Contents

1 Introduction . . . 1
1.1 Contents and Importance of Atomic Physics . . . 1
1.2 Molecules: Building Blocks of Nature . . . 3
1.3 Survey on the Concept of this Textbook . . . 4
References . . . 4

2 The Concept of the Atom . . . 7
2.1 Historical Development . . . 7
2.2 Experimental and Theoretical Proofs for the Existence of Atoms . . . 8
2.2.1 Dalton's Law of Constant Proportions . . . 9
2.2.2 The Law of Gay-Lussac and the Definition of the Mole . . . 10
2.2.3 Experimental Methods for the Determination of Avogadro's Constant . . . 12
2.2.4 The Importance of Kinetic Gas Theory for the Concept of Atoms . . . 16
2.3 Can One See Atoms? . . . 18
2.3.1 Brownian Motion . . . 19
2.3.2 Cloud Chamber . . . 22
2.3.3 Microscopes with Atomic Resolution . . . 22
2.4 The Size of Atoms . . . 27
2.4.1 The Size of Atoms in the Van der Waals Equation . . . 27
2.4.2 Atomic Size Estimation from Transport Coefficients . . . 27
2.4.3 Atomic Volumes from X-Ray Diffraction . . . 29
2.4.4 Comparison of the Different Methods . . . 30
2.5 The Electric Structure of Atoms . . . 31
2.5.1 Cathode Rays and Kanalstrahlen . . . 32
2.5.2 Measurement of the Elementary Charge e . . . 33
2.5.3 How to Produce Free Electrons . . . 34
2.5.4 Generation of Free Ions . . . 35
2.5.5 The Mass of the Electron . . . 38
2.5.6 How Neutral is the Atom? . . . 40
2.6 Electron and Ion Optics . . . 42
2.6.1 Refraction of Electron Beams . . . 42
2.6.2 Electron Optics in Axially Symmetric Fields . . . 43
2.6.3 Electrostatic Electron Lenses . . . 45
2.6.4 Magnetic Lenses . . . 46
2.6.5 Applications of Electron and Ion Optics . . . 48
2.7 Atomic Masses and Mass Spectrometers . . . 48
2.7.1 J.J. Thomson's Parabola Spectrograph . . . 49
2.7.2 Velocity-Independent Focusing . . . 50
2.7.3 Focusing of Ions with Different Angles of Incidence . . . 52
2.7.4 Mass Spectrometer with Double Focusing . . . 53
2.7.5 Time-of-Flight Mass Spectrometer . . . 54
2.7.6 Quadrupole Mass Spectrometer . . . 56

2.7.7 Ion-Cyclotron-Resonance Spectrometer . . . 57
2.7.8 Isotopes . . . 59
2.8 The Structure of Atoms . . . 59
2.8.1 Integral and Differential Cross Sections . . . 60
2.8.2 Basic Concepts of Classical Scattering . . . 61
2.8.3 Determination of the Charge Distribution within the Atom from Scattering Experiments . . . 65
2.8.4 Thomson's Atomic Model . . . 65
2.8.5 Rutherford's Scattering Experiments . . . 66
2.8.6 The Rutherford Atomic Model . . . 67
2.8.7 Rutherford's Scattering Formula . . . 68
Summary . . . 71
Problems . . . 72
References . . . 73

3 Development of Quantum Physics . . . 75
3.1 Experimental Hints to the Particle Character of Electromagnetic Radiation . . . 75
3.1.1 Blackbody Radiation . . . 76
3.1.2 Cavity Modes . . . 77
3.1.3 Planck's Radiation Law . . . 79
3.1.4 Wien's Law . . . 81
3.1.5 Stefan–Boltzmann's Radiation Law . . . 81
3.1.6 Photoelectric Effect . . . 82
3.1.7 Compton Effect . . . 84
3.1.8 Properties of Photons . . . 86
3.1.9 Photons in Gravitational Fields . . . 87
3.1.10 Wave and Particle Aspects of Light . . . 88
3.2 Wave Properties of Particles . . . 89
3.2.1 De Broglie Wavelength and Electron Diffraction . . . 90
3.2.2 Diffraction and Interference of Atoms . . . 91
3.2.3 Bragg Reflection and the Neutron Spectrometer . . . 92
3.2.4 Neutron and Atom Interferometry . . . 93
3.2.5 Application of Particle Waves . . . 94
3.3 Matter Waves and Wave Functions . . . 94
3.3.1 Wave Packets . . . 95
3.3.2 The Statistical Interpretation of Wave Functions . . . 97
3.3.3 Heisenberg's Uncertainty Principle . . . 99
3.3.4 Dispersion of the Wave Packet . . . 102
3.3.5 Uncertainty Relation for Energy and Time . . . 102
3.4 The Quantum Structure of Atoms . . . 104
3.4.1 Atomic Spectra . . . 104
3.4.2 Bohr's Atomic Model . . . 105
3.4.3 The Stability of Atoms . . . 108
3.4.4 Franck–Hertz Experiment . . . 109
3.5 What are the Differences Between Classical and Quantum Physics? . . . 111
3.5.1 Classical Particle Paths Versus Probability Densities in Quantum Physics . . . 111
3.5.2 Interference Phenomena with Light Waves and Matter Waves . . . 112
3.5.3 The Effect of the Measuring Process . . . 114
3.5.4 The Importance of Quantum Physics for our Concept of Nature . . . 115
Summary . . . 117
Problems . . . 118
References . . . 118

