

Contents

<i>Preface</i>	xiii
<i>Introduction</i>	xv
Part 1: Energy Spectrum of Many-electron Atom. Radiative and Autoionizing Transitions (Initial Formulas)	1
1 Non-relativistic atomic Hamiltonian and relativistic corrections	3
1.1 Schrödinger equation	4
1.2 Non-relativistic atomic Hamiltonian and wave function	6
1.3 Relativistic corrections	8
2 Relativistic atomic Hamiltonian. New wave function	10
2.1 Role of relativistic effects	10
2.2 Relativistic atomic Hamiltonian	11
2.3 Relativistic wave functions. New type of angular parts of non-relativistic and relativistic wave functions	13
3 Perturbation theory for the energy of an atom	16
3.1 Methods of accounting for correlation effects	16
3.2 Brillouin–Wigner (BW) and Rayleigh–Schrödinger (RS) expansions	18
4 Radiative and autoionizing electronic transitions. Generalized expressions for electric multipole (Ek) transition operators	25
4.1 Interaction of atomic electrons with electromagnetic radiation	25
4.2 Generalized expressions for relativistic electric multipole (Ek) transitions	27
4.3 Non-relativistic operators of electronic transitions	29
4.4 Relativistic corrections to various forms of the electric multipole (Ek) radiation operator	31
4.5 Autoionizing transitions	33

Part 2: Foundations of the Angular Momentum Theory.	
Graphical Methods	35
5 Angular momentum and tensorial algebra	37
5.1 Central field approximation, angular momentum and spherical functions	37
5.2 Irreducible tensorial sets	39
5.3 Tensorial products and their matrix elements	42
5.4 Unit tensors	44
6 Main quantities of angular momentum theory	48
6.1 Clebsch–Gordan coefficients	48
6.2 $3nj$ -coefficients	50
6.3 Transformation matrices	53
7 Angular momentum theory for relativistic case	57
7.1 Angular momentum	57
7.2 Unit tensors in a relativistic approach	58
8 Graphical methods: their generalization for perturbation theory	63
8.1 The graphs of Jucys, Levinson and Vanagas (JLV graphs)	63
8.2 The graphs of Jucys and Bandzaitis (JB graphs)	65
Part 3: Description of Complex Electronic Configurations	71
9 Non-relativistic and relativistic cases of a shell of equivalent electrons	73
9.1 A shell of equivalent electrons	73
9.2 Wave function of equivalent electrons and coefficients of fractional parentage	75
9.3 s^N , p^N , d^N and f^N shells. Seniority quantum number	77
9.4 A shell of equivalent electrons in jj coupling (a subshell)	80
9.5 Quasispin	81
10 Two and more shells of equivalent electrons	85
10.1 Two non-equivalent electrons. Representation of coupled momenta	85
10.2 Several shells of equivalent electrons	87
11 Classification of energy levels	91
11.1 Electronic interactions as interactions of momenta	91
11.2 Various coupling schemes	92
11.3 Classification of the energy levels using various coupling schemes	94
12 Relations between various coupling schemes	97
12.1 A shell of equivalent electrons l^N	99
12.2 Two shells of equivalent electrons	102
12.3 Optimization of the coupling scheme	106

Part 4: Second-quantization in the Theory of an Atom. Quasispin and Isospin	107
13 Second-quantization and irreducible tensorial sets	109
13.1 General remarks	109
13.2 Second-quantization. Electron creation and annihilation operators	111
13.3 Commutation relations. Occupation numbers	113
13.4 Operators and wave functions in second-quantization representation	114
13.5 Particle-hole representation	117
13.6 Phase system	118
14 Operators and matrix elements in second-quantization representation	121
14.1 Irreducible tensors in the space of occupation numbers. One-particle states	121
14.2 Second-quantization operators as irreducible tensors. Tensorial properties of electron creation and annihilation operators	122
14.3 Unit tensors	124
14.4 Group-theoretical methods of classification of the states of a shell of equivalent electrons. Casimir operators	126
14.5 Commutation relations for various tensors	128
14.6 One-particle operators of physical quantities	131
14.7 Two-particle operators of physical quantities	132
14.8 Operator of averaged electrostatic interaction	135
15 Quasispin for a shell of equivalent electrons	138
15.1 Wave functions in second-quantization representation	138
15.2 Submatrix elements of creation and annihilation operators. Coefficients of fractional parentage	140
15.3 Many-particle coefficients of fractional parentage	142
15.4 Quasispin	145
15.5 Tensors in quasispin space	147
15.6 Connection of quasispin method with other group-theoretical methods	150
15.7 Expansion of operators of physical quantities in quasispin space	158
16 Algebraic expressions for coefficients of fractional parentage (CFP)	160
16.1 Wave functions in quasispin space	160
16.2 Reduced coefficients (subcoefficients) of fractional parentage	163
16.3 Relationship between states of partially and almost filled shells	170
16.4 Transposition of spin and quasispin quantum numbers	173
16.5 Algebraic expressions for some specific CFP	175
16.6 Algebraic expressions for CFP of $l^N vLS$ shells	176
16.7 Algebraic expressions for CFP of the $f^N(u_1 u_2) vLS$ shell	178

