

- **Preface** (p. xix)
- **Acknowledgments** (p. xxiii)
- **1 Basic Principles of Paramagnetic Resonance** (p. 1)
- **1.1 Introduction** (p. 1)
- **1.2 Historical Perspective** (p. 3)
- **1.6 Quantization of Angular Momenta** (p. 13)
- **1.3 A Simple EPR Spectrometer** (p. 4)
- **1.4 Scope of the EPR Technique** (p. 7)
- **1.5 Energy Flow in Paramagnetic Systems** (p. 11)
- **1.7 Relation Between Magnetic Moments and Angular Momenta** (p. 14)
- **1.8 Magnetic Field Quantities and Units** (p. 15)
- **1.9 Bulk Magnetic Properties** (p. 18)
- **1.10 Magnetic Energies and States** (p. 20)
- **1.11 Interaction of Magnetic Dipoles with Electromagnetic Radiation** (p. 21)
- **1.12 Characteristics of the Spin Systems** (p. 23)
- **1.12.1 The g Factor** (p. 23)
- **1.12.2 Characteristics of Dipolar Interactions** (p. 27)
- **1.13 Parallel-Field EPR** (p. 28)
- **1.14 Time-Resolved EPR** (p. 29)
- **1.15 Computerology** (p. 29)
- **1.16 EPR Imaging** (p. 30)
- **References** (p. 30)
- **Notes** (p. 32)
- **Further Reading** (p. 34)
- **Problems** (p. 35)
- **2 Magnetic Interaction Between Particles** (p. 36)
- **2.1 Introduction** (p. 36)
- **2.2 Theoretical Considerations of the Hyperfine Interaction** (p. 38)
- **2.3 Angular-Momentum and Energy Operators** (p. 40)
- **2.3.1 Spin Operators and Hamiltonians** (p. 41)
- **2.3.2 Electronic and Nuclear Zeeman Interactions** (p. 43)
- **2.3.3 Spin Hamiltonian Including Isotropic Hyperfine Interaction** (p. 46)
- **2.4 Energy Levels of a System with One Unpaired Electron and One Nucleus with  $I = 1/2$**  (p. 47)
- **2.5 Energy Levels of a System with  $S = 1/2$  and  $I = 1$**  (p. 50)
- **2.6 Signs of Isotropic Hyperfine Coupling Constants** (p. 53)
- **2.7 Dipolar Interactions Between Electrons** (p. 54)
- **References** (p. 54)
- **Notes** (p. 55)
- **Further Reading** (p. 56)
- **Problems** (p. 56)
- **3 Isotropic Hyperfine Effects in EPR Spectra** (p. 58)
- **3.1 Introduction** (p. 58)
- **3.2 Hyperfine Splitting from Protons** (p. 59)
- **3.2.1 Single Set of Equivalent Protons** (p. 59)
- **3.2.2 Multiple Sets of Equivalent Protons** (p. 62)

- **3.3 Hyperfine Splittings from Other Nuclei with  $I = 1/2$**  (p. 68)
- **3.4 Hyperfine Splittings from Nuclei with  $I > 1/2$**  (p. 69)
- **3.5 Useful Rules for the Interpretation of EPR Spectra** (p. 74)
- **3.6 Higher-Order Contributions to Hyperfine Splittings** (p. 75)
- **3.7 Deviations from the Simple Multinomial Scheme** (p. 77)
- **3.8 Other Problems Encountered in EPR Spectra of Free Radicals** (p. 77)
- **3.9 Some Interesting [Pi]-Type Free Radicals** (p. 78)
- **References** (p. 79)
- **Notes** (p. 79)
- **Further Reading** (p. 80)
- **Problems** (p. 80)
- **4 Zeeman Energy (g) Anisotropy** (p. 85)
- **4.1 Introduction** (p. 85)
- **4.2 Systems with High Local Symmetry** (p. 88)
- **4.3 Systems with Rhombic Local Symmetry** (p. 90)
- **4.4 Construction of the g Matrix** (p. 92)
