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Chapter 4

Theoretical Spectroscopy of Rare-Earth Elements: Spectra and Autoionization Resonances

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.69314

Abstract

An investigation of spectra, radiative and autoionization characteristics for the rare-earth elements is of a great interest as for development atomic spectroscopy as different applications in plasma chemistry, astrophysics, laser physics, quantum electronics etc. We present and review the results of studying spectra and autoionization resonance characteristics of a few lanthanide elements (ytterbium and thulium). Computing the spectra and autoionization resonance parameters is carried out within the relativistic many-body perturbation theory (RMBPT) and generalized relativistic energy approach. The accurate results on the autoionization resonance energies and widths are presented with correct accounting for the exchange-correlation and relativistic corrections and compared with other available theoretical and experimental data. In this chapter, we present a brief review of the theoretical and experimental works on spectroscopy of some lanthanide atoms. Spectroscopy of the Rydberg autoionization resonances in rare-earth atoms in an external electromagnetic field is expected to be very complex and unusual.

Keywords: rare-earth elements, spectroscopy, relativistic many-body perturbation theory, spectra, autoionization resonances

1. Introduction

An investigation of spectra, optical and spectral, radiative and autoionization characteristics for the rare-earth elements (REEs) (isotopes) and corresponding ions is traditionally of a great...
interest due to the further development of quantum optics and atomic spectroscopy and their different applications in the plasma chemistry, astrophysics, laser physics, quantum and nanoelectronics, etc. (see Refs. [1–8]). As it was indicated in many information sources on the rare-earth elements, they make possible the high-tech world—everything from the miniaturization of electronics, to the enabling of green energy and medical technologies, to supporting a myriad of essential telecommunications and defence systems [1, 2]. Besides, it is worth to mention that such industrial operations such as mining, refining and recycling of rare earths can have serious environmental consequences in a case of the improper operations and management. As it was indicated in Ref. [1, 2] that the rare-earth elements all tend to occur together in the same mineral deposits with radioactive elements, particularly thorium and uranium, and because they have similar properties, it is difficult to separate them from one another. Let us remember that according to the modern IUPAC definition, the rare-earth element (REE) is one of a set of 17 chemical elements in the Mendeleev’s periodic table, specifically the 15 lanthanides, as well as scandium and yttrium.

Below we will present the results of theoretical investigation of a few lanthanide atoms, namely, ytterbium and thulium. The detailed review of studying energetic, spectral and radiative characteristics of these atoms is presented in a number of monographies and articles [11, 14–86]. One should mention the detailed theoretical studying of the lanthanide atoms by Cowan and pioneer studying by King and Meggers et al., who studied atomic spectra of rare-earth elements and reported wavelengths and relative intensities of more than 1600 lines and estimated intensities of more than 1700 lines of Yb I (see [6–9] and references therein). Camus [14] and Wyart and Camus [15] measured more than 70 absorption lines in the ultraviolet region and obtained the even-parity states with \( J = 0 \) and \( J = 2 \) belonging to the series \( 4f^{14}6sns(n = 13–62) \), \( 4f^{14}6snd(n = 11–64) \) and \( 4f^{14}6snd(n = 11–21) \). Moreover, these authors fulfilled new additional observations of the neutral ytterbium spectrum in the infrared region and measured the Zeeman resonance parameters in the visible and near ultraviolet regions. In fact, these measurements allow to propose a new classification of the \( 4f^{14}6snl \) Rydberg series in the Yb spectrum. The configurations \( 4f^{13}6s^26p \) and \( 4f^{14}6p^2 \) have been complete and the lowest levels of \( 4f^{13}5d^26s \) and \( 4f^{14}5d6p \) have been recognized, as well as new low members of the Rydberg series. Spector [16] identified the energy levels of \( 4f^{13}5d6s^2 \) and \( 4f^{13}5d6p^2 \) configurations. Highly excited levels of the neutral ytterbium have been studied by means of the two-photon and two-step spectroscopy of even spectra [17] and theoretically by means of the multi-channel quantum defect analysis of the \( f^{\text{odd}} \) and even-parity spectra [18].

