Contents

Foreword xi

Preface xv

Introduction xix

Part 1. 1

Chapter 1. Different Photoionization Processes, Rydberg Series 3

1.1. Photoionization processes 3
1.1.1. Direct photoionization and resonant photoionization 3
1.1.2. Multiple photoionization 6
1.1.3. Illustration of the autoionization phenomenon in the case of two-electron atomic systems 7
1.1.4. Illustration of the processes of photoionization in the case of the carbon ion, C^+ 9
1.2. Rydberg Series 10
1.2.1. Definition and notation 10
1.2.2. Resonance energy and natural width 15

Chapter 2. Experimental and Theoretical Methods of Photoionization 21

2.1. Experimental methods 21
2.1.1. Ionic spectroscopy assemblies in collinear beams 21
2.1.2. New synchrotron radiation assemblies 22
2.2. Theoretical methods 22
2.2.1. General aspects 22
2.2.2. Resonant photoionization methods 23

2.3. Absolute photoionization cross-section 24
2.4. Analysis of resonance energies and quantum defect 28
2.4.1. Concept of quantum defect. 28
2.4.2. Standard quantum-defect formula 29

Chapter 3. General Formalism of the Screening Constant by Unit Nuclear Charge Method Applied to Photoionization 33

3.1. Genesis of the screening constant by unit nuclear charge method 33
3.1.1. Introduction to the screening constant by unit nuclear charge 33
3.1.2. General expression of the total energies of autoionizing states of helium-like systems 39
3.1.3. Procedures for determining the screening constant by unit nuclear charge 40
3.2. Expression of the total energy of three-electron atomic systems 43
3.2.1. Interaction model 43
3.2.2. Expression of the energy of the ground state 44
3.2.3. Expression of the energy of the autoionizing states 46
3.3. General expressions of the resonance energies and widths of Rydberg series of multi-electron atomic systems. 48
3.3.1. Expression of the resonance energies 48
3.3.2. Expression of the resonance widths 51
3.3.3. Analysis of the resonance energies 51
3.3.4. Principle of determining absolute errors 52

Part 2. Applications in the Calculations of Energies and Natural Widths of the Resonance States of Multi-Electron Atomic Systems 55

Introduction to Part 2 57

Chapter 4. Application to the Calculation of Energies of Two-electron Atomic Systems (Helium-like Systems) 59

4.1. Energy of the ground state of helium-like systems 59
4.2. Energy of the excited states, $1sns\ ^{1,3}S^e$, of helium-like systems 61
4.3. Energy of the doubly excited symmetric states, ns^2 and np^2, of helium-like systems 65

4.4. Calculation of the resonance energies and natural widths of the Rydberg series, $_2(1,0)_n^+$ $^1S^e$, of the helium atom 67
4.5. Effect of the nucleus on the accuracy of semi-empirical calculations 71
4.6. Resonance energy of the Rydberg series, $_2(1,0)_n^{\pm}$ $^{1,3}P^\circ$ and $_2(1,0)_n^-$ $^1P^\circ$, of the Li^+ helium-like ion 72
4.7. Resonance energies of the Rydberg series, $^{1,3}S^e$, of the Li^+ helium-like ion converging toward the excitation threshold, $n = 2$ 78
4.8. Calculation of the energies of the Rydberg states, $_3(1,1)_n^+$ $^1P^0$, of helium-like systems 80
4.9. Physical interpretation of the angular-correlation quantum number, K. 82

Chapter 5. Calculating the energies of Three-electron Atomic Systems (Lithium-like Systems) 117

5.1. Energy of the ground state of lithium-like systems 117
5.2. Energy of the doubly excited states, $1s2snl$ ^2L, of lithium-like systems 119
5.3. Energy of the doubly excited states, $1s^2sns$ ^2S, of lithium-like systems 123
5.4. Energy of the single excitation states, $1s^2nl$ $^2L^\pi$ $(1 \le l \le 3)$, of lithium-like systems 132
5.4.1. Energies of the excited states ($1s^2np$; $^2P^\circ$). 133
5.4.2. Energies of the excited states ($1s^2nd$; $^2D^e$) and ($1s^2nf$; $^2F^\circ$) 136
5.4.3. Results 137

