquid crystal solutions, (b) spin imaging and related topics, and (c) chemically-induced dynamic nuclear polarization. These areas are self-contained and may be considered somewhat away from mainstream chemical usage of NMR. Specifically biochemical applications of NMR have also been largely omitted, in spite of their importance, mainly because it is difficult to develop such aspects without extensive discussion of strictly biochemical principles. Some will doubtless be critical of these decisions, but I defy anyone to produce a set of topics for a book of this size which would not arouse similar criticisms! Some texts on the omitted topics are listed under 'Further reading' at the end of this book (p. 241).

Problems are also encountered in deciding the level of mathematical sophistication used. I have tried to combine a degree of rigour with a desire both to give a physically-meaningful description of NMR behaviour and to minimize the amount of mathematics that is needed. A deliberate decision was taken not to introduce density matrix formalism, in spite of its power. Throughout the book SI units and equations are used. The form of relaxation equations may on occasion seem unfamiliar because of the factors of  $(\mu_0/4\pi)$ , and many scientists still apparently find Gauss rather than Tesla come first to mind for units of magnetic field, but these problems are not usually of great significance. I believe familiarity with SI is now such that a more detailed discussion of units is not required, but readers should refer if necessary to the booklet by M. L. McGlashan entitled *Physico-Chemical Quantities and Units* (Royal Society of Chemistry Monographs for Teachers, Number 15, 1968). Lists of SI units and of fundamental constants, in tabular form, follow this preface. IUPAC recommendations for NMR have been used throughout the book (see *Pure Appl. Chem.*, **29**, 627 (1972) and **45**, 219 (1976)).

Chapters 1, 2 and 8 cover roughly the same ground as in the corresponding chapters of the earlier book. Chapter 1 is, indeed, a self-contained discussion of the simpler basic principles of NMR, as involved in the continuous wave (CW) mode of operation, and is intended for beginners of the subject. Chapter 2 discusses second-order spectral analysis, and it is largely possible for the student to omit detailed reading of this Chapter if it is not directly relevant to his or

her interests. Chapter 3 is largely new, and introduces the Fourier transform principle, together with the concept of relaxation. Chapter 4 continues the discussion of relaxation but concentrates on the dipolar interaction and on double resonance. The fifth chapter covers chemical exchange and the effects arising from quadrupolar interactions, in a form greatly expanded from the earlier book. Chapters 6 and 7 are entirely new. The former deals with NMR of solids, including the high-resolution techniques that are now finding increasing application. The latter discusses a number of special pulse sequences and develops the concepts of two-dimensional NMR. The final chapter is about the factors affecting chemical shifts and coupling constants. Problems are provided at the end of each chapter. A limited number of references, together with suggestions for further reading, are also included.

It is hoped that the whole volume provides a basis of understanding of NMR that will be valuable for chemists of many complexions, but particularly for those who value a physicochemical approach.

University of East Anglia  
5 April 1982

Robin Harris

# Acknowledgements

I am very grateful to Dr Ruth M. Lynden-Bell who joined me in writing a book on NMR in 1969. In particular, Chapter 2 of that book, which was written by Dr Lynden-Bell, has become, with modifications, Chapter 2 of the present book. Dr Lynden-Bell has also kindly read and commented on the present Chapter 3. I am also grateful to my colleagues Professors Norman Sheppard and Ken Packer who have, over the years, been the source of countless stimulating discussions of NMR. The work of many graduate students and other research workers at the University of East Anglia has also contributed to my enlightenment and has provided a number of the figures in the present book. Dr G. A. Webb has made some useful comments on Chapter 8 at galley-proof stage, which have resulted in improvements, and I thank him for his help. I would also like to thank Dr A. J. Jones of the National NMR Centre, the Australian National University, with whom I spent two months of sabbatical leave in 1981 during which the writing of this book was commenced. Some figures have been taken from the literature, and acknowledgements are given in the appropriate figure captions. A number of people have assisted with typing this book, but the largest share has been carried out by Mrs Janice Hancock, whom I would like to thank for all her work.