In Ref. [19], it has been used the method of photoionization laser spectroscopy of the ytterbium atoms in the presence of a direct current (DC) electric field on order to study the Yb photoionization near the first ionization threshold. Blondel et al. [19] had recorded a few spectra corresponding to ionization from the levels \( 4f^{14}6s7s \, ^1S_0 \) and \( ^3S_1 \), \( 4f^{14}6s6p \, ^1P_1 \) and \( 4f^{14}6s5d \, ^1D_2 \). The first observation of a long Rydberg series due to single excitation from the \( 4f^{14} \) subshell in Yb I was reported in Ref. [20] and additionally a two-channel multi-channel quantum defect analysis reveals a prominent series perturbation due to coupling with one particular \( 4f^{13}5dnf \) doubly excited series. Baig et al. [21] have studied the inner shell and double excitation spectrum of ytterbium involving the \( 4f \) and \( 6s \) subshells and reported more than 200 new levels. Theoretical analysis allowed to interpreter these lines as the \( 4f^{14}6s^2 \to 4f^{13}5d^2F_{7/2,5/2}^{14} \) inner
shell transitions and the $4f^{14}6s^{2} \to 4f^{14}5d(CD_{312,512})np,nf$ and $4f^{14}6s^{2} \to 4f^{14}6p(CP_{112,312})ns,nd$
doubly excited ones. All the observed levels lie above the first ionization threshold and can be
ordered into Rydberg series converging onto six limits. The interchannel interactions between
the overlapped series have been parametrized using multi-channel quantum defect theory.

In Ref. [22], Karaçoban and Özdem carried out the total relativistic computing the energies,
Landé factors, lifetimes for a group of the excited levels outside the neutral ytterbium core
[Xe]. These authors have used the relativistic Hartree-Fock (RHF) method (the Cowan’s
atomic code) and the multi-configuration Hartree-Fock (MCHF) method with accounting of
the relativistic effects within the Breit-Pauli (BP) scheme (the Fischer’s atomic code).

Maeda et al. [23] have used a method of optical-microwave double-resonance spectroscopy to
study the highly excited Rydberg states of ytterbium. In Refs. [24, 25], the methods of two-
photon ionization and three-photon polarization spectroscopy have been applied to studying
the autoionization states (ASs) of the ytterbium atom. The ytterbium atom in the $6s^{2}1S_{0}$
ground state was excited to the $6s6p^{3}P_{1}$ excited state by a photon with a visible wavelength
(555.648 nm), and it was ionized by absorbing an ultraviolet photon with a wavelength of
260–285 nm. The Rydberg and autoionization states of neutral ytterbium are also considered
in Ref. [27]. In Ref. [27], the authors reported the results of a reinvestigation of the
$6snf^{1,3}F_{3}$ ($9 < n < 16$), $6snp^{1}P_{1}$ ($12 < n < 56$), $6snp^{3}P_{1}$ ($12 < n < 21$) and $6snp^{3}P_{2}$ ($12 < n < 19$) Yb Rydberg
states using a two-colour three-photon resonant excitation technique through the $4f^{14}6s5d^{1}D_{2}$
intermediate level. The novelty of this studying is in the identification of the new levels in the
vicinity of the $6snf^{1,3}F_{3}$ ($9 < n < 16$) Rydberg levels.

The laser spectroscopy method has been effectively applied by Letokhov [28, 29] and
Letokhov and co-workers [30, 31] to studying narrow doubly excited autoionization states
of ytterbium and other lanthanide atoms. An analysis is made of doubly excited
autoionization states of an atom with two valence electrons. The results of experimental and
theoretical investigations of narrow autoionization states are reported for ytterbium atoms
near the ionization threshold. The method of multi-stage photoionization of atoms by tun-
able laser radiation was used to detect experimentally and identify narrow autoionization
states $^{1}P_{1}$ and $^{3}P_{0,1,2}$ of the $7s6p$ configuration. In Refs. [32–48], it has been performed the
detailed computing energies and widths of the autoionization resonances, Rydberg levels for
ytterbium and thallium. The positions and widths of the autoionization states belonging to
the $7s6p$, $6p5d$, $6p^{2}$ and $5d^{2}$ configurations were calculated using the method of relativistic
perturbation theory (PT) with the model potential (MP) zeroth approximation [49–79]. In
Refs. [63–68, 85, 86], it has been discovered a principally new spectroscopic effect of a giant
broadening autoionization resonances of the lanthanide atoms (thulium and gadolinium) in
a sufficiently weak external electric (laser) field. This new effect is of a great importance for
problem of laser separation of heavy isotopes and nuclear isomers, spectroscopy and photo-
chemistry [65, 66, 93, 94]. It is worth to note from theoretical viewpoint that computing
spectra, radiative transition and autoionization parameters of the rare-earth elements’ energy
is very complicated task because of the necessity of the correct accounting for the exchange-
correlation (including polarization and screening effects, a continuum pressure, etc.) and
relativistic corrections (and also radiative and nuclear effects in a case of the super heavy

