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Igor I. Sobelman

Atomic Spectra and Radiative Transitions

With 21 Figures

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Preface

My previous book on the theory of atomic spectra was published in Russian about fifteen years ago. Besides the traditional problems usually included in a book on atomic spectroscopy, some other problems arising in various applications of spectroscopic methods were also discussed in the book. These include, for example, continuous spectrum radiation, excitation of atoms, and spectral line broadening. Extensive revisions were made in the English version of the book published by the Pergamon Press in 1972, especially in the chapter devoted to the problem of excitation of atoms.

This book is intended as the first part of a two-volume presentation of the theory of atomic spectra, atomic radiative transitions, excitation of atoms, and spectral line broadening. The aim in preparing these new books has been to stress the problems connected with the most interesting applications of atomic spectroscopy to plasma diagnostics, astrophysics, laser physics, and other fields, which have been developed very intensively in recent years.

The content of this first volume, devoted to the systematics of atomic spectra and radiative transitions, is similar to that of Chapters 1-6, 8 and 9 of the old book, but considerable revision has been made. Some sections, such as those on the Hartree-Fock method, the Dirac equation, and relativistic corrections, have been deleted. At the same time, more attention is paid to radiative transitions. More extensive tables of oscillator strengths, probabilities, and effective cross sections of radiative transitions in discrete and continuous spectra are given.

The book is based on the courses of lectures on atomic spectroscopy and connected problems which the author and L. A. Vainshtein gave at the Moscow Physics and Technology Institute, and reflects the changes in these courses in recent years. As a rule references are made only to monographs, reviews, and papers whose results are used in the text.

In conclusion, I wish to express sincere thanks to Dr. V. I. Kogan, who prepared Section 9.5, and to Dr. E. A. Yukov who helped me to prepare Sections 9.6 and 9.7.

Moscow, November 1978

I. I. Sobelman

Contents

Part I

Elementary Information on Atomic Spectra

Chapter 1

The Hydrogen Spectrum

1.1 Schrödinger's Equation for the Hydrogen Atom	3
1.1.1 Energy Levels	3
1.1.2 Wave Functions	5
1.2 Series Regularities	7
1.2.1 Radiative Transition Selection Rules	7
1.2.2 Spectral Series of the Hydrogen Atom	8
1.2.3 Hydrogenlike Ions	9
1.3 Fine Structure	10
1.3.1 Velocity Dependence of Electron Mass	10
1.3.2 Electron Spin	11
1.3.3 Fine Structure	12
1.3.4 Lamb Shift	15

Chapter 2

Systematics of the Spectra of Multielectron Atoms

2.1 Central Field	16
2.1.1 Central Field Approximation	16
2.1.2 Parity of States	18
2.1.3 Systematics of Electron States in a Central Field	19
2.2 General Picture of Electrostatic and Spin-Orbit Splitting of Levels in the LS Coupling Approximation	20
2.2.1 Spectral Terms. LS Quantum Numbers	20
2.2.2 Fine Structure of Terms	21
2.2.3 Finding the Terms of Multielectron Configurations	23
2.2.4 Radiative Transitions	26
2.3 jj Coupling Approximation	27
2.3.1 Various Coupling Schemes	27
2.3.2 Systematics of Electron States with jj Coupling	29

Chapter 3

Spectra of Multielectron Atoms

3.1 Periodic System of Elements	32
3.2 Spectra of the Alkali Elements	34
3.2.1 Term Scheme of the Alkali Elements	34
3.2.2 Series Regularities	37
3.2.3 Fine Structure	37
3.2.4 Copper, Silver, and Gold Spectra	38
3.3 Spectra of the Alkaline Earth Elements	39
3.3.1 He Spectrum	39
3.3.2 Spectra of the Alkaline Earth Elements	40
3.3.3 Zinc, Cadmium, and Mercury Spectra	42
3.4 Spectra of Elements with p Valence Electrons	42
3.4.1 One p Electron Outside Filled Shells	42
3.4.2 Configuration p^2	43
3.4.3 Configuration p^3	44
3.4.4 Configuration p^4	45
3.4.5 Configuration p^5	46
3.4.6 Configuration p^6	46
3.5 Spectra of Elements with Unfilled d and f Shells	48
3.5.1 Elements with Unfilled d Shells	48
3.5.2 Elements with Unfilled f Shells	49

Part II

Theory of Atomic Spectra

Chapter 4	
Angular Momenta	
4.1 Angular Momentum Operator. Addition of Angular Momenta	53
4.1.1 Angular Momentum Operator	53
4.1.2 Orbital Angular Momentum	54
4.1.3 Electron Spin	54
4.1.4 Addition of Two Angular Momenta	55
4.1.5 Addition of Three or More Angular Momenta	57
4.2 Angular Momentum Vector Addition Coefficients	60
4.2.1 Clebsch-Gordan and Associated Coefficients	60
4.2.2 Summary of Formulas for $3j$ Symbols	62
4.2.3 Racah W Coefficients and $6j$ Symbols	66
4.2.4 Summary of Formulas for $6j$ Symbols	70
4.2.5 $9j$ Symbols	72

4.3 Irreducible Tensor Operators	74
4.3.1 Spherical Tensors	74
4.3.2 Matrix Elements	76
4.3.3 Some Examples of Calculation of Reduced Matrix Elements	78
4.3.4 Tensor Product of Operators	80
4.3.5 Matrix Elements with Coupled Angular Momenta	84
4.3.6 Direct Product of Operators	86

