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Collisional broadening and shift of the hyperfine lines for complex atomic systems in atmosphere of the buffer inert gases

An effective approach to determination of the collisional hyperfine lines shift and broadening in a buffer gas medium is presented and based on the generalized kinetic theory of spectral lines, the exchange perturbation theory and relativistic gauge-invariant perturbation theory with the optimized model potential approximation for computing the optimized basises of the relativistic wave functions.The results of calculating the shift and broadening of the hyperfine structure spectral lines due to collisions for complex atoms (here thallium is considered) in an atmosphere of inert gases (Kr, Xe) are presented and compared with other available alternative theoretical and experimental data. It is shown that the ratio of an adiabaticbroadening to a collisional shift for the pair of Tl–Kr (Γ_a/p)/ f_p is ~1/75 and for the pair of Tl- Xe(Γ_a/p)/f_p ~1/60.These estimates testify to a violation of well-known Foley relationship, which is, as a rule, inviolable in the standard atomic spectroscopy.

Keywords: *heavy atomic system in a buffer gas, kinetic theory of spectral lines, relativistic multi-particle perturbation theory, broadening and shift of ultrafine lines due to collisions.*

Introduction. Physics of interatomic collisions in gases and their manisfestations of collision effects in the energy, spectral and radiation parameters of atomic systems is quicly developing field of modern physics [1–5]. Data on the shifts and broadening of spectral lines due to the collision of active atoms with buffer ones can serve as a good additional way to better understanding the laws of interparticle interactions. Multiple application in physics of aerodispersed systems, atomic and molecular physics, astro- and plasmas physics, metrology etc require the highly precise information about the collisional broadening and collisional shift of the spectral lines for different elements (alkali, alkali-earth, lanthanides, actinides and others) in an atmosphere of the buffer (for example, inert) gases [1,2,6-16]. One of the most consistent and popular is a generalized kinetic theory of spectral lines in a buffer gas medium [1,5-7,16]. Its successful application to problem of studying the hyperfine structure (HFS) lines shift and broadening in an atmosphere of the buffer gas requires the knowledge of the corresponding matrix elements of the hyperfine interation operator. Naturally, the collisional spectral lines broadening and shift parameters due to a collision of the emitting atoms with the buffer atoms are very sensitive to a kind of the corresponding interatomic interaction. Different theoretical methods have been developed in order to describe the collisional shift and broadening of spectral lines in the buffer gas, including the solving the corresponding atomic task. The detailed nonrelativistic theory of the HFS lines collisional shift and broadening for a number of simple elements (such as different light elements etc.) has been presented in many papers (see, for example, Refs. [6,13-25]).

However, until now an accuracy of the corresponding information for heavy systems is not quite adequate to meet the requirements of different important physical

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and chemical applications. Moreover, in a case of middle and heavy elements a precise treatment of collisional spectral lines dynamics in a buffer gas medium requires the correct accounting for the relativistic and correlation effects.

In this paper, we present an effective approach to determination of the HFS spectral lines shift and broadening in a buffer gas medium, which is based on the generalized kinetic theory of spectral lines, the exchange perturbation theory (PT) and relativistic gauge-invariant PT with the optimized Dirac-Coulomb-Sturm plus the model potential (MP) approximation for computing the optimized basises of the atomic wave functions. The implementation of the latter within the kinetic theory of shift and broadening of spectral lines constitutes an element of novelty.

Optimized atomic perturbation theory and advanced kinetic theory of spectral lines. As the detailed description of the kinetic theory of spectral lines as well as the exchange PT formalism have been earlier presented in Refs. [6,7,17-19], here we will focus only on the key elements. In order to compute a collisional shift of the HFS spectral lines one can use the following expression known in the kinetic theory of spectral lines shape [6,7]):

$$f_p = \frac{D}{p} = \frac{4\pi w_0}{kT}\int_0^\infty [1+g(R)]dw(R)\exp\left(-U(R)/kT\right)R^2 dR\,, \tag{1}$$

$$g(R) = \begin{cases} \dfrac{2}{3\sqrt{\pi}}\left(-\dfrac{U(R)}{kT}\right)^{3/2}, & U<0, \\ 0, & U>0, \end{cases} \tag{2}$$

Here T is a temperature, w_0 is a frequency of the hyperfine structure transition in an isolated active atom; $U(R)$ is an effective interatomic potential, which has the central symmetry in a case of the diatomic system A-B (e.g., $A=Tl; B=Xe$); $d\omega(R)=Dw(R)/w_0$ is a relative local shift of the HFS spectral line; $1+g(R))$ is a temperature form-factor. In order to calculate an effective interatomic potential and the local collisional shift, the modified version of the exchange PT [6, 7] has been used. The interaction between an active atom and the buffer gas atom is considered in the adiabatic approximation.

