

Contents

1. Introduction

| | | |
|-----|---|---|
| 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 |

2. The Concept of the Atom

| | | |
|-------|--|----|
| 2.1 | Historical Development | 7 |
| 2.2 | Experimental and Theoretical Proofs for the Existence of Atoms .. | 9 |
| 2.2.1 | Dalton's Law of Constant Proportions | 9 |
| 2.2.2 | The Law of Gay-Lussac and the Definition of the Mole .. | 11 |
| 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 | 17 |
| 2.3 | Can One See Atoms? | 19 |
| 2.3.1 | Brownian Motion | 20 |
| 2.3.2 | Cloud Chamber | 23 |
| 2.3.3 | Microscopes with Atomic Resolution | 23 |
| 2.4 | The Size of Atoms | 28 |
| 2.4.1 | The Size of Atoms in the Van der Waals Equation | 28 |
| 2.4.2 | Atomic Size Estimation from Transport Coefficients | 28 |
| 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 | 37 |
| 2.5.5 | The Mass of the Electron | 39 |
| 2.5.6 | How Neutral is the Atom? | 42 |
| 2.6 | Electron and Ion Optics | 43 |
| 2.6.1 | Refraction of Electron Beams | 43 |
| 2.6.2 | Electron Optics in Axially Symmetric Fields | 45 |
| 2.6.3 | Electrostatic Electron Lenses | 47 |
| 2.6.4 | Magnetic Lenses | 48 |
| 2.6.5 | Applications of Electron and Ion Optics | 50 |

| | | |
|-------|---|----|
| 2.7 | Atomic Masses and Mass Spectrometers | 51 |
| 2.7.1 | J.J. Thomson's Parabola Spectrograph | 51 |
| 2.7.2 | Velocity-Independent Focusing | 53 |
| 2.7.3 | Focusing of Ions with Different Angles of Incidence | 54 |
| 2.7.4 | Mass Spectrometer with Double Focusing | 55 |
| 2.7.5 | Time-of-Flight Mass Spectrometer | 55 |
| 2.7.6 | Quadrupole Mass Spectrometer | 58 |
| 2.7.7 | Ion-Cyclotron-Resonance Spectrometer | 60 |
| 2.7.8 | Isotopes | 61 |
| 2.8 | The Structure of Atoms | 62 |
| 2.8.1 | Integral and Differential Cross Sections | 62 |
| 2.8.2 | Basic Concepts of Classical Scattering | 64 |
| 2.8.3 | Determination of the Charge Distribution within the Atom from Scattering Experiments | 68 |
| 2.8.4 | Thomson's Atomic Model | 68 |
| 2.8.5 | The Rutherford Atomic Model | 70 |
| 2.8.6 | Rutherford's Scattering Formula | 71 |
| | Summary | 74 |
| | Problems | 76 |

3. Development of Quantum Physics

| | | |
|-------|--|-----|
| 3.1 | Experimental Hints to the Particle Character of Electromagnetic Radiation | 79 |
| 3.1.1 | Blackbody Radiation | 80 |
| 3.1.2 | Planck's Radiation Law | 82 |
| 3.1.3 | Wien's Law | 86 |
| 3.1.4 | Stefan-Boltzmann's Radiation Law | 86 |
| 3.1.5 | Photoelectric Effect | 87 |
| 3.1.6 | Compton Effect | 89 |
| 3.1.7 | Properties of Photons | 91 |
| 3.1.8 | Photons in Gravitational Fields | 92 |
| 3.1.9 | Wave and Particle Aspects of Light | 92 |
| 3.2 | Wave Properties of Particles | 94 |
| 3.2.1 | De Broglie Wavelength and Electron Diffraction | 95 |
| 3.2.2 | Diffraction and Interference of Atoms | 96 |
| 3.2.3 | Bragg Reflection and the Neutron Spectrometer | 97 |
| 3.2.4 | Neutron and Atom Interferometry | 98 |
| 3.2.5 | Application of Particle Waves | 99 |
| 3.3 | Matter Waves and Wave Functions | 100 |
| 3.3.1 | Wave Packets | 100 |
| 3.3.2 | The Statistical Interpretation of Wave Functions | 103 |
| 3.3.3 | Heisenberg's Uncertainty Principle | 104 |
| 3.3.4 | Dispersion of the Wave Packet | 107 |
| 3.3.5 | Uncertainty Relation for Energy and Time | 108 |
| 3.4 | The Quantum Structure of Atoms | 109 |
| 3.4.1 | Atomic Spectra | 109 |
| 3.4.2 | Bohr's Atomic Model | 112 |