# List of SI units and related quantities

<i>Property</i>	<i>Symbol</i>	<i>SI unit</i>	<i>Symbol of unit</i>	<i>Equivalent SI units</i>	<i>Equivalents in other systems</i>
Length	$\ell, r$	metre	m	—	$10^2$ centimetres
Mass	$m$	kilogramme	kg	—	$10^3$ grammes
Time	$t$	second	s	—	—
Force	$F$	newton	N	$\text{kg m s}^{-2}$	$10^7$ dynes
Energy	$U$	joule	J	$\text{kg m}^2 \text{s}^{-2}$	$10^7$ ergs
Angle	$\theta$	radian	rad	$1/2\pi$ cycles	—
Frequency	$\nu$	hertz	Hz	—	1 cycle per second (c/s or cps)
Electric charge	$q$	coulomb	C	A s	$2.9979 \times 10^9$ e.s.u.
Electric current	$i$	ampere	A	—	$10^{-1}$ e.m.u.
Magnetic induction field	$B$	tesla	T	$\text{kg s}^{-2} \text{A}^{-1}$	$10^4$ gauss (e.m.u.)
Magnetic field intensity	$H$	ampere metre <sup>-1</sup>	—	$\text{m}^{-1} \text{A}$	$4\pi \times 10^{-3}$ oersted
Magnetic dipole moment	$\mu$	ampere metre <sup>2</sup>	—	$\text{m}^2 \text{A}$	$10^3$ e.m.u. sec <sup>-1</sup>
Magnetogyric ratio	$\gamma$	radian tesla <sup>-1</sup> second <sup>-1</sup>	—	rad kg <sup>-1</sup> s A	$10^{-4}$ rad gauss <sup>-1</sup> sec <sup>-1</sup>
Reduced coupling constant	$K$	newton ampere <sup>-2</sup> metre <sup>-3</sup>	—	$\text{kg m}^{-2} \text{s}^{-2} \text{A}^{-2}$	$10 \text{ cm}^{-3}$

# Fundamental constants<sup>(a)</sup>

Constant	Symbol	Value	Unit	
			SI	CGS
Elementary charge	$e$	1.602192 4.80325	$\times 10^{-19}$ C —	$\times 10^{-20}$ e.m.u. $\times 10^{-10}$ e.s.u.
Electron rest mass	$m_e$	9.10956	$\times 10^{-31}$ kg	$\times 10^{-28}$ g
Proton rest mass	$m_p$	1.67261	$\times 10^{-27}$ kg	$\times 10^{-24}$ g
Planck constant	$h$	6.62620	$\times 10^{-34}$ J s	$\times 10^{-27}$ erg s
	$\hbar = h/2\pi$	1.054592	$\times 10^{-34}$ J s	$\times 10^{-27}$ erg s
Charge-to-mass ratio for electron	$e/m_e$	1.758803	$\times 10^{11}$ C kg <sup>-1</sup>	$\times 10^7$ e.m.u.
Permeability constant	$\mu_0$	$4\pi$ 1	$\times 10^{-7}$ kg m s <sup>-2</sup> A <sup>-2</sup> —	— $\times 1$ e.m.u.
Free electron Landé splitting factor	$g_s$	2.00232	—	—
Magnetogyric ratio of proton	$\gamma_p$	2.675197 <sup>(b)</sup>	$\times 10^8$ rad s <sup>-1</sup> T <sup>-1</sup>	$\times 10^4$ rad s <sup>-1</sup> gauss <sup>-1</sup>
	$\gamma_p/2\pi$	4.25771 <sup>(b)</sup>	$\times 10^7$ Hz T <sup>-1</sup>	$\times 10^3$ s <sup>-1</sup> gauss <sup>-1</sup>
Bohr magneton	$\mu_B$	9.27410	$\times 10^{-24}$ J T <sup>-1</sup>	$\times 10^{-21}$ erg gauss <sup>-1</sup>
Nuclear magneton	$\mu_N$	5.05095	$\times 10^{-27}$ J T <sup>-1</sup>	$\times 10^{-24}$ erg gauss <sup>-1</sup>
Boltzmann constant	$k$	1.38062	$\times 10^{-23}$ J K <sup>-1</sup>	$\times 10^{-16}$ erg K <sup>-1</sup>
Avogadro constant	$N$	6.02217	$\times 10^{23}$ mole <sup>-1</sup>	$\times 10^{23}$ mole <sup>-1</sup>

<sup>(a)</sup> Taken from B. N. Taylor, W. H. Parker & D. N. Langenberg, *Rev. Mod. Phys.* **41**, 375 (1969), but quoted to fewer places.