4 Basic Concepts of Quantum Mechanics . . . 119
4.1 The Schrödinger Equation . . . 119
4.2 Some Examples . . . 121
4.2.1 The Free Particle . . . 121
4.2.2 Potential Barrier . . . 122
4.2.3 Tunnel Effect . . . 125
4.2.4 Particle in a Potential Box . . . 127
4.2.5 Harmonic Oscillator . . . 130
4.3 Two-and Three-Dimensional Problems . . . 133
4.3.1 Particle in a Two-dimensional Box . . . 133
4.3.2 Particle in a Spherically Symmetric Potential . . . 134
4.4 Expectation Values and Operators . . . 138
4.4.1 Operators and Eigenvalues . . . 138
4.4.2 Angular Momentum in Quantum Mechanics . . . 141
Summary . . . 144
Problems . . . 145
References . . . 145

5 The Hydrogen Atom . . . 147
5.1 Schrödinger Equation for One-electron Systems . . . 147
5.1.1 Separation of the Center of Mass and Relative Motion . . . 147
5.1.2 Solution of the Radial Equation . . . 149
5.1.3 Quantum Numbers and Wave Functions of the H Atom . . . 151
5.1.4 Spatial Distributions and Expectation Values of the Electron in Different Quantum States . . . 152
5.2 The Normal Zeeman Effect . . . 155
5.3 Comparison of Schrödinger Theory with Experimental Results . . . 158
5.4 Relativistic Correction of Energy Terms . . . 159
5.5 The Electron Spin . . . 161
5.5.1 The Stern–Gerlach Experiment . . . 162
5.5.2 Experimental Confirmation of Electron Spin . . . 163
5.5.3 Einstein–de Haas Effect . . . 164
5.5.4 Spin-Orbit Coupling and Fine Structure . . . 165
5.5.5 Anomalous Zeeman Effect . . . 168
5.6 Hyperfine Structure . . . 170
5.6.1 Basic Considerations . . . 170
5.6.2 Fermi-contact Interaction . . . 172
5.6.3 Magnetic Dipole-Dipole Interaction . . . 172
5.6.4 Zeeman Effect of Hyperfine Structure Levels . . . 173
5.7 Complete Description of the Hydrogen Atom . . . 173
5.7.1 Total Wave Function and Quantum Numbers . . . 174
5.7.2 Term Assignment and Level Scheme . . . 174
5.7.3 Lamb Shift . . . 176
5.8 Correspondence Principle . . . 179
5.9 The Electron Model and its Problems . . . 180
Summary . . . 183
Problems . . . 185
References . . . 185

6 Atoms with More Than One Electron . . . 187
6.1 The Helium Atom . . . 187
6.1.1 Approximation Models . . . 188
6.1.2 Symmetry of the Wave Function . . . 189
6.1.3 Consideration of the Electron Spin . . . 190

