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OPTIMIZED PERTURBATION THEORY TO CALCULATING THE HYPERFINE LINE SHIFT AND BROADENING FOR HEAVY ATOMS IN THE BUFFER GAS

It is presented review of a new consistent relativistic approach to determination of collisional shift and broadening hyperfine lines for heavy atoms in an atmosphere of the buffer inert gas. It is based on the atomic gauge-invariant relativistic perturbation theory and the exchange perturbation theory. As illustration, consistent approach is applied to calculating the interatomic potentials, hyperfine structure line collision shift and broadening for heavy atoms, in particular, atoms of alkali elements – rubidium, caesium, and thallium, ytterbium, in an atmosphere of the buffer inert gas.

1 Introduction

The broadening and shift of atomic spectral lines by collisions with neutral atoms has been studied extensively since the very beginning of atomic physics, physics of collisions etc [1–5]. High precision data on the collisional shift and broadening of the hyperfine structure lines of heavy elements (alkali, alkali-earth, lanthanides, actinides and others) in an atmosphere of the buffer (for example, 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 [1-10]. As a rule, the cited spectral lines shift and broadening due to a collision of the emitting atoms with the buffer atoms are very sensitive to a kind of the intermolecular interaction. It means that these studies provide insight into the nature of interatomic forces and, hence, they provide an excellent test of theory.

An accurate analysis of the spectral line profiles is a powerful technique for studying atomic and molecular interactions and is often necessary for probing matter in extreme conditions, such as in stellar atmospheres, ultracold traps and Bose–Einstein condensates [3,6]. Besides, calculation of the hyperfine structure line shift and broadening allows to check a quality of the wave functions (orbitals) and study a contribution of the relativistic and correlation effects to the energetic and spectral characteristics of the two-center (multi-center) atomic systems. From the applied point of view, the mentioned physical effects form a basis for creating an atomic quantum measure of frequency [10,12,14]. The corresponding phenomenon for the thallium atom has attracted a special attention because of the possibility to create the thallium quantum frequency measure. Alexandrov et al [10] have realized the optical pumping thallium atoms on the line of 21GHz, which corresponds to transition between the components of hyperfine structure for the Tl ground state. These authors have measured the collisional shift of this hyperfine line in the atmosphere of the He buffer gas.

The detailed non-relativistic theory of collisional shift and broadening the hyperfine structure lines for simple elements (such as light alkali elements etc.) was developed by many authors (see, for example, Refs. [1-14]). However, until now an accuracy of the corresponding available data has not been fully adequate to predict or identify transitions within accuracy as required for many applications. It is obvious that correct taking into account the relativistic and correlation effects is absolutely necessary in order to obtain sufficiently adequate description of spectroscopy of the heavy atoms in an atmosphere of the buffer gases. This stimulated our current investigation whose goals were to propose a new relativistic perturbation theory approach to calculating the interatomic potentials and hyperfine structure line collision shifts and broadening for the alkali and lanthanide atoms in an atmosphere of the inert gases. The basic expressions for the collision shift and broadening hyperfine structure spectral lines are taken from the kinetic theory of spectral lines [6,7,11,12].

The exchange perturbation theory (the modified version EL-HAV) has been used to calculate the corresponding potentials (see details in [1-5]). Let us note that sufficiently detailed reviews of the different versions of exchange perturbation theory are presented, for example, in Refs.[1-9]. It is worth to remind about the known difficulties of the exchange perturbation theory, associated with complex structure series, which contain the overlap integrals and exchange integrals [1]. Due to the ambiguity of the expansion in the antisymmetric functions it had been built a number of different formalisms of an exchange perturbation theory. Usually one could distinguish two groups in dependence on the zero-order approximation of the Hamiltonian. In the symmetry adapted theories the zeroth-approximation Hamiltonian is an asymmetric, but the zeroth- approximation functions have the correct symmetry. In symmetric formalisms there is constructed a symmetric zeroth-approximation Hamiltonian such as the antisymmetric function is its eigen function. Further formally standard Rayleigh - Schrodinger perturbation theory is applied. However, this approach deals with the serious difficulties in switching to systems with a number of electrons, larger than two. In addition, the bare Hamiltonian is not hermitian.

So the symmetry adapted theories gain more spreading. In particular, speech is about versions as EL-HAV (Eisenschitz-London-Hirschfeleder-van der Avoird), MS-MA (Murrel-Shaw-Musher-Amos) and others (see details in Refs. [4,5]). The detailed analysis of advantages and disadvantages of the exchange perturbation theory different versions had been performed by Batygin et al (see, for example, [11,12]) in studying the hyperfine structure line shift of the hydrogen atom in an atmosphere of an inert buffer gas. In our work the modified version of the EL-HAV exchange perturbation theory has been used to calculate the corresponding potentials (see details in [4]). On fact [4] this is the Schrödinger type perturbation theory for intermolecular or interatomic interactions, using the wave operator formalism. To include all exchange effects, wavefunctions are used whose symmetry with respect to permutations of both electronic and nuclear coordinates can be prescribed arbitrarily. The interaction energy is obtained as a series in ascending powers of the interaction operator. Further van der Avoird [4] has proved that every term in this series is real and that the terms of even order are negative definite for perturbation of the ground state. It has been also verified that up to and including third order the results of this theory, if they are restricted to electron exchange only, agree exactly with those of the Eisenschitz-London theory (see other details in Refs. [1-5]).

