## Contents

Preface xxi

Preface to the First Edition xxiii

Introduction 1

### Part 1 Nuclear Magnetism 3

#### 1 Matter 5

1.1 Atoms and Nuclei 5
1.2 Spin 5
   1.2.1 Classical angular momentum 6
   1.2.2 Quantum angular momentum 6
   1.2.3 Spin angular momentum 7
   1.2.4 Combining angular momenta 8
   1.2.5 The Pauli Principle 9
1.3 Nuclei 9
   1.3.1 The fundamental particles 9
   1.3.2 Neutrons and protons 10
   1.3.3 Isotopes 11
1.4 Nuclear Spin 12
   1.4.1 Nuclear spin states 12
   1.4.2 Nuclear Zeeman splitting 14
   1.4.3 Zero-spin nuclei 14
   1.4.4 Spin-1/2 nuclei 15
   1.4.5 Quadrupolar nuclei with integer spin 15
   1.4.6 Quadrupolar nuclei with half-integer spin 15
1.5 Atomic and Molecular Structure 15
   1.5.1 Atoms 15
   1.5.2 Molecules 16
1.6 States of Matter 17
   1.6.1 Gases 17
   1.6.2 Liquids 17
   1.6.3 Solids 19
# Contents

## Part 1 Magnetism

2 Magnetism 23

2.1 The Electromagnetic Field 23
2.2 Macroscopic Magnetism 23
2.3 Microscopic Magnetism 25
2.4 Spin Precession 26
2.5 Larmor Frequency 29
2.6 Spin–Lattice Relaxation: Nuclear Paramagnetism 30
2.7 Transverse Magnetization and Transverse Relaxation 33
2.8 NMR Signal 36
2.9 Electronic Magnetism 36

## Part 2 NMR Spectroscopy

3 NMR Spectroscopy 39

3.1 A Simple Pulse Sequence 39
3.2 A Simple Spectrum 39
3.3 Isotopomeric Spectra 42
3.4 Relative Spectral Frequencies: Case of Positive Gyromagnetic Ratio 44
3.5 Relative Spectral Frequencies: Case of Negative Gyromagnetic Ratio 46
3.6 Inhomogeneous Broadening 48
3.7 Chemical Shifts 50
3.8 $J$-Coupling Multiplets 56
3.9 Heteronuclear Decoupling 59

## Part 2 The NMR Experiment

4 The NMR Spectrometer 65

4.1 The Magnet 65
4.2 The Transmitter Section 66
  4.2.1 The synthesizer: radio-frequency phase shifts 67
  4.2.2 The pulse gate: radio-frequency pulses 68
  4.2.3 Radio-frequency amplifier 69
4.3 The Duplexer 69
4.4 The Probe 70
4.5 The Receiver Section 72
  4.5.1 Signal preamplifier 73
  4.5.2 The quadrature receiver 73
  4.5.3 Analogue–digital conversion 74
  4.5.4 Signal phase shifting 76
4.6 Overview of the Radio-Frequency Section 76
4.7 Pulsed Field Gradients 77
  4.7.1 Magnetic field gradients 78
  4.7.2 Field gradient coils 79
  4.7.3 Field gradient control 80
## 5 Fourier Transform NMR

5.1 A Single-Pulse Experiment  
5.2 Signal Averaging  
5.3 Multiple-Pulse Experiments: Phase Cycling  
5.4 Heteronuclear Experiments  
5.5 Pulsed Field Gradient Sequences  
5.6 Arrayed Experiments  
5.7 NMR Signal  
5.8 NMR Spectrum  
5.8.1 Fourier transformation  
5.8.2 Lorentzians  
5.8.3 Explanation of Fourier transformation  
5.8.4 Spectral phase shifts  
5.8.5 Frequency-dependent phase correction  
5.9 Two-Dimensional Spectroscopy  
5.9.1 Two-dimensional signal surface  
5.9.2 Two-dimensional Fourier transformation  
5.9.3 Phase twist peaks  
5.9.4 Pure absorption two-dimensional spectra  
5.10 Three-Dimensional Spectroscopy

