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Abstract. Theoretical studies of Rydberg autoionization resonances in spectra of lanthanides atoms (ytterbium) are carried out within the relativistic many-body perturbation theory in the generalized relativistic energy approach (Gell-Mann and Low S-matrix formalism). The accurate theoretical results on the autoionization $4f^{13}[^2F_{7/2}]6s^2np[5/2]_2$, $4f^{13}$ $[^2F_{7/2}]$ $6s^2nf[5/2]_2$ resonances energies and widths are presented and compared with experimental data, obtained by using laser polarization spectroscopy method.

1. Introduction

In this work, we present the results of our theoretical studies of spectra and spectroscopic parameters for heavy atoms, namely, lanthanides atoms (see, for example [1]). Investigations of spectra, optical and spectral, radiative and autoionization characteristics for heavy elements atoms and multicharged ions are traditionally of a great interest for further developments of quantum atomic optics and atomic spectroscopy and different applications in the plasma chemistry, astrophysics, laser physics etc. (see Refs. [1–23]). Different atomic spectroscopy methods have been used in describing radiative and autoionization characteristics of atomic systems. The well known classical multi-configuration Hartree-Fock method (relativistic effects are taken into account in the Pauli approximation or Breit Hamiltonian) allowed us to obtain a great number of useful spectral information about light and/or not-heavy atomic systems, yet it results in only qualitative description of spectra of the heavy atoms and ions. The multi-configuration Dirac-Fock method is the most reliable for multielectron systems with a large nuclear charge. In this calculation approach, the one- and two-particle relativistic effects are taken into account practically precisely. In essence, special attention should be given to two very general and important computer systems for relativistic and Quantum Electro-Dynamics (QED) calculations of atomic and molecular properties developed at Oxford, UK, known as GRASP ("GRASP", "Dirac"; "BERTHA") (see Refs. [1-4] and references therein). Relativistic many-body perturbation theory is effectively applied to the computation of spectra of low-lying states for lanthanides atoms [5-10].

Interpretation of spectra, radiative and autoionization characteristics for heavy atoms is quite challenging because it is required to correctly account for the exchange-correlation and relativistic corrections. Here we present the results of the Rydberg Yb $4f^{13}[^2F_{7/2}]6s^2np[5/2]_2$, $4f^{13}$ $[^2F_{7/2}]$ $6s^2nf[5/2]_2$ states energies, widths and compare with experimental laser polarization spectroscopy data [23].

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

As the method of computing has been presented in detail previously, here we summarize only the key elements. A model relativistic energy approach in a case of the multielectron atom has been proposed by Ivanov-Ivanova *et al.* [6-8] and its generalized gauge-invariant version has been developed in Refs. [9-12]. The approach is based on the Gell-Mann and Low S-matrix formalism, and the relativistic many-body perturbation theory that uses the optimized one-quasiparticle representation and an accurate account of the relativistic and exchange-correlation effects. In the relativistic case, the Gell-Mann and Low formula expressed an energy shift ΔE through the QED scattering matrix including the interaction of the photon vacuum field and of the laser field. The wave function zeroth basis is found from the Dirac equation with a potential, which includes *ab initio* optimized model potentials (Ivanov-Ivanova type [6]) or DF potentials, the electric potential of a nucleus – we usually use the Gaussian form of the charge distribution in a nucleus [4]. The correlation corrections of the perturbation theory of second and higher orders are taken into account with the polarization and screening potentials (see Refs. [10-16]).

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 applied for calculating the energy shifts ΔE of degenerate states. This procedure is connected to secular matrix M diagonalization [7, 8]. 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 perturbation theory (first order of the interelectron interaction). Their imaginary part of ΔE is connected to radiative decay. 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 published work by different authors, the 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 introduced previously [4, 13, 14]: 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 Perturbation Theory (PT) series for the interelectron interaction. The complex secular matrix M is represented in the form [7,8]:

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

Here, $M^{(0)}$ 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 real matrix, proportional to the unit matrix, but it determines only the general level shift. We assumed $M^{(0)} = 0$. The diagonal matrix $M^{(1)}$ can be represented 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 summed all the contributions of the one -quasiparticle diagrams of all orders of the formally exact QED perturbation theory. However, the necessary experimental quantities are not often available. The first two order corrections to Re$\{M^{(2)}\}$ have been analyzed [4] using Feynman diagrams. The contributions of the first-order diagrams have been completely calculated. In 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 account for the immediate quasiparticle interaction. 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 incorporated 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. Therefore, the secular matrix can be written as follows:

$$M \to \tilde{M}^{(1)} + \tilde{M}^{(2)}, \tag{2}$$

where $\tilde{M}^{(1)}$ is the modified one-quasiparticle matrix (diagonal), and $\tilde{M}^{(2)}$ the modified two-quasiparticle one. $\tilde{M}^{(1)}$ is calculated by substituting the modified one-quasiparticle energies, and $\tilde{M}^{(2)}$ by means of the first PT order formulae for $M^{(2)}$, putting the modified radial functions of the one-quasiparticle states in the radial integrals.

In QED theory, the photon propagator D(12) plays the role of the interaction. Naturally the analytical form of D(12) depends on the gauge, in which the electrodynamical potentials are written. The interelectron interaction operator that accounts for the Breit interaction has been taken as follows:

$$V(r_i r_j) = exp(i\omega r_{ij}) \cdot \frac{(1 - \alpha_i \alpha_j)}{r_{ij}} + V_{ee}^w, \tag{3}$$

where, as usual, α_i are the Dirac matrices. In general, the results of all approximate calculations depend on the gauge. Yet the correct result must be gauge-invariant. The gauge dependence of the amplitudes of the photo processes in the approximate calculations is well known. This is investigated in detail by Grant, Armstrong, Aymar and Luc-Koenig, Glushkov-Ivanov *et al.*, see Refs. [1-4,9-15]. 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. These results remain true in the energy approach because the final formulae for the probabilities coincide in both approaches. Glushkov-Ivanov developed a new relativistic gauge-conserved version of the energy approach [11]. Here we apply this approach for generating the optimized relativistic orbitals basis in the zeroth approximation of the many-body perturbation theory [1]. Below we will be interested in studying the spectra of the autoionization resonances in the ytterbium atom and calculate their energies and widths. The excited states of the ytterbium atom can be treated as the states with two-quasiparticles above the electron core [Xe]4f^{14}.

Within the standard energy approach [8-11], the autoionization width is determined by the square of an electron interaction matrix element having the form:

$$V_{1234}^{\omega} = [(j_1)(j_2)(j_3)(j_4)]^{1/2} \sum_{\lambda\mu} (-1)^{\mu} \begin{pmatrix} j_1 j_3 & \lambda \\ m_1 - m_3 & \mu \end{pmatrix} \times \mathrm{Re}\, Q_{\lambda}(1234) \tag{4}$$

The real part of the electron interaction matrix element is determined using expansion in terms of Bessel functions [17-19, 26]:

$$\frac{\cos|\omega|r_{12}}{r_{12}} = \frac{\pi}{2\sqrt{r_1 r_2}} \sum_{\lambda=0} (\lambda) J_{\lambda+1/2}(|\omega|r_<) J_{-\lambda-1/2}(|\omega|r_>) P_{\lambda}(\cos\widehat{\mathbf{r}_1 \mathbf{r}_2}) \cdot \tag{5}$$

The Coulomb part Q_{λ}^{Qul} is expressed in terms of radial integrals R_{λ}, angular coefficients S_{λ}:

$$\mathrm{Re}\, Q_{\lambda}^{Qul} = \frac{1}{Z} \mathrm{Re}\left\{ R_l(1243)S_{\lambda}(1243) + R_{\lambda}(\tilde{1}\, 24\tilde{3})S_{\lambda}(\tilde{1}\, 24\tilde{3}) + R_{\lambda}(1\tilde{2}\tilde{4}3)S_{\lambda}(1\tilde{2}\tilde{4}3) + R_{\lambda}(\tilde{1}\,\tilde{2}\tilde{4}\tilde{3})S_{\lambda}(\tilde{1}\,\tilde{2}\tilde{4}\tilde{3}) \right\}$$

$$\tag{6}$$

As a result, the autoionization decay probability is expressed in terms of $\mathrm{Re}Q_{\lambda}(1243)$ matrix elements. We present an example below:

$$\mathbf{Re}\, R_{\lambda}(1243) = \iint dr_1 r_1^2 r_2^2 f_1(r_1) f_3(r_1) f_2(r_2) f_4(r_2) Z_{\lambda}^{(1)}(r_<) Z_{\lambda}^{(1)}(r_>). \tag{7}$$

