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Intermediate coupling in relativistic atomic calculations: Average of configuration and the nonrelativistic limit

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Results of relativistic Dirac–Fock calculations of atoms using different coupling schemes are presented. Closed-form expressions are given for the atomic energies in the average of configuration approximation employing both the jj- and LS-coupling schemes. Using elements of groups 13 and 14 of the periodic table (the boron and carbon groups, respectively) as examples, it is shown by comparison with calculations in the intermediate coupling scheme that the energy level structure of group 14 atoms is not correctly reproduced in the jj-coupling scheme up to Sn (Z=50), while it is reproduced with good precision for the superheavy element Fl (Z=114). It is demonstrated that the average of configuration in LS-coupling, in contrast to jj-coupling, has the correct nonrelativistic limit. Furthermore, it is shown that the LS-term energies of open-shell atoms obtained by the Dirac–Fock method in the intermediate coupling scheme, when taken in the nonrelativistic limit, may slightly differ from the corresponding term energies computed by the nonrelativistic Hartree–Fock method. This effect is accompanied by a lowering of the symmetry of the one-electron central field wavefunctions.

Keywords: Hartree–Fock and Dirac–Fock methods, average of configuration, jj-coupling, LS-coupling.

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1. Introduction

The calculations of atomic thermal energies using the basis of single-electron Hartree-Fock functions (HF) or Dirac-Fock (DF) functions, are provided, in general, for LS- or jj-couplings. In LS-coupling, the first stage usually involves calculating the atom using the non-relativistic single-configuration HF method with further accounting for correlation effects [1]. In LS-coupling, relativistic effects, in particular spin-orbit splitting, are taken into account at the second stage by methods of disturbance theory. This approach is justified for valence electrons of light atoms, where small relativistic corrections can be considered as disturbance.

In jj-coupling, the relativistic four-component DF method with Dirac–Coulomb or Dirac–Coulomb–Breit Hamiltonians [2,3] or their two-component counterparts are usually used to determine the single-electron wave. However, for valence electrons in their pure form, jj-coupling is realized only in heavy and superheavy atoms. This is due to the fact that several relativistic configurations with similar energy (further in the text - jjconfigurations) corresponding to a single non-relativistic configuration (further in the text - LSconfigurations) are intensively mixed when allowing for the configuration interaction. As a result, calculations of the open-shell atoms in pure jjcoupling may incorrectly predict the arrangement and structure of atomic terms. In addition, it should be stressed that in the general jj-coupling does not transform into LS-coupling in the non-relativistic limit. To get the correct results and correct non-relativistic limit in relativistic atomic analysis, the multi-configuration methods should be applied that allow mixing various jj configurations corresponding to a single LSconfiguration, in other words, using an intermediate type of coupling (IC-coupling).

Where HF or DF method is used to determine the single-electron wave functions, which later serve as a single-electron basis in multi-configuration analysis, the approximation of the configuration's center of gravity (CCoG) is usually used. This approximation makes it possible to construct a common single-electron basis for all terms of the same configuration. The main idea of CCoG approximation is that, due to the conservation of the matrix trace during its diagonalization, the one-configuration expression for the total energy obtained by averaging the energy of all terms of one configuration, taking into account their multiplicity, coincides with the average value of all diagonal matrix elements of the complete Hamiltonian of an atom in the basis of Slater determinants of one configuration. As a result, we may obtain an explicit expression for the total energy of an atom in terms of Slater–Condon F_k and G_k integrals [4], varying of which leads to a system of integro-differential equations for determination of radial wave functions. It should be emphasized that CCoG is not an additional approximation for configurations containing only one term, i.e., for configurations with closed shells and configurations containing one electron or one hole outside closed shells. For the non-relativistic HF method, CCoG approximation is described in detail in [4]. It should be noted that in CCoG approximation, the Koopman's theorem [5] holds for atoms with any number of open shells [6].