## Part 3 Quantum Mechanics

6 Mathematical Techniques

6.1 Functions  
6.1.1 Continuous functions  
6.1.2 Normalization  
6.1.3 Orthogonal and orthonormal functions  
6.1.4 Dirac notation  
6.1.5 Vector representation of functions  
6.2 Operators  
6.2.1 Commutation  
6.2.2 Matrix representations  
6.2.3 Diagonal matrices  
6.2.4 Block diagonal matrices  
6.2.5 Inverse  
6.2.6 Adjoint  
6.2.7 Hermitian operators  
6.2.8 Unitary operators  
6.3 Eigenfunctions, Eigenvalues and Eigenvectors  
6.3.1 Eigenequations  
6.3.2 Degeneracy  
6.3.3 Eigenfunctions and eigenvalues of Hermitian operators  
6.3.4 Eigenfunctions of commuting operators: non-degenerate case  
6.3.5 Eigenfunctions of commuting operators: degenerate case  
6.3.6 Eigenfunctions of commuting operators: summary  
6.3.7 Eigenvectors
6.4 Diagonalization
   6.4.1 Diagonalization of Hermitian or unitary matrices 135

6.5 Exponential Operators
   6.5.1 Powers of operators 135
   6.5.2 Exponentials of operators 136
   6.5.3 Exponentials of unity and null operators 136
   6.5.4 Products of exponential operators 137
   6.5.5 Inverses of exponential operators 137
   6.5.6 Complex exponentials of operators 137
   6.5.7 Exponentials of small operators 137
   6.5.8 Matrix representations of exponential operators 138

6.6 Cyclic Commutation
   6.6.1 Definition of cyclic commutation 138
   6.6.2 Sandwich formula 139

7 Review of Quantum Mechanics 143

7.1 Spinless Quantum Mechanics
   7.1.1 The state of the particle 143
   7.1.2 The equation of motion 144
   7.1.3 Experimental observations 144

7.2 Energy Levels 145

7.3 Natural Units 146

7.4 Superposition States and Stationary States 147

7.5 Conservation Laws 148

7.6 Angular Momentum
   7.6.1 Angular momentum operators 149
   7.6.2 Rotation operators 149
   7.6.3 Rotation sandwiches 151
   7.6.4 Angular momentum eigenstates and eigenvalues 152
   7.6.5 The angular momentum eigenstates 154
   7.6.6 Shift operators 154
   7.6.7 Matrix representations of the angular momentum operators 156

7.7 Spin
   7.7.1 Spin angular momentum operators 157
   7.7.2 Spin rotation operators 158
   7.7.3 Spin Zeeman basis 158
   7.7.4 Trace 159

7.8 Spin-1/2
   7.8.1 Zeeman eigenstates 160
   7.8.2 Angular momentum operators 160
   7.8.3 Spin-1/2 rotation operators 160
   7.8.4 Unity operator 161
   7.8.5 Shift operators 161
   7.8.6 Projection operators 161
   7.8.7 Ket-bra notation 162

7.9 Higher Spin
   7.9.1 Spin $I = 1$ 163
   7.9.2 Spin $I = 3/2$ 164
   7.9.3 Higher spins 165
## Part 4 Nuclear Spin Interactions

### 8 Nuclear Spin Hamiltonian

8.1 Spin Hamiltonian Hypothesis 171
8.2 Electromagnetic Interactions 172
  8.2.1 Electric spin Hamiltonian 173
  8.2.2 Magnetic spin interactions 176
8.3 External and Internal Spin Interactions 177
  8.3.1 Spin interactions: summary 177
8.4 External Magnetic Fields 177
  8.4.1 Static field 179
  8.4.2 Radio-frequency field 179
  8.4.3 Gradient field 181
  8.4.4 External spin interactions: summary 181
8.5 Internal Spin Hamiltonian 182
  8.5.1 The internal spin interactions 182
  8.5.2 Simplification of the internal Hamiltonian 185
8.6 Motional Averaging 186
  8.6.1 Modes of molecular motion 186
  8.6.2 Molecular rotations 186
  8.6.3 Molecular translations 187
  8.6.4 Intramolecular and intermolecular spin interactions 189
  8.6.5 Summary of motional averaging 190

