SPIN-TEMPERATURE AND NUCLEAR-SPIN RELAXATION IN MATTER:

BASIC PRINCIPLES AND APPLICATIONS

BY

DIETER WOLF

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PREFACE

> 'Although all the first beginnings of things are in motion, the sum total seems nevertheless to abide in supreme quietude.' *Lucretius (94–40 BC), 'De Rerum Natura'*

The use of n.m.r. techniques in materials science, solid-state physics, and chemical physics has progressed considerably during the last two decades. By their nature, most n.m.r. experiments represent rather indirect probes to gain information on static and dynamic microscopic properties of solid, liquid, and gaseous materials. Therefore, to interpret n.m.r. experiments in terms of the underlying microscopic events which determine the n.m.r. relaxation behaviour, considerable theoretical efforts are required.

In the past, many of the necessary theoretical concepts have been developed by experimentalists. This has the advantage that the basic concepts and models have been formulated in a language easily comprehensible to those for whom the theory is finally developed; namely, for the experimentalists. The disadvantages of this development lie in the apparent conflicting diversity of the different theoretical concepts and the variety of different experimental techniques developed.

As a theorist, I have always considered the variety of ideas as a challenge to find a more unified concept which would allow me to bring some order into the manifold of theoretical approaches used, which are conflicting in some respects and compatible in other ways. However, as Professor Alfred Seeger once pointed out to me, for good communication between theorists and experimentalists to be possible, both have to speak the same language. He reminded me that the word 'theory' derives from the Greek word 'ϑεωρια', which means 'overview' or understanding from a superior point of view, perhaps what the Germans call 'Weltanschauung'. In the original sense of the word 'theory', nuclear magnetic resonance in solids represents an ideal playground for a theorist trying to achieve a comprehensive understanding of the basic physical concepts applied in a field in which, as in not too many other areas of physics, experimental and theoretical efforts may be so closely correlated. Keeping in mind this point of view, I wrote this book mainly for the experimentalist who is struggling to decide which kind of theoretical approach to apply to interpret his experimental results. In developing a language and a formalism which combines both intuitive and more formal theoretical concepts, my final goal was to encourage more physicists to adopt some of the extremely versatile n.m.r. techniques as a probe to gain a more microscopic picture of the static and dynamic properties of atoms, defects, and molecules in, for example, crystals.

In the past, the spin-temperature concept – a rather intuitive approach – has proved to be extremely fruitful in bringing some degree of order into the microscopic interpretation of a variety of different n.m.r. experiments performed in solids and liquids. However, because of the great number of different physical situations dealt with in these experiments, several apparently different types of spin-temperature theories have been developed. By reviewing the different approaches, a rather general spin-temperature formalism is developed in this book from which the different well known versions (which are restricted to particular experimental regimes) may be obtained as special cases. Since two weakly-coupled quantum systems may not interchange energy unless their interaction fluctuates, any kind of spin-temperature theory is only capable of describing the effects of 'lattice'-induced motions on the nuclear-spin system but not the static properties of matter. I shall therefore concentrate on situations in which, because of the motion-induced time dependence of the spin–lattice coupling, energy is exchanged between the spin system and the 'lattice'. Using the nuclear-spin system as a probe, we are able to gain microscopic insight into the mechanisms that allow atoms, molecules, point defects, dislocations, conduction electrons, etc. to move.

This book consists of four major parts. In Part 1, the basic interactions of spins with each other and with other degrees of freedom in a liquid or solid material are discussed. The basic ideas and assumptions underlying the spin-temperature concept are also reviewed and extended.

Part 2 begins with a summary of the basic assumptions common to all theories of motion-induced nuclear-spin relaxation. As an example, the early theory of Bloembergen, Purcell, and Pound ('BPP theory') is used to illustrate how these basic assumptions affect the nuclear spin–lattice relaxation behaviour (Chapter 4). In Chapters 5, 6, and 7, the three most fundamental theories of nuclear-spin relaxation (Kubo–Tomita, Bloch–Wangsness–Redfield, and Hebel–Slichter theories) are reviewed from a common point of view. Part 2 is concluded by a comparison of and synthesis from these theories. This leads to the formulation of a rather general type of nuclear-spin-relaxation theory which includes the relaxation equations in a 'rigid lattice' and from which the usual theories of motion-induced nuclear-spin relaxation may be derived as special cases. As a limiting case of the latter, a unified spin-temperature theory of motion-induced nuclear-spin relaxation may be formulated (Chapter 8).