The next important point is choice of the most reliable version of calculation for multielectron atomic field and generating the basis of atomic orbitals. In Refs. [17-30] a consistent relativistic energy approach combined with the relativistic many-body perturbation theory has been developed and applied to calculation of the energy and spectroscopic characteristics of heavy atoms and multicharged ions. This is the relativistic many-body perturbation theory with the optimized Dirac-Fock (Dirac-Kohn-Sham) zeroth approximation and taking into account the nuclear, radiation, exchange-correlation corrections. It is worth to remind that this approach has been successfully used to calculate the b-decay parameters for a number of allowed (super allowed) transitions and study the chemical bond effect on b-decay parameters [29]. This approach has been used in our work to generate a basis of relativistic orbiltals for heavy atoms. Besides, the correct procedures of accounting for the many-body exchange-correlation effects and relativistic orbital basis optimization (in order to provide a performance of the gauge-invariant principle) as well as accounting for the highly excited and continuum states have been used.

Earlier it was shown [21-30] that an adequate description of the energy and spectral characteristics of the multi-electron atomic systems requires using the optimized basis of wave functions. In Ref. [31] a new ab initio optimization procedure for construction of the optimized basis had been proposed and based on the principle of minimization of the gauge dependent multielectron contribution $ImdE_{ninv}$ of the lowest QED perturbation theory corrections to the radiation widths of atomic levels. The minimization of the functional $ImdE_{ninv}$ leads to the Dirac-Kohn-Sham-like equations for the electron density that are numerically solved. This procedure has been implemented into our approach. In result, the numerical data on the hyperfine line collision shifts and broadening for some alkali (Rb, Cs), thallium and ytterbium atoms in atmosphere of the inert gas (such as He, Ke, Xe) are presented and compared with available theoretical and experimental data (see, for example, [1-12]). Besides, new data on the van der Waals constavts and other parameters for the studied two-atomic systems are presented too.

2 Optimized atomic perturbation theory and kinetic theory of spectral lines

In order to calculate a collision shift of the hyperfine structure spectral lines one can use the following expression known in the kinetic theory of spectral lines shape (see Refs. [6,7,11,12]):

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

$$g(R) = \begin{cases} \frac{2}{3\sqrt{\pi}}\left(-\frac{U(R)}{kT}\right)^{3/2}, & U<0, \\ 0, & U>0, \end{cases} \tag{1b}$$

Here *U(R)* is an effective potential of interatomic interaction, which has the central symmetry in a case of the systems *A—B (*in our case, for example, A=Rb,Cs*;* B=He*)*; T is a temperature, w_0 is a frequency of the hyperfine structure transition in an isolated active atom; $dw(R)=Dw(R)/w_0$ is a relative local shift of the hyperfine structure line; $(1+g(R))$ is a temperature form-factor.

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

Since we are interested by the alkali (this atom can be treated as a one-quasiparticle systems, i.e. an atomic system with a single valence electron above a core of the closed shells) and the rare-earth atoms (here speech is about an one-, two- or even three-quasiparticle system), we use the classical model for their consideration. The interaction of alkali (A) atoms with a buffer (B) gas atom is treated in the adiabatic approximation and the approximation of the rigid cores. Here it is worth to remind very successful model potential simulations of the studied systems (see, for example, Refs. [32-41]).

In the hyperfine interaction Hamiltonian one should formally consider as a magnetic dipole interaction of moments of the electron and the nucleus of an active atom as an electric quadrupole interaction (however, let us remind that, as a rule, the moments of nuclei of the most (buffer) inert gas isotopes equal to zero) [6].

The necessity of the strict treating relativistic effects causes using the following expression for a hyperfine interaction operator H_{HF} (see, eg., [1,5]):

$$H_{HF} = a\sum_{i=1}^{N} I\frac{\alpha_i \times r_i}{r_i^3}, \quad a = -2\mu\frac{e^2 h}{2m_p c}, \tag{2}$$

where I – the operator of the nuclear spin active atom, a_i – Dirac matrices, m_p – proton mass, μ - moment of the nucleus of the active atom, expressed in the nuclear Bohr magnetons. Of course, the summation in (2) is over all states of the electrons of the system, not belonging to the cores. The introduced model of consideration of the active atoms is important to describe an effective interatomic interaction potential (an active atom – an passive atom), which is centrally symmetric (J_A=$^1/_2$) in our case (the interaction of an alkali atom with an inert gas atom).

Let us underline that such an approximation is also acceptable in the case system “thallium atom – an inert gas atom” and some rare-earth atoms, in spite of the presence of p-electrons in the thallium (in the case of rare-earth atoms, the situation is more complicated).

Next, in order to determine a local shift within the consistent theory it should be used the expression obtained in one of versions of the exchange perturbation theory, in particular, EL-HAV version (see [1-5,8,9]). The relative local shift of the hyperfine structure line is defined 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:

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

$$\overline{E}_{\alpha,b}=\left(I_{a,\,b}+E_{1a,\,b}\right)/2\,\cdot \qquad (3)$$

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 W_1, W_2 in Eq. (3a) are the first order non-exchange and exchange non-perturbation sums correspondingly. These values are defined as follows:

$$\Omega_1=\frac{2}{N(1-S_0)\rho_0}\sum_k{}' \frac{\langle\,\Phi'_0(1)\left|H'_{HF}\right|\Phi'_k(1)\,\rangle V_{k0}}{E_0-E_k} \qquad (4a)$$

$$\Omega_2=\frac{2}{N(1-S_0)\rho_0}\sum_k{}' \frac{\langle\,\Phi'_0(1)\left|H'_{HF}\right|\Phi'_k(1)\,\rangle U_{k0}}{E_0-E_k} \qquad (4b)$$

where $\acute{I}'_{H} = \frac{[a\times r_1]_z}{r^3}$ 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, $\Phi'_k(1)=F'_{k_a}(1)\varphi_{k_b}(2...N)$ are an energy and a non-symmetrized wave function of state $k=\{k_a,,k_b\}$ for the isolated atoms A and B.