- **4.5 Symmetry-Related Sites** (p. 96)
- **4.6 EPR Line Intensities** (p. 97)
- **4.7 Statistically Randomly Oriented Solids** (p. 99)
- **4.8 Spin-Orbit Coupling and Quantum-Mechanical Modeling of g** (p. 105)
- **4.9 Comparative Overview** (p. 110)
- **References** (p. 111)
- **Notes** (p. 112)
- **Further Reading** (p. 114)
- **Problems** (p. 114)
- **5 Hyperfine (A) Anisotropy** (p. 118)
- **5.1 Introduction** (p. 118)
- **5.2 Origin of the Anisotropic Part of the Hyperfine Interaction** (p. 120)
- **5.3 Determination and Interpretation of the Hyperfine Matrix** (p. 122)
- **5.3.1 The Anisotropic Breit-Rabi Case** (p. 122)
- **5.3.2 The Case of Dominant Electron Zeeman Energy** (p. 124)
- **5.3.2.1 General Case** (p. 126)
- **5.3.2.2 The Case of B [approximately] B<sub>hf</sub>** (p. 128)
- **5.3.2.3 The Case of B [greater than] B<sub>hf</sub>** (p. 141)
- **5.4 Combined g and Hyperfine Anisotropy** (p. 143)
- **5.5 Multiple Hyperfine Matrices** (p. 144)
- **5.6 Systems With  $I > 1/2$**  (p. 144)
- **5.7 Hyperfine Powder Lineshapes** (p. 145)
- **References** (p. 150)
- **Notes** (p. 151)
- **Further Reading** (p. 152)
- **Problems** (p. 152)
- **6 Systems With More Than One Unpaired Electron** (p. 158)
- **6.1 Introduction** (p. 158)
- **6.2 Spin Hamiltonian for Two Interacting Electrons** (p. 159)
- **6.2.1 Electron-Exchange Interaction** (p. 160)

- **6.2.2 Electron-Electron Dipole Interaction** (p. 162)
- **6.3 Systems with  $S = 1$  (Triplet States)** (p. 164)
  - **6.3.1 Spin Energies and Eigenfunctions** (p. 165)
  - **6.3.2 ' $\Delta M_s = \pm 2$ ' Transitions** (p. 172)
  - **6.3.3 Randomly Oriented Triplet Systems** (p. 173)
  - **6.3.4 Photo-excited Triplet-State Entities** (p. 177)
  - **6.3.5 Thermally Accessible Triplet Entities** (p. 182)
  - **6.3.6 Ground-State Triplet Entities** (p. 185)
    - **6.3.6.1 Carbenes and Nitrenes** (p. 185)
    - **6.3.6.2 Dianions of Symmetric Aromatic Hydrocarbons** (p. 187)
    - **6.3.6.3 Inorganic Triplet Species** (p. 188)
- **6.4 Interacting Radical Pairs** (p. 189)
- **6.5 Biradicals** (p. 190)
- **6.6 Systems with  $S > 1$**  (p. 195)
- **6.7 High-Spin and High-Field Energy Terms** (p. 196)
- **6.8 The Spin Hamiltonian: A Summing up** (p. 197)
- **6.9 Modeling the Spin-Hamiltonian Parameters** (p. 199)
- **References** (p. 200)
- **Notes** (p. 203)
- **Further Reading** (p. 204)
- **Problems** (p. 205)
- **7 Paramagnetic Species in the Gas Phase** (p. 208)
  - **7.1 Introduction** (p. 208)
  - **7.2 Monatomic Gas-Phase Species** (p. 209)
  - **7.3 Diatomic Gas-Phase Species** (p. 211)
  - **7.4 Triatomic and Polyatomic Gas-Phase Molecules** (p. 217)
  - **7.5 Laser Electron Paramagnetic Resonance** (p. 219)
  - **7.6 Other Techniques** (p. 219)
  - **Notes** (p. 222)
  - **7.7 Reaction Kinetics** (p. 220)
  - **7.8 Astro-EPR** (p. 220)
  - **References** (p. 221)
  - **Further Reading** (p. 222)
