Contents

Preface  XXIX
List of Contributors  XXXI

1 Introduction  1
Sushil K. Misra
1.1 Introduction to EPR  1
1.1.1 Continuous-Wave EPR  1
1.1.2 Pulsed EPR  2
1.1.3 EPR Imaging  2
1.2 Historical Background of EPR  2
1.2.1 Literature Pertinent to the Early History of EPR  3
1.3 Typical X-Band, Low-, and High-Frequency Spectrometers  3
1.3.1 EPR Spectrometer Design  3
1.3.2 X-Band Spectrometer  4
1.3.2.1 Source of Microwave Radiation  4
1.3.2.2 Transmission of Microwaves  6
1.3.2.3 The Cavity (Resonator) System  6
1.3.2.4 Magnetic Field System  7
1.3.2.5 Modulation and Detection System  8
1.3.3 EPR Line Shapes and Determination of Signal Intensity  9
1.3.4 Low-Frequency Spectrometers  9
1.3.5 High-Frequency Spectrometers  10
1.3.5.1 Sources of Radiation  10
1.3.5.2 Transmission of Submillimeter Waves  12
1.3.5.3 Resonators and Sensitivity  13
1.3.5.4 Magnetic Field  14
1.3.5.5 Detectors  14
1.3.6 Pertinent Literature  15
1.4 Applications of EPR  15
1.4.1 Pertinent Literature  20
Multifrequency Aspects of EPR

Sushil K. Misra

2.1 Frequency Bands

2.2 X-Band EPR

2.3 EPR at Higher Frequencies (HF)

2.3.1 Advantages

2.3.2 Disadvantages

2.4 Low-Frequency EPR

2.4.1 Advantages

2.4.2 Disadvantages

2.5 Multifrequency EPR

2.5.1 Advantages of Using Multifrequency EPR

2.5.2 Limitations of Using Multifrequency EPR

2.5.3 Size of Resonant Cavity at Different Frequencies

2.5.4 Signal-to-Noise Ratios at Different Frequencies

2.5.5 Multifrequency Aspects of Using Home-Built versus Commercial Spectrometers

2.5.6 Multifrequency Aspects of Sample-Related Problems

Basic Theory of Electron Paramagnetic Resonance

Sushil K. Misra

3.1 Introduction

3.2 Crystal-Field Theory

3.2.1 Introduction to CFT

3.2.2 Free Atoms and Ions

3.2.3 The Crystal-Field Description of Transition Group Ions in Crystals

3.2.3.1 p-Orbitals

3.2.3.2 d-Orbitals

3.2.4 Crystal Field Potential

3.2.5 Point Charge Model

3.2.5.1 Potentials for Cubic and Lower Symmetry

3.2.6 Equivalent Operators and the Wigner–Eckart Theorem

3.2.7 Properties of d-Electrons in Crystal Fields

3.2.7.1 Ions with Several d-Electrons: Strong- and Weak-Field Cases

3.2.7.2 Energies and Wave-Functions for d-Electrons

3.2.7.3 Crystal-Field Parameters for d-Electrons

3.2.7.4 Crystal-Field Splittings for 3d^1 and 3d^9 Configurations
3.2.7.5 The Ground State and its Relationship to EPR: Quenching of Orbital Angular Momentum and Calculation of g-Factors 78
3.2.8 The Rare-Earth Ions 80
3.2.8.1 Crystal Fields for Rare-Earth Ions: Dominant Spin–Orbit Coupling 81
3.2.9 Irreducible Representations for CF Energy Levels 81
3.2.10 Critique of Crystal-Field Theory 82
3.2.11 Kramers’ Theorem 82
3.3 Superposition Model (SPM) 83
3.4 Molecular Orbital (MO) Approach 85
3.4.1 Linear Combination of Atomic Orbitals (LCAO) 85
3.4.2 Extended Hückel Molecular Orbital Theory (EHMO) 88
3.4.3 Ligand Field Theory: The Angular Overlap Model (AOM) 88
3.5 The Jahn–Teller (JT) Effect 92
3.5.1 Theory of the JT Effect 95
3.5.1.1 General Theory of the JT Effect 96
3.5.2 Perturbation within the Vibronic Ground State 98
3.5.3 Three-State Model 100
3.5.4 Transition from Dynamic to Static JT Effect 101
3.6 The Spin Hamiltonian 102
3.6.1 The Abragam and Pryce Spin Hamiltonian for the Iron Group 102
3.6.1.1 Incorporation of Covalency 105
3.6.2 Zero-Field Splitting (ZFS) 105
3.6.2.1 Cubic Zero-Field Splitting (S > 3/2) 106
3.6.3 The Phenomenological Spin Hamiltonian 106
3.6.3.1 Triclinic Symmetry 107
3.6.3.2 Monoclinic Symmetry (C_{2h}, C_{2}, C_{2v}) 108
3.6.3.3 Orthorhombic Symmetry (D_{2h}, D_{2}, D_{2v}) 108
3.6.3.4 Tetragonal (D_{4h}, D_{4}, C_{4v}, D_{2h}, C_{4h}, S_{4}, and C_{4}) 108
3.6.3.5 Cubic (O_{h}, O, T_{d}, T_{h}, and T) and Spherical Symmetry 108
3.6.3.6 Additional Spin-Hamiltonian Terms with Higher Powers of Components of S 108
3.6.4 The Generalized Spin Hamiltonian 110
3.6.5 The Effective Spin Hamiltonian for EPR 110
3.7 Concluding Remarks 111
Acknowledgments 111
Pertinent Literature 111
References 111

Part One Experimental 115

4 Spectrometers 117
4.1 Zero-Field EPR 117
Sushil K. Misra
4.1.1 Introduction 117
4.1.2 Preliminary Theory of ZFR 118
4.1.3 The ZFR Spectrometer 119
4.1.3.1 Examples of ZFR Spectra 119
4.1.4 Advantages of Using Resonant Systems 121
4.1.5 Examples of ZFR 121
4.1.5.1 The Case of the Mn$^{2+}$ Ion 122
4.1.6 Concluding Remarks 125