6.1.4 The Pauli Principle . . . 191
6.1.5 Energy Levels of the Helium Atom . . . 192
6.1.6 Helium Spectrum . . . 193
6.2 Building-up Principle of the Electron Shell for Larger Atoms . . . 194
6.2.1 The Model of Electron Shells . . . 195
6.2.2 Successive Building-up of Electron Shells for Atoms with Increasing Nuclear Charge . . . 196
6.2.3 Atomic Volumes and Ionization Energies . . . 197
6.2.4 The Periodic System of the Elements . . . 201
6.3 Alkali Atoms . . . 203
6.4 Theoretical Models for Multielectron Atoms . . . 206
6.4.1 The Model of Independent Electrons . . . 206
6.4.2 The Hartree Method . . . 207
6.4.3 The Hartree–Fock Method . . . 208
6.4.4 Configuration Interaction . . . 208
6.5 Electron Configurations and Couplings of Angular Momenta . . . 209
6.5.1 Coupling Schemes for Electronic Angular Momenta . . . 209
6.5.2 Electron Configuration and Atomic States . . . 213
6.6 Excited Atomic States . . . 215
6.6.1 Single Electron Excitation . . . 216
6.6.2 Simultaneous Excitation of Two Electrons . . . 216
6.6.3 Inner-Shell Excitation and the Auger Process . . . 217
6.6.4 Rydberg States . . . 218
6.6.5 Planetary Atoms . . . 220
6.7 Exotic Atoms . . . 221
6.7.1 Muonic Atoms . . . 221
6.7.2 Pionic and Kaonic Atoms . . . 222
6.7.3 Anti-hydrogen Atoms and Other Anti-atoms . . . 223
6.7.4 Positronium and Muonium . . . 224
Summary . . . 226
Problems . . . 228
References . . . 228

7 Emission and Absorption of Electromagnetic Radiation by Atoms . . . 229
7.1 Transition Probabilities . . . 230
7.1.1 Induced and Spontaneous Transitions, Einstein Coefficients . . . 230
7.1.2 Transition Probabilities, Einstein Coefficients and Matrix Elements . . . 232
7.1.3 Transition Probabilities for Absorption and Induced Emission . . . 234
7.2 Selection Rules . . . 235
7.2.1 Selection Rules for Spontaneous Emission . . . 235
7.2.2 Selection Rules for the Magnetic Quantum Number . . . 236
7.2.3 Parity Selection Rules . . . 237
7.2.4 Selection Rules for Induced Absorption and Emission . . . 237
7.2.5 Selection Rules for the Spin Quantum Number . . . 238
7.2.6 Higher Order Multipole Transitions . . . 239
7.2.7 Magnetic Dipole Transitions . . . 240
7.2.8 Two-Photon-Transitions . . . 240
7.3 Lifetimes of Excited States . . . 240
7.4 Line Profiles of Spectral Lines . . . 242
7.4.1 Natural Linewidth . . . 243
7.4.2 Doppler Broadening . . . 245
7.4.3 Collision Broadening . . . 247

7.5 X-Rays . . . 250
7.5.1 Bremsstrahlung . . . 251
7.5.2 Characteristic X-Ray-Radiation . . . 252
7.5.3 Scattering and Absorption of X-Rays . . . 253
7.5.4 X-ray Fluorescence . . . 257
7.5.5 Measurements of X-Ray Wavelengths . . . 257
7.6 Continuous Absorption and Emission Spectra . . . 259
7.6.1 Photoionization . . . 260
7.6.2 Recombination Radiation . . . 262
Summary . . . 265
Problems . . . 267
References . . . 268

8 Lasers . . . 269
8.1 Physical Principles . . . 269
8.1.1 Threshold Condition . . . 270
8.1.2 Generation of Population Inversion . . . 272
8.1.3 The Frequency Spectrum of Induced Emission . . . 274
8.2 Optical Resonators . . . 274
8.2.1 The Quality Factor of Resonators . . . 275
8.2.2 Open Optical Resonators . . . 275
8.2.3 Modes of Open Resonators . . . 277
8.2.4 Diffraction Losses of Open Resonators . . . 279
8.2.5 The Frequency Spectrum of Optical Resonators . . . 279
8.3 Single Mode Lasers . . . 280
8.4 Different Types of Lasers . . . 283
8.4.1 Solid-state Lasers . . . 283
8.4.2 Semiconductor Lasers . . . 285
8.4.3 Dye Lasers . . . 286
8.4.4 Gas Lasers . . . 288
8.4.5 Free Electron Laser . . . 291
8.5 Nonlinear Optics . . . 292
8.5.1 Optical Frequency Doubling . . . 293
8.5.2 Phase Matching . . . 293
8.5.3 Optical Frequency Mixing . . . 294
8.6 Generation of Short Laser Pulses . . . 295
8.6.1 Q-Switched Lasers . . . 295
8.6.2 Mode-Locking of Lasers . . . 296
8.6.3 Optical Pulse Compression . . . 299
8.6.4 Measurements of Ultrashort Optical Pulses . . . 300
Summary . . . 302
Problems . . . 303
References . . . 303

