

Contents

Fundamental constants – Unit conversions	1
Chapter 1 – The electron paramagnetic resonance phenomenon	3
1.1 – What is a spectroscopy experiment?	3
1.1.1 – Exchange of energy between matter and radiation	3
1.1.2 – Spectroscopic techniques	4
1.2 – Magnetic spectroscopy techniques	6
1.3 – Diversity of paramagnetic centres	7
1.3.1 – Electrons have two magnetic moments	7
1.3.2 – Paramagnetic atoms	9
1.3.3 – Paramagnetic molecules	12
1.4 – Principle of electron paramagnetic resonance experiments	13
1.4.1 – Reduced angular momenta	13
1.4.2 – Interaction between a paramagnetic centre and a magnetic field.....	13
1.4.3 – EPR transitions	15
1.4.4 – Expression of the absorption signal	16
1.5 – Basic EPR spectrometry instrumentation	18
1.5.1 – A few orders of magnitude.....	18
1.5.2 – Simplified description of an EPR spectrometer	19
1.5.3 – Tuning the spectrometer	21
1.6 – Points to consider in applications	21
1.6.1 – Electronic and nuclear paramagnetism.....	21
1.6.2 – Importance of paramagnetic centres	22
1.6.3 – Continuous wave EPR and pulsed EPR.....	22

1.6.4 – Some observations	23
Complement 1 – Magnetic moment created by a rotating point charge	24
Complement 2 – Why are B₂ and O₂ paramagnetic molecules?	25
Complement 3 – How magnetic field modulation affects the signal detected	27
References	28
Exercises & Answers to exercises	29
Chapter 2 – Hyperfine structure of a spectrum in the isotropic regime	31
2.1 – The various origins of spectral features in EPR	31
2.2 – Hyperfine interactions	32
2.2.1 – The nuclear magnetic moment	32
2.2.2 – Hyperfine interactions between unpaired electrons and nuclei	35
2.2.3 – The isotropic regime	36
2.3 – EPR spectrum for a centre which interacts with a single nucleus in the isotropic regime	37
2.3.1 – Expression of the energy levels for the centre	37
2.3.2 – EPR spectrum for $S = \frac{1}{2}$ and $I = \frac{1}{2}$	38
2.3.3 – EPR spectrum for $S = \frac{1}{2}$ and $I = 1$	41
2.3.4 – General case	43
2.4 – EPR spectrum for a centre which interacts with several nuclei in the isotropic regime	45
2.4.1 – Hyperfine interactions with several equivalent nuclei	45
2.4.2 – Interaction with non-equivalent nuclei	50
2.5 – Important points for applications	51
2.5.1 – Importance of hyperfine interactions	51
2.5.2 – Free radicals	51
2.5.3 – Transition ion complexes	52
Complement 1 – The paramagnetic radical probes technique	53
Complement 2 – “Pascal’s triangles”	54

References	55
Exercises & Answers to exercises	56
Chapter 3 – Introduction to the formalism of the space of spin states. The Hamiltonian operator	61
3.1 – Introduction	61
3.2 – Space of spin states associated with an angular momentum	63
3.2.1 – Construction of linear operators from \mathbf{J} – Specific bases of \mathcal{E}_J	63
3.2.2 – The scalar product	65
3.2.3 – Representation of an operator by a matrix	65
3.2.4 – Eigenvectors and eigenvalues of an operator	67
3.2.5 – Application to a centre characterised by $J = \frac{1}{2}$	69
3.2.6 – How can we use the formalism of the space of spin states associated with an angular momentum?	73
3.3 – Spin states and allowed energy levels for a paramagnetic centre placed in a magnetic field	74
3.3.1 – Interaction between a centre with an isotropic magnetic moment and a field \mathbf{B}	74
3.3.2 – When the magnetic moment is anisotropic	75
3.4 – Transition probabilities and allowed transitions	78
3.5 – Possible spin states and allowed transitions in the presence of hyperfine interaction	79
3.5.1 – Determining the energy levels	80
3.5.2 – Allowed transitions	83
3.6 – Points to consider in applications	84
3.6.1 – Why is a spin Hamiltonian used in EPR and magnetic spectroscopies?	84
3.6.2 – What does the spin Hamiltonian do?	84
3.6.3 – Looking back to the procedure described in chapters 1 and 2	84
Complement 1 – Diagonalisation of $\tilde{\mathbf{H}}_{Zeeman}$ in any basis	86
Complement 2 – The principle of perturbation theory	88
References	93