Throughout Part 2 neither the spin nor the spin–lattice interaction Hamiltonian had to be specified. Except for those theories which explicitly assume the existence of a spin temperature, the relaxation theories reviewed are of a very general nature and apply to relaxation processes in many areas of physics (most of which do not involve spins at all).

In the second half of this book the consequences of the 'unified spin-temperature theory' of Chapter 8 on a variety of commonly encountered physical situations are developed. As illustrated here, in effect all correlation-function expressions for T_1 and $T_{1\rho}$ follow from a single starting equation which is practically identical to the Hebel–Slichter equation. This leads to the development of a fairly comprehensive formalism for the derivation of correlation-function expressions for the nuclear-spin-relaxation behaviour. As demonstrated in some detail, laboratory and rotating-frame relaxation properties may therefore be determined in completely identical manners. In addition, the relaxation rates in the limiting 'ultra-slow motion' and 'motionally narrowed' regimes, respectively, are found to follow quite naturally as special cases from our general starting expression.

In Part 3, the relaxation due to fluctuating dipolar and quadrupolar interactions in systems containing one or two spin species and in molecular crystals or liquids is investigated. The results of Chapters 9, 10, and 12 are applied to self diffusion in cubic crystals for which the dipolar and quadrupolar 'lattice' correlation functions are well known and particularly simple. Explicit analytical and numerical results for the entire relaxation behaviour (temperature, field, and orientation dependence of T_1 and $T_{1\rho}$) may thus be obtained.

Finally, Part 4 focuses on the relaxation properties associated with fluctuating hyperfine interactions. Owing to limited space, only the Fermi-contact interaction in metals or semiconductors and the relaxation due to fluctuating anisotropic chemical-shift interactions in non-cubic crystals are investigated. Common to the two related Hamiltonians is their linear nuclear-spin structure which is contrasted with the bilinearity of the dipolar and quadrupolar Hamiltonians. In spite of these differences it is found that the basic relaxation properties associated with fluctuating hyperfine interactions are very similar to those arising from time-dependent dipolar and quadrupolar interactions.

By developing both a language and the underlying formalism needed for the theoretical interpretation of n.m.r. experiments on the internal dynamical processes in solids, liquids, and gases, I hope that more experimentalists will in the future be inspired to use some of the very versatile n.m.r. techniques to investigate the microscopic dynamics of atoms, molecules, defects, and electrons in a great variety of materials.

I am grateful for the extremely helpful criticism and feedback which I have received from Professor Otmar Kanert of the University of Dortmund. During his sabbatical visit to the University of Utah, I benefited in numerous ways from his stimulating interest in this book and from his insistence on clarity and the use of a language familiar to experimentalists. During the two years in which I have focused a considerable share of my research efforts on this book, I have had two opportunities to test and improve its teachability: I am grateful for invitations from the 'Troisième Cycle de la Physique en Suisse Romande' to present a summer course in Lausanne in 1975, and from the Universidad Central de Venezuela to teach a course on the subject during the fall of 1976.

Salt Lake City,
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D.W.

