

| | |
|-------------------------------------------------|--------------|
| 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 |

| | | |
|----------|----------------------------------------------------|-----------|
| 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 |

| | | |
|----------|--------------------------------------------------------------------|-----------|
| 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 | <i>J</i> -Coupling Multiplets | 56 |
| 3.9 | Heteronuclear Decoupling | 59 |

Part 2 The NMR Experiment **63**

| | | |
|----------|-----------------------------------------------|-----------|
| 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 | 85 |
| 5.1 | A Single-Pulse Experiment | 85 |
| 5.2 | Signal Averaging | 86 |
| 5.3 | Multiple-Pulse Experiments: Phase Cycling | 89 |
| 5.4 | Heteronuclear Experiments | 90 |
| 5.5 | Pulsed Field Gradient Sequences | 91 |
| 5.6 | Arrayed Experiments | 91 |
| 5.7 | NMR Signal | 93 |
| 5.8 | NMR Spectrum | 96 |
| 5.8.1 | Fourier transformation | 96 |
| 5.8.2 | Lorentzians | 96 |
| 5.8.3 | Explanation of Fourier transformation | 100 |
| 5.8.4 | Spectral phase shifts | 102 |
| 5.8.5 | Frequency-dependent phase correction | 103 |
| 5.9 | Two-Dimensional Spectroscopy | 105 |
| 5.9.1 | Two-dimensional signal surface | 105 |
| 5.9.2 | Two-dimensional Fourier transformation | 105 |
| 5.9.3 | Phase twist peaks | 107 |
| 5.9.4 | Pure absorption two-dimensional spectra | 109 |
| 5.10 | Three-Dimensional Spectroscopy | 114 |

Part 3 Quantum Mechanics **119**

| | | |
|----------|------------------------------------------------------------|------------|
| 6 | Mathematical Techniques | 121 |
| 6.1 | Functions | 121 |
| 6.1.1 | Continuous functions | 121 |
| 6.1.2 | Normalization | 122 |
| 6.1.3 | Orthogonal and orthonormal functions | 122 |
| 6.1.4 | Dirac notation | 122 |
| 6.1.5 | Vector representation of functions | 123 |
| 6.2 | Operators | 125 |
| 6.2.1 | Commutation | 126 |
| 6.2.2 | Matrix representations | 126 |
| 6.2.3 | Diagonal matrices | 129 |
| 6.2.4 | Block diagonal matrices | 129 |
| 6.2.5 | Inverse | 130 |
| 6.2.6 | Adjoint | 130 |
| 6.2.7 | Hermitian operators | 131 |
| 6.2.8 | Unitary operators | 131 |
| 6.3 | Eigenfunctions, Eigenvalues and Eigenvectors | 131 |
| 6.3.1 | Eigenequations | 131 |
| 6.3.2 | Degeneracy | 131 |
| 6.3.3 | Eigenfunctions and eigenvalues of Hermitian operators | 132 |
| 6.3.4 | Eigenfunctions of commuting operators: non-degenerate case | 132 |
| 6.3.5 | Eigenfunctions of commuting operators: degenerate case | 132 |
| 6.3.6 | Eigenfunctions of commuting operators: summary | 133 |
| 6.3.7 | Eigenvectors | 134 |

| | | |
|-------|--------------------------------------------------|-----|
| 6.4 | Diagonalization | 134 |
| 6.4.1 | Diagonalization of Hermitian or unitary matrices | 135 |
| 6.5 | Exponential Operators | 135 |
| 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 | 138 |
| 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 | 143 |
| 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 | 148 |
| 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 | 157 |
| 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 | 160 |
| 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 | 162 |
| 7.9.1 | Spin $I = 1$ | 163 |
| 7.9.2 | Spin $I = 3/2$ | 164 |
| 7.9.3 | Higher spins | 165 |

8 Nuclear Spin Hamiltonian 171

| | | |
|-------|-----------------------------------------------------|-----|
| 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 195

| | | |
|--------|-------------------------------------------------------|-----|
| 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 | <i>J</i> -Coupling | 217 |
| 9.4.1 | Isotropic <i>J</i> -coupling | 219 |
| 9.4.2 | Liquid crystals and solids | 221 |
| 9.4.3 | Mechanism of the <i>J</i> -coupling | 222 |
| 9.4.4 | <i>J</i> -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 | <i>x</i> -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 |

| | | |
|--------|----------------------------------------|-----|
| 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 ϕ_p | 280 |
| 11.8.6 | Free precession for an interval τ | 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 |

| | | |
|--------|-------------------------------------------------|-----|
| 13.2 | Spin $I = 3/2$ | 334 |
| 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 | 359 |
| 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 | 363 |
| 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 | 376 |
| 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 | 381 |
| 15.6.1 | Construction of product operators | 382 |
| 15.6.2 | Populations and coherences | 383 |
| 15.6.3 | Spin orientations | 386 |
| 15.7 | Thermal Equilibrium | 389 |
| 15.8 | Radio-Frequency Pulses | 391 |
| 15.8.1 | Rotations of a single spin pair | 392 |
| 15.8.2 | Rotations of the spin density operator | 393 |

| | | |
|--------|-----------------------------------------|-----|
| 15.8.3 | Operator transformations | 395 |
| 15.9 | Free Evolution of the Product Operators | 397 |
| 15.9.1 | Chemical shift evolution | 399 |
| 15.9.2 | <i>J</i> -coupling evolution | 400 |
| 15.9.3 | Relaxation | 405 |
| 15.10 | Spin Echo Sandwich | 405 |

