

Contents

List of the Most Important Symbols Used	XV
1. Introduction	1
1.1 Classical Physics and Quantum Mechanics	1
1.2 Short Historical Review	1
2. The Mass and Size of the Atom	5
2.1 What is an Atom?	5
2.2 Determination of the Mass	5
2.3 Methods for Determining Avogadro's Number	7
2.3.1 Electrolysis	7
2.3.2 The Gas Constant and Boltzmann's Constant	7
2.3.3 X-Ray Diffraction in Crystals	8
2.3.4 Determination Using Radioactive Decay	9
2.4 Determination of the Size of the Atom	10
2.4.1 Application of the Kinetic Theory of Gases	10
2.4.2 The Interaction Cross Section	11
2.4.3 Experimental Determination of Interaction Cross Sections	14
2.4.4 Determining the Atomic Size from the Covolume	15
2.4.5 Atomic Sizes from X-Ray Diffraction Measurements on Crystals ..	15
2.4.6 Can Individual Atoms Be Seen?	20
Problems	25
3. Isotopes	27
3.1 The Periodic System of the Elements	27
3.2 Mass Spectroscopy	29
3.2.1 Parabola Method	29
3.2.2 Improved Mass Spectrometers	32
3.2.3 Results of Mass Spectrometry	33
3.2.4 Modern Applications of the Mass Spectrometer	34
3.2.5 Isotope Separation	35
Problems	36
4. The Nucleus of the Atom	37
4.1 Passage of Electrons Through Matter	37
4.2 Passage of Alpha Particles Through Matter (Rutherford Scattering) ...	39
4.2.1 Some Properties of Alpha Particles	39
4.2.2 Scattering of Alpha Particles by a Foil	39
4.2.3 Derivation of the Rutherford Scattering Formula	41
4.2.4 Experimental Results	46
4.2.5 What is Meant by Nuclear Radius?	47
Problems	48

5. The Photon	49
5.1 Wave Character of Light	49
5.2 Thermal Radiation	51
5.2.1 Spectral Distribution of Black Body Radiation	51
5.2.2 Planck's Radiation Formula	53
5.2.3 Einstein's Derivation of Planck's Formula	54
5.3 The Photoelectric Effect	58
5.4 The Compton Effect	60
5.4.1 Experiments	60
5.4.2 Derivation of the Compton Shift	62
Problems	64
6. The Electron	67
6.1 Production of Free Electrons	67
6.2 Size of the Electron	67
6.3 The Charge of the Electron	68
6.4 The Specific Charge e/m of the Electron	69
6.5 Wave Character of Electrons and Other Particles	72
6.6 Interferometry with Atoms	76
Problems	77
7. Some Basic Properties of Matter Waves	79
7.1 Wave Packets	79
7.2 Probabilistic Interpretation	83
7.3 The Heisenberg Uncertainty Relation	85
7.4 The Energy-Time Uncertainty Relation	87
7.5 Some Consequences of the Uncertainty Relations for Bound States	88
Problems	91
8. Bohr's Model of the Hydrogen Atom	93
8.1 Basic Principles of Spectroscopy	93
8.2 The Optical Spectrum of the Hydrogen Atom	95
8.3 Bohr's Postulates	98
8.4 Some Quantitative Conclusions	102
8.5 Motion of the Nucleus	103
8.6 Spectra of Hydrogen-like Atoms	105
8.7 Muonic Atoms	107
8.8 Excitation of Quantum Jumps by Collisions	109
8.9 Sommerfeld's Extension of the Bohr Model and the Experimental Justification of a Second Quantum Number	112
8.10 Lifting of Orbital Degeneracy by the Relativistic Mass Change	113
8.11 Limits of the Bohr-Sommerfeld Theory. The Correspondence Principle	114
8.12 Rydberg Atoms	115
Problems	117
9. The Mathematical Framework of Quantum Theory	119
9.1 The Particle in a Box	119
9.2 The Schrödinger Equation	123