| | | |
|-----------|---|-----|
| 3.4.3 | The Stability of Atoms | 115 |
| 3.4.4 | Franck–Hertz Experiment | 115 |
| 3.5 | What are the Differences Between Classical and Quantum Physics? | 117 |
| 3.5.1 | Classical Particle Paths Versus Probability Densities in Quantum Physics | 118 |
| 3.5.2 | Interference Phenomena with Light Waves and Matter Waves | 119 |
| 3.5.3 | The Effect of the Measuring Process | 121 |
| 3.5.4 | The Importance of Quantum Physics for our Concept of Nature | 122 |
| | Summary | 123 |
| | Problems | 124 |
| 4. | Basic Concepts of Quantum Mechanics | |
| 4.1 | The Schrödinger Equation | 127 |
| 4.2 | Some Examples | 129 |
| 4.2.1 | The Free Particle | 129 |
| 4.2.2 | Potential Barrier | 130 |
| 4.2.3 | Tunnel Effect | 133 |
| 4.2.4 | Particle in a Potential Box | 136 |
| 4.2.5 | Harmonic Oscillator | 139 |
| 4.3 | Two- and Three-Dimensional Problems | 142 |
| 4.3.1 | Particle in a Two-dimensional Box | 142 |
| 4.3.2 | Particle in a Spherically Symmetric Potential | 143 |
| 4.4 | Expectation Values and Operators | 147 |
| 4.4.1 | Operators and Eigenvalues | 148 |
| 4.4.2 | Angular Momentum in Quantum Mechanics | 150 |
| | Summary | 153 |
| | Problems | 154 |
| 5. | The Hydrogen Atom | |
| 5.1 | Schrödinger Equation for One-electron Systems | 157 |
| 5.1.1 | Separation of the Center of Mass and Relative Motion ... | 157 |
| 5.1.2 | Solution of the Radial Equation | 159 |
| 5.1.3 | Quantum Numbers and Wave Functions of the H Atom .. | 161 |
| 5.1.4 | Spatial Distributions and Expectation Values of the Electron in Different Quantum States | 163 |
| 5.2 | The Normal Zeeman Effect | 166 |
| 5.3 | Comparison of Schrödinger Theory with Experimental Results ... | 168 |
| 5.4 | Relativistic Correction of Energy terms | 170 |
| 5.5 | The Stern–Gerlach Experiment | 171 |
| 5.6 | Electron Spin | 172 |
| 5.6.1 | Einstein–de Haas Effect | 173 |
| 5.6.2 | Spin-Orbit Coupling and Fine structure | 174 |
| 5.6.3 | Anomalous Zeeman Effect | 177 |

| | | |
|-------|---|-----|
| 5.7 | Hyperfine Structure | 180 |
| 5.7.1 | Basic Considerations | 180 |
| 5.7.2 | Fermi-contact Interaction | 182 |
| 5.7.3 | Magnetic Dipole-Dipole Interaction | 182 |
| 5.7.4 | Zeeman Effect of Hyperfine Structure Levels | 183 |
| 5.8 | Complete Description of the Hydrogen Atom | 184 |
| 5.8.1 | Total Wave Function and Quantum Numbers | 184 |
| 5.8.2 | Term Assignment and Level Scheme | 184 |
| 5.8.3 | Lamb Shift | 185 |
| 5.9 | Correspondence Principle | 190 |
| 5.10 | The Electron Model and its Problems | 191 |
| | Summary | 193 |
| | Problems | 195 |