9 Diatomic Molecules . . . 305
9.1 The H_2^+ Molecular Ion . . . 305
9.1.1 The Exact Solution for the Rigid H_2^+ Molecule . . . 306
9.1.2 Molecular Orbitals and LCAO Approximations . . . 309
9.1.3 Improvements to the LCAO ansatz . . . 311
9.2 The H_2 Molecule . . . 312
9.2.1 Molecular Orbital Approximation . . . 313
9.2.2 The Heitler–London Method . . . 314
9.2.3 Comparison Between the Two Approximations . . . 314
9.2.4 Improvements to the Approximations . . . 315

9.3 Electronic States of Diatomic Molecules . . . 316
9.3.1 The Energetic Order of Electronic States . . . 317
9.3.2 Symmetry Properties of Electronic States . . . 317
9.3.3 Electronic Angular Momenta . . . 318
9.3.4 Electron Spins, Multiplicity and Fine Structure Splittings . . . 319
9.3.5 Electron Configurations and Molecular Ground States . . . 320
9.3.6 Excited Molecular States . . . 322
9.3.7 Excimers . . . 323
9.3.8 Correlation Diagrams . . . 323
9.4 The Physical Reasons for Molecular Binding . . . 324
9.4.1 The Chemical Bond . . . 325
9.4.2 Multipole Interaction . . . 325
9.4.3 Induced Dipole Moments and van der Waals Potential . . . 327
9.4.4 General Expansion of the Interaction Potential . . . 330
9.4.5 The Morse Potential . . . 330
9.4.6 Different Binding Types . . . 331
9.5 Rotation and Vibration of Diatomic Molecules . . . 332
9.5.1 The Born-Oppenheimer Approximation . . . 332
9.5.2 The Rigid Rotor . . . 334
9.5.3 Centrifugal Distortion . . . 335
9.5.4 The Influence of the Electron Motion . . . 336
9.5.5 Vibrations of Diatomic Molecules . . . 337
9.5.6 Interaction Between Rotation and Vibration . . . 338
9.5.7 The Dunham Expansion . . . 340
9.5.8 Rotational Barrier . . . 340
9.6 Spectra of Diatomic Molecules . . . 341
9.6.1 Transition Matrix Elements . . . 342
9.6.2 Vibrational-Rotational Transitions . . . 343
9.6.3 The Structure of Electronic Transitions . . . 346
9.6.4 Continuous Spectra . . . 350
Summary . . . 354
Problems . . . 355
References . . . 355

10 Polyatomic Molecules . . . 357
10.1 Electronic States of Polyatomic Molecules . . . 357
10.1.1 The H_2O Molecule . . . 357
10.1.2 Hybridization . . . 358
10.1.3 The CO_2 Molecule . . . 361
10.1.4 Walsh Diagrams . . . 362
10.2 Molecules with more than Three Atoms . . . 363
10.2.1 The NH_3 Molecule . . . 364
10.2.2 Formaldehyde and Other H_2AB Molecules . . . 365
10.2.3 Aromatic Molecules and π-Electron Systems . . . 365
10.3 Rotation of Polyatomic Molecules . . . 367
10.3.1 Rotation of Symmetric Top Molecules . . . 369
10.3.2 Asymmetric Rotor Molecules . . . 371
10.4 Vibrations of Polyatomic Molecules . . . 371
10.4.1 Normal Vibrations . . . 371
10.4.2 Quantitative Treatment . . . 372
10.4.3 Couplings Between Vibrations and Rotations . . . 374
10.5 Spectra of Polyatomic Molecules . . . 375
10.5.1 Vibrational Transitions within the Same Electronic State . . . 376
10.5.2 Rotational Structure of Vibrational Bands . . . 377
10.5.3 Electronic Transitions . . . 378

10.6 Molecular Symmetry and Spectroscopy . . . 379
10.7 Clusters . . . 380
10.7.1 Production of Clusters . . . 382
10.7.2 Physical Properties of Clusters . . . 383
10.8 Chemical Reactions . . . 384
10.8.1 First Order Reactions . . . 385
10.8.2 Second Order Reactions . . . 385
10.8.3 Exothermic and Endothermic Reactions . . . 386
10.8.4 Determination of Absolute Reaction Rates . . . 387
10.9 Molecular Dynamics and Wave Packets . . . 388
Summary . . . 390
Problems . . . 391
References . . . 391

