Contents

Preface, xii Acknowledgements, xv

1 The Basics of NMR, 1

- 1.1 The vector model of pulsed NMR, 1
 - 1.1.1 Nuclei in a static, uniform magnetic field, 2
 - 1.1.2 The effect of rf pulses, 3
- 1.2 The quantum mechanical picture: hamiltonians and the Schrödinger equation, 5
- Box 1.1 Quantum mechanics and NMR, 6

Wavefunctions, 6

Operators, physical observables and expectation values, 7

Schrödinger's equation, eigenfunctions and eigenvalues, 7

Spin operators and spin states, 8

Dirac's bra-ket notation, 11

Matrices, 11

- 1.2.1 Nuclei in a static, uniform field, 12
- 1.2.2 The effect of rf pulses, 15
- Box 1.2 Exponential operators, rotation operators and rotations, 19

Rotation of vectors, wavefunctions and operators

(active rotations), 20

Rotation of axis frames, 23

Representation of rf fields, 25

Euler angles, 25

Rotations with Euler angles, 26

Rotation of Cartesian axis frames, 27

- 1.3 The density matrix representation and coherences, 29
 - 1.3.1 Coherences and populations, 30

l .	CU	,,,	c	

2

	1.3.2	The density operator at thermal equilibrium, 33
	1.3.3	Time evolution of the density matrix, 34
1.4	Nuclea	ar spin interactions, 37
	1.4.1	Interaction tensors, 41
1.5	Genera	al features of Fourier transform NMR experiments, 43
		Multidimensional NMR, 43
		Phase cycling, 46
		Quadrature detection, 48
Box		The NMR spectrometer, 53
		Generating rf pulses, 53
		Detecting the NMR signal, 56
Note	es, 58	0
	rences,	59
	,	
Esse	ntial Te	echniques for Solid-State NMR, 60
2.1		uction, 60
2.2		-angle spinning (MAS), 61
	2.2.1	
	2.2.2	Rotor or rotational echoes, 67
		Removing spinning sidebands, 67
	2.2.4	Setting the magic-angle and spinning rate, 72
	2.2.5	Magic-angle spinning for homonuclear dipolar couplings, 75
2.3		onuclear decoupling, 77
		High-power decoupling, 78
	2.3.2	Other heteronuclear decoupling sequences, 81
2.4		onuclear decoupling, 83
	2.4.1	Implementing homonuclear decoupling sequences, 83
Box		Average hamiltonian theory and the toggling frame, 86
		Average hamiltonian theory, 86
		The toggling frame and the WAHUHA pulse sequence, 89
2.5	Cross-	polarization, 96
	2.5.1	Theory, 97
	2.5.2	Setting up the cross-polarization experiment, 101
Box	2.2	Cross-polarization and magic-angle spinning, 106
•		remainded and magic-angle spinning, 100

References, 114

2.6 Echo pulse sequences, 110

Notes, 113

3.1 Theory, 116

- 3.1.1 Introduction, 116
- 3.1.2 The chemical shielding hamiltonian, 117

- 3.1.3 Experimental manifestations of the shielding tensor, 120
- 3.1.4 Definition of the chemical shift, 123
- 3.2 The relationship between the shielding tensor and electronic structure, 125
- 3.3 Measuring chemical shift anisotropies, 131
 - 3.3.1 Magic-angle spinning with recoupling pulse sequences, 132
 - 3.3.2 Variable-angle spinning experiments, 135
 - 3.3.3 Magic-angle turning, 138
 - 3.3.4 Two-dimensional separation of spinning sideband patterns, 141
- 3.4 Measuring the orientation of chemical shielding tensors in the molecular frame for structure determination, 145

Notes, 149

References, 149

4 Dipolar Coupling: Theory and Uses, 151

- 4.1 Theory, 151
 - 4.1.1 Homonuclear dipolar coupling, 154
- Box 4.1 Basis sets for multispin systems, 156
 - 4.1.2 The effect of homonuclear dipolar coupling on a spin system, 157
 - 4.1.3 Heteronuclear dipolar coupling, 160
 - 4.1.4 The effect of heteronuclear dipolar coupling on the spin system, 162
 - 4.1.5 Heteronuclear spin dipolar coupled to a homonuclear network of spins, 163
 - 4.1.6 The spherical tensor form of the dipolar hamiltonian, 164
- Box 4.2 The dipolar hamiltonian in terms of spherical tensor operators, 164