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

$$V_{ko}=<\Phi'_k(1)\;|\;V(1)\;|\;\Phi'_0(1)>. \qquad (5a)$$

Correspondingly the exchange matrix element is as follows:

$$U_{k0}=\sum_{i=2}^{N}\langle\,\Phi'_k(1)\left|V(i)\right|\Phi'_0(i)\,\rangle \qquad (5b)$$

The operator $V(i)$ (for example, in a case of the system Rb(a)-He(b)) can be presented as follows:

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

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

The useful expressions for approximating the interaction potential and shift are presented in Refs. [11,12]:

$$U_{\text{A-B}}(R)=U^{\text{æ}}_{A-B}-C_6/R^6\,, \qquad (7)$$

$$\delta\omega^{(1)}_{\text{A-B}}(R)=\frac{2}{N\rho_0}(\chi^{1/2}(R)-\chi_0^{1/2})U^{\hat{\imath}\acute{a}\grave{\imath}}_{\text{A-B}}(R)+(\Omega_1^{3/2}+\Omega_2^{3/2})_{\text{A-B}}\sqrt{\frac{S_{0\text{A-B}}}{S_{0\text{A-B}}}} \qquad (8)$$

where the overlap integrals $S_{0\text{A-B}}$ are determined by the standard expressions, and the potential $U^{\text{æ}}_{\text{A-B}}$ is calculated in the framework of the exchange perturbation theory [12]:

$$U^{ex}=(V_{00}-U_{00})/(1-S_0). \qquad (9)$$

It should also be noted that as a rule, in the alternative non-relativistic theories of [6-9] the commutator technique [11] is used when calculating the sums of the type (4). Earlier the reason of using actually approximate non-relativistic methods was the lack of reliable information on the wave functions of the excited states of the complex atoms. Starting approximations in alternative theories [11,12] were rather simple approximations for the electronic wave functions of both active and passive atoms. In particular, in Refs. [11] the electronic wave functions were approximated by simple Slater expression (the approximation of the effective charge = Z-approximation) or simple analytical approximation formulas by Löwdin (L- approximation) and Clementi-Roothaan (C - approximation) [42] in studying the shift and broadening the hyperfine lines for such atoms as He, Rb, Cs etc. In Refs. [12] the wave functions had been determined within the Dirac-Fock approximation, however, these authors had used the approximate non-relativistic expressions to describe the interatomic interaction potential. Besides, determination of the polarizabilities and the van der Waals constants has been performed with using the following London's expressions [6,12]:

$$C_6^I = \frac{3}{2}\alpha_A \alpha_B \frac{I_A I_B}{\mathrm{I}_A + I_B}, \qquad (10a)$$

$$C_6^{\mathrm{I}} = \frac{3}{2}\alpha_A \alpha_B \frac{1}{\sqrt{\sqrt{\frac{\alpha_A}{n_A}} + \sqrt{\frac{\alpha_B}{n_B}}}}, \qquad (10b)$$

$$C_6^{III} = \frac{3}{2}\alpha_B I_B \sum_k \frac{f_{ko}}{(E_o - E_k)(E_o - E_k + I_B)}. \qquad (10c)$$

where f is the oscillator strength, other notations are the standard. However, sufficiently large error in definition of the van der Waals constants could provide a low accuracy of calculating the interatomic potentials. It is worth to note that the authors of the cited works indicate on the sufficiently large error (~ 50%) in the calculation of the collision shifts.

Let us return to consideration of the van der Waals coefficient C_6 for the interatomic *A-B* interaction. The van der Waals coefficient may be written as [13,43,44]:

$$C_6(L,M) = C_{6,0}(L) - \frac{3M^2 - L(L+1)}{(2L-1)(2L+3)} \cdot \mathrm{C}_{6,2}(\mathrm{l}) \quad , \qquad (10)$$

where $C_{6,0}$ *(L)* is the isotropic component of the interaction and $C_{6,2}$ *(L)* is the component corresponding to the $P_2(cosq)$ 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 [13]. In particular, one may write in the helium case as follows:

$$C_{6,0}(L) = \frac{3}{\pi} \cdot \int_0^\infty \alpha_0(L; iw)\overline{\alpha}_{He}(iw)dw, \qquad (11)$$

where $\overline{\alpha}_{He}$ is the dynamic polarizability of He. The polarizabilities at imaginary frequencies are defined in atomic units by the following formula:

$$\alpha_\parallel(L,M; iw) = 2\sum_{\gamma, M_\gamma} \frac{(E_\gamma - E_L)|< LM\,|\,\hat{z}\,|\,L_\gamma M_\gamma >|^2}{(E_\gamma - E_L)^2 + w^2} \qquad (12)$$

where E_g is the energy of the electronically excited state $|L_g M_g>$ and the *z* axis lies along the internuclear axis.

Obviously, generally speaking, the calculation of the dynamic polarizability and the resulting van der Waals constants is connected with a summation over infinite number of intermediate states (the states of the discrete spectrum and integrating over the states of the continuous spectrum).

On the other hand, it is known that the space of functions of the atomic states can be stretched over the space of the Sturm orbitals, which is both discrete and countable [6,35,43]. Thus, it allows to eliminate a problem of accounting the continuous spectrum within the formally exact approach.

Naturally, the set of Sturm orbitals should be introduced with specially prescribed asymptotics that is crucial for the convergence of the spectral expansion, including a spectral expansion of the corresponding Green's functions.

3 Relativistic many-body perturbation theory with the Kohn-Sham zeroth approximation and the Dirac-Sturm method

3.1 Relativistic many-body perturbation theory with the Kohn-Sham zeroth approximation

As it is well known (see also Refs. [1,7]), the non-relativistic Hartree-Fock method is mostly used for calculating the corresponding wave functions. More sophisticated approach is based on using the relativistic Dirac-Fock wave functions (first variant) [15,16]. Another variant is using the relativistic wave functions as the solutions of the Dirac equations with the corresponding density functional, i.e within the Dirac-Kohn-Sham theory [45-48]. In fact, the theoretical models involved the use of different consistency level approximations led to results at quite considerable variance.

