МІНІСТЕРСТВО ОСВІТИ І НАУКИ УКРАЇНИ
ОДЕСЬКИЙ ДЕРЖАВНИЙ ЕКОЛОГІЧНИЙ УНІВЕРСИТЕТ

Methodical instructions for practical work, test performance, distance learning of PhD students in the discipline "Atomic Optics and Spectroscopy", Part 8 (Training of PhD students of the specialty: 104 –"Physics and astronomy")

«Затверджено»
на засіданні групи забезпечення спеціальності
Протокол №1 від 28/08/2021 Голова групи_____Свинаренко А.А.

«Затверджено»
на засіданні кафедри вищої та прикладної математики
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Methodical instructions for practical work, test performance, distance learning of PhD students in the discipline “Atomic Optics and Spectroscopy”, Part 8. (Training specialty: 104 - “Physics and Astronomy”; 01.04.05- “Optics and Laser Physics” and others)

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PREFACE

Discipline "Atomic optics and spectroscopy" is a compulsory discipline in the cycle of professional training of postgraduate students (3 level of education) in specialty 104 – Physics and Astronomy (specialization: 01.04.05 -optics and laser physics). **It is aimed at** assimilating (assuring) a number of planned competences, including the study of the modern apparatus of Atomic optics and spectroscopy, as well as the development of new computational methods of determination and treating spectra of diatomic and multiatomic molecules, their energetic and spectroscopic characteristics on the basis of methods of quantum mechanics and quantum electrodynamics, the ability to analyze data of numerical experiments on the study of Atomic energetic, optical, spectroscopic characteristics that can be large and require the use of powerful computing resources, the use of modern existing and new advanced methods in order to achieve scientific results that create potentially new knowledge in Atomic optics and spectroscopy.

The place of discipline in the structural-logical scheme of its teaching: the knowledge gained during the study of this discipline is used in the writing of dissertations, the topics of which are related to determination and treating spectra of diatomic and multiatomic molecules, their energetic and spectroscopic characteristics on the basis of methods of quantum mechanics and quantum electrodynamics. **The basic concepts** of discipline are the fundamental tools of a specialist in the field of Physics and Astronomy (specialization: 01.04.05 - optics and laser physics).

The purpose of studying the discipline is assimilation (assurance) of a number of competencies, in particular, the achievement of the relevant knowledge, understanding and the ability to use the advanced methods of Atomic optics and spectroscopy, as well as the development of new computational methods of determination and treating spectra of diatomic and multiatomic molecules, their energetic and spectroscopic characteristics on the basis of methods of quantum mechanics and quantum electrodynamics, to the needs of the dissertation before - study, adapt, improve quantum (Atomic) methods to analyze data on Atomic spectra, results of numerical experiments on the study of Atomic energetic, optical, spectroscopic characteristics.

After mastering this discipline, the postgraduate student must be able to use modern or personally developed new methods, in particular, to analyze, simulate, predict, and program the spectra of diatomic and multiatomic molecules. These methodical instructions are for self-studying work of the second-year PhD students and tests performance in the discipline «Atomic optics and spectroscopy».

Topics: Multiplicity of splitting of energy levels. Classification of atoms with p-shells that are filled. Spectral regularities of atoms with p1 - and p5 - ground state configuration. Electronic configuration of ground and excited states Ne

Topics: Multiplicity of splitting of energy levels. Classification of atoms with p-shells that are filled. Spectral regularities of atoms with p1 - and p5 - ground state configuration. Electronic configuration of ground and excited states Ne

Топіки: Мультіплетність розщеплення енергетичних рівнів. Класифікація атомів з р-оболонками, які заповнюються. Спектральні закономірності атомів з p1 - і p5 - конфігурацією основного стану. Електронна конфігурація основного та збуджених станід Ne **(ЗБ- Л2.8)**

1. Introduction

It is well known that the correct data about different radiation, energetic and spectroscopic characteristics of the multielectron atoms and multicharged ions, namely, radiative decay widths, probabilities and oscillator strengths of atomic transitions, excitation and ionization cross-sections are needed in astrophysics and laboratory, thermonuclear plasma diagnostics and in fusion research. In this light, studying the spectral characteristics of the alkali elements attracts a special interest.