9.3	The Conceptual Basis of Quantum Theory	125
9.3.1	Observations, Values of Measurements and Operators	125
9.3.2	Momentum Measurement and Momentum Probability	126
9.3.3	Average Values and Expectation Values	127
9.3.4	Operators and Expectation Values	130
9.3.5	Equations for Determining the Wavefunction	131
9.3.6	Simultaneous Observability and Commutation Relations	133
9.4	The Quantum Mechanical Oscillator	136
	Problems	142
10.	Quantum Mechanics of the Hydrogen Atom	147
10.1	Motion in a Central Field	147
10.2	Angular Momentum Eigenfunctions	149
10.3	The Radial Wavefunctions in a Central Field*	155
10.4	The Radial Wavefunctions of Hydrogen	157
	Problems	163
11.	Lifting of the Orbital Degeneracy in the Spectra of Alkali Atoms	165
11.1	Shell Structure	165
11.2	Screening	167
11.3	The Term Diagram	168
11.4	Inner Shells	173
	Problems	173
12.	Orbital and Spin Magnetism. Fine Structure	175
12.1	Introduction and Overview	175
12.2	Magnetic Moment of the Orbital Motion	176
12.3	Precession and Orientation in a Magnetic Field	178
12.4	Spin and Magnetic Moment of the Electron	180
12.5	Determination of the Gyromagnetic Ratio by the Einstein-de Haas Method	182
12.6	Detection of Directional Quantisation by Stern and Gerlach	183
12.7	Fine Structure and Spin-Orbit Coupling: Overview	185
12.8	Calculation of Spin-Orbit Splitting in the Bohr Model	186
12.9	Level Scheme of the Alkali Atoms	190
12.10	Fine Structure in the Hydrogen Atom	191
12.11	The Lamb Shift	192
	Problems	196
13.	Atoms in a Magnetic Field:	
	Experiments and Their Semiclassical Description	199
13.1	Directional Quantisation in a Magnetic Field	199
13.2	Electron Spin Resonance	199
13.3	The Zeeman Effect	202
13.3.1	Experiments	202
13.3.2	Explanation of the Zeeman Effect from the Standpoint of Classical Electron Theory	204
13.3.3	Description of the Ordinary Zeeman Effect by the Vector Model	206

13.3.4 The Anomalous Zeeman Effect	208
13.3.5 Magnetic Moments with Spin-Orbit Coupling	209
13.4 The Paschen-Back Effect	211
13.5 Double Resonance and Optical Pumping	212
Problems	214
14. Atoms in a Magnetic Field: Quantum Mechanical Treatment	215
14.1 Quantum Theory of the Ordinary Zeeman Effect	215
14.2 Quantum Theoretical Treatment of the Electron and Proton Spins ..	217
14.2.1 Spin as Angular Momentum	217
14.2.2 Spin Operators, Spin Matrices and Spin Wavefunctions	218
14.2.3 The Schrödinger Equation of a Spin in a Magnetic Field	220
14.2.4 Description of Spin Precession by Expectation Values	222
14.3 Quantum Mechanical Treatment of the Anomalous Zeeman Effect with Spin-Orbit Coupling*	224
14.4 Quantum Theory of a Spin in Mutually Perpendicular Magnetic Fields, One Constant and One Time Dependent	228
14.5 The Bloch Equations	233
14.6 The Relativistic Theory of the Electron. The Dirac Equation	235
Problems	241
15. Atoms in an Electric Field	243
15.1 Observations of the Stark Effect	243
15.2 Quantum Theory of the Linear and Quadratic Stark Effects	245
15.2.1 The Hamiltonian	245
15.2.2 The Quadratic Stark Effect. Perturbation Theory Without Degeneracy*	246
15.2.3 The Linear Stark Effect. Perturbation Theory in the Presence of Degeneracy*	249
15.3 The Interaction of a Two-Level Atom with a Coherent Radiation Field	252
15.4 Spin- and Photon Echoes	255
15.5 A Glance at Quantum Electrodynamics*	258
15.5.1 Field Quantization	258
15.5.2 Mass Renormalization and Lamb Shift	263
Problems	270
16. General Laws of Optical Transitions	273
16.1 Symmetries and Selection Rules	273
16.1.1 Optical Matrix Elements	273
16.1.2 Examples of the Symmetry Behaviour of Wavefunctions	273
16.1.3 Selection Rules	278
16.1.4 Selection Rules and Multipole Radiation*	281
16.2 Linewidths and Lineshapes	284
17. Many-Electron Atoms	289
17.1 The Spectrum of the Helium Atom	289
17.2 Electron Repulsion and the Pauli Principle	291