It is obvious that more sophisticated relativistic many-body methods should be used for correct treating relativistic, exchange-correlation and even nuclear effects in heavy atoms. (including the many-body correlation effects, intershell correlations, possibly the continuum pressure etc [21-30]). In our calculation we have used the relativistic functions, which are generated by the

Dirac-Kohn-Sham Hamiltonian [18,27-30]. In a number of papers it has been rigorously shown that using the optimized basis in calculating the atomic electron density dependent properties has a decisive role. This topic is in details discussed in many Refs. (see, for example, [6,15,28-32,49]).

As usual, a multielectron atom is described by the Dirac relativistic Hamiltonian (the atomic units are used):

$$H = \sum_i h(r_i) + \sum_{i>j} V\left(r_i r_j\right). \tag{13}$$

Here, *h(r)* is one-particle Dirac Hamiltonian for electron in a field of the finite size nucleus and *V* is potential of the inter-electron interaction. In order to take into account the retarding effect and magnetic interaction in the lowest order on parameter a^2 (the fine structure constant) one could write [18]:

$$V\left(r_i r_j\right) = exp\left(i\omega_{ij} r_{ij}\right) \cdot \frac{\left(1-\alpha_i \alpha_j\right)}{r_{ij}}, \tag{14}$$

where w_{ij} is the transition frequency; a_i ,a_j are the Dirac matrices. The Dirac equation potential includes the electric potential of a nucleus and electron shells and the exchange-correlation potentials. The standard KS exchange potential is as follows [45]:

$$V_X^{KS}(r) = -(1/\pi)[3\pi^2 \rho(r)]^{1/3}. \tag{15}$$

In the local density approximation the relativistic potential is [45]:

$$V_X[\rho(r), r] = \frac{\delta E_X[\rho(r)]}{\delta \rho(r)}, \tag{16}$$

where $E_X[\rho(r)]$ is the exchange energy of the multielectron system corresponding to the homogeneous density $\rho(r)$, The corresponding correlation functional is [6, 28]:

$$V_C[\rho(r), r] = -0.0333 \cdot b \cdot \ln[1 + 18.3768 \cdot \rho(r)^{1/3}], \tag{17}$$

where *b* is the optimization parameter (for details see Refs. [6,31,32]).

As it has been underlined, an adequate description of the multielectron atom characteristics requires using the optimized basis of wave functions. In our work it has been used ab initio optimization procedure for construction of the optimized basis of the relativistic orbitals. It is reduced to minimization of the gauge dependent multielectron contribution $ImdE_{ninv}$ of the lowest QED perturbation theory corrections to the radiation widths of atomic levels.

The minimization of the functional $ImdE_{ninv}$ leads to the Dirac-Kohn Sham-like equations for the electron density that are numerically solved. According to Refs. [31], the gauge dependent multielectron contribution can be expressed as functional, which contains the multi-electron exchange-correlation ones. From the other side, using these functionals within relativistic many-body perturbation theory allows effectively to take into account the second –order atomic perturbation theory (fourth-order QED perturbation theory) corrections. In our work the corresponding functionals of Ref. [34] have been used. As a result one can get the optimal perturbation theory one-electron basis. In concrete calculations it is sufficient to use more simplified procedure, which is reduced to the functional minimization using the variation of the correlation potential parameter *b* in Eq. (16).

The differential equations for the radial functions *F* and *G* (components of the Dirac spinor) are:

$$\frac{\partial F}{\partial r} + \left(1+\chi\right)\frac{F}{r} - \left(\varepsilon + m - V\right)G = 0,$$
$$\frac{\partial G}{\partial r} + \left(1-\chi\right)\frac{G}{r} + \left(\varepsilon - m - V\right)F = 0, \tag{18}$$

where *F*, *G* are the large and small components respectively; *c* is the quantum number.

At large c, the functions *F* and *G* vary rapidly at the origin; we have $F(r), G(r) \approx r^{\gamma-1}$, $\gamma = \sqrt{\chi^2 - \alpha^2 z^2}$. This creates difficulties in numerical integration of the equations in the region $r \to 0$. To prevent the integration step from becoming too small it is usually convenient to turn to new functions isolating the main power dependence: $f = Fr^{1-|\chi|}$, $g = Gr^{1-|\chi|}$. The Dirac equations for *F* and *G* components are transformed as follows [18]:

$$f' = -(\chi + |\chi|)f/r - \alpha Z V g - (\alpha Z E_{n\chi} + 2/\alpha Z)g,$$
$$g' = (\chi - |\chi|)g/r - \alpha Z V f + \alpha Z E_{n\chi} f. \tag{19}$$

Here E_{nc} is one-electron energy without the rest energy. The boundary values are defined by the first terms of the Taylor expansion:

$$g=\left(V(0)-E_{n\chi}\right)r\alpha Z/(2\chi+1);\quad f=1 \text{ at } \chi<0,$$

$$f=\left(V(0)-E_{n\chi}-2/\alpha^2Z^2\right)\alpha Z;\quad g=1 \text{ at } \chi>0. \qquad (20)$$

The condition *f, g*®0 at *r*®∞ determines the quantified energies of the state E_{nc}. The system of equations (19) is numerically solved by the Runge-Kutta method. The details can be found in Refs. [21-30].