There have been sufficiently many reports of calculations and compilation of energies and oscillator strengths for these atoms and corresponding ions (see, for example, [1–28]). In many papers the standard Hartree-Fock, Dirac-Fock methods, model potential approach, quantum defect approximation etc in the different realizations have been used for calculating energies and oscillator strengths. However, it should be stated that for the heavy alkali atoms (such as caesium and francium and corresponding ions) and particularly for their high-excited (Rydberg) states, there is not enough precise information available in literature. The multi-configuration Dirac-Fock method is the most reliable version of calculation for multielectron systems with a large nuclear charge. In these calculations the one- and two-particle relativistic and important exchange-correlation corrections are taken into account (see Refs. [1] and Refs. therein). However, one should remember about very complicated structure of spectra of the lanthanides atoms and necessity of correct accounting for different correlation effects such as polarization interaction of the valent quasiparticles and their mutual screening, iterations of a mass operator etc.).The known method of the model relativistic many-body perturbation theory (RMBPT) has

been earlier effectively applied to computing spectra of low-lying states for some lanthanides atoms [5-11] (see also [12-22]). We use an analogous version of the perturbation theory (PT) to study spectroscopic characteristics of some Ne-like ions

2. Advanced relativistic many-body perturbation theory and energy approach

As the method of computing is earlier presented in detail, here we are limited only by the key topics [5-15]. Generally speaking, the majority of complex atomic systems possess a dense energy spectrum of interacting states with essentially relativistic properties. In the theory of the non-relativistic atom a convenient field procedure is known for calculating the energy shifts ΔE of degenerate states. This procedure is connected with the secular matrix M diagonalization [12-22]. In constructing M, the Gell-Mann and Low adiabatic formula for ΔE is used. In contrast to the non-relativistic case, the secular matrix elements are already complex in the second order of the electrodynamical PT (first order of the interelectron interaction).

The total energy shift of the state is usually presented as follows:

$$\Delta E = \mathrm{Re}\Delta E + \mathrm{i}\,\mathrm{Im}\Delta E, \qquad (1)$$

$$\mathrm{Im}\,\Delta E = -\Gamma/2, \qquad (2)$$

where Γ is interpreted as the level width, and the decay possibility

$$P = \Gamma. \qquad (3)$$

Their imaginary part of ΔE is connected with the radiation decay (radiation) possibility. In this approach, the whole calculation of the energies and decay probabilities of a non-degenerate excited state is reduced to the calculation and diagonalization of the complex matrix M. In the papers of different authors, the $\mathrm{Re}\Delta E$ calculation procedure has been generalized for the case of nearly degenerate states, whose levels form a more or less compact group. One of these variants has been previously introduced: for a system with a dense energy spectrum, a group of nearly degenerate states is extracted and their

matrix M is calculated and diagonalized. If the states are well separated in energy, the matrix M reduces to one term, equal to ΔE. The non-relativistic secular matrix elements are expanded in a PT series for the interelectron interaction. The complex secular matrix M is represented in the form [12-14]:

$$M = M^{(0)} + M^{(1)} + M^{(2)} + M^{(3)}. \qquad (4)$$

where $M^{(0)}$ is the contribution of the vacuum diagrams of all order of PT, and $M^{(1)}$, $M^{(2)}$, $M^{(3)}$ those of the one-, two- and three- quasiparticle diagrams respectively. $M^{(0)}$ is a real matrix, proportional to the unit matrix. It determines only the general level shift. We have assumed $M^{(0)} = 0.$

The diagonal matrix $M^{(1)}$ can be presented as a sum of the independent one-quasiparticle contributions. For simple systems (such as alkali atoms and ions) the one-quasiparticle energies can be taken from the experiment. Substituting these quantities into (1) one could have summarized all the contributions of the one -quasiparticle diagrams of all orders of the formally exact QED PT. However, the necessary experimental quantities are not often available.

