Collisional shift of the heavy atoms hyperfine lines in an atmosphere of the inert gas

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Abstract. New relativistic approach, based on the relativistic many-body perturbation theory (PT) with using the optimized wave functions sets, is applied to calculating the potentials and hyperfine structure collision shift for heavy atoms in atmosphere of inert gases. Data for the collisional shifts of the Cs, Tl and Yb atoms in atmosphere of the inert gases are presented.

1. Introduction
Studying the collisional shifts and broadening of the hyperfine structure lines for heavy elements (alkali, alkali-earth, lanthanides, actinides and others) in an atmosphere of inert gases is one of the important and actual topics of the modern quantum chemistry, atomic optics and spectroscopy [1-11]. It should be mentioned also that the heavy atoms are interesting from the point of view of studying a role of weak interactions in atomic optics and heavy-elements chemistry. Besides, calculation of the hyperfine structure line shift and broadening allows one to check the quality of wave functions and study a contribution of relativistic effects in two-center (multi-center) atomic systems. From the applied science point of view, the mentioned physical effects form a basis for creating an atomic quantum measure of frequency [8]. For a long time the corresponding phenomenon for thallium atom attracted a special attention because of possibility to create the thallium quantum frequency measure. Alexandrov and co-workers [8] have realized the optical pumping of the thallium atoms on the line of 21GHz, which corresponds to transition between the components of hyperfine structure for the ground state, and have measured the collisional shift of this line due to buffer (bath) gas. Naturally, the inert buffer gases (He, Ar etc.) were used. The detailed non-relativistic theory of the collisional shift and broadening of the hyperfine structure lines for simple elements (light alkali elements etc.) has been developed by many authors (see discussions in refs. [1-9]). However, consideration of heavy elements faces serious difficulties related with account for the relativistic and correlation corrections. By the way, in last years the lanthanide and actinide elements attract a great interest because of their perspectives in many applications, including the sensor physics and atomic optics devices (see refs. [2,10,11] and references there).

It is very curious that until now a consistent, accurate quantum mechanical approach for calculating main characteristics of the collisional processes was not developed though many different simplified models have been proposed (see, for example [2-11]). The most widespread approach is based on the calculation of the corresponding collision cross-section, in particular, in a case of the van der Waals interaction between colliding particles. However, such an approach does not factually define any difference between the Penning process and resonant collisional one and gives often non-correct results for cross-sections. More consistent method requires data on the process probability \( G( R ) \) as a function of inter nuclear distance. It should be noted that these data are practically absent at present.
time. In this paper a new relativistic optimized approach, based on the gauge-invariant perturbation theory (PT) with using the optimized wave functions basis’s, is applied to calculating the inter atomic potentials, hyper fine structure collision shift for alkali and ytterbium atoms in atmosphere of inert gases. The basic expressions for the collision shift and broadening of the hyperfine structure spectral lines are taken from the kinetic theory of spectral lines [6,7,11]. The exchange perturbation theory (the modified version EL-HAV) has been used for calculating the corresponding potentials (see details in [1]). New data for the collisional shifts of the Tl and Yb atoms in atmosphere of the inert gases are presented.

2. Hyperfine lines shift for system “heavy atom- inert gas”

To calculate the collision shift of hyperfine structure spectral lines one could use the following expression known from kinetic theory of spectral line form (see [5-7,11]):

\[ f_p = \frac{\Delta}{p} = \frac{4\pi \tilde{N}_b}{p} \int_0^\infty e^{-U(R)/kT} \left[ 1 + g(R) \right] \tilde{\delta}(R) R^2 dR, \]  