16 Experiments on AX Systems 409

| | | |
|--------|-----------------------------------------------|-----|
| 16.1 | COSY | 409 |
| 16.1.1 | The assignment problem | 409 |
| 16.1.2 | COSY pulse sequence | 411 |
| 16.1.3 | Theory of COSY: coherence interpretation | 411 |
| 16.1.4 | Product operator interpretation | 415 |
| 16.1.5 | Experimental examples | 418 |
| 16.2 | INADEQUATE | 418 |
| 16.2.1 | ¹³ C isotopomers | 418 |
| 16.2.2 | Pulse sequence | 423 |
| 16.2.3 | Theory of INADEQUATE | 424 |
| 16.2.4 | Coherence transfer pathways and phase cycling | 429 |
| 16.2.5 | Two-dimensional INADEQUATE | 431 |
| 16.3 | INEPT | 436 |
| 16.3.1 | The sensitivity of nuclear isotopes | 436 |
| 16.3.2 | INEPT pulse sequence | 437 |
| 16.3.3 | Refocused INEPT | 440 |
| 16.4 | Residual Dipolar Couplings | 443 |
| 16.4.1 | Angular information | 443 |
| 16.4.2 | Spin Hamiltonian | 443 |
| 16.4.3 | Orienting media | 444 |
| 16.4.4 | Doublet splittings | 446 |

17 Many-Spin Systems 453

| | | |
|------|-------------------------------------------|-----|
| 17.1 | Molecular Spin System | 453 |
| 17.2 | Spin Ensemble | 454 |
| 17.3 | Motionally Suppressed <i>J</i> -Couplings | 454 |
| 17.4 | Chemical Equivalence | 455 |
| 17.5 | Magnetic Equivalence | 458 |
| 17.6 | Weak Coupling | 461 |
| 17.7 | Heteronuclear Spin Systems | 462 |
| 17.8 | Alphabet Notation | 463 |
| 17.9 | Spin Coupling Topologies | 464 |

18 Many-Spin Dynamics 467

| | | |
|------|--------------------|-----|
| 18.1 | Spin Hamiltonian | 467 |
| 18.2 | Energy Eigenstates | 468 |

| | | |
|---------|----------------------------------------------|-----|
| 18.3 | Superposition States | 469 |
| 18.4 | Spin Density Operator | 470 |
| 18.5 | Populations and Coherences | 471 |
| 18.5.1 | Coherence orders | 471 |
| 18.5.2 | Combination coherences and simple coherences | 471 |
| 18.5.3 | Coherence frequencies | 472 |
| 18.5.4 | Degenerate coherences | 473 |
| 18.5.5 | Observable coherences | 473 |
| 18.6 | NMR Spectra | 475 |
| 18.7 | Many-Spin Product Operators | 477 |
| 18.7.1 | Construction of product operators | 477 |
| 18.7.2 | Populations and coherences | 478 |
| 18.7.3 | Physical interpretation of product operators | 480 |
| 18.8 | Thermal Equilibrium | 481 |
| 18.9 | Radio-Frequency Pulses | 481 |
| 18.10 | Free Precession | 482 |
| 18.10.1 | Chemical shift evolution | 482 |
| 18.10.2 | <i>J</i> -coupling evolution | 483 |
| 18.10.3 | Relaxation | 485 |
| 18.11 | Spin Echo Sandwiches | 485 |
| 18.12 | INEPT in an I_2S System | 488 |
| 18.13 | COSY in Multiple-Spin Systems | 491 |
| 18.13.1 | AMX spectrum | 492 |
| 18.13.2 | Active and passive spins | 493 |
| 18.13.3 | Cross-peak multiplets | 494 |
| 18.13.4 | Diagonal peaks | 496 |
| 18.13.5 | Linear spin systems | 497 |
| 18.14 | TOCSY | 497 |
| 18.14.1 | The ambiguity of COSY spectra | 497 |
| 18.14.2 | TOCSY pulse sequence | 499 |
| 18.14.3 | Theory of TOCSY | 499 |

Part 7 Motion and Relaxation

507

19 Motion

509

| | | |
|--------|-------------------------------------------|-----|
| 19.1 | Motional Processes | 509 |
| 19.1.1 | Molecular vibrations | 509 |
| 19.1.2 | Local rotations of molecular groups | 510 |
| 19.1.3 | Molecular flexibility | 510 |
| 19.1.4 | Chemical exchange | 510 |
| 19.1.5 | Molecular rotations | 511 |
| 19.1.6 | Translational motion | 512 |
| 19.1.7 | Mechanical motion | 513 |
| 19.2 | Motional Time-Scales | 513 |
| 19.3 | Motional Effects | 514 |
| 19.4 | Motional Averaging | 515 |
| 19.5 | Motional Lineshapes and Two-Site Exchange | 516 |

| | | |
|--------|----------------------------------------------------|-----|
| 19.5.1 | Slow intermediate exchange and motional broadening | 518 |
| 19.5.2 | Fast intermediate exchange and motional narrowing | 520 |
| 19.5.3 | Averaging of J -splittings | 523 |
| 19.5.4 | Asymmetric two-site exchange | 524 |
| 19.5.5 | Knight shift | 525 |
| 19.5.6 | Paramagnetic shifts | 527 |
| 19.6 | Sample Spinning | 527 |
| 19.7 | Longitudinal Magnetization Exchange | 529 |
| 19.7.1 | Two-dimensional exchange spectroscopy | 529 |
| 19.7.2 | Theory | 532 |
| 19.7.3 | Motional regimes | 539 |
| 19.8 | Diffusion | 539 |

20

Relaxation

543

| | | |
|--------|---------------------------------------------------------|-----|
| 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**599**

| | | |
|---------|----------------------------------------------|-----|
| 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 | <i>J</i> -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 |

| | | |
|--------|-----------------------------------------------|-----|
| 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**