17.3 Angular Momentum Coupling	292
17.3.1 Coupling Mechanism	292
17.3.2 <i>LS</i> Coupling (Russell-Saunders Coupling)	292
17.3.3 <i>jj</i> Coupling	296
17.4 Magnetic Moments of Many-Electron Atoms	298
17.5 Multiple Excitations	298
Problems	299
18. X-Ray Spectra, Internal Shells	301
18.1 Introductory Remarks	301
18.2 X-Radiation from Outer Shells	301
18.3 X-Ray Bremsstrahlung Spectra	302
18.4 Emission Line Spectra: Characteristic Radiation	304
18.5 Fine Structure of the X-Ray Spectra	306
18.6 Absorption Spectra	308
18.7 The Auger Effect	310
18.8 Photoelectron Spectroscopy (XPS), ESCA	312
Problems	313
19. Structure of the Periodic System. Ground States of the Elements	315
19.1 Periodic System and Shell Structure	315
19.2 Ground States of Atoms	322
19.3 Excited States and Complete Term Scheme	324
19.4 The Many-Electron Problem. Hartree-Fock Method*	325
19.4.1 The Two-Electron Problem	325
19.4.2 Many Electrons Without Mutual Interactions	330
19.4.3 Coulomb Interaction of Electrons. Hartree and Hartree-Fock Methods	331
Problems	334
20. Nuclear Spin, Hyperfine Structure	337
20.1 Influence of the Atomic Nucleus on Atomic Spectra	337
20.2 Spins and Magnetic Moments of Atomic Nuclei	338
20.3 The Hyperfine Interaction	340
20.4 Hyperfine Structure in the Ground States of the Hydrogen and Sodium Atoms	344
20.5 Hyperfine Structure in an External Magnetic Field, Electron Spin Resonance	346
20.6 Direct Measurements of Nuclear Spins and Magnetic Moments, Nuclear Magnetic Resonance	350
20.7 Applications of Nuclear Magnetic Resonance	354
20.8 The Nuclear Electric Quadrupole Moment	359
Problems	361
21. The Laser	363
21.1 Some Basic Concepts for the Laser	363
21.2 Rate Equations and Lasing Conditions	366
21.3 Amplitude and Phase of Laser Light	369
Problems	372

22. Modern Methods of Optical Spectroscopy	375
22.1 Classical Methods	375
22.2 Quantum Beats	376
22.3 Doppler-free Saturation Spectroscopy	378
22.4 Doppler-free Two-Photon Absorption	380
22.5 Level-Crossing Spectroscopy and the Hanle Effect	382
22.6 Laser Cooling of Atoms	384
23. Fundamentals of the Quantum Theory of Chemical Bonding	389
23.1 Introductory Remarks	389
23.2 The Hydrogen-Molecule Ion H_2^+	389
23.3 The Tunnel Effect	395
23.4 The Hydrogen Molecule H_2	397
23.5 Covalent-Ionic Resonance	404
23.6 The Hund-Mulliken-Bloch Theory of Bonding in Hydrogen	405
23.7 Hybridisation	406
23.8 The π Electrons of Benzene, C_6H_6	408
Problems	410
Appendix	411
A. The Dirac Delta Function and the Normalisation of the Wavefunction of a Free Particle in Unbounded Space	411
B. Some Properties of the Hamiltonian Operator, Its Eigenfunctions and Its Eigenvalues	415
C. Derivation of Heisenberg's Uncertainty Relation	416
Solutions to the Problems	419
Bibliography of Supplementary and Specialised Literature	449
Subject Index	453
Fundamental Constants of Atomic Physics (Inside Front Cover)	
Energy Conversion Table (Inside Back Cover)	