Chapter 5

Systematics of the Levels of Multielectron Atoms

5.1 Wave Functions	89
5.1.1 Central Field Approximation	89
5.1.2 Two-Electron Wave Functions in $LSMLM_S$ Representation	90
5.1.3 Two-Electron Wave Functions in $mm'SM_S$ Representation	93
5.1.4 Multielectron Wave Functions in a Parentage Scheme Approximation	93
5.1.5 Fractional Parentage Coefficients	96
5.1.6 Classification of Identical Terms of l^n Configuration According to Seniority (Seniority Number)	98
5.2 Matrix Elements of Symmetric Operators	106
5.2.1 Statement of the Problem	106
5.2.2 F Matrix Elements. Parentage Scheme Approximation	108
5.2.3 F Matrix Elements. Equivalent Electrons	109
5.2.4 Q Matrix Elements. Parentage Scheme Approximation	111
5.2.5 Q Matrix Elements. Equivalent Electrons	113
5.2.6 Summary of Results	115
5.3 Electrostatic Interaction in LS Coupling. Two-Electron Configuration	115
5.3.1 Coulomb and Exchange Integrals	115
5.3.2 Configuration Mixing	118
5.4 Electrostatic Interaction in LS Coupling. Multielectron Configuration	120
5.4.1 Configurations l^n and $l^n l'$	120
5.4.2 Shells More Than Half Filled	123
5.4.3 Filled Shells	123
5.4.4 Applicability of the Single-Configuration Approximation	124
5.5 Multiplet Splitting in LS Coupling	126
5.5.1 Preliminary Remarks	126
5.5.2 Landé Interval Rule	126
5.5.3 One Electron Outside Closed Shells	128
5.5.4 Configuration l^n	130
5.5.5 Parentage Scheme Approximation	132
5.5.6 Fine-Structure Splitting of Levels of He	133
5.5.7 Spin-Spin and Spin-Other Orbit Interactions	139

5.6 <i>jj</i> Coupling	141
5.6.1 Wave Functions	141
5.6.2 Spin-Orbit and Electrostatic Interactions	143
5.7 Intermediate Coupling and Other Types of Coupling	144
5.7.1 Transformations Between <i>LS</i> and <i>jj</i> Coupling Schemes	144
5.7.2 Intermediate Coupling	147
5.7.3 <i>jl</i> Coupling	152
5.7.4 Experimental Data	153
5.7.5 Other Types of Coupling	154

Chapter 6

Hyperfine Structure of Spectral Lines

6.1 Nuclear Magnetic Dipole and Electric Quadrupole Moments	156
6.1.1 Magnetic Moments	156
6.1.2 Quadrupole Moments	157
6.2 Hyperfine Splitting	159
6.2.1 General Character of the Splitting	159
6.2.2 Calculation of the Hyperfine Splitting Constant <i>A</i>	162
6.2.3 Calculation of the Hyperfine Splitting Constant <i>B</i>	168
6.2.4 Radiative Transitions Between Hyperfine-Structure Components	170
6.2.5 Isotope Shift of the Atomic Levels	170

Chapter 7

The Atom in an External Electric Field

7.1 Quadratic Stark Effect	173
7.2 Hydrogenlike Levels. Linear Stark Effect	177
7.3 Inhomogeneous Field. Quadrupole Splitting	181
7.4 Time-Dependent Field	183
7.4.1 Amplitude Modulation	183
7.4.2 The Hydrogen Atom in a Rotating Electric Field	187

Chapter 8

The Atom in an External Magnetic Field

8.1 Zeeman Effect	189
8.2 Paschen-Back Effect	194
8.2.1 Strong Field	194
8.2.2 Splitting of Hyperfine Structure Components in a Magnetic Field	198

Chapter 9

Radiative Transitions

9.1 Electromagnetic Radiation	200
9.1.1 Quantization of the Radiation Field	200
9.1.2 Radiative Transition Probabilities	201
9.1.3 Correspondence Principle for Spontaneous Emission	202
9.1.4 Dipole Radiation	203
9.1.5 Stimulated Emission and Absorption	203
9.1.6 Effective Cross Sections of Absorption and Stimulated Emission	205
9.2 Electric Dipole Radiation	205
9.2.1 Selection Rules, Polarization, and Angular Distribution	205
9.2.2 Oscillator Strengths and Line Strengths	208
9.2.3 <i>LS</i> Coupling Approximation. Relative Intensities of Multiplet Components	211
9.2.4 One Electron Outside Closed Shells	213
9.2.5 Multielectron Configurations. Different Coupling Schemes	214
9.2.6 Relative Intensities of Zeeman and Stark Components of Lines	215
9.3 Multipole Radiation	216
9.3.1 Fields of Electric and Magnetic Multipole Moments	216
9.3.2 Intensity of Multipole Radiation	220
9.3.3 Selection Rules	222
9.3.4 Electric Multipole Radiation	223
9.3.5 Magnetic Dipole Radiation	225
9.3.6 Transitions Between Hyperfine Structure Components. Radio Emission from Hydrogen	227
9.4 Calculation of Radiative Transition Probabilities	229
9.4.1 Approximate Methods	229
9.4.2 Three Ways of Writing Formulas for Transition Probabilities	230
9.4.3 Theorems for Sums of Oscillator Strengths	232
9.4.4 Semiempirical Methods of Calculating Oscillator Strengths	235
9.4.5 Electric Dipole Transition Probabilities in the Coulomb Approximation	236
9.4.6 Intercombination Transitions	237
9.5 Continuous Spectrum	239
9.5.1 Classification of Processes	239
9.5.2 Photorecombination and Photoionization: General Expressions for Effective Cross Sections	239
9.5.3 Bremsstrahlung: General Expressions for Effective Cross Sections	245
9.5.4 Radiation and Absorption Coefficients	248
9.5.5 Photorecombination and Photoionization: Hydrogenlike Atoms	251
9.5.6 Photorecombination and Photoionization: Nonhydrogenlike Atoms	255
9.5.7 Bremsstrahlung in a Coulomb Field	257