<sup>(b)</sup> Corrected for the diamagnetic shift of H<sub>2</sub>O.

# Symbols and abbreviations

These lists contain the symbols and abbreviations most frequently used in this book, but they are not expected to be exhaustive. Some specialized notation is only defined in the relevant chapter. An attempt has been made to standardize usage throughout the book as far as is feasible, but it must be borne in mind that the original research literature certainly is not standardized in this way, and some difficulties may arise from this fact. Trivial use of subscripts, etc. is not always mentioned in the symbols list below. Some of the other symbols used in the text, e.g. for physical constants such as  $h$  or  $\pi$ , or for thermodynamic quantities such as  $H$  or  $S$ , are not included in the list since they are reckoned to follow completely accepted usage. In general, vectors are in bold print, and quantum mechanical operators are indicated by circumflexes.

## Symbols

- $a$  hyperfine (electron-nucleus) coupling constant
- B** magnetic induction field (magnetic flux density)
- B**<sub>0</sub> static magnetic field of an NMR spectrometer
- B**<sub>1</sub>, **B**<sub>2</sub> r.f. magnetic fields associated with  $\nu_1$ ,  $\nu_2$ .
- B**<sub>L</sub> local magnetic field (components  $B_{xL}$ ,  $B_{yL}$ ,  $B_{zL}$ )—of random field or dipolar origin
- $c$  coefficient in linear expansion of wave functions
- C** spin-rotation interaction tensor
- $C_X$  (i) natural abundance of nuclide  $X$ , expressed as a %  
(ii) spin-rotation coupling constant of nuclide  $X$
- D** dipolar interaction tensor
- $D^C$  nuclear receptivity relative to that of carbon-13
- $D^p$  nuclear receptivity relative to that of the proton
- E** electric field
- $F$  spectral width
- $\hat{F}_X$  nuclear spin operator for a group,  $G$ , of nuclei (components  $\hat{F}_{Gx}$ ,  $\hat{F}_{Gy}$ ,  $\hat{F}_{Gz}$ ,  $\hat{F}_{G+}$ ,  $\hat{F}_{G-}$ )
- $F_G$  magnetic quantum number associated with  $\hat{F}_G$
- $g$  nuclear or electronic  $g$  factor (Landé splitting factor)
- $H_{ij}$  element of matrix representation of  $\mathcal{H}$
- $\mathcal{H}$  Hamiltonian operator (in energy units)—subscripts indicate the nature of the operator
- $i$   $\sqrt{-1}$
- $\hat{I}_i$  nuclear spin operator for nucleus  $j$  (components  $\hat{I}_{ix}$ ,  $\hat{I}_{iy}$ ,  $\hat{I}_{iz}$ )
- $\hat{I}_{j+}$ ,  $\hat{I}_{j-}$  'raising' and 'lowering' spin operators for nucleus  $j$
- $I_i$  magnetic quantum number associated with  $\hat{I}_i$
- $I$  moment of inertia