Let's name the CCoG approximation, which in relativistic analysis by DF method is easily generalized for the jj-configuration [2], following [6], the jj-average. In case of open shells jj-average, as well as the energies of individual terms, may have an incorrect non-relativistic limit. However, if we apply CCoG approximation in an intermediate type of coupling, i.e., when it is averaged over all terms of LS configuration, then we can obtain an explicit expression for the total energy in terms of Slater–Condon F_k and G_k relativistic integrals [1,2], and this expression will have correct non-relativistic limit. Following [6], we will call this approximation the relativistic LS-average over configuration. The scheme of relativistic LS-average over configuration was first proposed in [7,8] and then sequentially derived in general form in [6]. In [9–11], the scheme of relativistic LS-average was used to rewrite the expression for DF energy similar to the expression for the non-relativistic HF energy by replacing the non-relativistic Condon-Slater parameters F_k and G_k with the averaged relativistic integrals F_k and G_k. Yet, these expressions for energy were not presented in a general closed form. Later on, LS-average of the configuration was widely used in relativistic calculations of atoms (see, for example, the papers [12–14] and others).

In this paper, in the second section, we give expressions for energies in various CCoG variants, such as the non-relativistic LS-average in HF method, jj-average and the relativistic LS-average in DF method. Such expressions, presented in a closed form and collected together for different CCoG options, are not available in the literature. In the third section, we give the calculated energies of relativistic terms in jj- and IC couplings, as well as jj- and LS-CCoG energies in atoms of groups 13 and 14 of periodic table (boron and carbon groups, respectively). The elements of group 13 have a valence configuration s^2p^1, and the elements of group 14 — s^2p^2. In this paper, we also consider the non-relativistic limit of the energies of relativistic terms and CCoG energies of these atoms.

Atomic system of units ($m_e = e = \hbar = 1$) is used in the study.

2. Theory

Configuration center of gravity

The expression for E_{av} energy in CCoG approximation is defined as the average value of all terms of one or more configurations of an atom, taking into account their multiplicity, i.e.

$$E_{av} = \frac{1}{N_d}\sum_{\Gamma} n_\Gamma E_\Gamma, \qquad N_d = \sum_{\Gamma} n_\Gamma, \tag{1}$$

where Γ numbers all terms of one or more configurations, and n_Γ is the multiplicity (degeneracy) of the term Γ. If the term energies are calculated in a single basis for all Slater determinants N_d related to these configurations, then it follows from the condition of $\hat{H}$ Hamiltonian matrix trace conservation when diagonalizing it that

$$E_{av} = \frac{1}{N_d}\sum_{\alpha}\langle\alpha|\hat{H}|\alpha\rangle. \tag{2}$$

Here α enumerates the Slater determinants.

Further, we'll use the following designations. Let the indices A and B enumerate the shells of the nonrelativistic LS-configuration, and indices a and b — sub-shells of relativistic jj-configuration. The number of electrons on the shells of LS-configurations is denoted by q_A and q_B, and the number of electrons on the sub-shells of jj-configurations — by q_a and q_b.

The center of gravity of the configuration in non-relativistic HF method

The expression for CCoG energy in the non-relativistic HF method can be written as [4,6]

$$\begin{aligned} E_{av}^{HF} = &\sum_A q_A I_A^{HF} + \frac{1}{2}\sum_A q_A(q_A-1)F_0^{HF}(A,A) \\ &+ \frac{1}{2}\sum_{A\neq B} q_A q_B F_0^{HF}(A,B) \\ &+ \sum_A\sum_{k>0} q_A(q_A-1) f_k^{HF}(A,A) F_k^{HF}(A,A) \\ &+ \sum_{A<B}\sum_k q_A q_B g_k^{HF}(A,B) G_k^{HF}(A,B), \end{aligned} \tag{3}$$

where coefficients $f_k^{HF}(A,A)$ and $g_k^{HF}(A,B)$ are defined by the expressions

$$f_k^{HF}(A,A) = -\frac{1}{4}\frac{4l_A+2}{4l_A+1}\frac{\left(C^{k0}_{l_A0,l_A0}\right)^2}{2k+1},$$

$$g_k^{HF}(A,B) = -\frac{1}{2}\frac{\left(C^{k0}_{l_A0,l_B0}\right)^2}{2k+1}. \tag{4}$$