The first two order corrections to $\mathrm{Re}\, M^{(2)}$ have been analyzed previously using Feynman diagrams (look Ref. in [1,2]). The contributions of the first-order diagrams have been completely calculated. In the second order, there are two kinds of diagrams: polarization and ladder ones. The polarization diagrams take into account the quasiparticle interaction through the polarizable core, and the ladder diagrams take into account the immediate quasiparticle interaction [11-20].

Some of the ladder diagram contributions as well as some of the three-quasiparticle diagram contributions in all PT orders have the same angular symmetry as the two-quasiparticle diagram contributions of the first order. These contributions have been summarized by a modification of the central potential, which must now include the screening (anti-screening) of the core potential of each particle by the two others. The additional potential modifies the one-quasiparticle orbitals and energies.

3. The Dirac-Kohn-Sham Relativistic Wave Functions

Usually, a multielectron atom is defined by a relativistic Dirac Hamiltonian(the a.u. used):

$$H = \sum_i h(r_i) + \sum_{i>j} V(r_i r_j) \qquad (5)$$

Here, *h(r)* is one-particle Dirac Hamiltonian for electron in a field of the finite size nucleus and *V* is potential of the inter-electron interaction. The relativistic inter electron potential is as follows [7,8]:

$$V(r_i r_j) = \exp(i\omega_{ij} r_{ij}) \cdot \frac{(1 - \alpha_i \alpha_j)}{r_{ij}}, \qquad (6)$$

where α_{ij} is the transition frequency; α_i , α_j are the Dirac matrices. The Dirac equation potential includes the electric potential of a nucleus and exchange-correlation potential. One of the variants is the Kohn-Sham-like (KS) exchange relativistic potential, which is obtained from a Hamiltonian having a transverse vector potential describing the photons, is as follows [33]:

$$V_X[\rho, r] = V_X^{KS}(r) \cdot \left\{ \frac{3}{2} \frac{\ln[\beta + (\beta^2 + 1)^{1/2}]}{\beta(\beta^2 + 1)^{1/2}} - \frac{1}{2} \right\} \qquad (7)$$

$$\beta = [3\pi^2 \rho(r)]^{1/3} / c \qquad (8)$$

The corresponding correlation functional is [2,33]:

$$V_C[\rho, r] = -0.0333 \cdot b \cdot \ln[1 + 18.3768 \cdot \rho(r)^{1/3}], \qquad (9)$$

where *b* is the optimization parameter (see details in Refs. [2-4,9,10]).

One-particle wave functions are found from solution of the Dirac equation, which is written in the known two-component form:

$$\frac{\partial F}{\partial r} + (1 + \chi)\frac{F}{r} - (\varepsilon + m - v)G = 0$$

$$\frac{\partial G}{\partial r} + (1-\chi)\frac{G}{r} + (\varepsilon - m - v)F = 0 \qquad (10)$$

Here we put the fine structure constant α=1, χ - the Dirac number. At large χ the radial functions F and G vary rapidly as:

$$F(r), G(r) \approx r^{\gamma-1}$$
$$\gamma = \sqrt{\chi^2 - \alpha^2 z^2} \qquad (11)$$

This involves difficulties in numerical integration of the equations for $r \to 0$. To prevent it, it is convenient to turn to new functions isolating main power dependence: $f = Fr^{1-|\chi|}$, $g = Gr^{1-|\chi|}$. The Dirac equation for *F* and *G* components are transformed as:

$$f' = -(\chi + |\chi|) f/r - \alpha Z V g - (\alpha Z E_{n\chi} + 2/\alpha Z) g$$
$$g' == (\chi - |\chi|) g/r - \alpha Z V f + \alpha Z E_{n\chi} \qquad (12)$$

Here the Coulomb units (C.u.) are used. In Coulomb units the atomic characteristics vary weakly with Z; E_n is one-electron energy without the rest energy. The boundary values of the correct solution are as:

$$g = (V(0) - E_{n\chi}) r\alpha Z/(2\chi + 1); \quad f = 1, \ \chi < 0$$

$$f = (V(0) - E_{n\chi} - 2/\alpha^2 Z^2)\alpha Z; \quad g = 1, \ \chi > 0 \qquad (13)$$

The condition $f, g \to 0$ at $r \to \infty$ determines the quantified energies E_n. The asymptotics of *f,g* at $r \to \infty$ are: f ,$g \sim \exp(-r/n^*)$ with effective quantum number $n^* = \sqrt{1/2|E_{n\chi}|}$.