$\overset{\circ}{J}$	indirect coupling tensor
${}^nJ$	nuclear spin-spin coupling constant through $n$ bonds (in Hz). Further information may be given by subscripts or in brackets. Normally subscripts are only used for algebraic symbols for nuclei in spectral analysis cases, e.g. $J_{AX}$ . Brackets are used for indicating the species of nuclei coupled, e.g. $J(^{13}\text{C}, ^1\text{H})$ or, additionally, the coupling path, e.g. $J(\text{POCF})$
$J(\omega)$	spectral density at angular frequency $\omega$
${}^nK$	reduced nuclear spin-spin coupling constant (see the notes concerning ${}^nJ$ )
$m_e$	mass of the electron
$m_j$	eigenvalue of $\hat{I}_{jz}$ (magnetic component quantum number)
$m_T$	total magnetic quantum number for a spin system (eigenvalue of $\sum_j \hat{I}_{jz}$ )
$m_T(X)$	total magnetic quantum number for $X$ -type nuclei
$\mathbf{M}_0$	equilibrium macroscopic magnetization of a spin system in the presence of $B_0$
$M_x, M_y, M_z$	components of macroscopic magnetization
$M_n$	moment of a spectrum ( $M_2$ = second moment, etc.)
$n_\alpha, n_\beta$	populations of the $\alpha$ and $\beta$ spin states
$N$	total number of nuclei of a given type in the sample
$P$	(i) angular momentum (ii) transition probability
$\mathbf{q}$	electric field gradient tensor (principal components $q_{xx}, q_{yy}, q_{zz}$ )
$Q$	nuclear quadrupole moment
$r$	(i) general symbol for distance (ii) general symbol for spin state (as $\langle r $ or $ r\rangle$ )
$R$	dipolar coupling constant, $(\mu_0/4\pi)\gamma_1\gamma_2(\hbar/2\pi)r^{-3}$
$s$	general symbol for spin state (as $\langle s $ or $ s\rangle$ )
$S$	(i) signal height (ii) electron (or, occasionally, nuclear) spin—cf. $I$
$T$	temperature
$T_c$	coalescence temperature for an NMR 'spectrum
$T_1^X$	spin-lattice relaxation time of the $X$ nuclei (further subscripts refer to the relaxation mechanism)
$T_2^X$	spin-spin relaxation time of the $X$ nucleus (further subscripts refer to the relaxation mechanism)
$T_2'$	inhomogeneity contribution to the dephasing time for $M_x$ or $M_y$
$T_2^*$	total dephasing time for $M_x$ or $M_y$ ; $(T_2^*)^{-1} = T_2^{-1} + (T_2')^{-1}$
$T_{1\rho}^X$	spin-lattice relaxation time of the $X$ nuclei in the frame of reference rotating with $B_1$
$T_d$	pulse delay time (in FT NMR)
$T_{ac}$	acquisition time (in FT NMR)
$T_p$	period for repetitive pulses (= interpulse time = $T_{ac} + T_d$ if $\tau_p$ is negligible)
$u$	in-phase (dispersion mode) signal
$v$	out-of-phase (absorption mode) signal
$W_0, W_1, W_2$	relaxation rates between energy levels differing by 0, 1 and 2 (respectively) in $m_T$

$\alpha$	nuclear spin wave function (eigenfunction of $\hat{I}_z$ ) for a spin- $\frac{1}{2}$ nucleus
$\alpha_A^2$	s-character of hybrid orbital at atom A
$\alpha_E$	the Ernst angle (for optimum FT sensitivity)
$\beta$	nuclear spin wave function (eigenfunction of $\hat{I}_z$ ) for a spin- $\frac{1}{2}$ nucleus
$\gamma_X$	magnetogyric ratio of nucleus X
$\delta_X$	chemical shift (for the resonance) of nucleus of element X (positive when the sample resonates to high frequency of the reference). Usually in ppm. Further information regarding solvent, references or nucleus of interest may be given by superscripts or subscripts or in brackets.
$\Delta n$	population difference between nuclear states ( $\Delta n_0$ at Boltzmann equilibrium)
$\Delta\delta$	change or difference in $\delta$
$\Delta\nu_{1/2}$	full width (in Hz) of a resonance line at half-height
$\Delta\sigma$	(i) anisotropy in $\sigma$ ( $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$ ) (ii) difference in $\sigma$ for two different situations
$\Delta\chi$	(i) susceptibility anisotropy ( $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ ) (ii) difference in electronegativities
$\epsilon_0$	permittivity of a vacuum
$\eta$	(i) nuclear Overhauser enhancement (ii) asymmetry factor (e.g. in $e^2qQ/h$ ) (iii) viscosity
$\theta$	angle—especially for that between a given vector and $\mathbf{B}_0$
$\mu_0$	(i) magnetic dipole moment (component $\mu_z$ along $\mathbf{B}_0$ ) (ii) electric dipole moment
$\mu_0$	permeability of a vacuum
$\mu_B$	Bohr magneton
$\mu_N$	nuclear magneton
$\nu_c$	carrier frequency of the radiation
$\nu_j$	Larmor precession frequency of nucleus $j$ (in Hz)
$\nu_0$	(i) spectrometer operating frequency (ii) Larmor precession frequency (general, or of bare nucleus)
$\nu_1$	frequency of 'observing' r.f. magnetic field
$\nu_2$	frequency of 'irradiating' r.f. magnetic field
$\Xi_X$	resonance frequency for the nucleus of element X in a magnetic field such that the protons in TMS resonate at exactly 100 MHz
$\sigma$	shielding tensor
$\sigma_j$	shielding constant of nucleus $j$ (used sometimes in tensor form). Usually in ppm. Subscripts may alternatively indicate contributions to $\sigma$
$\sigma_{\parallel}, \sigma_{\perp}$	components of $\sigma$ parallel and perpendicular to a molecular symmetry axis
$\tau$	time between r.f. pulses (general symbol)
$\tau_A$	pre-exchange lifetime of molecular species A
$\tau_c$	correlation time, especially for molecular tumbling
$\tau_d$	dwell time
$\tau_e$	electronic correlation time
$\tau_{\text{null}}$	recovery time sufficing to give zero signal after a $180^\circ$ pulse
$\tau_p$	pulse duration