  - **Problems** (p. 223)
- **8 Transition-Group Ions** (p. 225)
  - **8.1 Introduction** (p. 225)
  - **8.2 The Electronic Ground States of d-Electron Species** (p. 227)
  - **8.3 The EPR Parameters of d-Electron Species** (p. 232)
  - **8.4 Tanabe-Sugano Diagrams and Energy-Level Crossings** (p. 240)
  - **8.5 Covalency Effects** (p. 243)
  - **8.6 A Ferroelectric System** (p. 244)
  - **8.7 Some f-Electron Systems** (p. 245)
  - **References** (p. 246)
  - **Notes** (p. 248)
  - **Further Reading** (p. 249)
  - **Problems** (p. 249)

- **9 The Interpretation of EPR Parameters** (p. 253)
- **9.1 Introduction** (p. 253)
- **9.2  $\pi$ -Type Organic Radicals** (p. 254)
- **9.2.1 Anions and Cations of Benzene and Some of its Derivatives** (p. 259)
- **9.2.2 Anions and Cations of Polyacenes** (p. 262)
- **9.2.3 g Factors of  $\pi$  Radicals** (p. 262)
- **9.2.4 Origin of Proton Hyperfine Splittings** (p. 263)
- **9.2.5 Sign of the Proton Hyperfine Splitting Constant** (p. 265)
- **9.5 Inorganic Radicals** (p. 276)
- **9.2.6 Methyl Proton Hyperfine Splittings and Hyperconjugation** (p. 268)
- **9.2.7 Hyperfine Splitting from Nuclei Other than Protons** (p. 270)
- **9.2.8 One-Dimensional Chain Paramagnets** (p. 272)
- **9.3  $\sigma$ -Type Organic Radicals** (p. 274)
- **9.4 Triplet States and Biradicals** (p. 275)
- **9.6 Electrically Conducting Systems** (p. 281)
- **9.6.1 Metals** (p. 281)
- **9.6.2 Metals Dissolved in Ammonia and Amine Solutions** (p. 282)
- **9.6.3 Semiconductors** (p. 283)
- **9.6.4 Graphitic Compounds** (p. 285)
- **9.7 Techniques for Structural Estimates from EPR Data** (p. 285)
- **9.7.1 The Newman Superposition Model** (p. 285)
- **9.7.2 The Pseudo-cube Method** (p. 286)
- **9.7.3 Distances from Parameter D** (p. 286)
- **9.7.4 Eatons' Interspin-Distance Formula** (p. 287)
- **9.7.5 Summary** (p. 287)
- **References** (p. 287)
- **Notes** (p. 291)
- **Further Reading** (p. 291)
- **Problems** (p. 292)
- **Appendix 9A Huckel Molecular-Orbital Calculations** (p. 294)
- **HMO References** (p. 298)
- **HMO Problems** (p. 299)
- **10 Relaxation Times, Linewidths and Spin Kinetic Phenomena** (p. 301)
- **10.1 Introduction** (p. 301)
- **10.2 Spin Relaxation: General Aspects** (p. 302)
- **10.2.1 Spin Temperature and Boltzmann Distribution** (p. 302)
- **10.2.2 Spin Dynamics** (p. 303)
- **10.2.3 Mechanisms for  $T_1$**  (p. 305)
- **10.3 Spin Relaxation: Bloch Model** (p. 308)
- **10.3.1 Magnetization in a Static Magnetic Field** (p. 309)
- **10.3.2 Addition of an Oscillating Magnetic Field** (p. 310)
- **10.3.3 Rotating Frame** (p. 311)
- **10.3.4 Steady-State Solutions of Bloch Equations** (p. 312)
- **10.4 Linewidths** (p. 316)
- **10.4.1 Homogeneous Broadening** (p. 316)
- **10.4.2 Inhomogeneous Broadening** (p. 316)

- **10.5 Dynamic Lineshape Effects** (p. 317)
- **10.5.1 Generalized Bloch Equations** (p. 318)
- **10.5.2 Other Theoretical Models** (p. 322)