### 9 Internal Spin Interactions

9.1 Chemical Shift 195
  9.1.1 Chemical shift tensor 196
  9.1.2 Principal axes 197
  9.1.3 Principal values 198
  9.1.4 Isotropic chemical shift 198
  9.1.5 Chemical shift anisotropy (CSA) 198
  9.1.6 Chemical shift for an arbitrary molecular orientation 200
  9.1.7 Chemical shift frequency 201
  9.1.8 Chemical shift interaction in isotropic liquids 201
  9.1.9 Chemical shift interaction in anisotropic liquids 203
  9.1.10 Chemical shift interaction in solids 204
  9.1.11 Chemical shift interaction: summary 206
9.2 Electric Quadrupole Coupling 206
  9.2.1 Electric field gradient tensor 207
  9.2.2 Nuclear quadrupole Hamiltonian 208
  9.2.3 Isotropic liquids 209
  9.2.4 Anisotropic liquids 209
  9.2.5 Solids 210
  9.2.6 Quadrupole interaction: summary 210
9.3 Direct Dipole–Dipole Coupling 211
  9.3.1 Secular dipole–dipole coupling 213
  9.3.2 Dipole–dipole coupling in isotropic liquids 215
9.3.3 Dipole–dipole coupling in liquid crystals 216
9.3.4 Dipole–dipole coupling in solids 216
9.3.5 Dipole–dipole interaction: summary 217
9.4 J-Coupling 217
  9.4.1 Isotropic J-coupling 219
  9.4.2 Liquid crystals and solids 221
  9.4.3 Mechanism of the J-coupling 222
  9.4.4 J-coupling: summary 223
9.5 Spin–Rotation Interaction 223
9.6 Summary of the Spin Hamiltonian Terms 224

Part 5 Uncoupled Spins 229

10 Single Spin-1/2 231
  10.1 Zeeman Eigenstates 231
  10.2 Measurement of Angular Momentum: Quantum Indeterminacy 232
  10.3 Energy Levels 233
  10.4 Superposition States 234
     10.4.1 General spin states 234
     10.4.2 Vector notation 234
     10.4.3 Some particular states 235
     10.4.4 Phase factors 237
  10.5 Spin Precession 238
     10.5.1 Dynamics of the eigenstates 239
     10.5.2 Dynamics of the superposition states 240
  10.6 Rotating Frame 241
  10.7 Precession in the Rotating Frame 245
  10.8 Radio-frequency Pulse 247
     10.8.1 Rotating-frame Hamiltonian 247
     10.8.2 x-pulse 248
     10.8.3 Nutation 251
     10.8.4 Pulse of general phase 252
     10.8.5 Off-resonance effects 253

11 Ensemble of Spins-1/2 259
  11.1 Spin Density Operator 259
  11.2 Populations and Coherences 261
     11.2.1 Density matrix 261
     11.2.2 Box notation 261
     11.2.3 Balls and arrows 262
     11.2.4 Orders of coherence 263
     11.2.5 Relationships between populations and coherences 263
     11.2.6 Physical interpretation of the populations 264
     11.2.7 Physical interpretation of the coherences 265
  11.3 Thermal Equilibrium 266
  11.4 Rotating-Frame Density Operator 268
## Contents

11.5 Magnetization Vector 269  
11.6 Strong Radio-Frequency Pulse 270  
  11.6.1 Excitation of coherence 271  
  11.6.2 Population inversion 273  
  11.6.3 Cycle of states 274  
  11.6.4 Stimulated absorption and emission 275  
11.7 Free Precession Without Relaxation 276  
11.8 Operator Transformations 279  
  11.8.1 Pulse of phase $\phi_p = 0$ 279  
  11.8.2 Pulse of phase $\phi_p = \pi/2$ 279  
  11.8.3 Pulse of phase $\phi_p = \pi$ 279  
  11.8.4 Pulse of phase $\phi_p = 3\pi/2$ 279  
  11.8.5 Pulse of general phase $\phi_p$ 280  
  11.8.6 Free precession for an interval $\tau$ 280  
11.9 Free Evolution with Relaxation 281  
  11.9.1 Transverse relaxation 281  
  11.9.2 Longitudinal relaxation 283  
11.10 Magnetization Vector Trajectories 285  
11.11 NMR Signal and NMR Spectrum 287  
11.12 Single-Pulse Spectra 289