Exercises & Answers to exercises	94
Chapter 4 – How anisotropy of the $\tilde{\mathbf{g}}$ and $\tilde{\mathbf{A}}$ matrices affects spectrum shape for radicals and transition ion complexes	101
4.1 – Introduction	101
4.2 – The $\tilde{\mathbf{g}}$ matrix	102
4.2.1 – How the molecule's symmetry properties affect the $\tilde{\mathbf{g}}$ matrix.....	102
4.2.2 – The principal values of the $\tilde{\mathbf{g}}$ matrix	103
4.3 – Shape of the spectrum produced by an ensemble of paramagnetic centres in the absence of hyperfine interaction	110
4.3.1 – Variation in g' values with the direction of \mathbf{B}	110
4.3.2 – Shape of the EPR spectrum depending on the nature of the sample	112
4.3.3 – Notes on the spectra produced by polycrystalline powders or frozen solutions.....	117
4.4 – How anisotropic hyperfine interaction affects the shape of the EPR spectrum	118
4.4.1 – The hyperfine matrix $\tilde{\mathbf{A}}$	118
4.4.2 – Expression of the resonance field in the presence of anisotropic hyperfine interaction.....	121
4.4.3 – Effect of $\tilde{\mathbf{g}}$ and $\tilde{\mathbf{A}}$ matrix anisotropy on the shape of the powder spectrum..	123
4.5 – How molecular movements affect the spectrum: isotropic and very slow motion regimes	129
4.5.1 – A hypothetical experiment.....	129
4.5.2 – Effects of rotational Brownian motion of paramagnetic molecules	132
4.6 – Points to consider in applications	133
4.6.1 – Spectrum for a single crystal.....	133
4.6.2 – Powder spectrum for centres of spin $\frac{1}{2}$	135
4.6.3 – Spectra for transition ion complexes.....	135
4.6.4 – Spectra for free radicals	136
4.6.5 – The EPR spectrum contains additional information	136

Complement 1 – Splitting of the energy levels for the electrons in an octahedral complex	137
Complement 2 – Possible values of g' when the \tilde{g} matrix is rhombic	139
Complement 3 – Expression for the density of resonance lines for a centre with axial symmetry	141
Complement 4 – Expression giving the energy levels for any direction of \mathbf{B} when the \tilde{g} and \tilde{A} matrices are anisotropic	144
Complement 5 – An example of a study of a single crystal: identification of the site of Ti^{3+} fluorescence in $LaMgAl_{11}O_{19}$	147
References	149
Exercises & Answers to exercises	151
Chapter 5 – Spectrum intensity, saturation, spin-lattice relaxation	155
5.1 – Introduction	155
5.2 – Spectrum intensity at thermal equilibrium	156
5.2.1 – Absorption signal and intensity of a resonance line	156
5.2.2 – Expressions for the absorption signal and the intensity of the spectrum for a powder or a frozen solution	163
5.2.3 – Intensity of the spectrum produced by a single crystal	165
5.2.4 – Intensity of the resonance lines and of the spectrum in the presence of hyperfine interactions	166
5.3 – Signal saturation	167
5.3.1 – Saturation of an EPR transition	167
5.3.2 – Expression for the absorption signal in the saturated regime	170
5.3.3 – Significance of the saturation phenomenon	172
5.4 – Spin-lattice relaxation	174
5.4.1 – The various spin-lattice relaxation processes	174
5.4.2 – How can the spin-lattice relaxation time T_1 be measured?	178
5.4.3 – Relaxation phenomena and EPR spectroscopy in practice	180
5.5 – Points to consider in applications	182