9.6 Formulas for Q Factors	274
9.6.1 Symmetry and Sum Rules	274
9.6.2 LS Coupling. Allowed Transitions	275
9.6.3 jl Coupling	279
9.7 Tables of Oscillator Strengths and Radiative Transition Probabilities	281
9.7.1 Transition Probabilities for the Hydrogen Atom	281
9.7.2 Radiative Transition Probabilities in the Bates-Damgaard Approximation	283
9.7.3 Oscillator Strengths and Probabilities of Some Selected Transitions	284
9.7.4 Effective Cross Sections and Rates of Photorecombination	284
References	303
List of Symbols	304
Subject Index	305

Part I

Elementary Information on Atomic Spectra

Summary. For the convenience of the reader, the main body of the book is prefaced by a summary of the elementary information on atomic spectra given in Part I. This section includes the description of atomic spectra in various groups of the periodic table beginning with hydrogen and hydrogenlike spectra, and a discussion of the main physical principles on which the theory of atomic spectra is based. Experimental data on atomic spectra are discussed for the purpose of illustrating the physical meaning and justifying the approximations used in the theory, such as the concept of the self-consistent field and different coupling schemes for angular momenta.

Chapter 1 The Hydrogen Spectrum

The hydrogen atom and its spectrum treated in this chapter are of special interest in atomic spectroscopy because only for the hydrogen atom can the Schrödinger and Dirac equations be solved analytically. So-called hydrogenlike approximations are widely used in the theory of atomic spectra.

1.1 Schrödinger's Equation for the Hydrogen Atom

1.1.1 Energy Levels

The problem of the relative motion of an electron (mass: m , charge: $-e$) and a nucleus (mass: M , charge: Ze) reduces, as is well known, to the problem of the motion of a particle with an effective mass $\mu = mM/(m + M) \approx m$ in a Coulomb field of $-Ze^2/r$. The Schrödinger equation for a particle in the field $-Ze^2/r$ has the form

$$\left(\frac{\hbar^2}{2\mu}\Delta + E + \frac{Ze^2}{r}\right)\psi = 0. \quad (1.1)$$

The wave function ψ , which is the solution of this equation, describes the stationary state with a definite value of the energy E . In the case of a centrally symmetric field the angular momentum is conserved. Because of that, we shall consider stationary states which are characterized by definite values of the quantities E , the square of the angular momentum, and the z component of the angular momentum. The wave functions ψ of these stationary states are eigenfunctions of the operators L^2 and L_z and must therefore satisfy the equations

$$L^2\psi = l(l+1)\psi, \quad (1.2)$$

$$L_z\psi = m\psi, \quad (1.3)$$

where $l(l+1)$ and m are eigenvalues of the operators L^2 and L_z . We recall that in quantum mechanics the square of the angular momentum can only take a discrete series of values $\hbar^2 l(l+1)$, where $\hbar = h/2\pi$; h is Planck's constant, and also $l = 0, 1, 2, \dots$. In exactly the same way, the z component of the momentum can have the values $\hbar m$, $m = 0, \pm 1, \pm 2, \dots$ with the additional condition $|m| \leq l$.

For brevity, we shall henceforth speak of the angular momentum l and the z component of the angular momentum m , meaning the angular momentum

whose square is equal to $\hbar^2 l(l+1)$ and whose z component equals $\hbar m$.

Let us seek the solution of (1.1) in the form

$$\psi = R(r) Y_{lm}(\theta, \varphi), \tag{1.4}$$

where $Y_{lm}(\theta, \varphi)$ is the spherical function. The radial part satisfies the equation

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{l(l+1)}{r^2} R + \frac{2\mu}{\hbar^2} \left(E + \frac{Ze^2}{r} \right) R = 0. \tag{1.5}$$

If $E > 0$, this equation has finite and continuous solutions for any value of E and l . If $E < 0$, such solutions are possible only at certain discrete values of energy

$$E = -\frac{1}{2} \frac{Z^2 \mu e^4}{n^2 \hbar^2}, \tag{1.6}$$

where n is an integer, and also $n \geq l + 1$. The number n is called the principal quantum number. For a given value of n , the quantum number l can take the values $0, 1, 2, \dots, n-1$. To each value of l there correspond $(2l+1)$ states, differing by the values of the quantum number m , which is usually called the magnetic quantum number. The energy of an atom in the state nlm is uniquely determined by the principal quantum number and does not depend on l or m . Thus, for a particle in a Coulomb field the energy levels are n^2 -fold degenerated. There are $n^2 = 1 + 3 + 5 + \dots + n-1$ states differing in the quantum numbers l and m . The independence of m for the energy has a simple physical meaning. In a central field, all directions in space are equivalent, and therefore the energy cannot depend on the spatial orientation of the angular momentum. The independence of l is a specific property of the Coulomb field and does not occur in the general case of a centrally symmetric field. The energy level diagram of the hydrogen atom corresponding to (1.6) is shown in Fig. 1.1.

In spectroscopy it is usual to denote states corresponding to the values $l = 0, 1, 2, \dots$ by letters of the Latin alphabet

$$s, p, d, f, g, h, i, k, \dots$$

Thus the state $n = 1, l = 0$ is denoted $1s$, the state $n = 2, l = 2$ is denoted $2d$, and so on. So the state $1s$ relates to the level $n = 1$, the states $2s, 2p$ relate to the level $n = 2$, the states $3s, 3p, 3d$ relate to the level $n = 3$, and so on.

If we neglect the difference between the reduced mass $\mu \approx m(1 - m/M)$ and the electron mass m , which is approximately $m/2000$, we obtain $E_n = - (me^4/\hbar^2) Z^2/2n^2$. The quantity $me^4/\hbar^2 = 4.304 \times 10^{-11}$ ergs (≈ 27.07 eV) is taken as the atomic unit of energy. The Rydberg unit of energy $Ry = me^4/2\hbar^2$ is also used in spectroscopy; hence $E_n = - RyZ^2/n^2$.

