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RELATIVISTIC SPECTROSCOPY OF ATOMIC SYSTEMS: SPECTRAL LINES BROADENING AND SHIFT FOR HEAVY ELEMENTS IN THE BUFFER GAS AND PLASMAS ENVIRONMENT

It has been developed a modified relativistic approach to describing the shift and broadening due to collisions of spectral lines of hyperfine structure for alkali atoms in an atmosphere of buffer (inert) gases. The approach is based on the generalized kinetic theory of spectral lines, exchange, relativistic perturbation theory with the Dirac-Hartree-Slater zeroth approximation and accounting for the complicated correlation effects by means of using the many-body polarization density-dependent functionals. The basic expressions for the collision shift and broadening hyperfine structure spectral lines are taken from the kinetic theory of spectral lines. The exchange perturbation theory (the modified version EL-HAV) has been used to calculate the corresponding potentials. The results of calculating the interatomic potentials, local shifts, temperature dependent spectral line shifts for the systems of the Rb, Cs-He are listed and compared with available theoretical and experimental data. The important feature of our scheme is correct taking into account the correlation (polarization) effects with using special effective functionals from. The difference between our theoretical data and other calculation results can be explained by using different perturbation theory versions and different approximations for calculating the wave functions basis's.

1. Introduction

The behavior of atomic and molecular systems in different gas and plasmas environments is an actual problem of modern physics, namely, molecular, physics, photoelectronic, optics and spectroscopy etc. On the one hand, sources of high-energy (e.g. ultraviolet) radiation have become widely used, including the technique of picosecond and femtosecond laser pulses. In particular, dyes have become widely used in various fields of optics , spectroscopy, atomic and molecular physics, quantum and photoelectronics (including for recording information (compact discs), dyeing fabrics, as working substances of lasers based on dyes, etc).

In the last two decades, a number of fundamentally new discoveries have been made in atomic physics, in particular, obtaining a Bose condensate in pairs of Rydberg atoms of alkaline elements (by the way, the question of the shift and broadening of the spectral lines of atoms in such a gas is an extremely urgent modern task), the creation of fountains of cold atoms, the possibility of building Tl quantum measure, and so on, which is largely due to the unprecedented progress in the development of new experimental methods of research (magneto-optical traps, accelerators, sources of intense laser radiation, etc.). This stimulates the possibilities of studying the spectroscopic characteristics of atoms, including the parameters of spectral lines for atoms in the external gas of plasmas environments, increasingly with higher accuracy. Although modern atomic spectroscopy has a wide range of different quantum methods (in particular, Hartree-Fock self-consistent field (HF) and Dirac-Fock (DF) methods, methods of quantum defect, model potential, density functional (DF), various variants of perturbation theory (PT), including the Rayleigh-Schrödinger, Möller-Plesset PT, various versions of the exchange PT, and even new methods such as mega-DF, "Bertha" and so on) for calculating the electronic structure of atoms, interatomic potentials, various spectroscopic characteristics, etc., however, most

of them still have a number of fundamental shortcomings.

High precision data for collisional shifts and broadening the hyperfine structure lines of heavy elements (alkali, alkali-earth, lanthanides, actinides and others) in an atmosphere of the inert gases are of a great interest for modern quantum chemistry, atomic and molecular spectroscopy, astrophysics and metrology as well as for studying a role of weak interactions in atomic optics and heavy-elements chemistry [1-27]. As a rule, the cited spectral lines shift and broadening due to a collision of the emitting atoms with the buffer gas or plasmas atoms and ions are very sensitive to a kind of the interatomic interaction potential. Besides, calculation of the hyperfine structure line shift and broadening allows to check a quality of the wave functions and study a contribution of the relativistic and correlation effects to the energetic and spectral characteristics of the two-center (multi-center) atomic systems.

Modern representations about the characteristics of spectral lines of atomic systems, the most widespread variants of the theory of spectral lines of atoms and, in particular, the theory of shift and broadening of spectral lines of the hyperfine transitions for atoms (ions) in an atmosphere of buffer (inert) gases are presented in Refs. [1-5].

An analysis of modern quantum methods for calculating the characteristics of the spectroscopic characteristics of atoms and ions is presented, taking into account correlation, relativistic and radiation corrections to one degree or another is given in Refs. [3-6].
In this paper it has been developed a modified
relativistic approach to describing the shift and broadening due to collisions of spectral lines of hyperfine structure for alkali atoms in an atmosphere of buffer (inert) gases. The approach is based on the generalized kinetic theory of spectral lines, exchange, relativistic PT with the Dirac-Hartree-Slater zeroth approximation and accouting for the complicated correlation effects by means of using the many-body polarization density-dependent functionals. The basic expressions for the collision shift and broadening hyperfine structure spectral lines are taken from the kinetic theory of spectral lines [1,9,10]. The

exchange perturbation theory (the modified version EL-HAV) has been used to calculate the corresponding potentials (see details in [2-8]).