- **10.5.3.3 Proton Transfer** (p. 326)
- **10.5.3 Examples of Line-Broadening Mechanisms** (p. 322)
- **10.5.3.1 Electron-Spin Exchange** (p. 323)
- **10.5.3.2 Electron Transfer** (p. 324)
- **10.5.3.4 Fluxional Motion** (p. 326)
- **10.5.4 Linewidth Variation: Dynamic Hyperfine Contributions** (p. 327)
- **10.5.4.1 Single Nucleus** (p. 328)
- **10.5.4.2 Multiple Nuclei** (p. 329)
- **10.5.5 Molecular Tumbling Effects** (p. 333)
- **10.5.5.1 Dipolar Effects** (p. 335)
- **10.5.5.2 Spin-Rotation Interaction** (p. 339)
- **10.5.6 General Example** (p. 340)
- **10.6 Longitudinal Detection** (p. 342)
- **10.7 Saturation-Transfer EPR** (p. 343)
- **10.8 Time Dependence of the EPR Signal Amplitude** (p. 343)
- **10.8.1 Concentration Changes** (p. 343)
- **10.8.2 Chemically Induced Dynamic Electron Polarization** (p. 345)
- **10.9 Dynamic Nuclear Polarization** (p. 347)
- **10.10 Bio-Oxygen** (p. 347)
- **10.11 Summary** (p. 347)
- **References** (p. 348)
- **Notes** (p. 351)
- **Further Reading** (p. 352)
- **Problems** (p. 353)
- **11 Noncontinuous Excitation of Spins** (p. 357)
- **11.1 Introduction** (p. 357)
- **11.2 The Idealized  $B_{1\text{[subscript 1]}}$  Switch-on** (p. 359)
- **11.3 The Single  $B_{1\text{[subscript 1]}}$  Pulse** (p. 362)
- **11.4 Fourier-Transform EPR and FID Analysis** (p. 364)
- **11.5 Multiple Pulses** (p. 368)
- **11.6 Electron Spin-Echo Envelope Modulation** (p. 369)
- **11.7 Advanced Techniques** (p. 375)
- **11.8 Spin Coherence and Correlation** (p. 375)
- **References** (p. 378)
- **Notes** (p. 380)
- **Further Reading** (p. 381)
- **Problems** (p. 382)
- **12 Double-Resonance Techniques** (p. 385)
- **12.1 Introduction** (p. 385)
- **12.2 A Continuous-Wave ENDOR Experiment** (p. 386)
- **12.5.1 The F Centers in the Alkali Halides** (p. 397)
- **12.3 Energy Levels and ENDOR Transitions** (p. 388)
- **12.4 Relaxation Processes in Steady-State ENDOR<sup>5</sup>** (p. 392)

- **12.5 CW ENDOR: Single-Crystal Examples** (p. 397)
- **12.5.2 Metal-Ion Tetrphenylporphyrins** (p. 401)
- **12.6 CW ENDOR in Powders and Non-Crystalline Solids** (p. 401)
- **12.7 CW ENDOR in Liquid Solutions** (p. 402)
- **12.11 Fluorescence-Detected Magnetic Resonance** (p. 407)
- **12.8 Pulse Double-Resonance Experiments** (p. 404)
- **12.9 Electron-Electron Double Resonance (ELDOR)** (p. 404)
- **12.10 Optically Detected Magnetic Resonance** (p. 406)
- **References** (p. 408)
- **Notes** (p. 410)
- **Further Reading** (p. 411)
- **Problems** (p. 411)
- **13 Other Topics** (p. 414)
- **13.1 Apologia** (p. 414)
- **13.2 Biological Systems** (p. 414)
- **13.3 Clusters** (p. 415)
- **13.4 Charcoal, Coal, Graphite and Soot** (p. 415)
- **13.5 Colloids** (p. 415)
- **13.6 Electrochemical EPR** (p. 415)
- **13.7 EPR Imaging** (p. 416)
- **13.9 Glasses** (p. 417)
- **13.10 Geologic/Mineralogic Systems and Selected Gems** (p. 417)