The standard hyperfine interaction Hamiltonian includes two main terms, which describe a magnetic dipole interaction of moments of an electron and a nucleus of an active atom as well as an electric quadrupole interaction. The hyperfine interaction operator H_{HF}has the following standard form (e.g., [21, 22]):

$$H_{HF} = a\sum_{i=1}^{N} I\frac{\alpha_i \times r_i}{r_i^3}\,, \tag{3a}$$

$$a = -2\mu\frac{e^2 h}{2m_p c}\,, \tag{3b}$$

where α_i – Dirac matrices, m_p– proton mass, μ – moment of the nucleus of the active atom, expressed in the nuclear Bohr magnetons; I – the operator of a nuclear spin of

the active atom. The relative local shift of the HFS line is determined with up to the second order in the potential V of the Coulomb interaction of the valence electrons and the cores of atoms as follows:

$$\delta\omega(R) = \frac{S_0}{1-S_0} + \Omega_1 + \Omega_2 - b\frac{C_6}{R_6}. \quad (4)$$

Here S_0 is the overlapping integral; C_6 is the van der Waals coefficient; b is the energy multiplier, determined by the potential of ionization and excitation energy of the corresponding atom; the quantities Ω_1, Ω_2 in Eq. (4) are the first order non-exchange and exchange non-perturbation sums correspondingly. The detailed formulas for determinetaion of these quantities are presented in Refs. [6,7]. In particular, the value Ω_1 is defined as follows:

$$\Omega_1 = \frac{2}{N(1-S_0)\rho_0}\sum_k \frac{\langle \Phi'_0(1)|H'_{HF}|\Phi'_k(1)\rangle V_{k0}}{E_0 - E_k} \quad (5)$$

where $H'_{HF} = [a \times r_1]_z / r_1^3$ is the transformed operator of the hyperfine interaction; $[a \times r_1]_z$ is Z component of the vector product; Z – quantization axis directed along the axis of the quasi-molecule; N is the total number of electrons, which are taken into account in the calculation; E_k, and $\Phi'_k(1) = F'_{k_a}(1)\varphi_{k_b}(2..N)$ are an energy and a non-symmetrized wave function of state $k = \{k_a,,k_b\}$ for the isolated atoms A and B, correspondingly. The detailed information about the corresponding matrix elements of the Coulomb interatomic interaction is presented in refs. [5-7, 17, 20, 25-28].

The master aspect of the whole theory is connected with method of computing the atomic wave functions. The non-relativistic Hartree-Fock method has been mostly used. More theoretically consistent approach is based on using the relativistic Dirac-Fock (DF) or Dirac-Kohn-Sham (DKS) methods (e.g. [15-20]). The key criterion of the choice of the method is determined by a necessity of the correct accouting for the relativistic, interelectron exchange-correlationand even nuclear effects in heavy atomic systems [1-5,21-25]. In our calculation we have used the relativistic functions, which are generated within the Dirac-Coulomb-Sturm approximation with the Ivanov-Ivanova and Miller-Green MP [24,25,29]. The MP parameter has been determined within the known ab initio optimization procedure [26] for construction of the optimized basis of the relativistic orbitals. It is reduced to minimization of the gauge dependent multielectron contribution into an imaginary part of an electron energy $Im\delta E_{ninv}$ of the lowest PT orders (see the detailes in Refs. [26-28, 30, 31]). The minimization of the $Im\delta E_{ninv}$ leads to the Dirac-like equations for the electron density that are numerically solved. The gauge-dependent multielectron contribution into imaginary part of an electron energy can be presented as the functional, which contains the multi-electron exchange-correlation ones (including polarization interquasiparticle interaction, effects of its shielding, effects of rapid "smearing" of the initial state by a non-zero set of configurations, essentially non-Coulomb grouping of levels in Rydberg spectra, pressure and accounting for continuum states) [3-8]. Using this functional within a relativistic many-body PT allows effectively to take into account

the second-and higher orders atomic PT (fourth-order QED PT) corrections. The whole procedure remains quite complicated. So, in concrete calculations it is sufficient to use more simplified approach, which is reduced to the functional minimization using the variation of the MP parameter *b*. The detailed description of the whole procedure can be found in Ref. [5-7,26-28,30,31].

Some results and conclusions. Below we present the results of calculating the shift and broadening of the HFS spectral lines due to collisions for complex atomic systems (thallium is considered) in an atmosphere of inert gases (Kr, Xe) and compare the obtained data with other available alternative theoretical and experimental ones. In Table 1 there are listed our theoretical values (Th.C) for the thallium atom HFS line collisional shift f_ρ(in Hz/Torr) at the temperature $T = 700^oK$ for the diatomic systems: TI - Kr, Tl-Xe. For comparison, there are also listed the results of calculation: Th.A- single-configuration DF method; Th. B – the optimized DF/DKS method, as well as experimental data Choron-Scheps-Galagher [2,13,14]. The qualitative estimate from Ref. [13] has been listed as well.

