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# Collisional shift of hyperfine line for thallium in an atmosphere of the buffer inert gases

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**Abstract.** A relativistic approach, based on the relativistic many-body perturbation theory (PT) with using the optimized Dirack-Kohn-Sham wave functions sets, is applied to computing the hyperfine structure collision shift for the thallium atom in atmosphere of the inert gases (A=He,Ar, Xe). Data for the collisional shifts of the Tl-A system are presented and compared with other available ones.

## 1. Introduction

This paper goes on our work on theoretical studying hyperfine lines shift and broadening for heavy atoms in an atmosphere of the buffer gases (see, for example [1-5]). Let us remind that 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 [6,7]. 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. The detailed non-relativistic theory of the hyperfine line collisional shift and broadening for simple elements (alkali elements etc) was developed by many authors (see Refs. [1,6-8]). However, consideration of heavy elements faces serious difficulties related with account for relativistic and correlation effects. In our paper a new relativistic optimized approach, based on the gauge-invariant perturbation theory (PT) with using the optimized Dirac-Kohn-Sham wave functions basis's and the exchange PT (modified version EL-HAV [1,7]), is applied to computing the hyperfine line collision shift for thallium atom in atmosphere of the inert gases. The basic expressions for the collision shift are taken from the kinetic theory of spectral lines [1,6].

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

As the method of computing hyperfine lines shift is earlier presented in details [1-4], here we are limited only by the key topics. 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 [6]):

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

Here  $U(R)$  is an effective central interatomic interaction potential of a system A-B (for example, A=Tl, B=He);  $T$  is a 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 on distance  $R$ ,  $\{1+g(R)\}$  is the temperature factor. To calculate interatomic interaction potential, the exchange PT method (modified version EL-HAV; see [1-3,7]) is used. Within exactness to 2<sup>nd</sup> order terms on potential of Coulomb interaction of the valent electrons and atomic cores one can write:

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

where  $C_6$  is the van der Waals constant for the A-B interaction;  $I, E_{Ia,b}$  are the ionization potential and excitation energy for atoms A,B correspondingly;  $S_0$  is the overlapping integral. The values  $\Omega_1, \Omega_2$  in Eq.(2) are the non-exchange and exchange non-perturbation sums of the first order correspondingly:

$$\begin{aligned} \Omega_1 &= \frac{2}{N(1-S_0)\rho_0} \sum_k \frac{\langle \Phi'_0(1) | H'_{CT} | \Phi'_k(1) \rangle V_{k0}}{E_0 - E_k}, \\ \Omega_2 &= \frac{2}{N(1-S_0)\rho_0} \sum_k \frac{\langle \Phi'_0(1) | H'_{CT} | \Phi'_k(1) \rangle U_{k0}}{E_0 - E_k}, \end{aligned} \quad (3)$$

$$\rho_0 = \langle \Phi'_0(1) | H'_{CT} | \Phi'_0(1) \rangle / \langle \Phi'_0(1) | \Phi'_0(1) \rangle$$

where  $H'_{CT}$  is the operator of hyperfine interaction,  $N$  is the total number of electrons taken into account in calculation;  $E_k, \Phi'_k(1)=F'_{k_a}(1)\varphi_{k_b}(2\dots N)$  — 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:  $V_{k0} = \langle \Phi'_k(1) | V(1) | \Phi'_0(1) \rangle$ . Correspondingly the exchange matrix element is:  $U_{k0} = \sum_{i=2}^N \langle \Phi'_k(1) | V(i) | \Phi'_0(i) \rangle$ . Operator  $V(i)$  is (for the system Tl-He) as follows:

$$V(i)=U_{SCF}(r_{a3})+U_{SCF}(r_{a4})-2U_{SCF}(R)+\frac{1}{r_{bi}}, \quad (4)$$

where  $U_{SCF}(r)$  is the self-conjunctive field, created by the thallium tomic core.

Let us return to consideration of the van der Waals constant  $C_6$  for the interatomic A-B interaction. As a rule, one uses 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 inter-atomic potentials calculation and further inaccuracies. The van der Waals constant may be written as [1]:

$$C_6(L, M) = C_{6,0}(L) - \frac{3M^2 - L(L+1)}{(2L-1)(2L+3)} \cdot C_{6,2}(L), \quad (5)$$

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. The coefficients  $C_{6,0}, C_{6,2}$  may be expressed in terms of the scalar and tensor polarizabilities evaluated at imaginary frequencies [8]. Usually (see [6]) the non-relativistic Hartree-Fock sets of the wave functions are used. More correct approach is based on using the relativistic Dirac-Fock (DF) wave functions or wave functions as the solutions of the Dirac equations with model potential (the Ivanov-Ivanova type) [2-10]). Here paper we used the set of the relativistic functions, generated by the Dirac-Kohn-Sham equation with the optimized exchange-correlation functional (see details in [11-19]).

### 3. Results

In table 1 we list our data for the shift  $f_p$  (Hz/Torr) for the Tl-He, Ar, Xe pairs. The observed value of the line shift ( $T=700\text{K}$ ) and other theoretical data, obtained with using the standard DF, optimized DF methods [2,3,6] are listed too. 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 heavy elements in an atmosphere of more heavy inert gases.

**Table 1.** The shift  $f_p$  (Hz/Torr) of the Tl hyperfine line for the pairs: Tl-He, Kr, Xe ( $T=700\text{ K}$ ).

System	Tl-He	Tl-Ar	Tl-Xe
Experiment	$130 \pm 30$	$-490 \pm 20$	$-1000 \pm 80$
Theory [6]	155.0	-850.0	-1420.0
Theory [2]	137.2	-504	-1052
Theory [3]	135.4	-501	-1044
This work	136.6	-503	-1048

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