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http://dx.doi.org/10.5772/intechopen.69314
atomic systems). Moreover, theoretical study of spectral properties of the lanthanide atoms is of a great importance for the development of new methods of atomic spectroscopy.

Let us remind that many different quantum-mechanical approaches in the on-relativistic and relativistic versions have been used in order to study energetic and spectroscopic parameters of the lanthanide elements. One should mention such known methods as a standard multi-configuration Hartree-Fock (HP) method with accounting of the relativistic effects within the Breit-Pauli scheme or the classical relativistic Hartree-Fock method or, at last, a multi-configuration Dirac-Fock method. These methods allow to obtain very useful spectral data about many light and heavy atoms. Nevertheless, studying the autoionization resonance characteristics for heavy elements with using the mentioned methods not always provides a precise description of the corresponding spectra. From the other side, at present time, the advanced versions of these methods have been developed, where the one- and two-particle relativistic and exchange-correlation effects are taken into account very precisely. It is worth to remind about computer codes for relativistic many-body calculations of atomic (molecular) properties developed in the Oxford group, Russian-German one, etc. (‘GRASP’, ‘Dirac’; ‘BERTHA’, ‘QED’; see Refs. [1–13] and references therein).

In Refs. [71–88], it has been developed a new formalism of the relativistic many-body PT with using the optimized one-quasiparticle (QP) representation and effective account of the exchange-correlation corrections of the PT second order and higher orders (polarization interaction, quasiparticles screening, etc.). The method of the relativistic many-body PT is constructed on the basis of the same ideas as the well-known PT with the model potential zeroth approximation by Ivanov et al. [49–64]. However, there are two key differences: namely, the PT zeroth approximation [81, 82, 85, 86] is in fact the Dirac-Kohn-Sham one. In order to calculate the radiative transition and autoionization resonance parameters, a new version of relativistic energy approach is used. It is important to remind that a model relativistic energy approach in a case of the multi-electron atom has been proposed by Ivanov et al. [49–56]. A generalized gauge-invariant relativistic energy approach in a case of the multi-electron atomic systems has been developed by Glushkov-Ivanov-Ivanova (see Refs. [71–76]). It should be noted that an energy approach uses the known Gell-Mann and Low S-matrix scheme. More exactly, a probability of any atomic state radiative decay is connected with an imaginary part of an electron energy shift $\Delta E$, which can be expressed through the Quantum electrodynamics (QED) scattering matrix (by means of the Gell-Mann and Low formula), including the interaction with the photon vacuum field (the spontaneous radiative decays) as an external electromagnetic field (the induced decays) [67–75, 85, 86, 91 92]. In Refs. [71–76], the new energy approach has been combined with a formalism of the relativistic many-body perturbation theory (RMBPT) with an optimized one-quasiparticle representation and an accurate accounting of the multi-electron exchange-correlation effects.

In this chapter, we present the results of application the optimized relativistic many-body PT with the Dirac-Kohn-Sham zeroth approximation and a generalized relativistic energy approach to studying spectra, radiative and autoionization resonance characteristics for lanthanide atoms, in particular, ytterbium and thulium. Data on the autoionization resonance energies and widths in the ytterbium and thulium are obtained with correct accounting for the
exchange-correlation and relativistic corrections and compared with other available theoretical and experimental data.

