

Contents

Preface	v
<i>one</i> The Essence of EPR	1
1-1 Magnetic Fields and Magnetic Moments	1
1-2 The Magnetic Moment of an Electron	3
1-3 The Two States of an Electron in a Magnetic Field	5
1-4 Electron Paramagnetic Resonance	7
1-5 Hyperfine Structure	9
1-6 Line Positions	10
1-7 Line Widths and Intensities	10
1-8 Substances Which Can Give EPR Signals	13
<i>two</i> Hamiltonians and Wave Functions	15
2-1 Wave Functions	15
2-2 Operators	16
2-3 Average Values in Quantum Mechanics	18
2-4 Matrices	19
2-5 Spin Operators	22
2-6 The Energy Operator	24
Supplementary References	26
<i>three</i> Hyperfine Splitting	27
3-1 Introduction	27
3-2 Angular Momentum Labels	28
3-3 Hyperfine Splitting of the Hydrogen Atom	30
3-4 Other Examples of Hyperfine Splitting	35
3-5 Dipolar Hyperfine Interactions	37
3-6 Fermi Contact Interaction	39

four	Relaxation Phenomena	41
4-1	Introduction	41
4-2	Spin State Populations	43
4-3	The Spin-Lattice Relaxation Time, T_1	45
4-4	The Spin-Spin Relaxation Time, T_2	47
4-5	Classification of Line Widths	49
4-6	Relaxation Mechanisms in Various Environments	51
4-7	Cause of Inhomogeneous Lines	56
4-8	Line Shape	58
	Answers to Problems	63
	Supplementary References	63
five	g Values	64
5-1	Anisotropy of g	66
5-2	g Values of Radicals	69
5-3	Two Different Signals or One Split Signal?	72
six	Intensity	73
6-1	Miscellaneous Factors Affecting Signal Intensity	73
6-2	Measurement of the Absolute Number of Unpaired Spins as Spins per Gram or Spins per Milliliter of Sample	75
seven	Organic Radicals and Their Spin Distribution	77
7-1	Advantages of the Liquid State in Studying Radicals	77
7-2	Hyperfine Splitting Caused by a Single Nucleus of Spin $\frac{1}{2}$	77
7-3	Relative Intensities of the Lines	78
7-4	Hyperfine Splitting Caused by a Single Nucleus of Spin 1 or Greater	79
7-5	Stability of the Nuclear Spin States	79
7-6	The Combined Effect of Several Equivalent Magnetic Nuclei on the Odd Electron	80
7-7	Spin Distribution and the Splittings	86
7-8	The Methyl Radical	87
7-9	The Ethyl Radical	91
7-10	The Naphthalene Negative Ion	94

7-11	The Pyrazine Negative Ion	97
7-12	Satellites from C ¹³ in Natural Abundance	97
7-13	An Experimental Example	100
	Problems	106
	Supplementary References	106
	Appendix: Rule for Calculating the Total Number of Lines in a Spectrum	107
<i>eight</i>	The Triplet State	108
8-1	Paramagnetism and the Triplet State	108
8-2	The Three Energy Levels of Triplet Molecules	111
8-3	A Particular Case: The Naphthalene Triplet	117
8-4	Calculation of <i>D</i> from the EPR Spectra	118
8-5	Determination of the Sign of <i>D</i>	118
8-6	Hyperfine Structure Superimposed on the Fine Structure	119
8-7	Variations in <i>D</i> with the Molecular Structure of the Triplet	119
8-8	Spectroscopy of Randomly Oriented Triplet in Dilute Frozen Solutions	124
8-9	Utility of the Parameter <i>E</i>	125
8-10	Temperature Effect on the Intensity of the Spectra of Low Lying Triplets	126
8-11	Metal-Organic Triplets	126
<i>nine</i>	The Inorganic World	127
9-1	Inorganic Radicals	128
9-2	Metal Complexes	134
9-3	Electron Paramagnetic Resonance in Insulators	139
9-4	Mössbauer Effect	145
9-5	Metals	146
<i>ten</i>	Double Resonance	151
10-1	Introduction	151
10-2	The Distribution of Molecules in Different Spin Energy States	154
10-3	Overhauser Effect	156
10-4	Electron Nuclear Double Resonance (ENDOR)	159
10-5	Optical Pumping	160
10-6	Level Crossing	162

<i>eleven</i>	Applications of EPR to Chemistry	164
11-1	Lifetime Broadening	164
11-2	Effect of Chemisorbed Hydrogen on the Ferromagnetic Resonance of Finely Divided Nickel	165
11-3	Aryloxy Radicals Produced by Ceric Oxidation of Phenols	167
11-4	The Role of Antimony Trichloride in the Oxidation of Hydrocarbons	167
11-5	Solvent Effect on Spin Distribution	168
11-6	Participation of the 3d Orbitals of Silicon in Molecular Bonds	168
11-7	Radicals from Illuminated Alkoxide Ions	169
11-8	Disproportionation of Olefins and Dianions to Form Monoanion Radicals	169
11-9	Hyperconjugation of the Methyl Group	170
11-10	Ion Pairs and Their Dissociation in Nonpolar Solvents	171
11-11	Electron Transfer Broadening: Rates and Activation Energies of Electron Transfer	171
11-12	Electron Transfer from Carbanions to Neutral Radicals	174
11-13	Electron Transfer from Neutral Radicals to Carbonium Ions	175
11-14	Electron Transfer Narrowing	175
11-15	Solvent Effects in Radical Ion Formation	176
11-16	Mechanism of Oxidation Inhibition by Diphenylamine	177
11-17	Electrochemical Reduction and Oxidation of Organic Compounds	178
11-18	The Reduction of Tetracyanoethylene	178
11-19	Formation of Nitroaromatic Radical Anions in the Presence of <i>t</i> -Butoxide Ion	180
11-20	Rotational Isomerism	181
11-21	Free Radicals and the Friedel-Crafts Reaction	182
11-22	Metal Ammonia Solutions	183
11-23	The Free Radicals of Irradiated Plastics	183
11-24	The Positive Ion of Duroquinol	184
<i>twelve</i>	Applications of EPR to Biology	187
12-1	Redox Enzymes and the Reactions Catalyzed by Them	187

12-2	Free Radicals as Intermediates in Enzymatic Dehydrogenation of Succinate	188
12-3	Identification of the Substrate Radicals in Peroxidase Catalyzed Oxidations	189
12-4	Environment of the Cu^{++} in Copper Enzymes	195
12-5	Photosynthesis	197
12-6	Effects of Radiation	199
12-7	EPR Signals of Whole Mammalian Tissues and Their Relation to Pathology	203
appendix A	Why EPR Instruments Give Derivatives of Absorption Lines	205
appendix B	Magnetic Dipolar Interactions	208
B-1	The Origin of the Dipolar Hyperfine Interaction	208
B-2	The Fermi Interaction	214
B-3	Calculation of the Hyperfine Interaction Terms	217
B-4	Spin Polarization	218
appendix C	Magnetic Energy Levels for a Two-Spin System	221
C-1	Matrix Elements	222
C-2	Wave Functions of the Levels	226
C-3	Selection Rules	226
C-4	The Hamiltonian	227
appendix D	Dipolar Line Shape in Powder EPR	234
appendix E	Hyperfine Splitting of Organic Radicals in Solution	238
	Index	271