For ionization of the hydrogen atom, i.e., for the detachment of an electron from the nucleus, it is necessary to impart to the atom the energy $|E_\infty - E_1| = \mu e^4/2\hbar^2$. This quantity is called the ionization energy (or ionization potential

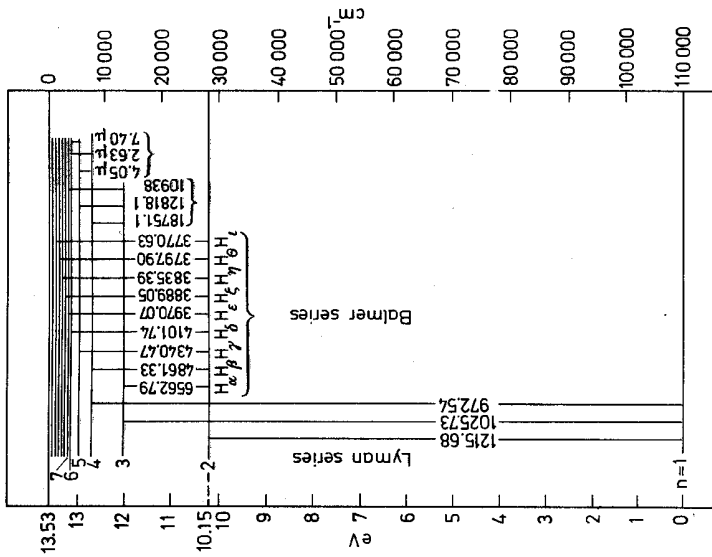


Fig. 1.1. Energy-level diagram for the hydrogen atom

if it is measured in electron volts) and is denoted by E_i . If the difference between μ and m is neglected, $E_1 = Ry$. The level $n = 1$ is called the ground level. The first excited level, nearest to the ground level, is called the resonance level. The energy necessary for excitation of the resonance level is called the resonance potential and is denoted E_r . For the hydrogen atom, $E_r = |E_2 - E_1| = 3/4 E_1$. This gives $E_1 \approx 13.53$ eV and $E_r \approx 10.15$ eV. In atomic spectroscopy, instead of the energy levels E_n , one usually uses the quantities $\sigma_n = E_n/2\pi\hbar c$ which are expressed in cm^{-1} as wave numbers. The values of the quantities σ_n for the energy levels of the hydrogen atom are given in Fig. 1.1.

1.1.2 Wave Functions

The angular functions $Y_{lm}(\theta, \varphi)$ can be expressed in terms of the associated Legendre polynomials P_l^m

$$Y_{lm}(\theta, \varphi) = \Theta_{lm}(\theta) \Phi_m(\varphi),$$

$$\Theta_{lm} = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} P_l^m(\cos \theta), \quad \Phi_m = \frac{e^{im\varphi}}{\sqrt{2\pi}}. \tag{1.7}$$

Here it is assumed that $m \geq 0$. For $m < 0$, $\Theta_{l, -|m|} = (-1)^m \Theta_{l, |m|}$. The functions Y_{lm} are orthogonal and normalized

$$\int_0^{2\pi} \int_0^\pi Y_{l'm'}^* Y_{lm} \sin \theta \, d\theta \, d\varphi = \delta_{l'l'} \delta_{m'm'} \quad (1.8)$$

The expressions for the functions Θ_{lm} when $l = 0, 1, 2$, are

$$\begin{aligned} \Theta_{00} &= \frac{1}{\sqrt{2}}, & \Theta_{10} &= \sqrt{\frac{3}{2}} \cos \theta, & \Theta_{1,\pm 1} &= \mp \sqrt{\frac{3}{4}} \sin \theta, \\ \Theta_{20} &= \sqrt{\frac{5}{2}} \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right), & \Theta_{2,\pm 1} &= \mp \sqrt{\frac{15}{4}} \cos \theta \sin \theta, \\ \Theta_{2,\pm 2} &= \frac{1}{4} \sqrt{15} \sin^2 \theta \end{aligned} \quad (1.9)$$

The radial functions for the discrete spectrum are expressed in the terms of the generalized Laguerre polynomial

$$L_n^m(x) = (-1)^m \frac{n!}{(n-m)!} e^{x/2} x^{-m} \frac{d^{n-m}}{dx^{n-m}} e^{-x} x^n, \quad (1.10)$$

$$R_{nl}(r) = -\sqrt{\frac{(n-l-1)!}{(n+l)! 2^n}} \left(\frac{2Zr}{na_0} \right)^{\frac{l}{2}} e^{-\frac{Zr}{na_0}} L_{n-l}^{2+l} \left(\frac{2Zr}{na_0} \right), \quad (1.11)$$

where $a_0 = \hbar^2/mc^2 = 0.529 \times 10^{-8}$ cm is the atomic unit of length (Bohr radius). The functions $R_{nl}(r)$ are orthogonal and normalized

$$\int R_{nl}(r) R_{n'l'}(r) r^2 dr = \delta_{nn'} \delta_{ll'}. \quad (1.12)$$

For large r , the functions R_{nl} decrease exponentially: $R_{nl} \sim \exp(-Zr/na_0)$. If r is expressed in atomic units a_0 and the energy in Ry, then for $r \rightarrow \infty$, $R_{nl} \sim \exp(-\sqrt{|E_n|} r)$.