2. Method of relativistic many-body perturbation theory and relativistic energy approach

As our method of computing has been in detail presented previously, here we summarize only the key points. Generally speaking, the energy spectra for the majority of complex atomic systems (naturally including the rare-earth elements) are characterized by a great density. Moreover, these spectra have essentially relativistic properties. So, a correct theoretical method of their studying can be based on the convenient field procedure, which includes computing the energy shifts $\Delta E$ of the degenerate electron states. More exactly, speech is about constructing secular matrix $M$ (with using the Gell-Mann and Low adiabatic formula for $\Delta E$), which is already complex in the relativistic theory, and its further diagonalization [49, 50, 55, 56]. In result, one could compute the energies and decay probabilities of a non-degenerate excited state for a complex atomic system [49–64]. The secular matrix elements can be further expanded into a PT series on the interelectron interaction. Here, the standard Feynman diagrammatic technique is usually used.

Generally speaking, the secular matrix $M$ can be represented as follows:

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

where $M^{(0)}$ is the contribution of the vacuum diagrams of all PT orders (this contribution determines only the general levels spectrum shift); $M^{(1)}$, $M^{(2)}$ and $M^{(3)}$ are contributions of the 1-, 2- and 3-quasiparticle (QP) diagrams, respectively. The matrix $M^{(1)}$ can be presented as a sum of the independent one-QP contributions. Substituting these quantities into Eq. (1) one could have summarized all the one-QP diagram contributions. In the empirical methods here, one could use the experimental values of one-electron energies; however, the necessary experimental quantities (especially for the rare-earth and other elements) are not often available. The detailed procedure for computing $\text{Re} M^{(2)}$ is presented, for example, in Refs. [51–56].

We will describe an atomic multi-electron system by the relativistic Dirac Hamiltonian (the atomic units are used) as follows [17, 18]:

$$H = \sum_i \left( \alpha \mathbf{p}_i - \beta c^2 - Z/r_i \right) + \sum_{i<j} \exp(i\omega_{ij})/r_{ij}(1 - \alpha_i \alpha_j)/r_{ij} \quad \hfill (2)$$

where $Z$ is a charge of nucleus, $\alpha_i$ and $\alpha_j$ are the Dirac matrices, $\omega_{ij}$ is the transition frequency, $c$ is the velocity of light. The interelectron interaction potential (the second term in Eq. (3)) takes into account the retarding effect and magnetic interaction in the lowest order on the parameter of the fine structure constant. In the PT zeroth approximation, it is used ab initio mean-field potential:
with the standard Coulomb, exchange Kohn-Sham $V_X$ and correlation Lundqvist-Gunnarsson $V_C$ potentials (see details in Refs. [75–79]). An effective approach to accounting the multi-electron polarization contributions is described earlier and based on using the effective two-QP polarizable operator, which is included into the PT first-order matrix elements.

In order to calculate the radiation decay probabilities and autoionization energies and widths, a gauge invariant relativistic energy approach (version [71–76]) is used. In particular, a width of the state, connected with autoionization decay, is determined by coupling with the continuum states and calculated as square of the matrix element [73–76]:

$$V_{DKS}(r) = [V_{Coul}^D(r) + V_X(r) + V_C(r)]$$  

(3)

Here $Q_a = Q^{Coul}_a + Q^{Br}_a$, where $Q^{Coul}_a$ and $Q^{Br}_a$ correspond to the Coulomb and Breit parts of the relativistic interelectron potential in Eq. (3) and express through Slater-like radial integrals and standard angle coefficients. Other details can be found in Refs. [71–92].

The most complicated problem of the relativistic PT computing the rare-earth element spectra is in an accurate, precise accounting for the multi-electron exchange-correlation effects (including polarization and screening effects, a continuum pressure, etc.), which can be treated as the effects of the PT second and higher orders. Using the standard Feynman diagrammatic technique, one should consider two kinds of diagrams (the polarization and ladder ones), which describe the polarization and screening exchange-correlation effects. The detailed description of the polarization diagrams and the corresponding analytical expressions for matrix elements of the polarization QPs interaction (through the polarizable core) potential is presented in Refs. [51–56]. An effective approach to accounting of the polarization diagram contributions is in adding the effective two-QP polarizable operator into the PT first-order matrix elements. In Refs. [55, 56], the corresponding non-relativistic polarization functional has been derived. More correct relativistic expression has been presented in Refs. [11, 81, 82] and used in our computing. The corresponding polarization potential looks as follows [81, 82]:

$$V_{pol}^{DKS}(r_1r_2) = X \left\{ \frac{d^3r'}{|r_1 - r'| \cdot |r' - r_2|} \theta(r') \right\}$$