Let us remind that in the QED theory, the photon propagator D(12) plays the role of this interaction. Naturally the analytical form of D(12) depends on the gauge, in which the electrodynamical potentials are written. Interelectron interaction operator with accounting for the Breit interaction has been taken as follows:

$$V(r_i r_j) = exp(i\omega r_{ij}) \cdot \frac{(1 - \alpha_i \alpha_j)}{r_{ij}} \quad , \qquad (14)$$

where, as usually, αi are the Dirac matrices. In general, the results of all approximate calculations depended on the gauge. Naturally the correct result must be gauge-invariant.

The gauge dependence of the amplitudes of the photo processes in the approximate calculations is a well known fact and is in details investigated by Grant, Armstrong, Aymar and Luc-Koenig, Glushkov-Ivanov et al (see reviews in [5-7] and Refs. therein). Grant has investigated the gauge connection with the limiting non-relativistic form of the transition operator and has formulated the conditions for approximate functions of the states, in which the amplitudes of the photo processes are gauge invariant [3]. Glushkov-Ivanov have developed a new relativistic gauge-conserved version of the energy approach [14]. In ref. [25, 29-35] it has been developed its further generalization.

Here we applied this approach for generating the optimized relativistic orbitals basis in the zeroth approximation of the many-body PT. Optimization has been fulfilled by means of introduction of the parameter to the Fock and Kohn-Sham exchange potentials and further minimization of the gauge-non-invariant contributions into radiation width of atomic levels with using relativistic orbital bases, generated by the corresponding zeroth approximation Hamiltonians.

Other details can be found in Refs. [1-5,36-44].

4. Some results and conclusion

In tables 1 and 2 we present the values of probabilities of the transitions between levels of the configurations 2s22p53s,3d,4s,4d and 2s2p63p,4p in the Ne-like ions of the Ni XIX, Br XXVI (in s-1; total angle moment J=1): a – the MCDF method; b- relativistic PT with the empirical zeroth approximation (RPTMP); c1 – REA-PT data (without correlation corrections); c2 – REA-PT data (with an account for the correlation); exp.- experimental data (look [1-6] and Refs therein); This work -our data.

Table 1.

Probabilities of radiation transitions between levels of the configurations 2s22p53s,3d,4s,4d and 2s2p63p,4p in the Ne-like ion of Ni XIX (in s-1; total angle moment J=1): a – the MCDF method; b- relativistic PT with the empirical zeroth approximation (RPTMP); c1, c2 – REA PT data (without and with account for correlation effects); exp. - experiment; this work-our data (see text)

Level J=1	Exp.	a-MCDF	b-RPTMP
2p3/23s1/2	7.6+11	9.5+11	1.3+12
2p1/23s1/2	6.0+11	1.8+12	1.0+12
2p3/23d3/2	1.4+11	2.2+11	1.5+11
2p3/23d5/2	1.2+13	2.1+13	1.2+13
2p1/23d3/2	3.2+13	4.8+13	3.6+13
2s1/2 3p1/2			8.5+11
2s1/2 3p3/2			5.1+12
2p3/24s1/2	3.3+11		3.6+11
2p1/24s1/2	2.0+11		3.0+11
2p3/24d3/2	4.5+10		5.2+10
2p3/24d5/2	8.3+12		8.3+12
2p1/24d3/2	8.1+12		7.9+12
Level J=1	c1-REA PT	c2-REA PT	This work
2p3/23s1/2	9.7+11	8.1+11	7.9+11
2p1/23s1/2	7.6+11	6.2+11	6.1+11
2p3/23d3/2	1.7+11	1.4+11	1.3+11
2p3/23d5/2	1.5+13	1.2+13	1.1+13
2p1/23d3/2	4.0+13	3.3+13	3.2+13
2s1/2 3p1/2	9.5+11	8.1+11	8.0+11
2s1/2 3p3/2	5.6+12	4.7+12	4.6+12
2p3/24s1/2	4.1+11	3.4+11	3.3+11
2p1/24s1/2	3.1+11	2.4+11	2.2+11
2p3/24d3/2	5.4+10	4.8+10	4.6+10
2p3/24d5/2	9.2+12	8.2+12	8.1+12
2p1/24d3/2	8.9+12	8.0+12	8.0+12
2s1/24p1/2	6.3+11	5.7+11	5.6+11
2s1/24p3/2	2.7+12	2.4+12	2.3+12

Analysis of the data shows that the computational method used provides a physically reasonable agreement between the theoretical and experimental data.