$\tau_{sc}$	correlation time for relaxation by the scalar mechanism
$\tau_{sr}$	correlation time for spin-rotation relaxation
$\tau_{  }, \tau_{\perp}$	correlation times for molecular tumbling parallel and perpendicular to a symmetry axis
$\chi$	(i) magnetic susceptibility (ii) electronegativity (iii) nuclear quadrupole coupling constant ( $=e^2qQ/h$ )
$\omega_i, \omega_0, \omega_1, \omega_2, \omega_c$	as for $\nu_i, \nu_0, \nu_1, \nu_2, \nu_c$ but in $\text{rad s}^{-1}$
$\Omega_1, \Omega_2$	the strength of a radiofrequency magnetic field, expressed in angular frequency units for a nucleus of magnetogyric ratio $\gamma$ ( $\Omega_1 = \gamma B_1, \Omega_2 = \gamma B_2$ )

## Abbreviations

acac	acetylacetonato
ASIS	aromatic solvent-induced shift
CIDNP	chemically-induced dynamic nuclear polarization
CPMG	Carr-Purcell pulse sequence, Meiboom-Gill modification
CW	continuous wave
DD	dipole-dipole (interaction or relaxation mechanism)
DMSO	dimethylsulphoxide
EFG	electric field gradient
en	ethylenediamine
ESR	electron spin resonance
FID	free induction decay
fod	1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato
FT	Fourier transform
LCAO	linear combination of atomic orbitals
MO	molecular orbital
mol. wt.	molecular weight
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
NQR	nuclear quadrupole resonance
o.d.	outside diameter
ppm	parts per million
QF	quadrupole moment/field gradient (interaction or relaxation mechanism)
r.f.	radiofrequency
r.m.s.	root mean square
SA	shielding anisotropy
S/N	signal-to-noise ratio
SPI	selective population inversion
SPT	selective population transfer
SR	spin-rotation (interaction or relaxation mechanism)
tmhd	2,2,6,6-tetramethylheptane-3,5-dionato (also known as dpm, dipivaloylmethanato)
TMS	tetramethylsilane
UE	unpaired electron relaxation mechanism
WAHUA	Wagh, Huber and Haeberlen (pulse sequence)

# Contents

2-  
0611.

H-

<i>Preface to revised reprint</i>	x
<i>Preface</i>	xi
<i>Acknowledgements</i>	xiv
<i>List of SI units and related quantities</i>	xv
<i>Fundamental constants</i>	xvi
<i>Symbols and abbreviations</i>	xvii

## Chapter 1 The fundamentals

1-1	Introduction	1
1-2	Quantization of angular momentum	2
1-3	Electron and nuclear spin	3
1-4	Nuclear magnetic moments	5
1-5	Nuclei in a magnetic field	7
1-6	Larmor precession	8
1-7	The intensity of an NMR signal	9
1-8	Electronic shielding	11
1-9	Chemical shifts	12
1-10	Reference standards and solvents	14
1-11	Spin-spin coupling	17
1-12	Basic product functions	19
1-13	First-order energies and spectra	20
1-14	Equivalence	22
1-15	Notation for spin systems	24
1-16	First-order spectra involving magnetic equivalence	26
1-17	Abundant spins and dilute spins	27
1-18	Decoupling	28
1-19	The multiscan principle	29
1-20	Continuous-wave NMR: the spectrometer	30
1-21	Experimental aspects: the sample and the spectrum	33
	Notes and references	35
	Further reading	36
	Problems	36

## Chapter 2 Analysis of NMR spectra for isotropic solutions

2-1	Introduction	38
2-2	Operators	39
2-3	Wave functions	40
2-4	Spin operators and spin functions	42