2.2 The Dirac-Sturm approach

The basic idea of the Dirac-Sturm approach is as follows [6,9,35,43]. In the usual formulation as basis functions used system of eigenfunctions of the generalized eigenvalue problem for the family of operators:

$$(H_0-\varepsilon)\Phi_\nu=\Lambda_\nu\hat{g}\Phi_\nu, \qquad (21)$$

where H_0 – unperturbed Hamiltonian of a system, $\hat{g}$ is a weighting operator, generally speaking, do not commute with the operator H_0; Λ_ν,Φ_ν - eigenvalues and eigenfunctions of equation (21). A weighting operator in Eq. (21) is usually chosen so that unlike a spectrum of H_0, the spectrum of (21) is a purely discrete. Using the orthogonality and completeness conditions, it is easy to show that the Green operator of the unperturbed problem is diagonal in a representation, defined by a set of functions Φ_ν and the corresponding expansion is as follows:

$$G_0(\varepsilon)=\sum_\nu|\Phi_\nu\rangle\langle\Phi_\nu|/\Lambda_\nu(\varepsilon) \qquad (22)$$

and contains only a single summation over the quantum numbers *{n}*. As the operator H_0 we use the Dirac-Kohn-Sham Hamiltonian. The Dirac-Kohn-Sham equation can be written in the next general form [9]:

$$[h_{DKS}(x)-\varepsilon_n]u_n(x)=0 \qquad (23)$$

Along with discrete spectrum ($e=e_n£e_F$) there is a continuous spectrum of the eigenvalues ($e>e_F$), corresponding to the Dirac-Kohn-Sham virtual orbitals. In the Sturmian formulation of the problem one should search for the eigen-values and eigen-functions of the equation:

$$[h_{DKS}(x)-\varepsilon]\varphi_\nu=\lambda_\nu\rho(x)\varphi_\nu \qquad (24)$$

where

$$\varepsilon=E-\sum_{k=1}^{N-1}\varepsilon_{n_k} \qquad (25)$$

When $e<0$ equation (24) has a purely discrete spectrum eigenvalues $l_n=l_n(e)$.

As the weight of the operator there are commonly used operators, proportional to a part or even all potential energy in the Hamiltonian H_0. Further, it is easily to understand that the Fourier-image of the one-particle Green's function in the Dirac-Kohn-Sham approximation can be represented as an expansion on the eigenfunctions of (24) [6,9]:

$$G^{(+)}=(x,x';\varepsilon)=\sum_\nu\frac{\tilde{\varphi}_\nu(x)\tilde{\varphi}^*_\nu(x')}{\lambda_\nu(\varepsilon)-1}, \qquad (26)$$

where $\tilde{\varphi}_\nu(x)$ is the Sturm designed function:

$$\tilde{\varphi}_\nu(x)=\varphi_\nu(x)-\sum_{k=1}^{N}u_{n_k}(x)<u_{n_k}|\varphi_\nu> \qquad (27)$$

In the case of the single-particle perturbed operator, say,

$$W(x)=\sum_{a=1}^{N}w_a(x) \qquad (28)$$

the second-order correction to an energy of the atom is determined by the standard expression of the following type:

$$\delta E^{(2)}=-\sum_{k=1}^{N}<u_{n_k}|wG^{(+)}(\varepsilon_{n_k})w|u_{n_k}>=$$

$$=-\sum_{k=1}^{N}\sum_\nu|<\tilde{\varphi}_\nu|w|u_{n_k}>|^2/[\lambda_\nu(\varepsilon_{n_k})-1] \qquad (29)$$

and it actually contains only the summation over the occupied states (core) and virtual orbitals of the Dirac-Kohn-Sham-Sturm type relating to a purely discrete spectrum.

If the operator $w_a(x)$ is an interaction with an external electric field, the expression (29) determines the many-electron atom polarizability. Let us illustrate the specific numerical implementation of relativistic method of the Sturm expansions on the example of the rubidium atom. Calculation of the static polarizability is actually reduced to two stages. In the first stage one should solve the system of relativistic Dirac-Kohn-Sham equations with respect to the Dirac radial functions and the Lagrange diagonal parameters e^{5s},e^{4p}, e^{4s} etc. In the second stage of the calculation procedure the system of equations equivalent to (24) is solved numerically:

$$(-i\alpha c\nabla + V_N(r) + \delta_i V_C(r) + V_X(r\,|\,b_i) - \varepsilon_i)\varphi_i = 0 \tag{30}$$

where, as above, V_N is the potential of the electron-nuclear interaction, V_C is a mean-field potential generated by the other electrons; V_X is the Kohn-Sham potential.

Two parameters e_i, d_i correspond to each orbital "i" of a real or Sturmian state. The parameter d_i =1 for orbitals of the real states. It is also important to emphasize that all orbitals of the Sturmian supplement of the Eq. (26) have an exponential asymptotic behavior as *r*®¥, which coincides with the asymptotic behavior of the last real state orbitals in the corresponding basis of the real state orbitals. In each case, the functions of the accounted real states represent a reduced spectral expansion of the Green's function G. The residual part decreases as exp[$-r(-2e)^{1/2}$] for *r*®¥ (*e* is the eigen energy of the explicitly accounted last real state). All orbitals of the Sturm supplement have absolutely the same asymptotic in the corresponding basis. This fact is very significant in terms of convergence of the method. Number of explicitly accounted real state functions is determined by concrete numerical application of method to computing studied atomic characteristics. Other details can be found in Refs. [6,9,35].