In Table 2 there are listed our theoretical data on the Tl HFS line collisional shift f_ρ(in Hz/Torr) in dependence upon a temperatures (T^0K) for the systems TI – Kr and Tl-Xe. Analyzing thelisted data, it is of a considerable interest to estimate the ratio of the adiabatic broadening to a collisional shift $(\Gamma_a/p)/f_\rho$.

In the standard theory of atomic spectral lines (e.g.,[5-9]) it is well-known so-called Foley relationship for lines of the visible optical part of spectrum, when the value of a collisional broadening is practically of the same order as the magnitude of

Table 1. The collisional shift fρ (in Hz/Torr) of the thallium hyperfine line for pairs TI - He, TI - Kr, Tl-Xe at $T = 700^oK$; Experiment and Theory: Th.A- single-config. DF method; Th. B – the optimized DF/DKS method; Th.C- our scheme (see text).

System	Exp.	Th.A (DF)	Th.B (DKS)	Th.C (MP)
T1-Kr	–490±20	–850.0	–504 –488	–512.4
T1-Xe	–1000±80	–1420.0	–1052 –1024	–1036.2

Note. Qulaitative estimate: -5500 Hz/Torr

Table 2. The temperature dependence of the HFS collisional shift f_ρ(in Hz/Torr) and adiabatic broadening Γ_a/p (inHz/Torr) due to collsison for diatomic pairs Tl–Kr, Tl–Xe in the temperature interval 700-1000°K (our data);

Diatomic Pair	Tl-Kr f_ρ	Tl-Xe f_ρ	Tl-Kr Γ_a/p	Tl-Xe Γ_a/p
700	-512.4	-1036.2	6.84	17.32
800	-431.8	-896	5.93	14.62
850	-402.5	-843	5.61	13.76
900	-375.3	-798	5.30	12.92
1000	-323.1	-720	5.27	11.53

a collisional shift. It is easily to to estimate the ratio of the broadening to a collisional shift for the pair Tl – Kr(Γ_a/p)/f_p ~1/75and for the pair Tl- Xe- (Γ_a/p)/f_p ~1/60. These estimates testify to the violation of well-known Foley relationship , which is , as a rule, inviolable in the usual atomic spectroscopy (for ordinary spectral lines in the visible spectrum part). In the sense of what has been said, it is very interesting to provide data on the Foley ratio (Γ_a/p)/f_p in the case of a shift and broadening of the 535 nm Tl line ($72S_{1/2}$ -$62P_{3/2}$ transition) in the atmosphere of the inert buffer gases Kr, Xe, respectively: – 0.35 ÷ –0.39 [14].

Conclusions. It should be concluded that dynamics of the HFS spectral lines collisional shift and broadening of the Tl (possibly, as well as other heavy atoms) in a buffer inert gas medium demonstrate very unusual fetures.

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Уширення та зсув за рахунок зіткнень ліній надтонкої структури складних атомних систем в атмосфері буферних інертних газів

АНОТАЦІЯ

Представлено ефективний підхід до визначення зсуву та уширення надтонких спектральних ліній у буферному газовому середовищі, який базується на узагальненій кінетичній теорії спектральних ліній, обмінній теорії збурень та релятивістській калібрувально-інваріантній теорії збурень з оптимізованим модельним потенціалом нульового наближення для обчислення відповідних атомних релятивістських хвильових функцій. Наведені результати розрахунку зсуву та уширення спектральних ліній надтонкої структури внаслідок зіткнень для складної атомної системи (розглянуто атом талію) в атмосфері інертних газів (зокрема, Kr, Xe) які порівнюються з альтернативними теоретичними та експериментальними даними. Показано, що для спектральних ліній надтонкої структури талію відношення величини адіабатичного уширення до відповідного зсуву за рахунок зіткнень для пари Tl–Kr(Γ_a/p)/f_p становить ~1/75, а для пари Tl-Xe – (Γ_a/p)/ f_p ~1/60. Ці оцінки свідчать про порушення відомого у стандартній атомній спектроскопії співвідношення Фолі у випадку зсуву та уширення за рахунок зіткнень спектральних ліній надтонкої структури атомних систем.

Ключові слова: *важкий атом у буферному газі, кінетична теорія спектральних ліній, релятивістська багаточастинкова теорія збурень, уширення та зсув надтонких ліній за рахунок зіткнень.*