Here, f is the large component of radial part of single electron state Dirac function and the function Z is connected with the Bessel functions. The angular coefficient is defined in the standard way as above [26]. The Breit part of Q is defined in similar way as above, but our interest focuses on the real part. The Breit interaction is known to change considerably the Auger decay dynamics in some cases (see, for example, Refs. [8]). Determination of the radiation decay probabilities (oscillator strengths) simplifies to calculating the imaginary matrix elements of the interaction. The calculation of radial integrals $\mathbf{Re}R_\lambda(1243)$ is reduced to the solution of a system of differential equations according to the Ivanova-Ivanov method [26]. The system of differential equations includes also equations for functions $f/r^{|æ|-1}$, $g/r^{|æ|-1}$, $Z_\lambda^{(1)}$, $Z_\lambda^{(2)}$. The formulas for the autoionization (or "Auger") decay probability include the radial integrals $R_\alpha(\alpha k\gamma\beta)$, where one of the functions describes electron in the continuum state. When calculating this integral, the correct normalization of the function Ψ_k needs attention. The correctly normalized function should have the following asymptotic behaviour for $r\to 0$:

$$\left.\begin{array}{c} f \\ g \end{array}\right\} \to (\lambda\omega)^{-1/2} \left\{\begin{array}{l} \left[\omega + (\alpha Z)^{-2}\right]^{-1/2} sin(kr + \delta), \\ \left[\omega - (\alpha Z)^{-2}\right]^{-1/2} cos(kr + \delta). \end{array}\right. \tag{10}$$

It is important to note that the calculation is carried out in the jj-coupling scheme representation. The transition to the intermediate coupling scheme has been accomplished by diagonalizing the secular matrix. Indeed, only Re{M} should be diagonalized. The imaginary part is converted by means of the matrix of eigenvectors $\{C_{mk}\}$, obtained by diagonalization of Re{M}:

$$\mathrm{Im}\,M_{mk} = \sum_{ij} C_{mi}^* M_{ij} C_{jk} \tag{12}$$

M_{ij} are the matrix elements in the jj-coupling scheme, and M_{mk} in the intermediate coupling scheme representation. Other details can be found in Refs. [6-11,13-19].

3. Results
In Table 1 we present the experimental data (Jong-Hoon et al [22,23]) and theoretical results for energies and widths of the excited (autoionization) states of the $4f^{13}$ $[^2F_{7/2}]6s^2np[5/2]_2$ and $4f^{13}$ $[^2F_{7/2}]$ $6s^2$ $nf[5/2]_2$ states (because of excitation of the 4f shell) .

Table 1. Energies E (cm^{-1}) and widths Γ (cm^{-1}) of the $4f^{13}$ $[^2F_{7/2}]6s^2np[5/2]_2$ and $4f^{13}$ $[^2F_{7/2}]$ $6s^2$ nf $[5/2]_2$ states.

N	$4f^{13}$ $[^2F_{7/2}]$ $6s^2$ $np[5/2]_2$				$4f^{13}$ $[^2F_{7/2}]$ $6s^2$ $np[5/2]_2$			
	Exp. E_{exp}	Exp. Γ_{exp}	Theory E	Theory Γ	Exp. E_{exp}	Exp. Γ_{exp}	Theory E	Theory Γ
12	70120.5	1.5	70121	1.7	70963.6	0.5	70965	0.7
13	70482.0	0.4	70483	0.5	71105.0	0.4	71107	0.5
15	70914.8	1.2	70916	1.4	71312.2	1.4	71313	1.6
20	71428.1	0.6	71429	0.7	71559.1	0.8	71561	0.9
25	71612.5	1.3	71611	1.5	71672.5	0.5	71673	0.8
26	71633.3	0.6	71631	0.8	71687.5	0.5	71689	0.7
30	71698.8	0.5	71697	0.7	71732.4	0.4	71734	0.5
46	-	-	71797	0.4	-	-	71813	0.3

The smallness of the resonance widths requires attention. In our interpretation, narrow resonances are related to the complex energy structure of the 4f-shell atoms. Consequently, unusual behavior occurs for autoionization resonances and their decay mechanisms, especially in comparison with the standard spectroscopy (for inert gases, alkali atoms). We emphasize that that our theory provides a physically reasonable agreement with experimental results. Finally, it should be noted that the studied autoionization resonances (Rydberg states are more preferable) can be very useful, for example, in new laser photo-ionization schemes of separating the Yb isotopes and nuclear isomers [24].

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