5.5.1 – Intensity of the resonance lines and the spectrum	182
5.5.2 – Use of spin-lattice relaxation.....	183
Complement 1 – Fermi’s golden rule.....	185
Complement 2 – Expression of the intensity factor for an axially symmetric centre of spin $\frac{1}{2}$.....	187
Complement 3 – Homogeneous and inhomogeneous lines.....	189
References	192
Exercises & Answers to exercises	193
Chapter 6 – The zero-field splitting term. EPR spectrum for paramagnetic centres of spin greater than $\frac{1}{2}$	197
6.1 – Introduction	197
6.2 – The zero-field splitting term.....	198
6.2.1 – The $\tilde{\mathbf{D}}$ matrix.....	198
6.2.2 – The D and E parameters	200
6.3 – Definition and general characteristics of “high-field” and “low-field” situations	202
6.3.1 – The energy levels for a centre with axial symmetry for the canonical directions of the magnetic field	202
6.3.2 – “High-field” and “low-field” situations.....	205
6.4 – General properties of the spectrum in the high-field situation	207
6.4.1 – Energy levels and allowed transitions.....	207
6.4.2 – Intensity of the resonance lines and the spectrum	208
6.5 – Shape of the powder spectrum in the high-field situation	210
6.5.1 – Expression for the resonance field in axial symmetry	210
6.5.2 – Shape of the spectrum in axial symmetry	211
6.5.3 – The “half-field” line for $S = 1$	215
6.5.4 – Shape of the spectrum in “rhombic” symmetry	217
6.6 – EPR spectrum for complexes of half-integer spin in the low-field situation. Kramers doublet.....	218

6.6.1 – Case of a complex with axial symmetry	218
6.6.2 – Generalisation to a complex of any geometry	223
6.7 – EPR spectrum for integer-spin complexes in the low-field situation	224
6.8 – Points to consider in applications	225
6.8.1 – Organic molecules in a triplet state	226
6.8.2 – Transition ion complexes in the high-field situation	226
6.8.3 – Transition ion complexes in the low-field situation	227
6.8.4 – Spin-lattice relaxation for centres of spin greater than $\frac{1}{2}$	227
Complement 1 – Intensity of the resonance line at high temperature in the high-field limit	229
Complement 2 – Shape of the low-field spectrum for a centre of spin $S = 1$	231
References	233
Exercises & Answers to exercises	235
Chapter 7 – Effects of dipolar and exchange interactions on the EPR spectrum. Biradicals and polynuclear complexes	241
7.1 – Introduction	241
7.2 – Origin and description of intercentre interactions	242
7.2.1 – The true nature of exchange interaction	242
7.2.2 – Phenomenological description of exchange interaction	248
7.2.3 – “Anisotropic components” of exchange interaction	249
7.2.4 – Magnetic dipolar interaction	250
7.3 – Effects of weak intercentre interactions on the spectrum	250
7.3.1 – Effects of the dipolar interactions	251
7.3.2 – Effects of the exchange interaction	256
7.3.3 – General case	261
7.4 – Effects of strong exchange interaction on the spectrum Biradicals and polynuclear complexes	262
7.4.1 – Introduction	262

7.4.2 – Construction of equivalent Hamiltonians for a pair of paramagnetic centres	263
7.4.3 – Equivalent Hamiltonians and EPR spectra for a few typical pairs	267
7.5 – How intercentre interactions affect the intensity of the spectrum and the relaxation properties	274
7.5.1 – EPR spectrum intensity	274
7.5.2 – Relaxation properties.....	275
7.6 – Points to consider in applications	277
7.6.1 – How weak intercentre interactions affect the spectra.....	277
7.6.2 – How strong exchange interaction affects the spectrum	277
7.6.3 – Dynamic effects of intercentre interactions.....	278
Complement 1 – Equivalent Hamiltonian for a trinuclear complex	279
References	282
Exercises & Answers to exercises	284
Chapter 8 – EPR spectrum for complexes of rare earth and actinide ions	289
8.1 – Rare earth ions.....	289
8.1.1 – Magnetic moment of free rare earth ions.....	290
8.1.2 – Hyperfine interaction with the nucleus.....	291
8.2 – Complexes of rare earth ions: effect of interaction with ligands	293
8.2.1 – Expression describing the interaction of electrons in the $4f$ subshell with ligands	293
8.2.2 – Effects of interaction with ligands on the ground multiplet.....	295
8.3 – The EPR spectrum for complexes of rare earth ions with half-integer J values	298
8.3.1 – Introduction	298
8.3.2 – Expression for the effective parameters	299
8.3.3 – The case of cations in an S state.....	300
8.3.4 – Application: analysing the data obtained for ethyl sulfates	301
8.3.5 – Spin-lattice relaxation for complexes with half-integer spin.....	305