References 128

4.2 Low-Frequency CW-EPR Spectrometers: 10 MHz to 100 GHz 128

Harvey A. Buckmaster

4.2.1 Introduction 128
4.2.2 CW-EPR Spectrometer Configurations 132
4.2.3 Theoretical Sensitivity 146
4.2.4 EPR Lineshapes and Modulation Broadening 148
4.2.5 Microwave Power Sources 149
4.2.6 Reflex Klystrons 151
4.2.7 Solid-State Devices 151
4.2.8 Frequency Synthesizers 153
4.2.9 Microwave CW-EPR Sample Cavity Designs 153
4.2.10 Transmission Cavities 156
4.2.11 Reflection Cavities 157
4.2.12 Re-Entrant Cavities 159
4.2.13 Loop–Gap Cavities 160
4.2.14 Other Resonant Structures 163
4.2.15 Microwave Detectors or Demodulators 164
4.2.15.1 Point Contact Diodes 164
4.2.15.2 Schottky Barrier Diodes 165
4.2.15.3 Backward Diodes 165
4.2.15.4 Bolometers 165
4.2.16 Electromagnets 166
4.2.17 Zero-Field CW-EPR 167
4.2.18 Support Instrumentation 168
4.2.19 Concluding Remarks 168
4.2.20 Pertinent Literature 169

References 169

Appendix 4.2.I 171
Appendix 4.2.II 173
Appendix 4.2.III 174

4.3 High-Frequency EPR Spectrometers 175

Edward Reijerse

4.3.1 Introduction 175
4.3.2 High-Frequency EPR Spectrometer Configurations 176
4.3.3 Sensitivity Considerations 182
4.3.3.1 Cavity and Sample Holder  183
4.3.3.2 Reflection Cavity with Square-Law Detector  184
4.3.3.3 Reflection Cavity with Linear Detector  184
4.3.3.4 Spectrometer Bridge and Detector  185
4.3.4 Conclusions and Future Perspectives  188

Pertinent Literature  188
References  188

4.4 Pulsed Techniques in EPR  190
Sankaran Subramanian and Murali C. Krishna

4.4.1 Introduction  190
4.4.2 Components of a Pulsed EPR Spectrometer  193
4.4.2.1 Kα-Band (26.5–40 GHz) Pulsed EPR Spectrometer  194
4.4.2.2 Radiofrequency Pulsed EPR Spectrometers Operating at 300, 500, and 750 MHz  197
4.4.3 Resonators  199
4.4.4 Pulsed Excitation and Relaxation  202
4.4.5 Fourier Transform in Magnetic Resonance  202
4.4.6 Simple Pulsed EPR Experiments  203
4.4.6.1 Inversion Recovery and Hahn Echo Pulse Sequences, T1 and T2  204
4.4.7 Pulsed ENDOR, ESEEM, and HYSCORE  208
4.4.7.1 Nuclear Modulation Effects Leading to ENDOR and ESEEM  209
4.4.7.2 Mims and Davis Pulsed ENDOR Sequences  211
4.4.8 Electron Spin Echo Envelope Modulation (ESEEM) and Hyperfine Sublevel Correlation Spectroscopy (HYSCORE)  214
4.4.9 Electron–Electron Double Resonance (ELDOR), Double Electron–Electron Resonance (DEER), or Pulsed ELDOR (PELDOR)  218
4.4.10 Double-Quantum EPR  220
4.4.11 Concluding Remarks  222

Pertinent Literature  224
References  225

5 Multifrequency EPR: Experimental Considerations  229

5.1 Multiarm EPR Spectroscopy at Multiple Microwave Frequencies: Multiquantum (MQ) EPR, MQ-ELDOR, Saturation Recovery (SR) EPR, and SR-ELDOR  229
James S. Hyde, Robert A. Strangeway, and Theodore G. Camenisch

5.1.1 Introduction  229
5.1.2 Review of Frequency-Translation Techniques  231
5.1.3 Review of Multiarm Bridges  233
5.1.4 Multiarm Bridges at Higher Millimeter-Wave Frequencies  236
5.1.5 Resonator Considerations for Multiarm Experiments  238
5.1.6 Reference Arm and Receiver Design Considerations for Multiarm Experiments  239
5.1.7 Discussion  241

Pertinent Literature  243
5.2 Resonators for Multifrequency EPR of Spin Labels 244
James S. Hyde, Jason W. Sidabras, Richard R. Mett
5.2.1 Introduction 244
5.2.2 Methods 247
5.2.2.1 Computer-Based Simulations 247
5.2.2.2 Fabrication and Testing 251
5.2.3 Aqueous Samples 252
5.2.3.1 The Complex Dielectric Constant as a Function of Frequency and Temperature 252
5.2.3.2 Dielectric Loss Types and Parallel and Perpendicular E-Field Geometries 253
5.2.3.3 Results in Commercial Resonators at X-Band Using Extruded Sample Tubes 255
5.2.3.4 Multichannel Design 256
5.2.4 Uniform Field Cavities and Loop–Gap Resonators 258
5.2.4.1 Intrinsic Uniformity 258
5.2.4.2 Uniform Field Cavities 258
5.2.4.3 Uniformity in Two Dimensions 258
5.2.4.4 Loop–Gap Resonators 259
5.2.5 Coupling 261
5.2.5.1 Coupling at Low Frequencies 262
5.2.5.2 Coupling at High Frequencies 262
5.2.6 Field Modulation Penetration 263
5.2.7 Sample Access Stacks 265
5.2.8 Conclusions 268
Pertinent Literature 269
Acknowledgments 269
References 269
5.3 Multifrequency EPR Sensitivity 270
George A. Rinard, Richard W. Quine, Sandra S. Eaton, and Gareth R. Eaton
5.3.1 Introduction 270
5.3.1.1 Nomenclature 271
5.3.2 Frequency Dependence of Sensitivity for an Ideal Spectrometer, at the Thermal Noise Limit 272
5.3.2.1 General Expression for SNR 272
5.3.2.2 Explanation of Table 5.3.2 275
5.3.2.3 On Beyond the Predictions of Table 5.3.2 276
5.3.2.4 Dependence of SNR on g-Anisotropy 277
5.3.2.5 Source Noise 277
5.3.3 Experimental Validation of Predicted Dependence of Sensitivity on Frequency 279
5.3.3.1 CW Spectrometers at Frequencies <10 GHz 279
5.3.3.2 Pulsed EPR Spectrometers in the Frequency Range 250 MHz to 9.5 GHz  279
5.3.3.3 Summary of Experimental Validation of SNR of CW and Pulsed Spectrometers at Frequencies of <10 GHz  280
5.3.4 Reference Samples for SNR: Weak Pitch  281
5.3.5 Performance of High-Frequency (≥94 GHz)/High-Field EPR Spectrometers  282
5.3.5.1 CW Spectrometers  282
5.3.5.2 Pulsed EPR Spectrometers  282
5.3.6 Reported Sensitivities of CW and Pulsed Spectrometers at Various Frequencies  285
5.3.6.1 Further Details on CW EPR Sensitivity  286
5.3.7 Sensitivity Aspects Beyond the Minimum Detectable Number of Spins: Frequency Dependence of Pulse and CW Measurements Related to Distances Between Spins  288
5.3.7.1 Electron–Electron Coupling  288
5.3.7.2 Electron–Nuclear Coupling  289
5.3.7.3 Summary  289
5.3.8 Limitations of Sensitivity Considerations  289
5.3.8.1 CW Spectrometers  289
5.3.8.2 Resonators  290
5.3.8.3 Samples  290
5.3.8.4 Pulse Spectrometers  290
5.3.9 Conclusions  290
Acknowledgments  291
Pertinent Literature  291
References  292