### 12 Experiments on Non-Interacting Spins-1/2 295

12.1 Inversion Recovery: Measurement of $T_1$ 295  
12.2 Spin Echoes: Measurement of $T_2$ 298  
  12.2.1 Homogenous and inhomogenous broadening 298  
  12.2.2 Inhomogenous broadening in the time domain 299  
  12.2.3 Spin echo pulse sequence 299  
  12.2.4 Refocusing 302  
  12.2.5 Coherence interpretation 303  
  12.2.6 Coherence transfer pathway 305  
12.3 Spin Locking: Measurement of $T_{1\rho}$ 305  
12.4 Gradient Echoes 306  
12.5 Slice Selection 307  
12.6 NMR Imaging 309

### 13 Quadrupolar Nuclei 319

13.1 Spin $I = 1$ 319  
  13.1.1 Spin-1 states 319  
  13.1.2 Spin-1 energy levels 320  
  13.1.3 Spin-1 density matrix 321  
  13.1.4 Coherence evolution 323  
  13.1.5 Observable coherences and NMR spectrum 325  
  13.1.6 Thermal equilibrium 326  
  13.1.7 Strong radio-frequency pulse 326  
  13.1.8 Excitation of coherence 328  
  13.1.9 NMR spectrum 328  
  13.1.10 Quadrupolar echo 331
Contents

13.2 Spin $I = 3/2$
  13.2.1 Spin-$3/2$ energy levels 335
  13.2.2 Populations and coherences 336
  13.2.3 NMR signal 338
  13.2.4 Single pulse spectrum 339
  13.2.5 Spin-$3/2$ spectra for small quadrupole couplings 341
  13.2.6 Second-order quadrupole couplings 342
  13.2.7 Central transition excitation 343
  13.2.8 Central transition echo 345

13.3 Spin $I = 5/2$ 345

13.4 Spins $I = 7/2$ 349

13.5 Spins $I = 9/2$ 350

Part 6 Coupled Spins 353

14 Spin-$1/2$ Pairs 355
  14.1 Coupling Regimes 355
  14.2 Zeeman Product States and Superposition States 356
  14.3 Spin-Pair Hamiltonian 357
  14.4 Pairs of Magnetically Equivalent Spins
    14.4.1 Singlets and triplets 359
    14.4.2 Energy levels 360
    14.4.3 NMR spectra 362
    14.4.4 Dipolar echo 363
  14.5 Weakly Coupled Spin Pairs
    14.5.1 Weak coupling 363
    14.5.2 AX spin systems 364
    14.5.3 Energy levels 364
    14.5.4 AX spectrum 365
    14.5.5 Heteronuclear spin pairs 366