6. Atoms with More Than One Electron

| | | |
|-------|---|-----|
| 6.1 | The Helium Atom | 197 |
| 6.1.1 | Approximation Models | 198 |
| 6.1.2 | Symmetry of the Wave Function | 199 |
| 6.1.3 | Consideration of the Electron Spin | 200 |
| 6.1.4 | The Pauli Principle | 201 |
| 6.1.5 | Energy Levels of the Helium Atom | 202 |
| 6.1.6 | Helium Spectrum | 204 |
| 6.2 | Building-up Principle of the Electron Shell for Larger Atoms | 205 |
| 6.2.1 | The Model of Electron Shells | 205 |
| 6.2.2 | Successive Building-up of Electron Shells for Atoms with Increasing Nuclear Charge | 206 |
| 6.2.3 | Atomic Volumes and Ionization Energies | 208 |
| 6.2.4 | The Periodic System of the Elements | 211 |
| 6.3 | Alkali Atoms | 214 |
| 6.4 | Theoretical Models for Multielectron Atoms | 217 |
| 6.4.1 | The Model of Independent Electrons | 217 |
| 6.4.2 | The Hartree Method | 218 |
| 6.4.3 | The Hartree-Fock Method | 219 |
| 6.4.4 | Configuration Interaction | 219 |
| 6.5 | Electron Configurations and Couplings of Angular Momenta | 220 |
| 6.5.1 | Coupling Schemes for Electronic Angular Momenta | 220 |
| 6.5.2 | Electron Configuration and Atomic States | 225 |
| 6.6 | Excited Atomic States | 227 |
| 6.6.1 | Single Electron Excitation | 227 |
| 6.6.2 | Simultaneous Excitation of Two Electrons | 228 |
| 6.6.3 | Inner-Shell Excitation and the Auger Process | 229 |
| 6.6.4 | Rydberg States | 229 |
| 6.6.5 | Planetary Atoms | 232 |
| 6.7 | Exotic Atoms | 233 |
| 6.7.1 | Myonic Atoms | 233 |
| 6.7.2 | Pionic and Kaonic Atoms | 235 |

| | | |
|-----------|--|-----|
| 6.7.3 | Anti-hydrogen Atoms and Other Anti-atoms | 235 |
| 6.7.4 | Positronium and Myonium | 237 |
| | Summary | 238 |
| | Problems | 240 |
| 7. | Emission and Absorption of Electromagnetic Radiation by Atoms ■■■■■ | |
| 7.1 | Transition Probabilities | 242 |
| 7.1.1 | Induced and Spontaneous Transitions, Einstein Coefficients | 242 |
| 7.1.2 | Transition Probabilities and Matrix elements | 244 |
| 7.1.3 | Transition Probabilities for Absorption and Induced Emission | 246 |
| 7.2 | Selection Rules | 247 |
| 7.2.1 | Selection Rules for the Magnetic Quantum Number | 248 |
| 7.2.2 | Parity Selection Rules | 249 |
| 7.2.3 | Selection Rules for the Spin Quantum Number | 250 |
| 7.2.4 | Higher Order Multipole Transitions | 251 |
| 7.2.5 | Magnetic dipole transitions | 252 |
| 7.2.6 | Two-Photon-Transitions | 253 |
| 7.3 | Lifetimes of Excited States | 253 |
| 7.4 | Line Profiles of Spectral Lines | 255 |
| 7.4.1 | Natural Linewidth | 256 |
| 7.4.2 | Doppler Broadening | 258 |
| 7.4.3 | Collision Broadening | 260 |
| 7.5 | X-Rays | 263 |
| 7.5.1 | Bremsstrahlung | 264 |
| 7.5.2 | Characteristic X-Ray-Radiation | 266 |
| 7.5.3 | Scattering and Absorption of X-Rays | 266 |
| 7.5.4 | X-ray Fluorescence | 271 |
| 7.5.5 | Measurements of X-Ray Wavelengths | 271 |
| 7.6 | Continuous Absorption and Emission Spectra | 273 |
| 7.6.1 | Photoionization | 274 |
| 7.6.2 | Recombination Radiation | 277 |
| | Summary | 279 |
| | Problems | 280 |
| 8. | Lasers ■■■■■ | |
| 8.1 | Physical Principles | 283 |
| 8.1.1 | Threshold Condition | 284 |
| 8.1.2 | Generation of Population Inversion | 286 |
| 8.1.3 | The Frequency Spectrum of Induced Emission | 288 |
| 8.2 | Optical Resonators | 289 |
| 8.2.1 | The Quality Factor of Resonators | 289 |
| 8.2.2 | Open Optical Resonators | 290 |
| 8.2.3 | Modes of Open Resonators | 291 |
| 8.2.4 | Diffraction Losses of Open Resonators | 294 |
| 8.2.5 | The Frequency Spectrum of Optical Resonators | 294 |