(1)

where \( U(R) \) is the effective potential of the interatomic interaction, which has a central symmetry in a case of the systems A-B (in our case, for example, B=He; A=Yb); \( T \) is a temperature, \( w_0 \) is a frequency of the hyperfine structure transition in the isolated active atom; \( d\omega(R) = D\omega(R)/w_0 \) is the relative local shift of the hyperfine structure lines, which is arisen due to the disposition of the active atoms (say, atom of ytterbium Yb and helium He) on a distance \( R \), \( \{ 1 + g(R) \} \) is a temperature factor. To calculate an effective potential of the interatomic interaction a method of the exchange perturbation theory (the modified version EL-HAV) [1] has been used. Within exactness to second order terms on potential of Coulomb interaction of the valent electrons and atomic cores one can write:

\[ \tilde{\delta}(R) = \frac{S_0}{1 - S_0} + \Omega_1 + \Omega_2 - \frac{C_6}{R^6} \left( \frac{2}{E_a} + \frac{1}{E_a + E_B} \right), \]  

(2)

where \( C_6 \) is the van der Waals constant for interaction A-B (e.g., a pair of Yb-He; look below); \( I, E_{iab} \) are the ionization potential and excitation energy on the first level for atoms A, B correspondingly; \( S_0 \) is the overlapping integral. The value of \( E_{iab} \) can be simply defined as follows [7]:

\[ E_{iab} = (E_{ia} + E_{ib})/2. \]

The values \( \Omega_1, \Omega_2 \) in the expression (2) are the non-exchange and exchange non-perturbation sums of the first order correspondingly, which are defined as follows:

\[ \Omega_1 = \frac{2}{N(1 - S_0)\rho_0} \sum_k \frac{\langle \Phi_i | H_{CT} | \Phi_i \rangle V_{iab}}{E_a - E_b}, \]

\[ \Omega_2 = \frac{2}{N(1 - S_0)\rho_0} \sum_k \frac{\langle \Phi_i | H_{CT} | \Phi_i \rangle U_{iab}}{E_a - E_b}, \]

\[ \rho_0 = \langle \Phi_0 | H_{CT} | \Phi_0 \rangle / <\Phi_0 | H_{CT} | \Phi_0 \rangle \]
where $H_{CT}$ is the operator of hyperfine interaction, $N$ is the total number of electrons taken into account in calculation; $E_0$, $\Phi'_k(1)=\langle \Phi_k(1)|\Phi'_0(1) \rangle$ — energy and non-symmetrized wave function of state $k = \{k_a, k_b\}$ for isolated atoms A and B.

The non-exchange matrix element of the Coulomb interatomic interaction is as follows:

$$V_{k0} = \langle \Phi'_k(1) | V(1) | \Phi'_0(1) \rangle.$$ 

Correspondingly the exchange matrix element is as follows:

$$U_{k0} = \sum_{i=1}^{N} \langle \Phi_i(1) | V(1) | \Phi_i(1) \rangle.$$ 

Operator $V(1)$ is, for example, in a case of system Yb-He, as follows:

$$V(1) = U_{SCF}(r_{a1}) + U_{SCF}(r_{a4}) - 2U_{SCF}(R) + \frac{1}{r_{bi}}, \quad (3)$$

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

Let us return to consideration of the van der Waals constant $C_6$ for the interatomic A-B interaction. As a rule, one could use the approximate values for the van der Waals constant $C_6$ etc. Often the sufficiently great mistake in determination of the van der Waals constants provides non-high accuracy of the interatomic potentials calculation and further inaccuracies. The van der Waals constant may be written as follows \cite{10}:

$$C_6(L, M) = C_{6,0}(L) - \frac{3M^2 - L(L+1)}{(2L-1)(2L+3)} C_{6,2}(L), \quad (4)$$

where $C_{6,0}(L)$ 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 \cite{7,11}. In particular, for the helium case one may write:

$$C_{6,0}(L) = \frac{3}{\pi} \int_0^\infty \alpha_0(L; iw) \overline{\alpha}_{He}(iw) dw, \quad (5)$$

where $\overline{\alpha}_{He}$ is the dynamical polarizability of helium. The polarizabilities at imaginary frequencies are given in atomic units as follows:

$$\alpha_0(L, M; iw) = 2 \sum_{\gamma, \alpha, \beta} \frac{(E_\gamma - E_L)<LM|\vec{\gamma}\cdot\vec{M}_\gamma>^2}{(E_\gamma - E_L)^2 + w^2}, \quad (6)$$