(5a)

$$\frac{d^3r'}{|r_1 - r'|} \frac{d^3r'}{|r' - r_2|} \frac{d^3r''}{|r'' - r_2|} \theta(r'' \theta(r') \theta(r'')) \right\}$$

(5b)

$$\left\langle \rho^{(0)}_c \right\rangle^{1/3} = \int dr \rho^{(0)}_c (r)^{1/3} \theta(r),$$

(5c)

$$\theta(r) = \left\{ 1 + [3n^2 \cdot \rho^{(0)}_c (r)^2]^{1/2} \right\}^{1/2}$$
where \( \rho^0 \) is the core electron density (without account for the quasiparticle), \( X \) is numerical coefficient and \( c \) is the light velocity. The contribution of the ladder diagrams (these diagrams describe the immediate QPs interaction) is summarized by a modification of the PT zeroth approximation mean-field central potential (see below), which include the screening (anti-screening) of the core potential of each particle by the two others. The details of this contribution can be found in Refs. [71–92]. All computing were performed with using the modified PC code ‘Superatom-ISAN’.

3. Spectra and autoionization state characteristics for the ytterbium and thulium atoms

3.1. Spectroscopy of excited and autoionization states in ytterbium

The Yb \((Z = 70)\) atom has the external electron configuration \(4f^{14}6s^2\) in the ground state and any excited states of the ytterbium atom can be treated as the states with two- or three quasiparticles above the electron core \([Xe]4f^{14}\). **Figure 1** shows a qualitative spectrum of the ytterbium, according to Ref. [30, 31].

In the Yb spectrum, it is possible to define two main types of the autoionization states (ASs) [28, 29]. The state of the first type arises with the excitation of inner shells, the condition of the second type with the double excitation of the valence shell. Those arising from the excitation of the \(4f\)-shell belong to the intermediate type. Autoionization decay in single-particle approximation can be represented as follows: \( \alpha_1\alpha_2 \rightarrow \alpha_3k \), where \( \alpha_i \) \((i = 1, 2, 3)\) describes the set of quantum numbers of bound states, \( k \) is the state of free electron. The decay is possible only in a state of continuum, which matches the original AS by parity and value of a total momentum \( J \).

![Figure 1](http://dx.doi.org/10.5772/intechopen.69314)
Low-lying AS of the Yb atom, arising from the double excitation of 6s\(^2\) shell, decays under the scheme \(n_1 l_1 n_2 l_2 \rightarrow 6skl\). State with electronic configuration \(4f^{14}6s^{2}7nl\) is a low-lying auto-ionization state AS with excitation of electron-hole type. The energy areas of these states and states with excited 6s\(^2\)-shell match. The decay of such AS takes place under the scheme: \(4f^{14}6s^{2}7nl \rightarrow 4f^{14}6skl'\). Wide low-lying AS (\(\Gamma \approx 100\) cm\(^{-1}\)) observed in the experiment by Letokhov and co-workers [30, 31] are attributed to such states. The estimation of the AS energy with configurations \(6p5d, 6p7, 5d^2, 7s6p\) in one-particle approximation indicates that these states should be located in the area of 0–15,000 cm\(^{-1}\) above Yb ionization threshold. As one could see from Figure 1, it is clear that in this case, even configurations \(6p^5, 5d^2\) can be excited in two stages, and the odd \(6p5d, 7s6p\) can be excited in three stages. This fact has been used in the experiments by Letokhov and co-workers [30, 31]. In this experiment, the Yb atoms were excited into the AS by radiation of three dye lasers. The laser of the first stage (\(\lambda_1 = 5556.5\) Å) excited transition \(6s^{2}1S_0 \rightarrow 6s6p\) \(P_0^0\) (see Figure 1). The second laser provided the further excitation to the one of selected intermediate states. The wavelength of the third laser was rebuilt in a such range it provided AS excitation in the studied area 0–15,000 cm\(^{-1}\) above the ionization threshold. In particular, upon AS excitation through \(6s6d\)\(^1D_2\) state the wavelength of the third stage varied in the range 7100–4100 Å, which allowed to ionize Yb atoms, excited in \(^1D_2\) state and carry out search of AS in the area of 3700–14,000 cm\(^{-1}\). Figure 2 shows the dependence of ion current on the third stage laser wavelength, under excitation of the AS \(7s6p\) \(^3P_0^0\) from the \(6s6d\)\(^1D_1\) state by laser radiation with the line width of ~1 cm\(^{-1}\). Figure 2 also shows the AS \(^3P_0^0\) with the width of the laser line of the three stage ~0.1 cm\(^{-1}\).