Table 2.

Probabilities of radiation transitions between levels of the configurations 2s22p53s,3d,4s,4d and 2s2p63p,4p in the Ne-like ion of Br XXVI (in s-1; total angle moment J=1): a – the DF method; b- RPTMP; c1,2 – REA PT data (without and with account for correlation effects); exp. - experiment; this -our data

Level J=1	Exp.	a-MCDF	b-RPTMP
2p3/23s1/2	4.5+12	6.2+12	4.4+12
2p1/23s1/2	3.1+12	4.8+12	2.8+12
2p3/23d3/2	2.8+11	3.9+11	2.9+11
2p3/23d5/2	6.1+13	8.0+13	6.3+13
2p1/23d3/2	8.6+13	9.5+13	8.7+13
2s1/2 3p1/2	3.9+12		4.2+12
2s1/2 3p3/2	1.4+13		1.5+13
2p3/24s1/2	1.1+12		1.2+12
2p1/24s1/2	2.1+12		2.5+12
2p3/24d3/2	2.8+10		7.3+10
Level J=1	c1-QED PT	c2-QED PT	This work
2p3/23s1/2	5.5+12	4.4+12	4.3+12
2p1/23s1/2	3.6+12	2.7+12	2.6+12
2p3/23d3/2	3.5+11	2.8+11	2.7+11
2p3/23d5/2	7.5+13	6.1+13	6.1+13
2p1/23d3/2	9.9+13	8.6+13	8.5+13
2s1/2 3p1/2	4.7+12	4.0+12	3.9+12
2s1/2 3p3/2	1.8+13	1.4+13	1.3+13
2p3/24s1/2	1.5+12	1.1+12	1.1+12
2p1/24s1/2	2.8+12	2.3+12	2.2+12
2p3/24d3/2	6.9+10	6.3+10	6.0+10
2p3/24d5/2	2.7+13	2.3+13	2.2+13
2p1/24d3/2	2.3+13	2.0+13	1.9+13
2s1/24p1/2	2.9+12	2.6+12	2.5+12
2s1/24p3/2	8.9+12	8.0+12	7.8+12

Tests performance

Test Option 1.

1). Give the key features of sspectra of atoms with s-p-shells that are filled such inert gases atoms. Explain an influence of relativistic effects (spin-orbit interaction) on the structure of spectra of the atoms with p-shells that are filled: i) mathematical and physical essense of the structure of spectra of the atoms with p-shells that are filled; ii) calculation and interpratation of Spectra of the structure of spectra of the atoms with p-shells that are filled, iii) calculation of the relativistic and exchange-correlation contributions into Spectra of the structure of spectra of the atoms with s-p-shells that are filled v) the technical details of the computation code.

2). Explain all fundamental features of energy and spectroscopic characteristics of inert gases atoms, preliminarily describing the corresponding spectra.

3). Perform its pracrical comnputational realization (using Fortran Power Station , Version 4.0; PC Code: “Superatom” for Spectra of lanthanide and actinide atoms **on example of the neon** (all necessary numerical parameters should be self-taken).

Test Option 2.

1). Give the key features of sspectra of atoms with s-p-shells that are filled such inert gases atoms. Explain an influence of relativistic effects (spin-orbit interaction) on the structure of spectra of the atoms with p-shells that are filled: i) mathematical and physical essense of the structure of spectra of the atoms with p-shells that are filled; ii) calculation and interpratation of Spectra of the structure of spectra of the atoms with p-shells that are filled, iii) calculation of the relativistic and exchange-correlation contributions into Spectra of the structure of spectra of the atoms with s-p-shells that are filled v) the technical details of the computation code.