Chapter 6. Application in the Resonant Photoionization of Atomic Systems of Atomic Numbers Z = 4–12 149

6.1. Resonance energies of the Rydberg series, (2pns $^1P^\circ$) and (2pnd $^1P^\circ$), of beryllium 149
6.1.1. Preliminary text 149
6.1.2. Resonance energies of the Rydberg series, 2pns and 2pnd, of beryllium 151
6.2. Resonance energies of the excited states, $1s2p^4$ $^{2,4}L$, of five-electron atomic systems (boron-like systems) 153
6.3. Energies and widths of the Rydberg series, 2pns $^{1,3}P^\circ$ and 2pnd $^{1,3}P^\circ$, of the beryllium-like B^+ ion 164
6.3.1. Expressions of the resonance energies 165
6.3.2. Expressions of the natural widths 166

6.3.3. Results and discussion 168
6.4. Energies and widths of the Rydberg series, $2pnl\ ^{1,3}P^{\circ}$, of beryllium-like ions C^{2+}, N^{3+}. ….. and Ar^{14+} 181
6.4.1. Expressions of the resonance energies 182
6.4.2. Expressions of the natural widths 183
6.4.3. Results and discussion 184
6.5. Resonance energies of the Rydberg series, $2s^22p^4\ (^1D_2)ns$, nd, $2s^22p^4\ (^1S_0)ns$, nd and $2s2p^5\ (^3P_2)np$, of the Ne^+ ion. 206
6.5.1. Expressions of the resonance energies 207
6.5.2. Results and discussion 209
6.6. Energies of the Rydberg series, $2s^22p^2\ (^1D)nd\ (^2L)$, $2s^22p^2\ (^1S)nd\ (^2L)$, $2s2p^3(^5S_0)np\ (^4P)$ and $2s^22p^3\ (^3D)np$, of the F^{2+} ion 222
6.6.1. Expressions of the resonance energies 222
6.6.2. Results and discussion 223
6.7. Energies and widths of the Rydberg series, $3pns\ ^{1.3}P$, $3pnd\ ^{1.3}P$ and $3pnd\ ^3D$, of magnesium (Mg) 230
6.7.1. Expressions of the resonance energies 231
6.7.2. Expressions of the resonance widths 232
6.7.3. Results and discussion 234
6.8. Energies and widths of several resonance states resulting from the photoexcitation $1s \rightarrow 2p$ of the N^{3+} and N^{4+} ions 245
6.8.1. Expressions of the resonance energies 247
6.8.2. Expressions of the resonance widths 248
6.8.3. Results and discussion 249

Chapter 7. Resonant Photoionization of Sulfur (S) and Ar^+, Se^+, Se^{2+} and Kr^+ Ions 255

7.1. Photoionization of sulfur 255
7.1.1. Expressions of the resonance energies 256
7.1.2. Results 257
7.2. Photoionization of the krypton ion (Kr^+) 264
7.2.1. Expressions of the resonance energies 265
7.2.2. Results 265
7.3. Photoionization of the Argon ion (Ar^+) 270
7.3.1. Expressions of the resonance energies 271
7.3.2. Expression of the natural widths. 272
7.3.3. Results 272
7.4. Resonant photoionization of the selenium ions, Se^+, Se^{2+} and Se^{3+}. 283
7.4.1. Photoionization of the selenium ion (Se^+) 283
7.4.2. Photoionization of the selenium ion (Se^{2+}) 301
7.4.3. Photoionization of the selenium ion (Se^{3+}) 308

Conclusion 319

Appendices 325

Appendix 1. Detailed Calculation of the Screening Constant by Unit Nuclear Charge Relative to the Ground State of Two-electron Atomic Systems 327

Appendix 2. Formalism of Slater's Atomic Orbital Theory 335

Appendix 3. Modified Formalism of the Atomic Orbital Theory 341

Bibliography 353

Index 371