4 Shift and broadening of the hyperfine spectral line for multielectron atoms in an atmosphere of the buffer gas

4.1 Shift and broadening of the thallium and ytterbium hyperfine line in an atmosphere of the inert gas

At first, let us consider the thallium atom in atmosphere of the inert gas. Its studying is of a great interest as this atom a sufficiently heavy. In contrast to more simple alkali atoms (look below) the thallium atom contains p-electrons outside closed shells and has a nuclear charge Z = 81. In Table 1 the theoretical values of the van der Waals constants (in atomic units) respectively, for atom Tl (Tl - He, Kr, Xe) are listed. There are presented our results (*) obtained from our relativistic calculation by the optimized Dirac-Kohn-Sham method combined with the Dirac-Sturm approach, the calculation results by Batygin et al, based on the approximation formulas (10a)-(10c), the Hartree-Fock data by Penkin et al, as well as experimental data (from refs. [8,9,10-13]).

It is noteworthy sufficiently large error for values of the van der Waals constants, obtained during calculating on basis of formula (10), and standard Hartree-Fock method.

Table 1

Theoretical values of the van der Waals constants (in atomic units) respectively, for atom Tl (Tl - He, Kr, Xe); see explanations in the text.

	TI – He	TI – Ar	TI-Kr	TI-Xe
C_6^{I} (10a)	17.5	129	180	291
C_6^{II} (10b)	20.5	148	212	318
C_6^{III} (10c)	20.33	133	193	296
C_6 (Hartree-Fock)	6.59	48	71	111
C_6 (our data ^{a})*	12.1	106	157	265
C_6 (our data^{b})*	14.5	119	173	289
C_6 (experiment)	-	100	150	260

Note:^{a} – calculation with optimization*; ^{b} – calculation without optimization;

The calculation shows the importance of the quality of the atomic wave functions (using an optimization and correct account for the exchange-correlation effects and continuum "pressure" etc.) for an adequate description of the corresponding constants

In Table 2 there are listed the results of our calculation of the interatomic interaction potential *U* (*R*) and the values of the local shift δ*ω* (*R*) (all values are in atomic units) of the thallium hyperfine spectral line for different values of the internuclear distance in the system TI - He. For comparison, similar results of the calculation of the potential *U* (*R*) and the local shift $\delta\omega$ (*R*) with using the single-configuration Dirac-Fock method [12] are presented too.

Table 2

Local shift and interatomic interaction potential (in atomic units) for the pair TI - He.

R	Dirac-Fock method [12]		Our theory [8,9]	
	$\delta\omega(R)\bullet10^2$	$U(R)\bullet10^3$	$\delta\omega(R)\bullet10^2$	$U(R)\bullet10^3$
5	4.22	7.6	3,92	6.93
6	1.34	2.0	1,21	1.76
7	0.329	0.44	0.27	0.38
8	0.0788	0.099	0.070	0.085
9	0.0032	0.024	0.0025	0.020
10	-0.0145	-0.076	-0.0131	- 0.067
11			- 0.0119	-0.008

In Table 3 we list the results of our calculation (as all values are given in atomic units) interatomic interaction potential *U (R)* and the values of the local shift *δω (R*) for pairs TI-Kr, TI-Xe.

Table 3

Local shift and interatomic interaction potential (in atomic units) for the pair TI – Kr, Xe (see text)

R	T1-Kr (Our theory)		T1-Xe (Our theory)	
	$\delta\omega(R)\bullet10^2$	$U(R)\bullet10^3$	$\delta\omega(R)\bullet10^2$	$U(R)\bullet10^3$
5	-14.30	13.24	-19,05	18.31
6	-2.88	6.10	-8.22	5.95
7	-1.44	1.72	-2.67	2.04
8	-0.67	0.49	-1.52	0.65
9	-0.48	0.06	-0.74	0.01
10	-0.35	-0.03	-0.48	- 0.08
11	-0.24	- 0.04	- 0.37	-0.09

Further in Table 4 we present our theoretical values (theory C) for the thallium atom hyperfine line collisional shift at the temperature T = 700K for a number of the diatomic systems, in particular, the pairs of TI - He, TI - Kr, Tl-Xe.

Table 4

The collisional shift f_r (in Hz/Torr) of the thallium hyperfine line for pairs TI - He, TI - Kr, Tl-Xe at T = 700^{o}K; Experiment and the qualitative estimate by Choron-Scheps-Galagher (Virginia group); Theory: A- single-configuration Dirac-Fock method; B – the optimized Dirac-Fock method; C- our theory (see text).

System	T1-He	T1-Kr	T1-Xe
Experiment	130 ± 30	-490±20	-1000±80
Qualitative estimate	-	-	-5500
Theory A	155.0	-850.0	-1420.0
Theory B	139.0	-	-
Theory C	137.2	-504	-1052

In Table 5 we present the theoretical data on the collisional shift f_r (in Hz/Torr) the thallium atom hyperfine line at different temperatures (T^{0}K) for the systems TI - He, TI - Kr, Tl-Xe: Theory A - the single-configuration Dirac-Fock method Batygina DF et al. [12]; C- our theory [8,9].

As can be seen from the presented data, our theory provides a physically reasonable agreement with experimental data on the hyperfine line collisional shifts for the pairs of TI-He, TI-Kr, Tl-Xe.

Table 5

The temperature dependence of the collisional shift f_r (in Hz/Torr) for pairs TI - He, TI - Kr, Tl-Xe; Theory: A- single-configuration Dirac-Fock method; C- our theory;

Pair	T1—He	T1—He	T1—Kr	T1—Xe
T, K	Theory A	Theory C	Theory C	Theory C
700	155	137,2	-504	-1052
750	153.0	135,3	-461	-964
800	151	134,1	-422	-899
850	149	133,3	-391	-841
900	147.5	131,4	-362	-794
950	146	129,1	-330	-751
1000	143	126,2	-308	-713

For comparison, in this table there are also listed the results of calculation on the basis of the single-configuration Dirac-Fock method Batygina DF et al. [12] (theory A), the optimized DF-like method [8] (theory B), as well as experimental data Choron-Scheps-Galagher (the Virginia group) . The qualitative estimate from Ref. [10] has been listed as well. In Table 6 we present our calculated values for adiabatic broadening Γ_a/p (in Hz / Torr) of the thallium atom hyperfine line at different temperatures for the TI – He pair: C - our theory; A theory [12]. In Table 7 we list the similar theoretical data on the Tlatom hyperfine line adiabatic broadening of Γ_a/p (in Hz / Torr) for the pairs TI - Kr, TI-Xe.