Part Two  Theoretical  295

6  First Principles Approach to Spin-Hamiltonian Parameters  297
Frank Neese
6.1 Introduction  297
6.2 The Spin Hamiltonian  298
6.3 Electronic Structure Theory of Spin-Hamiltonian Parameters  300
6.3.1 Electronic Structure Methods  300
6.3.2 Additional Terms in the Hamiltonian  305
6.3.3 Sum-Over States Theory of Spin Hamiltonian Parameters  307
6.3.4 Linear Response Theory  310
6.3.5 Expression for Spin-Hamiltonian Parameters for Self-Consistent Field Methods  314
6.3.6 Practical Aspects  320
6.3.6.1 Choice of Molecular Model  320
6.3.6.2 Choice of Geometry  320
Contents

6.3.6.3 Choice of Theoretical Method 321
6.3.6.4 Choice of Basis Set 322
6.3.6.5 Summary and Recommendations 323
6.4 Concluding Remarks 323
Acknowledgments 324
Pertinent Literature 325
References 325

7 Spin Hamiltonians and Site Symmetries for Transition Ions 327
Sushil K. Misra
7.1 Introduction 327
7.2 Spin Hamiltonians 328
7.3 Spin-Hamiltonian Terms for Various Site Symmetries 332
7.4 Transition Ions 333
7.4.1 Introduction to Transition-Metal Ions 333
7.4.2 First-Transition Series Ions (3d \(n\), Iron-Group Ions) 333
7.4.3 Second and Third Transition Series (The 4d, Palladium and 5d, Platinum Groups) 345
7.4.4 Rare-Earth Ions 347
7.4.4.1 Odd Number of 4f Electrons 350
7.4.4.2 Even Number of 4f Electrons 350
7.4.5 Actinide Ions (5f \(n\)) 354
7.4.5.1 5f\(^1\) Configuration 354
7.4.5.2 5f\(^2\) Configuration 356
7.4.5.3 5f\(^3\) Configuration (\(1\Omega_{1/2}; U^{+\nu}, Np^{4+}\)) 357
7.4.6 S-State Ions 358
7.4.6.1 Introduction 358
7.4.6.2 Spin Hamiltonian 358
7.4.6.3 Theoretical Considerations 359
7.5 Concluding Remarks 363
Acknowledgments 363
Pertinent Literature 363
References 363
Appendix 7.1 Spin Operators and Their Matrix Elements 365
Appendix 7.1I Descent of Symmetry 381
Appendix 7.1II Site Symmetries of Host Crystals 382

8 Evaluation of Spin-Hamiltonian Parameters from Multifrequency EPR Data 385
Sushil K. Misra
8.1 Introduction 385
8.2 Perturbation Approach 386
8.2.1 Spin Hamiltonian 387
8.2.1.1 \(S = 7/2\) 390
8.2.1.2 \(S = 5/2\) (Fe\(^{3+}\)) 391
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.3.4 Resonance Eigenpairs</td>
<td>424</td>
</tr>
<tr>
<td>9.3.5 Integrals</td>
<td>425</td>
</tr>
<tr>
<td>9.3.6 $(\theta, \phi)$ Grid</td>
<td>426</td>
</tr>
<tr>
<td>9.3.7 Steps Required in Simulation of Powder Spectrum</td>
<td>426</td>
</tr>
<tr>
<td>9.3.7.1 Calculation of First-Derivative EPR Spectrum</td>
<td>428</td>
</tr>
<tr>
<td>9.3.8 Illustrative Example</td>
<td>429</td>
</tr>
<tr>
<td>9.3.9 Additional remarks</td>
<td>429</td>
</tr>
<tr>
<td>9.4 Evaluation of Spin-Hamiltonian (SH) Parameters and the Linewidth from a Polycrystalline EPR Spectrum</td>
<td>429</td>
</tr>
<tr>
<td>9.4.1 Estimation of Spin-Hamiltonian Parameters from a Polycrystalline Spectrum</td>
<td>430</td>
</tr>
<tr>
<td>9.4.1.1 Estimation of D and E Parameters for the Mn(^{2+}) Ion from Forbidden Hyperfine Doublet Separations in Polycrystalline Samples in the Central Sextet</td>
<td>430</td>
</tr>
<tr>
<td>9.4.1.2 Rigorous Evaluation of SH Parameters from a Polycrystalline Spectrum by Using Matrix Diagonalization and Least-Squares Fitting</td>
<td>432</td>
</tr>
<tr>
<td>9.4.1.3 Evaluation of SH Parameters and Linewidths for the Case of Two Magnetically Inequivalent Species</td>
<td>436</td>
</tr>
<tr>
<td>9.4.1.4 Illustrative Example</td>
<td>436</td>
</tr>
<tr>
<td>9.4.1.5 General Remarks</td>
<td>437</td>
</tr>
<tr>
<td>9.5 Simulation of EPR Spectra in Disordered Materials: Application to Glassy Materials</td>
<td>437</td>
</tr>
<tr>
<td>9.5.1 Introduction</td>
<td>437</td>
</tr>
<tr>
<td>9.5.2 Computer Simulation of EPR Spectra in Glasses</td>
<td>437</td>
</tr>
<tr>
<td>9.5.3 Computer-Simulated Spectra and Comparison with Experiment</td>
<td>440</td>
</tr>
<tr>
<td>9.5.4 Shape of EPR Spectra in Glasses: Effect of SH Parameters</td>
<td>442</td>
</tr>
<tr>
<td>9.5.4.1 Distribution of the Fine-Structure Parameters D and E</td>
<td>442</td>
</tr>
<tr>
<td>9.5.4.2 Sharp Features in Spectra</td>
<td>447</td>
</tr>
<tr>
<td>9.5.4.3 Broad Resonances in Spectra</td>
<td>448</td>
</tr>
<tr>
<td>9.6 Simulation of EPR Spectra in Disordered Random Network Materials</td>
<td>448</td>
</tr>
<tr>
<td>9.6.1 Introduction</td>
<td>448</td>
</tr>
<tr>
<td>9.6.2 CW-EPR Spectrum for Random Distribution of SH Parameters at Various Sites in Glasses</td>
<td>449</td>
</tr>
<tr>
<td>9.6.2.1 Calculation of Eigenvectors $</td>
<td>i\rangle$ and $</td>
</tr>
<tr>
<td>9.6.3 Limitations of the Original Implementation and its Assumptions</td>
<td>450</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>451</td>
</tr>
<tr>
<td>Pertinent Literature</td>
<td>451</td>
</tr>
<tr>
<td>References</td>
<td>451</td>
</tr>
<tr>
<td>Appendix 9.1 The Eigenfield Equation</td>
<td>453</td>
</tr>
</tbody>
</table>