| | | |
|-------|---|-----|
| 8.3 | Single Mode Lasers | 295 |
| 8.4 | Different Types of Lasers | 298 |
| 8.4.1 | Solid-state Lasers | 299 |
| 8.4.2 | Semiconductor Lasers | 300 |
| 8.4.3 | Dye lasers | 301 |
| 8.4.4 | Gas Lasers | 304 |
| 8.5 | Nonlinear Optics | 307 |
| 8.5.1 | Optical Frequency Doubling | 308 |
| 8.5.2 | Phase Matching | 308 |
| 8.5.3 | Optical Frequency Mixing | 309 |
| 8.6 | Generation of Short Laser Pulses | 310 |
| 8.6.1 | Q-Switched Lasers | 310 |
| 8.6.2 | Mode-Locking of Lasers | 311 |
| 8.6.3 | Optical Pulse Compression | 314 |
| 8.6.4 | Measurements of Ultrashort Optical Pulses | 316 |
| | Summary | 318 |
| | Problems | 318 |

9. Diatomic Molecules

| | | |
|-------|--|-----|
| 9.1 | The H_2^+ Molecular Ion | 321 |
| 9.1.1 | The Exact Solution for the Rigid H_2^+ Molecule | 322 |
| 9.1.2 | Molecular Orbitals and LCAO Approximations | 325 |
| 9.1.3 | Improvements to the LCAO ansatz | 327 |
| 9.2 | The H_2 Molecule | 329 |
| 9.2.1 | Molecular Orbital Approximation | 329 |
| 9.2.2 | The Heitler–London Method | 331 |
| 9.2.3 | Comparison Between the Two Approximations | 331 |
| 9.2.4 | Improvements to the Approximations | 332 |
| 9.3 | Electronic States of Diatomic Molecules | 333 |
| 9.3.1 | The Energetic Order of Electronic States | 333 |
| 9.3.2 | Symmetry Properties of Electronic States | 334 |
| 9.3.3 | Electronic Angular Momenta | 335 |
| 9.3.4 | Electron Spins, Multiplicity and Fine Structure Splittings | 336 |
| 9.3.5 | Electron Configurations and Molecular Ground States | 337 |
| 9.3.6 | Excited Molecular States | 338 |
| 9.3.7 | Excimers | 340 |
| 9.3.8 | Correlation Diagrams | 340 |
| 9.4 | The Physical Reasons for Molecular Binding | 341 |
| 9.4.1 | The Chemical Bond | 341 |
| 9.4.2 | Multipole Interaction | 342 |
| 9.4.3 | Induced Dipole Moments and van der Waals Potential | 344 |
| 9.4.4 | General Expansion of the Interaction Potential | 347 |
| 9.4.5 | The Morse Potential | 347 |
| 9.4.6 | Different Binding Types | 348 |
| 9.5 | Rotation and Vibration of Diatomic Molecules | 349 |
| 9.5.1 | The Adiabatic Approximation | 349 |
| 9.5.2 | The Rigid Rotor | 350 |

