

Contents

List of the Most Important Symbols Used	XIX
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	69
6.1 Production of Free Electrons	69
6.2 Size of the Electron	69
6.3 The Charge of the Electron	70
6.4 The Specific Charge e/m of the Electron	71
6.5 Wave Character of Electrons and Other Particles	74
6.6 Interferometry with Atoms	78
Problems	79
7. Some Basic Properties of Matter Waves	81
7.1 Wave Packets	81
7.2 Probabilistic Interpretation	85
7.3 The Heisenberg Uncertainty Relation	87
7.4 The Energy-Time Uncertainty Relation	89
7.5 Some Consequences of the Uncertainty Relations for Bound States	90
Problems	93
8. Bohr's Model of the Hydrogen Atom	95
8.1 Basic Principles of Spectroscopy	95
8.2 The Optical Spectrum of the Hydrogen Atom	97
8.3 Bohr's Postulates	100
8.4 Some Quantitative Conclusions	104
8.5 Motion of the Nucleus	105
8.6 Spectra of Hydrogen-like Atoms	107
8.7 Muonic Atoms	109
8.8 Excitation of Quantum Jumps by Collisions	111
8.9 Sommerfeld's Extension of the Bohr Model and the Experimental Justification of a Second Quantum Number	114
8.10 Lifting of Orbital Degeneracy by the Relativistic Mass Change	115
8.11 Limits of the Bohr-Sommerfeld Theory. The Correspondence Principle	116
8.12 Rydberg Atoms	117
8.13 Positronium, Muonium, and Antihydrogen	119
Problems	121
9. The Mathematical Framework of Quantum Theory	125
9.1 The Particle in a Box	125
9.2 The Schrödinger Equation	129

Contents	XIII
9.3 The Conceptual Basis of Quantum Theory	131
9.3.1 Observations, Values of Measurements and Operators	131
9.3.2 Momentum Measurement and Momentum Probability	132
9.3.3 Average Values and Expectation Values	133
9.3.4 Operators and Expectation Values	136
9.3.5 Equations for Determining the Wavefunction	137
9.3.6 Simultaneous Observability and Commutation Relations	139
9.4 The Quantum Mechanical Oscillator	142
Problems	148
10. Quantum Mechanics of the Hydrogen Atom	153
10.1 Motion in a Central Field	153
10.2 Angular Momentum Eigenfunctions	155
10.3 The Radial Wavefunctions in a Central Field *	161
10.4 The Radial Wavefunctions of Hydrogen	163
Problems	169
11. Lifting of the Orbital Degeneracy in the Spectra of Alkali Atoms	171
11.1 Shell Structure	171
11.2 Screening	173
11.3 The Term Diagram	174
11.4 Inner Shells	179
Problems	179
12. Orbital and Spin Magnetism. Fine Structure	181
12.1 Introduction and Overview	181
12.2 Magnetic Moment of the Orbital Motion	182
12.3 Precession and Orientation in a Magnetic Field	184
12.4 Spin and Magnetic Moment of the Electron	186
12.5 Determination of the Gyromagnetic Ratio by the Einstein-de Haas Method	188
12.6 Detection of Directional Quantisation by Stern and Gerlach	189
12.7 Fine Structure and Spin-Orbit Coupling: Overview	191
12.8 Calculation of Spin-Orbit Splitting in the Bohr Model	192
12.9 Level Scheme of the Alkali Atoms	196
12.10 Fine Structure in the Hydrogen Atom	197
12.11 The Lamb Shift	198
Problems	202
13. Atoms in a Magnetic Field: Experiments and Their Semiclassical Description	205
13.1 Directional Quantisation in a Magnetic Field	205
13.2 Electron Spin Resonance	205
13.3 The Zeeman Effect	208
13.3.1 Experiments	208
13.3.2 Explanation of the Zeeman Effect from the Standpoint of Classical Electron Theory	210
13.3.3 Description of the Ordinary Zeeman Effect by the Vector Model	212

13.3.4	The Anomalous Zeeman Effect	214
13.3.5	Magnetic Moments with Spin-Orbit Coupling	215
13.4	The Paschen-Back Effect	217
13.5	Double Resonance and Optical Pumping	218
	Problems	220
14.	Atoms in a Magnetic Field: Quantum Mechanical Treatment	223
14.1	Quantum Theory of the Ordinary Zeeman Effect	223
14.2	Quantum Theoretical Treatment of the Electron and Proton Spins	225
14.2.1	Spin as Angular Momentum	225
14.2.2	Spin Operators, Spin Matrices and Spin Wavefunctions	226
14.2.3	The Schrödinger Equation of a Spin in a Magnetic Field	228
14.2.4	Description of Spin Precession by Expectation Values	230
14.3	Quantum Mechanical Treatment of the Anomalous Zeeman Effect with Spin-Orbit Coupling *	232
14.4	Quantum Theory of a Spin in Mutually Perpendicular Magnetic Fields, One Constant and One Time Dependent	236
14.5	The Bloch Equations	241
14.6	The Relativistic Theory of the Electron. The Dirac Equation	243
	Problems	249
15.	Atoms in an Electric Field	251
15.1	Observations of the Stark Effect	251
15.2	Quantum Theory of the Linear and Quadratic Stark Effects	253
15.2.1	The Hamiltonian	253
15.2.2	The Quadratic Stark Effect. Perturbation Theory Without Degeneracy *	254
15.2.3	The Linear Stark Effect. Perturbation Theory in the Presence of Degeneracy *	257
15.3	The Interaction of a Two-Level Atom with a Coherent Radiation Field	260
15.4	Spin and Photon Echoes	263
15.5	A Glance at Quantum Electrodynamics *	266
15.5.1	Field Quantization	266
15.5.2	Mass Renormalization and Lamb Shift	271
	Problems	278
16.	General Laws of Optical Transitions	281
16.1	Symmetries and Selection Rules	281
16.1.1	Optical Matrix Elements	281
16.1.2	Examples of the Symmetry Behaviour of Wavefunctions	281
16.1.3	Selection Rules	286
16.1.4	Selection Rules and Multipole Radiation *	289
16.2	Linewidths and Lineshapes	292
17.	Many-Electron Atoms	297
17.1	The Spectrum of the Helium Atom	297
17.2	Electron Repulsion and the Pauli Principle	299