15 Homonuclear AX System 369
  15.1 Eigenstates and Energy Levels 369
  15.2 Density Operator 370
  15.3 Rotating Frame 375
  15.4 Free Evolution
    15.4.1 Evolution of a spin pair 376
    15.4.2 Evolution of the coherences 377
  15.5 Spectrum of the AX System: Spin–Spin Splitting 378
  15.6 Product Operators
    15.6.1 Construction of product operators 381
    15.6.2 Populations and coherences 383
    15.6.3 Spin orientations 386
  15.7 Thermal Equilibrium 389
  15.8 Radio-Frequency Pulses
    15.8.1 Rotations of a single spin pair 391
    15.8.2 Rotations of the spin density operator 393
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Sections</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.8</td>
<td>Operator transformations</td>
<td>395</td>
</tr>
<tr>
<td>15.9</td>
<td>Free Evolution of the Product Operators</td>
<td>397</td>
</tr>
<tr>
<td>15.9.1</td>
<td>Chemical shift evolution</td>
<td>399</td>
</tr>
<tr>
<td>15.9.2</td>
<td>J-coupling evolution</td>
<td>400</td>
</tr>
<tr>
<td>15.9.3</td>
<td>Relaxation</td>
<td>405</td>
</tr>
<tr>
<td>15.10</td>
<td>Spin Echo Sandwich</td>
<td>405</td>
</tr>
<tr>
<td>16</td>
<td>Experiments on AX Systems</td>
<td>409</td>
</tr>
<tr>
<td>16.1</td>
<td>COSY</td>
<td>409</td>
</tr>
<tr>
<td>16.1.1</td>
<td>The assignment problem</td>
<td>409</td>
</tr>
<tr>
<td>16.1.2</td>
<td>COSY pulse sequence</td>
<td>411</td>
</tr>
<tr>
<td>16.1.3</td>
<td>Theory of COSY: coherence interpretation</td>
<td>411</td>
</tr>
<tr>
<td>16.1.4</td>
<td>Product operator interpretation</td>
<td>415</td>
</tr>
<tr>
<td>16.1.5</td>
<td>Experimental examples</td>
<td>418</td>
</tr>
<tr>
<td>16.2</td>
<td>INADEQUATE</td>
<td>418</td>
</tr>
<tr>
<td>16.2.1</td>
<td>$^{13}$C isotopomers</td>
<td>418</td>
</tr>
<tr>
<td>16.2.2</td>
<td>Pulse sequence</td>
<td>423</td>
</tr>
<tr>
<td>16.2.3</td>
<td>Theory of INADEQUATE</td>
<td>424</td>
</tr>
<tr>
<td>16.2.4</td>
<td>Coherence transfer pathways and phase cycling</td>
<td>429</td>
</tr>
<tr>
<td>16.2.5</td>
<td>Two-dimensional INADEQUATE</td>
<td>431</td>
</tr>
<tr>
<td>16.3</td>
<td>INEPT</td>
<td>436</td>
</tr>
<tr>
<td>16.3.1</td>
<td>The sensitivity of nuclear isotopes</td>
<td>436</td>
</tr>
<tr>
<td>16.3.2</td>
<td>INEPT pulse sequence</td>
<td>437</td>
</tr>
<tr>
<td>16.3.3</td>
<td>Refocused INEPT</td>
<td>440</td>
</tr>
<tr>
<td>16.4</td>
<td>Residual Dipolar Couplings</td>
<td>443</td>
</tr>
<tr>
<td>16.4.1</td>
<td>Angular information</td>
<td>443</td>
</tr>
<tr>
<td>16.4.2</td>
<td>Spin Hamiltonian</td>
<td>443</td>
</tr>
<tr>
<td>16.4.3</td>
<td>Orienting media</td>
<td>444</td>
</tr>
<tr>
<td>16.4.4</td>
<td>Doublet splittings</td>
<td>446</td>
</tr>
<tr>
<td>17</td>
<td>Many-Spin Systems</td>
<td>453</td>
</tr>
<tr>
<td>17.1</td>
<td>Molecular Spin System</td>
<td>453</td>
</tr>
<tr>
<td>17.2</td>
<td>Spin Ensemble</td>
<td>454</td>
</tr>
<tr>
<td>17.3</td>
<td>Motionally Suppressed J-Couplings</td>
<td>454</td>