| | | |
|-------|--|-----|
| 9.5.3 | Centrifugal Distortion | 352 |
| 9.5.4 | The Influence of the Electron Motion | 353 |
| 9.5.5 | Vibrations of Diatomic Molecules | 354 |
| 9.5.6 | Interaction Between Rotation and Vibration | 355 |
| 9.5.7 | The Dunham Expansion | 357 |
| 9.5.8 | Rotational Barrier | 357 |
| 9.6 | Spectra of Diatomic Molecules | 358 |
| 9.6.1 | Transition Matrix Elements | 358 |
| 9.6.2 | Vibrational-Rotational Transitions | 360 |
| 9.6.3 | The Structure of Electronic Transitions | 362 |
| 9.6.4 | Continuous Spectra | 367 |
| | Summary | 370 |
| | Problems | 371 |

10. Polyatomic Molecules

| | | |
|--------|--|-----|
| 10.1 | Electronic States of Polyatomic Molecules | 373 |
| 10.1.1 | The H ₂ O Molecule | 373 |
| 10.1.2 | Hybridization | 374 |
| 10.1.3 | The CO ₂ Molecule | 378 |
| 10.1.4 | Walsh Diagrams | 379 |
| 10.2 | Molecules with more than Three Atoms | 380 |
| 10.2.1 | The NH ₃ Molecule | 380 |
| 10.2.2 | Formaldehyde and Other H ₂ AB Molecules | 381 |
| 10.2.3 | Aromatic Molecules and π -Electron Systems | 382 |
| 10.3 | Rotation of Polyatomic Molecules | 384 |
| 10.3.1 | Rotation of Symmetric Top Molecules | 386 |
| 10.3.2 | Asymmetric Rotor Molecules | 388 |
| 10.4 | Vibrations of Polyatomic Molecules | 388 |
| 10.4.1 | Normal Vibrations | 388 |
| 10.4.2 | Quantitative Treatment | 389 |
| 10.4.3 | Couplings Between Vibrations and Rotations | 392 |
| 10.5 | Spectra of Polyatomic Molecules | 392 |
| 10.5.1 | Vibrational Transitions within the Same Electronic State | 393 |
| 10.5.2 | Rotational Structure of Vibrational Bands | 395 |
| 10.5.3 | Electronic Transitions | 395 |
| 10.6 | Clusters | 396 |
| 10.6.1 | Production of Clusters | 398 |
| 10.6.2 | Physical Properties of Clusters | 399 |
| 10.7 | Chemical Reactions | 401 |
| 10.7.1 | First Order Reactions | 401 |
| 10.7.2 | Second Order Reactions | 401 |
| 10.7.3 | Exothermic and Endothermic Reactions | 402 |
| 10.7.4 | Determination of Absolute Reaction Rates | 404 |
| 10.8 | Molecular Dynamics and Wave packets | 405 |
| | Summary | 406 |
| | Problems | 408 |