17.3	Angular Momentum Coupling	300
17.3.1	Coupling Mechanism	300
17.3.2	<i>LS</i> Coupling (Russell-Saunders Coupling)	300
17.3.3	<i>jj</i> Coupling	304
17.4	Magnetic Moments of Many-Electron Atoms	306
17.5	Multiple Excitations	307
	Problems	307
18.	X-Ray Spectra, Internal Shells	309
18.1	Introductory Remarks	309
18.2	X-Radiation from Outer Shells	309
18.3	X-Ray Bremsstrahlung Spectra	310
18.4	Emission Line Spectra: Characteristic Radiation	312
18.5	Fine Structure of the X-Ray Spectra	314
18.6	Absorption Spectra	316
18.7	The Auger Effect	318
18.8	Photoelectron Spectroscopy (XPS), ESCA	320
	Problems	322
19.	Structure of the Periodic System. Ground States of the Elements	323
19.1	Periodic System and Shell Structure	323
19.2	From the Electron Configuration to the Atomic Term Scheme. Atomic Ground States	330
19.3	Excited States of Atoms and Possible Electronic Configurations. Complete Term Schemes	333
19.4	The Many-Electron Problem. Hartree-Fock Method*	335
19.4.1	The Two-Electron Problem	335
19.4.2	Many Electrons Without Mutual Interactions	340
19.4.3	Coulomb Interaction of Electrons. Hartree and Hartree-Fock Methods	341
	Problems	344
20.	Nuclear Spin, Hyperfine Structure	347
20.1	Influence of the Atomic Nucleus on Atomic Spectra	347
20.2	Spins and Magnetic Moments of Atomic Nuclei	348
20.3	The Hyperfine Interaction	350
20.4	Hyperfine Structure in the Ground State of the Hydrogen Atom, the Sodium Atom, and the Hydrogen-like Ion ${}_{83}\text{Bi}^{82+}$	354
20.5	Hyperfine Structure in an External Magnetic Field, Electron Spin Resonance	356
20.6	Direct Measurements of Nuclear Spins and Magnetic Moments, Nuclear Magnetic Resonance	361
20.7	Applications of Nuclear Magnetic Resonance	364
20.8	The Nuclear Electric Quadrupole Moment	369
	Problems	371
21.	The Laser	373
21.1	Some Basic Concepts for the Laser	373
21.2	Rate Equations and Lasing Conditions	376

21.3 Amplitude and Phase of Laser Light	379
Problems	382
22. Modern Methods of Optical Spectroscopy	385
22.1 Classical Methods	385
22.2 Quantum Beats	386
22.3 Doppler-free Saturation Spectroscopy	388
22.4 Doppler-free Two-Photon Absorption	390
22.5 Level-Crossing Spectroscopy and the Hanle Effect	392
22.6 Laser Cooling of Atoms	394
22.7 Nondestructive Single-Photon Detection – An Example of Atomic Physics in a Resonant Cavity	399
Problems	401
23. Progress in Quantum Physics: A Deeper Understanding and New Applications	403
23.1 Introduction	403
23.2 The Superposition Principle, Interference, Probabilily and Probability Amplitudes	403
23.3 Schrödinger's Cat	405
23.4 Decoherence	405
23.5 Entanglement	406
23.6 The Einstein-Podolsky-Rosen (EPR) Paradox	407
23.7 Bell's Inequalities and the Hidden-Variable Hypothesis	408
23.8 Experiments to Test Bell's Inequalities	411
23.9 Quantum Computers	412
23.9.1 Historical Remarks	412
23.9.2 Review of Digital Computers	413
23.9.3 Basic Concepts of the Quantum Computer	414
23.9.4 Decoherence and Error Correction	416
23.9.5 A Comparison Between the Quantum Computer and the Digital Computer	418
23.10 Quantum Information Theory	418
23.11 The Bose-Einstein Condensation	418
23.11.1 Review of Statistical Mechanics	418
23.11.2 The Experimental Discovery	419
23.11.3 The Quantum Theory of the Bose-Einstein Condensation	421
23.12 The Atom Laser	422
Problems	423
24. Fundamentals of the Quantum Theory of Chemical Bonding	425
24.1 Introductory Remarks	425
24.2 The Hydrogen-Molecule Ion H_2^+	425
24.3 The Tunnel Effect	431
24.4 The Hydrogen Molecule H_2	433
24.5 Covalent-Ionic Resonance	440
24.6 The Hund-Mulliken-Bloch Theory of Bonding in Hydrogen	441
24.7 Hybridisation	442
24.8 The π Electrons of Benzene, C_6H_6	444

Contents	XVII
Problems	446
Appendix	
A. The Dirac Delta Function and the Normalisation of the Wavefunction of a Free Particle in Unbounded Space	447
B. Some Properties of the Hamiltonian Operator, Its Eigenfunctions and its Eigenvalues	451
C. Derivation of Heisenberg's Uncertainty Relation	452
Solutions to the Problems	455
Bibliography of Supplementary and Specialised Literature	458
Subject Index	493
Fundamental Constants of Atomic Physics (Inside Front Cover)	
Energy Conversion Table (Inside Back Cover)	