2). Explain all fundamental features of energy and spectroscopic characteristics of inert gases atoms, preliminarily describing the corresponding spectra.

3). Perform its pracrical comnputational realization (using Fortran Power Station , Version 4.0; PC Code: “Superatom” for Spectra of lanthanide and actinide atoms **on example of the krypton** (all necessary numerical parameters should be self-taken).

Test Option 3.

1). Give the key features of sspectra of atoms with s-p-shells that are filled such inert gases atoms. Explain an influence of relativistic effects (spin-orbit interaction) on the structure of spectra of the atoms with p-shells that are filled: i) mathematical and physical essense of the structure of spectra of the atoms with p-shells that are filled; ii) calculation and interpratation of Spectra of the structure of spectra of the atoms with p-shells that are filled, iii) calculation of the relativistic and exchange-correlation contributions into Spectra of the structure of spectra of the atoms with s-p-shells that are filled v) the technical details of the computation code.

2). Explain all fundamental features of energy and spectroscopic characteristics of inert gases atoms, preliminarily describing the corresponding spectra.

3). Perform its pracrical comnputational realization (using Fortran Power Station , Version 4.0; PC Code: "Superatom" for Spectra of lanthanide and actinide atoms **on example of the xenon** (all necessary numerical parameters should be self-taken).

Test Option 4.

1). Give the key features of sspectra of atoms with s-p-shells that are filled such inert gases atoms. Explain an influence of relativistic effects (spin-orbit interaction) on the structure of spectra of the atoms with p-shells that are filled: i) mathematical and physical essense of the structure of spectra of the atoms with p-shells that are filled; ii) calculation and interpratation of Spectra of the structure of spectra of the atoms with p-shells that are filled, iii) calculation of the relativistic and exchange-correlation contributions into Spectra of the structure of spectra of the atoms with s-p-shells that are filled v) the technical details of the computation code.

2). Explain all fundamental features of energy and spectroscopic characteristics of inert gases atoms, preliminarily describing the corresponding spectra.

3). Perform its pracrical comnputational realization (using Fortran Power Station , Version 4.0; PC Code: "Superatom" for Spectra of lanthanide and actinide atoms **on example of the radon** (all necessary numerical parameters should be self-taken).

Test Option 5.

1). Give the key features of sspectra of atoms with s-p-shells that are filled such inert gases atoms. Explain an influence of relativistic effects (spin-orbit interaction) on the structure of spectra of the atoms with p-shells that are filled: i) mathematical and physical essense of the structure of spectra of the atoms with p-shells that are filled; ii) calculation and interpratation of Spectra of the structure of spectra of the atoms with p-shells that are filled, iii) calculation of the relativistic and exchange-correlation contributions into Spectra of the structure of spectra of the atoms with s-p-shells that are filled v) the technical details of the computation code.

2). Explain all fundamental features of energy and spectroscopic characteristics of inert gases atoms, preliminarily describing the corresponding spectra.

3). Perform its pracrical comnputational realization (using Fortran Power Station , Version 4.0; PC Code: "Superatom" for Spectra of lanthanide and actinide atoms **on example of the helium** (all necessary numerical parameters should be self-taken).

Test Option 6.

1). Give the key features of sspectra of atoms with s-p-shells that are filled such inert gases atoms. Explain an influence of relativistic effects (spin-orbit interaction) on the structure of spectra of the atoms with p-shells that are filled: i) mathematical and physical essense of the structure of spectra of the atoms with p-shells that are filled; ii) calculation and interpratation of Spectra of the structure of spectra of the atoms with p-shells that are filled, iii) calculation of the relativistic and exchange-correlation contributions into Spectra of the structure of spectra of the atoms with s-p-shells that are filled v) the technical details of the computation code.

2). Explain all fundamental features of energy and spectroscopic characteristics of inert gases atoms, preliminarily describing the corresponding spectra.

3). Perform its pracrical comnputational realization (using Fortran Power Station , Version 4.0; PC Code: "Superatom" for Spectra of lanthanide and actinide atoms **on example of the argon** (all necessary numerical parameters should be self-taken).

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Methodical instructions
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