Here and further, the coefficients $C^{j\mu}_{j_1\mu_1,j_2\mu_2}$ — are Clebsch-Gordan coefficients. The coefficients $f_k^{HF}(A,A)$ are different from zero, if k — an even number, and coefficients $g_k^{HF}(A,B)$, if $l_A + l_B + k$ – an even number. Parameter I_A^{HF} in expression (3) is a non-relativistic radial matrix element of the single-electron part of the Hamiltonian, and $F_k^{HF}(A,B)$ and $G_k^{HF}(A,B)$ are Coulomb and exchange integrals, respectively:

$$F_k^{HF}(A,B) = \int_0^\infty dr \int_0^\infty dr' \rho_A(r)\,\frac{r_<^k}{r_>^{k+1}}\,\rho_B(r')\,dr\,dr',$$

$$G_k^{HF}(A,B) = \int_0^\infty dr \int_0^\infty dr' \rho_{AB}(r)\frac{r_<^k}{r_>^{k+1}}\rho_{AB}(r')dr\,dr', \tag{5}$$

where

$$\rho_A(r) = P_A^2(r), \qquad \rho_{AB}(r) = P_A(r)\,P_B(r). \tag{6}$$

Here $P_A(r)$ and $P_B(r)$ — radial wave functions, and $r_< = \min(r, r')$, $r_> = \max(r, r')$.

The center of gravity of jj-configuration in the relativistic DF method

Similarly, we can write the expression for CCoG energy in jj-couplings within the framework of DF method:

$$\begin{aligned} E_{\mathrm{av}}^{\mathrm{DF}} &= \sum_a q_a\, I_A^{\mathrm{DF}} + \frac{1}{2}\sum_a q_a(q_a-1)\,F_0^{\mathrm{DF}}(a,a) \\ &+ \frac{1}{2}\sum_{a\neq b} q_a\, q_b\, F_0^{\mathrm{DF}}(a,b) + \\ &+ \sum_a \sum_{k>0} q_a\,(q_a-1)\, f_k^{\mathrm{DF}}(a,a)\, F_k^{\mathrm{DF}}(a,a) \\ &+ \sum_{a<b}\sum_k q_a\, q_b\, g_k^{\mathrm{DF}}(a,b)\, G_k^{\mathrm{DF}}(a,b)\,, \end{aligned} \tag{7}$$

where

$$\begin{aligned} f_k^{\mathrm{DF}}(a,a) &= -\frac{(2j_a+1)(2l_a+1)^2}{4j_a(2k+1)} \\ &\times \left(C^{k0}_{l_a0,l_a0}\right)^2 \begin{Bmatrix} j_a & j_a & k \\ l_a & l_a & \frac{1}{2} \end{Bmatrix}^2, \qquad a=b \end{aligned} \tag{8}$$

and

$$\begin{aligned} g_k^{\mathrm{DF}}(a,b) &= -\frac{(2l_a+1)(2l_b+1)}{2k+1} \\ &\times \left(C^{k0}_{l_a0,l_b0}\right)^2 \begin{Bmatrix} j_a & j_b & k \\ l_b & l_a & \frac{1}{2} \end{Bmatrix}^2, \qquad a\neq b. \end{aligned} \tag{9}$$