The important feature of our scheme is correct taking into account the correlation (polarization) effects with using special effective functionals from [1,4-7,16-18]. The difference between our theoretical data and other calculation results can be explained by using different PT schemes and different approximations for calculating the wave functions. Some of the obtained results of calculating the interatomic potentials, local shifts, temperature dependent observed spectral hyperfine line shifts for the systems of the Rb, Cs-He are listed and compared with available theoretical and experimental data.

2. Fundamentals of the method

As the key features of the presented approach gave been described in Ref. [10-12], below we will concentrate on the original moments of our approach.
As usually, in order to compute a collision shift of the hyperfine structure spectral lines one should use the following expression, which is known in the kinetic theory of spectral lines shape (see Refs. [7-9]):

$$f_p = \frac{D}{p} = \frac{4\pi w_0}{kT} \int_0^\infty dw(R) \exp\left(-U(R)/kT\right) R^2 dR$$

(1)

Here T is a temperature, $U(R)$ is an effective potential of the a-b interatomic interaction, w_0 is a frequency of the hyperfine structure transition in an isolated active atom; $d\omega(R) = Dw(R)/w_0$ is a relative local shift of the hyperfine structure line.

The local shift is caused due to the disposition of the active atoms (say, the atoms of lead Pb and helium He) at the distance R. In order to calculate an effective potential of the interatomic interaction further we use the exchange PT formalism (the modified version EL-HAV) [1,8,9].

The relative local shift of the hyperfine structure line is defined as follows:

$$\delta\omega(R)=\frac{S_0}{1-S_0}+\Omega_1+\Omega_2-\frac{C_6}{R^6}\left(\frac{2}{\overline{E}_a}+\frac{1}{\overline{E}_a+\overline{E}_B}\right),(2a)$$

$$\overline{E}_{\alpha,b}=\left(I_{a,b}+E_{1a,b}\right)/2 \qquad (2b)$$

Here S_0 is the overlapping integral; C_6 is the van der Waals coefficient; I is the potential of ionization; $E_{1a,b}$ is the energy of excitation to the first (low-lying) level of the corresponding atom. The values Ω_1, Ω_2 in Eq. (2) are the first order non-exchange and exchange non-perturbation sums correspondingly [8-10]. These quantities can be determined by the following way:

$$\Omega_1=\frac{2}{N(1-S_0)\rho_0}\sum_k{}'\frac{\langle\Phi_0'(1)|H_{HF}'|\Phi_k'(1)\rangle V_{k0}}{E_0-E_k}$$

$$\Omega_2=\frac{2}{N(1-S_0)\rho_0}\sum_k{}'\frac{\langle\Phi_0'(1)|H_{HF}'|\Phi_k'(1)\rangle U_{k0}}{E_0-E_k}$$

$$\rho_0=<\Phi_0^1(1)|H_{HF}'|\Phi_0'(1)>/<\Phi_0^1(1)|\Phi_0'(1)>$$
$$(3)$$

where H_{HF}' is the operator of hyperfine interaction; N is the total number of electrons, which are taken into account in the calculation; E_k, $\Phi_k'(1)=F_{k_a}'(1)\phi_{k_b}(2\dots N)$ are an energy and a non-symmetrized wave function of state $k=\{k_a, k_b\}$ for the isolated atoms a and b.
The non-exchange matrix element of the Coulomb interatomic interaction is as:

$$V_{ko}=<\Phi'_k(1)\mid V(1)\mid\Phi'_0(1)>. \qquad (4)$$

Correspondingly the exchange matrix element is as follows:

$$U_{k0}=\sum_{i=2}^N\langle\Phi_k'(1)|V(i)|\Phi_0'(i)\rangle \qquad (5)$$

The operator $V(i)$ (for example, in a case of the system "a-b") is as follows:

$$V(i)=U_{SCF}(r_{a3})+U_{SCF}(r_{a4})-2U_{SCF}(R)+\frac{1}{r_{bi}}\cdot(6)$$

where $U_{SCF}(r)$ is the self-consistent field, created by the lead atomic core.

The van der Waals coefficient C_6 for the interatomic a-b interaction can be computed on the basis of the standard definition (see details. For example, in refs. [2,9-12,23]:

$$C_6(L,M)=C_{6,0}(L)-\frac{3M^2-L(L+1)}{(2L-1)(2L+3)}\cdot C_{6,2}(l) ,$$
$$(7)$$

Here $C_{6,0}(L)$ is the isotropic component of the interaction and $C_{6,2}(L)$ is the component corresponding to the $P_2(cos\ \theta)$ term in the expansion of the interaction in Legendre polynomials, where the angle specifies the orientation in the space-fixed frame. The dispersion coefficients $C_{6,0}(L)$ and $C_{6,2}(L)$ may be expressed in terms of the scalar and tensor polarizabilities $\alpha_0(L;iw)$ and $\alpha_2(L;iw)$ evaluated at imaginary frequencies [9]. Other details can be found in Refs. [8-21].

The key original moment of any computational scheme is connected with the method of calculation the electron wave functions.

