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SPECTROSCOPY OF AUTOIONIZATION RESONANCES IN SPECTRA OF BARIUM: NEW SPECTRAL DATA

We applied a generalized energy approach (Gell-Mann and Low S-matrix formalism) combined with the relativistic multi-quasiparticle (QP) perturbation theory (PT) with the Dirac-Kohn-Sham zeroth approximation to studying autoionization resonances (AR) in complex atoms and ions, in particular, energies for the Rydberg barium with accounting for the exchange-correlation, relativistic

1. Introduction

Here we continue our investigations of studying the autoionization state and AR in spectra of complex atoms and ions. Let us note [1] that traditionally an investigation of spectra, spectral, radiative and autoionization characteristics for heavy and superheavy elements atoms and multicharged ions is of a great interest for further development atomic and nuclear theories and different applications in the plasma chemistry, astrophysics, laser physics, etc. (look Refs. [1–10]). Theoretical methods of calculation of the spectroscopic characteristics for heavy atoms and ions may be divided into a few main groups [1-6]. First, the well known, classical multi-configuration Hartree-Fock method (as a rule, the relativistic effects are taken into account in the Pauli approximation or Breit hamiltonian etc.) allowed to get a great number of the useful spectral information about light and not heavy atomic systems, but in fact it provides only qualitative description of spectra of the heavy and superheavy ions. Second, the multi-configuration Dirac-Fock (MCDF) 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 effects are taken into account practically precisely. In this essence it should be given special attention to two very general and important computer systems for relativistic and QED calculations of atomic and molecular properties developed in the Oxford group and known as GRASP ("GRASP", "Dirac"; "BERTHA", "QED") (look [1-5] and refs. therein). In particular, the BERTHA program embodies a new formulation of relativistic molecular structure theory within the framework of relativistic QED. This leads to a simple and transparent formulation of Dirac-Hartree-Fock-Breit (DHFB) self-consistent field equations along with algorithms for molecular properties, electron correlation, and higher order QED effects. The DHFB equations are solved by a direct method based on a relativistic generalization of the McMurchie-Davidson algorithm [4].

In this paper we applied a new relativistic approach [11-15] to relativistic studying the autoionization characteristics of the barium atom. Let us note that new approach in optics and spectroscopy of heavy atomic systems is the combined the generalized energy approach and the gauge-invariant QED many-QP PT with the Dirac-Kohn-Sham (DKS) "0" approximation (optimized 1QP representation) and an accurate accounting for relativistic, correlation, nuclear, radiative effects. In refs. [11-15, 17-20]. It has been in etails presented, so here we give only the fundamental aspects. The generalized gauge-invariant version of the energy approach has been further developed in Refs. [12,13].

2. Relativistic approach in autoionization spectroscopy of heavy atoms

In relativistic case the Gell-Mann and Low formula expressed an energy shift DE through the QED scattering matrix including the interaction with as the photon vacuum field as the laser field. The first case is corresponding to definition of the traditional radiative and autoionization characteristics of multielectron atom. The wave function zeroth basis is found from the Dirac-Kohn-Sham equation with a potential, which includes the ab initio (the optimized model potential or DF potentials, electric and polarization potentials of a nucleus; the Gaussian or Fermi forms of the charge distribution in a nucleus are usually used) [5]. Generally speaking, the majority of complex atomic systems possess a dense energy spectrum of interacting states with essentially relativistic properties. Further one should realize a field procedure for calculating the energy shifts DE of degenerate states, which is connected with the secular matrix *M* diagonalization [8-12]. The secular matrix elements are already complex in the second order of the PT. Their imaginary parts are connected with a decay possibility. A total energy shift of the state is presented in the standard form:

$$\Delta \mathrm{E} = \mathrm{Re}\,\Delta E + i\,\mathrm{Im}\,\Delta E \qquad \mathrm{Im}\,\Delta E = -\Gamma/2\,, \quad (1)$$

where Γ is interpreted as the level width, and the decay possibility $\mathrm{P} = \Gamma$. The whole calculation of the energies and decay probabilities of a non-degenerate excited state is reduced to the calculation and diagonalization of the *M*. The *jj*-coupling scheme is usually used. The complex secular matrix *M* is represented in the form [9,10]:

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

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-QP 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 1QP contributions. For simple systems (such as alkali atoms and ions) the 1QP energies can be taken from the experiment. Substituting these quantities into (2) one could have summarized all the contributions of the 1QP diagrams of all orders of the formally exact QED PT. However, the necessary experimental quantities are not often available. So, the optimized 1-QP representation is the best one to determine the zeroth approximation. The correlation corrections of the PT high orders are taken into account within the Green functions method (with the use of the Feynman diagram's technique). All correlation corrections of the second order and dominated classes of the higher orders diagrams (electrons screening, polarization, particle-hole interaction, mass operator iterations) are taken into account [10-14]. In the second order, there are two important kinds of diagrams: polarization and ladder ones. Some of the ladder diagram contributions as well as some of the 3QP diagram contributions in all PT orders have the same angular symmetry as the 2QP diagram contributions of the first order [10-12]. 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 two others. The additional potential modifies the 1QP orbitals and energies. Then the secular matrix is : $M \simeq \tilde{M}^{(1)} + \tilde{M}^{(2)}$, where $\tilde{M}^{(1)}$ is the modified 1QP matrix (diagonal), and $\tilde{M}^{(2)}$ the modified 2QP one. $\tilde{M}^{(1)}$ is calculated by substituting the modified 1QP energies), and $\tilde{M}^{(2)}$ by means of the first PT order formulae for $M^{(2)}$, putting the modified radial functions of the 1QP states in the interaction radial integrals. Let us remind that in the QED theory, the photon propagator D(12) plays the role of this interaction. Naturally, an analytical form of D depends on the gauge, in which the electrodynamic potentials are written. 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 photoprocesses in the approximate calculations is

a well known fact and is in details investigated by Grant, Armstrong, Aymar-Luc-Koenig, Glushkov-Ivanov [1,2,5,9]. 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 are gauge invariant. These results remain true in an energy approach as the final formulae for the probabilities coincide in both approaches. In ref. [16] it has been developed a new version of the approach to conserve gauge invariance. Here we applied it to get the gauge-invariant procedure for generating the relativistic DKS orbital bases (abbreviator of our method: GIRPT). The autoionization width is defined by the square of interaction matrix element [9]:

$$V^{\omega}_{1234} = [(j_1)(j_2)(j_3)(j_4)]^{1/2} \sum_{\lambda\mu} (-1)^{\mu} \begin{pmatrix} j_1 & j_3 & \lambda \\ m_1 & -m_3 & \mu \end{pmatrix} \times \mathrm{Re}\, Q_{\lambda}(1234) \tag{3}$$

The real part of the interaction matrix element can be expanded in terms of Bessel functions [5,8]:

$$\frac{\cos|\omega|r_{12}}{r_{12}} = \frac{\pi}{2\sqrt{r_1 r_2}} \sum_{\lambda=0} (\lambda) J_{\lambda+1/2}(|\omega| r_<) J_{-\lambda-1/2}(|\omega| r_>) P_{\lambda}(\cos \mathbf{r}_1 \mathbf{r}_2) \tag{4}$$

The Coulomb part $Q^{\mathrm{Qul}}_{\lambda}$ is expressed in the radial integrals R_1, angular coefficients S_1 as follows:

$$\begin{aligned} \mathrm{Re}\, Q^{\mathrm{Qul}}_{\lambda} \sim \mathrm{Re}\{ & R_l(1243) S_{\lambda}(1243) + R_{\lambda}(\tilde{1}24\tilde{3}) S_{\lambda}(\tilde{1}24\tilde{3}) \\ & + R_{\lambda}(1\tilde{2}\tilde{4}3) S_{\lambda}(1\tilde{2}\tilde{4}3) + R_{\lambda}(\tilde{1}\tilde{2}\tilde{4}\tilde{3}) S_{\lambda}(\tilde{1}\tilde{2}\tilde{4}\tilde{3}) \} \end{aligned} \tag{5}$$

where $\mathrm{Re}Q_1(1243)$ is as follows:

$$\mathbf{Re}\, R_{\lambda}(1243) = \iint dr_1 r_1^2 r_2^2 f_1(r_1) f_3(r_1) f_2(r_2) f_4(r_2) Z^{(1)}_{\lambda}(r_<) Z^{(1)}_{\lambda}(r_>) \tag{6}$$

where f is the large component of radial part of the 1QP state Dirac function and function Z is :

$$Z^{(1)}_{\lambda} = [2/|\omega_3|\alpha Z]^{\lambda+1/2} J_{\lambda+1/2}(\alpha|\omega_3|r) [r^{\lambda} \Gamma(\lambda + 3/2)]. \tag{7}$$

The angular coefficient is defined by standard way as above [3]. The calculation of radial integrals $\mathbf{Re}R_1(1243)$ is reduced to the solution of a system of differential equations:

$$\left.\begin{aligned} y_1' &= f_1 f_3 Z^{(1)}_{\lambda}(\alpha|\omega|r) r^{2+\lambda}, \\ y_2' &= f_2 f_4 Z^{(1)}_{\lambda}(\alpha|\omega|r) r^{2+\lambda}, \\ y_3' &= [y_1 f_2 f_4 + y_2 f_1 f_3] Z^{(2)}_{\lambda}(\alpha|\omega|r) r^{1-\lambda}. \end{aligned}\right\} \tag{8}$$

In addition, $y_3(\infty)=\mathbf{Re}R_1(1243)$, $y_1(\infty)=X_1(13)$. The system of differential equations includes also equations for functions $f/r^{|æ|-1}$, $g/r^{|æ|-1}$, $Z^{(1)}_{\lambda}$, $Z^{(2)}_{\lambda}$. The formulas for the autoionization (Auger) decay probability include the radial integrals $R_a(akgb)$, where one of the functions describes electron in the continuum state. When calculating this integral, the correct normalization of the function Y_k is a problem. The correctly normalized function should have the following asymptotic at $r \to 0$:

$$\left.\begin{matrix} f \\ g \end{matrix}\right\} \to (\lambda\omega)^{-1/2} \begin{cases} [\omega + (\alpha Z)^{-2}]^{-1/2} \sin(kr + \delta), \\ [\omega - (\alpha Z)^{-2}]^{-1/2} \cos(kr + \delta). \end{cases} \tag{9}$$

When integrating the master system, the function is calculated simultaneously:

$$N(r) = \{\pi\omega_k [f_k^2 [\omega_k + (\alpha Z)^{-2}] + g_k^2 [\omega_k + (\alpha Z^{-2})]]\}^{-1/2} \tag{10}$$

It can be shown that at $r \to \infty$, $N(r) \to N_k$, where N_k is the normalization of functions f_k, g_k of continuous spectrum satisfying the condition (9). Other details can be found in refs.[10-13,16-20].

3. Results and conclusions

In table 1 we present the data for energies (cm^{-1}) of the barium autoionization resonances 4fnf, n = 15 (averaged over the fine structure) measured experimentally and calculated on the basis of our theory and multichannel quantum defect method (MCQD) with the empirical fit (de Graaf et al) [2]. An analysis shows quite physically reasonable agreement between the theoretical and experimental results. But some difference, in our opinion, can be explained by different accuracy of estimates of the radial integrals, using the different type basises (gauge invariance conservation or a degree of accounting for the exchange-correlation effects) and some other additional calculation approximations. In our theory there are used more optimized basises of the orbitals in comparison with the MCQD).

In ref. [14] (see also [5,12]) it has been predicted a new spectroscopy effect of the giant changing of the AS ROD width in a sufficiently weak electric field (for two pairs of the Tm, Gd AR).

Following to [5], let us remind that any two states of different parity can be mixed by the external electric field. The mixing leads to redistribution of the autoionization widths. In the case of degenerate or near-degenerate resonances this effect becomes observable even at a moderately weak field.

Table 1.