</tr>
<tr>
<td>17.4</td>
<td>Chemical Equivalence</td>
<td>455</td>
</tr>
<tr>
<td>17.5</td>
<td>Magnetic Equivalence</td>
<td>458</td>
</tr>
<tr>
<td>17.6</td>
<td>Weak Coupling</td>
<td>461</td>
</tr>
<tr>
<td>17.7</td>
<td>Heteronuclear Spin Systems</td>
<td>462</td>
</tr>
<tr>
<td>17.8</td>
<td>Alphabet Notation</td>
<td>463</td>
</tr>
<tr>
<td>17.9</td>
<td>Spin Coupling Topologies</td>
<td>464</td>
</tr>
<tr>
<td>18</td>
<td>Many-Spin Dynamics</td>
<td>467</td>
</tr>
<tr>
<td>18.1</td>
<td>Spin Hamiltonian</td>
<td>467</td>
</tr>
<tr>
<td>18.2</td>
<td>Energy Eigenstates</td>
<td>468</td>
</tr>
<tr>
<td>18.3 Superposition States</td>
<td>469</td>
<td></td>
</tr>
<tr>
<td>---------------------------</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td>18.4 Spin Density Operator</td>
<td>470</td>
<td></td>
</tr>
<tr>
<td>18.5 Populations and Coherences</td>
<td>471</td>
<td></td>
</tr>
<tr>
<td>18.5.1 Coherence orders</td>
<td>471</td>
<td></td>
</tr>
<tr>
<td>18.5.2 Combination coherences and simple coherences</td>
<td>471</td>
<td></td>
</tr>
<tr>
<td>18.5.3 Coherence frequencies</td>
<td>472</td>
<td></td>
</tr>
<tr>
<td>18.5.4 Degenerate coherences</td>
<td>473</td>
<td></td>
</tr>
<tr>
<td>18.5.5 Observable coherences</td>
<td>473</td>
<td></td>
</tr>
<tr>
<td>18.6 NMR Spectra</td>
<td>475</td>
<td></td>
</tr>
<tr>
<td>18.7 Many-Spin Product Operators</td>
<td>477</td>
<td></td>
</tr>
<tr>
<td>18.7.1 Construction of product operators</td>
<td>477</td>
<td></td>
</tr>
<tr>
<td>18.7.2 Populations and coherences</td>
<td>478</td>
<td></td>
</tr>
<tr>
<td>18.7.3 Physical interpretation of product operators</td>
<td>480</td>
<td></td>
</tr>
<tr>
<td>18.8 Thermal Equilibrium</td>
<td>481</td>
<td></td>
</tr>
<tr>
<td>18.9 Radio-Frequency Pulses</td>
<td>481</td>
<td></td>
</tr>
<tr>
<td>18.10 Free Precession</td>
<td>482</td>
<td></td>
</tr>
<tr>
<td>18.10.1 Chemical shift evolution</td>
<td>482</td>
<td></td>
</tr>
<tr>
<td>18.10.2 J-coupling evolution</td>
<td>483</td>
<td></td>
</tr>
<tr>
<td>18.10.3 Relaxation</td>
<td>485</td>
<td></td>
</tr>
<tr>
<td>18.11 Spin Echo Sandwiches</td>
<td>488</td>
<td></td>
</tr>
<tr>
<td>18.12 INEPT in an I$_2$S System</td>
<td>488</td>
<td></td>
</tr>
<tr>
<td>18.13 COSY in Multiple-Spin Systems</td>
<td>491</td>
<td></td>
</tr>
<tr>
<td>18.13.1 AMX spectrum</td>
<td>492</td>
<td></td>
</tr>
<tr>
<td>18.13.2 Active and passive spins</td>
<td>493</td>
<td></td>
</tr>
<tr>
<td>18.13.3 Cross-peak multiplets</td>
<td>494</td>
<td></td>
</tr>
<tr>
<td>18.13.4 Diagonal peaks</td>
<td>496</td>
<td></td>
</tr>
<tr>
<td>18.13.5 Linear spin systems</td>
<td>497</td>
<td></td>
</tr>
<tr>
<td>18.14 TOCSY</td>
<td>497</td>
<td></td>
</tr>
<tr>
<td>18.14.1 The ambiguity of COSY spectra</td>
<td>497</td>
<td></td>
</tr>
<tr>
<td>18.14.2 TOCSY pulse sequence</td>
<td>499</td>
<td></td>
</tr>
<tr>
<td>18.14.3 Theory of TOCSY</td>
<td>499</td>
<td></td>
</tr>
</tbody>
</table>