where $E_\gamma$ is the energy of the electronically excited state $|L, M_\gamma>$ and the $z$ axis lies along the internuclear axis.
Usually (see [2]) the non-relativistic Hartree-Fock sets of the wave functions are used. More sophisticated approach is based on using the relativistic Dirac-Fock wave functions (first variant) [5-7,11-15]. Another variant is using the relativistic wave functions as the solutions of the Dirac equations with different density functionals (the Kohn-Sham DFT theory) and effective potentials [2,10,12,16-19]. In this paper we have used the set of the relativistic functions, generated by the Dirac equation with the optimized Ivanov-Ivanova model potential [20]. The detailed approbation of this model potential in studying spectra and radiative characteristics of the ytterbium and thallium atoms is given in refs. [17-19]. In a number of papers it has been rigorously shown that using the optimized sets in calculating the atomic electron density dependent properties has a decisive role (see discussions in refs. [21,22]). Here we will not in details discuss this question.

3. Results and conclusions

In table 1 we present our theoretical results for the line shift $f_p$ (1/Torr) for the Cs-He pair. The observed value of the line shift (T=323K) and other theoretical results for $f_p$ are given in table 1 too. Other theoretical data are obtained on the basis of the exchange PT with using the wave functions sets in Clementi et al and Hartree-Fock approximations [6,7,23]. The important feature of our scheme is a correct account of the correlation and polarization effects with using special effective functionals from [17,21]. A difference between our theoretical data and other calculation data is explained by using the different sets of wave functions and different PT schemes. For other temperatures there are no quite precise data. It is obvious that using the gauge-invariant optimized sets of the wave functions and correct version of the exchange PT will be necessary in a case of the alkali elements in an atmosphere of more heavy inert gases.

| System | Cs-He | Cs-He | Cs-He | Cs-He | Cs-He |
|--------|-------|-------|-------|-------|-------|
| $T$, K | Experiment | Our theory | Theory [3] | Theory [6] | Theory [6] |
| 323 | 135 | 134 | 137 | 126 | 109 |
| 423 | — | 121 | 123 | 111 | 96 |
| 523 | — | 109 | 112 | 100 | 85 |
| 623 | — | 103 | 105 | 94 | 78 |

In table 2 we present our theoretical results for the shift $f_p$ (Hz/Torr) for the Tl-He, Ar, Xe pairs. The observed value of the line shift (T=700K) and other theoretical results with using the Dirac-Fock and optimized Dirac-Fock methods are listed in table 2 too [3,7].

| System | Tl-He | Tl-Ar | Tl-Xe |
|--------|-------|-------|-------|
| Experiment | $130 \pm 30$ | $-490 \pm 20$ | $-1000 \pm 80$ |
| Theory [7] | $155.0$ | $-850.0$ | $-1420.0$ |
| Theory [5] | $137.2$ | $-304$ | $-1052$ |
| Our theory | $135.4$ | $-301$ | $-1044$ |

The ground configuration for ytterbium is: [Xe]$4f^{14}6s^2$ (term: $^1S$). First of all, let us present our results for the scalar static polarizability $\alpha_0$ (in units of $a_0^3$, $a_0$ is the Bohr radius) and isotropic dispersion coefficient $C_{6,0}$ (in units of $E_H a_0^6$, $E_H$ is the Hartree unit of energy). Our results are as follows: $C_{6,0}$= 45, $\alpha_0$=168. For comparison let us present the data (from ref. [10]) by Dalgarano et al: $C_{6,0}$= 39.4, $\alpha_0$=157.3 and by Buchachenko et al: $C_{6,0}$= 44.5. In table 3 we present our preliminary calculation results for the observed $f_p$ (Hz/Torr) shift for the system Yb-He. It is obvious that the
Table 3. The observed $f_\rho$ (Hz/Torr) shift for the system Yb-He.

| $T$, K | $f_\rho$ |
|--------|---------|
| 700    | 146.8   |
| 750    | 144.1   |
| 800    | 141.3   |
| 850    | 139.0   |
| 900    | 136.2   |

pair Yb-He is significantly more complicated system. Until now there are no any experimental or theoretical data for this system. Thus, our data may be considered as the first preliminary reference.

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