In Table 1, we present the experimental [51, 54] and theoretical data for the energy (energy count from ground state \(4f^{14}6s^2\) \(^1S_0\)) of some YbI singly excited states: MCHF-BP, data obtained on the basis of multi-configuration Hartree-Fock (MCHF) method with Breit-Pauli (BP) adjustments (A, B + D, D different sets of configurations included in the calculation by the method MCHF-BP [22]); RHF—the relativistic Hartree-Fock data [1, 2]; DF—analysis of Wyart-Camus

![Figure 2. Dependence of ion current on the third stage laser wavelength, under excitation of the AS \(7s6p\) \(^3P_0^0\) from the \(6s6d\)\(^1D_1\) state by laser radiation with the line width of ~1 cm\(^{-1}\).](image-url)
The analysis of the calculated data (Table 1) shows that the role of exchange-correlation effects for the studied atom is extremely significant. The HF method with a small number of considered configurations gives an error of more than 100 cm$^{-1}$. In Table 2, we list the experimental and theoretical data of Letokhov and co-workers [30, 31] for the energy and width of the excited (AS) states of the 7s6p configuration in the YbI spectrum (counted from the ground state 4f146s21S0 Yb):

Table 1. Energies (cm$^{-1}$) of YbI singly excited states: MCHF-BP, with Breit-Pauli (BP) adjustments (A, B + D, D, different sets of configurations); RHF, relativistic Hartree-Fock method; RPTMP (E1), relativistic perturbation theory with model potential (MP) zeroth approximation [30, 31]; DF, analysis of Wyart-Camus [15]; RPT-DKS (E2), our theory and experiment data (Exp).

<table>
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<tr>
<th>Config.</th>
<th>J</th>
<th>MCHF + BP(A)</th>
<th>MCHF + BP(C)</th>
<th>MCHF + BP(BD)</th>
<th>RHF</th>
<th>RPTMP</th>
<th>Our theory</th>
<th>DF</th>
<th>Exp</th>
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$E = -14,8710$ cm$^{-1}$; $E_1 = -14,7800$ cm$^{-1}$; $E_2 = -14,6955$ cm$^{-1}$ [45–48].

Table 2. Energies E (cm$^{-1}$) and widths $\Gamma$ (cm$^{-1}$) of the autoionization resonances of configuration YbI 7s6p (see text).
pressure. In Table 3, we list the data on energies (counted from the energy of the ground state Yb 4f$^{14}$) excited AS with double excited valence shell: E1—RMBPT data (Ref. [30, 31]), E2—our theory.

In Tables 4 and 5, we list the analogous data for energies and widths of the other AS. In whole, analysis of these data shows that the results of our theory and the theory of Ivanov et al. regarding energies are in reasonable agreement with the experimental data.

However, in respect of the AS widths there is a reasonably large discrepancy between the theories, which is associated with the use of different basis of orbitals, different degree of accounting for the correlation effects, including continuum pressure (accounted channels nln'-n'nlp,d,f).

<table>
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Table 3. Energies (10$^5$ cm$^{-1}$) of the YbI AS with the double excited valence shell (see text).

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Table 4. Energies (10$^5$ cm$^{-1}$) of the YbI AS with the double excited valence shell (see text).
The analysis shows that the state of the $5d_{3/2}$ $(J=1)$ having an abnormally small width is AS, due to the fact that its decay is prohibited in the non-relativistic limit. This remarkable fact has been found by Ivanova et al. for the first time. From the numerical viewpoint, this effect can be linked with the presence of multiple oscillations of the wave functions in the electron core area.

On the other hand, we are talking about the phenomenon, inherent in heavy atoms and associated with a complex energetics of their valence shells. This fact in principle largely explains unusual and very rich physics of the AS in the lanthanide (rare-earth) atoms. Furthermore in Tables 6 and 7, we list the results of computing the energies and widths of autoionization resonances $4f^{13} [^2F_{7/2}] 6s^2 np[5/2]_g$, $4f^{13} [^2F_{7/2}] 6s^2 np[5/2]_g$, resulting from the excitation of electrons in 4f-shell. For comparison, there is data from experimental measurements via three-photon laser polarization spectroscopy method (see [24, 25] and references therein).