If in formulae (8) and (9) we use the following expression for $6j$-symbol [15]:

$$C^{k0}_{l_a0,l_b0} \begin{Bmatrix} j_a & j_b & k \\ l_b & l_a & \frac{1}{2} \end{Bmatrix} = \frac{1}{\sqrt{(2l_a+1)(2l_b+1)}}\, C^{k0}_{j_a\frac{1}{2},j_b-\frac{1}{2}}\,, \tag{10}$$

then, for the coefficients $f_k^{\mathrm{DF}}(a,a)$ and $g_k^{\mathrm{DF}}(a,b)$ we may get a more simple expression:

$$f_k^{\mathrm{DF}}(a,a) = -\frac{1}{2}\,\frac{2j_a+1}{2j_a}\,\frac{\left(C^{k0}_{j_a\frac{1}{2},j_a-\frac{1}{2}}\right)^2}{2k+1}\,,$$

$$g_k^{\mathrm{DF}}(a,a) = -\frac{\left(C^{k0}_{j_a\frac{1}{2},j_b-\frac{1}{2}}\right)^2}{2k+1}. \tag{11}$$

Here, the coefficients $f_k^{\mathrm{DF}}(a,a)$ are also different from zero, if k — is an even number, and coefficients $g_k^{\mathrm{DF}}(a,b)$, if $l_a + l_b + k$ — is an even number.

Relativistic Coulomb and exchange integrals are defined by an expression similar to (5), where

$$\rho_a^{\mathrm{DF}}(r) = P_a^2(r) + Q_a^2(r)\,,$$

$$\rho_{ab}^{\mathrm{DF}}(r) = P_a(r)\,P_b(r) + Q_a(r)\,Q_b(r). \tag{12}$$

Here, $P_a(r)$, $P_b(r)$ and $Q_a(r)$, $Q_b(r)$ — the large and small components of the radial Dirac wave function, respectively.

The center of gravity of LS-configuration in the relativistic DF method

The expression of LS-average for DF energy in the intermediate $E_{\mathrm{av}}^{\mathrm{IC}}$ coupling can be obtained by averaging all diagonal matrix elements (1) in the basis of Slater determinants for all jjconfigurations belonging to the same nonrelativistic LS-configurations. This is equivalent to averaging the expressions for jj-average energies (7) over all jj-configurations of a single LS-configuration [6]:

$$\begin{aligned} E_{\mathrm{av}}^{\mathrm{IC}} &= \sum_a \widetilde{q}_a\, I_a^{\mathrm{DF}} + \frac{1}{2}\sum_a \widetilde{q}_a(\widetilde{q}_a - w_a) F_0^{\mathrm{DF}}(a,a) \\ &+ \sum_{a<b} \widetilde{q}_a \widetilde{q}_b\, \omega_{AB}\, F_0^{\mathrm{DF}}(a,b) \\ &+ \sum_a\sum_{k>0} \widetilde{q}_a(\widetilde{q}_a - w_a)\, f_k^{\mathrm{DF}}(a,a)\, F_k^{\mathrm{DF}}(a,a) \\ &+ \sum_{a<b}\sum_k \widetilde{q}_a\, \widetilde{q}_b\, \omega_{AB}\, g_k^{\mathrm{DF}}(a,b)\, G_k^{\mathrm{DF}}(a,b)\,, \end{aligned} \tag{13}$$

where

$$\widetilde{q}_a = \frac{2j_a+1}{4l_A+2}\, q_A\,, \qquad w_a = \frac{q_A - \widetilde{q}_a + 2j_a}{4l_A+1},$$

$$\omega_{AB} = \begin{cases} \frac{4l_a+2}{4l_a+1}\,\frac{q_A-1}{q_A} & A = B. \\ 1 & A \neq B. \end{cases} \tag{14}$$

The expression for the relativistic LS-average (13) can be rewritten similar to expression (3) for the CCoG in the non-relativistic HF method. For this purpose, let's express the relativistic coefficients $f_k^{\mathrm{DF}}(a,a)$ and $g_k^{\mathrm{DF}}(a,b)$ (8), (9) through the nonrelativistic coefficients — $f_k^{\mathrm{HF}}(a,a)$ and $g_k^{\mathrm{HF}}(a,b)$ (4):

$$\begin{aligned} f_k^{\mathrm{DF}}(a,a) &= \frac{(2j_a+1)(2l_a+1)(4l_a+1)}{2j_a} \\ &\times \begin{Bmatrix} j_a & j_a & k \\ l_a & l_a & \frac{1}{2} \end{Bmatrix}^2 f_k^{\mathrm{HF}}(A,A), \end{aligned} \tag{15}$$

and

$$\begin{aligned} g_k^{\mathrm{DF}}(a,b) &= \frac{1}{2}\,(2l_a+1)(2l_b+1) \\ &\times \begin{Bmatrix} j_a & j_b & k \\ l_b & l_a & \frac{1}{2} \end{Bmatrix}^2 g_k^{\mathrm{HF}}(A,B). \end{aligned} \tag{16}$$