We shall give explicit expressions for the functions $R_{nl}(r)$ when $n = 1, 2, 3$, expressing r in units a_0 (for this it is sufficient to make the substitution $r/a_0 \rightarrow r$) and omitting the factor $Z^{3/2} a_0^{-3/2}$ common to all the functions,

$$\left. \begin{aligned} R_{10} &= 2e^{-r}, \\ R_{20} &= \frac{1}{\sqrt{2}} e^{-\frac{r}{2}} \left(1 - \frac{1}{2} r \right), & R_{21} &= \frac{1}{2\sqrt{6}} e^{-\frac{r}{2}} r, \\ R_{30} &= \frac{2}{3\sqrt{3}} e^{-\frac{r}{3}} \left(1 - \frac{2}{3} r + \frac{2}{27} r^2 \right), \end{aligned} \right\} \quad (1.13)$$

¹ Definition of the phases of functions (1.7) corresponds to that adopted in [1].

$$R_{31} = \frac{8}{27\sqrt{6}} e^{-\frac{r}{3}} r \left(1 - \frac{r}{6} \right), \quad R_{32} = \frac{4}{81\sqrt{30}} e^{-\frac{r}{3}} r^2.$$

By using (1.11), one can calculate the mean values of the quantities r^k , which will be necessary later

$$\left. \begin{aligned} \langle r^k \rangle &= \int R_{nl}^2 r^{k+2} dr, \\ \langle r \rangle &= \frac{1}{2} [3n^2 - l(l+1)] \frac{a_0}{Z}, \\ \langle r^2 \rangle &= \frac{n^2}{2} [5n^2 + 1 - 3l(l+1)] \frac{a_0^2}{Z^2}, \\ \langle r^3 \rangle &= \frac{n^2}{8} [35n^2(n^2 - 1) - 30n^2(l+2)(l-1) \\ &\quad + 3(l+2)(l+1)l(l-1)] \frac{a_0^3}{Z^3}, \\ \langle r^{-1} \rangle &= \frac{1}{n^2} \frac{Z}{a_0}, \\ \langle r^{-2} \rangle &= \frac{1}{n^2} \frac{Z^2}{\left(l + \frac{1}{2} \right) a_0^2}, \\ \langle r^{-3} \rangle &= \frac{1}{n^2} \frac{Z^3}{\left(l + 1 \right) \left(l + \frac{1}{2} \right) l a_0^3}. \end{aligned} \right\} \quad (1.14)$$

The radial functions for the continuous spectrum $R_{E\ell}(r)$ can be expressed in terms of confluent hypergeometric functions. Different representations of these functions are given in [2,3].

1.2 Series Regularities

1.2.1 Radiative Transition Selection Rules

The radiative transitions between the states nlm , $n'l'm'$ are possible only if the quantum numbers l, m change by the quantities

$$\Delta l = l' - l = \pm 1, \quad \Delta m = m' - m = 0, \pm 1. \quad (1.15)$$

There are no limitations on the quantum numbers n, n' .

Relations (1.15) are called the selection rules for dipole radiation. Transitions satisfying conditions (1.15) are called allowed transitions. If conditions (1.15)

are not fulfilled, then dipole radiation is forbidden. In this case, quadrupole or magnetic dipole radiation may be possible. The probability of such transitions, however, is approximately 10^5 times less than probabilities of dipole transitions. They are called forbidden transitions. The probabilities of radiative transitions for the hydrogen atom are given in Section 9.7.

1.2.2 Spectral Series of the Hydrogen Atom

The selection rules (1.15) enable one to find out what transitions are responsible for the series of lines observed in the hydrogen spectrum. The hydrogen spectrum consists of clearly defined series of lines with wavelengths λ satisfying the following formulas:

$$\begin{aligned} \frac{1}{\lambda} &= R \left(1 - \frac{1}{n^2} \right), & n &= 2, 3, 4, \dots & \text{Lyman series} \\ \frac{1}{\lambda} &= R \left(\frac{1}{2^2} - \frac{1}{n^2} \right), & n &= 3, 4, 5, \dots & \text{Balmer series} \\ \frac{1}{\lambda} &= R \left(\frac{1}{3^2} - \frac{1}{n^2} \right), & n &= 4, 5, 6, \dots & \text{Paschen series} \\ \frac{1}{\lambda} &= R \left(\frac{1}{4^2} - \frac{1}{n^2} \right), & n &= 5, 6, 7, \dots & \text{Brackett series} \\ \frac{1}{\lambda} &= R \left(\frac{1}{5^2} - \frac{1}{n^2} \right), & n &= 6, 7, 8, \dots & \text{Pfund series} \end{aligned}$$

Here R is a constant called the Rydberg constant, equal to $109677.581 \text{ cm}^{-1}$.

The longest-wavelength lines of these series are, respectively, $\lambda = 1215.68 \text{ \AA}$ (vac.), 6562.79 \AA , $1.8751 \text{ }\mu\text{m}$, $4.051 \text{ }\mu\text{m}$ and $7.456 \text{ }\mu\text{m}$ ($1 \text{ }\mu\text{m} = 10^{-4} \text{ cm} = 10^4 \text{ \AA}$). The line $\lambda = 12.37 \text{ }\mu\text{m}$, corresponding to the sixth series, was observed in absorption. The general form of the series is shown in Fig. 1.2. The distance between the lines decreases as λ decreases. A continuous spectrum adjoins the short-wave edge of the series. The limits of the first three series are located respectively at $\lambda = 912 \text{ \AA}$, 3648 \AA , 8208 \AA . Thus the Lyman and Balmer series are separated from the others; the other series partially overlap.

It is easy to see that for any two levels n, n' there exist states n', n'' between

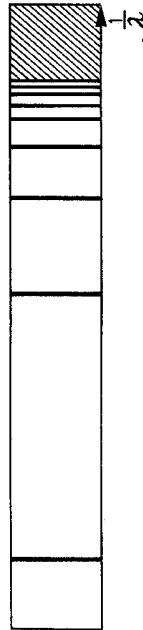


Fig. 1.2. General picture of a series in the hydrogen spectrum

which radiative transitions are allowed. Thus, for $n = 2, n' = 1$, transitions are allowed between the states $2p$ and $1s$, for $n = 3$ and $n' = 2$, transitions are allowed between the states $3s$ and $2p$, $3p$ and $2s$, $3d$ and $2p$, and so on.