Table 6

Adiabatic broadening Γ_a/p (in Hz / Torr) for the TI - He: Theory A- single-configuration Dirac-Fock method; C- our theory.

T, K	TI – He Theory A	TI – He Theory C
700	2.83	2.51
800	2.86	2.54
900	2.90	2.58
1000	2.89	2.56

Table 7

Adiabatic broadening Γ_a/p (in Hz / Torr) for the TI – Kr, Yl-Xe (our theory).

T, K	TI- Kr	TI- Xe
700	6.81	17.3
800	5.89	14.6
900	5.26	12.9
1000	5.24	11.5

It is easily to estimate that the ratio values (Γ_a/p) / f_p ~ 1/50 for the system TI - He, (Γ_a/p) / f_p ~ 1/70 for the system TI - Kr and (Γ_a/p) / f_p ~ 1/60 for the TI-Xe. These estimates (at first it had been noted in Ref.[12]) show that well-known in the theory of optical range spectral line broadening Foley law $\Gamma_a \sim |\Delta|$ (see, for example, [6]) is incorrect for the spectral lines of transitions between components of the hyperfine structure. At least this fact is absolutely obvious for the thallium atom.

In any case we suppose that more detailed experimental studying are to be very actual and important especially a light of availability of the theoretical data on temperature dependences of the thallium hyperfine line collisional shift and broadening. Obviously, this is also very actual from the point of view of the construction the thallium quantum frequency measure, as well as studying a role of the weak interactions in atomic physics and physics of collisions (see, for example, [6,10]).

Now let us consider the pair ‘Yb-He”. The ground configuration for the ytterbium atom is: [Xe]$4f^{14}6s^2$ (term: ^1S). Further we present our results for the scalar static polarizability a_0 (in units of a_0^3, a_0 is the Bohr radius) and isotropic dispersion coefficient $C_{6,0}$ (in units of $E_H \times a_0^6$, E_H is the Hartree unit of energy). Our data are as follows [9]: $C_{6,0}$= 45.2 and a_0=169.3. For comparison let us present the corresponding data by Dalgarno et al [13]: $C_{6,0}$= 39.4, a_0=157.3 and by Buchachenko et al [44]: $C_{6,0}$= 44.5.

In table 8 we present our calculation results for the observed f_r (in Hz/Torr) shift for the system of Yb-He.

Table 8

The observed f_r (in, Hz/Torr) shift for the system Yb-He (see text)

T, K	f_ρ
700	148.1
750	146.0
800	143.8
850	141.5
900	138.9

It is obvious that the pair Yb-He is more complicated system in comparison with the pair of Tl-He or “alkali atom-He”. Until now there are no any experimental or theoretical data for this system. So, we believe that our data may be considered as the first useful reference

4.2 Shift and broadening of the alkali atom hyperfine line in an atmosphere of the inert gas

Here we present the results of our studying hyperfine line collisional shift for alkali atoms (rubidium and caesium) in the atmosphere of the helium gas. In Table 9 we present our data on the van der Waals constants in the interaction potential for alkali Rb, Cs atoms with inert gas atoms Ne, Kr, Xe, and also available in the literature experimental data [10,11]. In Table 10 we list the results of our calculating (in atomic units) interatomic potentials, local shifts $dw(R)$ for the pair Cs-He. Noteworthy is the fact that an accuracy of the experimental data for the van der Waals constants does not exceed 10 % for heavy alkali atoms. Calculation has shown that the optimization of the relativistic orbitals basis and accounting for the exchange-correlation effects seem to be very important for obtaining adequate accuracy of the description of the constants.

Table 9

The van der Waals constants (in atomic units.) for alkali atoms, interacting with inert gas atoms Ne, Kr, Xe (see text).

Pair of atoms	Our theory	Experiment
Rb-He	42	41
Rb –Kr	484	470
Rb –Xe	758	-
Cs-He	52	50
Cs-Kr	582	570
Cs-Xe	905	-

Table 10. **The interatomic potential (10^5) and local δω(R) shift (10^5) for Cs-He pair (in atomic units; see text)**

R	$\delta\omega(R)$	U (R)
8	4280	610
9	2845	336
10	1890	169
11	955	77
12	482	32
13	251	12.8
14	113	4.1
15	59	1.9

In Table 11 and 12 we present our theoretical results for the hyperfine line observed shift f_p (1/Torr) in a case of the Rb-He and Cs-He pairs. The experimental and alternative theoretical results by Batygin et al [11] for f_p are listed too. At present time there are no precise experimental data for a wide interval of temperatures in the literature.

Table 11

The observed f_r (10^{-9} 1/Torr) shifts for the systems of the Cs-He and corresponding theoretical data (see text).

T, K	Experiment	Our theory	Theory[a] [11]	Theory[b] [11]	Theory[c] [11]
223	-	178	164	142	169
323	135	137	126	109	129
423	-	123	111	96	114
523	-	112	100	85	103
623	-	105	94	78	96
723	-	98	-	-	-
823	-	92	-	-	-

Note:[a] –calculation with using the He wave functions in the Clementi-Rothaane approximation; [b] – calculation with using the He wave functions in the Z-approximation;

[c] –calculation with using the He wave functions in the Löwdin approximation;

Table 12

The observed f_r (10^{-9} 1/Torr) shifts for the systems of Rb-He and corresponding theoretical data (see text).