10 Relaxation of Paramagnetic Spins

Sushil K. Misra

10.1 Introduction 455
10.2 Equilibrium Magnetization of a Paramagnetic Spin System 457
10.3 Relaxation Phenomena: Spin–Lattice and Spin–Spin Relaxation Times 458
10.3.1 Bloch’s Equations 459
10.4 Rotating Frame 459
10.5 Experimental Techniques to Measure Relaxation Times 460
10.5.1 CW-EPR Techniques (Bertini, Martini, and Luchinat, 1994) 461
10.5.1.1 CW Saturation 461
10.5.2 Longitudinally Detected Paramagnetic Resonance (LODEPR) to Measure Short Relaxation times (10^{-8} s) (Giordano et al., 1981) 463
10.5.3 Amplitude Modulation Technique to Measure Very Short Relaxation Times (10^{-8} – 10^{-9} s) (Misra, 2005) 463
10.5.4 Pulsed EPR Techniques to Measure Relaxation Times 463
10.5.5 Long Pulse Saturation Recovery Using CW Detection (Huisjen and Hyde, 1974; Percival and Hyde, 1975; Eaton and Eaton, 2000) 464
10.5.6 Inversion Recovery (Eaton and Eaton, 2000) 464
10.5.7 Electron Spin Echo (ESE) Technique (Schweiger and Jeschke, 2001) 464
10.5.8 Long-Pulse Saturation with Spin-Echo Detection 465
10.5.9 Picket-Fence Excitation (Eaton and Eaton, 2000) 465
10.5.10 Echo Repetition Rate (Eaton and Eaton, 2000) 465
10.5.11 Three-Pulse-Stimulated Echo (Eaton and Eaton, 2000) 466
10.5.12 Longitudinally Detected Pulsed EPR (LODPEPR) (Schweiger, 1991; Schweiger and Ernst, 1988) 466
10.5.13 Other Pulse Techniques 466
10.5.14 Measurements of Relaxation Time by Line-Shape Analysis: Linewidth and Spin–Spin Relaxation Time 466
10.5.15 Temperature-Dependent Contribution to EPR Linewidth (Poole and Farach, 1971) 467
10.5.16 Non-EPR Techniques to Measure Relaxation Times 467
10.6 Relaxation Mechanisms 468
10.6.1 Spin-Lattice Relaxation in Diluted Ionic Solids in the Crystalline State 468
10.6.1.1 General Background 468
10.6.1.2 The Direct Process 469
10.6.1.3 The Orbach Process (Orbach and Stapleton, 1972; Orbach, 1961a, 1961c) 471
10.6.1.4 Two-Phonon Raman Process 471
10.6.1.5 SLR due to Exchange Interaction 473
10.6.2 Relaxation in Amorphous Systems 474
10.6.2.1 Relaxation via TLS Centers 475
10.6.2.2 SLR Effected by Electron–Nuclear Dipolar Coupling to a TLS Center 477
10.6.2.3 SLR due to Fermi-Contact Hyperfine Interaction with a TLS Center 478
10.6.2.4 Temperature Dependence of Relaxation Rate in Amorphous Materials due to Exchange Interaction 478
10.6.2.5 Relaxation for the Case of Strong Cross-Relaxation and Weak Spin-Lattice Relaxation of Single Ions in Amorphous Materials (Al’tshuler, 1956) 478
10.6.3 Relaxation in Diluted Liquid Solutions 479
10.6.4 Effect of Intramolecular Dynamics of Molecular Species on Relaxation 483
10.6.4.1 Dephasing by Methyl Groups in Solvent or Surroundings 483
10.6.4.2 Shape of the Echo-Decay Curve 484
10.6.4.3 Averaging of Electron-Nuclear Couplings due to Rotation of Methyl Groups 484
10.6.4.4 Effect of a Rapidly Relaxing Partner on Electron–Electron Spin–Spin Coupling 484
10.6.4.5 Librational Motion 484
10.6.4.6 Molecular Tumbling 484
10.6.4.7 Biomolecules 485
10.6.4.8 Macromolecules 485
10.6.5 Relaxation among Different Paramagnetic Centers in Concentrated Solution 485
10.6.6 Spin-Fracton Relaxation 485
10.6.6.1 One-Fracton Emission 486
10.6.6.2 Two-Fracton Inelastic Scattering (Localized Electronic State) (Alexander, Entin-Wohlman, and Orbach, 1985a) 487
10.6.7 Frequency/Field Dependence of Paramagnetic Relaxation 489

Pertinent literature 490
Acknowledgments 491
References 491
Appendix 10.1 Early History of Paramagnetic Spin-Lattice Relaxation 494