According to (1.6) in the transition of a one-electron atom from the level n to the level n' , there is radiated the quantum

$$\hbar\omega = E_n - E_{n'} = \frac{\mu e^4 Z^2}{2\hbar^2} \left(\frac{1}{n'^2} - \frac{1}{n^2} \right). \quad (1.16)$$

Since the radiation frequency ω is connected with the wavelength λ by the relation $\omega = 2\pi c/\lambda$, where c is the velocity of light, we obtain (for $Z = 1$)

$$\frac{1}{\lambda} = \frac{E_n - E_{n'}}{2\pi\hbar c} = \sigma_n - \sigma_{n'} = \frac{\mu e^4}{4\pi c \hbar^3} \left(\frac{1}{n'^2} - \frac{1}{n^2} \right). \quad (1.17)$$

The quantity $\mu e^4/4\pi c \hbar^3$ with the accuracy determined by the accuracy of measurement of the constants m, e, c, \hbar coincides with the experimentally found value of the Rydberg constant R .

For $n' = 1$, (1.17) gives the wavelengths of the lines of the Lyman series (transitions $1s \rightarrow np$), for $n' = 2$, the wavelengths of the lines of the Balmer series (transitions $2s \rightarrow np, 2p \rightarrow ns, 2p \rightarrow nd$), and so on. The continuous background adjoining the limit of the series is due to transitions from the states of the continuous spectrum ($E > 0$) to the states of the discrete spectrum.

Special notations have been adopted for the lines of the hydrogen spectrum. The Lyman series lines, in order of decrease of wavelengths, are denoted by means of $L_\alpha, L_\beta, L_\gamma$, and so on; the Balmer series lines by means of $H_\alpha, H_\beta, H_\gamma$, and so on. The longest-wavelength line of the Lyman series $L_\alpha, \lambda = 1215.68 \text{ \AA}$, is obviously the resonance line of the hydrogen atom, i.e., the line corresponding to a transition from the first excited level to the ground level. This line is located in the vacuum ultraviolet region of the spectrum. The following lines of the Balmer series are the main lines in the visible and near ultraviolet regions of the hydrogen spectrum:

H_α	6562.73 Å,	H_ϵ	3970.07 Å,
H_β	4861.33 Å,	H_ζ	3889.06 Å,
H_γ	4340.47 Å,	H_η	3835.39 Å,
H_δ	4101.74 Å,	H_θ	3797.90 Å.

1.2.3 Hydrogenlike Ions

The level systems of the one-electron ions $\text{He}^+, \text{Li}^{++}, \text{Be}^{+++}$, etc., are similar to the level system for hydrogen. These ions are called hydrogenlike. The constant $R = \mu e^4/4\pi c \hbar^3$ depends on the reduced mass $\mu = mM/(m + M)$ and, consequently, on the nuclear mass M . Since $m \ll M$, the difference between the

constants R for two different masses M_1 and M_2 is not great. Thus, for H and He⁺ spectra, according to (1.17) the ratio $R_{\text{H}}/R_{\text{He}} = 0.999596$, which agrees well with experiment. For $M/m \rightarrow \infty$, $\mu \rightarrow m$. The corresponding value of R is denoted by R_∞ . The constant R_∞ is connected with the Rydberg unit of energy, Ry, by the relation $R_\infty = \text{Ry}/2\pi\hbar c$. It is easy to see that for a finite nuclear mass M

$$R_M = R_\infty \left(1 + \frac{m}{M}\right)^{-1}. \quad (1.18)$$

Experimental values of R for hydrogen, deuterium, and a series of ions are given in Table 1.1.

According to (1.6), $E_n \propto Z^2$. Thus, for an ion with a nuclear charge Z the potentials E_1, E_2 are Z^2 times greater than for hydrogen, and the wavelength of the resonance transition λ_{res} is Z^2 times less. The values of λ_{res} for a series of hydrogenlike ions are given in Table 1.2. In this table the spectroscopic system of notation is used. The spectra of neutral atoms are denoted by the Roman numeral I following from the symbol of the chemical element, the spectra of singly charged ions by the numeral II, and for doubly charged ions, by the numeral III, and so on.

Table 1.1. Values of the constant R for hydrogenlike ions

R	cm^{-1}
R_∞	$109,737,311 \pm 0.012$
R_{H}	$109,677,575 \pm 0.012$
R_{D}	$109,707,420 \pm 0.012$
R_{He^+}	$109,717,346 \pm 0.012$
$R_{\text{He}^{2+}}$	$109,722,268 \pm 0.012$

Table 1.2. Values of λ_{res} for hydrogenlike spectra

Z	Spectrum	$\lambda_{res}, \text{\AA}$
1	H I	1215.68
2	He II	303.78
3	Li III	135.02
4	Be IV	75.94
5	B V	48.58
6	C VI	33.74

1.3 Fine Structure

1.3.1 Velocity Dependence of Electron Mass

For the hydrogen atom and hydrogenlike ions with not very large nuclear charge Z , relativistic effects are not great and can be taken into account within the

limits of perturbation theory. The relativistic effects are the velocity dependence of electron mass and the splitting of the levels connected with electron angular momentum, the spin s . Expanding the relativistic expression for the energy of a particle of mass m in a field $U(r)$, $\mathcal{E} = U + \sqrt{c^2 p^2 + m^2 c^4}$ in a series in powers of $p^2/m^2 c^2 = (v/c)^2$, we obtain $E = \mathcal{E} - mc^2 \approx p^2/2m + U - p^4/8m^3 c^2$. The perturbation $V = -p^4/8m^3 c^2 \approx 1/2 mc^2 (E^{(0)} - U)^2$ where $E^{(0)}$ is the nonrelativistic energy $p^2/2m + U$ results in the level shift

$$\Delta E_{nl}^{(1)} = - (E_n^2 + 2E_n Z e^2 \langle r^{-1} \rangle_{nl} + Z^2 e^2 \langle r^{-2} \rangle_{nl}) / 2mc^2.$$

Using (1.6) and (1.14) we obtain

$$\Delta E_{nl}^{(1)} = -\alpha^2 \left(\frac{1}{j+1/2} - \frac{3}{4n} \right) \frac{Z^4}{n^3} \text{Ry}. \quad (1.19)$$

Here $\alpha = e^2/\hbar c \approx 1/137$.