- **13.10.1 Amethyst** (p. 417)
- **13.10.2 Beryl and Chrysoberyl** (p. 417)
- **13.10.3 Diamond** (p. 417)
- **13.10.4 Emerald** (p. 418)
- **13.10.5 Opal** (p. 418)
- **13.10.6 Rock Crystal ([alpha]-Quartz)** (p. 418)
- **13.10.7 Ruby** (p. 418)
- **13.10.8 Sapphire** (p. 418)
- **13.10.9 Topaz** (p. 418)
- **13.10.10 Tourmaline** (p. 419)
- **13.10.11 Turquoise** (p. 419)
- **13.10.12 Zircon** (p. 419)
- **13.11 Liquid Crystals** (p. 419)
- **13.12 "Point" Defects** (p. 419)
- **13.12.1 Insulators** (p. 419)
- **13.12.1.1 Alkali Halides** (p. 419)
- **13.12.1.2 Oxides** (p. 419)
- **13.12.2 Semiconductors** (p. 420)
- **13.13 Polymers** (p. 420)
- **13.14 Radiation Dosage and Dating** (p. 420)
- **13.15 Spin Labels** (p. 421)
- **13.16 Spin Traps** (p. 421)
- **A.1 Complex Numbers** (p. 422)
- **13.8 Ferromagnets, Antiferromagnets and Superparamagnets** (p. 416)

- **13.17 Trapped Atoms and Molecules** (p. 421)
- **Appendix A Mathematical Operations** (p. 422)
- **A.2 Operator Algebra** (p. 423)
- **A.2.1 Properties of Operators** (p. 423)
- **A.2.2 Eigenvalues and Eigenfunctions** (p. 426)
- **A.3 Determinants** (p. 428)
- **A.4 Vectors: Scalar, Vector, and Outer Products** (p. 430)
- **A.5 Matrices** (p. 432)
- **A.5.1 Addition and Subtraction of Matrices** (p. 434)
- **A.5.2 Multiplication of Matrices** (p. 434)
- **A.5.3 Special Matrices and Matrix Properties** (p. 438)
- **A.5.4 Dirac Notation for Eigenfunctions and Matrix Elements** (p. 438)
- **A.5.5 Diagonalization of Matrices** (p. 440)
- **A.5.6 Matrix Invariants** (p. 446)
- **A.6 Perturbation Theory** (p. 446)
- **A.7 Dirac Delta Function** (p. 449)
- **A.8 Group Theory** (p. 450)
- **References** (p. 450)
- **Notes** (p. 451)
- **Further Reading** (p. 451)
- **B.2 Angular-Momentum Operators** (p. 457)
- **Problems** (p. 451)
- **Appendix B Quantum Mechanics of Angular Momentum** (p. 455)
- **B.1 Introduction** (p. 455)
- **B.3 Commutation Relations for General Angular-Momentum Operators** (p. 458)
- **B.4 Eigenvalues of  $J^2$  and  $J_z$**  (p. 459)
- **B.5 Superposition of States** (p. 464)
- **B.6 Angular-Momentum Matrices** (p. 464)
- **B.7 Addition of Angular Momenta** (p. 466)
- **B.8 Notation for Atomic and Molecular States** (p. 472)
- **B.9 Angular Momentum and Degeneracy of States** (p. 473)
- **B.10 Time Dependence** (p. 475)
- **B.11 Precession** (p. 475)
- **B.12 Magnetic Flux Quantization** (p. 477)
- **B.13 Summary** (p. 478)
- **References** (p. 479)
- **Notes** (p. 480)
- **Further Reading** (p. 480)
- **Problems** (p. 481)
- **Notes for Problem B.12** (p. 483)
- **Appendix C The Hydrogen Atom and Selected Radicals  $RH_n$**  (p. 484)
- **C.1 Hydrogen Atom** (p. 484)
- **C.1.1 Spin Hamiltonian** (p. 484)
- **C.1.2 The Spin Eigenkets and Energy Matrix** (p. 485)
- **C.1.3 Exact Solution for the Energy Eigenvalues** (p. 487)
- **C.1.4 Energy Eigenstates and Allowed Transitions** (p. 489)