Substituting expressions (15) and (16) for the coefficients $f_k^{\mathrm{DF}}(a,a)$ and $g_k^{\mathrm{DF}}(a,b)$ in (13), we obtain an expression for the relativistic *LS* average, similar to the non-relativistic formula (3):

$$E_{\mathrm{av}}^{\mathrm{IC}} = \sum_A q_A I_A^{\mathrm{IC}} + \frac{1}{2}\sum_A q_A(q_A-1)\,F_0^{\mathrm{IC}}(A,A) + \frac{1}{2}\sum_{A\neq B} q_A q_B\,F_0^{\mathrm{IC}}(A,B) + \sum_A\sum_{k>0} q_A\,(q_A-1)\,f_k^{\mathrm{HF}}(A,A)\,F_k^{\mathrm{IC}}(A,A) + \sum_{A<B}\sum_k q_A q_B\,g_k^{\mathrm{HF}}(A,B)\,G_k^{\mathrm{IC}}(A,B)\,, \quad (17)$$

where

$$I_A^{\mathrm{IC}} = \sum_{a\in A}\frac{2j_a+1}{4l_a+2}\,I_A^{\mathrm{DF}}\,. \quad (18)$$

The Coulomb $F_0^{\mathrm{IC}}(A,B)$ and exchange $G_k^{\mathrm{IC}}(A,B)$ integrals included in expression (17) have the meaning of Slater-Condon parameters in the intermediate coupling and are defined as follows:

$$F_0^{\mathrm{IC}}(A,B) = \begin{cases} \sum\limits_{a\in A}\sum\limits_{b\in A}\frac{(2j_a+1-\delta_{j_a,j_b})(2j_b+1)}{(4l_A+2)(4l_A+1)}\,F_0^{\mathrm{DF}}(a,b) & A=B,\\ \sum\limits_{a\in A}\sum\limits_{b\in B}\frac{(2j_a+1)(2j_b+1)}{(4l_a+2)(4l_b+2)}\,F_0^{\mathrm{DF}}(a,b) & A\neq B, \end{cases} \quad (19)$$

and

$$G_k^{\mathrm{IC}}(A,B) = \frac{1}{2}\sum_{a\in A}\sum_{b\in B}(2j_a+1)(2j_b+1) \times \begin{Bmatrix} j_a & j_b & k\\ l_b & l_a & \frac{1}{2}\end{Bmatrix}^2 G_k^{\mathrm{DF}}(a,b)\,,$$

$$F_k^{\mathrm{IC}}(A,A) = G_k^{\mathrm{IC}}(A,A)\,. \quad (20)$$

Nonrelativistic limit of the CoG of *LS*-configuration in DF method

Let's assume that in the non-relativistic limit ($c\to\infty$) the large radial components $P_a(r)$ and $P_b(r)$ are independent of the quantum number j, i.e. they are the same for all $a\in A$ and $b\in B$, respectively, and the small components $Q_a(r)$ and $Q_b(r)$ tend to zero. Then, at $c\to\infty$ integrals $F_k^{\mathrm{DF}}(a,b)$ and $G_k^{\mathrm{DF}}(a,b)$ depend only on indices A and B and tend to the nonrelativistic integrals $F_k^{\mathrm{HF}}(A,B)$ and $G_k^{\mathrm{HF}}(A,B)$ (5). In this case, the radial integrals can be taken off the signs of the sums in expressions (19) and (20). By using the equalities