11 Molecular Motions 497
Sushil K. Misra and Jack H. Freed
11.1 Introduction 497
11.2 Historical Background 498
11.3 High-Field Multifrequency CW-EPR Experiments to Unravel Molecular Motion 500
11.3.1 Determination of the Axes of Motion from High-Field, High-Frequency (HFHF) EPR Spectra: Orientational Resolution 503
11.3.2 Observation of Motion as a Function of Frequency 504
11.3.3 Virtues of Multifrequency EPR in Studying Molecular Motion 504
11.3.4 Stochastic Liouville Equation (SLE) to Describe Slow-Motional EPR Spectra 505
11.3.4.1 Calculation of Slow-Motion Spectrum 506
11.3.4.2 MOMD and SRLS Models 511
11.4     Pulsed EPR Study of Molecular Motion  514
11.4.1  $T_2$-Type Field-Swept 2D ESE  515
11.4.2  Magnetization Transfer by Field-Swept 2-D-ESE  515
11.4.3  Stepped-Field Spin-Echo ELDOR  517
11.4.4  2-D Fourier Transform EPR  517
11.4.4.1 Lineshapes of the Auto and Cross-Peaks: Homogeneous (HB) and Inhomogeneous Broadening (IB)  518
11.4.5  MOMD and SRLS Models and 2-D-ELDOR  520
11.4.6  Extension of 2-D-ELDOR to Higher Frequencies  522
11.5  Simulation of Multifrequency EPR Spectra Using More Atomistic Detail Including Molecular Dynamics and Stochastic Trajectories  522
11.5.1  Augmented SLE  522
11.5.2  MD Simulations Using Trajectories  524
11.5.3  Use of Dynamic Trajectories to Simulate Multifrequency EPR Spectra  525
11.5.4  Numerical Integrators  526
11.5.4.1 Integration of the Quantal Spin Dynamics  526
11.5.4.2 Generation of Stochastic Trajectories for Rotational Diffusion  531
11.5.4.3 Testing the Integrators: Generation of Trajectories for Typical Stochastic Models of Spin-Label Dynamics  535
11.6  Concluding Remarks  541
Acknowledgments  541
Pertinent Literature  541
References  542

12  Distance Measurements: Continuous-Wave (CW)- and Pulsed Dipolar EPR  545
Sushil K. Misra and Jack H. Freed

12.1  Introduction  545
12.2  The Dipolar Interaction and Distance Measurements  547
12.2.1  Unlike Spins  547
12.2.2  Like Spins  548
12.2.3  Intermediate Case  548
12.3  CW EPR Method to Measure Distances  548
12.4  Pulsed Dipolar EPR Spectroscopy (PDS)  549
12.5  Double Electron–Electron Resonance (DEER)  550
12.5.1  Orientation-Selection Considerations in DEER  552
12.5.2  Three-Pulse DEER  553
12.5.3  Four-Pulse DEER  555
12.5.4  Merits and Limitations of DEER as Compared to CW-EPR and FRET  557
12.6  Six-Pulse DQC  559
12.6.1  Theoretical Background and Computation of Six-Pulse DQC Signal  562
12.6.2  Illustrative Examples  566
<table>
<thead>
<tr>
<th>Part</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Contents</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>586</td>
</tr>
<tr>
<td>12</td>
<td>12.6.3 Conclusions and Future Prospects of Six-Pulse DQC Echo Signal Simulation</td>
<td>566</td>
</tr>
<tr>
<td></td>
<td>12.7 Sensitivity Considerations: Multifrequency Aspects</td>
<td>570</td>
</tr>
<tr>
<td></td>
<td>12.7.1 Frequency Dependence of Sensitivity of PDS</td>
<td>572</td>
</tr>
<tr>
<td></td>
<td>12.8 Distance Distributions: Tikhonov Regularization</td>
<td>573</td>
</tr>
<tr>
<td></td>
<td>12.9 Additional Technical Aspects of DEER and DQC</td>
<td>574</td>
</tr>
<tr>
<td></td>
<td>12.10 Concluding Remarks</td>
<td>576</td>
</tr>
<tr>
<td></td>
<td>Acknowledgments</td>
<td>576</td>
</tr>
<tr>
<td></td>
<td>Pertinent Literature</td>
<td>576</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>576</td>
</tr>
<tr>
<td></td>
<td>Appendix 12.I Density-Matrix Derivation of Echo Signal for Three-Pulse DEER</td>
<td>578</td>
</tr>
<tr>
<td></td>
<td>Appendix 12.II Density-Matrix Derivation of the Echo Signal for Four-Pulse DEER</td>
<td>582</td>
</tr>
<tr>
<td></td>
<td>Appendix 12.III Spin Hamiltonian for Coupled Nitroxides Used in Six-Pulse DQC Calculation</td>
<td>584</td>
</tr>
<tr>
<td></td>
<td>Appendix 12.IV Algorithm to Calculate Six-Pulse DQC Signal</td>
<td>586</td>
</tr>
<tr>
<td></td>
<td>Appendix 12.V Approximate Analytic Expressions for 1-D DQC Signal</td>
<td>587</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Part Three Applications</strong></td>
<td>589</td>
</tr>
<tr>
<td>13</td>
<td>Determination of Large Zero-Field Splitting</td>
<td>591</td>
</tr>
<tr>
<td></td>
<td>By Sushil K. Misra</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13.1 Introduction</td>
<td>591</td>
</tr>
<tr>
<td></td>
<td>13.2 ZFS of Kramers and Non-Kramers Ions in Different Environments</td>
<td>592</td>
</tr>
<tr>
<td></td>
<td>13.3 Concluding Remarks</td>
<td>596</td>
</tr>
<tr>
<td></td>
<td>Acknowledgments</td>
<td>597</td>
</tr>
<tr>
<td></td>
<td>Pertinent Literature</td>
<td>597</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>597</td>
</tr>
<tr>
<td>14</td>
<td>Determination of Non-Coincident Anisotropic $\tilde{g}$, $\tilde{A}$, $\tilde{D}$, and $\tilde{P}$ Tensors: Low-Symmetry Considerations</td>
<td>599</td>
</tr>
<tr>
<td></td>
<td>By Sushil K. Misra</td>
<td></td>
</tr>
<tr>
<td></td>
<td>14.1 Introduction</td>
<td>599</td>
</tr>
<tr>
<td></td>
<td>14.2 Spin Hamiltonian</td>
<td>599</td>
</tr>
<tr>
<td></td>
<td>14.3 Eigenvalues</td>
<td>601</td>
</tr>
<tr>
<td></td>
<td>14.3.1 Perturbation Approach</td>
<td>601</td>
</tr>
<tr>
<td></td>
<td>14.3.1.1 Complexities Associated with the Use of Second-Order-Perturbed Eigenvalues in the Application of Least-Squares Fitting (LSF) Procedure</td>
<td>604</td>
</tr>
<tr>
<td></td>
<td>14.3.2 Exact Matrix Diagonalization</td>
<td>605</td>
</tr>
<tr>
<td></td>
<td>14.4 Evaluation of SHPs by the LSF Technique</td>
<td>606</td>
</tr>
<tr>
<td></td>
<td>14.4.1 First-Order Perturbation</td>
<td>606</td>
</tr>
</tbody>
</table>
14.4.2 Second-Order Perturbation  607
14.4.3 Use of Special Coordinate Axes  609
14.4.3.1 “Allowed” Line Positions  609
14.4.3.2 “Forbidden” Line Positions  611
14.4.4 Use of Arbitrary Coordinate Axes  612
14.4.5 Simultaneous LSF Fitting of Both the “Allowed” and “Forbidden” Line Positions  613
14.5 Numerical Evaluation of the Derivatives Required in the LSF Procedure  614
14.6 General Remarks  616
Acknowledgments  618
Pertinent Literature  618
References  618