17	Tensorial properties and quasispin of complex configurations	182
17.1	Irreducible tensors in the space of complex configurations	182
17.2	Tensorial properties of operators of physical quantities	184
17.3	Wave functions and matrix elements	188
17.4	Operators in quasispin space of separate shells	191
17.5	Superposition of configurations in quasispin space	193
17.6	Tensors in the space of total quasispin and their submatrix elements	194
18	Isospin in the theory of an atom	200
18.1	Isospin	200
18.2	Isospin basis and its properties	202
18.3	Additional classification of terms in isospin basis	208
18.4	Electron interaction energy in isospin basis	212
	Part 5: Matrix Elements of the Energy Operator	217
19	The energy of a shell of equivalent electrons	219
19.1	Expression of the energy operator in terms of irreducible tensors	219
19.2	Matrix elements of the energy operator in the case of a shell l^N	223
19.3	Relativistic Breit operator and its matrix elements	231
20	Interaction energy of two shells in LS coupling	235
20.1	Electrostatic interaction	237
20.2	Relativistic energy operator	241
21	Semi-empirical methods of calculation of the energy spectra	248
21.1	Least squares fitting	248
21.2	Accounting for relativistic and correlation effects as corrections	251
21.3	Dependence of the energy operator matrix elements on nuclear charge Z	256
21.4	Semi-empirical method of model potential	258
22	Hyperfine structure of the energy spectra, isotopic and Lamb shift	261
22.1	Hyperfine interactions in non-relativistic approximation	261
22.2	Hyperfine structure in relativistic approximation	265
22.3	Isotopic and Lamb shifts of the energy levels	268
23	Quasispin and isospin for relativistic matrix elements	273
23.1	Relativistic approach and quasispin for one subshell	273
23.2	Quasispin for complex electronic configurations	281
23.3	Isospin basis for two $n_1 l_1 j^{N_1} n_2 l_2 j^{N_2}$ subshells	285
23.4	Relativistic energy of electron–electron interaction in isospin basis	288

Part 6: Electric and Magnetic Multipole Transitions	291
24 General expressions for electric (E_k) and magnetic (M_k) multipole radiation quantities	293
24.1 Line and multiplet strengths	293
24.2 Oscillator strength, transition probability, lifetime and line intensity	295
24.3 'Exact' selection rules for electronic transitions	297
24.4 'Approximate' selection rules. Intermediate coupling. Intercombination lines	299
24.5 Sum rules	301
25 Non-relativistic matrix elements of the E_k-transitions	305
25.1 E_k -transitions of electrons above the core configurations	305
25.2 Selection and sum rules	308
25.3 E_k -transitions between levels of one and the same configuration	310
25.4 E_k -transitions with participation of core electrons	310
26 Relativistic matrix elements of E_k-transitions	315
26.1 E_k -transitions of electrons above the core configurations	315
26.2 E_k -transitions with participation of core electrons	318
26.3 Selection and sum rules	320
27 M_k-transitions. Particular cases of $E2$- and $M1$-transitions	323
27.1 Relativistic and non-relativistic M_k -transitions	323
27.2 $E2$ - and $M1$ -transitions between levels of one and the same configuration	326
Part 7: Calculation of Energy Spectra and Electronic Transitions in the Case of Complex Configurations	331
28 Methods of determination of radial orbitals	333
28.1 Non-relativistic numerical radial orbitals	333
28.2 Relativistic Hartree–Fock radial orbitals	338
28.3 Analytical radial orbitals	339
28.4 Collapse of the orbit of the excited electron	341
28.5 Non-orthogonal radial orbitals	344
29 Correlation effects. Perturbation theory	346
29.1 Methods of accounting for correlation effects	346
29.2 Matrix elements connecting different electronic configurations	351
29.3 Perturbation theory	354
30 The role of gauge dependence, relativistic and correlation effects in electronic transitions	357
30.1 Electronic transitions in intermediate coupling	357
30.2 Relativistic and correlation effects, gauge dependence	360
30.3 Perturbation theory	363

31	Peculiarities of the structure and spectra of highly ionized atoms	368
31.1	Peculiarities of multiply charged ions	368
31.2	Isoelectronic sequences	372
31.3	Astrophysical applications	377
32	Global methods in the theory of many-electron atoms	380
32.1	Mean characteristics of atomic spectra	380
32.2	Average, variance, asymmetry, excess of a spectrum	384
32.3	Configuration mixing	387
32.4	Statistical characteristics of radiation spectra	389
33	Peculiarities of configurations with vacancies in inner shells	392
33.1	Autoionization	392
33.2	Production of excited states in atoms	394
33.3	X-ray absorption spectra	395
33.4	Photoelectron spectra	397
33.5	Characteristic X-ray spectra	398
33.6	Auger spectra	400
33.7	Width and shape of spectral lines. Fluorescence yield	401
	<i>Epilogue</i>	404
	<i>References</i>	407
	<i>Index</i>	422