$$\sum_{a\in A}(2j_a+1) = 4l_a+2\,, \qquad \sum_{b\in B}(2j_b+1) = 4l_b+2, \quad (21)$$

and enumeration ratios for $6j$-symbols [16]

$$\sum_{j_a}(2j_a+1)\begin{Bmatrix} j_a & j_b & k\\ l_b & l_a & \frac{1}{2}\end{Bmatrix}^2 = \sum_{j_a}(2j_a+1)\begin{Bmatrix} k & j_b & j_a\\ \frac{1}{2} & l_a & l_b\end{Bmatrix}^2 = \frac{1}{2l_b+1}\,, \quad (22)$$

we may get

$$\sum_{a\in A}\sum_{b\in A}\frac{(2j_a+1-\delta_{j_a,j_b})(2j_b+1)}{(4l_A+2)(4l_A+1)} = 1\,,$$

$$\sum_{a\in A}\sum_{b\in B}\frac{(2j_a+1)(2j_b+1)}{(4l_a+2)(4l_b+2)} = 1\,, \quad (23)$$

and

$$\frac{1}{2}\sum_{a\in A}\sum_{b\in B}(2j_a+1)(2j_b+1)\begin{Bmatrix} j_a & j_b & k\\ l_b & l_a & \frac{1}{2}\end{Bmatrix}^2 = 1\,. \quad (24)$$

Taking into account equalities (23) and (24) in the non-relativistic limit of the intermediate coupling, we obtain for integrals (19) and (20)

$$F_0^{\mathrm{IC}}(A,B) = F_0^{\mathrm{HF}}(A,B)\,, \qquad G_k^{\mathrm{IC}}(A,B) = G_k^{\mathrm{HF}}(A,B)\,,$$

$$F_k^{\mathrm{IC}}(A,B) = F_k^{\mathrm{HF}}(A,B)\,. \quad (25)$$

Thus, expression (17) for the CCoG energy in the intermediate coupling in the non-relativistic limit coincides with expression (3), i.e. it has the correct non-relativistic limit.

3. Calculation results

In this paper, calculations were performed using program [17], which was generalized to the case of an intermediate coupling. In this approach, all jj-configurations corresponding to a single non-relativistic *LS* configurations were included in the calculation within the multi-configuration method of the self-consistent DF (MCDF) field.

In our analysis, we used the Fermi model for the nuclear density distribution [18]. The root-mean-square radii of the nuclei for the most common isotopes were taken from [19]. The RMS radius of Fl atom was taken to be 6.2705 fm.

Tables 1 and 2 present the results of calculations of *LS*-average total energies of atoms of groups 13 and 14 of the periodic table using DF and HF methods. The third columns of these tables contain data obtained using standard light velocity ($c = 137.0359991$). The fourth columns present the results of calculations using DF method with a 10,000-fold increase of the light velocity. As can be seen from the tables, these results are in very good agreement with the data obtained by the non-relativistic HF method shown in the last columns of table 1 and 2. This comparison indicates that *LS*-average has a correct non-relativistic limit.

In Table 3, the third and fourth columns provide the thermal energies of the elements of group 14 of the periodic

Table 1. *LS*-average energies of atoms of group 14, calculated by DF method with standard and increased values of the light velocity, as well as the non-relativistic HF method

Z		DF *LS*-average $c = 137.0359991$	DF *LS*-average $c \times 10000$	HF $c = \infty$
6	C	-37.67604078	-37.6596946	-37.6596946
14	Si	-289.461336	-288.834437	-288.834437
32	Ge	-2097.47037	-2075.33148	-2075.33148
50	Sn	-6176.13021	-6022.84352	-6022.84352
82	Pb	-20913.7029	-19523.2664	-19523.2664
114	Fl	-49709.5886	-42688.1130	-42688.1130

Table 2. *LS*-average energies of atoms of group 13, calculated by DF method with standard and increased values of light velocity, as well as the non-relativistic HF method