**Part 7 Motion and Relaxation**

**19 Motion**

<table>
<thead>
<tr>
<th>19.1 Motional Processes</th>
<th>509</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.1.1 Molecular vibrations</td>
<td>509</td>
</tr>
<tr>
<td>19.1.2 Local rotations of molecular groups</td>
<td>510</td>
</tr>
<tr>
<td>19.1.3 Molecular flexibility</td>
<td>510</td>
</tr>
<tr>
<td>19.1.4 Chemical exchange</td>
<td>510</td>
</tr>
<tr>
<td>19.1.5 Molecular rotations</td>
<td>511</td>
</tr>
<tr>
<td>19.1.6 Translational motion</td>
<td>512</td>
</tr>
<tr>
<td>19.1.7 Mechanical motion</td>
<td>513</td>
</tr>
<tr>
<td>19.2 Motional Time-Scales</td>
<td>513</td>
</tr>
<tr>
<td>19.3 Motional Effects</td>
<td>514</td>
</tr>
<tr>
<td>19.4 Motional Averaging</td>
<td>515</td>
</tr>
<tr>
<td>19.5 Motional Lineshapes and Two-Site Exchange</td>
<td>516</td>
</tr>
</tbody>
</table>
20 Relaxation

20.1 Types of Relaxation 543
20.2 Relaxation Mechanisms 543
20.3 Random Field Relaxation 545
  20.3.1 Autocorrelation functions and correlation times 545
  20.3.2 Spectral density 548
  20.3.3 Normalized spectral density 549
  20.3.4 Transition probabilities 550
  20.3.5 Thermally corrected transition probabilities 551
  20.3.6 Spin–lattice relaxation 552
20.4 Dipole–Dipole Relaxation 556
  20.4.1 Rotational correlation time 556
  20.4.2 Transition probabilities 557
  20.4.3 Solomon equations 561
  20.4.4 Longitudinal relaxation 564
  20.4.5 Transverse relaxation 565
20.5 Steady-State Nuclear Overhauser Effect 566
20.6 NOESY 570
  20.6.1 NOESY pulse sequence 570
  20.6.2 NOESY signal 570
  20.6.3 NOESY spectra 573
  20.6.4 NOESY and chemical exchange 575
  20.6.5 Molecular structure determination 576
20.7 ROESY 577
  20.7.1 Transverse cross-relaxation 577
  20.7.2 Spin locking 578
  20.7.3 Transverse Solomon equations 578
  20.7.4 ROESY spectra 580
  20.7.5 ROESY and chemical exchange 582
  20.7.6 ROESY and TOCSY 583
20.8 Cross-Correlated Relaxation 584
  20.8.1 Cross-correlation 584
  20.8.2 Cross-correlation of spin interactions 585
  20.8.3 Dipole–dipole cross-correlation and angular estimations 586
  20.8.4 TROSY 590
## Appendix A: Supplementary Material

A.1 Euler Angles and Frame Transformations 599
   A.1.1 Definition of the Euler angles 599
   A.1.2 Euler rotations: first scheme 599
   A.1.3 Euler rotations: second scheme 600
   A.1.4 Euler rotation matrices 601
   A.1.5 Reference-frame orientations 601
   A.1.6 Consecutive reference-frame transformations 602
   A.1.7 Passive rotations 602
   A.1.8 Tensor transformations 603
   A.1.9 Intermediate reference frames 604
A.2 Rotations and Cyclic Commutation 604
A.3 Rotation Sandwiches 605
A.4 Spin-1/2 Rotation Operators 606
A.5 Quadrature Detection and Spin Coherences 608
A.6 Secular Approximation 611
A.7 Quadrupolar Interaction 614
   A.7.1 Full quadrupolar interaction 614
   A.7.2 First-order quadrupolar interaction 614
   A.7.3 Higher-order quadrupolar interactions 615
A.8 Strong Coupling 615
   A.8.1 Strongly-coupled Spin-1/2 pairs 615
   A.8.2 General strongly coupled systems 620
A.9 J-Couplings and Magnetic Equivalence 621
A.10 Spin Echo Sandwiches 623
   A.10.1 Short-duration limit 625
   A.10.2 Long-duration limit 625
   A.10.3 Two spin echo sequences 626
   A.10.4 Heteronuclear spin echo sequences 627
A.11 Phase Cycling 629
   A.11.1 Coherence transfer pathways 629
   A.11.2 Coherence transfer amplitudes 630
   A.11.3 Coherence orders and phase shifts 631
   A.11.4 The pathway phase 632
   A.11.5 A sum theorem 633
   A.11.6 Pathway selection I 634
   A.11.7 Pathway selection II 635
   A.11.8 Pathway selection III 637
   A.11.9 Selection of a single pathway I 638
   A.11.10 Selection of a single pathway II 639
   A.11.11 Dual pathway selection 640
   A.11.12 Internal phases I 641
   A.11.13 Internal phases II 642
   A.11.14 Nested phase cycles I 644
   A.11.15 Nested phase cycles II 645
   A.11.16 Different ways of constructing phase cycles 648
## Contents

A.12 Coherence Selection by Pulsed Field Gradients 649
   A.12.1 Field gradient dephasing 649
   A.12.2 Pathway phase 651
   A.12.3 Coherence transfer echoes 652
   A.12.4 Pathway selection 652
   A.12.5 Heteronuclear coherence transfer echoes 652
A.13 Bloch Equations 653
A.14 Chemical Exchange 654
   A.14.1 The incoherent dynamics 655
   A.14.2 The coherent dynamics 655
   A.14.3 The spectrum 656
   A.14.4 Longitudinal magnetization exchange 658
A.15 Solomon Equations 660
A.16 Cross-Relaxation Dynamics 662

**Appendix B: Symbols and Abbreviations** 665

**Answers to the Exercises** 681

**Index** 693