11 Experimental Techniques in Atomic and Molecular Physics . . . 393
11.1 Basic Principles of Spectroscopic Techniques . . . 394
11.2 Spectroscopic Instruments . . . 395
11.2.1 Spectrometers . . . 395
11.2.2 Interferometers . . . 400
11.2.3 Detectors . . . 404
11.3 Microwave Spectroscopy . . . 408
11.4 Infrared Spectroscopy . . . 410
11.4.1 Infrared Spectrometers . . . 410
11.4.2 Fourier Transform Spectroscopy . . . 410
11.5 Laser Spectroscopy . . . 414
11.5.1 Laser-Absorption Spectroscopy . . . 414
11.5.2 Optoacoustic Spectroscopy . . . 415
11.5.3 Optogalvanic Spectroscopy . . . 416
11.5.4 Cavity-Ringdown Spectroscopy . . . 417
11.5.5 Laser-Induced Fluorescence Spectroscopy . . . 419
11.5.6 Ionization Spectroscopy . . . 420
11.5.7 Laser Spectroscopy in Molecular Beams . . . 422
11.5.8 Nonlinear Laser Spectroscopy . . . 423
11.5.9 Saturation Spectroscopy . . . 424
11.5.10 Doppler-Free Two-Photon Spectroscopy . . . 426
11.6 Raman Spectroscopy . . . 428
11.6.1 Basic Principles . . . 428
11.6.2 Coherent Anti-Stokes Raman Spectroscopy . . . 429
11.7 Spectroscopy with Synchrotron Radiation . . . 431
11.8 Electron Spectroscopy . . . 433
11.8.1 Experiments on Electron Scattering . . . 433
11.8.2 Photoelectron Spectroscopy . . . 434
11.8.3 ZEKE Spectroscopy . . . 437
11.9 Measurements of Magnetic and Electric Moments in Atoms and Molecules . . . 437
11.9.1 The Rabi-Method of Radio-Frequency Spectroscopy . . . 438
11.9.2 Stark-Spectroscopy . . . 440
11.10 Investigations of Atomic and Molecular Collisions . . . 441
11.10.1 Elastic Scattering . . . 441
11.10.2 Inelastic Scattering . . . 444
11.10.3 Reactive Scattering . . . 445

11.11 Time-Resolved Measurements of Atoms and Molecules . . . 446
11.11.1 Lifetime Measurements . . . 446
11.11.2 Fast Relaxation Processes in Atoms and Molecules . . . 449
Summary . . . 450
Problems . . . 451
References . . . 451

12 Modern Developments in Atomic and Molecular Physics . . . 453
12.1 Optical Cooling and Trapping of Atoms . . . 453
12.1.1 Photon Recoil . . . 453
12.1.2 Optical Cooling of Atoms . . . 455
12.1.3 Cooling Limits . . . 456
12.1.4 Optical Trapping of Atoms . . . 457
12.1.5 Bose–Einstein Condensation . . . 459
12.1.6 Atomic Fountain . . . 461
12.1.7 Molecular Spectroscopy in a MOT . . . 461
12.1.8 Optical Lattices . . . 462
12.2 Time-resolved Spectroscopy in the Femtosecond Range . . . 463
12.2.1 Time-resolved Molecular Vibrations . . . 463
12.2.2 Femtosecond Transition State Dynamics . . . 464
12.2.3 Coherent Control . . . 465
12.3 Optical Metrology with New Techniques . . . 467
12.3.1 Frequency Comb . . . 467
12.3.2 Atomic Clocks with Trapped Ions . . . 469
12.4 Squeezing . . . 470
12.5 New Trends in Quantum Optics . . . 476
12.5.1 Which Way Experiments . . . 476
12.5.2 The Einstein–Podolski–Rosen Paradox . . . 477
12.5.3 Schrödinger's Cat . . . 478
12.5.4 Entanglement and Quantum Bits . . . 478
12.5.5 Quantum Gates . . . 480
Summary . . . 483
Problems . . . 484
References . . . 484

Chronological Table for the Development of Atomic and Molecular Physics . . . 487

Solutions to the Exercises . . . 491

Index . . . 541