Z		DF *LS*-average $c = 137.0359991$	DF *LS*-average $c \times 10000$	HF $c = \infty$
5	B	-24.5365543	-24.5290592	-24.5290592
13	Al	-242.330751	-241.876580	-241.876580
31	Ga	-1942.56376	-1923.25348	-1923.25348
49	In	-5880.43224	-5740.10506	-5740.10506
81	Tl	-20274.8437	-18961.1412	-18961.1412
113	Nh	-48504.1069	-41806.1514	-41806.1514

table, calculated by DF method in jj- and IC-couplings. Valence configuration of these atoms – s^2p^2. The atomic terms in *LS*coupling are ^3P, ^1D, and ^1S. The energies of these terms are counted from the energies of *LS*-average over the configurations that are provided in the third column of Table 1. The data in the third and fourth columns of Table 3 compared indicate that up to and including Sn atom (Z=50), the calculation results in jj coupling absolutely incorrectly convey the order and structure of atomic terms. Pure jj coupling is realized with good accuracy only in the superheavy atom Fl (Z=114). The degree of realization of jjcoupling in atoms of group 14 can be estimated using the populations of relativistic valence $p_{1/2}$ and $p_{3/2}$-subshells. Populations of $p_{1/2}$-sub-shell designated through $q_{1/2}$, were analyzed in jj- and IC-couplings. They are given in the 5-th and 6-th columns of Table 3. We do not give the population $p_{3/2}$, since it is easily determined by the formula $q_{3/2} = 2 - q_{1/2}$. The populations of jj-sub-shells are integers from zero to two. As can be seen by comparing the data in the 5th and 6th columns of Table 3, in its pure form jj-coupling is realized only for the term $^3P_1$. This is due to the fact that the total moment $J = 1$ of this term differs from the total moments of all other terms of this configuration, and therefore is not mixed with them by inter-electron interaction. Moreover, as mentioned before, jj-coupling is realized in the super-heavy atom of Fl.

In our calculated total energies of the elements of groups 13 and 14, there is a slight effect of decline in the energies of

Table 3. Energies of terms of the elements of group 14 counted from *LS*-average (Table 1), $q^{jj}_{1/2}$ and $q^{IC}_{1/2}$ — populations of the valence $p_{1/2}$ shell in jj- and IC-couplings, respectively (c=137.0359991)

	Term	DF jj	DF IC	$q^{jj}_{1/2}$	$q^{IC}_{1/2}$
C	$^3P_0$	0.0186224	-0.0290902	2.0	1.33
	$^3P_1$	-0.0290024	-0.0290024	1.0	1.00
	$^3P_2$	-0.0094026	-0.0288277	1.0	0.33
	$^1D_2$	0.0094285	0.0283610	0.0	0.66
	$^1S_0$	0.0654752	0.1100634	0.0	0.66
Si	$^3P_0$	0.0114976	-0.0204919	2.0	1.35
	$^3P_1$	-0.0201031	-0.0201031	1.0	1.00
	$^3P_2$	-0.0058443	-0.0193846	1.0	0.35
	$^1D_2$	0.0061457	0.0194045	0.0	0.65
	$^1S_0$	0.0453865	0.0754959	0.0	0.65
Ge	$^3P_0$	0.0044036	-0.0239556	2.0	1.44
	$^3P_1$	-0.0214924	-0.0214924	1.0	1.00
	$^3P_2$	-0.0023045	-0.0174993	1.0	0.41
	$^1D_2$	0.0043000	0.0192614	0.0	0.59
	$^1S_0$	0.0477715	0.0743313	0.0	0.56
Sn	$^3P_0$	-0.0085912	-0.0298937	2.0	1.59
	$^3P_1$	-0.0227756	-0.0227756	1.0	1.00
	$^3P_2$	0.0006568	-0.0140413	1.0	0.55
	$^1D_2$	0.0495462	0.0189211	0.0	0.44
	$^1S_0$	0.0042913	0.0693715	0.0	0.42
Pb	$^3P_0$	-0.0565372	-0.0682630	2.0	1.86
	$^3P_1$	-0.0348880	-0.0348879	1.0	1.00
	$^3P_2$	-0.0126826	-0.0175138	1.0	0.90
	$^1D_2$	0.0292379	0.0344964	0.0	0.10
	$^1S_0$	0.0721256	0.0823468	0.0	0.15
Fl	$^3P_0$	-0.1965942	-0.2009824	2.0	1.98
	$^3P_1$	-0.0726660	-0.0726661	1.0	1.00
	$^3P_2$	-0.0563699	-0.0570748	1.0	1.00