8.4 – The EPR spectrum for complexes of rare earth ions with integer J values	306
8.4.1 – Intradoublet transitions	306
8.4.2 – Transitions between singlets	307
8.5 – Actinide complexes	307
8.5.1 – Introduction	307
8.5.2 – Comparison of spectra for complexes of trivalent rare earth and actinide cations	309
8.5.3 – Complexes of high valence actinides: example of cations with a $5f^1$ configuration	310
8.6 – Points to consider in applications	313
8.6.1 – Comparison of the EPR characteristics of transition ion and rare earth ion complexes with a half-integer spin	313
8.6.2 – Interpreting spectra for rare earth complexes	314
8.6.3 – Actinide complexes	315
Complement 1 – Rare earth elements and actinides: etymological considerations	316
References	317
Exercises & Answers to exercises	319
Chapter 9 – How instrumental parameters affect the shape and intensity of the spectrum.	
Introduction to simulation methods	323
9.1 – Introduction	323
9.2 – How field sweep and field modulation affect the shape of the spectrum	324
9.2.1 – Effects of modulation at the level of the sample	325
9.2.2 – Effects of magnetic field modulation and sweep at the level of the detection chain	326
9.3 – How the power and frequency of the radiation affect the spectrum. The temperature parameter	329
9.3.1 – Effect of the power and frequency of the radiation	329

9.3.2 – Temperature-related effects	332
9.3.3 – Case study: seeking the origin of line splitting in an EPR spectrum	333
9.4 – Simulating spectrum saturation	335
9.4.1 – Simulating saturation of a homogeneous Lorentzian line	336
9.4.2 – Simulating saturation of an inhomogeneous line	338
9.4.3 – Simulating saturation of a powder spectrum	340
9.5 – Introduction to numerical simulation of the EPR spectrum	341
9.5.1 – Why simulate a spectrum?	341
9.5.2 – How can the spectrum be numerically calculated?	343
9.5.3 – The linewidth problem	344
9.6 – Points to consider in applications	345
9.6.1 – How should the modulation and sweep parameters be selected?	345
9.6.2 – How can a saturation curve be simulated?	346
9.6.3 – How can an EPR spectrum be simulated?	347
Complement 1 – Some properties of the convolution product	348
Complement 2 – Quantitative analysis of the saturation curve for an inhomogeneous line	350
Complement 3 – Quantitative study of relaxation broadening	352
Complement 4 – Using standard samples in EPR spectroscopy	354
Complement 5 – Numerical simulation software	357
References	359
Exercises & Answers to exercises	361
Appendix 1 – Expression of the magnetic moment of a free atom or ion	363
First step: electrostatic interactions to which electrons are subjected	363
1 – Microstates	363
2 – (L , S) terms	364
Second step: magnetic interactions to which electrons are subjected	367
1 – Multiplets	367

2 – Expression for the magnetic moment	368
Appendix 2 – Expression of \tilde{g} and \tilde{A} matrices given by ligand field theory for a transition ion complex.....	371
1 – Electrostatic interactions in free ions	371
2 – Electrostatic interactions with ligands.....	372
3 – Magnetic interactions	374
3.1 – Effects of spin-orbit coupling and interaction with a magnetic field	374
3.2 – Effects of hyperfine interactions.....	377
3.3 – The case of complexes of cations in an S state	379
Appendix 3 – Dipolar interactions between a nuclear magnetic moment and electron spin magnetic moments	381
1 – The dipolar matrix \tilde{T}	381
Case where the $\varphi(\mathbf{r})$ orbital is spherically symmetric relative to the nucleus	382
2 – Principal axes and principal values of the \tilde{T} matrix.....	383
2.1 – $\varphi(\mathbf{r})$ is an atomic orbital centred at 0.....	384
2.2 – $\varphi(\mathbf{r})$ is centred at a point C which is remote from the nucleus.....	384
3 – Case with several unpaired electrons	385
Appendix 4 – Some properties of angular momentum operators. Spin coupling coefficients and equivalent operators. Application to Landé's formula and to dipolar hyperfine interactions.....	387
1 – Definition of coupled bases and spin coupling coefficients	387
1.1 – Product bases and coupled bases	387
1.2 – Construction of the matrices representing operators defined from \mathbf{J}_1 and \mathbf{J}_2 in the coupled basis	389
1.3 – Spin coupling coefficients	390
1.4 – Application to the energy of multiplets. Demonstration of the Landé formula ...	392
2 – Calculation of the dipolar components of the hyperfine interaction within an (L, S) term	393

Appendix 5 – The notion of spin density	397
1 – Definition	398
2 – Spin density in a mononuclear complex.....	400
3 – Spin density in a dinuclear complex	402
Appendix 6 – Example of calculation of the spin-lattice relaxation time T_1: the direct process	407
Appendix 7 – Matrix elements of operators defined from components of an angular momentum	411
Glossary	413
Index	417