2-5	The nuclear spin Hamiltonian operator	44
2-6	The nuclear resonance spectrum of a single nucleus	46
2-7	Spectra of molecules with two coupled nuclei	47
2-8	Systems with more than two nuclei	52
2-9	The X approximation (a) General principles	54
	(b) Systems with one X-nucleus	55
	(c) Satellite spectra	56
	(d) Coupled carbon-13 spectra	57
2-10	Equivalent nuclei	57
2-11	The composite particle method for systems containing magnetically equivalent nuclei	59
2-12	Analysis of observed spectra	61
	Notes and references	63
	Further reading	64
	Problems	64

### Chapter 3 Relaxation and Fourier transform NMR

3-1	Introduction	66
3-2	The Bloch equations	66
3-3	The rotating frame of reference	68
3-4	Steady state (CW) experiments	70
3-5	Saturation	72
3-6	Nuclear receptivity	73
3-7	The effects of radiofrequency pulses	74
3-8	The free induction decay and Fourier transform NMR spectra	75
3-9	Multipulse operation	77
3-10	Other operational facets of Fourier transform NMR	79
3-11	Cosmetic improvements by computer	80
3-12	Measurement of $T_1$ by the inversion-recovery method	81
3-13	Spin-echoes and the measurement of $T_2$	82
3-14	The origins of relaxation for spin- $\frac{1}{2}$ nuclei	84
3-15	The theory of relaxation	85
3-16	Relaxation mechanisms for spin- $\frac{1}{2}$ nuclei	88
3-17	Spin-locking and $T_{1\rho}$	91
	Notes and references	93
	Further reading	94
	Problems	94

### Chapter 4 Dipolar interactions and double resonance

4-1	Dipole-dipole coupling	96
4-2	Averaging by molecular tumbling	97
4-3	Relaxation induced by dipolar interactions	98
4-4	Double resonance—introduction	101
4-5	Selective population transfer	101
4-6	The double resonance Hamiltonian	102
4-7	Tickling experiments	105
4-8	Spin decoupling	106
4-9	The Solomon equations	107
4-10	The nuclear Overhauser effect	108
4-11	Carbon-13 relaxation times and the $^{13}\text{C}\{-^1\text{H}\}$ NOE	111

4-12	Quantitative $^{13}\text{C}$ NMR intensities	112
4-13	Anisotropic molecular tumbling—the Woessner Equations	114
	Notes and references	116
	Further reading	117
	Problems	117

## Chapter 5 Chemical exchange and quadrupolar effects

<b>5A</b>	<b>Chemical exchange</b>	
5-1	Introduction	119
5-2	Slow-exchange and fast-exchange regimes	120
5-3	Near the exchange rate limits	122
5-4	Intermediate rates of exchange: the $A \rightleftharpoons X$ case	123
5-5	More complicated exchange cases	125
5-6	Kinetic information	127
5-7	Chemical exchange information from spin-lattice relaxation in the rotating frame	129
5-8	Chemical exchange involving paramagnetic species	130
<b>5B</b>	<b>Quadrupolar effects</b>	
5-9	Nuclear electric quadrupole moments	131
5-10	Nuclear quadrupole energy	132
5-11	NMR of quadrupolar nuclei in solids	133
5-12	NMR of quadrupolar nuclei in solution	134
5-13	Quadrupole coupling constants and asymmetry factors	137
5-14	The effect on spin- $\frac{1}{2}$ spectra of coupling to quadrupolar nuclei	139
	Notes and references	142
	Further reading	142
	Problems	142

## Chapter 6 NMR of the solid state

6-1	The two-spin system	144
6-2	Magic-angle rotation	145
6-3	Second moments and the effects of molecular motion	146
6-4	Motional effects on relaxation times in solids	148
6-5	Cross-polarization	150
6-6	Shielding anisotropy	153
6-7	High-resolution NMR of dilute spins	154
6-8	Non-quaternary suppression	158
6-9	Discriminating techniques	159
6-10	Multiple-pulse techniques for abundant spins	162
	Notes and references	163
	Further reading	164
	Problems	164

## Chapter 7 Special pulse sequences and two-dimensional NMR

7-1	Introduction	165
7-2	Spin-echoes in coupled spin systems	165
7-3	Attached proton tests	169
7-4	The effects of selective pulses	170
7-5	The INEPT experiment	176
7-6	Two-dimensional NMR—basic principles	179