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NEW RELATIVISTIC APPROACH TO CALCULATING THE HYPERFINE LINE SHIFT AND BROADENING FOR HEAVY ATOMS IN THE BUFFER GaS

It is presented a new consistent relativistic approach, based on the atomic gauge-invariant relativistic perturbation theory and the optimal construction of the interatomic potential function within exchange perturbation theory . As illustration it is applied to calculating the interatomic potentials, hyperfine structure line collision shift and broadening for heavy atoms in an atmosphere of the buffer inert gas. The accurate account for the relativistic and exchange-correlation and continuum pressure effects is necessary for an adequate description of the energetic and spectral properties of the heavy atoms in an atmosphere of the heavy inert gases.

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 [1–16]. 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 [1-14]. As a rule (see [15]), 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. 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.

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. [1-3,15]). 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 precise relativistic approach 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].

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. [11,12,15]):

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

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

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) [1]).

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).

As it is well known (see also Refs. [1, 2]), 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) [12]. 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 [8,15]. 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]). In our calculation we have used the relativistic functions, which are generated by the Dirac Hamiltonian [8]. The potential of the inter-electron interaction with accounting the retarding effect and magnetic interaction in the lowest order on parameter a^2 (the fine structure constant) is as follows:

$$V(r_i r_j) = exp(i\omega_{ij} r_{ij})\cdot\frac{(1-\alpha_i\alpha_j)}{r_{ij}}, \tag{3}$$

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 in the Kohn-Sham approximation. Besides, we introduce into the zeroth order Hamiltonian the corresponding correlation functional [5]

$$V_C[\rho(r),r] = -0.0333\cdot b\cdot \ln[1+18.3768\cdot \rho(r)^{1/3}], \quad (4)$$

where b is the optimization parameter (for details see Refs. [5,8,15]). The optimization is reduced to minimization of the gauge dependent multielectron contribution $ImdE_{ninv}$ of the lowest relativistic 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. The further elaboration of the method can be reached by means of using the Dirac-Sturm approach [5]. To calculate an effective potential of the interatomic interaction we use a method of the exchange perturbation theory (in the modified version EL-HAV [1]). Within exactness to second order terms on potential of Coulomb interaction of the valent electrons and atomic cores a local shift can be written as:

$$\delta(R) = \frac{S_0}{1-S_0} + \Omega_1 + \Omega_2 - \sum_n \frac{C_n}{R^n}, \quad (5)$$

where values W_1, W_2 are the non-exchange and exchange non-perturbation sums of the first order correspondingly, which express through the matrix elements of the hyperfine interaction operator. The other details are in Refs.[1,8,15].

Further we present some test results of our studying hyperfine line collisional shift for alkali atoms (rubidium and caesium) in the atmosphere of the helium gas. In Table 1 and 2 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. 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]).

Table 1.

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

T, K	Exp.	[13]	[11] a	[11] b	[11]c	This
223	-	113	79	67	81	116
323	105	101	73	56	75	103
423	-	89	62	48	64	91
523	-	80	55	43	56	83
623	-	73	50	38	50	75
723	-	-	-	-	-	73
823	-	-	-	-	-	71

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 2.

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

T, K	Exp	[11] a	[11] b	[11]c	This
223	-	164	142	169	175
323	135	126	109	129	136
423	-	111	96	114	122
523	-	100	85	103	110
623	-	94	78	96	103
723	-	-	-	-	96
823	-	-	-	-	91

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

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).

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Abstract

It is presented a new consistent relativistic approach to hyperfine structure line collision shift and broadening for heavy atoms in an atmosphere of the buffer inert gas, based on the atomic gauge-invariant relativistic perturbation theory and the optimal construction of the interatomic potential function within exchange perturbation theory . As illustration it is applied to calculating the interatomic potentials, hyperfine structure line collision shift for heavy atoms in an atmosphere of the buffer inert gas. The accurate account for the relativistic and exchange-correlation and continuum pressure effects is necessary for an adequate description of the energetic and spectral properties of the heavy atoms in an atmosphere of the heavy inert gases.

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

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НОВЫЙ РЕЛЯТИВИСТСКИЙ ПОДХОД К ОПРЕДЕЛЕНИЮ СДВИГА И УШИРЕНИЯ ЛИНИЙ СВЕРХТОНКОЙ СТРУКТУРЫ В ТЯЖЕЛЫХ АТОМАХ В БУФЕРНЫХ ГАЗАХ

Резюме

Представлен новый релятивистский подход к определению сдвига и уширения линии сверхтонкой структуры тяжелых атомов в атмосфере буферных газов. Метод основан на атомной калибровочно-инвариантной теории возмущений и оптимальной конструкции межатомного потенциала в обменной теории возмущений. В качестве иллюстрация приведены результаты расчета сдвига сверхтонких линий ряда тяжелых атомов, в частности, щелочных атомов в атмосфере буферных инертных газов. Аккуратный учет релятивистских, обменно-корреляционных и эффектов давления континуума необходим для адекватного описания энергетических и спектральных свойств тяжелых атомов в атмосфере тяжелых инертных газов.

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

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НОВИЙ РЕЛЯТИВІСТСЬКИЙ ПІДХІД ДО ВИЗНАЧЕННЯ ЗСУВУ ТА УШИРЕННЯ ЛІНІЙ НАДТОНКОЇ СТРУКТУРИ У ВАЖКИХ АТОМАХ В БУФЕРНИХ ГАЗАХ

Резюме

Представлено новий релятивістський підхід до визначення зсуву та уширення лінії надтонкої структури важких атомів в атмосфері буферних газів. Метод базується на атомній калібрувально-інваріантній теорії збурень та оптимальній конструкції міжатомного потенціалу в обмінній теорії збурень. Як ілюстрація наведені результати розрахунку зсуву надтонких ліній ряду важких атомів, зокрема, лужних атомів в атмосфері буферних інертних газів. Акуратний облік релятивістських, обмінно-кореляційних і ефектів тиску континууму необхідний для адекватного опису енергетичних і спектральних властивостей важких атомів в атмосфері важких інертних газів.

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