11. Experimental Techniques in Atomic and Molecular Physics

| | | |
|---------|---|-----|
| 11.1 | Basic Principles of Spectroscopic Techniques | 410 |
| 11.2 | Spectroscopic Instruments | 411 |
| 11.2.1 | Spectrometers | 411 |
| 11.2.2 | Interferometers | 417 |
| 11.2.3 | Detectors | 421 |
| 11.3 | Microwave Spectroscopy | 425 |
| 11.4 | Infrared Spectroscopy | 428 |
| 11.4.1 | Infrared Spectrometers | 428 |
| 11.4.2 | Fourier Transform Spectroscopy | 428 |
| 11.5 | Laser Spectroscopy | 432 |
| 11.5.1 | Laser-Absorption Spectroscopy | 432 |
| 11.5.2 | Optoacoustic Spectroscopy | 434 |
| 11.5.3 | Optogalvanic Spectroscopy | 435 |
| 11.5.4 | Cavity-Ringdown Spectroscopy | 436 |
| 11.5.5 | Laser-Induced Fluorescence Spectroscopy | 438 |
| 11.5.6 | Ionization Spectroscopy | 439 |
| 11.5.7 | Laser Spectroscopy in Molecular Beams | 441 |
| 11.5.8 | Nonlinear Laser Spectroscopy | 443 |
| 11.5.9 | Saturation Spectroscopy | 444 |
| 11.5.10 | Doppler-Free Two-Photon Spectroscopy | 446 |
| 11.6 | Raman Spectroscopy | 447 |
| 11.6.1 | Basic Principles | 447 |
| 11.6.2 | Coherent Anti-Stokes Raman Spectroscopy | 449 |
| 11.7 | Spectroscopy with Synchrotron Radiation | 451 |
| 11.8 | Electron Spectroscopy | 453 |
| 11.8.1 | Experiments on Electron Scattering | 453 |
| 11.8.2 | Photoelectron Spectroscopy | 455 |
| 11.8.3 | ZEKE Spectroscopy | 457 |
| 11.9 | Measurements of Electric and Magnetic Moments in Atoms and Molecules | 457 |
| 11.9.1 | The Rabi-Method of Radio-Frequency Spectroscopy | 458 |
| 11.9.2 | Stark-Spectroscopy | 459 |
| 11.10 | Investigations of Atomic and Molecular Collisions | 461 |
| 11.10.1 | Elastic Scattering | 462 |
| 11.10.2 | Inelastic Scattering | 465 |
| 11.10.3 | Reactive Scattering | 466 |
| 11.11 | Time-Resolved Measurements of Atoms and Molecules | 466 |
| 11.11.1 | Lifetime Measurements | 467 |
| 11.11.2 | Fast Relaxation Processes in Atoms and Molecules | 470 |
| | Summary | 471 |
| | Problems | 472 |

12. Modern Developments in Atomic and Molecular Physics

| | | |
|--------|---|-----|
| 12.1 | Optical Cooling and Trapping of Atoms | 473 |
| 12.1.1 | Photon Recoil | 473 |
| 12.1.2 | Optical Cooling of Atoms | 475 |

| | | |
|--------|---|------------|
| 12.1.3 | Optical Trapping of Atoms | 477 |
| 12.1.4 | Bose–Einstein Condensation | 479 |
| 12.1.5 | Molecular Spectroscopy in a MOT | 481 |
| 12.2 | Time-resolved Spectroscopy in the Femtosecond Range | 482 |
| 12.2.1 | Time-resolved Molecular Vibrations | 482 |
| 12.2.2 | Femtosecond Transition State Dynamics | 483 |
| 12.2.3 | Coherent Control | 484 |
| 12.3 | Optical Metrology with New Techniques | 485 |
| 12.3.1 | Frequency Comb | 486 |
| 12.3.2 | Atomic Clocks with Trapped Ions | 487 |
| 12.4 | Squeezing | 489 |
| 12.5 | New Trends in Quantum Optics | 495 |
| 12.5.1 | Which Way Experiments | 495 |
| 12.5.2 | The Einstein–Podolski–Rosen Paradox | 497 |
| 12.5.3 | Schrödinger’s Cat | 498 |
| 12.5.4 | Entanglement and Quantum Bits | 498 |
| 12.5.5 | Quantum Gates | 500 |
| | Summary | 501 |
| | Problems | 502 |
| | Chronological Table | 503 |
| | Solutions to the Exercises | 507 |
| | References | 555 |
| | Subject Index | 563 |