Here, one should pay attention to the smallness of the widths of desired resonances, which has not been explained in the literature in detail. In our opinion, this is due to the complex energetics of the studied atom (heavy multi-electron core), causing some unusual physics of AS and mechanisms of their decay, especially in comparison with the usual standards of

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Table 5. Widths (cm$^{-1}$) of the YbI AS with the double excited valence shell.

The analysis shows that the state of the $5d_{3/2} 5d_{5/2} (J=1)$ having an abnormally small width is AS, due to the fact that its decay is prohibited in the non-relativistic limit. This remarkable fact has been found by Ivanova et al. for the first time. From the numerical viewpoint, this effect can be linked with the presence of multiple oscillations of the wave functions in the electron core area.

On the other hand, we are talking about the phenomenon, inherent in heavy atoms and associated with a complex energetics of their valence shells. This fact in principle largely explains unusual and very rich physics of the AS in the lanthanide (rare-earth) atoms. Furthermore in Tables 6 and 7, we list the results of computing the energies and widths of autoionization resonances $4f^{13} [^2F_{7/2}] 6s^2 np[5/2]_g$, $4f^{13} [^2F_{7/2}] 6s^2 np[5/2]_g$, resulting from the excitation of electrons in 4f-shell. For comparison, there is data from experimental measurements via three-photon laser polarization spectroscopy method (see [24, 25] and references therein).

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<table>
<thead>
<tr>
<th>$n$</th>
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<th>$\Gamma_{exp}$</th>
<th>$E$ (our theory)</th>
<th>$\Gamma$ (our theory)</th>
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Table 6. Energies and widths (cm$^{-1}$) of autoionization resonances $4f^{13} [^2F_{7/2}] 6s^2 np[5/2]_g$, resulting from the excitation of electrons in 4f-shell.
atomic spectroscopy (typical AS widths for the He atom, atoms of the inert gases, alkali and alkali-earth atoms reach dozens and hundreds cm$^{-1}$).

3.2. Spectroscopy of excited and autoionization states in thulium

In contrast to the ytterbium atom, the thulium atom has been studied to a much lesser extent. Moreover, it is not difficult to understand that this atom is theoretically more complex than the ytterbium atom. In Refs. [32–41], it has been shown that two pairs of low-lying ionization limits (with vacancy states in the 4$^{13}f$ shell: 4$^{15}f$ and 4$^{17}f$) cause two main types of autoionization decay (Figure 3):

1. the classical decay channel of Beutler-Fano (BFD)

\[ 4f^{13}_j 6s_{1/2}(J_{12})nl \rightarrow 4f^{13}_j 6s_{1/2}(J_{12})Tm^+ + \epsilon l_{j'} n > 7, J_{12} = 2; 3, J_{12'} = 3; 4, \]  

2. the re-orientation-type decay (ROD) channel

\[ 4f^{13}_j 6s_{1/2}(J_{12})nl \rightarrow 4f^{13}_j 6s_{1/2}(J_{12})Tm^+ + \epsilon l_{j'} n > 25, J_{12} = 3, J_{12'} = 2; 4, j = 5/2; 7/2. \]  

Here ROD refers to re-orientation-type AS decay. The states $4f^{13}_j 6s_{1/2}(J_{12} = 3)nl$ are exposed simultaneously to BFD and ROD-decays. In contrast to BFD-decay, ROD-decay is a low energy process, preserving one-electron quantum numbers of the atomic core: 4$^{13}_j f$ and 6$s_{1/2}$. The ROD-decay can be of both monopole and quadrupole nature.