15 Biological Systems  619
Boris Dzikovski
15.1 Introduction  619
15.2 VHF EPR as the g-Resolved EPR Spectroscopy  620
15.2.1 Spectral Resolution of g-Factor Differences  620
15.2.2 Precise Determination of the g-Tensor Principal Values  621
15.2.3 Resolution of g-Factors of Different Paramagnetic Centers  622
15.3 Effect of Polarity of the Environment on the g-Factor  623
15.3.1 Examples  623
15.3.1.1 Derivatives of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)  623
15.3.1.2 Spin-Labeled Phospholipid Membranes: 1,2-Dipalmitoyl-sn-Glycero-3-Phosphocholine (DPPC) and 1-Palmitoyl-2-Oleoyl-sn-Glycero-3-Phosphocholine (POPC)  625
15.3.1.3 Bacteriorhodopsin (BR)  625
15.3.1.4 Azurin  626
15.3.1.5 Tyrosyl and Tryptophan Radicals  626
15.3.1.6 Flavin  626
15.3.1.7 Biliverdin Radical  627
15.3.2 Polarity Measurements Outside of Rigid Limit Conditions  627
15.4 Improvement in Orientational Resolution for Spin Labels  628
15.5 Simulation of EPR Spectra at Various Frequencies: Simple Limiting Cases  630
15.6 Macroscopically Aligned Phospholipid Membranes  631
15.6.1 A “Shunt” Fabry–Pérot Resonator. The study of DMPC and DMPS (1,2-dimyristoyl-sn-glycero-3-phospho-L-serine) Membranes with 3-doxyl-5(-cholestane) (CSL) Spin Label  632
15.6.2 Microtome Technique on Isopotential Spin-Dry Ultracentrifugation (ISDU)-Aligned Membranes  633
15.6.3 Other Membrane-Alignment Techniques  635
15.7 Metalloproteins  636
15.7.1 Fe$^{3+}$ Systems  638
16 Copper Coordination Environments 647
William E. Antholine, Brian Bennett, and Graeme R. Hanson
16.1 Introduction 647
16.2 Multifrequency EPR Toolkit 649
16.2.1 \( g \)-Value Resolution and Orientation Selection 649
16.2.2 Magnitude of the Microwave Frequency 650
16.2.3 State Mixing 650
16.2.4 Angular Anomalies 652
16.2.5 Distribution of Spin Hamiltonian Parameters 653
16.2.6 Numerical Differentiation and Fourier Filtering 655
16.2.7 High-Resolution EPR Techniques 655
16.2.8 Computer Simulation 656
16.2.9 Computational Chemistry 658
16.3 Multifrequency EPR Simulation of Square–Planar-Based Cu(II) 660
16.3.1 EPR of Square–Planar-Based Cu(II) 660
16.3.2 Multifrequency EPR of Square–Planar-Based Cu(II): S- and L-Band EPR 660
16.3.3 Multifrequency EPR of Square–Planar-Based Cu(II): Very Low-Frequency EPR 661
16.3.4 Multifrequency EPR of Square–Planar-Based Cu(II): Experimental Considerations for Low-Frequency EPR 663
16.3.5 Introduction to Multifrequency EPR Simulations of Square–Planar Cu(II) 664
16.3.6 Optimum Frequency Selection 665
16.3.7 Sensitivity Analysis 668
16.3.8 Global Fitting 669
16.3.8.1 Mo(V) Complexes 671
16.3.8.2 Low-Spin Co(II) Crossover Complexes 673
16.3.8.3 Future Developments 675
16.3.9 Heterogeneity 675
16.4 Copper-Coordination Environments: Multifrequency EPR of Three-Coordinate Copper and Mixed-Valence Dinuclear Copper [Cu(1.5\(^+\)) ... Cu(1.5\(^+\))] 677
16.4.1 Introduction: Spectrum and Structure 677
16.4.1.1 X-Band EPR Spectrum for Mononuclear, Light Blue Cu\(^{2+}\) 677
16.4.1.2 Peisach–Blumberg-Like Table (EPR Parameters Assembled by the Author) 677
16.4.1.3 Type 1 (Blue) Copper Centers, Three-Coordinate Cu 678
16.4.2 EPR for New Three-Coordinate Copper Complexes 681
16.4.2.1 Three-Coordinate CuL(SCPh3) and Copper(II)Phenolate Complexes 681
16.4.2.2 CuPPN, Three-Coordinate Copper Amido and Aminyl Complexes (More Like a Free Radical) 681
16.4.2.3 Simulation of Spectra for CuPPN (Quenched EPR Parameters Expected for a Radical) 682
16.4.2.4 EPR Parameters for CuPPN (Unpaired Electron Density Delocalized as Expected for a Radical) 685
16.4.3 Spectra for Mixed-Valence Dinuclear Copper Complexes 686
16.4.3.1 Nitrous Oxide Reductase, N2OR (15N Example) 686
16.4.3.2 Perturbation of the EPR Spectrum of CuA, H120X 689
16.4.3.3 Cytochrome c Oxidase (CcO): Best Demonstration of the Use of Low-Frequency for Mixed-Valence Sites 691
16.4.3.4 Model Diamond Core Complexes, {Cu(LXL)}2+ 695
16.4.3.5 X-Band EPR Spectra of {Cu(PPP)}2+, {Cu(PNP)}2+, and {Cu(SNS)}2+ 695
16.4.3.6 Q-Band EPR Spectra of {Cu(PPP)}2+, {Cu(PNP)}2+, and {Cu(SNS)}2+ 695
16.4.3.7 S-Band Spectra of {Cu(PPP)}2+, {Cu(PNP)}2+, and {Cu(SNS)}2+ 697
16.4.3.8 EPR Parameters and Simulations for {Cu(SNS)}2+ 697
16.4.3.9 First-Harmonic S-Band Spectrum for {Cu(PPP)}2+ 697
16.5 Structural Characterization of Copper(II) Cyclic Peptide Complexes Employing Multifrequency EPR and Computational Chemistry 699
16.5.1 Copper(II) Complexes with Marine Cyclic Peptides 701
16.5.2 Copper(II) Complexes with Westiellamide and Synthetic Analogs 707
16.6 Summary 711
Acknowledgments 711
Pertinent Literature 712
Section 16.3 712
Section 16.4 713
References 714