Energies (cm^{-1}) of autoionization resonances 4fnf, n = 15 (averaged over the fine structure) measured experimentally and calculated on the basis of our theory and multichannel quantum defect method (MCQD) with the empirical fit (de Graaf et al)

AC	J	Exp.	MCQD	Our work
$4f_{5/2}15f_{7/2}$	6	89 758.4±0.5	89759.1	89758.8
$4f_{7/2}15f_{5/2}$	6	89 993.6±0.5	89992.4	89993.6
$4f_{7/2}15f_{7/2}$	6	89 926.6±5.0	89937.1	89926.8
$4f_{5/2}15f_{7/2}$	5	89 726.3±1.0	89718.7	89726.9
$4f_{5/2}15f_{5/2}$	5	89 749.2±0.5	89748.6	89749.7
$4f_{7/2}15f_{7/2}$	5	89 951.0±0.5	89952.9	89951.6
$4f_{7/2}15f_{5/2}$	5	-	-	89942.3
$4f_{5/2}15f_{5/2}$	4	89 705.6±0.5	89706.8	89705.4
$4f_{5/2}15f_{7/2}$	4	-	-	89718.5
$4f_{7/2}15f_{5/2}$	4	89 937.8±2.0	89937.2	89937.6
$4f_{7/2}15f_{7/2}$	4	89 951.0±2.0	89951.8	89951.5
$4f_{5/2}15f_{5/2}$	3	-	-	89728.5
$4f_{5/2}15f_{7/2}$	3	89 741.5±2.0	89738.0	89740.9
$4f_{7/2}15f_{7/2}$	3	89 969.3±2.0	89972.0	89969.8
$4f_{7/2}15f_{5/2}$	3	-	-	89953.4
$4f_{5/2}15f_{7/2}$	2	89 766.5±5.0	89774.7	89767.8

In the Tm one could deal with ROD *nd* and *nf* series, converging to the same ionization limit, i.e. they are nearly degenerate states of different parity. Among them one can find some pairs of *nd* and *nf* states with widths Γ, differing by several orders. So, we could suggest that the phenomenological effect of giant broadening of the Rydberg AS could take a place in the barium atom too, however, the corresponding detailed investigation is required.

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SPECTROSCOPY OF AUTOIONIZATION RESONANCES IN SPECTRA OF HE-LIKE IONS AND ALKALI-EARTH ATOMS: NEW SPECTRAL DATA AND CHAOS EFFECT

Abstract

We applied a generalized energy approach (Gell-Mann and Low S-matrix formalism) combined with the relativistic multi-quasiparticle (QP) perturbation theory (PT) with the Dirac-Kohn-Sham zeroth approximation to studying autoionization resonances (AR) in complex atoms and ions, in particular, energies for the Rydberg barium with accounting for the exchange-correlation, relativistic corrections.

Key words: spectroscopy of autoionization resonances, relativistic energy approach

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СПЕКТРОСКОПИЯ АВТОИОНИЗАЦИОННЫХ РЕЗОНАНСОВ В СПЕКТРАХ БАРИЯ: НОВЫЕ СПЕКТРАЛЬНЫЕ ДАННЫЕ

Резюме

Обобщенный энергетический подход (S-матричный формализм Гелл-Мана и Лоу) и релятивистская теория возмущений с дирак-кон-шэмовским нулевым приближением применены к изучению автоионизационных резонансов в сложных атомах, в частности, энергий автоионизационных резонансов в ридберговом барии с учетом обменно-корреляционных и релятивистских поправок.

Ключевые слова: спектроскопия автоионизационных резонансов, релятивистский энергетический подход

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СПЕКТРОСКОПІЯ АВТОІОНІЗАЦІЙНИХ РЕЗОНАНСІВ В СПЕКТРАХ БАРІЯ: НОВІ СПЕКТРАЛЬНІ ДАНІ

Резюме

Узагальнений енергетичний підхід (S-матричний формалізм Гелл-Мана та Лоу) и релятивістська теорія збурень з дірак-кон-шемівським нульовим наближенням застосовані до вивчення автоіонізаційних резонансів у складних атомах, зокрема, енергій автоіонізаційних резонансів у в рідберговому барії з урахуванням обмінно-кореляційних і релятивістських поправок.

Ключові слова: спектроскопія автоіонізаційних резонансів, релятивістський енергетичний підхід