1.3.2 Electron Spin

The existence of a magnetic moment of the electron, connected with electron spin s

$$\mu = -\frac{e\hbar}{mc} s = -2\mu_0 s, \quad (1.20)$$

where $\mu_0 = e\hbar/2mc$ is the Bohr magneton, leads to an additional interaction $\mu \cdot H$ between the electron and nucleus. H is the magnetic field which is associated with the electron moving in the electric field E . Since $H = -[E, v]/c$, $E = (\partial U/\partial r)r/r$, $m[r, v] = \hbar l$, this additional interaction $V \propto l \cdot s$. Thus this interaction is usually called spin-orbital interaction or simply spin-orbit interaction. The resulting expression for V is

$$V = \frac{\hbar^2}{2m^2 c^2} \frac{\partial U}{\partial r} \frac{1}{r} l \cdot s. \quad (1.21)$$

Since $s = 1/2$ the eigenvalue of the square of the spin s^2 is

$$s(s+1) = 3/4$$

and the z component of the spin s_z can take two values $\pm 1/2$.

Spin-orbit interaction depends not only on the value of the angular momentum l , but also on the mutual orientation of the angular momenta l and s , i.e., on the value of the total angular momentum of the atom, $j = l + s$. This value is obtained according to the general quantum mechanical rules for the addition of angular momenta.

The eigenvalue of the square of the total angular momentum j^2 equals $j(j+1)$, where for a given value of $l, j = l \pm 1/2$ (for $l = 0, j = 1/2$). The z component of the total angular momentum m_j is the sum of the z components of the orbital angular momentum m_l and spin m_s , i.e., $m_j = m_l + m_s$. In the following we shall drop the subscript j of m_j , understanding by m the z component of the total angular momentum.

For a given value of j , the quantum number m can take $(2j+1)$ different values $j, j-1, \dots, -j$. Thus, to a level nlj there belong $2j+1$ states, differing in the value of the quantum number m . The quantity $2j+1$ is called the statistical weight of the level j . The value of j is usually written as a subscript after the spectroscopic notation of l . Thus, the state $n, l = 1, j = 1/2$ is denoted $np_{1/2}$, the state $n = 4, l = 2, j = 3/2$ is $4d_{3/2}$, and so on.

The total angular momentum of any isolated system is conserved; therefore, the state of an atom can be characterized by the value of the total angular momentum j even in the case when the orbital and spin angular momenta are not separately conserved. Due to the spin-orbit interaction, the energy of an atom in the states $j = l + 1/2$ and $j = l - 1/2$ is different. Thus, the spin-orbit interaction leads to the splitting of the level nl into two components $l + 1/2$ and $l - 1/2$. Before passing on to the calculation of energy of splitting, we shall express the dependence of the spin-orbit interaction on j in explicit form. Since $\mathbf{j} = \mathbf{l} + \mathbf{s}$

$$j^2 = l^2 + s^2 + 2\mathbf{l} \cdot \mathbf{s}, \quad \mathbf{l} \cdot \mathbf{s} = (j^2 - l^2 - s^2)/2.$$

Remembering also that $U = -Ze^2/r$, we obtain

$$V = \frac{Ze^2\hbar^2}{2m^2c^2} \frac{1}{r^3} \frac{1}{2} (j^2 - l^2 - s^2). \quad (1.22)$$

The mean value of the perturbation (1.22) in the state n, l, j equals obviously

$$\frac{Ze^2\hbar^2}{2m^2c^2} \left\langle \frac{1}{r^3} \right\rangle_n \frac{1}{2} [l(l+1) - l(l+1) - s(s+1)].$$

Therefore, for the correction to the energy due to spin-orbit interaction, we obtain (the value of the matrix element $\langle r^{-3} \rangle_n$ has been given above)

$$\Delta E_{nlj}'' = \alpha^2 j(j+1) - l(l+1) - \frac{s(s+1)Z^4}{n^3} \text{Ry} \quad (1.23)$$

$$2l(l+1) \left(l + \frac{1}{2} \right)$$

1.3.3 Fine Structure

Comparison of (1.19) and (1.23) shows that both effects, connected with electron-mass velocity dependence and with electron spin, have the same order of mag-

nitude. It is easy to see that in both possible cases, $j = l + 1/2$ and $j = l - 1/2$, the total correction to the energy $\Delta E' + \Delta E''$ is given by one and the same expression

$$\Delta E_{nlj} = \Delta E' + \Delta E'' = \alpha^2 \left(\frac{3}{4n} - \frac{1}{j+1/2} \right) \frac{Z^4}{n^3} \text{Ry} \quad (1.24)$$

Thus, owing to the relativistic effects, the level nl splits into two components, $j = l + 1/2$ and $j = l - 1/2$. This splitting is called fine or multiplet splitting. The dimensionless constant $\alpha = e^2/\hbar c \approx 1/137$ defining the scale of the splitting is called the fine-structure constant. It is significant that whereas each of the corrections $\Delta E'$ and $\Delta E''$ separately depends on l , the total correction ΔE does not depend on l . Thus, for all n, l levels differing only by the value of l , the fine-structure components with one and the same value of j coincide. The fine splitting of levels $n = 1, 2, 3$ is shown in Fig. 1.3. As follows from (1.24), fine splitting decreases with increase of n approximately as $1/n^3$, therefore this splitting is particularly important for lower levels.