LS-terms found by DF method in the non-relativistic limit, compared to the energies obtained by the non-relativistic HF method. This is due to the fact that the space of variable functions in the relativistic DF method is larger than in HF method. Even in the non-relativistic limit, in DF method, the functions $P_{nlj}(r)$ for different $j = l \pm 1/2$ vary independently, whereas in HF method they correspond to one variable function $P_{nl}(r)$, the same for different j. This may lead to a slight decrease in the energy of the terms (due to a lower symmetry) for atoms with open shells. The effect of energy reduction and symmetry breaking can also be explained by the fact that electrons of different jj-subshells of the same valence shell polarize the backbone in different ways.

Table 4 shows the calculated total energies of *LS*-terms of the elements of group 13 of the periodic table. These energies are counted from the energies of *LS*-averages calculated in similar way and given in the Table 2. Despite

Table 4. Nonrelativistic limit. Energies of terms of the elements of group 13 counted from the energy of *LS*-average (Table 1)

	Term	DF DF $c = 137.0359991$	DF DF $c \times 10000$	HF HF
B	$^2P_{1/2}$	-0.0000620	0.0000000	0.0
	$^2P_{3/2}$	0.0000310	0.0000000	0.0
Al	$^2P_{1/2}$	-0.0003687	-0.0000113	0.0
	$^2P_{3/2}$	0.0001759	-0.0000027	0.0
Ga	$^2P_{1/2}$	-0.0024558	-0.0000440	0.0
	$^2P_{3/2}$	0.0011907	-0.0000109	0.0
In	$^3P_{1/2}$	-0.0065473	-0.0000584	0.0
	$^3P_{3/2}$	0.0032122	-0.0000145	0.0
Tl	$^3P_{1/2}$	-0.0234708	-0.0000183	0.0
	$^3P_{3/2}$	0.0115394	-0.0000735	0.0
Nh	$^3P_{1/2}$	-0.0780977	-0.0000695	0.0
	$^3P_{3/2}$	0.0378175	-0.0000171	0.0

the fact that for a single electron outside a closed shell, jj-coupling is completely equivalent to IC-coupling, the energies calculated by DF method in the non-relativistic limit and presented in the 5th column of Table 4 are systematically lower than HF energies equal to zero in this case. As mentioned above, this is due to the different polarization of the backbone by electrons of $p_{1/2}$- and $p_{3/2}$-shells. Atom B (Z=4) that has no any backbone p-shells is an exclusion here.

4. Conclusions

In this paper, we have given closed expressions for the total energies of atoms in various types of couplings. The expression for *LS*-average configuration in DF method is presented in the form similar to *LS*-average over configuration in the non-relativistic HF method. The difference is that the non-relativistic Slater-Koster $F_k(A, B)$ and $G_k(A, B)$ parameters have been replaced by their relativistic counterparts. It is shown that the non-relativistic limit of *LS*-average expression for the energy in DF method coincides with the energy of CCoG in the non-relativistic HF method. This is not true for *LS*-terms of the open shell atoms where in the non-relativistic limit a decline in symmetry and a decrease in energy occurs as compared to HF energy. This is because different jjsubshells of the same valence shell polarize the backbone differently.

The energies of CCoG and energies of the atomic terms of the elements of group 13 and group 14 of the periodic table in various couplings and also in the non-relativistic limit were calculated to illustrate and prove the theoretical analysis. The results of non-relativistic calculations using HF method were compared.

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Conflict of interest

The authors declare no conflict of interest.

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