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## Collisional shift of hyperfine line for rubidium in an atmosphere of the buffer inert gas

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**Abstract.** New relativistic approach, based on the relativistic many-body perturbation theory using optimized wave functions sets, is applied to calculate the hyper fine structure collision shift for rubidium atom in atmosphere of the helium inert gas. Data for the collisional shifts of the Rb-He system are presented and compared with data available in the literature.

### 1. Introduction

This paper presents our recent progress in the theoretical study of hyperfine lines shift and broadening for heavy atoms, namely, alkali and others, in atoms in an atmosphere of the buffer gases (see, for example, Refs. [1-5]). The study of 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 current topics of modern quantum chemistry, atomic optics and spectroscopy [5-8]. Furthermore, heavy atoms are interesting from the point of view of studying the 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. For a long time, the corresponding phenomenon for thallium atoms attracted a special attention because of possibility to create the thallium quantum frequency measure. 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. [5-9]). However, consideration of heavy elements faces serious difficulties in accounting for the relativistic and correlation corrections.

It is noteworthy 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 [5-9]). 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 hyperfine structure collision shift for rubidium atom in atmosphere of the helium inert gas. The basic expressions for the collision shift and broadening of the hyperfine structure spectral lines are taken from the kinetic theory of spectral lines [5-7]. The exchange perturbation theory (the modified version EL-HAV) has been used for calculating the corresponding potentials (see details in [5,6]).

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

As the method of computing hyperfine lines shift is presented in detail earlier[1-5], here we highlight key elements. To calculate the collision shift of hyperfine structure spectral lines one can use the following expression known from kinetic theory of spectral line form (see [5-7]):

$$f_p = \frac{\Delta}{P} = \frac{4\pi N_b}{P} \int_0^{\infty} e^{-U(R)/kT} [1 + g(R)] \delta\omega(R) R^2 dR, \quad (1)$$

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=Rb);  $T$  is the temperature,  $w_0$  is a frequency of the hyperfine structure transition in the isolated active atom;  $d\omega(R) = Dw(R)/w_0$  is the relative local shift of the hyperfine structure lines, which is arisen due to the disposition of the active atoms (say, atom of Rb and He) on a distance  $R$ ,  $\{1 + g(R)\}$  is a temperature factor. To calculate an effective potential of the interatomic interaction, the method of the exchange perturbation theory (the modified version EL-HAV) (see details in [1,7] has been used. Accurate to second order terms in the potential of the Coulomb interaction of the valent electrons and atomic cores one can write:

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

where  $C_6$  is the van der Waals constant for interaction A-B;  $I, E_{1a,b}$  are the ionization potential and excitation energy on the first level for atoms A, B correspondingly;  $S_0$  is the overlap integral. The value of  $\bar{E}_{a,b}$  can be simply defined as follows:

$$\bar{E}_{a,b} = (I_{a,b} + E_{1a,b})/2,$$

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:

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

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

$$\rho_0 = \langle \Phi_0^1(1) | H_{CT}' | \Phi_0^1(1) \rangle / \langle \Phi_0^1(1) | \Phi_0^1(1) \rangle$$

where  $H'_{CT}$  is the operator of hyperfine interaction,  $N$  is the total number of electrons taken into account in the calculation;  $E_k$ ,  $\Phi'_k(\mathbf{l}) = F'_{k_a}(\mathbf{l})\varphi_{k_b}(2\dots N)$  — 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:

$$V_{ko} = \langle \Phi'_k(\mathbf{l}) | V(\mathbf{l}) | \Phi'_o(\mathbf{l}) \rangle.$$

and, correspondingly, the exchange matrix element is as follows:

$$U_{k0} = \sum_{i=2}^N \langle \Phi'_k(\mathbf{l}) | V(i) | \Phi'_0(i) \rangle.$$

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

$$V(i) = U_{SCF}(r_{a3}) + U_{SCF}(r_{a4}) - 2U_{SCF}(R) + \frac{1}{r_{bi}}, \quad (3)$$

where  $U_{SCF}(r)$  is the self-conjunctive 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 large errors in determination of the van der Waals constants leads to low accuracy of the inter-atomic potentials calculation and may introduce further inaccuracies. The van der Waals constant may be written as follows [10]:

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

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 [5,8]. In particular, for the helium case one may write:

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

where  $\bar{\alpha}_{He}$  is the dynamical polarizability of helium. The polarizabilities at imaginary frequencies are given in Ref. [3].

Usually (see [6]) the non-relativistic Hartree-Fock sets of the wave functions are used. A more sophisticated approach is based on using the relativistic Dirac-Fock wave functions (first variant) [5-7]. Another variant is using the relativistic wave functions as the solutions of the Dirac equations with different model potentials (of the Ivanov-Ivanova type) and effective potentials [6,10-15]. In this paper we have used the set of the relativistic functions, generated by the Dirac equation with the optimized Dirac-Kohn-Sham exchange-correlation functionals [16]. The detailed treatment of this approach in studying spectra and radiative characteristics of different atomic systems is given in Refs. [1-3, 16].

### 3. Results and conclusions

In Table 1 we present our theoretical results for the line shift  $f_p$  (1/Torr) for the Rb-He pair. The observed value of the line shift (T=323K) and other theoretical results for  $f_p$  are also included in Table 1. Other theoretical data are obtained on the basis of the exchange PT [6] with using the wave functions sets in Clementi et al [17] and Hartree-Fock approximations. The important feature of our scheme is a correct account of the correlation and polarization effects with using special effective functionals from [12,14,16]. 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.

**Table 1.** Observed and theoretical  $f_p$  ( $10^{-9}$  1/Torr) shift data for pair of Rb-He.

T, K	Experiment	This work	Theory [1]	Theory [6]	Theory [6]
223	-	116	113	81	79
323	105	103	101	75	73
423	-	91	89	64	62
523	-	82	80	56	55
623	-	75	73	50	50
723	-	73	71	47	47
823	-	70	69	-	-

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