T, K	Experiment	Our theory	Theory[a] [11]	Theory[b] [11]	Theory[c] [11]
223	-	113	79	67	81
323	105	101	73	56	75
423	-	89	62	48	64
523	-	80	55	43	56
623	-	73	50	38	50
723	-	71	47	36	47
823	-	69	-	-	-

Note:[a] –calculation with using the He wave functions in the Clementi-Rothaane approximation; [b] – calculation with using the He wave functions in the Z-approximation;

[c] –calculation with using the He wave functions in the Löwdin approximation;

The theoretical data from Refs. [11] are obtained on the basis of calculation within the exchange perturbation theory with using the He wave functions in the Clementi-Rothaane approximation [42] (column: Theory[a]), and in the Z-approximation (column: Theory[b]), and in the Löwdin approximation (column: Theory[c]).

The important feature of the developed optimized perturbation theory approach is using the optimized relativistic orbitals basis, an accurate accounting for the exchange-correlation and continuum pressure effects with using the effective functionals [18,34].

The difference between the obtained theoretical data and other alternative calculation results can be explained by using different perturbation theory schemes and different approximations for calculating the electron wave functions of heavy atoms. It is obvious that the correct account for the relativistic and exchange-correlation and continuum pressure effects will be necessary for an adequate description of the energetic and spectral properties of the heavy atoms in an atmosphere of the heavy inert gases (for example, such as Xe).

5 Conclusion

In this chapter a brief review of the experimental and theoretical works on the hyperfine structure line collision shifts for heavy atoms in an atmosphere of the buffer inert gases is given. A new, consistent relativistic perturbation theory combined with the exchange perturbation theory, is presented and applied to calculating the interatomic potentials, van der Waals constants, hyperfine line collision shift and broadening for some heavy atoms in an atmosphere of the buffer inert gases. It should be noted that the presented approach can be naturally generalized in order to describe the energy and spectral characteristics of other atomic systems and buffer mediums.

The calculation results on the hyperfine line collision shift and broadening for the alkali (Rb, Cs), thallium, and ytterbium atoms in an atmosphere of the inert gas (He, Kr, Xe) are listed and compared with available alternative theoretical and experimental results. The obtained data for the $(\Gamma_a/p)\,/\,f_p$ ratio allowed to confirm that the well-known Foley law $\Gamma_a \sim f_p$ in the theory of optical range spectral line broadening is incorrect for the spectral lines of transitions between components of the hyperfine structure of the heavy multielectron atoms.

The studying hyperfine structure line collision shifts and widths for different heavy atomic systems in the buffer gases opens new prospects in the bridging of quantum chemistry and atomic and molecular spectroscopy and physics of collisions. These possibilities are significantly strengthened by a modern experimental laser and other technologies [10,50-56]. Really, new experimental technologies in physics of collisions may provide a measurement of the atomic and molecular collision spectral parameters with very high accuracy.

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OPTIMIZED PERTURBATION THEORY TO CALCULATING THE HYPERFINE LINE SHIFT AND BROADENING FOR HEAVY ATOMS IN THE BUFFER GAS

Abstract

It is presented review of a new consistent relativistic approach to determination of collisional shift and broadening hyperfine lines for heavy atoms in an atmosphere of the buffer inert gas. It is based on the atomic gauge-invariant relativistic perturbation theory and the exchange perturbation theory. As illustration, consistent approach is applied to calculating the interatomic potentials, hyperfine structure line collision shift and broadening for heavy atoms, in particular, atoms of alkali elements – rubidium, caesium, and thallium, ytterbium, in an atmosphere of the buffer inert gas.

Key words: Relativistic many-body perturbation theory, hyperfine line collision shift

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ОПТИМИЗИРОВАННЯ ТЕОРИЯ ВОЗМУЩЕНИЙ ДЛЯ ОПРЕДЕЛЕНИЯ СДВИГА И УШИРЕНИЯ ЛИНИЙ СВЕРХТОНКОЙ СТРУКТУРЫ В ТЯЖЕЛЫХ АТОМАХ В БУФЕРНЫХ ГАЗАХ

Резюме

Представлен обзор нового последовательного релятивистского подхода к определению столкновительного сдвига и уширения линии сверхтонкой структуры тяжелых атомов в атмосфере буферных инертных газов. Метод основан на атомной калибровочно-инвариантной теории возмущений и обменной теории возмущений. В качестве иллюстрации приведен пример расчета межатомных потенциалов, столкновительного сдвига и уширения сверхтонких линий для тяжелых атомов, в частности, атомов щелочных элементов, таллия, иттербия в атмосфере буферных инертных газов.

Ключевые слова: релятивистская теория возмущений, столкновительный сдвиг линий сверхтонкой структуры

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ОПТИМІЗОВАНА ТЕОРІЯ ЗБУРЕНЬ ДЛЯ ВИЗНАЧЕННЯ ЗСУВУ ТА УШИРЕННЯ ЛІНІЙ НАДТОНКОЇ СТРУКТУРИ У ВАЖКИХ АТОМАХ В БУФЕРНИХ ГАЗАХ

Резюме

Представлено огляд нового послідовного релятивістського підходу до визначення зсуву та уширення лінії надтонкої структури важкого атома в атмосфері буферних інертних газів. Метод базується на атомній калібрувально-інваріантній теорії збурень та обмінній теорії збурень. Як ілюстрація наведено приклад розрахунку міжатомних потенціалів, зсуву та уширення за рахунок зіткнень надтонких ліній для важких атомів, зокрема, атомів лужних елементів, таллія, іттербія в атмосфері буферних інертних газів.

Ключові слова: релятивістська теорія збурень, зсув за рахунок зіткнень ліній надтонкої структури