NOTATION

$A_{ij}^{(q)}$	dipolar spin operators
A, B	spin operators
$\tilde{A}$	symmetrical second-rank tensor
$B_{j_I i_S}^{(q)}$	dipolar spin operators for different spin species I and S
C	Curie's constant
C_d	concentration of point defects in a crystal
e	elementary charge
$E = \langle \mathcal{H} \rangle$	energy (expectation value of Hamiltonian $\mathcal{H}$)
$F_{ij}^{(q)}$	dipolar (geometrical) lattice functions
$G^{(q)}(t)$	'lattice' correlation function
$\mathbf{H}_0$	external constant magnetic field
$\mathbf{H}_1$	external rotating field
H_L	internal local field
H_D	dipolar local field
H_Q	quadrupolar local field
$\mathcal{H}_\mathrm{D}$	dipolar-interaction Hamiltonian
$\mathcal{H}_\mathrm{ex}$	exchange-coupling Hamiltonian
$\mathcal{H}_\mathrm{ind}$	indirect magnetic-dipole Hamiltonian
$\mathcal{H}_\mathrm{L}$	'lattice' Hamiltonian
$\mathcal{H}_\mathrm{psd}$	pseudo-dipolar interaction Hamiltonian
$\mathcal{H}_\mathrm{psex}$	pseudo-exchange interaction Hamiltonian
$\mathcal{H}_\mathrm{Q}$	quadrupolar Hamiltonian
$\mathcal{H}_\mathrm{S}$	Hamiltonian of the completely isolated spin system
$\mathcal{H}_\mathrm{SL}$	spin—lattice interaction Hamiltonian
$\mathcal{H}_\mathrm{Z}$	Zeeman Hamiltonian
I, S	spin quantum numbers for two-spin systems

I, $\vec{S}$	total angular-momentum operator
J	exchange integral
$J^{(q)}(\omega)$	dipolar spectral density (Fourier transform of $G^{(q)}(t)$
$\tilde{K}$	Knight-shift anisotropy tensor
$\mathbf{M}$	nuclear magnetization
Q	nuclear quadrupole moment
$Q_n^{(p)}$	quadrupolar spin operators
$Q_{\alpha\beta}$	quadrupole tensor
$\boldsymbol{r}$	internuclear vector
T	absolute temperature
T_1	spin-lattice relaxation time
$T_{1\rho}$	spin-lattice relaxation time in the rotating frame
T_2	spin-spin relaxation time
T_{IS}	cross-relaxation time
T_m	thermal-mixing time
$V_{\alpha\beta}$	electric field gradient (e.f.g.) tensor
Z	Zeeman
γ	gyromagnetic ratio
$\delta_{\alpha\beta}$	Kronecker's symbol
η	asymmetry parameter of an electric field gradient
θ	off-resonance angle
θ_L	thermal-equilibrium 'lattice' temperature
θ_S	spin temperature
$\vec{\mu}$	magnetization operator
$\rho(t)$	hermitian density operator of the entire system (spins plus 'lattice')
$\sigma(t)$	density matrix of spin system
τ_c	correlation time
τ	mean time between successive jumps of an atom
τ_d	mean time between successive jumps of a point defect

χ_{eq}	thermal-equilibrium or 'Curie' susceptibility
$\psi_n(t)$	wave function of a spin n
ω	angular precession frequency
ω_0	Larmor angular precession frequency due to $\mathbf{H}_0$
ω_1	Larmor angular precession frequency due to $\mathbf{H}_1$
ω_D	precession frequency in the dipolar local field
ω_L	local-field precession frequency
ω_Q	precession frequency in a quadrupolar local field
$\langle\ \rangle_{\theta,\phi}$	solid-angle average

Subscripts and superscripts

′	transformed
*	interaction representation
★	complex conjugate
(0)	secular part of Hamiltonian
c	correlation
cr	cross relaxation
CS	chemical shift
D	dipolar
e	electronic
eq	thermal equilibrium
ext	external
FC	Fermi contact
HF	hyperfine
ind	induced
int	internal
L	'lattice'
(n)	non-secular part of Hamiltonian
orb	orbital

Q	quadrupolar
r	rotating frame
rf	radio frequency
ρ	doubly rotating frame
RL	rigid lattice
S	spin
SL	spin-lattice

CONTENTS

PART 2: BASIC THEORIES OF NUCLEAR-SPIN RELAXATION

PART 3: APPLICATION TO SPIN–LATTICE RELAXATION ASSOCIATED WITH FLUCTUATING DIPOLAR AND QUADRUPOLAR INTERACTIONS

PART 4: SPIN–LATTICE RELAXATION VIA FLUCTUATING HYPERFINE INTERACTIONS