17 Multifrequency Electron Spin-Relaxation Times 719
Gareth R. Eaton and Sandra S. Eaton
17.1 Introduction and Scope of the Chapter 719
17.2 Spin–Spin Relaxation, T2 and Tm 720
17.2.1 Tm for Fremy’s Salt in Glassy Solvents 723
17.2.2 Exchange-Narrowed Species and the 10/3 Effect 724
17.2.3 Conducting Systems 725
17.2.4 Metal Ions in Solution 726
17.2.5 Pb2+ in Calcite 726
17.3 Spin–lattice Relaxation, T1 726
17.3.1 Phonon Densities 727
17.3.2 Practical Interpretation of Relaxation Time Data as a Function of Temperature 729
17.3.3 Glasses versus Crystals 729
17.3.4 Spectral Diffusion and Cross-Relaxation 731
17.3.5 Effect of Pairs and Clusters 732
17.3.6 Magnetic Field Dependence of Relaxation 732
17.3.6.1 The Direct Process 732
17.3.6.2 The Raman Process 734
17.3.6.3 The Orbach Process 734
17.3.6.4 The Thermally Activated Process 735
17.3.6.5 Local Modes 735
17.3.7 Dependence of Relaxation on Magnetic Field Position in a CW-EPR Spectrum 736
17.3.8 Case Studies of Experimental Data 737
17.3.8.1 Nitroxyl Spin Labels 737
17.3.8.2 Semiquinones 741
17.3.8.3 Triarylmethyl (Trityl) Radicals 742
17.3.8.4 DPPH 742
17.3.8.5 Conducting Spin Systems 742
17.3.8.6 Metal ions in Fluid Solution 743
17.3.8.7 Relaxation at 2 mm Wavelength (150 GHz) 746
17.3.9 Fullerenes 747
17.3.10 Summary 747
Acknowledgments 748
Pertinent Literature 748
References 748

18 EPR Imaging: Theory and Instrumentation 755
Rizwan Ahmad and Periannan Kuppusamy
18.1 Introduction 755
18.2 EPR Principle: Zeeman Effect 756
18.2.1 Hyperfine Splitting 757
18.2.2 Spin Relaxation 759
18.2.3 Comparison to NMR 759
18.2.4 EPR Probes 759
18.3 CW-EPR Imager 760
18.3.1 Magnets and Magnetic Field Control 761
18.3.2 Gradient Coil Assembly 762
18.3.3 RF Bridge 764
18.3.4 EPR Resonator 765
18.3.5 Signal Channel 768
18.4 Data Acquisition for CW-EPR and EPRI 769
18.4.1 Spectroscopy 769
18.4.2 Spatial EPRI 770
18.4.3 Spectral–Spatial EPRI 772
18.5 Important Imaging Parameters 774
18.5.1 Time Constant of Lock-In Amplifier 774
18.5.2 Modulation Amplitude 775
18.5.3 Gradient Strength 775
18.6 Image Reconstruction 776
18.6.1 Direct Methods 777
18.6.1.1 Filtered Backprojection (FBP) Method 777
18.6.1.2 Fourier-Based Reconstruction 778
18.6.2 Iterative Methods 779
18.6.3 Spectral–Spatial Reconstructions 781
18.6.4 Image Quality and Resolution 782
18.7 Other Data Collection Modalities 783
18.7.1 Pulsed-EPR 783
18.7.2 Single Point Imaging 784
18.7.3 Rapid Scan 784
18.7.4 Spinning Gradient 784
18.8 Constraints for Biological Applications 785
18.9 Special Imaging Applications 786
18.9.1 EPR Oximetry Mapping 786
18.9.2 Imaging Redox Metabolism in Tissues 788
18.9.2.1 Differential Distribution of Nitroxide Probes in Normal versus Tumor Tissue 788
18.9.2.2 Differential Metabolism of Nitroxide Probes in Normal versus Tumor Tissue 789
18.10 Scope and Limitations 790
Acknowledgments 791
Pertinent Literature 791
References 791

19 Multifrequency EPR Microscopy: Experimental and Theoretical Aspects 795
Aharon Blank
19.1 General 795
19.2 Introduction 795
19.2.1 Definition 795
19.2.2 Historical Overview 796
19.2.3 “Induction Detection” versus Other Detection Methods 797
19.3 General Experimental Aspects of EPR Microscopy 798
19.3.1 CW-EPR Microscopy 798
19.3.1.1 System Configuration 798
19.3.1.2 Signal-to-Noise Ratio 803
19.3.1.3 Resolution 805
19.3.2 Pulsed-EPR Microscopy 805
19.3.2.1 System Configuration 805
19.3.2.2 SNR 808
20  EPR Studies of Nanomaterials  825
   Alex Smirnov
   20.1  Introduction  825
   20.2  EPR Studies of Magnetic Nanostructures  827
   20.3  Characterization of Nanostructured Oxide Semiconductors for
         Photoactivated Catalysis and Solar Energy Conversion  832
   20.4  Surface Radicals, Catalytic Activity, Cytotoxicity, and Radical-
         Scavenging Properties of Nanomaterials  833
   20.4.1  Catalytic Activity  833
   20.4.2  Cytotoxicity  834
   20.4.3  Radical-Scavenging Properties  835
   20.5  Spin-Labeling EPR Studies of Ligand-Protected Nanoparticles and
         Hybrid Nanostructures  835
   20.6  Summary and Future Perspectives  841
   Acknowledgments  842
   Pertinent Literature  842
   References  842

21  Single-Molecule Magnets and Magnetic Quantum Tunneling  845
   Sushil K. Misra
   21.1  Introduction  845
   21.1.1  Intramolecular Coupling  846
   21.1.2  Examples of SMMs Reported in the Literature  847
   21.1.3  Applications  851
   21.2  Multifrequency EPR of SMMs: Magnetic Hysteresis and MQT  852
   21.2.1  The Effective Spin Hamiltonian  853
   21.2.2  Magnetic Quantum-Mechanical Tunneling (MQT) and MF-EPR  854
   21.2.3  Zero-Field EPR with Variable Frequency  854
21.2.4 Low-Field (X-band) EPR 854
21.2.5 MF High-Frequency EPR 855
21.2.5.1 EPR Spectrometers with MF Cavity (40–350 and Extended Range 18–350 GHz), and up to 650 GHz Without a Cavity 855
21.2.5.2 Polycrystalline Powder EPR Spectrum 855
21.2.5.3 The Virtues of Single-Crystal Measurements 855
21.2.5.4 A Typical SMM Spectrum 857
21.2.5.5 EPR Linewidth Measurements: Effect of D-Strain, g-Strain, Dipolar and Exchange Interactions 857
21.2.5.6 Study of Intermolecular Exchange Interactions and Dipolar Interactions 860
21.2.5.7 EPR Spectra for Mn₆ Family 861
21.2.6 Effect of Molecular Site Symmetry on Tunneling Phenomenon (MQT) as Revealed by EPR 863
21.3 Magnetic Quantum Tunneling (MQT): Pure and Thermally Assisted Tunneling 867
21.3.1 Relaxation of Magnetization for SMMs 867
21.3.2 Magnetic Hysteresis, Resonant Magnetization Tunneling in High-Spin Molecules and Thermally Assisted Resonant Tunneling Between Quantum States 868
21.4 Concluding Remarks 872
Acknowledgments 872
Pertinent Literature 872
References 872