According to (1.24), the distance between the levels $j' = l + 1/2$ and $j'' = l - 1/2$ equals

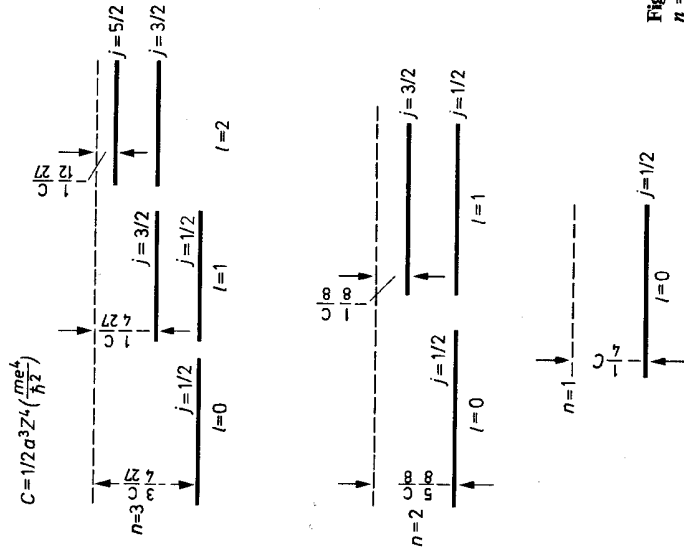


Fig. 1.3. Fine structure of levels $n = 1, 2, 3$

$$\delta E_{j,j''} = \frac{\alpha^2 Z^4}{n^2(l+1)} \text{Ry}. \tag{1.25}$$

Thus, for the hydrogen atom the splitting of the levels $j = 1/2$ and $j = 3/2$ for $n = 2, 3$ and 4 is, respectively, 0.36 , 0.12 , and 0.044 cm^{-1} .

The set of lines arising from the transitions between the fine-structure components of the levels nl and $n'l'$ (transitions $nlj \rightarrow n'l'j'$) is called a multiplet. The selection rule with respect to the quantum number j is

$$\Delta j = 0, \pm 1. \tag{1.26}$$

Using this rule, it is easy to find the character of the fine splitting of the lines of the hydrogen spectrum. For example, the multiplet $n'p \rightarrow nd$, shown in Fig. 1.4, in accordance with (1.26) consists of three components.

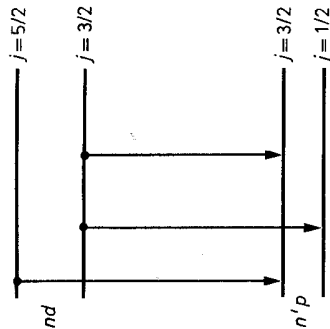


Fig. 1.4. Diagram of allowed transitions in the multiplet $nd \rightarrow n'p$

Further, for the transitions responsible for the Lyman series, both of the following transitions are permitted by the selection rules with respect to j

$$1s_{1/2} \rightarrow np_{1/2}, \quad 1s_{1/2} \rightarrow np_{3/2}.$$

In the case of the Balmer series, the following transitions are permitted:

$$2s_{1/2} \rightarrow np_{1/2}, \quad 2p_{1/2} \rightarrow ns_{1/2}, \quad 2p_{1/2} \rightarrow nd_{3/2},$$

$$2p_{3/2} \rightarrow nd_{3/2},$$

$$2s_{1/2} \rightarrow np_{3/2}, \quad 2p_{3/2} \rightarrow ns_{1/2}, \quad 2p_{3/2} \rightarrow nd_{5/2}.$$

The transition diagram for H_α lines is given in Fig. 1.5. Owing to the fact that the levels $ns_{1/2}$ and $np_{1/2}$, $np_{3/2}$ and $nd_{3/2}$ coincide, each of the Balmer lines must consist of five components in the general case. Since, however, the splitting of

the lower level considerably exceeds the splitting of the higher levels, the Balmer lines consist of two groups of closely spaced lines. The distance between these two groups equals 0.36 cm^{-1} and is constant for all lines of the series. The magnitude of splitting within each group falls rapidly in passing from the initial lines of the series to higher ones. For hydrogenlike ions the splitting $\Delta E \propto Z^4$.

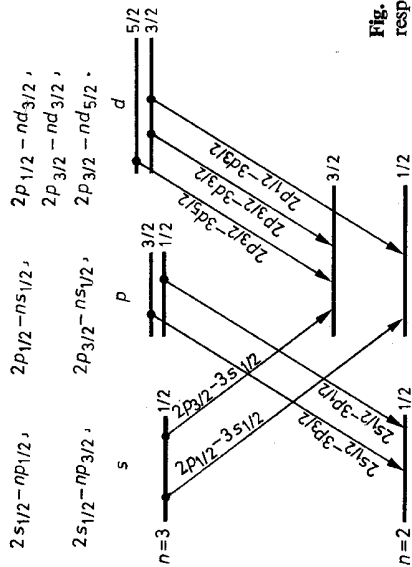


Fig. 1.5. Diagram of transitions responsible for the H_α line

1.3.4 Lamb Shift

Lamb and Retherford discovered (1947) that the splitting of the hydrogen levels $2s_{1/2}$ and $2p_{1/2}$ equals 0.034 cm^{-1} . Later it was shown that this splitting is caused by the interaction of the electron with the radiation field (see [2]). The theoretical value of the shift (Table 1.3) and experimental value coincide with great accuracy. For hydrogenlike ions the shift is proportional to Z^4 .

Table 1.3. Radiative splitting of the level $n = 2$

Level	Radiative shift [Mc/s]	Difference [Mc/s]
$2s_{1/2}$	+1040	1057
$2p_{1/2}$	-17	
$2p_{3/2}$	8	