This refers to the QPs interaction multi-polarity that causes the AS decay. The states with $J_{12} = 2; 4$ are unable to disintegrate through ROD channel. However, their mixing with the states of the

<table>
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<th>$n$</th>
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Table 7. Energies and widths (cm$^{-1}$) of autoionization resonances $4f^{13}_j [2F_{7/2},6s\pi3j(5/2)]_p$, resulting from the excitation of electrons in 4$s$-shell.
ROD decaying type can greatly improve monopole ROD decay of the latter. For these Rydberg series, there is only possible AS decay channel—re-orientation one ROD. In Table 8, we list the results of computing the energies $E_2$ (10 cm$^{-1}$) and widths $\Gamma_2$ (cm$^{-1}$) of the AS $4f^{13} 6s_{1/2}(3)ns_{1/2}$, for which the ROD-decay is the only autoionization decay channel. For comparison, we list the calculated data obtained by Ivanov et al. (E1, $\Gamma_1$) [32–41] and Glushkov et al. (E, $\Gamma_3$) [6].

In Tables 9 and 10, we list our data on the widths and energies of the Tm AS $4f^{13} 6s_{1/2}(3)np_{1/2}$ and $4f^{5/2} 6s_{1/2}(2)ns_{1/2}$, for which BFD is the only autoionization decay channel. In Table 10,

$$\begin{array}{cccccccc}
 n & \Gamma_1 & \Gamma_3 & \Gamma_2 & E1 & E3 & E2 & \Gamma_2 & E2 \\
25 & 1.18 \text{ (}–5\text{)} & 1.29 \text{ (}–5\text{)} & 1.25 \text{ (}–5\text{)} & 4985 & 4981 & 4983 & 1.58 \text{ (}–2\text{)} & 4986 \\
26 & 1.13 \text{ (}–5\text{)} & – & – & 4975 & 1.34 \text{ (}–2\text{)} & 4988 \\
30 & 6.72 \text{ (}–6\text{)} & 6.12 \text{ (}–6\text{)} & 4995 & 4993 & 4994 & 3.98 \text{ (}–3\text{)} & 4995 \\
33 & 3.79 \text{ (}–6\text{)} & – & – & 4996 & 1.58 \text{ (}–2\text{)} & 4998 \\
35 & 3.21 \text{ (}–6\text{)} & – & – & 4998 & 3.18 \text{ (}–3\text{)} & 5000 \\
\end{array}$$

Table 8. Widths and energies of the Tm AS $4f^{13} 6s_{1/2}(3)ns_{1/2}$. 

**Figure 3.** Position of the low-lying Tm atom $4f^{5} 6s_{1/2}$ ionization limits and scheme of autoionization decay of Tm atom Rydberg states $4f^{5} 6s_{1/2}$. 

Theoretical Spectroscopy of Rare-Earth Elements: Spectra and Autoionization Resonances

http://dx.doi.org/10.5772/intechopen.69314
we list our data on the widths and energies (in cm\(^{-1}\)) of AS \(f_{13/2}^1 s_{1/2}(3) m_f | f\) (our data), which can decay in both the ROD and the BFD channels.

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Table 10. The widths (cm\(^{-1}\)) and energies (10\(^2\) cm\(^{-1}\)) of the Tm AS \(4 f_{13/2}^1 s_{1/2}(2) m_f | f\).

4. Conclusions

We have presented a brief review of the theoretical and experimental papers on spectroscopy of the rare-earth elements of ytterbium and thulium and some results of theoretical studying their spectra. Computing energy level positions and autoionization resonance widths and energies is fulfilled on the basis of the generalized relativistic energy approach and relativistic many-body PT with the Dirac-Kohn-Sham zeroth approximation and accurate accounting for the exchange-correlation and relativistic corrections. Spectral data for some autoionization resonances, such as the Rydberg ones, or autoionization states with the double excited valence shell and others are of a great interest as they reveal a sufficiently
high complexity of rare-earth elements (in particular, ytterbium and thulium) from the atomic spectroscopic viewpoint, indicating a rather complex dynamics of the decay of such states. Namely, these states play an important role in various atomic elementary processes in plasmas and gases. The Rydberg autoionization states are of considerable interest, for example, for the creation of new types of lasers, studies on the laser separation of heavy isotopes and nuclear isomers and the corresponding applications such as an analysis of trace quantities of rare-earth elements, etc. It should also be noted that the dynamics of the decay of autoionization resonances in ytterbium, thallium and other rare-earth elements in an external electromagnetic (laser) field is expected to be extremely complex and unusual. In any case, further study of the spectra, characteristics of the radiation and autoionization decay of the autoionization states in spectra of the rare-earth atoms is extremely important and actual.

Author details

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Odessa State Environmental University, Odessa, Ukraine

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