Spherical tensor operators, 165

Interaction tensors, 167

The homonuclear dipolar hamiltonian under static and MAS conditions, 167

- 4.2 Introduction to the uses of dipolar coupling, 172
- 4.3 Techniques for measuring homonuclear dipolar couplings, 175
 - 4.3.1 Recoupling pulse sequences, 175
- Box 4.3 Analysis of the DRAMA pulse sequence, 180 Simulating powder patterns from the DRAMA experiment, 184
 - 4.3.2 Double-quantum filtered experiments, 185
- Box 4.4 Excitation of double-quantum coherence under magic-angle spinning, 189

The form of the reconversion pulse sequence: the need for time-reversal symmetry, 191

Analysis of the double-quantum filtered data, 195

Jonienis			

Box 4.5 Analysis of the C7 pulse sequence for exciting double-quantum coherence in dipolar-coupled spin pairs, 196 Rotational resonance, 199 4.3.3 Theory of rotational resonance, 202 Box 4.6 Effect of \hat{H}_{Λ} term on the density operator, 203 The hamiltonian in the new rotated frame, 204 The average hamiltonian, 205 Techniques for measuring heteronuclear dipolar couplings, 207 4.4.1 Spin-echo double resonance (SEDOR), 207 4.4.2 Rotational-echo double resonance (REDOR), 208 Box 4.7 Analysis of the REDOR experiment, 210 4.5 Techniques for dipolar-coupled quadrupolar-spin-½ pairs, 215 Transfer of population in double resonance (TRAPDOR), 216 4.5.1 4.5.2 Rotational-echo adiabatic-passage double-resonance (REAPDOR), 219 4.6 Techniques for measuring dipolar couplings between quadrupolar nuclei, 220 4.7 Correlation experiments, 221 4.7.1 Homonuclear correlation experiments for spin-½ systems, 221 4.7.2 Homonuclear correlation experiments for quadrupolar spin systems, 224 4.7.3 Heteronuclear correlation experiments for spin-½, 226 4.8 Spin-counting experiments, 227 4.8.1 The formation of multiple-quantum coherences, 228 4.8.2 Implementation of spin-counting experiments, 231 Notes, 232 References, 233 Quadrupole Coupling: Theory and Uses, 235 Introduction, 235 5.2 Theory, 237 5.2.1 The quadrupole hamiltonian, 237 Box 5.1 The quadrupole hamiltonian in terms of spherical tensor operators: the effect of the rotating frame and magic-angle spinning, 242 The quadrupole hamiltonian in terms of spherical tensor operators, 242 The effect of the rotating frame: first- and second-order average hamiltonians for the quadrupole interaction, 243 The energy levels under quadrupole coupling, 248 The effect of magic-angle spinning, 248 5.2.2 The effect of rf pulses, 249

The effects of quadrupolar nuclei on the spectra of spin-1/2 5.2.3 nuclei, 252 High-resolution NMR experiments for half-integer quadrupolar 5.3 nuclei, 255 5.3.1 Magic-angle spinning (MAS), 256 5.3.2 Double rotation (DOR), 259 5.3.3 Dynamic-angle spinning (DAS), 260 5.3.4 Multiple-quantum magic-angle spinning (MQMAS), 263 5.3.5 Satellite transition magic-angle spinning (STMAS), 268 5.3.6 Recording two-dimensional datasets for DAS, MQMAS and STMAS, 275 5.4 Other techniques for half-integer quadrupole nuclei, 280 5.4.1 Ouadrupole nutation, 282 Cross-polarization, 285 5.4.2 Notes, 290 References, 291 NMR Techniques for Studying Molecular Motion in Solids, 293 Introduction, 293 6.1 Powder lineshape analysis, 296 6.2 Simulating powder pattern lineshapes, 297 6.2.1 Resolving powder patterns, 305 6.2.2 Using homonuclear dipolar-coupling lineshapes - the WISE 6.2.3 experiment, 311 Relaxation time studies, 313 6.3 Exchange experiments, 316 6.4 Achieving pure absorption lineshapes in exchange spectra, 318 Interpreting two-dimensional exchange spectra, 320 6.4.2 ²H NMR, 322 6.5 6.5.1 Measuring ²H NMR spectra, 323 6.5.2 ²H lineshape simulations, 328 6.5.3 Relaxation time studies, 329 6.5.4 ²H exchange experiments, 330 Resolving ²H powder patterns, 332 6.5.5 Notes, 334 References, 335 NMR Properties of Commonly Observed Nuclei, 336 Appendix A

The General Form of a Spin Interaction Hamiltonian in Terms of

Spherical Tensors and Spherical Tensor Operators, 337

Appendix B

References, 343