As a rule, (see, for example, Ref. [8]), the non-relativistic Hartree-Fock or relativistic Dirac-Fock methods are used for calculating the corresponding wave functions [8-14]. Another variant is using the relativistic wave functions as the solutions of the Dirac equations with the corresponding density functional (the Dirac-Kohn-Sham theory) and effective potentials [7,14,15]. In our calculational scheme the relativistic optimized Dirac-Hartree-Slater scheme with basis formulas [10-12] is used.

3. Results and conclusions

In Tables 1,2 we present our theoretical results for the line shift f_p (1/Torr) in a case of the Rb-He and Cs-He pairs. The observed value (experiment) of the line shift (T=323K) and other theoretical results [6,10] for f_p are listed too. The theoretical results in Ref. [8] are obtained on the basis of calculation within the exchange PT with using the He wave functions in the approximation by Clementi et al (Theory[a] [8]) and wave functions in the Hartree-Fock approximation Theory[b] [8]). The

Dirac-Kohn-Sham scheme gas been used in Ref.[10].

Table 1. The observed $f\times$ (10^{-9} 1/Torr) shift for the diatomic system Rb-He: data of [8a] with using the He wave functions in the approximation by Clementi et al; (see text).

a-b	Rb-He	Rb-He	Rb-He	Rb-He
T, K	Experi-ment	Theory [10]	Theory[a] [6]	This work
323	105	101	75	102
423	-	89	64	91
523	-	80	56	82
623	-	73	50	75

The important feature of our scheme is correct taking into account the correlation (polarization) effects with using special effective functionals from [19,22]. The difference between our theoretical data and other calculation results can be explained by using different PT schemes and different approximations for calculating the wave functions. It is obvious that the using correct version of the exchange PT was well as the optimized basis's of wave functions and correct accounting for the exchange-correlation effects is principally necessary for an adequate description of the energetic and spectral properties of

Table 2. The observed $f\times$ (10^{-9} 1/Torr) shift for the diatomic system Cs-He: data of [8a] with using the He wave functions in the approximation by Clementi et al; [8b] -wave functions in the Hartree-Fock approximation (see text).

a-b	Cs-He	Cs-He	Cs-He	Cs-He	Cs-He
T, K	Experi-ment	Theory [a] [6]	Theory [b] [6]	Theory[a] [10]	This work
323	135	126	109	137	137
423	-	111	96	123	123
523	-	100	85	112	112
623	-	94	78	105	105

the alkali elements in an atmosphere of the heavy inert gases. It is represented a great interest a generalization of the presented approach on energy and radiation properties

and studying spectral lines characteristics for atomic and ionic systems in the corresponding plasmas environments.

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Summary. It has been developed a modified relativistic approach to describing the shift and broadening due to collisions of spectral lines of hyperfine structure for alkali atoms in an atmosphere of buffer (inert) gases. The approach is based on the generalized kinetic theory of spectral lines, exchange, relativistic perturbation theory with the Dirac-Hartree-Slater zeroth

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Key words: relativistic spectroscopy, spectral lines shift and broadening, atomic systems, relativistic theory, perturbation theory, gas and plasmas environments,

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РЕЛЯТИВІСТСЬКА СПЕКТРОСКОПІЯ АТОМНИХ СИСТЕМ: РОЗШИРЕННЯ ТА ЗСУВ СПЕКТРАЛЬНИХ ЛІНІЙ ДЛЯ ВАЖКИХ ЕЛЕМЕНТІВ У БУФЕРНОМУ ГАЗОВОМУ ТА ПЛАЗМОВОМУ СЕРЕДОВИЩАХ

Резюме. Розроблено модифікований релятивістський підхід до опису зсуву та розширення за рахунок зіткнень спектральних ліній надтонкої структури для лужних атомів в атмосфері буферних (інертних) газів. Підхід базується на узагальненій кінетичній теорії спектральних ліній, обміну, релятивістській теорії збурень з нульовим наближенням Дірака-Хартрі-Слетера та врахуванням складних кореляційних ефектів за допомогою використання поляризаційних багаточастинкових залежних від густини функціоналів. Основні вирази для колізійного зсуву та розширення спектральних ліній надтонкої структури взяті з кінетичної теорії спектральних ліній. Для розрахунку відповідних потенціалів використано теорію обмінних збурень (модифікована версія EL-HAV). Наведено результати розрахунків локальних зсувів, температурно-залежних повних зсувів спектральних ліній для систем Rb, Cs-He та проведене порівняння з наявними теоретичними та експериментальними даними. Важливою особливістю нашої схеми є коректне урахування кореляційних (поляризаційних) ефектів із застосуванням спеціальних ефективних функціоналів густини. Різницю між нашими теоретичними даними та іншими результатами розрахунків можна пояснити використанням різних версій теорії збурень і різних наближень для розрахунку базису хвильових функцій.

Ключові слова: релятивістська спектроскопія, зміщення та розширення спектральних ліній, атомні системи, релятивістська теорія, теорія збурень, газове та плазмове середовища.