- **C.1.5 Resonant Frequencies in Constant Magnetic Field** (p. 493)
- **C.1.6 Resonant Magnetic Fields at Constant Excitation Frequency** (p. 493)
- **C.1.7 Calculation of Spin Energy Levels by Perturbation Theory** (p. 495)
- **C.2 RH Radicals** (p. 497)
- **C.3 RH<sub>2</sub> Radicals** (p. 498)
- **C.3.1 Spin Hamiltonian and Energy Levels** (p. 499)
- **C.3.2 EPR Transitions** (p. 499)
- **References** (p. 501)
- **Notes** (p. 501)
- **Further Reading** (p. 502)
- **Problems** (p. 502)
- **Appendix D Photons** (p. 505)
- **D.1 Introduction** (p. 505)
- **D.2 The Physical Aspects of Photons** (p. 505)
- **Appendix E Instrumentation and Technical Performance** (p. 512)
- **D.3 Magnetic-Resonance Aspects** (p. 508)
- **References** (p. 510)
- **Notes** (p. 510)
- **E.1 Instrumental: Background** (p. 512)
- **E.2 CW EPR Spectrometers** (p. 515)
- **E.2.1 Magnet System** (p. 516)
- **E.2.2 Radiation Source** (p. 517)
- **E.2.3 Microwave Transmission** (p. 518)
- **E.2.4 Coupling of the Source to the Resonator** (p. 519)
- **E.2.5 Resonator System** (p. 520)
- **E.2.6 Field Modulation System** (p. 525)
- **E.2.7 Coupling of the Resonator to the Detector** (p. 525)
- **E.2.8 Detection System** (p. 526)
- **E.3 Pulsed EPR Spectrometers** (p. 529)
- **E.4 Computer Interfacing with EPR Spectrometers** (p. 530)
- **E.5 Techniques for Temperature Variation and Control** (p. 531)
- **E.6 Techniques for Pressure Variation** (p. 532)
- **References** (p. 533)
- **Notes** (p. 535)
- **Further Reading** (p. 535)
- **Problems** (p. 536)
- **Appendix F Experimental Considerations** (p. 537)
- **F.1 Techniques for Generation of Paramagnetic Species** (p. 537)
- **F.2 Lineshapes and Intensities** (p. 539)
- **F.2.1 Lineshapes** (p. 539)
- **F.2.2 Signal Intensities and Spin-Concentration Standards** (p. 545)
- **F.3 Sensitivity and Resolution** (p. 548)
- **F.3.1 Optimum Sensitivity** (p. 548)
- **F.3.2 Sample Temperature** (p. 550)
- **F.3.3 Microwave Frequency** (p. 550)
- **F.3.4 Q Factor of the Resonator** (p. 551)



- **F.3.5 Microwave Power Level and Measurements of  $B_{1}$**  (p. 553)
- **F.3.6 Modulation Amplitude** (p. 554)
- **F.3.7 Modulation Frequency** (p. 557)
- **F.4 Measurements** (p. 557)
- **F.4.1 g Factors and Hyperfine Splittings** (p. 557)
- **F.4.2 Relaxation Time** (p. 559)
- **F.4.3 Spin-Number Determinations** (p. 561)
- **References** (p. 561)
- **Notes** (p. 564)
- **Further Reading** (p. 565)
- **Problems** (p. 565)
- **Appendix G EPR-Related Books and Selected Chapters** (p. 567)
- **Appendix H Fundamental Constants, Conversion Factors, and Key Data** (p. 577)
- **Appendix I Miscellaneous Guidelines** (p. 588)
- **I.1 Notation for Symbols** (p. 588)
- **I.2 Glossary of Symbols** (p. 590)
- **I.3 Abbreviations** (p. 600)
- **I.4 Exponent Nomenclature** (p. 602)
- **I.5 Journal Reference Style** (p. 602)
- **Author Index** (p. 603)
- **Subject Index** (p. 624)