22 Multifrequency EPR on Photosynthetic Systems 875
Sushil K. Misra, Klaus Möbius, and Anton Savitsky
22.1 Introduction 875
22.2 Nonoxygenic Photosynthesis 880
22.3 Multifrequency EPR on Bacterial Photosynthetic Reaction Centers (RCs) 882
22.3.1 X-band EPR Experiments 882
22.3.2 95-GHz EPR on Primary Donor Cations P⁺⁺ in Single-Crystal RCs 883
22.3.3 360-GHz EPR on Primary Donor Cations P⁺⁺ in Mutant RCs 884
22.3.4 Results of g-tensor Computations of P⁺⁺ 885
22.3.5 95-GHz EPR and ENDOR on the Acceptors Q₅⁻ and Q₆⁻ 885
22.3.6 95-GHz ESE-Detected EPR on the Spin-correlated Radical Pair P⁺⁺Q₅⁻ 892
22.3.7 95-GHz RIDME and PELDOR on the Spin-Correlated Radical Pair P⁺⁺Q₆⁻ 893
22.3.8 Multifrequency EPR on Primary Donor Triplet States in RCs 895
22.4 Oxygenic Photosynthesis 897
22.4.1 Multifrequency EPR on Doublet States in Photosystem I (PS I) 897
22.4.2 Multifrequency EPR on Doublet States in Photosystem II (PS II) 900
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.5 Concluding Remarks</td>
<td>902</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>904</td>
</tr>
<tr>
<td>Pertinent Literature</td>
<td>904</td>
</tr>
<tr>
<td>References</td>
<td>905</td>
</tr>
<tr>
<td>23 Measurement of Superconducting Gaps</td>
<td>913</td>
</tr>
<tr>
<td><em>Sushil K. Misra</em></td>
<td></td>
</tr>
<tr>
<td>23.1 Introduction</td>
<td>913</td>
</tr>
<tr>
<td>23.2 The Superconducting Gap</td>
<td>913</td>
</tr>
<tr>
<td>23.3 Measurement of SCG</td>
<td>914</td>
</tr>
<tr>
<td>23.4 Concluding Remarks</td>
<td>917</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>918</td>
</tr>
<tr>
<td>References</td>
<td>919</td>
</tr>
<tr>
<td>24 Dynamic Nuclear Polarization (DNP) at High Magnetic Fields</td>
<td>921</td>
</tr>
<tr>
<td><em>Thomas Prisner and Mark J. Prandolini</em></td>
<td></td>
</tr>
<tr>
<td>24.1 Introduction</td>
<td>921</td>
</tr>
<tr>
<td>24.2 Historical Aspects (Metals, Solids and Liquids) at Lower Magnetic Fields</td>
<td>922</td>
</tr>
<tr>
<td>24.3 Theory</td>
<td>924</td>
</tr>
<tr>
<td>24.3.1 The Overhauser Effect (OE)</td>
<td>924</td>
</tr>
<tr>
<td>24.3.2 Two-Spin Cross-Polarization: Solid Effect (SE)</td>
<td>930</td>
</tr>
<tr>
<td>24.3.3 Many-Spin Cross-Polarization: Thermal Mixing (TM)</td>
<td>931</td>
</tr>
<tr>
<td>24.3.4 Three-Spin Cross-Polarization: Cross Effect (CE)</td>
<td>933</td>
</tr>
<tr>
<td>24.3.5 Beyond Classical DNP Methods: Coherent Polarization Transfer</td>
<td>935</td>
</tr>
<tr>
<td>24.4 Hardware (High-Frequency Microwave Equipment, SS-MAS DNP, HF-Liquid DNP, Dissolution DNP, Shuttle-DNP)</td>
<td>936</td>
</tr>
<tr>
<td>24.4.1 High-Frequency Microwave Sources</td>
<td>936</td>
</tr>
<tr>
<td>24.4.2 Transmission Lines</td>
<td>937</td>
</tr>
<tr>
<td>24.4.3 Spectrometer Types</td>
<td>938</td>
</tr>
<tr>
<td>24.4.3.1 Solid-State Magic Angle Spinning (MAS) DNP</td>
<td>938</td>
</tr>
<tr>
<td>24.4.3.2 Low-Temperature Dissolution Polarizer</td>
<td>939</td>
</tr>
<tr>
<td>24.4.3.3 In-Situ Temperature-Jump DNP (Laser Melting)</td>
<td>940</td>
</tr>
<tr>
<td>24.4.3.4 High-Field (HF) Liquid-DNP Spectrometers</td>
<td>940</td>
</tr>
<tr>
<td>24.4.3.5 Shuttle DNP</td>
<td>941</td>
</tr>
<tr>
<td>24.5 First Applications and Outlook</td>
<td>942</td>
</tr>
<tr>
<td>24.5.1 Application Areas of High-Field DNP</td>
<td>942</td>
</tr>
<tr>
<td>24.5.2 Outlook</td>
<td>943</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>943</td>
</tr>
<tr>
<td>Pertinent Literature</td>
<td>943</td>
</tr>
<tr>
<td>References</td>
<td>944</td>
</tr>
<tr>
<td>25 Chemically Induced Electron and Nuclear Polarization</td>
<td>947</td>
</tr>
<tr>
<td><em>Lawrence J. Berliner and Elena Bagryanskaya</em></td>
<td></td>
</tr>
<tr>
<td>25.1 Introduction</td>
<td>947</td>
</tr>
</tbody>
</table>
26.3 Desirable Applications of EPR  1003
26.4 Future of EPR  1003
Acknowledgments  1004

Appendix A1 Fundamental Constants and Conversion Factors used in EPR  1005
Index  1009